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Proceeding Of The Seventeenth Annual EPA Conference On Analysis Of Pollutants In The Environment

May 3 - 5, 1994

Proceedings Of The Seventeenth Annual EPA Conference On Analysis Of Pollutants In The Environment

May 3-5, 1994

INTRODUCTION

I am pleased to present the proceedings of the 17th Annual EPA Conference on Analysis of Pollutants in the Environment. This year's conference, which was held in Norfolk, VA on May 3-5, 1994, was jointly sponsored by the EPA Office of Water and the Water Environment Federation. The result wan an enormously successful conference that provided more than 400 participants with an opportunity to meet and discuss contemporary issues concerning the measurement of environmental pollutants.

Once again, conference participants represented a broad spectrum of the environmental community, including Federal, State, and local regulatory authorities, environmental laboratories, regulated industries, wastewater treatment facilities, and environmental groups. This diversity has always been and continues to be an integral aspect of the conference in that it fosters small, group discussions among individuals representing different analytical or regulatory perspectives.

The proceedings contained in this document reflect the 31 presentations given at the Conference. These presentations, which were chosen because they reflect current areas of concern in the water pollution control arena, included discussions on: efforts to replace the use of Freon 113 in methods for the determination of oil and grease and total petroleum hydrocarbons in environmental samples; the development of alternate techniques for measurement of these parameters; techniques and current efforts to make reliable measurements of trace metals at ambient water quality criteria levels; research concerning the effects of interferences on cyanide measurements; new procedures for measuring biochemical oxygen demand; new techniques for determination of volatile organic compounds, polynuclear aromatic compounds, and total organic halides; statistical procedures used to derive numerical effluent limitations; the results of recent studies to evaluate the performance of several methods for measuring organic pollutants; and current issues and developments concerning the implementation of performance-based methods and analytical detection limits.

I would like to take this opportunity to thank Ms. Jan Kourmadas of Ogden Environmental, Ms. Cindy Simbanin of DynCorp Viar, Mr. Dale Rushneck of Interface, and the staff at the Water Environment Federation for their assistance in making this conference such a resounding success. I would also like to extend my thanks to all who participated in this conference; I look forward to seeing you at the 18th Annual Conference next May!

William A. Telliard

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PROCEEDINGS

May 3, 1994

MR. TELLIARD: I would like to welcome you to the 17th annual meeting of measuring pollutants in the environment. This meeting is sponsored by the Office of Water and also co-sponsored this year by the Water Environment Federation.

There are a couple of housekeeping rules I need to tell you about. First of all, my name is Bill Telliard. I am from EPA, and I am here to help you.

During the sessions, if you have any questions, there are microphones spaced around the room. If you would, please go to those microphones, identify yourself, and ask your question.

There is no limit on questions. That is covered in your registration fee.

This year is our first effort at a co-sponsorship. The Water Environment Federation has been involved in a number of activities with the Office of Water over the years, not surprisingly. In addition to workshops and other committees that they serve on, the Water Environment Federation has been a long-time source of information and consulting to the Agency.

So, we are very pleased to initiate this program this year, and we look forward to having a number of other years where we will be co-sponsoring with the Water Environment Federation.

I would be happy to get your comments later on after this meeting on what you think of it, how we can improve it, and how we can make it better. We are all interested in that.

I would like to introduce at this time Bob Wyeth. Bob is Chairman of the Laboratory Practices Committee of the Water Environment Federation, and in his spare time, he is Senior Vice President for Recra Environmental, Incorporated, a laboratory which does work in the environmental field. So, I would like to introduce Bob at this time.

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17th ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

INTRODUCTION AND WELCOME

Robert K. Wyeth
Senior Vice President and Principal
Recra Environmental, Inc.
Laboratory Practices Committee Chairperson
Water Environmental Federation

On behalf of the Water Environment Federation, it gives me great pleasure to welcome all of you to the 17th Annual Conference on Analysis of Pollutants in the Environment.

The Water Environment Federation is very pleased to be able to co-sponsor this prestigious conference with the United States Environmental Protection Agency.

The Water Environment Federation, formerly the Water Pollution Control Federation, is a not-for-profit technical and educational organization that was founded in 1928. Its mission is to preserve and enhance the global water environment. Federation members number more than 40,000 water quality specialists from around the world. Included in this membership are environmental, civil and chemical engineers, biologists, chemists, government officers, treatment plant managers and operators, laboratory analysts and technicians, college professors, researchers, students and equipment manufacturers and distributors.

The strengths of the Water Environment Federation, in addition to its size, are:

1) Active volunteer leadership
2) Quality technical materials
3) Technically diverse membership
4) Organizational culture responsive to change
5) Financial stability and strong staff resources

Other strengths include:

6) Geographically broad base
7) Worldwide reputation
8) A track record of success and credibility
9) Continuous growth in quality member services

And most importantly:

10) Both individual and organizational commitment to water quality!

In support of attaining their mission the Water Environment Federation established a number of strategic initiatives:

- Create and sustain a quality improvement philosophy
- Explore new methodologies and technologies for delivery of services
- Develop a system for comprehensive technological information exchange and dissemination
- Provide leadership for environmental policy information
- Educate the public
- Support and encourage research and development
- Expand the focus to include all issues related to the water environment

Co-sponsorship of this conference is totally consistent with these initiatives and the American Water Works Association mission.

I mentioned active volunteer leadership. The Water Environment Federation generates much of its strengths from its committee activities. The Water Environment Federation has over 40 standing committees, including Toxic Substances, Standard Methods (which works jointly with American Public Health Association and the American Water Works Association), Ecology and Groundwater, to name a few.

Another of these committees is the Laboratory Practices Committee of which I am chairperson. Our committee consists of approximately 30 active members from across the country. Members include predominantly chemists from the commercial laboratory industry, industrial laboratories, municipal, state and federal government laboratories and agencies.

Activities of the Laboratory Practices Committee include participation in such issues as: National Environmental Laboratory Certification, Performance Based Methods, and application of Method Detection Limits. Significant committee efforts are also focused on training and education and sponsorship of a Laboratory Practices Committee Specialty Conference. These specialty conferences are focused strictly on issues and concerns of the laboratory professional and have consistently received exceptional ratings from the participants and attendees.

With the specific intention of a plug or commercial, please allow me to state that the Laboratory Practices Committee's next specialty conference will be in August of 1995 in

Cincinnati, Ohio. I assure you that you will receive information about our specialty conference. I hope you'll be able to attend.

In reviewing the program for the 17th Annual Norfolk Conference, it is clear that the content and quality of materials will once again meet the high standard for which this Conference has become known.

Issues of environmental sampling, analysis and discharge monitoring are critically important to the government, to industry and to all laboratories. As a principal of Recra Environmental, Inc., which is a commercial environmental laboratory with locations in Buffalo New York, Cleveland Ohio, Detroit Michigan and Columbia, Maryland, I have to deal with these types of concerns and issues each and every day.

As many of you may know, the commercial laboratory industry, particularly in the Environmental Sector, has its own set of problems, including greater demands from our clients, continually eroding prices and shortened turnaround time, which exacerbate the operational and management difficulties that we face. An example of one of these problems, which is being addressed at the conference, is the question of Freon use. As an environmentalist, I share the concern over use and control of Freon and all CFC's. As a scientist, I need to insure its replacement is appropriate, efficient and capable of providing reasonably comparable data. As a laboratory operation person, I need to insure that replacement technologies can be implemented to produce high quality results in an effective and productive manner. And lastly as a laboratory owner I must be concerned over the costs of performance of any new procedures, but anxiously await changing from a method where my solvent costs alone are $1000/gallon.

Likewise, in order to remain competitive and increase marketshare, I have to provide capital for new technologies and procedures like Immunoassay, SPE, SFE, Ion-Trap GC/MS, post-column derivitization HPLC with various detectors, some of which are new in their application to the environmental analysis arena.

All of these issues, of course, also have to be considered in concert with the long term trend in ever decreasing limits of quantification and ever increasing requirements of analytical certainty. - *Oh, what a tangled web we weave*! - Over the years, the Norfolk Conference, as much as any other I am familiar with has continued to assist in untangling our web.

In closing, let me state that the Vision of the WEF is for the federation to be the pre-eminent organization dedicated to the preservation and enhancement of the global water

environment.

The membership of the organization, while in pursuit of this mission, are committed to the principals of providing technical information to a worldwide audience, expanding quality services for its members and building alliances with other organizations.

This Conference provides an ideal forum for attainment of our mission and realization of our vision. As a principal in Recra Environmental, Inc. and the Chairperson of the Water Environmental Federation Laboratory Practice Committee and a co-sponsor of the Conference, I want to thank you for your attendance, invite your active participation in the proceedings, and once again, welcome you to the 17th Annual Norfolk Conference.

MR. TELLIARD: Thanks, Bob.

This afternoon's session is going to focus on the cutting edge of science. None of this high resolution mass spectrometry. We are going to talk about oil and grease.

For those of you who were here last year and heard my presentation, you know that as part of the effort to find a suitable replacement solvent for Freon in oil and grease methods, EPA had conducted Phase I of the Freon Replacement Study. Today I am going to present the results of Phase II of the Freon Replacement Study. My talk will be followed by a number of other speakers, including vendors and industry representatives, who will be presenting information on additional studies related to this effort.

FREON REPLACEMENT STUDY PHASE II

MR. TELLIARD: First I am going to provide you with some background information pertaining to the Freon Replacement Study. I will quickly review the objectives and conclusions of Phase I of the study, and then I will focus the remainder of my presentation on Phase II of the study and bring you up to date on the present status of this project.

As a party to the Montreal Protocol on Substances that Deplete the Ozone Layer and as required by law under the Clean Air Act Amendments of 1990, the United States is committed to controlling and eventually phasing out chlorofluorocarbons, which have been shown to cause depletion of the stratospheric ozone layer. Freon-113 is a CFC whose use as an extraction solvent is mandated under some EPA methods for the determination of oil and grease. As part of the effort to eliminate the use of CFCs, the EPA initiated studies to find a suitable replacement for Freon-113 in these methods.

Phase I of the Freon Replacement Study was the result of a cooperative effort between the Office of Water, the Office of Solid Waste and Emergency Response, the Office of Air and Radiation, and the Office of Research and Development. The objective of Phase I of the Freon Replacement Study was to either find a solvent that gave results equivalent to Freon-113 for gravimetric determination of oil and grease in both aqueous and solid samples, or to select a solvent or alternative technique for further study. Results of this study demonstrated that of the five solvents tested, none produced results equivalent to Freon-113 when the sample results were evaluated collectively. If the aqueous samples were separated into petroleum and non-petroleum subcategories, however, values produced when n-hexane and perchloroethylene were used as the extraction solvent were not significantly different from results produced when Freon-113 was the extraction solvent.

As a result, n-hexane was retained as a candidate solvent for further study of gravimetric oil and grease and total petroleum hydrocarbons determination, and perchloroethylene was retained for consideration in future studies related to the measurement of oil and grease and TPH by infra-red techniques. Perchloroethylene was not considered for further testing as a replacement solvent for gravimetric purposes because of its high boiling point, which would require a higher temperature for evaporation and therefore result in a loss of anything that evaporates below 121°C, and because it is more toxic than n-hexane.

Phase II of the Freon Replacement Study focused on the gravimetric determination of both oil and grease and TPH in aqueous samples. The purpose of this phase was to further assess the suitability of n-hexane as a replacement solvent and, based on comments received about the neurotoxicity of n-hexane, to consider cyclohexane as an alternative solvent.

Oil and grease analysis was performed using MCAWW Method 413.1, with modifications to compensate for the lighter density and higher boiling points of n-hexane and cyclohexane as compared to Freon-113. TPH analysis was performed using Standard Methods 5520F. Each sample was analyzed in triplicate and 1600-series method QC requirements were added to the analytical protocol to monitor laboratory performance.

In addition, other techniques were examined independently by vendors and included solid phase extraction, both column and disk, non-dispersive IR, and immunoassay. EPA supplied these vendors with splits of the same samples used for EAD study purposes.

In Phase II, 34 samples from 25 facilities covering 15 industrial categories were collected. Sample collection activities ended in April, so we have not received all of the data from this study. This presentation is based on what data we have available. In addition to these efforts, a round robin study has been initiated to test the new method, Method 1664, with a group of laboratories located in the Minneapolis-St. Paul area known as the Twin Cities Round Robin Group.

Samples were collected from a number of industrial categories in order to test a variety of sample matrices. In Phase I we learned that many of the effluents sampled did not contain detectable levels of oil and grease. In order to avoid the statistical problems associated with nondetect values, and to ensure that analyses would produce measurable values that could be evaluated, samples were prepared by mixing the influent to treatment with the effluent from the facilities. Facilities were surveyed to determine the average oil and grease values in the effluent, and based on the information provided, a portion of influent was added to the effluent to hopefully produce a sample with oil and grease concentrations in the range of 40-300 mg/L.

Hexane and cyclohexane results were compared to Freon-113 results by calculating the root mean square deviation of the results from the alternative solvents around the results

from Freon-113. Acceptance limits indicate whether or not the hexane and cyclohexane results are comparable to the Freon-113 results. A smaller RMSD indicates better agreement with Freon-113. The results from Phase II show that both hexane and cyclohexane produced results significantly different from Freon, except for TPH analysis using hexane as the extraction solvent.

Another way to compare the hexane and cyclohexane results to Freon results is to look at the mean absolute deviation of the alternative solvent results from the Freon results. The calculated values show that in general, the deviation of the hexane and cyclohexane results from Freon are often less than 20%, which is within the acceptance criteria for deviation of duplicate analysis results. This indicates that, although the hexane and cyclohexane results are statistically different from the Freon results, they are close enough in value to the Freon results to be within the variability of duplicate analyses.

As part of the Phase II data evaluation, we also determined the percentages of the hexane and cyclohexane results that were above or below the Freon results. As you can see, analysis for oil and grease using either hexane or cyclohexane produced results less than the results generated with Freon for approximately 80% of the samples, and analysis for TPH using either hexane or cyclohexane produced results less than the results generated with Freon for over half of the samples.

This means that approximately 20% of the hexane and cyclohexane oil and grease values are above the Freon values, which raises some concerns about the effect of a solvent change on compliance monitoring and the ability to meet permit limits. We plan to look at this particular data more closely to further evaluate how much of an effect this may have on compliance monitoring.

Based on our evaluation of the Phase II data, we have concluded that both hexane and cyclohexane produce results that are different from Freon, but that hexane and cyclohexane results are equivalent to one another.

Since hexane and cyclohexane had similar extraction efficiencies, when determining the most suitable solvent to replace Freon more practical issues were considered, namely analytical conditions. Due to the lower boiling point of hexane, the solvent evaporation step took much less time for hexane than cyclohexane. The wide range of evaporation times presented on this slide is the result of laboratories using various evaporation techniques, such as water baths, steam baths, and rotovaps.

We also determined that the toxicity of hexane was not that much higher than that of cyclohexane, and that by using good laboratory practices, this health and safety issue should be manageable.

Based on all of these considerations, the Agency is recommending the use of n-hexane to replace Freon as the extraction solvent for gravimetric determination of oil and

grease and TPH. Though we have not yet analyzed the data from other studies, such as those that API and the Uniform and Textile Service Association will be presenting, our evaluation of the data we have collected to date has led us to recommend the use of n-hexane.

A comparison of the n-hexane extracted oil and grease data from Phase I and Phase II demonstrates that Phase II results had much less deviation between replicate analyses than the Phase I data. This improved performance in Phase II analysis can be attributed to the more stringent quality control objectives that were implemented in Phase II, which resulted in more careful and thorough application of analytical technique.

These quality control criteria were incorporated into the new method for gravimetric oil and grease and TPH determination, Method 1664. Analysis consists of a series of three extractions with hexane and requires that both the sample bottle and cap be rinsed to ensure removal of all extractable material that may adhere to the sample container. Sodium sulfate is used to remove any residual water from the solvent after extraction of the sample. For the TPH procedure, the amount of silica gel used increases proportionately with the amount of HEM in the sample at a ratio of 30:1. Method 1664 also requires the use of hexadecane and stearic acid as reference standards, which were used for the QC analyses in Phase II of the study.

Quality control is more entailed than previously used methods and consists of a two point calibration of the analytical balance, calibration verification every ten samples, initial precision and recovery analysis prior to the analysis of field samples, ongoing precision and recovery with each batch of samples, a reagent water method blank with the IPR analysis and with each batch of samples, and a matrix spike/matrix spike duplicate with each batch. A batch consists of ten samples.

As I stated earlier, hexadecane and stearic acid are used as reference standards for QC analyses. These compounds were chosen over materials such as Wesson oil or fuel oil because they are standards of known composition and purity that can be readily obtained from vendors. In addition, the use of stearic acid serves to verify the adsorptive properties of the silica gel.

Method 1664 is a performance-based method, so it allows the use of alternate extraction and concentration techniques, as long as the performance meets the specifications in Method 1664. The laboratory that chooses to use alternate techniques must demonstrate equivalency by meeting the data quality objectives for the specified QC tests in Method 1664 which, among others include the method detection limit, initial precision and recovery analysis, ongoing precision and recovery, and matrix spike/matrix spike duplicate analysis. In addition, detailed records of the method changes and QC analyses must be maintained. These recordkeeping specifications are provided in Section 9.1.2.2 of Method 1664.

As I mentioned earlier, an interlaboratory study of Draft Method 1664 is currently being conducted by the Twin City Round Robin Group. Approximately 16 laboratories that are part of this group are voluntarily participating to analyze two samples, one from an olive packaging plant and one from a shore reception facility, each in triplicate, for oil and grease using Method 1664. Prior to analyzing field samples, the laboratories were required to demonstrate their ability to meet method protocol by performing initial precision and recovery analyses. We are in the process of receiving the IPR data and, of the data that have been submitted, almost all meet the data quality objectives of Draft Method 1664. We anticipate that analyses will be completed and data submitted within a month or so.

In the future, we plan to conduct an MDL study using hexadecane and stearic acid to determine the MDLs and Minimum Levels for Method 1664. Other related projects under consideration include an interlaboratory study to compare solid phase extraction techniques with liquid/liquid extraction techniques, and a study to evaluate infra-red techniques for the analysis of oil and grease and TPH using perchloroethylene as the extraction solvent.

Method 1664 will be proposed in the Federal Register as the Freon replacement method for oil and grease and TPH. We will distribute copies of Draft Method 1664 at the end of this presentation, and would be glad to receive your comments on this method. In addition, a questionnaire is being distributed in an effort to collect additional comments, information, and suggestions on the Freon replacement study. Please complete the questionnaire and submit it to us before you leave.

If there are any questions, I will be happy to answer them at this time. Thank you.

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EPA Efforts to Replace Freon-113 Phase II

William A. Telliard
USEPA

Regulatory History

- Montreal Protocol on Substances that Deplete the Ozone Layer regulates the use of chlorofluorocarbons (CFCs), with an eventual phase out by 1996.

Regulatory History (cont'd)

- The Clean Air Act Amendments of 1990 (CAAA) commit EPA to phase out CFCs and other ozone depleting chemicals by 1996.

- Freon-113 is the only CFC used in laboratory testing that falls under these regulations.

Study Plan: Phase I

- Find a solvent (if any) that gives results equivalent to Freon-113, or
- Select solvent or alternative technique for further study

Summary of Results from Phase I

- All Solvents Were Significantly Different From Freon When Samples Were Not Segregated By Sample Category

- Hexane and Perchloroethylene Were Not Significantly Different From Freon For Aqueous Non-Petroleum Samples

Study Plan: Phase II

- Further Assess Precision, Accuracy, and Comparability of n-Hexane in Gravimetric Oil & Grease Analyses of Aqueous Samples

- Evaluate Cyclohexane as an Alternative Solvent (Based on Concerns About Neurotoxicity of n-Hexane)

- Evaluate n-Hexane and Cyclohexane as Alternative Solvents For Gravimetric Total Petroleum Hydrocarbons (TPH) Analysis (Silica Gel Procedure) of Aqueous Samples

Solvents and Techniques: Phase II

- Freon 113
- Freon 113 + silica gel adsorption procedure
- n-Hexane
- n-Hexane + silica gel adsorption procedure
- Cyclohexane
- Cyclohexane + silica gel adsorption procedure

Overview of Sampling Plan: Phase II

- 34 Samples From 25 Facilities Covering 15 Industrial Categories Have Been Collected
- Sampling Ongoing Through April, 1994
- Twin City Round-Robin Study Began in April, 1994
  - 16 Laboratories Participating

Industrial Categories Sampled: Phase II

Non-Petroleum Sources:

4	Meat Product Plants
2	Coil Coating Plants
2	Miscellaneous Foods
2	Textile Manufacturers
2	Leather Tanning Plants
1	Metal Molding and Casting
1	Meat Processing Plant
1	Soap & Detergent Manuf.
1	POTW

Petroleum Sources:

3	Metal Finishing Plants
3	Shore Reception Facilities
2	Petroleum Refineries
2	Transportation Facilities
2	Drum Reconditioning Fac.
2	Organic Chemical Plants
1	Industrial Laundry

Phase II
Comparison of Solvents Alternative to Freon
Following Natural Log Transformation

Category	Analysis	Normalized RMSD* Hexane	Normalized RMSD* Cyclohexane	Acceptance Limit
All Samples	Oil & Grease	3.7	3.4	1.5
	TPH	1.7	2.4	1.5
Non-Petroleum	Oil & Grease	4.1	2.8	1.8
	TPH	1.5**	2.3	1.8
Petroleum	Oil & Grease	5.0	4.2	1.8
	TPH	2.3	2.4	1.8

* Root Mean Square Deviation; Significantly Different Than Freon If Exceeds Acceptance Limit

** Value Within Acceptance Limit

Phase II
Mean Absolute Deviation From Freon Of Alternative Solvents
Following Natural Log Transformation

Category	Analysis	Percent Deviation From Freon-113 of: Hexane†	Cyclohexane†	N
All Samples	O & G	10.4 ± 2.1	9.7 ± 3.1	29
	TPH	15.9 ± 3.3	25.9 ± 11.9	29
Non-Petroleum	O & G	11.0 ± 2.7	8.4 ± 1.7	14
	TPH	25.8 ± 6.7	38.4 ± 15.3	14
Petroleum	O & G	14.4 ± 4.8	8.7 ± 3.4	15
	TPH	6.7 ± 1.9	14.5 ± 6.7	15

† Mean ± Standard Error of the Mean (S.E.M.)
Percent Deviation =
| (100 x Conc derived with Hexane* / Conc derived with Freon) - 100 |
* or Cyclohexane

Phase II
Percentages of Solvent Results Above and Below Freon Results
Following Log Transformation

Analysis	Solvent	Solvent Result < Freon Result	Solvent Result > Freon Result
O & G	Hexane	79.3%	20.7%
	Cyclohexane	79.3%	20.7%
TPH	Hexane	68.0%	32.0%
	Cyclohexane	53.8%	46.2%

Conclusions: Phase II

- Both n-Hexane and Cyclohexane Produce Results Which Are Different From Freon
- n-Hexane and Cyclohexane Results Are Equivalent

Comparison of Analytical Conditions: Phase II

n-Hexane

- Boiling Point = 69° C
- Solvent Evaporation Time ≈ 30 - 150 Minutes, With Water Bath at 85 - 90° C

Cyclohexane

- Boiling Point = 81° C
- Solvent Evaporation Time ≈ 80 - 240 Minutes, With Water Bath at 90 - 95° C

Recommendation: Phase II

- EPA Recommends the Use of n-Hexane as a Replacement For Freon in Gravimetric Oil & Grease and TPH Analyses of Aqueous Samples

Summary of Hexane Results For Analyses Of Total Oil & Grease

Aqueous Samples

Study Phase	Sample Category	Similar to Freon?	% Freon Recovery*
I	All Samples	No	117 ± 20
	Non-Petroleum	Yes	145 ± 52
	Petroleum	No	102 ± 15
II	All Samples	No	95 ± 3
	Non-Petroleum	No	97 ± 4
	Petroleum	No	97 ± 6

* Mean ± S.E.M.

Draft Method 1664—Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT-HEM) By Extraction and Gravimetry

Characteristics:

- Hexane Used As Extraction Solvent (Purity > 95%)
- Bottle and Cap Rinsed 3x With Extracting Solvent
- Sodium Sulfate Used to Remove Residual Water
- Set Ratio of Silica Gel to HEM at 30:1
- Reference Standards—Hexadecane and Stearic Acid

Draft Method 1664

Quality Control:

- Two Point Calibration of Analytical Balance
- Calibration Verification Every 10 Samples
- Initial Precision and Recovery (IPR; 4 Reps)
- Ongoing Precision and Recovery (Each Batch)
- Reagent Water Method Blank (With IPR and With Each Batch)
- Matrix Spike/Matrix Spike Duplicate Each Batch
- Batch Size = Maximum of 10 Field Samples

Draft Method 1664

Hexadecane and Stearic Acid as Reference Standards:

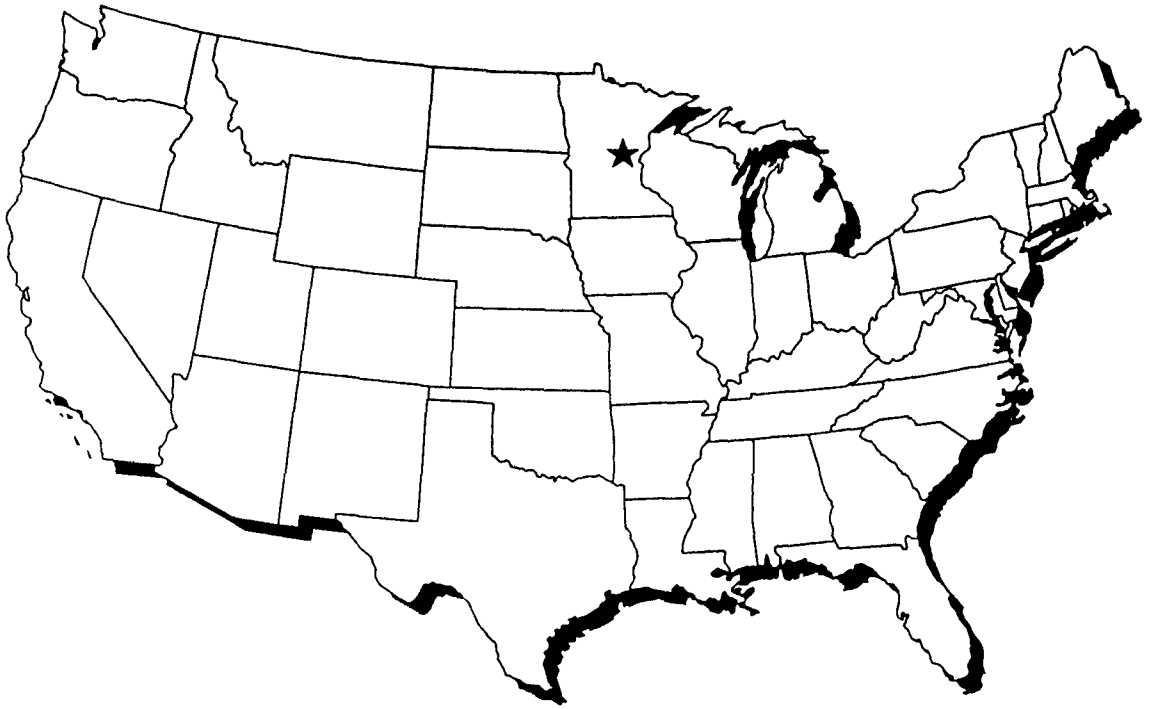
- Standards of Known Composition and Purity That Can Be Readily Obtained From Vendors
- Adsorptive Properties of Silica Gel Are Verified Using Stearic Acid

Draft Method 1664

Performance-Based Approach

- Sect 9.1.2 Allows for the Use of Alternative Extraction and Concentration Devices and Procedures, as Long as Performance is Equivalent to Draft Method 1664
- Equivalency is Demonstrated by Meeting Data Quality Objectives in Draft Method 1664 for:
  - Sensitivity (Method Detection Limit; Sect 9.2.1)
  - Precision (Sect 9.2.2 & 9.3.5)
  - Accuracy (Sect 9.2.2 & 9.3.4)
  - and Other Criteria
- Required Recordkeeping is Specified in Sect 9.1.2.2

Twin City Round-Robin Group



Interlaboratory Study of Draft Method 1664

51-001-28

EPA
Engineering & Analysis Division

Future Plans

- Conduct MDL and ML Study For Draft Method 1664 Using Hexadecane and Stearic Acid as Analytes
- Conduct an Interlaboratory Study to Compare Solid Phase Extraction Techniques With Liquid/Liquid Extraction Techniques
- Evaluate Infra-Red Techniques For the Analysis of Oil and Grease and TPH Using Perchloroethylene as the Extraction Solvent

MR. TELLIARD: Our next speaker is presenting on behalf of the American Petroleum Institute or, as we refer to it in government, the big API, not to be confused with the little API. Harold Rhodes is going to talk about a study that they conducted looking at 30 facilities and comparing solvents. Harold has just recently retired from Texaco, but he is going to say Texaco things to us, so please give him your attention. Thank you.

NOTHING IN LIFE IS FREON

MR. RHODES: The title of our study was Nothing in Life is Freon, and this can be attributed to the old philosopher from API, Roger Claff, or you can blame me for it also.

Last year at this meeting, we saw what Bill has just finished telling you again, that the Phase I study was done and gave us some ammunition to conduct our own study for the petroleum industry. We did this in support of EPA so they could have some information for their decision making. A contractor was contacted to do this for us.

Our API project goals were to seek an alternative solvent to Freon 113 and Method 413.1 only. This is a gravimetric method, and we were going to report the findings to EPA in response to their request.

Now, what we already knew when we started is that oil and grease is a defined parameter and is just used to monitor effluent quality. In our industry, it is many different compounds and many different classes of compounds.

These include the crude oil from produced waters or refinery products from our refineries or our finished products from our marketing terminals, but the petroleum facilities in our industries are all different. Each one of those effluents is different, so we were going to conduct a study of different sectors of our industry.

Our goal was, can we find another solvent which is either equivalent to or proportional to Freon 113?

After listening to Bill, we probably made the wrong choices, but it looks like we came out pretty close. We were going to try n-hexane and cyclohexane and perchloroethylene, all in the gravimetric test. Also in our scope, we wanted to take three different industry sectors, the marketing terminals, production platforms, and refineries.

Our original goal was to select 10 sites from each sector. We almost made it in, that, one biotreater was out at a marketing terminal, so we had 29 samples.

Triplicate samples were taken from each site at each location for each solvent. The data were duly compared against results for Freon 113 for each of the solvents.

Our operating procedures we have gone through already, so I will show you exactly what we did. Method 413 we followed rigorously and made some observations as to what was going to be different for each one of our solvents. We did a quality control daily, method blanks, all of the good QA/QCs that you are supposed to do.

If you use cyclohexane, one of the first things you run into is it is lighter than water. This causes a perturbation in the Freon extraction procedure, because it, being heavier than water, is easier to handle.

Some of the things that you had to take care of were that, at each serial extraction, you had to drain the solvent back into the bottle and remove the water, and do some more handling. Of course, the solvent is highly flammable and has a flash point of about -20. It requires a higher water bath temperature to remove, but it is relatively low cost in disposals.

Again, here are some observations using hexane. The same low density is a problem. It is a known neurotoxin. We had to take this and the flammability into consideration. Again, it has a relatively low price and disposal costs.

For perchloroethylene, we go back to the greater density, so it was a lot easier to handle, but its high boiling point required the use of a heating mantle in order to remove the solvent. It is a little more toxic than the Freon, but it is not known as a neurotoxin.

One observation we made was we used a quality control standard, that we ran with each batch on each day, which is a 33 API gravity crude and is about 0.86 density, and the means you can compare results for recovery.

Now, this crude oil has some volatile components. As you can see, none of the solvents gave as good a recovery as with Freon of your gravimetric residue. This may be due to the higher boiling point or analyte loss at different stages.

Here are some real data. This is data plotted as a function of Freon for each sector. This particular one is a production platform wastewaters. Only one of the sites had any significant...Bill, you would like that...had significant oil and grease in it, but this data point was included into the pooled data for our decision.

In refinery effluents, we tried to select, again, streams that were upstream of our final effluent. The refinery 104 is a final effluent, and you can see we find none in it. This is really a comparison study for the solvents more than the sites.

In the marketing terminals, we had a lot of non-detects and one super-detect. This point was rejected in our statistical data due to the fact that it had floating oil in it and was not representative.

Now, what did we do to check for equivalency of oil and grease concentrations? This is the data evaluation. What we did was take all of the data, and we took it for each solvent at each site and for all the sites.

We did the mean square error of the natural logs of the concentrations. We did the mean square deviation of the natural logs and calculated for each candidate solvent relative to Freon. For each solvent, an F-test was used to test the null hypothesis that no significantly difference between the candidate solvent and Freon based on the ratio of the mean square deviation.

So, what did that say? No candidate solvent was shown to be equivalent to Freon... we have already heard this from Bill... from refinery or production effluents. The perchloroethylene and cyclohexane were equivalent to Freon for marketing terminals, but this may really be due to the fact that there were many non-detects.

Were they proportional to Freon in any case? This is what we did to determine that.

We found that the data variability increased with concentration. So, we did the natural logs of the oil and grease concentration for each candidate solvent. They were regressed against natural logs of the concentrations using Freon.

Coefficients of determination were 0.8 and above. (A regressed slope of 1 indicated solvent behavior proportional to Freon.) The 95 percent confidence intervals were estimated for all of the calculated correction factors.

What we found here was that, sure enough, all three candidate solvents were proportional in some manner to Freon within the three individual petroleum sectors. The exception was cyclohexane with the terminal effluents. Again, that may be due to the non-detects.

Only hexane and perchloroethylene were proportion to Freon for all of the pooled data. The only rejected point was that one marketing terminal.

However, the confidence intervals for this made of the correction factors for each of the concentrations were very large. This is just an example from our main report of the confidence intervals concerning hexane and PCE.

We did one more test sort of as a sideline because of the boiling point differences of the solvents. We did a little experiment here with analyte loss as a function of evaporation temperature.

What we did was take one milligram of our general oil standard, take it up in the solvent, evaporate it, and take the residue up in methylene chloride and run a GC on it. This is the comparison of the GC data as a function of temperature and carbon number.

This study was a one-time shot, and it needs further study to evaluate.

What did we learn? What we learned for production refinery effluents, none of the candidate solvents was equivalent to Freon for 413.1 and that the marketing terminals had too many non-detects.

With the exception of cyclohexane on marketing terminals, all of them were proportional to Freon. For the pooled data, hexane and perchloroethylene were proportional.

The main thing we found out was the confidence intervals for the estimated correction factors were very large, and it is amazing, but perchloroethylene, in our test, showed to be the closest to being proportional to Freon.

This is our recommendation from our study, and Bill has already made his recommendation, so this is whatever you want to do with it. Even though we did the statistical analysis on all of our data and tried to make it either equivalent to or proportional to Freon, the confidence intervals were so great that this was not possible.

So, we are strongly recommending against correction factors, and I was glad to find out in our previous speaker that this is not being done.

I would like to thank all of these people who worked on this project, and if there are any questions within the API sector, I would be glad to answer them.

MR. TELLIARD: Any questions?

(No response.)

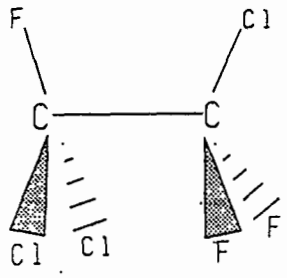
MR. TELLIARD: Thank you.

NOTHING IN LIFE IS FREON !

ANALYSIS OF OIL AND GREASE

FOR

PETROLEUM INDUSTRY EFFLUENTS



API PROJECT GOALS

THROUGH A LABORATORY STUDY OF CANDIDATE SOLVENTS,

1. To ~~seek~~ an alternative solvent to Freon 113 in EPA Method 413.1, Oil and Grease;

2. To report the study findings to EPA in response to their request for industry recommendations on a Freon replacement.

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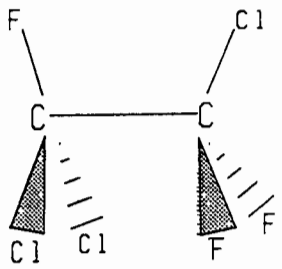

WHAT WE ALREADY KNEW

* O&G is a method-defined parameter used to monitor effluent quality

* O&G is many different compounds and classes of compounds

* Petroleum industry facility effluents are not alike

WHAT WE ASKED

* Can another solvent produce results equivalent to or proportional to Freon for EPA Method 413.1 ?

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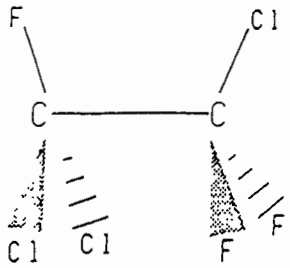


PROJECT SCOPE

Candidate solvents:
- perchloroethylene
- n-hexane
- cyclohexane

Petroleum industry facility types:
- marketing terminals (9)
- production platforms (10)
- refineries (10)

Triplicate samples were collected at each location.

Effluent samples were analyzed using modified methods 413.1 for each candidate solvent. Data were compared against results from methods 413.1 with Freon®, to identify an equivalent or proportional solvent.

OIL AND GREASE DETERMINATIONS USING CYCLOHEXANE

* NO APPARENT BACKGROUND INTERFERENCE IN REAGENT GRADE SOLVENT.

* NO SEVERE EMULSIONS OBSERVED. LOW DENSITY SOLIDS AND POTENTIAL FOR WATER TRANSPORT IN SOME SAMPLES MADE FILTRATION OF EXTRACT NECESSARY STEP.

* DENSITY LESS THAN WATER COMPLICATES ANALYSIS. FLOATING SOLVENT ADDS MANIPULATION STEPS TO PROCEDURE (REQUIRES DRAINING OF SAMPLE INTO ORIGINAL CONTAINER AND RINSING WITH SOLVENT AFTER EACH SERIAL EXTRACTION). ADDITIONAL MANIPULATION COULD LEAD TO LOSS OF ANALYTE.

* BOILING POINT 81°C COULD CONTRIBUTE TO ANALYTE LOSS, i.e., LOW RECOVERY.

* HIGHLY FLAMMABLE, FLAMMABILITY LIMITS IN AIR 1.3 - 8.4% V/V. FLASH POINT IS -20°C.

* LONGEST ANALYSIS TIME OBSERVED, 73 MINUTES, WITH WATER BATH USED IN STRIPPING STEP, 95°C.

* LEAST TOXIC OF SOLVENTS EXAMINED TLV = 300 PPM (TWA). SKIN IRRITANT AND NARCOTIC AT HIGH CONCENTRATIONS.

* RELATIVELY LOW PRICE AND DISPOSAL COSTS.

OIL AND GREASE DETERMINATIONS USING HEXANE

* NO APPARENT BACKGROUND INTERFERENCE IN REAGENT GRADE SOLVENT.

* NO SEVERE EMULSIONS OBSERVED. LOW DENSITY SOLIDS AND POTENTIAL FOR WATER TRANSPORT IN SOME SAMPLES MADE FILTRATION OF EXTRACT NECESSARY STEP.

* DENSITY LESS THAN WATER COMPLICATES ANALYSIS. FLOATING SOLVENT ADDS MANIPULATION STEPS TO PROCEDURE (REQUIRES DRAINING OF SAMPLE INTO ORIGINAL CONTAINER AND RINSING WITH SOLVENT AFTER EACH SERIAL EXTRACTION). ADDITIONAL MANIPULATION COULD LEAD TO LOSS OF ANALYTE.

* BOILING POINT (69°C) COULD CONTRIBUTE TO MINOR ANALYTE LOSS, i.e., LOW RECOVERY. BP CLOSEST TO FREON OF THREE STUDIED. LOW POLARITY MAY AFFECT PERFORMANCE RELATIVE TO FREON.

* FLAMMABLE, FLASH POINT IS - 26°C.

* ANALYSIS TIME OBSERVED, 40 MINUTES, WITH WATER BATH USED IN STRIPPING STEP, 90°C. SIMILAR TO FREON.

* MORE TOXIC THAN FREON, TLV = 50 PPM (TWA). RESPIRATORY TRACT IRRITANT AND NARCOTIC AT HIGH CONCENTRATIONS.

* RELATIVELY LOW PRICE AND DISPOSAL COSTS.

OIL AND GREASE DETERMINATIONS USING PERCHLOROETHYLENE

* NO APPARENT BACKGROUND INTERFERENCE IN REAGENT GRADE SOLVENT.

* NO SEVERE EMULSIONS OBSERVED. HIGH DENSITY SOLIDS OF SOME SAMPLES MADE FILTRATION OF EXTRACT NECESSARY STEP. EXTRACT APPEARED HAZY IN BLANK RUNS.

* DENSITY GREATER THAN WATER SIMPLIFIES ANALYSIS. SETTLING SOLVENT IS CONSISTENT WITH STANDARD SEP FUNNEL TECHNIQUES.

* BOILING POINT (121°C) COULD CONTRIBUTE TO MAJOR ANALYTE LOSS, i.e., LOW RECOVERY. LOW POLARITY MAY AFFECT PERFORMANCE RELATIVE TO FREON.

* NONFLAMMABLE.

* ANALYSIS TIME OBSERVED, 40 MINUTES, WITH HEATING MANTLE USED IN SOLVENT STRIPPING STEP, 130°C. ANALYSIS TIME EQUIVALENT TO FREON.

* MORE TOXIC THAN FREON TLV = 50 PPM (TWA) AND EQUAL TO HEXANE. DEFATTING ACTION ON SKIN AND NARCOTIC AT HIGH CONCENTRATIONS.

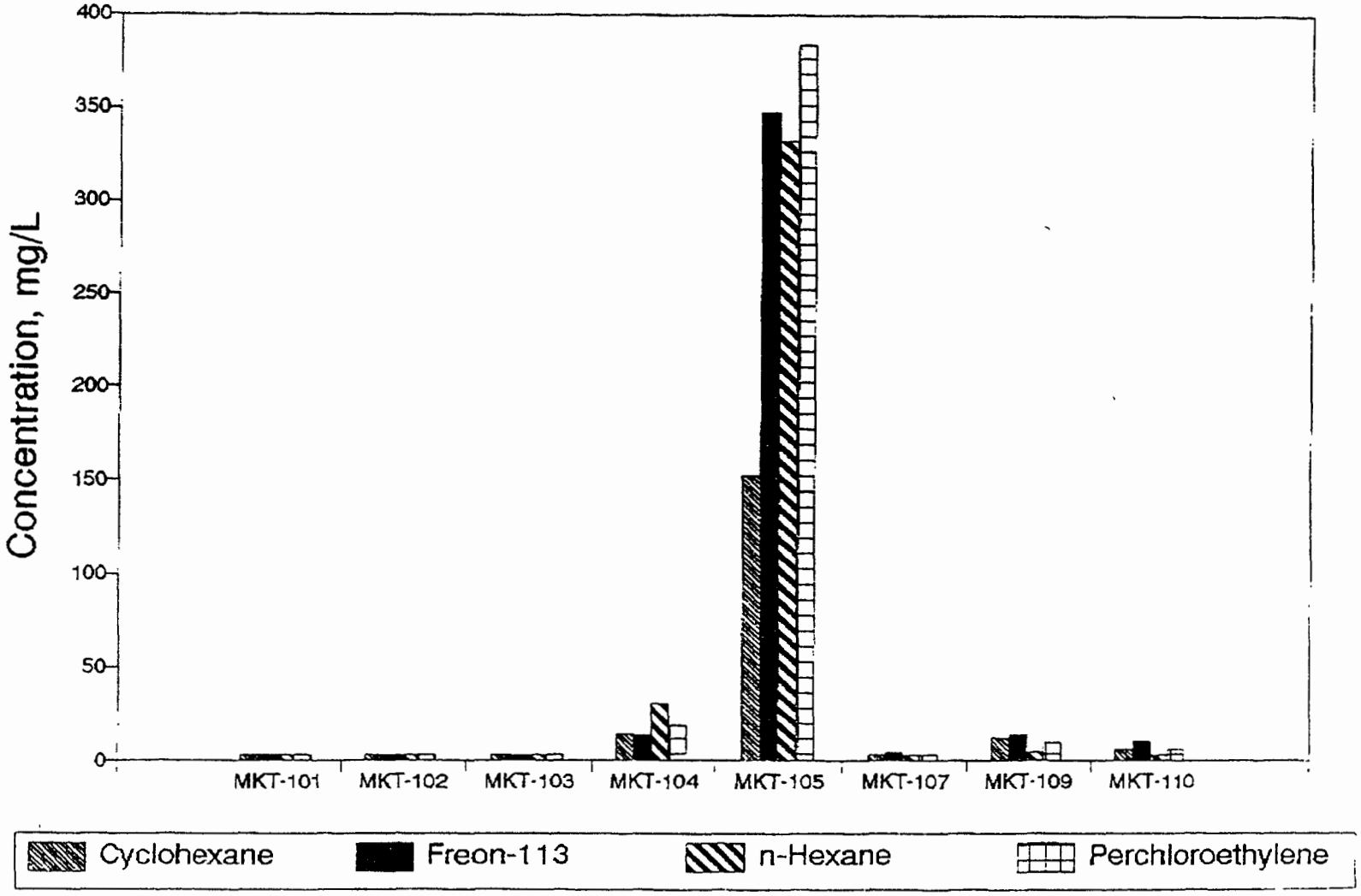
* RELATIVELY LOW PRICE, BUT DISPOSAL COSTS ARE HIGH MAY QUALIFY FOR RECYCLING.

TABLE A-4. QUALITY CONTROL MEASUREMENTS:
PERCENT RECOVERY OF REFERENCE OIL

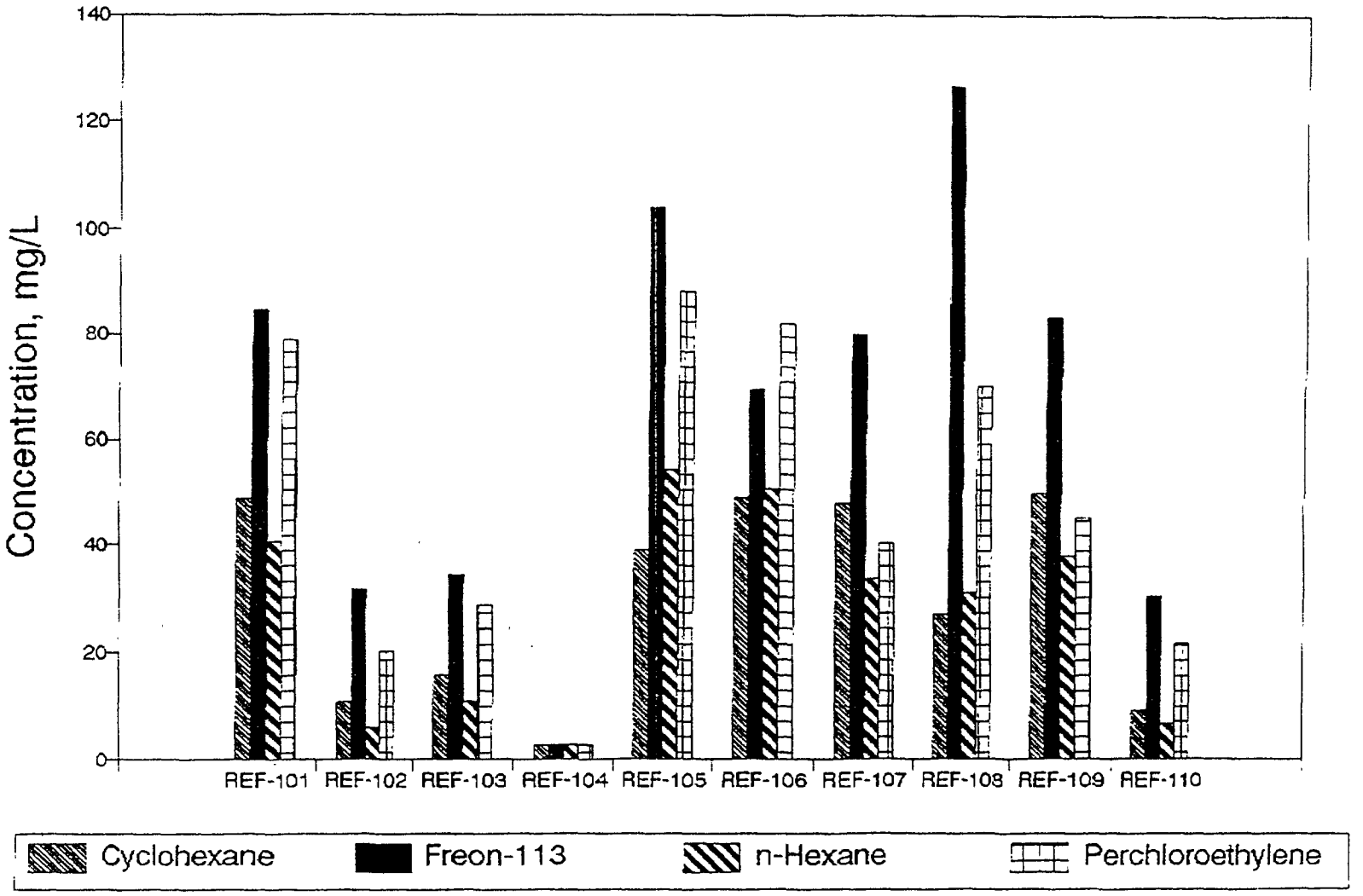
QC SAMPLE NO.	FRE	HEX	CYC	PCE
1	65	44	59	59
2	69	42	56	56
3	70	44	56	55
4	70	44	56	55
5	62	47	52	51
6	62	50	44	52
7	56	51	56	53
8	70	46	54	54
9	60	55	60	54
10	71	48	56	58
11	60	54	52	58
12	63	49	64	63
13	73	68	64	75
14	66	54	55	
MEAN	66	50	56	57

FRE = Freon-113®; HEX = n-Hexane; CYC = Cyclohexane; PCE = Perchloroethylene

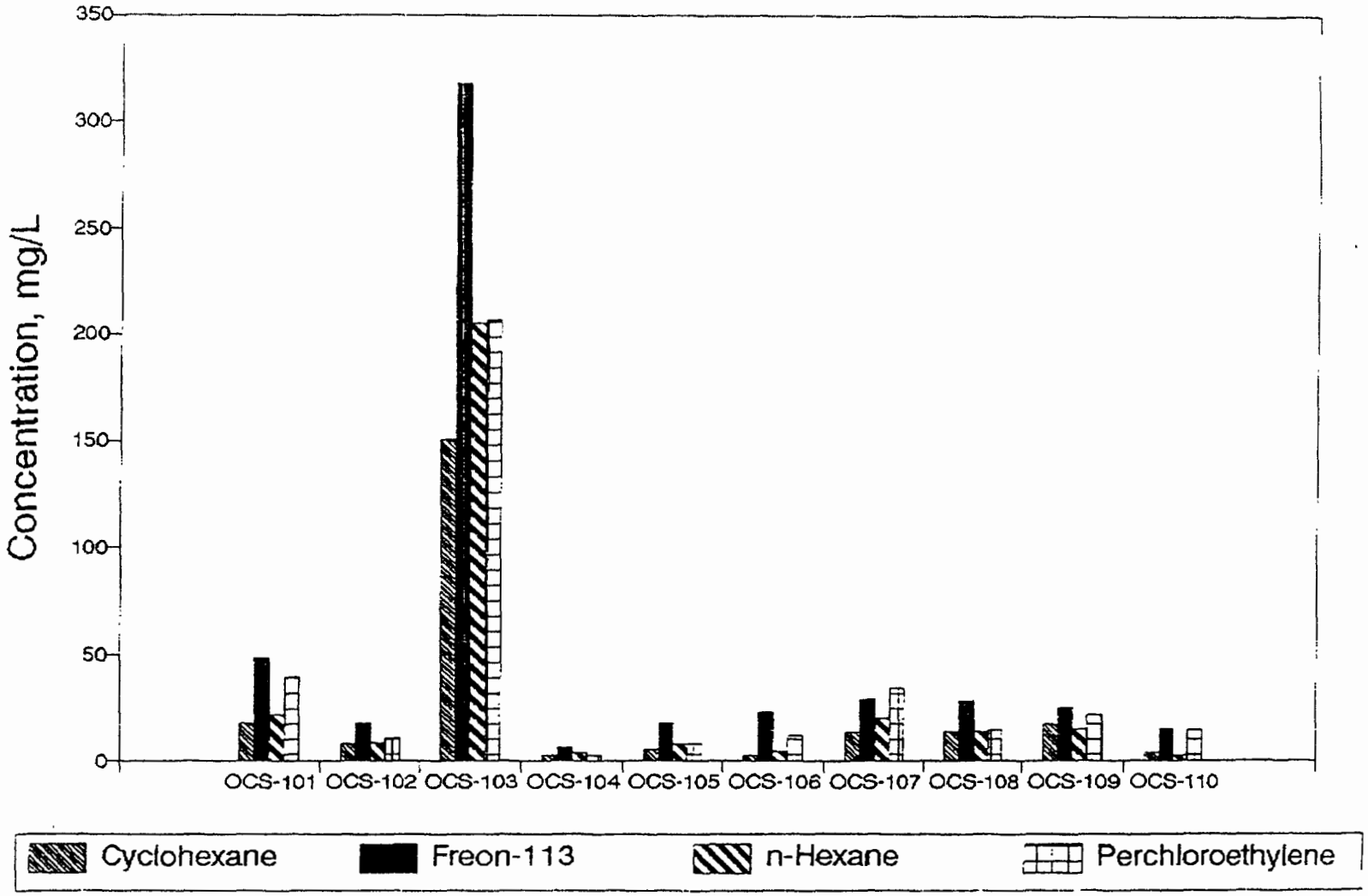
METHOD 413.1 FREON REPLACEMENT STUDY
MARKETING TERMINAL WASTEWATER SAMPLES

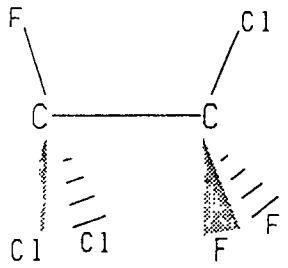


METHOD 413.1 FREON REPLACEMENT STUDY
REFINERY WASTEWATER SAMPLES



METHOD 413.1 FREON REPLACEMENT STUDY
PRODUCTION PLATFORM WASTEWATER SAMPLES





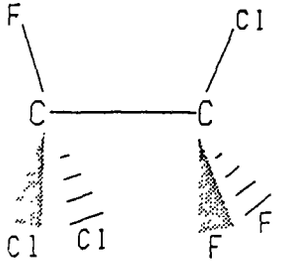
EQUIVALENT OIL AND GREASE CONCENTRATIONS WITH METHOD 413.1?

Data Evaluation for Each Industry Sector

- Mean square error of the natural logs of O&G concentrations was calculated.

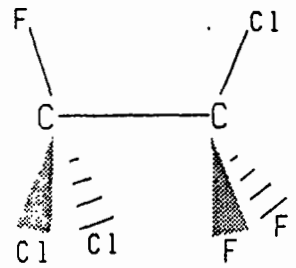
- Mean square deviation of the natural logs of O&G concentrations was calculated for each candidate solvent relative to Freon®.

- For each solvent, an F-test was used to test the null hypothesis of no statistically significant difference between the candidate solvent and Freon®, based on the ratio of the mean square deviation to the mean square error.



EQUIVALENT OIL AND GREASE CONCENTRATIONS WITH METHOD 413.1?

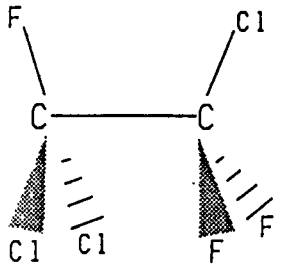
- No candidate solvent was equivalent to Freon® in O&G concentrations for refinery or production effluents. Perchloroethylene and cyclohexane were equivalent to Freon® for marketing terminal effluents; however, this may be an artifact of the many NDs.



PROPORTIONAL OIL AND GREASE CONCENTRATIONS WITH METHOD 413.1?

Data Evaluation

- Data variability increased with concentration.
- Natural logs of O&G concentrations by each candidate solvent were regressed against natural logs of O&G concentrations using Freon®.
- Coefficients of determination (r^2) were 0.8 and above.
- Regressed slope of 1 indicated solvent behavior proportional to Freon®. If the regressed slope was not statistically significantly different from 1, the y-intercept of the regression line was identified as the natural log of the correction factor.
- 95% confidence intervals were estimated for calculated correction factors.



PROPORTIONAL OIL AND GREASE CONCENTRATIONS WITH METHOD 413.1?

- All three candidate solvents were proportional to Freon® within each of the three individual petroleum industry sectors. Exception: cyclohexane with marketing terminal effluents.

- Only hexane and perchloroethylene were proportional to Freon® for pooled data.

- The confidence intervals for the estimated correction factors for the candidate solvents were large.

TABLE C-6. CORRECTION FACTORS

Solvent	Estimate of k	95% Confidence Interval
HEX	0.662	(0.352, 1.247)
PCE	0.737	(0.519, 1.046)

These correction factor estimates and confidence intervals were obtained by an exponential transformation of the corresponding estimates and confidence intervals for ln(k). For completeness the estimates, standard errors, and confidence intervals for ln(k) are provided below. The confidence intervals for ln(k) are based on the Student's t distribution with 26 degrees of freedom and the appropriate critical value is 2.056.

Solvent	Estimate of ln(k)	Standard Error	95% Confidence Interval
HEX	-0.412	0.308	(-1.045, 0.221)
PCE	-0.305	0.171	(-0.656, 0.045)

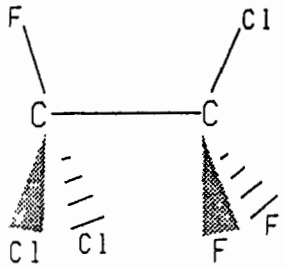
FRE = Freon-113®; HEX = n-Hexane; CYC = Cyclohexane; PCE = Perchloroethylene

TABLE D-1. COMPONENT LOSS RELATIVE TO FREON-113®

Component	RT (min)	B.P.,°C	Loss CYC	Loss HEX	Loss PCE
n-C_{10}	7.98	174	72%	71%	57%
n-C_{11}	11.79	196	70%	70%	44%
n-C_{12}	14.06	216	65%	65%	36%
n-C_{13}	15.83	235	61%	61%	33%
n-C_{14}	17.38	254	55%	55%	31%
n-C_{16}	20.06	-	41%	43%	24%
n-C_{18}	22.39	-	29%	32%	24%
n-C_{20}	24.51	-	21%	25%	21%
n-C_{22}	26.46	-	19%	23%	23%
n-C_{24}	28.22	-	16%	20%	20%
		AVG	45%	46%	31%

OBSERVATIONS

1. These data show that cyclohexane and n-hexane residues experienced severe losses relative to Freon-113® residues. The bulk of these analyte losses were observed in components with boiling points less than 254°C (nC-14).
2. Perchloroethylene residues experienced severe relative losses of components with boiling points below 174°C (nC-10).
3. These data suggest that losses of "light end" crude oil components caused by evaporation temperature modifications made to Method 413.1 may be related to low temperature azeotropic conditions that apparently exist between the low boiling oil components and the non-halogenated solvents.
4. Perchloroethylene residues displayed moderate to low relative losses overall despite the 130°C evaporation temperature. This finding appears consistent with QC data presented in Table A-4 of (Appendix A).
5. Further study would be required to verify these findings.



WHAT WE LEARNED - METHOD 413.1

- For production and refinery effluents, none of the candidate solvents tested was equivalent to Freon® in EPA Method 413.1. Findings for marketing terminal effluents may be influenced by the large number of NDs.

- With the exception of cyclohexane on marketing terminal effluent samples, all three candidate solvents were proportional to Freon® within each of the three individual petroleum industry sectors. For pooled data, hexane and perchloroethylene were proportional to Freon®.

- Confidence intervals for the estimated correction factors were large.

- Perchloroethylene was the candidate solvent which appeared closest to proportional behavior relative to Freon® for pooled data by EPA Method 413.1.

Even though stastical analysis demonstrated proportional relationships between each of the candidate solvents and Freon-113, the application of correction factors based on this study is not recommended.

Statistical analysis showed large uncertainties associated with correction factors.

The 95% confidence intervals for the correction factors were found to be excessively broad for use.

ACKNOWLEDGEMENTS

The following people are recognized for their contributions of time and expertise during this study and in the preparation of this report:

API STAFF CONTACTS

Alexis Steen, HESD
Roger Claff, HESD

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Larry Henry, Chevron USA, Inc.
Zara Khatib, Shell Development Co.
David LeBlanc, Texaco Exploration and Production, Inc.
Francis C. McElroy, Exxon Research and Engineering Co.
David W. Pierce, Chevron Research and Technology Co.
James P. Ray, Shell Oil Co.
Harold A. Rhodes, Texaco Research and Development Co.
Joseph P. Smith, Exxon Production Research Co.
George H. Stanko, Shell Development Co.
Allen Verstuyft, Chevron Research and Technology Co.

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MR. TELLIARD: Our next speaker is Dave Clampitt from the Uniform and Textile Services Association. Dave's group looked at the application of the solvents as it relates to their particular wastewater and, in particular, the impact of surfactants and detergents as it relates to the method and the method application.

IMPACT OF DETERGENTS ON DETERMINATION OF OIL AND GREASE BY GRAVIMETRIC AND INFRA-RED ANALYSIS

MR. CLAMPITT: Good afternoon. I am Dave Clampitt, Director of Environmental Regulatory Services for the Uniform and Textile Service Association or UTSA. My presentation today is entitled "Impacts of Detergents on the Determination of Oil and Grease by the Gravimetric and Infrared Analysis".

UTSA is a national trade association representing the industrial laundry industry. Most industrial launderers are small, family-owned businesses. Several are large, publicly traded organizations. These companies rent and launder uniforms, coveralls, jackets, shop towels, roll towels, floor mats, bed and table linens, kitchen dish towels, health care, and other items.

The product mix among companies and individual facilities is highly diversified. Industrial launderers service a wide range of industrial and commercial industries such as auto repair shops, gas stations, printing facilities, machine shops, special trade contractors, restaurants, hotels, and agricultural services, to name a few.

In the course of use, these rented textile products become soiled with a wide range of materials, including grease, solvents, oils, inks, food, blood, medical products, and other chemical substances.

A textile supplier picks up these soiled textiles in their fleet of company-owned or operated vehicles, furnishes clean replacements, transports these soiled textiles to a central plant for laundering or dry cleaning, and provides replacements for worn out textiles.

After arrival at the laundry, the textiles are put through a various laundering and maintenance process. The wastewater from the laundry process is discharged to publicly owned treatment works or POTWs.

Because of the wide variety of customers served, contaminants and product mixes, no two laundry effluents are alike. Even within each laundry facility, the wastewater characteristics change daily, hourly, and even by the minute, depending upon the types of textiles that are being processed at that time.

UTSA believes that the oil and grease content in industrial laundry wastewater, as measured by the current required method of USEPA 413.1, yields biased high results. Since the solvent, Freon, cannot distinguish between oil and grease and other extractable materials, it is believed that a significant amount of oil and grease now being measured on these discharges is actually Freon soluble materials from chemical detergents and other sources.

If so, UTSA contends that the contribution of these other materials should not be regulated as oil and grease. Although Freon will no longer be available after 1994, it is unlikely that any of the EPA-proposed replacement solvents will alter this situation.

The detection of detergents by the oil and grease analysis was demonstrated by one of our members in California. This company basically took a 600-pound washing machine, loaded it with the water level required to process textiles and detergents for those loads. They ran the machine for basically 30 seconds, and then took samples out of the wash wheel.

These are the analyses for those samples in parts per million of oil and grease (O&G) with just water and detergents. As you can see, by whatever method they used, they ranged from 30 ppm all the way up to 926 ppm for just water and detergents.

With these results, UTSA met with EPA on September 13, 1993 to discuss the problem with the current oil and grease test methods. As a result of this meeting, UTSA volunteered to conduct some testing to evaluate the impact of detergents on the determination of oil and grease by gravimetric and infrared analysis.

In addition, industrial laundry wastewater was sampled and tested, using Freon, hexane, and cyclohexane to assist EPA in their determination of a replacement solvent for the 413.1 test method.

A total of 12 laundry effluent samples from UTSA members were shipped to ETS Analytical Services of Roanoke, Virginia. The 12 plants were from different areas of the country, which included different product mixes, customer bases, and wastewater treatment processes.

The plants were located in the following States: 2 samples came from California, 3 from West Virginia, Illinois, Texas, Ohio, Washington State, Louisiana, North Carolina, and Massachusetts.

Some of the laundries processed high volumes of wipers used in the printing and auto industries which contain high levels of toxics such as toluene and xylenes, while others mainly process uniforms which are considered light soiled products.

Wastewater treatment at these plants ranged from simple techniques such as pH control and shaker screens all the way up to dissolved air floatation systems. Each sample was extracted in triplicate with the three different solvents, Freon, hexane, and cyclohexane. Each extract was split into two equal fractions and one treated with a silica gel clean-up step.

In all, a total of 216 samples were measured for oil and grease content using EPA Method 413.1. Six samples that were extracted with Freon were also measured using the IR analysis.

In addition, 7 chemical suppliers were asked to send 3 different detergent samples to the lab, but, actually, one sent 4 samples. Therefore, we had 22 products that went through the test.

Of the 22 products, 20 were powders, 2 were liquids. Each detergent was sampled and analyzed with the 3 solvents and with and without the silica gel, according to Method 413.1, the gravimetrical analysis. Five of the detergents that were extracted with Freon were also measured with the IR analysis.

The following results that I am going to cover are preliminary. The analysis was just basically completed last week, and everything was faxed to me. The final report should be done in the next couple of weeks.

The 12 wastewater samples analyzed using the 413.1 Method with Freon for O&G basically ranged from 20 ppm all the way up to 792 with an average of 270 ppm.

The 12 wastewater samples that were analyzed with the modification of a silica gel with the Freon extraction ranged from 5 to 425 ppm with an average of 112 ppm which is more than a 50 percent reduction from the 270 ppm with the normal test procedure.

The wastewater results from the analysis of the 413.1 Method modified with n-hexane for O&G ranged from 12 to 865 ppm, with an average of 222; and the samples for TPH with the silica gel clean-up ranged from 4 to 464 with 100 ppm average, again, a greater than 50 percent reduction.

The wastewater results with the 413 Method with cyclohexane for O&G ranged from 18 to 588 ppm with an average of 228 ppm and, when modified with a silica gel clean-up step, it went from 6 to 389 ppm with an average of 94, again, as the other test results showed, a greater than 50 percent reduction in numbers.

Using the IR techniques, 3 of the total oil and grease samples and 3 of the TPH were analyzed. You can see from the slide that the numbers greatly reduced with the silica gel clean-up step.

This study concludes that industrial laundry wastewater analyzed by USEPA Method 413.1 and 418.1 modified with a silica gel clean-up step consistently produced lower numbers than the standard 413.1 and 418.1 methods.

What was the clean-up step removing? We believe some of the materials removed were detergents. So, let us go over what our detergent analysis determined.

The results varied across the board for mg/kg of product. For Freon, you can see it went from 14 all the way up to 419,000 mg/kg. TPH was 7 to 101,000 mg/kg. Hexane, under oil and grease was 28 to over 189,000 mg/kg. TPH was less than 7 to 14,894 mg/kg. Cyclohexane was 32 to over 240,000 mg/kg, and cyclohexane with TPH was less than 7 to over 75,000 mg/kg.

Five detergent samples were analyzed using infrared analysis techniques. For total oil and grease analysis using Method 418.1 modified with the use of silica gel, the numbers were as the chart shows, ranging from less than 17 mg/kg all the way up to 253,703 mg/kg. For TPH, all five samples were under the limit of detection.

The limit of detection was high on the detergent samples due to the foaming of the detergents during the analysis.

Using the chemical supplier's recommended amount of 2 gallons of water per pound of textiles laundered, it was calculated for two detergents how much they will contribute to the analysis using the 413.1 method for total oil and grease and TPH.

The first sample, it was calculated that the Freon extraction yielded 226 ppm. Under TPH, it dropped down to 127 ppm. For n-Hexane extract for total oil and grease, it yielded 168 ppm; and for TPH, it was less than 10 ppm, below the detection limit. Cyclohexane extraction for oil and grease yielded 309 ppm, the TPH was 40.

For the second sample that we did, again, everything with the silica gel clean-up step was lower. Whichever solvent we used for extraction, the results always produced a lower number with the silica gel clean-up step.

Detergents that yielded high numbers using the standard 413.1 method were those having glycols, alcohols, and various solvents. Since these materials are polar, the silica gel was able to remove them. Detergents that yielded low numbers were caustics and silicates.

Therefore, the addition of a silica gel clean-up step to the 413.1 method may reduce the impact of detergents during the analysis. As a concern to the industry, the contribution of detergents in the wastewater can cause the results of the analysis to exceed regulatory limits.

Talking about regulatory limits, another part of our study addressed the compliance and enforcement issue that deals directly with the oil and grease measurement. Some municipalities are requiring the use of infrared analysis 413.2 for the analysis of total oil and grease and method 418.1 for petroleum hydrocarbons. This has been required even though these methods are not approved by EPA for use in the NPDES permit program.

Arguments have been made by local and State regulatory agencies that since EPA has published the 418.1 method in the EPA manual Methods for Chemical Analysis of Water and Waste, that it is therefore, validated and, therefore, does not require approval. It is assumed that it is not necessary to follow promulgated approval procedures for alternative methods set out by Part 136 regulations.

This raises several questions by our members. Why is it that regulators do not comply with their own regulations? Why would EPA documents such as the manual of methods specifically point out that method 418.1 is not approved for the use in NPDES permits but is still being used? Finally, why would Part 136 regulations go to the trouble to lay out approval procedures if they are not meant to be followed?

The industrial laundry industry has been arguing that method 418.1 is inappropriate, not only because it is not approved but also that it consistently gives much higher numbers. This puts many facilities in violation and in jeopardy of enforcement actions, including substantial penalties without any real basis.

The value found in most local ordinances for total oil and grease is 100 ppm. When this historical value was chosen, the method of analysis was hexane extractable compounds determined by gravimetric analysis. The value in ordinances has been slow to change to correspond with a change to Freon as a solvent and the ability to use the IR analysis.

Some municipalities have chosen to change their ordinances to limit petroleum hydrocarbons instead of total oil and grease, usually at the same 100 ppm. Some, however, have chosen 25 ppm, no doubt to protect the environment, but still without a scientific basis.

Also, many municipalities have specified the use of infrared 418.1 method in their issued permits. Some cities have promulgated higher oil and grease limits. Most of these limits are still arbitrary. To our knowledge, only a few municipalities have actually studied the impact of total oil and grease or TPH on POTWs based on accepted criteria as pass-through and sludge impacts, et cetera.

Unfortunately, the value, having been around for so long, has been assumed to be based on some actual authority.

In our study, the Freon extracts of 12 samples were analyzed using the 418.1 infrared method modified without the use of silica gel for total oil and grease and for 418.1 method

petroleum hydrocarbons. The data suggest that the total oil and grease values in IR analysis is 45 percent higher than the approved 413.1 gravimetric method.

The petroleum hydrocarbon fraction was compared in the same fashion. The analysis shows an increase of over 120 percent over the gravimetric method. We realize that there are many factors that may account for this difference, including volatization of lighter fractions during solvent evaporation, the presence of different materials... industrial laundry wastewater is one of the most variable imaginable... and the contribution of detergent products.

The oil and grease limit in municipal ordinances and permits is the major source of enforcement problems for industrial laundries and many municipalities. In one northeastern city, industrial user violations for total oil and grease limits account for over 50 percent of the total violations. Of course, USEPA, the State, and the environmental groups are after the city to enforce their limits or face Federal enforcement action against them and the industry.

The sad thing is that there actually is no evidence of environmental impact on the POTW or the receiving waters from the oil and grease normally found in POTW influent.

UTSA hopes that the results of this study will assist EPA in their decision on a replacement for Freon in the 413.1 method. However, we believe that the test method proves that other materials, such as detergents, interfere with the test method which results in biased high numbers.

It is also our hope that, with a change in solvent, EPA will modify the approved Part 136 oil and grease method to include the silica gel option to measure petroleum hydrocarbons.

Resolving the analytical problem will not completely solve the problems associated with these limits, but it will go far in alleviating the excessive numbers of non-environmental threatened oil and grease violations.

As I stated earlier, these are only preliminary test results. Anyone who would like to get a copy of this final report with all the statistical information, just give me a business card and put O&G study on the back.

Also, you can write to me at the Uniform and Textile Service Association, 1730 M Street, N.W., Suite 610, Washington, D.C. 20036. Thank you. I can take any questions.

QUESTION AND ANSWER SESSION

MR. PARANJAPE: Can you go back to your slides in the beginning? I got confused over the fact that you have taken averages anywhere from 20 to 900 or something, and this does not fit some of the other.

MR. CLAMPITT: Well, I am not a lab person. I am a compliance guy, so I averaged them just for my own numbers to compare.

MR. PARANJAPE: Because, you see, normally, if the analysis is performed, let us say, on the same samples collected four or five times during the day, I can understand taking an average, but if you have performed analysis on a sample, let us say, the first of the month and the last day of the month, taking an average for the industrial surcharge purposes is also okay, but for scientific purposes, taking an average from below 20 anywhere and another at 800, somehow or the other, I fail to understand how one can take that average. Can you explain that.

MR. TELLIARD: Excuse me. Can you identify yourself and your organization, please?

MR. PARANJAPE: Oh, yes. I am Bhal Paranjape from the City of Solon, Ohio, and we have an industry in town, a laundry industry with whom we do not have the problem.

MR. CLAMPITT: I just averaged them for myself. I was not sure if it was correct or not, but if you get a copy of the final report, you will see each sample, if it was one number under the normal 413.1 method, when you use the clean-up step, that same sample showed a lower result. So, I just averaged it just for this presentation, but the report will have each one. I was not going to put 12 samples on a slide, because I figured people in the back would not be able to see it. But, as I said, I am not a lab statistician.

MR. TELLIARD: Any other questions for Dave?

MR. BOURBON: I am John Bourbon from USEPA Region II. Dave, I agree with your study here, I think, the approach. I have been exposed to some things from other industries like the dye industry claiming the same type of thing, that there are interference. In a sense, I guess, you could look at it that way.

I guess I am just saying I think everybody realizes that oil and grease is an operationally defined parameter. It is sort of like a catch-all for a general rough indicator of the effluent, and I am just not so sure how much... maybe Bill can discuss more, I do not know... how much the EPA really can do about all of these so-called interferences.

You know, you are talking about compounds like these detergents or dyes or things like that. They themselves could be causing problems when they are being dumped into the ambient waters. So, I am just not so sure what...

MR. CLAMPITT: There are some cities, like Seattle, which have actually studied the impact of total oil and grease and petroleum oil and grease. For total oil and grease, they realize that it did not impact their system at all, and they waived the limit. For TPH, they have a limit of 100 ppm.

All we are trying to say with this study is that we would rather you analyze our wastewater for TPH and not for total oil and grease, because we do not think a lot of the cities have actually done analysis to determine total oil and grease on their systems.

MR. TELLIARD: Any other questions?

(No response.)

MR. TELLIARD: There is a study underway by our division to look at the industrial laundry group. We are looking at various measurement techniques, including silica gel and actually running detergents as part of the test, and so forth. How this is all going to shake out at the end only God knows at this point, but we are trying to make some of these considerations.

As was referred to, the method by itself is solvent dependent, you know, oil and grease is that which comes out in the solvent you use. As we all know, that could be ball bearings, that could be a lot of other things, but whatever is left on the balance when you are done is, by definition, oil and grease.

That does not make it right. That does not make it scientific. It is just the way it is, and we are trying to address some of those issues as we get into some of these studies.

In this particular one where surfactants and detergents are a very large part of the effluent, it is something we are going to look at. That is all I can tell you.

Somebody in the back?

MR. LEVY: Nathan Levy with A&E Testing in Baton Rouge. Hi, Bill. How are you doing? Happy 17th. Hope you have 17 more.

MR. TELLIARD: Thank you.

MR. LEVY: I have got three questions for you just to show you I was paying attention. The first one is your reference to MS and MSDs. Typically, that terminology has been used for organic analytes, and you have used it now in reference to an inorganic analyte. Is that a trend that we should be expecting in the future?

MR. TELLIARD: Yes.

MR. LEVY: Good answer. All right.

MR. TELLIARD: Even if it was not, it is now.

MR. LEVY: You also have taken the opportunity to use, if I could use the expression, SW846 syntax in naming the method. Is that a trend for the Office of Water?

MR. TELLIARD: No. Basically, the method format is that which the Agency has agreed on through their EMMC which is the Environmental Monitoring and Management Council. We have adopted a new format that, hopefully, all the methods will eventually end up in or something that looks a lot like it.

MR. LEVY: I was hoping you would say that. That is good.

My third question is that with hexane seeming to be the solvent of choice but the recoveries seem to be quite lower than Freon, do you think there will be an effort in the regulatory agency to reduce the NPDES limits for this analyte to correspond with the lower recoveries from hexane?

MR. TELLIARD: I do not know yet. We are not there yet. We are still playing science. We will get to policy a little bit down the road here.

That is certainly something we are going to solicit comment on when we propose the method is implementation issues, and I am sure we will hear a few words, probably. Thank you.

Anyone else for either one of these gentlemen? (No response.)

MR. TELLIARD: Well, you are a quiet crowd, and I would like to thank you for your attention. I would like to thank this afternoon's first batch of speakers, and we are going to take a ten-minute break to get a cup of coffee and get back in here. Thank you.

(A brief recess was taken.)

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IMPACT OF DETERGENTS ON THE DETERMINATION OF OIL AND GREASE BY GRAVIMETRIC AND INFRA-RED ANALYSIS

By: David L. Clampitt, Uniform & Textile Service Association

Robert B. Schaffer, Coyne Textile Services

David F. Tompkins, ETS Analytical Services

INTRODUCTION

- Industrial Laundry Industry
- Product Mix Highly Diversified
- Wide Range of Customers
- Wastewater Characteristics Vary

REASON FOR STUDY

- Method 413.1 Yields Bias Results
- Freon Soluble Materials - i.e., Detergents
- Replacement Solvent Will Not Alter Problem

CALIFORNIA LAUNDRY STUDY

SOAP	SOAP VOLUME	WATER VOLUME	418 IR PPM	503E PPM
Liquid	0.5 gal.	144 gal.	510	40
Powder	12 lbs.	144 gal.	620	170
Powder	12 lbs.	250 gal.	460	30

SOAP	SOAP VOLUME	WATER VOLUME	503A PPM	503E PPM
Liquid	1 gal.	125 gal.	926	642
Powder	12 lbs.	144 gal.	793	423
Powder	12 lbs.	250 gal.	461	89

SCOPE OF STUDY

- **12 Laundry Effluent Samples**
  - Freon
  - n-Hexane
  - Cyclohexane
  - Silica Gel
- **7 Chemical Suppliers**
  - 3 Detergents
  - 3 Solvents
  - Silica Gel

WASTEWATER RESULTS
413.1 METHOD/FREON
(mg/l)

	MEAN	SD	RMSD
LOW	20	2.1	10.1
MEDIAN	167	7.8	4.7
HIGH	792	18.1	2.3
AVERAGE	270	11.5	4.7

WASTEWATER RESULTS
413.1 METHOD WITH SILICA GEL
FREON
(mg/l)

	MEAN	SD	RMSD
LOW	5	0.9	17.7
MEDIAN	46	7.8	16.6
HIGH	425	31.3	7.4
AVERAGE	112	10.0	15.8

WASTEWATER RESULTS
413.1 METHOD/N-HEXANE
(mg/l)

	MEAN	SD	RMSD
LOW	12	1.7	13.8
MEDIAN	143	9.7	6.8
HIGH	865	38.2	4.4
AVERAGE	222	8.6	5.6

WASTEWATER RESULTS
413.1 METHOD WITH SILICA GEL
N-HEXANE
(mg/l)

	MEAN	SD	RMSD
LOW	4	1.6	40.8
MEDIAN	35	4.1	11.6
HIGH	464	19.7	4.2
AVERAGE	100	9.0	15.3

WASTEWATER RESULTS
413.1 METHOD/CYCLOHEXANE
(mg/l)

	MEAN	SD	RMSD
LOW	18	2.4	13.8
MEDIAN	154	4.3	2.8
HIGH	588	9.7	1.7
AVERAGE	228	17.2	7.6

WASTEWATER RESULTS
413.1 METHOD WITH SILICA GEL
CYCLOHEXANE
(mg/l)

	MEAN	SD	RMSD
LOW	6	1.7	30.0
MEDIAN	51	3.7	7.3
HIGH	389	28.3	7.3
AVERAGE	94	9.0	16.0

WASTEWATER RESULTS
INFRARED SPECTROSCOPY
(mg/l)

SAMPLE #	TEST	MEAN	SD	RMSD
152149	O&G	517	27.5	5.3
152150	O&G	1, 520	123.6	8.1
152151	O&G	429	9.0	2.1
152149	TPH	64	3.8	5.9
152150	TPH	1,283	77.6	6.0
152151	TPH	300	8.8	2.1

DETERGENT RESULTS
413.1 METHOD
(mg/kg)

SOLVENT	TEST	RANGE	AVERAGE
Freon	O&G	14 - 429,940	102,846
Freon	TPH	7 - 101,639	20,417
Hexane	O&G	28 - 189,793	54,030
Hexane	TPH	<7 - 14,894	4,110
Cyclohexane	O&G	32 - 240,147	71,584
Cyclohexane	TPH	<7 - 75,248	16,215

DETERGENT RESULTS INFRARED ANALYSIS (mg/kg)

SAMPLE #	O&G FREON	TPH FREON
152825	253,703	<9,683
152826	<17	<17
152930	20,158	<1,976
152931	16,288	<1,894
152932	17,200	<2,000

DETERGENT CALCULATION (mg/l)

SAMPLE #	TEST	SOLVENT	CONTRIBUTION
152462	O&G	Freon	226
	TPH	Freon	127
	O&G	Hexane	168
	TPH	Hexane	<10
	O&G	Cyclohexane	309
	TPH	Cyclohexane	40

DETERGENT CALCULATION
(mg/l)

SAMPLE #	TEST	SOLVENT	CONTRIBUTION
152825	O&G	Freon	193
	TPH	Freon	5
	O&G	Hexane	85
	TPH	Hexane	5
	O&G	Cyclohexane	108
	TPH	Cyclohexane	16

IMPACT OF DETERGENTS

- The Addition Of A Silica Gel Clean-Up Step To The 413.1 Method May Reduce Impact Of Detergent
- Contribution Of Detergents Can Exceed Regulatory Limits

COMPLIANCE & ENFORCEMENT

- Some Municipalities Require I/R
- Test Is "Validated"
- Method 418.1 Is Inappropriate
- Local Limits Of 100 mg/l

TOTAL O&G ANALYSIS GRAVIMETRIC VS. I/R (mg/l)

	SAMPLE #	GRAV.	I/R	IR/GRAV.
LOW	153672	43	59	1.37
MEDIAN	152149-1	384	485	1.26
HIGH	152150-3	813	1640	2.02
			AVERAGE	1.45

TPH ANALYSIS GRAVIMETRIC VS. I/R (mg/l)

	SAMPLE #	GRAV.	I/R	IR/GRAV.
LOW	153672	18	33	1.83
MEDIAN	152151-1	149	288	1.93
HIGH	152150-3	469	1380	2.94
			AVERAGE	2.23

CONCLUSION

- Assist EPA
- Detergents Interfere With Test Method
- Modify The Approved Part 136 Gravimetric Method To Include The Silica Gel Option

FOR COPY OF FINAL REPORT

Write To:

Uniform & Textile Service Association
1730 M Street, N.W.
Suite 610
Washington, D.C. 20036

Attn: David Clampitt

MR. TELLIARD: We would like to get going with our second session this afternoon which is going to focus primarily at the application of the solid phase extraction technique as it relates to the oil and grease analysis and the infrared application.

Our first speaker is... this is a replay of last year, although he says he has new data, though I am not a believer... Craig Markell from 3M who is here to talk about the application of the Empore disks.

SOLID PHASE EXTRACTION DISKS
A SOLUTION FOR THE FREON PROBLEM

MR. MARKELL: Thanks, Bill. It is a great pleasure to be here, and I do have new data, believe me. It is kind of nice to be here once again and speak in this airplane hangar.

You know, last year, if you were here... I know some of you were here... the first slide came up, and it was backwards. Well, this year, before I even got in the door, I had to arm wrestle a couple of people who said we want your slides and we want them now. We want to put them in the projector. Then, after I went through that humiliation, they actually went ahead and reviewed them for me. So, I think the slides are going to be in the proper order.

True to 3M traditions, we have a multi-media presentation today. We have got overheads which are manned by Professor Wisted down here, and slides. So, we will see how it works out.

What I wanted to do is start out by recapping a little bit of what we did in Phase I of the oil and grease study, then tell you how we used that information to go on and construct a new disk for Phase II which is specific for oil and grease analysis. Even though Bill refers to this as the cutting edge of science, it turns out that for solid phase extraction, it is the cutting edge, because you have got to extract just what you want to, nothing more, nothing less.

So, let us see how this works. In Phase I, we started out knowing absolutely nothing about oil and grease analysis. We knew all about pesticide analysis, but oil and grease was something new to us.

We started out by looking at a number of different options to see how well we could extract these extractable materials from water samples. What we looked at were three different parameters that we varied.

One was sorbents. We looked at a couple of different sorbents to extract the materials out of the water. We looked at C_{18} silica, and we also looked at styrene-divinylbenzene which is able to extract more polar materials.

We looked at a couple of different disk sizes to see what size was the most appropriate for these matrices. Finally, we looked at six different elution solvents. We looked at things as non-polar as hexane and Freon, then we went up to methylene chloride and methyl t-butyl ether, and it turns out that all these things make a difference.

In fact, when we were all done, we could give you any answer you wanted. That will be good for the industrial laundry people. Just kidding.

Now, for the Phase I recipe, this was the best one we found. We took a 90 mm C_{18} silica disk, washed it and conditioned it. We extracted the sample through the disk and eluted with hexane. That was the best elution solvent we found to get an answer somewhere in the ball park of Freon. We dried it, filtered it to get residual sodium sulfate out of there, and then evaporated it and weighed the residue. It is a very easy recipe. It worked pretty well.

Now, I think you are all familiar with disks. I will just show you what they are. Here is a 47 on the left and a 90 mm on the right. The sorbent you know of in solid phase extraction tubes, but here it is in disk form to give you more of a filtration type of process. It is very efficient. It is the newest technology in solid phase extraction.

This is a typical scattergram of our earlier results from Phase I. Let me explain how the graph is constructed. Bill, I hope I do not get you with this pointer.

What we have plotted here are the disk results eluting with methyl t-butyl ether versus the 413.1 results. This is a liquid-liquid extraction with Freon.

Now, if you get perfect 1:1 correspondence of the results, you will get a straight line which goes up with a slope of 1. These are the actual results from a number of matrices, and what you are seeing is that, although there is some scatter in the data, the results tend to track the Freon result. So, that was pretty encouraging.

After we knew the answer, we went back to the data, the results of the Phase I study, and looked at the hexane results only on the 90 mm disk, the recipe I showed you a minute ago. What we looked at was we took the Freon result as the target. This is the liquid-liquid extraction Freon result, and we said okay, how did these three techniques... hexane liquid-liquid, 90 mm C_{18}, and the SPE tubes, compare in closeness to the target and in what number of matrices were they closest?

So, the total number of samples is down here in the bottom in the parentheses, and we are looking at the three techniques. So, for hexane here, it turns out that for 27 samples

that were analyzed, 6 of them were closer to the Freon result than any of the two other techniques, and there were 6 ties with one of the other two techniques.

We looked at the disks. There were 10 closer to Freon than any other technique, and, again, 6 results were tied with other techniques. Finally, for the tubes, that result is a bit biased, because there were only 20 samples done by that technique.

The point is, clearly, we are on the right track with solid phase extraction.

So, armed with that knowledge, we went on and drew some conclusions, and we said okay, first of all, non-polar is good and polar is bad. We looked at the elution solvents. It was true for that. The methyl t-butyl ether and methylene chloride gave you much higher numbers than if you eluted with something like Freon or hexane.

Also, in the sorbents, polar was bad. The styrene-divinylbenzene can extract more of the polar materials that you really do not want in there with your results. Again, the number could be high using styrene-divinylbenzene.

So, based on those first two points, we decided we wanted to be as non-polar as possible in the sorbent, the disk matrix material, and also the elution solvent. That was what determined the way we went for Phase II.

Finally, you have heard this before, nothing duplicates Freon. That is becoming a fashionable statement to make at this meeting, and I am proud to say that we do not, either.

So, we went to Phase II. We were told by certain people very close to me that we wanted to use hexane and cyclohexane as the elution solvents. Do not bother with anything else. We were also told that we wanted to do 1-liter samples, so we did those, and we designed a new disk which was more appropriate for this analysis.

Here is what we came up with. We call it the oil and grease disk. Now, the marketing people are not going to like this, but let's call it the OG disk.

47 and 90 mm, you need both sizes, especially depending on if you are doing influent or effluents. Certainly, the 90 is good for the influents that are a little more chunky. It is C_{18} silica in a non-polar fibril matrix. Again, we wanted to keep the polarity as low as possible. With this disk, there are fewer plugging problems than we saw with the traditional Empore disk. Finally, we wanted to design it and price it so it was very cost-effective, because if you have got a $30 or $40 test, you just do not want to pay $50 for a new disk. No, it is not $50, not even close. So, that is the OG disk.

Also, as a part of the system, we have got to have more than just a disk, because, remember, you are dealing not only with dissolved species in the water. You are dealing

with the chunks floating around, and when you have high levels of oil and grease, those chunks have all the oil and grease agglomerated on them, and you have also got to extract those, just like you do with liquid-liquid extraction.

So, to extend the range of what you could do, we took some filter aid material and stuck it on top of the disk. These are small glass beads, and now what you have is an even higher surface area to sort of adsorb and absorb the free oil and grease in the system. It speeds the filtration, it helps your recoveries, and it certainly increases the capacity for free oil and grease in your system. So, that is the system we came up with.

Here are the directions. Number one, you assemble the disk. You put some filter aid on the disk after you have assembled it, about 1 cm of filter aid. Number 2, you wash and condition the disk. This is stuff you all know very well. You run the sample through. We found you could run it as quickly as you wanted, just like the traditional solid phase disks. Finally, we eluted it, and we blew it down. We did a filtration step, of course, to get rid of sodium sulfate fines that might be in your extract, and then we weighed the residue.

Now, certainly, you can use the old glass apparatus, but if you have multiple samples, it is nice to have an apparatus like this, and this is actually what we used for the evaluation, and this is Professor Wisted hard at work.

Spike recoveries. First of all, we started out by spiking some of our own samples. We wanted to see how it performed before we started using the precious EPA samples. So, we looked at the lubricating oil which we thought was a non-polar hydrocarbon, corn oil, and, finally, Eric went home and fried up some bacon, and we had bacon grease.

So, we have got a wide range of polarities from hydrocarbons to even a lot of fatty acids, and the results are very good out to about 1 g/L. So, that looked okay so far.

Ah, there is a hole here. That means we must have an overhead. You are on, big guy. And there is our first overhead.

The other thing is we kind of heard through the grapevine that maybe there would be a new spiking mixture for this analysis, hexadecane plus stearic acid, 20 ppm each, and that represents non-polar materials and polar materials. We did those. Eric just got the results of this last week. These are the triplicate results we got, 100 percent recovery plus or minus 2, certainly capable of meeting the QA/QC criteria in the new method.

The next slide shows the flow rates we found. Now, we have done about 25 of the samples so far. These... oops, 30. These are the results we got.

If we used a 47 mm disk, 21 samples gave the average flow time of about 55 minutes per liter, and, in fact, that was skewed to the high side by some very slow samples we

probably should have used a 90 for. In fact, if you use 21 of the samples, the average was 55 minutes. If you throw one data point out, for 20 samples, the average went down to 43 minutes. That shows you how skewed the result is. In fact, it was in the range of 15 or 20 minutes per liter for the typical sample that came in.

Now, 9 samples we did on 90 mm disks. These tended to be kind of the meat types of samples, meat packers, slaughter houses, things like that which had a kind of gelatinous material that really was very pluggy in terms of its behavior on the disk. So, we used 90s there. The average was 36 minutes if we used 9 samples. If we threw one data point out, it went down to 19 minutes. Again, it gives you a feeling for one or two bad samples in the batch. The longest flow time we had on a 90 which was the worst sample was 173 minutes.

Now, you have got to remember that these were blended by the master himself, so these are a blend of influent samples plus effluent samples. If you only had effluent samples, they are a lot cleaner, and I suspect we probably could have used 47s for all of them.

Why don't we look at a couple of slides first? All right, what we are looking at is some of the data points. We are comparing, again, this type of plot where we have Freon liquid-liquid results versus the new oil and grease disks.

Here is a scattergram going from zero to about 800 ppm. In fact, the highest data point we saw was down around 700. Again, you can see, certainly, a general correlation of our results with the Freon results with a fair bit of scatter.

Now, if we zoom in on the zero to 100 ppm part of that curve, this is what you see. The scatter increases, as you might expect, as you get down towards the detection limits. Still, over all, many of the data points are within a fairly reasonable envelope of comparing with the Freon number.

I have got all the data with me. If anyone wants to visit afterwards, we can certainly go over this.

Okay, we need another overhead.

Now, we also looked at hexane and cyclohexane as an eluting mixture to see if there was any difference. We like hexane a lot better, because you can blow it down much more quickly.

This is what we found, really very good correlation between the two solvents which should not be any surprise. They are very close in polarity. So, we like hexane much better.

Okay, now we have a slide. We also analyzed TPH and this is the way we did it. We redissolved the oil and grease residue in some hexane, and then we added silica gel, stirred it up as the method calls for, and then filtered, evaporated, and weighed the residue.

I do not have any of that data to show you. We are working on it now. The study is not quite complete yet, so we do not have all the data points, but, so far, the results look pretty good. It looks like it works just fine.

There is one other laboratory that has actually taken this a step further. They wanted to look at the infrared technique. So, what they did is at this point, they redissolved the residue in Freon. Now, I do not know what other solvent you are going to use if you are going to use infrared, but at any rate, they used Freon, and that worked out very nicely as well.

Every year when I come here, there is a character named Jack Cochran from Illinois. I think he has one of his cohorts here this year, and Jack always stands up at the end of the presentation and says yeah, great, well, what about surfactants?

Well, we actually did some work with a local Twin Cities company called Economics Laboratories or Ecolab to take a look at a design experiment to see how surfactants impact the oil and grease result. So, they spiked, I believe, 10 samples in a design experiment, and we took a look at surfactants.

Now, you can rationalize this any way you like. You can postulate perhaps we will get low results, because the surfactant solubilizes and complexes the oil and grease and makes it water soluble. Therefore, it stays in the water instead of partitioning into the organic phase.

You can also postulate that maybe you will get high results, because you are going to extract the surfactant and it is going to add to the oil and grease result.

Finally, you wonder if there is a dependence of the type of surfactant it is on the result.

The answer to all of those is yes, by the way. Ah, another hole. It must be overhead time.

Okay, these are the recoveries. Now, this was a 10-point design experiment. I am not a statistician, and I do not have a clue as to what it all means, but this is what the folks at Ecolab told us the findings were.

With one type of surfactant, we got an 88 percent recovery of the oil and grease. Because they spiked these, they knew what the number should be. The Freon liquid-liquid

extraction got a 135 percent recovery on the same sample. These are the RSDs you see here in parentheses.

With surfactant 2, we got 64 percent; Freon got 106. Finally, with surfactant 3, we got 72; Freon got 136.

So, certainly, it looks like we are extracting less of the polar materials in this case. Whether it is through selective extraction or whether it is through solubilization, we just do not know at this point, but it looks more attractive if you have got a lot of surfactant in the sample.

Jack Cochran is also looking at some of these in Illinois, doing some very creative work with selective elution, and we should have some interesting results next year for you.

This is also from that same study. What you are seeing here is the variation from 100 percent recovery. What we are doing, again, is using the target technique where we say the target is the Freon liquid-liquid extraction number. No, for this study, that is wrong. The target is the actual amount of oil and grease spiked into the sample, because in this case, we knew the answer, and we are looking at the variation from 100 percent.

So, the height of these bars really is how close the result is to the target. For the Empore here, this was certainly closer with surfactant 1 than the Freon was. In the second sample, that was reversed, and in the third with a third type of surfactant, it was more or less of a wash in closeness to the target.

Here what we are looking at is RSDs. Certainly, the RSDs look better using the disk technique in all three cases. So, that looked pretty good, too. That is all we have so far in the study, but it looks like it can work for surfactants.

The last thing I have for you is an overhead. This is what we have concluded from the study so far. We have got a couple of samples left to do, but it looks like the system works. It looks like it is certainly capable of extracting these extractable materials from the water samples.

It is user friendly. Certainly, a lot of people are not going to like going to hexane with the two separatory funnels and everything else.

Good RSDs. In fact, in our own internal evaluations of the EPA samples, the RSDs tend to be in the single digit range, so they look very good.

There is general agreement with the Freon result, and that is a very broad term, you understand. It is good for oil and grease or TPH, and there is potential for using it for infrared. In fact, perhaps if you chose the right elution solvent, you might be able to do with no further steps.

No emulsions. You will never have to worry about another emulsion.

It is cost effective, and we have done a little field testing so far with very positive results. People really like it in terms of comparing with their standard technique which is 413.1 and also just the handle-ability of the whole system.

So, thank you for inviting me, sir. Thank you all for coming.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MR. BANSAL: Kris Bansal from Conoco. I have two or three questions on your solid phase extraction technique. One is relating to the effect of solids.

I understand the samples that you have done basically are in the lab, but you are really not simulating the effect of the solids, or are you? Did you put any solids in to see whether the solid phase extraction plugging tendency will increase with solids?

MR. MARKELL: Yes, we have done about 25 samples that Bill has collected, and those samples, many of them have high solids, yes.

MR. BANSAL: When you say high solids, I am looking at small particle sizes also, because if you leave the sample for a long period of time, most of the solids will settle down, and if you are taking that extract, the results are really not comparable.

MR. MARKELL: Well, let me explain a little to you how we did it. We allowed the samples to settle first so all the solids went to the bottom. Then we extracted most of the sample so that it went through easily without the solids in the system. Then, finally at the end, we added the solids, and then we rinsed the bottle, shook it up well a couple of times with the hexane that we were using for elution.

So, I think we got a good extraction of things that were adsorbed on the solids, and there was a range of solid sizes from a fine precipitate or clay, perhaps from a formulating plant, all the way to large gels from meat processing.

MR. TELLIARD: Sausage maker.

MR. MARKELL: Sausage maker, yes.

MR. BANSAL: The second question I had is the effect of salinity on the performance of the solid phase extraction technique.

MR. MARKELL: I suspect there is. We have not looked at that, but we do know that in usual solid phase extraction, if you have polar materials, the more salt, the more salt strength there is in the solution, the more you will tend to partition from the water into the organic phase. So, there may be an effect. We just have not seen it.

MR. BANSAL: I come from the oil industry. In our case, the salinity really is anywhere from 30,000 to 200,000 ppm, so that is a very, very major concern.

MR. MARKELL: I suspect if it is a hydrocarbon type of material you are looking at, salt will not make any difference. If it is fatty acids, it could make a difference.

MR. BANSAL: The last question is, what is the volume of n-hexane which you used as an elutant? I am just comparing with the liquid-liquid extraction what is used for the solid phase.

MR. MARKELL: We used two 15 ml portions which not only was good for the elution, but it was also good for rinsing out all of the garbage in the bottle and desorbing things from the particulates. So, about 30 ml for the elution.

MR. TELLIARD: Yes, sir?

MR. SLENTZ: My name is Kurt Slentz. I am from Energy Laboratories in Rapid City, South Dakota.

Have you guys done any detection limit determinations on that at all to see how it acts below 20 ppm?

MR. MARKELL: We have done a little bit of work looking at MDLs but not extensive enough to give you an actual number. It certainly looks like it is good down to 5 ppm at any rate. That is something we have got to look at yet.

MR. PRONGER: This question may be more pertinent for Bill. My name is Greg Pronger with National Environmental Testing.

When you have a method that is... the result is clearly very method specific, what is EPA's position when you have clearly two different technologies to get the result?

MR. TELLIARD: Good question, thank you.

Hopefully, if we write this in a performance-based method format like we have said we would, we are going to be able to allow the option of using solid phase in whatever form it is or the liquid-liquid extraction phase for use in the measurement technique. Again, this is dependent upon review of the data and discovering that they are somewhat compatible. We do not know yet.

MR. PRONGER: Thank you.

MR. TELLIARD: You are welcome. Anyone else?

(No response.)

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Solid Phase Extraction Disks - A Solution for the Freon Problem

Craig Markell, Eric Wisted, Donald F. Hagen, 3M

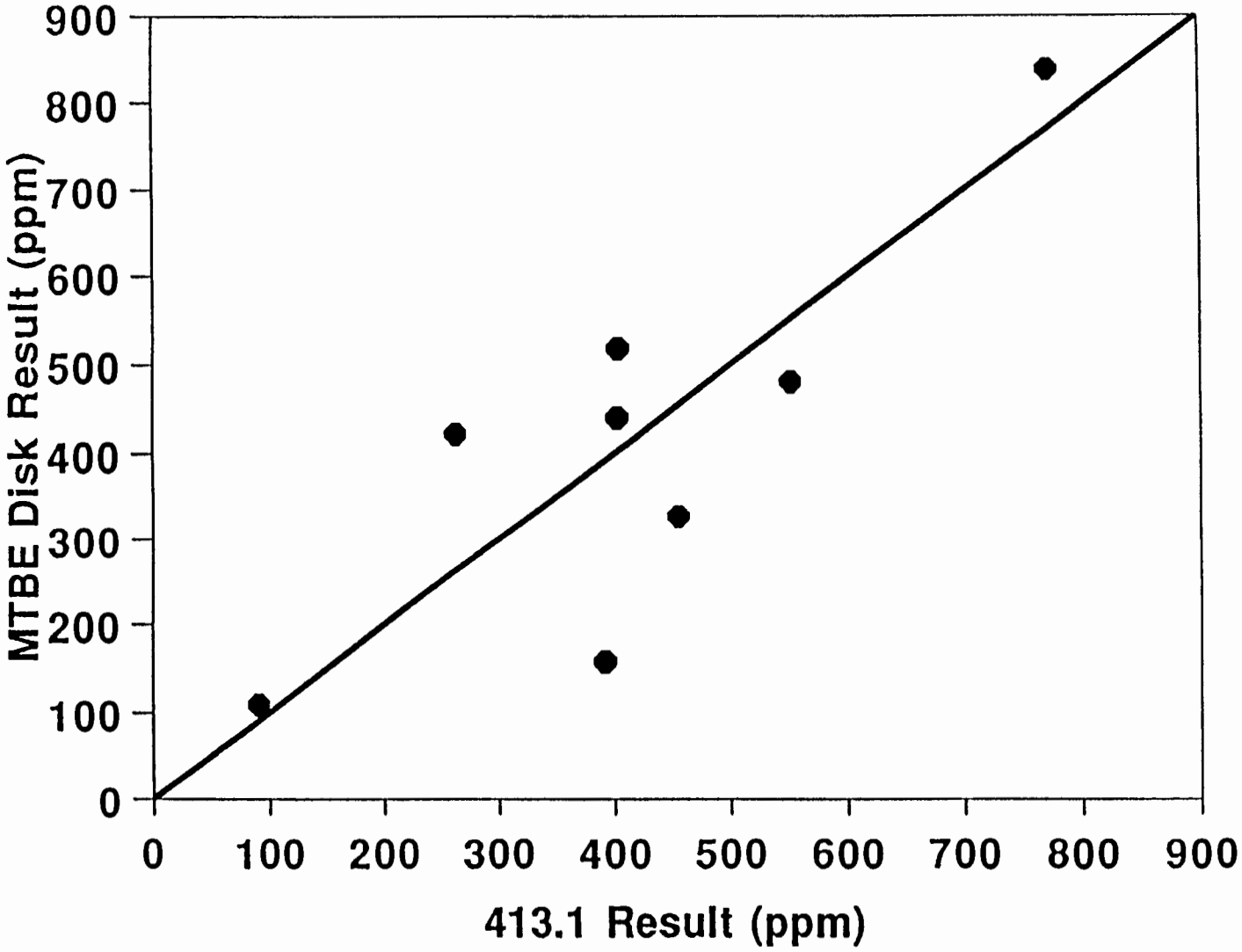
Phase I Study - Rangefinding

- Sorbents
- Disk Sizes
- Elution Solvents

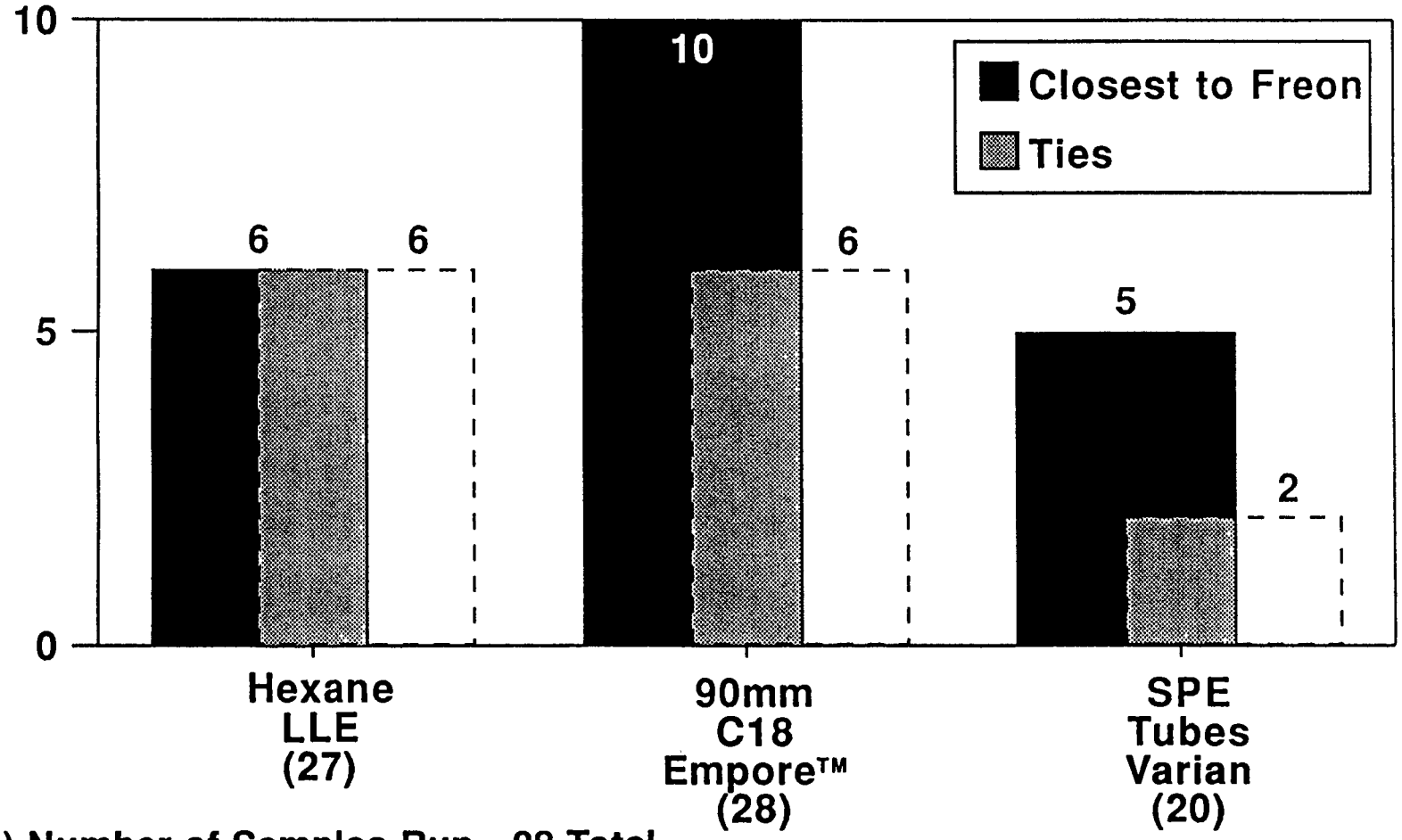
Phase I Recipe

1. Wash and Condition 90mm C18 Disk
2. Extract Sample Through Disk
3. Elute Disk With Hexane
4. Dry, Filter, and Evaporate Hexane
5. Weigh Residue

Results - Disk Vs. 413.1 - High Levels



Phase I Results - Correlation With Freon LLE



( ) Number of Samples Run - 28 Total

Phase I Conclusions

- Nonpolar is Good
- Polar is Bad
- Nothing Duplicates Freon

Phase II - Optimization

- Hexane or Cyclohexane
- 1 L Samples
- New Disk

Oil and Grease Disk

- 47 or 90mm
- C18 in a Non Polar Fibril Matrix
- Fewer Plugging Problems
- Cost Effective

Filter Aid 400

- 1 cm on Top of O and G Disk
- Speeds Filtration
- Helps Recoveries
- Increases Capacity for Free O and G

Spike Recoveries, % (RSD, n=3)

Sample	20 ppm	175 ppm	900 ppm
Lubricating Oil	101 (0)	100 (3.1)	95 (6.6)
Corn Oil	95 (11.8)	92 (2.3)	93 (5.0)
Bacon Grease	101 (4.5)	96 (3.1)	102 (5.1)

Spike Recoveries

- 20 ppm hexadecane + 20 ppm stearic acid

100%
98%
102%
100% ± 2%

Flow Rate

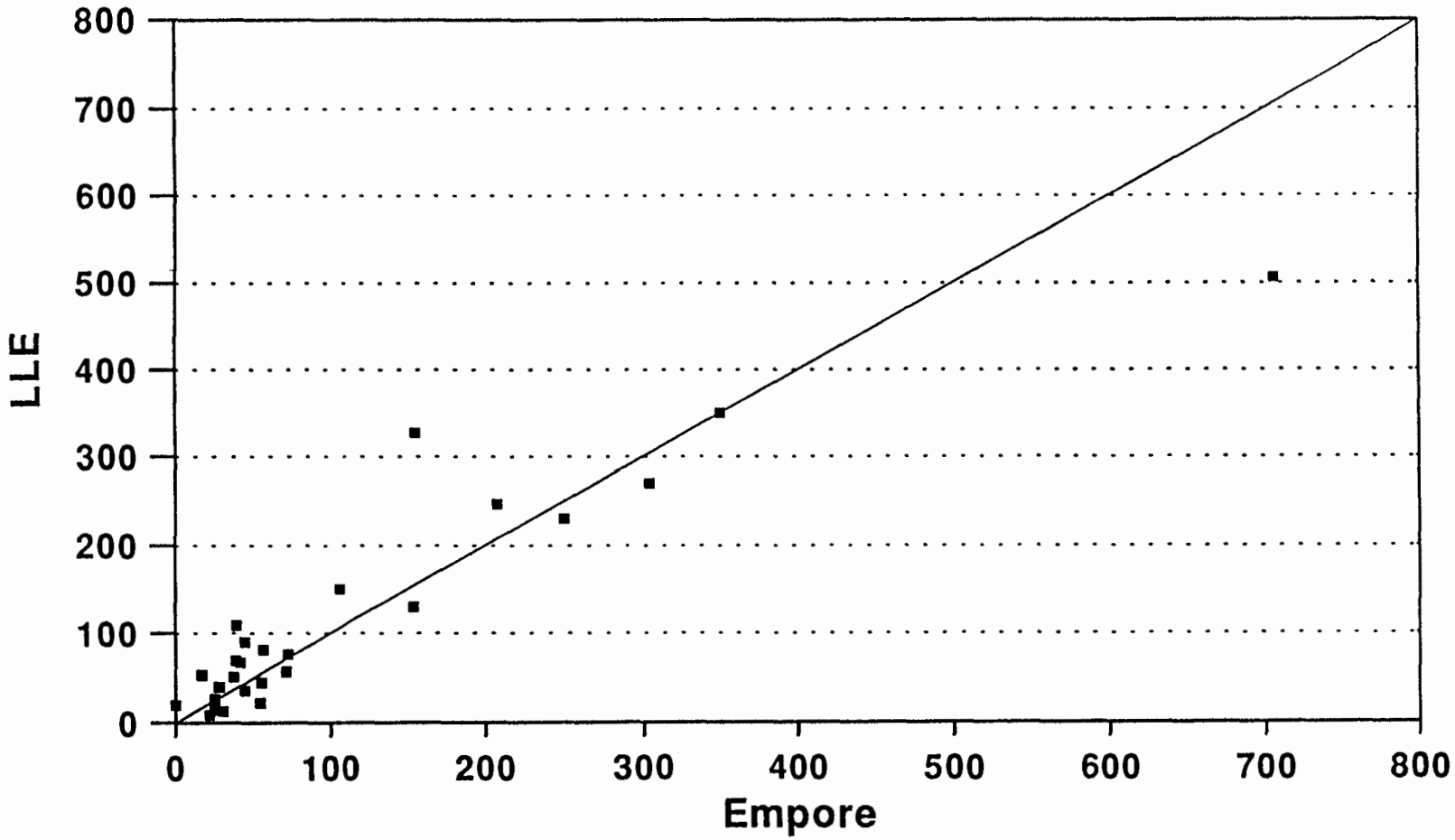
21 Samples on 47 mm	Average 55	(43)
	n = 21	n = 20
9 Samples on 90 mm	Average 36	(19)
	n = 9	n = 8

Longest Flow time on 90 mm was 173 min.

Influent + effluent blends

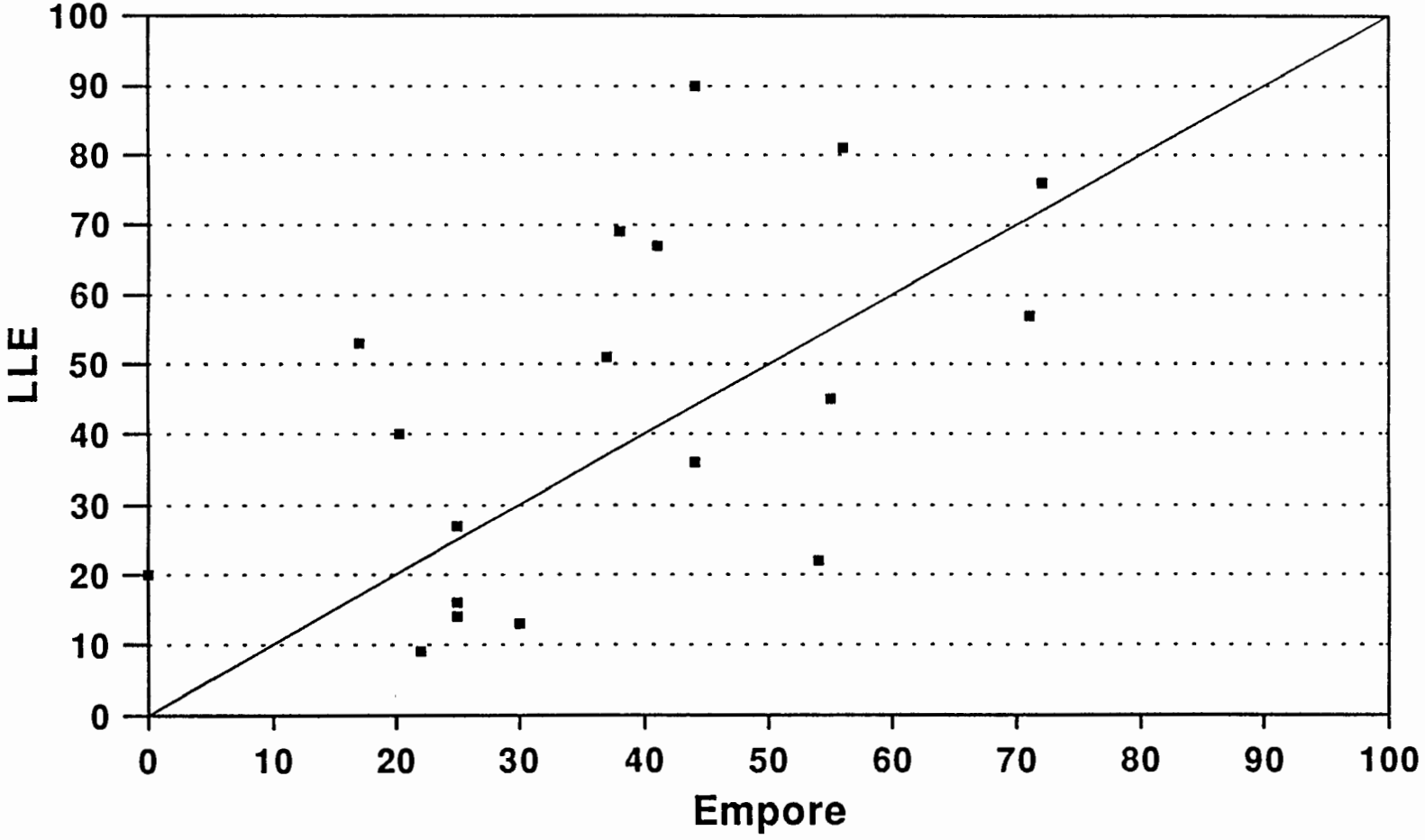
Oil and Grease Comparison

LLE Vs. Disk

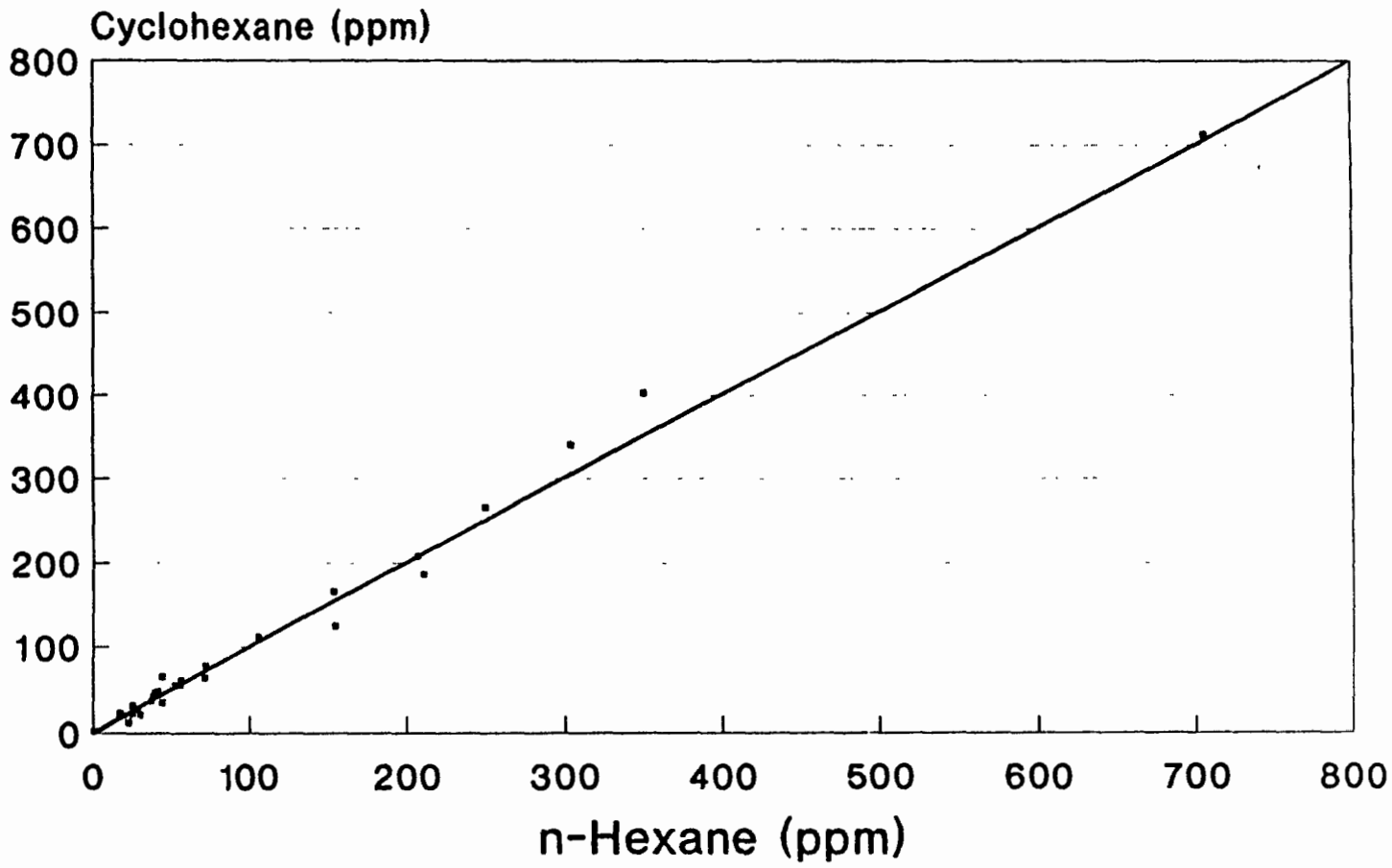


Oil and Grease Comparison

LLE Vs. Disk



Oil and Grease Disk
n-Hexane vs Cyclohexane



TPH Analysis

1. Redissolve Residue in Hexane
2. Add Silica Gel and Stir
3. Filter, Evaporate, Weigh Residue

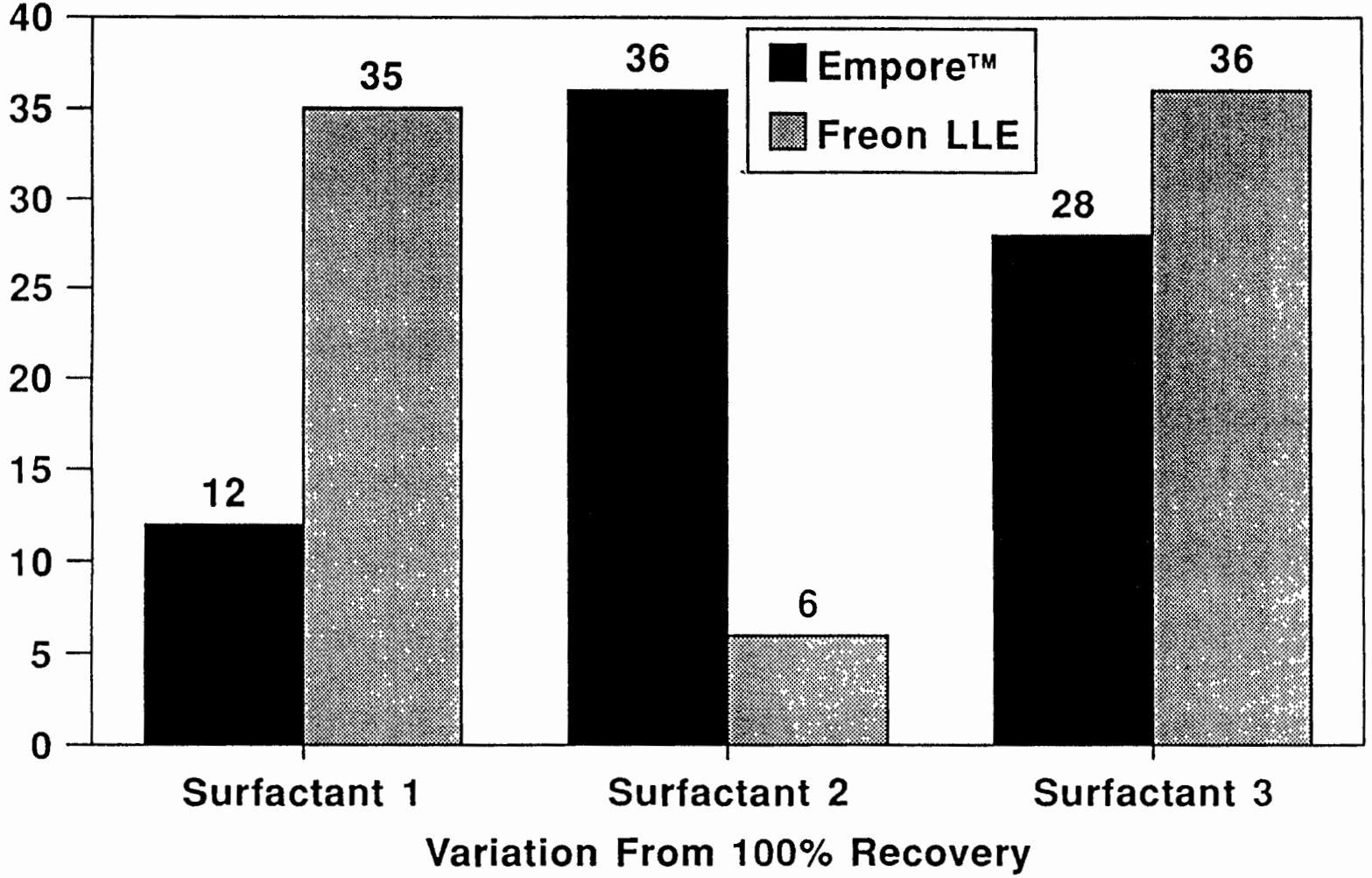
Oil and Grease Results in the Presence of Surfactants - Ecolab and 3M

- Low Results Because of O and G Solubilization?
- High Results Because of Surfactant Extraction?
- Surfactant Dependence?

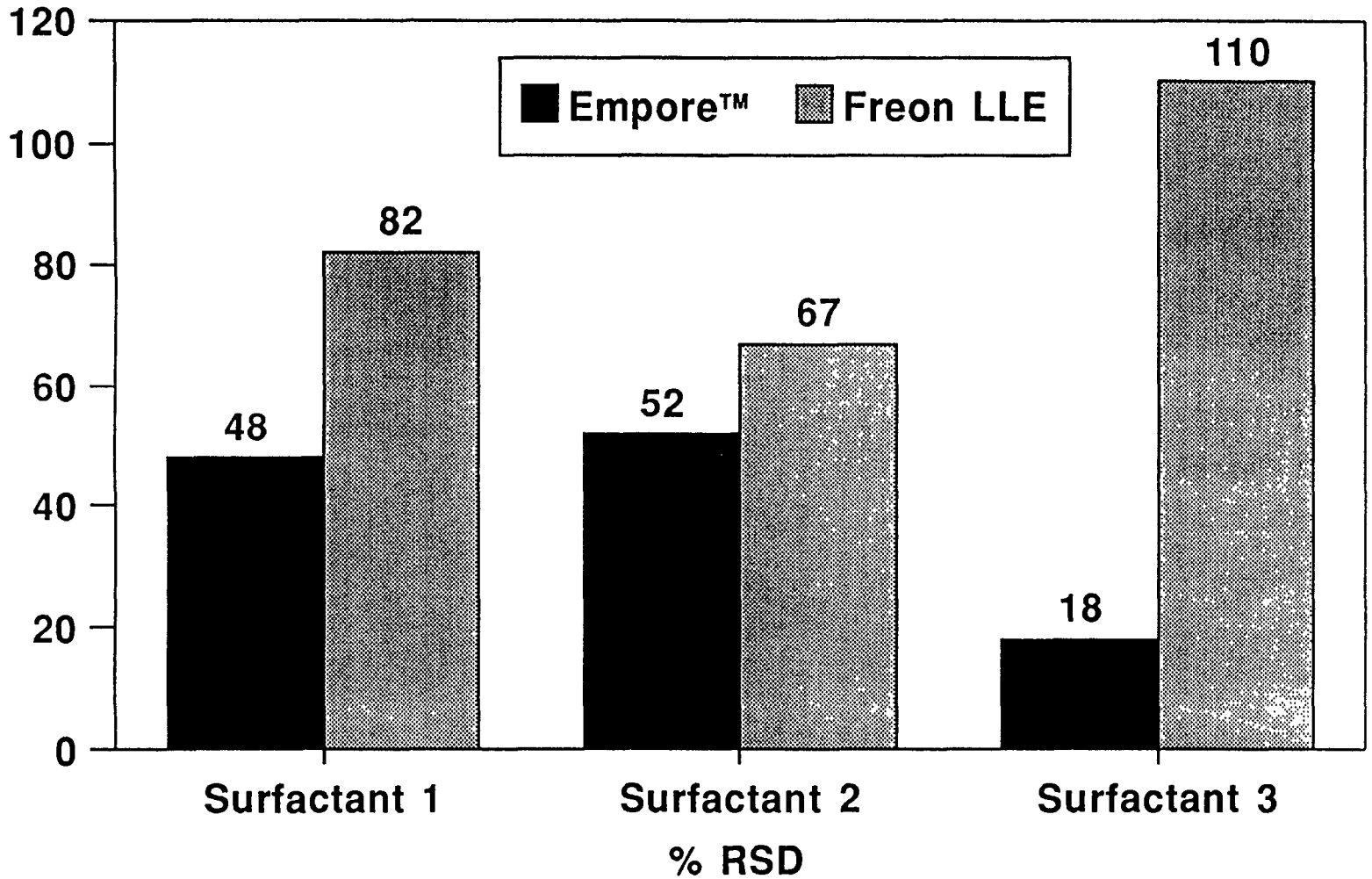
Recoveries (RSD)

	Empore™	Freon LLE
Surfactant 1	88 (48)	135 (82)
Surfactant 2	64 (52)	106 (67)
Surfactant 3	72 (18)	136 (110)

Oil and Grease Method Comparison



Oil and Grease Method Comparison



Conclusions

- System works
  - » User friendly
  - » Good RSD's & recoveries
  - » General agreement with 413.1
- Good for Oil and Grease or TPH
  - » IR potential
- No emulsions
- Cost effective
- <u>Very</u> positive field testing

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MR. TELLIARD: Our next speaker is Rex Hawley. Rex is with Varian Sample Preparation Products which you all know as Varian. Rex has been in the market development section of Varian forever, I guess, according to this resume. Could not find a real job; stayed at Varian, I guess.

Rex is going to describe a similar study that Varian has been carrying out looking at, again, application of solid phase extraction. Now, the samples that Rex is going to describe to you are the same samples that Craig analyzed and that we analyzed. So, these are all the same matrices; identical samples taken from the same locations.

OIL AND GREASE MEASUREMENT BY SOLID PHASE EXTRACTION

MR. HAWLEY: Thank you, Bill.

First of all, I have to thank Craig for saying almost everything I have to say. I think we would expect to have similar results, and, as you will see here, we tend to agree.

Last year, I stood here and presented information regarding a new method for determining oil and grease content from aqueous samples, and the technique involved solid phase extraction followed by gravimetric measurement of the analyte. Today, I am going to talk about the results of additional studies that were conducted over the last few months for further evaluation of the system.

Fortunately or unfortunately, I do not have a lot of new features to describe to you, simply because very few changes were really needed in order to have the unit function as designed.

Again, as a brief description, I would like to go through the fact that the system was based on three design parameters. First of all was simplicity, the ease of use. There are no large separatory funnels. It is compact in space requirements, and it is basically a cookbook approach.

The next slide is, as Craig has already talked about, the fact is that you want to have it to be cost effective. You have low solvent usage, again, of the order of 25 to 30 ml of solvent. You have a less expensive solvent, less expensive disposal costs.

The third parameter which is on the next slide is error reduction. We were attempting to minimize the potential for error wherever it may occur. We tried to use the same components, whether or not we were talking about sampling or running the test. We used full liter samples. We were not splitting samples. As Craig pointed out, we do not have emulsions because of the technology that is being used.

On the next slide is a brief flow chart, basically, for the procedure. If you cannot read it, do not worry about it. We are going to describe it in more detail here, because I found out one thing from last year's talk was that my verbal description of the apparatus and the procedure just was not sufficient to ignite your imagination so that you understood what I was talking about. So, I have some slides here that I would like to show, and it will give you a better idea of what I am going to be talking about over the next few minutes.

If I can get the first slide at this stage, the processor that we used comes in two stages. The first stage is basically set up for a single sample at a time. It comes with two stations, first of all, for sample application, and the second side over here is for elution, and you will see a little bit better in a few minutes what this means. It also has a version for six samples at a single time.

One of the keys that we talked about for error reduction was the fact that we are using similar components for both the sampling and the processing. The first of that is simply the bottle that is used.

We designed a special cap to fit this bottle. It is an 80 mm standard 1 liter bottle. You can buy it from any of the laboratory supply houses. As you can see, when you have a sample put into it, you have an insert plug to keep it from leaking.

As far as the extraction is concerned, we use a solid phase extraction cartridge which has filtration material built into it, a depth filter material, to remove the particulates, the gel or whatever it happens to be that you may have in the sample that you are working with.

The first step in the process is to condition the column and then to apply the sample. Now, as far as applying the sample, it is nothing more than removing the plug from the cap. It is a hexagonal key, as you may have noticed... I should have pointed it out on the cap... which fits into the holes in the apparatus. So, you simply put the cartridge on the top of the cap, invert the bottle, and, in this case, we open a vacuum line and suck all the fluid through.

As you can see, the filtration material itself really does hold most of the particulates prior to the extraction sorbent.

After the sample has gone through, you simply rinse the bottle with the elution solvent. In our case, we use 20 ml of elution solvent first, and then we rinse again with a second 10 ml aliquot which is then applied to the larger side.

Now, the reason we use two sides for this apparatus is because of the way we do the elution. Part of the simplicity factor of this is we are trying to make it easier for everything.

One of the problem areas that we have found and that Craig described was the fact that sodium sulfate inherently has some problems. Even if it does not have any problems, you still have to filter it out before you can do the measurement.

What we have ended up doing is we designed a new device which basically traps water and separates it from the organic phase. So, what we designed is an in-line process where you rinse the bottle out and invert the bottle again. The elution solvent goes through the particulates and the sorbent bed into this what we call aquaset which separates the organic from the aqueous phase.

Then you end up with a separation of the aqueous water up here and organic phase below it. It is all done in-line, single step. It is real simple as far as what happens.

So, you have a dried extract without having to filter it. To dry it down, we use the nitrogen blow-down system and then weigh the vial for your determination.

I think that is the end of the slides. Now we are back to the overheads.

This slide is nothing more than what Bill has already presented. It shows the industries and the description of the samples that we were sent. In a few minutes when the lamp brightens up there, you will be able to see it.

The bottom line is I can sit here and tell you that our system is the best thing since sliced bread, but the end performance is what is going to convince anybody about the validity of the technique. So, I would like to review some of the data that we have done in this Freon replacement study.

The direct answer right here is that all of these samples that you are going to see here are from real-world samples. By the way, if anybody gets picky, I know I misspelled maintenance down there at the bottom.

The studies that we did involved the use of a number of potential replacement solvents. This chart, again, we can talk about this afterwards. I would not worry too much about trying to read this, because I am going to show displays of the data in a few minutes differently.

The table is just an indication that the solvents that we investigated were hexane, cyclohexane, because, as Craig said, we had this little birdie here that said that might be something to investigate. We also looked at pentane, acetone, dichloromethane, and ethyl acetate.

In order to keep this presentation at a reasonable length, I am only going to show the pertinent data for hexane, but if anybody wants to discuss the other solvents and their results, please see me after the session. I will be glad to talk about it.

As far as calibration is concerned for these studies, we used vegetable oil. We did not use the hexadecane stearic acid standards.

I can tell you that as far as displaying the results of almost 30 samples at one time where everything is readable is somewhat challenging, so the presentation I finally decided to use is simplified. Since the results are method dependent on Freon, I decided to use Freon as my standard.

Now, what I have done here is this one is for less than 75 mg/L. The dark lines are an arbitrary band around the Freon results. The band is plus or minus 25 percent.

So, basically, the other two lines that are there are hexane done with liquid-liquid extraction and hexane used as an elution solvent for solid phase extraction.

As pointed out this afternoon, anything that tends to make hydrophobic more hydrophilic, such as alcohols or organic acids or surfactants, can affect recoveries negatively. On the other hand, compounds which are hydrophobic but not oils and greases, such as waxes and soaps and hydrocarbon species, et cetera, will be retained by SPE but may not be extracted by Freon liquid-liquid.

Now, there is a series of six overheads here. I think this is the third one. The first two had to do with all industries that were tested in this protocol, and then I broke it down a little bit into... and that is divided by less than 75 mg/L and over 75 mg/L, and I broke it down into petroleum industries and non-petroleum industries. This is based on the information that we were given as far as the breakdown is concerned.

You can see that there are exceptions that fall outside of this band, but, generally, the trend is definitely there. I think we can be more specific and say that the general conclusion is that we fall within this plus or minus 25 percent band.

Again, I will say that the 25 percent is an arbitrary evaluation from my standpoint. You can see this area right here is the solid phase extraction, and this one over here is the liquid-liquid hexane.

By the way, we know that certain things, such as glycerin and some surfactant compounds seem to clog the column, but, interestingly enough, we had more problems not with the sample application as much as trying to elute the sample off the column. Many times, the pentane or the cyclohexane just would not penetrate the organic barrier that basically had formed.

The best technique that we have been able to find is to raise the sample pH to neutral. This seems to neutralize any of the ionized species that may have been there, and it allows for better flow characteristics.

However, the results that you are looking at here, these are results that did not use that technique of increasing the sample pH. These were all pH 2.

One of the things that I am not going to present today is the results of the silica gel clean-up that we did. The data will be provided in a summary report that Bill will end up with.

Oh, I forgot this one. This is just simply a restatement of what you have heard from Craig and everybody else here, that the current Method 413.1 is a solvent dependent method. There are a lot of variations involved with all of these things to be considered.

As far as the silica gel results are concerned, I can say that the results were consistently low. They did not vary up and down as you might expect.

If I had hexane values for 413.1 that varied up and down, I did not get similar results when I did the silica gel study. I think everything except for one sample was lower. So, they were consistently low.

However, I did change the procedure. When I was using the solid phase extraction, I tried to take advantage of the fact that I could stack two columns. So, that may very well have changed the results and made them strange.

I am looking into why they are strange right now, but I still believe that a method can be developed, and I think that Craig's results indicate that if you simply take the residue obtained from Method 413.1 and reconstitute it that you can get similar results. I think it is a given that we can do that. Now, the question is, can I make it a simpler method than what is currently being used?

In conclusion, I think I am happy to state my belief that SPE is a viable alternative to Freon liquid-liquid extraction. Currently, the results indicate that hexane is suitable as an elution solvent. Generally, consistent results are obtained from what you looked at here.

What still needs to be done is solidifying the hydrocarbon fraction, but I do not think it will take very long to finish that study. Thank you for your time.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions for Rex?

MR. BANSAL: Kris Bansal from Conoco. I want to find out what is the cost for these cartridges compared to the disks that Craig mentioned.

MR. HAWLEY: Cartridges right now are running at $12 list. Craig, the list on yours is what, $5?

MR. MARKELL: Well, we have not quite decided that yet, but it will be somewhere in the neighborhood of $4 or $5.

MR. BANSAL: The second question is more in terms of my understanding of the elution process itself. The way you describe it, you have the cartridge. You put the solution through. Now you have a certain set volume of the hexane which is used as an eluant.

The way I look at the column is that the initial part, as it is being eluted, that is going to be adsorbed at the lower end. The question is, if you are varying the concentration of the stuff which is going to be removed, how can you really be sure that all of it is eluted by a certain fixed volume of this solvent that you are using, the n-hexane?

MR. HAWLEY: I think I will have to refer back to what I presented last year. When we determined the 30 ml or the two aliquats that total 30 ml, it was done by additional solvent rinses or elution steps where we went up to, I think it was, 70 or 80 ml altogether. We found that there was on the order of less than 5 percent, on average, was ever recovered after that 30 ml. So, that is how we determined that number.

MR. TELLIARD: Yes, sir?

MR. SLENTZ: My name is Kurt Slentz with Energy Labs. Have you guys, either one of you guys, done any studies on the relationship between total suspended solids and recoveries that you get off of these devices?

MR. HAWLEY: I can give you some information for what I have done, and Craig will have to speak for himself. We have done a little bit, I guess you would call it, of an informal investigation, and from what we have seen, the amount of solids and the type of solids are two different things.

The amount of solids, if I get something that is fairly granular, I have no problem either segregating it so that I can filter it out, and I have no problem with recovery. Again,

remember all of these numbers, when we talk about recovery, are based on comparison to the Freon method.

When you talk about something that is gelatinous or extremely fine particles... in fact, some of the samples that Bill sent to us did not look that bad, but they are the ones that ran slowly. Some of the stuff that came up, I mean, literally, the bottle was half full of crud, ran through without any problem at all.

So, simply looking at it or simply looking at total suspended solids did not really relate to how well the n-hexane ran through or how well it related to the overall recovery.

MR. SLENTZ: The reason I asked the question was that we seem to have a lot of difficulties that are, I guess you could call them, colloidal type particles plugging those disks up. I guess I am asking if you think it would be worth maybe taking some samples of those types of particles and spiking them up and seeing what effect that has on your recoveries that you get.

MR. HAWLEY: I would be interested in doing that. We just have not done it to date.

MR. MARKELL: If I can just add to that answer, you are absolutely right. The smaller particles seem to cause more problems than the larger ones.

We have not done a systematic study, but with some of the work which I will present on Thursday, we looked at Method 608, and we have looked at a lot of those kinds of samples. We have not seen a definite relationship between any recovery problems and total suspended solids.

On the other hand, clearly, there is going to be an upper limit where you have a certain amount of suspended solids, and if you have analytes that are very non-polar like the organochlorine pesticides or PAHs, they are going to be adsorbed to those suspended solids, maybe even incorporated into the body of the solid.

There is, obviously, no way in the world you can do that without a fairly extensive extraction like a Soxhlet. So, somewhere, there is a relationship there; you are right.

MR. SLENTZ: Have you guys noticed any channelization when you have and that in your pre-filtering part that would affect your recoveries at all when you eluted off your column?

MR. HAWLEY: For the filter that we use, it is a very loosely woven material. So, we do not tend to have the problems with channeling

because of the particle size. It tends to be distributed pretty evenly throughout the whole filter matrix.

MR. TELLIARD: Ditto.

MR. SLENTZ: Thank you.

MR. TELLIARD: Any other questions?

(No response.)

MR. TELLIARD: Thank you, Rex.

(Slides for this presentation were not available at the time of publication.)

MR. TELLIARD: Our next two speakers will be talking about the infrared effort that has been underway. Jim Vance is with Horiba Instruments. Jim, again, is going to be discussing analysis performed on the same sets of samples that Craig and Rex described and that I described earlier. So, these are all the same matrices from the same locations.

NONDISPERSIVE INFRARED ANALYSIS OF OIL AND GREASE AND TOTAL PETROLEUM HYDROCARBONS

MR. VANCE: Hello. I am Jim Vance with Horiba Instruments, and I am here to entertain you, unfortunately, with a pile of data. Perhaps I will enlighten you. I know I will raise some questions and, hopefully, will answer some.

Horiba had asked the EPA to be included in their efforts to replace Freon in the oil and grease test procedures, and the EPA graciously accepted, and sent us some of the dirtiest, the grungiest, the stinkiest samples they could find. Thanks a lot, Bill.

I would like to discuss our method of measurement. The nondispersive infrared technique is the same extraction procedure as in the gravimetric technique, but rather than evaporate and weigh the residue, we take the extract, put it into the nondispersive infrared spectrophotometer, and measure the absorbance in the infrared compared to known standards.

These known standards are oil that has been doped into the solvent. The EPA had asked us this time to use the same mixture you have seen, the 50/50 mixture of hexadecane and stearic acid. We did that by making a 40 ppm standard on our zero to 50.0 ppm analyzer and adjusting the readout to read exactly 40.

A midpoint was made by dilution of that standard to 20 ppm, and, of course, zero was tested.

The small aliquot method that we use is to put 30 ml in our extraction chamber which consists of both solvent and sample. The extraction chamber has a mixer that vigorously extracts the hydrocarbons automatically. When the extraction times out, the water goes to the top, the solvent goes to the bottom, except in the case of emulsions, as you are familiar with.

Later I will show graphically how we can treat emulsions and how the solvent to water volume affects emulsions. I will also present some data on residual measurement of

oil and grease, that is, the water that is left over after you have already done this extraction and measurement, and data on another technique of sparging the sample.

On this first overlay over there... I apologize to the people in the back that I did not make it quite big enough, but let's see if I can use this pointer. Episode it says there, and these numbers relate to the sample collection process.

Sample number is the next column, and you can see the same sample numbers that have been presented before. Lab ID, this is all Horiba. We did the testing.

The bottle number is identified in the next column, and then we start getting into some significant things like solvent. We used Freon-113, Horiba's S-316 solvent, and a special grade of perchloroethylene developed by J.T. Baker for this analysis.

This column says O&G 1. We have got O&G 2, O&G 3, and an average for oil and grease measurements.

Next to that I have a residual. This is the residual I was talking about where we take the water that has already been extracted and extract it again. These numbers should be zero, and in some cases, they are awfully close to zero, but some are not.

TPH 1, TPH 2, TPH 3, and average are the three columns for total petroleum hydrocarbons. The total petroleum hydrocarbon is tested right after the oil and grease. We have not done anything destructive to the oil and grease extract, so we simply drain it into a clean catch beaker, treat it with the silica gel, and then filter it, and put it back into the analyzer for measurement, and those are the TPH numbers.

The next couple of columns read SPG O&G and TPH SPG. SPG stands for sparged. What we did was take a small quantity, maybe 250 ml, of the water, raise it to 60 degrees centigrade, bubble it with air to drive off low-boiling hydrocarbons. In some cases, these numbers are much lower than the oil and grease numbers.

The first one here is 60 point something. This next sample is a couple tenths of a ppm higher than the O&G number. It should not be higher than the O&G number, but that is real world data.

As we go down the list, we see some drastic changes down to 121 ppm sparged from 174 ppm oil and grease.

This overlay is a continuation of the samples. We actually measured 30 samples so far, and I have 4 backlogged to do. These samples were measured from 25 to 30 analyses per bottle, so you are looking at a total of 750 or 900 samples on this data sheet. This is including the sparged and the residual measurements.

You might also notice that we tested these samples with three solvents. We have Freon-113, S-316, and perchloroethylene. Not all of the samples were tested with the perchloroethylene. We did not have copious quantities, unlimited supply, and there was a period when I did not have it at all. I have 30 samples measured with Freon and the S-316 solvent, and 19 samples ran with the perchloroethylene. We plan to do additional tests on the four back logged samples and more tests with perchloroethylene.

This overlay is an attempt to show the disparity of oil and grease by solvent. I have the sample number indicated here, and we come down this column and there is a hole in here, because there was not a sample number 24885.

At any rate, sample number, Freon-113. Now, what I am doing in this column is comparing the solvents to Freon-113, so this Freon-113 column, by definition, is zero disparity.

The S-316 solvent shows differences. This is the percent difference, and some of these percentages get kind of high. So, we decided also to show the difference in ppm, because at the low end of the analyzer, perhaps 1 ppm difference can represent as much as 10 percent disparity.

The Freon-113, again, for ppm difference is going to be zero. S-316 shows a maximum of, 24 percent here, and perchloroethylene -25. If you count the minuses and the pluses, you will find that the S-316 had 13 samples that were high, 17 that were lower than Freon-113. Perchloroethylene had 12 samples that were higher than the Freon-113, 6 samples that were lower, and 1 that was right on.

This overlay looks similar to the last one, except it is total petroleum hydrocarbon disparity by solvent. The disparity seems to be a little bit larger with the TPH number. Perhaps we needed to use more than 3 grams of silica gel. I am not sure if that is influenced there or not, to tell you the truth.

The differences are as high as -54 percent which means we should go back and look at that sample on the oil and grease to compare the difference.

On this overlay I have a sample description, and sample number. Here is the ID by type of sample, textile mill in this case, leather finishing, POTW, and so forth. The solvents, Freon-113, S-316, and perchloroethylene are listed here. Now I have listed in this column the volume sample and solvent.

We used no less than a 1:1 ratio of solvent to sample to assure maximum extraction efficiency. The first sample has 10 ml of water sample to 20 ml of solvent.

The next column tells if we treated it with sodium sulfate. Yes, means we had to do that. No, means we did not have to use sodium sulfate. This one I called coffee and

cream. It turned our extraction chamber totally brown, but it settled out after a couple of minutes. It did not require the anhydrous sodium sulfate treatment.

The residual numbers are also on this sheet and the extraction time. Normal extraction time was 1 minute except in some of the cases where we felt that the residual was getting too high, and we tried 2 and 3-minute extraction times.

The sample down at the bottom, again, I apologize that you probably will not be able to read that, but this one was interesting, at least to me. I named it green volcano. When we did our sparge technique, we had a green volcano.

The next one in this column was from the formulating plant and, when sparged, looked like a bubble bath. That one, as you can see, needed the anhydrous sodium sulfate treatment.

This overlay is a continuation. I could not put all the data on one page, so we have two pages. There is the sample description. I do not know that I need to go over this much, but I do have some that were very yellow, for instance. Several of these did need the treatment with sodium sulfate. The one from the olive plant, loved that one; Martini time. And the one from the bacon plant, we named that one the breakfast smell.

This slide shows the test set-up that we used, and you might notice some subtle hints there as to which solvent to put in which analyzer. We have perchloroethylene, S-316, and Freon-113. We have in the picture, tetrachloroethylene, otherwise known as perchloroethylene and the S-316 bottle. I do not have the Freon on the table top here.

The funnels that you see there, this one is supported by a stainless steel rod, and it is going directly into the analyzer. This can be used both for the treatment with the anhydrous sodium sulfate and the silica gel treatment.

We do the extract. If we have a cloudy extract or an emulsion, we drain it into a clean catch beaker underneath, treat it with sodium sulfate, pass it through the funnel back into the analyzer. We have three funnels set up for the three analyzers.

You can see a couple of burets set up to precisely measure the amount of solvent that goes into each one of those analyzers.

This slide is a work of art that I call tres ninos malos or three bad boys. These had to be done in the fume hood because they smelled so bad.

On the next slide are the three good boys. This one is the bacon, the olive plant, and the dye works. The dye works was kind of a paradise blue, so we have got breakfast, lunch, and paradise blue.

This slide is an attempt to show what the extract is supposed to look like in the extraction chamber. The extraction chamber holds 30 ml of sample, and you can see a line here, kind of a dirty, filmy line. I have got about 5 ml of water from that point to that point, and then the solvent, 25 ml, is pretty clear.

This slide shows the water sample a little greyer, but the solvent is still good and clear.

In this slide we have an emulsion down here. This needs to be treated with sodium sulfate. The water phase is from here to here.

I was not happy with the results of those slides, so we took three VOA vials, 40 ml VOA vials, filled them with a total of 30 ml of solvent and sample from one of the bottles. The one on the left has 20 ml of water, 10 ml of sample. The one in the center is 15 ml and 15 ml. The one on the right is 25 ml solvent and 5 ml sample, and you can see the difference there; the extract is clear.

As they settle, you see the bottom starts to clear out a little bit on these two. Of course, the one on the right is good and clear anyway.

This slide shows that the higher water to solvent ratio still has not cleared. The one in the center has cleared, but look at the levels. The water level on the center sample is slightly lower than the other two VOA vials. What we did was take the solvent phase out carefully with a syringe, treat it with the anhydrous sodium sulfate, and put it back into the VOA vials, now compare these two extracts for clarity.

This slide shows a technician taking a water sample with the proper pipette and pipette bulb. This is the buret that we used to carefully measure the solvent.

This is a guy who has the right equipment, lab coat, gloves, safety glasses, but he seems to be drinking the water.

In this slide, he has drank it all; all done. So, in conclusion, I can say that this has been a lot of fun doing these tests. Did we learn anything? Well, we did learn that our method using the small volume aliquot is fast, 2 to 20 minutes per test, generally repeatable, and still has an edge in this industry in that we can look at samples on a changing basis with fast analysis. You can take this machine to the field and add chemicals to your influent and look for reductions and that sort of thing.

Are there any questions?

QUESTION AND ANSWER SESSION

MR. BANSAL: Kris Bansal with Conoco. I want to ask you two questions. One, you used perchloroethylene to extract. Now, my understanding is that perchloroethylene has the capacity for water which makes it absorb in the infrared.

MR. VANCE: That is true. I am glad you raised that point. We had a special grade developed by J.T. Baker to do this analysis. It seems that perchloroethylene that is available on the market right now will not work for the IR tests because of just exactly what you are saying.

MR. BANSAL: I would be interested in getting a little bit more information on the special grade of perchloroethylene, because this is one of the problems, I think, that we have to find a suitable IR solvent when we do go to hexane as the preferred solvent for the gravimetric method.

The second question I had was that you said that you used a small aliquot from the entire sample. What did you do to make sure that your aliquot was a representative sample?

MR. VANCE: What we did to do that was to take several samples. I do realize that if there are a lot of particulates in the sample that this method is a little more shaky. Because of the tendency for the oil to adhere to the particulates, shaking the bottle does not assure that you are going to get a homogeneous number of particles in your small volume aliquot.

We did do at least one full bottle extraction on one of those samples which was one of the points I was going to bring up here and missed. I measured 13.2 ppm on the light blue bottle from the dye plant versus 15 by the oil and grease method, IR. And the dye plant sample had a lot of particulates in it. Any other questions?

MR. MARKELL: Craig Markell from 3M. Jim, I love the idea of naming the samples. That was great. You have got to explain martini time to us.

MR. VANCE: Oh, martini time. That has to do with the olives. Now, I know that could have been lunch, but I figured it was a double martini lunch.

MR. TELLIARD: Anyone else?

(No response.)

MR. TELLIARD: Thank you, Jim.

NON-DISPERSIVE INFRARED ANALYSIS
OIL & GREASE/T.P.H.

EPISODE	SAMPLE	LAB-ID	BOTTLE	SOLVENT	O&G 1	O&G 2	O&G 3	AVG.	RESIDUAL	TPH 1	TPH 2	TPH 3	AVG.	SPG O&G	SPG TPH
4546	24873	HORIBA	87349	FREON	62.4	64.2	55.8	60.8	22.6	70	65.6	55.8	63.8	64.4	55
	24873	HORIBA	87349	S-316	65.2	54.4	55.6	58.4	32	55.4	43.6	59.6	52.9		
	24873	HORIBA	87349	PERC	66.8	55.6		61.2		54.2	44.4		49.3		
4547	24874	HORIBA	87449	FREON	24.2	39.2	30.2	31.2	5.5	15.6	39	30	28.2	39	
	24874	HORIBA	87449	S-316	27.8	18.2	19.8	21.9	6.9	14.4	11.3	13.2	13		
	24874	HORIBA	87449	PERC	16.7	19.8		18.3		11.5	16.1		13.8		
4548	24875	HORIBA	87549	FREON	21.4	21.2	22.1	21.6	3	7.7	7.4	11	8.7	21.6	13.2
	24875	HORIBA	87549	S-316	22	22.3	22.4	22.2	4.1	8.4	7.3	8.2	8		
	24875	HORIBA	87549	PERC	23.5	21.6		22.6		9.8	8.8		9.3		
4549	24876	HORIBA	87649	FREON	251	247.5	247.5	249	35	197.5	202.5		200	187.5	124
	24876	HORIBA	87649	S-316	251.5	249	236	247	34.5	157	184	154	165		
	24876	HORIBA	87649	PERC	246	237.5		242		162.5	163		163		
4550	24877	HORIBA	87749	FREON	57	60.9	54.2	57.3	0.5	60	65	59.9	59.9	63.8	65.8
	24877	HORIBA	87749	S-316	44.6	46	42.3	44.3	1.2	45.4	46.3		45.8		
	24877	HORIBA	87749	PERC	42	42.2		42.1		42.7	44.2		43.4		
4550	24878	HORIBA	87879	FREON	170	162.8	171.6	168	0.3	172.4	167.2		170	172.8	
	24878	HORIBA	87879	S-316	129.2	136	130.4	132	3		129.2		129	102.8	96.8
	24878	HORIBA	87879	PERC	144.8	145.6		145		149.6	156.8		153		
4551	24879	HORIBA	87961	FREON	333	348	320.4	334	13.2	297.9	282		290	121.5	146.7
	24879	HORIBA	87961	S-316	412.2	334.8	336.6	361	14.2		316.8	290.7	304	166.5	128.7
4552	24880	HORIBA	88061	FREON	42.3	56.5	35.2	44.7	4.2		20.8	23.4	22.1	34.5	12.5
	24880	HORIBA	88061	S-316	36.3	35		35.7	5	13.4	12.8		13.1	30.22	11.4
4553	24881	HORIBA	88162	FREON	65.2	63.2	63.5	64	1.5	66	61.1	66	64.4	5.2	
	24881	HORIBA	88162	S-316	62.2	57.8	59.8	60	1.9	63.8	57.5		60.6	4.1	
4553	24882	HORIBA	88262	FREON	82	72	72.7	75.6		82.2	71.8		77	12.9	
	24882	HORIBA	88262	S-316	82.2	69.7	68.8	73.6	3.5	68.3	70.2		69.2	11.8	
4554	24883	HORIBA	88361	FREON	33.4	32.3	33.7	33.1	2.3	20.3	19.9	21.8	20.7	32.9	20
	24883	HORIBA	88361	S-316	29.2	30.1	31.4	30.2		15.5	17.1	16.4	16.3		
4555	24884	HORIBA	88461	FREON	132.5	127.2	124.6	128			87.6	60.4	74	115.2	38.4
	24884	HORIBA	88461	S-316		113	108.6	111	14.7		55.2	55.6	55.4	92.6	35
4556	24886	HORIBA	88661	FREON	60.8	64.2	64.2	63.1	16	10.4	10.5		10.4	20.7	2
	24886	HORIBA	88661	S-316	51.6	55.3	53.7	53.5	13.4	8.6	8		8.3	14	0.8
4557	24887	HORIBA	88755	FREON	155	157	150	154	**	61.6	14		37.8	74.2	33.6
	24887	HORIBA	88755	S-316	144.2	150		147	**	61.6	30.8		46.2	82.6	35
4558	24888	HORIBA	88855	FREON		81	79.6	80.3	3.1		15.2	13.6	14.4	33	14.6
	24888	HORIBA	88855	S-316	42.6	45.6	46	44.7	3.6	18	20.4	16	18.1	31.4	0.6

NON-DISPERSIVE INFRARED ANALYSIS
OIL & GREASE/T.P.H.

4559	24889	HORIBA	88955	FREON	88	87	81.8	85.6	7.8	14.2	14	11.2	13.1	2.4 **	
	24889	HORIBA	88955	S-316	96.6	101.2	101.8	99.9	8.4	16	17.6	13.6	15.7	3.8 **	
4560	24890	HORIBA	89055	FREON	14.5	14.8	15.7	15	1.5	6.5	3.6	4	4.7	7.5	3.6
	24890	HORIBA	89055	S-316	16.8	17.6	17.8	17.4	2.2	6	5.1	5	5.4	9.8	3.5
4561	24891	HORIBA	89155	FREON	8.8	7.4	8.1	8.1	3.5	3.8	2.8	3.1	3.2	3	2.6
	24891	HORIBA	89155	S-316	8.5	6.1		7.3	3.7	2.8	1.4		3.3	2.7	2.3
	24891	HORIBA	89155	PERC	9.5	9.7		9.6		2.4	4.4		3.4	3	
4562	24892	HORIBA	89255	FREON	208.4	362.5	168	246	31	99.2	101.6		100.4	43.6	9.4
	24892	HORIBA	89255	S-316	121.8	206.6	346.5	225	30	44	45.4	118	69.1	37	10.1
	24892	HORIBA	89255	PERC	377.5	342		240	39	156	115.5		135.8	36.5	8.2
4563	24893	HORIBA	89355	FREON	56.6	57.2	54.4	56	6.9	23.8	26.4	26.7	25.6	25.4	8.6
	24893	HORIBA	89355	S-316	61.1	60	58.9	60	6.6	23.3	22.3	22.2	22.6	27.8	8.6
	24893	HORIBA	89355	PERC	56	55.3		55.6	6.3	23	21.6		22.3	26.6	6.3
4564	24894	HORIBA	89455	FREON	167	224		196	40.5	71	39		55	141.6	80
	24894	HORIBA	89455	S-316	194	181.5		188	50	59	32		45.5	167.2	80.4
	24894	HORIBA	89455	PERC	174	168		171	20	171	10		90.5	155	21.5
4565	24895	HORIBA	89555	FREON	425	430		428	75	156	150		153	19.8	11.4
	24895	HORIBA	89555	S-316	451	454		452	80	178	215		196	21.8	10.6
	24895	FROIBA	89555	PERC	456	462		459	30	104	128		120	20.7	11.2
4566	24896	HORIBA	89655	FREON	62.4	50.4		56.4		24.4	24		24.2	62.4	14.4
	24896	HORIBA	89655	S-316	62.6	71.8		67.2	11.8	20.4	22.4		21.4	55.4	18
	24896	HORIBA	89655	PERC	60	54.8	57	57.3	16	22.2	28.4	28.8	26.5	56	14.2
4567	24897	HORIBA	89755	FREON	104	99	98.4	100.5	5	99.6	96.2	97.8	97.9	7.4	5.6
	24897	HORIBA	89755	S-316	102.8	103.2	102.4	102.8	4.6	79.2	91.2	93.6	88	6	3.6
	24897	HORIBA	89755	PERC	98.6	94.6		96.6	3	78.6	78.2		78.4	4.4	0.8
4568	24898	HORIBA	89855	FREON	44.9	46.8	45.8	45.8	12	15.2	12	14.2	13.8	30.6	12.*
	24898	HORIBA	89855	S-316	43.1	44.4	44.4	44	10.8	15	12.8	13	13.6	34.4	11
	24898	HORIBA	89855	PERC	46.1	45.4		45.8	8	12.8	15.1		13.9	29	12.2
4569	24899	HORIBA	89955	FREON	259	245	268	257	17	26.7	6.7	0	11.1		
	24899	HORIBA	89955	S-316	250	271	272	264	30	33.3	28.5	29.2	30.3		
	24899	HORIBA	89955	PERC	248	233		241	15.5	23.3	0		11.7		
4570	24900	HORIBA	90055	FREON	262	260	264	262	5	150	143	140	144	172	110
	24900	HORIBA	90055	S-316	278	298	296	290	13.2	179	198	160	179	191	112
	24900	HORIBA	90055	PERC	265	254		260	1.5	142	118	122	127	168	82
4571	24901	HORIBA	90155	FREON	182	159	150	164	13.8	150	156	148	151	100	79.2
	24901	HORIBA	90155	S-316	193	214	178	195	42	139	159	142	147	125	92
	24901	HORIBA	90155	PERC	154	161		158	20	121	150		136	113	69.8
4572	24902	HORIBA	90255	FREON	304	290	303	299	10		83.3	41.5	62.4	190	21
	24902	HORIBA	90255	S-316	305		306	306	42	70		53.5	61.8	192	40
	24902	HORIBA	90255	PERC	266	278		272	12.6	67.2	63.7		65.4	148	39
4573	25101	HORIBA	10155	FREON	69.2	69	68.2	68.8	1	69.2	69	69	69.1	1	
		HORIBA	10155	S-316	80.2	74.6	71	75.3	1.2	77	72.4	68.4	72.6	2.7	
		HORIBA	10155	PERC	75.6	68.4		72	0.6	66.6	65.6		66.1	1.5	

OIL & GREASE DISPARITY BY SOLVENT

OIL AND GREASE	%DIFF			DIFFERENC IN PPM		
SAMPLE	F-113	S-316	PERC	F-113	S-316	PERC
24873	0	-3.9	0.6	0	-2.4	0.4
24874	0	-30	-41	0	-9.3	-12.9
24875	0	-2.8	4.6	0	0.6	1
24876	0	-0.8	-2.8	0	-2	-7
24877	0	-23	-33	0	-13	-20.4
24878	0	-21	-14	0	-36	-23
24879	0	8.1		0	27	
24880	0	-20		0	-9	
24881	0	-6.2		0	-4	
24882	0	-2.6		0	-2	
24883	0	-8.8		0	-2.9	
24884	0	-13		0	-17	
24886	0	-15		0	-9.6	
24887	0	-4.5		0	-7	
24888	0	-44		0	-35.6	
24889	0	17		0	14.3	
24890	0	16		0	2.4	
24891	0	-9.9	19	0	-0.8	1.5
24892	0	8.5	-2.4	0	-21	-6
24893	0	7.1	-0.7	0	4	-0.4
24894	0	-4.1	-13	0	-8	-25
24995	0	5.6	7.2	0	24	31
24896	0	19	1.6	0	10.8	0.9
24897	0	2.3	-3.9	0	2.3	-3.9
24898	0	-3.9	0	0	-1.8	0
24899	0	2.7	-6.2	0	7	-16
24900	0	11	-0.8	0	28	-2
24901	0	19	-3.7	0	31	-6
24902	0	2.3	-9	0	7	-27
25101	0	9.4	4.6	0	6.5	3.2

TOTAL PETROLEUM HYDROCARBON DISPARITY BY SOLVENT

T.P.H.	%DIFF			DIFFERENC	IN	PPM
SAMPLE	F-113	S-316	PERC	F-113	S-316	PERC
24873	0	-17	-23	0	-10.9	-14.5
24874	0	-54	-51	0	-15.2	-14.4
24875	0	-8	6.9	0	-0.7	0.6
24876	0	-18	-18	0	-35	-37
24877	0	-23	-27	0	-14.1	-16.5
24878	0	-24	-10	0	-41	-17
24879	0	4.8		0	14	
24880	0	-41		0	-9	
24881	0	-5.9		0	-3.8	
24882	0	-10		0	-7.8	
24883	0	-21		0	-4.4	
24884	0	-25		0	-18.4	
24886	0	-20		0	-2.1	
24887	0	22		0	8.4	
24888	0	26		0	43.7	
24889	0	20		0	2.6	
24890	0	15		0	0.7	
24891	0	3.1	6.2	0	0.1	0.2
24892	0	-31	35	0	-31.3	35.4
24893	0	-12	-13	0	-3	-3.3
24894	0	-17	64	0	-9.9	35.5
24995	0	28	-22	0	43	-33
24896	0	-12	9.5	0	-2.8	2.3
24897	0	-10	-20	0	-9.9	-19.5
24898	0	-1.4	0.7	0	-0.2	0.1
24899	0	173	5.4	0	19.2	0.6
24900	0	24	-12	0	35	-17
24901	0	-2.6	-9.9	0	-4	-15
24902	0	-1	4.8	0	-0.6	3
25101	0	5.1	-4.3	0	3.5	-3

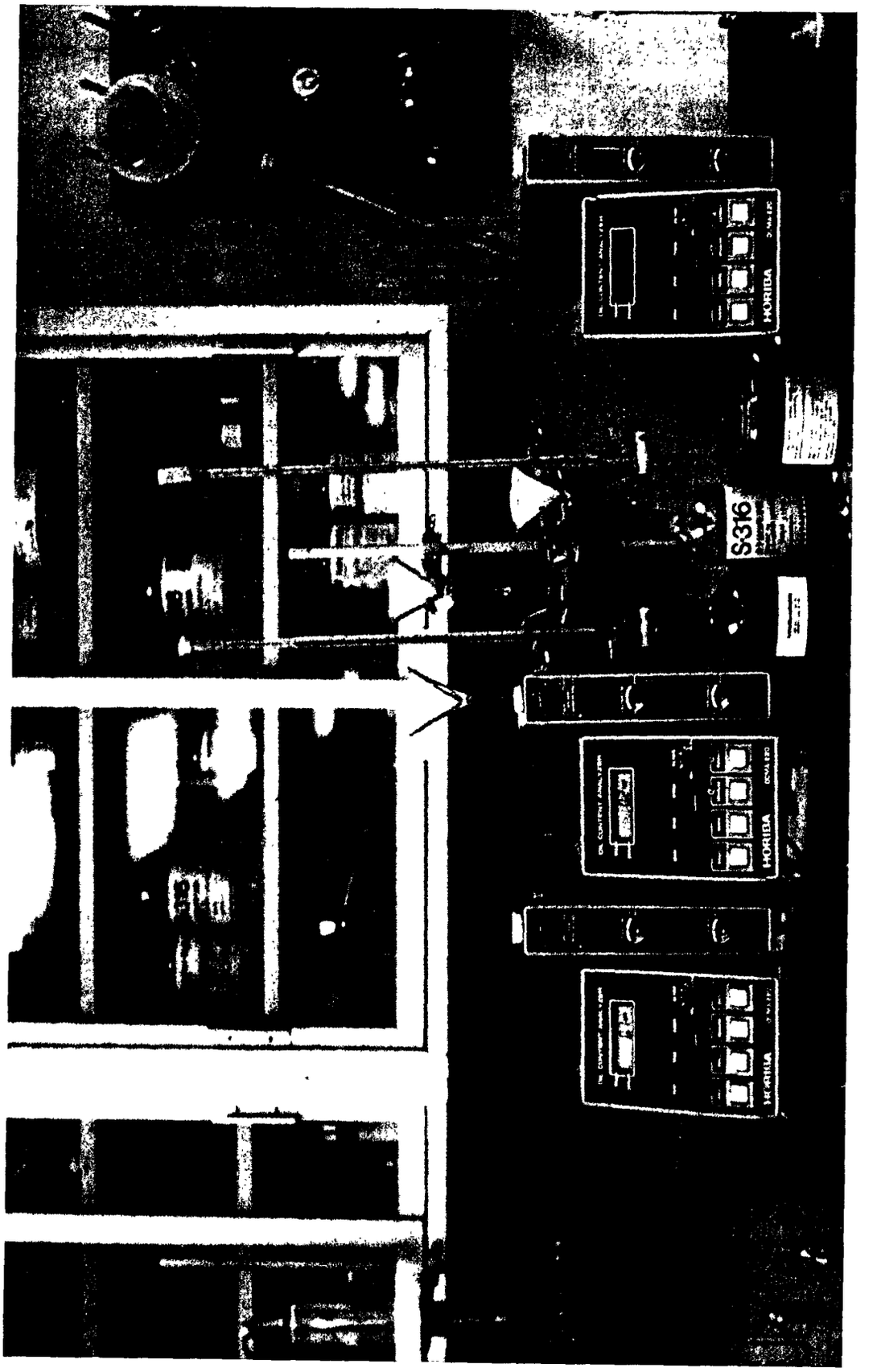
SAMPLE DESCRIPTION

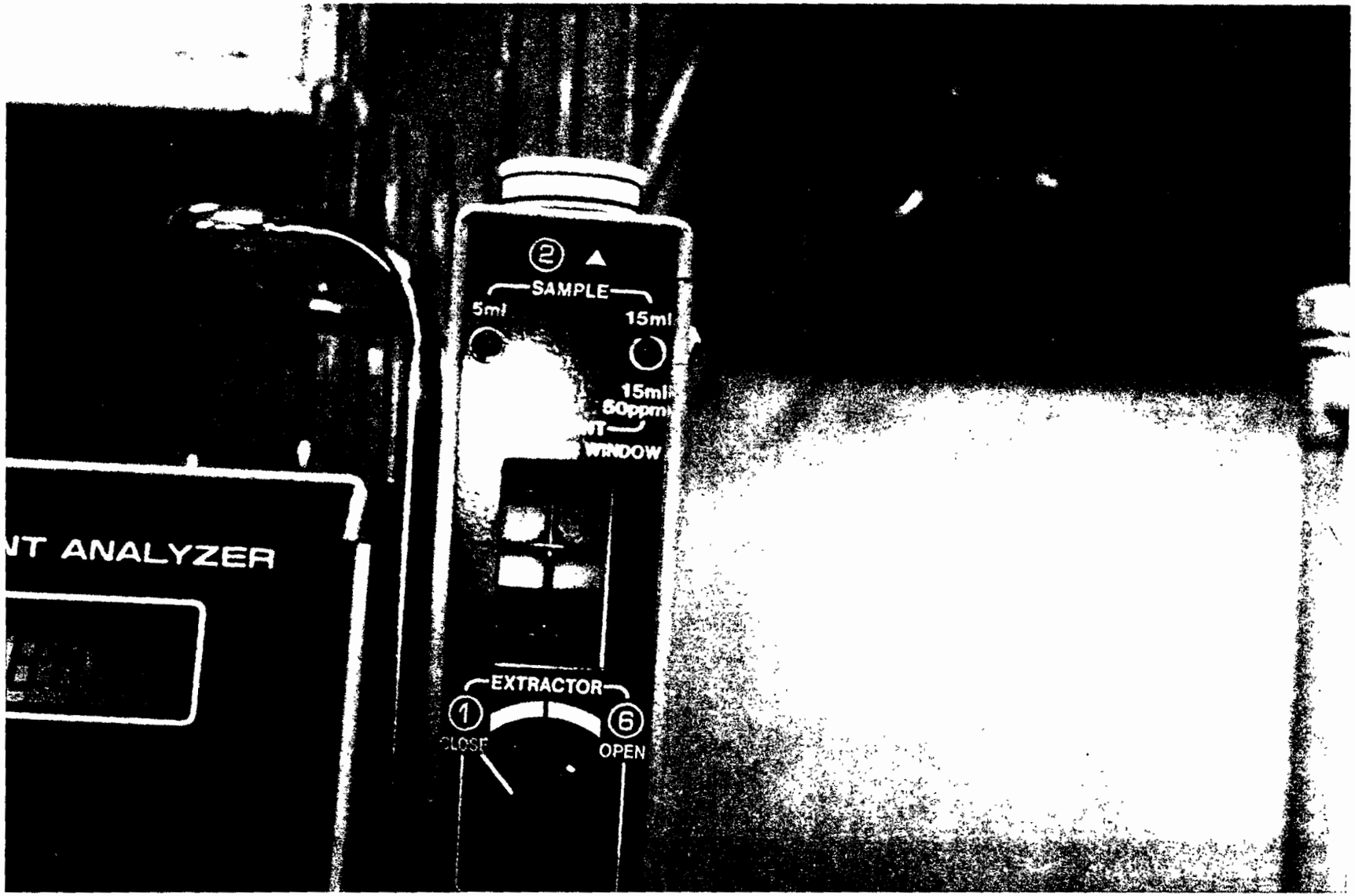
SAMPLE	ID	SOLVENT	ML SAMP	ML SOLV	NA2SO4	RESID.	EXT.TIME	COMMENTS
24873	TEXTL	FREON	10	20	YES	22.6	1	
24873	MILL	S-316	10	20	YES	32	1	
24873		PERC	10	20	YES		1	
24874	LEATHR	FREON	15	15	NO	5.5	1	COFFEE & CREAM
24874	FINISH	S-316	15	15	NO	6.9	1	
24874	PLANT	PERC	15	15	NO		1	
24875	POTW	FREON	15	15	NO	3	1	GREY W/ BLK PARTS
24875	POTW	S-316	15	15	NO	4.1	1	
24875	POTW	PERC	15	15	NO		1	
24876	DIE	FREON	5	25	NO	35	1	
24876	CASTING	S-316	5	25	NO	34.5	1	
24876	PLANT	PERC	5	25	NO		1	
24877	METAL	FREON	15	15	NO	0.5	1	DISPERSE PARICLES
24877	FINISH	S-316	15	15	NO	1.2	1	
24877	EFFL	PERC	15	15	NO		1	
24878	METAL	FREON	5	20	NO	0.3	1	MURKY WHITE
24878	FINISH	S-316	5	20	NO	3	1	
24878	PROCESS	PERC	5	20	NO		1	
24879	PUMP	FREON	3	27	NO	13.2	1	
24879	MFG	S-316	3	27	YES	14.2	1	
24880	BACON	FREON	15	15	NO	4.2		WHITE
24880	PROCESS	S-316	15	15	NO	5		
24881	SHORE	FREON	15	15	NO	1.5	1	GRAY
24881	RECEPT	S-316	15	15	NO	1.9	1	
24882	SHORE	FREON	15	15	NO		1	MORE GRAY
24882	RECEPT	S-316	15	15	NO	3.5	1	
24883	CAN MFG	FREON	15	15	NO	2.3	1	
24883	PROC.WW	S-316	15	15	NO		1	
24884	CAN MFG	FREON	10	20	YES		1	
24884	PROC.WW	S-316	10	20	YES	14.7	1	
24886	DRUM	FREON	15	15	NO	16	3	GREEN VALCANO
24886	HANDLN	S-316	15	15	NO	13.4	3	
24887	FORMUL	FREON	2	28	YES		1	BUBBLE BATH
24887	PLANT	S-316	2	28	YES		1	
24888	LEATHER	FREON	10	20	YES	3.1	1	BROWN COW
24888	TANNING	S-316	10	20	YES	3.6	1	SMELLY
24889	CHEMMFG	FREON	10	20	NO	7.8	1	SUSPEND COLLOID
24889	EFFL	S-316	10	20	NO	8.4	1	

PAGE 1

SAMPLE DESCRIPTION

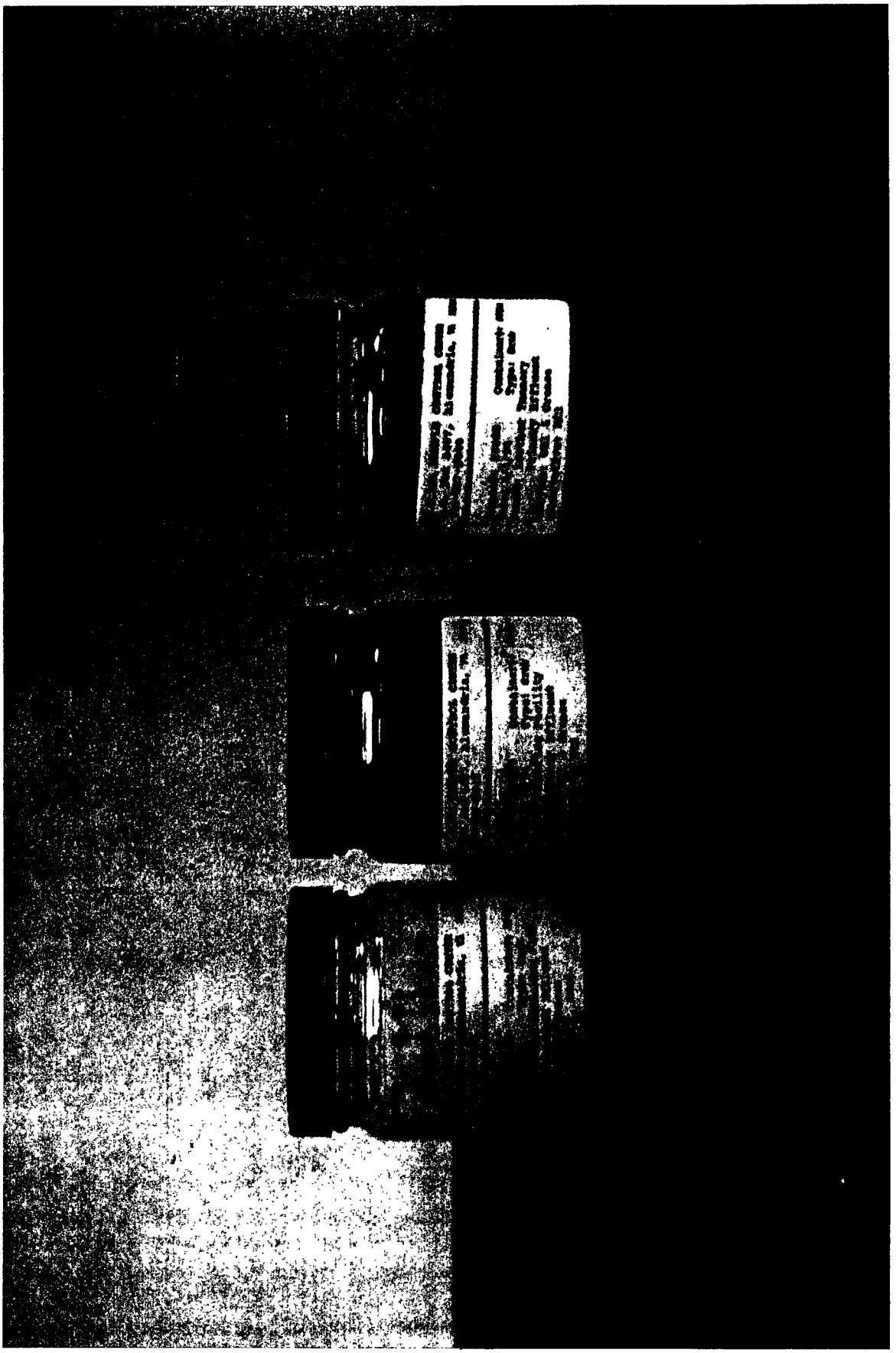
24890	DYE	FREON	15	15	NO	1.5	1	LT. BLUE	
24890	PLANT	S-316	15	15	NO	2.2	1	FULL BOTTLE EXT	13.2
24891	CHEMMFG	FREON	15	15	NO	3.5	1	OL YELLER	
24891	PRIME	S-316	15	15	NO	3.7	1		
24891	EFFL	PERC	15	15	NO				
24892	PACKING	FREON	5	25	NO	31	2		
24892	PLANT	S-316	5	25	NO	30	2		
24892	EFFL	PERC	5	25	NO	39	2		
24893	DRUM	FREON	15	15	NO	6.9	2		
24893	HANDLN	S-316	15	15	NO	6.6	2		
24893	EFF	PERC	15	15	NO	6.3	2		
24894	MEAT	FREON	5	25	NO	40.5	2	GR/WHT/BRN	
24894	PROCESS	S-316	5	25	NO	50	2		
24894	EFFL	PERC	5	25	NO	20	2		
24895	EXTRUSN	FREON	2	25	NO	75	1	ORANGE	
24895	PLANT	S-316	2	25	NO	80	1		
24895	PROC.WW	PERC	2	25	NO	30	1		
24896	OLIVE	FREON	10	20	YES		1	MARTINI TIME	
24896	PACKIN	S-316	10	20	YES	11.8	1		
24896	EFFL	PERC	10	20	YES	16	1		
24897	BUS	FREON	10	20	NO	5	1		
24897	MAINT	S-316	10	20	NO	4.6	1		
24897	EFFL	PERC	10	20	NO	3	1		
24898	MEAT	FREON	10	20	YES	12	1		
24898	PROCESS	S-316	10	20	YES	10.8	1		
24898	EFFL	PERC	10	20	YES	8	1		
24899	RENDER	FREON	3	25	NO	17	2	BRN/GRUNG FLT STUFF	
24899	FACIL	S-316	3	25	NO	30	2		
24899	EFFL	PERC	3	25	NO	15.5	2		
24900	INDUST	FREON	5	25	NO	5	2	GRY NO DEBRIS	
24900	LAUNDY	S-316	5	25	NO	13.2	2		
24900	EFFL	PERC	5	25	NO	1.5	2		
24901	RAILRD	FREON	5	25	NO	13.8	1		
24901	MAINT	S-316	5	25	NO	42	1		
24901	EFFL	PERC	5	25	NO	12.6	1		
24902	BACON	FREON	5	25	NO	10	1	BRKFAST SMELL	
24902	PLANT	S-316	5	25	YES	42	1		
24902	PROCESS	PERC	5	25	YES	12.6	1		
25101	SHORE	FREON	10	20	NO	1	1		
	RECEPT	S-316	10	20	NO	1.2	1		
	OILYWW	PERC	10	20	NO	0.6	1		

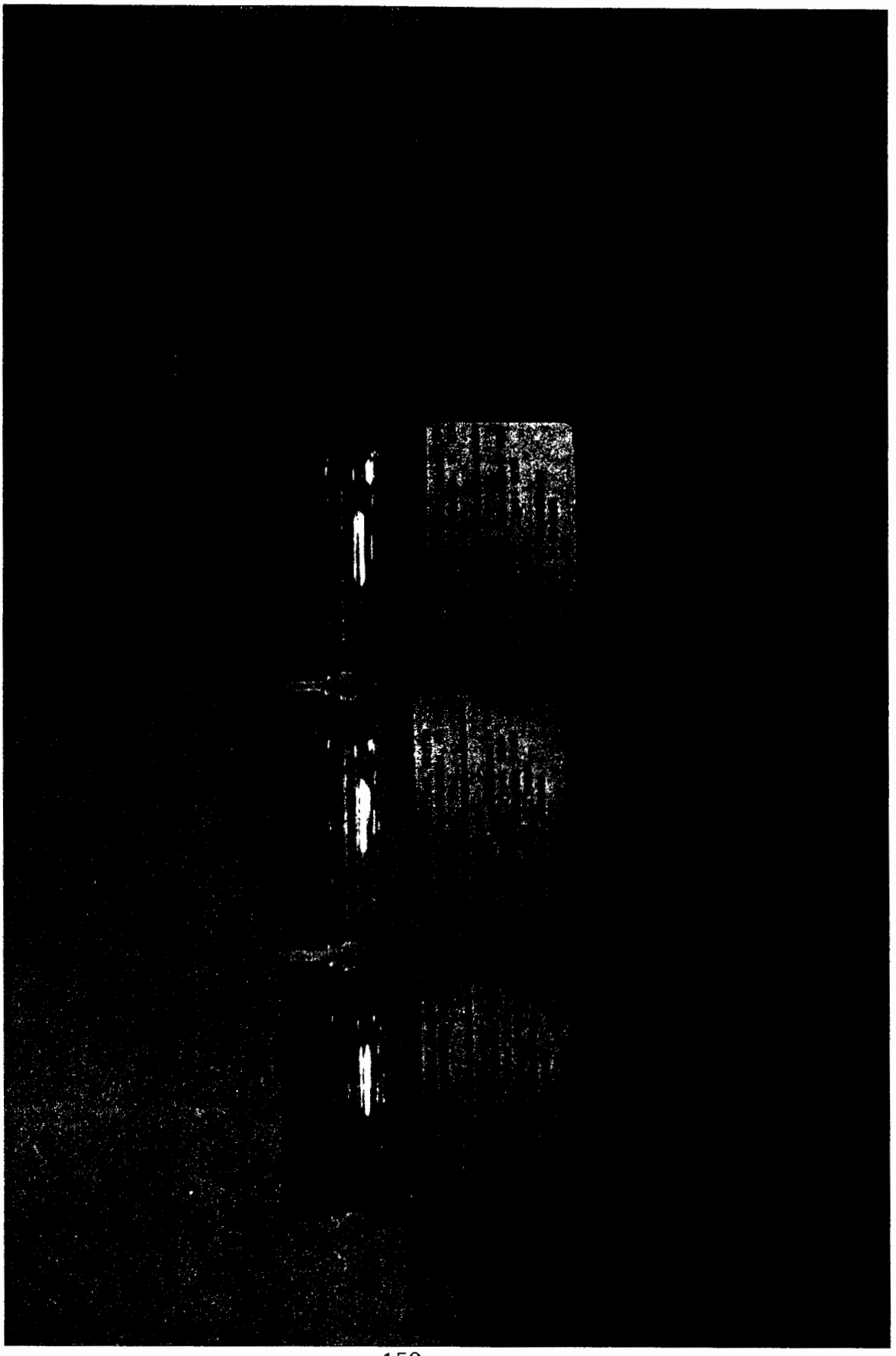

HORIBA
S316
HORIBA
HORIBA

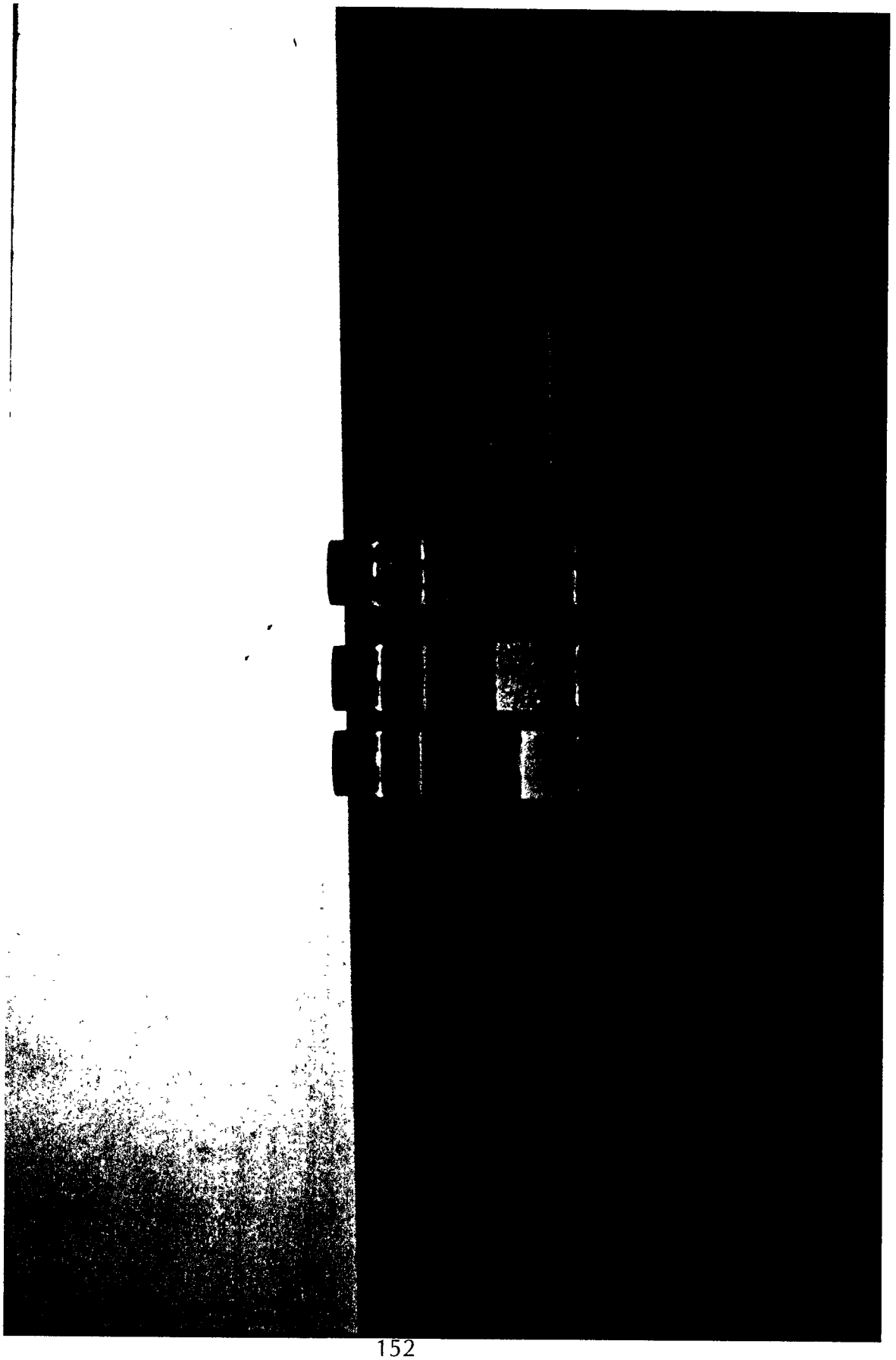

NT ANALYZER
2
SAMPLE
5ml
15ml
15ml
60ppm
WINDOW
EXTRACTOR
1
CLOSE
6
OPEN

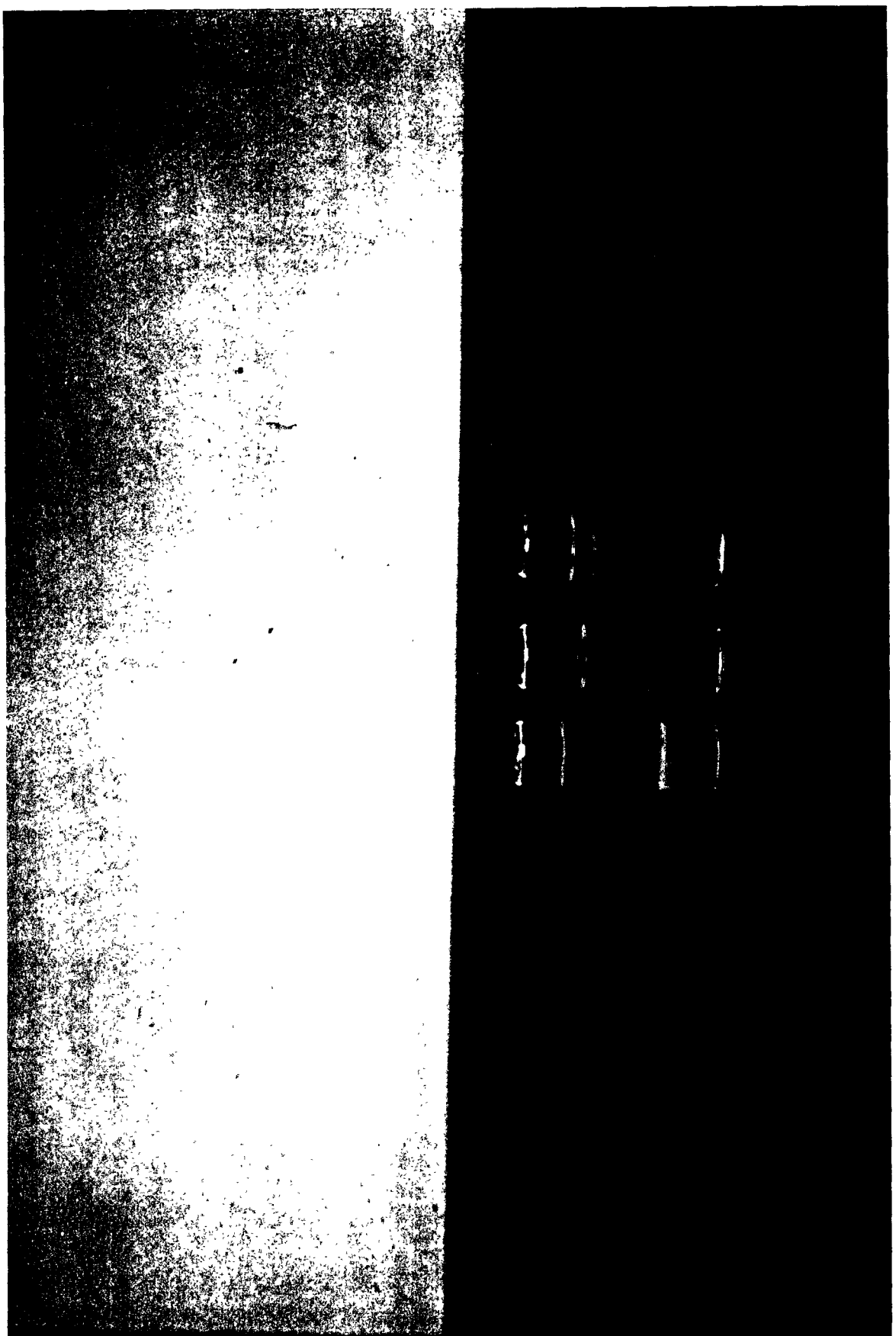
ENT ANALYZER
SAMPLE
15ml
15ml
EXTRACTOR
CLOSE
OPEN

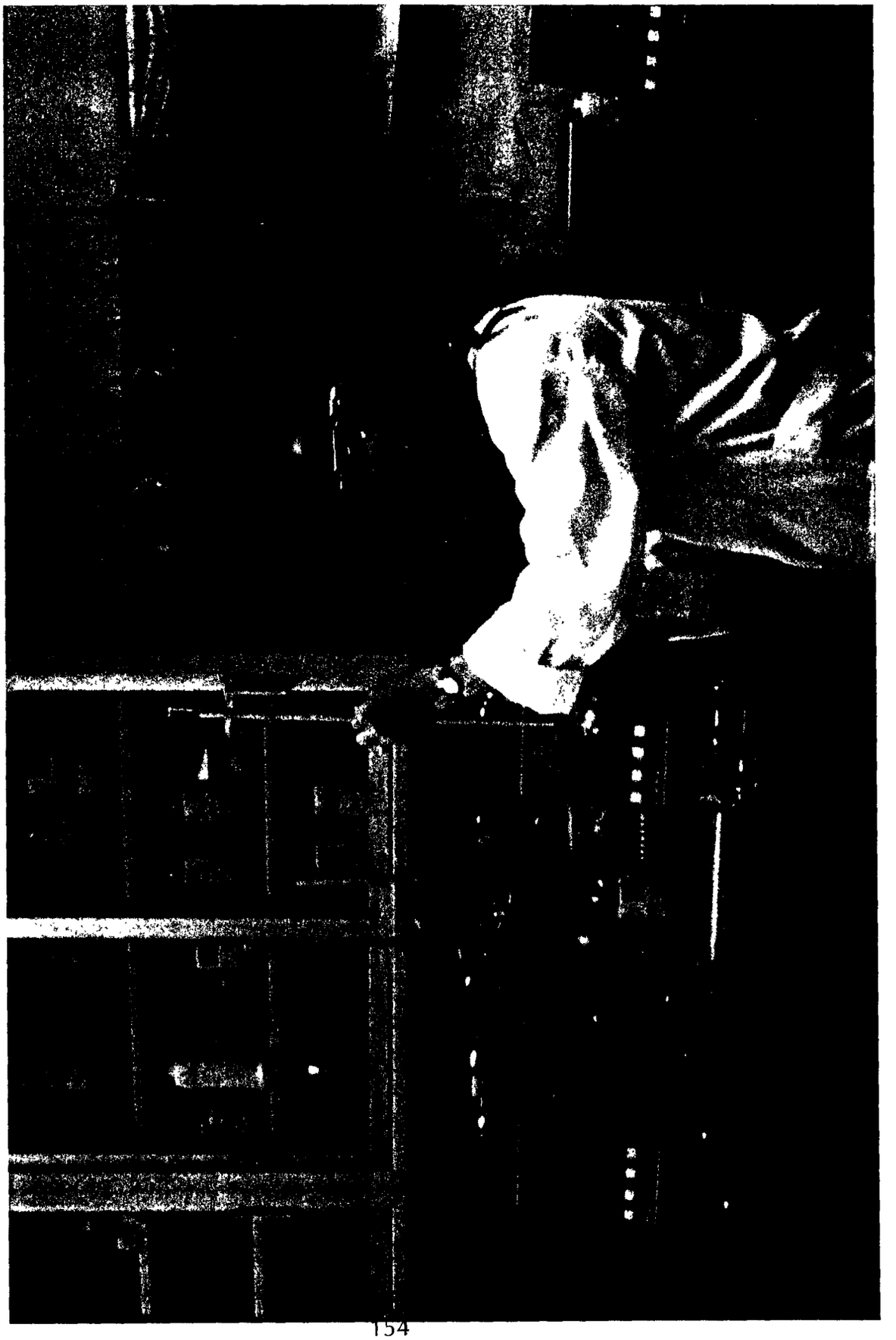
ALYZER
20ml
200ppm
15ml
50ppm
SOLVENT
WINDOW
CLOSE
OPEN











MR. TELLIARD: Our next speaker is going to also be discussing the nondispersive infrared technique, Jerry DeMenna. Jerry worked on this paper at home at night by the fireplace. Jerry's theory is that if you are going to do a paper and you have to submit it, do not let anyone know where you are, because that way, you do not have to worry about when to get it in, but, eventually, it did appear, and we are glad to have him here today. Jerry?

CURRENT ADVANCES IN OIL AND GREASE USING NDIR WITH THE "NEW" SOLVENTS"

MR. DEMENNA: I want to thank you all for coming, and I want to thank Bill for giving me the clean-up spot again for the third time in a row.

I started out in analytical chemistry as a food scientist years ago, so when you say oil and grease, that is sort of in my blood, both figuratively and literally, unfortunately, based on today's lunch.

When I started out with Bill Telliard and his group, I learned that a significant number of variables and parameters for oil and grease analysis is really somewhat unexplored territory.

My background is in analytical spectroscopy and food technology, so this area where practical applications do not usually follow the theory and where the instrumentation usually is not compatible with the chemistry is somewhat an area of concern, because it would be nice to have everything coordinated so that you can use a chemistry that is applicable to some instrumental technique or the theoretical mechanisms do predict how a sample should be prepared.

Current methodologies for oil and grease and TPH consist of the existing gravimetric methods, the modification using an infrared detection with a non-hydrocarbon based solvent, and some States are using gas chromatography with an FID detector for the TPH, not so much for the oil and grease, but I figured I would throw it in to be thorough.

Using the classical extraction or whatever extraction, be it solid phase disks or solid phase tubes, I tried to focus on a detection method that would be very quick and very reproducible and save the time involved with the classic gravimetric analysis.

We did a series of samples by separatory funnel, by Soxhlet, to judge the efficiency of the recovery, and we followed up with gravimetric analysis, and gas chromatographic analysis.

Unfortunately, in a GC, you do not get a single number like you do off an infrared at a fixed wavelength. You either get a group of peaks which, in this case, it was a kerosene sample from the State of Pennsylvania, or you get a big blob which is this. This is a grease sample coming off at 400 degrees.

So, really, chromatography is really not the way to go, and that was something that Bill was mentioning last year. So, I am glad to see no one else is talking about GC.

The infrared techniques that we utilize can be done on both FTIR, fixed wavelength nondispersive IR, or even scanning dispersive infrareds. As long as you can sit at the 3.42 micron hydrocarbon wavelength, you can get a reading, do calibrations, and judge your precision that way.

Here is a standard 1 cm liquid cell in an FTIR unit.

This is a fixed wavelength IR set at 3.42 microns, again, with an open sample compartment, and you can fit a variety of different sample cells in there to accommodate the concentration or pre-concentration of the sample.

Right now, the way I understand it, again not coming from an environmental lab environment, is that Bill and his people are looking for a safe solvent to use for gravimetric methods or a less hazardous non-Freon solvent to use for both infrared and gravimetric where you have good correlation and you do not damage the environment or ourselves too much.

What we did is we looked at a variety of materials using a couple of the solvents that have been floating around. Last year, it was mentioned that hexane and what was called the 80/20 hexane/MTBE mixture was going to be used but that it was not under serious consideration because of its neurotox...neurotox...neurotoxicity feature that Bill had brought up. Thank you for wanting me, Bill.

Our neighbors to the north had been using cyclohexane with some degree of success. I do not know how it has worked compared to Freon in our situation. Within the last month or two, the perchloroethylene came up.

So, we decided to look at all these materials compared to Freon-113.

Now, I am one of the few people from Rutgers University that got his Ph.D. and failed p-chem, so I cannot tell you what any of these things mean except to show that there are differences in something called the dipole moment, dielectric constant, magnetic susceptibility. Boiling point I know. I can figure that one out myself.

But trying to get an idea of why one solvent or solvent mixture gives good recovery for certain oil and greases and does not for another is still undiscovered country. Maybe Gene Roddenbury's ghost will come back this fall and do an episode on that for us.

What we did is try to modify the existing infrared version of the method so that we could use less solvent, be it Freon which is quite expensive and, technically, not supposed to be used, or whatever the new material would be and try to use instruments for detection so that we could maintain good detection limits and get a little bit faster turnaround than classical gravimetric techniques and keep our overall precision in acceptable ranges.

So, we prepared the samples by the standard procedure using the four solvents, the three proposed and the Freon. We downscaled the size of the sample and either the volume or weight of solvent used by from a factor of 2 to a factor of 10 which falls in line with the solvent reduction protocols from last year.

We did the analyses by, again, the gravimetric, by liquid cell infrared with a standard 1 cm cell, quartz cell, and by something called the cavity cell which we developed last year to allow us to use hydrocarbon based solvent in an infrared. Normally, you cannot do that, because a solvent has so much of an absorbance, it would swamp out the sample.

The tests were done on an HC-404 fixed wavelength hydrocarbon analyzer set at 3.42 microns. Again, the analyses were done with a standard 10 mm, 1 cm IR quartz liquid cell and what we call the cavity cell with a 250 uL depression in a quartz plate.

The gist of it was that we can utilize the gravimetric preparation with an infrared finish to it. So, we have the speed of an infrared determination, and we have the sensitivity of an infrared determination compared to gravimetric, and we do not have the interference of a hydrocarbon based solvent that the infrared would have.

This is the evaporation plate. It is a quartz plate with a depression of about 300 uL, and what we did is we followed through our extraction with some methylene blue, oil soluble methylene blue in the oil and grease sample. Basically, that is our 250 uL in the cell.

The back of the unit, the 404 unit, has a pair of heat fins that are about 45 degrees C. So, we put the plate on the heat fins which is a very constant temperature, and within about 30 seconds to 45 seconds, all of the solvents we evaluated were evaporated, leaving a residue of your grease, and you can see the little blue stain down there.

That whole cavity fits into the beam of the infrared. So, again, most dispersives and FTIRs have a fairly large beam, and we designed these plates so that the beam would encompass the entire area of it. So, whether the grease is on the bottom or on the side makes no difference. It is all going to be in the path of the infrared.

You place it in the unit, and you can see the large white area encompassing the depression in the cell.

I did not know Bill long enough to be blessed with some of his smelly, grungy samples that everybody else was, so I took some stuff that we had in New Jersey and did the three preparations. No disrespect to New Jersey. I am a native, but I used to be 6'5".

Using the four solvents and the three methods, we just came up with a table of correlations.

This was solid waste from a settling pond bed in Camden. I do not think it is Campbell Soup, but I cannot be sure. The 80/20, the cyclohexane, the perchloroethylene, and Freon.

By gravimetric, we could not do the perchloroethylene, because the boiling point was too high, so we could not draw it off without drawing off the grease. We could not use the 80/20 and the cyclohexane in the regular liquid infrared cell, because there is about 999,000 ppm of hydrocarbons in there. Likewise, the perchloroethylene we could not use in the evaporation plate because of the higher boiling point.

However, based on the classic method which would be Freon by gravimetric, we can see that the 80/20 and cyclohexane came out a little bit low, and the reproducibility on the cyclohexane was not that good. The liquid infrared by Freon came out higher. By perchloroethylene, it came out much higher.

The gravimetric technique using the 80/20 and the cyclohexane, because they are volatile, was not that good. The 80/20 came out significantly low, about 15 percent low. The cyclohexane was not too bad. And the Freon came out quite good compared to the gravimetric.

So, again, we have an evaporation preparation, a gravimetric preparation, with an infrared detection. So, you can combine the two technologies.

This was a residential soil from former farm land. There was a tremendous amount of organics in there from biomass decomposition and tilled manure and other material. Even with the silica gel treatment, we found some significant discrepancies.

Again, the classical value of Freon gravimetrically of 11 ppm, the 80/20 and cyclohexane again coming out low, but the evaporation by Freon coming out not too bad, 10 ppm versus 11, much closer than the 14 ppm by the liquid IR.

Again, you do not lose, as someone else mentioned on the panel here, some of the light organics that are extracted in a liquid-liquid extraction and not volatilized. So, that is a part of the problem.

This a solid sewage sludge that came from an area with a lot of petrochemical activity. Here, by the gravimetric technique, we got about 4 ppm. Our error was significantly bad there, because the water was actually quite clean. Excuse me, this is a water sample, not the solid waste.

By 80/20 and cyclohexane, we got nothing. By perchloroethylene in the liquid cell, we got about 5.6, a little bit higher, again, keeping in line with the other recoveries we saw. Freon by the liquid cell, again, higher.

Freon by the evaporation plate, because our detection limit by infrared is significantly better than by gravimetric, we were able to quantitate this to about 3.5 ppm quite precisely, and the gravimetric preparation with the infrared finish for the 80/20 and the cyclohexane were not too shabby. At least we saw some good reproducibility at the low levels.

This is a discharge process water that is cleaned up from a metal processing plant. Again, the classic value would be 17.7 ppm. The gravimetric with the 80/20 came out to be fairly close. Cyclohexane came out high. The perchloroethylene by the liquid cell came out high, again in keeping with all the other data.

The infrared with the Freon in the liquid cell came out significantly higher, showing there were a lot of volatile components that are maintained in the straight liquid running, but the correlation to the evaporation cell technique is quite good, 18.4 to 17.7 is a lot closer than 21.7 to 17.7.

This is a situation where some aerospace parts are being cleaned to check manufacturing QC for residual oil and grease, and here we have our classic value. Again, excellent precision by gravimetric analysis. Because this is mostly high molecular weight petroleum hydrocarbon greases, we see good correlation overall between the 80/20 and the cyclohexane gravimetrically, between the perchloroethylene and the Freon in the liquid cell, and even between the 80/20, the cyclohexane, and the Freon by the evaporation technique.

So, what we did was just tabulate a typical solvent usage. I think the hexane affected my eyes, also. Gravimetric techniques took about 100 ml of solvent, the liquid infrared about 50 ml, and the evaporation plate only about 25 ml of solvent. So, we were able to reduce our solvent usage and our costs there.

The analysis time, the gravimetric, depending upon the material, took about 40 minutes on average. The liquid IR technique, once a sample is prepared, takes only 3 minutes to transfer it to a cell, make sure it is filtered for no particulates because the liquid cell will give an absorbance if there are particulates that will scatter the light, and that is about 3 minutes. The evaporation plate technique took about 10 minutes.

So, here we have less solvent. It takes less time than gravimetric, a little bit more time than liquid, but the correlation to the gravimetric procedure is much higher.

So, based on some spike recoveries and using solvents with boiling points less than 81 degrees which is the 80/20, the cyclohexane, and the Freon, we calculated by running a series of blanks and spikes a method detection limit of 1.5 ppm which gives a 0.0044 absorbance unit signal...our sensitivity, rather, 1.5 ppm.

That gives us a detection limit of 4 ppm with 10 percent reproducibility at the 0.01A or 0.01 absorbance unit level which is quite low, and we are linear up to 250 ppm. We have pretty much a straight line at a 0.98 correlation.

So, this evaporation cell, cavity cell, technique is really applicable to all infrared units, filter infrareds, nondispersive, scanning dispersive, and FTIRs that have an open sample compartment to allow you to place a cavity cell in there.

We are working at developing a cell with a deeper cavity so we can use a larger sample aliquot, improving our reproducibility, because when you try to micro-pipette 250 uL of a volatile solvent, you will have some error, and also you can get a little bit larger residue which will give you, technically, a factor of 2 better improvement in sensitivity.

The current studies with the listed solvents and a variety of sample matrices, until Bill sends me some of his goops, show suitability for universal applications with minimal procedural changes and equipment modifications. So, for those of us that have infrareds, you know, let us not throw the baby out with the bath water, so to speak, till we figure out which solvent is going to be used.

Regardless of what solvent will be used, there are ways to still use your infrared so you can get the sensitivity and speed of the analysis without having to worry about the problems with the hydrocarbon based solvents.

Thanks. Any questions?

QUESTION AND ANSWER SESSION

MR. BANSAL: I want to find out does the thickness of the residue on the IR cell contribute any problems?

MR. DEMENNA: The thickness of the residue?

MR. BANSAL: Yes. I mean, is it to be uniform on the entire phase of the IR cells?

MR. DEMENNA: It does not make a difference. As long as the entire deposit is exposed to the infrared, you will get an absorbance. So, whether it is spread out 100 microns thick over 10 mm or 10 microns thick over 100 mm makes no difference, because the whole mass... it is a molecular absorption, so as long as all the molecules are hitting light, you will get the same absorbance.

MR. BANSAL: I see. How do you ensure that the residual, like if you are using cyclohexane, that all cyclohexane is gone, that it does not create any problems in the signal that you are getting from the IR?

MR. DEMENNA: Basically, just like gravimetric, you would basically evaporate to constant weight. Here, you just put the thing on the heat fins, stick it in the machine every 15 seconds until you have a constant absorbance, and then our studies have shown that that has drawn off all the solvent.

MR. TELLIARD: Yes, sir?

MR. SLENTZ: I am Kurt Slentz with Energy Labs. I have got a question for Bill of the EPA.

We have a number of clients that are required by their permits to run the 413.1 method, and if we phase out Freon, what is going to be their possibilities with your agency for some of these other techniques we have seen?

MR. TELLIARD: We are proposing to have 1664 proposed this summer and final by the end of the year. So, there is going to have to be, at least gravimetrically...I do not know if we are going to have NDIR, but, certainly, the gravimetric procedure has got to be ready by the end of the year.

MR. SLENTZ: What about the solid phase stuff that we were looking at? Are you guys taking a look at allowing us to use that, too?

MR. TELLIARD: Yes, we are. We do not know the answer yet, because, as you know, we have not all sat down and crunched the data. We will put out a Phase II report which will contain all of the data you have heard here today from API and from the industrial laundry folks and from the solid phase people and from the infrared folks. It will all be in a final report that we will have available, and we are working on that for proposal, as I say, during midsummer.

MR. SLENTZ: Then you are going to publish that in the Register so it is...

MR. TELLIARD: We will notice it in the Register. We will not publish it. It will be too expensive to publish it, but we will notice it, and you can write for it.

MR. SLENTZ: Then, do they have to modify their permits to use those methods?

MR. TELLIARD: We hope we can handle that through the way we notice the procedure.

MR. SLENTZ: Okay, thank you.

MR. TELLIARD: You are welcome.

ENVIRONMENTAL OIL & GREASE SESSION:

Current Advances in Oil & Grease Analysis using NDIR with the "New" Solvents"

Gerald J. DeMenna, Chem-Chek / BUCK
44 Stelton Road, Piscataway, NJ 08854
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16th. Annual EPA Conference // 3 May 1994
Norfolk, Virginia

CURRENT METHODOLOGIES:

[1] Extraction and Gravimetric Isolation of TPH materials

[2] Extraction and Liquid Cell IR Filter Photometry of TPH (C-H) Absorptions at 3.42 uM

[3] Gas Chromatographic Separation with FID Detection for TPH

STATUS of METHODOLOGY:

[1] Use a "safe" hydrocarbon-based solvent for gravimetric procedure only

[2] Use a "less hazardous" non-Freon, non-hydrocarbon solvent for both IR and gravimetric techniques

EVALUATION PROTOCOLS:

-=> Perform extractions on a variety of samples with assorted solvents [80/20 Hexane-MTBE, Cyclohexane, Perchloroethylene]

-=> Compare recovery of with previously approved method using Freon [trichlorotrifluoroethane]

EVALUATION PROTOCOLS:

[1] Prepare the sample and perform the extraction per standard protocols [SW-846 / #9070-9071]

[2] Decrease solvent utilization by downscaling the Volume or Weight of SOLVENT used for the extraction by a factor of 2 to 10 [dependant on sample matrix]

[3] Perform the analysis by Gravimetry, Liquid Cell IR and "Cavity Cell" IR [as proposed at 1993 meeting]

INSTRUMENTATION:

Model HC-404 Hydrocarbon analyzer [Filter IR Photometer w/ 20 cm-1 bandpass at 3.42 microns]

Normal Analyses w/ 10mm. IR-Quartz Liquid Cell
Evaporative Analyses w/ 250uL IR Cavity Cell

Items purchased from BUCK Scientific, Inc., E. Norwalk, CT

PRINCIPLES:

Like the existing gravimetric procedure, the "evaporation method" will allow the chosen SOLVENT to volatilize and leave the TPH, Oil & Grease as a film residue in a IR-transparent Quartz plate.

BENEFITS of MODIFIED PROCEDURE:

[1] Allows use of significantly lower volumes of regulated & proposed solvents.

[2] Allows user to achieve faster results, better D.L.s and overall precision.

EXPERIMENTAL SET-UP:

Samples of solid wastes and liquid effluents were examined by the 3 defined methods GRAV, LIQ-IR, EVAP-IR using the 4 existing or proposed solvents 80/20, cyclohexane, Perc & Freon

Sample #1: Settling Pond Bed, Camden, NJ / discharge line

Data is AVERAGE in PPM from triplicate preps w/ [%RSD]

	[1] GRAV	[2] LIQ-IR	[3] EVAP-IR
80/20	68 (4.7%)	n/a	70 (5.1%)
Cyclohex	75 (5.2%)	n/a	85 (4.3%)
Perc	>250 (n/a)	94 (2.9%)	>250 (n/a)
Freon	81 (3.4%)	86 (1.9%)	79 (3.2%)

Sample #2: Residential Soil,
Piscataway, NJ / past farm usage, biomass

Data is AVERAGE in PPM from triplicate preps w/ [%RSD]

	[1] GRAV	[2] LIQ-IR	[3] EVAP-IR
80/20	9.8 (6.3%)	n/a	9.5 (4.4%)
Cyclohex	8.7 (4.5%)	n/a	9.1 (3.7%)
Perc	>100 (n/a)	12 (2.9%)	>100 (n/a)
Freon	11 (2.9%)	14 (2.2%)	10 (3.1%)

Sample #3: Post-treatment Sewage Discharge,
Metarie, LA / petrochemical activity

Data is AVERAGE in PPM from triplicate preps w/ [%RSD]

	[1] GRAV	[2] LIQ-IR	[3] EVAP-IR
80/20	< 10 (n/a)	n/a	4.5 (5.6%)
Cyclohex	< 10 (n/a)	n/a	5.9 (4.2%)
Perc	>100 (n/a)	5.6 (4.0%)	>100 (n/a)
Freon	~ 4 (6.8%)	5.1 (3.3%)	3.5 (3.6%)

Sample #4: Metal Finishing Facility,
Skokie, IL / process water, recycled

Data is AVERAGE in PPM from triplicate preps w/ [%RSD]

	[1] GRAV	[2] LIQ-IR	[3] EVAP-IR
80/20	16.8 (4.9%)	n/a	15.9 (5.3%)
Cyclohex	20.7 (4.4%)	n/a	21.0 (3.8%)
Perc	>100 (n/a)	19.2 (4.8%)	>100 (n/a)
Freon	17.7 (3.8%)	21.7 (2.9%)	18.4 (3.2%)

Sample #5: Aeronautical Parts Cleaning
Schenectady, NY / manufacturing QC program

Data is AVERAGE in PPM from triplicate preps w/ [%RSD]

	[1] GRAV	[2] LIQ-IR	[3] EVAP-IR
80/20	29 (3.4%)	n/a	30 (4.2%)
Cyclohex	32 (2.5%)	n/a	31 (3.8%)
Perc	>100 (n/a)	34 (3.1%)	>100 (n/a)
Freon	33 (2.4%)	35 (2.2%)	32 (2.9%)

EXPERIMENTAL METHOD COMPARISONS:

METHOD Type	AVERAGE Solvent Use	AVERAGE Analysis Time
GRAV	~100 ml.	~40 mins.
LIQ-IR	~50 ml.	~3 mins.
EVAP-IR	~25 ml.	~10 mins.

SOLVENT CHARACTERISTICS:

SOLVENT Type	DIPOLE Moment	DIELECTRIC Constant	MAGNETIC Suscept.	BOILING Point
80/20	0.77	2.13	64	65
Cyclo	0	1.80	68	80
Perc	0	3.89	82	121
Freon	0.87	4.22	57	46

EVAP-IR PERFORMANCE:

[based on 250uL aliquot in 5mm x 4mm cavity, for solvents w/ BP < 81 degrees C]

Sensitivity: 1.5 PPM gives 0.004A signal

Detection Limit: 4 PPM gives 10% reproducibility at approx. 0.01A

Linearity: Correlation of 0.98 up to 250 PPM

CONCLUSIONS:

This technique is adaptable to all IR Photometric units with an open sample compartment to allow use of the "cavity cell" evaporation plate.

Current studies with listed solvents and a variety of sample matrices shows suitability for "universal" applications with minimal procedural and equipmental modification.

MR. TELLIARD: At this point in the proceedings, we are going to pass out the method for your review. There are two issues. First, there is a questionnaire on oil and grease with it. It will take you three to four minutes to fill it out. I would like your input, and we would like to get it, before you leave. Unless you want to spend the evening, you have got to fill out the form.

Secondly, we are looking for a few good labs to participate in a round-robin testing of both the solid phase procedure and 1664 as it is presently written. We would like some feedback after you folks get a chance to look at it. Tomorrow, I will give you my address, phone number, and box number, and if you want to drop me a line, I would appreciate it.

If you work in a laboratory or are associated with a laboratory and would like to participate in a round-robin on oil and grease, the cutting edge of science, please stop me, Dale, or Marion while you are here and give us your name and information. We will be glad to contact you, make arrangements to ship you the samples, tell you the data recording requirements, and so forth.

I want to thank all the speakers for today. I hope you enjoyed it. I hope you learned something. We will see you tomorrow morning, but you cannot leave until you fill out the form.

Thank you.

(The Conference was recessed at 4:22 p.m., to reconvene the following day, May 4, 1994, at 8:45 a.m.)

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MR. TELLIARD: Good morning. I would like to get started with today's session, please.

A couple of brief announcements. Last year, for those who attended, you remember that we had a small hole in the program regarding the policy that relates to the application of method detection limits and minimum levels and its relation to water quality based limits and, more specifically, those limits that are below the method detection limit that are water quality based limits.

We have made available on the back table copies of the memo that went out on that policy. It is a draft proposal. You are welcome to any of those copies. If, for some reason, you do not get one, if you will let the folks know at the table outside, we will make arrangements to mail you one.

Also, in addition to that, there are copies of the Martha Prothro memo floating around back there, as well. This memo focusses on today's subject, which is the application of trace metals and the issue of the dissolved versus the total metals or available metals as it relates to the water quality standards.

So, those documents are available. If, for some reason, you do not get one of those, again, check with the folks at the table outside at the break, and we will make arrangements to get you one.

Our first speaker this morning is Jim Hanlon. Jim is the Deputy Director of the Office of Science and Technology in the Office of Water. Jim has been with the Agency for quite a while. In his former life, he was the Director of the Construction Grants Program upstairs. For those of you who dealt with that program, you probably know Jim pretty well.

Jim is going to speak to you this morning on an overview of what is happening in the regulatory field as it relates to metals and a few other tidbits of information that he has brought down from Washington. Thank you. Jim?

REGULATORY BACKGROUND DETERMINATION OF METALS AT AMBIENT WATER QUALITY CRITERIA LEVELS

MR. HANLON: Good morning. This is the 17th Annual Analytical Methods Conference. As many of you may know, Bill has been involved,

I think, in all 17 of these, but I want to make sure you all know that he started this as a high school project. So, basically, even though he has been involved in the whole series of conferences, he started at a very young age and is looking forward to the next 17 conferences.

We, at EPA as well as the rest of the Federal Government, have gone through a political transition and turnover over the last 18 months. Carol Browner is now the Administrator of the Environmental Protection Agency, and Bob Perciasepe is the Assistant Administrator for Water. In government, as you go through these transitions, you observe the list of themes and directions that each administration brings in with them.

A theme, however, that has carried over, clearly, from the Bill Reilly tenure at EPA to Carol Browner's tenure is that of sound science. A very high priority on an Agency-wide basis is that our programs be founded in sound science, and I think the subjects that you are dealing with during this conference in terms of our ability to identify and measure not only where we are at but where our objectives are at, where we are going, has never been more critical.

Basically, the investments that our society makes in pollution control activities is continuing to increase as our knowledge about how pollutants and contaminants interact in the environment increases, and it is ever more important that we are able to measure where we are at and, again, where we are going.

What I am going to talk about this morning is the issue of metals and metals measurement and metals policy issues in our water quality programs.

Metals issues have been around since the beginning. Those of us who have been in the water quality programs over the last 20 years basically recall that the focus early in the '70s, after the passage of the Clean Water Act, was on the more conventional pollutants; BOD and suspended solids. Not to forget those favorite target pollutants, I notice on your agenda this afternoon, there is the ever-present session, on BOD measurement.

This morning, we want to focus on metals and how the Office of Water is dealing with metals in our regulatory programs and where we are going from a policy perspective.

A basic and fundamental responsibility of the Clean Water Act that is assigned to the States is the management of the water quality standards program. By definition, water quality standards include three components: designated uses of individual water bodies; an anti-degradation policy; and numeric and narrative criteria.

Water quality criteria, therefore, are fundamental building blocks in the foundation of the water quality program that is laid out within the structure of the Clean Water Act. It is those criteria that EPA develops that are adopted by the States in their water quality standards that are the basis for point source permitting actions that are taken under the

Clean Water Act through the National Pollutant Discharge Elimination System permitting program, the NPDES program.

Currently, all States are responsible for implementation of water quality standards, and 38 States have the responsibility for issuing individual point source permits.

Water quality criteria become enforceable instruments when they are adopted by States into their water quality standards and then are enforceable on a point source basis as they are incorporated into permits.

Currently, EPA has developed two types of water quality criteria. Basically, each of these criteria types measure water column concentrations of pollutants.

The first type of criteria currently available is for the protection of aquatic life. We currently have 30 criteria issued that are aimed at the protection of aquatic life. Another set of criteria are designed to protect human health. The Agency has issued 91 criteria aimed at human health protection.

Our future or the work in progress, illustrates that we are headed towards several other different types of criteria that you will be hearing about in time to come. The first is sediment criteria, basically, criteria documents that would allow the measurement and set objectives for contamination in sediment.

Secondly, we have criteria documents that would again be water column criteria aimed at the protection of wildlife.

Criteria are developed in the laboratory setting with the objective of determining acceptable levels or protective levels of contaminants, in this case, in the water column. When you go through that protocol, it is possible and often the case that the concentration that ends up in the criteria document is below our current levels of detection. Basically, we are not able to measure at the criteria levels.

This brings us to the metals issue. Many of the metals fall into the category of criteria levels being below the level of detection. In addition, metals management in the aquatic environment is further complicated by the site-specific nature of metals toxicity.

We have found in our efforts to manage metals in water quality limited water bodies that we are often calling for an ability to measure at almost 300 times lower than levels that have historically been required in the context of technology-based limits.

Metals in the environment exist and can be measured in total form, in total recoverable form, and in a dissolved form. Metals also appear in both organic and inorganic forms. The bioavailability and the related toxicity of metals varies, depending on all the variables we have just talked about including form and speciation.

It is also often necessary to determine more than one form of a metal in a particular setting. In doing so, it could require multiple procedures for sample handling, preservation, preparation, and analysis.

Essentially, what we are doing here is setting the table in terms of the whole myriad of complications that we are faced with and, I am sure, you are faced with as you look at the need to assess concentrations and appropriate levels in samples representing conditions in the environment.

From a policy perspective, EPA's role was to determine from a metals management standpoint, first of all in the ambient environment, what form of metals are we concerned about? Historically, the Agency's position was...to base all criteria on total recoverable metals. That was the best information available in the mid '80s when those criteria documents were developed.

In January of 1993, we convened a workshop of experts representing industry, academia, States, other Federal agencies to talk about metals management and to provide recommendations in terms of the aquatic environment and what were appropriate approaches for metals measurement.

Based, in large part, on the advice of the assembled experts at that meeting that EPA issued a memo in October of 1993 that expressed the policy preference of EPA's Office of Water to use the dissolved form of metals in the measurement of metals in the ambient aquatic environment.

That was a change in policy that had been brewing for some time and was clearly articulated in that October 1993 memo.

What the memo goes on to say, however, is that, if you reflect back to the role of the States in implementing the water quality program, this form of metals management is a State decision. The October memo sets out EPA's recommendation, but States may choose to use dissolved or total recoverable forms of metals in establishing and adopting their water quality standards.

The October memo is basically EPA's best advice to the States in terms of how those standards should be set and what form of metal to measure.

What we have also covered in the October memo is an update of the conversion factors. Recognizing that all the criteria documents that have been issued to date are based on total recoverable metals, it is necessary to be able to convert those criteria documents from total recoverable to dissolved.

The attachments to the October memo laid out our best advice for those conversion

factors, and we expect to have out in midsummer, an updated set of conversion factors based on some additional analysis we are currently doing.

Going beyond water quality standards, it is also necessary to make a decision in terms of what form of metal you use for managing metals across a water body in the development of total maximum daily loads (TMDL). Again, our best advice is that dissolved be used, but you would need to be able, when you get into the TMDL process, to go back and forth between dissolved and total recoverable. When you get into TMDLs, it is also important to continue to recognize the variable nature of metals and how they behave in the environment.

However, when you get to the NPDES program, EPA's permit regulations require that permit limits for metals be issued as total recoverable. The reason for that is the dynamic nature of metals and their relationship to the chemistry of the effluent, the chemistry of the ambient water the effluent would be discharged into, and the interrelationship of the effluent and the ambient water at the point of discharge, in the mixing zone, and then as the mix moves down stream. So it is, and continues to be, EPA policy that permits use total recoverable as the method of measurement for metals.

We have also recognized that it is necessary to go beyond a recognition of or a measurement of dissolved metals which takes into some account the site-specific nature of metals toxicity. We have issued additional guidance that will further allow site-specific calculations of criteria for metals management.

These guidance documents include recalculation procedures, and indicator species-based procedure, also known as the water effect ratio guidance that has recently been updated.

That is where the National Program is. Our challenge is, as we discuss metals management and metals measurement throughout the day today, is to assess our ability to go beyond current techniques to be able to approach the capability of measuring at the criteria level. That is where we would like to be.

We recognize that metals are essentially ubiquitous in the environment. We all know there are many metals that are required as trace dietary elements. It is extremely important, as we get into the clean and so-called ultra-clean techniques, that we are conscious of the potential for sample contamination and preclude the identification of false positives.

I think we are aware of some of the incidents or examples that have come to light in terms of historical data that has been subject to sample contamination. That has occurred with some USGS data. We are also aware that it has been the case with some EPA data where we have not been or as sensitive as we should have been to sample contamination potential.

We need to improve laboratory capability. Our current assessment is that our best capabilities in terms of metals measurement exists in our marine research laboratories.

We also are of the opinion, and correct us if we are wrong, that there are no laboratories out there that are currently able to reliably measure metals at criteria levels.

So, what are we doing about this? Our office, under the direction of Mr. Telliard, is developing guidance that will describe sample handling and quality control procedures necessary to avoid contamination. We are utilizing techniques capable of achieving MDLs or method detection limits that are 1/10th the criteria levels. That is the objective to demonstrate freedom from contamination.

We are describing the data reporting and data review requirements necessary to define the quality of data prior to EPA's use of that data for guidance, policy, or regulatory activities.

The first of these documents addresses sampling methods and a QC supplement and is currently in peer review within the Agency, and we project it to be available in June of this year.

Additional efforts are underway to develop new analytical methods and data reporting and data review requirements for your use.

A reasonable question at this time is, why now? Why metals in 1994?

A quick review of the history of the water program would show that the metals criteria that we have talked about for the protection of aquatic life were developed in the mid '80s. In the 1987 amendments to the Clean Water Act, Congress required the States to adopt all available toxics criteria into their water quality standards. Remember the criteria to standard to permits relationship we talked about earlier.

Given the State procedures for changing water quality standards and recognizing that Congress laid out a three-year window within which the States were to adopt these toxic criteria into their standards. It was not until the early 1990s that metals limits began to appear in many permits.

A survey we did back in 1988 to take a snapshot of where the industry was at the time showed that there were very few metals limits or toxics limits in permits that had been issued to municipalities (POTWs).

It was, then, in the early '90s that EPA, after the three-year window that Congress laid out for adopting the criteria had expired, that we began a regulatory action to require States or to promulgate for the States toxic criteria into their standards.

In 1991 when we issued the proposed regulations, there were still 22 States that had not adopted the full suite of criteria into their standards. We issued the final regulation in December of 1992, and in the final regulation, only 14 States were included. So, between November of '91 and December of '92, an additional eight States had adopted toxic criteria, the full suite of toxic criteria into their standards.

With the promulgation of the final regulation, all States had in their water quality standards toxic criteria, the full suite of toxic criteria. That included the 91 human health and the 30 aquatic life criteria I talked about earlier.

A 1994 survey performed by our permits office, identified that, as of right now, approximately one in three municipalities has toxic limits which include metals in their permits. So, you can see between '88, almost none, and '94, up to a third of the municipalities have toxic limits in permits.

It is really at the point in time when a discharger receives a proposed permit in the mail that says you have now a numeric limit for zinc or copper or cadmium or whatever the pollutant of concern is in the effluent, that their attention is focused on the impact of the limit. What does it mean? How do I measure it? Am I going to be responsible for additional control technologies?

That is why, I think, we are dealing with metals in 1994 in terms of the importance of being able to accurately measure where we are at.

Another interesting fact is that under Section 304(l) of the Clean Water Act, the States were required to list impaired water bodies. That process resulted in some 680 water bodies being listed as impaired, and our count is that approximately 600 of those listings were attached to metals contaminations. Therefore, 90 percent or so of the listed water bodies are listed because of metals concerns.

The next slide is an eye chart. Basically, what this shows down the left-hand column is a list of metals and, in the right-hand column, the yes/no(s), indicating which of those metals we are currently able to measure at the criteria level, given approved EPA methods. Of that total list, there are seven of those down the right-hand column that we are not currently able to measure at criteria levels.

That is our perspective in terms of where our measurement capabilities are today.

Who do you call with any follow-up questions? This list outlines the folks at EPA who have lead responsibilities for issues associated with metals and metals management.

That summarizes where EPA's Office of Water is at with the metals management and metals issues. What I wanted to do for just a second this morning before I turn the podium

back to Bill is give you a quick update in terms of where the Clean Water Act is going, because, as we have discussed, it was the Clean Water Act requirements within Titles III and IV that have set the framework for management of metals within our water quality program.

Currently, there are two bills active on the Hill. In the Senate, Senator Baucus has issued S.B. 1114 which has been through committee markup, and we are expecting the committee report to be out within the next week or so that outlines a rather sweeping set of changes for the Clean Water Act.

In the House, Congressman Minetta who is chairmen of the House Public Works and Transportation Committee has introduced H.R. 3948. That bill is not as far along in the legislative process. There are hearings scheduled on that bill on the 16th of this month, and the process of the bill going to markup has been on again, off again, within the last month or so, but it is now expected that they will not go to markup until after the May 16th hearing.

Also, the Administration has issued a publication that is the Clinton Administration's vision for Clean Water Act reauthorization. It is in that document where we lay out a proposal for the water quality criteria and standards program. It would require the Agency to prepare a five-year outline of where the Agency is going in terms of criteria development.

It is that criteria development process, that would drive our need for additional laboratory and analytical support to assess where we are and more importantly, where we are going with those criteria.

In terms of the likelihood for either of the bills in the Congress or elements of the Administration's proposal to be incorporated into the Clean Water Act, the bet now is probably 50/50 whether, within this session of Congress, the Clean Water Act amendments will make it through the legislative process.

That concludes what I wanted to say formally this morning. Bill, do we have a couple of minutes for questions if anyone has one?

MR. TELLIARD: Sure.

QUESTION AND ANSWER SESSION

MR. HANLON: Why don't we turn the lights back up and the slides off. Certainly, if anyone has any questions, I will attempt to answer them. If I cannot, I am sure Bill can.

MR. TELLIARD: Please identify yourself and your organization. There are mics around.

MR. HANLON: Yes, ma'am?

MS. ASHCROFT: Navy Public Works Center in Norfolk, Virginia. I have a couple of questions, maybe not really directed at you guys, but we are getting ready to have our NPDES permit reauthorized or...

MR. HANLON: Reissued, yes.

MS. ASHCROFT: And they have limits that are lower than drinking water. Why are our permits being written that the water that goes into a body of water has to be less toxic than what we drink?

MR. HANLON: I will give you my answer to that, and then we will ask for other clarifications or Bill can get me out of trouble.

Did everyone hear the question? Okay.

The reason those numbers can come out that way is that, when you go into a laboratory and you run the full suite of tests that are required to develop criteria for the protection of aquatic life, it is possible, and it does happen, that you will get concentrations of particular pollutants that may be demonstrated in the laboratory, to be toxic to aquatic life that, in fact, may not harm you or me if we have it in the pitcher of water on the table.

So, although, at first blush, there is an intuitive reaction that says that doesn't make any sense, how can I be less sensitive than the fish, I think, in fact, what the folks who run the tests in the lab tell us is that that is exactly what can happen and does happen, and that is the reason the numbers are different.

MS. ASHCROFT: My concern is not only that it is less toxic that we are allowed to drink, but the fact is that the body of what to which it discharges has higher concentrations than that normally.

MR. HANLON: What is important is that if the State, in your case, I assume, has sent you the proposed reissuance of the permit, if those

permit limits are a result of a direct interpretation or lifting numbers directly out of EPA criteria documents which the States have adopted into their standards, it may be necessary and appropriate to go through some of the site-specific protocols that we talked about in terms of assessing what the appropriate criteria may be for the receiving water that you are discharging into because of local water chemistry.

When the criteria documents are developed, most of the fresh water criteria were developed in our lab in Duluth. The marine criteria were developed in our lab at Narragansett.

The criteria are developed in relatively clean or pristine water samples so that if there are background concentrations of solids or other elements in the ambient environment that you are dealing with, it may affect the toxicity of whatever the parameters are in your permit, and if you use directly the numbers that are in the criteria document, one could very well get limits that may be lower or more restrictive than are necessary for the protection of aquatic life at your site.

The only way to do that is getting into a site-specific calculation of what that local toxicity is. Your State permit writer, if he is sitting in Richmond, cannot do it. Our scientists in Duluth or Narragansett cannot do it. That has to be a local decision based on local chemistry.

MS. ASHCROFT: What the problem is that they look for this guidance from EPA, and, often, they do pick these numbers exactly as if the body of water was a lake and we are discharging to an ocean.

MR. HANLON: If you have not had a chance to look at the October '93 guidance or policy document that was issued, you now have a copy, and I would suggest you take a look at that and have a talk with your State permit writer. That is the best guidance I can give you this morning.

One more question?

MS. ASHCROFT: I have two more questions.

MR. HANLON: Okay.

MS. ASHCROFT: On the dissolved metals issue, we are trying to wrestle that, because that is in our permit now. One of the things I would like to ask you is, would it be possible, rather than to do field filtering for these dissolved metals and then preservation, to perhaps put these samples on ice, take them back to the laboratory with a six-hour holding time, and then filter under better conditions?

The metals concentration really should not change that greatly in a six-hour period. What are your feelings on this?

MR. TELLIARD: That is something we are looking at. We realize if you take water out of a well or someplace where you have an oxygen-starved environment, there are going to be significant changes. If you are taking it out a water body where everything is basically at equilibrium, there probably is a safe period of time. Whether it is 6 hours, whether it is 12 hours, whether it is 55 minutes we do not know yet, but that is one of the things we are going to be looking at this summer.

Nobody likes to do it on the back of a truck or hanging from the corner of your car. It is no fun. If we can do it in the laboratory and that is a viable option, we are going to let you do that, but we have to generate some data first.

MS. ASHCROFT: And what is EPA's policy on ICPMS? Are they looking at that? Are they forcing us all to buy these?

MR. TELLIARD: ICPMS is an accepted technique. You are going to hear some methods today that will revolve around the application and expansion of the ICPMS approach, and, yes, it is the coming thing. My sister does not have one yet, but they are coming down the road.

MS. ASHCROFT: Okay, thank you.

MR. HANLON: Yes, sir?

MR. BLOOM: I have a question and a comment. My name is Nicolas Bloom from Frontier Geosciences. My comment is that just in the last five minutes, I have been able to jot down seven laboratories that can measure all of the EPA criteria pollutants and trace metals at ambient levels.

MR. HANLON: Great.

MR. BLOOM: I do not think it is that difficult to do, and it brings up a question of why doesn't the EPA go to the people who have been able to, for the last 15 years, measure these metals at ambient levels to develop their new rounds of methods rather than trying to develop them internally?

MR. TELLIARD: The application or development of the methods, when we say internally, as you know, is done by contract support. So, we would look to these laboratories for that support and effort.

Where possible, we would still use our own research capability if it can be done in a timely manner, and that is what we are doing. You are going to hear some papers from our folks in Cincinnati today on some updated methods.

There are some big holes in the table that Jim showed you, and, yes, for those areas where we have to resolve some things, we are going to be out there soliciting help from the user community and the application community.

MS. DINSMORE: Donalea Dinsmore from the State of Wisconsin. Some of the toxicity-based limits for human health are based on total metals data. So, we have total and total recoverable.

What I am seeing is that the current methods have phased out some of the total metals procedures, and preliminary indications I have from technical people is that those two things are equivalent. I am trying to weigh what is really true based on your presentation of the three different forms.

Are the toxicity people talking to the methods people, and what is going on there?

MR. HANLON: They sure should be talking. In most cases, my understanding is that total and total recoverable are not the same and that, if that is an issue, you can follow up with us or follow up with the people in your State or region, and they should be able to provide you some advice on that.

Okay, thank you. One thing I wanted to do when we started is to get a sense of who is here and maybe help the audience get a sense of that also.

How many folks are here from States? (Show of hands.)

From municipalities? (Show of hands.)

From consultants? (Show of hands.)

From the laboratory folks, whether it is analytical? (Show of hands.)

Other Federal agencies other than EPA? (Show of hands.)

Okay. What I want you to do is look around now. All the people from EPA, stick up your hand. These are resource people, to let you know who is here during the day. We are all going to try to answer all your questions before you leave town. My plans are to be here all day and participate in the festivities this evening. Hopefully, the weather is going to cooperate. Thank you.

MR. TELLIARD: Thanks, Jim.

Metals—Regulatory Background and Policy Perspective

James A. Hanlon
Deputy Director
USEPA Office of Science and Technology

Regulatory Background

- States are required to adopt water quality standards that designate the uses of each water body and to adopt water quality criteria (WQC) necessary to protect those uses.
- Water quality criteria are essential tools for implementing water quality standards.
- CWA requires NPDES permits that contain an integrated approach to the control of toxic pollutants through technology-based controls and water quality-based controls.
- WQC become enforceable when they are adopted in a State water quality standard.

Regulatory Background (Cont.)

- Numeric WQC are set to protect aquatic life and human health
  - WQC represent a scientific assessment of the ecological and human health effects associated with pollutants in surface water
  - Because analytical detection limits are not related to actual environmental impacts, they are not a consideration when determining WQC.
- Implementation of WQC for trace metals is highly complex due to:
  - The site-specific nature of metals toxicity
  - The need for measurement at levels as much as 280 times lower than those levels required by technology-based controls or obtainable by routine analyses in environmental laboratories.

Metals Forms and Speciation

- Metals form and speciation varies by site, depending on the chemical, physical, and biological conditions of the site.
- Metals exist in total, total recoverable, and dissolved forms.
- Metals appear in both organic and inorganic forms, e.g., methyl mercury vs. mercury:
  - Organic forms can exist as one or more organo-metallic compounds, e.g., tributyltin vs. phenyltin;
  - Inorganic forms can exist in one or more oxidation states, e.g., chromium (VI) vs. chromium (III).
- Bioavailability and toxicity of a metal varies, depending on its form and speciation.
- Determination of more than one form may require multiple procedures for sample handling, sample preservation, sample preparation, and sample analysis.

Metals Forms and Speciation (Cont.)

- A major issue in the implementation of metals criteria for protection of aquatic life is whether, and how, to use dissolved metals or total recoverable metals concentrations in setting State water quality standards.

- EPA Office of Water policy recommends the use of the **dissolved** metal to set and measure compliance with water quality standards
  - Policy reflects widely held belief that the dissolved metal more closely approximates the bioavailable fraction of metal in the water
  - EPA will also approve State risk management decisions to adopt standards based on total recoverable metal, if those standards are otherwise approvable by law.

- Because the currently approved WQC are articulated as total recoverable metals, EPA has issued guidance for translating the published total recoverable metals criteria to dissolved criteria.

Metals Forms and Speciation (Cont.)

- Although EPA recommends the use of dissolved metals criteria to calculate Total Maximum Daily Loads (TMDLs) across a watershed or waterbody, EPA's NPDES regulations require that limits of metals in permits be stated as total recoverable metals.
  - This is because the chemical conditions in ambient waters frequently differ substantially from those in effluent, and
  - There is no assurance that effluent particulate metal would not dissolve after discharge.
- NPDES regulations require permit writers to translate between different metals forms in the calculation of permit limits so that a total recoverable limit can be established.

Metals Forms and Speciation (Cont.)

- EPA has also recognized that while the use of the dissolved form will correct some site-specific factors affecting metals toxicity, additional refinements may be necessary.

- EPA has issued guidance describing three methods for development of site-specific criteria:
  - A recalculation procedure
  - An indicator species procedure (also known as the water-effect ratio or WER)
  - A resident species procedure.

Measurement Difficulties

- Although the CWA does not require WQC levels to reflect analytical capability, our objective is to be able to measure at these levels.
- Trace metals are ubiquitous in the environment, and therefore, measurements at WQC levels require extensive precautions to preclude false positives that may arise from contamination during sampling or analysis:
  - USGS recently discovered that some metals data in one of its major databases may be the result of contamination; similar concerns have been raised about data gathered during EPA's New York/New Jersey Harbor studies.
  - This suggests the need for EPA to take steps to ensure that similar results are not produced as EPA continues to measure metals at WQC levels.
- Laboratory Capability
  - Expertise in metals determinations at the WQC levels currently exists only in marine research laboratories.
  - No laboratories are known to be capable of reliably measuring all metals at required WQC levels.

Requirements for Implementing Measurements at Ambient WQC Levels

- To address these concerns, OW's Engineering and Analysis Division (EAD) is developing guidance documents and methods that:
  - Describe sample handling and quality control procedures necessary to avoid contamination of samples during collection and analysis;
  - Utilize techniques capable of achieving method detection limits (MDLs) that are one-tenth of WQC levels in order to demonstrate freedom from contamination;
  - Describe the data reporting and data review requirements necessary to define the quality of data prior to EPA use.
- The first of these documents, a draft sampling method and a QC supplement to existing EPA analytical methods, are currently undergoing peer review within the Agency; release is scheduled for June, 1994.
- Additional efforts to develop new analytical methods and data reporting/data review requirements are currently underway.

Summary of WQC Levels vs. Current Technology

Metal	EPA WQC (ug/L)[1]	EPA Method[2]	Technique	MDL (ug/L)	ML (ug/L)	MDL Needed (ug/L)[3]	WQC Achieved?
Sb	14	200.8	ICP/MS	0.4	1	1.4	Yes
As	0.018	200.9	STGFAA	0.5	2	0.0018	No
Cd	0.32	200.13	CC/STGFAA	0.016	0.05	0.032	Yes
Cr (III)	57	None[4]	N/A	---	---	5.7	No
Cr (VI)	10.5	218.6	IC	0.3	1	1.05	Yes
Cu	2.5	200.10	CC/ICP/MS	0.023	0.05	0.25	Yes
Pb	0.14	200.10	CC/ICP/MS	0.074	0.2	0.014	No
Hg	0.012	245.7	CVAF	0.01	0.02	0.0012	No
Ni	7.1	200.10	CC/ICP/MS	0.081	0.2	0.71	Yes
Se	5	200.9	STGFAA	0.6	2	0.5	No
Ag	0.31	200.8	ICP/MS	0.1	0.2	0.031	No
Tl	1.7	200.8	ICP/MS	0.3	1	0.17	No
Zn	28	200.9	STGFAA	0.3	1	2.8	Yes

CC = Chelation/Concentration
CVAF = Cold Vapor Atomic Fluorescence
IC = Ion Chromatography
ICP/AES = Inductively Coupled Plasma/Atomic Emission Spectroscopy
ICP/MS = ICP/Mass Spectrometry
STGFAA = Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry

[1]Lowest of freshwater, marine, and human health WQC promulgated at 40 *CFR* Part 131 (57 *FR* 60848). Hardness-dependent freshwater criteria were recalculated at a hardness of 25 mg/L $CaCO_3$, and all appropriate aquatic life criteria were adjusted for dissolved metals criteria.

[2]If multiple EPA methods provide the detection levels required to reliably measure at WQC levels for a given metal, only the method with the lowest detection level is cited.

[3]The MDL needed in order to achieve WQC levels must be at least one-tenth of the lowest WQC level for that analyte.

[4]None = No EPA method exists for analysis of species of interest.

Points of Contact

- Copies of the full Office of Water guidance released in October 1993, can be obtained by contacting the Water Resource Center at (202) 260-7786.
- General questions about the guidance should be directed to me at (202) 260-5400.
- Specific questions should be directed as follows:

Subject	Contact	Phone
Water quality criteria	Bob April	(202) 260-6322
Water quality standards	Dave Sabock	(202) 260-1315
Monitoring & data issues	Elizabeth Fellows	(202) 260-7046
TMDL issues	Don Brady	(202) 260-7074
Permit issues	Jim Pendergast	(202) 260-9537
Modeling and translators	Russ Kinerson	(202) 260-1330
Analytical methods	Bill Telliard	(202) 260-7134

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MR. TELLIARD: Now that you have the overview, we will try to get into the nuts and bolts, and the first person I have is Carlton Hunt. Carlton is a Senior Research Scientist with Battelle.

Carlton is going to speak today on some of the problems with trace analysis.

Carlton?

TRACE METAL CLEAN TECHNIQUES: PROBLEM, QUALITY ASSESSMENTS, COMPARISONS

MR. HUNT: Thank you, Bill, and also the organizers of this for inviting me to give this talk.

What I would like to do, if I can have the first slide, is talk a little bit about the problem of trace metal analysis using clean and ultra-clean techniques. I think most of us know what the problem is, poor data quality. What I really want to do is focus at a high level of quality assessments, on those procedures that are necessary to achieve good metal results in waters, and also provide you with some comparisons of recent results that we have generated over the last year or so, as laboratories and people have asked us to, in fact, apply clean technologies and compare our methods to their standard methods to see what the problems might be in their labs.

My objectives are four-fold. One is to discuss major roadblocks that the labs might encounter in achieving accurate trace metal results, again, at a fairly high level. The details, having talked with Bill a little bit about what EPA is doing, I will be included in some really nice detailed guidance that is coming out shortly.

I would also like to convey required quality control assessments. This is really critical to have good quality control early in your program.

I will also show comparative results of some recent sampling and bottle comparisons.

Finally, I would like to start to focus, because of questions I have been asked over the last year or so, on thresholds for initiating clean methods. However, I do not want people to leave and say there is a point where you do not have to pay attention to cleanliness in trace metal analysis, but I think there are places where you start to begin to apply a lot more stringent control.

I have some data from our comparative studies to talk about. It is very preliminary. It is also incomplete. We need to do, I think, a lot more work in terms of identifying when we trigger these really clean techniques.

A couple of definitions. First of all, I think achieving accurate trace metal results is not necessarily application of new procedures. I think the procedures are out there, and the techniques are out there. It is a matter of appropriately implementing those technologies and techniques. It is execution more than it is new methods.

In my own way of thinking, and this is an evolving type of definition, the definition of clean methods is basically trying to apply sampling and laboratory techniques that accurately quantify contaminant levels at somewhere around the 20 μg/L and down to around the 0.1 μg/L level.

Basically, that includes achievement of a consistent, low blank contribution from your sampling and from your analytical procedures. So, the goal is really blank control and contamination control.

The ultra-clean techniques which are really getting down into the sub-part per billion and the part per trillion range, to me, is really a targeted zero contribution of contaminants to your sample. It is an intensive effort to identify where contamination gets into your sample, either at the sampling phase or at the analytical level and at the processing level.

We all probably know what the problems are in terms of high results, false positives. There are sampling errors, containers can be a problem, the reagents in the processing steps can be a problem, and the analytical interferences on the instruments can be a problem if not properly controlled for.

Sampling errors. A lot of people are using improper sampling devices, devices that are not built for trace metal collection.

Cleaning of sampling devices, even if it is constructed of the proper materials, is a critical issue. You have to also be able to clean sampling equipment properly.

Sampling and sampler deployment. Back when we first started doing a lot of trace metals sampling, people were deploying their sample bottles off the back end of a boat where lead-tainted gas was exhausted right into your bottles. This caused major lead contamination problems. So, how you deploy a sampler and where you deploy it, must be understood and you must know how to control the inputs of contamination.

Atmospheric contamination. This is why people are using clean rooms. Labs, inside and outside, are very dirty oftentimes because of the types of materials that have come through a lab.

There are some horror stories where people have been using contaminated soil sediments in a lab where they are also trying to do water quality measurements. The two are incompatible.

Clothing and gloves are the critical things I talk about in terms of contamination control. Gloves must be non-talc. Talc has a lot of zinc in it, and it immediately will contribute zinc to your sample and result in a false positive.

Finally, some sample transfer and handling procedures.

This is a recent comparison of a teflon sampler against a stainless steel sampler used for mercury collections. You can see that the stainless steel sampler that was used, this was a side-by-side collection, contributed a significant amount of mercury to the sample.

I do not know if you can read the scale in the back. This is 30 ng. This was 10 ng. The teflon sampler, with proper acids and control, resulted in a signature of about 2 or 2.5 ng/L, whereas we were getting ten times that with the stainless steel sampler. This is a recent study within the last year.

In terms of processing, we do much of our work on board ships. Because of the numbers of samples and the distance we have to ship samples, we, in fact, do process on board, but we do implement stringent control techniques, including Class-100 clean benches and non-talc gloves. All labware used is cleaned on board the vessel after each use.

Sampling concerns. Sampling up the contaminant gradient is critical. Do not start at the effluent and work down into a receiving water that has lower metal concentrations. Rather, work up the gradient especially if you have to reuse samples and sample bottles. Common sense in terms of contamination control will go a long way towards reducing contamination.

Containers. The basic rule of thumb here is to work with non-contaminating materials. In the movie Good-bye, Columbus a number of years ago, the key word was plastics. That still holds with metals today. Plastics are your first choice.

Compatibility of the metal with the plastic material or the teflon material is critical. The guys who do the really low-level mercury measurement, do all of their work in teflon, because it does not allow mercury to pass through the bottle walls, as allowed, by linear polyethylene and high density polyethylene.

Most of the other metals are very much compatible with the standard plastics that you might use.

You can buy commercially cleaned containers, but I advise everyone to check the blank on those bottles, and if you need to, institute a cleaning procedure to clean the bottles.

Finally, one of the things that we find very effective is to store cleaned bottles with a dilute acid until you use the bottle. You dump the dilute acid out in the field, do a quick

rinse of the bottle with sample, and then put your sample in it. That goes a long way to controlling contamination.

This slide shows a recent comparison of preservation acids and collection containers. We were asked to compare one type of sampling equipment with acid preservation against our clean techniques.

The metals are mercury and zinc. The scale here is 200 ng/L. This is 50 ng/L.

What you have in the green is reagent grade acid in a polyethylene container. The yellow is ultra-pure acids in a teflon container. Again, the metals are mercury and zinc.

You can see, for the mercury, certainly, the reagent grade acid in the polyethylene gives a very high signal relative to the teflon. The same thing holds for zinc.

I think the critical point here is the contamination that is evident here is the difference between possibly being in compliance and out of compliance, if you had a standard of 10 μg/L. At this level, a contaminated sample would kick you into an action, I think, whereas a clean sample probably would pass if that were the standard you were working against.

Reagents and processing and use of high purity reagents. If you are chelating a sample, if you are spiking with acids, the solvents you use to extract or otherwise work with a sample, must be clean. High purity reagents are commercially available and should be applied. The caveat here is check the blank, check the amount of metal that is in that particular reagent, because some of them are a little better for some metals than other metals, but they are available, and if you need to go to the ultra level, sometimes you need to, in fact, purify the acid in your own lab.

Routine use of highest purity deionized water is an absolute requirement. The guys who do the ultra-low trace level work, ultra-clean methods, in fact, sub-boil in quartz to get the highest quality acids.

However, this procedure is way down the hierarchy for ultra-clean techniques that need to be applied. I think, generally, deionized water is adequate for most of the work we do, but you do have to understand what is in the sample or in the deionized water.

Identification of reagent and procedural blanks prior to conducting analysis. This is critical to getting good numbers. Before you turn a sample in a lab, you need to do a procedural blank whereby you identify where potential contamination is coming in and then control for that.

The procedural blanks, then, routinely check that your analysis is in control.

Again, consistent blanks that are less than 10 percent of the lowest value that you expect to get are really a requirement in order to get good numbers.

This is just a quick summary table of results that we generated during the New York/New Jersey Harbor waste load allocation program. On the left are three analytical methods that we were evaluating. One was total recoverable, one was the draft acid soluble technique that EPA had potential to apply, and one is the dissolved method.

This is the blank level in ng/L for four metals. The lowest measured value in the program is listed on this line. I will focus on copper in this case.

This is the minimum blank contribution to this sample from the total recoverable measurement.

What you see is that the total recoverable method requires more manipulation of the sample, and the procedure allows open beaker digestion with 10 fold concentration of the sample, digestion down to about 20 ml from a 100 ml sample, followed by reconstitution.

The acid soluble and dissolved methods have equivalent steps. The difference is when you acidify the sample. The dissolved, you filter before you acidify; for acid soluble, then filter.

What you see is basically the blank contribution from these two steps. Using clean technique, the blank is reasonably consistent for these metals for dissolved and acid soluble, but the total recoverable blank is much higher, sometimes five to six to ten times. In terms of contribution to the sample, this number right here is in error. This should be 440. The contribution to the sample from the total recoverable ran anywhere from 90 percent down to 15 percent, depending on the element.

This slide is a more recent study. Again, this is total recoverable copper in a recent site-specific copper criteria development that we did. We did 60 blank samples during the total recoverable digestion.

16 of those 60 samples had contamination, these were processed in a fume hood using normal procedures. 16 of those 60 samples had detectable copper contribution from the procedure blank above the detection limit which is right here. The other 44 samples were below the detection limit.

The issue is, (a), it is highly variable which means there was a problem controlling for the contamination and understanding contribution source. If your sample only had 1 μg copper in it, these blanks would contribute over 50 percent to that concentration. So, you have a false number at the low end.

If you had 500 μg/L in terms of the spiked sample, there is really not a problem. You have to make sure you are working at the right levels of concentration.

Down at the bottom is a graph that just shows the same kind of procedures where we worked in a clean room. The bottom line is that these were extracted samples. The detection limit was 0.05 ug/L, and, basically, we saw no contribution of copper to that particular set of samples.

Analytical interferences. I think again, the messages are basically that you need to use the appropriate quantification techniques, because metals have notorious interferences at the instrument level, depending on the instrument you are working with. You have to know what those are and how to control for them.

I have jumped on somewhat of a bandwagon that I get on in terms of standard curves and standard additions and when to apply them, and I will show you a couple data points where we compared those methods.

Basically, you need to know the matrix you are working with, and you really cannot mix a variety of matrices together when you load them on the instruments. A lake water, a river water, and sea water do not necessarily have the same analytical interferences and should not be run in the same batch of samples.

Matrix modifiers are available and should be applied in all cases, and appropriately applied.

This graph will take me a little bit of time to explain. What you see is the concentration of copper in six samples that were collected for a field comparison and laboratory comparison. The solid line is samples that were collected by Battelle for EPA Region II and analyzed in our lab using extraction techniques and metal clean techniques.

The comparison is with three other sets of samples. If they were perfect comparisons, they would fall upon that solid line obtained by extraction using clean techniques.

The triangles here are EPA samples that were collected and analyzed by New York City for the required monitoring in New York Harbor. Basically, for the samples that we collected and provided to them in clean bottles, they came up with a reasonable comparison of concentrations to ours.

New York City also came in with a boat right beside the EPA's OSV *Anderson* that we used to collect the samples. New York City collected samples within 50 feet of the *Anderson*, and we then exchanged bottles. They used their techniques, and we used ours.

In this case, we see that there is a slight elevation in terms of the copper contribution when the New York City samples were run by Battelle. When New York City ran their own

samples, there was somewhat of a reasonable comparison here but a big difference in terms of the concentrations they were getting in the lab. Those are basically lab interferences because of the techniques they were using.

So, we had a bit of a problem determining whether or not they had a sample collection issue with their numbers or lab issue, and the lab issue had to be dealt with before we could really get to the field issue.

This slide addresses my bandwagon in terms of instrument calibration methods. It is the same type of a plot as before. The solid line is the extracted samples from a number of samples from New York Harbor.

In this case, we quantified the samples with a standard curve. These data are shown with the pluses, they fall on the solid line. The stars represent samples that were determined by standard additions.

In this case, the metal is cadmium. When analyzed by standard curve, we achieved very good agreement with the extracted samples, but when we ran the samples using standard additions, we started seeing high results. That is a non-specific interference at the instrument level.

Recently, I was looking at a report that was published in 1975 that basically called out this kind of a problem when you are working with standard additions and standard curves. So, the issue has been known for a long time. We just have not, I think, appropriately dealt with them over the last 15 or 20 years.

This is another instrument calibration method. This line is the extracted sample. The metal is copper. In this case, we see that the standard curve gave us consistently low results relative to the extracted sample where various ions that interfered with the sample were removed.

This is the standard additions curve. Good agreement at the lower end of the curve, and some disagreement up to the top in terms of concentrations. Basically, we see a negative comparison in terms of concentration using the standard curve as opposed to an extracted sample.

Let me quickly summarize what I have gone through here, and then I am going to step into the threshold argument. Successful application of clean methods requires (a) systematic identification and control of your contamination sources during sampling and analysis. Systematic means going in and identifying it before you turn a sample and collect a sample.

It is an awareness in the application of specialized cleanup procedures for storage containers and labware. This has been known and published on 15 years ago in a number

of books, one by the National Bureau of Standards and one by Morris and Zeit. The NBS book is titled *Contamination Control in Trace Metal Analysis*. Contamination control techniques are also in the literature and have been around for the last 15 or 20 years.

Use of high purity reagents, appropriate reagents, in cleanup steps is essential.

Isolation of samples from atmospheric contamination is required.

Control of analytical interferences are necessary. You just cannot throw a sample on an instrument without knowing the matrix that you are putting into the intrument and controlling for those instrumental interferences.

Finally, as I have said repeatedly, early evaluation and application of appropriate QA/QC techniques to include the procedural blanks and analysis of standard reference materials are essential. It is a performance-based type of comparison. You need to be able to measure what is in a certified standard appropriately before you really start the procedure, and then you need to apply that during the whole analytical train.

It also includes matrix spike recoveries and replicates. I think we will hear a little bit more about some of those things today.

The next sequence of slides presents data for a number of inter-comparison studies in a variety of types of effluents. To explain the sequence of graphs, the x-axis plots samples collected and run by Battelle using clean techniques.

The y-axis is a ratio of the other participating lab to our numbers. If you have perfect agreement, the ratio would be 1 which, on all these graphs, would be right here.

The concentration range for this set of copper in municipal effluent is somewhere between 55 and 100 μg/L. The samples were taken independently. Sample was placed into our clean bottles, put into their bottles, sent to the labs, and the numbers provided for comparison.

Essentially, for copper in this effluent... and these are total numbers...we see fairly good agreement between the two labs at this concentration range. There was not a comparability problem at that level.

As we move to lower concentrations... this is another study of effluents... you can see that at around 30 to 40 and up μg/L that the concentrations between the two labs are comparable.

However, as we move to the 30 μg/L and lower range... this is about 5 to 10 μg/L... we start to see the ratio go up. That means that the other lab, in our opinion, the other lab was contributing metals to the sample in some way.

The best study that I can present to you is one that Herb Allen provided the comparative data for.

You can see that at 6 to 8 μg/L copper, there was good agreement. The ratio was about 1:1. As we move to lower concentrations, between 6 and 1 μg/L, there is a very strong increase in the ratio, indicating false positives in the samples not processed using clean techniques.

This slide shows an inter-comparison for lead using the same samples. This is lead at about 40 to 100 μg/L. Fairly good agreement was achieved, but we start to see noise develop at the 40 μg/L. We also see noise down below 10 μg/L. Especially here at even lower concentrations, there is a very strong increase of extraneous lead in some of the samples, and a lot of variability. There is not a really good inter-comparison there.

I do not have a comparison for zinc below 60 μg/L but the labs were getting about a 1:1 ratio at below 60 μg/L.

This slide shows another problem. In this particular study, the reporting limit for chromium in the effluent was 10 μg/L. We were detecting chromium at around 0.5 to 1 μg/L.

The smooth curve here is basically our result divided into 10, so you get a very smooth curve, indicating that this is a detection limit problem. However, there were three samples that showed high chromium, that fell off the detection limit driven line, again, indicating analytical error or contamination error.

We need to do a little bit more of this type of comparisons. Actually, quite a bit more of this type of work is needed in order to really understand the threshold. I think the threshold for kicking in clean methods is probably somewhere in the 10 to 20 μg/L and down, and ultra-clean is, obviously, below 1 μg/L.

So, the take-home messages from my talk today is that contamination can be controlled through proper sample handling and analytical procedures. The methods have been around for 20 years.

Clean methods are required when metals concentrations, I think, are less than 20 ppb. I think the threshold may be metal-specific, and I think more study is needed to identify where those thresholds might be applied. However, I am not trying to imply that you can get away without some serious attention to clean metals analysis regardless of the actual level of metal in the sample.

Clean room benches and closed processing of samples and digestion are needed to control lab contamination.

I think your choice of samplers and sample containers is critical to high quality results. Again, there is literature that tells you what you should use, and EPA is, I think, bringing that together in some of the new guidance that they are developing.

Finally, method detection limits must be lower than presently required for routine monitoring. I think that is a given we heard about a little bit ago.

Finally, knowledge of matrix-specific interferences at the instrument level is critical to achieving good quality trace metal results.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Do we have any questions?

MR. SLENTZ: My name is Kurt Slentz. I am with Energy Labs in Rapid City, South Dakota. I guess I have one question. We have a lot of our samples that come through by UPS, and when you are talking ultra-low levels for mercury, let's say, would you recommend a trip blank for those samples?

MR. HUNT: A properly identified trip blank, I think, would be appropriate. Again...and I think Nick Bloom is here and could give you a lot more guidance in terms of specific mercury handling procedures, but those sample bottles need to be bagged properly, double bagged to control for any extraneous input, but I think a trip blank would be advisable.

MR. SLENTZ: Also, do you think that it would be possible for people without chemistry backgrounds to successfully sample at those levels?

MR. HUNT: I very much think people can be trained as long as they are sensitized to the appropriate way to handle the sample. It is not a one-day training, however. It is going to require some intensive effort to teach people how to touch a sample, where to touch a sample, but it is certainly possible.

MR. HORNG: My name is Albert Horng from HTMA, Colmar, Pennsylvania. You mentioned the importance of sampling. If you have to do both organics and metals and you have no choice but to use one container, the way we do it now is we use glass, a glass container. The problem is boron.

If we have no choice, do you know of any company that makes 2 or 3-gallon teflon containers?

MR. HUNT: I know there are 2-liter bottles. Whether or not you can get a 12-liter sample bottle I am not sure.

It seems awfully expensive to me to have to sample that way. I think you can use a cheaper way of going about it. I am not sure exactly what that would be, though. I would need to sit down and think a bit about it.

MR. HORNG: Sacrifice boron?

MR. HUNT: Again, please?

MR. HORNG: Sacrifice boron?

MR. HUNT: I do not know.

MS. ASHCRAFT: I believe I can understand what a clean room is, but I am not sure what you meant by a clean bench. Can you describe what you would call a clean bench to us?

MR. HUNT: Yes, a clean bench is simply a lab bench that has, in most cases, a HEPA filter that removes particles to a certain level. Class 100 means, I think it is, 100 particles per cubic meter.

There are two styles. There is one where the HEPA filter is on top and the air is brought down to the working area of the bench and it exits the front. The other one is where the HEPA filter and the air blower is in the back side, and it blows out to the analyst.

MS. ASHCRAFT: So, it would be like biological cabinets?

MR. HUNT: Yes, essentially that, and they are commercially available.

MR. EPSTEIN: Paul Epstein, National Sanitation Foundation. Have you noticed any problem with sample bottles now that there is an awful lot of recycled plastic out in the world? We have had one case where...these were not bottles. These were little molds that we were molding cement cubes in, and the plastic was recycled from battery cases. So, there was a severe lead problem in these molds.

MR. HUNT: That is scary. I do not have any evidence one way or the other, so I cannot say. In our labs, we reuse bottles, and we clean them, so we may not have that problem.

I can relate back in the early '70s, there used to be a polyethylene bottle that was black or brown, and had a horrible cadmium problem, because that was the plasticizer that was in the plastic.

So, yes, it may be something we need to look at, but I do not know of any studies that are really looking at this issue. That, again, is why bottle blanks should be run on the bottles you have.

MR. EPSTEIN: Thank you.

MR. BERNARD: John Bernard, Alexandria Sanitation. For Mr. Telliard, in your protocols, a question about in calibration standards, running them through the digestion process. Could you comment on that?

MR. HUNT: Calibration standards through the digestion process, normally, our calibration standards are not run through the digestion. It is an instrument calibration, and samples are run in the matrix that is the final matrix that we extract from a sample.

MR. TELLIARD: And that is similar to what the draft methods are right now. They do not go through the digestion.

MR. BERNARD: Would it make a difference?

MR. TELLIARD: Probably.

MR. HUNT: It might, but the critical thing there, to me, is running procedural blanks as well as spike recoveries. Those are the techniques that are designed to pick up any problems in the digestion.

MR. BERNARD: But your whole, your instrument response is based on your calibration standards. Shouldn't they be treated the same as your samples?

MR. HUNT: No, I don't think they need to be, because if you are matching up your matrices properly and the chemicals you are using to standardize your instrument, again, are traceable, you should not have a problem with that.

MS. DINSMORE: Donalea Dinsmore from Wisconsin. Are your samples collected with composite techniques, or are these all grabs?

MR. HUNT: That is usually specific to the various programs that we are working with. The municipal studies that I showed you were generally 24-hour composites, but the work that we did in New York Harbor were grab samples, and a lot of our work is based on grab samples.

MS. DINSMORE: Thank you.

MR. TELLIARD: Thank you, sir.

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Trace Metal Clean Techniques:
Problems, Quality Assessments, and Comparisons

Carlton D. Hunt
Dion A. Lewis

Battelle
... Putting Technology To Work

Ocean Sciences
Duxbury, MA

Objectives

- Discuss major roadblocks to achieving accurate metals results
- Convey required Quality Control assessments
- Present recent comparative results
- Identify preliminary thresholds for initiating clean methods

Achieving accurate results using clean metals techniques is primarily a function of the *execution* of appropriate analytical techniques rather than the application of new procedures!

Definition of "Clean" Methods

The application of sampling and laboratory techniques that are necessary to accurately quantify contaminant concentrations in the low and sub part per million range ($\approx$20 to 0.1 μg/L) in fresh and marine waters.

Includes the attainment of a consistently low, known metals contribution from sampling and analytical procedures.

Definition of Ultra-Clean Methods

Targeted zero contribution of extraneous contamination to the analytical result at the sub part ber billion and part per trillion concentrations through the use of clean room technologies and intensive contamination control strategies at all stages of sample collection, storage, processing, and analysis.

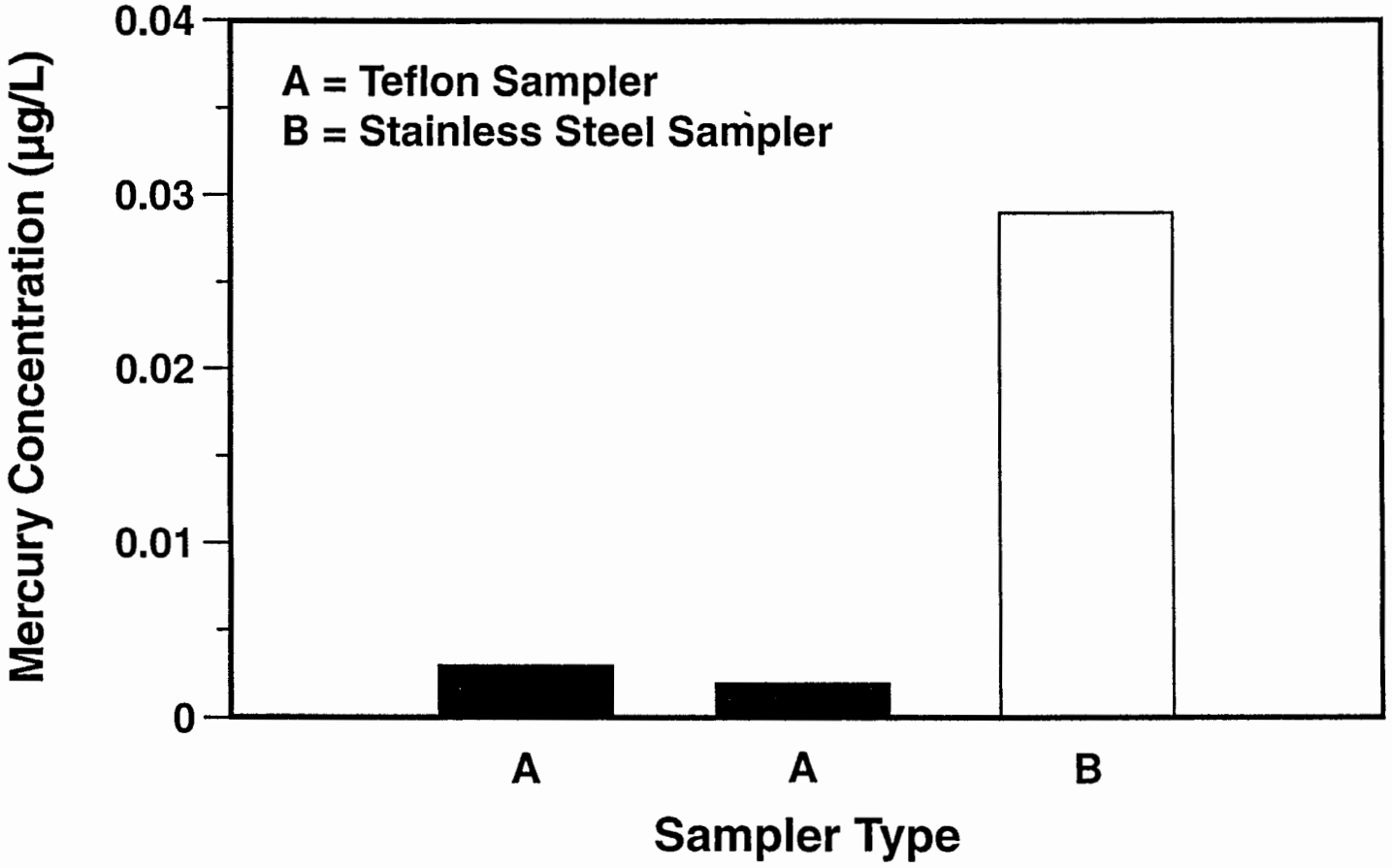
Causes of High Results

- Sampling errors
- Containers
- Reagents/processing
- Analytical interferences

Sampling Errors

- Improper sampling devices
- Poorly cleaned sampling devices
- Improper sampler deployment
- Uncontrolled atmospheric contamination
- Improper clothing and gloves
- Poor sample transfer and handling procedures

Mercury Field Blanks - Stainless vs Teflon Samplers

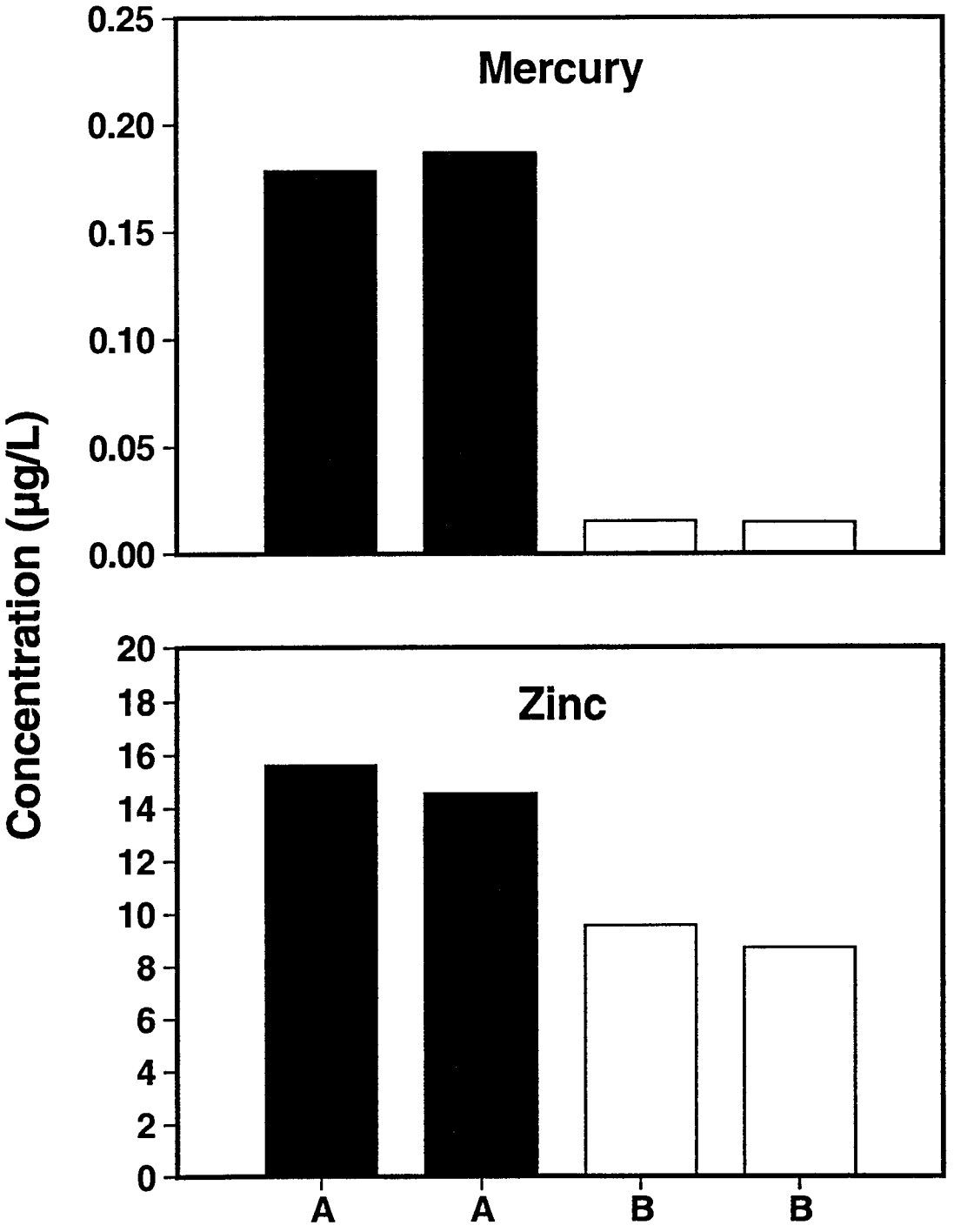


PErs/Hunt/20-5

Containers

- Non-contaminating materials — plastics are first choice
- Compatibility with metal — Teflon for Hg; LDPE, HDPE other metals
- Cleaned containers
  - Commercially available; independent bottle blanks
  - Additional hot acid cleanup for low level analysis
  - Shelf storage with high purity dilute acids

Preservation Acid and Collection Container Comparisons



A = Polyethylene; Reagent Grade Acid

B = Teflon; High Purity Acid

CD3/Hunt/20-7

Reagents and Processing

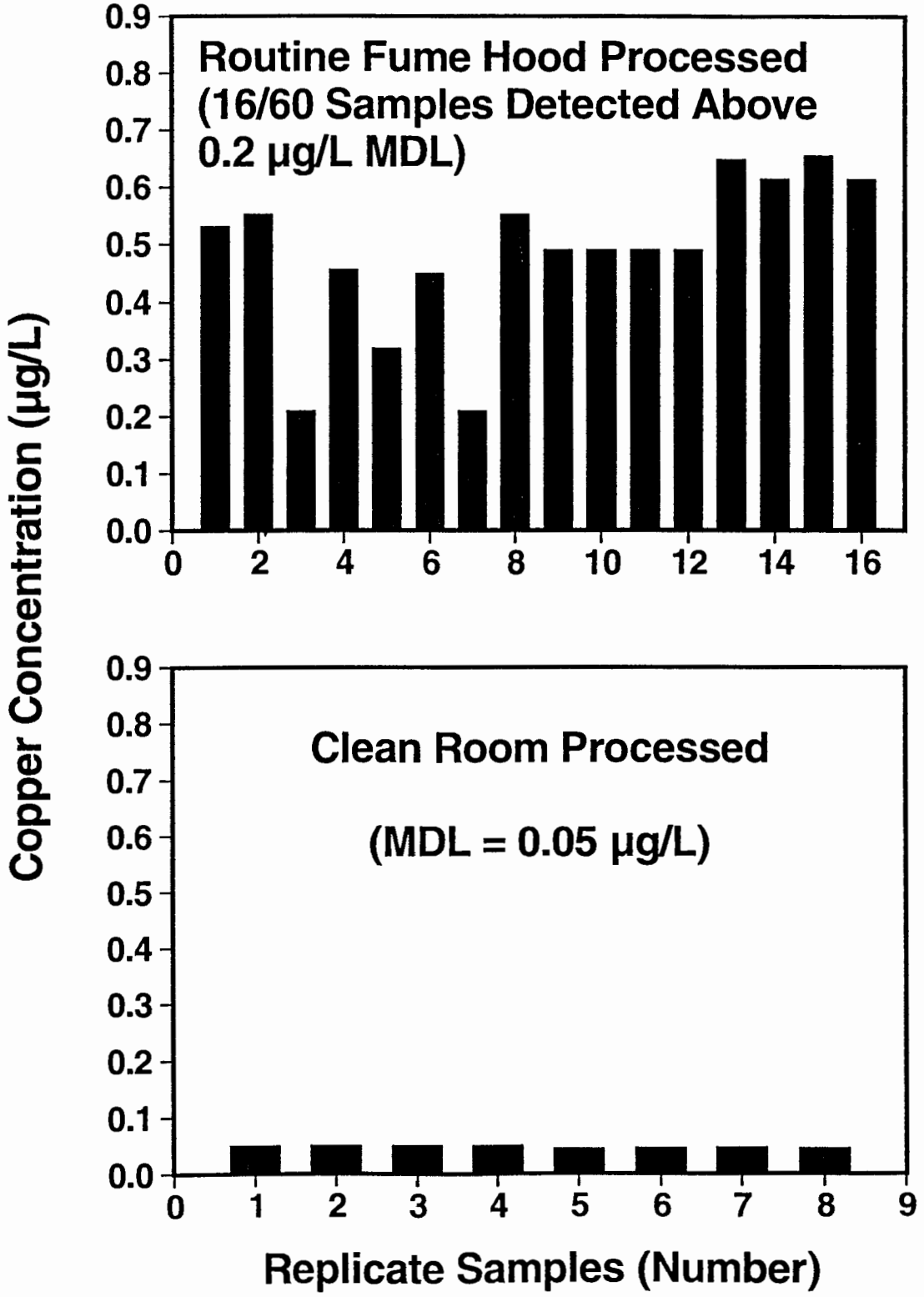
- Use of high purity reagents: chelator, acids, solvents
  - Commercially available; blanks must be checked
  - Purification via extraction; blanks must be checked
- Routine use of highest purity deionized water
  - Subboiling distillation for ultra-clean
- Identification of reagent and procedural blanks prior to conducting analysis
- Routine use of procedural blanks
- Know the potential sources of the contamination and causes of blank variability
- Consistent and low blanks relative to analytical signal <10% of lowest value expected

NKA/Hunt/19-06

Procedural Blanks (ng/L)
Ambient NY/NJ Harbor WLA Study (n = 6)

	Metal			
Method	Cu	Pb	Zn	Ni
Total Recoverable	60 ± 60	9 ± 1	180 ± 90	220 ± 300
Acid Soluble	9 ± 1	4 ± 3	80 ± 40	60 ± 40
Dissolved	12 ± 6	<2	60 ± 20	60 ± 30
Lowest Measured Value	400	40	44	250
Blank Contribution (%)	15	23	41	88

Total Recoverable Copper Method Blanks



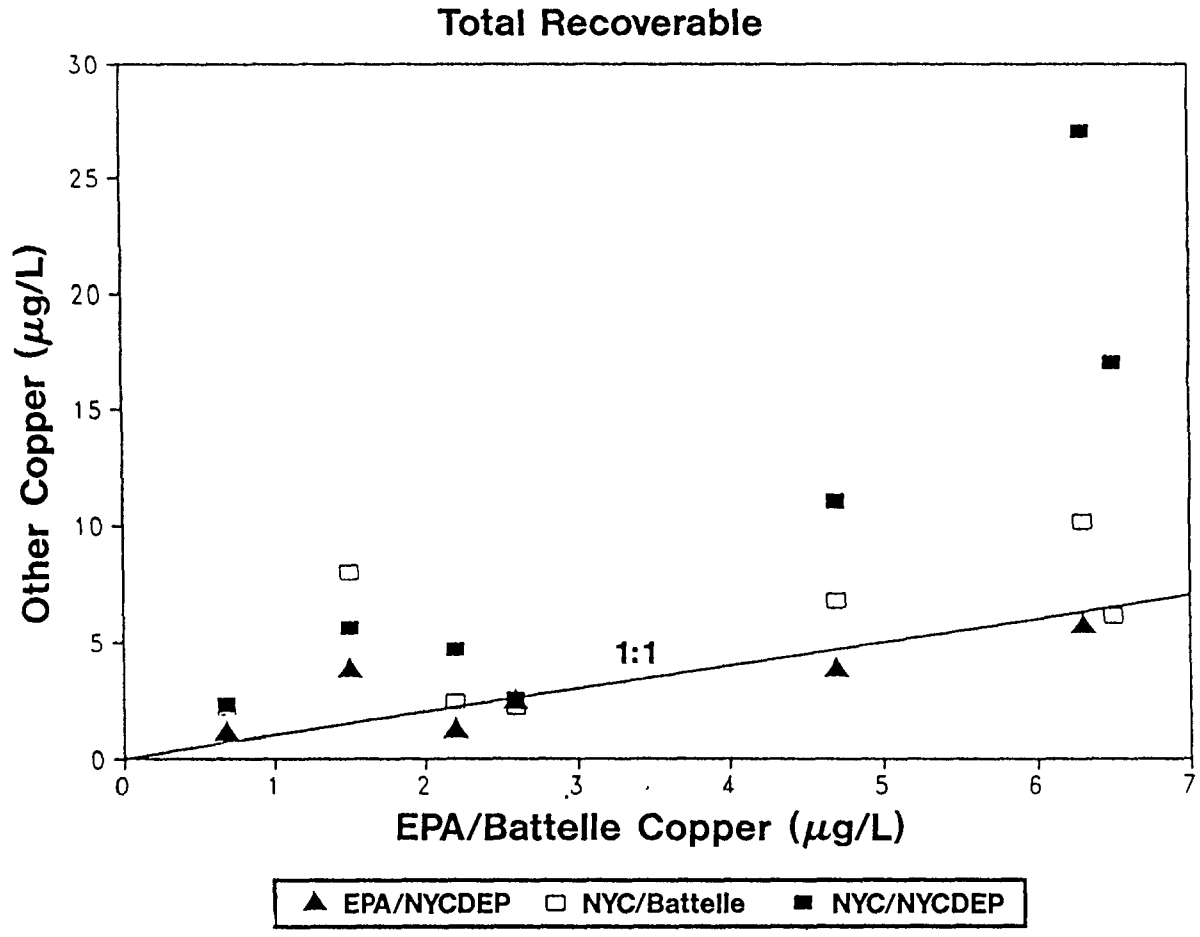
CD3/Hunt/20-6

Analytical Interferences

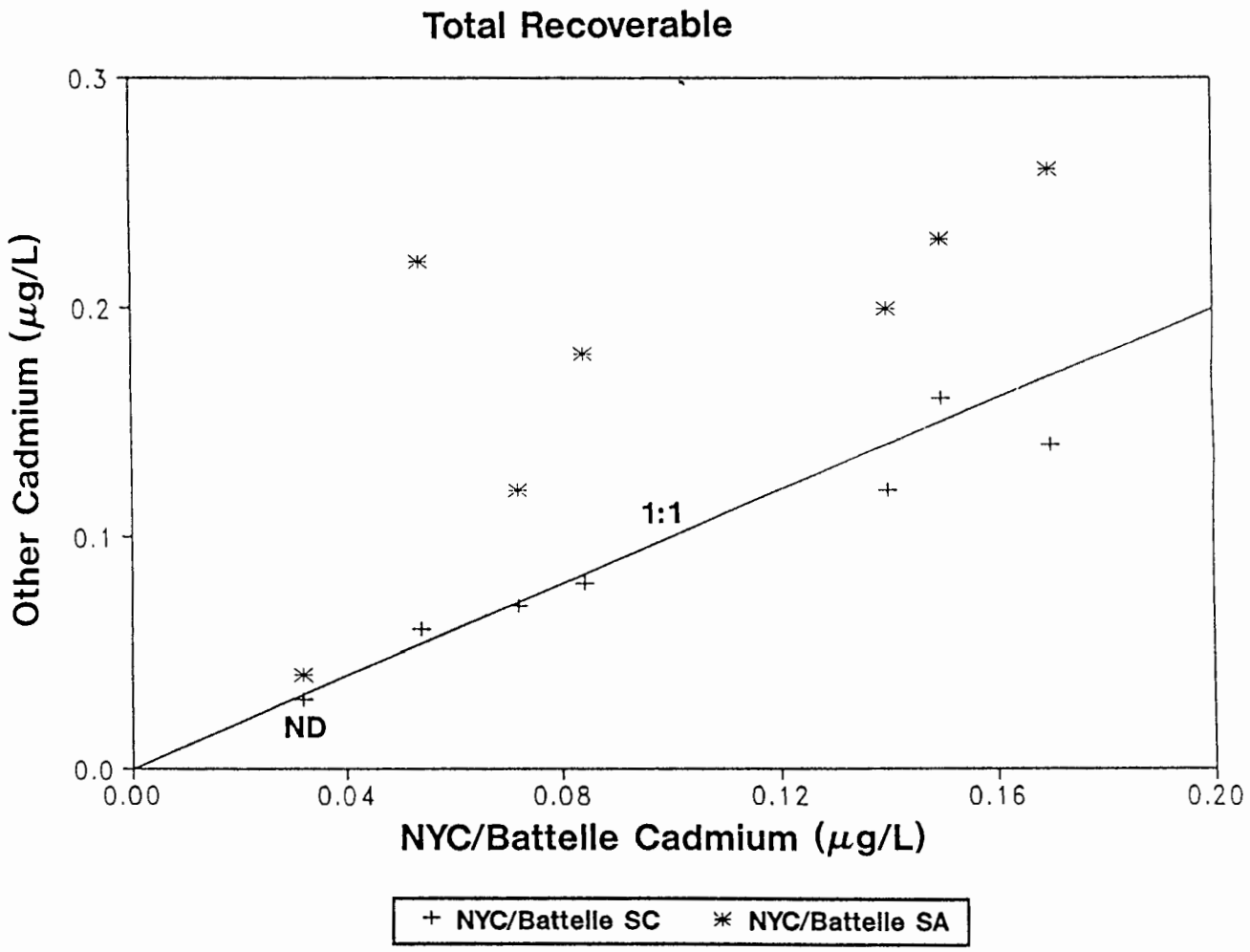
- Application of appropriate quantification techniques to metal level expected
  - Graphite furnace, ICP/MS, flame AAS, etc.
- Appropriate use of standard, standard addition or standard addition calibration curves
  - Know the matrix being analyzed, calibration curves appropriate to the sample type
- Use matrix modifiers to reduce interferences
  - Know when to use these and the applicable matrix
  - Don't assume matrix modifiers work for all matrices and instrument settings

NKA/Hunt/19-04

Analytical Comparison

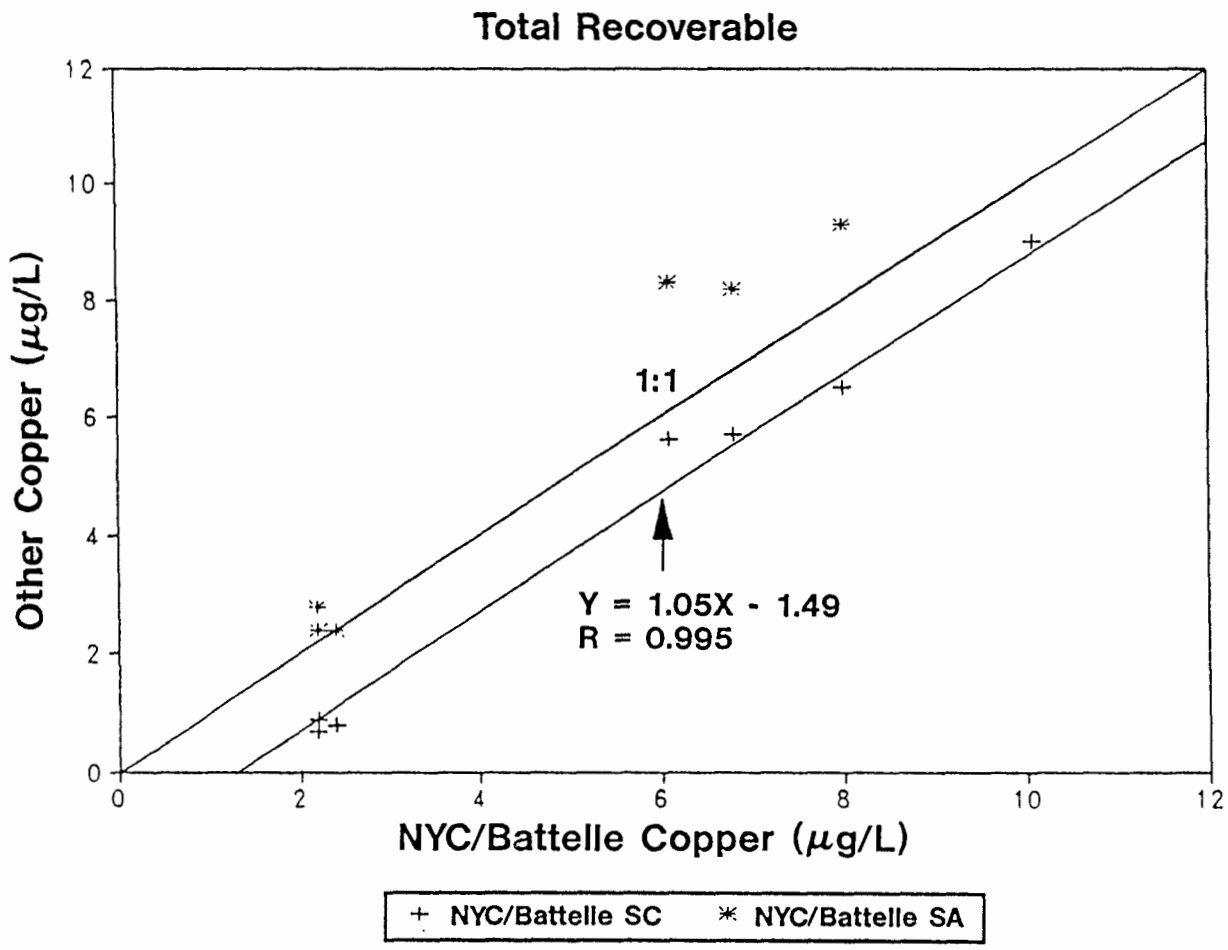


Instrument Calibration Methods



1:1 = Extracted Sample

Instrument Calibration Methods



1:1 = Extracted Sample

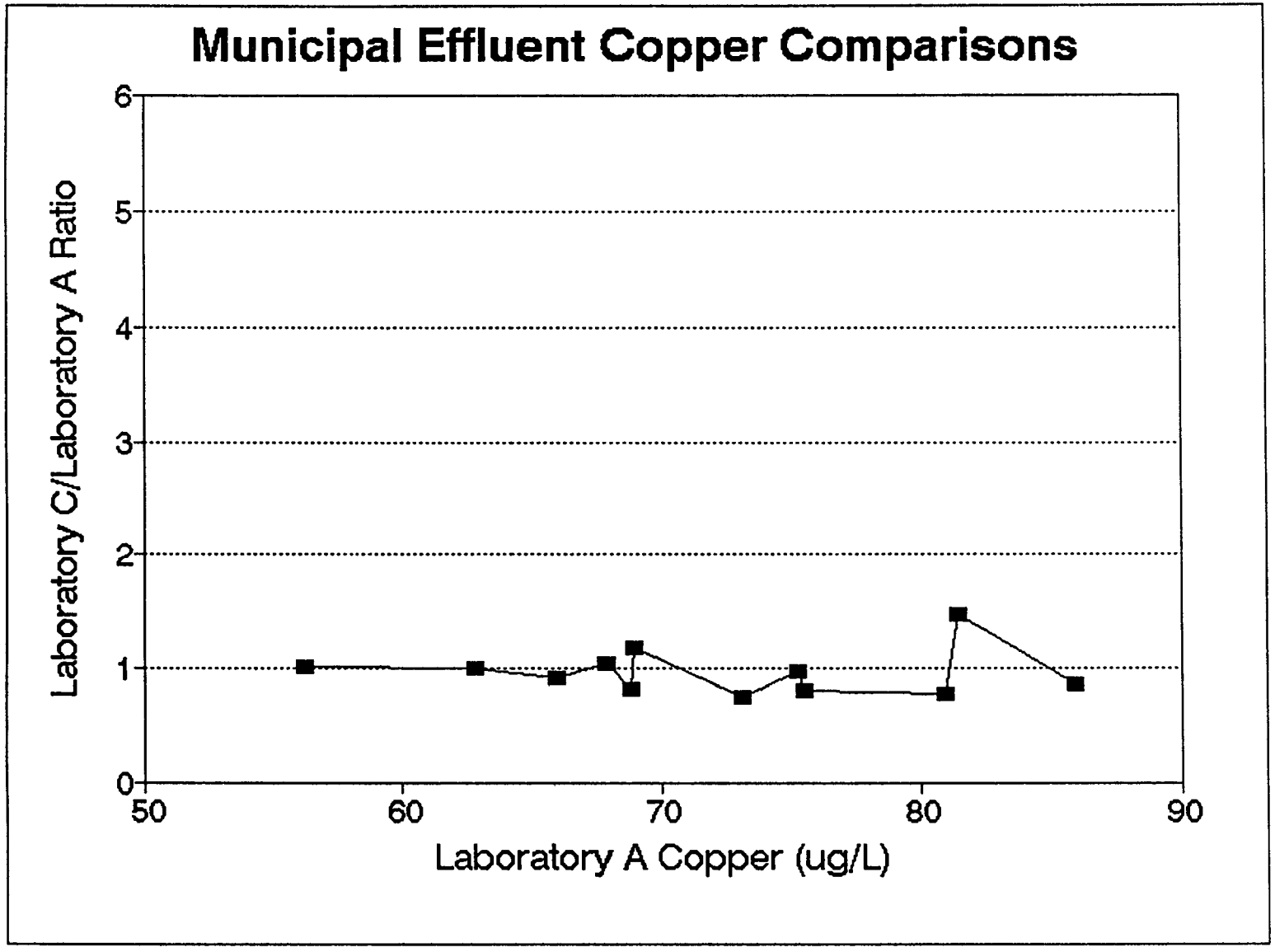
Successful Application of Clean Methods Requires

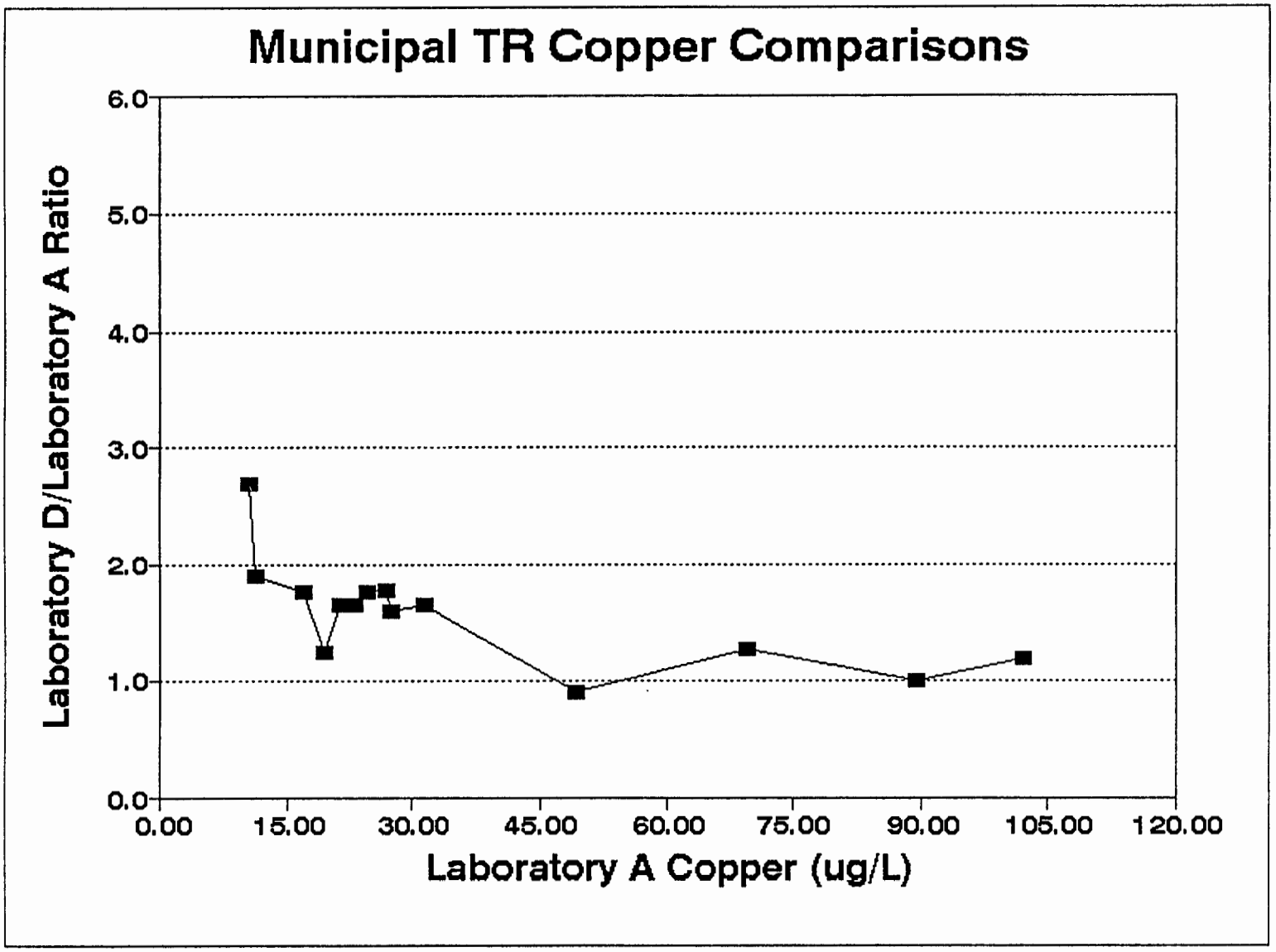
- Systematic identification and control of extraneous contaminant sources during sampling and analysis
- Awareness and application of specialized cleanup procedures for storage containers and laboratory ware
- Use of high purity reagents, reagent cleanup procedures, or both
- Isolation of samples from atmospheric contamination sources

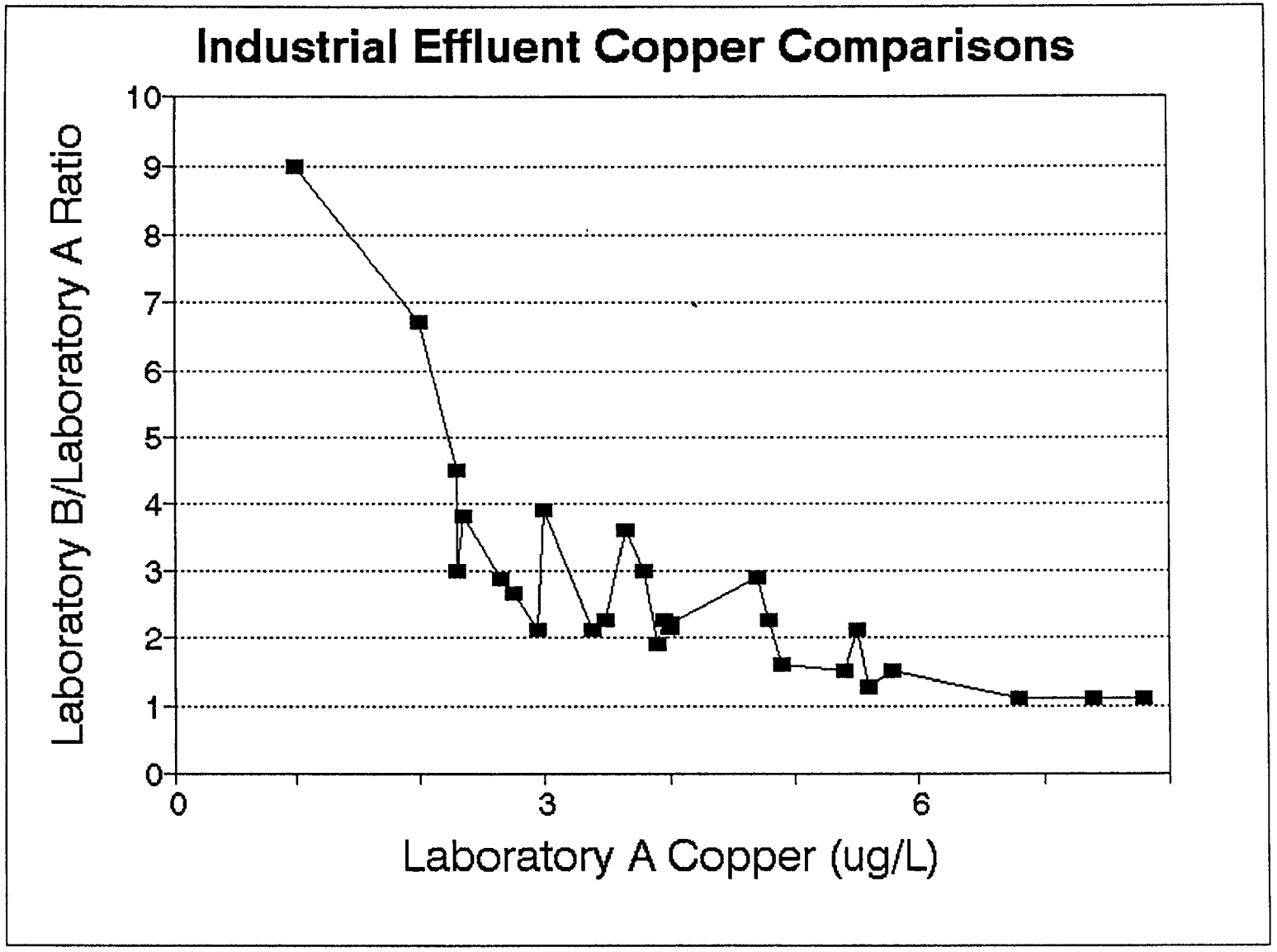
Successful Application of Clean Methods Requires (Continued)

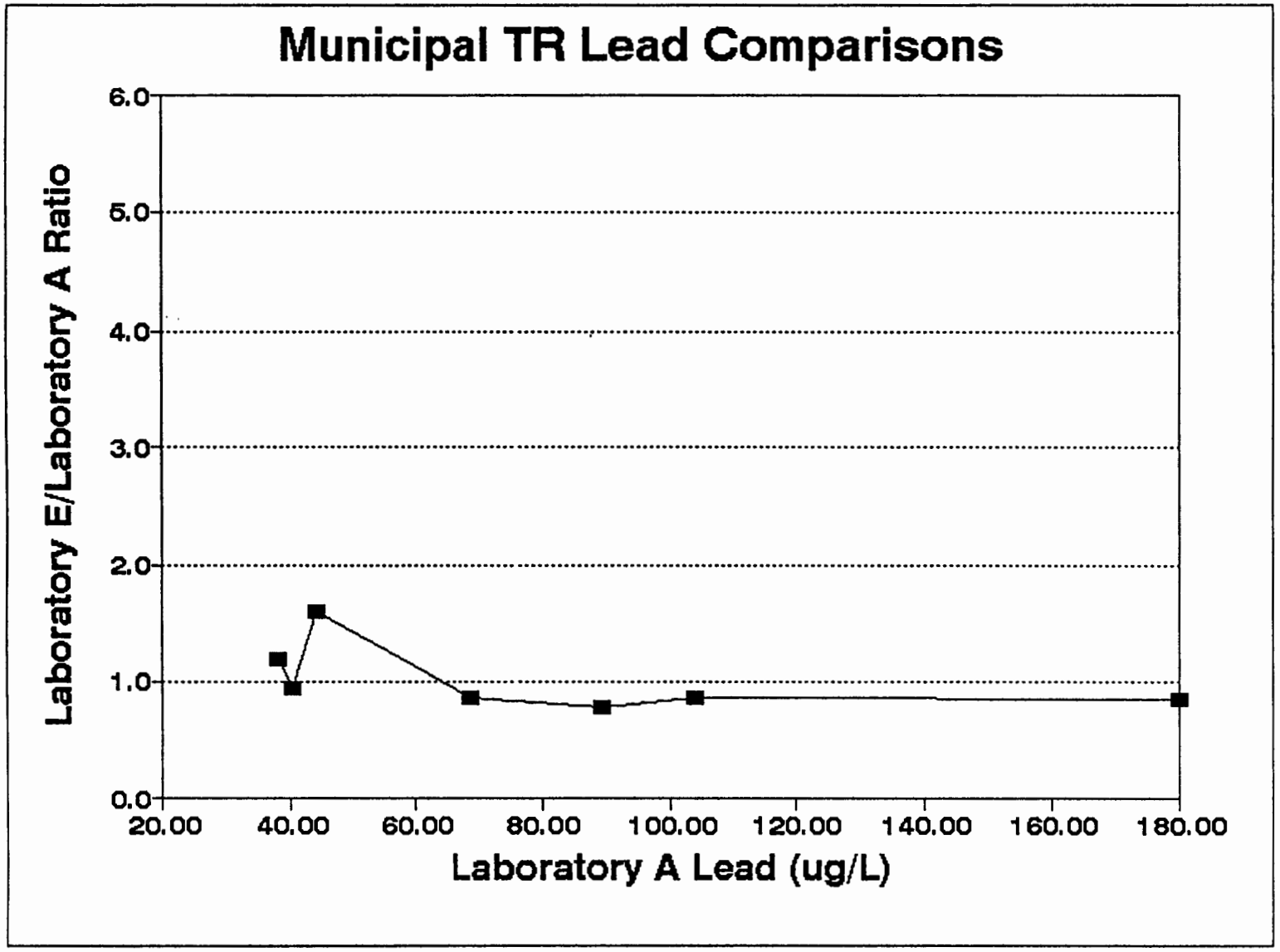
- Control of analytical interferences
- Early evaluation and application of appropriate QC techniques procedures including
  - Procedural blanks
  - SRMs
  - Matrix spike recoveries
  - Replicates

NKA/Hunt/19-10


Municipal Effluent Copper Comparisons
Laboratory C/Laboratory A Ratio
0
1
2
3
4
5
6
50
60
70
80
90
Laboratory A Copper (ug/L)


Municipal TR Copper Comparisons
Laboratory D/Laboratory A Ratio
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.00
15.00
30.00
45.00
60.00
75.00
90.00
105.00
120.00
Laboratory A Copper (ug/L)


Industrial Effluent Copper Comparisons
Laboratory B/Laboratory A Ratio
10
9
8
7
6
5
4
3
2
1
0
0
3
6
Laboratory A Copper (ug/L)


Municipal TR Lead Comparisons
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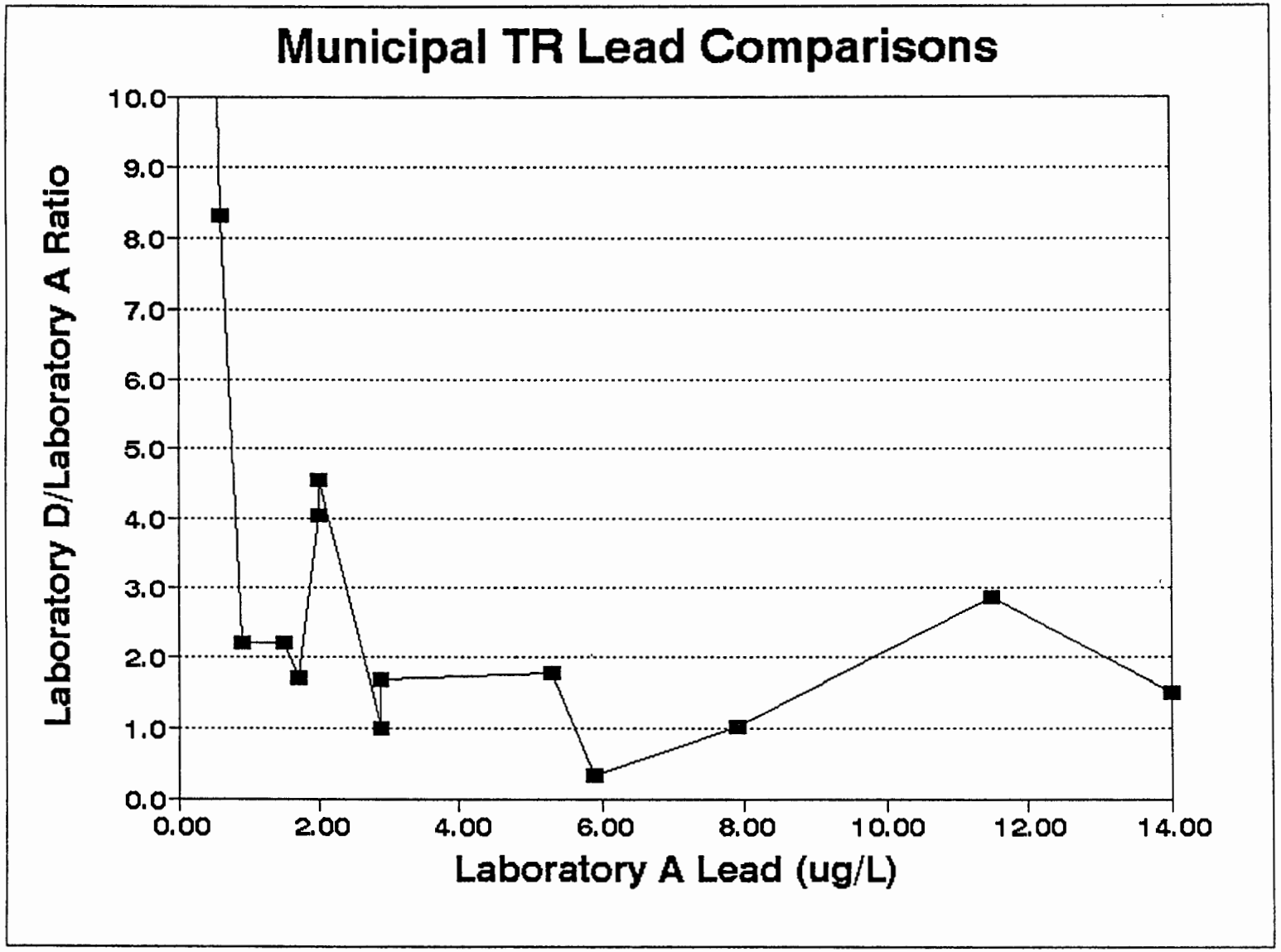
5.0
4.0
3.0
2.0
1.0
0.0
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
Laboratory A Lead (ug/L)


Municipal TR Lead Comparisons
Laboratory D/Laboratory A Ratio
10.0
9.0
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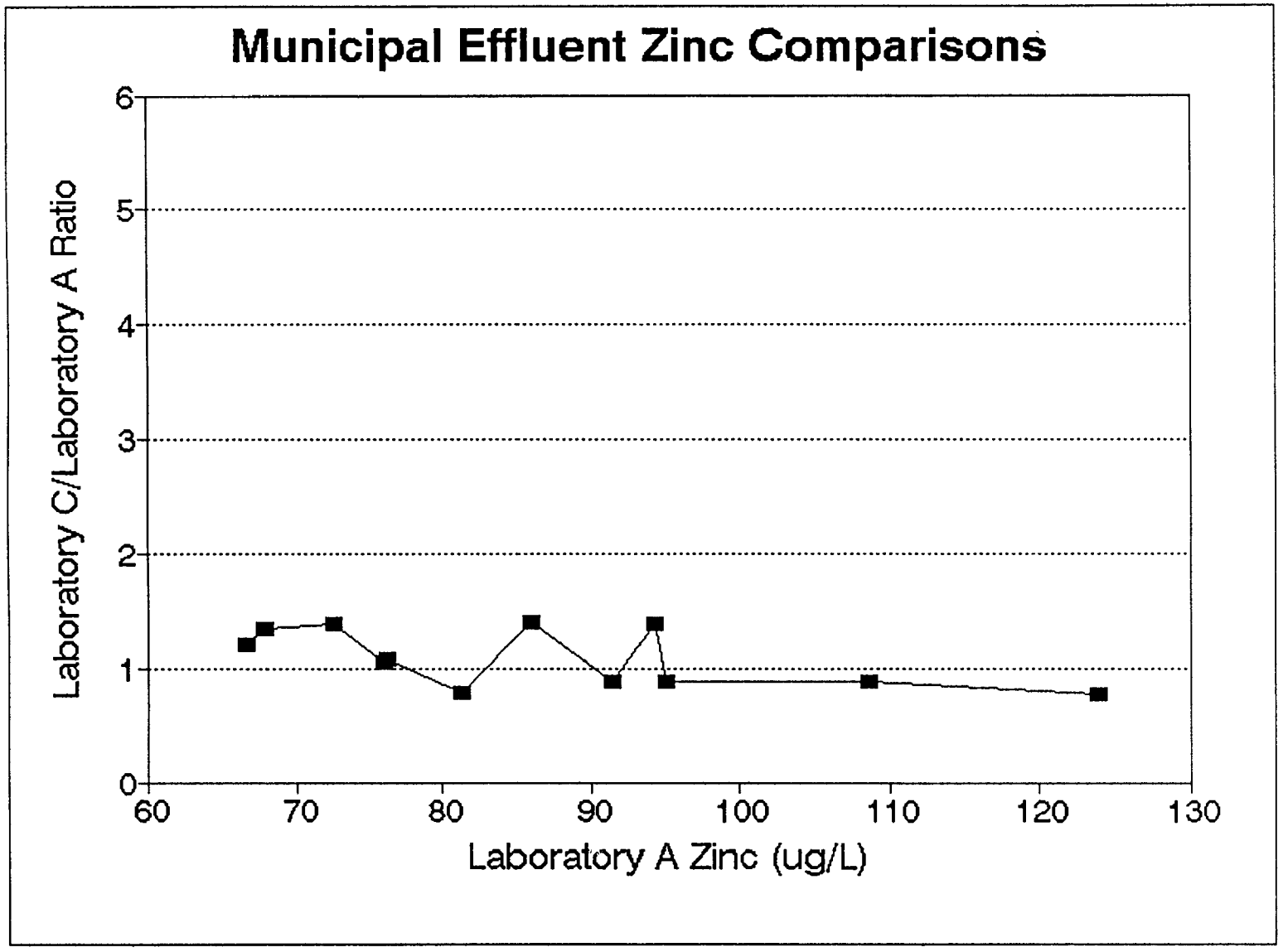
10.00
12.00
14.00
Laboratory A Lead (ug/L)


Municipal Effluent Zinc Comparisons
Laboratory C/Laboratory A Ratio
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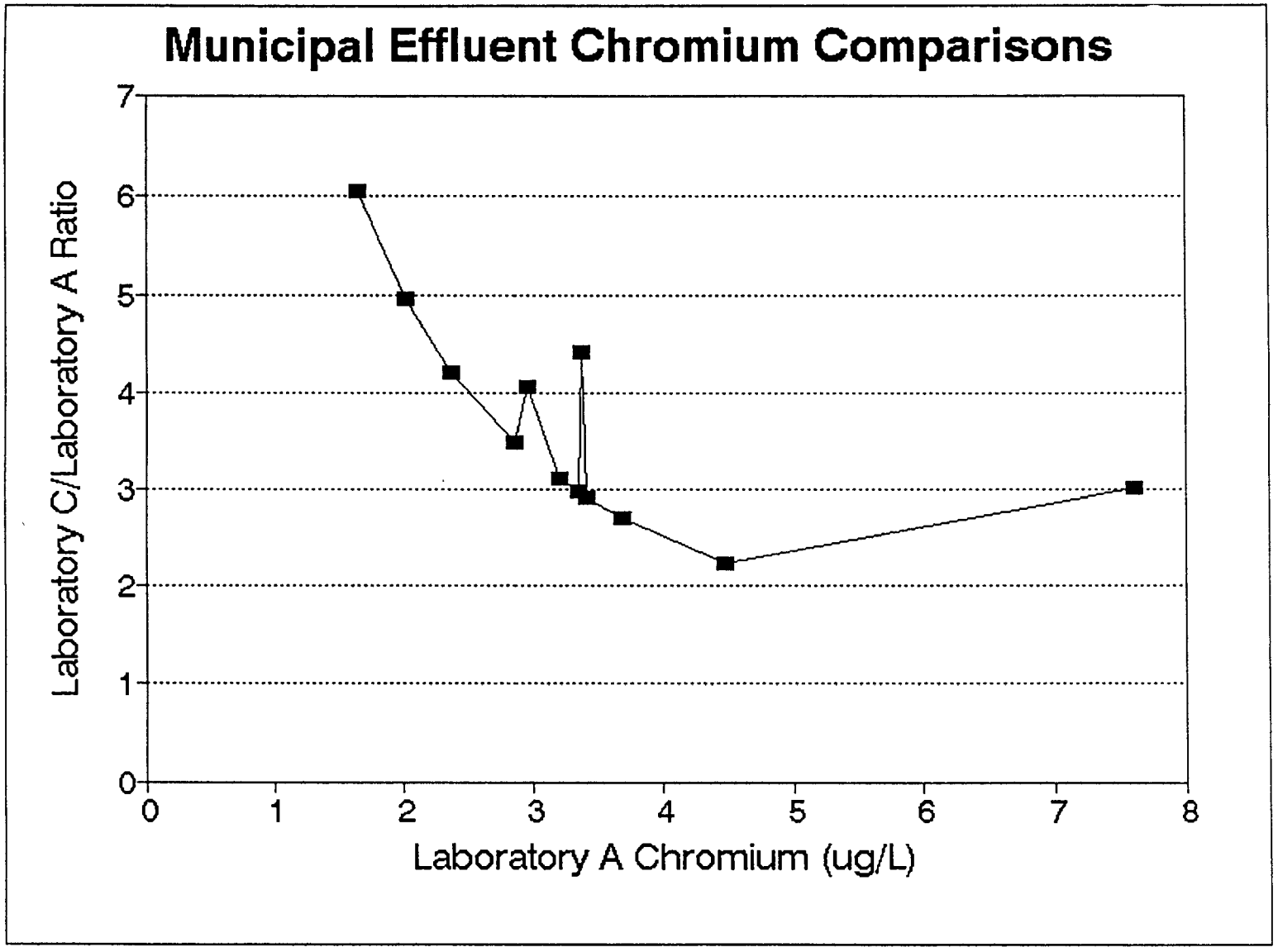
2
3
4
5
6
60
70
80
90
100
110
120
130
Laboratory A Zinc (ug/L)


Municipal Effluent Chromium Comparisons
Laboratory C/Laboratory A Ratio
0
1
2
3
4
5
6
7
0
1
2
3
4
5
6
7
8
Laboratory A Chromium (ug/L)

Take Home Messages

1. Contamination can be controlled through proper sample handling and analytical procedures.
2. Clean methods are required when metals concentrations are <20 µg/L.
   - Threshold is metal specific
   - More study to identify metal specific thresholds
3. Cleanrooms (benches) or closed processing and digestion are needed to control blanks.
4. Choice of samplers and sample containers is critical to high quality results.
5. Method detection limits must be lower than presently required for routine monitoring.
6. Knowledge of matrix specific interferences at the instrument level is critical.

Table 1
EPA WQC, Riverine Metal Levels, RLGs and MDLs (µg/L)

Analyte	Cd	Cu	Hg	Pb	Zn
EPA Freshwater WQC	1.1	12	0.012	3.2	110
Ambient Riverine[1,2]	0.03	2.76	0.001	0.13	3.33
Recommended RLG	0.006	0.6	0.0002	0.03	0.67
ICP MDL	1	3	7	10	2
GFAA/Hydride MDL	0.05	0.5	–	0.3	0.5
ICP-MS MDL	0.5	0.5	–	0.6	1.8
CVAAS	–	–	0.02	–	–
MDL with Preconcentration	0.005	0.02	0.0002	0.02	0.02

[1]Ottawa River Cd, Cu, Pb, and Zn (Canadian Research Council, 1990)
[2]Mobile River Hg (Battelle, unpublished)

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MR. TELLIARD: Our next speaker is from the U.S. Geological Survey. Tim Miller is the Assistant Chief of the USGS' Office of Water Quality.

Over the last few months, EPA and USGS have been looking at protocols both for sampling and for analysis. We felt... I am sorry to say this... that it probably was not worthwhile reinventing the wheel. Now, that goes against our previous policies. We have a number of wheel factories that are downsizing. We have been... I know this again shocks you... talking to our brothers at the U.S. Geological Survey and trying to get input from them, again, both from the field and the analytical end.

So, Tim is going to specifically address their efforts and, hopefully, shed some light on the problem.

U.S. GEOLOGICAL SURVEY PROTOCOL FOR MEASURING LOW LEVELS OF INORGANIC CONSTITUENTS INCLUDING TRACE ELEMENTS IN AMBIENT WATER SAMPLES

MR. MILLER: Thank you, Bill.

I am glad to be here. This is the first time I have had a chance to attend this conference, and I have got to say I am very impressed. For the first full day of presentations, Bill arranged for the weather outside to ensure that all of you would be in here listening to the speakers, and we appreciate that.

I think the presentations so far have made my job a little easier this morning because they have already discussed contamination sources and problems. I am going to tell you about a protocol for collecting inorganic surface-water samples that we have implemented in the Geological Survey this year. For those of you looking at the abstract, you can change the title. It should say trace elements in ambient water samples instead of waste samples. The USGS protocol focuses really on working in ambient waters.

Basically, Carlton Hunt has identified many of the contamination problems that we were facing. In addition, Jim Hanlon mentioned that the quality of some of the USGS data has been questioned in the literature. Indeed, going back to 1987, there was an article by Shiller and Boyle and then, subsequently, another by Flegal and Coale, and a recent article by Herb Windom. We have discussed the critical comments with a number of the authors, and found their concerns were justified.

What we are talking about, are problems that we have had in our operational program, not in our research program. Sampling for trace elements in our operational program probably includes more than 600 to 700 people.

In some cases, we have had to convince people that this change is really necessary, and then, also, to provide the training so they understand what needs to be done is quite a daunting task. So, what we are talking about is essentially changing our operational program culture.

We are now in the process of convincing people that the culture needs to change, the field process needs to change, and the analytical process in our laboratory needs to change as well. What I will tell you about this morning are many of the changes that have recently been put into place.

We often work in river systems where, in contrast to marine systems, trace element concentration changes in time and space are highly variable because of suspended sediments, and organic carbon. So, we typically collect depth and width integrated, composite samples, that are flow weighted or volume weighted for the cross section. Why have we introduced a ppb protocol? Many of the Federal water-quality criteria are at or near the ppb level. Our intent is to upgrade our sampling program so that we can collect samples relatively inexpensively and clean.

We have several key messages. I am going to highlight these as I would to individuals in our organization. What are the key messages from the protocol?

One is we want to make sure that people understand that inorganic samples can easily be contaminated; and that those sources of contamination can be identified and controlled through proper cleaning, proper sample equipment selection, proper analytical techniques, much of what Carl was talking about just a few minutes ago.

In addition to that, the next key message is ensuring that you have adequate quality control data. Following the protocol is not enough; quality control data is needed to quantitatively determine that contamination is within the desired level of control. Historically, our operational program did not collect quality control data to demonstrate contamination was adequately controlled.

The protocol that we have developed has been predicated on about five years of work, following much of the critical comments both from outside USGS and also internally to our organization. A series of experiments were employed to determine our level of contamination problems, and to test various equipment and cleaning procedures. The decisions that we have made in designing and implementing this protocol have been based on these experimental data.

One of our major experiments was a 1990 inter-calibration study on the Mississippi river; where we took our standard techniques that are used in the field by the operational program and compared results from that approach to results from what we were using in our research program.

We also invited along on that experiment, Alan Schiller, who was one of our initial critics in the literature, and who is now at the University of Southern Mississippi. We did a complete cross-comparison of the techniques including sample collection, processing, and analytical techniques; and the result from that comparison was the basis on which we argued within our agency, that we needed to make major changes to the field protocols we were then using. All of the changes for our protocol have been substantiated by field tests, by quality control samples, and have been tested in many different hydrologic and atmospheric environments.

The protocol that we have released is targeted towards filtered samples. Filtered samples present more of a sampling challenge because ambient trace element concentrations are low in these samples. So, we focused on filtered samples to be sure our procedures were adequate for easily contaminated samples.

Even for unfiltered samples, we know there are samples that have very low to moderate suspended sediment concentrations. Unfiltered samples with low sediment concentrations are susceptible to contamination; so, the protocol is needed for unfiltered samples too. For unfiltered samples, the protocol is applicable even if the concentrations of sediment are high. We have shown in a number of our trials that there can be adequate contamination to bias samples with high sediment concentrations as well. So, our argument is that even for the unfiltered samples, whether the sediment concentration is low or high, cleaner techniques need to be used.

The field protocol that we are employing has the following components: first, we have a certified list of equipment and supplies; second, there are four procedures which I will briefly go over in a few minutes, two are for cleaning, one for field rinsing, and one for processing and preservation; third, we have a very substantial emphasis on training, and although it does take a few days of training the protocol can be used even by relatively inexperienced people; and finally, we are recommending a minimum level of quality control data be collected, and we are providing guidelines for how those quality control data can be used.

The equipment that we suggest for this protocol are sampling devices that will allow us to collect a depth and width integrated sample in a river system. These are D77 samplers. I will show you a slide at the end of the overheads that illustrates what this equipment looks like. They basically have teflon or plastic internal components that can be adequately cleaned. There are a number of environments that we cannot sample right now with this sampler. For example, under ice sampling, and in some large rivers with depths of 50 to 70 feet, and flow rates as high as 15 to 20 feet per second.

The next overhead is a list of the supplies that we have recommended in the protocol. It is similar to the types of supplies Carl mentioned to you. Gloves are a requirement, the non-powdered type. We are also specifying certain types of filters in order to simplify the filtering process and minimize contamination. The list of supplies identifies

what has been tested to date and what we are certifying for our protocol which is set at 1 ppb right now.

The protocol also emphasizes to make sure that the equipment is adequately cleaned. Preferably, we want people to clean the equipment in the office before it goes out to the field. We also have an acceptable approach for cleaning between sites; because we realize in our operations, people are often out in the field for a week at a time, and it is not convenient to go back to the office and clean the equipment.

I will quickly run through the process for cleaning equipment in the office. The equipment is broken down, soaked, and cleaned with a detergent like liquinox, then copiously rinsed with hot tap water, followed by a cleaning and soaking in 5 percent hydrochloric acid, three rinses with deionized water, and then the equipment is double bagged and stored until it is used.

I want to digress a moment and mention that we have modified some of our equipment such as a compositing device to better shield samples from atmospheric contamination. We are suggesting that our field offices set aside a dedicated vehicle for water-quality sampling; that will alleviate historical problems when vehicles are used for purposes incompatible with water-quality sampling. In addition, we have specified using a processing enclosure which is very inexpensive to construct; it is made largely out of plastic, but some people have constructed them out of PVC and wood.

We are also specifying the use of a preservation chamber. Our samples are collected, processed, and preserved in the field, because, it is often 48 to 72 hours before they can be mailed to the laboratory. Preservation can be done using glass vials with ultra-pure nitric acid at $5 each; however, the acid is contaminated by the glass for some elements such as aluminum, boron, and sodium. If contamination of those elements is a problem, an alternative at $16 each are teflon vials with acid contamination well below 200 ng/L.

We also looked at the filtration process. We recommend use of a capsule filter. The product we have tested happens to be a Gelman Supore capsule. It is very easy to clean, and filtering is easier because of the large filter surface area.

A capsule filter is relatively inexpensive. It does cost more than the plate type filters that we have been using in the past, but when you consider the amount of time and effort it takes to clean plate filter holders, the capsule is really a cost-effective approach. I n addition, the cost difference is more than compensated by the reduced potential for contamination using a capsule filter.

Now, I want to return to the four field procedures that are included in the protocol. I mentioned the office preparation cleaning and briefly discussed the components of that. In addition, we have a field cleaning procedure used between sites when you cannot return

to the office. The field cleaning requires that the equipment be cleaned while it is still wet, at the site, using hydrochloric acid and deionized water. Both of the cleaning procedures at the part per billion level have been shown in our field tests to work well.

Next, we have a procedure for sample processing and preservation. Processing and preservation is carried out in a work space with specified requirements; and the sequence for preserving samples is also specified. Finally, there is a procedure for field rinsing of the sampling equipment prior to sample collection. That is, conditioning the equipment for sampling at the site using native water.

The other major change for USGS is the protocol requires using two people. The rationale is: probably one of the major ways contamination is introduced into a sample is from a person's hands. At a site that is difficult to sample, it is easy for one person working alone to contaminate a sample. It is too difficult for one person to keep their hands contaminant free with all the equipment they touch. Therefore, a procedure using two people has been deemed necessary by many practitioners of the ultra-clean method, especially when collecting a depth and width integrated sample.

At the site, one person is clean hands and the other dirty hands. The person with the clean hands changes their gloves frequently, and they are responsible for touching the sample bottle, and anything that comes in close contact with the sample. The other person who has dirty hands is responsible for all the rest of the work. With the types of sampling equipment that we use, there is a fair amount of manipulation that the person with dirty hands is required to do.

We have found that the process with two people works quite well. It does take a bit of practice, but with one to two days of training, the comfort level is quite high.

The protocol requires quality control samples. We want an equipment blank run at least annually or with every new crew that handles the equipment to demonstrate that they have the capability of cleaning the equipment. On each run out in the field, then, field blanks are taken. Those deionized blanks are run through the same equipment process and used for the environmental sample so that we have an understanding of the contamination levels introduced in the field.

In addition, we ask that samples be split periodically so that we have better information on laboratory precision. We also request concurrent samples be taken to identify how much variability there is in sample collection and processing.

Finally, in the laboratory, we have done a fair amount of work. All of our trace element samples, even for the ppb protocol, are handled in a Class 100 clean room. We do not use a concentration step in the methods that are currently applying for the ppb protocol. We are using the ICP/MS, and they are about 17 trace elements that are approved in our ICP/MS method.

We are doing two things. First, we are using the ICP/MS on deionized water matrices down around 100 to 200 ng/L for quality control and blanking purposes. Then for the protocol, we are using the ICP/MS to analyze the environmental samples with a reporting level of 1 ppb for most of the elements. The exceptions, I believe, are zinc and aluminum which are at 3 ppb. We are confident right now that, at 1 ppb, we can handle matrix interferences; but down below that, we still have some additional work to do. So, for deionized water, we will go down to the 100 to 200 ng/L level but not for the environmental samples yet.

I will take just a few minutes, to show some slides. This is a D77 sampler; a 65-pound fish made out of either aluminum or brass. It is coated in an epoxy paint, and that is a nalgene or teflon 3-liter bottle that fits inside. We have found that these samplers can be adequately cleaned, but all of the hardware is made out of aluminum and has to be handled. That is the responsibility of the person with the dirty hands. So, the person with the clean hands does not touch any of the metal, metal parts of the bridge or sampling environment.

We also have a wading bottle sampler. Again, in this case, many of the components are all made out of teflon. The rod is aluminum and is coated in a teflon sheath.

The compositing device that I mentioned is made out of plastic. We call it a churn splitter, because it allows you to homogenize samples. It has a modification, a funnel on top, in order to make it easier to introduce the sample to the churn instead of removing the entire churn cover. There is much less area, then, exposed to the atmosphere. The churn, then, is housed in a carrier which is all plastic. The reason we have gone to this extent to protect the compositing vessel is that many of the environments in which we sample are quite dirty. We are either on bridges or near roads.

These efforts to clean up the environment in which we are doing the sampling, actually works quite well. Contaminant levels are well below a ppb which is our target.

The chambers we use for field processing and preservation are constructed of half inch plastic pipe covered with a clear plastic bag. The outside plastic covering is changed whenever we change gloves or preservative, and we have found these chambers cost maybe $3 to $4 to construct. We have found that they work quite well.

That is where we are right now. Where we are heading is development of a protocol for the part per trillion level. We do not anticipate that that will be deployed any time soon. It will probably be another two years before we are ready to distribute that type of protocol within our division.

We have been talking with Bill Telliard and others at EPA on the development of the protocols that they are working on. The protocol that we distributed in February is an internal document, but if you are interested in taking a look at it, you can write to me at the

Geological Survey. If you look at the abstract, just insert below U.S. Geological Survey, 412 National Center, and the zip code is 22092. We will be happy to try and fulfill any requests that you have.

Thank you very much for listening.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Do we have any questions?

MR. VARNELL: David Varnell with the Tennessee Valley Authority Environmental Chemistry Lab. I was wondering if you could give an estimate of how much additional time all of this preparation and sampling requires for the field people.

MR. MILLER: That is an excellent question.

If a site is normally sampled right now with only one person, then the cost increase is fairly substantial to get a second person to the site. In those cases, we are looking at probably somewhere on the order of 50 to 75 percent increase in cost because of the second person and the added cleaning that goes along with the protocol.

However, if a site is sampled with two people, for example, from a boat or from a bridge now, then the increased costs are relatively minor. They are on the order of 20 to 30 percent increase for the cleaning and for the additional equipment that is required.

Our simple answer to folks in our agency when there is a concern raised on the cost issue is that we would rather have the 20 to 30 percent, even the 50 to 75 percent increase to have data of known and adequate quality than to have data that are questionable. So, we see it as a reasonable cost to pay.

MR. VARNELL: And, basically, the EPA relative to NPDES sampling for compliance, ICP/MS is not presently acceptable. Is that correct?

MR. TELLIARD: I do not know. I think Bill Potter is here from EMSL. I cannot remember Part 136.

MS. KNOX: Excuse me. That was my question also. My name is Robin Knox. I am with Geraghty & Miller, and I looked it up recently in the Federal Register, and ICP/MS by Method 200.8 was not listed as an approved NPDES method unless there has been some update to the regulation that was not available to me.

That was my question also, because there is a need to achieve those detection limits, but yet that methodology is not approved for NPDES as far as I can tell.

MR. TELLIARD: I will check on that and get back to you. I am sure that the update on Part 136, which only happens every eon probably is not the answer, but we will check on it for you and get back to you.

SPEAKER: Depending on which of the methods that will be used, it is going to be considered for the variance in each of the situations?

MR. VARNELL: A variance.

SPEAKER: A variance.

MR. VARNELL: Yes, you can always do that.

SPEAKER: No, but it is a matter of simply from my reading experience or the writing of items...

MR. TELLIARD: This is basically the 8.1.2 in the metals method that says you can change the method or the 9.1.2 in the format that the EMMC has used. It allows you to change the method on a site-by-site basis, but it is not for, quote, national approval.

So, you can use it. It tells you basically you have to do the start-up tests over again and what data you have to generate and put in your binder so that when we kick in your door, you say yes, I am using this thing, and here is the data to show that I have standardized on it.

MR. VARNELL: Okay, and if you do use ICP/MS, are you using hydrochloric acid for preparation and solubilization of the samples? You are only dealing with dissolved right now, so you do not need to do the total recoverable digestion?

MR. MILLER: No, in our case, hydrochloric acid is used simply for cleaning the equipment. Preservation is done in nitric acid, the reason for that being that we collect samples for nutrients and other constituents simultaneously. So, the cleaning protocol specifies hydrochloric acid. The preservation for trace elements is nitric acid.

MR. VARNELL: Okay, thank you.

SPEAKER: And I understand that a letter went out to the regions where, on a regional level, they are allowed the liberty of approving the

ICP/mass spec or something to that extent. You might want to talk to the region that you work within, because I believe the regions have the liberty to approve the ICP/mass spec.

The USGS filtration method eliminates filtration artifacts or reduces them due to the size of the filter that you are using. Is EPA addressing that in the methods that you are looking at?

MR. TELLIARD: Yes. We basically are using USGS studies on the filters. They had like four of them. We are using that data to look at the filters that we are looking at.

One of the things that you noticed in the USGS presentation is that they have these funny numbers, a BJ2642. You have to go find out what that is. Okay? And that is one of the things that we are doing, to clarify what Tim has put in his procedures. Like he says, that is a Gelman number or whatever.

SPEAKER: Thank you. Is anybody looking at another definition of dissolved metals because of the problems related to having a physical separation to define a biochemical type parameter?

MR. TELLIARD: No. It is still a 0.45 micron filter. By definition and by God's law, that is a dissolved metal.

SPEAKER: Thank you.

MR. TELLIARD: You are welcome. Shier?

MR. BERMAN: Shier Berman, National Research Council of Canada in Ottawa. I can see the horrific tremors through the audience about the increased cost of performing these new protocols. I would suggest that you look at the use of polypropylene as your containers in place of teflon in many cases.

We have about two decades of experience with these kinds of containers, and except for mercury, they are quite adequate to meet the requirements for ultra-trace level if properly cleaned. You can just throw them away and not worry about the expense.

Especially, a case in point is the ampules of acid that you are preparing. They can be adequately prepared quite well in polypropylene bottles that can be thrown away, and they only cost a few pennies rather than several dollars.

MR. TELLIARD: Thank you, sir.

MR. BERNARD: John Bernard, Alexandria Sanitation for Mr. Miller. What sort of filters? You said Gelman capsule filters?

MR. MILLER: Yes. I cannot tell you what the exact number is. They are Gelman capsule filters, and they are the Supore filter material, because I believe that is the only material that Gelman is currently producing that can be acid cleaned.

In our case for part per billion, however, we have found that the capsules are adequately prepared by simply washing them with high quality deionized water. Somewhere around a liter or liter and a half of water through the capsule filter will get you well down in the 100 to 200 ng/L range.

MR. HUNT: Carlton Hunt. Are those the filters that are about the size of your fist there?

MR. MILLER: Yes, and as a matter of fact, we were led to those type of filters by Herb Windom. He has been using them at Skidaway for a number of years.

MR. HUNT: I would like to add one thing. With the nuclepore filters that a lot of people use, you have to be very careful, because there is a lot of trace metal on those filters, and they do have to be cleaned. Which is why you are moving to capsule filters, and the cleaning for nuclepore has to be in a fairly warm acid environment.

MR. COMO: Joe Como from NK Testing Services. I am interested in knowing if microwave digestion techniques have a role in preparation of low level metals where you have fairly closed systems involved and teflon liners, you know, to protect the sample. Have you checked at all into that?

MR. MILLER: No, we have not.

MR. HUNT: I thought that...and correct me, Bill, if I am wrong, but I thought microwave technology had been approved for the total recoverable.

MR. TELLIARD: Yes.

MR. HUNT: And it is available and it works quite nicely.

MR. BOURBON: I am John Bourbon from Region II. Bill, I just want to let everybody else know about the ICP/mass spec. I talked to James Lichtenburg about a month ago. For those of you here, he is the head of the committee or work group that proposes methods for NPTE's updates, not very often, just like Bill said.

The package that is up now that they are going to propose, includes the 200.8 which is the ICP/mass spec and includes 200.9 which is a more advanced furnish procedure, ion chromatography, and two or three other inorganic methods.

I just wanted to at least give you that. It should be a few months before it gets to the proposal stage, and I think it is on a fast-track, where it will only be proposed for comment less than the normal six months.

The other thing is the gentleman from Fisons is right, and the lady that just spoke earlier. In case anybody is interested, any laboratory that wants to use the ICP/mass spec method, should contact the region you are in, because each of the regions, for the ICP/mass spec method, have flexibility on the requirements.

It is not going to be standard right now from region to region. That might be nice, but we have the flexibility.

So, one region might require just that you keep documentation in the lab for comparison, and another region may require a full-blown alternate test procedure. So, you should check within your region if you are interested in using the ICP/mass spec method.

Thanks.

MR. TELLIARD: Thank you. Tim, thanks so much.

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A PROTOCOL FOR THE COLLECTION AND PROCESSING OF SURFACE-WATER SAMPLES FOR THE SUBSEQUENT DETERMINATION OF INORGANIC CONSTITUENTS IN FILTERED WATER

WHY A MICROGRAM-PER-LITER PPB PROTOCOL?

- PPB is the concentration level at which most Federal drinking water regulations have been established.

WHY NUTRIENTS AND MAJOR IONS ARE INCLUDED

- Several nutrients have 0.01 or 0.001 mg/L reporting limits, which are actually μg/L levels. The cleaning, QC, and other items in the protocol are necessary to produce good-quality nutrient data at these levels.

- Counterproductive to use separate equipment and protocols for nutrients and major ions vs trace elements.

KEY MESSAGES OF THE PROTOCOL

- Inorganic samples can be contaminated, but sources of contamination can be reduced through proper planning, use of tested equipment/supplies, proper cleaning, and specified QA measures.

- Collection of adequate QC data can identify whether problems still exist.

KEY MESSAGES OF THE PROTOCOL, continued

- Development
  - All decisions made on supplies, procedures, and need for QC are supported by data from laboratory tests and actual field trials conducted in a number of different atmospheric and hydrologic environments.

HOW THE PROTOCOL APPLIES TO UNFILTERED SAMPLES

- Sample collection in the old approach was a major source of TE contamination.
- Therefore, for samples having low to moderate suspended sediment concentrations (fairly low total concentration of TE), the protocol is necessary.
- For high sediment concentration samples, might not need the protocol (TE on sediment might swamp contamination).
- However, never certain of suspended sediment concentration before sampling, so always use the protocol for unfiltered samples.

FIELD PROTOCOL

- Certified list of equipment and supplies
- Four procedures
- Heavy emphasis on training
- Recommended and minimally acceptable collection of "field" QC data
- Guidelines for use of QC data as basis to using and interpreting the environmental data

ACCEPTABLE SAMPLERS FOR THE COLLECTION OF INORGANIC SAMPLES FOR LOW-LEVEL ANALYSES[1,2,3]

D77 Teflon
D77 Frame
D77 bag (Teflon or Reynolds Oven Bag)
D77 standard (plastic)
DH 81 (with "shrink-wrapped" handle)

[1]These samplers are acceptable only following rigorous use of the specified cleaning procedures.

[2]No through-the-ice sampler presently certified.

[3]USGS is discussing development of a new generation of flow representative, noncontaminating samplers.

Equipment List for the ppb-Protocol

Item
Churn Splitter (8 or 14L)
Concentrated Hydrochloric Acid
Wash Bottles for Acid and DIW
Liquinox
Non-Powdered Vinyl Gloves
Clear/White Plastic Wash Basins
Non-metallic Brushes
Sealable Plastic Bags w/o colored strips
Capsule Filters
142mm 0.45-µm Cellulose Acetate Filters
142mm Filtration System preferably w/ white/clear plastic/teflon inlet/outlet valves
Peristaltic Pump for Filtration
Pump Tubing (C-Flex or silicon
Non-metallic (ceramic) forceps
Non-metallic (Kel-F)) forceps
Processing/Preservation chamber covers
Churn Splitter Carrier
Processing/Preservation Chamber Frames (plans available)

CLEANING OF FIELD EQUIPMENT

- Preferable: Separate sets of office-cleaned sample collection and sample processing equipment for each site.

- Acceptable: Cleaning between field sites to prevent cross contamination.

MODIFICATION/CONSTRUCTION OF FIELD EQUIPMENT

- Funnel on churn splitter

- Processing enclosure
  - To reduce/eliminate atmospherically derived contamination
  - Permanent in a dedicated vehicle; otherwise portable
  - Materials: PVC or wood frame; disposable plastic cover

- Preservation chambers
  - To prevent contamination during sample processing, cross contamination from preservatives, and atmospheric contamination
  - Same materials as processing enclosure

FILTERS

- Capsule filters are preferred because
  - Minimum precleaning
  - Less potential for atmospheric contamination
  - Large surface area to prevent filtration artifacts
  - No post-cleaning (one use)

- Cost is ~6 times more expensive than plate filters ($12 vs $2)

- The initial cost is more than compensated by
  - Labor savings from reduced field handling and no need to clean between sites
  - Need for fewer QC blanks because of the lessened potential for contamination

"FIELD" PROCEDURES

PROCEDURE 1. Office Preparations and Cleaning of Equipment

PROCEDURE 2. Field Rinsing of Equipment Prior to Sampling

PROCEDURE 3. Sample Processing and Preservation

PROCEDURE 4. Field Cleaning to Prevent Cross-Contamination Between Sites

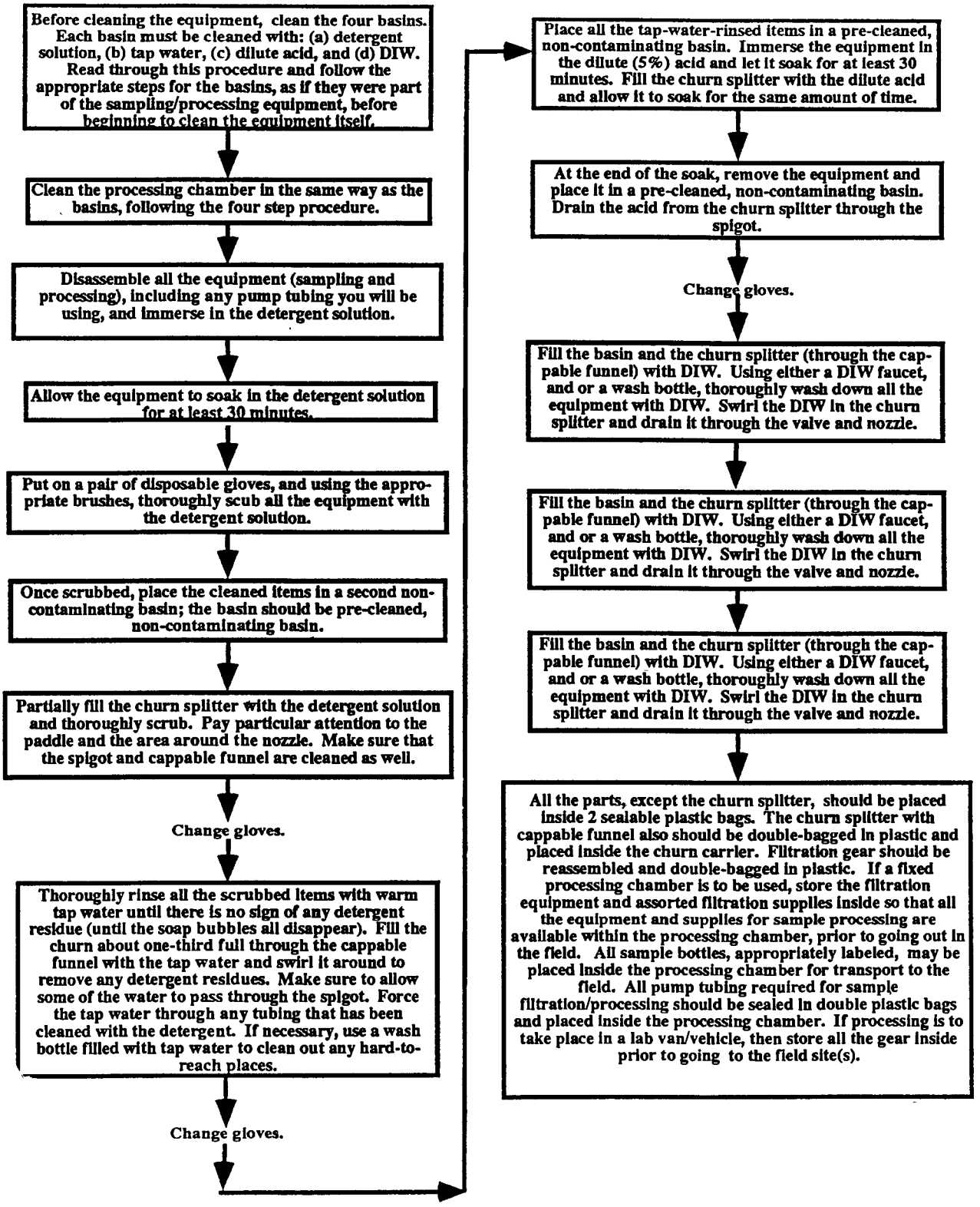


FIGURE 6--PROCEDURE 1: OFFICE PREPARATIONS AND CLEANING OF EQUIPMENT

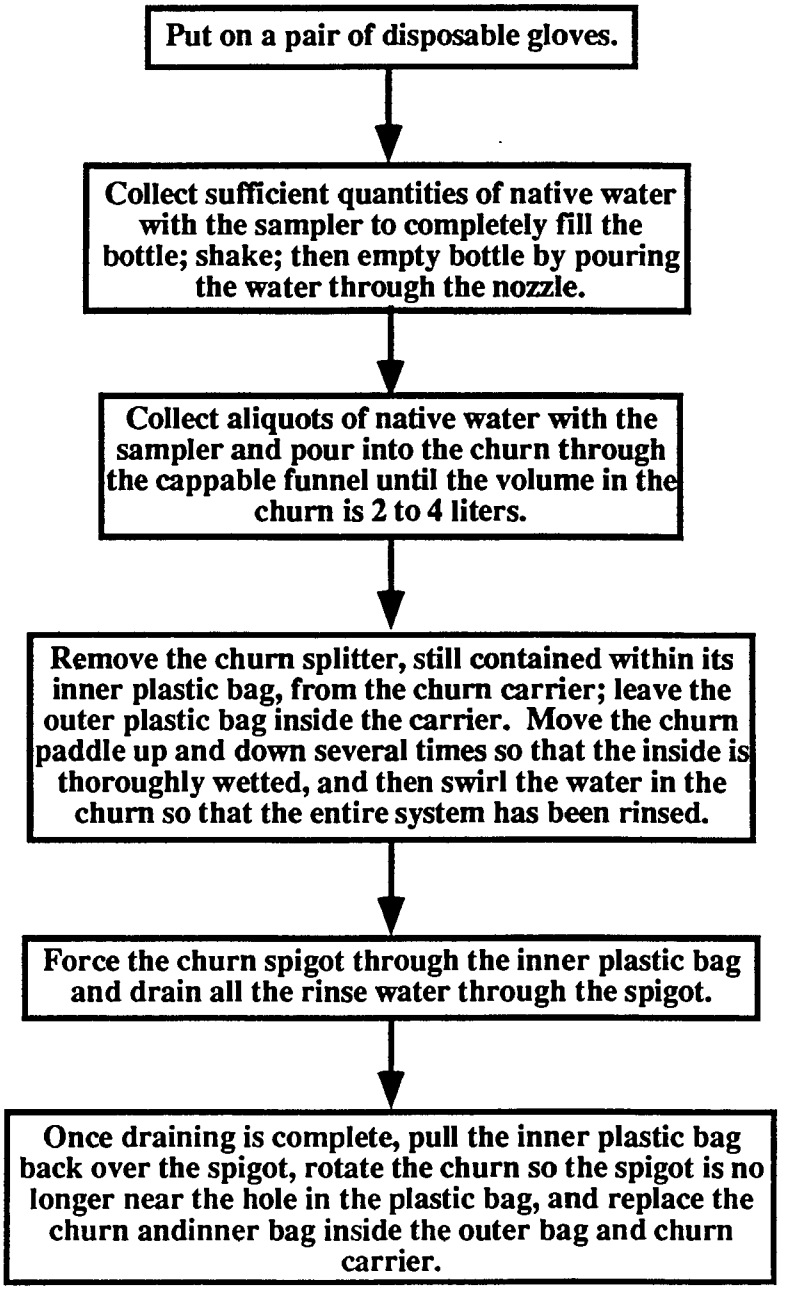


FIGURE 7--PROCEDURE 2: FIELD RINSING OF EQUIPMENT PRIOR TO SAMPLING

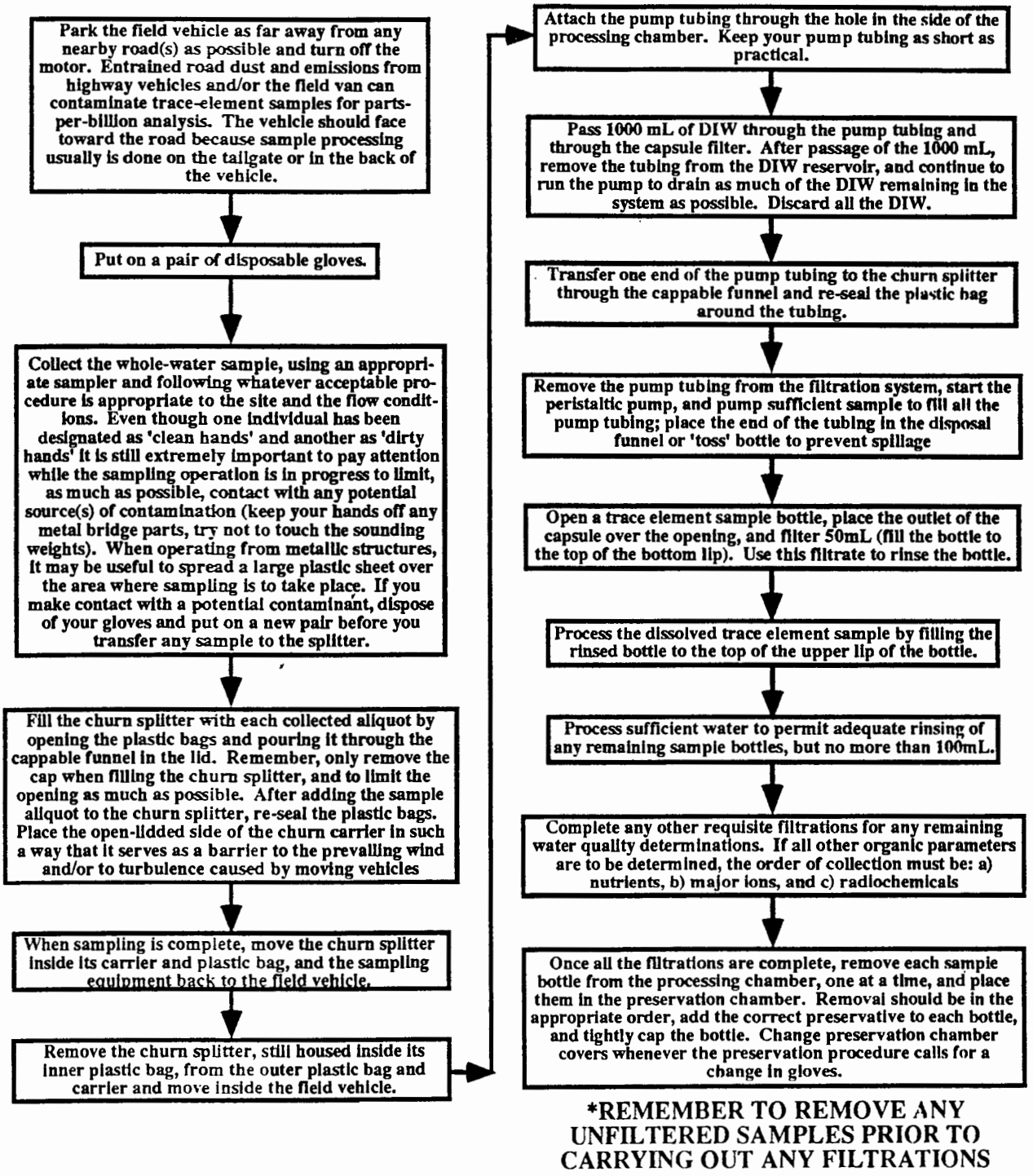
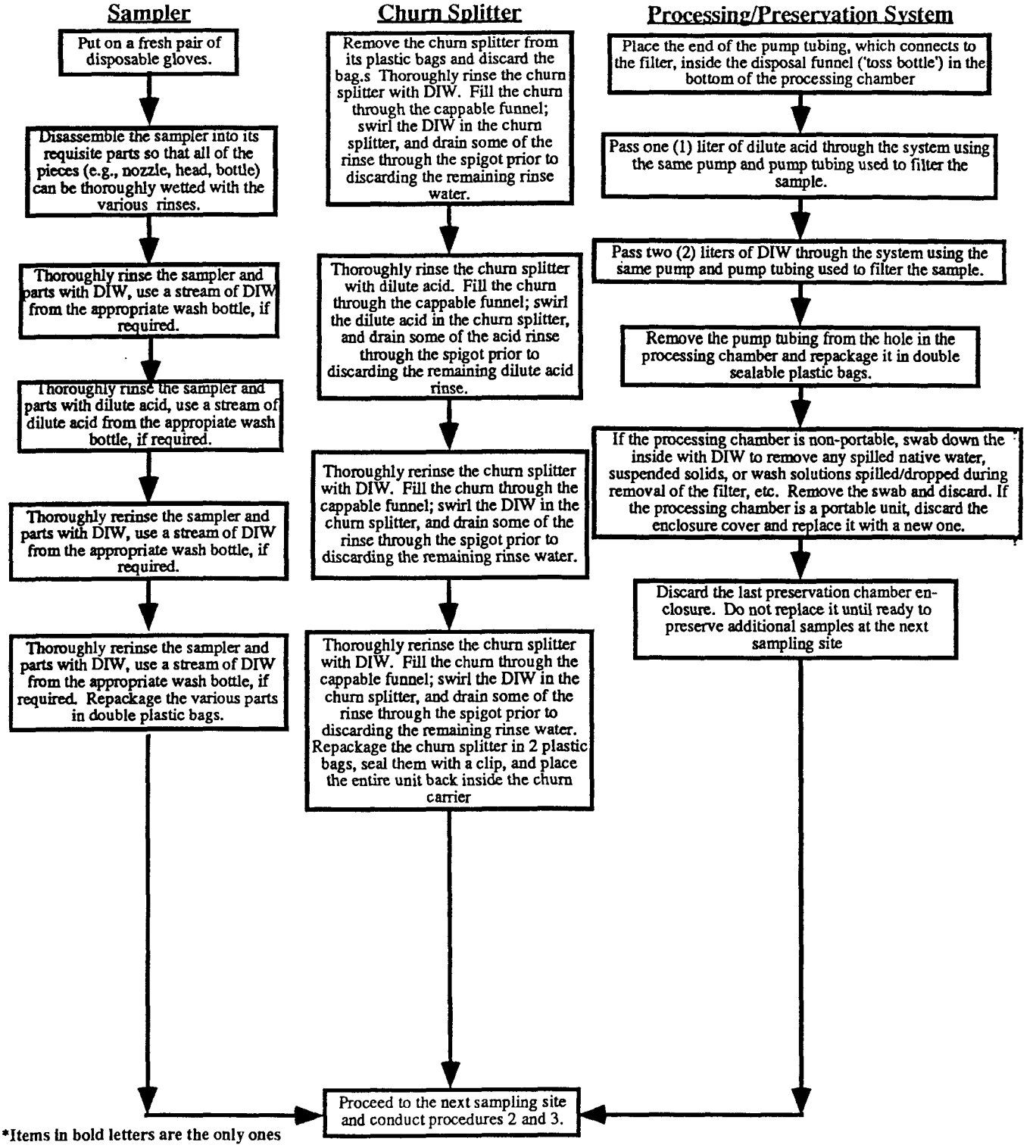


FIGURE 8--PROCEDURE 3: SAMPLE PROCESSING AND PRESERVATION CAPSULE FILTER OPTION *

THIS PROCEDURE SHOULD BE CARRIED OUT AT THE FIRST SAMPLING SITE WHEN THE EQUIPMENT IS STILL WET, AND BEFORE DRIVING TO THE SECOND SITE.



*Items in bold letters are the only ones that differentiate this procedure from Procedure 3

FIGURE 9--PROCEDURE 4: FIELD CLEANING TO PREVENT CROSS-CONTAMINATION BETWEEN SITES - CAPSULE FILTER OPTION

TWO-PERSON SAMPLING CREWS AT ALL TIMES--RATIONALE

- Aside from improperly cleaned equipment, use of one person represents the greatest potential source of contamination in sample collection and processing

- Deemed necessary by developers/practioners of all clean protocols used to date

TWO-PERSON SAMPLING CREWS--JOBS

- Clean Hands: All operations concerned with
  - Sampler bottle
  - Transfer of sampler bottle to churn splitter
  - Actual sample processing
- Dirty Hands
  - Preparation of the sampler
  - Actual collection of the sample
- Not clear cut, requires coordination and practice

SAMPLE PROCESSING SPACE

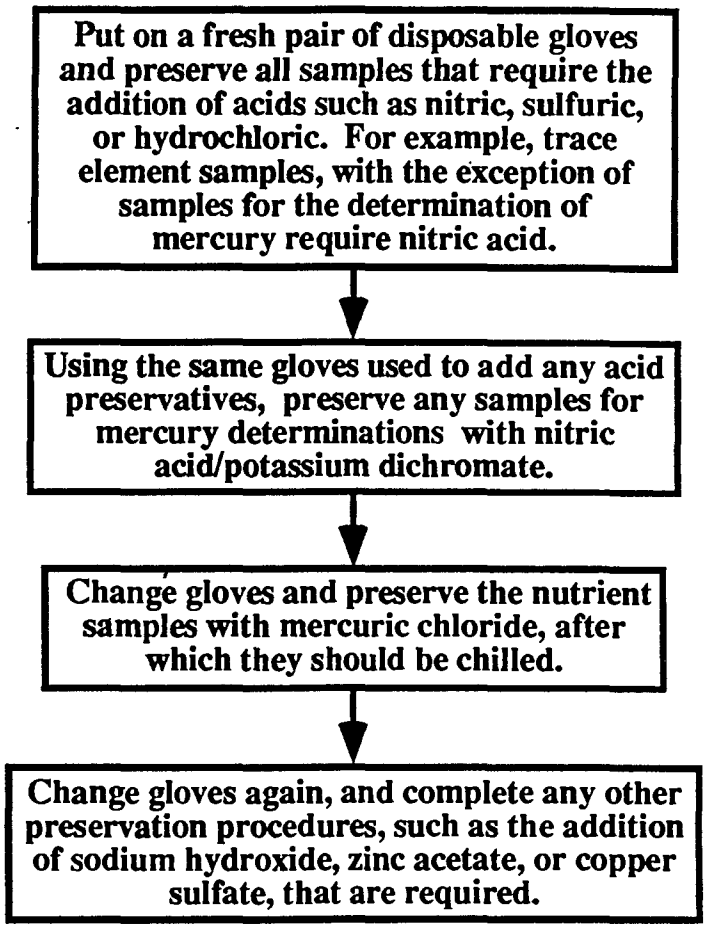
- Specifically cleaned space is necessary
- Dedicated vehicle is preferable

SAMPLE PRESERVATION

- Standard: highest quality nitric acid in borosilicate glass ampules
  - Found to have low levels of Al, Ba, B, Ca, Cr, Mg, Si, and Na from the glass (at MDLs of ICP/MS)
  - Cost: $5 per ampule
  - Tried other types of glass--same TE's at about the same levels

- Alternative: highest quality nitric acid in Teflon vials
  -- No contamination (at the MDL's of ICP/MS)
  -- Cost: $16 per vial

Figure 1--Order of Sample Preservation*



*Remember, change the preservation chamber cover every time you change gloves.

Always store your preservatives in separate sealed containers, preferably away from each other and away from any samples.

Preservative containers, once used, should be stored in separate sealed containers such as screw-cap bottles until proper disposal can be arranged.

Used gloves should also be stored in sealed containers, such as a lidded pail, until proper disposal can be arranged.

FIELD QC SAMPLES

- *Equipment blank*. To test whether equipment is clean:
  - Before crew goes to field first time to ensure crew is capable of cleaning equipment properly
  - When new equipment is used
  - At least once per year

- *Field blank*. To test for contamination during sample collection and processing
  - At least one per sampling trip
  - If a sampler is used several times during a trip, collect after the prescribed between-site cleaning and just before the last environmental sample

FIELD QC SAMPLES--continued

- *Split sample*. To test for precision in shipping and analysis
  - At least one per sampling trip
  - Split after the preservation step
- *Concurrent samples*. To test the reproducibility of sample collection
  - At least one per two sampling trips

Figure 2--Equipment Blanks

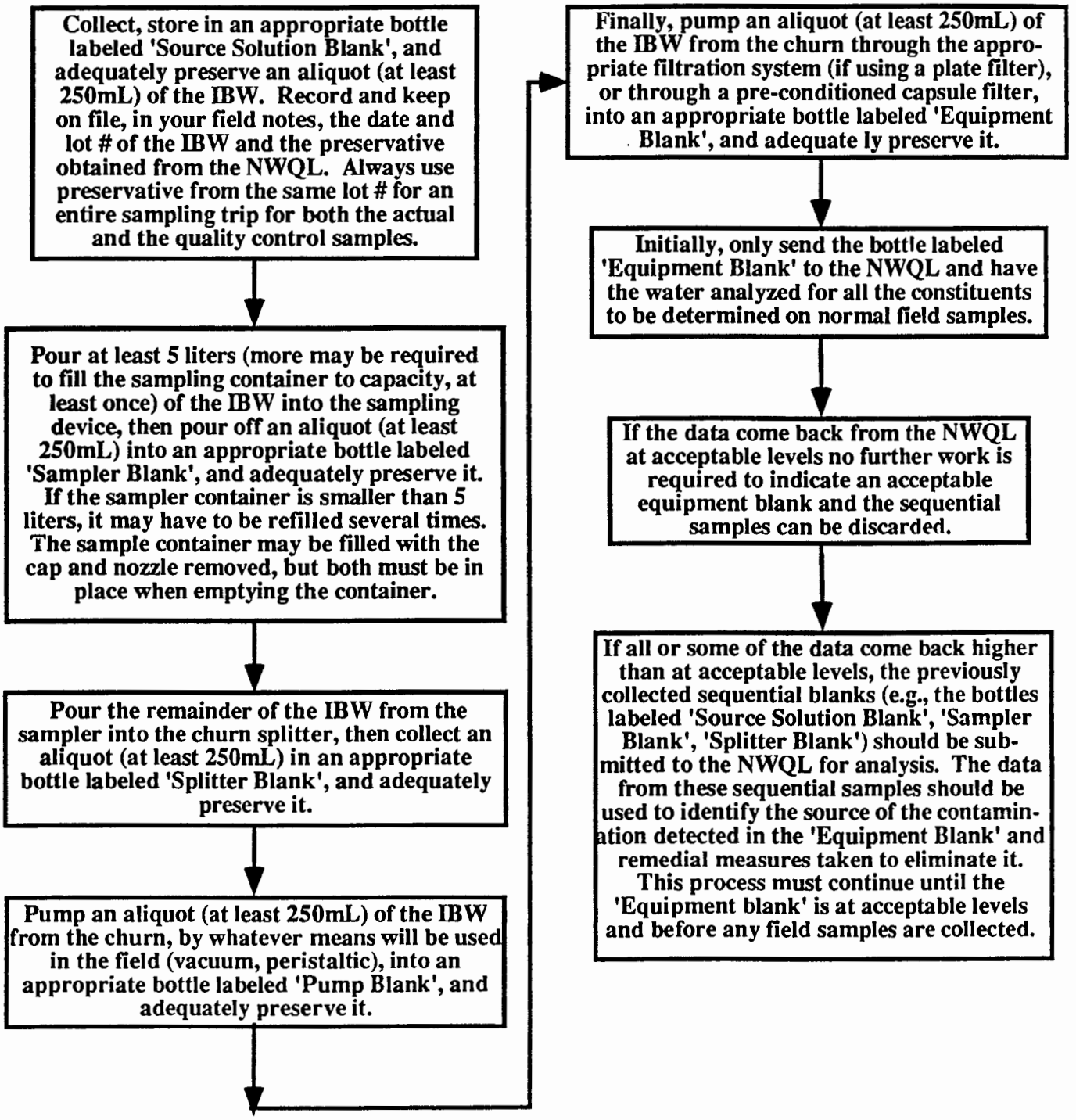


Figure 3--Field Blanks

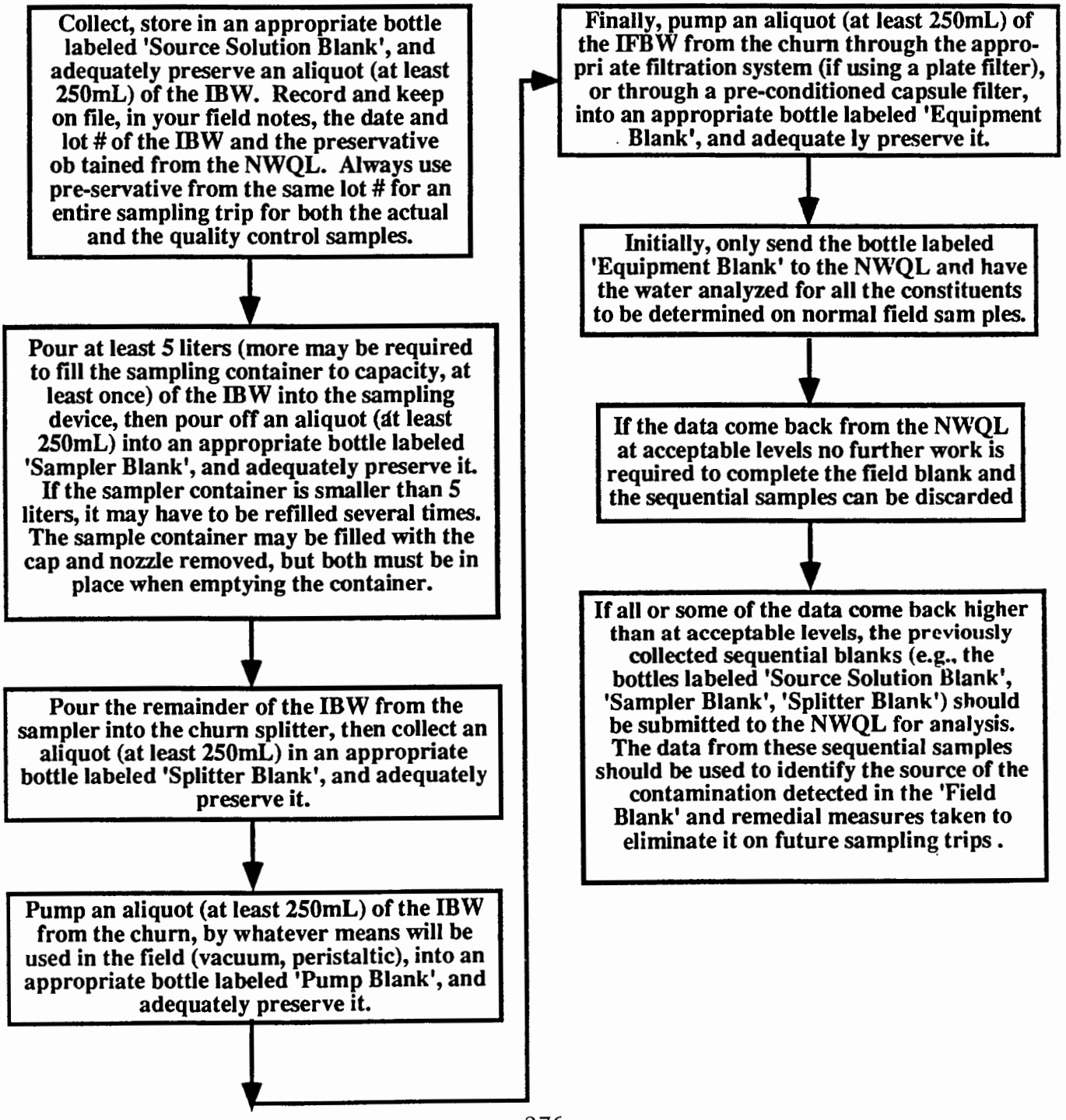


Figure 4--Split Field Samples

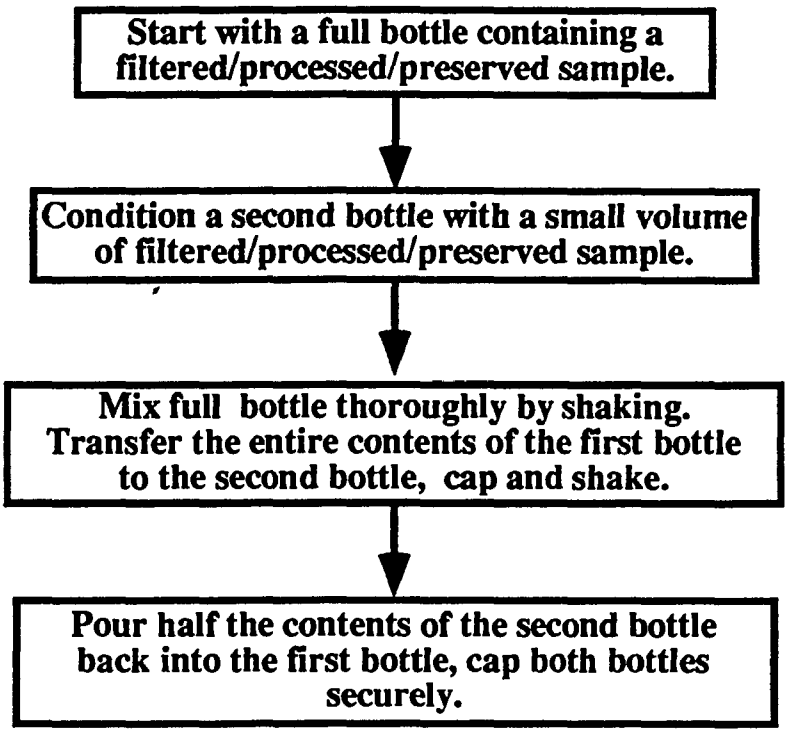
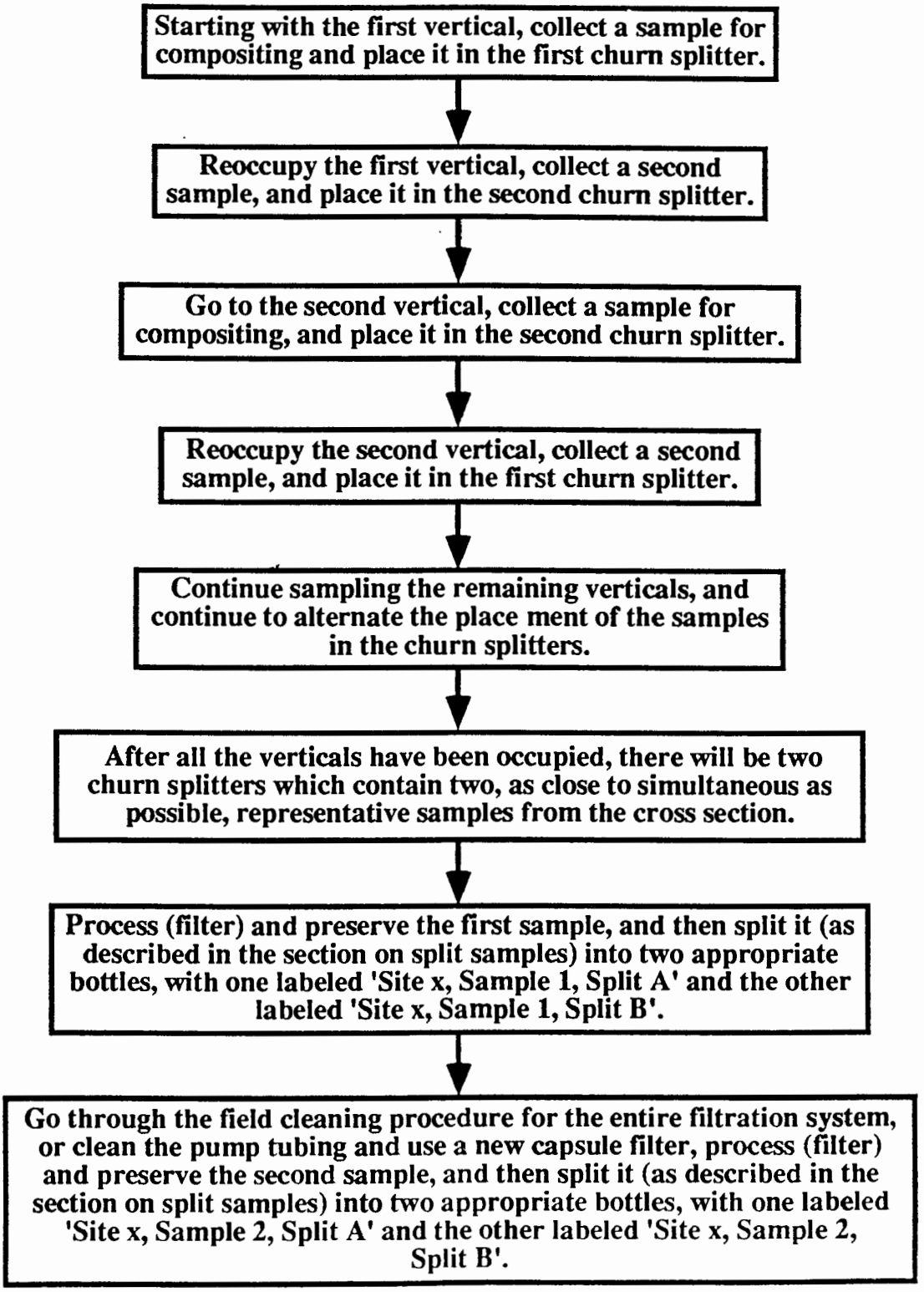


Figure 5--Concurrent Field Samples



LABORATORY PROTOCOL

- Class 100 clean room to:
  - Prepare equipment and supplies
  - Prepare samples
- ICP/MS to measure concentrations of 17 TE's in DIW blanks at MDL's of 0.1-0.5 μg/L
- ICP/MS to measure 15 TE's in environmental samples at reporting level of 1.0 μg/L
- Standard lab QC
  - Blanks
  - Reference Samples
  - Duplicates

METHOD DETECTION LIMITS AND REPORTING LIMITS FOR THE VARIOUS CONSTITUENTS COVERED BY THE PROTOCOL

Constituent	Analytical Instrument	Schedule 172 MDL	Environmental Sample RL
Aluminum (µg/L)	ICP-MS	0.3	3
Ammonia (N, mg/L)	ASF	0.002	0.002
Antimony (µg/L)	ICP-MS	0.2	1
Barium (µg/L)	ICP-MS	0.2	1
Beryllium* (µg/L)	ICP-AES	0.2	0.5
Boron (µg/L)	ICP-AES	2	2
Cadmium (µg/L)	ICP-MS	0.3	1
Calcium (mg/L)	ICP-AES	0.002	0.002
Cobalt (µg/L)	ICP-MS	0.2	1
Chromium (µg/L)	ICP-MS	0.2	1
Copper (µg/L)	ICP-MS	0.2	1
Iron (µg/L)	ICP-AES	3	3
Lead (µg/L)	ICP-MS	0.3	1
Magnesium (mg/L)	ICP-AES	0.001	0.001
Manganese (µg/L)	ICP-MS	0.1	1
Molybdenum (µg/L)	ICP-MS	0.2	1
Nickel (µg/L)	ICP-MS	0.5	1
Nitrate (N, mg/L)	ASF	0.001	0.001
Nitrite+Nitrate (N, mg/L)	ASF	0.005	0.005
Orthophosphate (P, mg/L)	ASF	0.001	0.001
Silver (µg/L)	ICP-MS	0.2	1
Sodium (mg/L)	ICP-AES	0.025	0.025
Strontium (µg/L)	ICP-MS	0.1	1
Thallium (µg/L)	ICP-MS	0.1	1
Uranium (µg/L)	ICP-MS	0.2	1
Zinc (µg/L)	ICP-MS	0.5	3
Silica (mg/L)	ICP-AES	0.02	0.02

* Be also can be determined by ICP-MS but the RL will be 1µg/L

MR. TELLIARD: We are going to take a 15-minute break, after the break please return for Session 2.

(A brief recess was taken.)

DR. FIELDING: We are now to talk of the rest of this morning's session. The next paper will be presented by Dr. Shier Berman, entitled the Preparation of NRC Certified Reference Materials.

Shier was appointed director of the Environmental Measurement Science program or EMS of the National Research Council Institute for Environmental Chemistry, now the Institute for Environmental Research and Technology, in June of 1990.

The EMS program is an internationally recognized center of excellence for analytical chemistry, especially for trace analysis. The program is responsible for the inorganic aspects of the NRC Marine Analytical Chemistry Standards program which is the world's foremost producer of marine certified reference materials.

Shier?

(Verbatim Transcript)

THE PREPARATION OF NRC CERTIFIED REFERENCE MATERIALS

MR. BERMAN: Thank you, Mr. Chairman, ladies and gentlemen. As soon as I figure out modern technology, we will get going.

I guess I should give a little bit of background to who we are. We are a national laboratory, and I guess the closest analogy to us in the United States is NIST, although there are great differences between us and NIST, but in the field of reference materials, we have a lot in common.

In fact, our institute has an informal memorandum of understanding with the standard reference material program of NIST regarding cooperation and exchange in the preparation of environmental certified reference materials.

About 15, 16, 17 years ago... I have not done the arithmetic... the National Research Council was approached by what was then the Canadian Committee on Oceanography to look into what they called the chaotic state of analytical chemistry with respect to the analysis of marine materials. Well, we soon discovered, in an ad hoc committee that

looked into this, that it was not only a Canadian problem, but it was a worldwide problem, and the National Research Council of Canada set up what became known as the Marine Analytical Chemistry Standards program, a very successful program which has done some very nice things, as I will tell you about some of them in this talk.

One of the reasons for the concern... and I use this slide as one of my favorite ones for introducing the topic... is that, as we know, as pollution was proceeding in this world... and it is an old slide, but it serves the point... that the oceans seemed to be getting cleaner and cleaner and cleaner and cleaner as we went through the decades from 1940 to the 1980s.

Of course, that really was not happening, but we just did not have the protocols in place in most of the laboratories which were described earlier this morning. This is a case of water analysis where cleanliness is next to godliness, and that is the message that has been given this morning.

In fact, when we first got into it... and I did not know a thing about marine things in 1975 or so... I remember reading this great treatise by a very prominent physical oceanographer on how wonderful it was that no matter where you measured zinc in the world's oceans, the concentration was 5 ppb and how this had to be based on the physical chemistry and the exchange in the chemistry that was going on in the ocean.

So, part of the problem is getting good values in order to get rid of all this folklore.

If you think it is the marine scientists who were in bad shape and those of you who deal with inland waters or fresh waters can smirk at them, we had the same problem. This is work complied at the University of Michigan, and here we look at Lake Huron, how it has been getting cleaner and cleaner and cleaner over the decades.

By 1980, the people at the University of Michigan were reaching something which was approaching the truth, and one has to give them a great deal of credit for being able to do that some 14, 15 years ago. It also dispels the folklore that the fresh waters are much higher concentrations than seawaters. Pristine fresh waters come awfully close to seawaters in concentration.

As a result of our work over the last decade and a half in this, we have developed what we call a quality assurance program for environmental analytical measurement of which the marine analytical chemistry program is a part.

We have four basic things that we do. One is the provision of certified reference materials for environmental samples, and we stay only in the environmental field. In fact, we are really limited to the aquatic environment which includes waters, sediments, and the biota that live therein.

We are very interested in the intercomparison of laboratories. This is from an enabling point of view. We want to ensure that the laboratories are able to get the right answer.

There are two reasons for this. One is that decisions are made on these answers which involve the expenditure of millions and even mega-millions of dollars by our masters. Two, we want to ensure that the laboratories get the work. If you get the right answer, you will get the contracts, and that is why we work with Canadian laboratories in this respect but also with a lot of American and other international laboratories.

Two other factors in our program are the development of reliable methodologies for the analysis of environmental samples, and I am not going to talk too much about this today save to say that we have probably, in the last decade, published about 250 papers on methodologies in reviewed peer literature and that in our laboratories lives the guru of electrothermal atomization atomic absorption, one Ralph Sturgeon, and down the hall from him is one if the pioneers in the ICP emission and ICP/mass spectrometry, Jim McLaren.

So, we are well suited. In fact, we are very experienced in these fields. The laboratory celebrated its 50th anniversary a few years ago. We are a product of World War II, and we entered the war some two years before you people did. We have even an edge on that.

We also develop analytical instrumentation, and I will not talk about this at all today.

I am going to talk about point 2 first, because it reflects back to point 1. The major part of my talk is going to be about certified reference materials, but the intercomparison exercises have set our philosophy of what we think we have to do in order to improve the quality of analytical measurement.

Over the last dozen years, we have conducted international studies, specifically, for the International Council for the Exploration of the Sea. We are in our eighth year of a very successful continuing program with NOAA where we share with NIST the responsibility for their quality assurance program with respect to the National Status and Trends program, and many USEPA laboratories participate in that study, and if you do not, I would suggest you get in touch with NOAA to talk to them about it.

And we even do some work in our home country of Canada.

As an example of what we do with the intercomparisons, I am using a rather old study, but it is an extreme example of what we are after. In 1981, about the time we got involved with the International Council, they were already carrying out an intercomparison on the determination of trace metals in seawater, and in front of you are the results for lead in 1981.

15 laboratories submitted results, and among these 15 were a good number of the world's, quote, best laboratories. They produced a consensus value. However, a sample had been sent to Clive Patterson, the guru of lead analysis in this world, especially at that time, and there is no doubt that lab 3 which was Patterson had a very good estimate of what was the true value.

The consensus value was wrong, and that is a lesson we learned early in the game. Democracy may be fine for the United States and Canada and even South Africa at the moment, but it has no place in analytical chemistry. If you are wrong, you are wrong even if you are the majority. If you are right, you are right even if you are a minority of one.

That was lesson one. You had to have in an intercomparison exercise some way of getting a look at the approximation to the truth in order to estimate the accuracy of the laboratories, not only their ability to reproduce each other or their variance between laboratories.

The other thing about this slide is if you look at the concentrations, even the true value is about 0.15 ppb, and in open ocean water, we have never seen anything close to that in all our experience. So, the sample was obviously contaminated during collection.

Even if the consensus value and the true value had been close to each other, it was a useless experiment, because you never analyze open ocean water at such high concentrations. So, we would have got no information about the ability of the laboratories to perform the analysis at that point.

At the time we got involved with high seas, and we ran two intercomparisons for trace metals in seawater over the next seven years, with the feedback to the laboratories that it entailed. By the end of the second one, we had something like this.

About 20 laboratories taking part with concentrations at true open ocean level. You see that about 15 of the 20 labs seven years later, with proper consultation and feedback and discussion, were now able to analyze the material, and the consensus value and the true value are certainly not far apart.

That is the basis of it all. You have to have good inter-laboratory consensus, but you have to have accuracy also. Too many intercomparisons leave out the accuracy factor.

Moving on to the reference material program, I just want to remind you what we mean when we talk about reference materials and certified reference materials. There is nothing magic about our reference material. In fact, most of you in your own laboratory prepare one. It just has to be a homogeneous material, and it has to have a well-established track record.

Then you can use it for your own purposes, for your quality control charts, for your own internal calibration, or for whatever purpose you want to use it.

However, you notice that in the official international standards organization definition of a reference material, there is no reference to accuracy. That is, it does not have to have an accurate value attached to it. It has to be homogeneous so that you can reproduce it, but it does not have to be accurate.

Now, a certified reference material is a subset of reference materials. NIST insists on calling theirs SRNs; the rest of the world talks about CRNs. It is a reference material which is accompanied by a certificate, that is, somebody is putting his name on the dotted line. The properties have been certified by a procedure which established a traceability.

It is like buying a dog. You have to establish its pedigree, its lineage. You have to relate it back to a national standard, an international standard, an SI unit, or what have you.

That is not all that easy to do at times, because the international unit is the mole, and who the hell ever measures anything in moles? So, we have debates these days about traceability, and it is a big word.

But it has to be an accurate manifestation or realization of the unit in which you express it. So, each certified value is also useless unless it has an uncertainty associated with it at a given level of confidence.

So, a number that does not have a plus or minus and is traceable back to a national or an international standard or an international unit is not a certified reference material, and they are a little tougher to make than the reference materials themselves.

We have manufactured and produced three types of reference materials, natural waters, sediments, and marine biota. Well, no, they are not all marine; they are aquatic biota.

All the materials we produce are taken from the environment. We do not believe in spiking. We do not believe in synthetic reference materials.

We have four types of water. The NASS is an open ocean water taken several hundred kilometers off the coast of Nova Scotia in the North Atlantic. The CAS is a coastal water taken near Halifax Harbor. The SLEW is an estuarine water, and the SLRS is a river water.

So, we have essentially a range of salinities, ocean water from 35 parts per thousand to coastal water at roughly 20 parts per thousand, estuarine about 12 or 13, and, of course, the river water of zero salinity. We cover the range, and they each give different problems in analysis, as many of you well know.

The collection is a problem. It was alluded to this morning. This was the first research vessel we had at our disposal to collect ocean open water. You can see what one of the problems is, because it had to keep its engines going to operate the winches for our sampling.

A closer view of the problem, scraping the rust off the deck. Now, we collect in 50-liter carboys. One ug of iron into any of those 50-liter carboys would increase our iron content by 10 percent, and 1 ug of lead into any of our carboys would increase the lead content by 100 percent.

So, how do you collect off a terrible collection platform like that? I am not going to take... we developed a system in which the water never saw the atmosphere. We either take samplers or now, if we can, if we are not going too deep, we pump by peristaltic pumping through silicone tubing which is all very well cleaned, through the filter system, through the automatic acidifying, and into the carboys which have been stored with acidified water to the same pH as we acidify our seawater. All is sealed in wooden crates, and the carboys are wrapped in plastic bags.

So, all we do on site is reach our hand in on top of the plastic, loosen the top of the container, connect the hose to the spigot on the bottom of the carboy, open the spigot, and pump backwards into the tube and expel the air that was in there.

It seems to work quite well, but it took us a long time to get there. In fact, it took us five years to decide that we were capable of storing seawater and of analyzing it with the aim of certification.

There is a picture of the on-board pumping apparatus, all enclosed. Those are Gelman filter cartridges, by the way, which were referred to in the last talk. They may not be the same size and shape, but they are enclosed capsules.

We have three or four water samples, as I said before. They are each, the three seawaters are certified for about a dozen trace metals, the river water with respect to 22 trace metals.

It is not that we favor the river water in our work, but it is a lot easier to work with a non-saline matrix. So, economically, we can afford to certify for more metals. Working in a 3.5 percent saline solution for analytical chemistry at concentrations which are extremely low is very challenging.

This is a coastal seawater, not quite as low concentrations as an open ocean water, but you see the concentrations that we are looking at. Most are fractional and low fractional parts per billion. In many cases, those numbers are cleaner than the water quality in many, many laboratories in North America. So, the blank problem becomes a very, very significant part of the analytical procedure.

All of these, of course, must be separated from the salt matrix. There is no instrument available today that you can shove seawater into at one end and get the answers out the other end without both a separation from the saline matrix and a concentration procedure.

With respect to sediments, we have three of them taken at various parts of the Canadian coastline, an east coast sediment, an Arctic Ocean sediment, and a west coast sediment.

The west coast sediment is very special, because it comes from a Canadian naval dockyard. It is contaminated to all hell, and it is a very practical one for those working in very contaminated harbors, and it has a special feature which I will tell you about in a moment.

Oddly enough, the geological matrix of the Arctic Ocean sediment and the east coast sediment are barely distinguishable. Maybe it is not oddly enough. It is just the Canadian shield being deposited by two river systems, the McKenzie in the north and the St. Lawrence in the southeast. It is probably just the same ground rock being taken out to sea.

The mucky mess you start with, and I am sure some of you are familiar with this, after freeze drying, the bits of plastic and the sticks that have to be taken out, and then it is ground a bit and screened through 100 mesh and then homogenized and bottled and certified.

The three sediments, anywhere from 16 to 20 trace metals certified in each. As the time goes on, we tend to be certifying more elements in our sediments. The last designation is the batch number, so we are already on our second generation of MESS, and you see we have added a few elements to the list.

The others are the major and minor constituents such as aluminum and silica which are the main features of these sediments or phosphate and sulfur and that like.

Another thing as time goes on, we find people are not interested in the major and minor constituents as much as in the trace metals. So, in that MESS-2, you see there are only six others. We have dropped some from the list for economic reasons. We just cannot afford to do everything all the time, especially if we feel that people are not using the numbers.

A typical...this is the Beaufort Sea sediment, but it is a typical aluminum silicate concentration. It is fairly clean but not pristine. They are probably the easiest of the types of materials that we certify to certify because of the relatively high concentrations. These are parts per million.

I have just listed 11 of the 20 certified metals. These are, I thought, the ones you might be more interested in that some of the other obscure ones.

The sediment from the west coast from the dockyard was a real eye opener, because it had about 40 ppm tin in it, and because navies like to paint their ships with butyltins and tributyltin as an anti-fouling agent, we found there was enough butyltin in this particular sediment to certify the specie of it butyltins.

This is a unique material. It was the first material ever certified for the three butyltins, and it remains unique for the three. There are not...there is a Japanese fish certified for tributyltin and dibutyltin which is available from NIAS in Japan.

We are trying, as much as possible, and the future wave is toward the speciation of metals rather than the total, and we are trying to do all we can to move in that direction.

Our third set of materials are biological tissues, a dogfish muscle, a dogfish liver, two types of lobster, and the difference between the two is the first one has been defatted so it does not turn into peanut butter or look like peanut butter sitting in your jar. The second one is not defatted, but we have developed a process for stabilizing these very fat materials and issuing them as a homogeneous slurry which is very close to what you do in the laboratory.

The last one is our first foray in Ottawa, anyway, into the organic contaminant realm. The carp sample has been just released about three weeks ago, certified for furans and dioxins and will soon be certified for a range of PCBs.

The dogfish liver and the muscle come from the same fish, essentially, and it is just a matter of homogenizing, spray drying, defatting... you must get the fat out, or it will not keep... and then blending, bottling, and then we do radiation sterilize at the end or we cannot ship them. Well, to keep them for our own purposes, but then you need to have the certificate for shipping to foreign countries.

A typical concentration in the dogfish liver, because liver is about the only thing that is monitored around the U.S. coast. They are quite low concentrations.

These are parts per billion, and they are, indeed, a challenge. You will see that tin does not have a plus or minus. So, as far as tin is concerned, this is only a reference material; it is not a certified reference material.

We did not have a big enough data base in order to consider certification of that material. The number is probably a fairly good one, but we did not assign a plus or minus range to it.

The range is the most important part of the number. You do not even need the number itself; you just need the range.

The other thing to look at, because we have complaints that your ranges are so narrow that we cannot seem to get within them, and that should not be what you are looking at. You should be looking at whether the range of the reference material that you are analyzing is within your plus or minus, and then look at it from that point of view and see whether your plus or minus is too big for your purposes, but if your range is within your plus or minus and your uncertainty, it is good enough for your purpose. You are probably accurate enough to do the job.

Most people tend to look at it the other way on and worry about the fact that they cannot get within the uncertainty range of the producers.

We ran into a problem, and it is a philosophical problem. We produce these materials. We defat them. We get a nice white powder, and they dissolve up easily, because we have defatted them and everything, but that it not a real sample, and it bothers us.

The question is, how do we get the fish really into the bottle? It is a perplexing problem. Of course, we cannot really do that, because we cannot find a homogeneous population of fish, or we would try it.

So, we developed a methodology with the people at the Technical University of Nova Scotia where we homogenized the material, added a bit of antioxidant, again homogenizing but diluting it with a bit of water because that is necessary for the process, and then emulsification in the same kind of machine that is used to produce homogenized milk or chocolate milk or ice cream so that you have a true emulsion that lasts forever, add a quality sealing, autoclaving to kill the enzymes that promote rancidity, and then packaging.

It works, and we have produced a beautiful material which you see in the ampule, and then it can be removed from the ampule, transferred to a volumetric flask where the suspension will stay homogeneous for as long as you desire. You can pipette it.

There is only one problem with it. Nobody buys it. It is something different. It is a second generation reference material, as we call it. We got great accolades from our colleagues and international producers, but nobody seems to want to use it.

That is one of the problems, how to transfer it to the client market. We do not know how to overcome that one. Maybe we are not good enough salesmen.

All our biological materials are certified with respect to methyl mercury, again, because we think that this is the way to go, and, again, we are unique in this business.

Some sediments are beginning to appear from Europe certified with respect to methyl mercury.

You can see in some cases in dogfish muscle that the methyl mercury is almost the total mercury. In other cases, it is only one third or one half.

This is not trace metals, but I am so proud of my guys for having been able to do this, because these concentrations, these are ng/k. That is about a thousand-fold less than the PCB concentrations you may be working with.

When you consider that they took from a 9 gram sample and they were following less than half a total nanogram of dioxins and furans through a horrendous clean-up and separation procedure and could come out with plus or minuses as low as that in order to certify it, along with the collaborating five or six Canadian labs that cooperated with us in this certification, it was, indeed, a feat that we are rather proud of.

I am just going to... I will not spend any time with this. I am just going to end up with two slides which demonstrate what we think is the ability to comply with the new MDLs which are being foisted upon you by EPA.

The required MDL list may not be entirely accurate, because I understand there was a revision to it recently following the list I had, but you see, if the required MDL for the six metals on the left are in blue, that pneumatic nebulization by ICP/MS is quite able to meet them for those six. Ultrasonic nebulization is even better but probably not necessary, and on-line preconcentration certainly does it also.

Why, you might ask, do we need an on-line concentration for these materials? Well, even the pneumatic and ultrasonic nebulization requires a separation and a preconcentration of the materials. The on-line concentration, if you do it directly into your ICP/MS, takes you out of the clean room. It gets you away from that horrendous cost that has been scaring you all morning.

We do that on-line preconcentration on the 5 ml sample in the instrument room, and I thought I would like to impart that information to you.

Now, there are other metals on the list, and here we have some problems. Obviously, antimony, we can meet that just by pneumatic nebulization into ICP/MS. The arsenic... the red numbers are we are getting close but not quite there yet. The yellow, we are not there. The white, we are there.

When I last saw the arsenic number, it was 0.2 ng/L. We can with a hydride generation going directly into the ICP/MS. Now, no preconcentration is necessary here. We can get down to 0.3 ng/L. So, we are getting awfully close.

We are getting close with mercury, and we are probably there already with selenium and silver even with pneumatic nebulization, because these required MDLs are a bit hazy and hairy on their own. Certainly, with hydride generation, we are there for selenium.

That is the talk there, Mr. Chairman. I think I have overstepped my time. Thank you.

QUESTION AND ANSWER SESSION

DR. FIELDING: Are there any questions? Before you ask the questions, may I remind you we do have microphones, and you should try to speak directly into the microphone and also give your name and affiliation before you start asking questions.

Are there any questions?

MS. BURGESSER: My name is Lisa Burgesser. I am with Environmental Research Associates. I was just wondering why you do not believe in spiked samples.

MR. BERMAN: We are never sure that a spiked sample behaves the same way in the analytical process as a sample that has been tied up by Mother Nature, and God knows what the speciation or what combination. So, while you might be able to easily extract 100 percent of your spike, you may not be able to extract 100 percent of the analyte of interest.

There is no way of your getting it in there in the right form.

MS. ASHCRAFT: What is the price range of the...

DR. FIELDING: Please give your name and affiliation.

MS. ASHCRAFT: Merrill Ashcraft, Navy Public Works Center. What are the price ranges of these standard reference materials?

MR. BERMAN: They range somewhere from $140 to $165 Canadian dollars for substantially sized bottles. The waters are 2-liter bottles. Multiply by 0.75 to get it into real money, and you will see that you get a real bargain.

MS. ASHCRAFT: Are you going to be leaving a card or something or your full address so we can contact your agency to purchase these?

MR. BERMAN: Our full address is in the list of attendees, but if you want, I will give you a card.

DR. FIELDING: Are there any other questions?

(No response.)

DR. FIELDING: Thank you, Shier.

(Slides for this presentation were not available at the time of publication.)

DR. FIELDING: Our next speaker is Dr. Diane Blake who will present a paper entitled Enzyme Immunoassay to Determine Heavy Metals using Antibodies to Specific Metal-EDTA Complexes.

Diane is an Associate Professor for the Departments of Ophthalmology and Biochemistry at Tulane University School of Medicine. She has worked as an assistant professor at the Department of Biochemistry at Meharry Medical College, a research scientist at Ames Division of Miles Laboratory, and a lecturer for the Department of Biological Chemistry at the University of Michigan.

She received her doctorate degree in biochemistry from the University of Michigan and her B.S. degree in biochemistry from Ohio State.

Diane?

ENZYME IMMUNOASSAY TO DETERMINE HEAVY METALS USING ANTIBODIES TO SPECIFIC METAL-EDTA COMPLEXES

DR. BLAKE: This is going to be somewhat different from what you have heard so far.

I would like to thank Dale Rushneck and the other organizers for inviting me here today, because what I want to describe to you is really an emerging technology that is not yet out of the laboratory. I was quite excited to be invited here so I could talk to the ultimate end-users of this technology and get some feedback about how we should be directing our experiments.

Today, I would like to tell you about an assay we are developing in our laboratory that will permit rapid, inexpensive, on-site analysis of specific heavy metal ions in wastewater effluents and ambient water samples.

This assay uses antibodies and applies a technology called ELISA technology. I would like to spend the first couple of minutes just reviewing the general features of ELISA technology and then go on to explain how we have adapted this technology for the assay of heavy metals.

ELISA technology requires an antibody that binds tightly and specifically to the material that you want to analyze, and from now on, I will call that material an antigen. The antigen, which I have designated as the little triangle on top of the circle in Figure 1 is insolubilized on the bottom of a plastic plate.

The antibody (inverted Y in Figure 1) is linked covalently to an enzyme (shown in Figure 1 as an arrow) that provides the signal for the assay. That signal is usually a color.

When you add the antigen to this plastic plate that has the antigen immobilized on the bottom surface, the antibody binds, and it binds tightly enough to remain bound through several washes of the plate.

When you add a substrate to the solution for the enzyme, color will develop, and the more antibody you have bound to the plate, the more color that will develop. So, that is your assay. You measure color formation.

We are using a variation of this particular ELISA technology called antigen inhibition ELISA, and which is shown in the second part of Figure 2. In this variation, in addition to the immobilized antigen on the plate, you also have soluble antigen in the solution, and the antibody has a choice of binding either to the immobilized antigen or to the soluble antigen.

When the antibody binds to the soluble antigen, it will be removed during the wash procedures. So, as you add more and more soluble antigen in your solution, you generate less and less color in the assay.

In antigen inhibition ELISA's, if you keep the antibody concentration constant and increase the concentration of soluble antigen, you generate inhibition curves where the color decreases in proportion to the concentration of soluble antigen in the solution. You can make standard curves and read your unknowns off these standard inhibition curves.

Of course, these assays are only as good as your antibody. Our first problem in developing this technology was obtaining an antibody that would recognize heavy metals.

Heavy metals, as you probably know, are not in themselves antigenic, but we discovered that if you bind them to a chelator like EDTA and then covalently link that metal chelate complex to a carrier protein and inject it into a mouse, the complex is antigenic, and it will elicit very specific antigen responses.

This was first done in the mid 1980s by a researcher in California named Claude Meares who first generated an antibody that was specific to indium-EDTA.

I would first like to tell you about some of our model system studies with the indium-EDTA antibody that we got from Dr. Meares; and these data have recently been published in Analytical Biochemistry. Then I will go on to talk about a new anti-cadmium antibody that we have generated in our own laboratory, and tell you some of the characteristics of that antibody as well.

The first problem in developing an ELISA, once you have an antibody, is to make sure that your antigen can be immobilized to the bottom of the plate. Free metal chelates

will not stick to the bottom of ELISA plates, so we solved that problem by covalently conjugating the metal chelates to a protein. We used a carrier protein called bovine serum albumin which is abbreviated as BSA in some of my figures.

Once the metal chelate has been covalently attached to the protein, then the conjugate sticks very nicely to commercially available ELISA plates. All of our ELISA plates have been pre-washed in 3 molar HCl to make them metal-free.

One of the first studies we did, shown in Figure 2, is to ask how much of this indium-EDTA complex can be immobilized onto our BSA carrier molecule. Figure 2 shows how different degrees of substitution of the BSA carrier protein effects color development in the assay.

We have plotted color on the y-axis, and reciprocal antibody dilution on the x-axis. We started at a 1:1000 dilution of the antibody and we went up to 1:64,000 dilution.

You can see that as we increased the extent of conjugation on the carrier protein, we increased the color the assay produced until we got up to a conjugate with 31 percent substitution. At 53 percent substitution, the color formation starts to decrease. We interpreted this result to be due to stearic hindrance to antibody binding at very high levels of substitution.

On the basis of these data, we used the 31 percent substituted material for the rest of the studies I am going to tell you about today.

So, we had a standard assay that could detect indium-EDTA chelate bound to the bottom of the plate, and we could get adequate color formation in our assay.

The next thing we want to do was to add soluble antigen and see if we could generate standard inhibition curves. The first standard curves we generated with the indium-EDTA are shown in Figure 3. Indium-EDTA was the soluble antigen we used to inhibit color formation and increasing indium, shown as ppm on the x-axis, decreased color in the assay.

You can see that in this particular assay, if we went up to 320 ppm of indium, we got complete inhibition of color formation, that is, no antibody binding to the well. This particular assay detects cadmium down to about 0.075 ppm. The sensitivity of this assay, which we defined as two standard deviations above the minimal detectable concentration, was 0.6 ppm.

This is a very simple assay. You dilute your sample into 5 mM EDTA, preincubate the sample with the antibody, add the mixture to precoated ELISA plates, develop the color, and read the indium concentration from the standard inhibition curve.

Now, this is a nice assay, but it is really not very sensitive, because it only detects indium down to 0.6 ppm. So, we next looked for ways that we could easily increase the sensitivity of this assay.

One of the best and cleanest ways to increase the sensitivity of an immunoassay is to obtain an antibody with a very high affinity for its ligand.

Well, we knew that this particular antibody had not been made just to indium-EDTA. It had been made to a conjugate which consisted of indium-EDTA (shown as a little spider web in Figure 4) up there, linked to a benzo group that was subsequently linked to a carrier protein, in this case, keyhole limpet hemocyanin. This three-part conjugate (shown at the top of Figure 4) is what we injected into mice to get an immune response.

So, we reasoned that indium-EDTA may be a very poor binder, but if we started adding more of what was actually used as the antigen, we would increase the affinity of our antibody for the antigen and, hence, make a more sensitive immunoassay.

So we next prepared inhibition curves using indium-(p-nitrobenzyl)-EDTA as the soluble antigen, as shown in Figure 5. You can see from the figure that we get about a five-fold increase in sensitivity in this assay when we use indium-(p-nitrobenzyl)-EDTA as the soluble antigen. Indium at a concentration of 120 ppm completely inhibited color formation and the limit of sensitivity in this particular assay was 0.1 ppm, so we were getting our limits of sensitivity into the high ppb range.

To make the assay even more sensitive, we added the entire indium-(p-nitrobenzyl)-EDTA-protein conjugate as the soluble antigen. As shown in Figure 6, we now have a very sensitive assay. The sensitivity of this assay goes from 2000 ppb down to about 0.001 ppb. The limit of the sensitivity in this assay format was 0.005 ppb.

These data demonstrate that we could develop a very sensitive immunoassay for indium. We next wanted to study the specificity of the assay. In Figure 7, we show the specificity of the assay for indium. Color formation is plotted on the y-axis and metal concentration (plotted on a log scale) is shown on the x-axis. You can see that this assay is about 100 times more sensitive for indium (shown as the circles in Figure 7) than it is for either the copper (triangles) or manganese-EDTA (squares). These two metals were tested because they were present in the growth media for a bacterium that we wanted to use in our field test of the indium ELISA.

Indium is a rare metal present at very low concentrations in the environment and we felt that using water samples or soil extracts to field test the assay would only give only negative results. We did, however, happen to have a bacterial culture in the laboratory that metabolized indium arsenide and solubilized the indium during its growth cycle. We therefore decided to test for indium solubilization during bacterial growth as a field test for our new immunoassay. Figure 8 shows some of our solubilization data.

On the x-axis we have plotted day of incubation of this particular bacteria with insoluble indium arsenide. On the y-axis we show the amount of indium solubilized by bacteria growth, assayed by both ELISA and atomic absorption spectroscopy. As you can see, the values for indium were very similar by both methods of analysis.

If you plot the AA data versus the ELISA data, you get a pretty good correlation. If it were perfect correlation, you would get a slope of 1 and an intercept through zero. Our slope was 0.9, and we had a non-zero intercept.

Of course, we like to think that the AA data was wrong, because bacterial solutions had particulates in them. Both indium arsenide, the substrate, and indium arsenate, the product of bacterial metabolism, are relatively insoluble, and although we had filtered our solutions through a 0.45 micron filter, we could not be sure that we had gotten out all the particulates.

The ELISA procedure only assays soluble, dissolvable metals or metals that can be solubilized with 5 mM EDTA, whereas the atomic absorption method would look at total metals, including any particulates. So, we think that the slight difference that we saw in the two methods might be due to particulates in our bacterial solutions.

Now, as I said, these data have been recently published in Analytical Biochemistry, and I will be happy to make reprints available to anyone who is interested.

While we were doing these model system studies, however, we were also in the process of making a monoclonal antibody to a metal that we knew was a priority pollutant. We chose cadmium, because it has such a high renal toxicity.

So, the procedure for antibody production was very similar to that used for indium. We covalently conjugated the EDTA to a carrier protein, loaded it with cadmium, and injected it into mice. Then we screened the clones to get a hybridoma that made a cadmium-specific monoclonal antibody.

In Figure 10, I show an antigen inhibition curve similar to those generated for indium, but now we are measuring a priority pollutant. This curve was generated using a cadmium-EDTA complex as the inhibiting antigen.

It appears that the cadmium-specific monoclonal antibody gave better sensitivity than the indium antibody. We are down in the ppb range, and this particular assay goes from about 6000 down to 0.7 ppb.

We hoped to increase the sensitivity of the assay by changing the nature of the soluble antigen, and in Figure 11 we have a p-nitrobenzyl EDTA derivative of cadmium as the soluble antigen. We did not get the increase in sensitivity that we observed with the indium antibody. Again, the limit of sensitivity was about 0.7 ppb, but the shape of the

curve had changed, and I will discuss this curve in relation to assay sensitivity when I present Table 1.

When we added the cadmium-EDTA-protein conjugate as the soluble antigen, the sensitivity of the assay was in the parts per trillion range, as shown in Figure 12. This was done in the laboratory with atomic absorption grade reagents, so I am not making any claims to how it is going to work in a field test, but the cadmium ELISA looks to be a very, very sensitive test.

Using cadmium-EDTA-protein as the soluble inhibiting antigen, we could detect cadmium from about 26 to 330 ppt in a very simple immunoassay format.

When we began generating our anti-cadmium antibodies we did a literature review on cadmium and where it occurs, and we discovered that it often occurred as a contamination in zinc ores, and also a contaminant in metal plating plants.

So, when we screened hybridomas for this antibody production, we wanted to make very sure that we did not get any cross-reactivity with zinc, because we thought the end users might be very interested in distinguishing zinc versus cadmium.

In Figure 13, I show metal ion specificity of our anti-cadmium antibody. This assay is two to three orders of magnitude more sensitive for cadmium than it is for either zinc or mercury-EDTA complexes.

The final table (Table 1) shows a quick summary of the data we have obtained so far with the anti-indium and the anti-cadmium antibodies in this antigen inhibition ELISA. The anti-indium antibody that we got from Claude Meares is actually inhibited by free indium ions to some extent, but since we run our tests in 5 mM EDTA, that is really not a problem for the assay as presently formatted.

With indium-EDTA as the soluble antigen, the concentration required for 50 percent inhibition of color formation is around 20 ppm. If you use p-nitrobenzyl EDTA as the soluble antigen, 6.8 ppm is required for 50% inhibition, and if you add the complete indium-EDTA protein conjugate, only to 0.6 ppb is required.

Now, the anti-cadmium antibody which was made specifically for metal ion immunoassays provides a more sensitive ELISA. The antibody does not react at all with free cadmium. With cadmium-EDTA as the soluble antigen, we get a 50 percent inhibition at about 83 ppb. When we used cadmium-(p-nitrobenzyl)-EDTA, only 15 ppb were required to inhibit color formation by 50 percent. This is a 5-fold increase in sensitivity when we changed the structure of the soluble antigen, just as we saw with the anti-indium antibody. The limit of detection was not lower in this assay because when these assays were assembled, the antibody concentration exceeded the cadmium concentration. That is the

reason that we got a curved inhibition plot when cadmium-(p-nitrobenzyl)-EDTA was used as the soluble antigen.

Finally, when we get use to the cadmium-EDTA-BSA, we are down in the parts per billion range here as well.

Now, I am at the point where I would like to bring this assay out of the lab and actually start looking at real samples, especially with the cadmium antibody. One of the reasons I was happy to be asked to speak here today was to see whether I could generate some interest in people sending me some samples, so I could test my new cadmium assay and compare it with ICP or AA assays that are already available.

We do not envision this test as replacing ICP/MS or AA, but we envision this as being a useful adjunct to those procedures that would allow you to do on-site analyses and get a general idea of how much metal contamination there is at a site.

It is a very simple assay to perform. It is very portable. The test is performed in a little plastic plate about 3 by 4 inches long, and with an inexpensive plate reader. And it is very quick. It only takes a couple of hours to do these assays.

At this point, I would really appreciate feedback from people who might be final users of the technology about what we should do next to make this assay useful to you, the end-users.

I would like to stop here. I would like to thank my collaborators, Drs. Chakrabarti, Hatcher, and Blake who participated in this study and also thank the EPA who supported this research.

Thank you.

QUESTION AND ANSWER SESSION

DR. FIELDING: Are there any questions?

MR. PLOSCYCA: I am Jim Ploscyca with IEA Laboratories. What matrices do you consider this to be applicable to in the future? We are talking, I guess, water at this point?

DR. BLAKE: Well, yes. We are thinking of wastewater. The assay presently detects soluble metals or any metals that can be solubilized with 5 mM EDTA. You dilute your sample into 5 mM EDTA.

So, I guess I need some help from you folks, about what matrices I should be testing.

All of the inhibition curves I showed today were done in ultra-purified water with AA standards. That is what we used to generate these standard curves.

MR. PLOSCYCA: Just so I make sure I understand this, you need one of these for every particular metal you are testing for. Correct?

DR. BLAKE: Yes. What metals do you think would be most applicable? What metals do you need quick and fast that go in the concentration ranges that I am able to detect?

MR. PLOSCYCA: Well, what I mean is one test would test for, say, chromium, cadmium.

DR. BLAKE: Yes. It is not like an ICP where you can get the whole spectrum. You get one metal at a time.

MR. PLOSCYCA: Thank you.

MR. KIMBROUGH: My name is David Kimbrough, and I am with the California Environmental Protection Agency.

I had a question for you. I did not quite catch on the earlier slide, how much selectivity do you have between these different metals? Will they interfere with each other? I did not quite get that off your slide there.

DR. BLAKE: Well, we can go back. It depends on the antibody you are looking at. This is the one we did for cadmium, and this is just a preliminary one, because if you put too many metals on one slide, it gets really complicated

to look at, but in this we have about a thousand-fold selectivity of cadmium over zinc or mercury.

So, at a concentration of 1 ppm here, we are down to 30 percent of total color formation with 1 ppm of cadmium, and we have to go up to 100 ppm or either zinc or mercury.

MR. KIMBROUGH: Those other metals do give you color formation, though?

DR. BLAKE: Pardon me?

MR. KIMBROUGH: These other metals do give you color formation?

DR. BLAKE: They do inhibit color formation at a 100 to 1000-fold higher concentrations than cadmium.

MR. KIMBROUGH: Have you considered using different chelating agents instead of EDTA which might give you more specificity and selectivity?

DR. BLAKE: Yes, we have something going right now on this idea. One of the problems with EDTA is it does not bind some metals tightly enough to give you a stable complex that survives when you inject it in the animals. EDTA is a first generation chelaters, and there are second generation chelaters that are more highly specific for certain metals. We are thinking about making monoclonals for those second generation chelaters as well that will give us a higher specificity.

Yes?

MS. ASHCRAFT: Merrill Ashcraft with the Navy Public Works Center. Just a word of caution to you. You will not be able to look at solubilized and dissolved as being equal if you use something like EDTA, because once you enter that chelating agent into the water, it will immediately solubilize some of the metals that may be adhering to particulates that would not be seen by regular dissolved metals. You need to look at that.

DR. BLAKE: Okay, that is the sort of feedback I need when I am starting field tests. Thank you.

Yes?

MR. HUNT: Carlton Hunt with Battelle. To follow that up, I think what you are going to find is EDTA is going to compete with natural organic ligands to release metals.

DR. BLAKE: So, we are going to get something more like total metals?

MR. HUNT: Right, so I do not know if you are measuring this against the free metal, the Cd^{+2}?

DR. BLAKE: Yes.

MR. HUNT: In a natural environment, in wastewaters particularly, you are going to have an awful lot of competing reactions for that EDTA, and you are going to have to take that into account at some point. That is just in the dissolved phase let alone the particulate issue.

DR. BLAKE: Now, if we have 5 mM EDTA in our reaction, the association constant of cadmium for EDTA is up in the 10^{24} range.

MR. HUNT: You are probably going to pull it out, but I think you are going to have to look at that fairly carefully to see if you are getting, quote, an absolute number. You are going to have to look at whether or not you are getting 20 percent, 80 percent, 90 percent out as sample.

DR. BLAKE: Since these assays are not inhibited by EDTA, we can even increase the concentration of EDTA if we need to.

MR. HUNT: Well, when you move to natural waters, I think you are going to have to do a sequence that looks at that issue.

DR. BLAKE: Yes. We have not done anything with natural waters yet.

MR. HUNT: Thank you.

DR. FIELDING: Are there any other questions?

(No response.)

DR. FIELDING: Thank you.

Figure 1

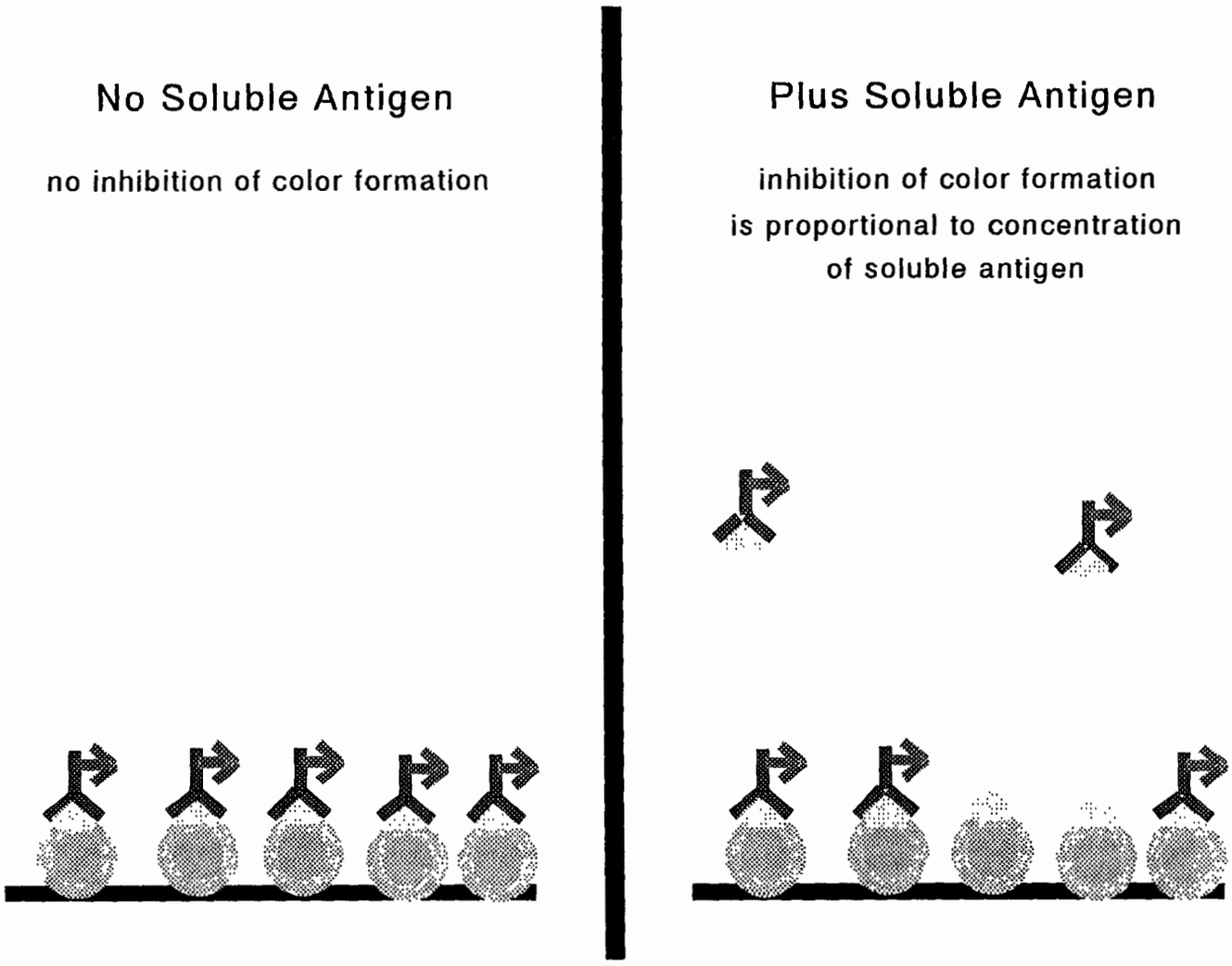

No Soluble Antigen
no inhibition of color formation
Plus Soluble Antigen
inhibition of color formation
is proportional to concentration
of soluble antigen

Figure 2

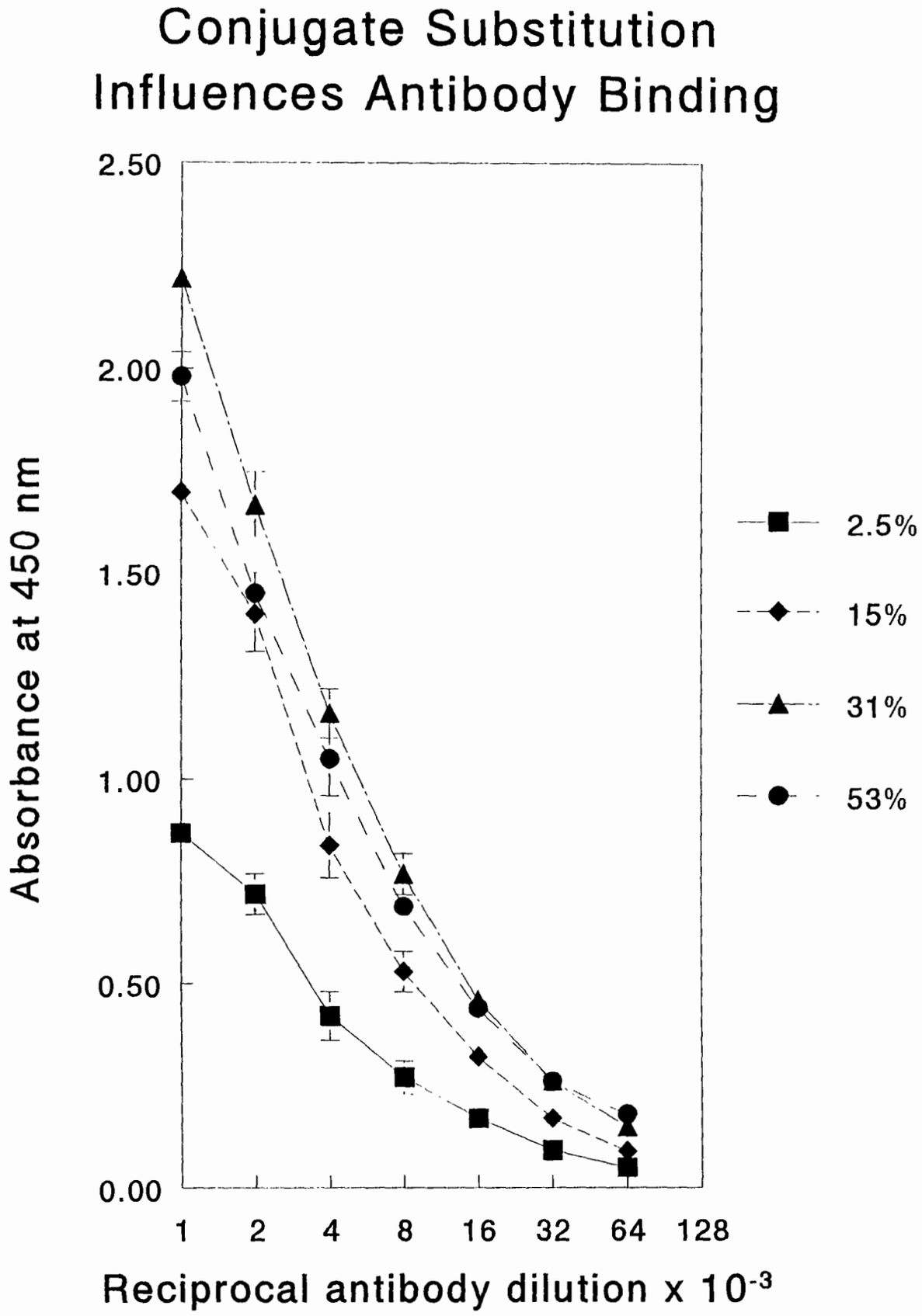

Conjugate Substitution
Influences Antibody Binding
Absorbance at 450 nm
2.50
2.00
1.50
1.00
0.50
0.00
1
2
4
8
16
32
64
128
Reciprocal antibody dilution x 10-3
2.5%
15%
31%
53%

Figure 3

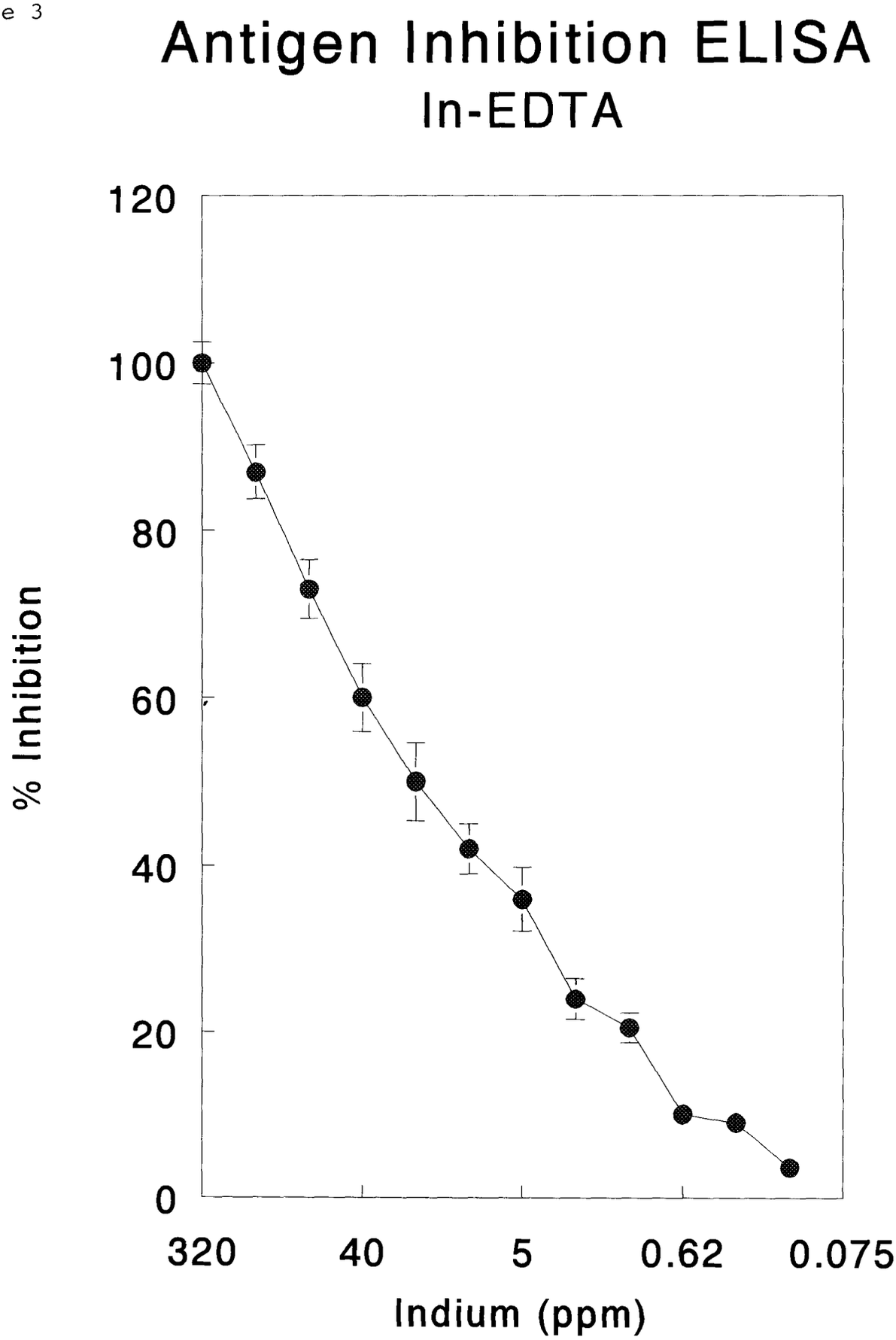

Antigen Inhibition ELISA
In-EDTA
120
100
80
60
40
20
0
% Inhibition
320
40
5
0.62
0.075
Indium (ppm)

Figure 4

Ligand Affinity Decreases when Ligand Occupies Less of the Binding Site

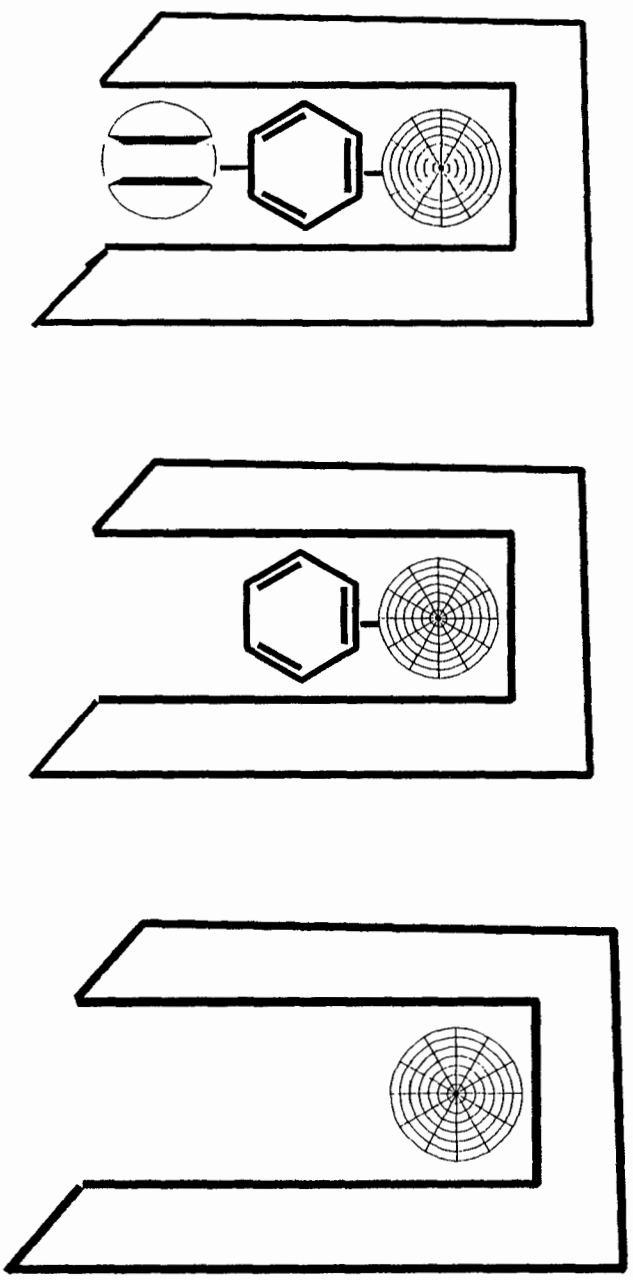


Figure 5

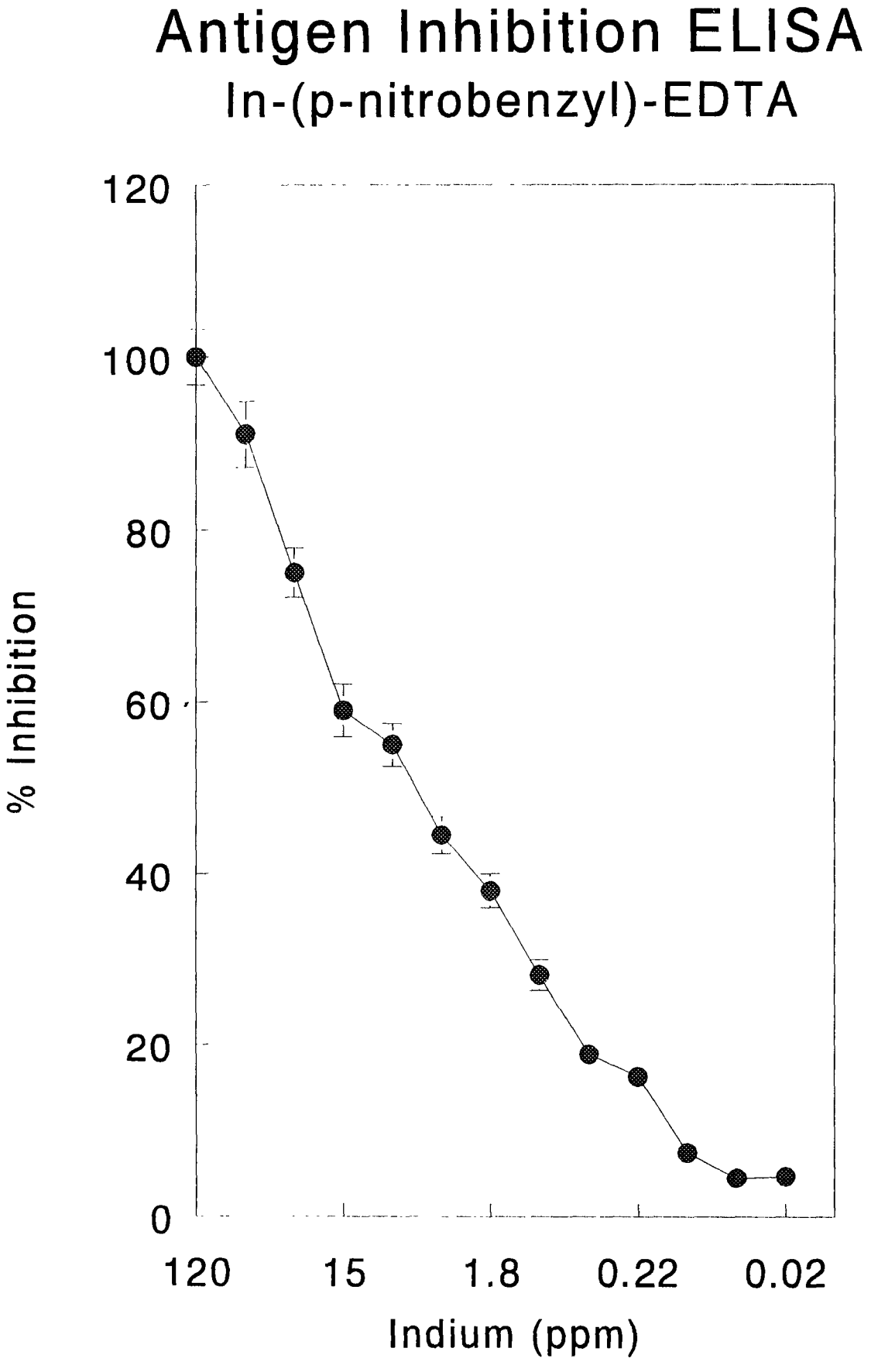

Antigen Inhibition ELISA
In-(p-nitrobenzyl)-EDTA
% Inhibition
120
100
80
60
40
20
0
120
15
1.8
0.22
0.02
Indium (ppm)

Figure 6

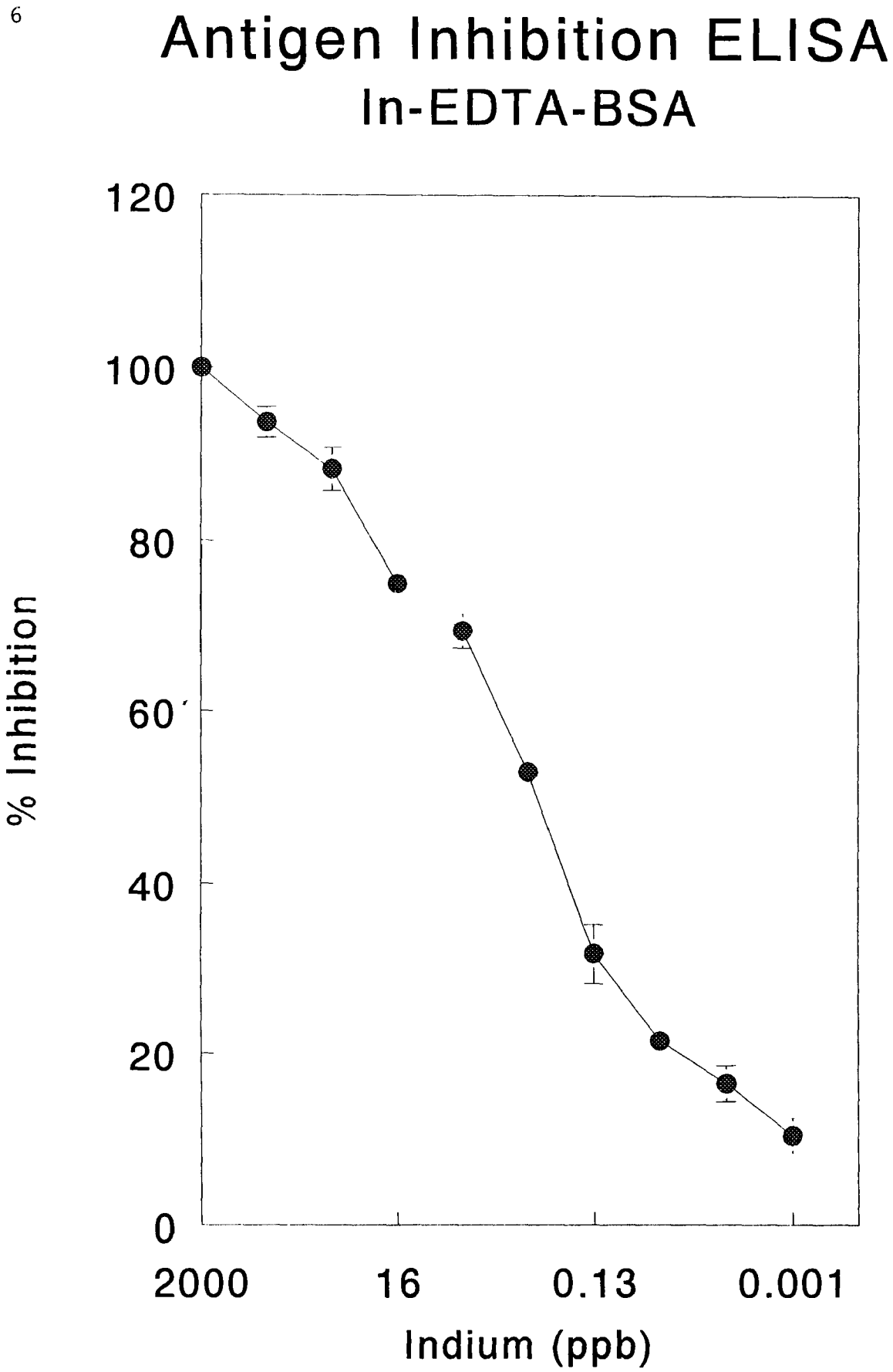

Antigen Inhibition ELISA
In-EDTA-BSA
120
100
80
60
40
20
0
% Inhibition
2000
16
0.13
0.001
Indium (ppb)

Figure 7

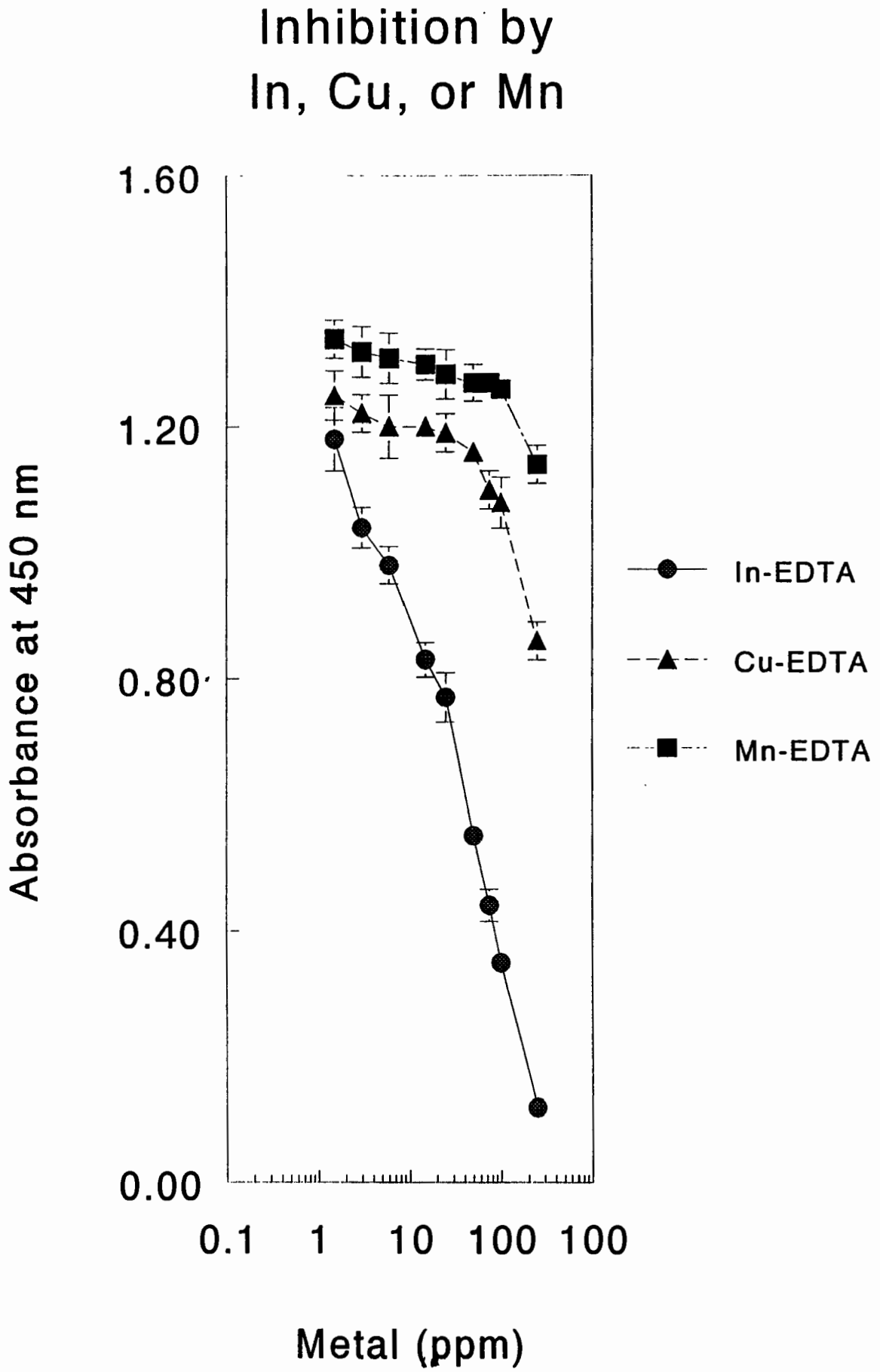

Inhibition by
In, Cu, or Mn
1.60
1.20
0.80
0.40
0.00
Absorbance at 450 nm
0.1
1
10
100
100
Metal (ppm)
In-EDTA
Cu-EDTA
Mn-EDTA

Figure 8

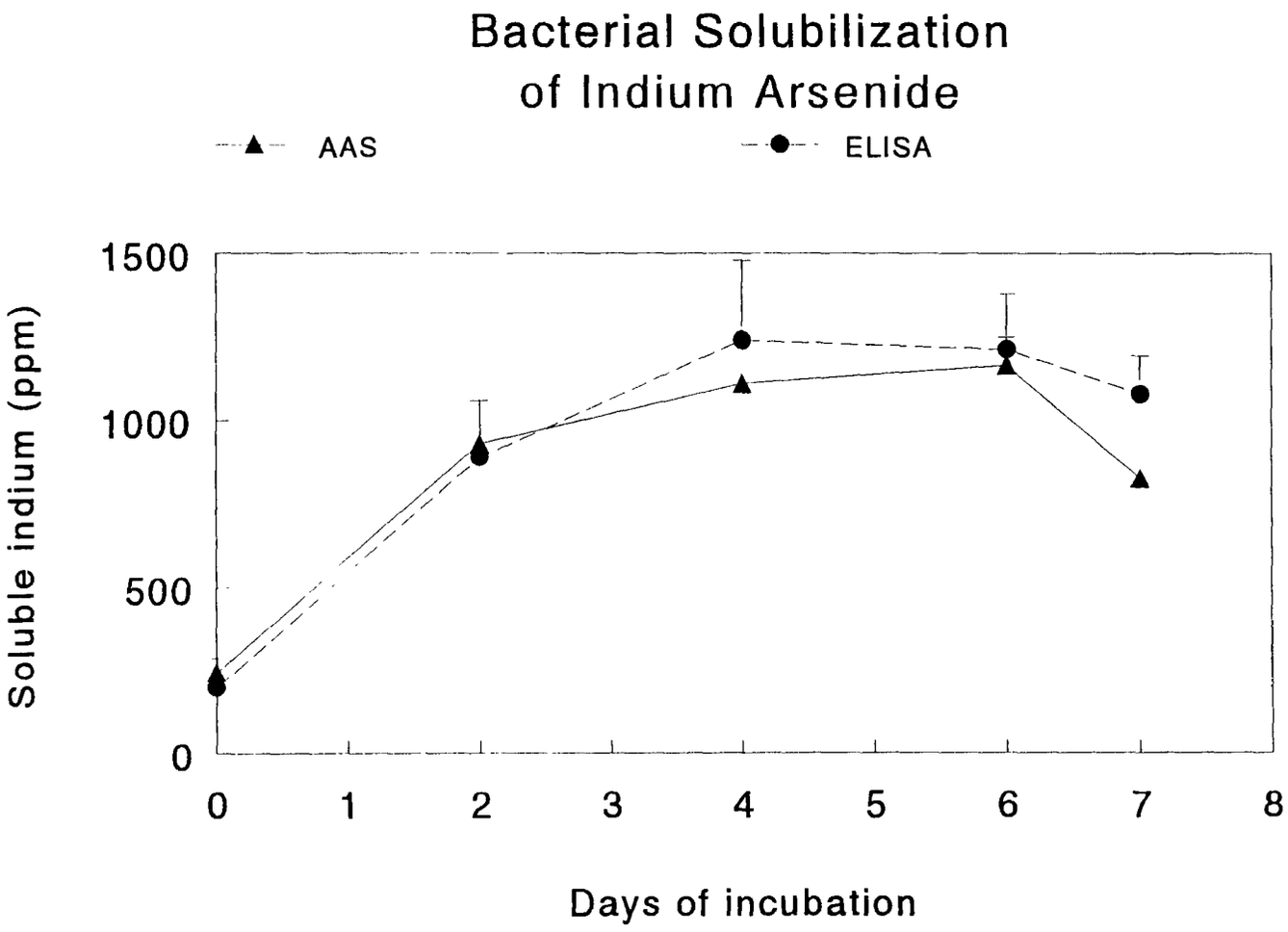

Bacterial Solubilization
of Indium Arsenide
AAS
ELISA
Soluble indium (ppm)
1500
1000
500
0
0
1
2
3
4
5
6
7
8
Days of incubation

Figure 9

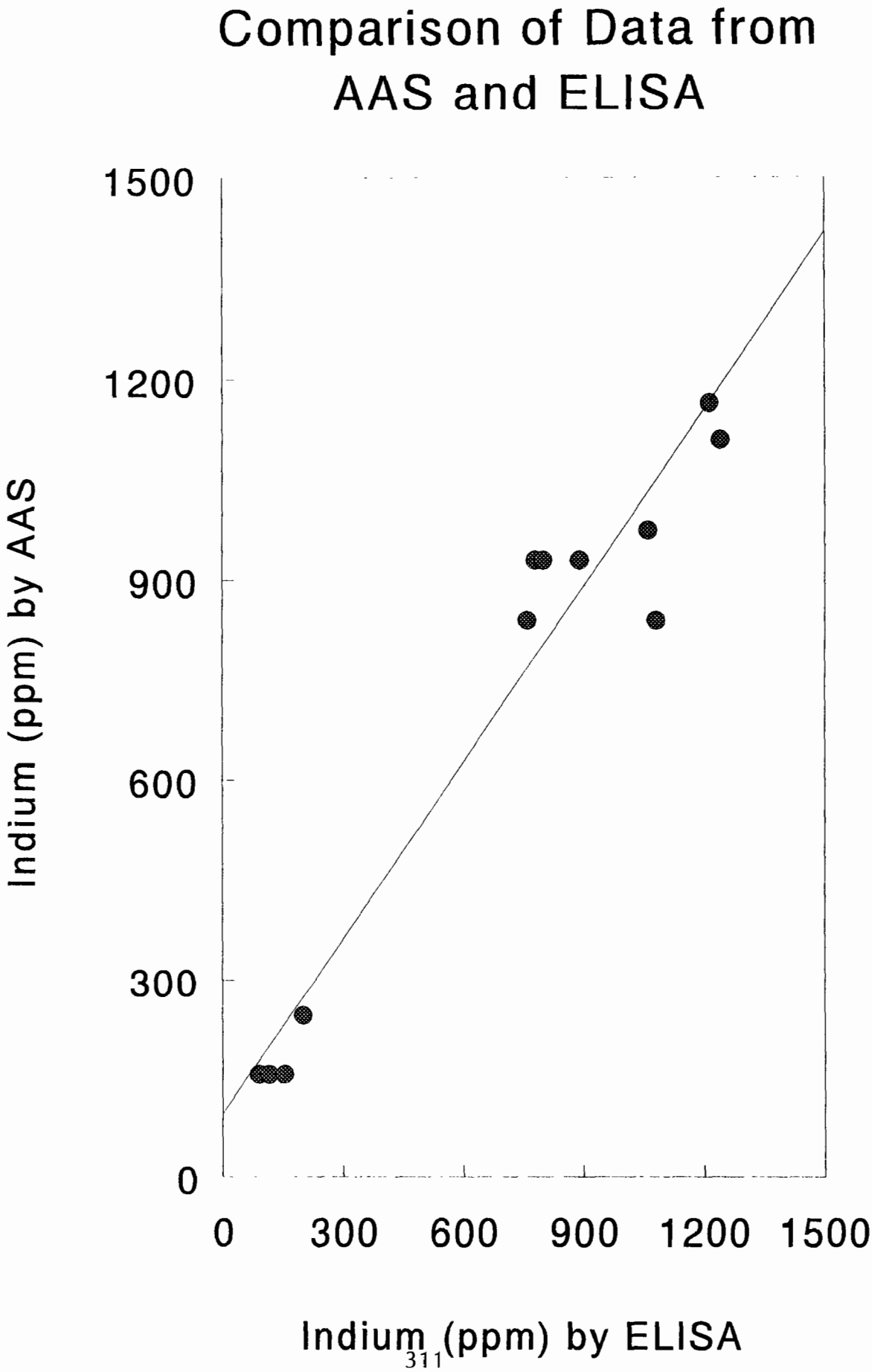

Comparison of Data from
AAS and ELISA
1500
1200
900
600
300
0
Indium (ppm) by AAS
0
300
600
900
1200
1500
Indium (ppm) by ELISA

Figure 10

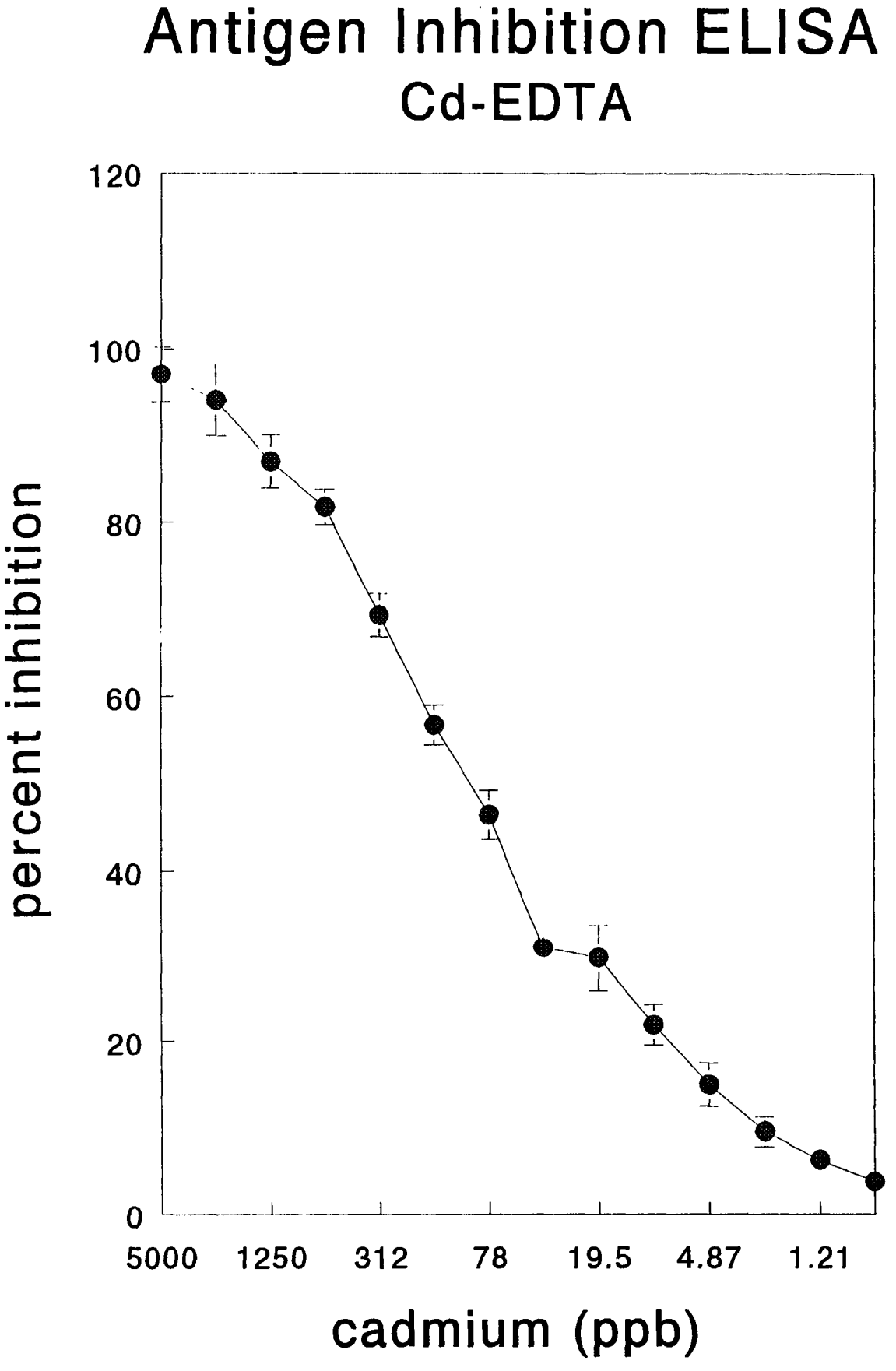

Antigen Inhibition ELISA
Cd-EDTA
percent inhibition
120
100
80
60
40
20
0
5000
1250
312
78
19.5
4.87
1.21
cadmium (ppb)

Figure 11

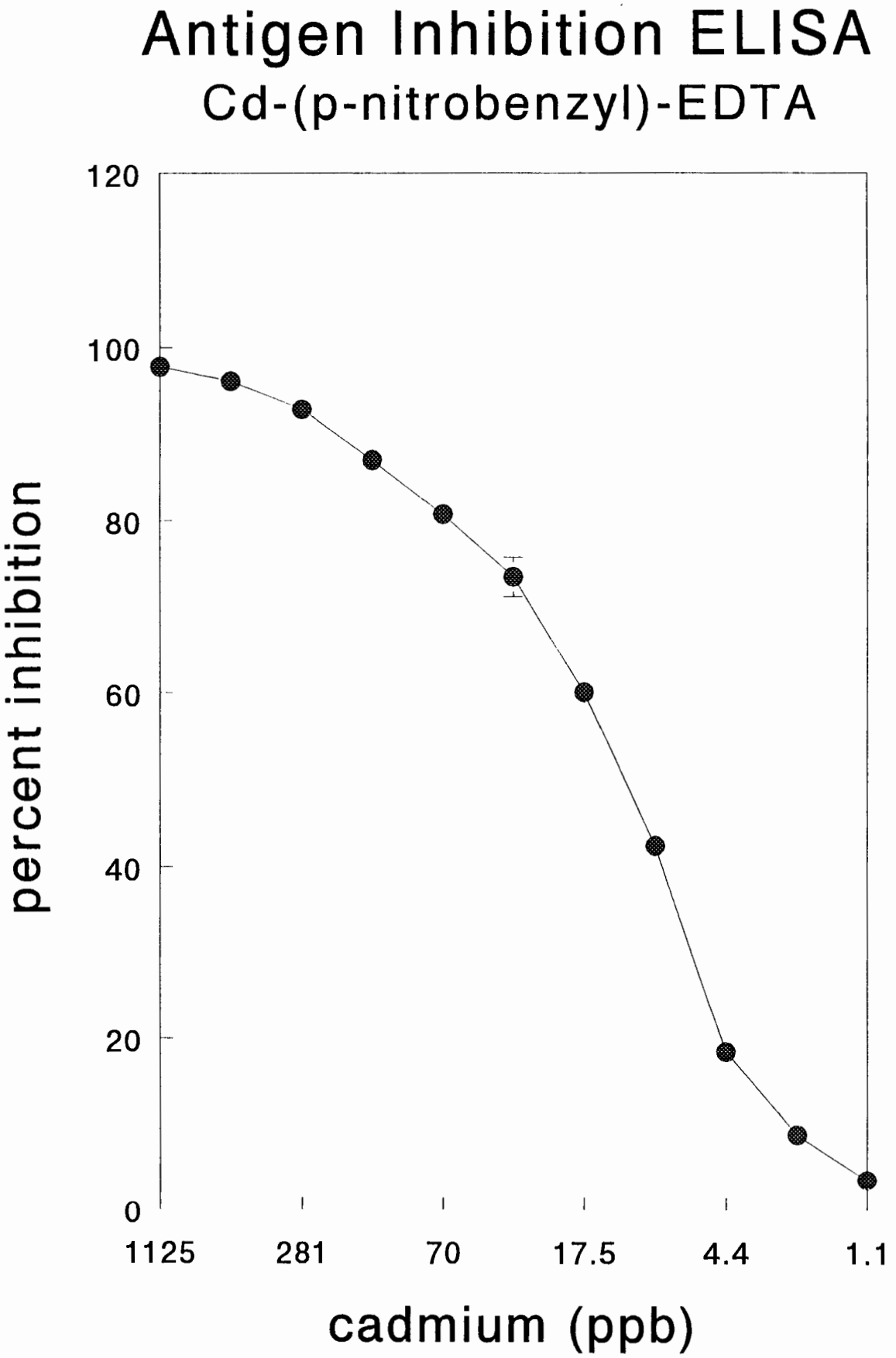

Antigen Inhibition ELISA
Cd-(p-nitrobenzyl)-EDTA
percent inhibition
120
100
80
60
40
20
0
1125
281
70
17.5
4.4
1.1
cadmium (ppb)

Figure 12

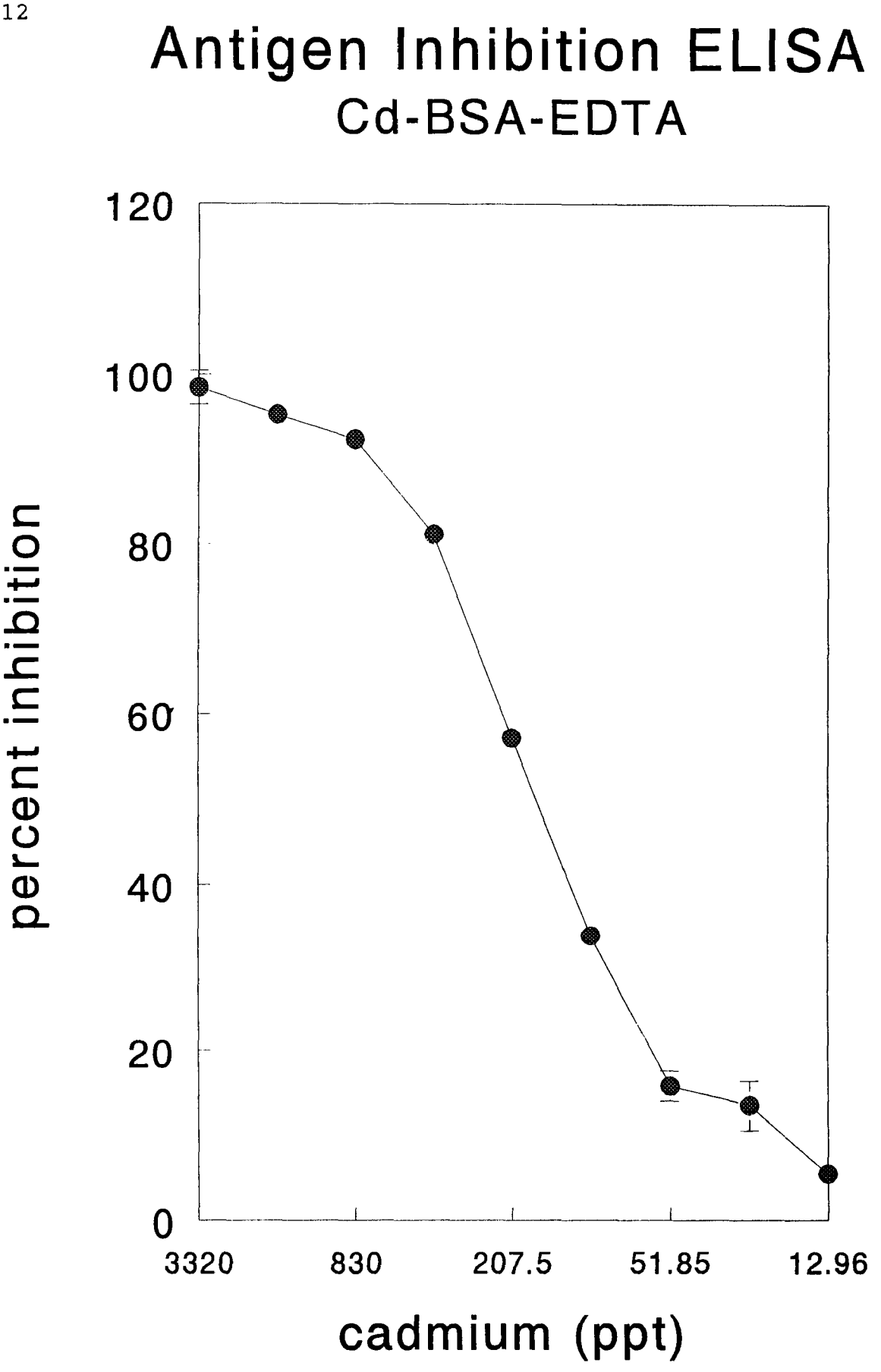

Antigen Inhibition ELISA
Cd-BSA-EDTA
120
100
80
60
40
20
0
percent inhibition
3320
830
207.5
51.85
12.96
cadmium (ppt)

Figure 13

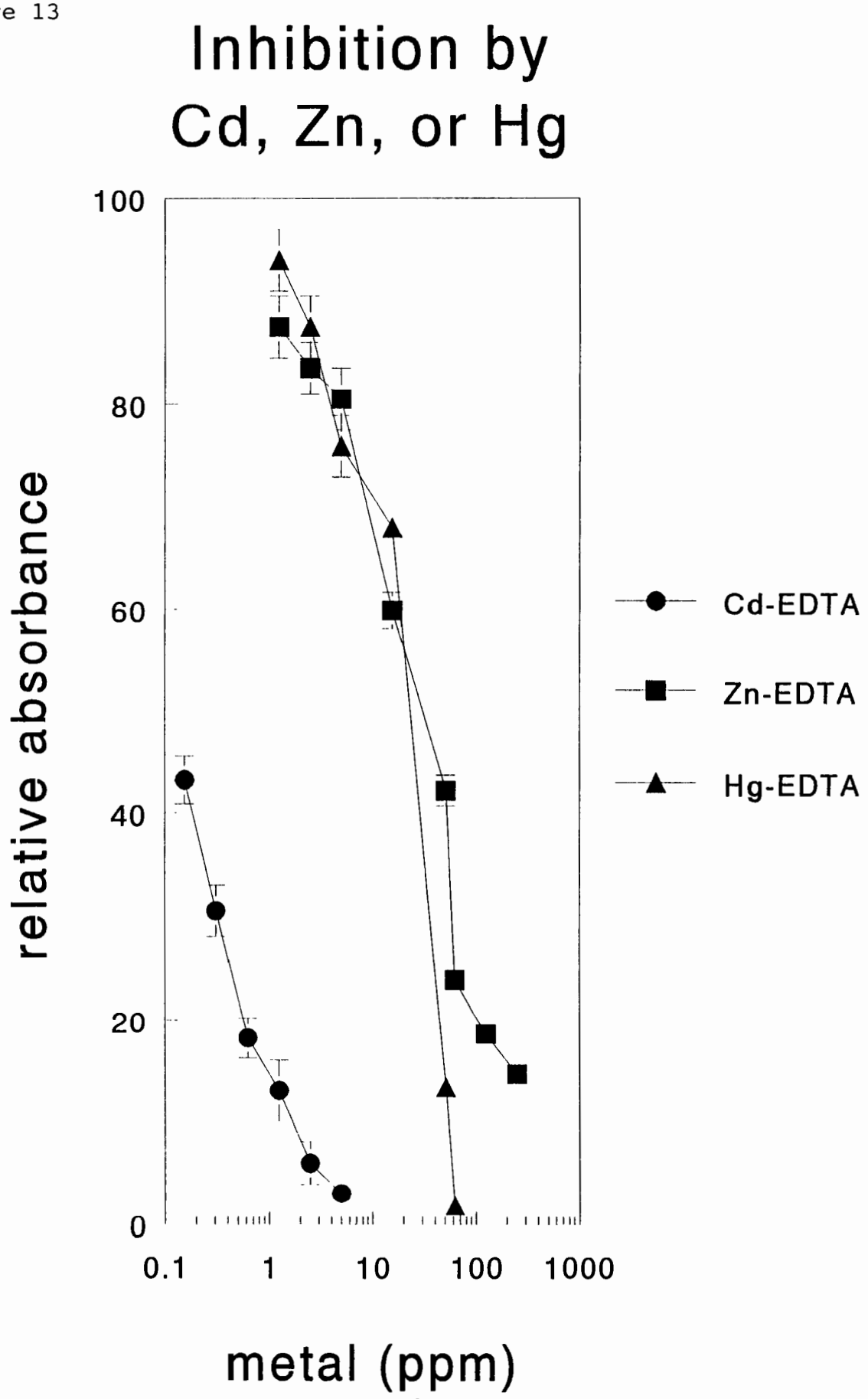

Inhibition by
Cd, Zn, or Hg
100
80
60
40
20
0
relative absorbance
0.1
1
10
100
1000
metal (ppm)
Cd-EDTA
Zn-EDTA
Hg-EDTA

Table I

Comparison of Anti-Indium and Anti-Cadmium Antibodies in Antigen Inhibition ELISA

Antibody	Soluble Antigen	Concentration Required for 50% Inhibition (ppm)
Anti-Indium (CHA255)	In	> 60
	In-EDTA	20
	In-(p-NBZ)-EDTA	6.8
	In-EDTA-BSA	0.0006
Anti-Cadmium (2A81G5)	Cd	>500
	Cd-EDTA	0.083
	Cd-(p-NBZ)-EDTA	0.015
	Cd-EDTA-BSA	0.00018

DR. FIELDING: Our last paper this morning will be presented by Billy Potter, entitled the Determination of Total Mercury for the Water Quality Based Approach.

Billy is a Research Chemist in the Inorganic Chemistry Branch of the Chemistry Research Division of EPA's Environmental Monitoring Systems Laboratory in Cincinnati.

He is responsible for the development of new methods and the improvement of existing methods for the analysis of parameters required by the Clean Water Act. This involves the renovation of existing methods to meet regulatory demand for the reduction of laboratory waste, lowering method detection limits, and increasing method reliability.

He received a B.S. degree in Chemistry and a B.A. degree in English from Central State College.

Billy?

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(SLIDE 1)

TITLE: **Determination of Total Mercury for the Water Quality Based Approach.**

SPEAKER: B.B. Potter

AUTHORS: Billy B. Potter, Inorganic Chemistry Branch, Chemistry Research Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati Ohio.

Winslow J. Bashe, Miguel D. Castellanos, Stephen E. Long and Jane A. Doster, Technology Applications, Inc., Cincinnati, Ohio.

(SLIDES 2-3)

ABSTRACT: The U.S. Environmental Protection Agency (USEPA) has developed the proposed EPA Mercury Method 245.7 for the determination of total mercury found in water, wastewater and sediment at the part per trillion (ppt) level. The total mercury method has an estimated method detection limit (MDL) of 5 ppt to 20 ppt of mercury. The MDL is made possible by digesting the sample using bromide/bromate reagent followed by detection of elemental mercury by cold vapor atomic fluorescence spectrometry at 253.7 nm. Method 245.7 may be used for the monitoring NPDES permits established by Water Quality Based Effluent Limits.

INTRODUCTION

METHOD 245.7, DETERMINATION OF MERCURY BY AUTOMATED COLD VAPOR, ATOMIC FLUORESCENCE SPECTROMETRY is written in the Environmental Monitoring Management Council (EMMC) method format. The EMMC format consists of the following sections:

(SLIDES 4-5)

1.0 **SCOPE AND APPLICATION**
2.0 **SUMMARY OF METHOD**
3.0 **DEFINITIONS**
4.0 **INTERFERENCES**
5.0 **SAFETY**
6.0 **APPARATUS, EQUIPMENT, LABORATORY AND CLEANING REQUIREMENTS**
7.0 **REAGENTS AND CONSUMABLE MATERIALS**
8.0 **SAMPLE COLLECTION, PRESERVATION, AND STORAGE**
9.0 **QUALITY CONTROL**
10.0 **CALIBRATION AND STANDARDIZATION**
11.0 **PROCEDURE**
12.0 **DATA ANALYSIS AND CALCULATIONS**
13.0 **METHOD PERFORMANCE**
14.0 **POLLUTION PREVENTION**
15.0 **WASTE MANAGEMENT**
16.0 **REFERENCES**
17.0 **TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA**

Each section addresses the details of the method application, procedures and quality control issues necessary for the proper execution of the method.

Method 245.7 describes procedures for the determination of mercury (organic + inorganic) total recoverable or dissolved (filtered 0.45μ), in drinking water, surface and ground water, sea and brackish water, industrial and domestic wastewaters. The chemistry of sample digestion is based on the brominating reagent producing bromine monochloride:

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl + 3KCl + 3H_2O$$

In the presence of excess bromide ions and acid, the bromine monochloride is converted to free bromine[1]:

$$BrCl + \text{excess } KBr \rightarrow Br_2 + KCl$$

Inorganic mercury compounds are rapidly oxidized by bromine and organomercury species are degraded by the oxidizing properties of bromine releasing mercury (II)[2,3] as follows:

$$HgR_2 + Br_2 \rightarrow RHgBr + RBr$$

$$RHgBr + Br_2 \rightarrow HgBr_2 + RBr$$

The excess Br_2 reacts to oxidize mercury, forming a complex. After the oxidation reactions are complete, the excess bromine is removed by the addition of hydroxylamine hydrochloride.

Elemental mercury vapor is generated from the digested sample by reduction with stannous (tin II) chloride in the presence of hydrochloric acid.[4] High purity argon gas is used to purge the mercury vapor from a gas/liquid separator, driving the equilibrium to the right as follows:

$$Sn^{+2} + Hg^{+2} \rightarrow (Ar\uparrow), Hg^{o}\uparrow + Sn^{+4}\downarrow$$

The excess $Sn^{+2}\downarrow$, $Hcl\downarrow$, solution is discharged to a waste container and the mercury vapor is carried by the argon flow to either a mercury concentrator/ detector or directly to the detector. The liquid containing spent reagents and sample are flushed continuously from the gas/liquid separator to a waste container. This waste contains tin and hydrochloric acid and does not contain mercury. The elemental mercury vapor is then purged from solution by a carrier stream of argon through a semi-permeable dryer tube[5] that removes water vapor. The vapor passes directly to the detector and is measured as a change in the rise (height) from the baseline. The mercury vapor concentration is determined by atomic fluorescence spectrometry at 253.7 nm.[6,7,8]

The key to the successful analysis of mercury at the method detection limits (MDL) is the control of mercury contamination of reagents and samples from laboratory sources. Control of contamination sources requires that the method procedures should be conducted in an ultra clean laboratory environment. Many laboratories have source contamination from common mercury reagents such as the reagents used in the Kjeldahl method and chemical oxygen demand method. The mercury vapors generated by these methods can permeate the air ventilation systems of the laboratory. Method 245.7 requires that equipment, reagents and samples be isolated from laboratory facilities that may have mercury contamination.

(SLIDE, Photographs, 6-7 not shown)

Some laboratories have designed soft wall clean rooms using air filtration systems Federal Standard 209d: clean room class 10,000 filtration with activated carbon filtration for instrument and changing areas with class 100 zones. Other laboratories use hard wall, Class 100, "metal free" clean room with forced air activated carbon filtration.

The Environmental Monitoring Systems Laboratory, Cincinnati Ohio evaluated Method 245.7 using a metal free glove box\dry box, purged by argon gas with activated carbon filtration. This approach for the control of mercury contamination from laboratory sources provides a low cost alternative to clean room storage of reagents and preparation of samples.

The Method 245.7 procedure is based on a method used by the Yorkshire Water Authority (YWA) in the United Kingdom.[9] The Method 245.7 procedure is simplified and summarized as follows:

(SLIDES 8-9)

(1) Add 5 mL (1 + 1) hydrochloric acid and 1 mL 0.1N potassium bromate/potassium bromide solution to a 50 mL conical vial.

(2) Transfer of sample to conical vial, filling to the 50 mL mark.

(3) Allow samples to stand for at least 30 minutes before analysis.

(4) Add 50 μL hydroxylamine hydrochloride solution to each conical vial.

(5) Turn on the automated instrument/detector and allow to stabilize.

(6) The sample enters gas/liquid separator with $SnCl_2$ to form mercury vapor.

(7) The vapor is analyzed by cold vapor atomic fluorescence spectrometry.

Method 245.7 was optimized using a statistically-based experimental design or chemometric approach as described by Deming and Morgan (1987).[10] The chemometric experimental approach was applied to this mercury method to speed the process of method evaluation. The chemometric approach is dynamic (modifiable) and recursive (experiments may be repeated). During the execution of the experiments an evaluation of each "phase" of an experiment is required. When a modification of the experiment was required, it was strongly supported by the statistical evidence. The experimental design consisted of the following phases:

(SLIDES 10-11)

Phase 1 - Familiarization Study.
Phase 2 - Automated Instrument Optimization Study.
Phase 3 - Automated Instrument Linearity Study.
Phase 4 - Mercury Precision and Recovery Study.
Phase 5 - Instrument Stability Study.
Phase 6 - Initial Interference Study.
Phase 7 - Sample Preservation Study.
Phase 8 - Single Laboratory Validation Study.
Phase 9 - Establish Instrument Control Charts.
Phase 10 - Establish Clean Laboratory Protocol.

In the familiarization and optimization phase of the experiments, the mercury analyzer was optimized for maximum sensitivity and/or signal-to-noise ratio. The use of Simplex optimization was investigated using the carrier gas and sheath gas flow rates as selected variables. A range for optimized settings was found as described in Table 1. These settings may be changed periodically to optimize the instrument. Small changes, when they remain within the specified ranges, do not adversely effect the instrument's performance. However, one setting was made and procedures were held constant for the remaining experiments.

(SLIDES 12-14)

INSTRUMENT CONTROL SETTING AND ARGON GAS FLOW SETTINGS	
Fluorescence Instrument Parameters	PSA *Merlin* Series AFS Range of Settings
Delay Time	5 to 15 seconds
Rise Time	20 to 30 seconds
Analysis Time	30 seconds
Memory Time	60 seconds
Argon Gas Control	Range of Settings
Gas Regulator	20 to 30 psi.
Carrier Flow	150 to 450 mL/minute
Drier Tube Flow	2.5 to 3.5 L/minute
Sheath Flow	150 to 250 mL/minute

The automated instrument is generally configured as shown below.

(SLIDE 15)

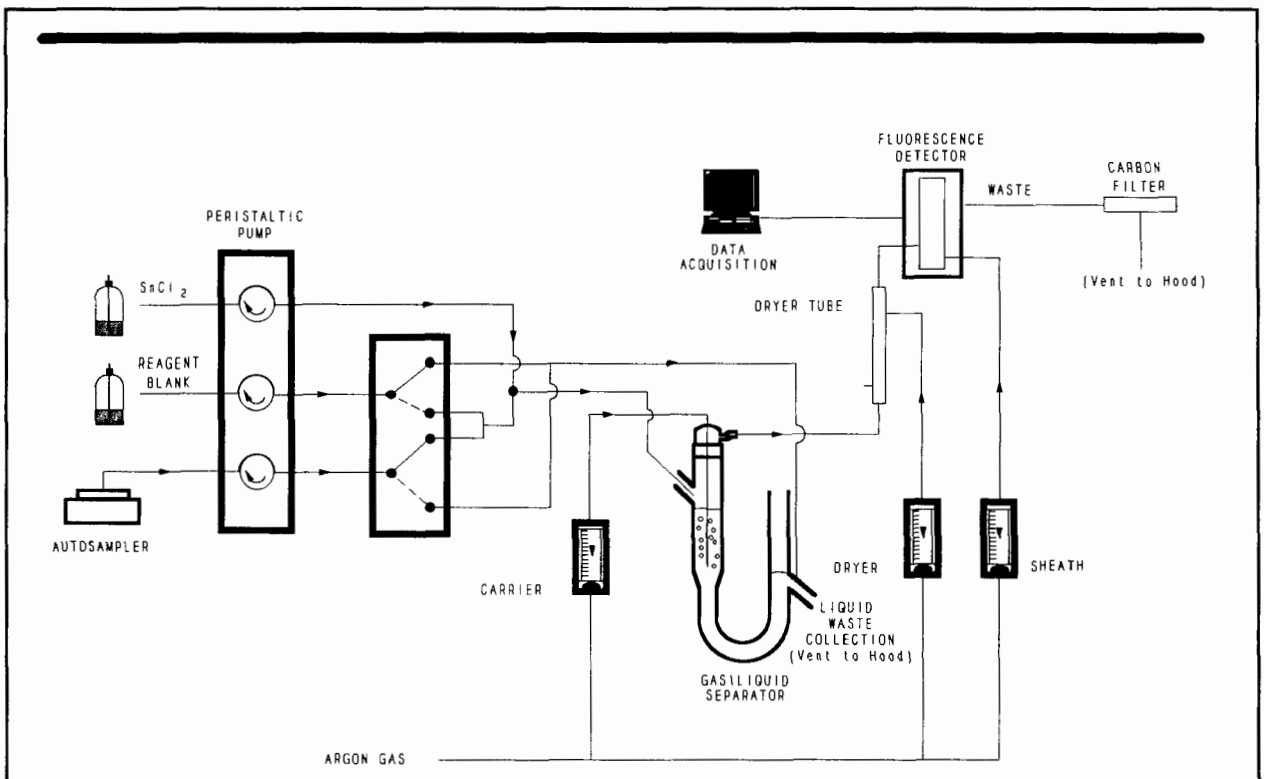

FIGURE 1 PSA AUTOMATED MERCURY FLUORESCENCE SYSTEM

After the experimental design (Phases 1-5) was completed, Method 245.7 was tested for ruggedness. Control charts were used to regulate the instrument and method procedures. It was necessary to find a sample container that would allow stable transport and storage of samples containing mercury concentration at near the MDL (1 to 20 ppt). A plastic container, polyethylene terphathalate copolyester (PETG), was selected. This plastic container's performance was measured at the 10 ppt-Hg, preserved in 1% HCl and sealed with Teflon™ tape. The PETG containers maintained a mean concentration of 10.6 $\pm$ 0.8 ppt-Hg over a period of 72 hours. This type of container is recyclable or disposable.

An important part of the ruggedness testing involves Phase 6, interference testing. The use of brominating digestion coupled with atomic fluorescence detection overcomes many interferences (chloride, sulfide) and molecular absorption interferences[11,12] inherent

in previous methods. No interferences were noted for sulfide concentrations below 24 mg/L.[13] The only significant interferences observed are for samples containing gold, silver and iodide.[14]

(SLIDE 16)

INTERFERENCES OBSERVED		
Interferant	Level	% Hg Recovery
Gold (100 ppt Hg)	1 ppm	76.1
Silver (100 ppt Hg)	1 ppm	183.2
Iodide (10 ppt Hg)	5 ppm	9.0

DISCUSSION

EPA Method 245.7 was developed to serve as a monitoring method for the ecological assessment of the Florida Everglades. Is this method adequate for a new role of supporting water quality-based effluent limitations (WQBELs)? To explore this possibility consider the following scenario:

(SLIDE 17)

(1) Methylmercury poisoning of humans and cats in Japan known as "Minamata" disease (1950-1970) was caused by the consumption of mercury (10 to 24 parts per million [ppm]) contaminated fish. This environmental catastrophe marked the beginning of world-wide concern that mercury may be a global pollution problem. The history, hazards, and concerns about mercury pollution have been documented since 1972.[15]

(SLIDE 18)

(2) The death of a Florida panther (110 parts per million [ppm]) in 1989 from mercury poisoning was the impetus for the completion of a tissue survey in 1990, of panthers, raccoons, otters and alligators found in the southern Florida Everglades. The findings of this survey "MERCURY CONTAMINATION IN FLORIDA PANTHERS"[16] documented widespread mercury contamination of wildlife in the southern part of the Everglades. Mercury contaminated food chain (fish and raccoons) is the suspected cause for the death of the Florida panther. The State of Florida has determined that many sport fish caught in the South Florida Everglades are contaminated with

high levels (0.5 to 4 ppm) of mercury. This has caused a fish advisory to be issued for the Florida Everglades.

(3) The mercury is concentrated in the aquatic food chain from natural waters and sediment.[17,18,19] For fish, this represents roughly a bio-magnification of 1,000,000 times the concentration of mercury found in natural waters. A comparison of which may be seen in the next slide.

(SLIDE 19)

ONE MILLION TIMES
BIO-MAGNIFICATION OF MERCURY
BY FISH
FROM NATURAL WATER

A. Fish 0.5 to 20 μg Hg/g (ppm, 10^{-3} g/kg), 10^{6} conc. factor,

B. Insects 7 to 265 ng Hg/g (ppb, 10^{-6} g/kg), 10^{3} conc. factor,

C. Biological-mass, 10 to 210 ng Hg/g (ppb, 10^{-6} g/kg), 10^{3} conc. factor,

D. Sediment, 34 to 753 ng Hg/g (ppb, 10^{-6} g/kg), 10^{5} conc. factor,

E. Water, 0.05 to 1 ng Hg/L (ppt, 10^{-9} g/L).

(SLIDE 20)

(4) There are at least 32 States with existing fish consumption advisories for mercury.[20] The screening value (SV) for mercury in fish is established at 0.6 ppm. The SV is based on calculations that include fish consumption of the U.S. population and other risk factors such as fish density (population). These risk factors may lead to the issuance of a fish consumption advisory.[21]

Using the above information, high concentrations of mercury (5 to 24 ppm) can lead to death of man (Japan) and predators (Everglades) that depend on the aquatic food chain. If using the SV of 0.6 ppm Hg for fish and the mercury is bio-magnified 1,000,000 fold in fish from the aquatic food chain, it is possible to back-calculate the upper limit for the concentration of mercury acceptable in natural water. The calculated upper minimal limit (ML) would be roughly 0.6 ppt-Hg.

Using the mercury in fish scenario to set an effluent limit at 0.6 ppt-Hg may be setting mercury at a concentration to high to protect the aquatic environment. Ecological risk factors and target populations other than the consumption of fish by humans should be considered and included in the calculation. Until all of the risk factors are included,

another approach of setting an interim effluent limit using Method 245.7's method detection limit (MDL) is suggested.

The MDLs as listed below also may be used for enforcement of water quality-based effluent limitations (WQBELs) by establishing the interim minimum level (Interim ML) for mercury. The MDLs are as follows:

(SLIDE 21)

METHOD DETECTION LIMITS FOR MERCURY (ng Hg/L)			
LOCATION MATRIX	EPA\EMSL Cincinnati Ohio Glove Box	EPA\Region 4 Athens Georgia Hard Wall Clean Room	S.E. Environ. Research, Florida International University Soft Wall Clean Room
Reagent Water	1.8	0.3 to 1.0	0.3 to 0.6
Florida Marsh Water	3.3		
Synthetic Sea Water	2.6		
Sea Water			1.4
Lake Water			0.3
Waste Water			0.4

The Interim ML is calculated when a method-specific ML does not exist. It is calculated by multiplying the MDL by 3.18. The factor of 3.18 is derived from the ACS definition of level of quantitation (LOQ) that is 10 standard deviations above the average blank signal and is divided by the 3.14 (student t value) for the MDL, i.e. $3.18 = 10/3.14_t$ for $n = 7$. The calculated ML is then rounded up to 1, 2, 5, 10, 20, 50, etc. The Interim ML for mercury would then range from 5 to 20 ppt-Hg depending on the water matrix and the laboratory's skill. Method 245.7 would satisfy the need for the Interim ML for mercury and the concentration value is near the levels found in natural waters. The interim ML for mercury concentrations would be 10 to 20 times higher than most ambient concentrations found in natural waters.

To summarize, if the risk-based water quality criteria (based on fish consumption of the U.S.) is used to establish effluent guidelines, the minimum level (ML) of 0.6 ppt-Hg may be set to near the Method 245.7 method detection limit (MDL) of 0.3 to 3.3 ppt-Hg. If the risk-based approach includes the protection of the aquatic food chain and other

endangered target populations, it is conceivable that the ML would be set below the MDL. To satisfy this need will require a revision of the method that will include a sample pre-concentration step to increase the sensitivity of the method. Method 245.7 is an acceptable method for monitoring of the Interim ML of 5 to 20 ppt-Hg.

ACKNOWLEDGEMENTS

(SLIDE 22)

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(SLIDE 23)

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QUESTION AND ANSWER SESSION

DR. FIELDING: Do we have any questions?

MR. XIE: My name is Jack Xie from Water Chemistry at Roanoke, Virginia. I am just wondering whether we can get a copy of EPA Method 245.7.

MR. POTTER: It will be published probably about midsummer. I cannot release this method at this time, because it has not received its second peer review which is a policy of the Office of Research and Development. The Method is in limited use at this time, and we are doing field testing on it.

MR. XIE: Okay, thanks.

MR. PEIST: I am Ken Peist, Region II laboratory in Edison, New Jersey. We have been doing some work with fluorescence detection following digestion using the permanganate digestion, and we are going to be doing a study this year where we compare the bromate/bromide versus the permanganate digestion, but also, we are looking into the microwave digestion prior to the fluorescence detection.

I was wondering if ORD was planning on doing any work with the microwave. I think a gentleman before had mentioned, you know, it is a closed vessel system and it has teflon liners, and it would probably be pretty good for the mercury contamination problems.

MR. POTTER: The only work we are doing right now with the microwave is with fish, fish tissue. We are trying to introduce disposable containers so that you use it only once. At the part per trillion (ppt) level, if you use a bomb to do your digestion in, you will have cleaning problems, and you increase your workload.

I am trying to get to the procedure where we are using inexpensive disposable plastics so that we can cut the cost and reduce the time.

The bromide/bromate method, for most samples, the digestion is almost instantaneous, that is, it occurs within 1 to 2 minutes.

The sample in the procedure is digested for 30 minutes. That is a conservative time for the digestion, and that is to applied for things that contain high humic materials.

MR. PEIST: I think what we are hoping to see is the recoveries on marine sediments improving with the microwave digestion being that you can digest at higher temperatures and pressures.

MR. POTTER: Now, on sediment, that is a different topic altogether, because now you are not at the parts per trillion level. Oftentimes, you are at the parts per billion level, and cleanliness of the bomb is not as critical as it would be at the part per trillion level.

MR. PEIST: Exactly. Thanks.

MR. POTTER: Yes, ma'am?

MS. ALLEN: I am Linda Allen from the Minnesota Department of Health. My question was I have heard a lot of talk today about clean rooms. The USGS has one definition, and you now have another definition of clean room.

I think some kind of document describing exactly what an environmental clean room means as opposed to...I am sure some of us are familiar with biological clean rooms from that aspect, but what, exactly, connotes an environmental clean room for analysis?

Obviously, when you were saying $10,000 to $100,000, that is a lot of money to be investing, and we would kind of like to know what we need to be looking at.

MR. POTTER: At this time, I have a work assignment with a contractor, Research Triangle Institute, to try to answer that question. We do not believe that you have to go to a $200,000 clean room to do a lot of the metals analysis. What we are trying to do is bring it down to an affordable price of, let's say, around $10,000.

With that, let me say if you are running a whole bunch of different kinds of samples, your laboratory may be better off going to a more expensive clean room to increase throughput. These clean rooms are typically polypropylene constructed or soft-wall constructed clean rooms.

The hoods have absolutely no metal parts in them. The electrical outlets don't have any metal things sticking out. You generally go through Class 10,000 clean room to get to a Class 100 metal free laboratory environment.

For volatile metals, it also requires filtration with carbon or gold or some other type of system.

I am working on a "low-end budget" controlled laboratory room. I am trying to get the price down so your lab can afford to work in a laboratory that has some mercury contamination. The technology being evaluated is glove box.

MR. BERMAN: I would just like to comment on the remark about sediments. It is true, if you look at a sediment, they seem to have about

100 times more mercury in them than a water sample. However, there is no way of getting 1 gram of sediment into 1 milliliter of solution.

So, when you prepare a sediment, you generally are diluting your concentration by about a factor of 50 to 100, and you are right back to where you started with the original water samples. So, you have to be just as diligent when you analyze sediments for mercury as you do analyzing waters.

DR. FIELDING: Are there any other questions?

(No response.)

DR. FIELDING: If not, this morning's session is over. The afternoon session is scheduled for 1:30. It is now 12:30 which gives us barely an hour for lunch. Let's try to get back by 1:45.

Speaking of which, next door is a very nice set of fast and good food places to eat, and they have, since last time I was here, put in a nice covered walk over there so it is not quite as bad as it might seem.

We will try again about 1:45.

(A luncheon recess was taken.)

MR. TELLIARD: Our first speaker this afternoon is Greg Cutter. Greg is an Associate Professor and Assistant Chairman and Graduate Program Director for the Department of Oceanography for the Old Dominion University which is here in town across the river, up the road, wherever. Greg is going to be talking about, again continuing in the same frame, the metals concentration and also the issue of speciation.

Greg?

DETERMINATION OF METALLOID CONCENTRATIONS AND SPECIATION IN NATURAL WATERS

MR. CUTTER: What I want to talk about today is, in fact, a group of elements that are not quite metals and are not quite non-metals; they are the metalloids. The metalloids are the elements of group IV, V, and VI on the periodic table and include germanium, arsenic, antimony, selenium, and tellurium.

Currently, most of the environmental interest in the metalloids centers on arsenic and selenium, and today I will talk focus on these elements. However, I would like to suggest to you that the other metalloids are quite interesting environmentally, and actually have some utility as tracers of different inputs to the aquatic environment.

What I will do first is review a little bit about the chemistry and the environmental behavior of these metalloids so that you can understand, or help to choose, an appropriate analytical technique.

To begin this review let me talk a little bit about the chemical forms of dissolved arsenic and selenium in natural waters. Selenium has four principal oxidation states, +VI, +IV, elemental or zero, and -II. In most natural waters at pHs of between 5 and 8, you would find that most of the Se(VI) will form selenate, because it is a strong Lewis acid. This form is roughly equivalent to sulfate in the sulfur series.

Next is Se(IV), primarily as selenite. You would find it in these two ionic forms (refer to Figure 1). What I want you to note is that rather than being cations such as mercury or lead, these trace elements are oxyanions, and, therefore, behave very differently.

The next selenium species is elemental selenium. Now, I am talking about dissolved ions, and the operational definition of dissolved is something that passes through a 0.45 μm filter. Because this is an operational definition, we have to include the possibility that there could be some elemental selenium, which is insoluble, in a colloidal form and pass through your filter. So, rigorously, we have to include elemental selenium in this dissolved metalloid series

Finally, selenium in the -II oxidation state, roughly equivalent to sulfide, would exist primarily in the form of organic selenides. Examples would be the dissolved free amino acids such as selenomethionine, which would be just like sulfur's methionine, and could be either free or bound in soluble peptides. There is another form of selenide that has been of concern, especially to atmospheric chemists, and that is dimethyl selenide; this is a volatile liquid.

If we go down to arsenic, and by analogy, antimony which is just below arsenic on the periodic table, we have As(V). It also exists as an oxyanion arsenate. There are also some organic forms of As(V), methylarsonic acid and dimethylarsinic acid. These are both found pervasively in the environment.

Finally, we have a reduced form of arsenic, As(III) which would be the arsenite oxyanion. There are some other organic forms of arsenic including arsenobetaine and arsenocholine which are produced by zooplankton and can be found in water samples.

So, what we have with the metalloids is a very potentially complex chemistry. We have multiple oxidation states, and then within a given oxidation state, you have different chemical forms. Thus, the speciation of the metalloids is potentially quite complex.

Now, superimposed upon this is the fact that, in natural waters, the interconversion between these metalloid species, for example, from Se(VI) to Se(IV) and the reverse, tends to be kinetically relatively slow. What this means is that simple thermodynamic calculations using, for example the pH and the oxygen concentration, cannot be used to predict the concentration of a given metalloid species. Thus, you have a lot of non-thermodynamic processes affecting these elements.

Finally, the other point to consider is the bioavailability or bioreactivity of these elements. It turns out, for example, that arsenate is almost chemically identical to phosphate. In fact, that is the basis of arsenic toxicity is its similarity to phosphate.

Therefore, we would be interested in the environment to know the concentration of arsenate as opposed to the concentration of total arsenic in water.

Selenium has similar considerations. It largely follows the biogeochemistry of sulfur, so it can get carried along in the natural sulfur cycle.

So, we need to know the speciation from a geochemical standpoint, that is, the reactivity of these different elements in the absence of biota and, as well, how their biological reactivity changes with the speciation. Overall, speciation is very important for the metalloids.

What I have done is to put forth some of the considerations that you need to think about when selecting appropriate analytical methods for determining the metalloids in natural waters (refer to Figure 2).

First of all, you have to consider the concentrations. Now, what I have selected here is natural range concentrations of selenium on the order of somewhere below 2 to 350 ng/L for selenium which is subdivided into at least three different major chemical forms, selenate, selenite, and selenide.

Arsenic has a very large concentration range, 50 to about 4800 ng/L, and you have at least four major chemical forms with arsenic. So, we have quite a large concentration range, and we have a diversity of species.

The other thing to consider is the natural cycling of these elements. There are processes such as selective biological uptake, that is, the conversion of dissolved selenium or arsenic into solid phases, and then the reverse, remineralization or regeneration of this organically-bound selenium or arsenic back into the water column.

You have to consider that the species can interconvert and that you have multiple inputs, atmospheric inputs, riverine inputs, streams, input from sediment pore waters, as well as anthropogenic inputs, of which the largest is fossil fuel combustion. It turns out the metalloids are very enriched in fossil fuels, especially in high sulfur coals.

Then, considering all these things, the analytical methods must be able to accurately and precisely determine the concentrations.

Well, the accuracy goes without saying. Shier Berman talked about that. You need to use standard reference materials, and you want to have the right number.

You need to have good precision. The natural variability of these elements is on the order of perhaps 20 to 30 percent. Therefore, if you have precision that is worse than that, you are not going to see anything; you are not going to see changes.

And, as I said, you have to understand the speciation of these metalloids, and we are working in a wide concentration range and in a variety of matrices.

What I want to do, then, is go over some major types of techniques that you can use to determine selenium, and I want to then argue for what I feel to be the technique of choice based on these criteria and go over the methodology.

What I have selected is five different common methods for determining selenium in natural waters (Figure 3). I have selected standard inductively coupled argon plasma, gas chromatography with electron capture detection, fluorimetry, graphite furnace-atomic absorption, and then hydride generation-atomic absorption.

I have put in some of the analytical figures of merit that one needs to consider, detection limits, precision, then the ability or not to do speciation, which species you can determine, and then some of the kinds of laboratory details you like to consider, the analysis and preparation time. Finally, a very important issue are interferents, analytical interferences in natural waters.

First of all, if you remember the concentration range of selenium is somewhere below 2 ng/L to up to 300, you can see right away that techniques such as argon plasma or graphite furnace are going to be right on the edge. So, they have some problems. You can also see that their precision is not so good.

Finally, the other thing that you have to consider with these is that typical techniques are incapable of doing speciation. As I say, they can do total selenium, but they are incapable of determining the VI, the IV, and the -II.

So, that leaves us with the ones to consider, gas chromatography, fluorimetry, and hydride generation-atomic absorption. There are other hyphenated techniques that we can modify. You could do hydride generation with ICAP, for example, but I am going to try to stick to the relatively straightforward techniques.

If we look at the gas chromatography, fluorimetry, and hydride generation methods, we see that the detection limits are extremely low using a sample size volume of on the order of 100 ml, except for fluorimetry, that we have very good precision (relative standard deviation), and that all are pretty much capable of doing the speciation for the IV and the VI.

You start to see differences when you want to try to determine the organic selenium. Fluorimetry has been developed to do that and hydride generation, but not gas chromatography. If we want to start doing species such as dimethyl selenide, only hydride generation has been used.

If we wanted to start looking at speciation on the solid phase (particles), the speciation methods have only been exploited for hydride generation. However, the speciation methods are applicable to these other techniques.

Finally, we have to look at the kind of prep time versus analysis time. Hydride generation has the longest analysis time, but it has one of the shortest preparation times. So, I would suggest to you that, in fact, you can kind of even this out in terms of prep time versus analysis time.

Finally, in terms of interferents, there have been very few studies, or none that I am aware of, for the gas chromatographic and fluorimetric techniques. There have been quite a few studies on the hydride generation method. The worst interferent for that is free chlorine, so it can pose a problem with the analysis of drinking waters.

Now, anybody who knows me is going to know that hydride generation is my favorite technique, and that is what I am going to focus on. If you want to quickly jot down the references here, they are the ones that go with that table (Figure 4). All of the methods, gas chromatography, hydride generation-atomic absorption, and gas chromatography have been published in the peer review literature and are readily available to everyone.

What I want to now do is focus a little bit on the hydride generation-atomic absorption method. This is the hydride generation setup for doing selenium speciation (slide). This is set up on a Perkin & Elmer instrument. We have set it up on IL's and Varian's.

It consists of the hydride generator which is what we call a gas stripper here. It has a Teflon septum into which you inject sodium borohydride. The sample is acidified, and you generate hydrogen selenide, the gas, which is swept out with helium into a U-tube that is immersed in -60 degree isopropanol; that removes water vapor. It is then swept into a glass U-tube that is immersed in liquid nitrogen which freezes out the hydrogen selenide.

This is a closeup of the burner (slide). What we do is use an open quartz tube burner that is burning an air/hydrogen flame. The hydrogen is coming in on the back side of the burner. The air is coming in here, and the effluent from the liquid nitrogen trap is coming in right here, so you have an open flame here.

Finally, the data are processed on a chromatographic integrator. Here is a little selenium peak you might not be able to make out. What we want to do with this integrator is to determine the peak area rather than the peak height. The reason for this is that we obtain a much larger linear working range, and the precision is infinitely improved over peak height.

The other question you may be wondering about, as a lot of people are familiar with hydride generation, is why do we include this liquid nitrogen trap? Well, the liquid nitrogen trap effects a preconcentration that you do directly on the instrument. You generate the hydrogen selenide. A commercial available hydride generator will then sweep it immediately into the flame. The problem with that is that at the same time you are producing hydrogen in the reaction of acid and sodium borohydride, and you actually dilute your hydride signal with that of hydrogen. You also have some other non-atomic interferences.

By using the liquid nitrogen trap and isolating the hydrogen selenide uniquely, you can remove these interferences. You also affect the preconcentration and have much better detection limits.

Now, you may ask the question, why do you want to have really good detection limits? Well, good detection limits, first of all, are needed if you are analyzing a natural water and you want to know the baseline.

But the other advantage, even if you are analyzing something such as a refinery effluent, which we have done, or something as contaminated as Kesterson Reservoir water in California, you can use an extremely small sample size and dilute it, and you dilute out all the interferences. An important advantage to having low detection limits is simply diluting out any problems in your analysis.

What we have here (Figure 5) is a flow diagram for processing a water sample. First of all, in terms of the definition, we are going to filter the sample through a polycarbonate filter; this operationally defines dissolved and particulate.

The other step is to take that filter and use it for the analysis of total selenium and the selenium species.

I would argue and recommend that you do particulate analyses directly on the filter rather than taking an unfiltered sample and a filtered sample and doing it by difference. The reason why is because you have a small difference between two large numbers and your errors are huge. So, it is much better to take the filter and analyze it directly for selenium. In addition, you can do selenium speciation if you so desire.

The filtrate is then placed in borosilicate glass bottles. We acidify it using hydrochloric acid to about pH 2, and we have found that it is stable up to at least six months under these storage conditions.

We use borosilicate glass bottles, because the selenium species, as anions, behave differently than cations, and they tend to absorb. For example, if you are doing metal analysis, and Russ will be telling us about this, you want to use low density polyethylene bottles, for example, which are very clean for trace metals. It turns out they are very absorptive for metalloids.

So, you need to use a different container, and we use borosilicate glass for selenium. We have found it has the lowest absorptive loss during storage. We use hydrochloric acid because if you use nitric acid, it interferes with the hydride generation technique.

The sample is acidified to 4M with hydrochloric acid. You add sulfanilamide. Sulfanilamide reacts with nitrite. Nitrite is another severe interferent with the hydride generation. However, if you react it with sulfanilamide, it removes the nitrite interference very simply.

You then add sodium borohydride. You generate the hydrogen selenide, liquid nitrogen trap it, sweep it into your AA, and you directly get Se(IV).

You take another aliquot of the sample, you acidify it, you boil it for 15 minutes, and then you follow this procedure again. That gives you the concentration of Se(IV) + VI.

You then take another aliquot, and you add an oxidant, potassium persulfate, boil it for up to 1 hour. You can experiment with your sample; you can do it in as little as 20 minutes, depending on how refractory the organics are. This oxidizes the -II selenium forms up to IV and VI. Then the persulfate, after about 20 minutes of boiling is gone, and then the acidic boiling reduces it all to IV. You then do the analysis, and that gives you the total selenium.

By difference, the Se(VI) is the IV + VI minus the IV fraction, and the -II + 0 is the total minus the IV + VI.

The reason why I included the Se0 here is because there is a possibility, again, that you have colloidal elemental selenium passing through your filter. So, rigorously, in practical purposes, this fraction is mainly selenide, but you have to include the possibility that some colloidal elemental selenium passed through the filter, and that is why we defined that fraction in such a fashion (Se -II + 0).

The analysis time for this is 12 minutes. The prep time is a maximum of 1 hour.

The apparatus that I showed you had a single hydride generator with a single liquid nitrogen trap. We have hooked up in our laboratory a three hydride generator setup with a special Valco valve, and it allows us to have three samples run simultaneously, because the instrument time, the chromatographic time, and the time that the AA uses is only a minute. So, most of the time is spent in generating and collecting the hydride so that you can maximize or minimize the instrument time, depending on which way you look at it, by having three samples running simultaneously and then just switching and selecting each hydride trap and sweeping it into your AA. In this way, you can process many more samples in a day.

The other thing I wanted to add is that we do all our analysis in triplicate. One must rigorously assess what the precision is. Therefore, you need at least three determinations.

And, we regularly use the standard additions method of calibration to assure accuracy. However, you also must include SRMs that are appropriate for the type of sample that you are analyzing.

Now, we will go on to arsenic. It is a similar type of thing that I did for selenium (Figure 6). I have selected the kinds of standard methods that people have in their laboratories, graphite furnace; hydride generation, this time with argon plasma; HPLC; hydride generation with atomic absorption, just like the selenium; and then a newer method I want to try to sell which is hydride generation coupled with gas chromatography with photoionization detection. I will tell you in a minute why I think that is good.

First of all, detection limit-wise, hands down it is the two hydride generation methods in terms of the detection limits. Again, this gives you an advantage of diluting out interferences and analyzing any sample you want.

The graphite furnace and argon plasma have other problems with precision, and they, at the current level, are incapable of doing speciation. The analysis is a relatively short one, however.

HPLC is interesting, because it has very poor detection limits, but it is capable of doing many species. In fact, it can do some of these complex organic arsenic species such as arsenobetaine or choline.

The only problem is that detection limits are not very good. This could be improved if one coupled it to, for example, an ICP/MS.

The hydride generation technique is capable of doing all the species, and the one thing I want to add here is the simultaneous determination of antimony. Antimony is right below arsenic on the periodic table. It is interesting to look at element pairs. The other interesting thing to look at with antimony is that it is used as a plasticizer and has been proposed as a good tracer for municipal waste incineration when you burn plastics.

So, if you can get antimony at the same time as arsenic, you get more than twice as much information. The advantage here is that this hydride generation gas chromatography technique gives us simultaneous antimony, so I would suggest that is an advantage.

There is essentially no prep time for arsenic. For the HPLC, standard hydride generation, and this hydride generation technique, there are effectively no interferences.

Now, while you are writing down references (Figure 7), I will say something else.

One of the things, unlike selenium whose species are generally stable during storage, arsenic is not. Now, you will find conflicting information in the literature, but we have been looking at this a lot, and it turns out that As(III) is not stable even if you rapidly freeze the sample. You cannot store it more than several weeks or you get speciation change.

If you have speciation change, in other words, if the As(III) oxidizes, you are going to overestimate the concentration of arsenate. This is usually the species that most people are interested in because of its similarity to phosphate and its toxicity.

So, one of the problems with arsenic is that you have species that are not stable with storage, and it means immediate analysis. Therefore, we developed a technique that is portable or relatively portable, and you do not have to lug an atomic absorption spectrometer along with you.

What you have is a very small little portable gas chromatograph with a photoionization detector (slide). You have your hydride generator setup much like the selenium with the hydride generator, a water trap, and a liquid nitrogen trap. You have your chromatographic integrator, and you have this little gas chromatograph here with a photoionization detector.

This is in a box here (referring to slide). Actually, this is out in the Black Sea. We have lugged this thing all over the world. It was in Iceland this last summer, and it is pretty sturdy.

It is relatively inexpensive. The whole setup is less than $8000.

This is a closeup (slide). The only thing you have to do here, because you have the high pressure gas chromatograph and you have a relatively low pressure stripping apparatus, you have to interface the high pressure and low pressure with this six-way valve that you switch from strip/trap where you collect the hydride in the liquid nitrogen trap to injecting it into the column. It is relatively simple, but the only trick is this six-way valve.

Here we have the kind of analytical scheme for arsenic (Figure 8). We again have the filtration step. I recommend the filter itself be used for total and arsenic and antimony speciation in the solid phases rather than doing it by difference.

We take the filtered sample and we split it. Because we have unstable As(III), we put the sample in teflon bottles, we refrigerate it, and no later than 24 hours do an immediate determination.

Now, the determination involves adjusting the pH with a buffer, Tris buffer, to pH 6, and adding sodium borohydride. That selectively volatilizes the arsenic or antimony (III) to their respective hydrides. They are trapped and determined with the GC/PID system simultaneously.

You then take another aliquot, add potassium iodide, acidify with HCl to pH 1.6, add sodium borohydride, and you get the arsenic and antimony (III + V).

Now, you could sequentially do this analysis where you do the tris analysis, get the (III), then add the KI, the HCl, and do the reduction step again. What we have found is that the determination of (V) comes out a little low. What we believe is that some of the arsenic and antimony (V) get reduced to elemental arsenic and elemental antimony and are then not subject to being reduced to the hydrides.

So, we recommend that you, in fact, do a (III), and then you do a (III + V) determination rather than doing a (III) and then sequentially a (V) determination.

So, this is the procedure you use with the gas chromatograph-photoionization detection system. You can do it in the field, or you can run it back to your home laboratory, but the important thing is that because of the instability of the species, you need to do the analyses pretty fast.

You can also take samples, acidify with HCl to pH 2 and then store in polyethylene or borosilicate glass up to six months. On the stored sample, you can do the arsenic and antimony (III + V) determinations. You can also go back to the more traditional hydride generation-atomic absorption and add the same reagents to get the methyl species, and what we did not include on this drawing is the As(III + V). The interesting thing here is doing the methyls and the (III + V) on your AA, you are performing a kind of semi-intercalibration between your photoionization determination of (III + V) and the determination on a completely different detector.

So, if you want to determine the methyl species, you get the inorganic arsenic at the same time, and then you can check your numbers from your field-determined (III + V). So, there is an advantage to this situation.

Finally, the arsenic and antimony (V) is the difference between the (III + V) and the unique (III) determinations.

That is about it. What I want to just briefly conclude with is that I argue that the hydride generation techniques are the best because of their wide application. We have analyzed refinery effluents, any kind of nasty water you can imagine, down to seawater, Antarctic ice cores, atmospheric deposition samples, and aerosols and rainwater in urban and pristine environments. We have applied these techniques to a wide variety of samples, and we know they work. They have excellent precision, excellent accuracy, and they meet all the analytical requirements listed previously.

What is the future of this? Well, everybody has been talking a lot about ICP/MS here. ICP/MS can be used for the metalloids. There are some problems, however. The first, with arsenic, is that it is mono-isotopic, and you have a problem with isobaric interferents with the argon oxide. So, arsenic is a little bit of a problem via hydride generation with ICP/MS.

The advantage with the ICP/MS is that we could in theory do all the metalloids simultaneously. However, you need to get rid of these interferences, and the isobaric interferences are a major problem with arsenic. You also have some isobaric interferences with selenium. The other thing is that the hydride generation conditions are somewhat mutually exclusive. What you need to do, then, is isotope dilution to correct your recoveries.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Questions? Yes, sir?

MR. LOVETT: Is it possible to go back to your selenium slide a second?

MR. CUTTER: You mean the...

MR. LOVETT: The schematic.

MR. CUTTER: Okay.

MR. LOVETT: I am confused about something, and I wondered if you would explain it to me. If you have selenide there to start with, it would seem that pH 2 would generate hydrogen selenide which I presume is the product desirable from the borohydride reduction. If it does not generate hydrogen selenide in that step, what would prevent the subsequent hydrochloric acid step from generating hydrogen selenide, and why wouldn't the selenide actually be part of those other ones or is, in fact, the sodium borohydride not producing selenide?

MR. CUTTER: I am a little fuzzy on the question, but let me try and answer, and you tell me if this answers your question.

If you mean at...if you are referring to this first step here, first of all, it is not pH 2, or are you referring to...

MR. LOVETT: In the filtered sample.

MR. CUTTER: Okay, in the filtered. Okay, now I understand.

MR. LOVETT: Wouldn't the acid generate H_2Se immediately?

MR. CUTTER: H_2Se does not exist in aqueous systems. It is a stronger reductant than water. So, H_2Se does not exist in water unless you have extremely strong reducing conditions such as you have in the hydride generator with the sodium borohydride. In a natural water sample, you would not have hydrogen selenide.

The selenide is almost exclusively covalently bound to carbon.

MR. LOVETT: So, it is, in fact, an organic.

MR. CUTTER: That is right.

MR. LOVETT: Okay.

MR. CUTTER: Yes, so you do not have hydrogen selenide.

MR. LOVETT: That was not clear exactly.

MR. CUTTER: In fact, if you have a water sample that goes anoxic...by the way, this is a hint for people who want to do water treatment...if you make the sample anoxic, you precipitate elemental selenium. Elemental selenium is the stable form in anoxic conditions. It will not produce selenide.

MR. LOVETT: Okay. It just was not clear that it was an organic determination.

MR. CUTTER: Yes, sorry.

MR. TELLIARD: Other questions?

MR. LOVETT: Another question. Selenium in teflon bottles, you don't recommend it?

MR. CUTTER: Part of my concern is the absorption of the organics onto the teflon, but we have done it. I just find that the borosilicate bottles are a little more rigorous and cheaper.

MR. LOVETT: Well, the concern was that we have a bunch of samples in our lab that were collected for mercury that we retroactively were asked to run selenium on. Would you recommend...

MR. CUTTER: Part of the problem with selenium, by the way, is that when it adsorbs, it is very hard to desorb. It is irreversible adsorption, and once it goes on a surface, it is harder than heck to get off. So, I guess, no, I wouldn't.

MR. NELSON: Would you go to your last overhead, please?

MR. CUTTER: Arsenic?

MR. NELSON: The very last one.

MR. TELLIARD: Tell us who you are, please?

MR. NELSON: John Nelson from Klohn-Crippen Consultants, Vancouver, Canada.

MR. CUTTER: That one?

MR. NELSON: Yes. That last overhead to determine the methyl arsenic for the stored sample, you add potassium iodide, HCL, and sodium borohydride.

MR. CUTTER: That is correct.

MR. NELSON: If you were not to add the potassium iodide, you would measure the inorganic plus the methyl arsenic. What does the potassium iodide do to eliminate the measurement of the inorganic arsenic species?

MR. CUTTER: The iodide is actually added for the antimony. The antimony (V) will not reduce without the addition. You need the extra reductant, so the KI is added to get the antimony.

In other words, you will have incomplete recovery of the...oh, for the methyls, it does not matter. Is that your question?

MR. NELSON: Won't you also get some measurement of arsenate under those conditions?

MR. CUTTER: Yes, you do. I am sorry. I pointed out that this slide was missing that. With the methyl thing here, the methyl should include (III + V) down here as well.

MR. NELSON: So, you measure all three of them?

MR. CUTTER: Yes. In fact, what you do...and I did not say this, because this is someone else's technique...is that you have...your liquid nitrogen trap actually has a little bit of a chromatographic packing, OV3, in it, and then you make a poor man's gas chromatograph. You wrap it with nichrome wire and then hook up a Variac to it. So, you pull it out of liquid nitrogen and heat it up, and you get the inorganic arsenic comes off first or antimony, and then you get the methyls come out.

MR. NELSON: Okay, thank you.

MR. TELLIARD: Thanks, Greg.

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THE CHEMICAL FORMS OF DISSOLVED METALLOIDS IN NATURAL WATERS

SELENIUM

Se(VI) Selenate (SeO_4^{2-})

Se(IV) Selenite ($HSeO_3^- + SeO_3^{2-}$)

Se(0) Elemental selenium (insoluble, but may be colloidal and pass through a 0.4 μm filter

Se(-II) Selenide, primarily in the form of organic selenides such as dissolved free seleno amino acids (e.g., selenomethionine, $CH_3Se(CH_2)_2CH(NH_3)CO_2H$) or dissolved peptides, and dimethyl selenide ($(CH_3)_2Se$)

ARSENIC (and ANTIMONY)

As(V) Inorganic: Arsenate (AsO_4^{3-})
Organic: Methylarsonic acid ($CH_3AsO(OH)_2$)
Dimethylarsinic acid ($(CH_3)_2AsOOH$)

As(III) Arsenite ($HAsO_3^{2-}$)
Other organic forms:
Arsenobetaine $[(CH_3)_3AsCH_2COOH]^+Cl^-$
Arsenocholine $[(CH_3)_3As(CH_2)_2OH]^+Cl^-$

FACTORS TO CONSIDER FOR SELECTING APPROPRIATE ANALYTICAL METHODS FOR DETERMINING METALLOIDS IN NATURAL WATERS

- TOTAL DISSOLVED SELENIUM CONCENTRATION RANGE IN UNCONTAMINATED WATERS: <2 - 350 ng/L; AT LEAST 3 MAJOR DISSOLVED CHEMICAL SPECIES
- TOTAL DISSOLVED ARSENIC CONCENTRATION RANGE IN UNCONTAMINATED WATERS: 50 - 4,800 ng/L; AT LEAST 4 MAJOR DISSOLVED CHEMICAL SPECIES
- THE BIOGEOCHEMICAL CYCLES OF THESE ELEMENTS INCLUDE: BIOTIC UPTAKE AND REMINERALIZATION; SPECIES INTERCONVERSIONS; INPUT FROM THE ATMOSPHERE, RIVERS AND STREAMS, SEDIMENTS, AND ANTHROPOGENIC SOURCES (FOSSIL FUEL COMBUSTION)
- THEREFORE, ANALYTICAL METHODS MUST BE ABLE TO ACCURATELYAND PRECISELY DETERMINE THE CONCENTRATIONS AND SPECIATION OF METALLOIDS OVER A WIDE RANGE OF CONCENTRATIONS AND IN A VARIETY OF MATRICES

Analytical Techniques for Selenium Determinations

Parameter	ICAP	GC	Fluor.	GFAA	HAA
Detection Limit (ng/L)	32	0.8	0.16	2,000.0	0.16
Sample Volume (mL)	100.0	100.0	1000.0	0.1	100.0
Precision (RSD)	10.0%	2.4%	8.0%	6.7%	2.7%
$\sum$ Se	Y	Y	Y	Y	Y
Se(VI)	N	Y	Y	N	Y
Se(IV)	N	Y	Y	N	Y
Se(-II)	N	N	Y	N	Y
Dimethyl Se	N	N	N	N	Y
Part. Speciation	N	N	N	N	Y
Analysis Time (min.)	3	8	1	2	12
Preparation Time (hrs.)	5	12	8	0	<1
Severe Interferents	?	?	?	MANY	Cl_2
Reference	1	2	3	4	5

Fluor. - Fluorimetry
GC - Gas Chromatography with Electron Capture Detection
GFAA - Graphite Furnace-Atomic Absorption Spectrometry
HAA - Hydride Generation-Atomic Absorption Spectrometry
ICAP - Inductively Coupled Argon Plasma

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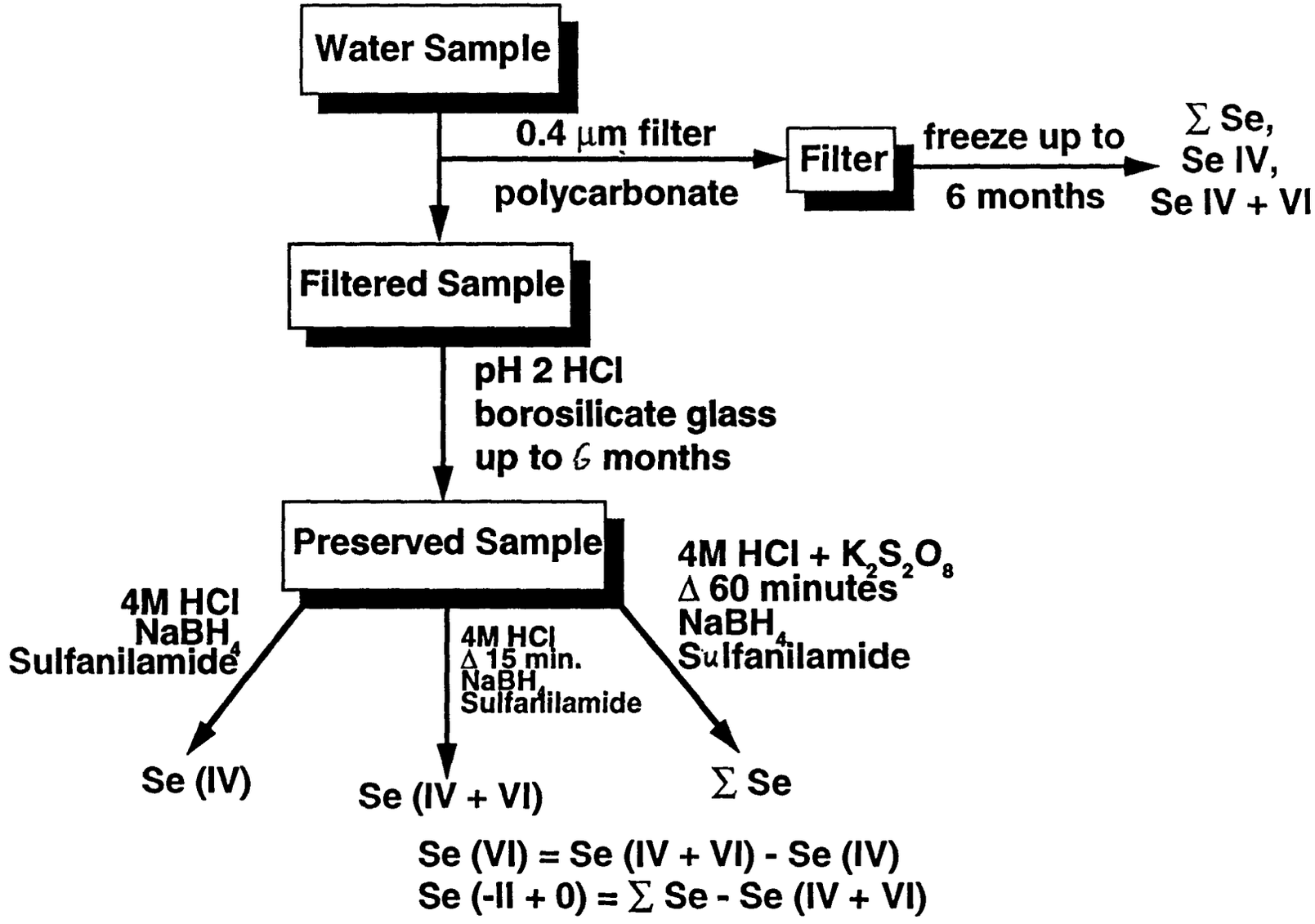
Selenium


Water Sample
0.4 μm filter
polycarbonate
Filter
freeze up to
6 months
∑ Se,
Se IV,
Se IV + VI
Filtered Sample
pH 2 HCl
borosilicate glass
up to 6 months
Preserved Sample
4M HCl
NaBH4
Sulfanilamide
Se (IV)
4M HCl
Δ 15 min.
NaBH4
Sulfanilamide
Se (IV + VI)
4M HCl + K2S2O8
Δ 60 minutes
NaBH4
Sulfanilamide
∑ Se
Se (VI) = Se (IV + VI) - Se (IV)
Se (-II + 0) = ∑ Se - Se (IV + VI)

Analytical Techniques for Arsenic Determinations

Parameter	GFAA	HICAP	HPLC	HAA	HGC
Detection Limit (ng/L)	900.0	800.0	13,000.0	1.0	0.8
Sample Volume (mL)	0.1	5.0	0.1	50.0	50.0
Precision (RSD)	15%	?	8%	9%	3%
$\sum$ As	Y	Y	N	Y	Y
As(III)	N	N	Y	Y	Y
As(V)	N	N	Y	Y	Y
Methyl As	N	N	Y	Y	N
Part. Speciation	N	N	N	Y	Y
Simultaneous Sb	N	Y	Y	N	Y
Analysis Time (min.)	2.0	2.0	27.0	10.0	12.0
Preparation Time (hrs.)	0	0	0	0	0
Severe Interferents	MANY	?	-	-	-
Reference	1	2	3	4	5

HGC - Hydride Generation-Gas Chromatography with Photoionization Detection
GFAA - Graphite Furnace-Atomic Absorption Spectrometry
HAA - Hydride Generation-Atomic Absorption Spectrometry
HICAP - Hydride Generation-Inductively Coupled Argon Plasma
HPLC - High Performance Liquid Chromatography-ICAP, GFAA, etc. Detectors

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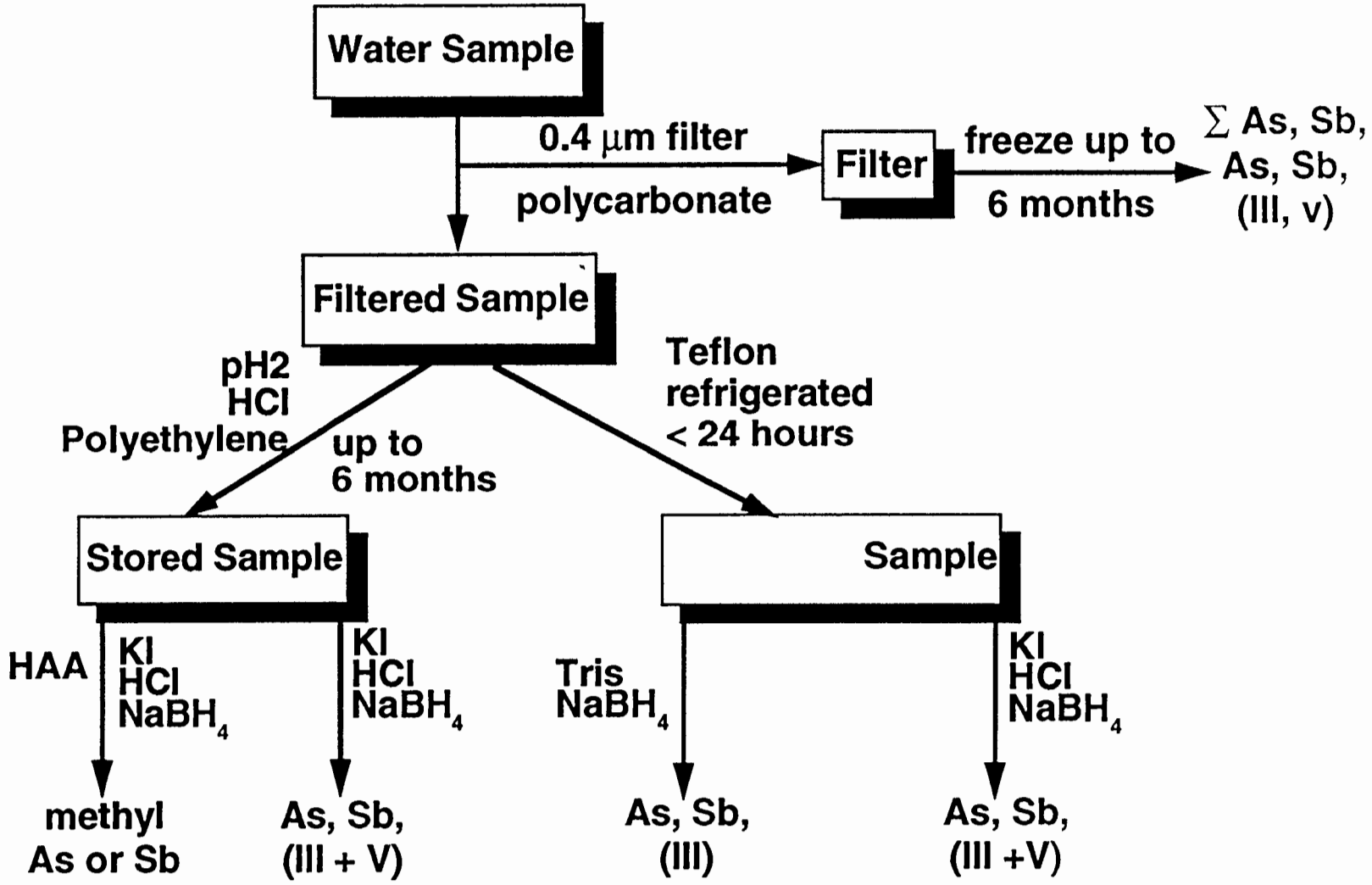
Arsenic and Antimony



As, Sb, (V) = As, Sb (III + V) - As, Sb (III)

MR. TELLIARD: Our next speaker is Russ Flegal, Professor of Toxicology at the University of California at Santa Cruz and visiting scientist at Lawrence Livermore National Laboratories.

Russ is going to be speaking on adaptation of ultra-clean techniques for an environmental monitoring program for establishing site-specific water quality criteria for San Francisco Harbor.

Russ?

(Verbatim Transcript)

ADAPTATION OF ULTRA-CLEAN TECHNIQUES FOR AN ENVIRONMENTAL MONITORING PROGRAM AND ESTABLISHING SITE-SPECIFIC WATER QUALITY CRITERIA IN SAN FRANCISCO BAY

MR. FLEGAL: I would like to thank Dale Rushneck whom I met at the EPA workshop on developing new methodologies for inviting me, and I certainly thank all of you for sitting around to listen to me.

I have a couple of comments prior to my talk in response to some of the questions raised in the previous talks, and my comments are also consistent with those brought up by Greg Cutter in his talk just a minute ago.

We use conventional polyethylene or low density polyethylene sampling bottles. For several metals, they are actually lower in their trace element concentration than the teflon bottles, and the obvious acknowledged exception is for mercury.

We reuse the bottles, because every time they are used, they come cleaner, because the concentrations of trace metals in water are so low that actually by sampling the water, if it is filtered water, you are actually cleaning the bottles before you use it the next time.

We number each bottle on the side and on the cap so that if we get an outlier, we can go back and we can trace and determine whether that bottle is actually the source of contamination for that sample.

I am going to be presenting data from several studies but concluding with the data for San Francisco Bay, and this is in response to the questions on instrumentation.

We use a 15-year old Perkin & Elmer 5000 which the California Department of Fish and Game surplused 10 years ago so that they could do better analyses at the ppm measurements of trace metals in organisms.

Then, in terms of the methodology, I was not able to come here Monday, because I was being deposed in a class action suit on lead contamination in lead crystal beakers or glasses, and the attorneys representing these manufacturers are going to great lengths to invalidate my data. They have gone to extensive questioning for four hours and fifteen minutes on why I did not use the certified acetic acid leach procedure to measure the lead concentrations coming out of the lead crystal.

I told the lawyers that I did not know anyone that went out and bought lead crystal so they could drink acetic acid out of it and that the method that they were using was certified in 1973, it had questionable value then, and it has no scientific validity now.

If you look at Greg's slides and listen to his talk, the important points are we do not care what instrument is used. We do not care what method is used. We only care if the data is accurate.

In fact, historically, the way the initial accuracy of these samples was demonstrated was by using intercalibrations with independent methods and different instruments.

My co-author is Mike Carlin who provided the support of our work in San Francisco Bay with the San Francisco Region of the California Regional Water Quality Control Board, and I have several people that I would like to acknowledge: Ken Brulin, John Donak who is now at Old Dominion, Kathy Lau who did the speciation studies on copper in San Francisco Bay, and Hunt & Associates who did studies on the bioavailability of copper in San Francisco Bay.

As I indicated, prior to Shier Berman developing these standard reference materials which, in the US of A, Shier, we refer to as SRMs, the only way we could demonstrate whether the data that we were reporting was accurate or reasonably accurate was to determine whether or not the data actually exhibited biogeochemical consistency and whether or not the data that we generated could be reproduced by someone using a different instrument and a different analytical methodology.

This is the very first measurements of lead in the oceans. The one on the far right was the Shall and Patterson reference that Berman reported in 1981. The subsequent ones were the ones that we made in the central and south Pacific and reported in 1983.

Now, at this time, there had been no previous data, so the only thing we could do was we could look at the data and determine whether or not it was reasonable. If you look at it, these are profiles going down to 4 km in depth and concentrations. So, they would go out to about 35 ng/kg in the Atlantic and to about 17 in the Pacific, and then they would drop down to values of 0.08 ng/kg at depth in the Pacific and higher levels of about 3 ng/kg in the Atlantic.

What we were able to do, though, was we were able to look at the fluxes of lead in the sediments during the Pleistocene period and calculate what the lead flux was, what the lead residence time in the ocean was, and then what the contemporary EO and input of industrial lead was, so the data were biogeochemically consistent.

This was how we came upon the idea that possibly we were using the right procedures. These analyses have since been corroborated by numerous researchers using multiple methodologies and multiple instrumentations.

Now, the common criticism of this work was that it was too expensive and too difficult. That certainly was the case.

The first samples we collected in the middle of the Pacific Ocean, we would get in a rubber raft, and we would row at least 5 kilometers away from the ship, and then we would take the person who had, theoretically, the clean hands, and they would put on the long plastic gloves that vets use to inspect horses, and then they would put other plastic gloves that had been cleaned in acid on top of those.

Then, the person with the dirty hands would pour subboiling quartz distilled acid over that individual, and while he lay over the bow of the boat, the one with the dirty hands would row the boat forward.

This was not an especially efficient way to collect samples, but it did provide the first accurate measurements of trace metals in the Pacific Ocean and the Atlantic Ocean.

I do not have a picture of the first generation deep water profiler. This is the second generation. The first generation was about the size of a German tank and had a few more moving parts, but we could take...the insides were made out of teflon, and we were literally only able to take a single sample out of each unit, and it cost about $10,000, and each unit inside cost about $10,000, so it cost us 6 weeks at sea and hundreds of thousands of dollars to make those initial samples that you saw.

The samples were then brought aboard the ship and processed in a trace metal clean laboratory that had been loaded onto the ship. The entire insides of these labs are, because we are looking at metals, not organics, they are metal free. They are HEPA filtered. They have an entry room, and the water is passed into it with purified nitrogen gas and then analyzed.

The initial analyses were done by thermal ionization, mass spectrometry using isotope dilution. This is the mass spectrometer at Cal Tech which was initially built in the 1950s by hand, and we got so that we could actually run sample a week on it.

That is no longer the case. In San Francisco Bay now, you can never row 5 kilometers away from the ship without hitting land, so what we have is a teflon peristaltic

pumping system where we extend the sampling hand over one side of the ship, process it through a peristaltic filter, and it is collected, after going through this cartridge that everyone is talking about, right here into the acid cleaned bottles.

We have determined that that has been sufficient. We have never found any substantial sources of contamination from the sampling collection in this procedure.

Again, as I said, the only way we can demonstrate the accuracy of our data to the level that we are satisfied is by independent intercalibrations using different methodologies and instrumentation. In this case, this is replicate samples with our group and then Ken Brulin and John Donak. John is now at Old Dominion with Greg.

I do not have the standard deviations, but they are about 0.05 on each of those analyses. So, these are not replicate samples. These are duplicate samples taken concurrently rather than splits of bottles.

When we finished the Pacific Ocean stuff, I was very interested in working in San Francisco Bay. This was the time that Greg Cutter was actually looking at the selenium problem in the Central Valley and the possibility of elevated levels of selenium in the San Francisco Bay area.

He told the groups that he was working with, that it would be most appropriate to have complimentary trace metal data so that we could actually look at the biogeochemical cycles of selenium and normalized trace metals as one way of determining whether or not his data was biogeochemically consistent.

We intercalibrated with the groups that were doing the trace metal measurements at that time. We took duplicate samples...I mean, a split of a sample, so they are replicate aliquots, and in that intercalibration, our measurements of trace metals were 10 or 100 or 1000 or 10,000 times lower than that of the other laboratory.

So, we were encouraged to write a small grant to do these analyses, and then it was determined that our analyses were too expensive, so they continued to fund the other group that generated different data.

The other criticisms that we encountered were that our data were unnecessary. You did not need trace metal clean techniques. They were inaccurate. We were getting low values because we were missing the metals. They invalidated existing water data, and they invalidated bioassays, because those had not been used with trace metal clean techniques or accurate measurements of the trace metal concentrations that they were measuring the bioassays with. So, they also invalidated water quality criteria.

My favorite criticism of our proposed analyses in San Francisco Bay was by an anonymous administrator who is now retired who stated that so what, she did not care if

our data were...if the data that they were generating were inaccurate; she only cared that they were reproducible.

So, we bagged San Francisco Bay, and about the same time, a friend of mine, Jerome Riagu who was then in Canada asked me if I would be interested in looking at the trace metal concentrations of lead in the Great Lakes, because he had some concerns about the data that had been published.

This is the data that had been published in 1987, values of -3 to 416 ng/L. Now, conclusions, if you look at that data, you come to some very straightforward conclusions.

The Great Lakes represent the ultimate solution to the lead problem. They contain anti-lead, so we can throw batteries in them and bring them up to neutral. The concentration of lead in the Great Lakes varied by 1000 to 100,000-fold, in contrast to the two orders of magnitude we saw throughout the world's oceans. In fact, the concentrations of lead in the Great Lakes were, depending on which data you used, if -26 actually counts as minus two orders of magnitude or not, the values ranges from either 10 to 10,000 times the concentrations of lead in the world's oceans.

When we went and measured the trace metals concentrations of lead in the Great Lakes using the same methodology we had used in the oceans, we found that, in fact, in the middle of Lake Ontario right here, you had concentrations...this is in picomoles, but that is about 2 ng/L which is as low as the middle of the north Pacific Ocean.

Similarly, the data was geochemically consistent. You had low concentrations in the middle of the Great Lakes where you have high levels of primary productivity that scavenged lead out of solution, and you have elevated levels of lead near primary industrial sources in the Great Lakes.

We also looked at isotopic composition of that lead, and we can actually fingerprint the lead so that we can show the lead in this area was coming from the industrial lead used by the Canadians, and the lead in the lower reaches of the Great Lakes was consistent with the industrial lead used by the United States. The values in the intermediate levels of Lake Erie then represent a confluence of industrial aerosols from the United States and Canada.

Now, this is another plot of the data that Shier Berman showed you before with the reported baseline concentrations of lead in the Great Lakes going from 1965 through 1989.

I initially tried to put this on a scale, but that does not work, because we go through three orders of magnitude. So, if you see this, you do not see this.

Oh, excuse me. It is important to note that at the same time that we were making these measurements of less than 2 ng/L in Lake Erie, a publication was picked up and published nationally and carried by the wire services about the dramatic decreases of lead

concentrations in U.S. waters. Unfortunately, the lead blank in those measurements was 1000 times higher than the concentrations of lead in the middle of Lake Erie.

This is a recent report, a summary of the data we have for silver in San Francisco Bay. Again, it is in picomolar, but the importance of this slide is to familiarize you with San Francisco Bay and to illustrate some of the problems we have.

San Francisco Bay, the estuary, consists of a positive estuary with the confluence of the Sacramento and San Joaquin Rivers here that drain, I believe, 85 percent of the watershed of California and go out through the Golden Gate. The South Bay, then, is a negative estuary. Its primary sources of fresh water are the San Jose sewage treatment plant and the Santa Clara sewage treatment plant.

San Francisco Bay is also referred to as the urban estuary in contrast with what you see out the window here. The only vegetation you see in San Francisco is in the fern bars.

When we looked at copper concentrations, what we found, by station, was elevated levels in the South Bay, low levels at the Golden Gate which were consistent with oceanographic data, and intermediate levels at the confluence of the Sacramento and San Joaquin Rivers. So, this, again, was very consistent with what I showed you previously for the distributions of silver. It was also reproducible.

Now, the thing with copper and most metals is that they are surface reactive which means that they tend to be removed from the water column just as you remove trace metals from a sewage treatment plant. You have both a geochemical sink where the copper would be adsorbed onto particles coming down the rivers and then a biogeochemical sink further on in the estuary where the copper is adsorbed onto phytoplankton produced within the bay.

Unfortunately, you cannot see the x axis, but it is plotted against salinity. Again, this is because we always normalize our data to biogeochemical parameters to see if it makes sense.

So, again, this is a plot of copper with salinity in two cases. This is the Sacramento-San Joaquin River coming down. Instead of a sink, we see a small source, intermediate source, within the estuary, and then the low levels you see at the Golden Gate Bridge or the open ocean.

Conversely, if you go to the South Bay, the copper concentrations go up off scale, much higher. So, in fact, these levels seasonally exceed the water quality criteria for copper.

By seasonality, here are three plots of copper. This is the dissolved copper at the top, total copper at the bottom, and similar plots from the Sacramento-San Joaquin to the Golden

Gate. The white represents what we see in the South Bay, a negative estuary, where the wastewater discharge is the primary source of fresh water to the system.

It is highest during the low flow periods and lowest during the high flow periods. That is high flow out of the rivers, not the treatment plants.

The other thing is that our samples were taken during the protracted drought, so what we were able to do is we were able to plot the hydrographic data of the flushing of the system with what we saw in the copper, and it was consistent. The copper concentrations built up in the South Bay when the flushing out of the North Bay was lowest.

Because we are able to accurately measure the metals, we can actually calculate what the residence time of the metals in the water column is. This illustrates, again, the problem with the South Bay.

Residence times of silver and lead in the South Bay are only 13 days. That is the residence time of the metals in the dissolved phase, whereas the hydraulic residence time in the South Bay is four months during the high flow discharge periods and up to six months and actually infinity during the low flow periods.

So, it is real, you know, regulators problem in how do you get these metals out of the bay when they stay in the South Bay, you know, essentially infinitely compared to the water.

The other thing we can do, then, with Mike Carlin is that we can calculate what the relative loadings of the South Bay are by source. Because we can actually measure what is in the river, we can figure out that the river loading is much smaller than previously reported, and the storm water loading is much higher than previously believed, and the municipal and industrial dischargers which have historically been blamed for all the elevated levels of copper in the South Bay actually represent a distant second to what is coming in from the storm water.

The other thing pointed out by this is that the water quality criteria for copper in drinking water is...what is that, almost three orders of magnitude greater than it is for the invertebrates in the South Bay, and that is, of course, because copper is relatively non-toxic to humans and is extremely toxic to some phytoplankton and some invertebrates.

So, what they are doing now is that they are using copper in the drinking water systems of the Bay Area to keep the water clean of the phytoplankton in it, but in order to reduce the copper loadings to the South Bay, they have realized that they can actually decrease the amount of copper put into the drinking water systems of the bay, and then that would decrease the amount of copper coming out of the effluent.

Again, here is the water quality criteria, the concentrations that we measure by station relative to the existing water quality criteria.

But we told them it does not matter what your existing water quality criteria is, because the concern you have with copper is the free copper. That is copper that is biologically available to the organisms.

There have been studies by Ken Brulin that showed essentially 95 to 99 percent of the copper in the ocean is so tightly bound to organics that it is not available to the phytoplankton at any immediate term.

Now, this is my failure to show the distribution of copper in aquatic systems, but, literally, you have inorganic complexes that are not available, you have free copper ions which are biologically available, and you have organic complexes of copper which are generally not that available based on sundry studies.

So, the plankton in filter feeders are getting copper only as the free ions, and they represent a relatively, we believe, relatively small fraction of the total dissolved copper in the water column.

Ken Brulin looked at the speciation of copper with John Donak using two different methodologies. The labile or relatively free copper ranged from 4 to 25 percent, depending on what definition you used and what methodology you used, but substantially less than the 100 percent that had been used in the water quality criteria.

So, new water quality criteria are being used based on bioassays with the endemic species, Midels californianis, and those toxicity studies were used with trace metal clean techniques where we actually measured the concentrations of copper in the bioassays using those same techniques.

In summary today, ultra-clean analyses are not too expensive. They are scientifically defensible. They follow the Clean Water Act guidance, and they stand up in court.

In conclusion, ultra-clean techniques are required for scientifically defensible water quality management.

Thank you.

(Slides and overhead transparencies for this presentation were not available at the time of publication.)

MR. TELLIARD: Our next speaker is Nicolas Bloom. Nick was here last year to talk about one of his favorite subjects, mercury. Nick is the Senior Research Scientist and Vice President of Frontier Geosciences, and he is going to ask the ever-abiding question, can mercury be routinely monitored at the parts per trillion level?

CAN Hg BE ROUTINELY MONITORED AT THE PARTS PER TRILLION LEVEL

MR. BLOOM: I was here last year talking about ultra-clean methods as they applied to mercury, and I believe at that time I voiced some pessimism as to whether the part-per-trillion level could be realized in a routine monitoring capacity based on the amount of effort and incentive that one has to have to apply clean techniques correctly.

Since then, I have been working on a project with the Central Valley Regional Water Quality Control Board in Sacramento, trying to do just that; monitor the rivers through the City of Sacramento at ambient levels, and I believe we have met with a large degree of success which has caused me to revise my pessimism, and I now believe that it is quite possible to do this, given the incentive on the part of the people who are collecting the data.

My co-workers on this project are Eva Butler from Brown and Caldwell, and Val Conner from the Central Valley Water Quality Control Board. Both of them are field workers for their respective organizations and have never had any past experience with trace metal work before embarking on this project. I have never met either of them, and all of the information concerning techniques was communicated over the telephone.

Before I go on, I might want to just ask the question why is it that we want to measure at ambient levels? Ambient mercury levels are typically in the range of 0.5 to 5 ppt in water which is several orders of magnitude lower than the current standard methodology and at least on a par or even lower than some of the newer methodologies that have been suggested, for example, the modified EPA method suggested by Dr. Potter earlier.

It turns out that even in very contaminated systems, mercury in the water is quite low. In a system that may have naturally had 1 ppt of mercury, elevation to 2 ppt could represent a major environmental degradation.

Unlike most metals, I believe evidence is now starting to build that mercury may be exhibiting toxicity to organisms at ambient levels, and the ambient levels today are

enhanced by about a factor of 4 over pre-anthropogenic times, and that factor of 4 may be enough to be pushing us today to chronic toxicity.

These studies have been wide-ranging. They have included studies on fishery production by Dr. Jim Wiener at the National Biological Survey. They have included human effects on fish eating populations in the Seychelles conducted through the World Health Organization and Dr. Clarkson at the University of Rochester Medical School. They have also included field correlational evidence linking mercury levels to degradation of loon reproduction in the Midwest and the death of the Florida panthers in the Everglades.

In all of these cases, the water bodies being measured contained total mercury concentrations of less than 3 ng/L of total mercury.

I should also note before going on that this talk is going to be about total mercury. It is likely that really what needs to be measured at ambient levels to get at some of these issues is methylmercury. Dr. Cutter discussed speciation for arsenic and selenium, and much the same is true for mercury as well. The biologically active species for mercury is methylmercury, and it is much more strongly correlated to biota concentrations than is total mercury.

When going out to measure mercury today, the only methods sensitive enough to even begin to come close to ambient mercury concentrations are based on the cold vapor technique where mercury is volatilized from the sample as elemental mercury and then detected by some form of atomic spectroscopy.

I have listed here several methods and their relative standard deviations. The technique that we have been using involves gold amalgamation. We are using an atomic fluorescence detector currently. Previously, we had used an atomic absorption detector.

The detection limit based on 2 standard deviations of the blank noise is about 0.05 to 0.15 ng/L. That has not changed in about 15 years. I want to emphasize that these methods have been used for quite some time since they were developed mainly in Bill Fitzgerald's lab at the University of Connecticut.

The difference between the use of AFS and the use of atomic absorption in this case is largely a function of how big of a sample volume you process, but in both cases, the detection limits are limited by mercury in the blanks.

Another technique that has been used, and this is similar to the one that was described earlier today, is to directly purge the sample into an AFS or an AAS detector without preconcentration on gold. This gives you detection limits ranging from, for AA using the standard EPA method, about 200 ng/L down to somewhere in the range of 0.2 to 1 for using an atomic fluorescence detector.

Then there is this somewhat unique method developed by Gary Glass for the EPA which uses AA but recirculates the gas stream through the bubbler, collecting all the mercury, ultimately, into the analyzer, therefore eliminating the dilution effect of the purge from the water. We have actually intercalibrated with his laboratory, and he has an effective detection limit of about 0.3 ng/L.

I should note that these methods that give you detection limits of, say, 0.3 or so, imply that the limit of quantitation is maybe 1 to 2 ng/L, which is too high to accurately measure mercury at ambient levels. Especially if you are going to want to measure methylmercury, which exists at about 1 to 20 percent of the total mercury concentration, then really the only method available currently involves a preconcentration and AFS detection.

The method we use, just very briefly, is that the sample is oxidized with bromine monochloride, which is essentially the same reagent that was discussed in the earlier presentation, and then it is pre-reduced with hydroxylamine hydrochloride.

The mercury is reduced to elemental mercury with stannous chloride and purged onto a gold trap. The mercury is collected by amalgamation, and then the trap is placed in line with a second smaller trap, and by thermal desorption, the mercury is removed from this trap onto the second trap. From the second trap, a similar step passes it into the atomic fluorescence detector.

Through the combination of these steps and the atomic fluorescence detection method, the method is virtually interference free, and all of the typical interferences that you have with the direct flow systems related to chlorine or hydrocarbons and so forth are avoided.

In addition, an interference that is not thought of too often but is quite real in the direct purge technologies is that the peak shape of the mercury being purged from the liquid varies as a function of the matrix. Very often, in techniques where a direct purge technique is used, it is necessary to use a method of standard additions on samples of different types to account for the different elution characteristics.

Using this method, since we purge an excessive amount of time and then have all of the mercury released from essentially the same matrix, all of the interferences related to things such as iodide and other trace metals and so forth are completely eliminated.

This is a diagram of a sampling system that was used by the California Regional Water Quality people in their studies. It was in place before we started the project. They had routinely been measuring other trace metals using this sampling equipment and, in a couple studies before ours, had attempted to measure mercury in the same system.

We were actually called in after they got some bizarre results where, in one year, they had very high and variable numbers from all of their sites, and then the next year, they switched laboratories and got less than detects from all of their sites, and they were trying to figure out whether those two data sets were consistent and, if not, where the problems were.

This sampling system just consists of a polyethylene box with an acrylic window. It is a glove box. These boxes are located at the sites along the rivers where samples are to be collected, and they have rigid PVC tubing going out into the lake or into the river, and each time they collect samples, they string a new piece of acid-cleaned PVC tubing out into the water and sample that through a peristaltic pump.

Early in the study, they filtered it in this chamber. Since then, we have filtered in the laboratory.

They then collect these bottles, these samples, into bottles of a type appropriate for the metals that they are studying.

Prior to our participation in the study, we had nothing to do with the development of this method, so our role was largely to assess how well this was working, and we will have some data to indicate how well it works so far and what might be done to improve matters as time goes along.

This is a photograph of the system in operation.

As part of our study, we felt it was quite necessary to have a lot of QA, both in the field and in the lab, and I will be reporting some of that information.

I want to note that this project was largely performed by people of relatively low level of technical expertise. The sampling crews at the consulting firms had no expertise in trace metal work at all, and the analytical technician at our laboratory essentially analyzed these samples blind and relied purely on QA measures of this type to ensure whether the data quality was good or not.

Later, actually much later, I was given a key as to the sample and QA locations from the people in California, and we went back and interpreted the results geochemically.

So, within this, we had method blanks. We run at least three per sample batch. Filtering blanks, since all the samples are filtered in our laboratory using a disposable polycarbonate filtering device similar to the ones used for sterilizing blood serum, for each sample batch, we measured the blank, introduced mq water passing through that filtering device.

Spike recoveries on all batches. Duplicate, lab duplicates and the field. Blank spikes were done once so far. We are not reporting those, because, apparently, there was an error on the part of the people in the field in spiking, and they spiked the samples with 100 times more mercury than they desired to, and it made that study a bit meaningless.

Then we have done some specific studies on the field equipment and on the interlab comparisons to verify the accuracy of the method.

One of the things that is really difficult with mercury is that at ambient levels, there is no certified standard for mercury in water that is close to ambient concentrations. So, the only real test of accuracy that you have is intercomparison with other reputable laboratories.

Unfortunately, virtually all of those other laboratories use the same methodology that we are reporting here. So, that intercomparison does serve to compare standards and technician skills and so forth, but it does not necessarily get at the root question of whether this method is inherently accurate.

To start off when I was asked to begin the project or, actually, before I was asked to begin the project, I was called about sample containers. As you recall, I said the very first data set was extremely high and variable, and they went to another lab, and the values dropped to less than detects in the second lab.

One of the differences between the use of that first lab and the second lab was that the first lab was using I-Chem polyethylene bottles for collecting the samples, and the second lab was using acid-cleaned teflon bottles. It had been reported long ago by Robertson and Bothner that polyethylene bottles did, indeed, allow mercury to pass through in the vapor phase and contaminate the samples, although that work was done at very high room concentrations of mercury.

So, one of the first things that we did was actually try to replicate that work in our clean room to give a more rigorous test as to how well polyethylene bottles were suited to mercury work. We used some of these I-Chem type polyethylene bottles and rigorously acid cleaned them, filled them with natural lake water, and we used teflon bottles as well.

Then I kept them in our clean room bench where the average mercury concentration in the air was known to be about 4 ng/m^3 and monitored the concentration of mercury in these bottles over two months. There is actually another data point out here.

This line is the polyethylene bottle, indicating a strong increase in time, even at very low atmospheric mercury concentrations from about 1 ng/L at the initial time up to 15. After 60 days, it was up to 24, and we noted a much smaller but statistically significant increase in methylmercury in this sample as well.

These are actually replicates of...these are means of four replicates.

On this bottom line right here are presented the results of the same sample stored in teflon bottles with and without acidification. In those cases, the results are essentially identical over three months with no change whether the samples are acidified or not.

So, the first conclusion was that yes, probably the first data set was compromised by the use of polyethylene bottles which I would assert should never be used for mercury sampling. They will invariably give you bad results.

Because we wanted to avoid the chance of contamination of the samples in the field by inexperienced technicians adding acid to preserve them and filtering them in the field and so forth, we decided to incorporate a procedure where the samples would be sent by overnight mail at 4 degrees C in teflon bottles and filtered on the day of arrival in our laboratory in the clean room.

We had used this method on other projects previously, and, anecdotally, it seemed to work quite well for oxic waters, although we had never really proved that in a rigorous way.

So, for the purpose of this project, we ran some tests on two different kinds of water, Duwamish River water...these are both western Washington waters now, because in order to get t = 0, we had to be close to the source, so we were using water from close to our lab.

Duwamish River water contained a lot of tertiary sewage effluent, and Lake Union water is quite, oligotrophic, although it is impacted by boating activities and shipping activities even in this water.

What we did, we had already established that total mercury was preserved in these samples for a long time period, so we looked at just the dissolved fraction over a period of about six days in order to ensure that the dissolved-to-total ratio would remain similar in the 24-hour time involved in shipping the samples from California to our laboratory.

For each of these two waters, we have time zero and 18 hours, 36 hours, and 168 hours. These are the mean of four replicates of each of the dissolved species.

The dissolved species are, in these samples, running about 0.5 ng/L which is quite common for mercury in water that contains about 4 or 5. So, that is 10 percent dissolved which is pretty typical for mercury in water.

Although the noise is rather high in this scale, given how low these concentrations are, essentially, this data indicates that, for the purposes of our project, filtering in the laboratory gives us sufficient data quality to meet the needs of the project. In the actual project data that I will show you later, typical total numbers are from 20 to 20 and dissolved values are from 0.5 to 4 or so.

I should note a caveat in this. This, again, seems to work rather well for natural oxic waters. We got a little too cocky once and applied this to groundwater samples, and it was a disaster. All of the mercury went to the walls of these groundwater samples in 24 hours, as did a lot of the manganese and iron.

We have since repeated that study by going to the source of the well and collecting dissolved samples at the wellhead, and in that case, the mercury in those samples was 100 percent dissolved in the wellhead and greater than 90 percent on the walls.

So, this kind of methodology may, in fact, apply well to oxic surface waters, but I do not think it can be universally applied.

I have here now a couple quality control charts for this project, and I bring them up, in part, to show the level of precision and accuracy that we are having in our project and also to indicate the importance of keeping this kind of information.

These are the method blanks for these two projects combined with another project that we use the same QA protocols on for the National Mercury Deposition program and over a five-month period. These are the method blanks from bromine monochloride and purging and so forth, and about right here, about where it says 20, this is a different batch of reagents than this, and it is slightly cleaner.

As you can see, excluding this bit of stuff right here, these values are quite tightly constrained and enable us to have very low laboratory detection limits.

What is perhaps of more interest is what happened right there, and it turns out that this event is correlated with a time when samples were sent to our lab that we had believed were about 100 ppm mercury in sediments from a contaminated sewage treatment plant, and they actually contained 10 percent mercury.

They were put in a drying oven and dried four rooms down from the analytical lab where we do this work. It raised the room air from about 10 to 2500 ng/m^3 during the course of that event, and it shut down our lab for over a month.

These data were collected after that, not during the event. We were not crazy enough to actually try to analyze samples during the event, but these data were collected when we thought that we were clean enough to start back up routine operations, and this is a two-week period after room air concentrations had come down to about 40 ng/m^3 and we thought we were safe, but we were not. There is a lesson here.

One lesson is always to measure your room air for mercury, because you never know when somebody dropped a thermometer in the room next door.

This is a similar set of data for recovery of mercury on spike recoveries during this project. These spikes are at 8 ng/L, and they are matrix spikes, and they show the mean, as you can see, is 99.6 plus or minus 6.3 percent over the entire range.

Interestingly, there is this excursion right here. That corresponds to the same time period that we had contamination due to the other system, and there is actually a reason why recoveries are low during the same time period that the contamination was high, and it has to do with when we ran the samples compared to when we ran the spike recoveries, which were separated by several days, and the level of contamination in the room was higher on the day that we ran the samples than on the day that we ran the spike recoveries. Therefore, subtracting the two resulted in a dip in the recovery.

So, this kind of event where you have mercury contamination in your air can compromise your data in many ways, both in terms of blanks which affect your detection limit and also in terms of recovery which, if you were to apply a correction factor using that information, would be considerably in error overestimating the mercury in the samples.

As I said, we do not have any quality assurance materials for mercury in water at ambient concentrations, so we have to rely on participating and intercomparison exercises, and we try to intercompare with other state-of-the-art labs often.

The data that is shown here is actually part of an intercomparison exercise that was sponsored by the Electric Power Research Institute, and it involved samples being sent to 22 of the most sophisticated mercury labs in the country. Each lab was sent three bottles of water that was collected from the surface of a quiescent lake without filtration.

We had already had enough experience to know that, on a given day, the surface water of lakes does not change very much, certainly far less than the analytical variability of laboratories which makes the collection of an SRM for mercury in water rather easy. All you do is pump a bunch of bottles full, and they all have the same concentration.

We pumped 120 consecutive bottles and randomly assigned them to each of the laboratories, and then there were 30 bottles retained by our laboratory to get a measure of the variability between bottles at the beginning of the experiment and four months later at the end of the experiment.

That is our mean right there. This is our laboratory, 30 bottles, 3 replicates on each bottle, for a total of 90 determinations in this lake. The value for the total mercury in this lake water is about 1.29 ng/L. Excluding these three outliers, the consensus value is very similar to the value that we obtained.

This is practically the only kind of evidence that you can have today for verifying the accuracy of your methods, given the absence of standards.

This bar chart was completed quite recently, and it is our first investigation of sources of contamination potentially involved with the California Water Quality Control Board sampling devices. Essentially, the thrust of the thing is here, this is deionized water that was sent to them in the field from our laboratory in acid-cleaned glass carboys, and then they ran this water through their sampling equipment and sent the results back to us.

Upon analysis, these items here labeled I#1, I#2, and I#3, these represent the concentrations of mercury in water that had just passed through their 25 feet of acid-cleaned tubing, through the peristaltic pump, into the box, and directly collected into the sample bottles. So, that is sort of the blank that is associated with this pumping system.

Then these ones that have a C attached to them add another feature that they were using. They were actually taking a 10-liter integrated sample before they would collect the sample into the bottles. They would actually collect it into a 10-liter polyethylene carboy.

So, these two and this one which was performed on natural lake water rather than on deionized water represent the entire system blank.

Given the magnitude of the numbers that they actually have in their rivers, these blanks are actually quite reproducible. Without the integrating carboy, the blank contribution is about 0.5 ng/L, and with the carboy included, it is about 1 ng/L.

They, I believe, feel that this level of contamination is acceptable and not necessarily worth changing their procedures which seem to work well for their other metals, although I have suggested to them that they go to acid-cleaned teflon tubing and a longer flush time, and that could probably drop these values considerably.

However, one of the values of this kind of information is at least they know. They actually can quantify what the level of contamination on their samples is, and that puts bounds on their accuracy and interpretation.

This is a summary of the QA statistics over the first five months of this project. We have reagent blanks, the mean at 0.14 ng/L and a standard deviation of 0.04 over four months. This is, again, I want to emphasize, without sophisticated world class scientists making these measurements.

Filtering blanks, the mean is 0.00 plus or minus 0.09 using this very simple disposable filter holder that we have used, and we have actually checked this with other metals, and it seems to be quite a clean technique for other metals as well.

Spike recoveries, the mean is 99.6 with a small standard deviation of 6.3. These spikes are at levels that are typically twice the concentration of mercury in the sample.

Lab duplicates, the mean variation between the two lab duplicates is 4.9 percent. For field duplicates, the mean variation is 13.3 percent. That includes the effect of both contamination and different water, perhaps, that is passing the sampling at the time they do their reps.

Then our intercomparison exercise, we intercompared with 13 labs with a deviation of 4 percent.

One other thing I did not mention about all this. Not only is this all being done by non-well known geochemist type personnel, but it is also being done at a price...we won the contract on a competitive bid against the other two companies that produced the odd numbers. So, this is economical. This is not unrealistic, by any means.

I have to apologize for this rather odd map of San Francisco...I mean Sacramento. The people from the Water Quality Board sent it to me. I picked it up at the airport. I never saw it until today, and I do not know why Sacramento is blotted out there, but it says it right there, so they are not hiding anything.

I am going to present some results that we have found in the first five months of the study not so much to tell you a lot about Sacramento but to give you an idea of the kind of knowledge that you can gain by getting numbers that are actual rather than numbers that are less than detect or random contamination events.

This is the City of Sacramento right here. There are two rivers, the Sacramento River and the American River, that meet in the center of the city and then form the Sacramento River which comes down into San Francisco Bay.

There are sampling points up here near Folsom Dam upstream of the city, assumed to be pristine by this study, and up here on the American River, and there is a sampling point in the middle of the city and several sampling points downstream.

The last sampling point here is at Greene's Landing, and what is called RM44, River Mile 44, are also downstream of the sewage treatment plants for the City of Sacramento and a large suburban community.

In this slide, the data from Greene's Landing are presented. The scale in mercury is now going from zero to 20 ng/L. In the very first study they had, all of the numbers were less than 200. In the more recent study, all of their noise numbers were noise up here in the 20 to 50 range, and then in the study immediately before this one, all of their values were reported back at less than 2 ng/L, and none of that seemed to make very much sense.

So, upon applying ultra-clean techniques and high levels of QA and so forth, we have now generated a mercury profile for the river at Greene's Landing which is traced by this curve right here, and you will notice it has these episodic peaks. These peaks correlate

almost with a R^2 of 1 to increases in total suspended matter which is directly correlated with river flow.

I do not think there is anything too surprising about that, but the point that is being made here is that you can actually see this now if you have a good data set, and that gives you geochemical confidence that your data is really saying something and it is not randomly distributed.

Finally, I have plotted here the mean and standard deviation of mercury concentrations in sampling sites above and below the City of Sacramento. The scale here now goes up to...our highest mean is about 7.5 ng/L, well below the quantitation levels of most methods. Given that the water upstream of the city is about 2 ng/L, this 7.5 could represent a significant degradation of the water resource in terms of impacts on fish and, ultimately, on people who might eat those fish, if they do eat the fish from that river.

Clearly, there is a definite impact of both the city here...this is the city center point...and, more importantly, downstream of the sewage treatment plants on the mercury concentration in that river.

I was asked to note, because the people in Sacramento were surprised that the sewage could have an impact like this, they did not have any idea why they could have mercury in their sewage, since they do not have a large industrial base.

It turns out that a large fraction of the mercury in sewage comes from human excrement as a result of emissions of mercury from dental amalgams. In a non-industrial city, that may be 50 to 70 percent of the total mercury in the sewage flow.

I thought that was common knowledge, but they said they had never heard of that, and they wanted me to mention it. So, there it is.

That is it.

MR. TELLIARD: Thank you, Nick.

Any questions? (No response.)

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Can Mercury be Routinely Monitored at the Parts per Trillion ($ng \cdot L^{-1}$) Level?

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Can Mercury be Routinely Monitored at the Parts per Trillion ($ng \cdot L^{-1}$) Level?

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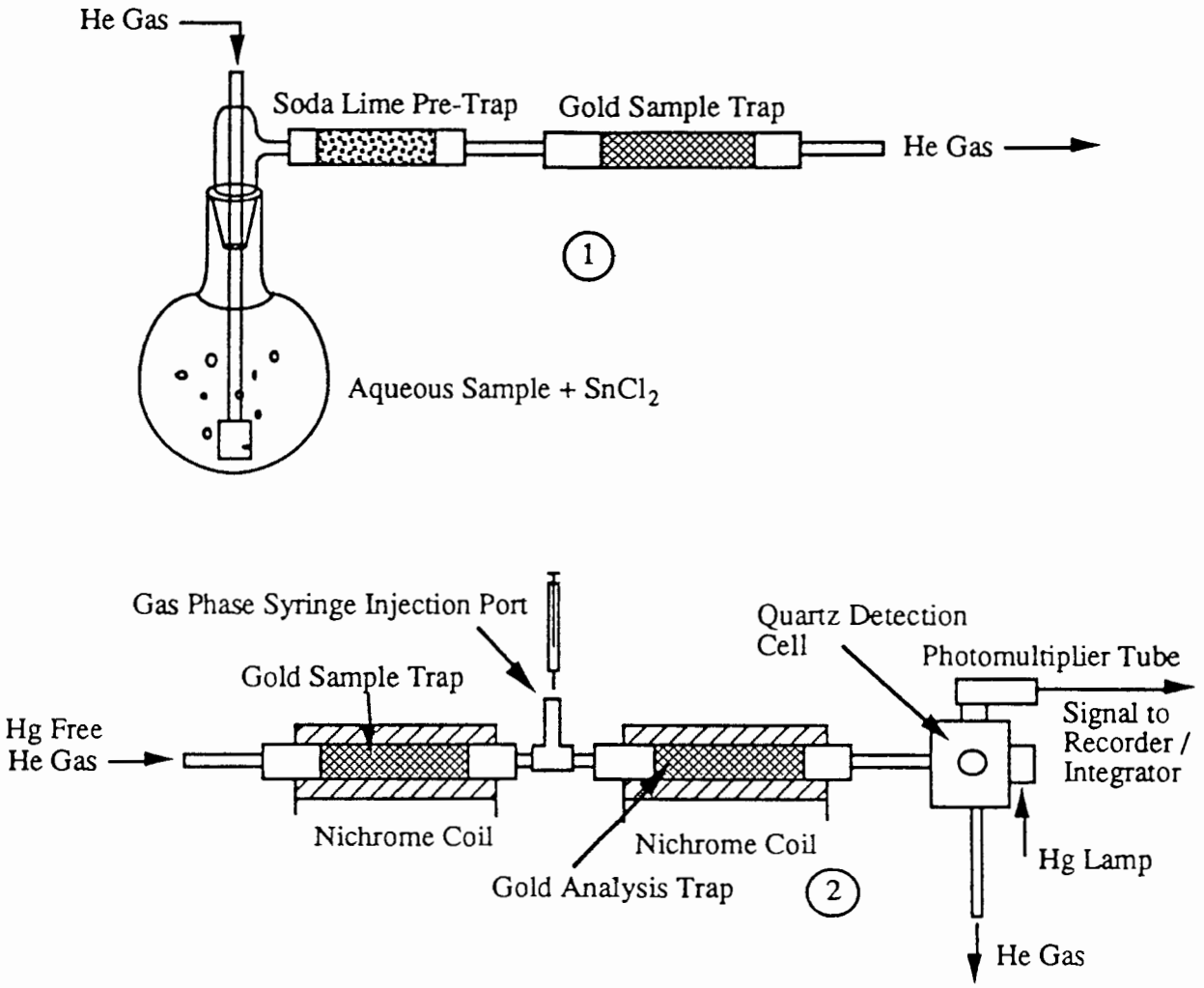
Recent advances in ultra-clean sample handling technique and analytical methods have shown that environmental levels of aquatic mercury are far lower than previously estimated by regulatory bodies. Rivers and lakes unpolluted by direct point source emissions are now understood to contain Hg concentrations in the range of 1-5 $ng \cdot L^{-1}$. Methylmercury generation sufficient to adversely impact commercial and sport fish tissue concentrations may occur in waters containing 1-5 $ng \cdot L^{-1}$ total Hg depending upon other ancillary parameters such as pH, DOC, and alkalinity. Even grossly polluted water bodies may contain water concentrations of only 10-50 $ng \cdot L^{-1}$ Hg, far below currently regulated levels (0.2-2.0 $\mu g \cdot L^{-1}$) With these findings in mind, the City and County of Sacramento and the Central Valley Water Quality Control Board (CA), sought to monitor rivers in the region for Hg at ambient concentrations. Through careful attention to clean technique in field sampling, especially in the use of pre-cleaned and tested Teflon bottles, and overnight shipping to an ultra-clean Hg laboratory for processing and preservation, reproducibility at the $ng \cdot L^{-1}$ level was attained with little additional cost to the program over standard protocols. Extensive field and laboratory QA revealed the existence of a small (< 1 $ng \cdot L^{-1}$) additional source of sample contamination due to the use of non-ultra-clean sample collection equipment, which has not yet been rectified. Also, this work reveals that the use of HNO_3 as a preservative may result in the loss of Hg from the samples by volatilization, and that polyethylene sample bottles are unacceptable for sample storage, as at the $ng \cdot L^{-1}$ level, dramatic increases in Hg are seen as a function of storage time. Ambient aqueous Hg concentrations for Sacramento Valley rivers are observed to be in the range of 2-20 $ng \cdot L^{-1}$ (unfiltered) and 0.5-5 $ng \cdot L^{-1}$ (0.2 μ filtered).

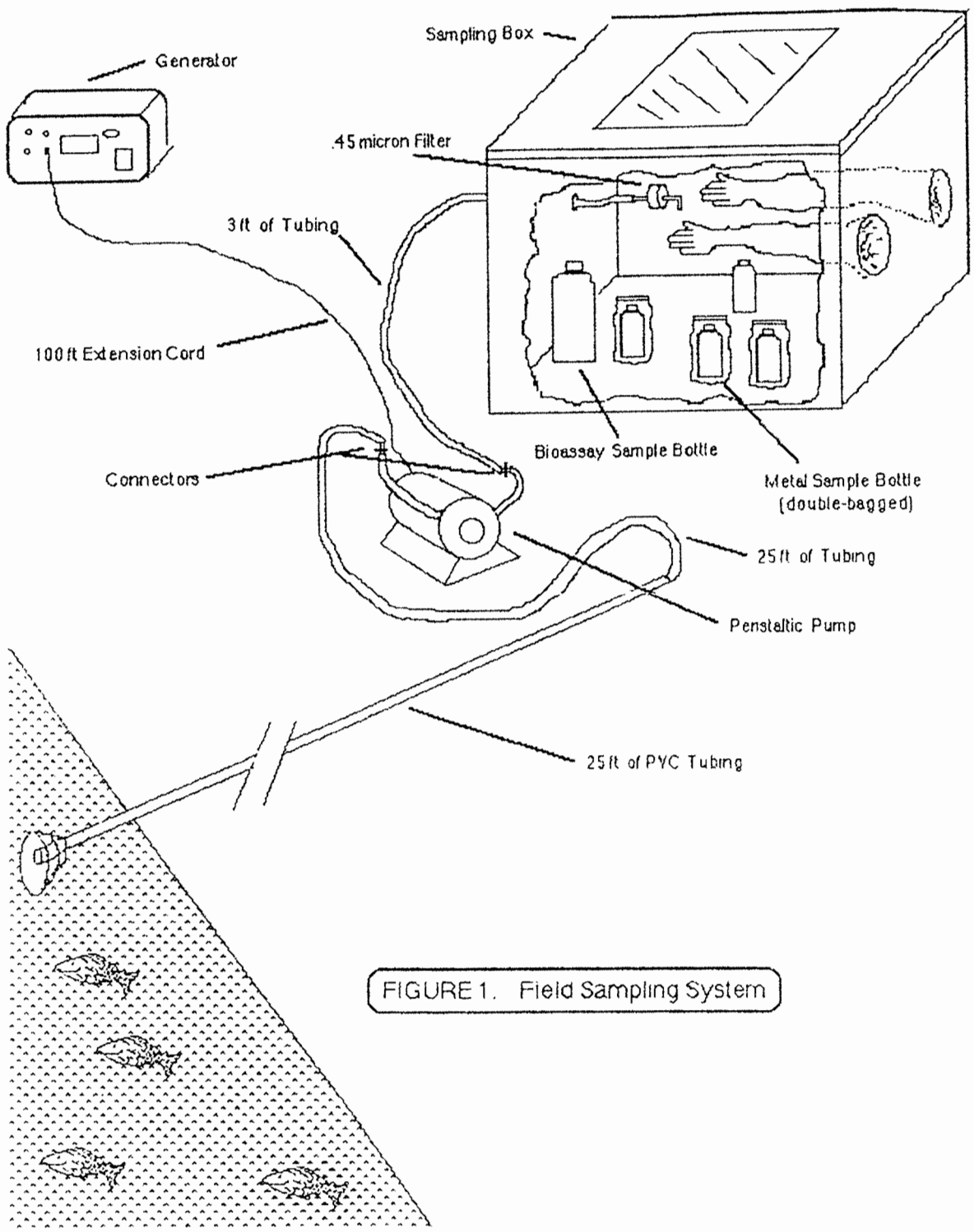
Options for Cold Vapor Hg Detection

method	detector	3 s DL's (ng/L)	comments
gold amalgamation	AFS or AAS	0.05-0.15	reagent blank limited, almost interference free
direct purge	AFS	0.2 (Pichet, et. al) 1-2 (Merlin)	potential quenching from molecular species
direct-purge (recirculation)	AAS	0.3 (G. Glass)	modified EPA method
direct purge	AAS	200	EPA standard method

Slide 1. Comparison of detection limits for various methods of Hg analysis. Note that typical concentrations of Hg in water are 1-10 ng/L, meaning that less than detects will always occur using the standard EPA method.



Slide 2. Schematic diagram of dual amalgamation/cold vapor atomic fluorescence spectroscopy (CVAFS) method. The aqueous sample is oxidized with bromine monochloride to release all Hg, and pre-reduced with hydroxylamine prior to analysis.

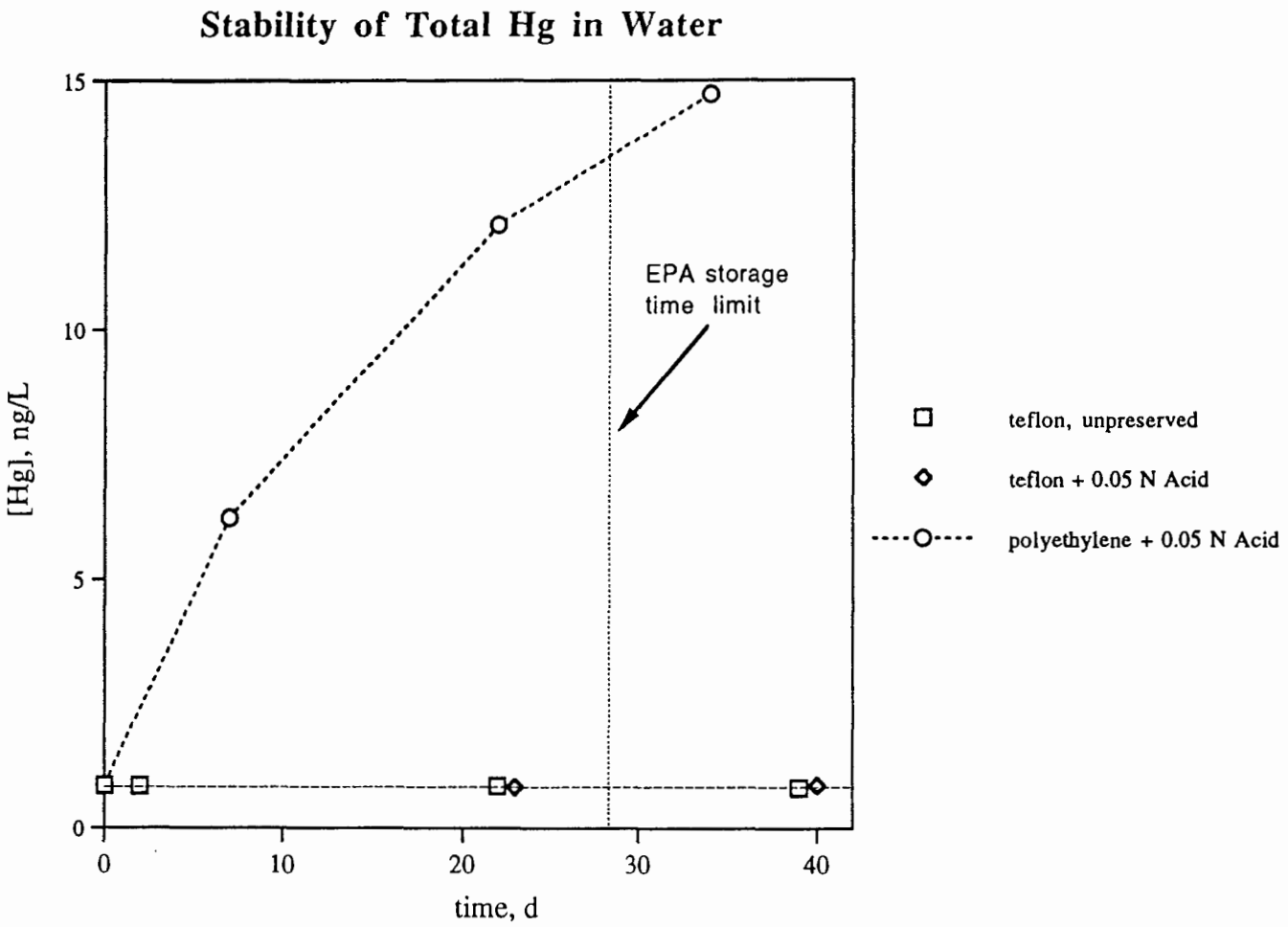


Slide 3. Water sampling system employed on the Sacramento Rivers Project.

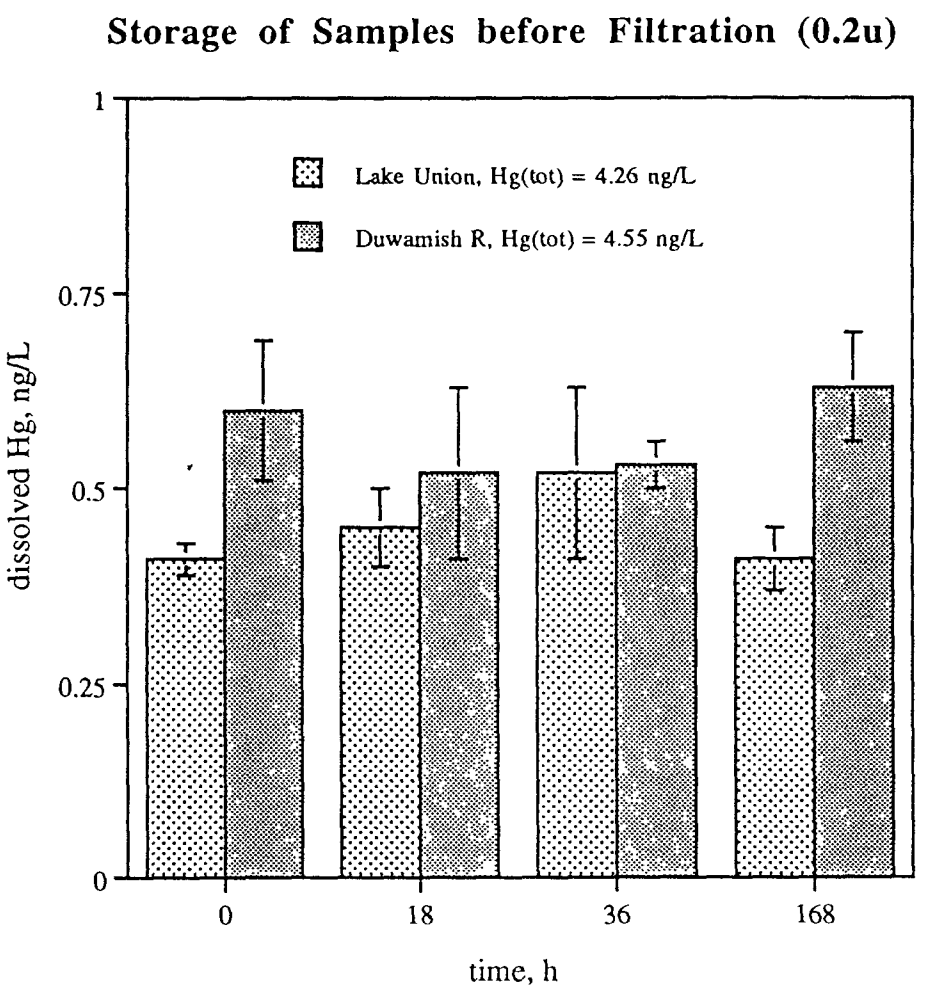
Quality Assurance Measures

parameter	minimum frequency
method blanks	3 per sample batch
filtering blank	1 per sample batch
spike recovery (4-11 ng/L)	1 per sample batch or 10 samples
laboratory duplicates	1 per sample batch or 10 samples
field duplicates	1 per sample batch
blind (field) spikes	once during study
storage experiments	once during study
field equipment blanking	as needed for method development
interlab intercomparison	as needed for method development

Slide 4. Quality assurance measures routinely employed.



Slide 5. Stability of total Hg in river water as a function of bottle material and preservation acid. Samples were stored in a cleanroom with an atmospheric Hg concentration of 5 ± 2 ng/m^3.



Slide 6. Effect on dissolved Hg concentration of storage unpreserved in Teflon bottles. Two different Western Washington waters were employed in the study (the Duwamish River contains 20-70% tertiary sewage effluent depending upon season).

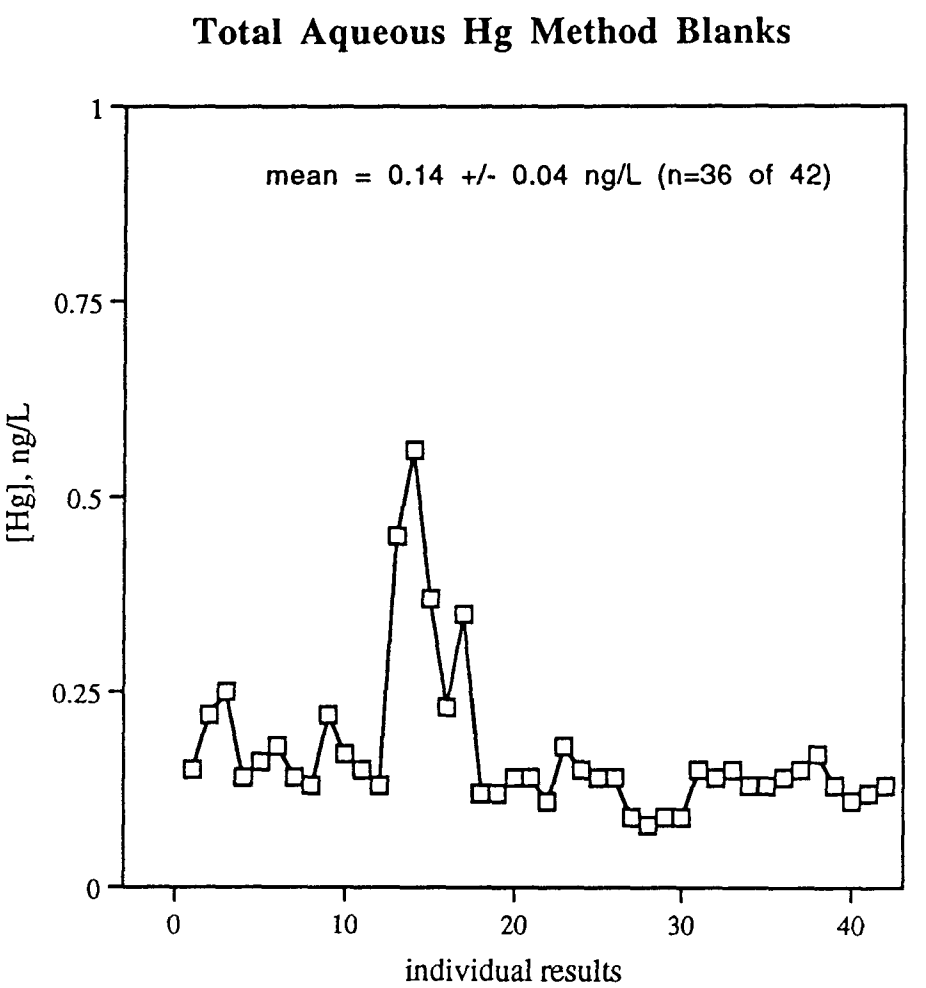
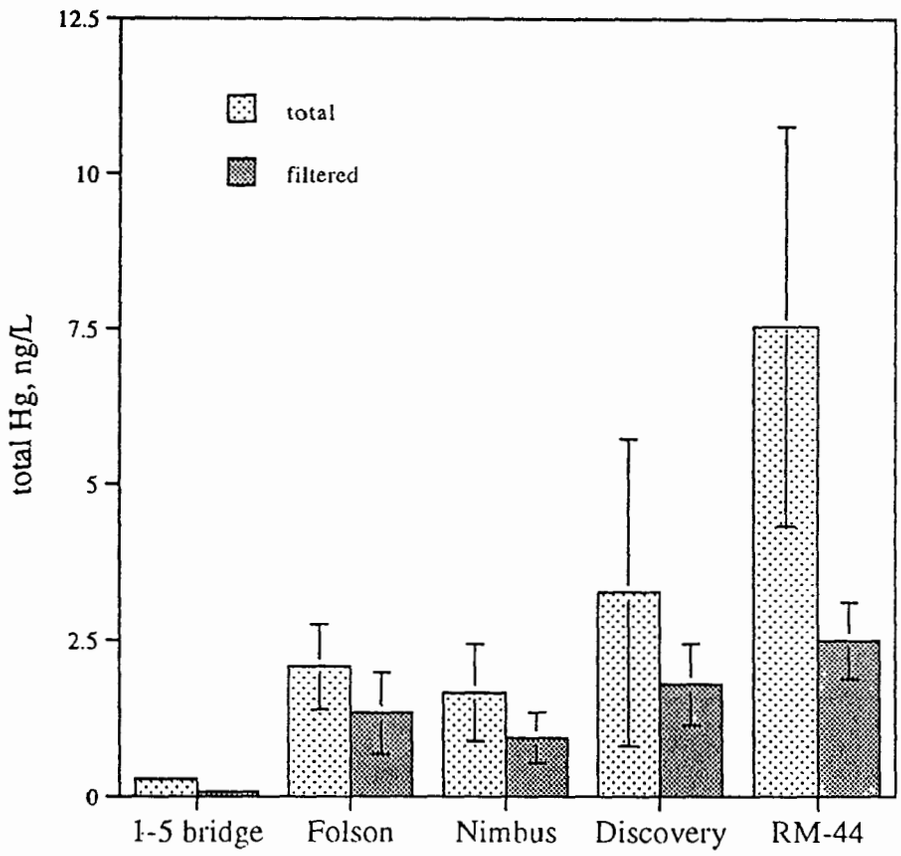
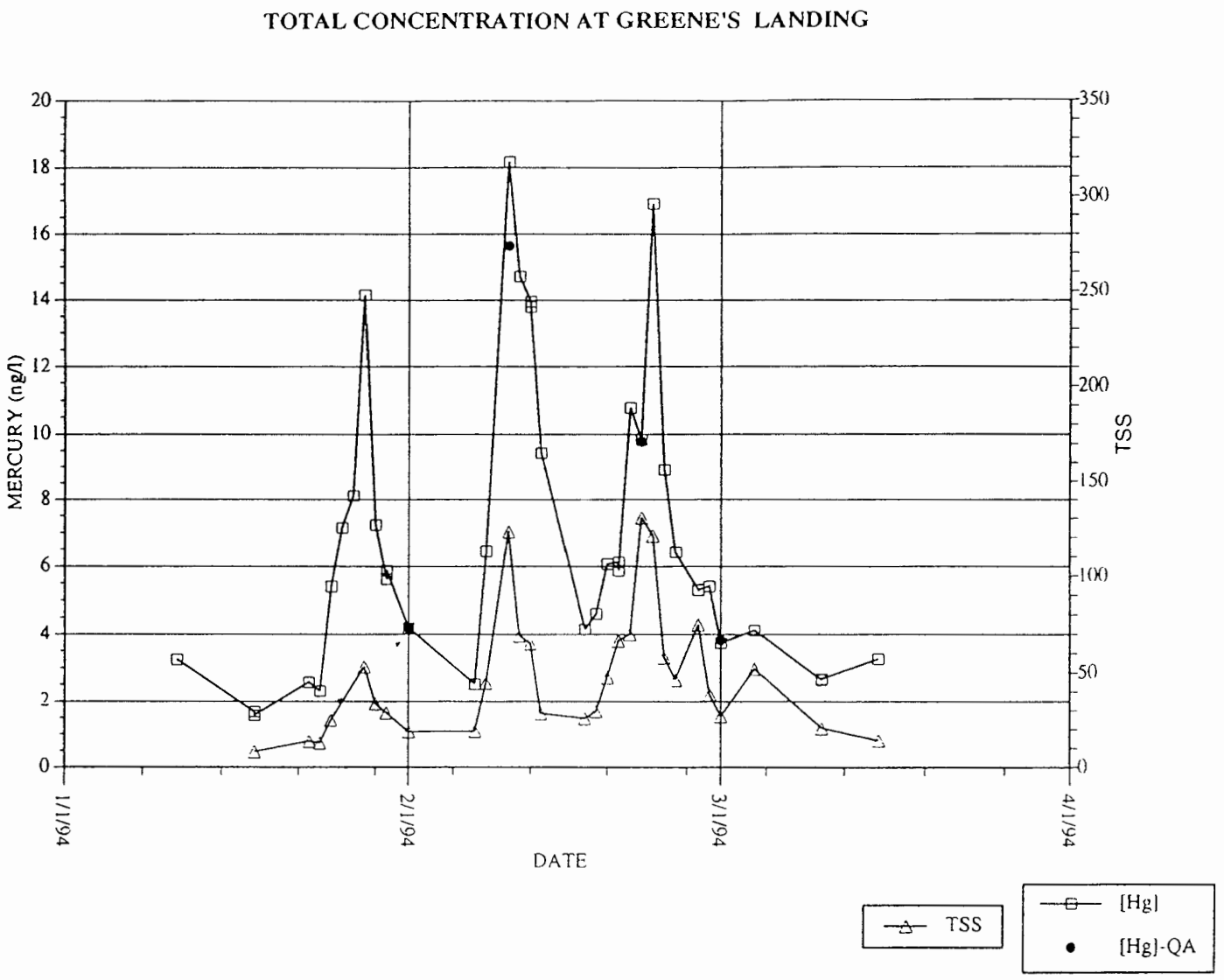


Figure 7. Control chart for total Hg method blanks, December 1993 to April 1994. The excursion in January was the result of a lab-wide atmospheric Hg^0 contamination from metallic Hg containing sediments.



Slide 13. Mean and variability of total Hg above and below the city of Sacramento. The I-5 bridge site is on the American River and the Folson and Nimbus sites on the Sacramento River, upstream of Sacramento. The Discovery site is in the City of Sacramento, where the two rivers merge. The RM-44 site is downstream of the city and its Sewage treatment discharge, near the Green's Landing site detailed on the previous slide. All values except the I-5 site (n=1 event) are means of 5-7 biweekly events.



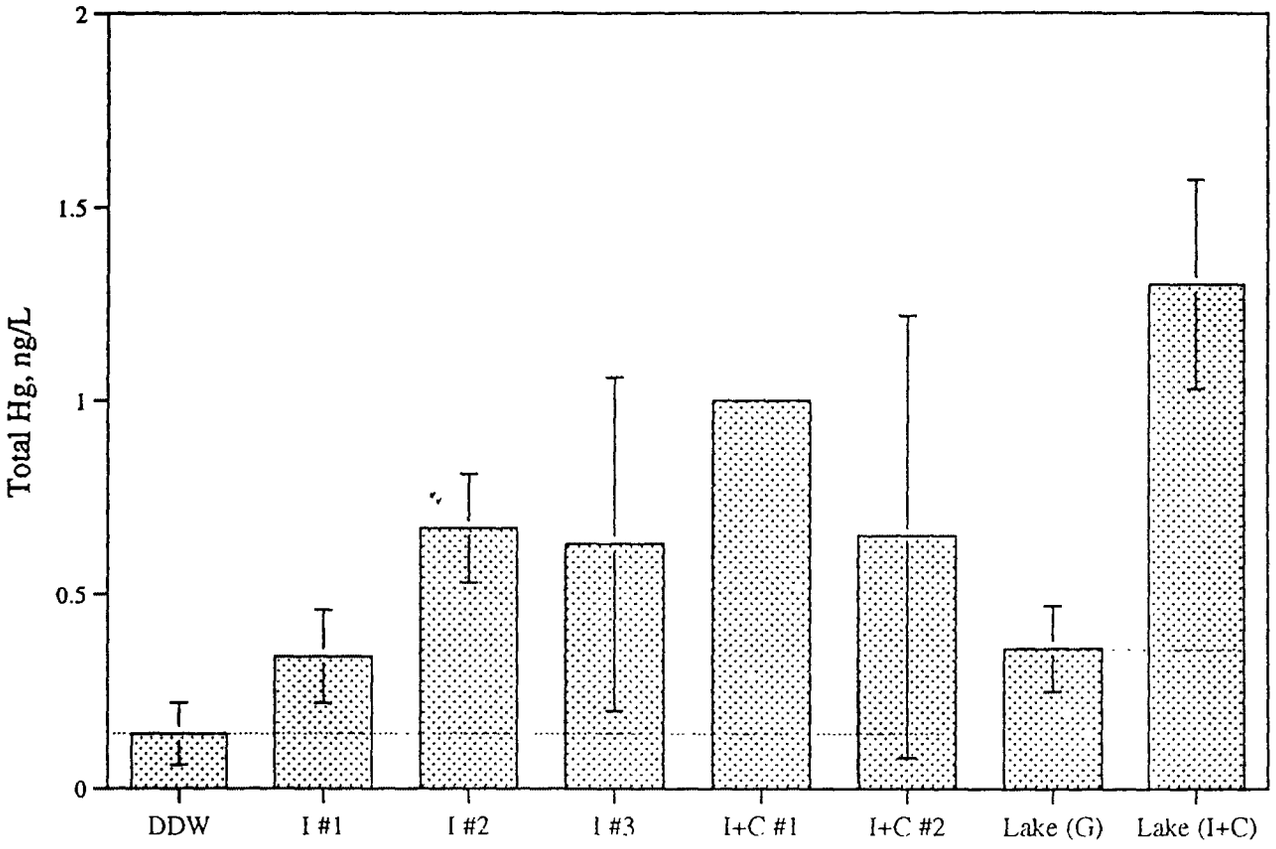
Slide 12. Variability of observed total Hg in the Sacramento River downstream of Sacramento, CA. The upper line is the Hg concentration, while the lower line is the total suspended solids, which correlate with total river flow (rainfall).

Summary QA Statistics

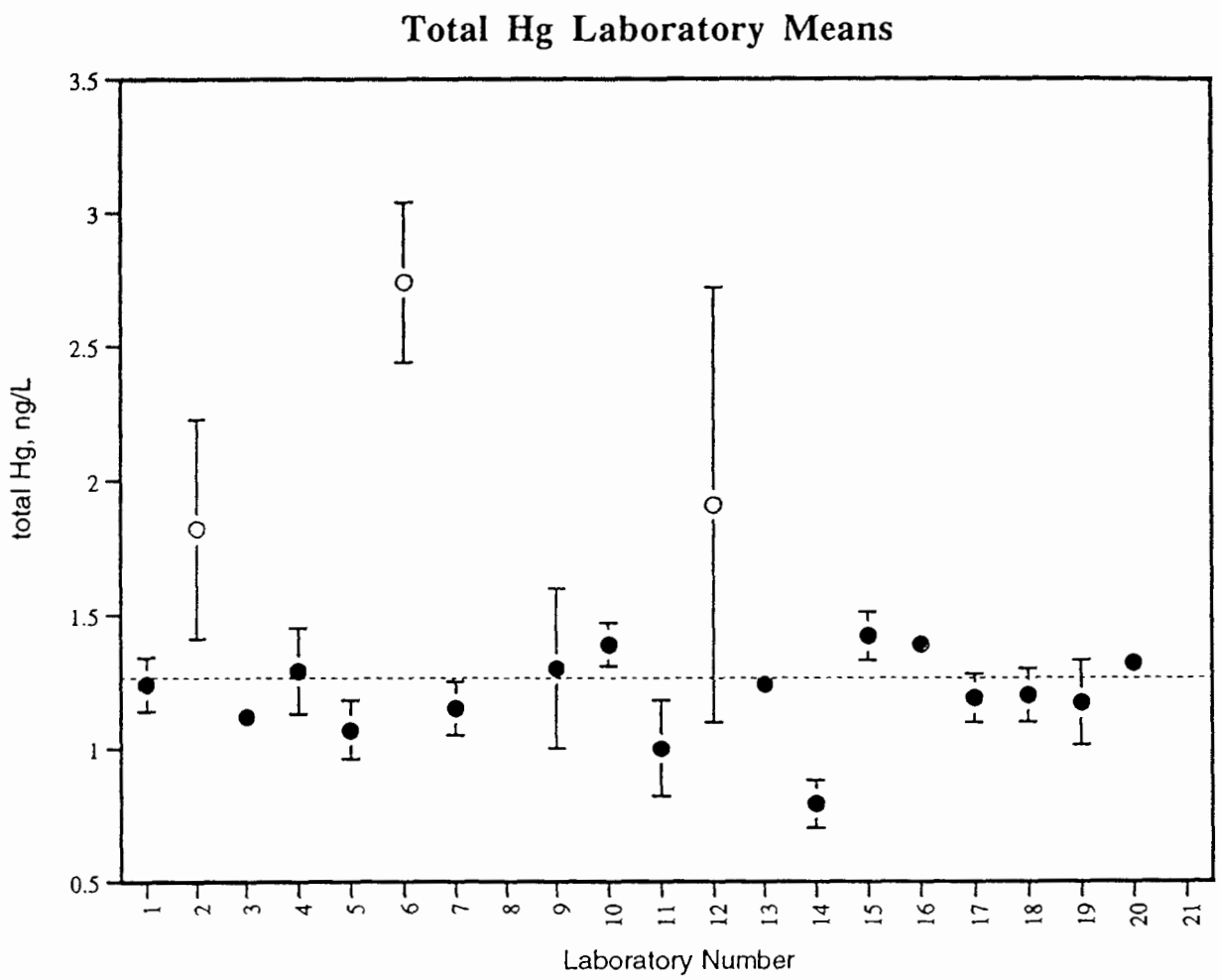
Parameter	units	mean	SD	N	Conc. Range
Reagent Blanks	ng/L	0.14	0.04	36	---
Filtering Blanks	ng/L	0.00	0.09	15	---
Spike Recoveries	%	99.6	6.3	60	4-11 ng/L
Lab Duplicates	Δ%	4.9	6.6	49	0.2-20 ng/L
Field Duplicates	Δ%	13.3	14.6	33	0.2-20 ng/L
Intercomparison	% [a]	-4.1	13.3	13 labs	1.2 ± 0.1 ng/L

[a] Difference between lab means in ICE intercomparison samples

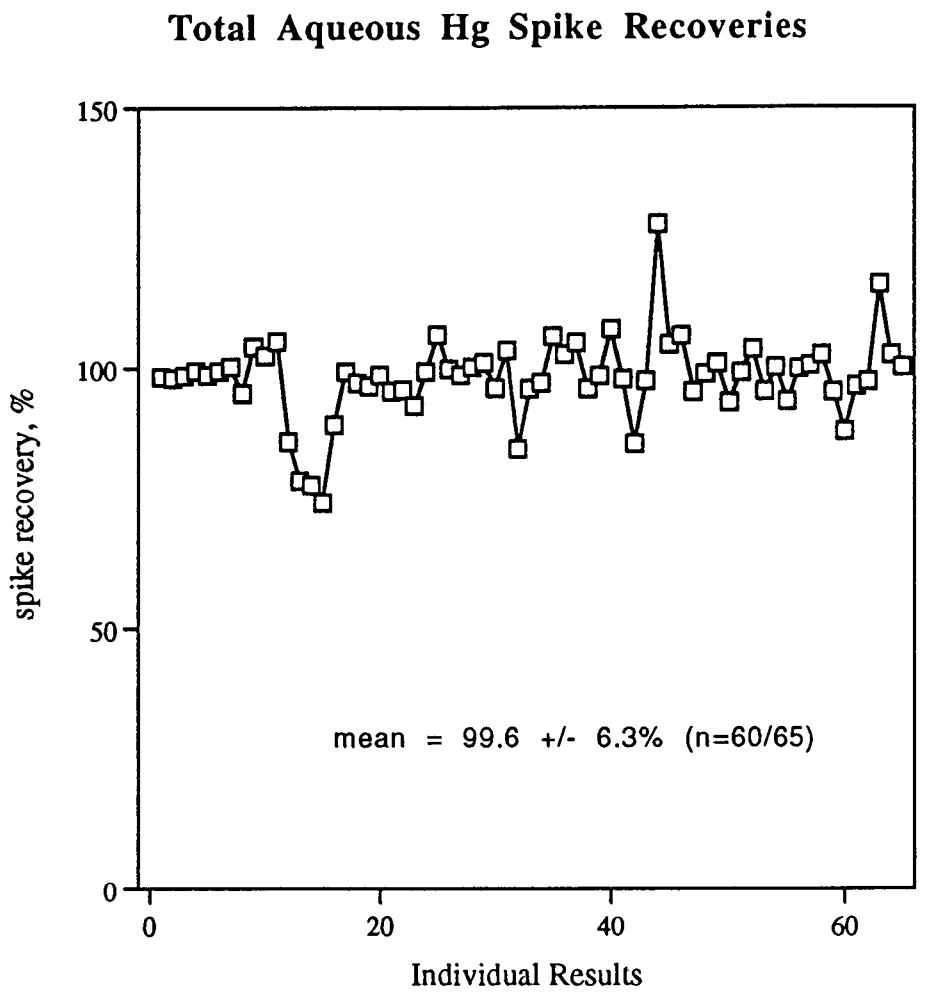
Slide 11. Summary of Laboratory QA statistics for December 1993 to April 1994.



Slide 10. Sampling induced contamination of water samples. Lab double deionized water (DDW) was passed through the sample tubing of the Isco sampler (I#), and then a 10 L polyethylene integrating carboy (C), as an ordinary sample. The results are means of three replicates conducted at different times throughout the project. In the last pair, the Isco sampler was compared with sub-surface ultra-clean grab sampling at an upstream lake site. Overall, the tubing of the Isco sampler and the integrating carboy are seen to each contribute approximately 0.5 ng/L contamination to the sample. Over the first five months of the study, this level has dropped by about 50%.



Slide 9. Intercomparison with other laboratories on a natural low-level Hg lake water sample. All laboratories represented are world-class research laboratories. Frontier Geosciences Inc. is laboratory #1 (the Control Lab), and the mean represents 30 individual bottles of the same water, analyzed in triplicate over a 4 month period. All other laboratories analyzed 3 bottles of the same water.



Slide 8. Control chart for Hg spike recovery at the 8 ng/L level (December 1993 to April 1994). The downward excursion in January occurred during a lab-wide atmospheric Hg^0 contamination from metallic Hg containing sediments.

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MR. TELLIARD: We have one quick announcement before you get to go get your coffee.

MS. ROMNEY: Hi, I am Jackie Romney from the Office of Wastewater Enforcement and Compliance from EPA headquarters office, and I wanted to just give you a brief status of the document that is on the table outside. It is the draft national guidance for the permitting, monitoring, and enforcement of water quality-based effluent limits set below the analytical detection or quantitation level.

Many of you have received copies. The document was released by the Office of Wastewater Enforcement and Compliance on March 22nd. We sent that document out for comment to the regions, State NPDES directors, our work group, and headquarters. We ended the comment period last Friday, April 29, 1994.

Our plans are to finalize the document by the end of this summer. If anybody has any questions or if you would like to talk to me about the document, I will be here until the end of the conference. My phone number is area code (202) 260-9528, or you can reach Cathy Smith who handles the enforcement issues in that document, and her number is area code (202) 260-0252.

Thank you.

MR. TELLIARD: Sure, Jackie.

Okay, we are going to take a 15-minute break, and let's try to make it 15 minutes.

Thank you.

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MR. TELLIARD: This afternoon, we are going to be talking a little bit about cyanide and BODs.

Our first speaker this afternoon is Margaret Goldberg from Research Triangle Institute. Margaret is going to speak on the effects of multiple interferences on the determination of total cyanide. For all of those who have them in your permits and are being regulated by them, this will probably make your day.

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THE EFFECT OF MULTIPLE INTERFERENCES ON THE DETERMINATION OF TOTAL CYANIDE IN SIMULATED ELECTROPLATING WASTE BY EPA METHOD 335.4

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INTRODUCTION

The U.S. Environmental Protection Agency approved test procedures for cyanide determination are listed in the Code of Federal Regulations 40, Ch.1, Pt.136, Appendix B, Table 1B. The test procedures are used for the reporting of results of analyses as required by the National Pollutant Discharge Elimination System (NPDES) permits. The methods listed for total cyanide in water all share similar chemistries and interferences. These interferences have resulted in many modifications of the procedures that are included in Standard Methods[1], ASTM[2], and the EPA methods.[3,4] The application of these modifications requires prior knowledge of the interference. Procedures to remove the interferences generally work well when a single interference is present. However, when multiple interferences are present, the total cyanide methods produce questionable analytical results.

The objective of this study was to evaluate the performance of the method when applied to simulated waste effluent that contained known concentrations of cyanide and multiple interferences. Electroplating waste effluent was studied because there have been many problems reported by analysts for that waste, and because it was known to contain a large number of method interferences. In brief, the problems reported included low recovery of cyanide spikes, suspected false positive results, and poor precision for replicate analyses.

OVERVIEW OF THE CYANIDE METHOD

Method 335.4 consists of two discrete analytical steps: (1) MIDI distillation of an acidified solution into an alkaline collector, and (2) colorimetric analysis.[4] In the first step, cyanide is converted to HCN at pH 1 by addition of sulfuric acid to the sample. The gas is purged from the sample solution into an alkaline absorber solution where it is stabilized as the cyanide anion. The purpose of this distillation step is to remove cyanide from method interferences that are present in the sample, and stabilize it in a clean matrix. The second step is a colorimetric analysis procedure using pyridine-barbituric acid reagent to form a colored adduct.

The MIDI distillation and analysis procedures were used to the extent possible. MIDI distillation was performed with an automated, 10 sample, temperature-controlled, heating block (Cyan-Ten, Andrews Glass Co.). Analysis was performed with an automated flow injection analysis colorimetric analyzer (QuikChem AE, Lachat Instrument, Inc.).

METHOD INTERFERENCES

Electroplating industry waste contains many interferences that affect the cyanide method. Table 1 contains a list of nine types of interferences that have been reported to be problematic in electroplating waste. Note that while some of the interferences listed are discrete chemicals (e.g. sulfide, thiocyanate, carbonate), others include entire categories of compounds (e.g. oxidizers, surfactants, metals). In the design phase of this study, we

performed preliminary experiments to identify five of the most significant interferences. We did not include metals in this testing because they were being studied separately. The five interferences selected were sulfide, hypochlorite, bisulfite, formaldehyde, and thiocyanate.

For some interferences, Method 335.4 recommends interference recognition tests ("spot tests") and/or interference removal methods. This information is summarized in Table 2, with"YES" listed if the method recommends a spot test for that interference, and "NO" if no test is recommended. The active reagent in the interference removal method is also listed if one is recommended by the method. Note that thiocyanate and bisulfite do not have spot tests. However, the Standard Methods 4500-CN procedure recommends addition of lead carbonate to the absorber tube of samples with sulfur-containing compounds, and thus lead carbonate is added to samples with thiocyanate and bisulfite.

RANGE FINDING STUDIES

In order to design the multiple interference study, it was first necessary to perform a series of range finding experiments to identify the most significant interferences and estimate the range of concentrations over which the interference had a measurable effect on cyanide recovery. The range finding studies were very limited tests of each interference individually. Typically, five solutions were prepared in duplicate with either 0 or 100 μg/L CN and a series of concentrations of a single interference; in some cases, more than five solutions were prepared and tested. In order to determine if the recommended interference removal method improved the recovery of cyanide, we treated some samples with the interference removal reagent and did not treat others. Samples were then distilled and analyzed according to Method 335.4. Results are shown in Figures 1 to 5 for sulfide, hypochlorite, formaldehyde, bisulfite, and thiocyanate, respectively. Samples designated as "Treated" were treated with the interference removal method; those designated "Untreated" were not. Data presented in the figures represent measured cyanide based on instrument calibration with undistilled KCN standards, and have not been blank-subtracted or otherwise corrected.

In the case of sulfide (Figure 1), samples contained either 0 or 100 ppb (μg/mL) CN, and 0, 7.8×10^{-5}, 1.6×10^{-4}, 3.1×10^{-4}, or 6.3×10^{-4} M sulfide. Treated samples contained lead carbonate in the absorber tube; untreated samples did not. Results shown in Figure 1 illustrate that:

(1) reagent blanks (0 ppb CN, Untreated) contained very little cyanide (approximately 2 ppb CN); (2) "Treated" blanks (0 ppb CN, Treated) had high measured cyanide (approximately 15 ppb CN); (3) In the absence of interference or treatment (100 ppb CN, Untreated, 0 Sulfide), cyanide was recovered at approximately 80% of nominal, but when sulfide was present (100 ppb CN, Untreated, 1.6E-04 Sulfide) the recovery decreased to approximately 50% of nominal; (4) Treated samples generally had higher recovery of cyanide than Untreated samples (even after blank subtraction); and (5) higher concentrations of sulfide resulted in lower recovery of cyanide.

As shown in Figure 2, hypochlorite had a much stronger effect on cyanide recovery than did sulfide. At the lowest concentration of hypochlorite tested, 3.4×10^{-6} M, cyanide recovery from a 100 ppb CN solution (100 ppb CN, Untreated, 3.4×10^{-6} M Hypochlorite) was approximately 80%. However, at all higher concentrations of hypochlorite tested, the recovery of cyanide was approximately 0% whether the sample was treated with ascorbic acid or not.

Figure 3 shows that for 100 ppb CN, Untreated samples, formaldehyde had little effect on cyanide recovery at the lowest formaldehyde concentration tested (3.7×10^{-7} M), but did substantially reduce recovery of cyanide from 77% to 60% when formaldehyde concentration increased from 3.7×10^{-7} to 3.7×10^{-6} M. Treatment of samples with ethylenediamine was effective in removing the effect of the interference at a formaldehyde concentration of 3.7×10^{-5} M (78% recovery), but not at 3.7×10^{-4} M (10% recovery).

In the case of bisulfite, a threshold response is observed in Figure 4 for the effectiveness of the lead carbonate in removing the effects of bisulfite on cyanide recovery. At 3.2×10^{-5} and 3.2×10^{-4} M bisulfite, cyanide recovery from 100 ppb CN solutions treated with lead carbonate was approximately 45%. At higher concentrations of bisulfite (1.6×10^{-3} and 3.2×10^{-3} M), cyanide recovery was reduced to approximately 11%.

Results for thiocyanate are shown in Figure 5. When the concentration of thiocyanate was increased from 3.9×10^{-7} to 3.9×10^{-5} M, the recovery of cyanide in 100 ppb CN, Untreated samples decreased from approximately 90% to 70%. The high cyanide concentration measured in the blank solution treated with lead carbonate (21 ppb) makes the interpretation of lead carbonate treatment uncertain, but in general, lead carbonate treatment increased the recovery of cyanide relative to untreated samples at the same thiocyanate concentration.

SAMPLE HOLDING TIME

A limited Sample Holding Time Study was also performed prior to the Multiple Interference Study. The sample holding time is the time between sample collection (or preparation of simulated samples) and analysis. If interferences react with cyanide at room temperature or refrigerated temperatures during this period, the final concentration of cyanide determined by the method will not accurately represent the initial cyanide content. Method 335.4 recommends a 14 day sample holding time for cyanide analysis. However, we believed that significant sample alteration could occur within 48 hours, and so conducted a brief study of the effect of holding time on cyanide recovery.

A set of simulated electroplating waste samples was analyzed on the same day they were prepared (Day 0). Half of the samples were analyzed again after one day refrigerated storage (Day 1), and the other half were analyzed after two days refrigerated storage. Percent recovery of the nominal cyanide was calculated for each sample analysis. Selected

results are shown in Table 3. The difference values presented were calculated as the difference between the percent recovery determined on Day 0 and that determined on either Day 1 or Day 2, and are indicators of the stability of the sample over that period. As can be seen in Table 3, the results are highly dependent on the sample composition, and clearly demonstrate that holding time has a large effect on cyanide recovery for some samples.

MULTIPLE INTERFERENCE STUDY

The Multiple Interference Study was a statistically designed study that enabled the estimation of the effects of 6 factors simultaneously on measured cyanide concentrations. Five of the factors were the interference levels, and the sixth factor was the actual cyanide concentration. In addition to statistical aspects, the design also incorporated chemical considerations and results from the Sample Holding Time Study and the Interference Range Finding Studies.

Chemical Aspects of Study Design

The concentrations of cyanide and the five interferences used in the Multiple Interference Study were selected based on three factors that are discussed below: (1) the current regulatory levels for cyanide; (2) the concentrations of interferences that were found to interfere in cyanide analysis in the range finding experiments; and (3) the molar ratios of interferences to cyanide.

Cyanide concentrations were chosen to cover a range of current regulatory discharge levels. For example, discharge to municipal sewer systems requires analysis of cyanide at low concentrations, typically 5-50 ppb CN, while permit levels for electroplating industry discharge are typically around 700 ppb CN. As indicated in Table 4, the study design included cyanide concentrations from 0 to 1000 ppb (0 to 3.8×10^{-5} M). As explained below, the statistical design enabled the best predictions over the range 49 to 500 ppb (1.9×10^{-6} to 1.9×10^{-5} M).

The range of interference concentrations was determined from the results of the preliminary range finding experiments. In general, cyanide recovery was affected by the interference when the interference was at a concentration between 3×10^{-7} M and 3×10^{-4} M. As indicated in Table 4, the range of interference concentrations used in this study was 0 to 1.14×10^{-4} M.

The molar ratio of interference to cyanide was important because the extent of the interference reaction depends on the molar ratio of interference to cyanide as well as on the magnitude of their concentrations. Thus, the study design includes samples with a stoichiometric excess of interferences, a stoichiometric excess of cyanide, and 1:1 stoichiometry of cyanide to interference. The molar ratios of interference:cyanide included in the study ranged from 0.068:1 to 185:1.

Experimental Methods

The results of the Sample Holding Time Study demonstrated the importance of regulating the time between sample preparation and analysis. Thus, each group of samples was prepared and analyzed within a period of approximately 24 hours. On the first day, ten samples (half of a study "block") were prepared, allowed to sit at room temperature for one hour, and then stored refrigerated for approximately 16 hours. On the second day, the samples were brought to room temperature, tested for interferences using the recommended spot tests, and those in which interferences were detected were treated using the recommended interference removal method. Then all ten samples were distilled and analyzed. The same process was then repeated for the second half of the study "block."

Statistical Study Design

The statistical study design consisted of 120 samples (trials) arranged in six blocks of 20. Each block had 18 samples containing cyanide and two blank samples. Of the 72 non-blank samples in blocks 1 through 4, 64 samples contained cyanide (factor Z_1; Table 4) at either 49 or 500 ppb, and each of the interferences (factors Z_2, Z_3, Z_4, Z_5, and Z_6; Table 4) at either 0 or 1.14×10^{-4} M. These 64 trials represent a complete 2^6 factorial arrangement (i.e., all possible combinations of high and low levels of each of six factors). In addition to the 64 factorial points and the blanks, each of the first four blocks also contained two "center points," with cyanide concentration of 160 ppb and interference concentration of 1.07×10^{-6} M for all five interferences. When the mathematical transformation used in this study (i.e., a logarithmic transformation) is applied to these concentrations, the "center points" fall near the center of the factorial design (i.e., about half way between the low and high levels of each factor). Blocks 5 and 6 each consisted of three center points, 6 pairs of points in which each factor was varied about the center point one factor at a time, and three points chosen to examine stoichiometric relationships.

Two deviations from the experimental design were performed. First, the actual concentration of interferences in some of the block 5 and 6 samples was 2.6×10^{-6} M rather than 1.07×10^{-6} M. Second, an additional block of samples was prepared and analyzed. The extra block was a re-run of block 1 with the exception that samples were analyzed immediately after preparation, rather than 24 to 48 hours later. The effect of this difference on the final model was negligible, so the additional samples were included in the data analysis.

Statistical Analysis

The goal of the statistical analysis was to characterize how measured cyanide concentrations were affected by actual cyanide concentrations and by the concentrations of one or more of the interferences. After considering a number of candidate model forms, we selected the following class of models for detailed analysis:

$$\ln[Y+1] = \ln[1+A+BZ_1] + \epsilon$$

where Y denotes the measured cyanide concentration, Z_1 is the KCN concentration, ϵ is a random error term, and A and B are functions of the interferences having the form:

$$A = B_0 + f_1(Z_2,Z_3,Z_4,Z_5,Z_6)$$

$$B = B_1 + f_2(Z_2,Z_3,Z_4,Z_5,Z_6)$$

where B_0 and B_1 are constants and f_1 and f_2 are polynomial functions of the interference concentrations that are zero when none of the interferences are present. The model allows each interference (a) to have an additive effect (i.e., to change the intercept) with the incremental amount being proportional to its concentration; (b) to have a multiplicative effect (i.e., to change the slope) with the increment being proportional to its concentration; and (c) to have both effects (a) and (b). In addition, the interferences are allowed to interact with one another (e.g., by including cross-product terms in the f_1 and f_2 functions) and thereby jointly affect either A or B or both.

Thus the objectives of the statistical analysis were first to determine "good" forms for the A and B functions and then to estimate the parameters of those functions. Nonlinear least squares estimations were performed using the SAS NLIN procedure.

Results

Statistical analysis of the data resulted in the following representations for A and B:

$$A = B_0 + B_2Z_2 + B_3Z_3 + B_4Z_4 + B_5Z_5 + B_6Z_6 + B_{22}Z_2^2 + B_{33}Z_3^2 + B_{55}Z_5^2 + B_{24}Z_2Z_4 + B_{36}Z_3Z_6 + B_{45}Z_4Z_5$$

and

$$B = B_1 + B_{12}Z_2 + B_{13}Z_3 + B_{14}Z_4 + B_{15}Z_5 + B_{16}Z_6 + B_{123}Z_2Z_3 + B_{133}Z_3^2$$

Thus the final model is given by:

$$Predicted\ [CN] =$$

$$B_0 + B_1\ [CN] + B_2\ [S] + B_3\ [OCl] + B_4\ [HCHO] + B_5\ [HSO_3] + B_6\ [SCN]$$

$$+ B_{12}\ [CN]\ [S] + B_{13}\ [CN]\ [OCl] + B_{14}\ [CN]\ [HCHO] + B_{15}\ [CN]\ [HSO_3] + B_{16}\ [CN]\ [S$$

$$+ B_{22}\ [S]^2 + B_{33}\ [OCl]^2 + B_{55}\ [HSO_3]^2$$

$$+ B_{24}\ [S]\ [HCHO] + B_{36}\ [OCl]\ [SCN] + B_{45}\ [HCHO]\ [HSO_3]$$

$$+ B_{123}\ [CN]\ [S]\ [OCl] + B_{133}\ [CN]\ [OCl]^2$$

The estimated parameters are given in Table 5, along with an estimate of their standard errors and approximate 95 percent confidence intervals. Asterisks are used to identify those coefficients which are statistically significant. The model results are presented in 3-dimensional graphs in Figures 6 to 11, with each graph presenting the predicted percent recovery of cyanide as a function of the actual KCN concentration and the concentration of one interference. The other interferences are held at a concentration of 0 for these simulations, except where noted.

As can be seen in Figure 6, increasing the concentration of sulfide results in decreasing the percent recovery of cyanide. The effect is most dramatic at low concentrations of KCN, and less so as the concentration of KCN increases. This general pattern is repeated to a lesser extent for bisulfite (Figure 7), formaldehyde (Figure 8), and thiocyanate (Figure 9). In the case of hypochlorite (Figure 10), the effect of increasing the hypochlorite concentration is a highly significant decrease in predicted percent recovery of cyanide, such that at the highest concentrations of hypochlorite and cyanide included, the predicted percent recovery approaches 0.

One effect that was not originally anticipated was the combined effect of hypochlorite and thiocyanate. As illustrated in Figure 11, for a fixed concentration of hypochlorite (0.1 mM) and variable concentration of thiocyanate, the predicted percent recovery of cyanide ranges from approximately 0 to 1000%. The explanation for this pattern is that, at low concentrations of thiocyanate, hypochlorite rapidly oxidizes cyanide to carbon dioxide and thus very little cyanide is present at the time of the analysis. At high concentrations of thiocyanate, hypochlorite oxidizes thiocyanate to sulfate plus cyanide, and thus increases the concentration of cyanide prior to analysis. Thus, the actual concentration of cyanide present at the time of analysis depends on the ratios of hypochlorite to thiocyanate and hypochlorite to KCN as well as the ratio of thiocyanate to KCN.

During the Multiple Interference Study, we tested each sample for the presence of each interference using the recommended interference recognition tests. The results are summarized in Table 6 and show that the interference recognition tests failed to correctly identify the presence of sulfide, hypochlorite, or formaldehyde in over half of the samples containing those interferences. In general, the presence of more than one interference caused each of the interferences to be "masked" during interference recognition testing.

CONCLUSIONS

Several conclusions were drawn from these studies:

1. As demonstrated in the Interference Range Finder Studies, individual interferences caused a substantial reduction in recovery of cyanide in some cases, even after application of the interference removal method.

2. Sample holding time was an important parameter that lead to an increase or a decrease in cyanide recovery as a function of time. The effect was a function not only of the interferences present in the sample, but also of the concentration of each interference and the length of time the sample was held. The fact that significant sample alteration was observed within 48 hours suggests that the 14 day holding time recommended in Table II of Method 335.4 and 40 CFR Part 136.3 is excessive.

3. In the Multiple Interference Study, it was observed that the interference recognition tests worked properly in less than 50% of the samples when multiple interferences were present.

4. The effect of the interferences on cyanide and on each other was complex. Not only was the effect of each interference on cyanide recovery statistically significant, but there were also statistically significant 2-way interactions between sulfide and formaldehyde, hypochlorite and thiocyanate, and formaldehyde and bisulfite, and a statistically significant 3-way interaction among cyanide, sulfide, and hypochlorite.

5. Hypochlorite was not considered a method interference by itself. It caused a rapid removal of cyanide prior to analysis, but if the excess hypochlorite was adequately removed in the pretreatment stage, then the method did accurately determine the concentration of cyanide present at the start of the analysis. However, in the presence of other oxidizable interferences, such as thiocyanate, sulfide, or formaldehyde, the effect of hypochlorite was more complex and time dependent, and the method did not provide reproducible or reliable results.

6. The word "Total" in the Total Cyanide Methods may be interpreted absolutely and lead to improper treatment of cyanide wastewater. Clearly the word "Total" is not representative of the results produced by these cyanide methods when multiple interferences are present and/or when interferences are not identified and removed.

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2. Annual Book of ASTM Standards, Vol. 11.02, American Society for Testing and Materials, Philadelphia, PA.

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QUESTION AND ANSWER SESSION

MR. LOEWE: Jeff Loewe with Daily Analytical Labs. Is the holding time before or after the distillation?

MS. GOLDBERG: It is before the distillation.

MR. LOEWE: Were the samples held after distillation?

MS. GOLDBERG: No, we did not. We always analyzed the samples the same days that they were distilled.

MR. LOEWE: Okay, thank you.

MR. JOHNSON: Mike Johnson with Dupont. I am one of the poor people in the regulated community that has to use this method, and I applaud you, because you have found exactly what we have found.

The question is right now, that method is the only method EPA has approved for cyanide, and what we are seeing is negative values which I do not mind as long as EPA lets us use it in our average, but that is another topic. We are seeing positive interferences. It is just all over the map.

Is there any recommendation on another method? We have been experimenting with the weak acid dissociable test and getting a lot better results from that. It seems to be ignoring a lot of the interferences, but from a regional standpoint, they do not recognize that as a method. So, what is somebody to do?

MS. GOLDBERG: I think we will have two responses to that. I will tell you my answer, and then I will ask Bill Potter to speak for EPA.

The first answer is that we are working on method improvements to this, and we have actually seen some improvements by using weaker oxidants than the hypochlorite.

The goal there is to oxidatively decompose the interferent but not oxidize the cyanide, and we have had very good success adding sodium vanadate as an interferent removal oxidant. It does not work with the thiocyanate. So, it will remove the other interferences for you but not the thiocyanate. For that, we have no recommendation.

We are currently exploring other methods, and I cannot give you any results from those yet. One of the studies we have not even started yet, and others are just in the process, so I cannot give you that recommendation, but maybe Bill can tell you some more.

MR. TELLIARD: Bill?

MR. POTTER: In response to coming up with different methods, right now, we are not funded for looking or exploring other methods. This particular project was designed only to find out if the classical method could be improved or if the interferences could be identified and handled in some way.

What this study has shown is that the method is dysfuntionate as written.

MR. TELLIARD: If you have a suggestion as to a method or an application, if you would send it to me, I would do what I can to get it addressed. No promises, but we are certainly interested, in the industrial industries that we regulate and are writing regulations for; we have to have a method. I have been waiting for this paper all day.

MR. TELLIARD: Thank you. The gentleman in the back?

MR. STRAKA: My name is Mike Straka, and I am with Perstorp Analytical Environmental. A couple of comments. First of all, I am very glad to hear that response to the request for better methods. We, as an instrumentation manufacturing company, are devoting a lot of energy to this specific problem, that is, the cyanide problem.

We have, in cooperation with the University of Nevada-Reno Mackey School of Mines, begun to commercialize a new weak acid dissociable chemistry that precludes the need to do a distillation and, therein, cures a lot of ills and evils.

The distillation plus colorimetric finish can take up to an hour or more, more like an hour and a half per sample. With this new method, we can get results identical to a distillation followed by ion chromatography finish in two minutes per analysis, and I promise you the interferences are what you would expect.

So, my question actually to Bill is I have the method that you are looking for. Now, tell me how I can get it through the EPA or get it evaluated rapidly.

MR. TELLIARD: We would be glad to take a look at it.

MR. STRAKA: Anything that I can do to help, I would appreciate it.

MR. TELLIARD: I understand.

MR. STRAKA: One comment, actually, to Margaret. Is it really fair to classify bisulfite and hypochlorite and those other oxidizers as interferences? As you mentioned, they are clearly oxidizing the cyanide, and they would only be expected to be in the sample because someone is trying to actually destroy the cyanide before it becomes an effluent.

MS. GOLDBERG: Well, in the case of the hypochlorite, that is true. The hypochlorite is added to remove the cyanide to enable discharge, and that was, I think, the comment that I made at the end, that it is not really considered an interference in itself, because it really is removing the cyanide.

The difficulty with the hypochlorite is that it is also oxidizing the other interferences present and that there are very complicated reaction pathways proceeding. It makes it very difficult to regulate on a method where you can get between zero and 1000 percent recovery.

So, I think, in that sense, we do have to consider the interactions of the hypochlorite with the other interferences as method interferences.

The bisulfite itself is not added as an oxidant deliberately to remove the cyanide, typically. Usually, that is present as a brightener or other component by the electroplaters. So, that is in the sample and is not added as an oxidant.

MR. STRAKA: In some industries, it actually is, but my final comment, and I will let you go, is it has been our observation that by adding lead sulfide to the accepter or the scrubber solution that we can have some interesting chemical kinetics going on there, too, which catalyze the cyanide and actually produce thiocyanate which may be a mechanism for giving rise to your lower recovery in the total procedure. That is to say that the sulfide plus cyanide yields thiocyanate.

I just make that general observation, because I know a lot of people traditionally do that for the total distillation, whereas if you do an amenable or WAD distillation, they do not use that practice, and sometimes, more often than not, you can end up getting WAD cyanide results that are higher than your totals, and that may be a very real mechanism for that interference.

Thank you.

MS. GOLDBERG: You are right. Thank you.

MR. TELLIARD: Thank you.

MR. SAWYER: My name is Bernard Sawyer. I am with the Metropolitan Water Reclamation District of Chicago. We have done a lot of work

on cyanide analysis using a UV lamp with the thin film distillation, and it breaks down the thiocyanate. That method is approved in the ASTM manual, and it was sent in at one point or another to EPA, but it never made it, for whatever reason, as being an approved EPA method, but we have used it for many years, especially on industrial waste samples.

It seems to eliminate a lot of these interferences, and it totally eliminates your thiocyanate problem, because you actually run the analysis twice. It is done on a Technicon train, and you basically have the UV lamp turned on, and then you turn the lamp off, and the difference in the two gives you your thiocyanate value which you then can subtract out.

A lot of work has been done with that at our labs, I know, to show the percent recoveries of all the different thiocyanate complexes, et cetera, and it has been published in the Water Pollution Control Federation Journal from many years ago.

So, there is some information out there.

MR. TELLIARD: Yes. The other thing is that, of course, there is a rule in ASTM that no method can go final while the author is alive.

MR. POTTER: Let me say something about that. That was, I believe, Nebi Kelada's method, and the purpose of this particular paper was just to look at the method that was already approved. So, we are now, since we have completed this experimentation, starting to look at Kelada's method, along with many other techniques, some of them UV techniques. There are membrane separation techniques.

With the remaining amount of money that we have in the contract, we may be able to review some of those on a very cursory sort of a quick look or snapshot.

MR. TELLIARD: Thanks, Bill.

MR. XIE: Jack Xie from Water Chemistry in Roanoke, Virginia. My question is I have percent recovery from zero percent here to 1000 percent. How do you record for your QA/QC data? Because some EPA methods require that the percent recovery should fall into a certain range, like 60 percent to 120 percent, but when you have a situation when your percent recovery is from zero to 1000, how do you deal with that?

MS. GOLDBERG: Well, I think, as Bill has said, the fact that we had 1000 percent recovery really is just showing that the method is dysfunctional. There is no way to show that those are good values. In fact, they are fairly non-reproducible. We can get 1000 percent recovery today, and we can get 1200 percent recovery tomorrow.

I did not speak at all about the quality control activities that we used in this lab. We have used a lot of procedures to establish our quality control levels.

Each day that we ran the cyanide distillation blocks with ten samples in them, we also ran a whole quality control block which contained four blanks plus four cyanide samples dosed at 100 ppb. Half of each of those groups were with the lead carbonate and the other half without, so that we tracked on a daily basis the performance of our entire process.

We kept quality control charts for that and for undistilled KCN just on a colorimetric analyzer as well so that we were able to distinguish on a daily basis if there were any problems with the distillation block or if there were any problems with the colorimetric analysis.

We felt that the quality control was well under control for that study and the observed 1000 percent recovery really were oxidative effects of the interferences.

MR. XIE: Okay, thanks.

MR. TELLIARD: Thank you. Thanks, Margaret.

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TABLE 1. POTENTIAL INTERFERENCES IN ELECTROPLATING INDUSTRY WASTE

- Sulfide (S^{2-})
- Thiocyanate (SCN^-)
- Carbonates (HCO_3^-, CO_3^{2-})
- Nitrite (NO_2^-)
- Oxidants (ClO_4^-, O_3, H_2O_2)
- Bisulfite (HSO_3^-)
- Formaldehyde (HCHO)
- Surfactants
- Metals

TABLE 2. ELECTROPLATING INTERFERENCES STUDIED

INTERFERENCE	SPOT TEST	REMOVAL METHOD
Sulfide	Yes	$PbCO_3$
Hypochlorite	Yes	Ascorbic Acid
Formaldehyde	Yes	Ethylenediamine
Thiocyanate	No	None ($PbCO_3$)
Bisulfite	No	None ($PbCO_3$)

TABLE 3. HOLDING TIME STUDY

SAMPLE	SAMPLE COMPOSITION (10^6 M)						PERCENT RECOVERY (%)			DIFFERENCE (%)
	CN	S	OCl	HCHO	HSO_3	SCN	DAY 0	DAY 1	DAY 2	
A	1.9	0	0	0	114	114	79		72	-7
B	1.9	0	114	114	0	0	40	29		-11
C	1.9	0	114	114	114	114	989		1101	+112
D	1.9	114	0	114	0	114	83		56	-27
E	1.9	114	0	114	114	0	78	90		+13
F	1.9	114	114	0	0	114	56	1089		+1033
G	19.2	0	0	114	0	114	71	75		+4
H	19.2	0	114	0	0	114	122	95		-26
I	19.2	0	114	0	114	0	4.0		2.8	-1.2
J	19.2	114	0	0	0	0	59	69		+10
K	19.2	114	0	0	114	114	59		70	+11
L	19.2	114	114	114	0	0	32	40		+8
M	19.2	114	114	114	114	114	78	146		+68
N	6.15	1.07	1.07	1.07	1.07	1.07	91		64	-27
O	6.15	1.07	1.07	1.07	1.07	1.07	90		58	-32

TABLE 4. STUDY DESIGN

CHEMICAL	FACTOR	CONCENTRATION RANGES	
		DESIGN	PREDICTION
KCN	Z_1	0-1000 μg/L (ppb)	49-500 μg/L (ppb)
Sulfide	Z_2	$0 - 1.14 \times 10^{-3}$ M	$0 - 1.14 \times 10^{-4}$ M
Hypochlorite	Z_3	$0 - 1.14 \times 10^{-3}$ M	$0 - 1.14 \times 10^{-4}$ M
Formaldehyde	Z_4	$0 - 1.14 \times 10^{-3}$ M	$0 - 1.14 \times 10^{-4}$ M
Bisulfite	Z_5	$0 - 1.14 \times 10^{-3}$ M	$0 - 1.14 \times 10^{-4}$ M
Thiocyanate	Z_6	$0 - 1.14 \times 10^{-3}$ M	$0 - 1.14 \times 10^{-4}$ M

TABLE 5. ESTIMATED MODEL PARAMETERS

	PARAMETER ESTIMATE	ASYMPTOTIC STD. ERROR	95% CONFIDENCE INTERVAL LOWER	95% CONFIDENCE INTERVAL UPPER
B0	1.21697E+01***	9.28269E-01	1.03311E+01	1.40082E+01
B1	6.72741E-01***	2.82236E-02	6.16841E-01	7.28642E-01
B2	-1.56419E-03***	3.01774E-04	-2.16189E-03	-9.66490E-04
B3	9.26762E-04***	2.62156E-04	4.07529E-04	1.44600E-03
B4	-5.13696E-04***	1.80544E-04	-8.71286E-04	-1.56107E-04
B5	-8.85959E-04***	2.70073E-04	-1.42087E-03	-3.51046E-04
B6	-6.20955E-04*	3.53309E-04	-1.32073E-03	7.88193E-05
B22	9.85605E-09***	3.57131E-09	2.78263E-09	1.69295E-08
B33	-1.82170E-08***	2.44597E-09	-2.30615E-08	-1.33724E-08
B55	5.80259E-09**	2.71985E-09	4.15579E-10	1.11896E-08
B12	-5.79119E-07	1.81319E-06	-4.17036E-06	3.01212E-06
B13	-6.50880E-05***	2.93706E-06	-7.09053E-05	-5.92708E-05
B14	-9.21116E-07	9.47768E-07	-2.79829E-06	9.56058E-07
B15	1.13738E-06	8.57594E-07	-5.61196E-07	2.83595E-06
B16	6.67081E-07	2.67670E-06	-4.63447E-06	5.96863E-06
B24	8.09171E-08**	3.34711E-08	1.46234E-08	1.47211E-07
B36	4.48756E-06***	3.09200E-07	3.87515E-06	5.09997E-06
B45	7.55712E-08***	2.58539E-08	2.43644E-08	1.26778E-07
B123	3.27211E-09***	3.78161E-10	2.52312E-09	4.02111E-09
B133	5.11637E-10***	2.36651E-11	4.64766E-10	5.58509E-10

TABLE 6. INTERFERENCE RECOGNITION TESTS

	INTERFERENCE		
	S^{2-}	OCl^-	HCHO
Number of Interference-Containing Samples Tested	57	57	57
Number Correctly Identified	2	9	24
Percent Correctly Identified	4%	16%	42%

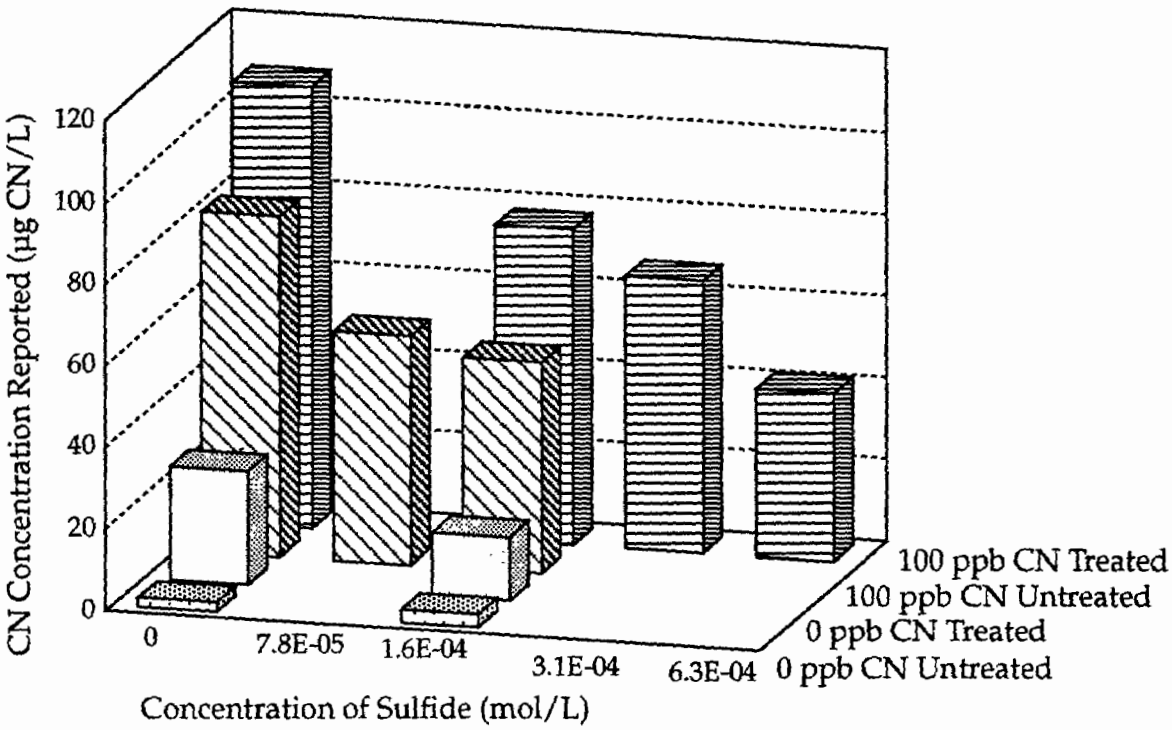

Figure 1. Sulfide: Treated samples contain $PbCO_3$ in the Absorber Tube.

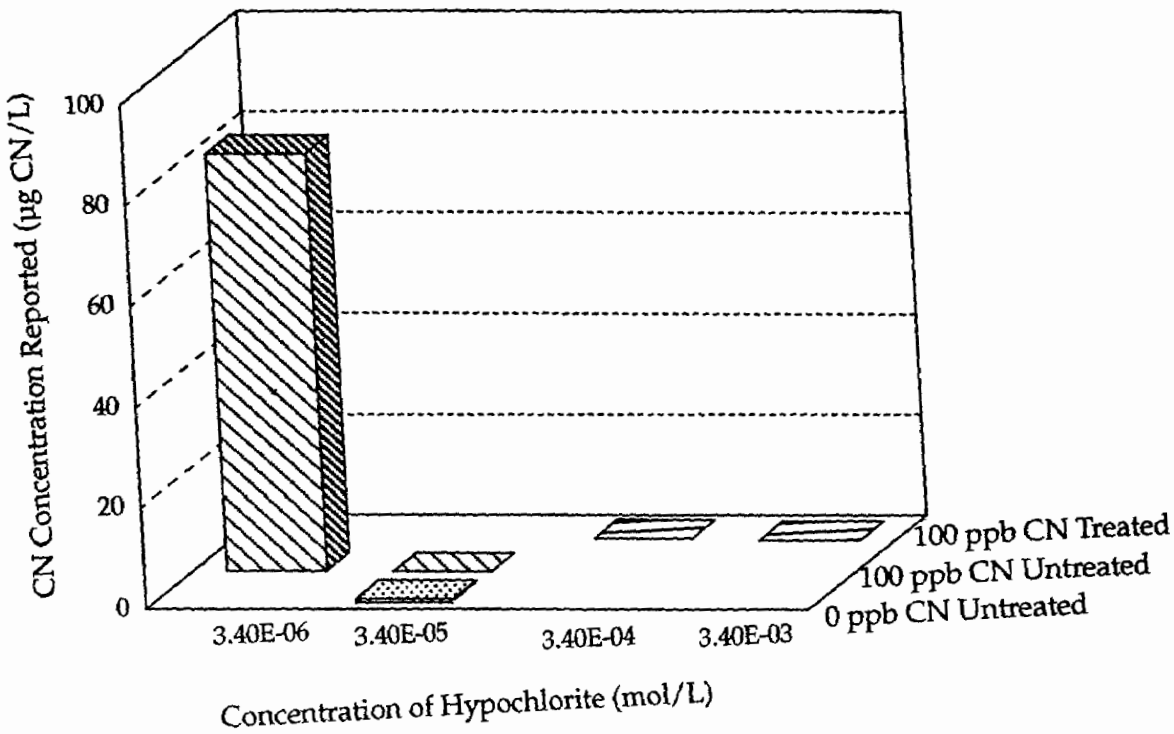

Figure 2. Hypochlorite: Treated samples contain Ascorbic Acid.

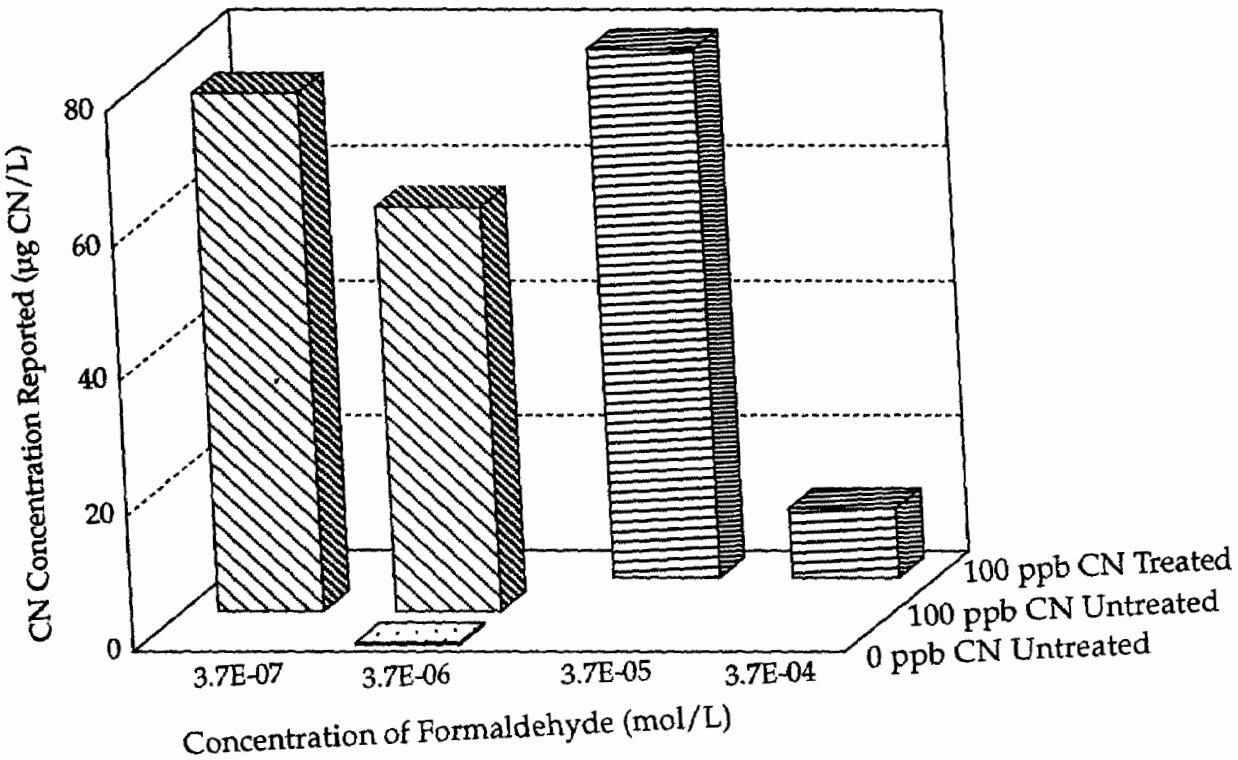

Figure 3. Formaldehyde: Treated samples contain Ethylenediamine.

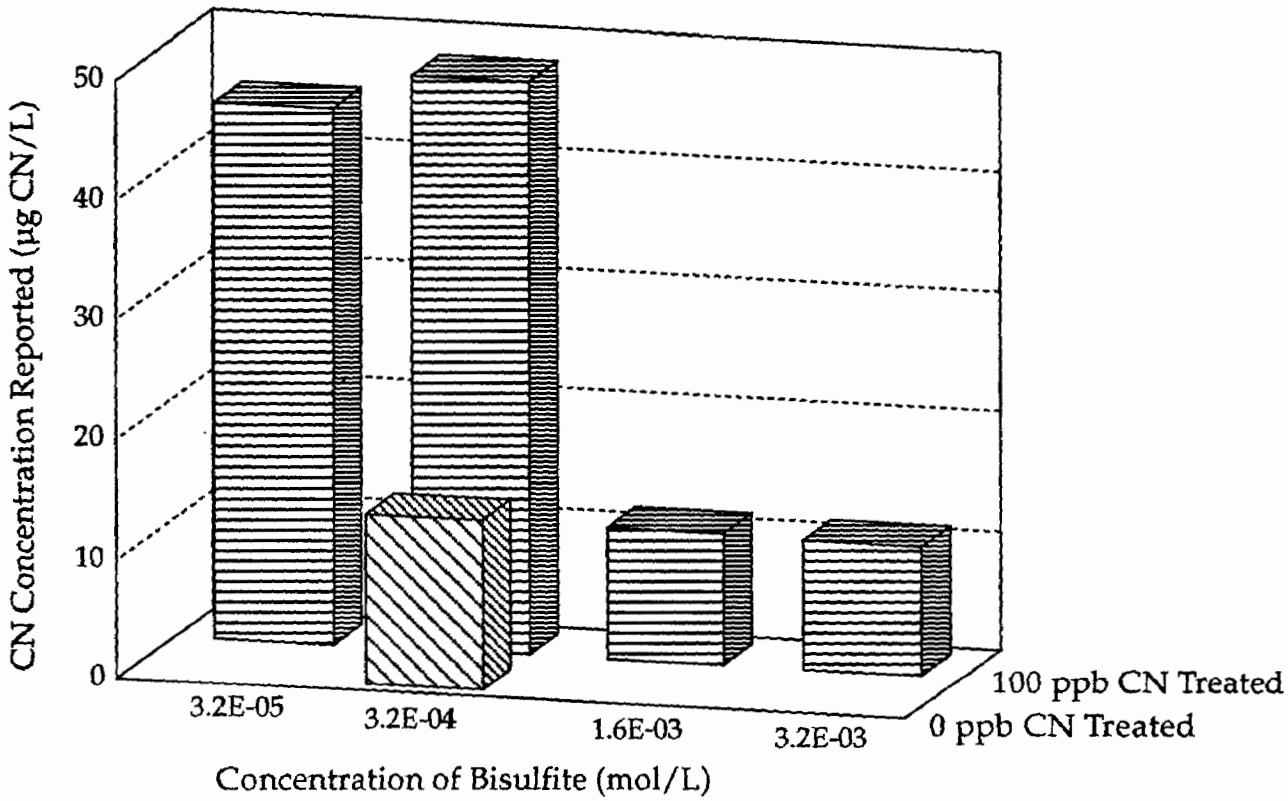

Figure 4. Bisulfite: All samples treated with $PbCO_3$ in each Absorber Tube.

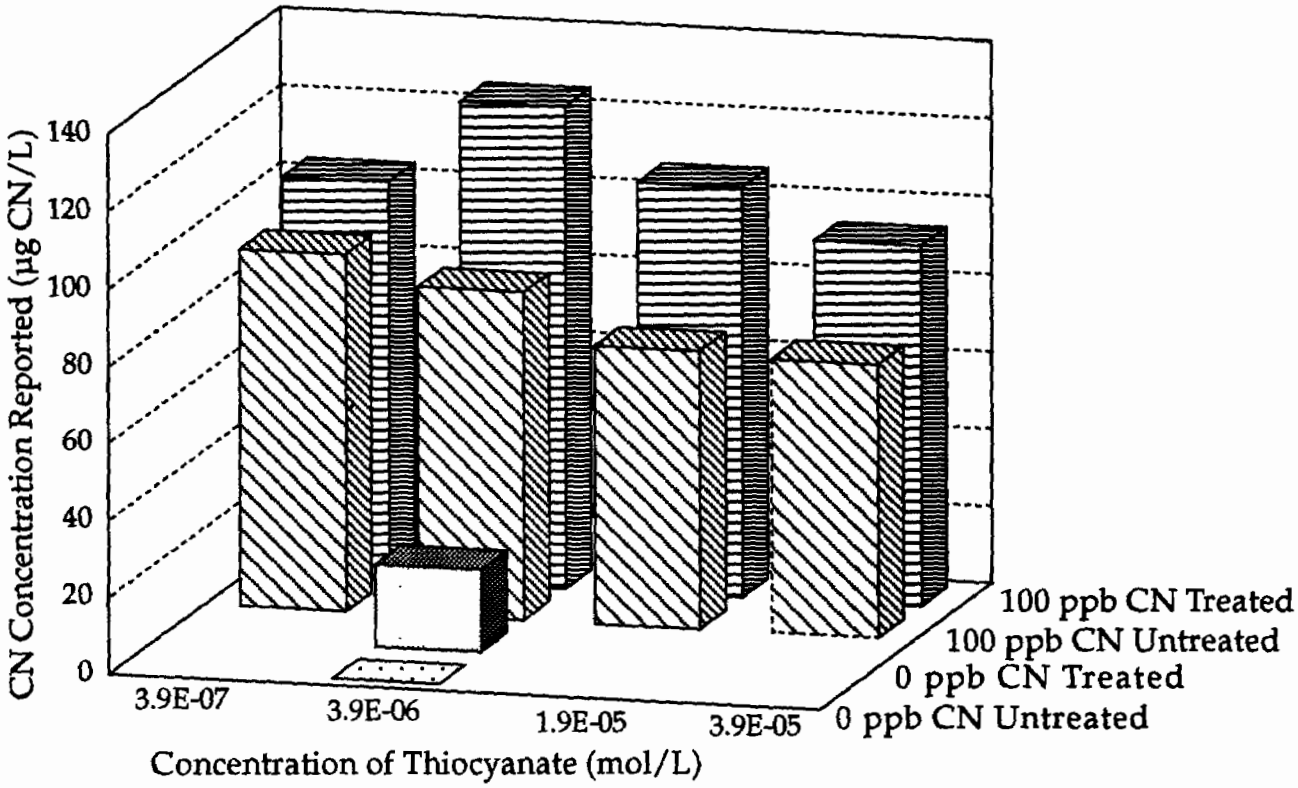

Figure 5. Thiocyanate: Treated samples contain $PbCO_3$ in the Absorber Tube.

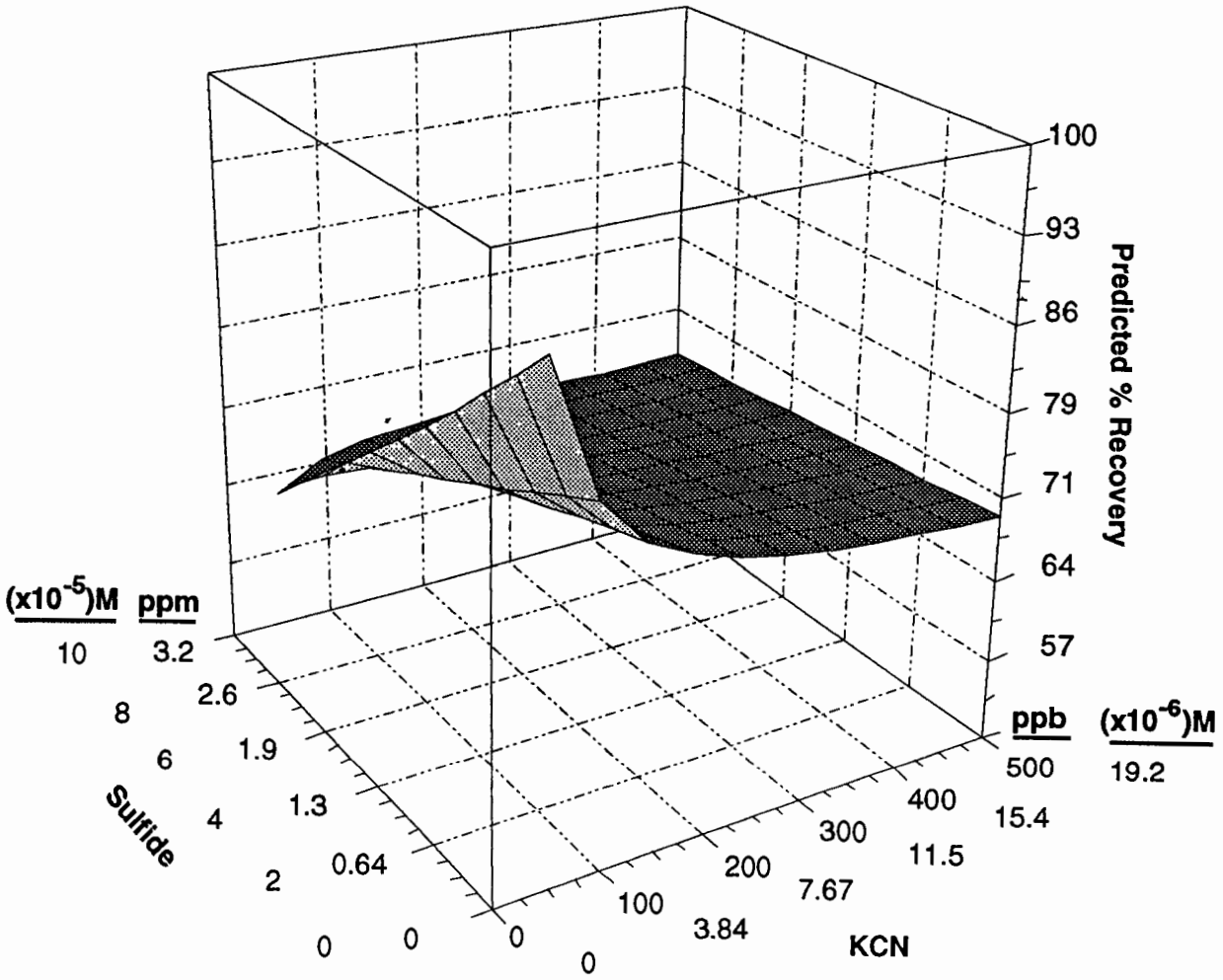

Figure 6. Sulfide: Predicted cyanide recovery.

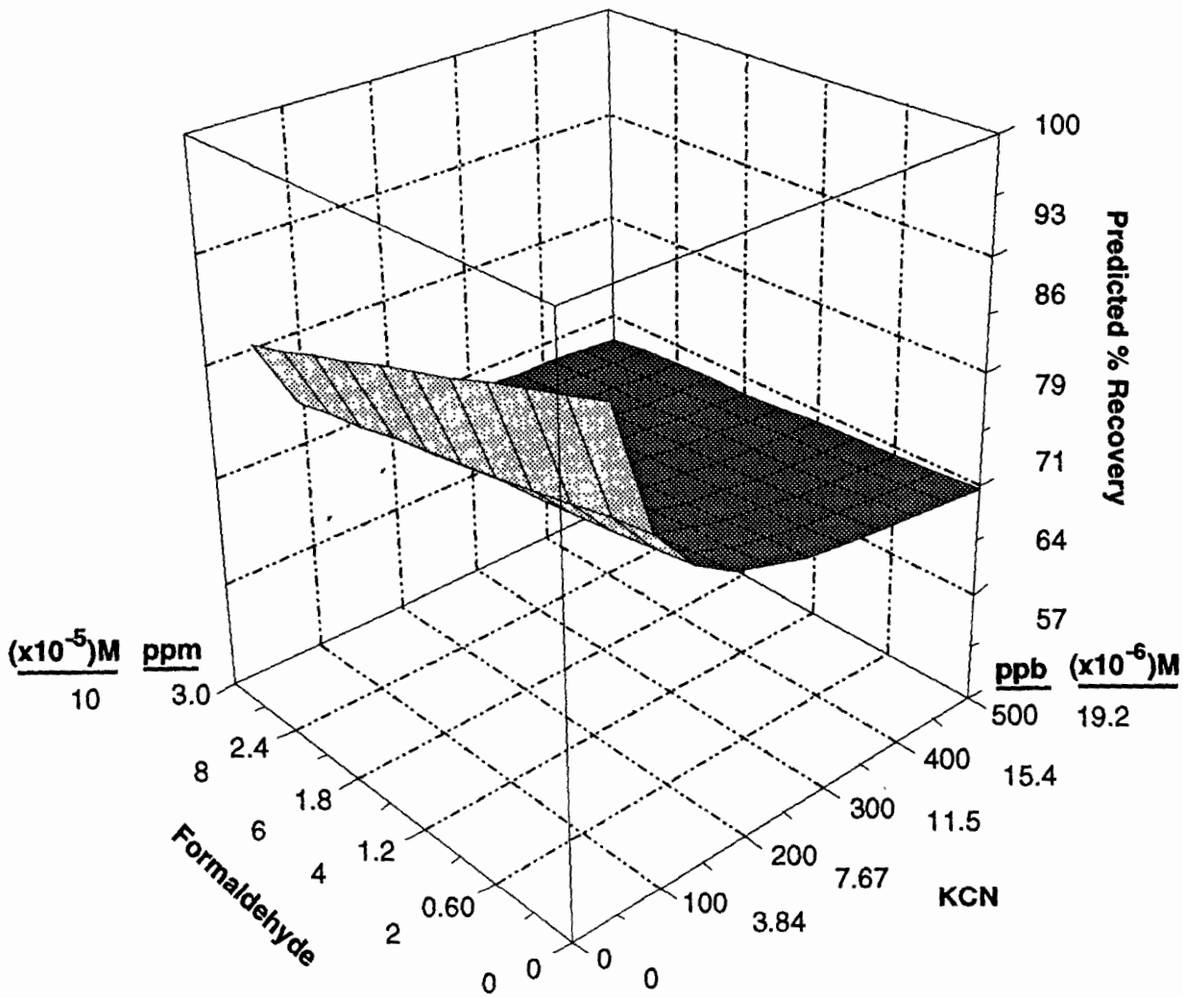

Figure 7. Formaldehyde: Predicted cyanide recovery.

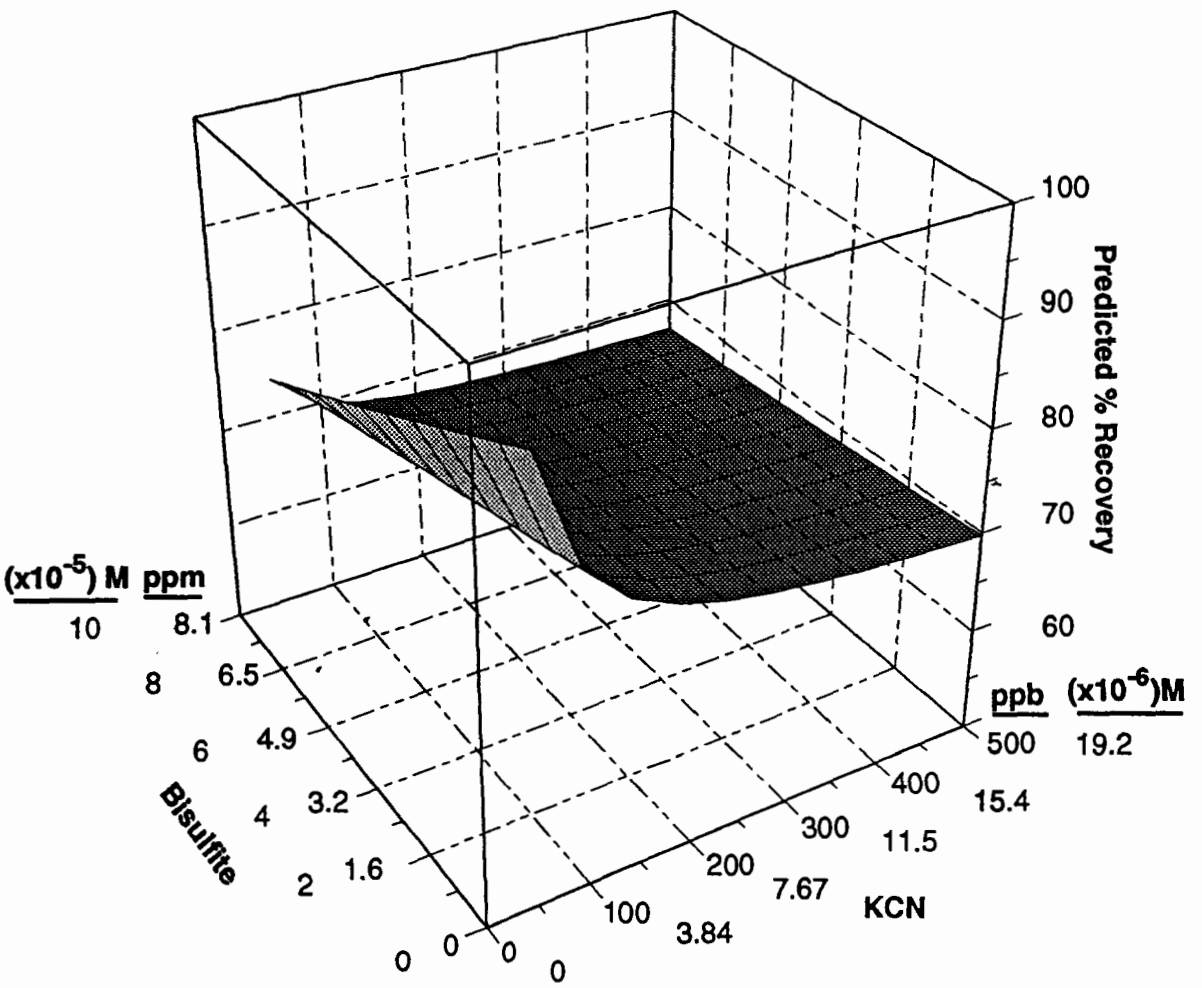

Figure 8. Bisulfite: Predicted cyanide recovery.

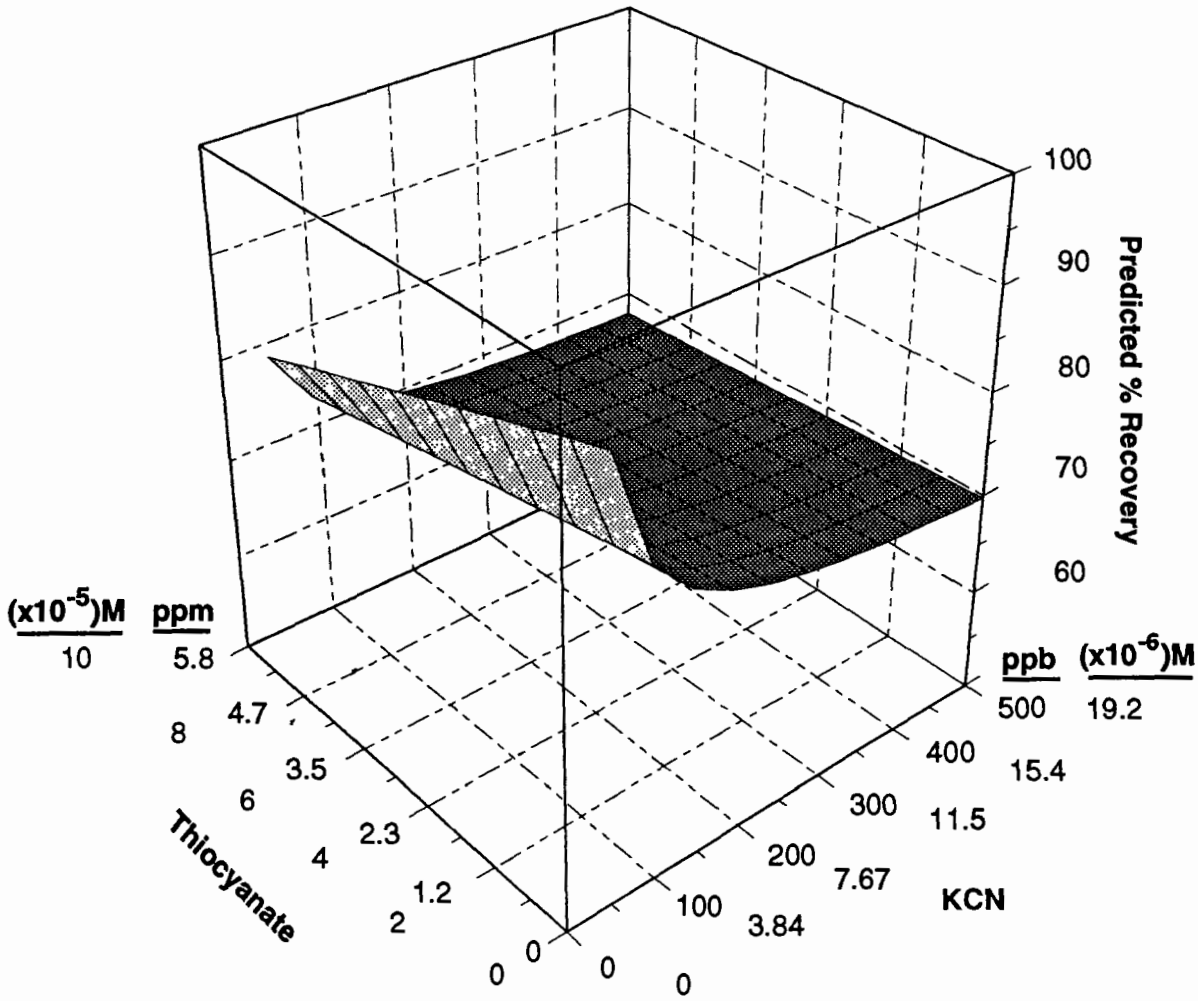

Figure 9. Thiocyanate: Predicted cyanide recovery.

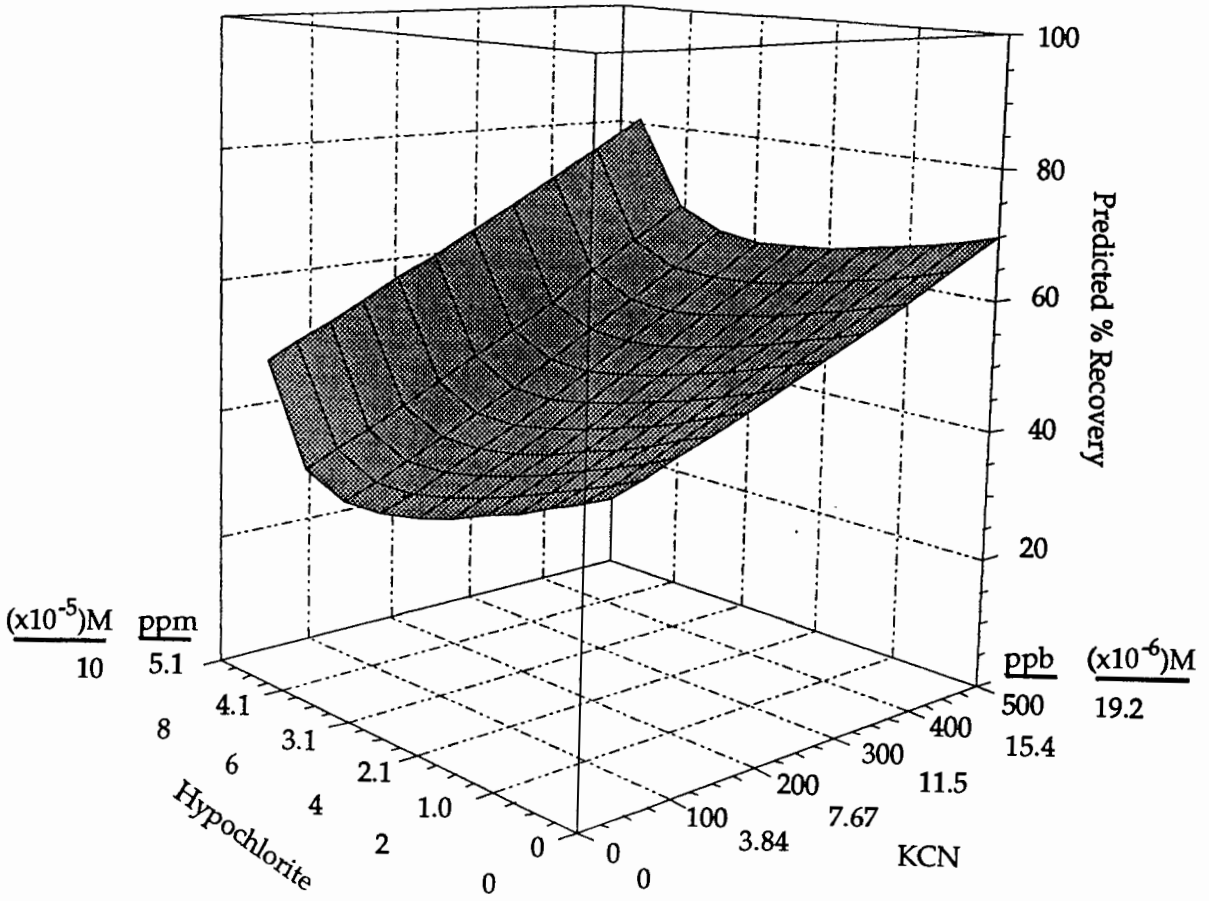

Figure 10. Hypochlorite: Predicted cyanide recovery.

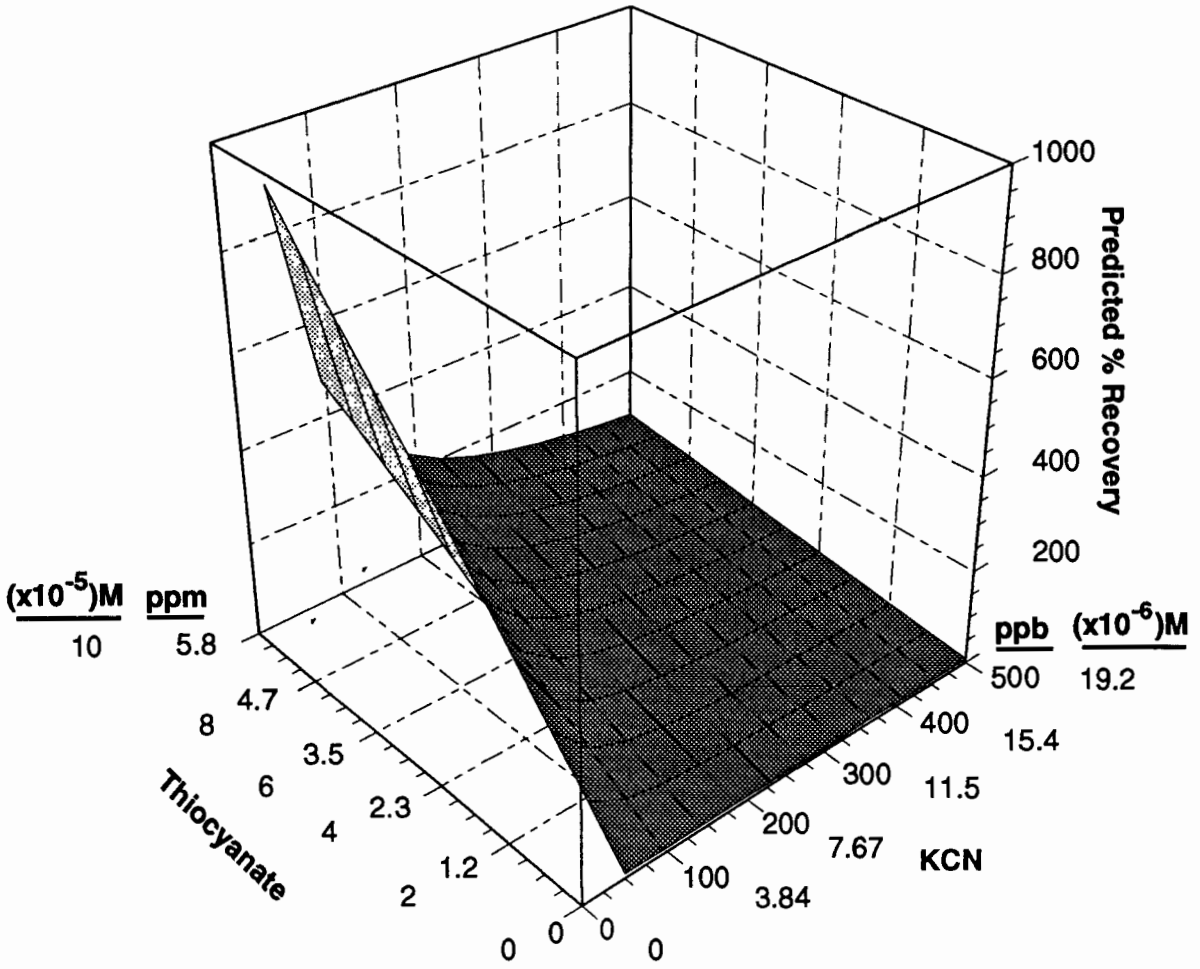

Figure 11. Thiocyanate with 0.1 mM hypochlorite: Predicted cyanide recovery.

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MR. TELLIARD: Our next speaker is Bruce Logan. He is Associate Professor of Environmental Engineering at the University of Arizona. He is going to talk about headspace analysis and BOD.

THE HEADSPACE BIOCHEMICAL OXYGEN DEMAND (HBOD) TEST: A NEW APPROACH FOR MEASURING BOD

MR. LOGAN: Well, isn't it amazing that, with all the improvements we have in analytical methods and procedures and materials that we do not do the BOD test a whole lot differently today than we did it 50 years ago?

There are certainly some problems associated with the test. It is labor intensive. It is glassware intensive and consumptive. It is bench space consumptive, incubator consumptive, dishwasher consumptive, time consumptive. I do not know if I have missed anything.

It is slow. It can take at least five days, as you know, and perhaps one of my biggest concerns, as an engineer who designs wastewater treatment systems, is that the results of the BOD test, because of the way we have modified it, no longer represent at all the conditions that are going on in the bioreactor. So, in terms of evaluating and changing wastewater treatment processes, it does not provide us the kind of information that we really need to evaluate the process.

So, what do we do? Well, there are some alternatives that have come up over the years. Respirometers, for one. Unfortunately, they are expensive, and they, because of their cost, provide few replicates.

There are on-line BOD measurements, but, again, those are also expensive and are usually limited to only one or two points in the treatment train.

There are automated BOD systems, and the next speaker will address the problems associated with those.

I am here today to present an alternative to the BOD test which I have called the HBOD test, H standing for headspace BOD test. I think it overcomes the problems with the BOD test. It is not a dilution technique, and it is fast, cheap, and relatively inexpensive.

Let's just spend a minute on what I consider the problems with the dilution technique. In diluting down the wastewater sample, we achieve less of an oxygen demand, but what we also do is slow the whole rate of oxygen exertion, BOD exertion, and substrate consumption down.

The rate of substrate utilization or the rate of organic matter decay is proportional to a couple constants and two things, X, which is the concentration of cells in the BOD bottle, and S, the concentration of substrate or the organic matter. When we dilute those down, we can slow down the reaction rate.

In a typical BOD test, if you are looking at BODs in the range of, say, 30 to 100 mg/L, you may dilute the sample as much as a factor of 10 to 100. So, you have really set up the game to work against you.

What do we do in the headspace BOD test? Well, as I said, it is not a dilution technique, so you do not need to change the concentration of the wastewater depending on the BOD.

The overall calculation of the headspace BOD is based on a mass balance, and the principle behind the test is that oxygen is replenished in the wastewater or the water sample in a sealed tube.

I have one of those sealed tubes, and unless you are sitting in the front row here, you will not be able to see this, but I can assure you I will have a slide of this in a moment.

The idea is that you take a tube, you fill it with a certain amount of wastewater, not diluted or in any way altered, and you leave a part of the tube open and just containing air, and then you seal that tube and let the reaction go on with time.

Now, one of the advantages of the test is, because I have not diluted it, the reaction will plateau out very quickly, typically within 24 to 36 hours, and this could allow you to take the sample on Monday morning and have your answer Tuesday afternoon.

Let me run through the test with you and then we can discuss how and why it works.

This is what you need to run the test. You need test tubes like this. A 28 ml test tube is the test tube that I use. This test tube was developed for work with anaerobic microorganisms, so it is airtight, gas tight, liquid tight.

Within one test tube rack, you can fit about 40 of these test tubes compared to, say, 3 or maybe 4 BOD bottles. You also need a cap for these tubes. We use teflon stoppers which were not around 50 years ago. And we use aluminum tops, and we crimp seal on the tops of the teflon stoppers to create and airtight seal.

So, how do you conduct the test? Get your wastewater, and put it in a bottle. You can put this bottle on a magnetic stirrer if you wish to keep everything well suspended. We use a little digital pipette or dispensette. We just set this for whatever volume of wastewater we want to put in the tube, say, 15 ml and just inject right into the test tube 15 ml of wastewater.

We put on the teflon top, crimp seal it, and we set these test tubes on their sides. This can be done by placing all the test tubes in this rack, putting a cover on to hold the test tubes in the rack, and putting the rack on a shaker table.

You need to agitate this sample so that you continuously re-aerate the sample with oxygen from the atmosphere.

Now, what do we do when we are done? We can wait 24 hours or 36 hours or 5 days and let this run, but how do we analyze oxygen in the liquid?

This is a standard YSI probe which most of you probably have in your labs. This probe will not fit down into that test tube. Moreover, even if it did, it would have to go through some sort of headspace at the top of the tube. So, the probe does not work for us.

So, if you want to run this test, you need to get a new DO probe. We use the Wheaton BOD analysis system, and this is the probe right here. It is a non-consumptive, non-stirring probe, so you do not need to stir the sample, and you do not consume any oxygen while the analysis is being done.

You just set the dial for the temperature of the laboratory and for the saturation concentration of oxygen.

When you are ready to analyze the sample, we give it a quick stir to make sure the water is equilibrium with the air on a vortexer. We then pour the sample out into a little plastic sampling cap. This is an incubator cap off a test tube.

And we insert the probe. The cap is actually sitting in the top of this BOD bottle and contains the wastewater sample. We insert the probe down into the wastewater sample and let it sit there about 60 seconds, and then we can read the DO directly from the machine.

When we are all done, we use a computer program to calculate the HBOD, although you can make the calculation on a calculator. To make the calculation you use the volume of the container, the volume of the liquid, the air pressure when you sealed the test tube, the temperature, the DO at the start which is usually insignificant, and the DO when you finish.

You input this data into the computer, and out pops your HBOD, in this case, 89.3 or 90 mg/L, and you can see that the DO at the start which is probably only 1 or 2 mg/L is insignificant compared to the final BOD.

Let me convince you that this analysis really works. It seems too simple. You probably think well, why didn't somebody think of this 50 years ago?

I do not know the answer to that, but the method is based on Henry's law. It is saying that the partial pressure of oxygen in the gas phase is related to the concentration in the liquid phase by a constant.

What this means is that the amount of oxygen in the air as it is used will drop the partial pressure of the concentration of the oxygen in air.

Now our intuition tells us that when the pressure changes in that test tube that the partial pressure of oxygen changes, but our intuition is based on a system where volume changes can occur, for example, injecting air into the bottom of the tank. You can compress or expand air bubbles depending on the pressure.

In this test tube, once it is sealed, the only way that the partial pressure can change is by consumption of oxygen. So, the total pressure in the tube, let's say the total pressure starts out at 1 atm, and let's say that, through production of CO_2, it ends up at 2 atm.

Let's say no oxygen was consumed. The mole fraction of oxygen went from being 1 to 0.5. So, the pressure went up, the mole fraction went down, and the partial pressure stayed the same.

So, the only way that the partial pressure of oxygen can change is by consumption of oxygen. So, I can either measure the concentration of oxygen in the air or the liquid. By measuring either one, I know both.

The oxygen consumption is calculated by first calculating the mass of oxygen in the air. That is calculated by nothing more complicated than the ideal gas equation, $pV = NRT$. We all remember that from freshman chemistry.

Then we calculate the moles of oxygen initially in the liquid phase. That is just the concentration times the volume.

To start out, we need the total moles of oxygen. We add up the moles in the liquid and the moles in the gas. We then have total moles of oxygen at the start of the test, and when we are done, we can go through the same calculation.

We measure the dissolved oxygen concentration in the liquid when we are done but we do not measure the concentration in the gas. There is no need to. We can calculate that from the Henry's law constant. So, we back-calculate the gas concentration.

So, the full calculation is that the headspace BOD is...well, you have this big equation, and I think if you look at this, you can appreciate why we put it on the computer, but all we need to know is the volume of the container, a couple of constants, the temperature, the initial concentration in the liquid, and the final concentration in the liquid.

You also need to know the saturation concentration of oxygen in the liquid. We can look that up in a book. If we don't believe it, we take our wastewater sample, put it on a stir plate for half an hour, and then we can go measure that in the exact sample that we have.

This is what the analogous dilution looks like for the headspace BOD concentration. Let's say that we run a test, and we end up with 2 mg/L of oxygen in the liquid. Well, if we had, say, 10 ml of liquid in a 28 ml container, our BOD is 100 mg/L. If we had 15 ml, it is 200, and so forth.

So, the final DO concentration and our choice of the volume of headspace tells us what the BOD was.

Varying the volume of wastewater or the volume of our sample in a tube, is intrinsically simpler than going through an extensive dilution procedure and perhaps guessing it wrong.

If you look at the DOC that is in a wastewater sample as a function of time, you can see the DOC rapidly, between 24 and 36 hours. Sometime later, but before our next sample, the DOC dropped down to zero, and the BOD exerted within that time came up and, over several more days, continued to increase, probably due to endogenous decay of microorganisms.

Now, we have run this comparison of the HBOD test to the conventional BOD test in a number of ways. We have looked at just primary effluent for domestic wastewater. We looked at the HBOD in six different experiments, on six different days at the waste treatment plant, and we compared our HBOD to what the operators reported for their BOD on that sample.

Of course, there is some variability and that is pretty typical of any BOD analysis, but the results are quite similar for both tests.

We also determined the HBOD after one day, and we recorded that number, and then, from the average of all these numbers versus the average of all these numbers, we got a constant ratio with an average of about 0.48. So, we are trying to anticipate what the final BOD is going to be after five days.

I will show you those same numbers in this graph. In triangles are the BODs here, and in boxes are the HBODs. You would expect that at this treatment plant, things should be pretty constant with time. All these numbers should be about the same, and our numbers, the HBOD numbers, compared very well to the BOD numbers.

The greatest outlier is the BOD, and it is a lot lower than these other ones. In fact, the operators thought that they had messed up, and our HBOD was right in line with all the other ones.

If we use the predictor, that one-day predictor, we divide by 0.48 and predict the five-day BOD and headspace BOD and compare it to the BOD, this is what our plot looks like. Surprisingly, our number drops down and tends to agree with that number, so it suggests to us that something unusual was going on in that sample.

We compared the one-day HBOD with itself. We hoped the agreement should be good and, indeed, it is, because this average is based on this data.

We also examined what the effect of the seed was. We wanted to look at a standard glucose:glutamic acid calibration procedure, so we looked at a variety of different seeds to see if there would be any appreciable difference in our procedures. We looked at some trickling filter seeds, some activated sludge seeds from two different plants, and a commercially available inoculant (Polyseed). We also looked at the effect of a nitrification inhibitor.

These are the HBOD and BOD results for the glucose:glutamic acid calibrations, and you can see, of course, typical of these tests, a fair scatter in the data. I think this represents our own relative inexperience in the method, but, again, certainly the variability we have with the HBOD test is no worse than the variability with the BOD test.

You can look at it this way. This is the BOD, and this is our HBOD on that glucose:glutamic acid solution, and if our numbers agreed completely, they would lie on this 45-degree line. Since they are close to this line there seems to be no statistical bias.

One problem that we do have is there seems to be a little bit of a bias towards the volume in the container. This comparison was done earlier on. We have run some more recent tests, and we do not see quite this bias, but there is a little bit of experience that one needs to go through with this test, also.

There are some other uses that you can make of this test. For instance, if you are trying to improve a wastewater treatment process, you can look at the effect of nutrient additions. Again, in the dilution test, the BOD test, you have stacked the deck against you. You have diluted out the sample, buffered it, added in lots of nutrients, and so forth. So, you really have no idea if your treatment process is nutrient lacking or nutrient poor.

pH changes will not occur in the BOD test; they will occur in the HBOD test, although we generally have not seen a big pH change.

If you want to measure things like volatile solids and total solids as a function of time in your HBOD bottle, you can do that, because you are not diluting it out, whereas in the

BOD test, you have perhaps either swamped out the suspended solids with your inoculant, or you are measuring a very small number.

Some people have questioned the need for a nitrification inhibitor in the HBOD test, because you have not diluted out the nitrifiers, and what we found when we compared a sample with no nitrification inhibitor to samples with nitrification inhibitor, was that for the first five days, those numbers were in good agreement, but by ten days, nitrification had kicked in, and the oxygen demand had gone up. So, as long as you are running five-day tests, there is no problem.

We also looked at comparing particulate versus soluble BOD. We chose to use a 5 um filter (a Millipore 5 um filter) because it actually passes particles about 1 um in size on average, and we were able to very easily measure soluble BOD. Since we have a very small volume of wastewater, we do not spend all day filtering it. Again, we see the same effect on additional oxygen demand at 10 days.

If you just put these results all on the same graph, you can compare them. This is the soluble BOD, this is the total BOD, and these both have nitrification inhibitors, so you can see what your fraction of the total is in the soluble form.

In conclusion, the HBOD test is very simple, it is very rapid, and it gives numbers that are equivalent to the BOD test.

The smaller test tubes that are used in the HBOD test can really be a space saver in your laboratory and allow you to run greater replicates or just free up a lot of space.

We have looked at wastewater samples, we have looked at the calibration tests, and we get comparable results in both those cases.

The 1-day test may yield results that are comparable to the 5-day with some sort of correlation factor that you probably have to put in for your own wastewater.

I would just say to all of you here today and to those people that you might know I would encourage you to try using the HBOD test and see that this test can actually update a test that has been virtually unchanged for 50 or 60 years.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions? Yes, ma'am?

MS. DINSMORE: Donalea Dinsmore of Wisconsin DNR. Have you tested very clean wastewaters? How sensitive is it? We have got effluent quality around 5 and 10 mg/L.

MR. LOGAN: Well, at 5 or 10 mg/L, you do not need to dilute your wastewater anyway, so you can just fill up the test tube and seal it and run your tests that way. If you still want to investigate the effects of buffering and pH and so forth, you can easily do a 50/50 dilution and run the test.

We have found fairly good replicates. If we run triplicates, we get very comparable results within the limitations of a BOD test, of course.

MR. HORNG: Albert Horng from HTMA, Colmar, Pennsylvania. My question was the opposite. How high did you go? I saw that 2250 was your limit. In some wastewaters, you have 5000 or 50,000. Have you checked into that?

MR. LOGAN: No, we have not gone to the other extreme, but it would be a very simple...actually, it is a much simpler approach at that point. I would say you fill up, instead of that jar that we have with wastewater, you fill that up with your dilution water, and you autodispense in 10 ml of that, and then you get a nice 100 uL pipette and put in your wastewater that way.

So, I think it would be very amenable to the higher concentrations, but if you have too little volume of your wastewater, you are going to run into problems, ultimately.

MR. HORNG: Another question is in diluting wastewater for the conventional method, you can find the toxicity from industrial waste very easily. Have you done anything with this method?

MR. LOGAN: No. Let me say two things. First of all, the point is finding toxicity. Typically, if you just dilute down to what you expect, you will dilute out toxicity problems, but if you are really after finding out if you have one, in this test, you could run one that you do not dilute out, one you do dilute out, and then you would have your answer very quickly. In fact, you would be able to find ways to get around that toxicity.

I do not know if I am being very clear on that, but the toxicity question is an important point, and you do not always address it when you immediately dilute it way down.

MR. TELLIARD: Yes? One more and we have got to get going.

MR. SLENTZ: Kurt Slentz with Energy Laboratories. I infer that you were incubating your samples at 20 degrees C. Is that correct?

MR. LOGAN: That is correct.

MR. TELLIARD: Thank you, Bruce.

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BOD TEST: A DILUTION TECHNIQUE

Rate of substrate utilization, and therefore oxygen demand, is decreased by dilution of substrate:

$$\frac{dS}{dt} = -\frac{\hat{\mu}\,X}{Y}\,\frac{S}{K+S}$$

where:
- $\hat{\mu}$ = maximum uptake rate,
- K = half-saturation constant,
- Y = yield coefficient,
- X = biomass concentration,
- S = substrate concentration.

First order approximation:

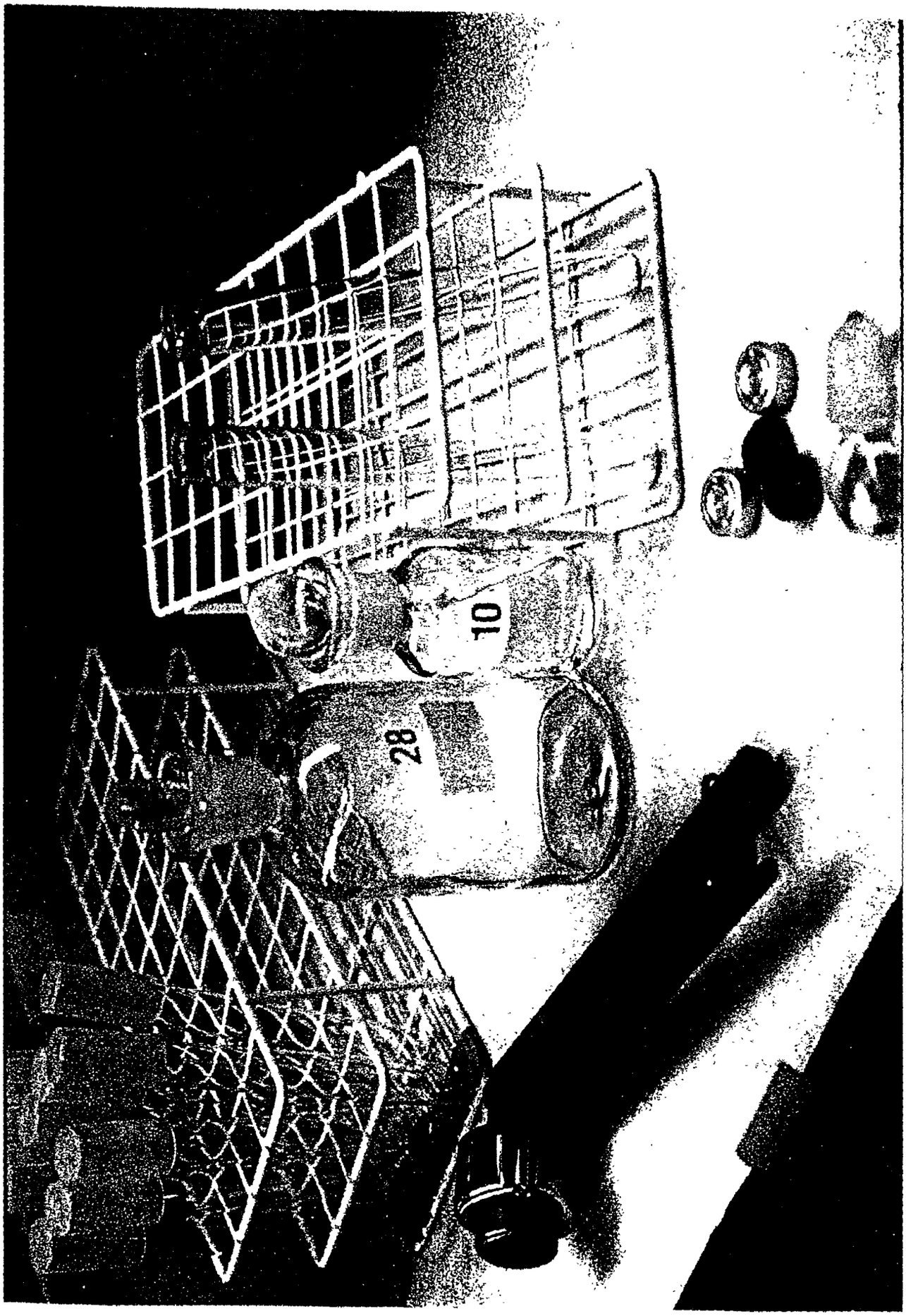
$$\frac{dS}{dt} = -\frac{\hat{\mu}}{Y\,K}\,X\,S$$

DILUTIONS NECESSARY TO DETERMINE BODs FOR PREPARING A BOD CURVE

Volume (ml) in 300 ml BOD bottle	Range of BOD test
300	0 - 7
100	6 - 21
50	12 - 42
20	30 - 105
10	60 - 210
5	120 - 420

THE HBOD TEST:

- Not a dilution technique, so composition of wastewater is not changed during determination of oxygen demand
- HBOD test is based on mass balance
- Oxygen in water is replenished by oxygen in air in a sealed tube
- Plateau at 24-36 h could allow a rapid (1 day) test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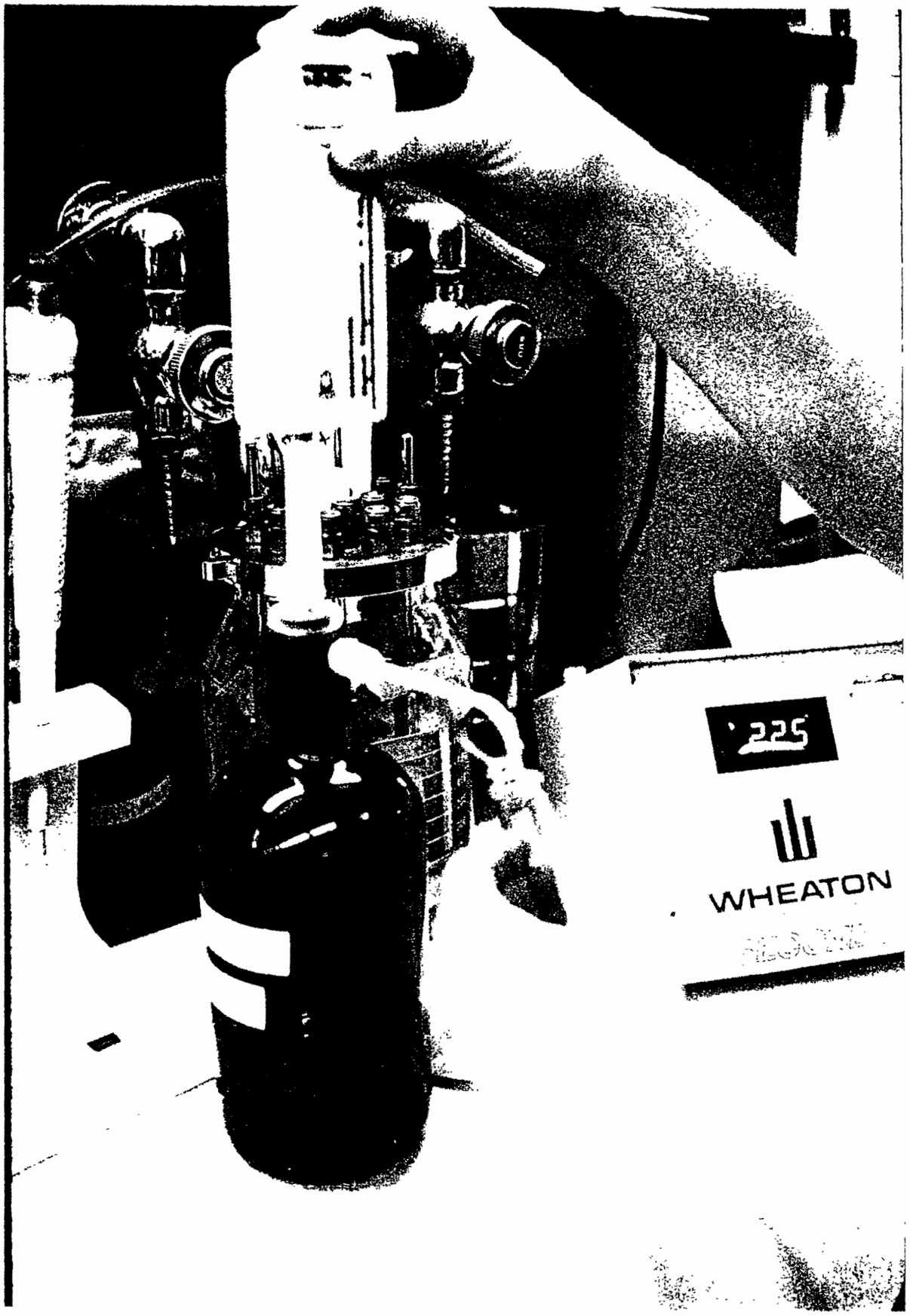
28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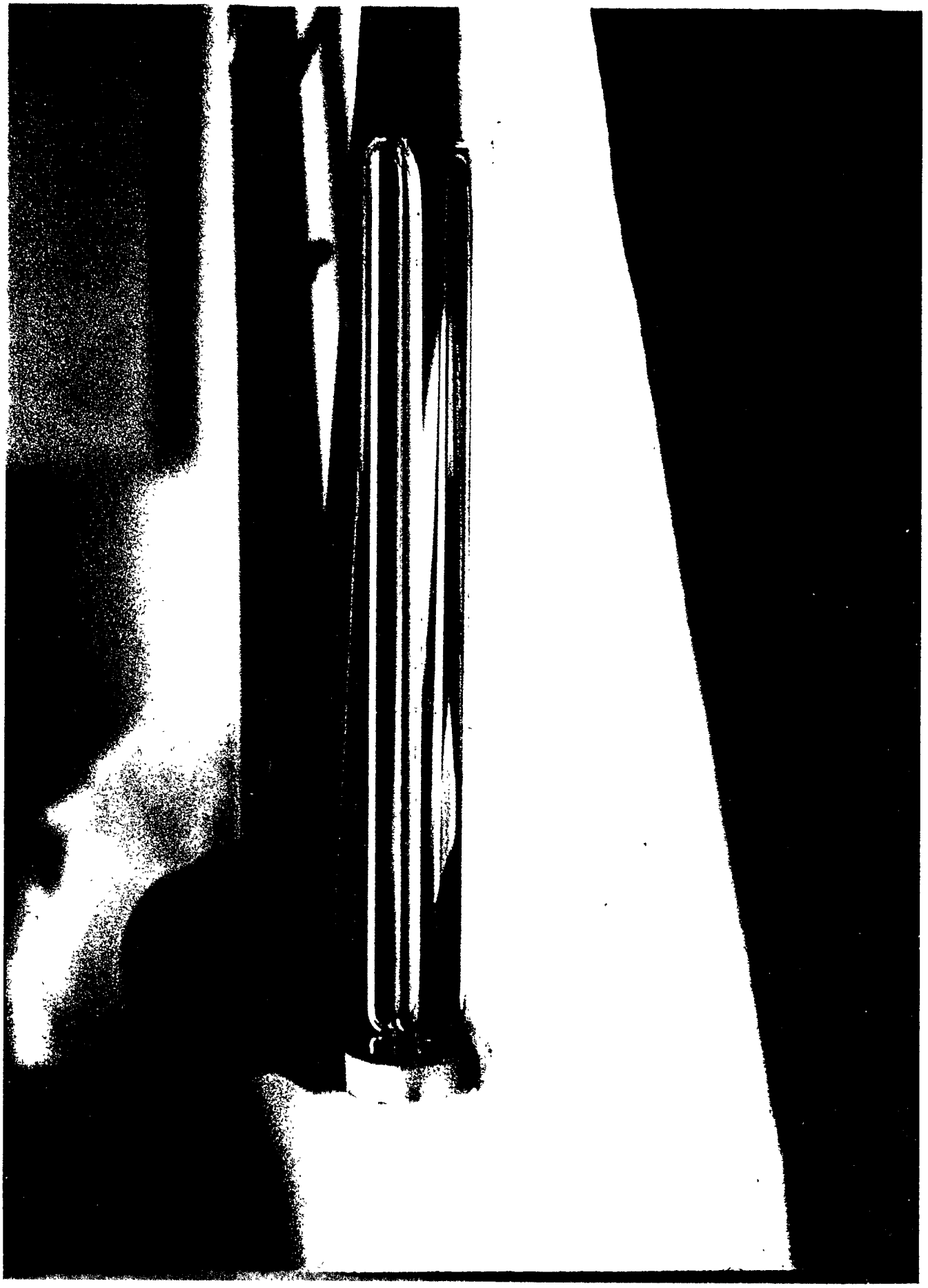
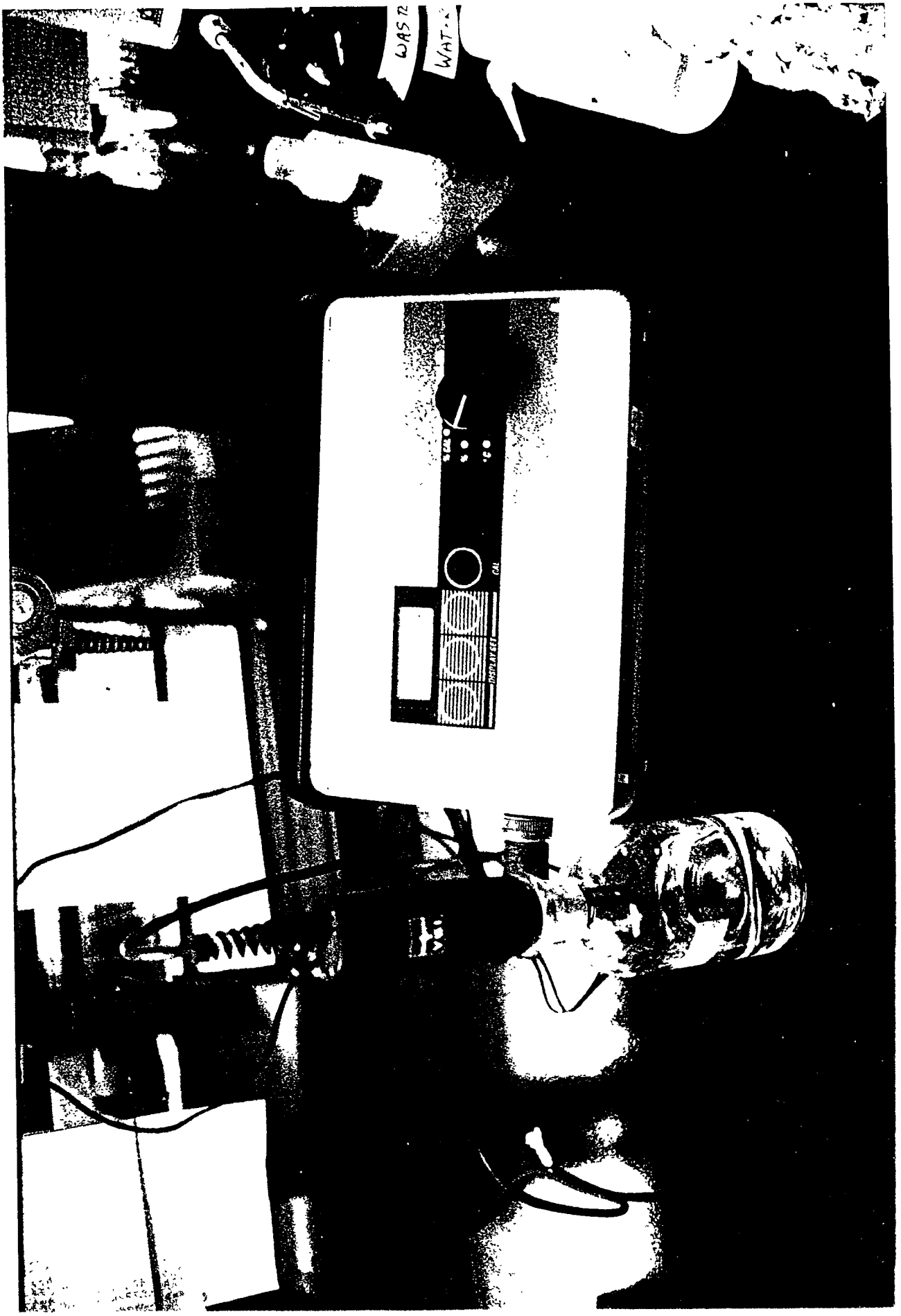
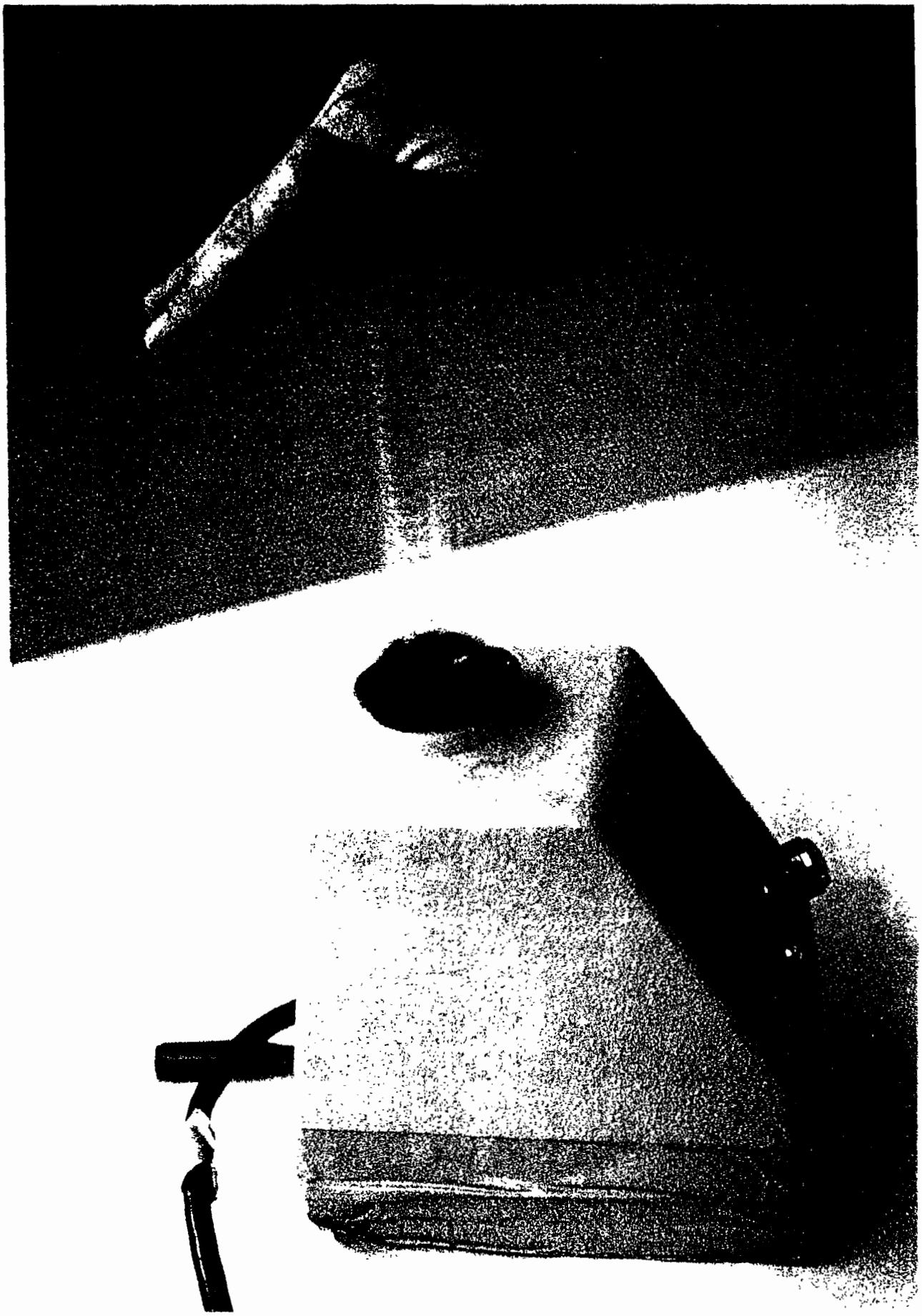
WHEATON




CAL
DISPLAY KEY

PROPERTY OF
UNIVERSITY OF ARIZONA
A228643
AC POWER
BATTERY TEST
TEMP. (°C)
AIR CAL
OXYGEN (PPM)
DISPLAY OFF
CALIBRATE
WHEATON
60 SECOND B.O.D. SYS



ONLY
PUNTER

07.5
WHEATON
60 SECONDS
AIR CAL
OXYGEN (PPM)
DISPLAY OF

HBOD INPUT DATA:

Volume of Container-	28	ml
Volume of Liquid-	15	ml
Air Pressure (initial)-	698	mmHg
Temperature-	20	degC
DO- start-	8.39	mg/l
DO- finish-	5.00	mg/l

HBOD CALULATIONS AND RESULTS:

O2 partial pressure	18.71	%
H2O partial pressure	17.53	mmHg
DO saturation(initial)-	8.31	mg/l
HBOD-	89.3	mg/l

1 HBOD 2 STOP! 3 4 5 6 7 8 9 10

Concentration of oxygen in liquid and air are related based on Henry's law:

$$p = H c$$

where: p = partial pressure of oxygen [atm]
H = Henry's law constant [atm-l mg^{-1}]
c = concentration of oxygen in the liquid phase [mg l^{-1}]

Note: pressure changes in tube do not affect p

$$p = y P_T$$

where: P_T = total pressure
y = the mole fraction of oxygen in the air

At the start of a HBOD test, the moles of oxygen in the gas phase, m_g, can be calculated from the ideal gas law as:

$$m_g = \frac{p_i V_g}{R T 10^3}$$

where: V_g = volume of air in the container [ml]
R = universal gas constant [0.0821 l-atm mol^{-1} $°K^{-1}$]
T = absolute temperature [°K].

The moles of oxygen initially in the liquid phase are:

$$m_l = \frac{c_i V_l}{M 10^6}$$

where: M = molecular weight of oxygen
V_l = volume of the liquid phase

The total moles of oxygen at the beginning of the test are:

$$m_i = (m_l + m_g) = \frac{p_i V_g}{R T 10^3} + \frac{c_i V_l}{M 10^6}$$

Similarly, the total moles of oxygen present in the sealed container at the end of a HBOD test m_f, are:

$$m_f = \frac{H c_f V_g}{R T 10^3} + \frac{c_f V_l}{M 10^6}$$

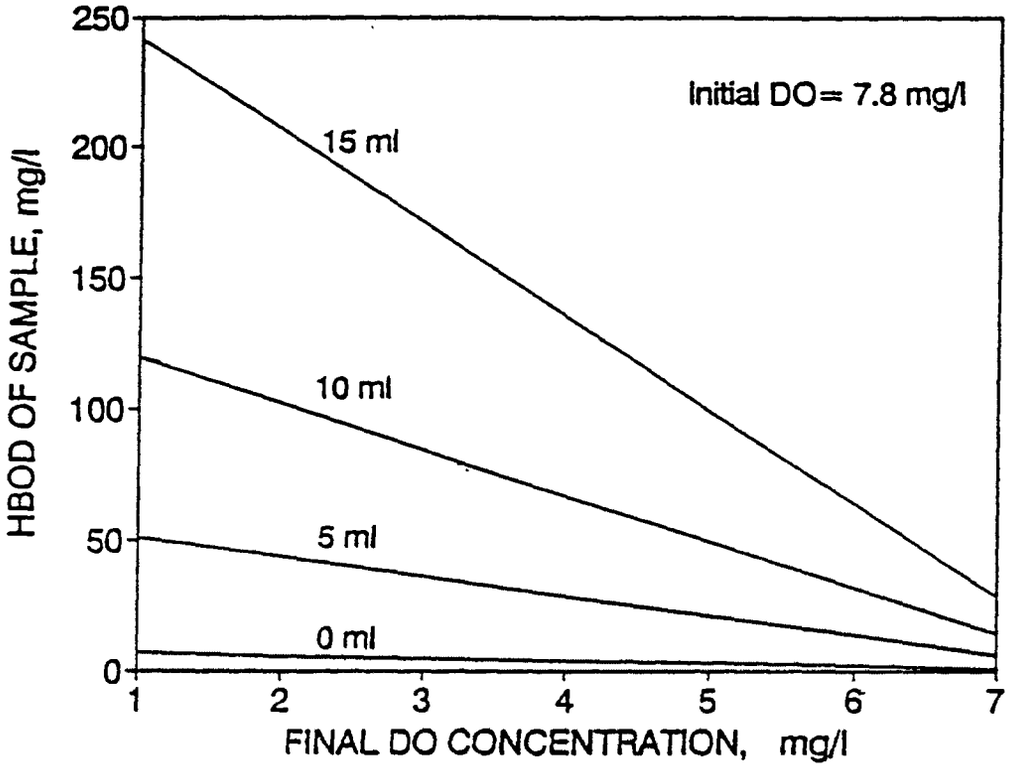
where: c_f = concentration of oxygen measured in the liquid phase (in equilibrium with the gas phase) at the end of the test

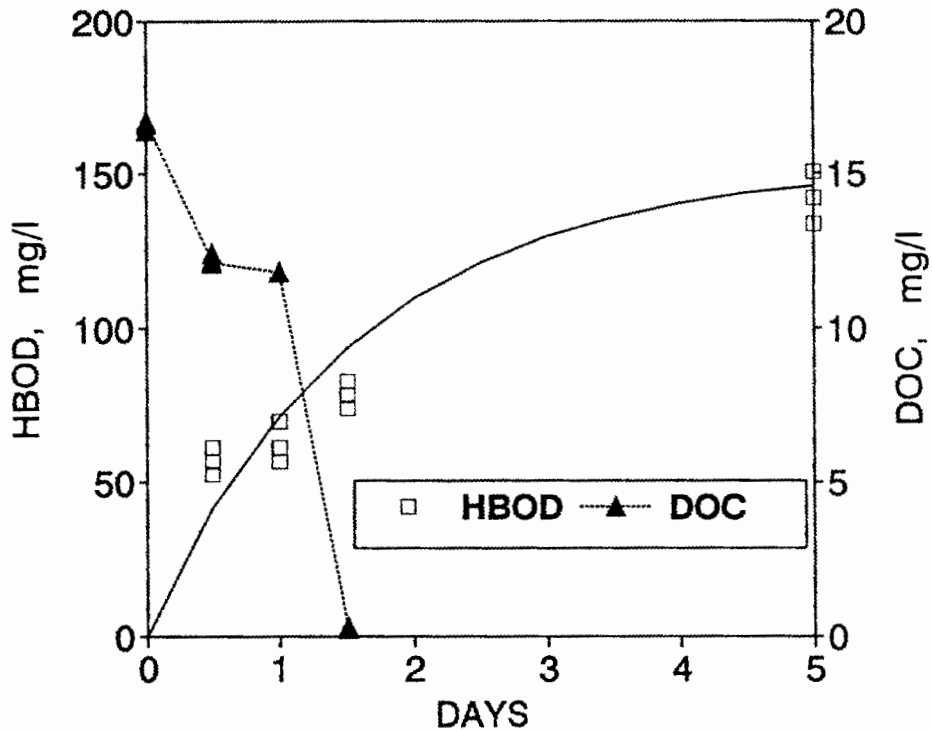
$$HBOD = \frac{V_g\, M\, p_i\, 10^3}{(V - V_g)\, R\, T} \left(1 - \frac{c_f}{c_{sat}}\right) + (c_i - c_f)$$

where:

V	=	$V_l + V_g$, the total volume of the container
M	=	molecular weight of oxygen
p_i	=	initial partial pressure of oxygen
R	=	universal gas constant
T	=	temperature
c_i	=	initial concentration of oxygen in solution
c_f	=	final concentration of oxygen in solution
c_{sat}	=	saturation concentration of oxygen (from Standard Methods)

The HBOD of samples for a 28-ml sample container containing 0, 5, 10 or 15 ml of headspace, as a function of final dissolved oxygen concentration.

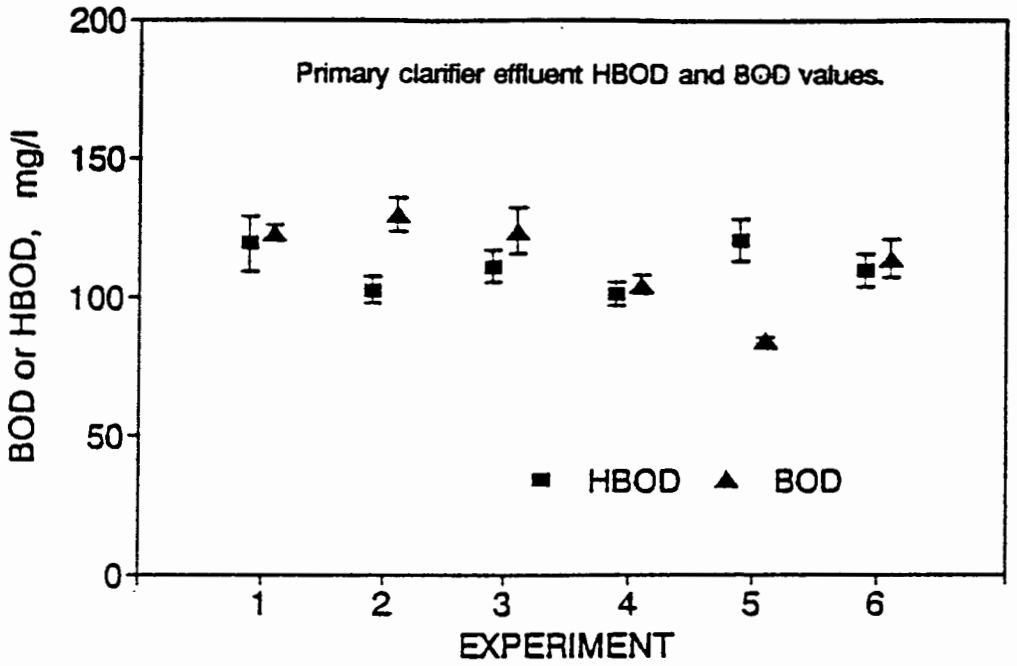


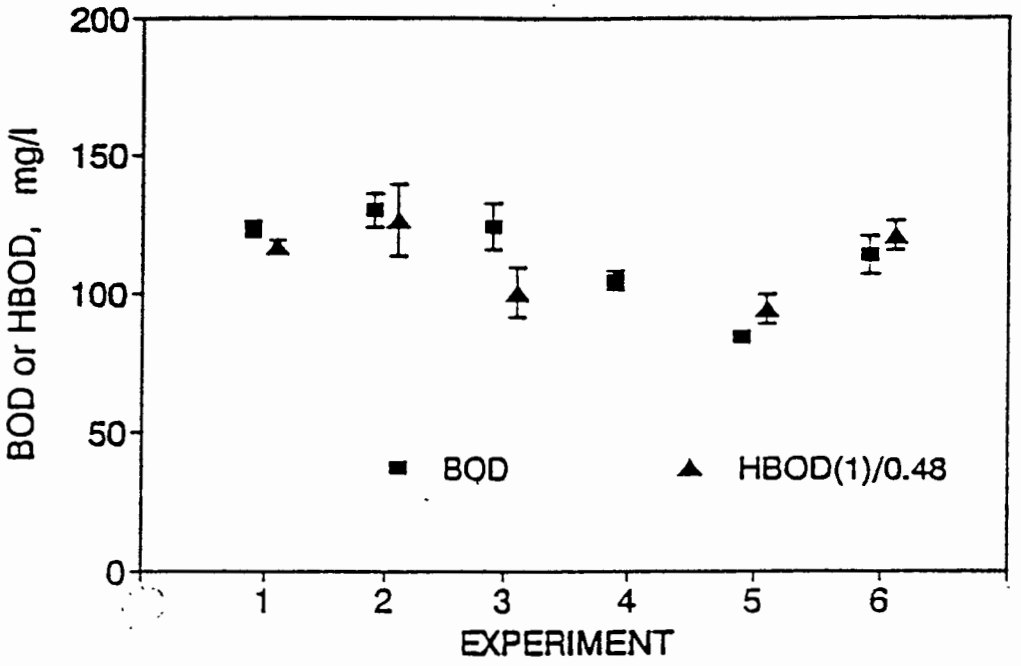

200
150
100
50
0
HBOD, mg/l
20
15
10
5
0
DOC, mg/l
0
1
2
3
4
5
DAYS
HBOD
DOC

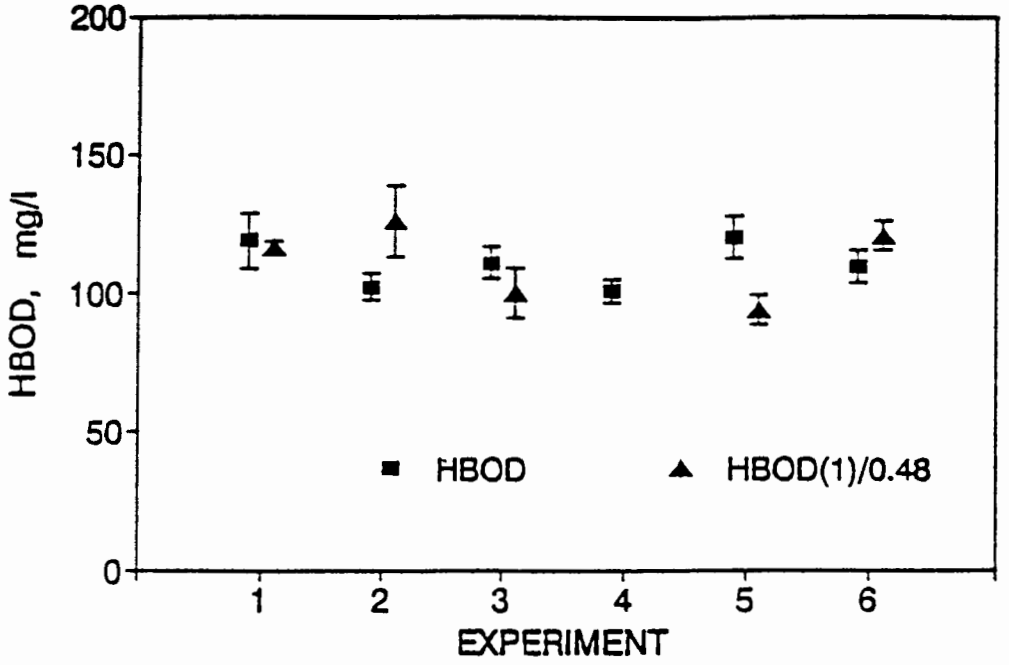
Comparison of HBOD and BOD tests using domestic wastewater (primary clarifier effluent, Ina Rd. Wastewater Treatment Facility).

Exp.	Range of Values[a]			$HBOD_1$/ HBOD
	$HBOD_1$	HBOD	BOD	
1	55-57 (n=3)	106-130 (n=3)	120-125 (n=3)	0.47
2	51-67 (n=5)	95-111 (n=6)	125-137 (n=3)	0.60
3	43-54 (n=5)	103-115 (n=5)	118-133 (n=3)	0.44
4	-----[b]	96-107 (n=5)	102-107 (n=2)	---
5	43-48 (n=5)	109-126 (n=4)	83-85 (n=2)	0.38
6	56-61 (n=3)	103-114 (n=5)	106-120 (n=3)	0.53
Avg[c]				0.48 (±0.08)

[a] n is the number of tests performed, [b] Data not taken, and [c] ± standard deviation based on averages of numbers in column.


Primary clarifier effluent HBOD and BOD values.
BOD or HBOD, mg/l
200
150
100
50
0
1
2
3
4
5
6
EXPERIMENT
HBOD
BOD

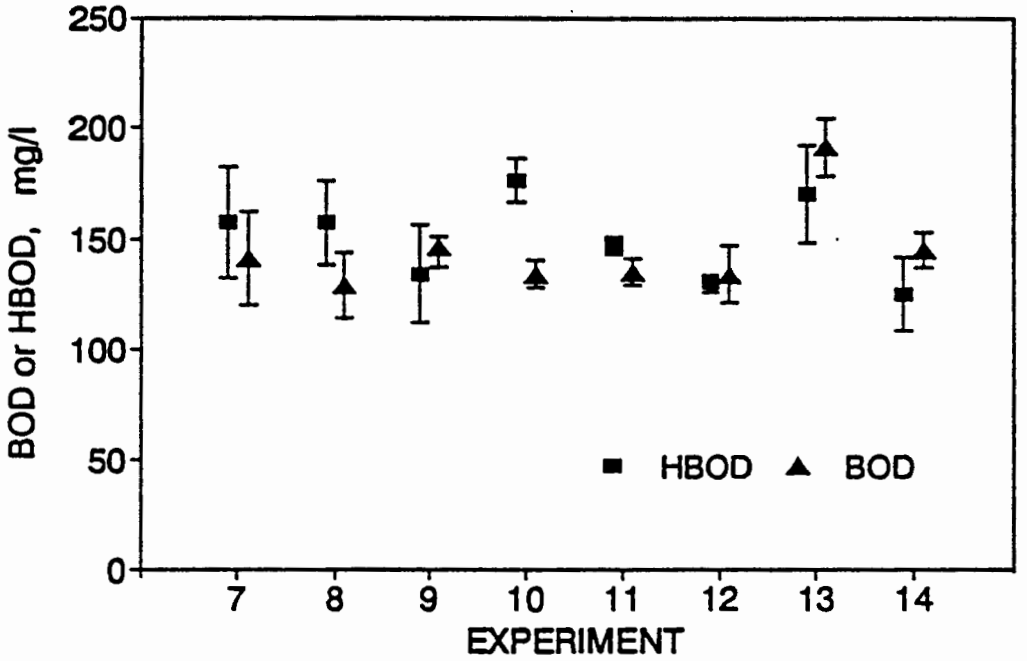

200
150
100
50
0
BOD or HBOD, mg/l
BOD
HBOD(1)/0.48
1
2
3
4
5
6
EXPERIMENT

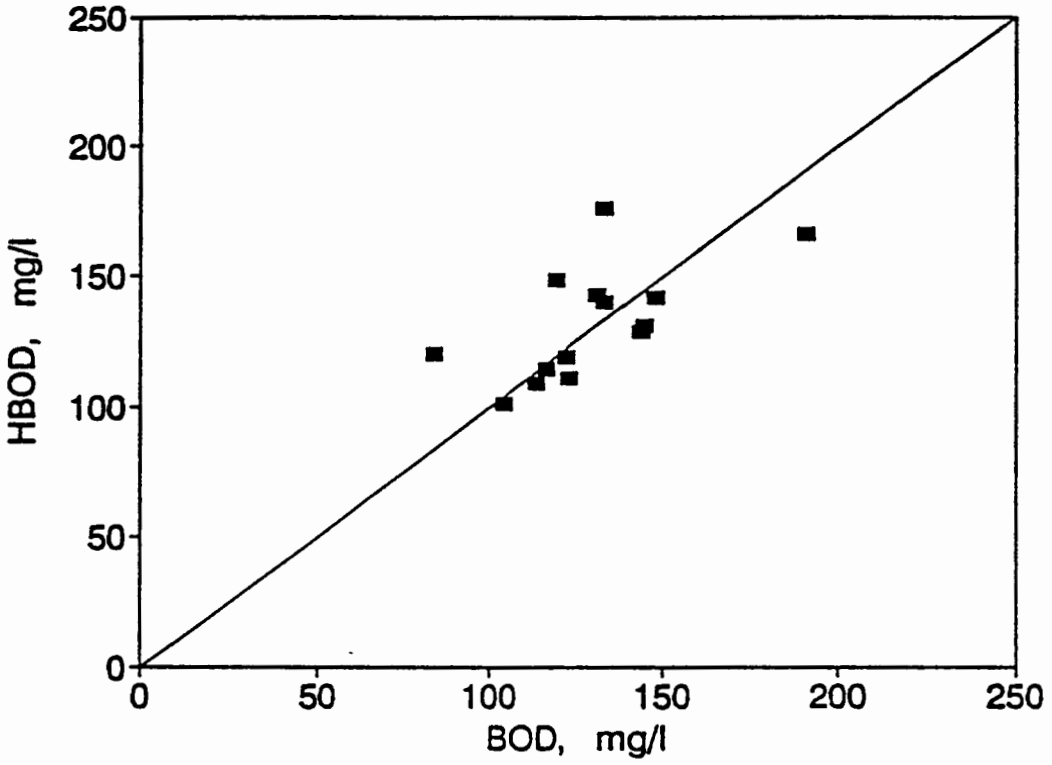

200
150
100
50
0
HBOD, mg/l
HBOD
HBOD(1)/0.48
1
2
3
4
5
6
EXPERIMENT

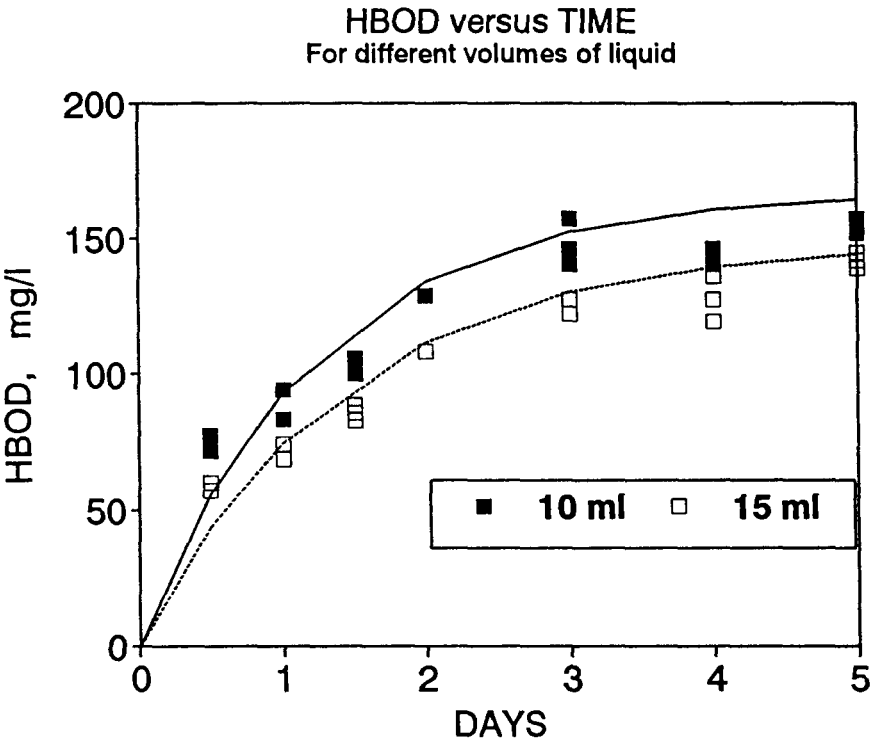
Comparison of HBOD and BOD tests using glucose:glutamic acid (150:150 mg l^{-1}) and different microbial seeds.

Exp.	Seed	Range of Values		Nitrification inhibitor
		HBOD	BOD	
7	Trickling Filter (Roger Rd.)	142-194 (n=4)	114-155 (n=8)	Yes
8	Trickling Filter (Roger Rd.)	143-179 (n=3)	108-126 (n=6)	Yes
9	Trickling Filter (Roger Rd.)	109-149 (n=3)	144-156 (n=6)	Yes
10	Activated Sludge (Randolf Park)	170-194 (n=4)	124-142 (n=3)	Yes
11	Activated Sludge (Randolf Park)	143-149 (n=3)	126-141 (n=4)	Yes
12	Activated Sludge (Randolf Park)	126-132 (n=3)	132-162 (n=6)	Yes
13	Activated Sludge (Ina Rd.)	151-192 (n=4)	175-206 (n=4)	No
14	Polyseed	113-137 (n=2)	139-154 (n=4)	No

HBOD and BOD measurements on a glucose:glutamic acid solution (150:150 mg l^{-1}).

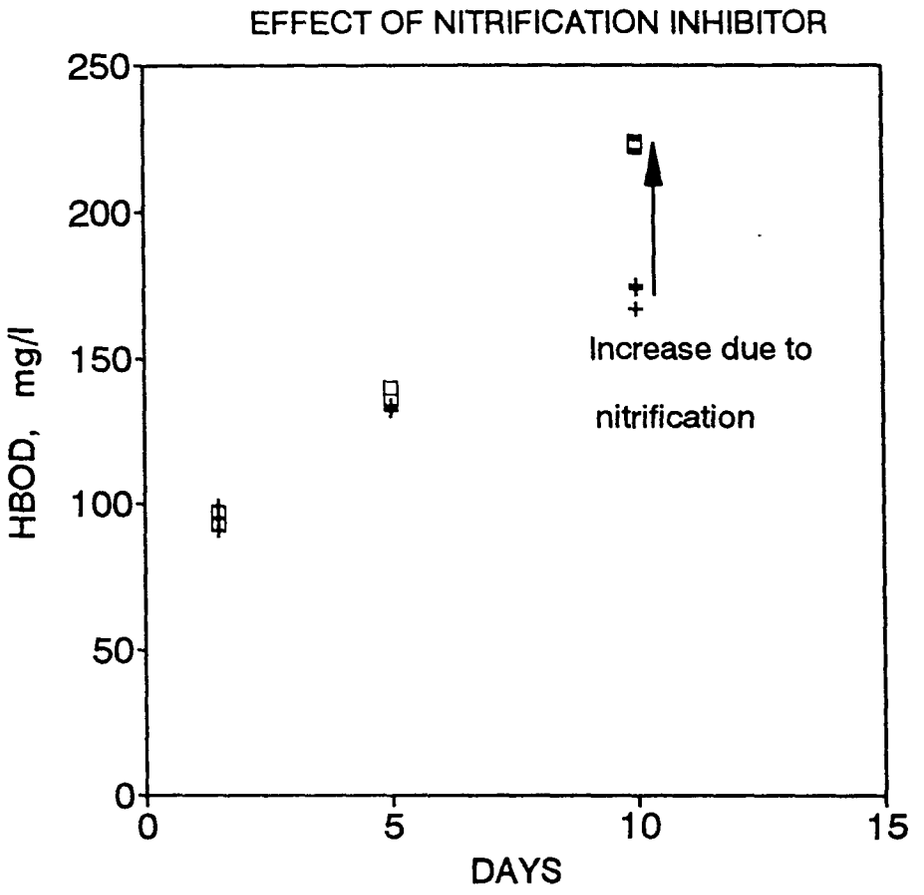


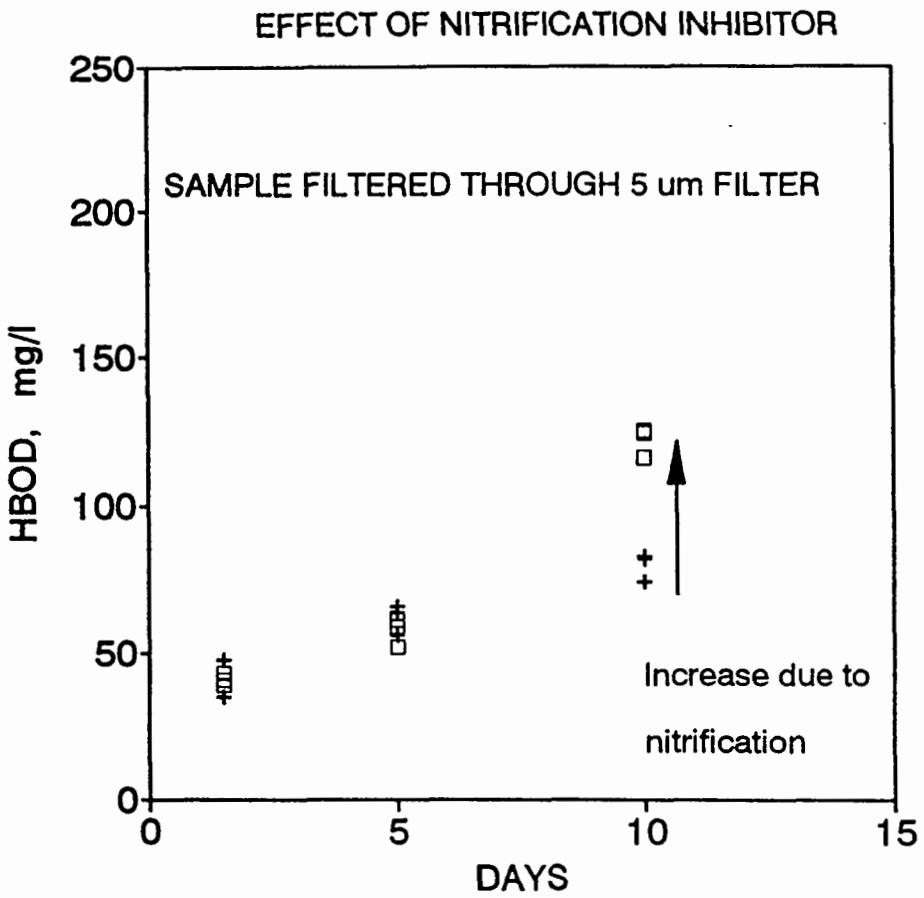

250
200
150
100
50
0
HBOD, mg/l
0
50
100
150
200
250
BOD, mg/l

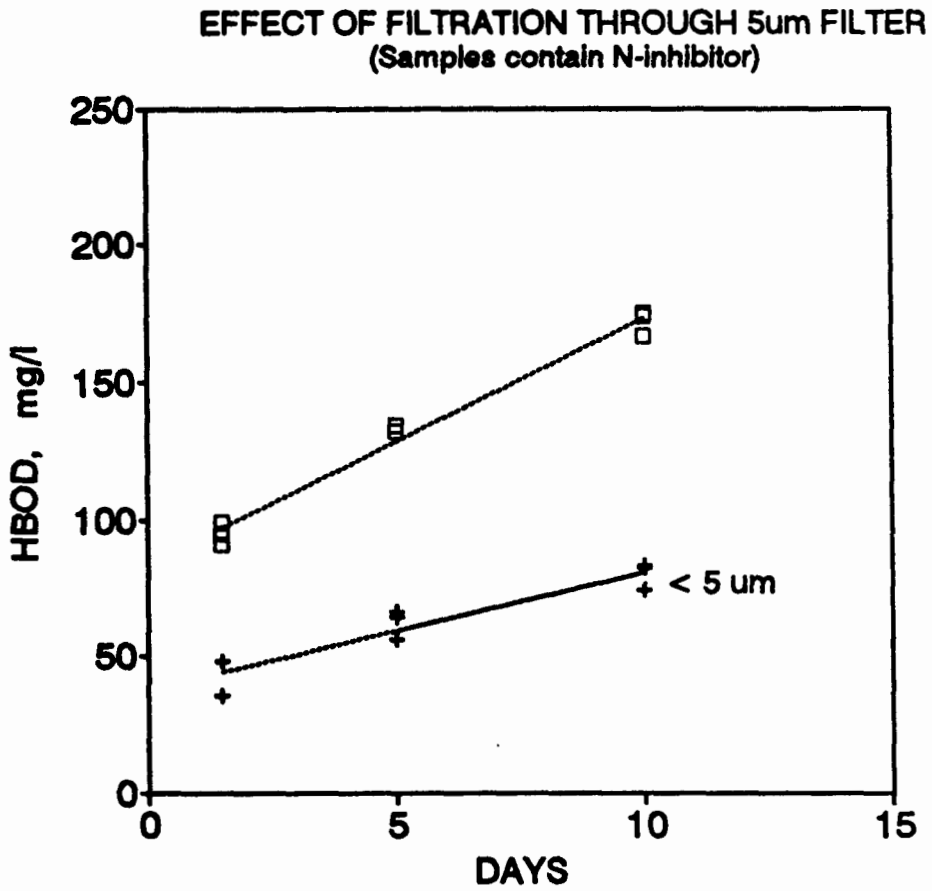

HBOD versus TIME
For different volumes of liquid
HBOD, mg/l
200
150
100
50
0
0
1
2
3
4
5
DAYS
10 ml
15 ml

OTHER USES OF HBOD TEST

- Test effects of nutrient additions
- Examine pH changes in undiluted samples mixed with wastewater
- Measure biomass concentrations (VSS and TSS)


EFFECT OF NITRIFICATION INHIBITOR
250
200
150
100
50
0
HBOD, mg/l
0
5
10
15
DAYS
Increase due to
nitrification


EFFECT OF NITRIFICATION INHIBITOR
SAMPLE FILTERED THROUGH 5 um FILTER
HBOD, mg/l
250
200
150
100
50
0
0
5
10
15
DAYS
Increase due to
nitrification


EFFECT OF FILTRATION THROUGH 5um FILTER
(Samples contain N-inhibitor)
250
200
150
100
50
0
HBOD, mg/l
< 5 um
0
5
10
15
DAYS

CONCLUSIONS

1. HBOD test is a very simple and rapid test for determining oxygen demand.

2. Smaller tubes required for test can reduce incubator space

3. HBOD and BOD results are comparable for:
   - wastewater samples,
   - glucose/glutamic acid tests.

4. 1-day HBOD test may yield much faster results than a conventional BOD test, but it requires correlation to a 5-day test.

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MR. TELLIARD: Our final speaker is going to be very quick, because he is talking about high speed automated BODs. Greg Hill is a Chemist with the Hampton Roads Sanitary District and is going to keep talking about BODs.

Greg?

A HIGH SPEED AUTOMATED BOD SYSTEM

MR. HILL: I will try to keep this short and sweet. I know we have all had a long day, and let's say we saved the best for last.

As Bill said, my paper or talk today will be on a high speed automated BOD system. For those of you who may have heard the original paper, I ask that you bear with me as I cover some background information. We feel it is important information that will help you in understanding why we would choose to pursue this project.

HRSD is a regional wastewater agency. We have 9 treatment plants with a combined flow capacity of over 2 million gallons a day. We service 13 cities and counties which have a total population of about 1.4 million. Currently, the CEL, Central Environmental Laboratory, is responsible for providing analytical support for these treatment plants as well as in-house programs and an aggressive industrial waste program.

Right now, we run 600 BODs a day. So, you can see that the BOD test, with its large number of high labor-intensive task, would be a primary candidate for automation.

What we considered the prime tasks of automation were reading of the initial and final DO concentrations, filling the BOD bottles with dilution water, adding the seed material to BOD bottles, capping, uncapping, calculating the BOD concentration, and monitoring QC data. You will notice this adds up to be 8 man-hours per day.

Based strictly on the salary for one person for one 8-hour day, not counting any benefits, that calculates to be about $44,000 a year savings. At this point, it was financially to our advantage to investigate this possibility.

After doing some market research, we found that automated systems could run between $100,000 and $200,000, with the average system cost being $150,000. We chose a five-year time period as the time frame in which we felt that whichever system we purchased should be able to provide us service without any major upgrades or modifications.

With that time frame in mind, you will notice that we could recover the cost of a $150,000 system in less than three and a half years.

At this point, we began investigating the market for systems that could do the tasks we wanted. The problem was there was no such system on the market that could meet the throughput demand that we had.

That left us with three basic approaches. We could either modify an existing system, we could have a system custom-designed, or we could do a three-phase custom design which was simply a detailed design study with a small working model with delivery of the final product.

We investigated all three, and found that the modification of an existing system was the best way to go for us.

Once we chose the method we wanted to go with, our next concern was finding a manufacturer willing to commit to this program as much as ourselves. We were looking for a commitment both financially and with technical resources.

This commitment came in written form. The manufacturer would provide to us a system and at the end of a set agreed-upon period, if the system did not perform as we felt it should or meet the written specifications, that it would be taken back at no cost to the district. Obviously, this would provide some incentive for the manufacturer to help us.

The first thing the manufacturer did was suggest that we go to multiple systems instead of one unit like we originally had thought of. This would allow the manufacturer to meet our system throughput, and it would give us the ability to have redundant systems so that if one system went down, we still could perform the BOD analysis but at a reduced speed.

One of the things we liked about the system was the simplicity of its mechanical parts. This, you will notice, is the rack movement system where it moves the BOD bottles to the probes. It is a simple carriage with a one-driven gear system.

We were doing so many bottles, it was very important to us that it be very simple and easy to work with.

The other main part was the manipulators. There was simply x, y. There was no z movement. Again, the movement was simplified, thus, hopefully, giving us less problems.

The next thing was, what time frame would it take for us to complete this project? You will notice side-by-side of our original time table compared to our actual time table. Originally, we felt the system would be delivered and the modifications completed in 60 days, with the system on-site setup in 7 days, system training in another 7 days, and 14 days for a system evaluation, which was not a method comparison since the methods were exactly the same. It was simply a performance evaluation to make sure there was no significant difference between the two ways that the analysis was being done.

We ended up with 90 days. Well, it did not...needless to say, it took 90 days before the system was actually delivered, 21 days for system setup, 7 days for training...that remained the same...and the system evaluation took 70 days, approximately, giving us a total of 188 which was basically double our initial estimates.

The reason the evaluation took longer was because of some problems that occurred, which I will address later.

The system evaluation was composed of three parts, first let us consider hardware. Under hardware, we have four areas of concern. First, the DO meter and probe. They were not what we had been using for years, so we had no feelings on how well they would compare to what we had been using or how well they would hold up over time.

Second was the stirring mechanism. It was an adaptation by the manufacturer to meet our specific needs. Thus, it had not been field tested.

The third was the bottle transfer system. Just because of the sheer volume of bottles we were doing every day, how well it would hold up over time.

The last one was the transfer pump, would it aerate the water causing it to become unstable.

We found that the third and fourth were not a problem at all. Things worked out much as we were hoping it would, but we did develop problems in the first and second which will be mentioned as we go.

Operational software, this is the second component. What we basically had to decide was whether or not we wanted a central control of all three systems through one computer system or a separate system at each instrument. Originally, we wanted the option to have both to see which one would work best for us. Unfortunately, the manufacturer could not develop this quick enough and get it into place before the system's delivery.

We are currently running the instruments specific with the manufacturer still working on trying to give us the ability to control them from one.

The second one is the initial and final DO operation steps. We consider BODs basically, in two parts, the initial steps before you place them into the incubator, and then the final readings once they came out. We were concerned how well they would work, how well our people would interface with these steps.

The third was the rack identification. This was another adaptation they did for us. We felt that, because of the sheer volume of bottles we did, we needed something that would help allow us to prevent human error.

The bar code tag on each rack would allow the bottles to be identified as they came across the bar code reader, keeping track of the incubation time, and if the rack was not in for the correct period of time, it would flag you to let you know that you had the wrong set of bottles. We also use color coded bottles as a visual aid, between the two, we were hoping to keep everything in order.

The last one was multitasking. Because we were trying to save as much time as possible, we wanted the system to be multitasking, that it could run while we used the computer to generate tables, check QC, things of that nature.

We wanted the ability to recalibrate. Again, this was a specialized item for us. We felt, and we still do feel, that recalibration is a very important process, that the meters will definitely drift, probes will drift, depending on the sample type, the reagent in the probes and a lot of other variables. So, we wanted the ability to reset or recalibrate at a set period of time. This was something new for them to address.

We entered the final, the major portion. This was the analytical performance. Again, we were not thinking of it as a method comparison. This was strictly an automated version of our same method compared to our manual version.

What we were after was to check the precision and accuracy of the new method compared to our current method. The parallel study basically consisted of samples run on both methods along with some of the glucose:glutamic acid standards.

Jumping right into the data evaluation. The first parallel study which was performed right after the instrument was delivered gave us a 29 percent RPD and a 19 percent positive bias. Obviously, this was well above what we considered acceptable.

Our in-house RPD level right now ranges between 5 and 8 percent, and we felt that we needed something under 10 percent from the automated system to even consider going this way.

The manufacturer thought that the recalibration problem was caused by the calibration vessel itself. If you will notice in the upper left, this is the calibration vessel for the automated, or it was. Those at the bottom right was the manufacturer's of the probes calibration vessel. They basically copied this calibration vessel.

The problem that came into play is that the stirring mechanism was not involved when you are originally calibrating the probe. Now that it was in the system and running, there was a stirring mechanism that was blocking the air flow from the water to the surface of the membrane.

Obviously, the membrane was not being correctly air calibrated at this point.

So, we added water to it to increase the level above the stirring mechanism so there was nothing blocking the flow from the surface of the water to the membrane, and a second run was done. At this point, the RPD has dropped to 17 percent with a 17 percent bias.

Again, this was very unacceptable, and we went back to the manufacturer. The manufacturer at this point went back to the calibration vessel, and stated that they needed to come up with a totally new calibration vessel. The stirring mechanism was bringing in water and taking out water as it went in and out, and that the vessel was so small that those changes in water would affect how much water was in it or whether or not it actually covered the stirring mechanism.

Amidst all this, they also wanted us to go away from recalibration. They wanted us to go to just a calibration check point at which time we would go back to a known value and just check for drift.

We decided we could try that. As long as we were monitoring for drift and we had the ability to calibrate, that was sufficient for us.

This is the new vessel. Obviously, it is just a miniature BOD bottle. It is filled to the top with known dilution water.

The instrument is brought up on line. At the check point, it goes back to the calibration bottle and monitors for drift. We can set the amount of drift that we feel is acceptable. If it does not meet that limit, it will flag itself, give an audible sound, and wait for recalibration.

We were hoping that this took care of our problem, and once it was brought on line, we found 9 percent RPD but a 15 percent positive bias. Well, a 9 percent RPD was great. We were really happy with that, but we were still concerned with the 15 percent positive bias.

We were really starting to get frustrated at this point. What the manufacturer did at this point was go to the meter's manufacturer and the probe manufacturer, showed them the stirring mechanism they were using, and the recommendation from the manufacturer was that the tension was too great on the membrane itself and was causing it to warp.

Excuses the artistry and it is off the screen, but the top one has a solid band which was clamped to the probe itself. According to how tight you had it pushed on and if it struck a bottle going in, the warping on the membrane might change. Thus, it would give you erratic results.

The second one is the modified version which is basically just a groove in the side of the first one to relieve the tension, hopefully, eliminating the warping of the membrane.

Well, with the new stirring mechanism, we still had 9 percent RPD and a 14 percent positive bias. At this point, we called the manufacturer back in. We said obviously, something is wrong. We cannot accept this, and they went off in search of improved stirring. They really felt that the problem was in the stirring.

At the same time, we got together with our group of people, and we said okay, obviously, there is not but so many things different between what we are doing now and what we are doing automated. It had to be something very simple.

We came up with three possibilities. It was either the calibration method itself, the stirring mechanism, or the filling and seeding. The filling and seeding tested not to be a problem. There was no statistical difference between automated versus manual seeding and filling.

That pointed back to the calibration or the stirring mechanism itself.

This graph may be a little tough to see. It shows the two meters. The middle one with the red line is what we are currently using with a Winkler calibration. The upper line was the new meter with this air calibration.

What you will notice is that the difference between the two does not stay consistent. It starts with a higher value, but because it is no longer consistent and the lines merge as they go towards the lower end, it would present an automatic positive bias.

The bottom line was the same meter with a calibration based on Winkler. You will notice this starts on the negative side, a lower value, and it merges as well toward the end.

At this time, the manufacturer had gotten back with us and said that they had found some real problems with the stirring mechanism, and they had developed a new one. We said let's try a new stirring mechanism, and what it is is simply dropped the stir bar in the bottom of the bottle, put the probe in, and you will notice a great difference, a bigger difference between the two meters, but the distance stayed consistent. By that difference being consistent, it cancelled each other out.

This gave us a 5 percent PRD and only a 1 percent positive bias. So, we were really happy. We thought we were on track here.

We had received the manufacturer's new stirrer, and it is hard to see here, but I put it in just to give you a visual of what we are looking at. The black item across the slide is the probe itself. The little piece on the end is the stirring mechanism, and that band is where the warping was occurring where it was attaching to the membrane itself.

I will go back to my famous art work. The lower one is the final version. Notice there are no guards on the front or the back. It allows for better transfer of water through it. The groove is still on the side to alleviate any warping of the membrane.

Once this was in place, we ran another study, and you will notice the lines became very tight. They tracked each other very well, and we found a 4 percent PRD and a 1 percent negative bias at this point.

At this point, it looked like we had really found the answer, and it was looking good.

So, in conclusion what we found is that the project grew from a simple turn-key into a joint system development. This was something we were not anticipating at all. We really thought that it was something that you brought in, set up, and should go since the methods were the same. So, it was very surprising that we had to spend as much time as we did on it.

The next one was the investment of the personnel resources. Again, this became something that was almost frustrating to us in that our 14 days became 70 days, and every time we did a parallel study, we were talking hours upon hours of extra work that was to be done in the normal working day. We had a 10 to 20 percent increase in our work load without increasing our personnel.

The only thing that saved us was that it was new and it was a challenge for our people, and we think that really helped them cope with the extra stress.

The third thing is that we may have entered into this with an overly optimistic view of implementation of the automation into the system.

The final thing is that the project has shown the ability to accomplish our original goals. The system has been on line. We have run it. It has saved us the 8 man-hours we were hoping it would.

So, what I think it has shown is that we had a realistic view, or our goals were very realistic in saving those 8 man-hours. We are hoping in the future to automate as much as we can, because, obviously, manpower is your greatest resource and where the most expense is in the lab.

I am sorry that I rushed through this. I knew it was getting late. I have a tendency to do that.

At this time, I will take any questions.

QUESTION AND ANSWER SESSION

MR. HILL: Yes, sir?

MR. STEVENS: Hank Stevens, Sacramento County Regional Sanitation District. I had a question on EPA's approval for this method and whether or not the bottle tops that are used are approved, because they are, I believe they are teflon coated and not ground stop.

MR. HILL: They are actually not teflon coated, no. The method is approved. We have a letter from EPA stating that it is an approved methodology. There again, it is no different than the standard methodology. It is exactly the same.

The stopper is a composite plastic, and it has a built-in water seal on the top. It is tough to visualize. I wish I had brought one with me, but we do have a letter of approval, yes.

MR. STEVENS: And what was the net savings overall on the...

MR. HILL: The net savings will be difficult to tell you at this moment, because we have not completed it. I still project that it should come out to be at least a $44,000 a year savings. Actually, I am expecting it to be more than that.

Any more? (No response.)

MR. TELLIARD: Thanks, Greg. Appreciate it.

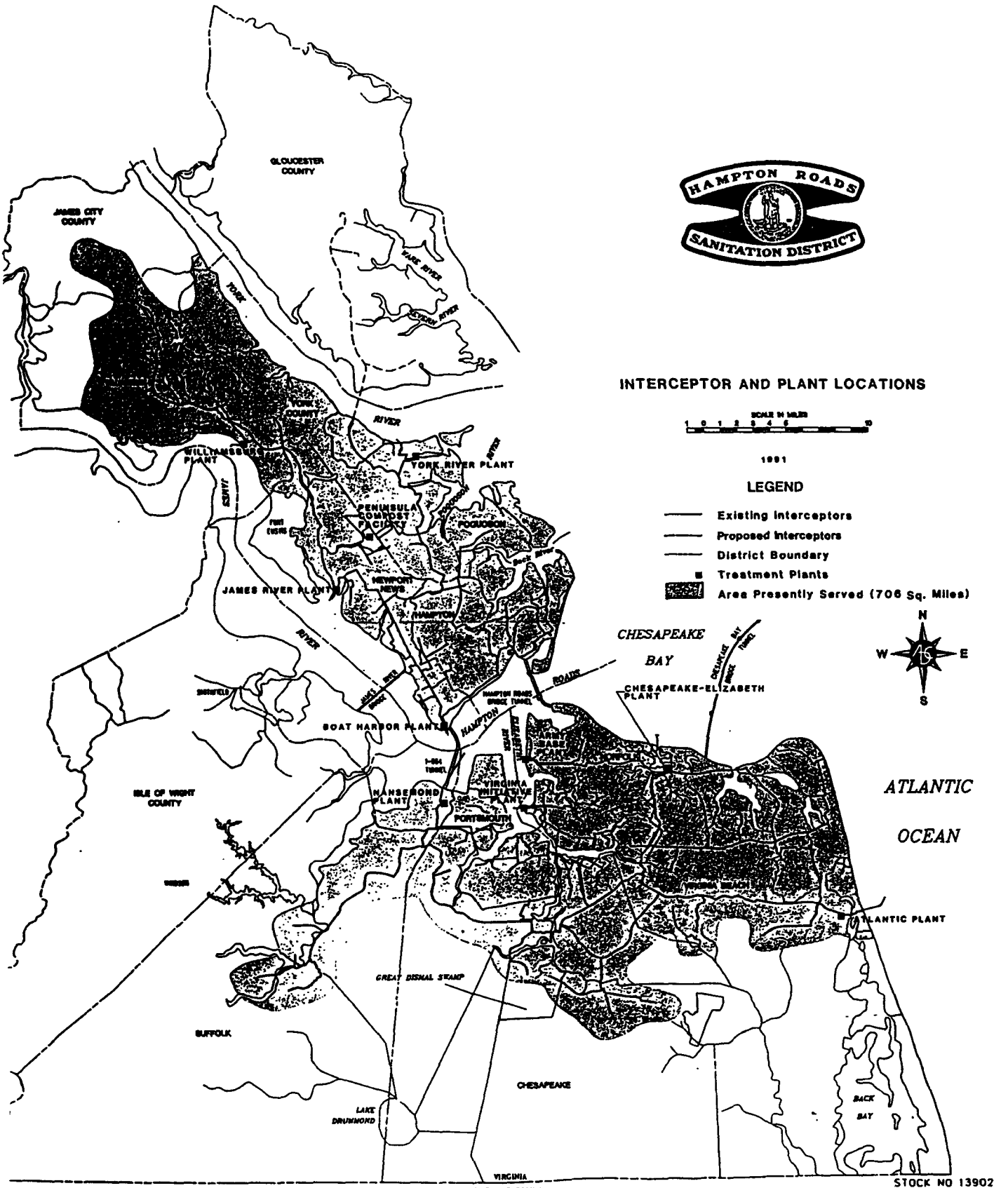
I would like to thank all the speakers today, and, if you would not mind, give them a round of applause.

Thank you.

(The Conference was recessed at 5:15 p.m., to reconvene the following day, May 5, 1994, at 8:45 a.m.)

HAMPTON ROADS SANITATION DISTRICT

" A HIGH SPEED AUTOMATED BOD SYSTEM "



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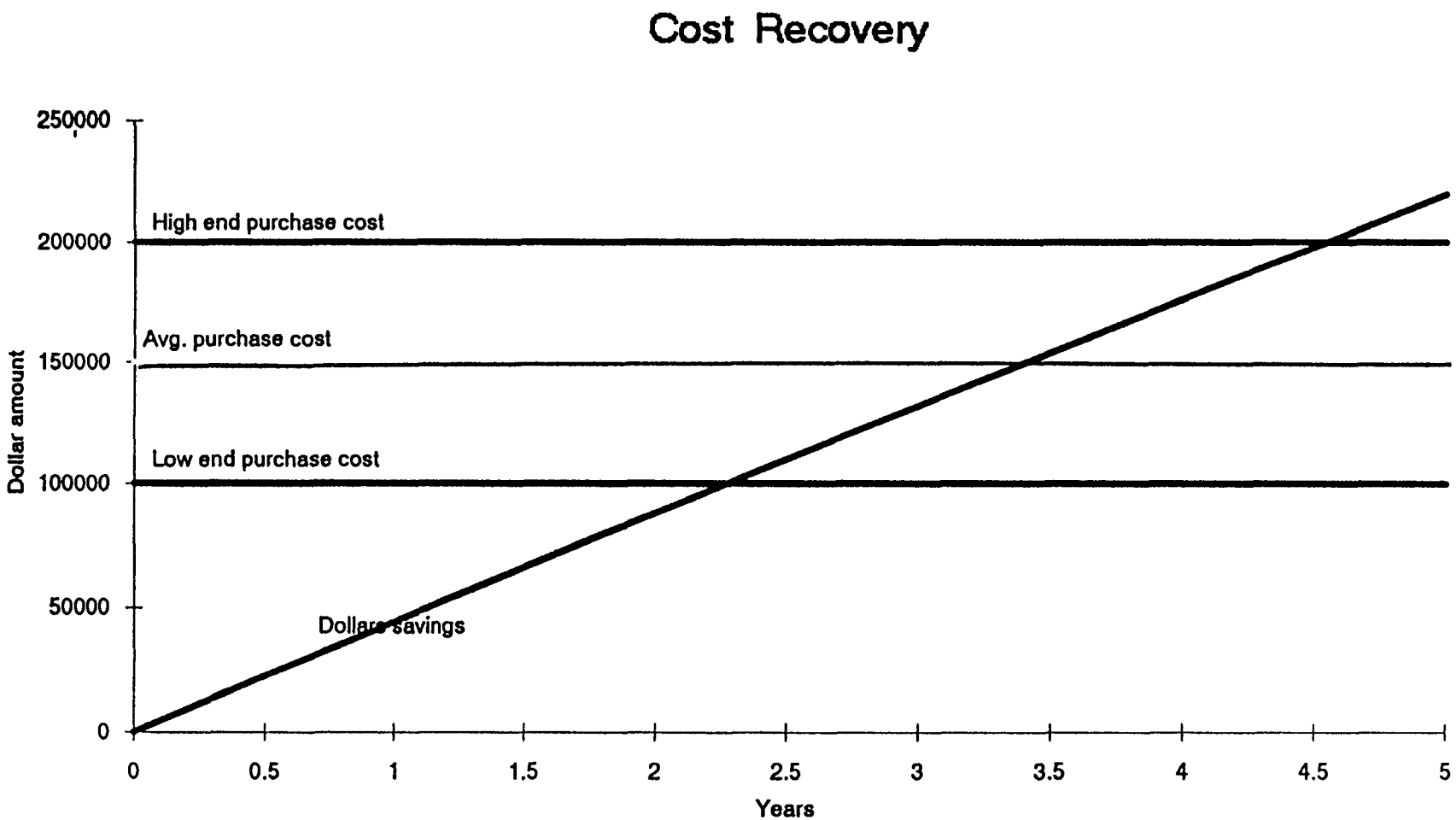
TASKS TO BE AUTOMATED

	TASK	TIME \ MANUAL PER DAY
1.	Reading (initial and final) D.O. conc	5.5 hours
2.	Filling BOD bottles with dilution water	45 minutes
3.	Adding seed material to BOD bottles	30 minutes
4.	Capping and uncapping bottles	15 minutes
5.	Calculating BOD concentrations	45 minutes
6.	Monitoring Q.C. data	15 minutes
	Total	**8 hours / Day**

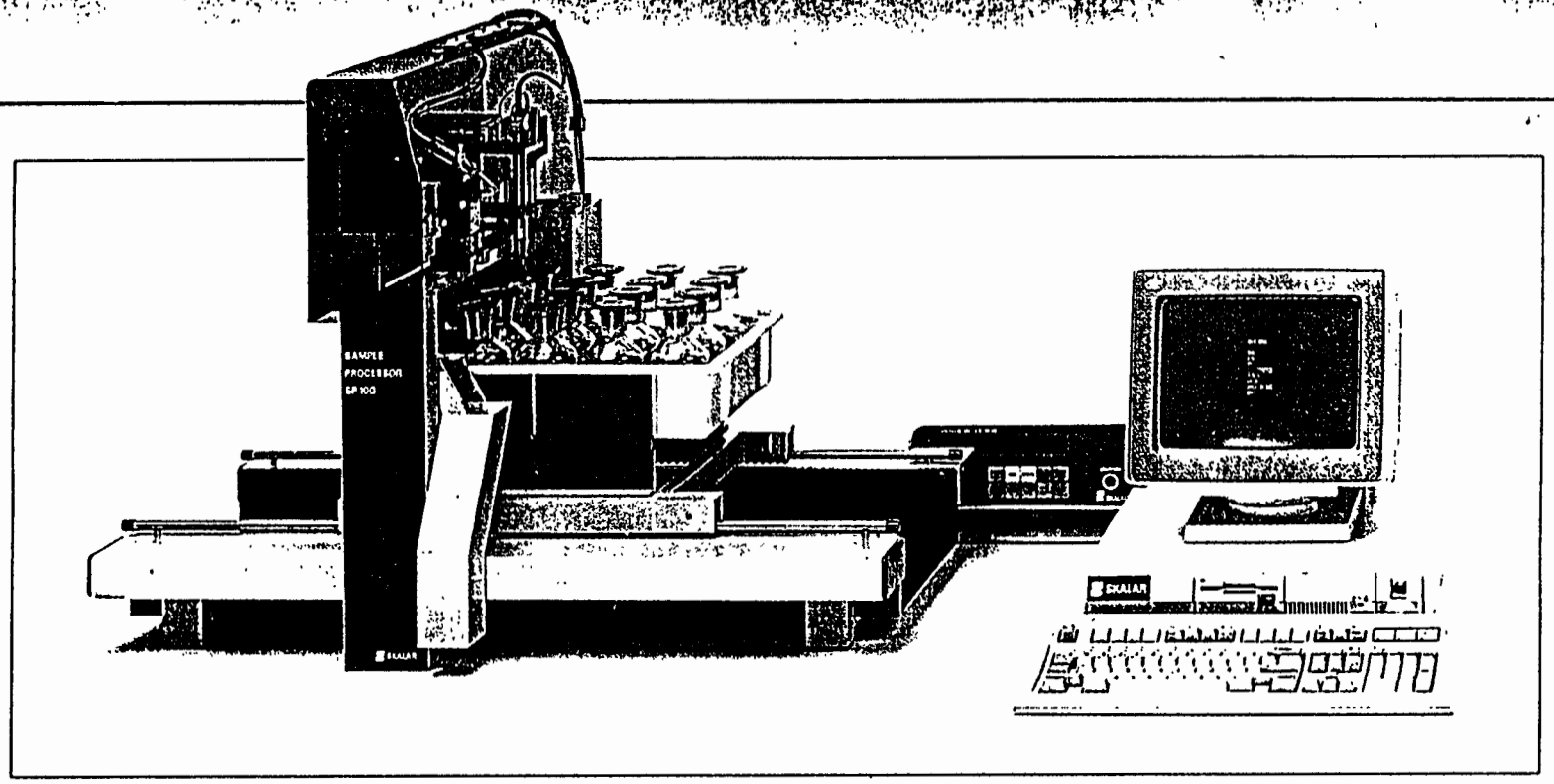

Cost Recovery
250000
200000
150000
100000
50000
0
Dollar amount
High end purchase cost
Avg. purchase cost
Low end purchase cost
Dollars savings
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Years

APPROACHES

1. Modification of an exiting system

2. Custom designed system

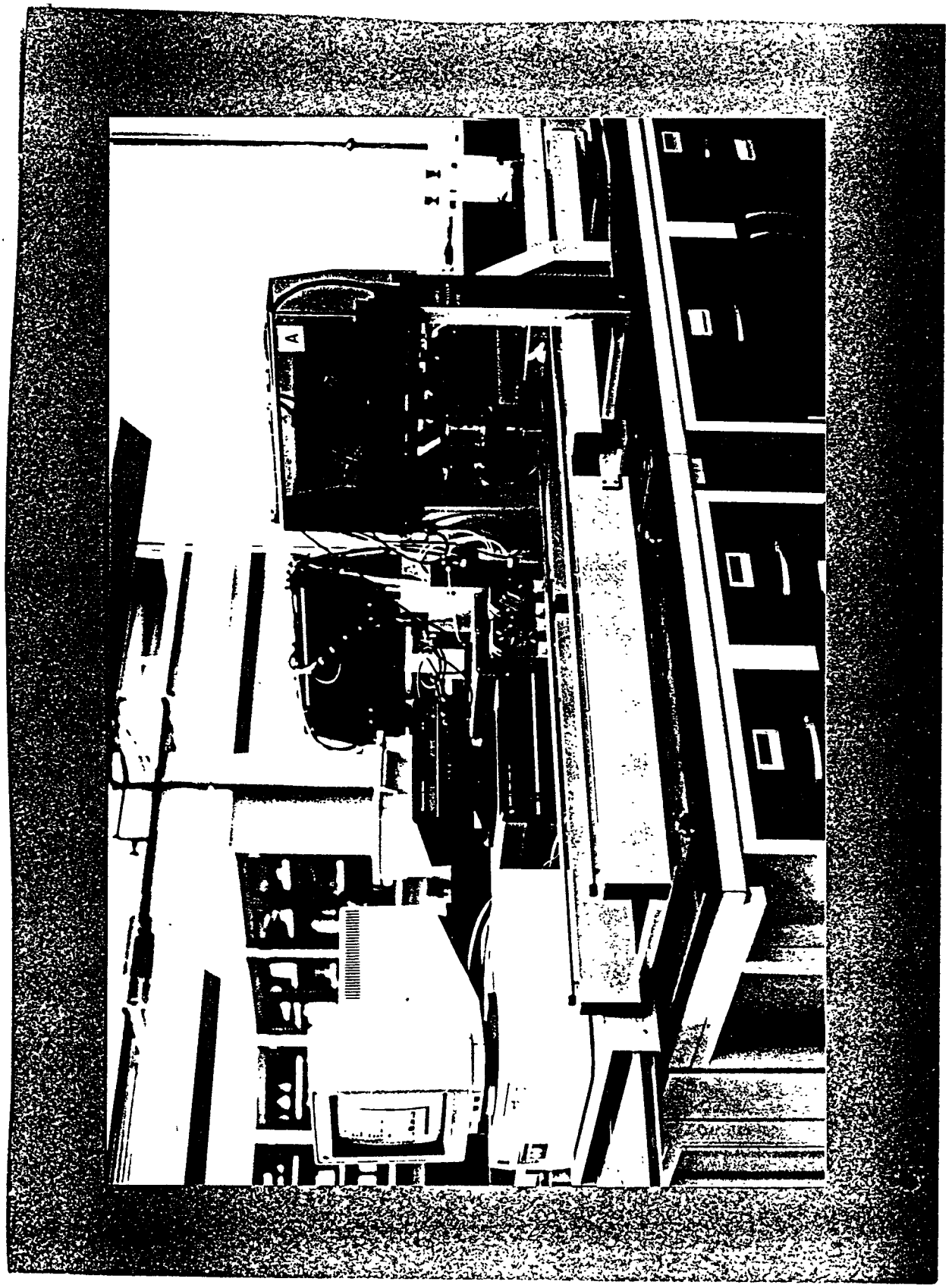
3. Three phase custom system

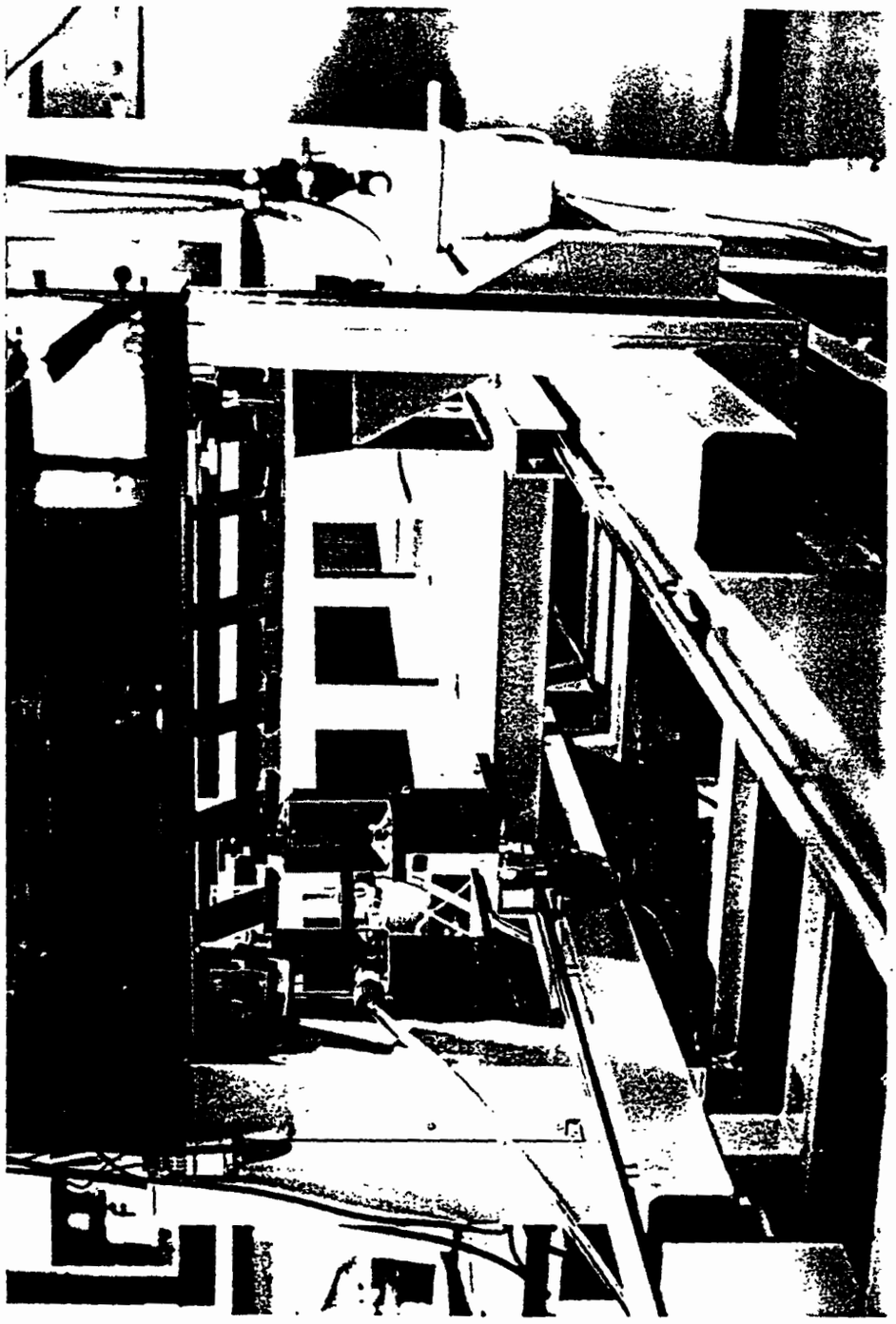


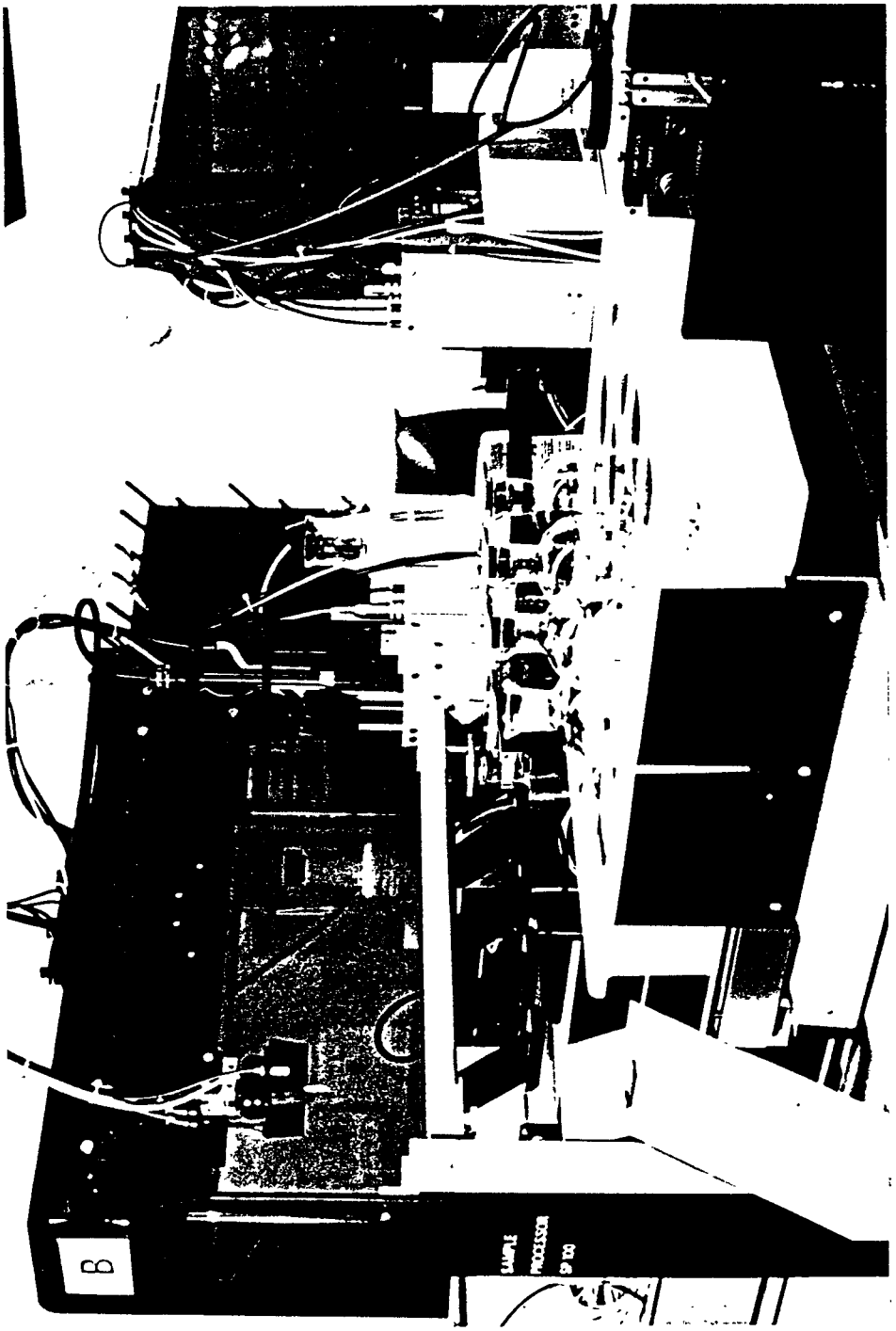
Application example - Biochemical Oxygen Demand

Sequence of operation:

- Sample I.D. s and dilutions are entered manually or via a


A
B




B
SAMPLE
PROCESSOR
SP 100

TIME TABLE COMPARISON

	Original	Actual
1. System' s modifications completed and delivered	60 days	90 days
2. System's on site set-up	7 days	21 days
3. System training for lab personnel	7 days	7 days
4. System evaluation	14 days	70 days (approx.)
Total time for automation conversion	**90 days**	**188 days (approx.)**

SYSTEM EVALUATION

Hardware

1. D.O. Meter and probe
2. Stirring mechanism
3. Bottle transfer system
4. Transfer pumps

Operational Software

1. Central control vs Instrument specific control
2. Initial and final D.O. operating steps
3. Rack I.D.
4. Multitasking
5. Recalibration

Analytical Performance

1. **Parallel Study**

   a. precision

   b. accuracy

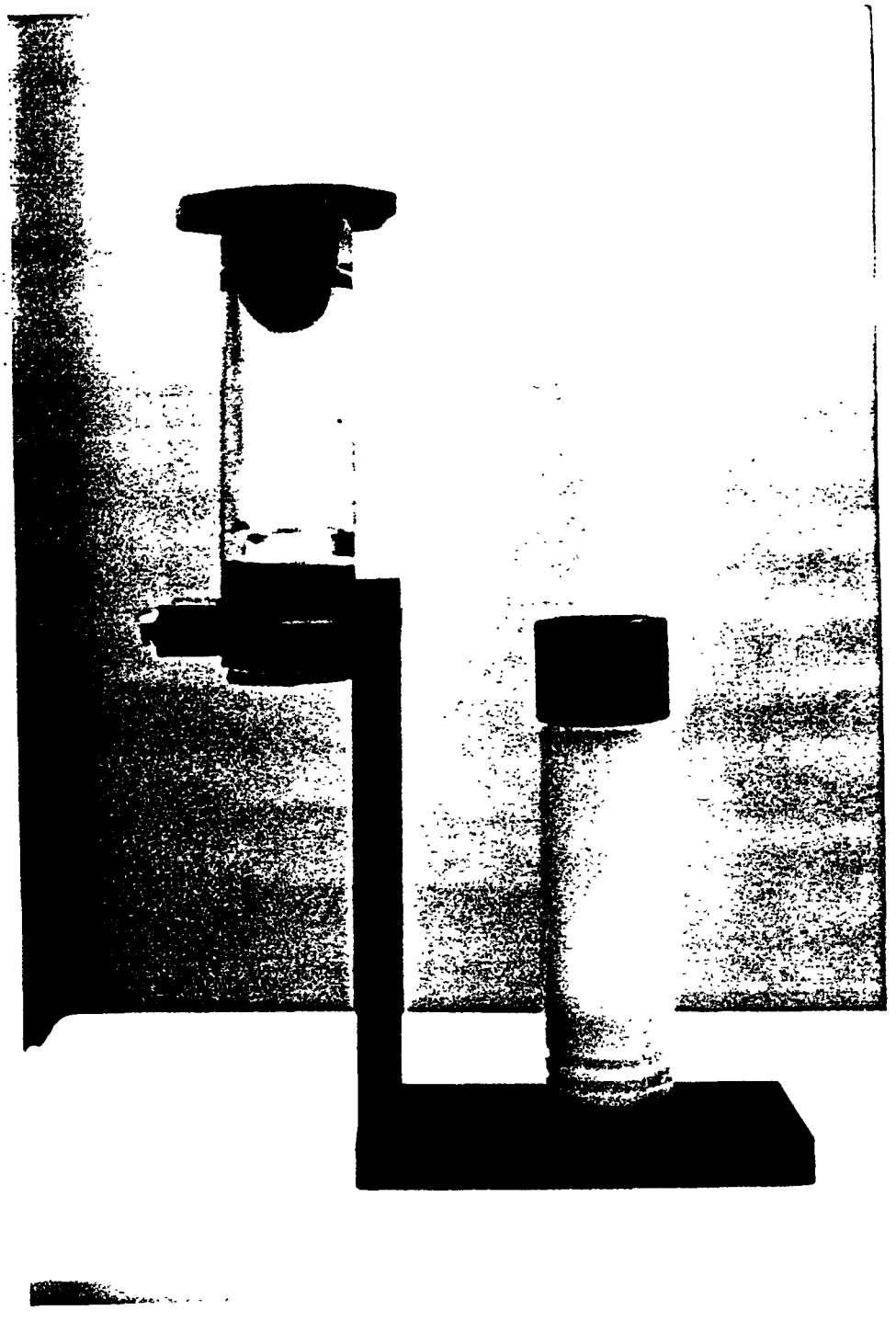
2. **Data evaluation**

   FIRST PARALLEL STUDY

   - 29% RPD
   - 19% Positive Bias

   Potential causes

   - Recalibration problem caused by calibration vessel



MODIFICATION OF CALIBRATION VESSEL

- 17% RPD
- 17% positive bias

Potential causes

- Calibration vessel and function

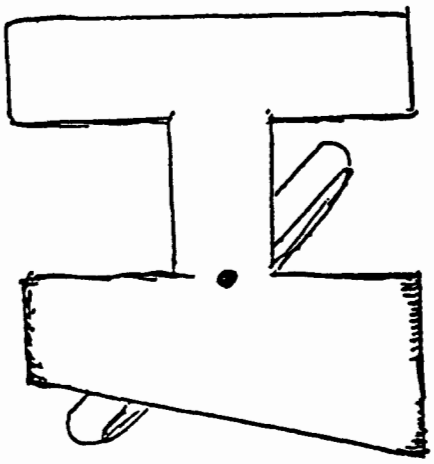
NEW CALIBRATION VESSEL

- 9% RPD
- 15% positive bias

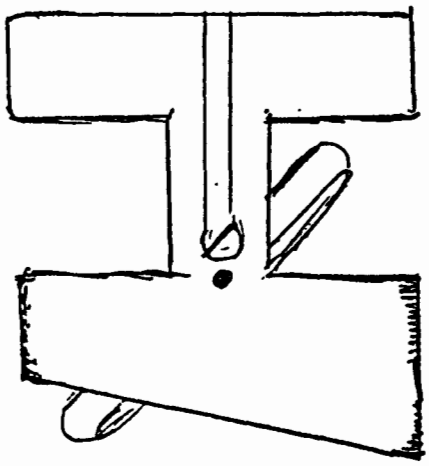
Potential causes

- Stirring mechanism causing membrane to warp

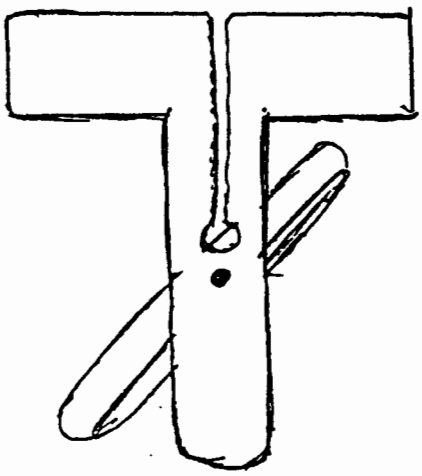
Original stirrer



Modified stirrer



Current stirrer



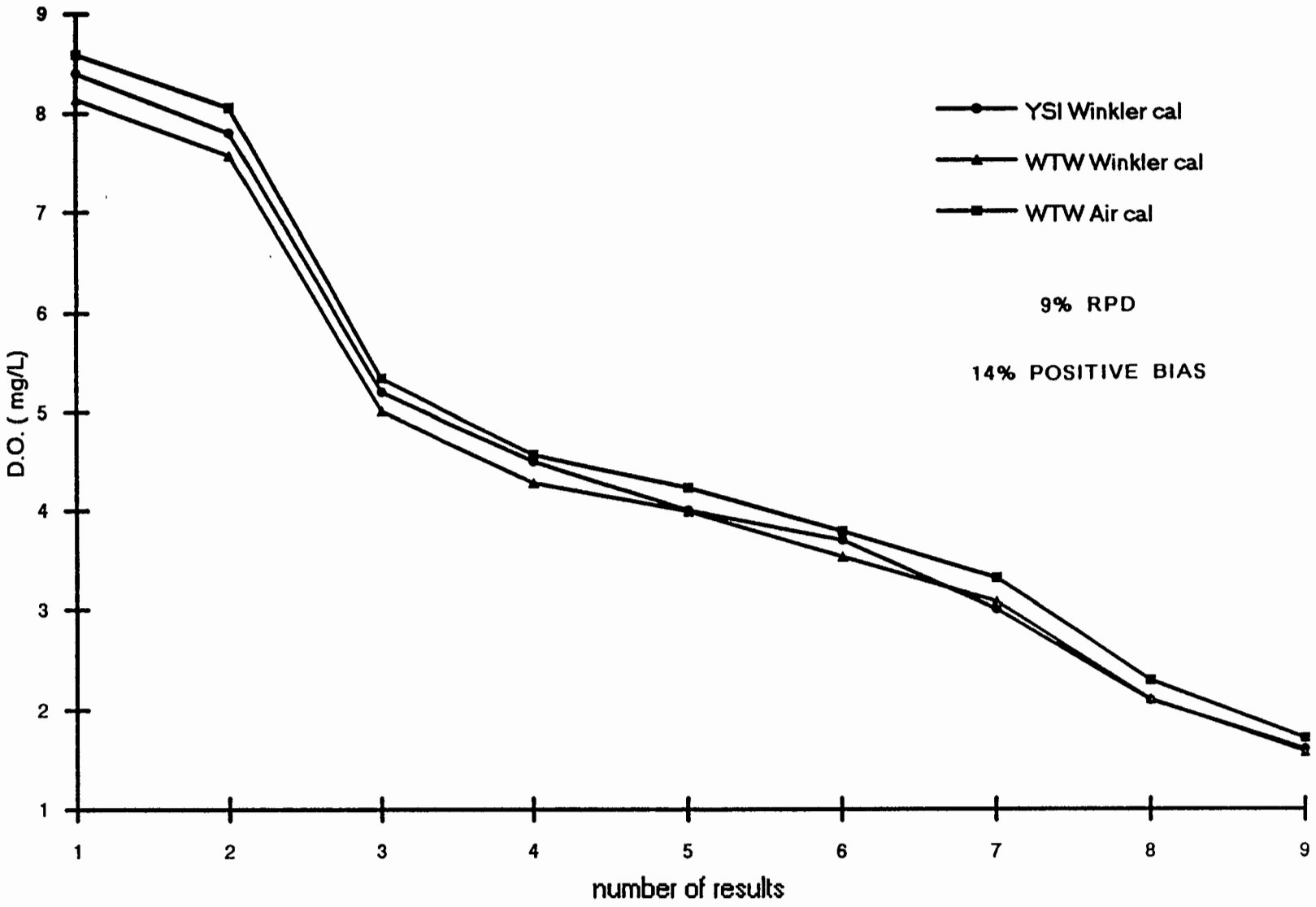
MODIFIED STIRRING MECHANISM

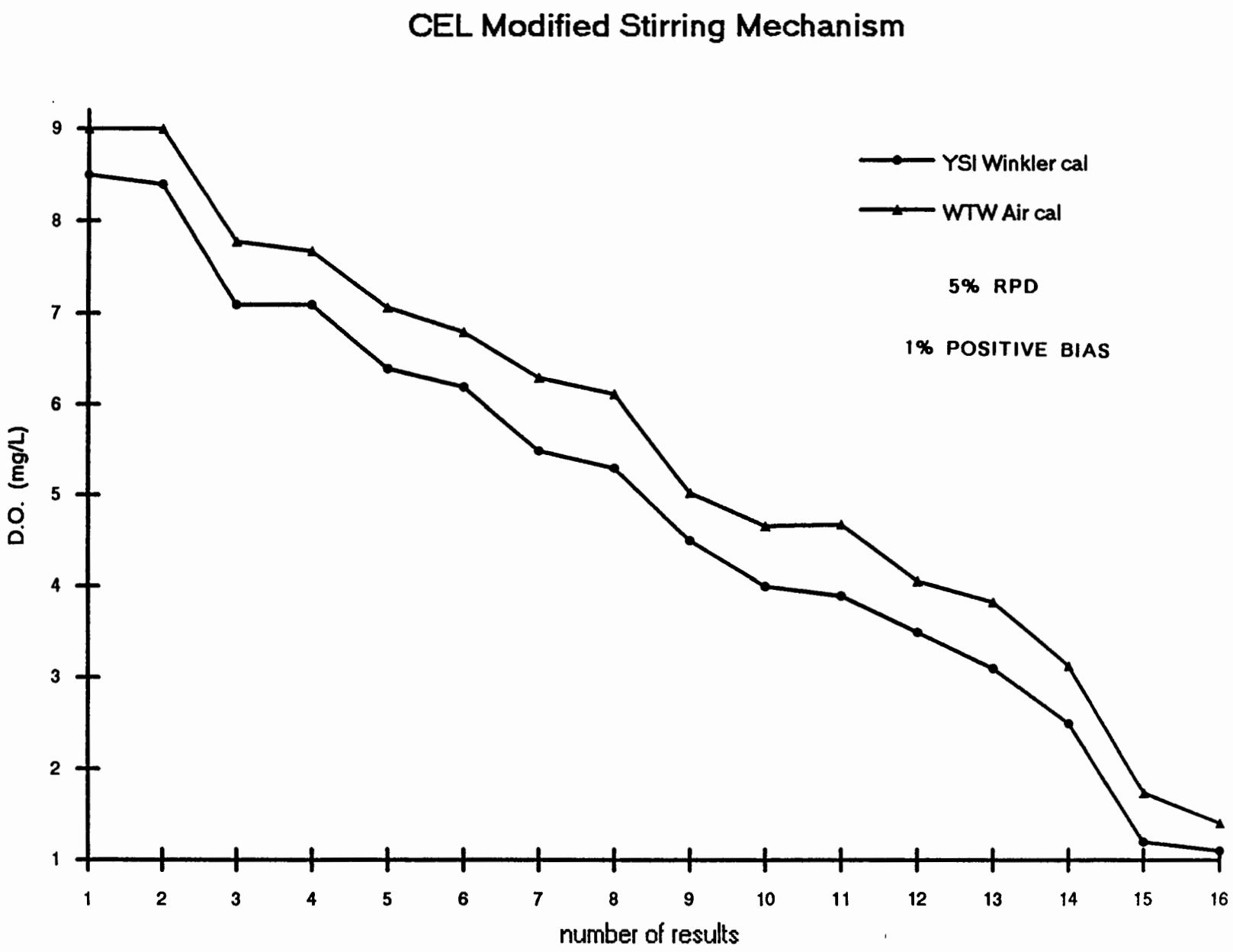
- 9% RPD
- 14% positive bias

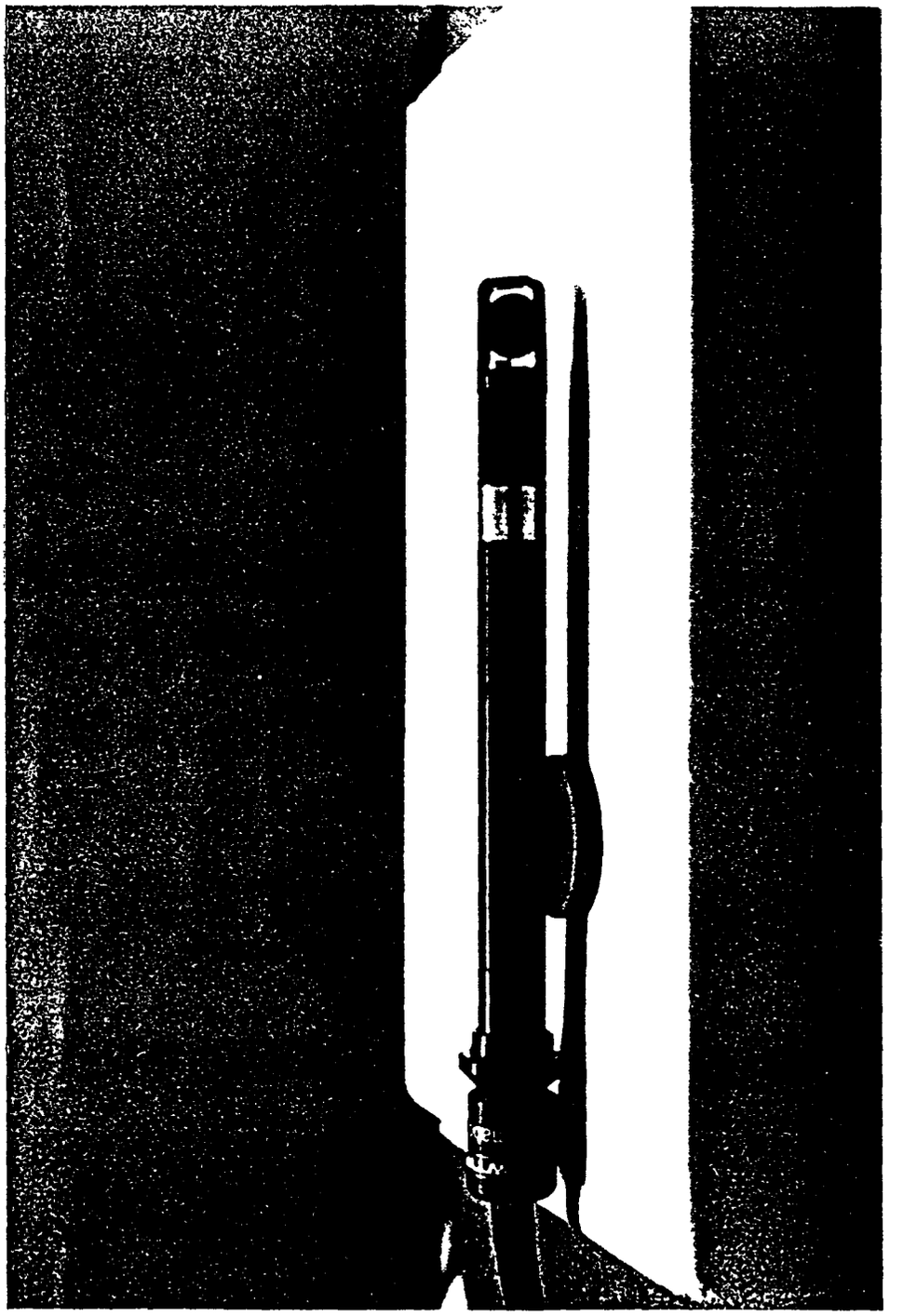
Potential causes

- Calibration method
- Stirring mechanism
- Filling and seeding

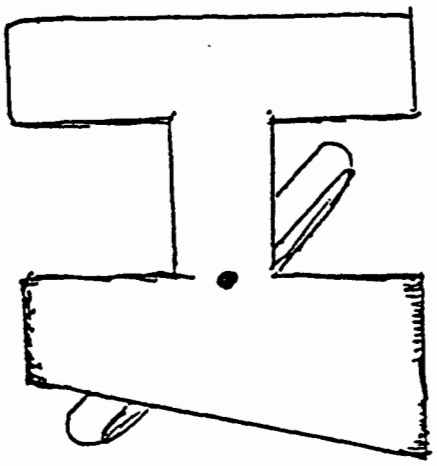
Meters and Calibration Comparison



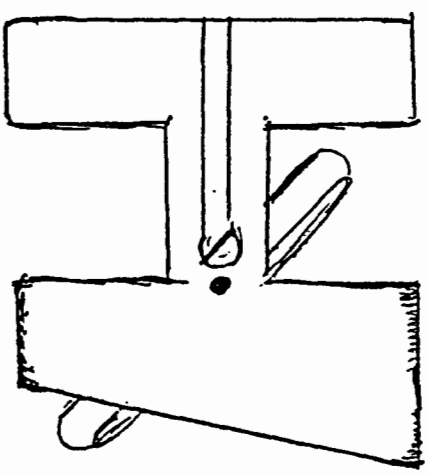

CEL Modified Stirring Mechanism
YSI Winkler cal
WTW Air cal
5% RPD
1% POSITIVE BIAS
D.O. (mg/L)
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
number of results



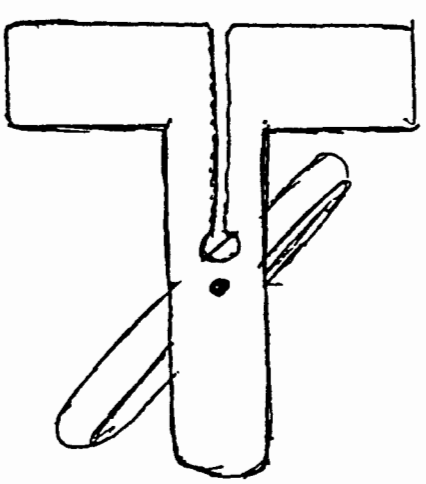
Original stirrer

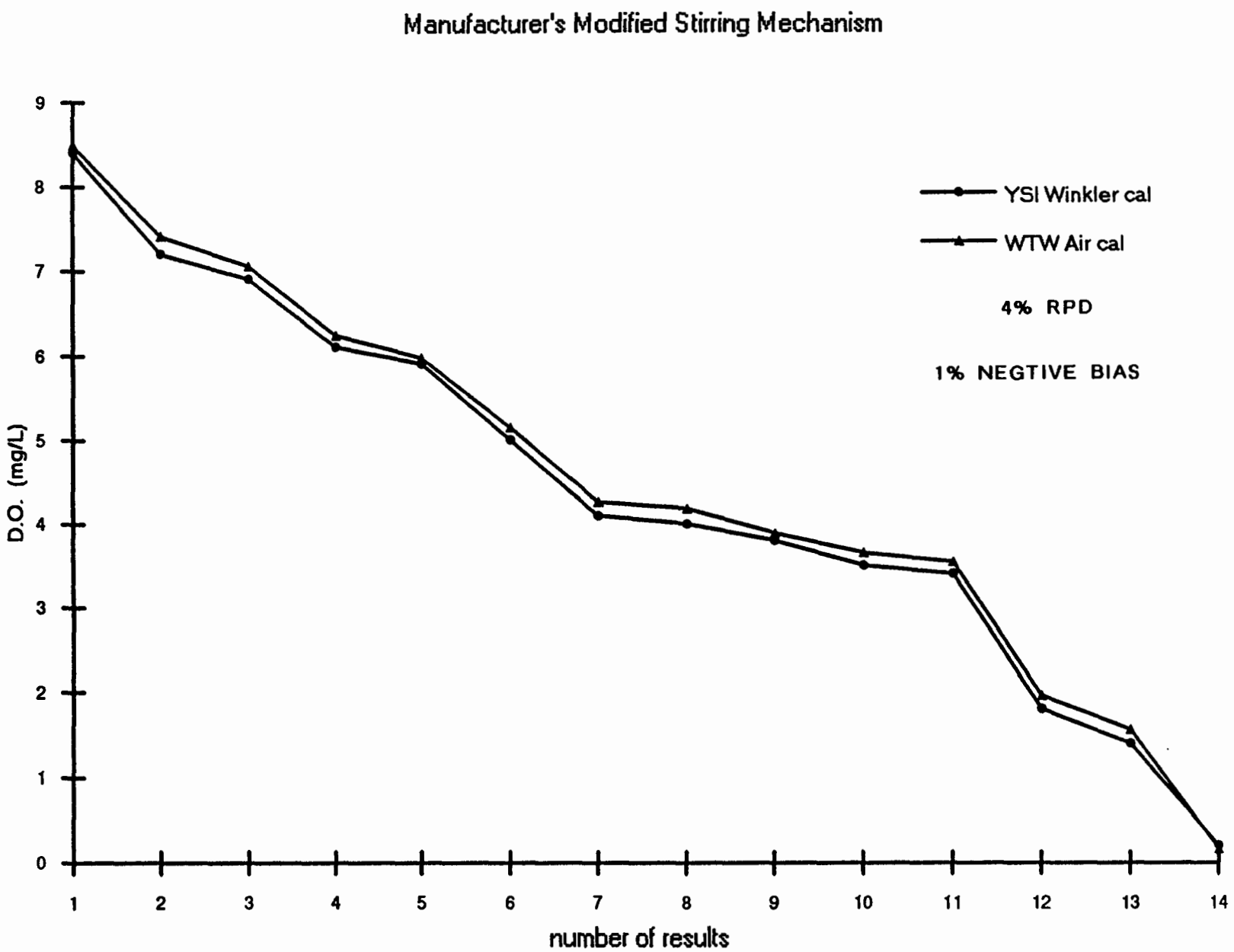


Modified stirrer



Current stirrer




Manufacturer's Modified Stirring Mechanism
YSI Winkler cal
WTW Air cal
4% RPD
1% NEGTIVE BIAS
D.O. (mg/L)
number of results
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

CONCLUSIONS

- Project size grew from a simple turn-key set-up into a joint system development.

- Large investment of personnel resources from the manufacturer and the District.

- Over-optimistic view of time frame needed for implementing automation.

- The project has shown the ability to accomplish our original goal of saving 8 manhours per day by successfully automating the repetitive, labor intensive tasks found in this analysis.

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MR. TELLIARD: Good morning. We would like to start our session today. As you notice, we have it broken up into a number of different areas. For those of you who have been pestering me all week about the statistical papers, you will have to wait a little while longer. Try to hold it together.

Our first speaker this morning is Bruce Colby. Bruce has been coming to these meetings probably about two meetings less than George Stanko. So, he is really an old-timer. At that time, Bruce had hair.

Bruce is going to be talking about the performance characteristics of isotope dilution as it relates to the dipstick, as I affectionately refer to it, and the volatiles method. As you know, over the years, Bruce has done a great deal of work for the Agency on the application and introduction of isotope dilution, so we welcome him back again this year.

Bruce?

PERFORMANCE CHARACTERISTICS OF AN ISOTOPE DILUTION HRGC/LRMS METHOD FOR VOLATILES

MR. COLBY: Thanks, Bill. I am glad to see everybody was able to get up after the cruise last night.

Actually, what I am going to be talking about is the incorporation of capillary columns into the method that the Office of Water uses internally and is available for people to use externally for measuring volatiles in wastewater. The method is isotope dilution GC/MS, and it is Method 1624.

The reasons...see that black thing forming in the middle of the slide? That is the film melting.

MR. TELLIARD: I think we have a...

MR. COLBY: We have a major meltdown here. We better shut that off, Lee.

MR. TELLIARD: These interactive graphics are really neat.

MR. COLBY: Okay, here we go. I have got to move these pretty quick, because it seems to melt them about as fast as they get up there.

Well, okay, why are we interested in high resolution gas chromatography or capillary columns? The real reasons are that wastewaters are pretty complex, usually, and they tend to have a lot of interferences in them. With the capillary columns, we can separate more components, one from the other, so we can minimize the interferences. Also, because the peaks are very narrow, typically, we will have better sensitivity. I will mention some more about sensitivity as we go along, however. In addition, the newer GC/MS instruments that are available typically do not support packed column interfaces except as sort of afterthought items, because the packed column technology seems to be fading into the background. The final thing is that the capillary column methods basically are more rugged than the packed column methods.

The goals of the work that we undertook were to retain as much of the method 1624 procedural steps as we could. We wanted to keep the calibration solutions. We wanted to keep the QC procedures, both initial and ongoing, the same as they were with the packed columns as much as possible. In order to do that, though, we had to back off on one thing, and that was the Method 1624 requirement that specifies analyte retention times. That was a requirement that was put into the method initially to make sure that people did not run their GC temperature programs at warp 9, get the run-over in 10 minutes and have all the compounds come out at one time. The goal was just to make sure that there was some decent chromatography going on.

Well, the way we elected to hook up the columns...and I am going to talk about both a narrow bore and a megabore setup and show you a comparison of the results from the two...was to hook the purge and trap device up to the GC/MS instrument via a splitter, and that can either be a splitter at the injection port of the instrument if you are hooking it up through an injection port, or it could be a swage lock T fitting with a needle valve on it or something like that.

This kind of a setup is pretty nice. It is very simple to work with. It works best with newer instruments that are very sensitive, because we are going to throw away a fair amount of the material going into the instrument.

The actual hardware that we used was an OI purge and trap, Hewlett-Packard 5890 GC and Fisons MD800 mass spec.

The way we set up an instrument like this involves an optimization process whereby we set the split ratio at some value. Typically, we would set it at some low split ratio, so we are not throwing away much of the material. We then run a standard and see what the peaks look like. What we are looking for are nicely shaped peaks.

One of the problems with capillary columns and purge and trap desorption instrumentation is that the flow rates from the purge and trap device typically are quite high, whereas the flow rate through the GC column is relatively low. We have got to match these things, so we use a splitter to match the flows.

Anyway, we look at the peak shape, and if it is not acceptable, we split off some more material, and we go through that cycle until we get good peak shape.

Then we run a set of five replicates. It could be a smaller number, but five is a good number. We look at the precision.

If the precision is not good enough and the method has some specifications in it, then we would increase the split again.

The reason that we increase the split is that it allows us to throw away more water. Basically, we are getting water out of the system by doing this. The more water we remove from the system, the more precise things are.

The water interacts with the column and affects retention time precisions. When water is co-eluted with analytes, it affects the precision. So, we want to throw away a fair amount of the water.

Well, what we see if we look at the peak width which is one of our key things, basically, in looking at peak shapes is that at low splits...here I went all the way down to a 1:1 split...we get fairly broad peaks, and as we increase the split ratio, things kind of narrow down. They continue to get narrower as you go out, and we only went out to about 20:1 there, I think, and things will get narrower as you continue on until you have split off everything and can't see anything at all anyway.

What is important here is to see that you can actually get away with a fairly small split. A 4:1 split will actually give you reasonable peak shapes.

If you look at this in terms of what I call sensitivity, the peak heights are smaller per unit material when the peaks are wide. That is what you expect. It is like a triangle. When it is wide at the bottom, it is not very tall.

So, as we increase the split, things go out until you get to a relatively constant situation at somewhere around 5 or 6:1 or so. So, it is clear that we can work with fairly small splits if we need to, but we can use very large splits as well.

If we look at the retention time precision that we get with a number of various splits, one thing we see with a 1:1 split is that the precision is not particularly good for the retention times.

The reason for that really goes back to the amount of water that is going on the column. The water interacts with the column material, and as you run and add more and more water to the system, if you don't really bake it out for a long time between runs, then the retention times start to shift a bit.

As we go to more split, then we start to see more precision in the retention time. So, clearly, there is something that we need to be pretty careful with here.

The precision of the areas that we get with these different kinds of splits is shown here. With the 1:1 split or a small split ratio, the precisions are not very good. Again, this is pretty much a function of the water that is in the system.

Now that we realize that, we could probably go back and put a long bake out cycle in between each run and improve the precision at a 1:1 split, but there are other things that cause us not to want to use that kind of a split anyway.

So, basically, anything that has got a split of about 5 or 6:1 or more gives us nicely reproducible results both in the retention time sense and in the area sense.

The conditions that we used for the narrow bore column are shown here. Basically, it is a 60-meter, 0.32 ID column, one that is geared towards volatiles analysis. We use a temperature program that starts out at 40. We hold that for 6 minutes, and then we use an 8 degree/minute ramp up to 160, and then ramp it up fairly quickly up to 250, and then we hold it.

We hold it for 10 minutes, again, to bake out the water. We want to make sure that water is out of the column. It is a really important thing to do.

The megabore setup is shown in the next slide. It is a bit more complex than the narrow bore, because we now are adding a second splitter to the system between the GC and the mass spec. This is effectively an open split interface type thing. In some circumstances, we actually might want to add some makeup here or some makeup here to adjust the flows around.

Now we have got flow from a purge and trap device that is reasonably compatible with the GC, but if we put all the water that the purge and trap device puts out into the GC column, we have reproducibility problems with the retention times and with the areas. So, we do have to eliminate some of the water and we do that using this first splitter, and then the second splitter is just to match the flow rate from the column with the gas load allowed into the mass spec.

The optimization process for the megabore system is a bit more complicated. Basically, we start out at some split and run a standard, check the peak shape, and if it is

not good enough, then we increase the split at the injector, the head of the column. We are trying to get that peak shape right.

Then we go and we start to run some replicates, and we look at retention time precision. If the retention time precision is inadequate, then we increase the split at the injector again. So, we are trying to increase the split at this stage to get our chromatography working well.

Once we have satisfied the chromatography requirements, then we start looking at the reproducibility of the areas that we get. If they are not reproducible enough, again, we probably want to get rid of more water somewhere.

We can do that either at the injector or at the open split end. It does not really matter too much. Typically, we would increase the open split a little bit and throw some material away there.

If you throw away too much material on a megabore and cut the flow rate on the column down, then the peak shapes starts to go away. Again, I want to emphasize that if too much water gets on the column, then we start to have a problem.

Well, the GC conditions for the megabore data that I am going to be showing are for a 75 meter, 0.53 ID column, same coating as the narrow bore. Temperature program is quite a bit similar to the other one. We have an initial 40 degree setup for 4 minutes, then 9 degrees to 200, and then we ramp it up fairly quickly to 250 and hold it, in this case, 20 minutes.

The megabore system gets a lot more material on column, so we have to hold that final temperature longer to bake the water off the column. It is quite a long hold.

The split ratios we ended up with were a 3:1 split at the injector and a 7:2 split at the...in between the mass spec and the GC. Total split for that actually comes out to be about 10:1, I think 10.5:1.

The chromatography that we get from these systems is shown here. You can see that the narrow bore produces a very nice set of peaks, as does the megabore, compared with the old packed column type runs. The runs are shorter, but, again, keep in mind that we had a bake out period involved in these.

Actually, this last peak in both of these is some hydrocarbon. I don't know why it is in there, because it is not a compound in the standard.

So, your run actually can end at about this point here, but you have got to bake the system out and make sure the water is gone.

One thing that is worth noting here is the water peak in the packed column is this. This is how much material would go on the column if we put everything in, and this is quite a bit of water.

When we go to the megabore now, we have thrown away quite a bit of the water, so we get a much smaller peak. It starts to look like a real GC peak, and with a narrow bore, it is just a very small amount of water that is getting in there, because we split away quite a bit of it at that point.

So, you can see that the water goes away very effectively as we go to the narrow bore arrangement.

The cycle times for the runs looking something like this. I put a packed column run up there. It is the little dotted line here. You can see that it runs out to 45 or 50 minutes, normally, in terms of cycling from one run to the next.

These long hold times are out here to get rid of water and, in some cases, to make sure that some of the heavier material that is purged from the sample actually is run through the system. So, we do that to make sure that run number 2 is not impacted by some of the chemicals that were in run number 1.

You can see that the narrow bore column does save some time, roughly 10 minutes, so your analytical efficiency can go up a bit.

The acquisition actually ends right about here where that higher ramp comes into play.

The things that we note in the chromatography in going to the capillary columns, well, obviously, there are going to be lot of changes in relative retention times. Also, we see things like separation of cis- and trans-1,2-dichloroethenes.

There is a swap between co-elution for packed column ortho- and para-xylene to meta- and para-xylene being co-eluted, and there are also a variety of separations that are challenging, and we have to pay attention to them. We need to be careful with dichloropropene or 3-chloropropene and carbon disulfide. They have to be separated. They have some common masses that can cause problems.

Chlorobenzene-d_5 and 1,1,1,2-tetrachloroethane, these are closely eluted if the chromatography is not good enough. Again, we run into some problems with the measurements. Isobutanol and benzene-d_6, and so on down the line.

One, in particular, that was interesting was that vinylchloride and methyl ether-d_6 were found to closely elute, and they come out very early in the run. The methyl ether-d_6 turns out to be an impurity in the methanol that the labeled analogs are spiked into, and it

has a spectrum that, unfortunately, looks quite similar to the vinylchloride. If one is not careful, it could be confused quite readily.

The analytical precision that we get out of the systems is shown in the next slide here. The solid line shows the required precision for the...these are the naturally abundant materials. This is the requirement for the method. You have to be essentially below this line to be producing acceptable data.

You can see that the data, both for megabore and for narrow bore are all well within the envelope. There are a few that have less precision than others. These are typically the more polar compounds that do not purge particularly well. Consequently, there is not as good a sensitivity for those compounds.

The recovery of the analytes that we are dealing with looks something like this. Here I have got another envelope, the upper acceptable level, and this blue line that is down in here, a little harder to see perhaps, is the lower acceptable level. Some of them, incidently, are down at zero, so if you do not see them, it is still okay. That is what the statisticians told us it was supposed to be.

Anyway, the results that we get are almost always right along the 100 percent recovery line which is what we would hope they would be, with an occasional deviation. Usually, those have something to do with some minor interference in a spectrum from some other material.

The recovery of the labeled analogs which, again, have acceptance criteria associated with them. Again, I have shown an envelope of what those recoveries are.

You can see that the labeled analogs that we have spiked in mostly come back at 100 percent. There are a few gaps in here that are not analogs that were not actually in the solution that we ran. So, those are not absent because we could not see them; they are absent from the data because they were not really there.

Again, everything is well within the Method 1624 acceptance criteria.

There are also some minimum levels that are identified for Method 1624, the minimum level being, I think, 3.18 times the MDL, and then you take that number and round it to some 25 or 10 type number.

Anyway, when we do the ML calculations, we come up with MLs that are all below the method requirements with the exception of one compound here. This is actually 2-chloroethylvinyl ether, and it is a fairly polar compound. It was only a problem in the megabore run, and I think that it is a consequence of some artifact in one of the runs. I believe if we re-ran it, it would fall inside with the rest of them.

We also have one compound that is quite high, but its ML does fall at the minimum level that is required by the method. I think that was dioxane, again, a polar compound with polar compounds not purging quite as well.

So, in conclusion with respect to capillary columns and Method 1624, it seems clear that the capillary columns satisfy all the Method 1624 acceptance criteria, again, with the exception of absolute retention times which, obviously, are going to be substantially different than they were with the packed column.

The capillary columns are quite easy to use. The narrow bore setup that we used was easier than the megabore setup, because there were not as many splits to control and fiddle around with. We really prefer the narrow bore to the other.

I should point out that neither of those systems required any cryogenics which was something we were very much interested in avoiding. They are one less thing to have to deal with.

The narrow bore column data, in general, was slightly better than the megabore data, but they were really quite similar.

I would like to thank Bill Telliard for supporting this work and answer any questions, if there are any.

QUESTION AND ANSWER SESSION

MR. COMO: Joe Como from HK Testing. What about the column head pressures and the total flow rates on the megabore? What were they and how did you deal with controlling those?

MR. COLBY: The head pressure on the megabore was controlled really with a needle valve at the splitter, and if we needed more head pressure, we would put makeup into it, just run it in with a regulator.

MR. COMO: How was the control dealt with in that situation?

MR. COLBY: I don't recall that right off hand. This work was done a while back, but it would be sort of normal for megabore, and you can adjust how much flow goes through and how much of your sample goes through by adding makeup if you need to. There is a lot of flexibility in there to control that.

MR. COMO: In the narrow bore?

MR. COLBY: We just split more and more off and jam more and more gas through in the other direction.

MR. BOLT: Dan Bolt, Cambridge Isotope Labs.

I just had a question. I know that in 1624, there is a means to deal with labeled surrogates which separate chromatographically from their native analytes, and whether you saw more of that with the cap columns. Maybe we should go to more 13_C instead of the deuterium.

MR. COLBY: There are more that are separated. It does not really seem to make much difference whether you use 13_C or whether we separate them or not. If they are separated or not separated, it doesn't seem to be too much of a problem, but there are some where a 13_C might be better, and there are some where none of the labels that we have available are really very attractive.

Acetone is probably one example. With acetone-d_6, all deuteria that are alpha to a carbonyl. They tend to exchange, so you have to be pretty careful with acetone, but that is really the only one that causes us much of a problem.

MR. CORL: Ed Corl with the Navy Public Works at Norfolk Naval Base. I don't believe I heard you say what type of trap you used in the purge and trap.

MR. COLBY: We were using the most recent trap that Sepelco is producing. It seems to be a little more effective with water than the others.

MR. PRONGER: Greg Pronger, National Environmental Testing. How did you interface a transfer to the column? Did you go direct to the column or through the injection port?

MR. COLBY: We just hook them up with a swagelock T fitting. We come out of the purge and trap with the existing tube into a T fitting. We actually try to run the end of the column up a little bit into the tube that comes from the purge and trap and then put a needle valve on the T sidearm.

MR. PRONGER: Thank you.

MS. KHALIL: Mary Khalil from the Metropolitan Water District of Chicago. In my lab, I have the VOC analysis by megabore column, capillary column, and the method jet separator, and I also do not use cryofocusing, and I have very good recovery of all the gases and everything. What is the advantage of with the split over what I do in lab? Like just to avoid the jet separator?

MR. COLBY: We went with the split because it is a very clean system to work with. The less material we get into the column and into the mass spec, the fewer times we have to take it apart and clean it, and the fewer times we have to replace the columns. We just did not want to use the cryofocusing, and it allowed us to avoid that.

I think there are ways you could do it with megabore and not use cryofocusing, but narrow bore gets pretty tricky if you do not use a split.

MS. KHALIL: Yes, but I think the method jet separator is doing the same thing, but I think the main...maybe the disadvantage of jet separator you have just to watch very carefully performing samples or something like that, but, still, it gives very good separation.

Thanks.

MR. TELLIARD: Thank you, sir.

Isotope Dilution HRGC/LRMS Volatiles Analysis

Bruce Colby & Lee Helms

Pacific Analytical
6349 Paseo Del Lago
Carlsbad, CA 92009
(619) 438-3100

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WHY HRGC

- Fewer interferences
- Better sensitivity
- Supported by newer instrumentation
- Generally more rugged with complex samples

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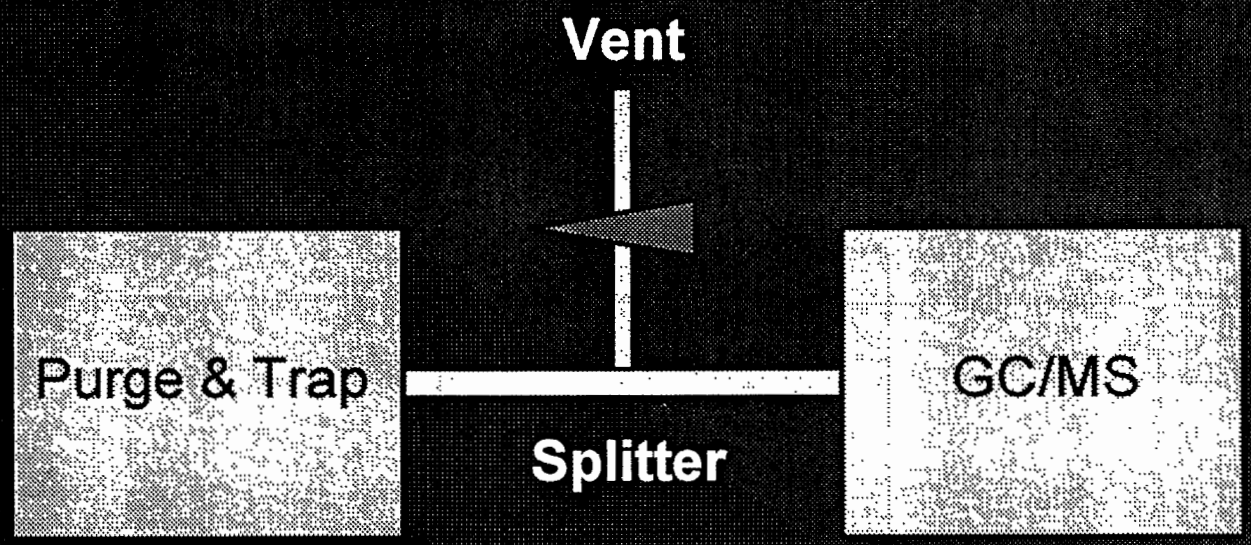
STUDY GOALS

- Retain calibration solutions & procedures
- Retain initial QC acceptance criteria
- Retain on-going QC acceptance criteria
- Allow flexibility with absolute retention times

PA

NARROW BORE HOOK-UP



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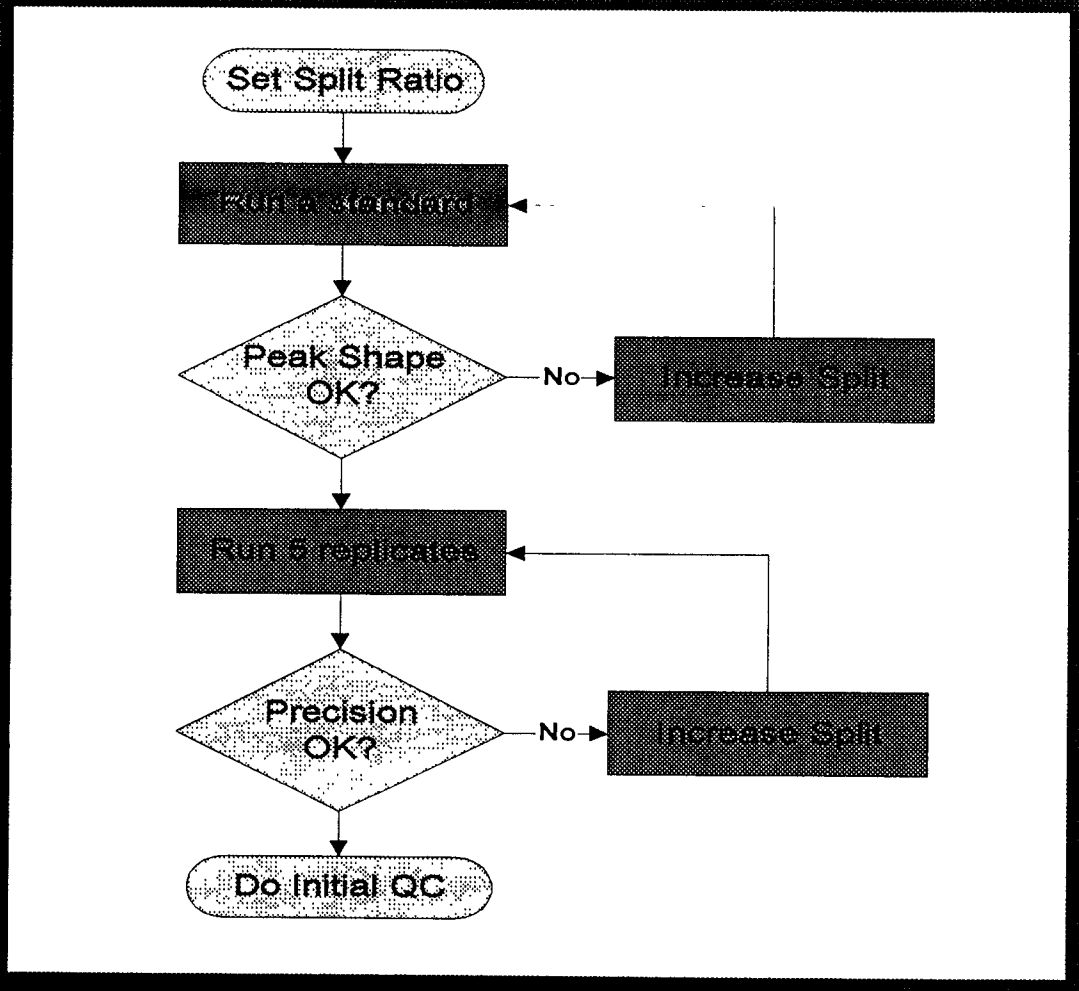
OPTIMIZATION PROCESS



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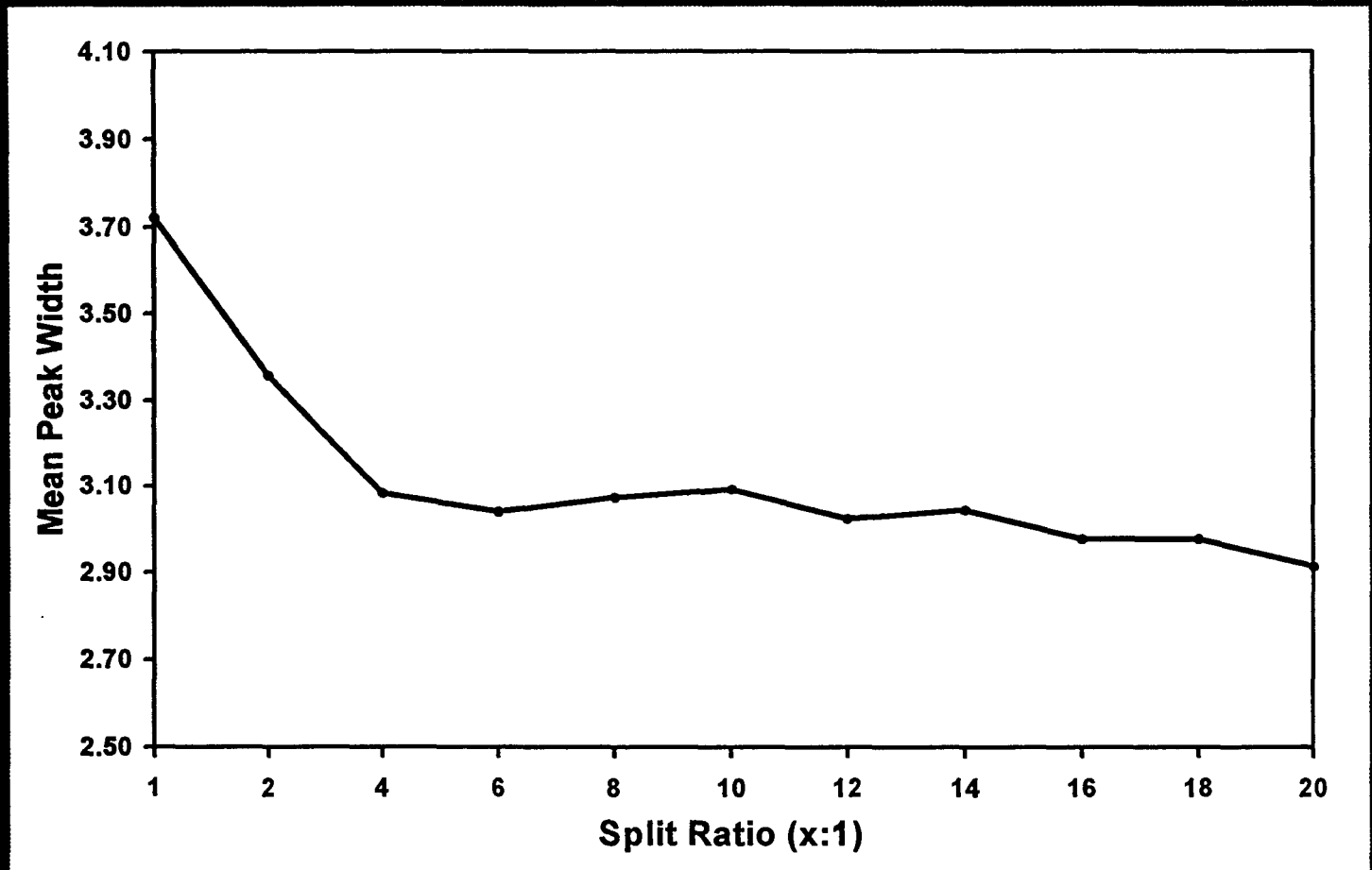
PEAK WIDTH (narrow bore)



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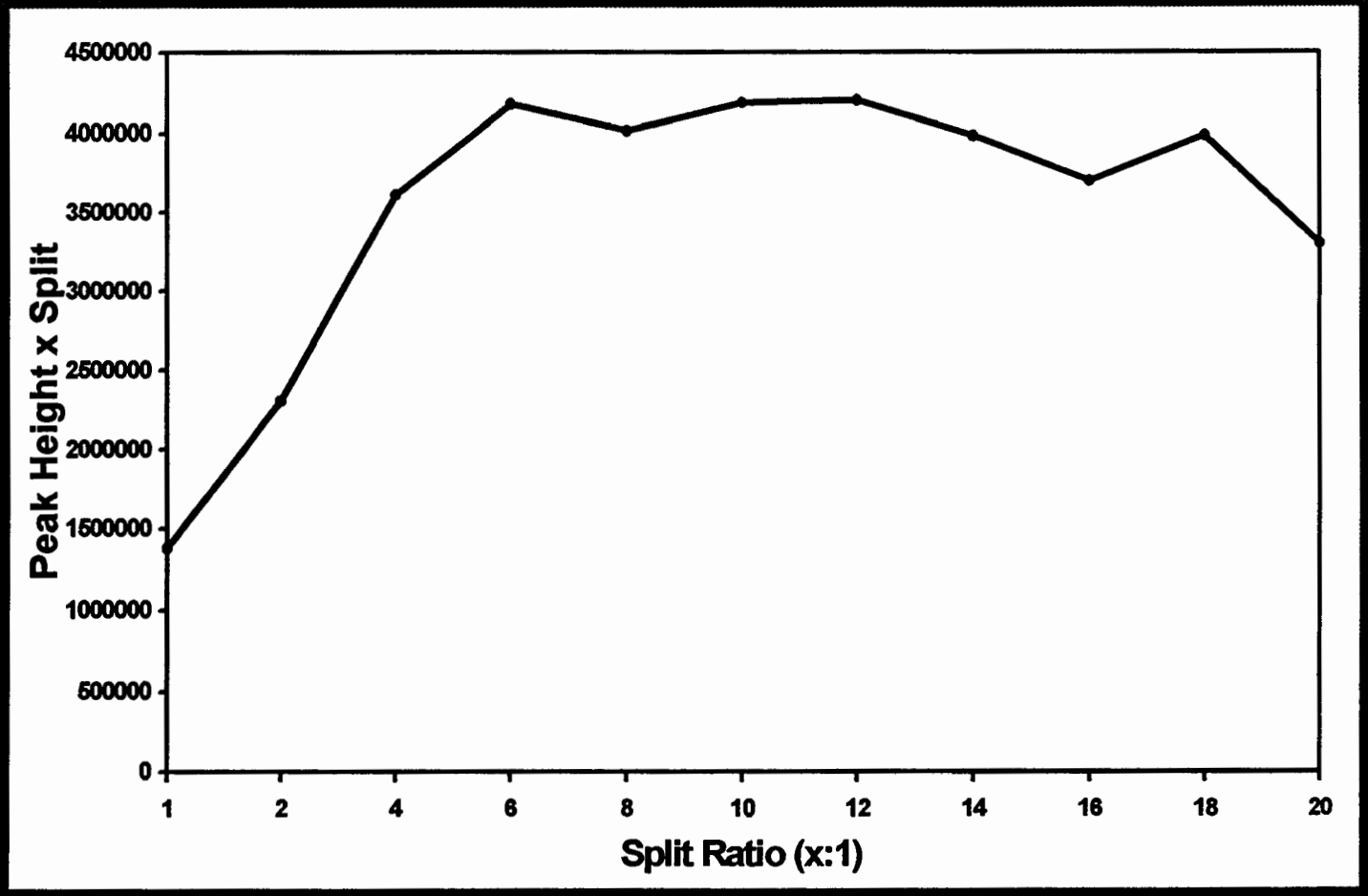
SENSITIVITY
(narrow bore)



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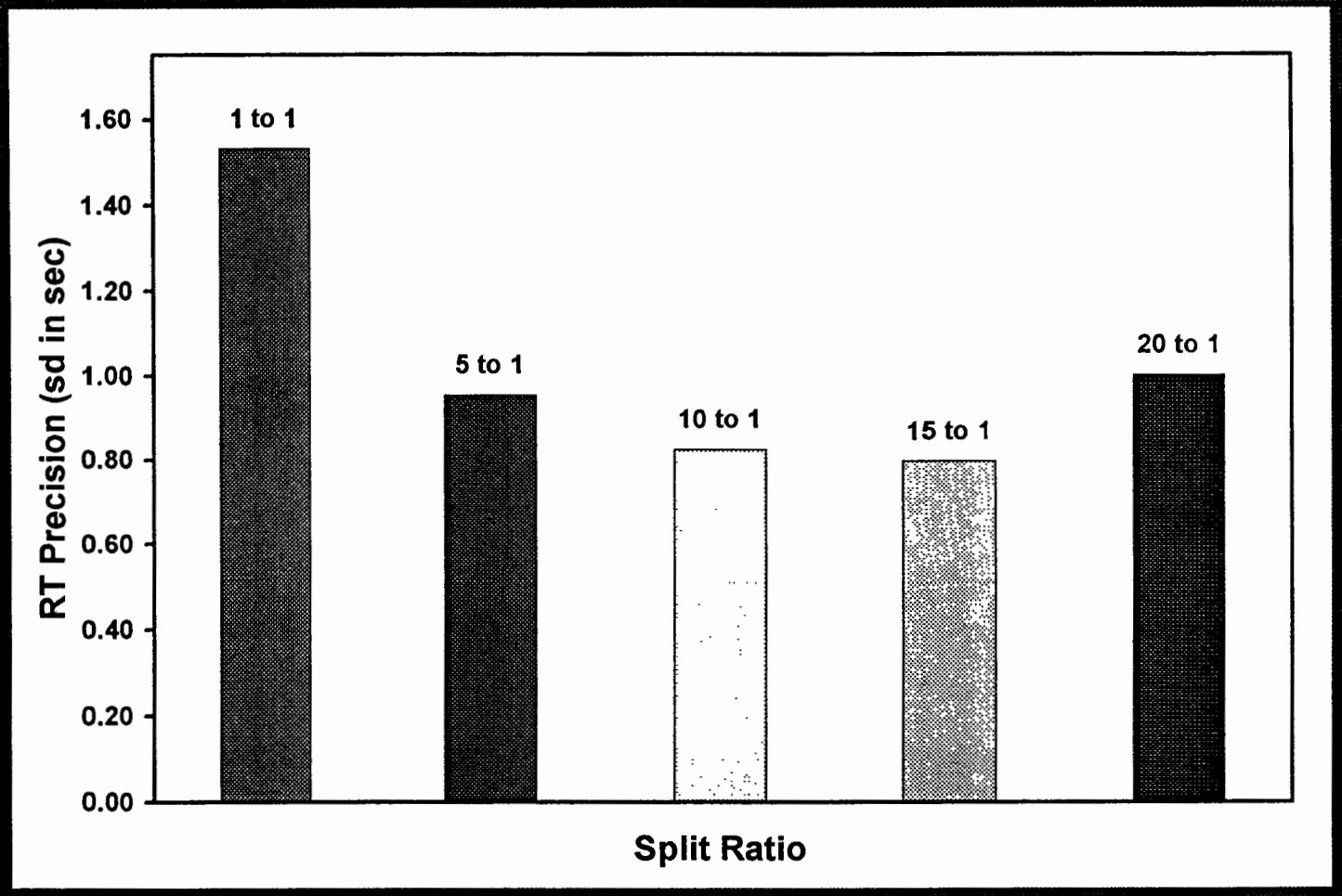
RETENTION TIME PRECISION (narrow bore)



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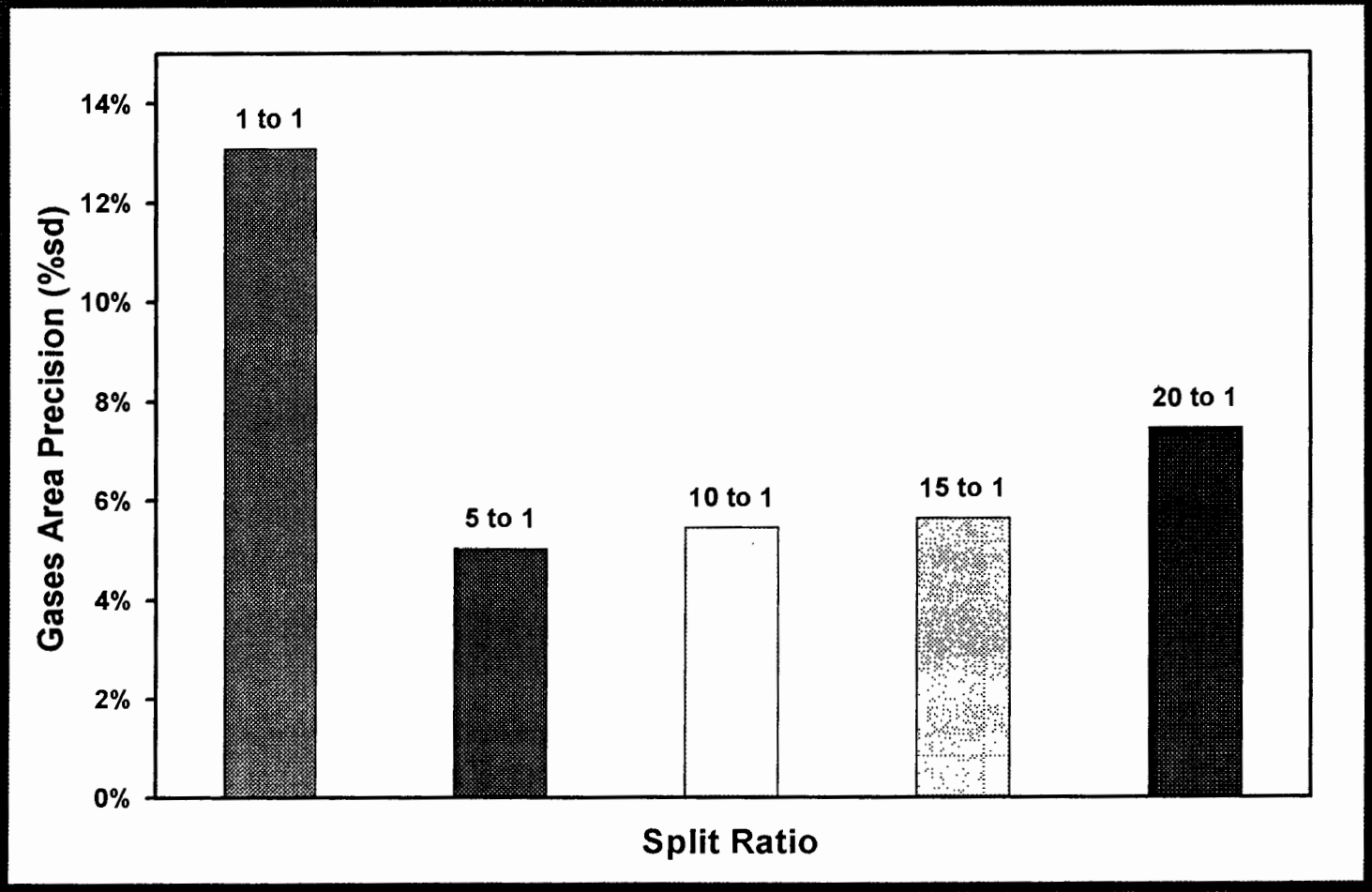
AREA PRECISION
(narrow bore)



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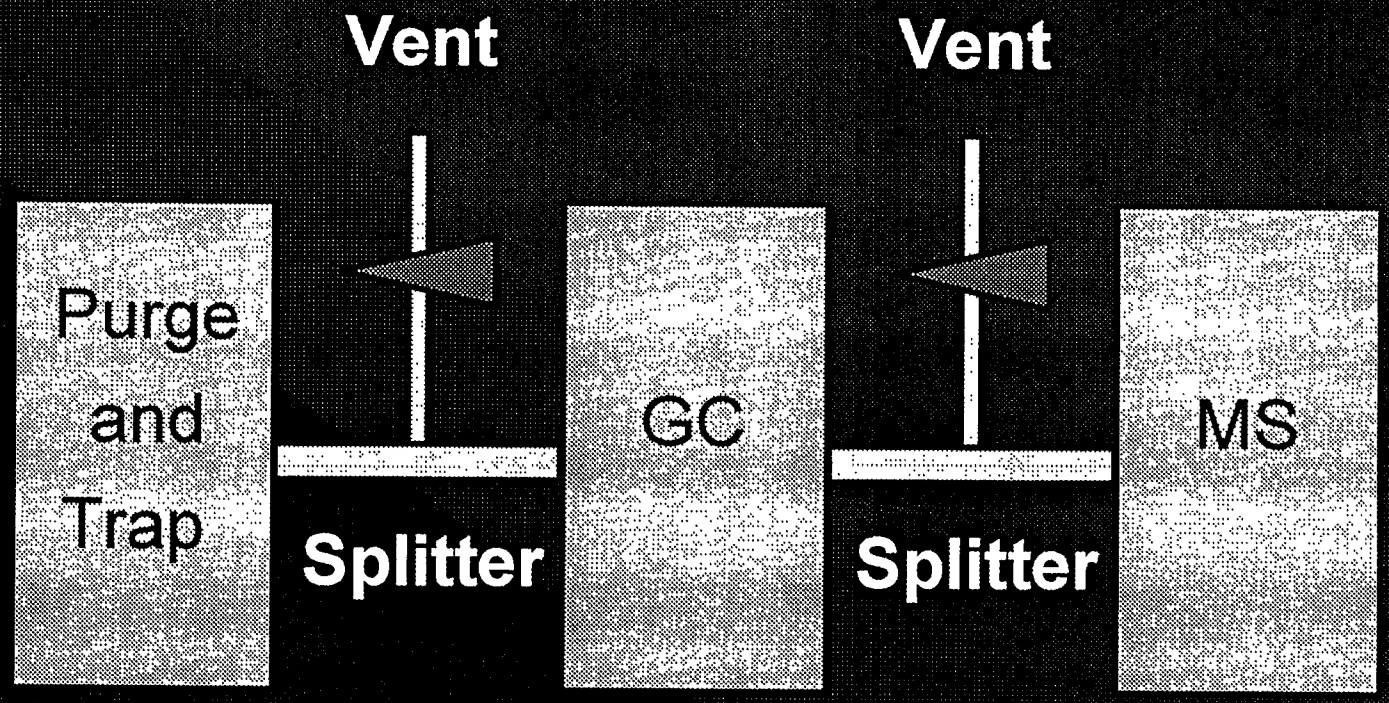
GC CONDITIONS

- 60 m x 0.32 mm 1.8 u DB-624
- Temperature Program
  - 40 deg for 6 min
  - 8 deg/min to 160 deg
  - 25 deg/min to 250 deg
  - 10 min hold
- 8:1 Split Ratio

PA

MEGABORE HOOK-UP



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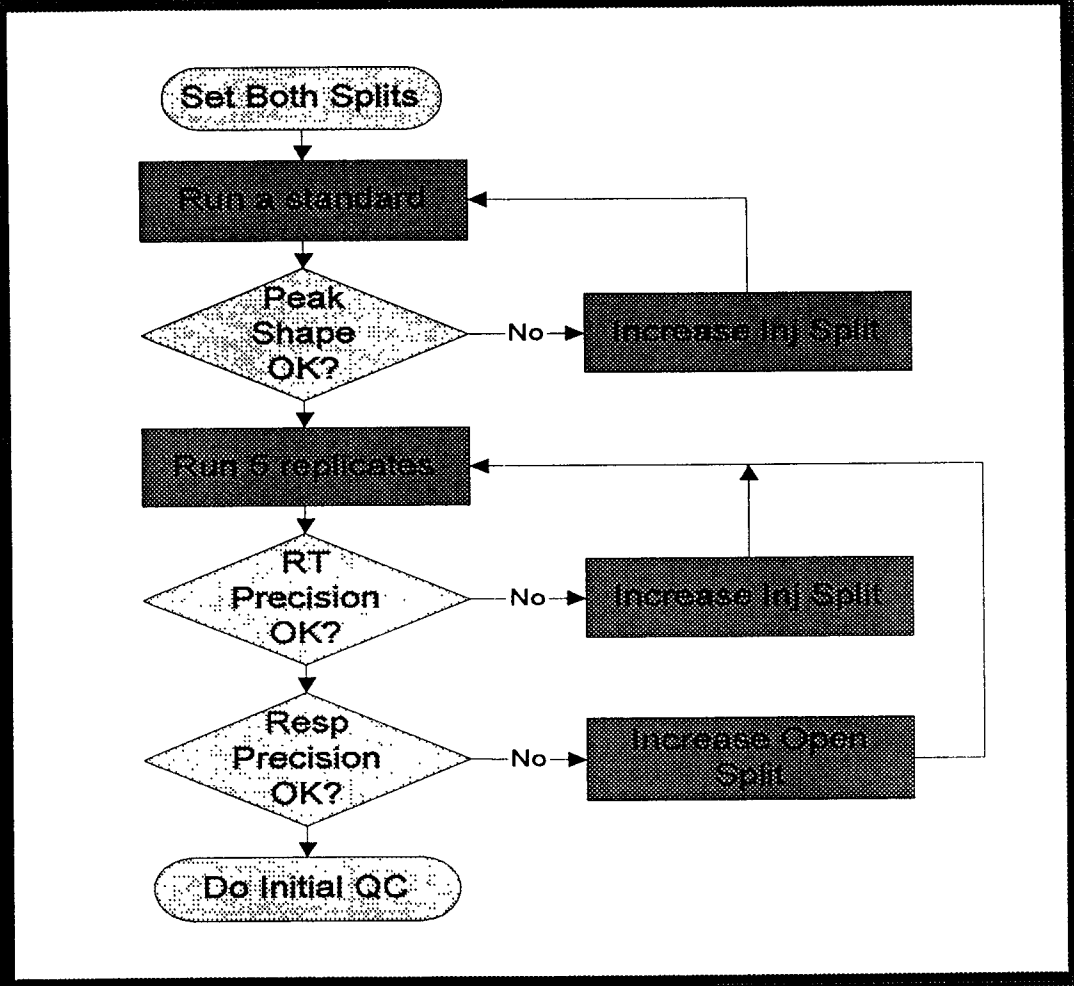
OPTIMIZATION PROCESS



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GC CONDITIONS

- 75 m x 0.53 mm 3 u DB-624
- Temperature Program
  - 40 deg for 4 min
  - 9 deg/min to 200 deg
  - 25 deg/min to 250 deg
  - 20 min hold
- 3:1 Injector Split Ratio
- 7:2 Open Split Ratio

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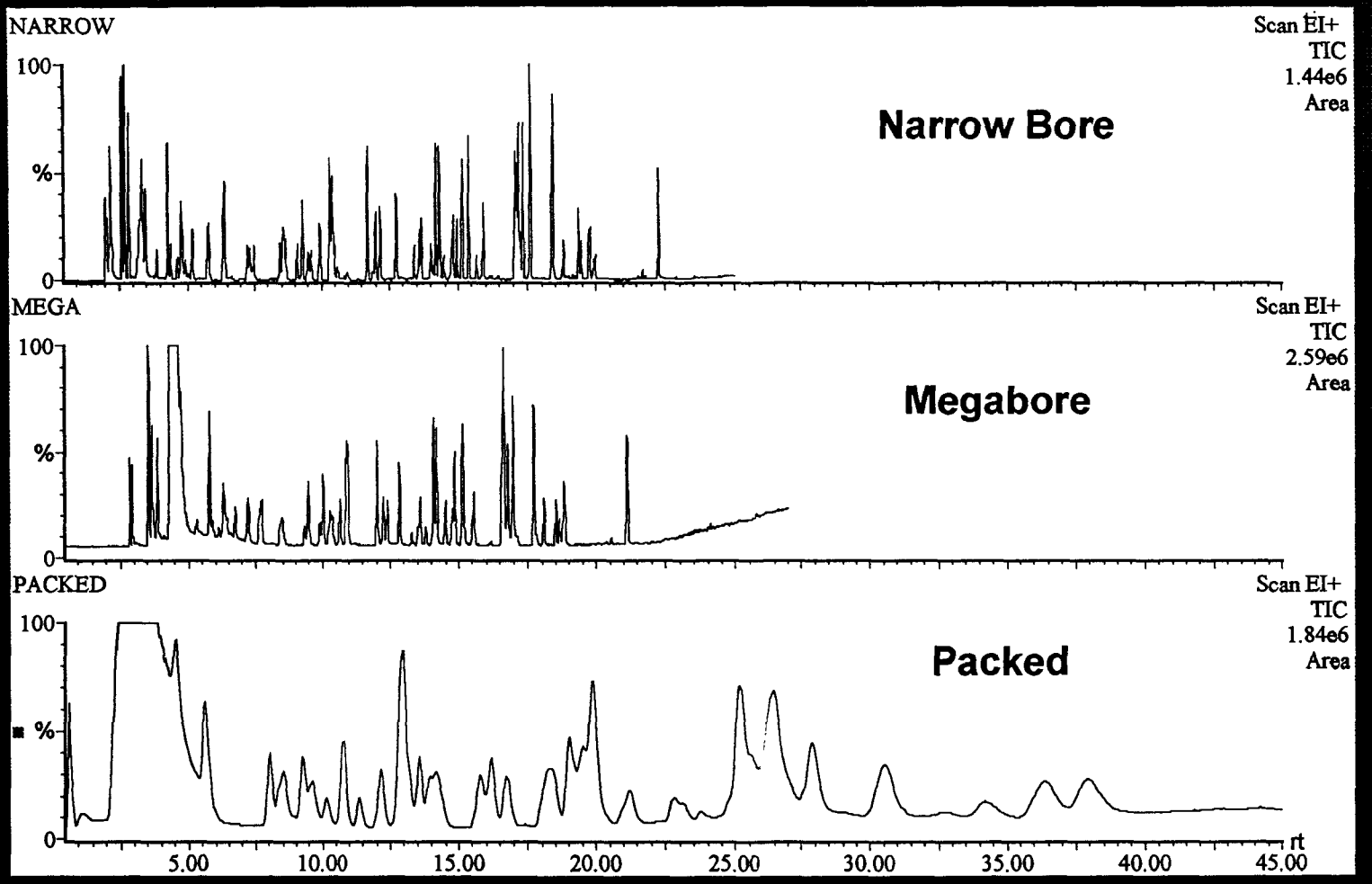
CHROMATOGRAMS



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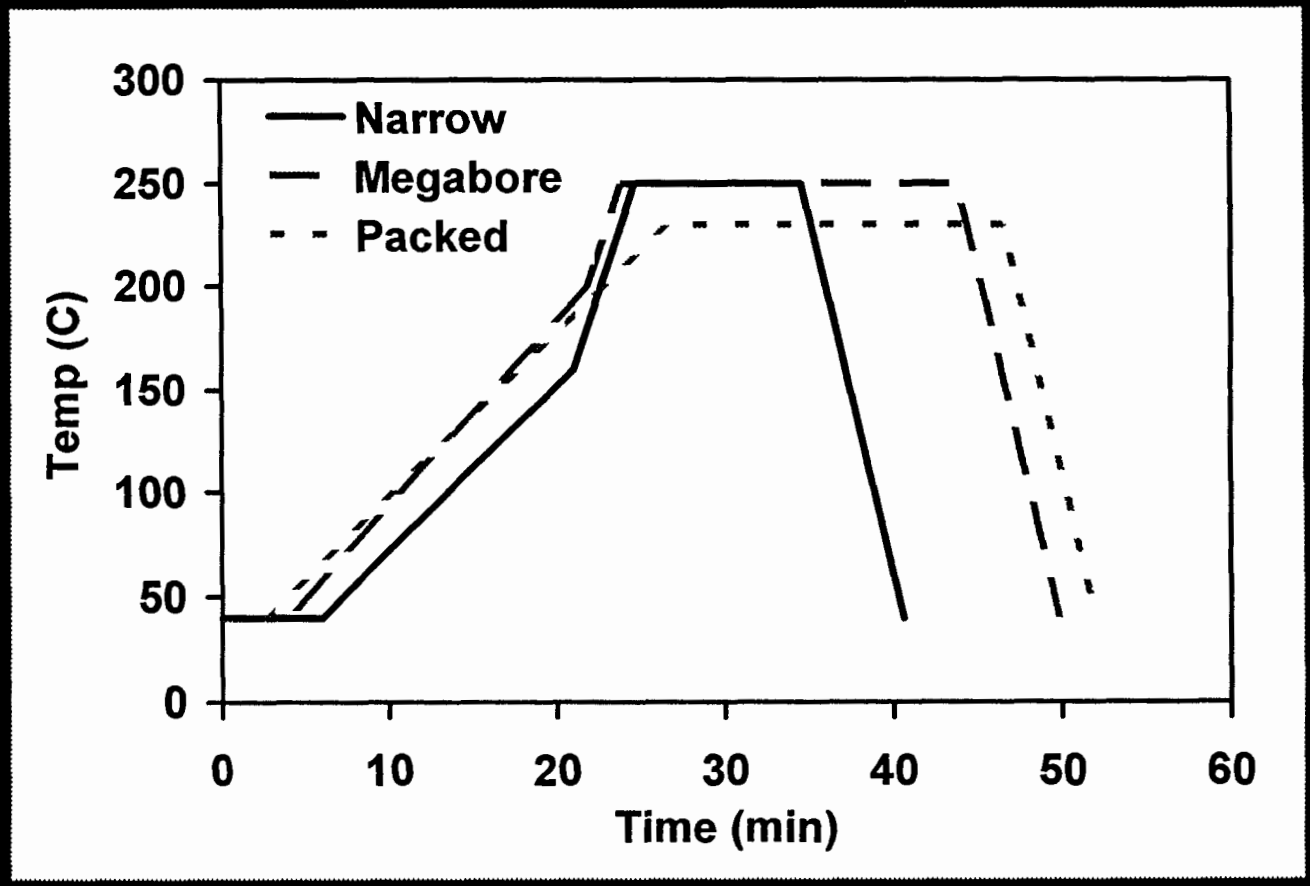
ANALYTICAL CYCLE TIMES



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RETENTION TIMES

- Numerous RRT changes
- Separation of cis- and trans-1,2-dichloroethenes
- m- and p-Xylene are coeluted rather than o- and p-xylene

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IMPORTANT SEPARATIONS

- 3-Chloropropene and carbon disulfide
- Chlorobenzene-d_5 and 1,1,1,2-tetrachloroethane
- Isobutanol and benzene d_6
- 2-Bromo-1-chloropropane and trans-1,3-dichloroporpene-d_4
- p-Dioxane and bromodichloromethane-$^{13}C_1$
- Vinylchloride and methyl ether-d_6

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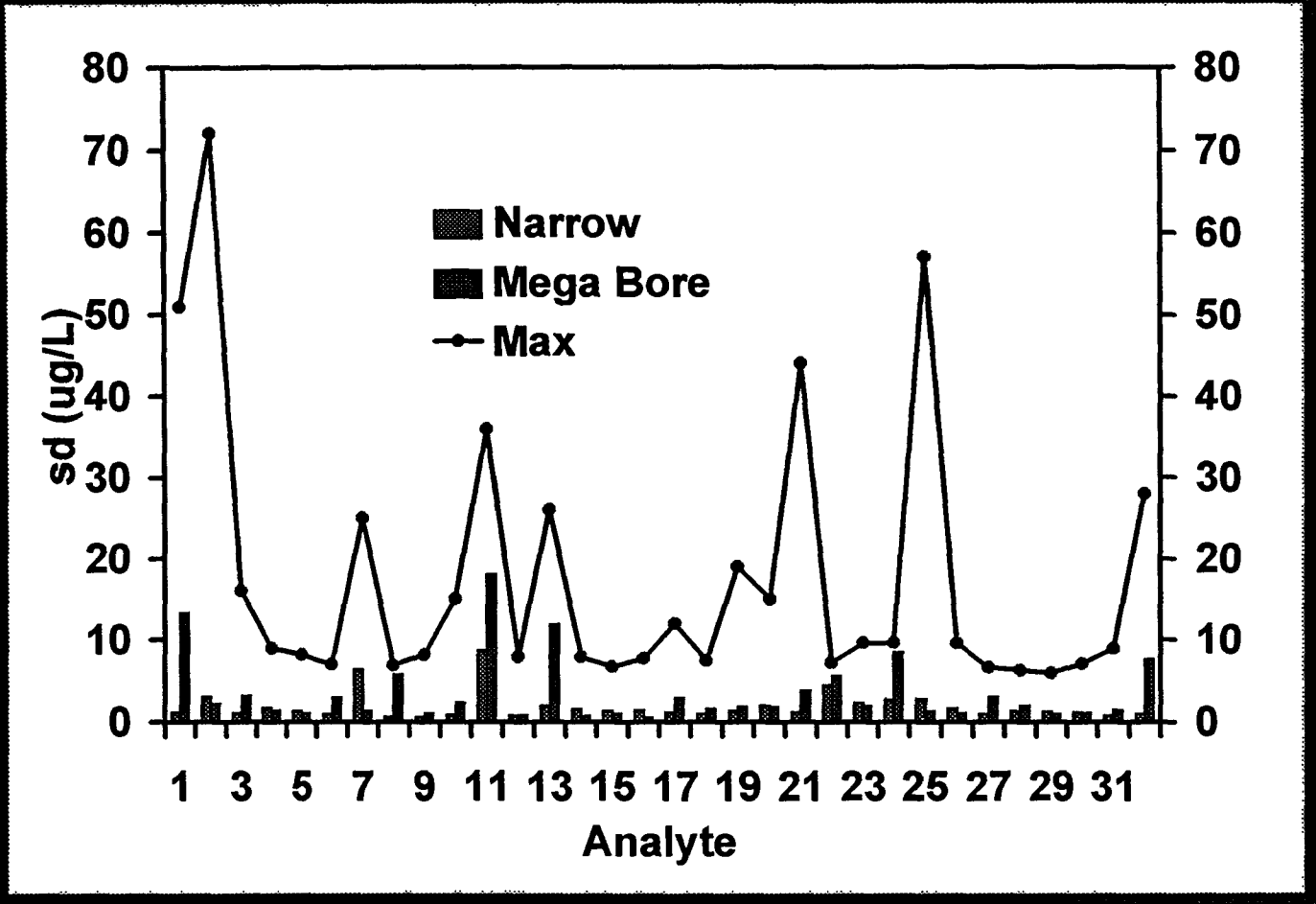
ANALYTICAL PRECISION



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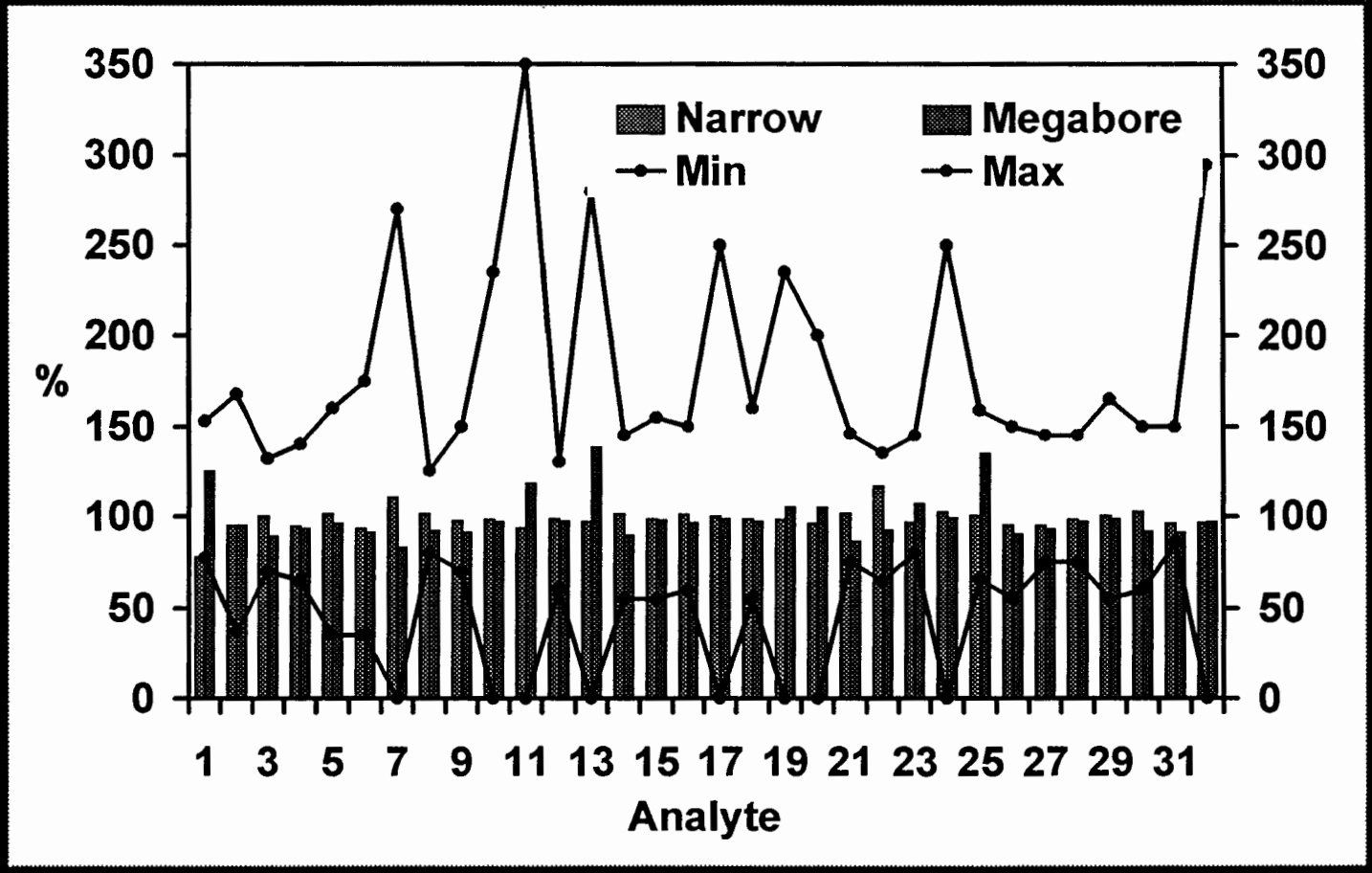
ANALYTE RECOVERIES



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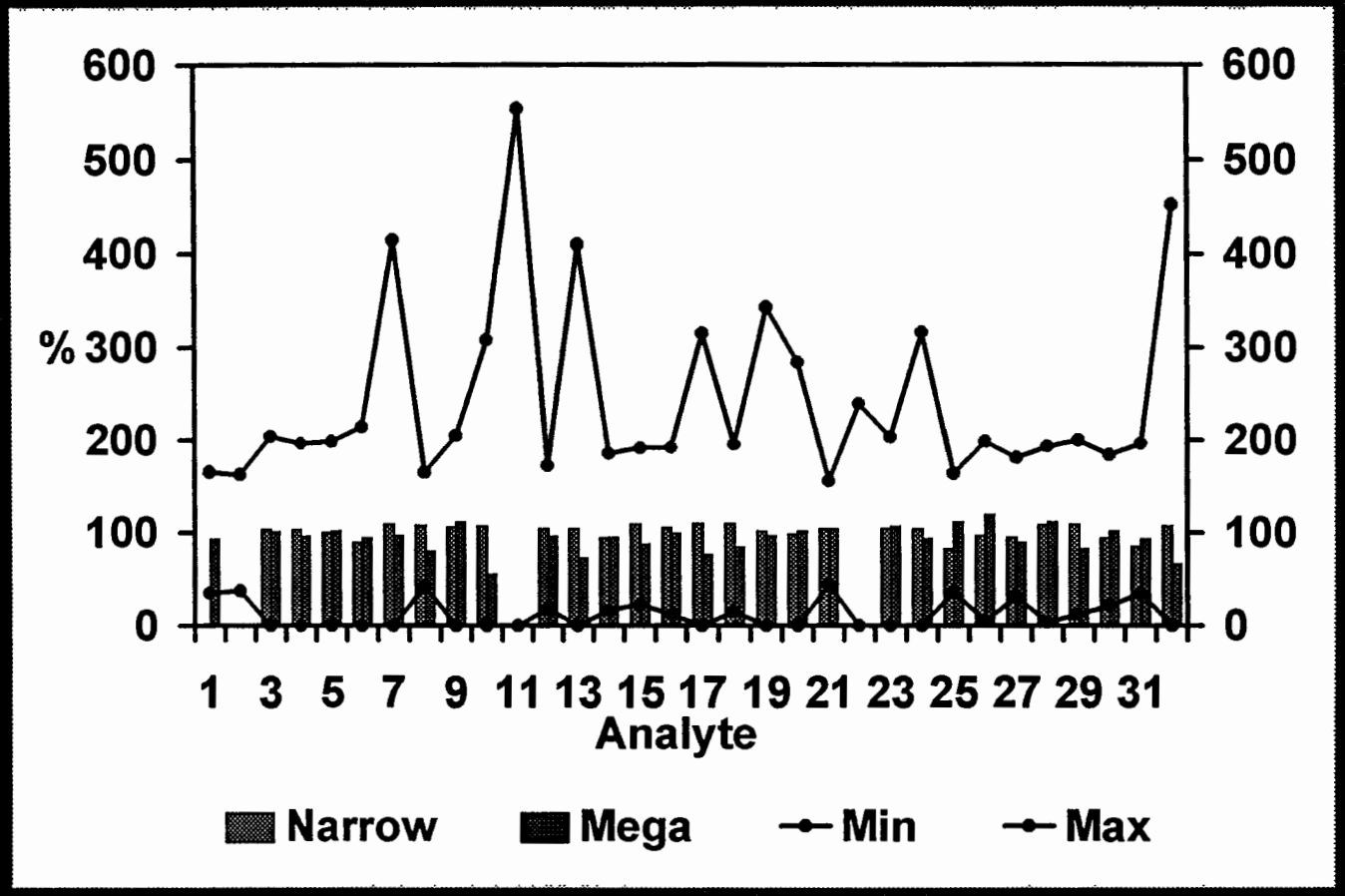
LABELED RECOVERIES



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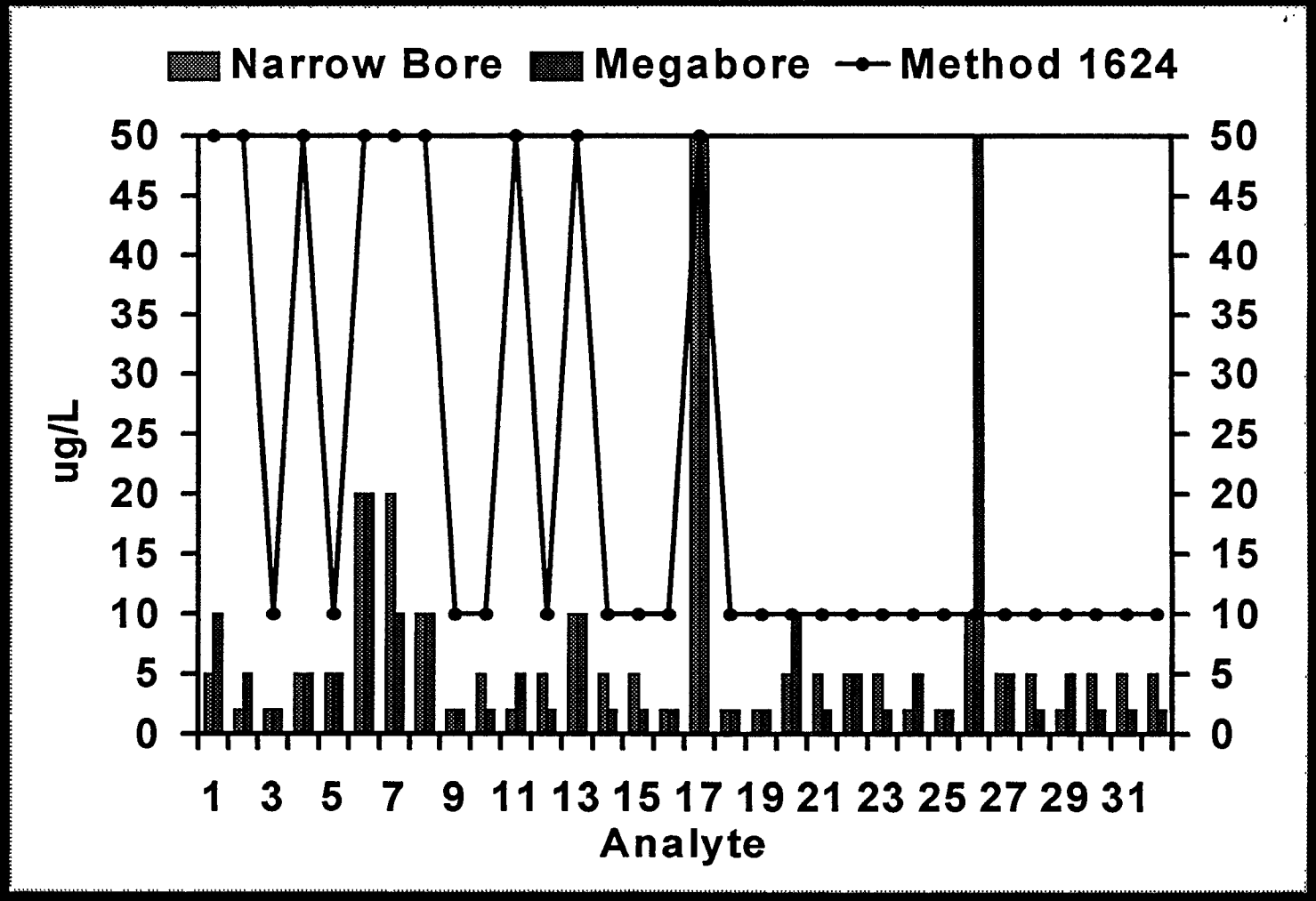
Minimum Levels



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CONCLUSIONS

- Capillary columns satisfy all Method 1624 QC criteria except absolute retention times.
- Capillary columns are easy to use and provide shorter analytical cycle times than packed columns.
- Narrow bore columns are more convenient to use than megabore columns.
- Narrow bore columns provide slightly better QC data than do megabore columns.

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Acknowledgment

The authors would like to thank
William A. Telliard of the USEPA
for his support and encouragement
in this effort.

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MR. TELLIARD: Our next speaker, Mike Sepaniak, is a Professor of Chemistry at the University of Tennessee, and his paper is entitled the Micellar Electrokinetic Capillary Chromatography: Application to Separations of Mycotoxins and Polynuclear Aromatic Compounds. There must be a shorter way to say that, but I think it is all there.

Mike?

MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY: APPLICATION TO SEPARATIONS OF MYCOTOXINS AND POLYAROMATIC COMPOUNDS

MR. SEPANIAK: I will add a few footnotes to that. I am glad I did not bring any expensive color slides.

Let me start out by thanking the organizers for giving me the opportunity to talk about some of our research at the University of Tennessee. The technique that I will be talking about is a separation technique. It is a technique that probably many of you are not that familiar with. It combines some of the attributes and characteristics of capillary electrophoresis with chromatography, in fact, with reversed-phase LC.

What I will do is talk a little bit about some of the principles and theory involved and then get into a couple of environmental applications.

I think the best way to understand the technique of micellar electrokinetic capillary chromatography is really to look at the apparatus and explain what the experiment involves.

The heart of the system is a capillary. It is not megabore or narrow bore. It is, I guess you would call it, microbore. We use columns, typically, that are about 50 um in ID, less than a meter in length, typically, 70 cm in length.

We will fill the capillary with an aqueous buffer solution, and place the ends of the capillary in reservoirs that contain that same solution. We will put numerous other additives in the system, too. We might add chelates, we might add soluble polymer, we might add micelles...and that is what most of this talk will be about...a variety of things we will put into the system.

When we apply a large voltage across the capillary, typically, 20,000 volts, 30,000 volts, what we observe is transport phenomenon referred to as electro-osmotic flow. That is a flow of solvent from one end of the capillary to the other. It is generally cathodic; that is generally goes towards the negative side of the capillary.

That electro-osmotic flow is fairly fast. It will move solutes from one end of the capillary to the other end in a matter of a few minutes.

So, imagine an experiment, now, where we place into this end of the capillary about a 1 mm plug of sample and turn on the voltage. Neutral species will migrate from one end of the capillary to the other due to this electro-osmotic flow. The velocity of the neutral species is equal to the velocity of the electro-osmotic flow. If we have cations, they are going to have an electrophoretic component that adds to the electro-osmotic flow, so they will move faster than the electro-osmotic flow. If we have anions in our sample, they will move slower, because they have, basically, a velocity component that is in opposition to the electro-osmotic flow. If we have two different cations with different mobilities, we may be able to separate them. In fact, if they stay as narrow plugs, as narrow bands, that is a likelihood.

At one end of the capillary, then, we are going to have our detection scheme, and I am showing laser-based detection. Whenever possible, we like to employ laser-based fluorescence detection, but a lot of the chromatograms that I will show in this talk are based on absorbance detection. The advantage of the laser is that its high intensity leads to better sensitivity to compensate for the short path lengths that are involved. When you perform on-column detection, the path length is essentially the diameter of the capillary.

The problem is in separating neutrals. Neutrals all move at the velocity of electro-osmotic flow, so they are not separated at all. But we can separate them if they associate in some manner with a charged species, in other words, if we cause them in some way to acquire an effective electrophoretic mobility.

The most common species that we will add to the mobile phase for that purpose is SDS, sodium dodecasulfate, C_{12}, an alkyl sulfate surfactant. SDS forms micelles at concentrations of about 8 mM. The micelles have aggregation numbers of about 60, and they have diameters of about 40 angstrom. So, typically, we will include in the mobile phase about 50 mM SDS and form micelles.

Another type of micelle that we can add to our system involves bile salts. We have gotten a lot of mileage out of the bile salts. They form smaller micelles. Moreover, they are more polar, which is an advantage in separating hydrophobic molecules. In addition to that, they are chiral which allows us to separate certain enantiomers.

Although they are not charged additives, I will show some data involving adding cyclodextrins to the mobile phase. Cyclodextrins are microcyclic sugar molecules that contain a hydrophobic cavity.

You can buy a cyclodextrin with a different number of sugar units in the macro cycle, and when you do, you have different cavity diameters, so you add a spatial component to

interactions. Since the cavity of the cyclodextrin is hydrophobic, it will interact with molecules in a very dispersive manner.

So, I am going to talk about using these things as additives to separate neutral species.

Here is the MECC experiment. That is a shorter title, so I guess I should have given it to you when you were introducing me. In this experiment, I have shown a section of the capillary here. Depicted is the rapid electro-osmotic flow.

Notice it is plug-like, too. Unlike hydrostatic flow which is parabolic, electro-osmotic flow is plug-like. That leads to better efficiency since there less dispersion due to resistance to mass transfer in the mobile phase.

This represents the electrophoretic velocity of the micelle. We generally use negatively charged micelles. This SDS would be negatively charged. And the little snowflakes here represent those micelles. So, they will have an electrophoretic component in the opposite direction. Generally, it is smaller than electro-osmotic flow, so the net velocity of the micelle is in the same direction as electro-osmotic flow; however, it is much slower.

So, we have a two-phase system that we have created here, the basis of chromatography. The secondary phase is not stationary, though. The secondary phase is moving slowly, and is composed of the micelles.

The two phases are an aqueous mobile phase and the very hydrophobic interior of the micelle. So, it is a lot like reversed-phase LC.

A solute that is neutral will distribute between the mobile phase and the micelle; for example if it is hydrophobic, it could largely dive into the hydrophobic core of the micelle. If it distributes between these phases, it will acquire a velocity that is somewhere intermediate between electro-osmotic flow and the net velocity of the micelles. Moreover, two solutes that have differing distributions between the micelle and the aqueous phase will be separated if they stay as narrow bands.

That is all depicted in this slide. V is the velocity of the band. This equation is general in nature, since it considers both charged and neutral species.

k′ is the familiar capacity factor. Basically, in this technique, it is the amount of solute that is in the micellar phase divided by the amount that is in the mobile phase.

There is a mobility term. That term is the mobility (Mb) of the analyte, and if the analyte is not charged, Mb will be zero. E represents the field that we are applying.

So, basically, what we have is a system that will allow us to separate neutral species based on differences in k′ and charged species based on differences in Mb.

Now, I know we do not like to look at equations unless we absolutely have to, but I like to bring the equations on this slide to your attention, mainly because I want to bring up that in achieving resolution, which is the object of any separation, there really are three important factors.

Efficiency, which we are all familiar with, is represented by the number of theoretical plates. With capillary electrophoresis, we can get efficiencies of greater than 1 million theoretical plates for a 1 M length of capillary. For this MECC technique, phase transfer is involved, so we never quite get to that efficiency, but in our best cases, we can achieve 500,000 to 600,000 plates for a 1 M long column. So, the efficiency is excellent. I will mention that a little bit later on, too.

Selectivity, the alpha factor in the illustrated equation, is the ratio of k′ for adjacent eluting peaks.

System retention is incredibly important with this technique. If you look here at the inner parenthetical term, you will note that it does not appear in the conventional expression for resolution in chromatography. It is not present in the conventional form of chromatography, because the stationary phase is just that. It is stationary.

The T_O and T_M represent the void time and the effective elution time of the micelles, respectively. It is important to note that the micelles are incorporated into the entire system. We are not injecting them; nevertheless they have an effective retention time, t_M.

This system retention term has a dramatic effect on the technique, and I will illustrate that shortly. You might notice that the first three terms in this equation are the same as in conventional chromatography.

What we have here, then, since the micelles are eluting from the system, is an elution window, and it is depicted here between T_O and T_M. What you see with the MECC technique is that hydrophobic molecules, the ones that would be retained the strongest, completely associate with the micelle, and "pile-up" near the end of the elution range. That is why this term, this elution range term, is so critically important.

Sometimes, it is beneficial to extend the elution range. It is also very important to reduce capacity factors to be in the optimum range. In conventional chromatography, resolution improves with increasing capacity factor. It means longer analysis, but it is better.

That is not true in MECC. With this technique, there is an optimum k′, generally in the range of about 1 to 5.

This slide demonstrates that effect. These are some derivatized n-alkylamines. I can tailor a sample here to have molecules with a range of hydrophobicities. So, what you are seeing is that the most hydrophobic molecules are piling up at the end of the elution range. We cannot separate them.

In the bottom chromatogram, we see easy separation of those compounds. What we have done is to add about 22% alcohol, isopropanol, to the mobile phase. The isopropanol has two effects. It reduces k' just like an organic modifier would do in reversed phase LC. It also extends the elution range by slightly reducing electro-osmotic flow. You will notice the last peak is coming out much later here.

The end of the elution range was about 30 minutes in the original one, and in this one, it is 80 minutes, but the last two peaks which are right on top of each other in the top chromatogram, now, they are easily separated. Actually, we have too much baseline between those compounds, which are labeled J and K.

So, that is the effect of the elution range. It is good to extend it and it is good to reduce capacity factors to get in the optimum range of about 1 - 5.

There is another illustration of the separation power of this technique and some of those same points. In fact, I will bring up a point about efficiency that is pretty critical as well.

This slide shows the separation of two binaphthyl compounds. This one happens to be charged. What we have here is a charged molecule and a neutral molecule, and we are separating them using the MECC technique. That is one of the advantages of MECC. Capillary electrophoresis is also operative.

These two binaphthyl molecules are chiral, so we are going to attempt a chiral separation by using a chiral micelle in our mobile phase. We are going to use a bile salt, sodium cholate.

In the first chromatogram shown, you do not see separation of the optical isomers of the neutral hydroxy binaphthyl or the charged phosphated binaphthyl/compounds. The efficiency is rather poor. It is not bad, but it is not adequate to resolve the optical isomers.

The reason efficiency is not high is because we do not have many micelles present in this system. The principal source of band dispersion with this technique results from the polydispersity of the micelles. The micelles are not all the same size. If they are not all the same size, they are not all moving at the same velocity and that causes band dispersion.

If you increase the concentration of surfactant, then the exchange of monomer with surfactant becomes rapid. Basically, what it does is it averages out the sizes of the micelles.

It is sort of like using a small diameter capillary or using small particles in conventional chromatography to minimize the effects of resistance to mass transfer in the mobile phase.

So, the difference between the separations labeled A and B is we doubled the concentration of surfactant. In this case, many more micelles are present and there is a dramatic effect on efficiency. We observe nearly baseline resolution of the optical isomers.

Now, we increase the concentration for the separation labeled C even further. What happens? Because we have increased the phase ratio, we have increased the amount of secondary phase and we pushed these components toward the back of the elution range.

I have nothing in here to mark T_O and T_M, but T_M would probably be somewhere around there. So, these binaphthyls have excessive k′ values. They are bunching up near the end of the elution range.

We add some methanol to the mobile phase and separation is achieved, because we have reduced the capacity factor. It does not look like it. They are coming out later, but we have reduced the capacity factor. If we were to look at the elution range now, it would probably extend from there to someplace out there. So, we have actually reduced the capacity factor even though retention time has increased.

What I should have done at this point is to add an organic solvent like acetonitrile which has a very small effect on the elution range but reduces the capacity factor. We probably could have achieved that same separation in a much less time.

Let me talk very quickly about a couple of applications. We tried to apply this MECC technique to the separation of mycotoxins. Collectively, the various mycotoxins shown in this slide are present in a lot of food samples. They are naturally occurring as they are produced by naturally occurring fungi. Collectively, this group is very toxic. Some of them are carcinogenic, some are mutagenic, some are terragenic. So, it is not particularly a good sample. There is a lot of "bad actors" in this group of compounds.

Notice that they are fairly polar, though. They dissolve in water moderately well, the aflatoxins not too well, but some of them are fairly polar. One or two of the mycotoxins even have acid or base functionalities and can be charged.

What I am showing you in this very busy slide is one of the characteristics of this MECC technique. You can change the separation system incredibly fast. It takes you a mere 10 seconds to fill the capillary with a different solution. Consequently, you can change the primary and stationary phases that you have in a matter of seconds.

So, this experiment involves either SDS or sodium deoxycholate, the bile salt, under changing acetonitrile concentration. The effects that these changes have on capacity factor are shown.

Same thing down here. We are changing both the pH and adding cyclodextrins in the mobile phase. All of that retention data can be collected in half a day.

I know you cannot see it very well, but this slide shows two separations. What we did is to look at that data in the previous slide and pick out two sets of conditions, one involving, on top here, an SDS mobile phase with some organic modifier and gama-cyclodextrin. The bottom one is a separation using sodium deoxycholate micelles.

Although you can barely see it, a lot of the lines here, these dashed lines, show how the components are changing positions.

Our goal was to pick two sets of conditions that yield rapid separations of all ten mycotoxins, which I do not think anybody has done previously, two sets of conditions that exhibit unique selectivities to enhance our qualitative capabilities for this technique.

The time axis is not shown, but both of these separations require about 12 minutes. In fact, using exactly the same instrumental setup, just simply squirting a different mobile phase into the capillary and allowing equilibration, both separations are possible in about 40 minutes. You can cycle back and forth between mobile phases. This enhances ones qualitative capabilities.

Reproducibility is not outstanding for this MECC technique because of the fact that retention times depend upon electro-osmotic flow which you can adjust by adjusting the field, but it also depends upon the surface condition of the capillary, and that is hard to control. Moreover, it depends upon the phase ratio which also depends on many interrelated parameters. So, reproducibility in retention time is not outstanding. Here we are showing RSD values of 2% and 4%.

We randomly generated five samples of mycotoxins that contained the mycotoxins that I showed and a number of polycyclic aromatic hydrocarbon interferences. By injecting standards using both sets of conditions and compare sample and standard retention times, we were able to identify every mycotoxin in these artificially generated samples with no misidentifications or missed mycotoxins.

So, the qualitative capabilities of this technique are quite good. Moreover, the technique is quite good at handling dirty samples.

Another advantage of the technique, is that it can be optimized for fast separations. The separation of four aflatoxins shown on this slide is accomplished in 20 seconds. So, incredibly fast separations are possible with the MECC technique as well.

However, I am misleading you a little bit. You have to use small diameter capillaries in order to achieve speed. It is often necessary to employ laser-based fluorescence detection with small capillaries. These aflatoxins, fortunately, can be excited using a He-Cd laser.

Switching gears very quickly, let me talk about some separations of, in this case, molecules that are extremely hydrophobic. They are hard to separate with this technique because of the fact that they like to dive into that micelle and stay there. In other words, they co-elute near the end of the elution range. I am going to mainly talk about some anthracene and benzopyrene separations, both benzo-a and benzo-e, as well as some separations of substitution isomers of these compounds.

As you probably know, these PAHs, especially benzo-a-pyrene, are carcinogenic, and they are released into the environment when we burn fossil fuels. So, they are important pollutants.

This is, again, an interesting slide in that it shows many of the characteristics of MECC technique. This sample contains anthracene, 2-methylanthracene, 9-methylanthracene, and benzo-a-pyrene.

What we show in the first chromatogram on this slide is everything co-eluting near the end of the elution range. We have a short elution range. In this case, we are using a short column, high voltages, and all four compounds co-elute with k′ that are too large.

When we switch to this system over here, we have added approximately 15% organic modifier to the mobile phase. Above about 30% organic modifier, you lose the micelles, and everything falls apart.

However, you notice here in the separation labeled b that we have reduced the capacity factors. The capacity factors are near optimum, but the two methyl-substituted anthracenes are still not separated. We have optimized system retention, but we have not achieved adequate selectivity.

So, the difference between the separation b and c is that we have added cyclodextrin to the mobile phase. The ability of the anthracene to insert into the hydrophobic core of the cyclodextrin is determined by the position of that methyl group.

Now, what does the cyclodextrin do? It is moving at the mobile phase's velocity. Thus, it is functioning as an organic modifier except that it is selective in the way that it interacts with the solutes.

This next slide shows a cyclodextrin and its interaction with benzo-a-pyrene and benzo-e-pyrene. Notice the numbering of the carbons on these PAHs. I am going to show separations of these two molecules, as well as a lot of substitutional isomers of benzo-a-pyrene.

Now, these molecules can then insert into the hydrophobic core of the cyclodextrin. The slide depicts gamma-cyclodextrin, which is the largest common cyclodextrin. When solutes insert into the cyclodextrin they are prohibited from associating with the micelle. The stronger the interaction with the cyclodextrin, the earlier the PAH will elute.

The mechanism for this separation is shown in the next slide. Benzo-a-pyrene, can interact with the micelle. When it does, it forms an adduct that is moving slowing towards the detector. When it is in the mobile phase, associated with cyclodextrin, it is moving rapidly towards the detector. Thus, the PAHs are distributing between the micelle and cyclodextrin phases.

This slide shows separations of benzo-a-pyrene and benzo-e-pyrene. The difference between the separations labeled a, b, and c is we are adding increasing concentrations of gamma-cyclodextrin to the mobile phase. By increasing the cyclodextrin concentration the resolution between these compounds is improved.

The separations of substitutional isomers of benzo-a-pyrene shown in this slide are quite impressive. The separation of methyl substituted isomers is particularly impressive in that high efficiency and excellent selectivity are observed. The position of the methyl substitution influences the ease with which the isomer can insert into the cyclodextrin.

The observed selectivity depends upon the type of cyclodextrin that is used. Beta-cyclodextrin is too small. Thus, the k′ values shown in this table are all quite large indicating poor interaction with the cyclodextrin. Conversely, the k′ values obtained using hydroxy-propyl-gamma cyclodextrin are all small. This large derivatized cyclodextrin does not discriminate between the isomers. However, by using gamma-cyclodextrin, we observe excellent selectivity. The values for the capacity factors vary greatly, and that is what is really needed for adequate separation.

I will entertain any questions you have.

MR. TELLIARD: Any questions? (No response.)

MR. TELLIARD: Thank you, Mike.

(Slides for this presentation were not available at the time of publication for these proceedings.)

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MR. TELLIARD: Our next speaker is Dr. Bruce R. Locke. Bruce is employed by the Department of Chemical Engineering at the Florida A&M/Florida State University College of Engineering in Tallahassee, Florida. His subject, the analysis of kraft mill effluent using non-purgeable total organic halide test, is very pertinent to a new regulation recently written.

So, this particular subject is very near and dear to our hearts at the present time and certainly topical for our meeting this year.

Bruce?

THE ANALYSIS OF KRAFT MILL EFFLUENT USING THE NON-PURGEABLE TOTAL ORGANIC HALIDE TEST

MR. LOCKE: I would like to thank the organizers of this session for inviting us to present our work here. I would like to acknowledge my co-author, Dr. Geoffrey Watts, currently employed by Geosolutions, Inc.

Dr. Watts performed much of the work presented here while he was an administrator for site investigation at the Florida Department of Environmental Regulation, and he subsequently used some of this work as a master's thesis in chemical engineering.

First, I would like to give an outline of the things we are going to cover today. I will begin with an introduction to the problem, and show why we are interested in this particular problem.

That will lead to consideration of the effluent water quality, both upstream and downstream of the plant. This will lead to a discussion of the NPTOX, non-purgeable total organic halide, analysis that we are considering here.

I will thereafter discuss the development of an analysis for what we have termed Fenextract which is a precipitate at low pH formed from the kraft mill effluent. We will talk about the preparation of this precipitate, its distribution in the river, the determination of its molecular weight, and some of its structural features. In addition, we will discuss some implications of this work on the chemistry of the bleaching process. Finally, we will end with conclusions and acknowledgements.

The next slide shows a picture of the area that we are interested in. There is a city called Perry, Florida, really a town, that is about 20 miles upstream from the Gulf of Mexico on the Fenholloway River shown in red. Upstream of the city is pretty much undeveloped pine land and swamp forest. There is really no industrial or residential development upstream of the town.

However, as shown in this figure, there is a large kraft mill that discharges into the river. We will consider the effluent water quality analysis both downstream and upstream of the discharge.

Before we do that, I would like to talk a little bit about, for those who are not familiar with it, the chemistry of the pulp process just to give you a feel for what it is we are trying to analyze.

The next slide shows the composition of the feed material that goes into a pulping plant. As you can see, the primary components are cellulose, about 41 percent, a linear polysaccharide, and lignin, about 29 percent, which is a highly colored brown aromatic polymer. In addition, there are some other compounds, including hemicellulose, and extractives at lower levels.

Of course, the product desired in a pulping process is cellulose. The lignin is covalently bonded to the cellulose and the other hemicellulose compounds. The next slide gives an idea of what the lignin looks like. This is just a schematic developed by Adler in 1977.

The lignin is not a simple compound, as you can see. There is a range of alkyl-alkyl ether linkages, also aryl alkyl ether linkages, and a number of aromatic groups. There is no repeating structure here, and it is a fairly complicated structure. It also extends to three dimensions. This just gives some structural features of what it looks like.

The next slide shows the pulping process. In a pulping plant, the wood is introduced, broken up, chipped, and the central heart of the process is a digester where, under high pH conditions and high temperature, the bonds are broken between the lignin and the cellulose compounds.

There are two streams coming out of the digester. One is the black liquor which is primarily your waste component containing large amounts of lignin. Much of the black liquor can be recovered and various products made from that.

However, the waste stream we are interested in arises from the subsequent downstream processing of the cellulose product. The cellulose product coming out of the digester contains still about 10 percent of the lignin compound which still needs to be removed.

There is a series of processes in the bleaching plant shown below where an alkali extraction that follows a chlorine dioxide oxidation process serves to remove the remaining amount of lignin.

There are other ways of oxidizing the material. However, the plant we are considering here uses chlorine dioxide.

The next slide shows the locations of the sampling sites. There is one sampling station a couple of miles upstream of the plant, and another sampling station downstream of the plant. In addition, some samples were taken at the confluence of the river with the Gulf of Mexico which is not shown on this slide.

The next slide shows some historical data for the facility taken by the DER from 1980 to 1988. I might mention that this plant has been in operation since 1953 and has essentially been discharging roughly 50 million gallons per day into the river. This is a significant portion of the river flow when the weather is fairly dry.

The top of the slide shows a color level right above the effluent discharge which is about 500 pcu, and just below the discharge to the river, it is about 1600. So, you can see there is a fairly significant increase in the color.

I might also mention that the impetus for this study was several years in the late 1980s when the river was very dry, when the weather was very dry, and the residents in and around the town of Perry found high levels of color, taste, and odor problems in their drinking water. The motivation for this study was to determine the source of these problems .

Primarily what I will talk about is the chemical characterizations of the river. Other work will address the connection between the well contamination and the river.

Now, you might also note in this slide that the dissolved oxygen drops slightly, and that the BOD level is fairly low, although it rises somewhat at station 2 below the discharge of the plant. However, it is not a real high level. Similarly, COD is not changed a whole lot upstream and downstream of the discharge.

You can see, of course, that due to the high salt content introduced in the plant, there is a very large increase in the conductance in the water. The pH level is approximately neutral, and this is due to the fact that the streams from the bleaching process, the alkali extraction and the chlorine dioxide treatment, are mixed together to give a fairly neutral solution that is introduced into the river.

Also shown are a high levels of sulfate and chloride ions.

The next slide just reiterates a little bit of this data that was taken at the beginning of this study. There is a fairly small change in temperature, the conductance is also very high, and the pH is very similar to that given before. Again, the high levels of sodium, sulfate, and chloride ions are what are important.

Now, of course, it is very important to note that the inorganic parameters are only going to get it so far. Really, the focus of this study has to be on organic materials, although we have already noted that the BOD and COD levels were not really very indicative of what is going on in the waste.

The next slide shows the results for the TOC analysis. The TOC upstream of the plant discharge is about 73 mg/L, and downstream it is about 140 mg/L. TOC gives us some idea of what is going on, however there still is a significant amount of TOC in the river due to the nature of the land above the plant.

You might note that this value, the 73 mg/L, is fairly similar to values obtained in the literature for undiluted streams.

The next slide shows some attempt here to try to determine some of the specific compounds that might be present in the water. This is the result of EPA Method 625 to analyze for extractable organics.

There are many compounds present, however they have very low concentrations. We are talking about 5 μg/L to 80 μg/L. There is approximately 300 μg/L of unidentified compounds. This gives us a total of about 0.5 mg/L.

Now, if you recall, in the last slide we had over 140 mg/L of TOC. So, we are really not making a lot of headway by trying to analyze for extractable compounds.

This leads us to try to look at a more global analysis of the waste, and this is the so-called NPTOX analysis that we are interested in here. This is a modification of EPA Method 9020 for total organic halogen. The method has a detection limit of roughly 10 μg/L of NPTOX as chlorine.

The procedure involves a modification to the EPA method by purging the sample with CO_2 or, preferably, helium to remove any volatile organics. I might mention that the waste discharge from the plant goes through an aeration lagoon with about a one-day residence time before it is discharged to the river, so many of the volatile organics are already removed. However, it is important to remove any remaining volatile organics, primarily chloroform, to have a good comparison with other samples.

This material is then passed through two activated carbon beds which adsorb the organic compounds. The column is then washed with potassium nitrate to remove any inorganic chlorides.

The columns are then combusted at 1000 degrees, producing combustion gases which can be precipitated with silver acetate to form silver halides. Finally, the decrease in silver is measured calorimetrically.

The results for the river water are shown in the next slide where the NPTOX level upstream of the plant discharge is roughly 90 μg/L, and downstream of the plant, it is roughly 15,000 to 16,000 μg/L. So, you can see that there is a very significant increase in the level of NPTOX from upstream to downstream.

The next slide shows the ratio of NPTOX to TOC. One of the important things to note is the elevated level for the upstream sample. Now, this is in line with some literature that was taken just about the same time that this work was performed. There are a number of works by Asplund and Grimvall in Sweden who reported adsorbable organic halide or total organic halide rather than the non-purgeable TOX per TOC to be roughly in the range of 1000 μg/g as shown here for the unpolluted river upstream of the plant.

So, we have roughly a factor of 100 increase in NPTOX to TOC ratio.

What we would like to do at this point is try to get an idea of the composition of NPTOX. This analysis was made somewhat simpler by the observation of workers who were trying to test for metals. They found that in lowering the pH of the river water, a precipitate was formed.

The next slide shows the procedure here that is used to purify lignin compounds from various sources. The river water is first filtered, then acidified to lower the pH, heated, and centrifuged to produce a precipitated compound. The compound is then redissolved and washed in several cycles

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So, what we have here is, finally, a redissolved and purified lignin compound. I might note at this point that this procedure is based very much on procedures used by Fricke and Martin and others for analyzing and purifying lignin compounds from black liquor. However, this work was the first work to try to apply this kind of procedure to the effluent from a bleaching plant.

The next slide shows the NPTOX distribution in the Fenholloway River as we have shown already, the 16.1 mg/L. Now, the supernate from the extraction purification process shown in the previous slide is about 11.1 mg/L which represents about 70 percent of the total NPTOX in the water.

There is about 31 percent of the NPTOX, by difference, therefore contained in the Fenextract.

The next slide shows the molecular weight distribution of the supernate from ultra-filtration. The species above 30,000 nominal molecular weight gives a value of NPTOX roughly 0.43 mg/L, and the values between 10,000 and 30,000 molecular weight give values of about 0. 37 mg/L. Finally, below the 10,000 molecular weight, there is about 7.2 mg/L.

The values on the right-hand side represent the recovery. There is somewhat of a loss of the sample during the filtration which is to be expected due to the nature of the compound. However, that 7.2 represents approximately 45 percent of the total 16.1 mg/L of Fenextract.

So, we have roughly about 45 percent of the NPTOX below 10,000 molecular weight, and the Fenextract is roughly 30 percent of the total NPTOX.

I might note also at this point that most of the color in the river, approximately 65 percent of the color of the sample, could be attributed to the Fenextract itself. I also will note that Fenextract could not be precipitated from water taken upstream of the plant.

The next slide shows the elemental composition of Fenextract. It can be seen to consist of primarily carbon, hydrogen, oxygen, and nitrogen. We also have elevated levels of sulfur and chlorine which indicated that we are getting chlorinated thiolignin compounds.

The next slide shows the distribution of different types of carbon types in the Fenextract as obtained using C_{13} NMR. The Fenextract is shown in the first column.

In the second column is indulin AT. This is a purified native lignin which would represent a lignin that would be found before any kind of bleaching process. Of course, the Fenextract is what is found downstream of a bleaching plant.

The important point to note here, is that the aliphatic character of the Fenextract is significantly increased from the 42 percent in the native lignin to 55 percent in the Fenextract. So, it is showing there is a significant increase in aliphatic content and, simultaneously, a decrease in aromatic groups.

The carbonyl and carboxyl groups also show an increase from the native. The methoxyl groups were not determined due to the fact that the signal on the NMR was not completely resolved. However, other methods found approximately 2 percent in the Fenextract.

It is important to note that we have both an increase of carboxyl groups as well as a decrease of the aromatic content. This gives us some indication of what is happening in the bleaching process.

The next slide shows a chemical reaction scheme developed by Lingren for various model lignin compounds. Compound 1 is a lignin guaiacol, and this compound is subjected to chlorine dioxide treatment to lead to a phenoxy radical, and this phenoxy radical, number 2, can either go through a chloride ester to form compound 6 which is a methyl muconate, or it can go to form a compound 4 which is a quinoid product.

Due to the information shown on the last slide where the aromatic content was very much decreased and the number of carboxylic acid groups was increased, we can see that the ring opening is very much what we would expect to be occurring in the bleaching plant.

So, we feel that the evidence from this study of the Fenextract gives us some idea that there is an increase of ring opening.

Finally, in conclusion, I would like to say that the chemical characterization of the water quality in the effluent from kraft mills has led to an improved measurement, termed NPTOX, of non-purgeable total organic halide. This is just a modification of EPA Method 9020. The ratio of NPTOX to TOC was elevated for the downstream by a factor of approximately 100 from the upstream to the downstream of the kraft mill.

Of course, there are other sources of NPTOX which are found in the literature also and that were found upstream of the plant. The NPTOX to TOC ratio is not a definitive way of showing the effluent.

However, an acid insoluble precipitate, termed Fenextract, could only be isolated from the downstream part of the effluent. This consists of large molecular weight chlorothiolignin derivatives.

Finally, the structure of this Fenextract, as obtained by the C_{13} NMR, indicates that the chlorine dioxide oxidation reaction in this pulping process leads to the aromatic ring cleavage and formulation of smaller lignin fragments.

Finally, in acknowledgements, I would like to acknowledge the support of the Florida Department of Environmental Regulation Water Quality Assurance Trust Fund for this work and also thank the organizers of this conference.

The work reported here has been published in *Environmental Science & Technology*, Volume 27, Number 12, 1993, pp 2311-2317.

MR. TELLIARD: Any questions out there? (No response.)

MR. TELLIARD: Are you sure? Bruce, thank you very much.

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THE ANALYSIS OF KRAFT MILL EFFLUENT USING THE NONPURGEABLE TOTAL ORGANIC HALIDE (NPTOX) TEST

by

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Paper presented at the EPA's 17th Annual Conference on Analysis of Pollutants in the Environment, Norfolk, VA, May 3 - 5, 1994.

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OUTLINE

- Introduction
- Effluent Water Quality Analysis
- NPTOX Analysis
- Fenextract Analysis
    - Preparation and elementary composition
    - Distribution in River
    - Molecular Weight Determination
    - Structural Features
- Implications for chemistry of bleaching
- Conclusions
- Acknowledgements

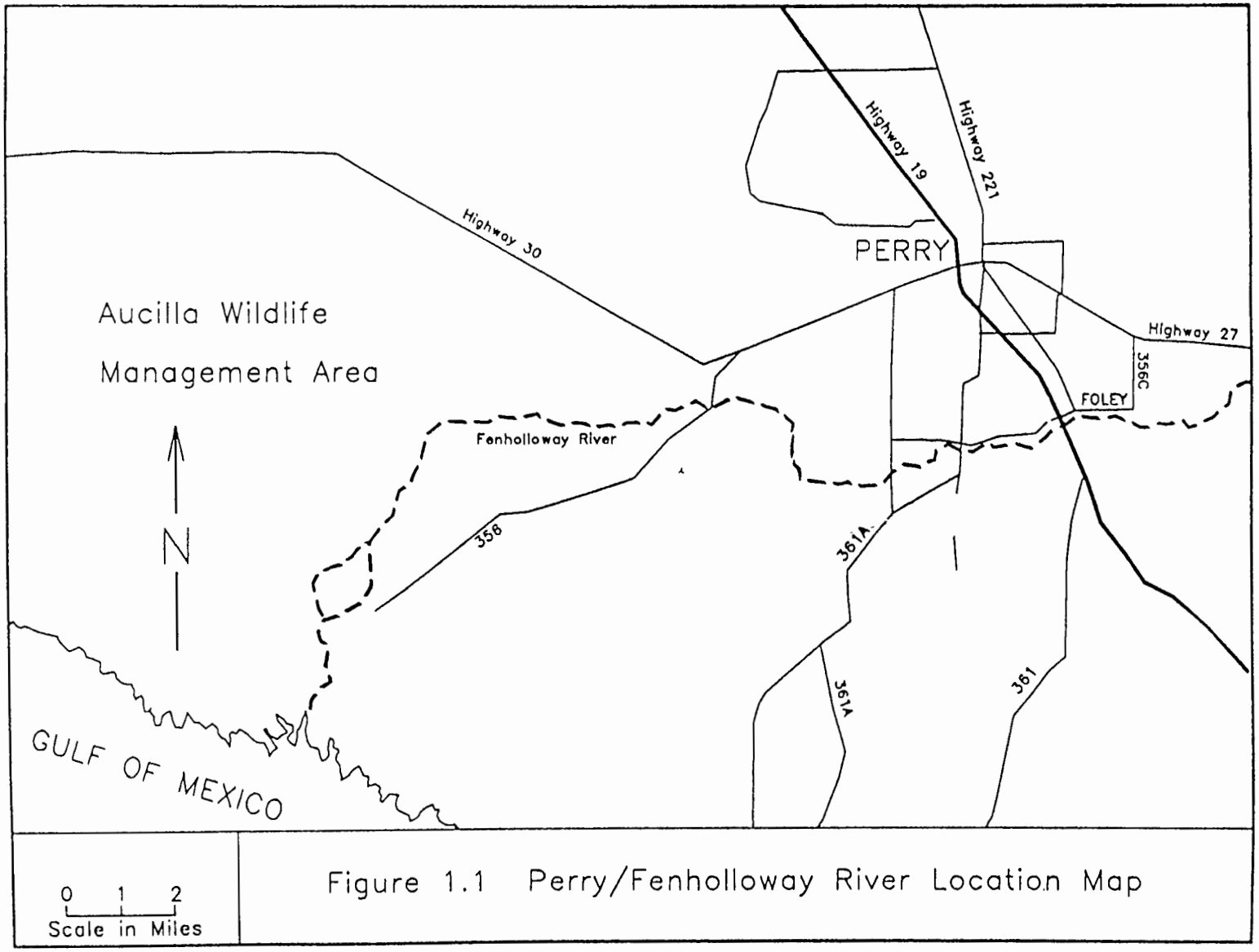
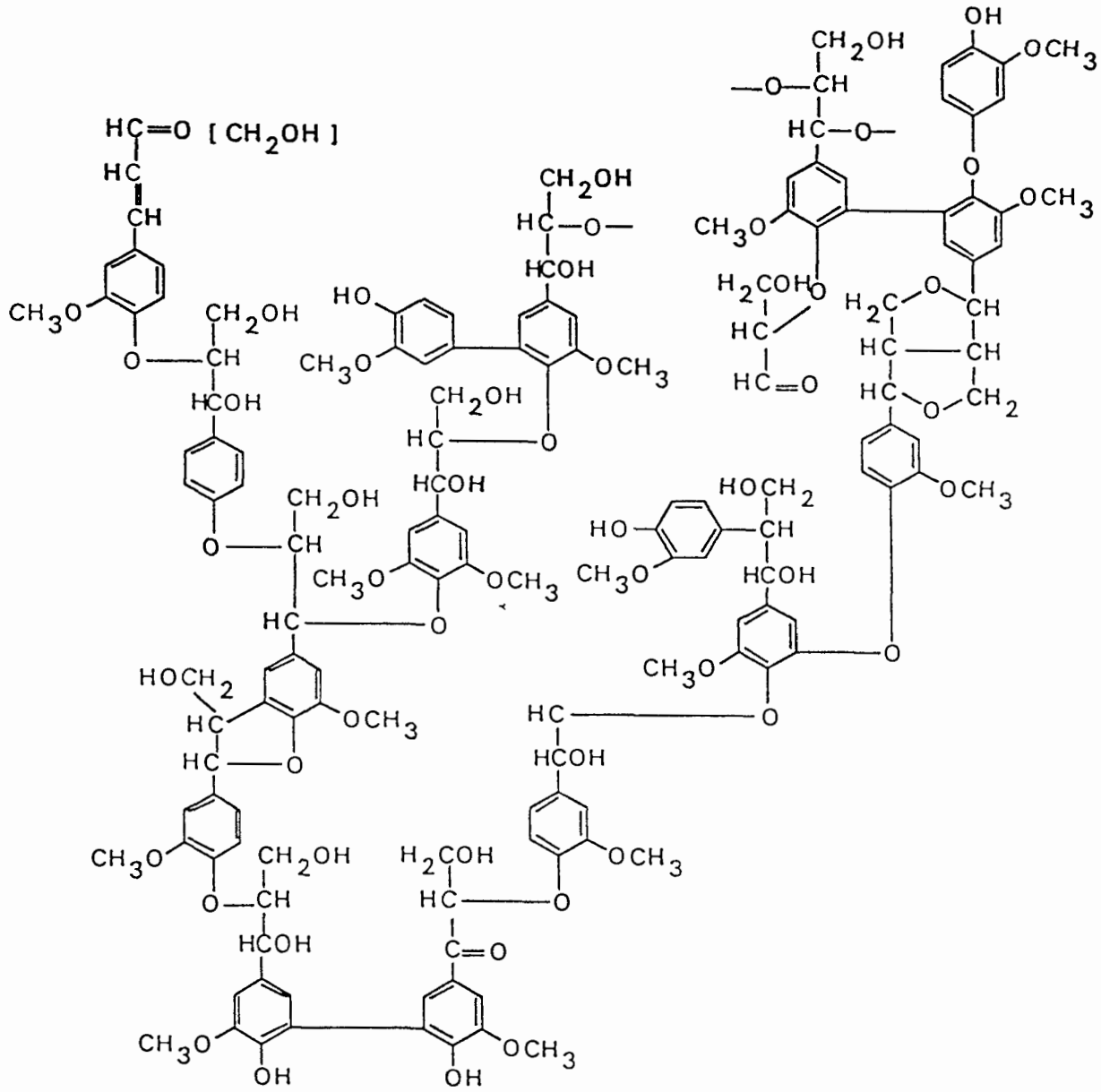


Figure 1.1 Perry/Fenholloway River Location Map

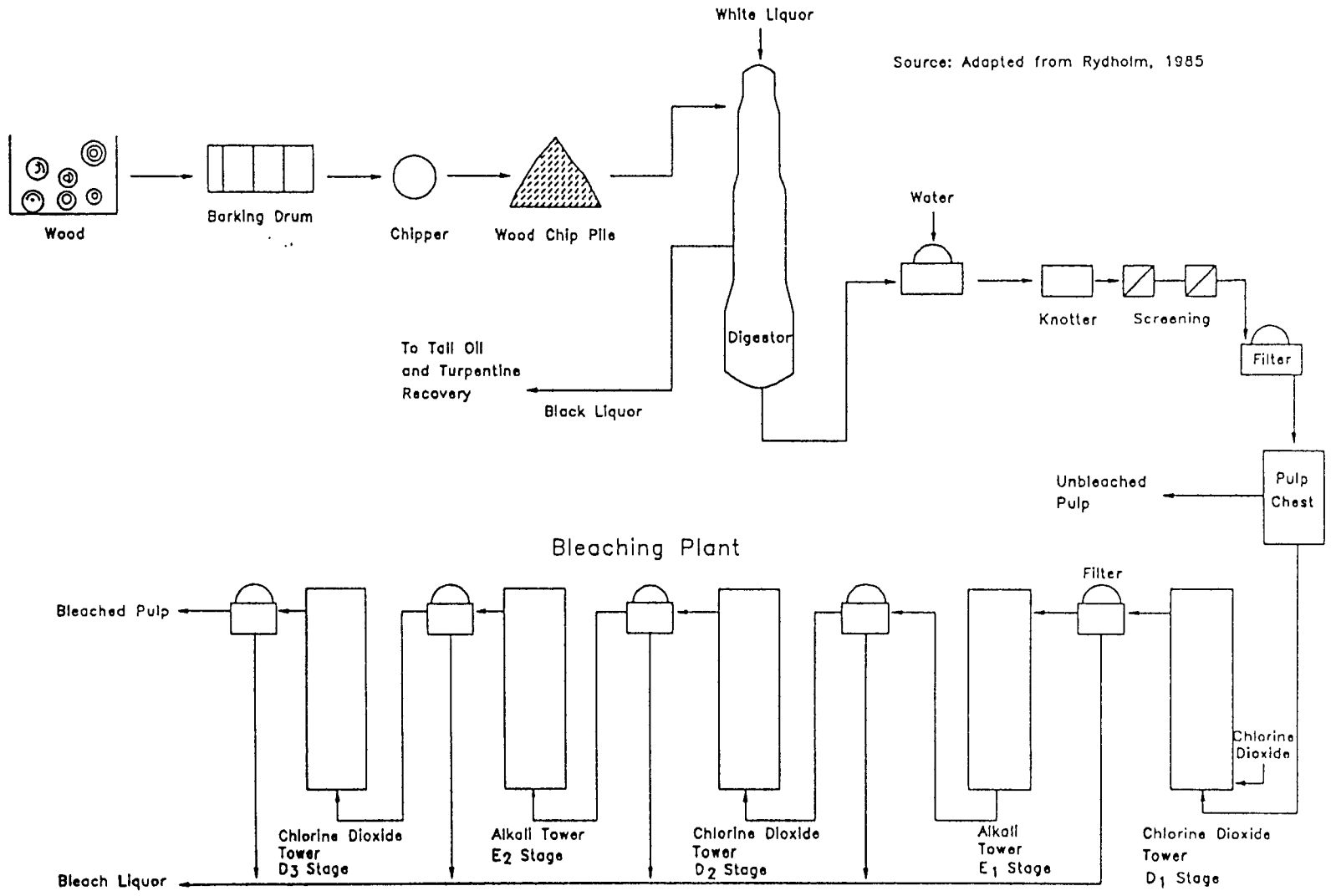
Composition of *Pinus Strobus*

(Timell, 1967)

Constituent	%
Cellulose	41
Lignin	29
Hemicellulose	
Arabino-4-O-Methylglucuronoxylan	9
O-Acetyl-Galactoglucomannan	18
Arabinogalactan	1
Extractives	1-2



Structural Features of Lignin (Adler, 1977)


White Liquor
Source: Adapted from Rydholm, 1985
Wood
Barking Drum
Chipper
Wood Chip Pile
Digestor
Water
Knotter
Screening
Filter
To Tall Oil
and Turpentine
Recovery
Black Liquor
Pulp
Chest
Unbleached
Pulp
Bleaching Plant
Filter
Bleached Pulp
Chlorine
Dioxide
Chlorine Dioxide
Tower
D3 Stage
Alkali Tower
E2 Stage
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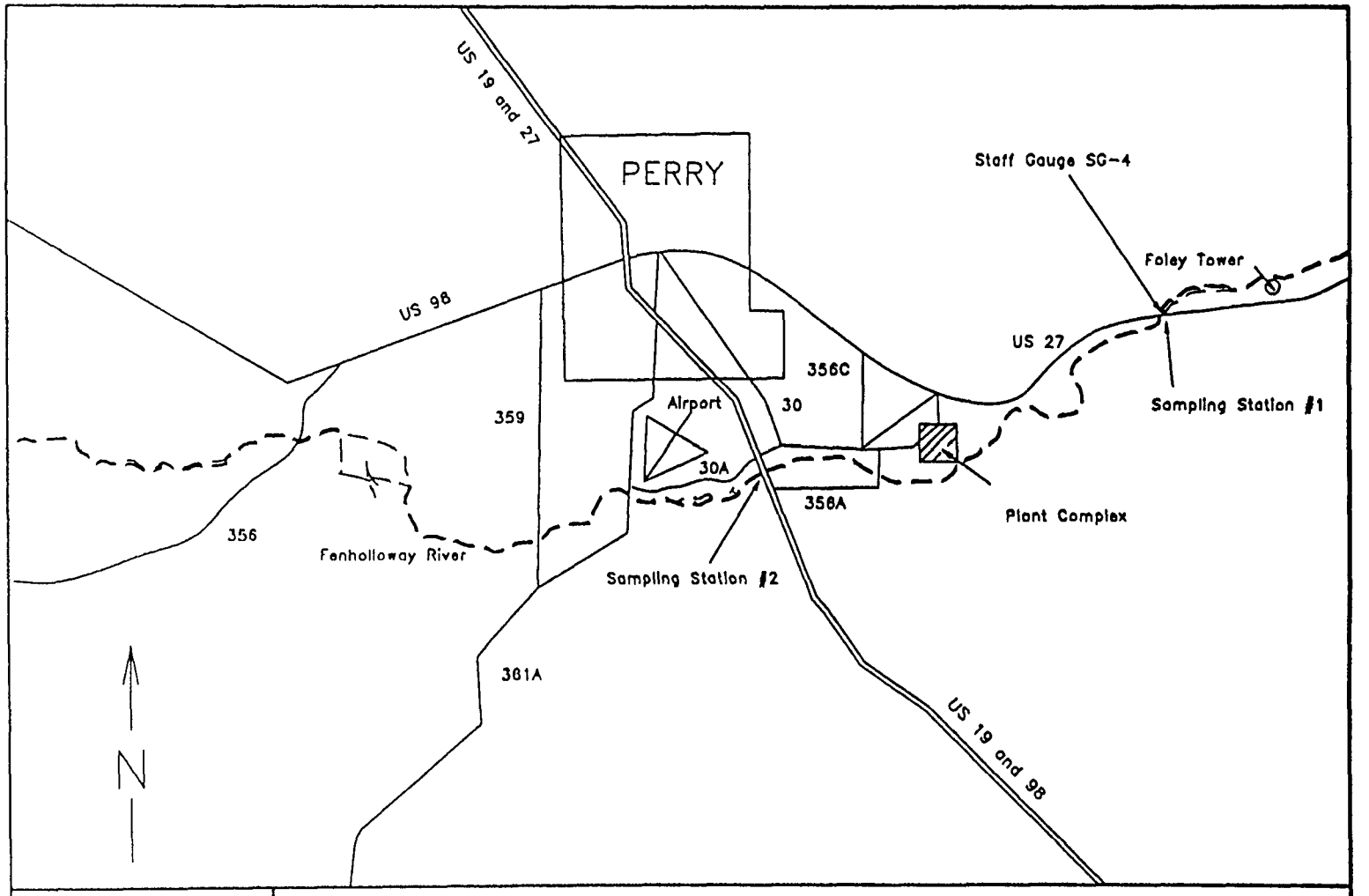
Tower
D1 Stage
Bleach Liquor



0 2
Scale in miles

Figure 3.1 Location of Fenholloway Sampling Stations

Fenholloway River-Median Water Quality Data 1980 - 1988 (FDER, 1990A)

Parameters	Station 1 US 27 Bridge	Station 2 US 19/98 Bridge	Station 3 Fishcamp
Color (PCU*)	499	1640	652
Dissolved Oxygen (mg/l)	3.1	1.9	1.2
BOD_5 (mg/l)	1.7	27.7	21.3
COD (mg/l)	413	422	195
Conductance (μmhos/cm.)	206	1993	931
pH (S.U.)	6.5	7.1	7.1
Sulfate (mg/l)	5.0	110	49
Chloride (mg/l)	8.6	345	205

*PCU = Platinum Cobalt Units

Inorganic Parameters

Parameter	Upstream Station # 1	Downstream Station # 2
Temperature (°C)	26.2	25.2
Conductance	72	1780
pH (S.U)	6.4	7.1
Chloride (mg/l)	10	590
Sulfate	35	260
Sodium	2.6	490
Iron (mg/l)	0.59	0.53
Manganese (mg/l)	0.008	0.19

Fenholloway River - TOC Analyses

Parameter	Station 1 US 27 Bridge (6/18/91)	Station 2 US 19/98 Bridge (1/19/90)
TOC (mg C/l)	73	140

Extractable Organic Components **

Extractable Organic	Concentration (μg/l)
2,4-Dichlorophenol	8
2,4,6-Trichlorophenol	24
2,3,4,6-Tetrachlorophenol	6
Bis (2-ethylhexyl)phthalate	26
Sulfonyl bismethane*	30
Dimethylcyclohexene*	40
Dimethyltrisulfide*	5
Dimethylhexadiene*	8
Trichlorodifluoroethane*	80
Methoxyphenylpropanone*	10
4-Hydroxy-3-methoxybenzaldehyde*	10
Tetrachloromethoxyphenol*	5
Hexadecanoic Acid*	10
Unidentified Components (#)	300 (7)
Total	< .5 mg/l

* Tentatively identified compound.
** Water sample taken from monitoring station 2

NPTOX Analysis

- Nonpurgeable total organic halide

- Modification of EPA Method 9020 for Total Organic Halogen

- Method detection limit of 10 μg/l NPTOX as chlorine

- Procedure:

    1) Purge with CO_2 (or He) to remove volatile organics

    2) Pass through two activated carbon beds

    3) Wash columns with potassium nitrate

    4) Combust columns at 1000° C

    5) Precipitate combustion gases with silver acetate to form silver halides

    6) Measure decrease in silver ions coulometrically

Fenholloway River - NPTOX Analysis

Sampling Station	NPTOX (μg/l)
Station 1 (upstream)	90
Station 2 (downstream)	15,000 - 16,100

Total NPTOX / TOC Ratio

Station 1 (upstream)	1200 μg/g
Station 2 (downstream)	112,000 μg/g

River Water

↓ Filtration

River Water

↓ Acidification with H_2SO_4

Lignin Precipitate

↓ Heat

Lignin Precipitate

↓ Centrifuge/Acid Wash/Centrifuge

Lignin Precipitate

↓ Dissolve in NaOH

Lignin Solution

↓ Acidification With H_2SO_4

Lignin Precipitate

↓ Heat

Lignin Precipitate

↓ Centrifuge/Acid Wash/Centrifuge (Three Times)

Lignin Precipitate

↓ Deionized Water Wash/Centrifuge

Lignin Precipitate

↓ Oven Dry

Lignin Sample

Figure 3.2 River Water Lignin Extraction/Purification Scheme

NPTOX / Distribution

Sample	NPTOX (mg/l)	Recovery
Fenholloway River Water (downstream)	16.1	
Supernatant (from extraction / purification)	11.1	(69%)
Fenextract (by difference)	5.0	(31%)

NPTOX Molecular Weight Distribution of Supernatant Ultrafiltration

	NPTOX (mg/l)	Recovery
Retentate > 30,000 NMWL	0.43	3.8%
30,000 > Rentenate > 10,000 NMWL	0.37	3.3%
Filtrate < 10,000 NMWL	7.2	65%
		72%

Elemental Composition of Fenextract

Element	Weight %
Carbon	54.27
Hyrdogen	5.20
Oxygen	29.12
Nitrogen	1.32
Sulfur	3.41
Chlorine	3.50

Carbon Distribution in Fenextract and Indulin AT by C-NMR

Carbon Type	Fenextract % (after bleaching)	Indulin AT % (before bleaching)
Aliphatic	55	42
Aromatic	34	56
Carboxyl	5	2
Carbonyl	6	ND
Methoxyl	NQ	~ 9

ND - Not detected NQ - Not quantified

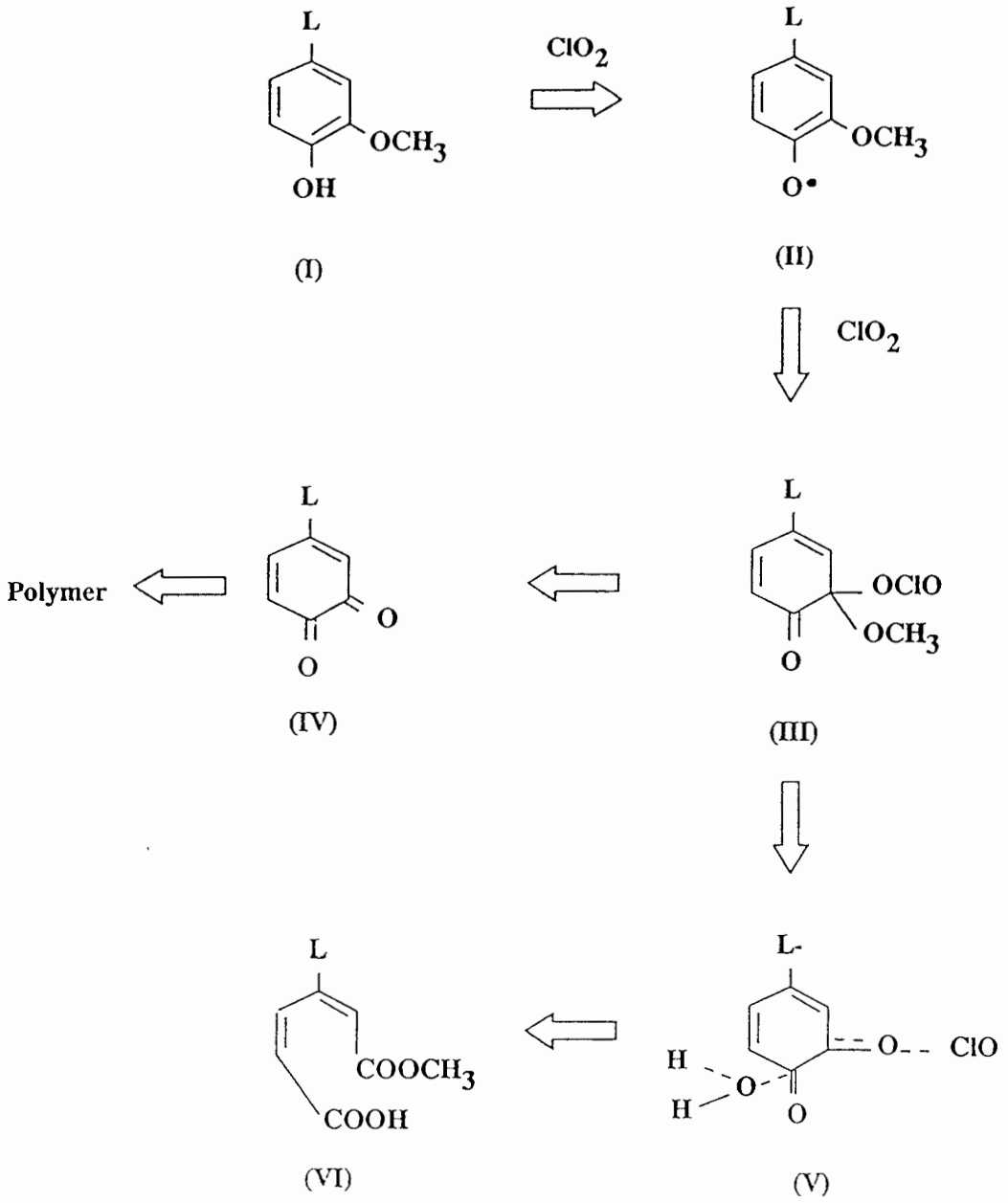


Figure 5. Chlorine Dioxide Oxidation of Lignin (Lindgren, 1971)

CONCLUSIONS

· Chemical characterization of the water quality in the outfall from a kraft mill has lead to an improved measurement, termed NPTOX, of the nonpurgeable total organic halide.

· NPTOX / TOC ratio allows organochlorine compounds derived from Kraft mills to be distinguished from naturally occurring organochlorine compounds from blackwater rivers.

· An acid insoluble precipitate, termed Fenextract, has been isolated and consists of large molecular weight chlorothiolignin derivatives.

· The structure of Fenextract gives indication that chlorine dioxide oxidation reaction in pulp bleaching leads to aromatic ring cleavage and polymerization of smaller lignin fragments.

ACKNOWLEDGEMENTS

· Support by the Florida Department of Environmental Regulation WQ005 Water Quality Assurance Trust Fund for this work is gratefully appreciated.

MR. TELLIARD: We would like to finish somewhere close to the schedule today. Some people have travel scheduled to deal with.

So, if we could take a break now and get back in here in 15 minutes, I would appreciate it. Thank you.

(A brief recess was taken.)

MR. TELLIARD: We would like to get going. Our next speaker is Ileana Rhodes from Shell Development. Ileana is a Research Chemist in the Analytical Chemistry Group there. I first met this young lady when she was working on drilling muds with us which was a few years ago. She started this, as was pointed out, as a high school project, so she was very young at the time. As part of her senior year field trip, she got to do drilling muds.

We are going to get a case study today on the pitfalls of using conventional TPH methods for source identification.

Thank you and welcome.

PITFALLS USING CONVENTIONAL TPH METHODS FOR SOURCE IDENTIFICATION: A CASE STUDY

Ileana A. L. Rhodes, E. M. Hinojosa, D. A. Barker, Robin A. Poole

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Abstract

A case study involving soil contaminated with used motor oil illustrates the problems in using conventional TPH methods for identification of source.

Background

There are several approaches for assessment of water and soil contamination. The terms "oil and grease" and "total petroleum hydrocarbons" (TPH) are used to describe the extent of contamination in water and soil. However, the actual value determined is method dependent and is defined by the method used. Most of the methods have been adapted from EPA methods that were originally developed for the determination of target analytes

at trace (ppb) concentrations in clean matrices. All methods involve some sort of extraction procedure followed by analysis of the extracts using gravimetry, infrared spectroscopy and/or gas chromatographic procedures. Gas chromatographic procedures either used selected components or a sum of all components detected within a given range. There are numerous publications documenting the problems and describing studies that emphasize the severe limitations with all of the commonly used "TPH methods[1-3]. The ability to interpret TPH data is only as good as the knowledge of the type of hydrocarbon contamination[2]. In addition, results are entirely dependent on the method used. Table 1 includes a summary of the most commonly used analytical methods for the determination of TPH. With the exception of ASTM Method 3328-90 (identification of waterborne oils), none of the methods listed have any provisions for product type identification[4]. This ASTM method does not include quantitation since it describes characterization of separate phase hydrocarbons and it is not a TPH method.

Most of the investigations involving potential contamination by petroleum hydrocarbons are related to underground storage tanks and pipeline releases. These types of investigations are primarily regulated by the states. Each state has its own criteria and methodology for determination of contamination based on analysis of the potentially affected media using methods such as those listed in Table 1. Some of the practical difficulties include the fact that notification/action/cleanup levels are different depending upon the type of contamination[5]. Typically, gasoline range material is considered more hazardous to human health and the environment than heavier distillates because of its monoaromatic content as well as its higher solubility and volatility. However, the methods specified by each state have no real protocol for identification of product type. Rather, some states simply require a combination of chromatographic techniques and define "gasoline" and "diesel" materials based on carbon ranges. Whatever elutes within a selected range is called "gasoline range" or "diesel range" whether or not the labels are applicable. As indicated in Table 2, there is a great deal of overlap in carbon ranges for all petroleum products.

Practical Limitations

The most frequently used approach is to use two methods, one for the volatile range and another for the semivolatile range. The volatile range analysis is usually done by analysis of water samples or soil extracts by purge and trap GC with flame ionization detector and often called "gasoline range organics" method, GRO, Modified EPA Method 8015, California LUFT 1, Wisconsin GRO, Washington GRO, etc. The methods typically quantitate anything eluting after C4, C5 or C6 and up to C10 or C12 depending on the state. The semivolatile range is done by analysis of a concentrated extract by direct injection GC with flame ionization detection. The method is often referred as "diesel range organics", DRO, Modified EPA Method 8015, California LUFT 2, Wisconsin DRO, Washington DRO, etc. Depending on the state, laboratory or analyst, the method may include a range C9, C10 or C12 up to C25 or up to C30.

Anything detected in the specified ranges is automatically called gasoline range or diesel range. In many cases the "range" qualifier is dropped or ignored and the final report often identifies the contamination as "gasoline" and/or "diesel". This can result in erroneous assessment of nature/source of contamination as well as false liabilities.

Many laboratories attempt to determine a product type by matching the chromatograms to other chromatograms obtained from analysis of reference products. This approach is referred to as "fingerprinting". This approach can be quite useful if there is appropriate expertise in recognizing different products' fingerprints. However, this can be difficult because the fingerprint is segmented (obtained from two different analyses), the products are weathered, there are bias due to sample preparation, evaporation, purging efficiency, and the great deal of overlap among product types. For example, a portion of diesel is in the gasoline range by the ranges defined in the methods. Conversely, a portion of gasoline is within the diesel range as defined in the methods.

A better approach to identify product type is to use a single chromatographic analysis that includes a wide carbon range that encompasses gasoline as well as diesel ranges and beyond. There are such methods that have been in used primarily by the oil industry to optimize refinery processes and product characterization. The methods can be modified to analyze extracts rather than neat materials[6]. Using a single chromatographic procedure, it is more convenient to evaluate fingerprints. Figures 1-3 and Tables 2-3 illustrate the degree of overlap of gasoline and diesel. Because different states have different carbon number cutoffs, results can vary a great deal. The distribution becomes even more complex with weathering of gasoline as shown in Figure 4 where a severely weathered gasoline would result in reporting of a significant concentration due to diesel. Without seeing and understanding the "picture" or chromatogram, it would be impossible to properly assess source. The common practice is to simply report gasoline range and diesel range concentrations for TPH without accompanying chromatograms. This information is often used incorrectly because it may be interpreted simply as a mixed gasoline and diesel release.

Additional Considerations

Even in cases where analysis identifies gasoline range material with the proper fingerprint for gasoline, there still could be significant problems in source identification without a deeper understanding of the nature of contamination. This is illustrated with a case study where gasoline range material was properly identified in the sample. However, the source of gasoline was not from an underground storage tank release but rather from used motor oil in soil.

Case Study

An investigation report indicated that there was soil contamination in a site that had been a service station for about 60 years and an auto repair shop for the last 20 years. There had

been several generations of underground storage tanks on the site through the years. Gasoline as well as used motor oils were stored at the site. Since the auto repair shop did not utilize the fuel tanks, they were removed. The contractor's report indicated that there was no evidence of leaks but there was some overall soil contamination at the site.

Conventional Approach

Soil analysis was done using California TPH methods where the gasoline range and the diesel range materials are determined by gas chromatography. Numerical TPH results indicated that there was gasoline present in the soil (anywhere from not detected up to 3000 ppm). There was limited information on the diesel range. This information was interpreted as a release from leaking tanks.

Chromatograms were requested and reviewed. Upon review of the chromatograms, it was evident that a weathered gasoline fingerprint was present in the gasoline range method and that material heavier than diesel fuel was also present in significantly higher amounts in the diesel range method. Some type of oil was the likely source of the heavy material which was not reported since the bulk of it is out of the diesel range. The fingerprint of this heavy material suggests the presence of motor oil.

After review of chromatographic fingerprints, the site was classified as containing gasoline range material as well as a heavy oil contamination. The implication was that the previous service station owner was liable since the current auto repair shop did not store fuels at the site. Both operators used a waste oil tank. Most of the analytical information was on the gasoline range and aromatics (BTEX) composition since the investigation was centered in finding gasoline. This is a typical situation where investigations are not conducted to determine what is really present but rather to look for specific components to support a case.

Interpretative Single Analysis Approach

It is quite important to use information from many sources when attempting to identify contamination source. Upon review of the contract laboratory data (particularly the chromatograms), it was evident that weathered gasoline range material was present in the soil. It was also evident that the bulk of contamination was a heavy oil whose chromatographic fingerprint and carbon number range resembled a motor oil. The main issue was whether or not leaky fuel tanks were the source of gasoline range soil contamination or were there other possible sources.

It is a well known and normal phenomenon that used motor oil becomes diluted with fuel during engine operation. Gaseous fuel from engine blowby and liquid fuel washing down the cylinder walls past the piston rings are introduced into the crankcase of the engine. Oil dilution is a factor in both gasoline and diesel engines, and allowances are made for its presence in oil formulations and engine performance testing. Blowby (combustion chamber

gases blowing past the piston rings) can be more pronounced in high mileage engines with worn piston rings. In addition, under cold start and warm-up conditions more liquid fuel will be transported past the rings and into the engine lubricant. As much as 10 percent of the motor oil can consist of gasoline[7]. After engine warm-up, some of the more volatile components of the gasoline will vaporize and be removed by the positive crankcase ventilation (PCV) system. The higher boiling fuel components will remain in the motor oil, and the appearance of the gasoline portion of a GC trace from analysis of such an oil will resemble heavily weathered gasoline. Oil dilution is a factor not only in high mileage vehicles and cold start conditions, but also in new vehicles driven at highway speeds. A study was initiated to obtain fingerprints of used motor oils and to understand how used motor oils could be interpreted using conventional GC TPH methods.

Used Motor Oil Study

Since samples from the site were not available, a study was initiated using new and used motor oils and spikes into soil. A protocol was developed to characterize the oils. Samples of new oils and used motor oil from different sources were analyzed using conventional gasoline range purge and trap GC methods and a single analytical method for the determination of petroleum hydrocarbons[6]. Figures 5-8 show the chromatograms from single gasoline to diesel range analysis of new oils. Figures 9-12 show the results obtained from analysis of used oils from Toyota, Honda, Ford and Chrysler engines. Clear evidence of weathered gasoline is observed in all chromatograms.

The four used motor oils and a new motor oil were spiked in soil at approximately 1% concentration. The soils were extracted with methanol and analyzed using the conventional volatiles method for gasoline range and using the single analysis for the entire gasoline to diesel range (up to ~C30). The results from both types of analyses are listed in Table 4. Figures 13-17 show the clear fingerprint of weathered gasoline in the spiked samples. All of the used oils contain 0.6 to 1.9% gasoline range material.

Figure 18 shows the chromatogram obtained from analysis of one of the soil spikes (1% used oil/Honda) using a conventional purge and trap TPH method that can only give information on the gasoline range. Clear evidence of gasoline range material is evident, however, the method does not provide any other pertinent information such as the presence of any additional material. The problem is that this is often the only type of analysis done. Even if diesel range analysis is done, the presence of other heavier materials may be disregarded because it may fall outside of the carbon number range that are defined by the methods. The project engineer typically gets a report indicating numerical results which in this case point overwhelmingly to a "gasoline" source.

Study Implications

This study clearly indicates that when used motor oil is present, it is also expected to find the fuel that the particular engine operated on. This is obviously a case where finding

gasoline does not automatically imply a leaking underground storage tank or a pipeline product release.

Summary

It is clear that to properly identify source, conventional TPH methods are inadequate and can lead to serious misidentification of sources. This has implications beyond legal liabilities and include impaired ability to correctly establish the source of major contamination, to stop the source, and to choose proper remediation technology. In this particular case study, conventional methods indicated that soil contamination was due to a leaking storage tank when in fact the source was used motor oil which had been improperly disposed of. Motor oil cannot be readily determined using conventional chromatographic methods for TPH but useful information about its presence can be obtained from the chromatographic fingerprint .

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QUESTION AND ANSWER SESSION

MR. WALLINGS: E. Wallings from Roy Airquest and Incorporated. My question here is to trace the target source contamination of the oil contamination. We do not have to identify it is diesel fuel or it is gasoline. All we have to do is see the whole patterns and compare to the nearby potential contaminated source.

So, to my knowledge, we should still be able to correctly trace to where the source of contamination.

The second thing I would like to say is it is on the chromatograms, sometimes they have other markers. Now, you can try to identify the source.

If you go back to your chromatograms, the C17 and C18 always have the phytane and the pristane over there, and the ratio of them is a characteristic of the source of oil. So, I don't know if you have looked into that kind of a marker to trace the source of the contamination?

MS. RHODES: The point that I am trying to make...we use all those things that you refer to when you have a reference material that you are trying to piece it back to, but in this particular case in the underground storage tanks investigations, you have a facility that has been in operation for, in this particular case, 80 years.

So, we do not have the original material, so all you have to do is look at a fingerprint and try to figure out what is there. The actual source, what I meant by source was, was it a gasoline spill or was it a motor oil spill? In this particular case, it was a motor oil spill, and the particular source, meaning the type of product, was misidentified because they were not looking for the right thing with the methodology they were using.

But, yes, I agree with you. If you have a reference material, we use all kinds of things to try to piece it back to the source, but they are not part of any conventional TPH methods that are used routinely.

MR. PEIST: Ken Peist, Region II Laboratory in Edison, New Jersey. I am aware of a few other people who have been using the fingerprinting techniques in our area of the country, and I was just curious if you were aware of any like perhaps national data bases where people can compare fingerprints to sort of eliminate a lot of the leg work that has to be done.

MS. RHODES: There are a lot of contractors that do the work, and, frankly, when anybody at Shell, for example, calls me and says we need an outside party to look at fingerprinting, I do not look towards the environmental

laboratories. I look at the laboratories that are doing characterization for petroleum products like the Southern Petroleum Labs, CORE, and others. People that have been doing work for the oil industry rather than for environmental purposes. Those are the ones that I think have a better chance of trying to identify what kind of material is present, not use an EPA-based method that was done for target compounds and then try to find what the product is.

But, yes, the fingerprints are not difficult. The problem is that the information is pieced from a purge and trap method and a direct injection method which has gone through an evaporation step. The resulting information can be skewed.

MR. PEIST: Thank you.

MR. TELLIARD: One more, hold on.

MR. VARNELL: I am David Varnell with the Tennessee Valley Authority. I was wondering if you had any information concerning the ability to differentiate between lubricating oil and what is commonly called mineral oil or what we use in our transformers which I think is from a similar source.

MS. RHODES: Sometimes you can look at the trace metals and the additives but you would have to know the different additives that different manufacturers use. There are ways to do it, but it is not something that you can just go to a contract lab and get it done, to my knowledge.

MR. VARNELL: Okay, thank you.

MR. TELLIARD: We came up with a method of looking at the distinction between mineral oil, diesel, and drilling muds, and we have a procedure that we had put together for the offshore oil and gas category when they insisted on our regulating them.

If you are interested, give me a buzz and I will send you a copy of that. It is not directly applicable, but you might be able to...it is a decision tree type of approach, and it might fit in or at least give you a starting point.

PITFALLS USING CONVENTIONAL TPH METHODS FOR SOURCE IDENTIFICATION:

A CASE STUDY

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Emiliano Hinojosa
Dave Barker
Robin Poole

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17th Annual Conference
Analysis of Pollutants in the Environment
Norfolk, May 1994

O&G / TPH ???

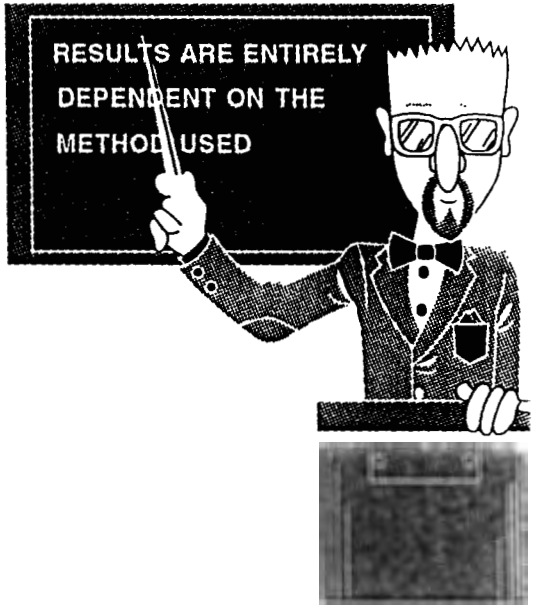
The terms "OIL & GREASE" and "TOTAL PETROLEUM HYDROCARBONS" are used to describe the extent of contamination in water, soil and wastes. However, the actual value determined is method dependent and thus must be defined by the method used

WHAT ELSE CAN BE MEASURED AS O&G / TPH ???

Any other organic compound (cleaning fluids, phthalates, mineral oils) and anything Freon soluble

WHAT IS NOT O&G / TPH ???

- It is not always "TOTAL" since heavy hydrocarbons are not always extracted, volatiles can be lost
- Not just petroleum
- Some methods underestimate aromatics
- Selected compounds are added in some methods (target compounds only)
- Limited information on product type which is often misinterpreted



O&G / TPH

INDICATOR METHODS WHICH PROVIDE INFORMATION
ON FREON EXTRACTABLE PETROLEUM HYDROCARBONS

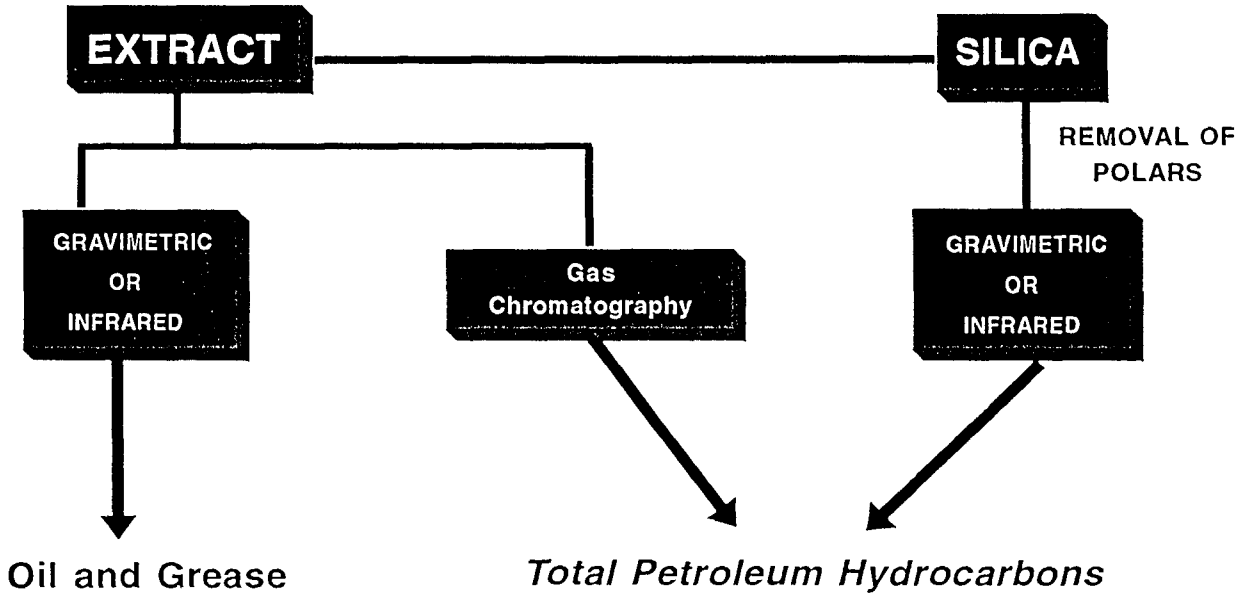


Table 1

SUMMARY OF CONVENTIONAL TPH METHODS

NO INFORMATION ON PRODUCT TYPE

GRAVIMETRIC TECHNIQUES

- EPA Methods: 413.1, 9070, 9071
- Standard Methods: 5520B, 5520D, 5520E, 5520F

INFRARED TECHNIQUES

- EPA Methods: 413.2, 418.1
- Standard Methods: 5520C

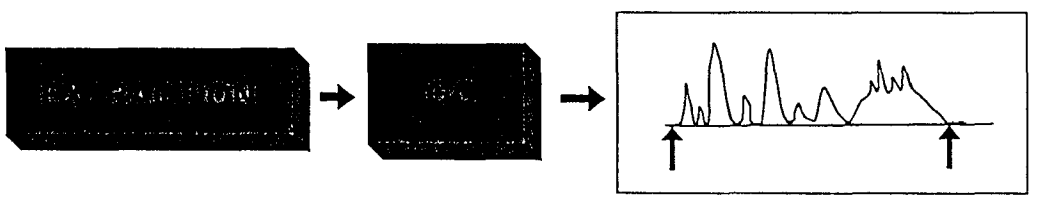
LIMITED INFORMATION ON PRODUCT TYPE (JUST C# RANGES)

GAS CHROMATOGRAPHIC TECHNIQUES

- Direct Injection Methods
  - Mod. EPA Method 8015 (GC–FID), CDHS, WDNR, WTPH, etc.
  - EPA Method 8270 (GC/MS)/Selected components
  - ASTM D3328–90 (GC–FID)/"Fingerprint" only. No quant.
- Purge & Trap and Headspace Methods (only Gasoline range)
  - Mod. EPA Method 8015 (GC–FID), CDHS, WDNR, WTPH, etc.
  - EPA Method 8020 (GC–PID)/Gives Only BTEX
  - EPA Method 8240 (GC/MS)/Selected Components

TPH
GC METHODS

- Sample is extracted with a solvent
- Extract is introduced into a gas chromatograph either by direct injection or by purge and trap techniques (the latter is only applicable for gasoline range organics)
- The chromatographic column separates components in the sample
- Total area of chromatogram is integrated and quantified by comparison

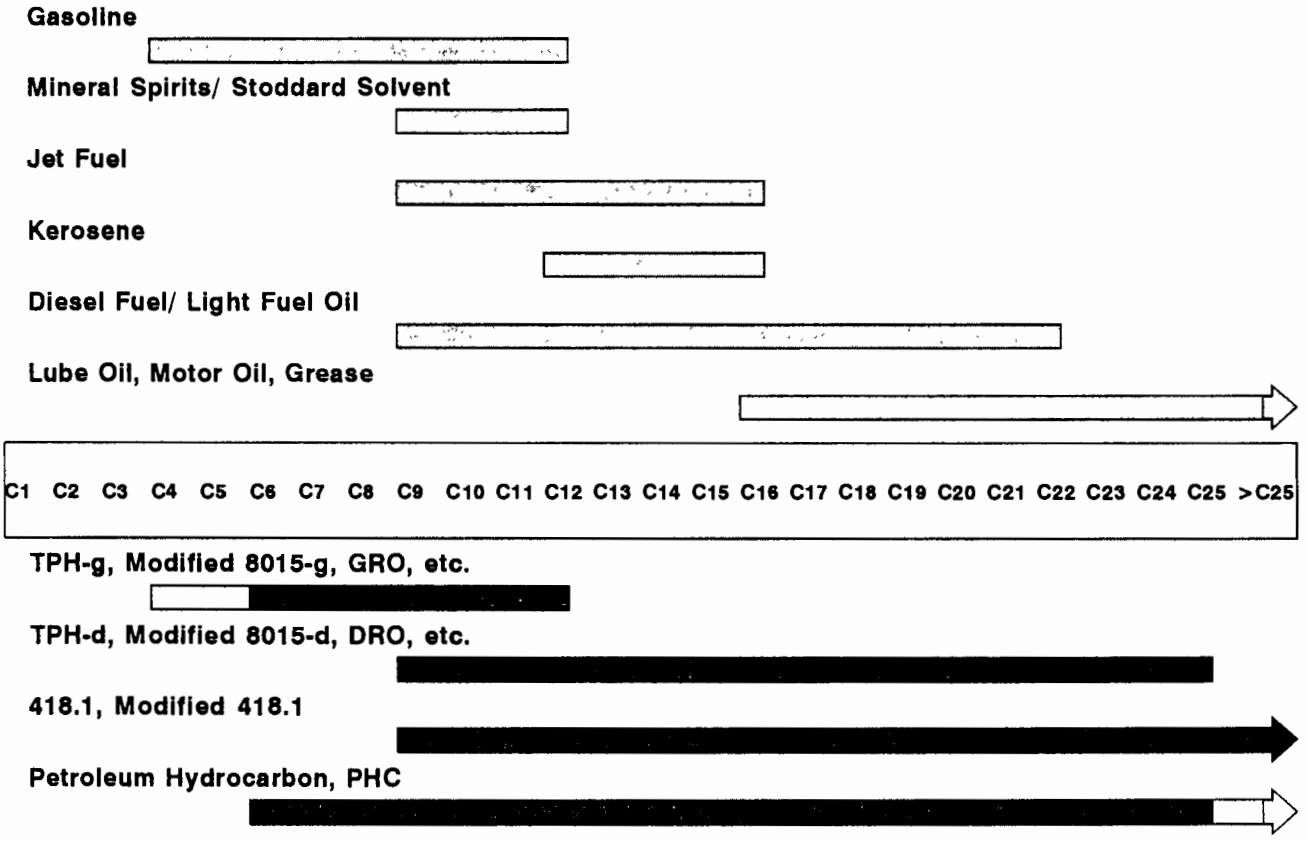


GC METHODS DO NOT INCLUDE A POLAR REMOVAL STEP

- SOME POLARS (S, N, O) WILL BE DETECTED
- SOME POLARS WILL NOT BE DETECTED (ACIDS)
- ONLY CHROMATOGRAPHABLE RANGE DETECTED (USUALLY ~~~<C40)

Table 2

Petroleum Product Carbon Number Range - Approximate



TPH Method Carbon Number Range - Approximate

Table 3

BOILING POINT DISTRIBUTION, CARBON NUMBER RANGES OVERLAP

Boiling Point	Approximate Carbon #	Cumulative % Composition: Gasoline	Jet/Kerosene	Diesel	
≤ 36°C	≈C5	13	0	0	
≤ 69°C	≈C6	27	0	0	
≤ 98°C	≈C7	43	0.2	0.05	
≤126°C	≈C8	59	1.2	0.2	
≤151°C	≈C9	62	3.6	0.5	
≤174°C	≈C10	84	9.8	1.2	C10
≤196°C	≈C11	93	23	8.9	
≤216°C	≈C12	98	44	22	C12
≤236°C	≈C13	99	63	30	
≤253°C	≈C14		79	40	
≤279°C	≈C15		91	57	
≤287°C	≈C16		98	69	
≤302°C	≈C17		99	78	
≤316°C	≈C18			85	
≤329°C	≈C19			90	
≤343°C	≈C20			94	
≤358°C	≈C21			97	
≤369°C	≈C22			98	
≤380°C	≈C23			99	
≤391°C	≈C24				
≤402°C	≈C25				

Table 4

SPIKED SOIL STUDY

SUMMARY OF BTEX AND TPH RESULTS: Gasoline Range TPH (up to C12)

Clean Soil Spiked with ~1% New and Used Motor Oil from Several Sources

Motor oil Source	Driving Conditions	Analysis Type	BTEX ppm	TPH/Gasoline Range, ppm	% Gasoline in Used Oil
New Oil	Not used	DI	<2	<20	
		P&T	<1	<10	
Toyota Used Oil	Suburban Driving	DI	16	170	1.7
		P&T	15	160	1.6
Honda Used Oil	Short Trips/City	DI	22	190	1.9
		P&T	23	140	1.4
Chrysler Used Oil	Suburban	DI	16	160	1.6
	Driving	P&T	17	140	1.4
Chrysler Used Oil (R)	Suburban	DI	16	160	1.6
	Driving	P&T	17	130	1.3
Ford Used Oil	Freeway	DI	12	80	0.8
	600 miles	P&T	13	60	0.6
	per day				

DI: Extraction followed by direct injection GC-FID
P&T: Extraction followed by purge and trap GC-FID

CHARACTERIZATION OF ORGANICS TO ~C30

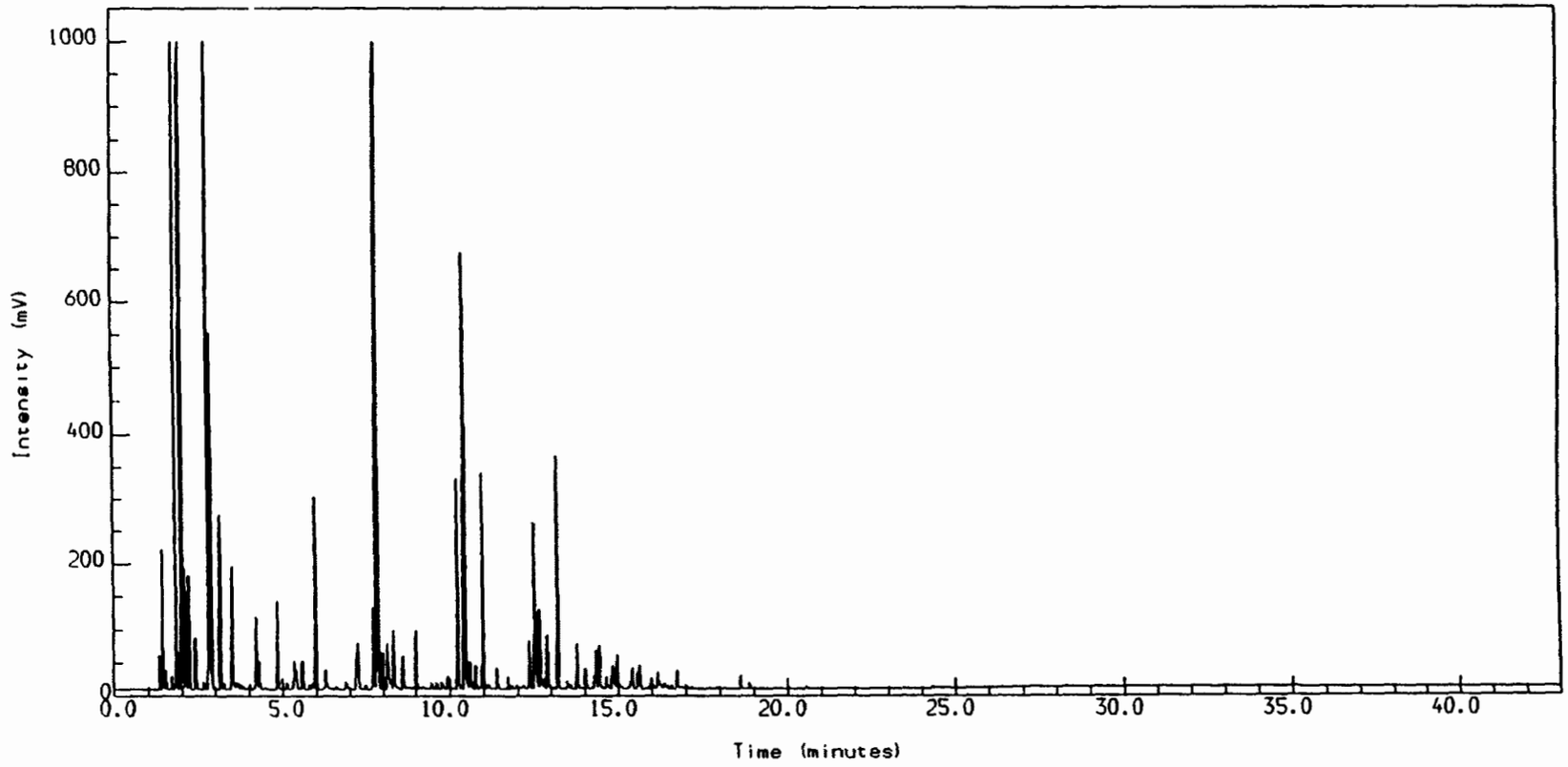


Figure 1: Chromatogram of fresh gasoline

CHARACTERIZATION OF ORGANICS TO ~C30

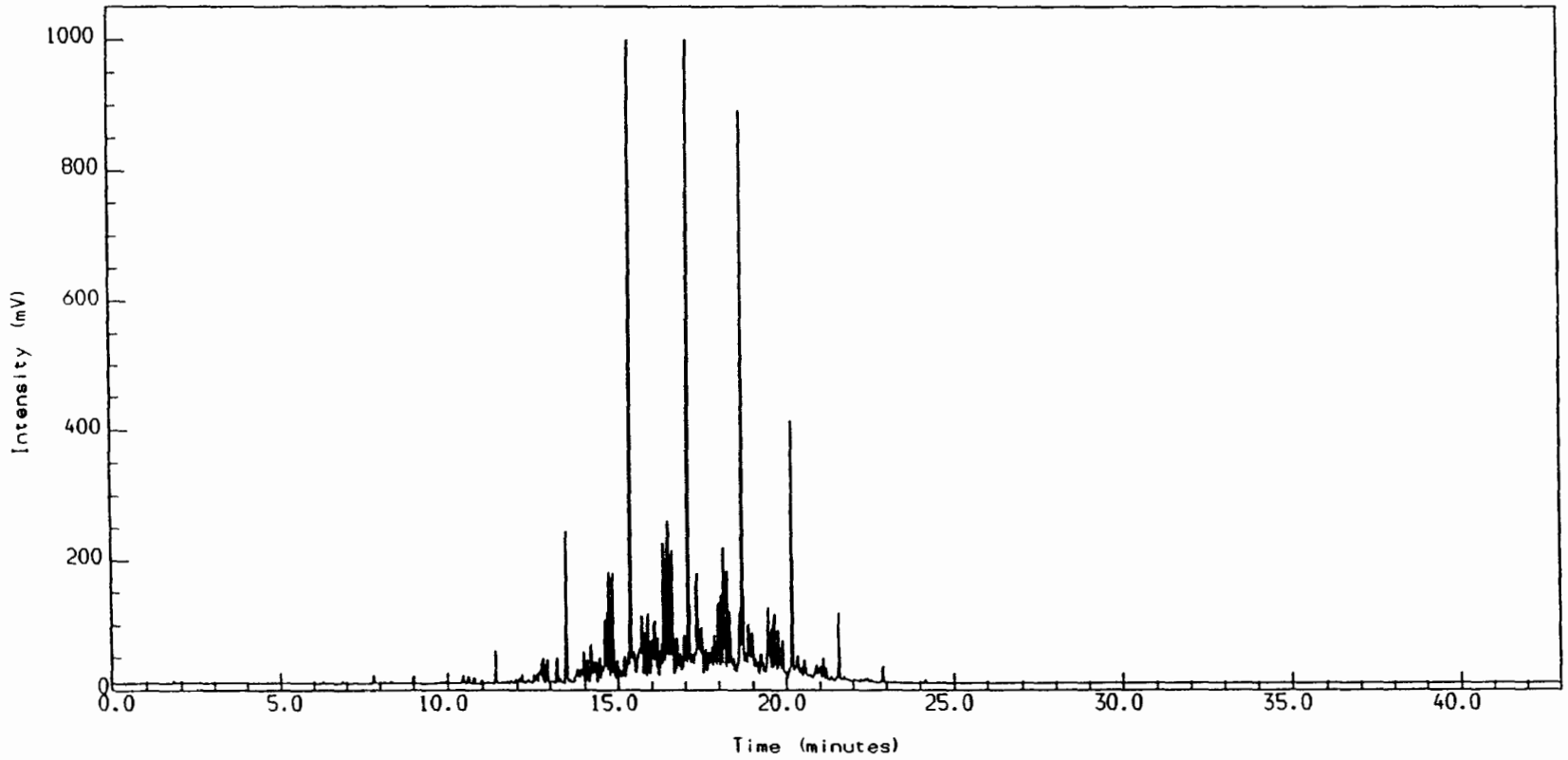


Figure 2: Chromatogram of fresh jet fuel

CHARACTERIZATION OF ORGANICS TO ~C30

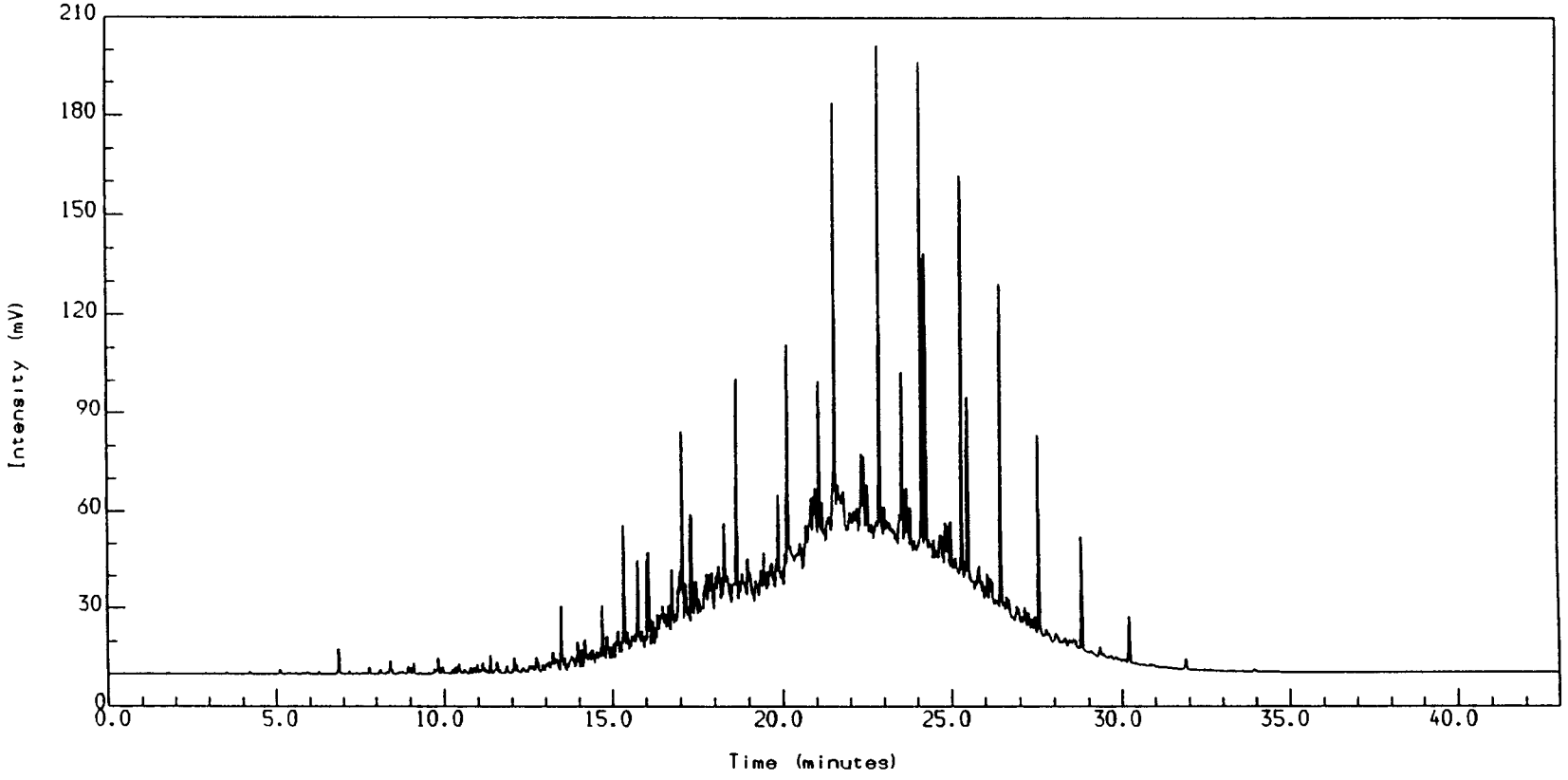


Figure 3: Chromatogram of fresh diesel fuel

CHARACTERIZATION OF ORGANICS TO ~C30

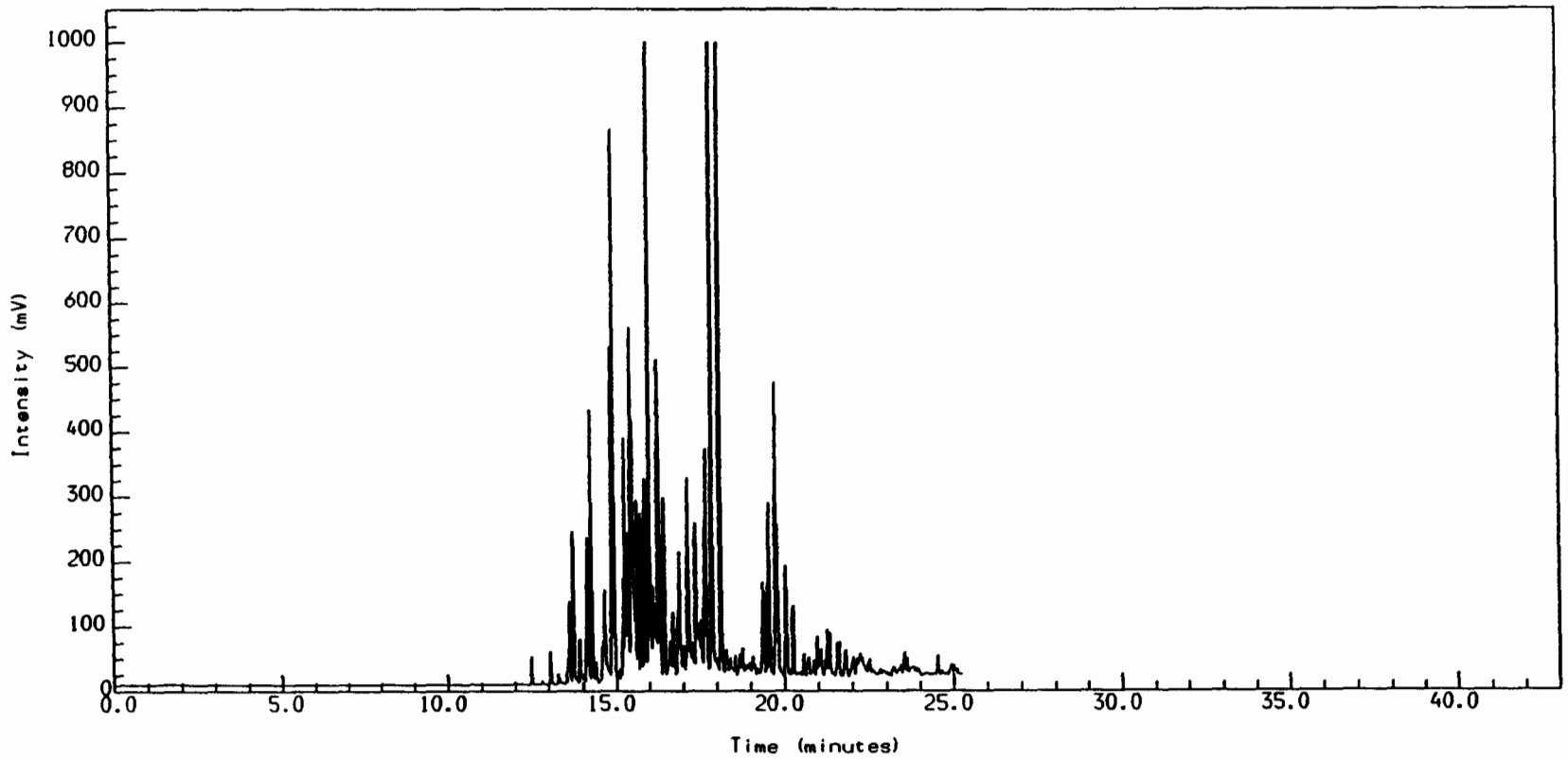


Figure 4: Chromatogram of severely weathered gasoline (~98%)

CHARACTERIZATION OF ORGANICS TO ~C30

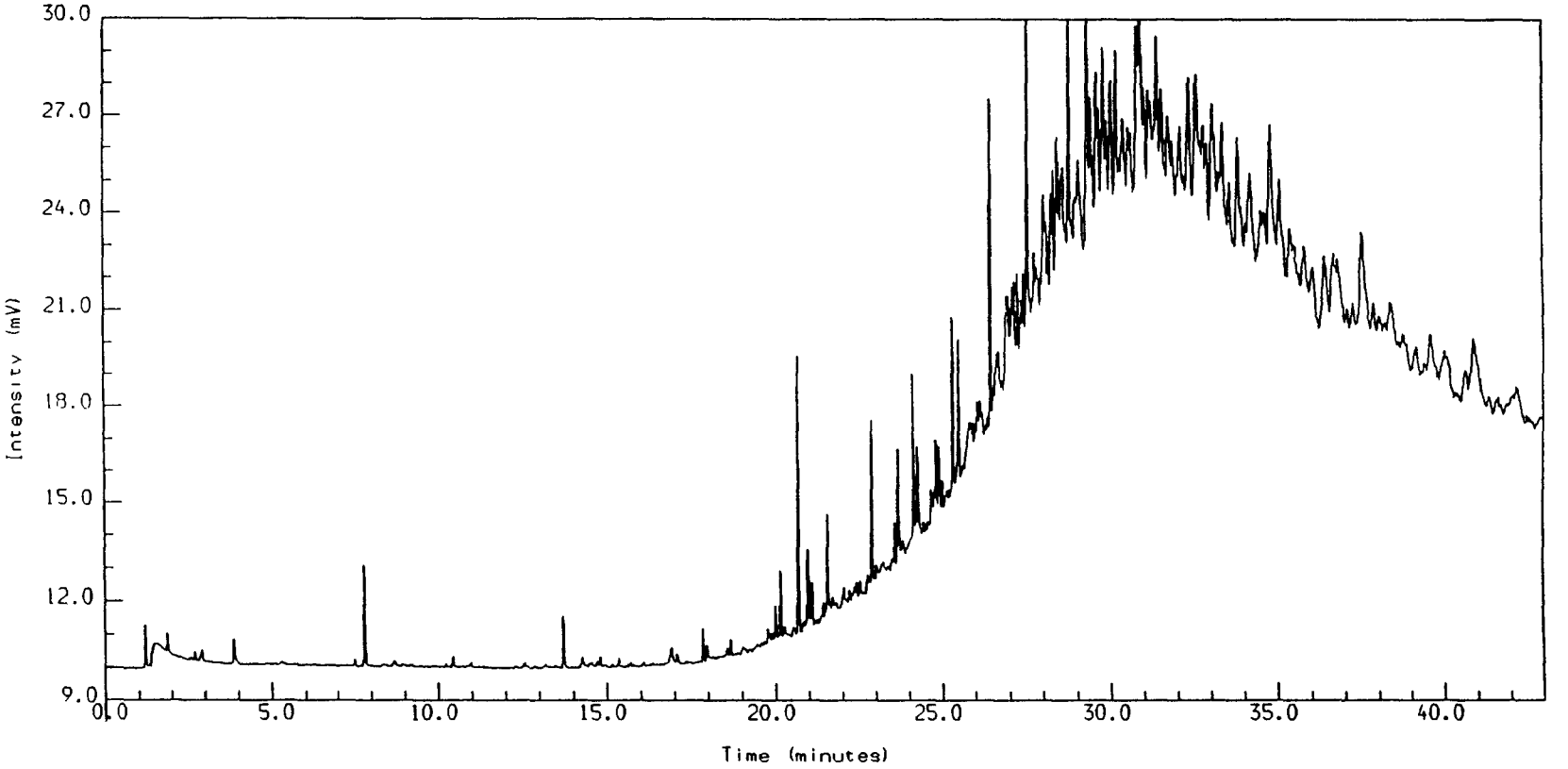


Figure 5: Chromatogram of new Motor Oil A

IMPORTANT FACTS ABOUT TPH

- The carbon number range of different products overlap.
- The carbon number ranges of the various methods overlap.
- Non-petroleum material may be measured as well.
- Laboratories may automatically assign the name of a product type to anything that elutes within a given range
- Because information is fragmented, results may point to wrong source(s)

CASE STUDY: CONVENTIONAL APPROACH

BACKGROUND

- Service station for ~60 years and then auto repair shop for the last 20 years
- Several generations of underground storage tanks through the years
- Service station USTs contained gasoline only
- Repair shop stored diesel only for a short time
- Repair shop no longer used the tanks. It was required to either permit the tanks or remove them

INITIAL ASSESSMENT

- Tanks removed. No evidence of leaks found but there was overall soil contamination
- Soil analysis:

- 418.1 (TPH/IR) - Mod. 8015 . Gasoline Range . Diesel Range	Results → Interpreted as	- Gasoline Range Organics - "Heavy" oil

INITIAL CONCLUSION

Soil contamination due to gas service station operation

↓

LAW SUIT

CASE STUDY

REVIEW OF DATA FROM CONVENTIONAL TPH METHODS

As previously stated...

- Information from conventional TPH methods is segmented and often misused
- "Product type" is simply as "defined by the method"

Problems...

- Results were reported as "gasoline range" and interpreted as "gasoline".

Chromatograms were requested. Review indicated that...

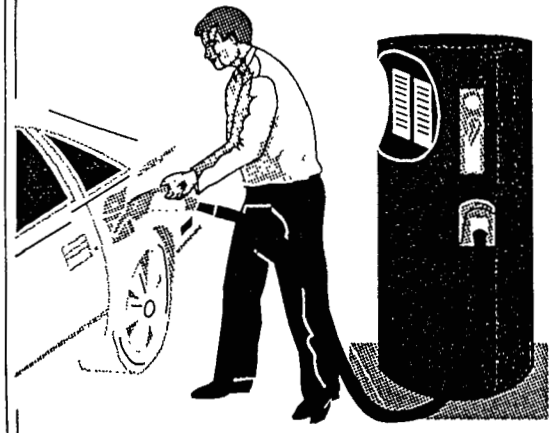
- There was indeed a weathered gasoline "fingerprint" in the soils
- Limited data on a few of the samples for "diesel range organics" indicated that the main contamination was due to a heavy material present in the soils
- The heavy material "fingerprint" resembled motor oil (Motor oil cannot be chromatographed in its entirety but sufficient "fingerprint" is obtained for potential identification)

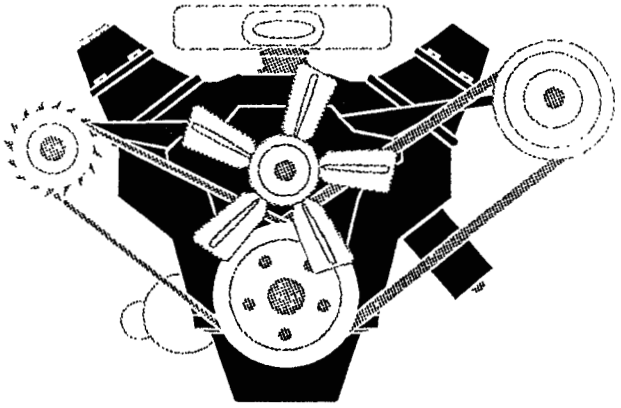
QUESTIONS???

- Is a leaking UST the source of gasoline in the soil?
- Could there be other sources (there was no evidence of leaks in the tanks)?
- Could the used motor oil be the source of gasoline?

?

HOW DOES FUEL GET IN THE MOTOR OIL?

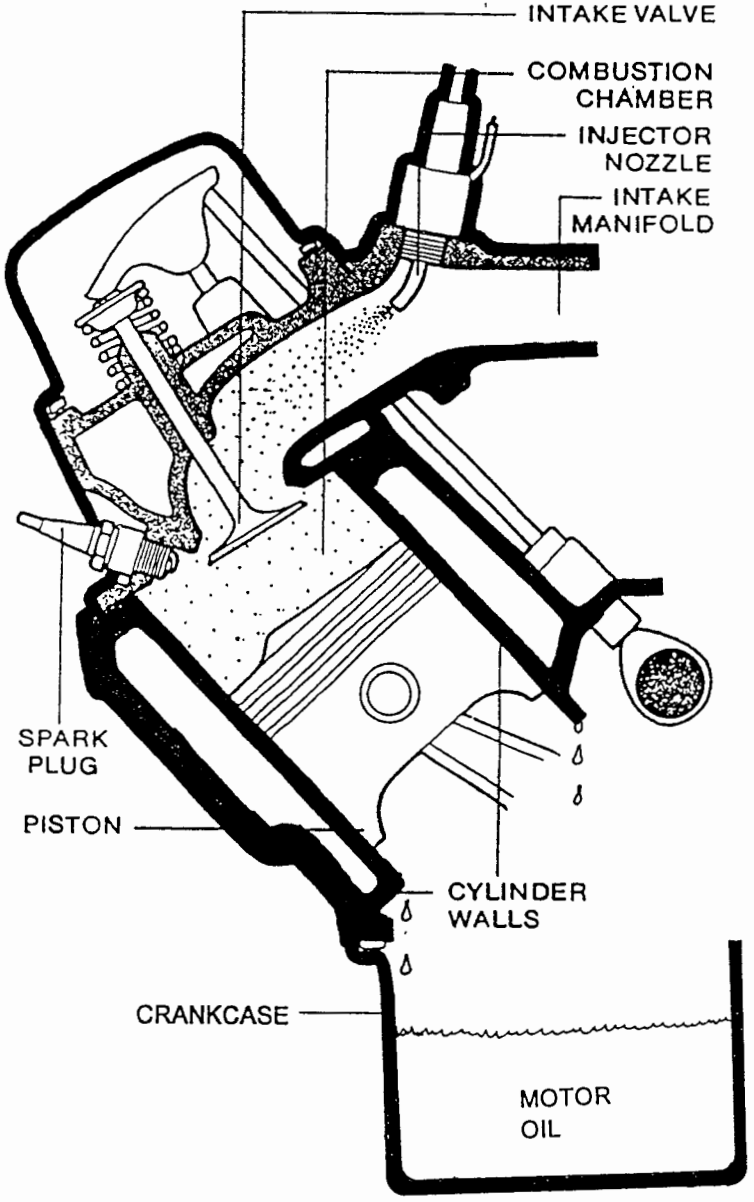




- Used motor oil is diluted with fuel during engine operation. Fuel gets into the crankcase of the engine by
  - Gaseous fuel from engine blowby
  - Liquid fuel washing down cylinder walls past the piston rings
- Oil dilution takes place with gasoline and diesel engines. Allowances are made for this in oil formulations and engine performance testing

HOW DOES FUEL GET IN THE MOTOR OIL?

- Blowby (combustion chamber gases blowing past the piston rings) can be more pronounced in high mileage engines with worn piston rings
- Under cold start and warm-up conditions, more liquid fuel is transported past the rings and into the oil
- After engine warm-up some of the more volatile components of gasoline vaporize and are removed from the oil via the positive crankcase ventilation system (PCV)
- Higher boiling components remain in the motor oil and will resemble heavily weathered gasoline. There can be 1 to 10% fuel in the used motor oil



CASE STUDY

CHARACTERIZATION OF FRESH AND USED MOTOR OIL

There were no samples available from the site

A study was conducted to...

- Characterize new and used motor oil
- Understand impact of used motor oil composition on source identification using conventional TPH methods

Approach:

- Neat new and used motor oil were analyzed using single GC TPH and "fingerprinting" method
- Spiked soil samples (1% motor oils) were analyzed using both
  - Single GC TPH and "fingerprinting" method
  - Conventional GC TPH methods for gasoline range

CHARACTERIZATION OF ORGANICS TO ~C30

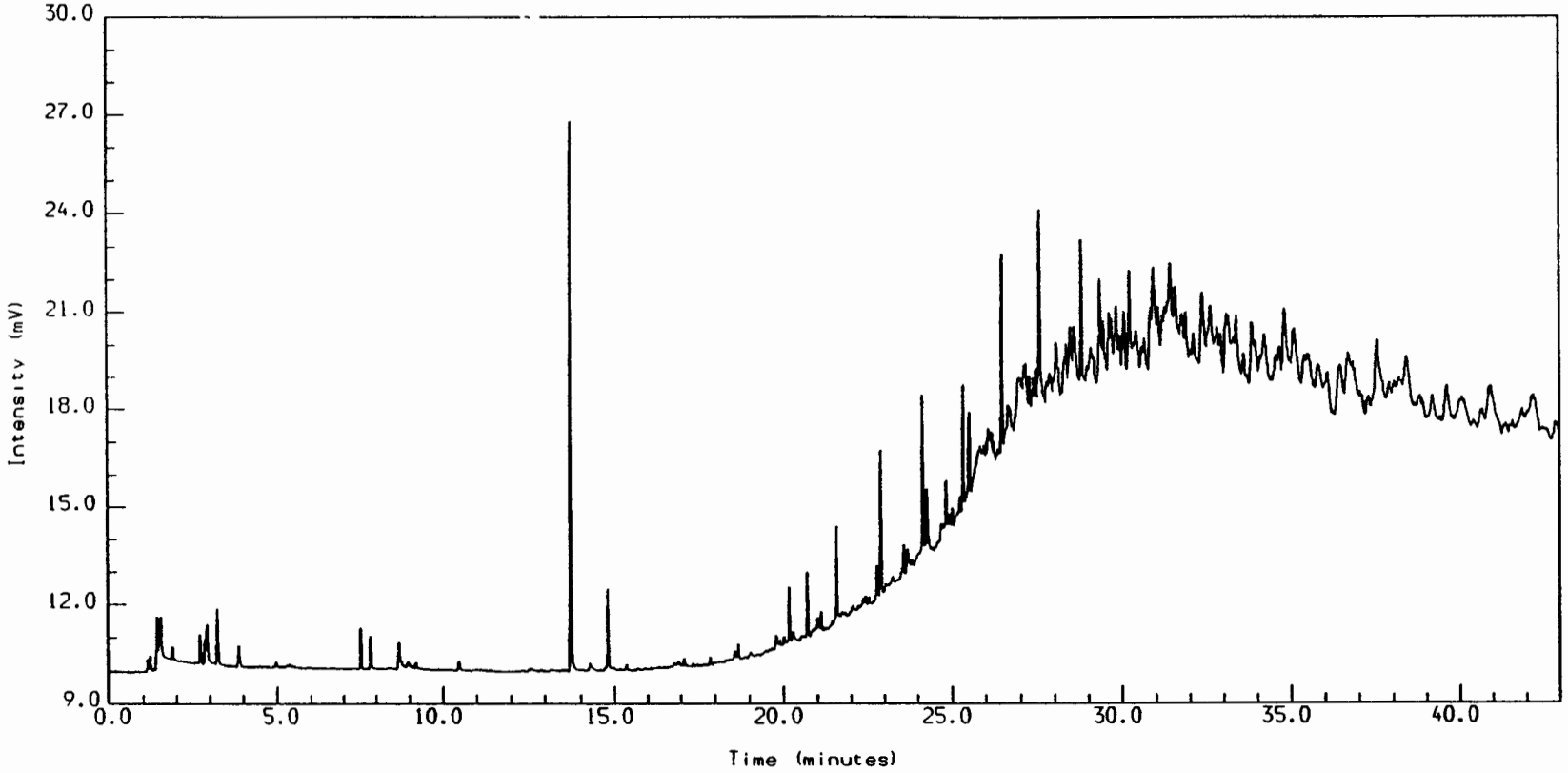


Figure 6: Chromatogram of new Motor Oil B

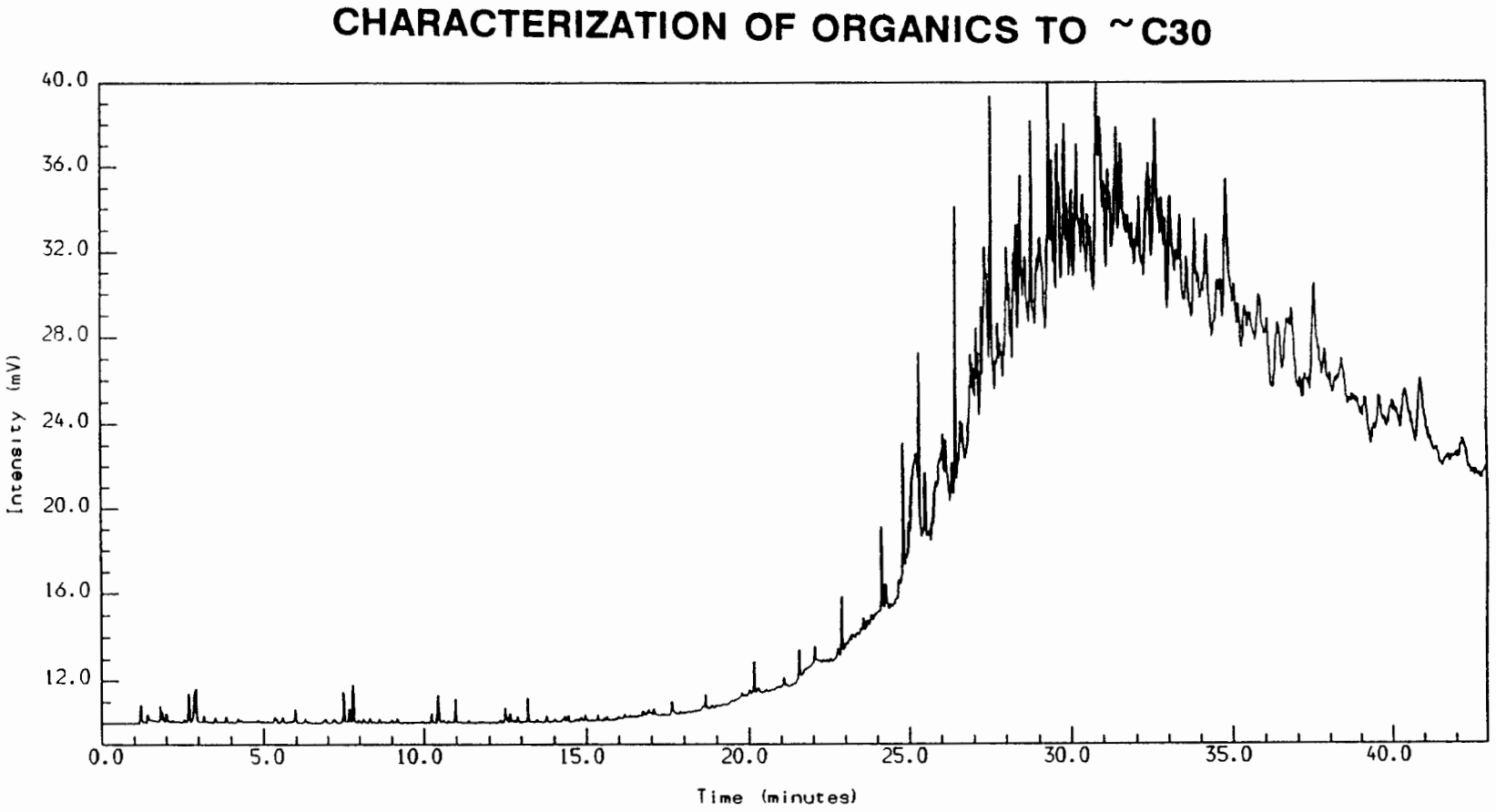


Figure 7: Chromatogram of new Motor Oil C

CHARACTERIZATION OF ORGANICS TO ~C30

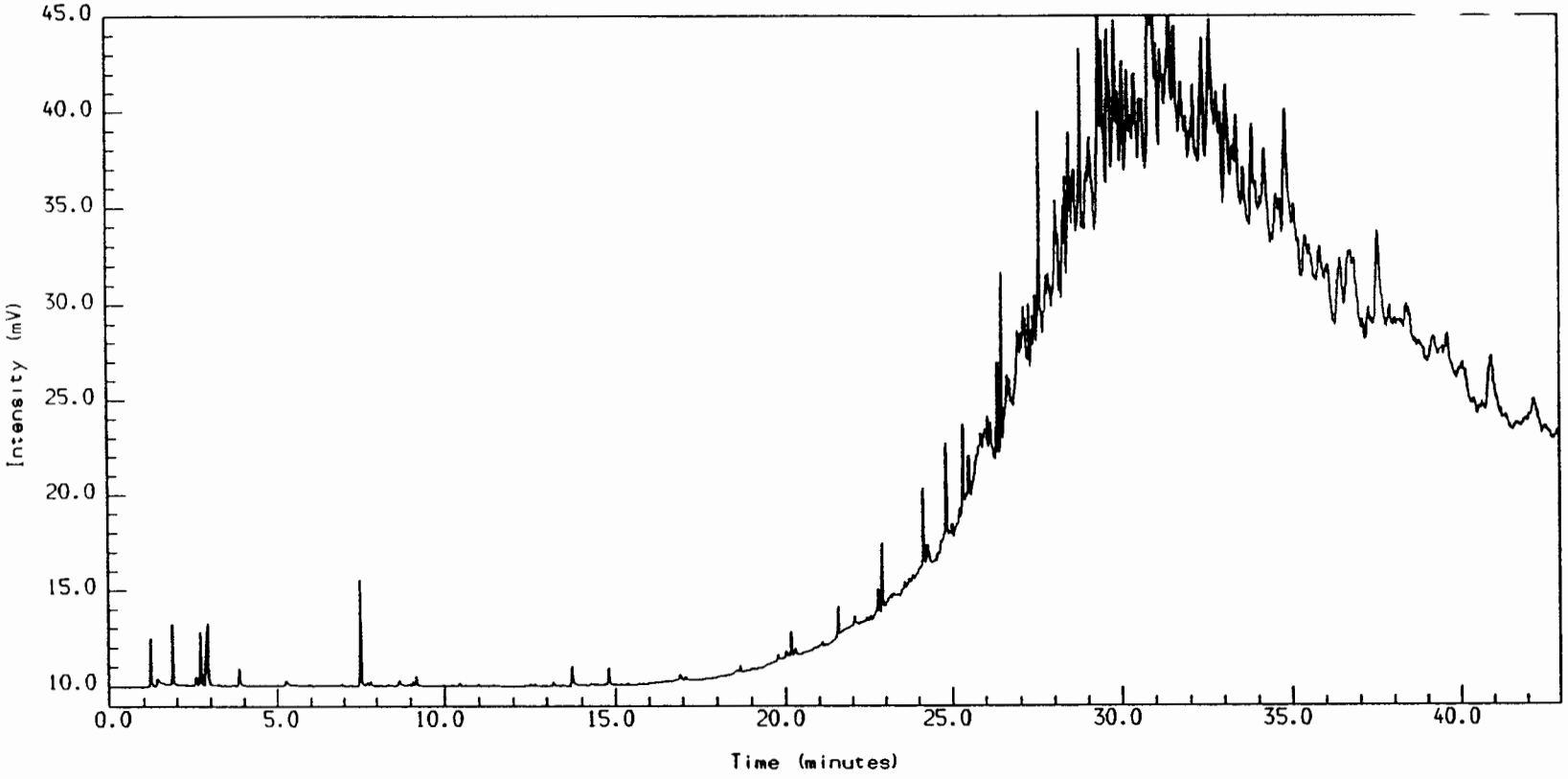


Figure 8: Chromatogram of new Motor Oil D

CHARACTERIZATION OF ORGANICS TO ~C30

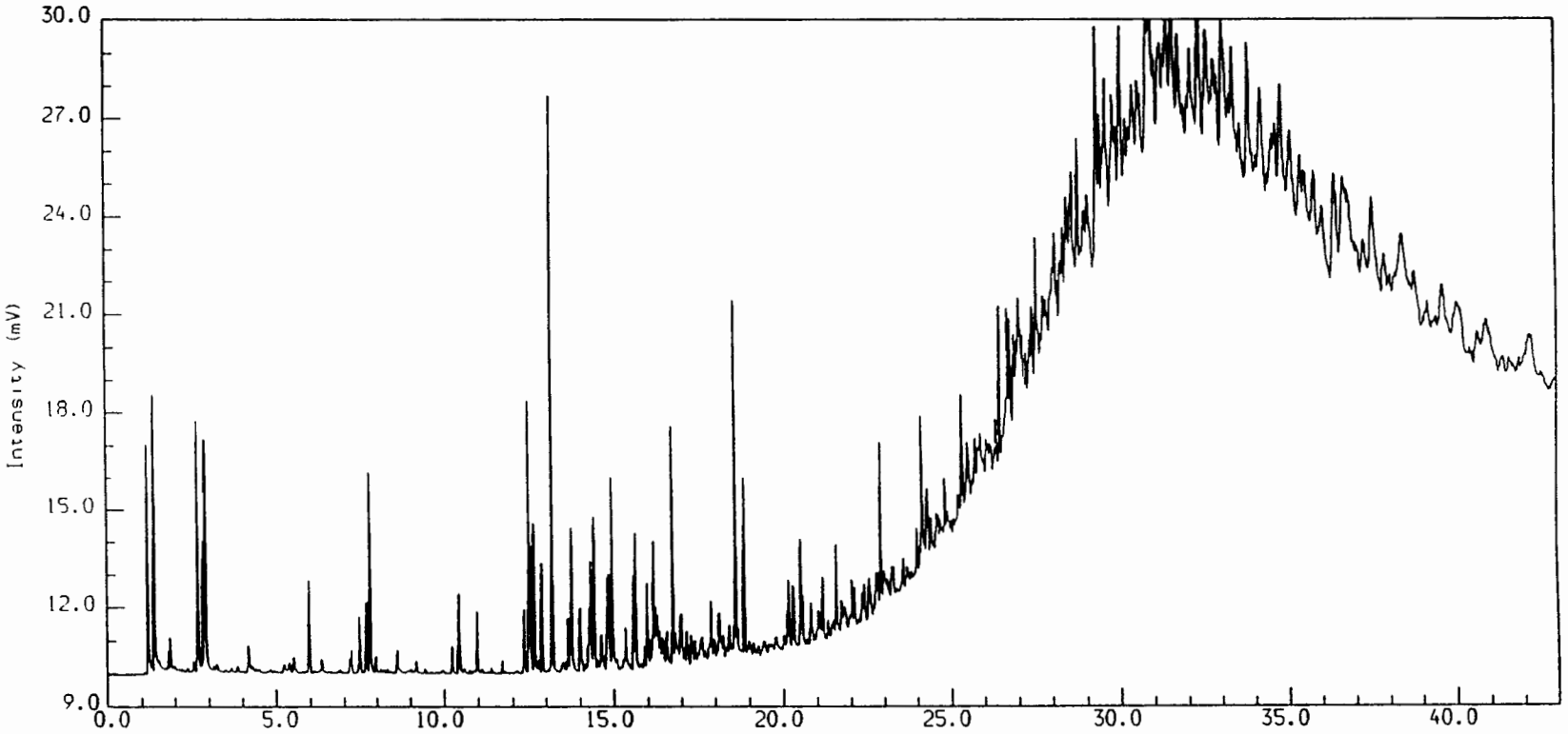


Figure 9: Chromatogram of used motor oil. Toyota Camry

CHARACTERIZATION OF ORGANICS TO ~C30

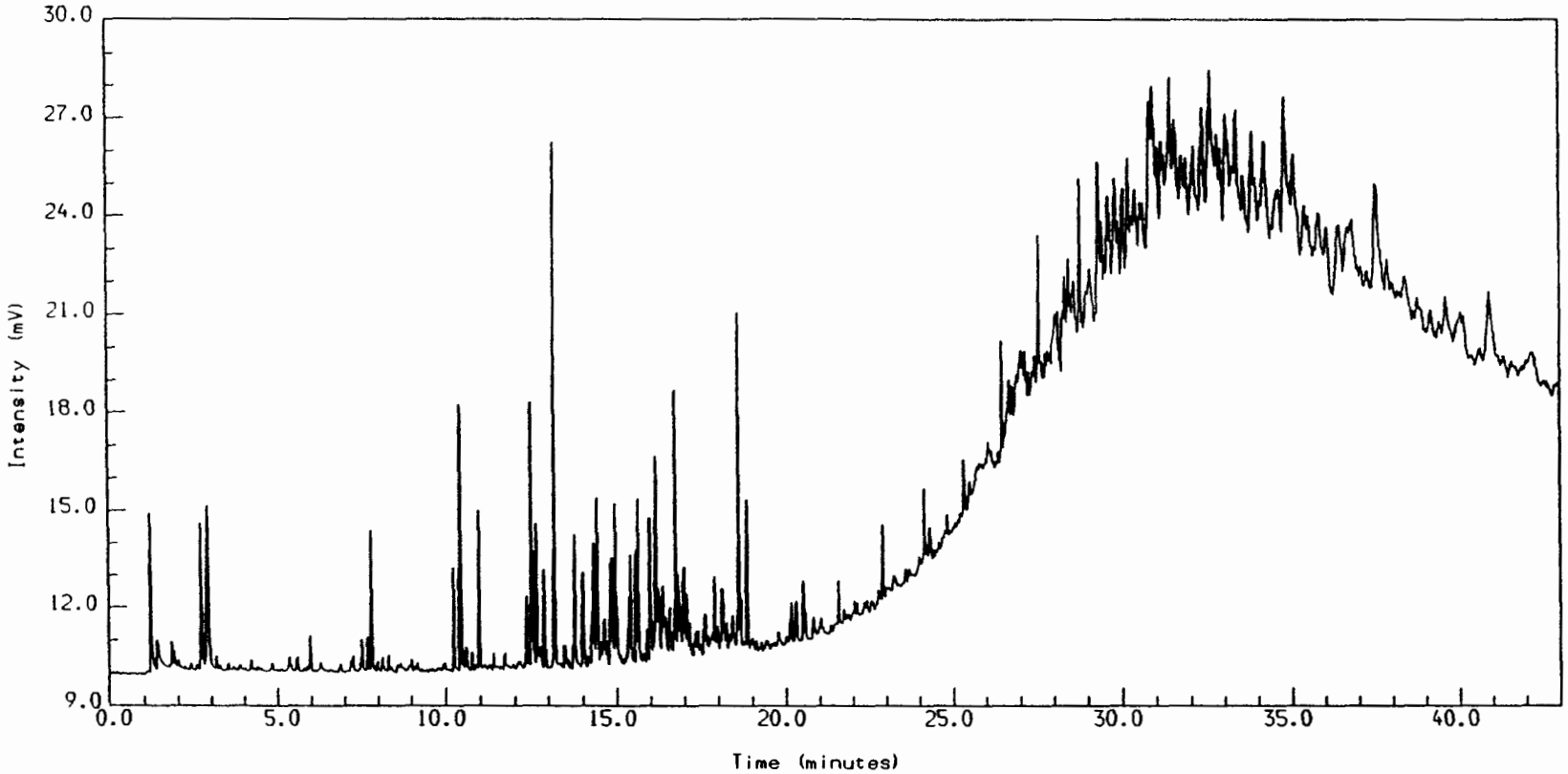


Figure 10: Chromatogram of used motor oil. Honda

CHARACTERIZATION OF ORGANICS TO ~C30

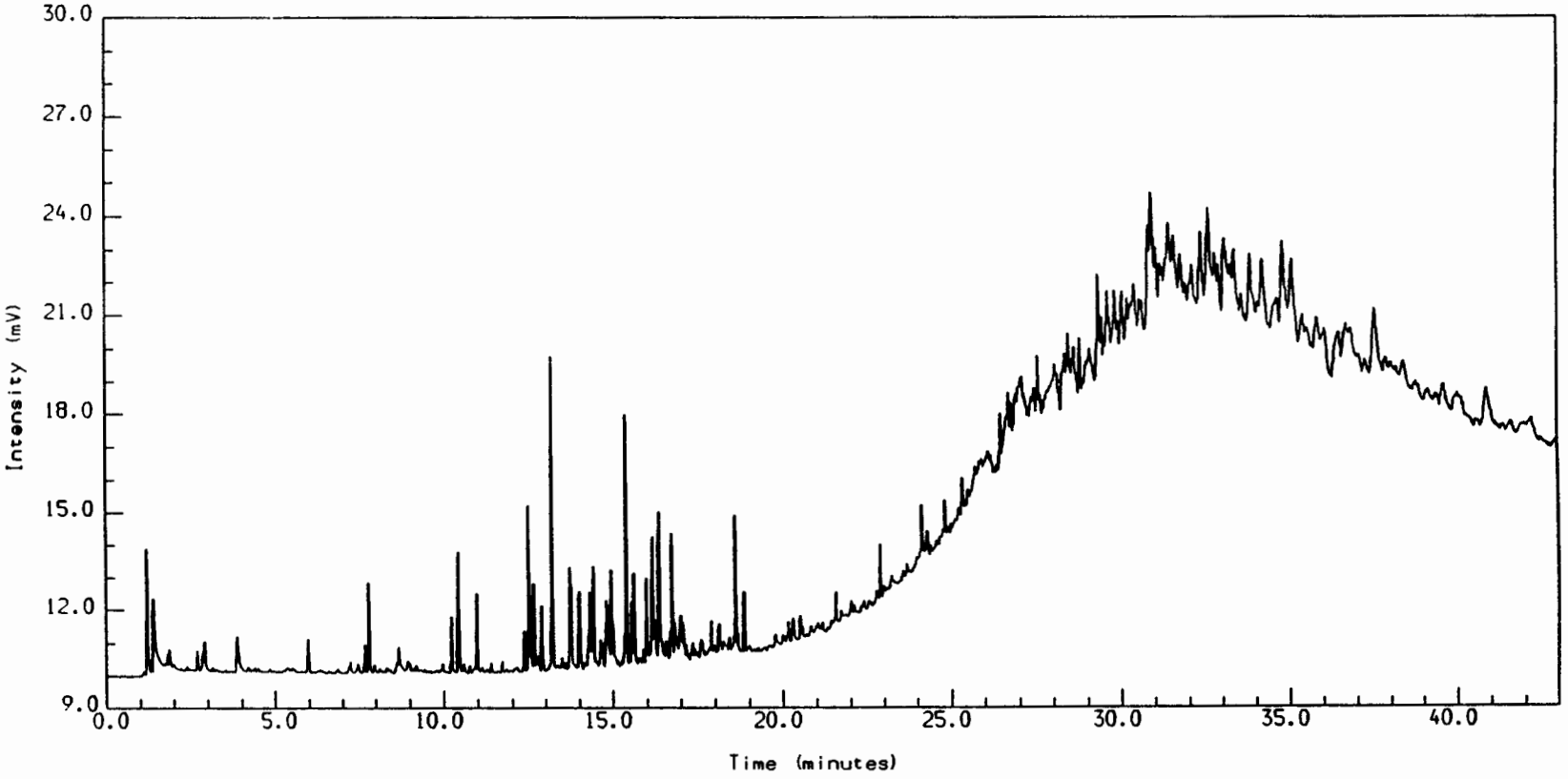


Figure 11: Chromatogram of used motor oil. Chrysler

CHARACTERIZATION OF ORGANICS TO ~C30

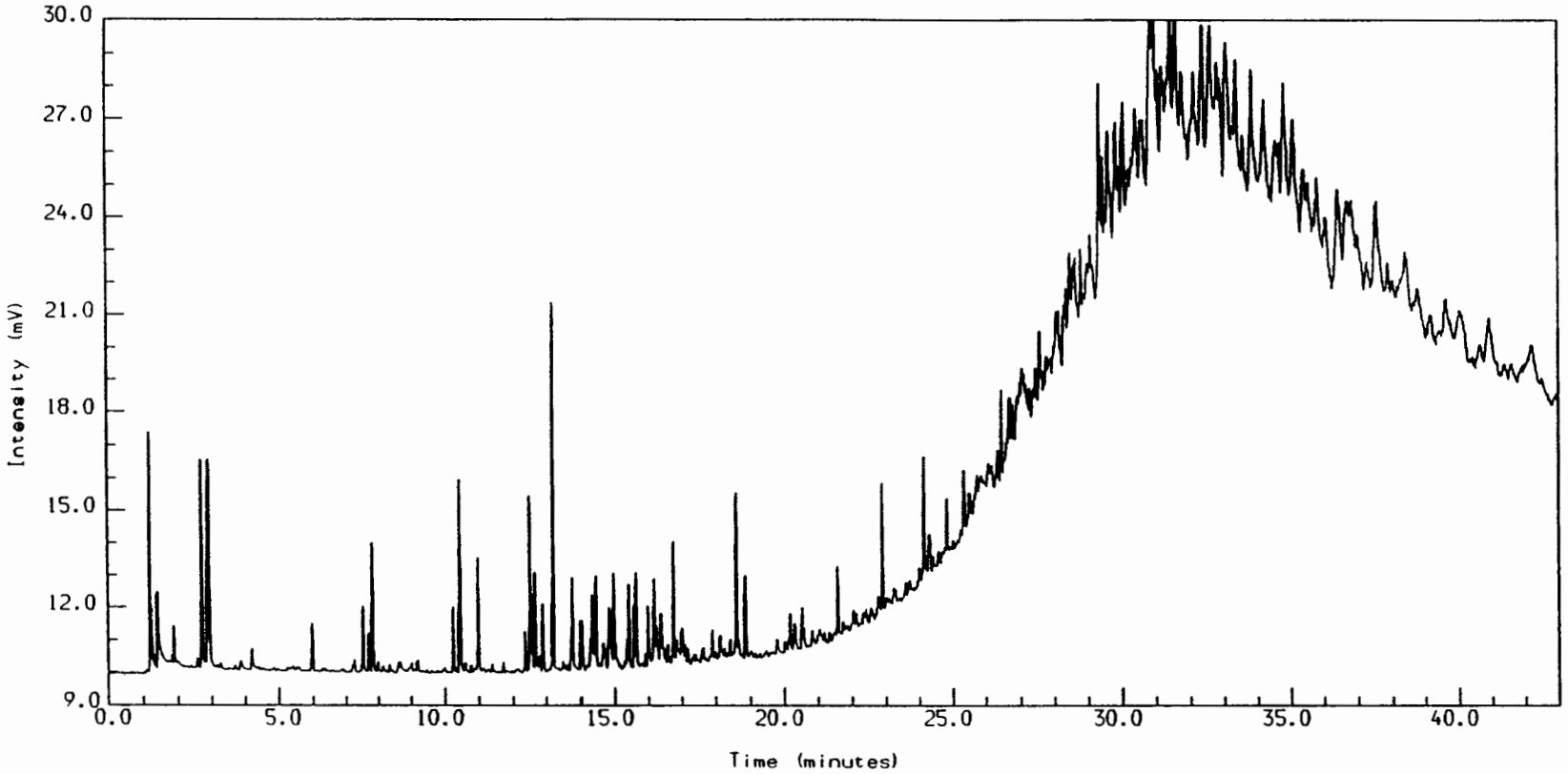


Figure 12: Chromatogram of used motor oil. Ford Taurus

CHARACTERIZATION OF ORGANICS TO ~C30

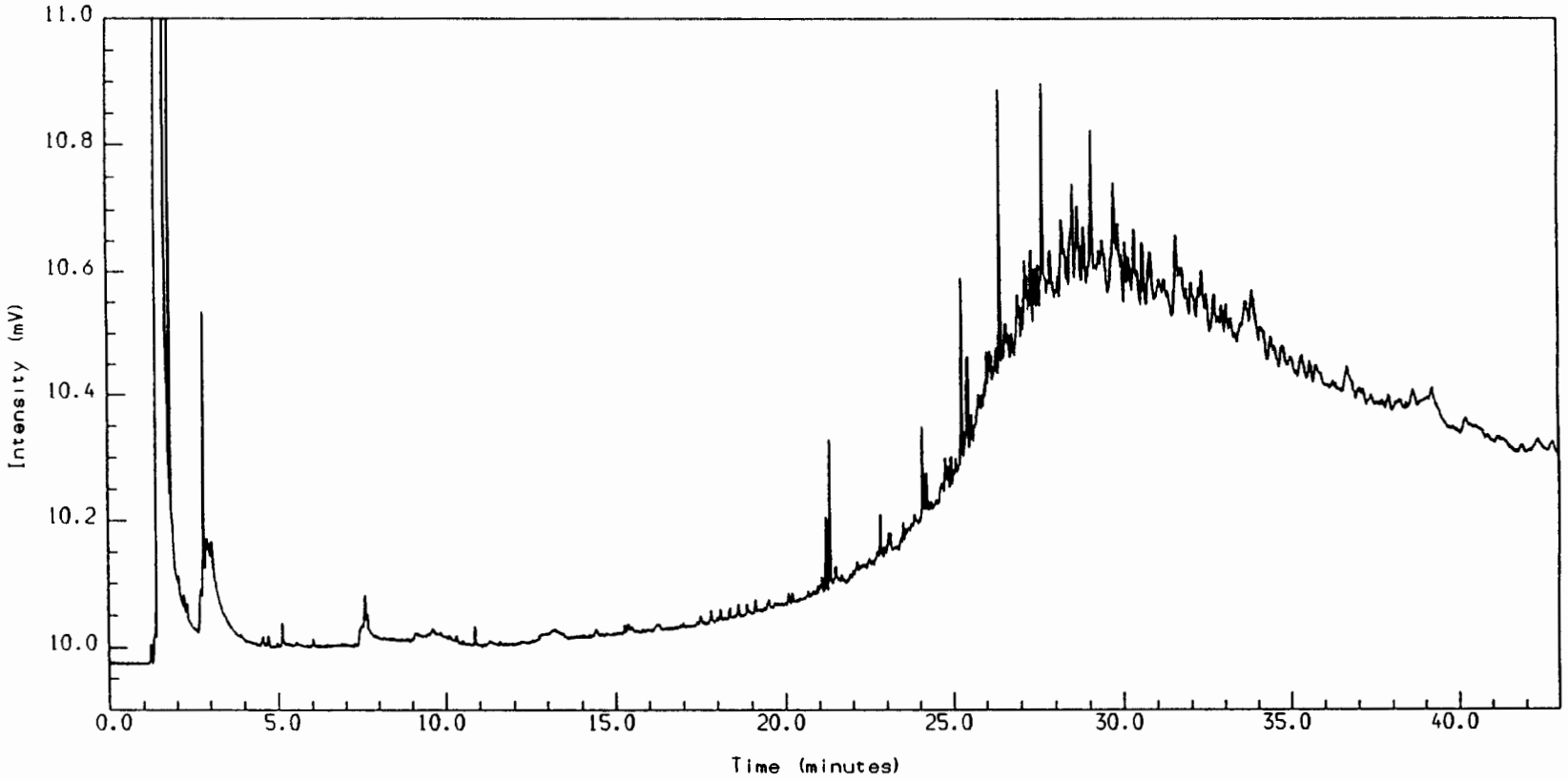


Figure 13: Chromatogram of soil extract. Soil spiked with 1% new motor oil

CHARACTERIZATION OF ORGANICS TO ~C30

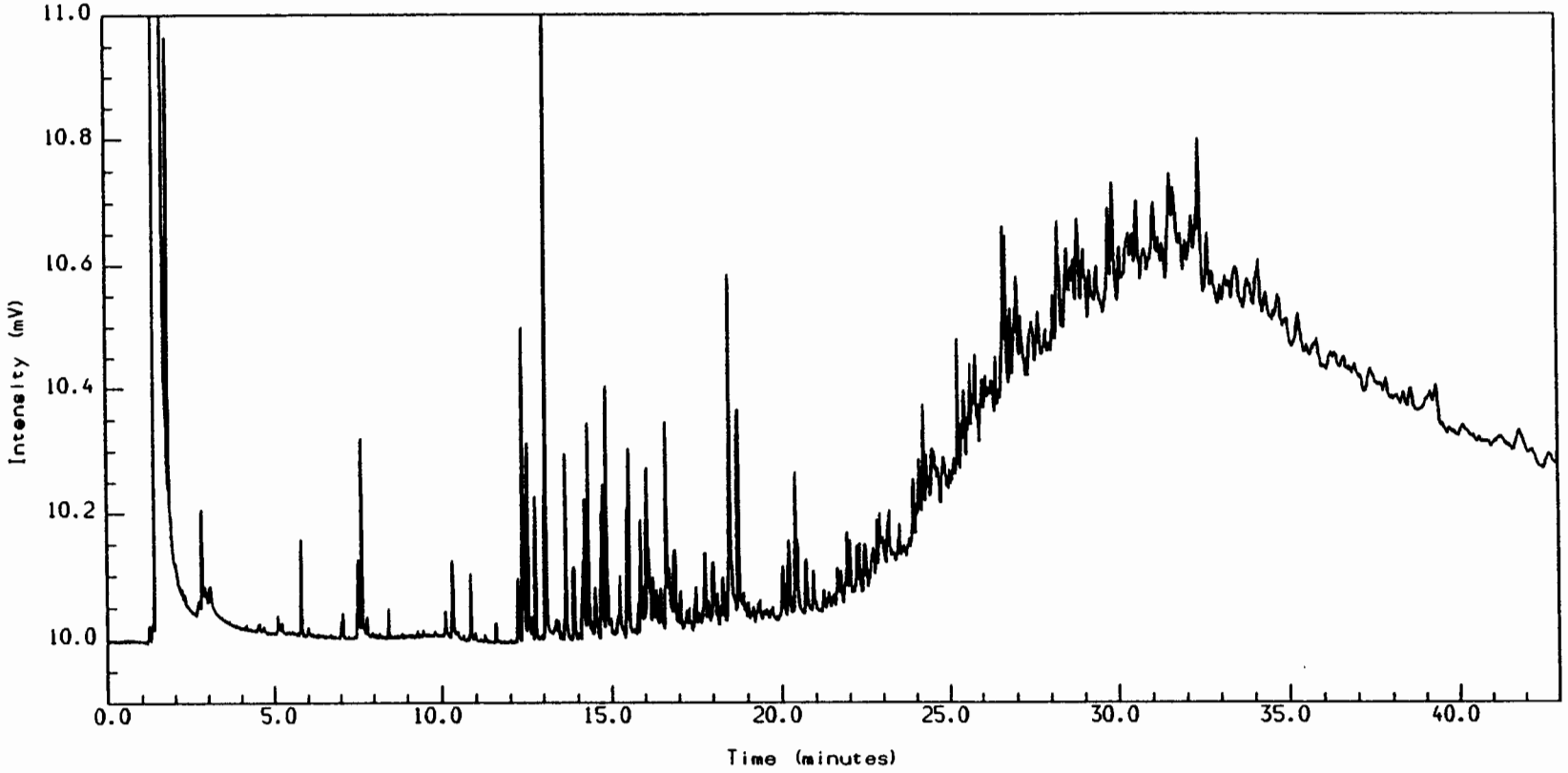


Figure 14: Chromatogram of soil extract. Soil spiked with 1% used motor oil. Toyota

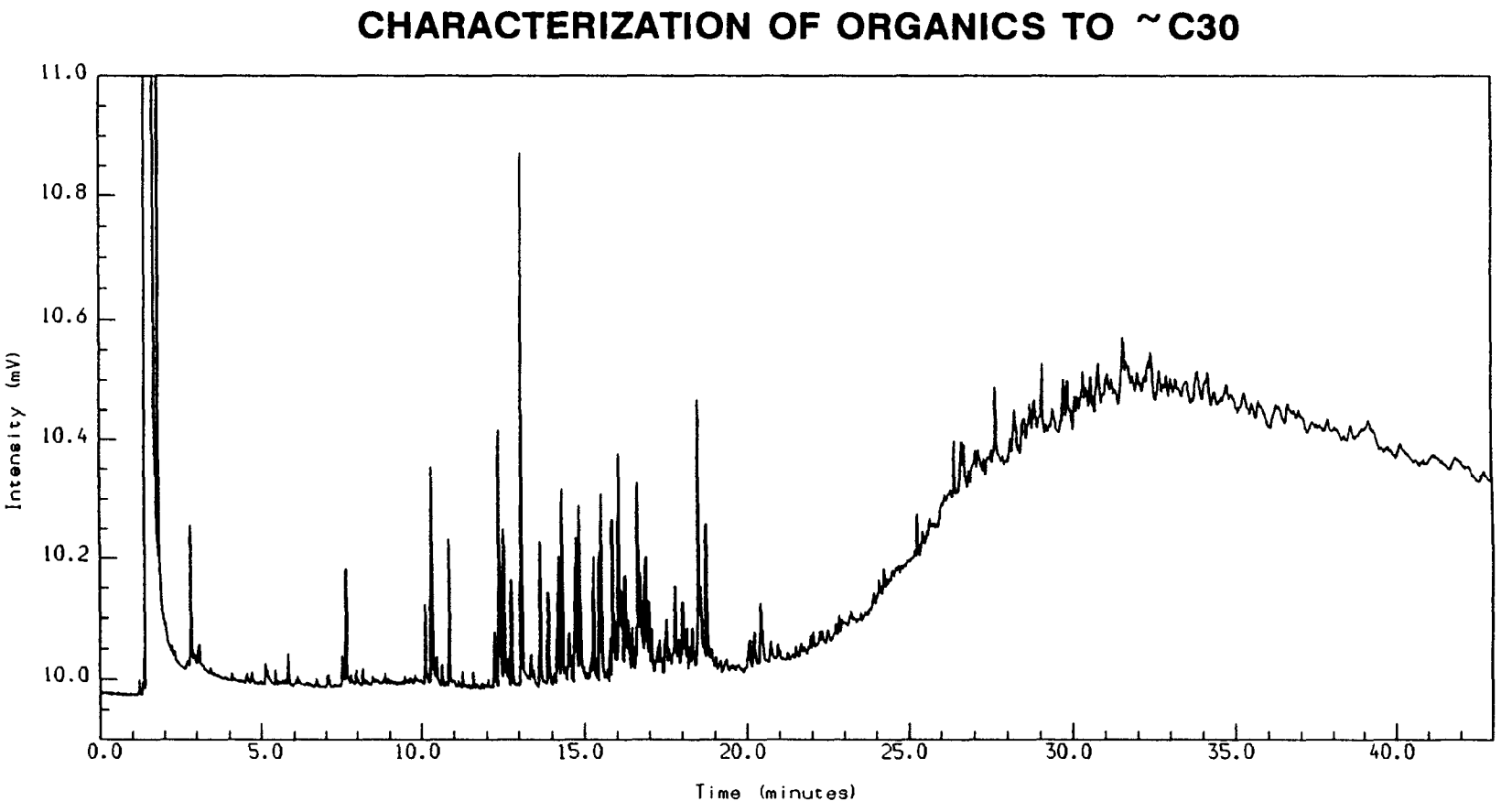


Figure 15: Chromatogram of soil extract. Soil spiked with 1% used motor oil. Honda

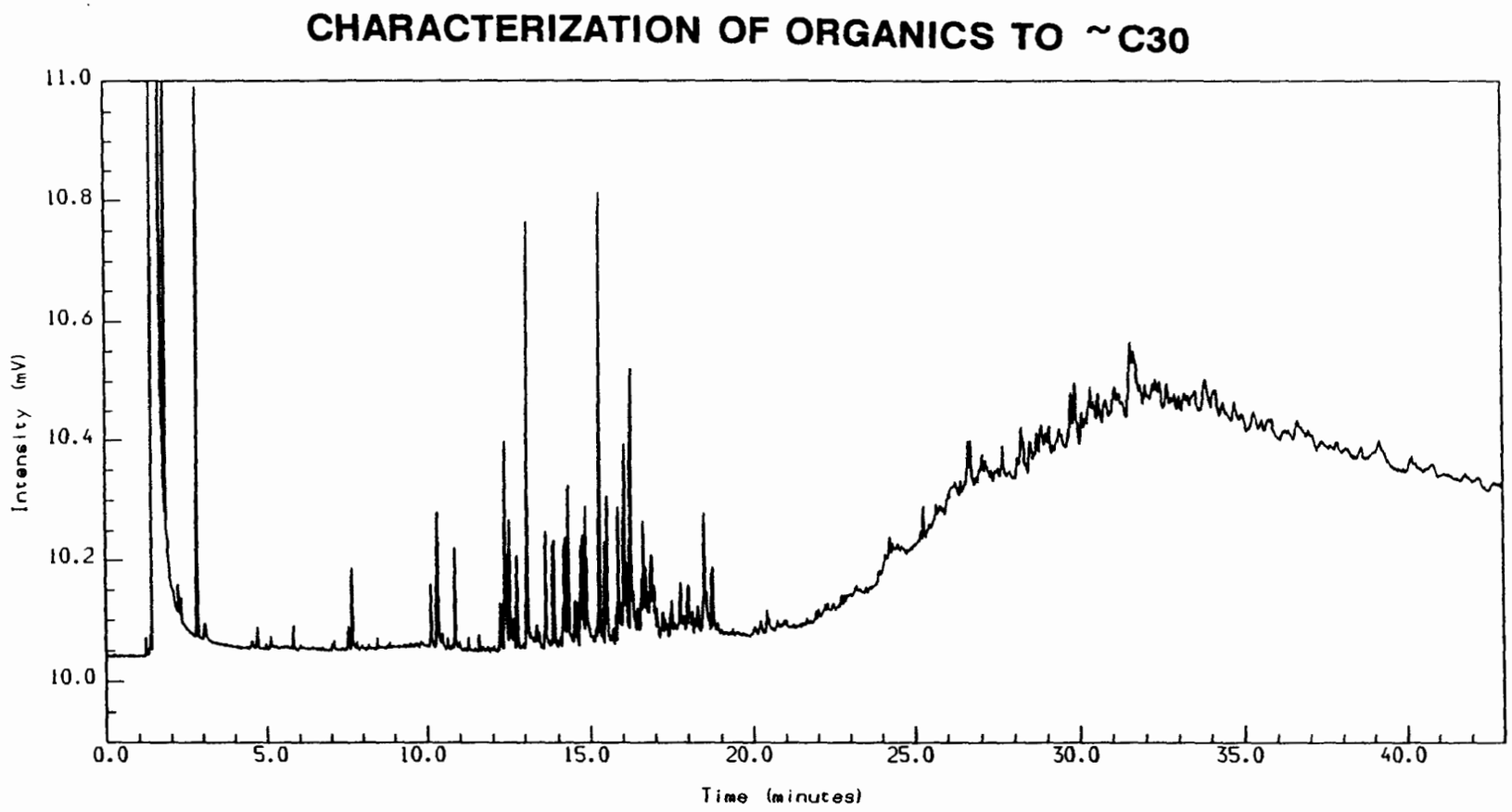


Figure 16: Chromatogram of soil extract. Soil spiked with 1% used motor oil. Chysler

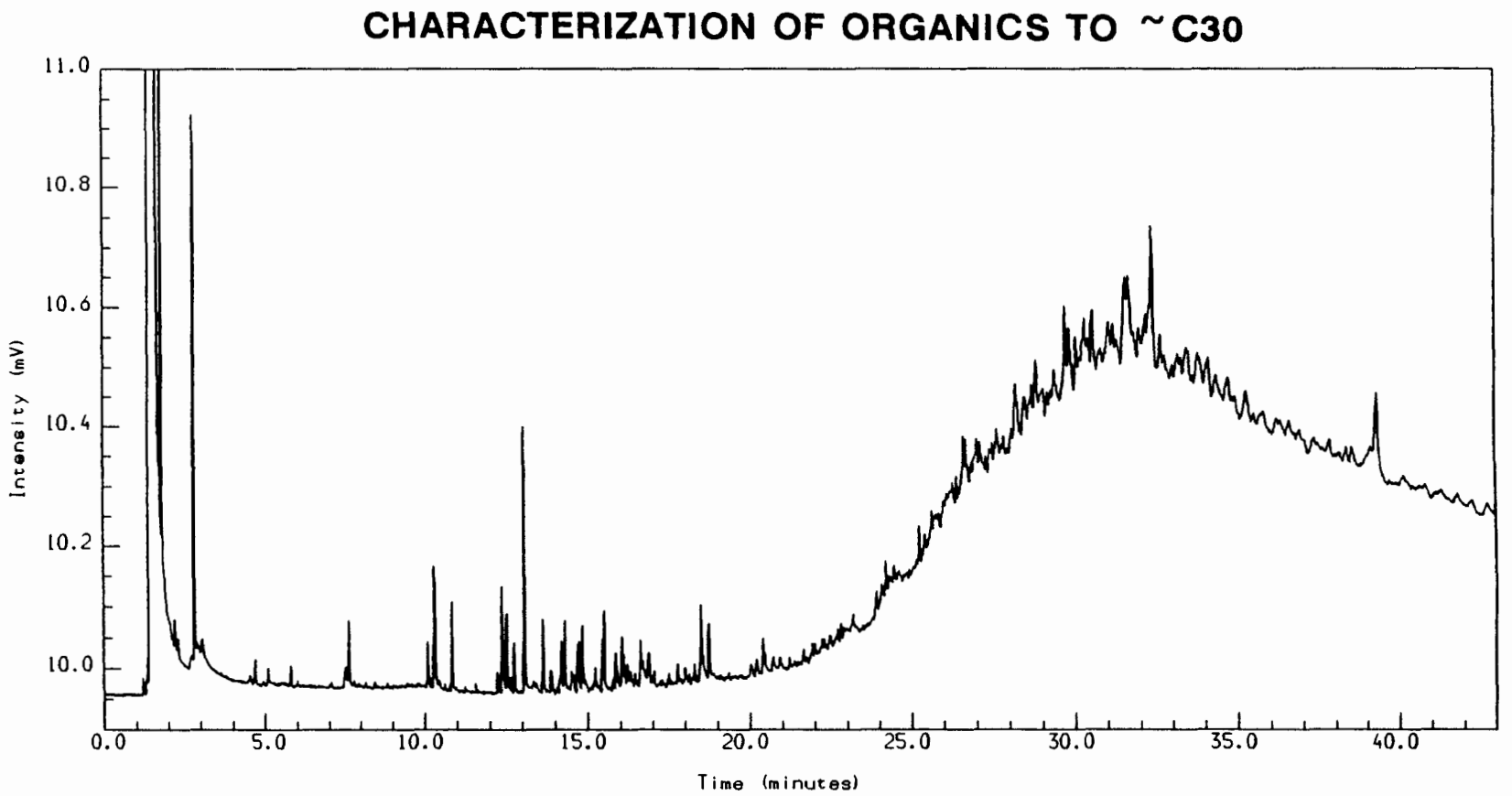


Figure 17: Chromatogram of soil extract. Soil spiked with 1% used motor oil. Ford Taurus

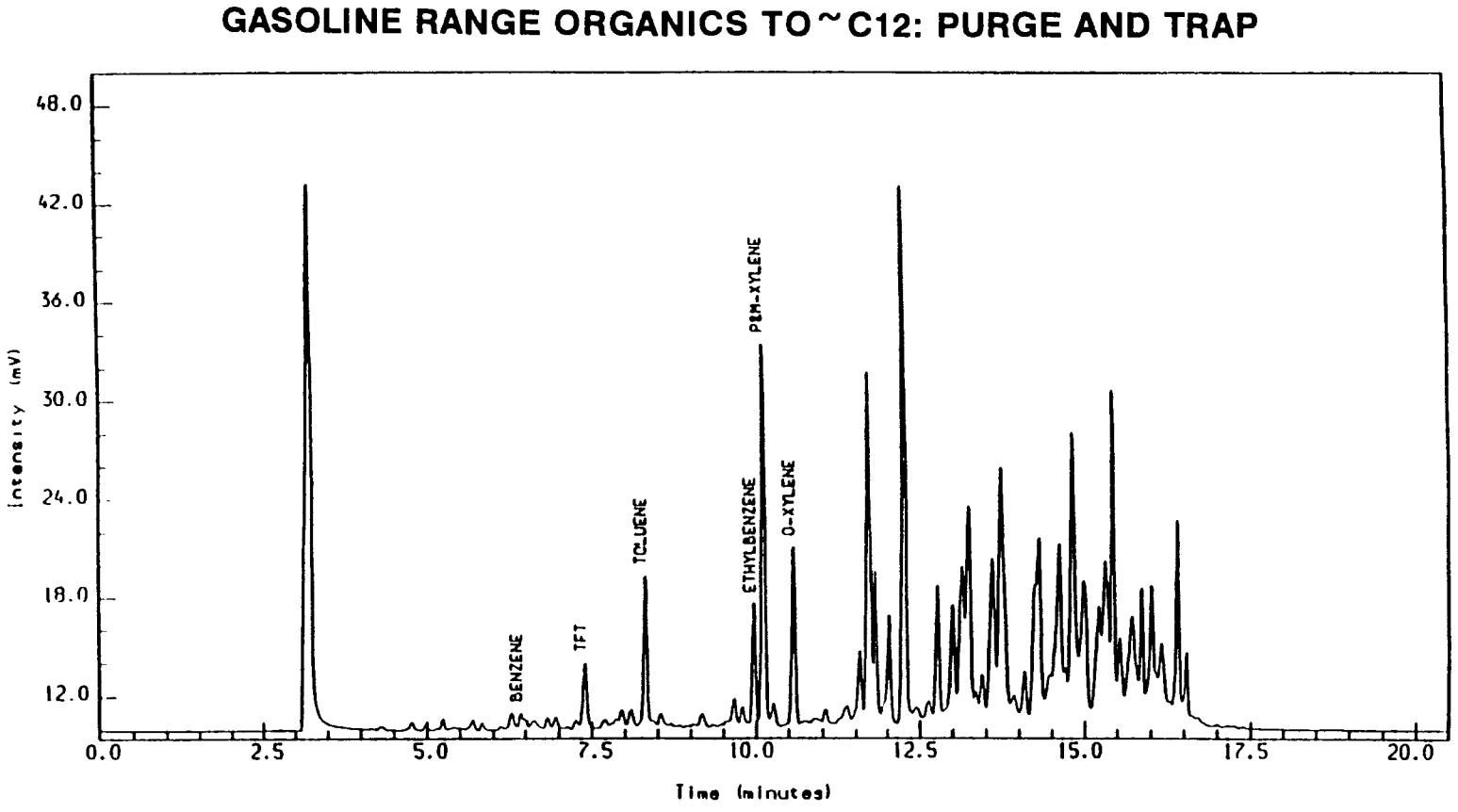


Figure 18: Chromatogram of soil extract using conventional TPH purge and trap method for determination of gasoline range organics. Soil spiked with 1% used motor oil. Honda

SPIKED SOIL STUDY

SUMMARY OF BTEX AND TPH RESULTS: Gasoline Range TPH (up to C12)
Clean Soil Spiked with ~1% Used Motor Oil from Several Sources

Motor oil Source	Driving Conditions	Analysis Type	BTEX ppm	TPH/Gasoline Range, ppm	% Gasoline in Used Oil
Fresh Oil	Not used	DI	<2	<20	
		P&T	<1	<10	
Toyota Used Oil	Suburban Driving	DI	16	170	1.7
		P&T	15	160	1.6
Honda Used Oil	Short Trips/City	DI	22	190	1.9
		P&T	23	140	1.4
Chrysler Used Oil	Suburban	DI	16	160	1.6
	Driving	P&T	17	140	1.4
Chrysler Used Oil (R)	Suburban	DI	16	160	1.6
	Driving	P&T	17	130	1.3
Ford Used Oil	Freeway	DI	12	80	0.8
	600 miles	P&T	13	60	0.6
	per day				

DI: Extraction followed by direct injection GC-FID
P&T: Extraction followed by purge and trap GC-FID

CASE STUDY

OBSERVATIONS/CONCLUSIONS

- As expected from knowledge of fuel dilution phenomenom, used motor oil contains gasoline range material
- Used motor oil from diesel engines are also expected to contain diesel range material
- The source of the gasoline and/or diesel may be misidentified:
  - If only gasoline range analysis is done
  - Even if diesel range analysis is done, the bulk of motor oil falls out of the range and may not even be reported, thus totally missing its presence
- It is extremely important to "see" the whole picture when attempting to "name" a source of product and not to rely solely on a "range"
- Results from conventional TPH methods could result in improper selection of remediation technology
  - Gasoline range usually remediated through soil venting
  - Used motor oil usually removed for offsite disposal or need to do risk assessment

SUMMARY

Conventional TPH methods as commonly applied are not adequate for source identification. This can lead to...

- Incorrect liability allocation
- Impaired ability to stop source
- Improper selection of remediation technique
- Failure to correctly identify source of contamination

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MR. TELLIARD: Our next speaker is Steve Hinton. Steve is a Research Engineer at the National Council of Air and Stream Improvement at Tufts University. He is going to be talking about the statistical analysis of environmental data sets that contain non-detect observations.

Not being a statistician, I tried to interpret what this means. Is this like how many non-detects will fit on the head of a pin, this sort of thing?

Steve?

STATISTICAL ANALYSIS OF ENVIRONMENTAL DATA SETS WHICH CONTAIN 'NON-DETECTED' OBSERVATIONS

MR. HINTON: Thank you, Bill.

Let me say, first of all, that there are no differential equations in this presentation today, so there is no reason to evacuate the room. I tried that a few times when I gave this talk a couple years ago, and I evacuated the room each time. So, I have learned my lesson, and could I have the first slide, please?

Let me tell you a little bit about the motivation for this work, as you may have heard a few references in the last day or two about the rulemaking for the paper industry that EPA is presently conducting. We have just gone through the first phase which concluded with the end of the comment period, and are now moving into Phase II. Understanding the potential effects of this rulemaking's data handling procedures was the motivation for some of my research.

In particular, the motivation for what I would characterize as methods development work for statistics, was to help us understand what might occur when averages and standard deviations were calculated from data sets that contained censored observations. As I am sure most of you in this room are aware, there are times when it is essential that a number be calculated, even, perhaps, when that does not make the best sense. We wanted to understand the consequences of that, and I am here today to alert you to some of the material which has been developed to address this issue.

As dischargers and regulatory agencies strive to reduce the concentrations of trace organics in wastewaters, there is a greater fraction of sample measurements that are being reported as non-detect. When this occurs, the data sets that they are a part of are called left censored data. Such data sets contain non-detected observations whose magnitude we do not really know but for which we do know their frequency of occurrence, as well as fully quantified measurements for which we know both their magnitude, or at least we have an estimate of their magnitude, and their frequency of occurrence.

The notion of left censoring arises because we do not have complete information about the frequency distribution of the sample. In the shaded area of Slide 2, we can characterize the frequency distribution quite well. These are the fully quantified measurements. Below the X_0 location, we simply do not know the shape of this curve. I should have drawn the curve below X_0 with a dotted line, because we really do not know the curve's shape in that region. About all that can be said in this situation is that we can estimate the relative area on the left versus the right based on the numbers of non-detects and fully quantified measurements, respectively. So, if we could back up one slide; I only do that once in a presentation, so it is forward from here on.

In a general context, there are really three types of observations; observations represent measurement attempts. These include: the non-detects, those things which we can count but we do not really know what their value is other than to say it is less than some censoring threshold; the fully quantified measurements, which we can also count for and which we have an estimate of their magnitude; and a third related type of measurement, which I characterize as uncertain measurements and which we will not discuss today, but they are similar to non-detected observation in that we know their frequency of occurrence, but we do not have a precise estimate of their magnitude. The most predominant type of such a measurement attempt is the greater than values that occur when you are above the linear calibration range of an instrument.

So, if we could go forward two slides to Slide 3, let's think about these left censoring thresholds. What could they be?

There are many definitions. Here are a few: the level of detection and the USEPA's minimum level values which are determined from subjective judgment about the analytical chemistry process. Then there are more formalized mathematically described definitions such as the method detection limit and the limit of quantitation which are determined from precise statistical and analytical chemistry procedures. There are many others. In fact, I believe later in today's program, you will hear a much more expanded discussion about this topic, so I will just simply say that it is fortunate for me and for those trying to apply the simple techniques that we are going to discuss that the censoring threshold definition itself, does not really have an impact on the results of a statistical analysis calculation.

The presence of censored observations in data sets does, however, make calculations of means and standard deviations more difficult, because we simply cannot incorporate the word non-detect (ND) into the common statistical procedures that we are all used to using like summing up numbers and dividing by n. This situation often leads people to substitute in a fixed value such as zero or the ND value for these missing observations and then to proceed with simple techniques that they are familiar with. This is not a sound practice. It produces biased estimates, and it is unnecessary because there are simple, unbiased, and easy-to-apply statistical methods.

So, if we could go forward to Slide 4, my objective today is to alert you to these statistical techniques and to show you some of their properties and limitations. To do that, we are going to delineate the problem setting, define some preliminary data analysis steps that will simplify the problem and make it easier to tackle, review three common approaches that can be used, and then show you the results of an evaluation of the bias and root mean square error properties of those three approaches.

When data comes from the laboratory, it often appears to be almost a puzzle. In Slide 5, you see four data sets for chlorophenolic compounds in chemically bleached pulp mill effluents. This is the way the data was received from the laboratory, and in its present form, little can be surmised about what might be going on.

In our next slide (Slide 6), we show what is often a good first step in data analysis which is to rank the data from lowest to greatest in magnitude. Then you can begin to see some trends in the data and begin to assess the complexity of the statistical analysis problem.

In data set 1, which represents our simplest case, we have, basically, observations or measurement attempts that were censored at approximately 1. We have four of those that were less than 1, and we have fully quantified measurements at 1 and above. In this case, we have a single censoring threshold. We can say these measurements can be characterized as either being below 1, or above 1 and fully quantified.

Data set 2 is slightly more complex, because there were actually three detection limits reported by the chemist. In a statistical sense, however, it is possible to treat the data set as if there were a single censoring location; in other words, all of our NDs are less than 12. This is an important property which we can exploit when performing statistical calculations, because it makes the applicable statistical methods much simpler.

In data set 3 of Slide 6, the chemists, have done it to us because they have reported this 500 ND, all these fully quantified observations between 56 and 281, and also a couple NDs at 50. Well, what do we do here? On first inspection, it is not immediately obvious how to reduce this problem and make it simpler. However, simplification is possible because we can eliminate the 500 ND from the data set given its distance from the median value of this data set which is 89; i.e. 500 is roughly five times the median value. In addition to that, it is more than a couple standard deviations away from the average of these observations which you would only know had you calculated it with and without consideration of 500 ND.

As a good rule of thumb, when you have ND observations which exceed the maximum value by several times, and if you have some suspicion about the credibility of the values, it is proper to eliminate them from the data set if your purpose is to calculate means and standard deviations. In this instance, elimination of the 500 ND value from data set 3, i.e. just ignoring it, would result in only a few percentage difference between the

estimates for the means and standard deviations. The 500 ND occurred in this particular data set because the sample was analyzed in several dilutions, and the analysis of strongest solution was lost. So, when the chemist reported the values, it was only possible for them to report the results for the dilution that made it through the analytical chemistry process, and that number was less than 500.

Saying something is less than 500 when the median value is 89 is equivalent to saying that it is less than infinity which is not particularly useful information and which is why ignoring the 500 ND does not have a big impact on the calculated means and standard deviations. You can show this mathematically by looking at the likelihood functions. I will not distract you at this time with that information.

The final data set in Slide 6 is the most complex and is not one that we can simplify. The ND at 100 is wedged in the middle of the fully quantified observations, and this requires a more powerful statistical technique than the ones that we will discuss today.

By performing the preliminary steps of ranking the data and determining the number of unique censoring thresholds, you can drastically simplify the problem into one that becomes more manageable; these are the first two preliminary data analysis steps listed in Slide 7. The remaining preliminary steps refer to testing for distributional properties and transforming the data, if it is needed, to conform to normality. The latter being necessary for many of the statistical procedures because they were developed and originally conceived for normally distributed data.

So, how do we determine what might be a good statistical distribution of our data? Well, a common and very useful way is to construct a probability plot like the one shown here on the right of Slide 8. It is made by calculating the cumulative probabilities based on the ranks, i, of the ordered information and then plotting the ranks or the cumulative probability and the data values on special paper which has been constructed for that purpose. When a straight line is formed, then the data are not inconsistent with the distribution assumption used to construct the paper. What is nice about this technique is it works for both a completely, fully quantified data set which is what you see here, and it also works when there are censored observations. You simply plot the fully quantified observations at their cumulative probabilities; some lower region of the curve is undefined.

Well, that is a nice textbook example; Slide 9 shows some real data. The normal distribution on the left is compared to the log normal distribution on the right. I might point out that these scales are switched compared to that previous slide in that the probability is on the x axis and the data values are on the y axis. Clearly, the log normal distribution provides a more linear fit, and of these two choices, it would be the preferred statistical distribution model for this data set. This outcome is very typical of low level concentration measurements of environmental quality data.

One last point about probability plots is that it is possible to use the slope of this line, as we will discuss in a minute, and the line's intercept with the 50th percentile to estimate means and standard deviations.

Going to Slide 10, suppose the data is log normally distributed. Well, what do we do? For many procedures, this involves an additional two steps which are to transform the data by calculating the logged values of the observations prior to applying the statistical procedure and then, returning the estimates of mean and standard deviation to the original scale of measurement.

What methods are available to us? Well, there are seven, listed in Slide 11, that I am aware of including: the maximum likelihood estimators of which there are three variations; regression of order statistics which is a mechanistic probability plot; delta-log normal; USEPA's D-log procedure which is an adaptation of the delta log normal statistics; balancing using either trimming or Winsorizing; graphical techniques which are just basically extracting the information you need from a manually constructed probability plot; and, finally, replacement techniques where the missing values are estimated in a probabilistic way and then conventional statistics are calculated with the replacement values. The replacement technique is different than the common practice of substituting in a fixed value which really does not make much sense.

The first of the three methods that we evaluated was Cohen's MLE method (Slide 12). Here, the starred quantities represent statistics calculated from the fully quantified observations. These are corrected based on the difference between the fully quantified mean and the censoring threshold and a function which incorporates the fraction of non-detected observations and the dispersion of the data represented by g. If we go back to the familiar picture shown in Slide 13, we can graphically observe the calculation process and what would happen if we calculated the mean only from the data in the shaded area; x bar is calculated for the shaded area. The true population mean which includes the missing or censored values has to be to the left of the calculated mean of the fully quantified measurements. In other words, the true mean has to be smaller and the objective of Cohen's method is to predict a correction factor to reduce this x bar to where it correctly estimates the population statistic.

Regression of normal order statistics is just a mechanization of the probability plot process. The quantity in the square brackets on Slide 14 is the cumulative probability based on the ranking of the data. The z function is the inverse normal function which linearizes the probability plot scale. Common regression techniques are applied to find the y intercept and slope of this equation which represent, respectively, the mean and the standard deviation of the parent population. This is perhaps the easiest process of the three to visualize.

The third and final approach that we evaluated was USEPA's D-log procedure which forms weighted estimates for the mean and standard deviation based on the average

properties for the fully quantified observations, assuming they were log normally distributed, that is this term on the left of Slide 15 plus a point value for the non-detects. The weighting factor used in this approach is delta which represents the fraction of non-detected observations. Inherent in this approach is the assumption that the observations or data which you are trying to model, arise from two distinct statistical populations.

Our research set about to test how these three statistical techniques, since they are probably the most commonly used ones around, work under a variety of situations so we might have some understanding of their bias and root mean square error when applied to real data. We did this with a Monte Carlo simulation study which calculated average bias and root mean square error for the mean and standard deviation estimators in 1000 trials. We actually performed some simulations on different numbers of trials up to, I think, 100,000 and found no difference, so we felt that 1000 was sufficient to characterize the statistical techniques. We used three different sampling sizes, 10, 15, and 20. This is unique to this work, to my knowledge, because most of the literature work on this topic have used sample sizes of 20, 50, and even larger. When samples cost $2000 apiece, you rarely find people that are willing even to pay for 10, let alone 20. So, I think this is an important issue since the results vary widely in this range, and it is important to consider them in this context.

Four distribution assumptions were used. We used a log normal distribution with a coefficient of variation of 1 and a log normal distribution with a coefficient of variation of 0.3. We chose this based on some preliminary analysis of paper industry data sets which I will describe in just a second and which seemed to have characteristics that were bracketed by this range of coefficients of variations; i.e. from 1 to 0.3. We also used data sets that contained 100 fully quantified observations and formed an empirical distribution from them; i.e. we drew values from them in groups of 10, 15, and 20 in order to test the three techniques under more realistic analysis conditions. Five levels of censoring were tested; these included censoring at the 5, 20, 40, 60 and 80 percentile values.

The simulation process described in Slide 16 work as follows: The computer program generates 10, 15, or 20 random numbers, depending on what condition you are simulating. If censoring is to occur at some fixed threshold, then the data set is scanned, and any value below that threshold is marked as an ND. The three statistical procedures are applied, and then the bias resulting from that application is stored. The process is repeated 1000 times, and then the average bias and the average root mean square error are calculated.

An important issue in evaluating simulation results is how well distribution assumptions such as the log normal model, characterize real data sets, because if they do not properly characterize real data sets, then you could be misled when interpreting the simulation results. One of the steps that has been taken, was to do distributional testing (Slide 17) for the log normal statistical model versus the bimodal feature of the D-log procedure using the effluent variability study data base generated from a cooperative effort

between USEPA and the paper industry. Just briefly, it involved sampling at 8 facilities with approximately 8 sampling locations per facility for approximately 18 events. So, we had a large pool of data to look at. You will hear more about this data base from the next speaker, I believe, during the in depth discussion of the effluent guidelines rulemaking. From that large data base, we selected data sets that met a particular criterion. In this case, we chose data sets that had at least two non-detected values and at least three fully quantified observations. We then constructed probability plots and examined the correlation coefficient values of those plots. When we did this test, we found that, by and large, the log normal distribution was superior to the D-log assumption for modeling the paper industry data sets and the EVS data base in particular.

As a further reality check, we also attempted to validate the notion that the single log normal distribution was the best choice for modeling paper industry data sets in a second way. We predicted the highest and the lowest fully quantified measurement in all of the data sets selected for regression analysis. Basically, we found that the log normal distribution model had one-sixth the error of the D-log assumption when applied to real paper industry data sets. So, we felt like, from this activity, that the log normal model used in our simulations is representative of the real world.

Slide 18 shows the results, at least for bias; time is short today, so I am going to skip the root mean square error results. For bias, we have our three techniques listed across the top; i.e. D-log, MLE, and RNOS. We have different sample sizes and different levels of population variability; CV = 1 being a more variable population than CV = 0.3.

For sample sizes of 10, we found that bias can range from as high as 28 percent for the D-log procedure to a high of 7 percent for the MLE procedure. These results are for the 5 to 60 percentile censoring range. Above 60 percentile censoring, none of the techniques worked particularly well, and they are really not recommended. Although with that caveat I mentioned at the beginning of my talk, sometimes it is necessary to calculate a number whether it makes sense or not. However, I only show here the bias for 5 to 60 percent censoring. The regression technique seems to be not nearly as effective as the MLE technique, and the MLE technique is definitely superior to D-log as well.

As sample size increases for the more variable samples with CV = 1 condition, we see that percent bias decreases with increasing sample size for both the MLE and RNOS procedures, whereas for the D-log procedure, the bias remains more or less constant. I am not sure we can detect the difference between 24 and 25.

When population variability is decreased, we see decreases in bias for all techniques. However, the decrease in bias seems to be strongest for the MLE and the regression techniques which seem to go down by factors of 3 to 5 compared to the D-log technique which only drops by a factor of 2. When we get into large sample sizes, we see that the bias is approaching zero quite nicely for the MLE and the RNOS techniques. Another thing

to notice about this slide is that all the methods, with the exception of this one case right here, overestimate mean standard deviations.

How well can these three techniques estimate standard deviations?

We find that, for the RNOS technique and sample size of 10, standard deviation estimation is terrible with 700 percent error; don't even use it (Slide 19). In general, biases are greater for standard deviation estimates; they are more difficult to estimate. Overall, the MLE is superior at estimating standard deviations. However, we have a peculiarity in that when population variability decreases, we see increasing bias for the D-log procedure and decreasing bias for the MLE and the regression techniques. Depending on the variability, the regression and MLE techniques seem to swing from positive to negative biases, whereas the D-log procedure always seems to underestimate.

In summary and conclusion (Slides 20, 21, & 22), all methods appear unreliable for data censoring greater than 60 percent. For estimating means, all approaches tend to overestimate; the MLE appears superior to the RNOS and the EPA D-log procedure with a bias, in the worst case, 2.5 times less than the D-log procedure. For estimating standard deviations, the MLE approach tends to over or underestimate standard deviations, and so does the regression technique while the EPA D-log procedure consistently underestimates standard deviations; in this case, the MLE was a superior method to both the regression and the D-log procedure with a bias that was 1.2 times less than the D-log procedure overall. In terms of sample size effect, the bias for the D-log procedure remained approximately constant while for the MLE and RNOS techniques, we saw a decrease in bias with increasing sample size.

In terms of population variability effect, for means, when you decrease the coefficient of variation, there is a decrease in bias for all the techniques while for standard deviations, the same occurs for the MLE and the RNOS techniques. However, for the D-log technique, we see an increase in standard deviation bias for a decrease in population variability.

That concludes my presentation today.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MS. DINSMORE: Donalea Dinsmore from State of Wisconsin. I would like to know, you talked about its not mattering where the values are censored, whether it be at the MDL minimum level or some other value. Are you talking about the absolute number that is censored? Did you deal at all with the uncertainty

around censoring when you are using an MDL and the numbers not being real numbers until you get to something that is like a quantitation limit?

MR. HINTON: The present statistical techniques that are available in the literature do not presently contain the sophistication to deal with that question which is why I said or should have said that, at this time, it does not matter which censoring threshold was used by the chemist. However, you are absolutely correct in that the choice of the censoring level and its uncertainty would make a difference if we could incorporate that into our calculations.

MR. TELLIARD: Thank you, Steve.

STATISTICAL ANALYSIS OF ENVIRONMENTAL DATA SETS WHICH CONTAIN 'NOT-DETECTED' OBSERVATIONS

(An Abstract for)
1994 Norfolk Conference

By
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March 1994

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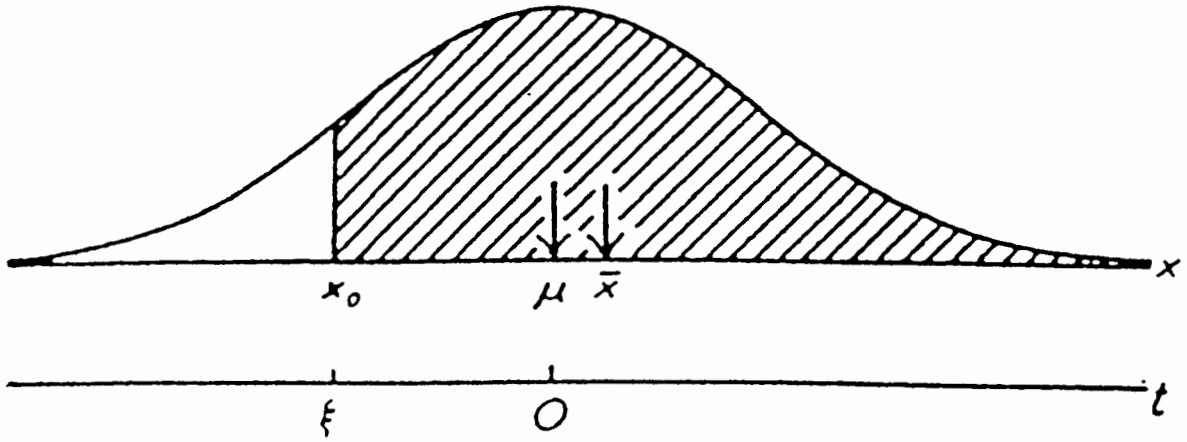
Special considerations and analysis techniques are needed to make rational decisions during regulation development or compliance monitoring when 'non-detected' observations are involved. The paper describes approaches for analyzing such data, limitations of the approaches and strategies to use when no 'detections' occur.

Introduction

- Increasing Occurence of Left Censored Data

- Types of Observations
  - Non-detects (NDs)
  - Fully Quant. Measurements (hits)
  - Uncertain Measurements (GTs)

Censoring on the Left at x_0



Slide 2

Introduction Cont.

- Left Censoring Thresholds
  - Level of Detection (LOD)
  - USEPA's Minimum Level (ML)
  - Method Detection Limit (MDL)
  - Limit of Quantitation (LOQ)
  - **Etc.....**

- Statistical Calculation Difficulties

Objective

- Delineate Problem Setting
- Define Preliminary Analysis Steps
- Review 3 Common Approaches
- Evaluate Bias and RMSE Properties

Slide 4

As Received Data

Set 1	Set 2	Set 3	Set 4
3	ND(11)	ND(50)	161
1	ND(10)	281	ND(100)
2	18	ND(500)	203
ND(1)	ND(11)	104	42
ND(1)	ND(12)	114	42
1	ND(12)	ND(50)	37
ND(1)	16	89	
ND(1)	ND(12)	61	
	ND(12)	80	
	ND(10)	134	
	15	56	

Ordered for Analysis

Set 1	Set 2	Set 3	Set 4
ND(1)	ND(10)	ND(50)	37
ND(1)	ND(10)	ND(50)	42
ND(1)	ND(11)	56	42
ND(1)	ND(11)	61	ND(100)
1	ND(12)	80	161
1	ND(12)	89	203
2	ND(12)	104	
3	ND(12)	114	
	15	134	
	16	281	
	18	ND(500)	

Slide 6

Preliminary Data Analysis

- Rank Data
- Determine Number of Unique Censoring Thresholds
- Test Distribution Assumptions
- Transform Data to Obtain Normality

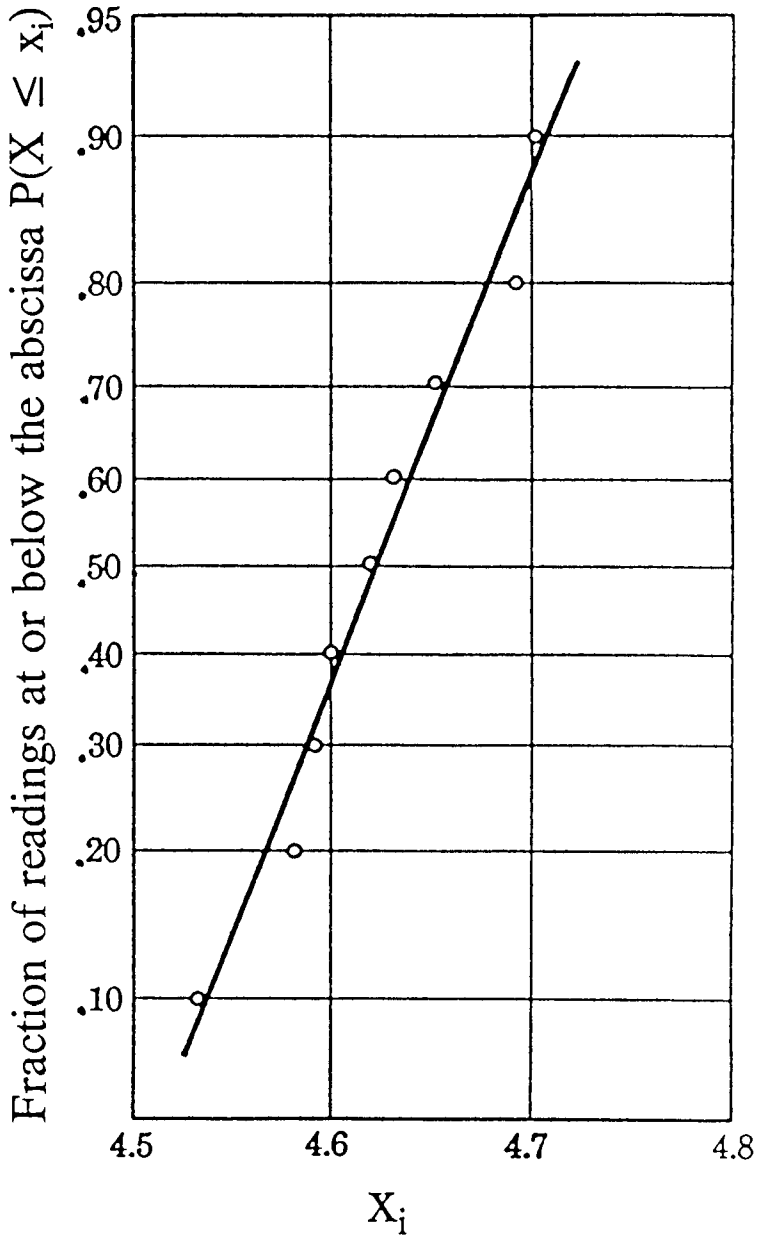
Slide 7

Probability Plot

$$P(X \le x_i) = \frac{i - 0.375}{n + 0.25}$$

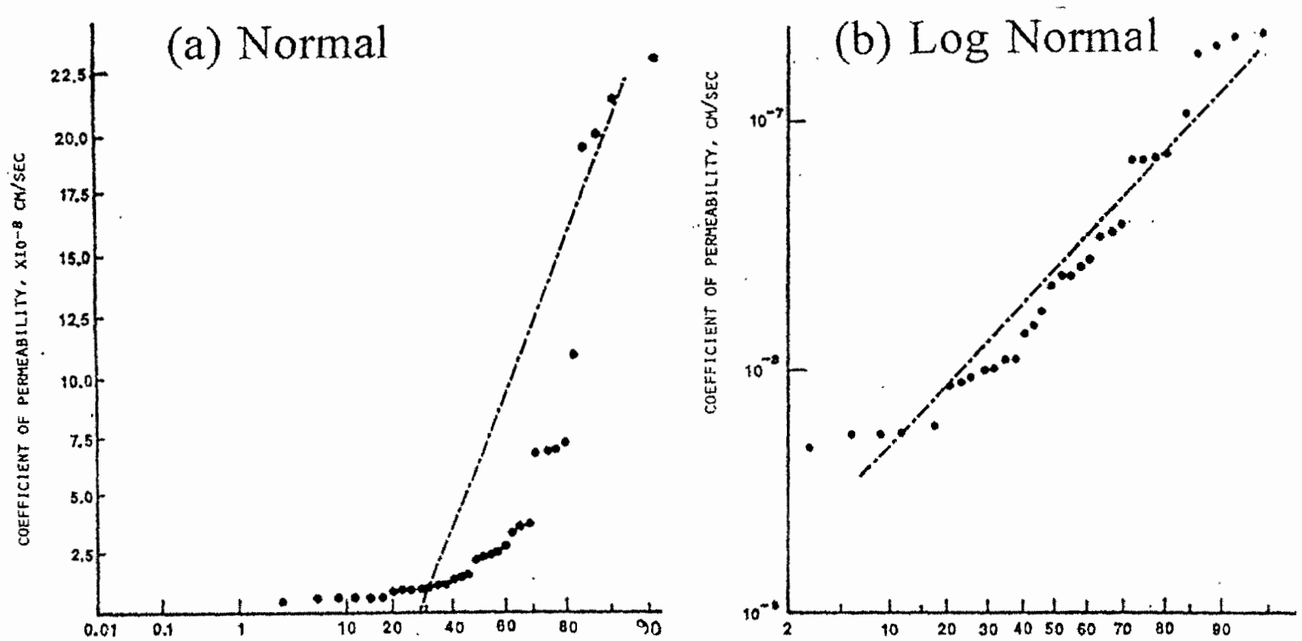
i = obs rank

n = total # of obs



Slide 8

Example Probability Plots



Slide 9

Log-Normal Data

- Transform w/ $y_i = \mathrm{Ln}(x_i)$
- Apply Statistical Procedure
- Untransform w/

$$\bar{x} = \exp(\bar{y} + 0.5 s_y^2)$$

$$s_x^2 = \bar{x}^2 [\exp(s_y^2) - 1.0]$$

Slide 10

Methods

- Maximum Likelihood Estimators (MLE)
  - Cohen - Restricted - Hald
- Regression of Order Statistics
- Delta - Log Normal
- USEPA D-Log
- Balancing
  - Trimmed & Winsorized Mean
- Graphical
- Replacement

Slide 11

Cohen's MLE Method

$$m_{ML} = m^* - (m^* - x_o)\ \Lambda\ [g,h]$$

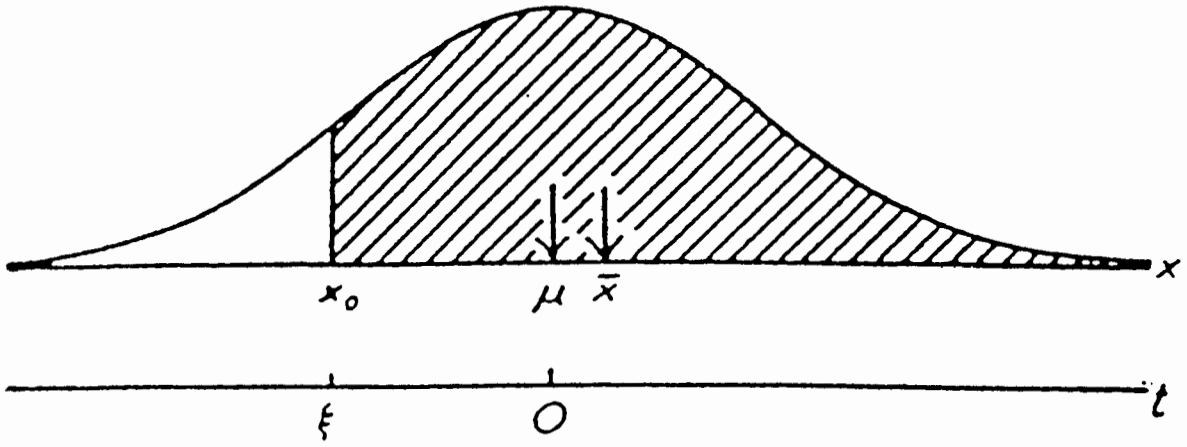
$$s^2_{ML} = s^{*2} + (m^* - x_o)^2\ \Lambda\ [g,h]$$

$$h = \textit{fraction of ND observations}$$

$$g = s^{*2}/(m^* - x_o)^2$$

Slide 12

Censoring on the Left at x_0



Slide 13

Regression of NOS

$$x_i = m_{RNOS} + s_{RNOS}\, z[(i - 0.375)/(n + 0.25)]$$

x_i = *ordered values of quantified observ*

z = *is the inverse normal function*

[ ] = *plotting position*

Slide 14

EPA's D-Log Approach

$$M_{EPA} = \hat{\delta} D + (1-\hat{\delta}) \exp(\bar{y}+0.5s^2)$$

$$\mathbf{s}^2_{EPA} = (1-\hat{\delta}) \exp(2\bar{y}+s^2)[\exp(s^2) - (1-\hat{\delta})] + \hat{\delta}(1-\hat{\delta})D[D-2\exp(\bar{y}+0.5s^2)]$$

where:

D = *detection limit*

$\hat{\delta}$ = *fraction of NDs*

y_i = $Ln(x_i)$ *for* $x_i > D$

Slide 15

Simulation Study Approach

- Average Bias and RMSE of $\bar{x}$ and S on 1000 trials
- Three Sampling Sizes 10, 15, & 20
- Four Distrib. Assumptions LN(cv=1), LN(cv=.3), 2346-TCP, 45-DCC
- Five Censoring Levels 5, 20, 40, 60 & 80 Percentile

Slide 16

Distribution Testing
LN vs D-LOG

- EVS Data Base
- Data Set Selection Criteria
- Prob Plot R^2 Values
- Relative Prediction Error

Slide 17

Mean Estimator Bias (%) *

	DLOG	MLE	RNOS
N=10			
CV=1	4 to 28	5 to 7	8 to 25
CV=.3	3 to 15	.6 to 2	2 to 5
N=15			
CV=1	2 to 25	3 to 4	5 to 12
CV=.3	.8 to 15	.3 to .4	1 to 3
N=20			
CV=1	.2 to 24	1 to 2	3 to 9
CV=.3	.3 to 15	-.1 to -.3	.5 to 2

* For 5 to 60% Censoring

Slide 18

SD Estimator Bias (%) *

	DLOG	MLE	RNOS
N=10			
CV=1	-1 to 20	10 to 25	17 to 756
CV=.3	-6 to -39	-2 to -7	-.5 to -2
N=15			
CV=1	-5 to -26	6 to 14	9 to 49
CV=.3	-6 to 39	-2 to -5	-.6 to -2
N=20			
CV=1	-7 to -27	3 to 11	6 to 36
CV=.3	-6 to -39	-2 to -3	.7 to 1

* For 5 to 60% Censoring

Summary & Conclusions

- All Methods Appeared Unreliable for Data Censoring > 60 Percentile

- Estimating Means
  - All Approaches Over Estimate
  - MLE Superior to RNOS & EPA-DLOG
  - $\text{Bias}_{\text{MLE}} \leq 1/2.5\ \text{Bias}_{\text{EPA-DLOG}}$

Slide 20

Summary & Conclusions Cont.

- Estimating Standard Deviations
  - MLE Over/Under Estimates
  - RNOS Over/Under Estimates
  - EPA-DLOG Under Estimates
  - MLE Superior to RNOS & EPA-DLOG
  - $\text{Bias}_{\text{MLE}} \leq 1/1.2\ \text{Bias}_{\text{EPA-DLOG}}$

Summary & Conclusions Cont.

- Sample Size Effect
  - $\text{Bias}_{\text{EPA-DLOG}} \approx$ Constant
  - Bias_{MLE} & $\text{Bias}_{\text{RNOS}}$ $\downarrow$ w/ n $\uparrow$

- Population Variability Effect
  - $\bar{x}$: Bias_{ALL} $\downarrow$ w/ cv $\downarrow$
  - s: Bias_{MLE} & $\text{Bias}_{\text{RNOS}}$ $\downarrow$ w/ cv $\downarrow$

    $\text{Bias}_{\text{EPA-DLOG}}$ $\uparrow$ w/ cv $\downarrow$

Slide 22

MR. TELLIARD: Our before luncheon speaker is one of our own. Henry Kahn is in the Office of Water and, more importantly, in the Engineering and Analysis Division.

Henry is going to speak on the statistics applied for developing the regulations covering the pulp and paper industry.

DETERMINATION OF PROPOSED EFFLUENT LIMITATIONS FOR THE PULP AND PAPER INDUSTRY

Henry D. Kahn and Marla D. Smith, U.S. EPA, and
Amy S. Brockman, Science Applications International Corporation

Presented on May 5, 1994 at EPA's 17th Annual Conference on Analysis of Pollutants in the Environment

ABSTRACT

Effluent guidelines regulations for the pulp, paper and paperboard industry were proposed by the U.S. Environmental Protection Agency in October, 1993. The proposed regulations contain numerical limitations on the amounts of pollutants in mill effluent. This paper provides a description of the characteristics of the data used to support the proposed limitations. This paper also includes a discussion of statistical methodology used in previous regulation development and modifications that were required to accommodate certain characteristics of the pulp and paper data. These modifications allowed for a mixture of various types of censoring in the data and for multiple detection limits.

INTRODUCTION

This paper provides a summary of the data and the statistical methodologies that were used in developing the effluent limitations contained in the proposed effluent guidelines regulations for the pulp, paper, and paperboard industry. In particular, this paper describes the data sources, the censoring of the data, aggregation of duplicate samples, calculation of production normalized loadings, the statistical modeling of the data, and special cases where the statistical methodologies were not used to develop the limitations. Detailed summaries of the data and statistical methodologies are presented in the "Statistical Support Document for Proposed Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard Point Source Category." [1]

DATA SOURCES

The data used in developing the limitations were obtained from three sources: the long-term study, short-term studies, and self-monitoring data. These data provided information about the concentration levels of various pollutants in wastewater. Samples of wastewater were analyzed for concentration levels of the following pollutants: volatile organic compounds, chlorinated phenolics, adsorbable organic halides (AOX), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 2,3,7,8-tetrachlorodibenzo-furan (TCDF), chemical oxygen demand (COD), color, total suspended solids (TSS), and biochemical oxygen demand (BOD_5).

Long-term Study

The long-term sampling study was undertaken as a cooperative effort between EPA and the industry. Representatives of the paper industry, the American Paper Institute (now the American Forest and Paper Association [AFPA]) and the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), cooperated with EPA in obtaining data to support EPA's effluent guidelines development. In this study, sampling data were collected and analyzed from eight pulp and paper mills.

The eight mills included in the long-term study were selected because they utilized particular pulping or bleaching technologies, wastewater treatment, or fiber furnishes. At each mill, sampling points were selected to characterize the bleach plant effluent and the final effluent. Samples were collected during one 24-hour period each week for nine weeks in the summer of 1991 and each week for nine weeks in the winter of 1991-1992. A total of about 540 samples was collected. These samples were chemically analyzed for chlorinated phenolics, chlorinated dioxins and furans, volatile organics, AOX, color, BOD_5, and TSS. All of the measurements were analyzed statistically, and the appropriate subsets of the data were used to develop the proposed effluent limitations and standards.

Short-term Studies

EPA conducted 13 short-term sampling episodes from 1988 through mid-1993. Each episode was either two or three days in length. Mills were selected for participation in the short-term sampling program because they utilized particular pulping or bleaching technologies, wastewater treatment, or fiber furnishes.

During these short-term episodes, samples were analyzed for chlorinated phenolics, chlorinated dioxins and furans, volatile organics, AOX, color, COD, BOD_5, and TSS. Depending on the mill, sampling location, and pollutant, 24-hour, two-day, or three-day composite samples were collected. The sampling points were selected to characterize wastewater discharges from various processes and treatments, including bleach plant filtrates and final effluent streams. All of the data from the short-term episodes were statistically

analyzed, and the appropriate subsets of the data were used to develop the proposed effluent limitations and standards.

Self-monitoring Data

Limitations for BOD_5, TSS, and COD are based, in part, on self-monitoring data collected from the 1990 National Census of Pulp, Paper, and Paperboard Manufacturing Facilities. In October 1990, this census was sent to all pulp, paper, and paperboard facilities in the United States and the self-monitoring data base was developed from the responses. In general, the questionnaire self-monitoring data base contains data provided by the mills in an approximate daily format (a few skipped days, samples for Monday through Friday only, etc.). These data were provided for time periods ranging from six months to one year for the time span from 1989 through 1992.

CENSORING OF DATA

The pulp and paper analytical data base (from the long-term study, short-term studies, and self-monitoring data) contained a mixture of measured values, non-detect measurements and right-censored measurements. These three different types of samples were delineated by certain qualifiers in the data base:

- Non-censored (NC): a measured value.
- Non-detect (ND): samples for which analytical measurement did not yield a concentration above a sample-specific detection limit (such measurements are, in effect, left-censored).
- Right-censored (RC): these samples were qualified with a greater than (>) sign, signifying that the reported value is considered a lower limit of the actual concentration.

The pulp and paper effluent concentration data were characterized by a large number of measurements reported as below the detection limit (ND). These detection limits were sample specific and, for many pollutants, covered a wide range of values.

The right-censored values occurred in the data for AOX, volatile organics, and chlorinated phenolics. For the AOX data, break-through is determined by comparing the results of two columns used in the chemical analysis of AOX. Ideally, all of the AOX is adsorbed in the first column. Break-through occurs when AOX is adsorbed in the second column. For the volatile organics and chlorinated phenolics data, right-censored values were reported when the measured values were beyond the highest calibration points.

AGGREGATION OF DUPLICATE SAMPLES

Both laboratory and field duplicate samples were provided in the data sources. Laboratory duplicates are samples that were divided at the laboratory, analyzed separately, and had the same sample number. Field duplicates are two or more samples collected for a particular sampling point at virtually the same time, assigned different sample numbers, and flagged as duplicates for a single episode number. For the statistical analysis, a single value was needed for each sample or episode number. Therefore, duplicates were aggregated using an averaging procedure. If a sample had both laboratory and field duplicates, the laboratory duplicates were averaged first.

In some cases, this aggregation produced another type of censoring which was called "mid-censoring." When a non-censored (NC) sample and a non-detected sample were averaged, the resulting average was labeled "mid-censored" (MC), that is, a censored sample whose true value lies between two non-zero bounds (lower and upper). For instance, the lower bound of the average is not zero (because one of the samples was detected at a measurable concentration), but instead would equal the average of the NC and zero (the lowest possible value of the non-detect). Similarly, the upper bound would equal the average of the NC and the detection limit of the non-detect sample (the highest possible value of the non-detect). Thus, the lower and upper bounds for this type of mid-censored data point are

lower:	NC/2
upper:	(NC + ND)/2

where the value of ND is the detection limit for the non-detected sample and the value of NC is the observed concentration value. For example, if one of the duplicate samples is non-censored with a concentration value of 44 ppq and the other duplicate sample is non-detect with a detection limit of 10 ppq, then the bounds of the mid-censored value would be:

lower = 44 ppq / 2 = 22 ppq
upper = (44 ppq + 10 ppq) / 2 = 27 ppq.

CALCULATION OF PRODUCTION NORMALIZED MASS LOADINGS

After all laboratory and field duplicates were averaged, production normalized mass loadings were calculated for each sample. Three types of information were used with appropriate conversion factors to calculate the production normalized mass loadings: an analytical concentration, a wastewater flow rate, and a brownstock flow rate. All subsequent calculations were computed using the production normalized mass loadings. The censoring associated with the concentration values was assigned to the corresponding production normalized value.

STATISTICAL MODELING OF DATA

The remainder of this paper describes the statistical methodologies that were used to develop the proposed limitations for the pulp and paper industry. The basic approach used was to fit observed data to various modifications of the lognormal distribution. These modifications were necessary to accommodate the different types of censoring present in the data. In certain cases, this basic approach was not suitable, and these special cases are also described.

Lognormal Distribution

The lognormal distribution is often appropriate for modeling effluent data (see figure of lognormal distribution) because such data are positively valued and the shape of their distribution is positively skewed. The BOD_5, TSS, and COD data were modeled using the lognormal distribution. Limitations were then calculated based on parameters of the lognormal distribution estimated from the data.

The presence of censored measurements in other pulp and paper effluent data sets led, for several reasons, to the consideration of modifications to the basic lognormal distribution. These modifications allow for the modeling of such data as mixtures of positive measurements that are lognormally distributed and measurements with values that are not known exactly ("censored" values).

Classical Delta-Lognormal Distribution

To incorporate censored data into the model, two modifications to the lognormal density model have been used by EPA in past effluent guidelines rulemakings. The first modification is known as the classical delta-lognormal model or delta distribution (see figure of classical delta-lognormal distribution), used in economic analysis to model income and revenue patterns (see reference [2]). In this adaptation of the usual lognormal distribution, the model is expanded to allow for the presence in the data of zero amounts. To do this, all positive (dollar) amounts are grouped together and fit to a lognormal density. Then all zero amounts are segregated into another group of measurements representing a discrete distributional "spike" or probability mass at zero. The resulting mixed distribution, combining a continuous density portion with a discrete-valued spike, is known as the delta-lognormal distribution. The delta in the name refers to the proportion of the overall distribution contained in the spike at zero; that is, the proportion of observed zero amounts.

Adapted Delta-Lognormal Distribution

EPA further adapted the classical delta-lognormal model ("adapted model") to account for non-detect measurements in the same fashion that zero measurements were handled in

the original delta-lognormal. Instead of zero amounts and non-zero, positive amounts, the data consisted of non-detects and detects. Rather than assuming that non-detects represented a spike of zero concentrations, these samples were allowed to have a single positive value (see figure of adapted delta-lognormal distribution and reference [3]). Because each non-detect was assigned the same positive value, the distributional spike in this adapted model was located not at zero, but at that single positive value. In the adapted delta-lognormal model, the delta again refers to those measurements contained in the discrete spike, this time representing the proportion of non-detect values observed in the data set.

The adapted model was used in developing limitations for the Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) and the Pesticides Manufacturing regulations promulgated in 1987 and 1993, respectively. For most data sets for these two rulemakings, the concentration data were fit to the adapted model (see references [4] and [5]). However, the distribution can also be used to model mass values as was done in two instances in the pesticides manufacturing rulemaking. Mass values and production-normalized mass values are typically lognormally distributed as are concentration data.

Modified Delta-Lognormal Distribution

The modified delta-lognormal model contains several modifications of the adapted model. The modifications allow for changes in three key assumptions underlying the adapted delta-lognormal. These assumptions relate to the discrete probability mass of the model, the continuous lognormal portion of the model, and non-censored values below the detection limit.

The first assumption is that the discrete spike portion of the adapted delta-lognormal model is a fixed, single-valued probability mass associated (typically) with all the non-detect measurements. If all non-detect samples in the pulp and paper data base had roughly the same reported detection limit, this assumption would be satisfied adequately. However, reported detection limits among sample measurements in the pulp and paper analytical studies varied substantially, especially when the non-detect concentrations were converted to "no detectable mass amounts" by multiplying the concentration detection limit by the effluent flow rate associated with the stream from which the sample was taken. Because of this variation in the reported concentration-based detection limits and "no detectable mass amounts", a single-valued discrete probability mass could not adequately represent the set of non-detect measurements observed in the pulp and paper data base and a modification of the model was used.

The second assumption of the adapted delta-lognormal model is that all non-censored values (i.e., measurements) reported below the detection limit (D) are set equal to the value chosen to represent non-detect measurements. For example, if this value for TCDD was 10 parts per quadrillion (ppq), then any non-censored samples reported below 10 ppq were set

to 10 ppq. The adapted model was modified to incorporate the presence of non-censored values below the detection limits.

The third assumption of the adapted delta-lognormal model is that all of the detected measurements comprising the continuous lognormal portion of the overall distribution are known concentration (or mass) amounts. In the pulp and paper data base, however, not all of the samples considered to be detects were associated with known numerical values. As an example, certain sample measurements within the AOX data base were known to have a concentration at least as large as some lower bound L, but the exact value could not be determined. In statistical terms, just as non-detect samples are referred to as left-censored measurements because they are known to be between zero and an upper bound (i.e., the detection limit), these AOX measurements were referred to as right-censored samples. In effect, left-censored values are censored on the left side of the distribution and right-censored values are censored on the right side. Another example occurred for mid-censored samples. These samples were known to have a concentration (or mass value) between some lower bound (L) and some upper bound (U) but the exact value was not known. As discussed previously, mid-censored values occurred due to averaging duplicates where one measurement was non-censored and the other measurement was non-detect.

The presence of measurements that are censored in some fashion, so that the exact values are indeterminate, makes it inappropriate to apply the adapted delta-lognormal model without further modifications. One approach that could be taken without changing the model would be to assign an "exact" measurement value to those samples that are censored. However, this tactic leads to arbitrary measurement value assignments and would have an uncertain and potentially arbitrary impact of the calculated estimates of the final model parameters. Instead of handling uncertain measurements in this fashion, the choice was made to modify the adapted delta-lognormal model to accommodate censored samples as well as non-censored samples (i.e., those detected measurements associated with "exact" or known concentration/mass values).

Modification of the Discrete Spike

To appropriately modify the adapted delta-lognormal model for the observed pulp and paper data base, the first modification was made to the discrete single-valued spike representing non-detect measurements (see figure of the modified delta-lognormal distribution). In order to model these values as production-normalized mass values, a production-normalized mass-based detection limit is defined as the reported concentration-based sample-specific detection limit multiplied by the flow rate associated with that sample, and divided by the corresponding production value. Because non-detect samples had wide variation in production-normalized mass-based detection limits, the single spike of the delta-lognormal model was replaced by a discrete distribution made up of multiple spikes. Each spike in this modification is associated with a distinct production-normalized mass-based detection limit observed in the pulp and paper data base. Thus, instead of assigning all non-

detects to a single, fixed value, as in the adapted model, non-detects can be associated with multiple values depending on how the production-normalized mass-based detection limits vary.

In particular, because the production-normalized mass-based detection limit associated with a non-detect sample is considered to be an upper bound on the true value, which could range conceivably from zero up to the detection limit, the modified delta-lognormal model used here assigns each non-detect sample to half its production-normalized mass detection limit.

This procedure of using half of the production-normalized detection limit was modified when the concentration-based detection limit was much larger than the majority of other concentration-based detection limits for that pollutant. Using the production-normalized mass loadings resulting from these high concentration-based detection limits caused instabilities in estimating the parameters of the distribution of the loadings. Therefore, twice the mode (i.e., the most commonly reported concentration-based detection limit) was substituted for any concentration-based detection limits that were reported as greater than the value of twice the mode of the set of detection limits for a pollutant. This substituted value was then used in calculating the production-normalized mass-based detection limit. For example, if one sample has a concentration-based sample-specific detection limit reported as 500 ug/l for pollutant XYZ and the mode of the set of detection limits for XYZ was 20 ug/l, then the value of 40 ug/l (i.e., two times the mode) was used in calculating the production-normalized mass-based detection limit.

The modified delta-lognormal used to model the production-normalized mass values is, in effect, a generalization of the adapted model that allows for more than one sample specific detection limit. In the adapted model, the delta portion represents the proportion of non-detects. In the modified model, the delta portion represents the proportion of non-detects, but is divided into the sum of smaller fractions, each representing the proportion of non-detects associated with a particular and distinct detection limit. While replacing the single discrete spike in the adapted delta-lognormal distribution with a more general discrete distribution of multiple spikes increases the complexity of the model, the discrete portion with multiple spikes plays a role in limitations development identically parallel to the single spike case and offers flexibility for handling multiple observed detection limits.

Modification of the lognormal portion

To accommodate detected observations that are censored in some fashion, the lognormal portion of the adapted delta-lognormal model also has been modified. A lognormal distribution is still used to represent the set of detected measurements, but the manner of estimating the distributional parameters has been changed to allow for mid- and right-censored observations and for non-censored values below the multiple detection limits. In general, the method typically used to estimate the parameters of the underlying lognormal

distribution is known as maximum likelihood estimation (MLE). The MLE method is based on assuming that a group of independent observations follow a particular distributional model, in this case the lognormal distribution. A mathematical function known as the "likelihood," is constructed from the mathematical formula for the lognormal distribution fit to the observed data. Data that are reported as either measured or censored can be incorporated into the likelihood function. The values of the parameters of the distribution that maximize the likelihood function for a given set of data are referred to as the maximum likelihood estimates.

SPECIAL CASES

The modified delta-lognormal was not used to model data sets that contained only non-detect measurements. For each of these data sets, the proposed effluent limitation is non-detect at the minimum level for the analytical method. EPA proposed non-detect limitations for some of the chlorinated phenolics, volatile organics, and TCDD when the data contained all non-detect measurements.

CONCLUSION

With two basic modifications to the adapted delta-lognormal distribution, it is possible to fit a wide variety of observed effluent data sets to the modified model. This model can accommodate data sets that contain a mixture of multiple detection limits for non-detects, detected samples with mid- and right-censored measurements, and non-censored values below the multiple detection limits. The same basic framework can be used even if there are no non-detect values or censored data. Thus, the modified delta-lognormal model offers a large degree of flexibility in modeling effluent data. This flexibility was necessary in order to model the data available to support the proposed pulp and paper rulemaking.

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QUESTION AND ANSWER SESSION

MR. MADELONE: Ray Madelone, TRW. What was the percentage of non-detects in the data sets?

MR. KAHN: It ran the gamut. There were so many different data sets with different percentages of non-detects. You saw the one with 100 percent non-detects. We had all the way from zero to 100 percent, depending on the analyte.

MR. MADELONE: Can you hazard a guess on what the typical value would be?

MR. KAHN: No, I would not want to do that.

MR. MADELONE: Okay.

MR. TELLIARD: It depended on the analyte, Ray. I mean, for example, AOX was always there. 2,3,7,8, as Henry pointed out, in most instances, was below the detection level.

MR. MADELONE: In your process of determining the true mean value of the data set, do you preserve the variability of the overall data set? In other words, if I were to take the non-detects and just set them to some number and then compute the standard deviation of that set, I would probably decrease it, because I loaded it, weighted it, with numbers that are all the same.

In the process that you are using here, do you maintain the variability that the rest of the true data set has in computing the numbers for the non-detect?

MR. KAHN: The short answer is yes.

MR. TELLIARD: Fellow in the back?

MR. SLENTZ: My name is Kurt Slentz with Energy Labs. I guess I had the same question, maybe formed a little bit differently, but if I understand it correctly, you are going to enforce their limits at non-detectable values. Is that correct?

MR. KAHN: The proposed compliance level for certain pollutants is at the minimum level for the analytical method which is the lowest level for quantification.

MR. SLENTZ: Have you taken into account the precision of the analytical method at that value?

MR. TELLIARD: Yes.

MR. KAHN: Bill says yes.

MR. TELLIARD: Yes.

MR. SLENTZ: You have accounted for that statistically?

MR. TELLIARD: Yes.

MR. KAHN: Yes. The variability inherent in the data is inherent in the values such as limitations, that we calculate from the data.

MR. SLENTZ: Do you require reporting of data that we produce that are below the detection that we flag, I mean, it is below our quantitation limit and we flag it as detectable? Do you count that?

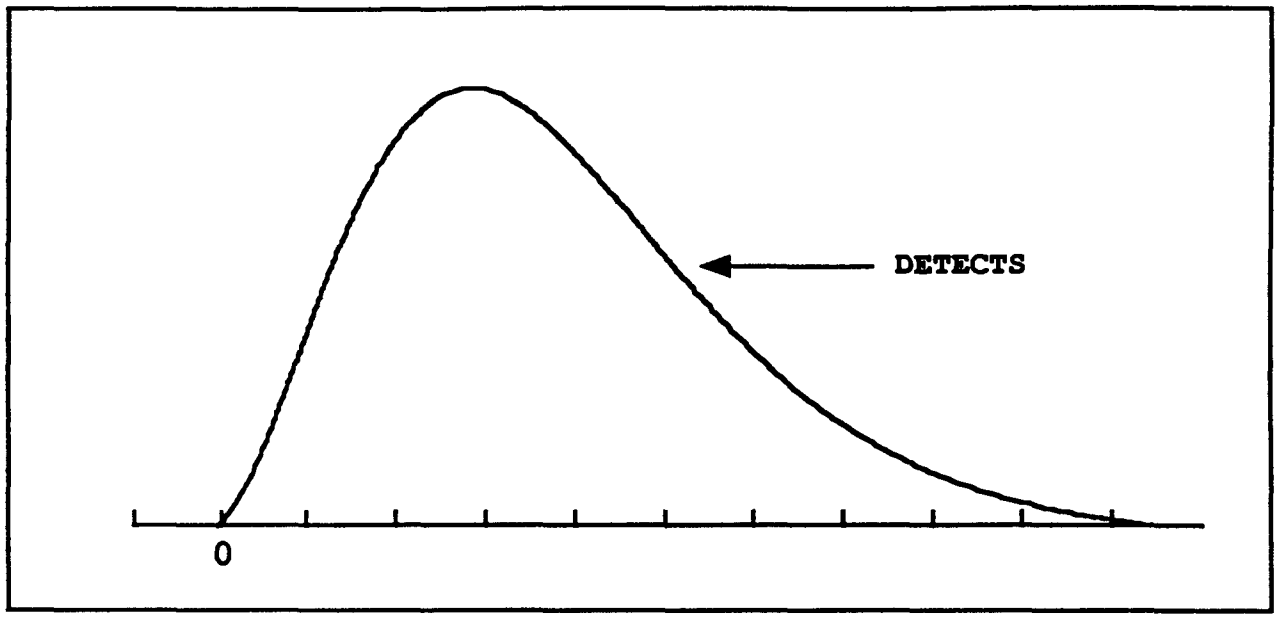
MR. TELLIARD: No.

MR. SLENTZ: If we detect something that is greater than our method detection, lower than our practical quantitation limit, do you count that as a number then?

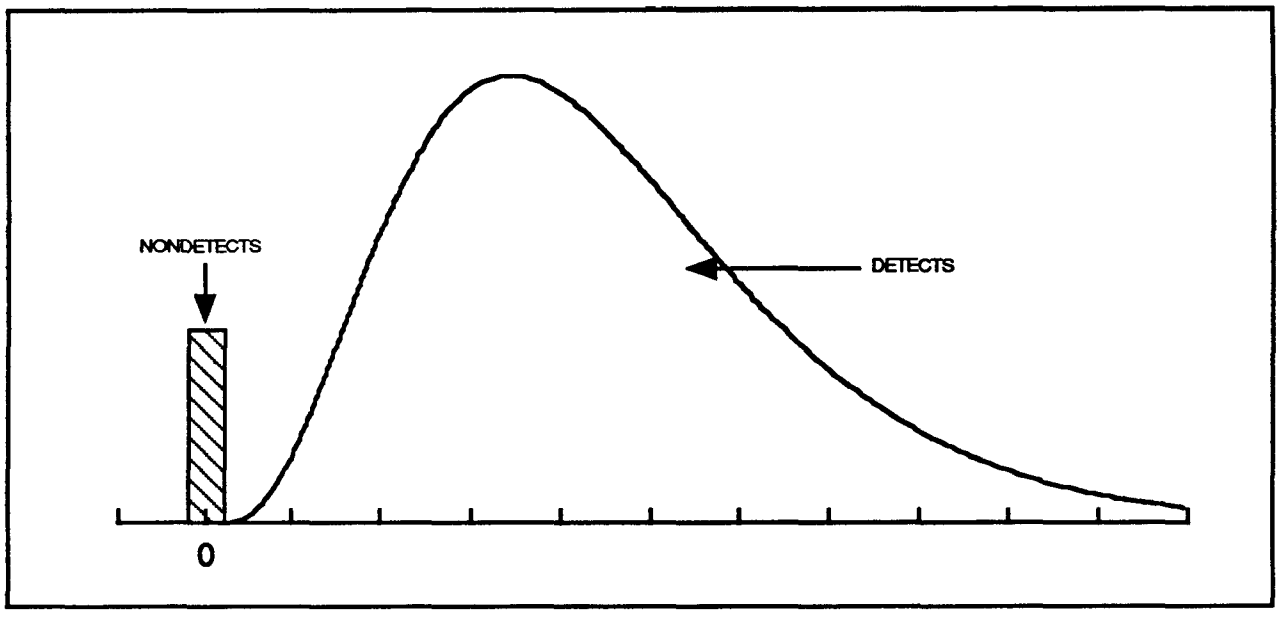
MR. TELLIARD: No.

MR. KAHN: We use a value that is at or above the minimum level which is our minimum level for quantification.

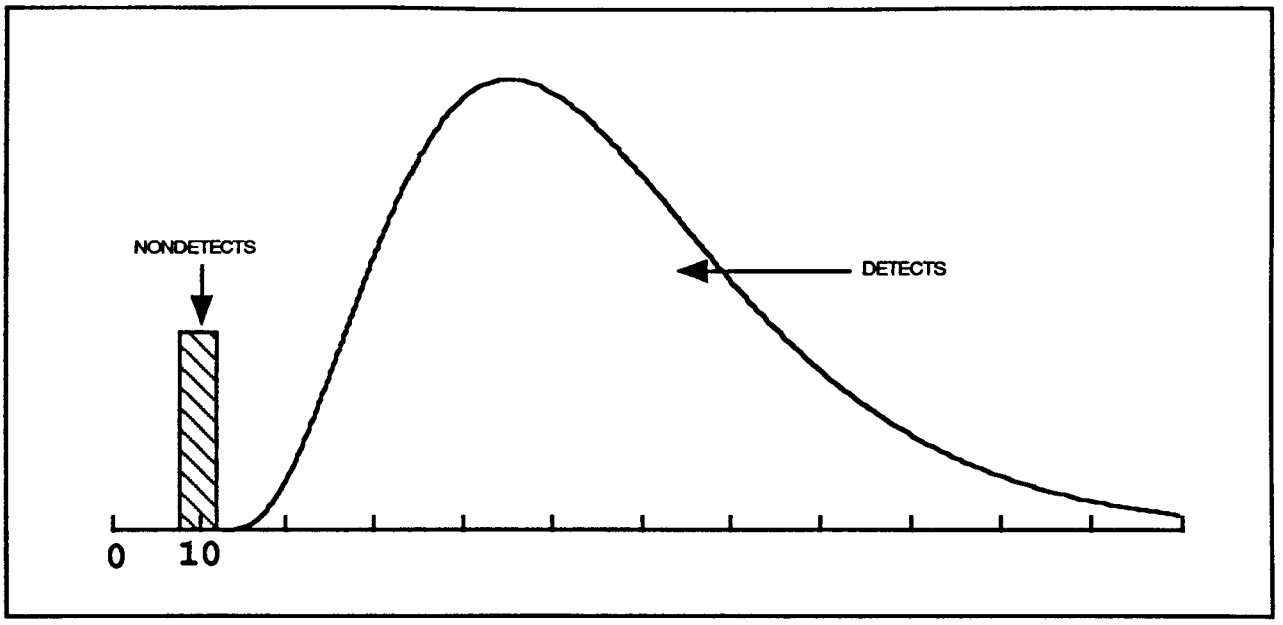
MR. TELLIARD: Thank you, Henry.



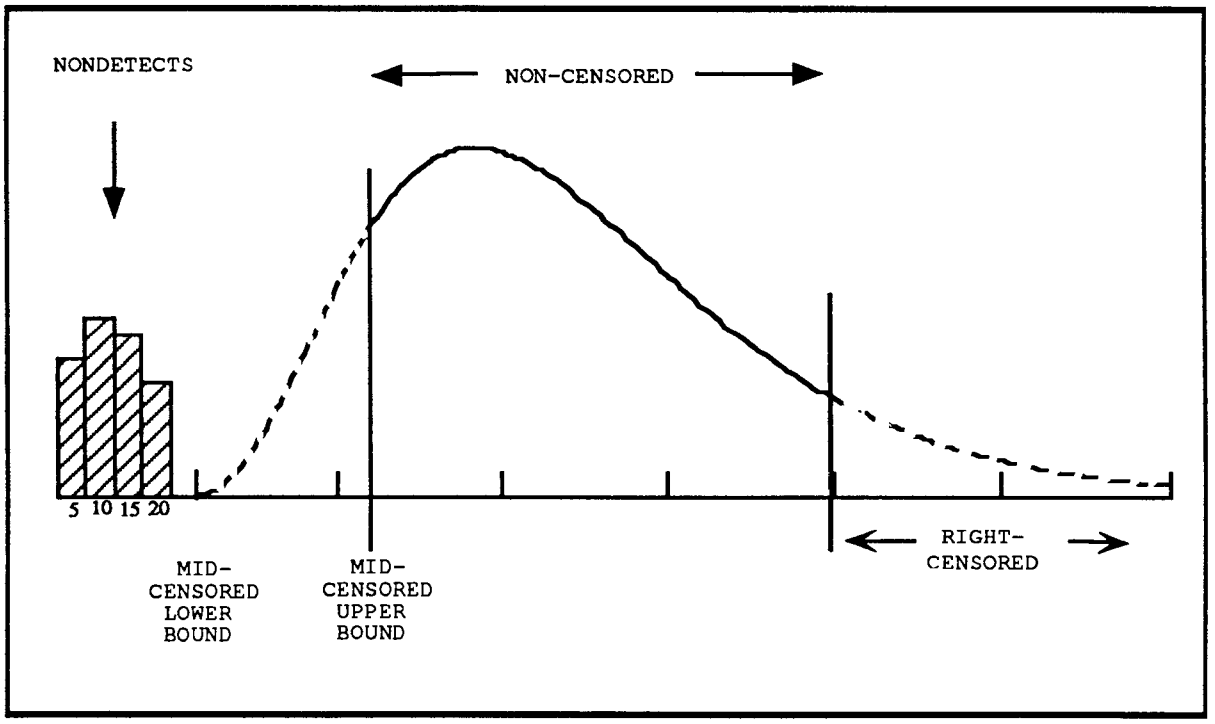
Standard Lognormal Distribution



Standard Delta-Lognormal Distribution



Adapted Delta-Lognormal Distribution



Modified Delta-Lognormal Distribution

MR. TELLIARD: Ileana has copies of her paper in the back of the room for anybody who wants to take a hard copy home with them.

It is lunch time. If you will, please be back here by 1:30. For those who are checking out and need to put your bags somewhere, feel free to bring them down, and we will find spaces for them around the room.

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MR. TELLIARD: Good afternoon to all of you who are back from the pizzeria, chocolate factory, or whatever else you were doing.

Our first speaker this afternoon is Bob Runyon. Bob is Chief of the Monitoring and Management branch of the Environmental Services Division (ESD) in Region II. Bob is also, in his spare time when he has nothing else to do, Co-chairman of the Methods Panel for the Environmental Monitoring Management Council, or, as we like to call it in government because we cannot use words, EMMC.

Bob is going to talk to us this afternoon about what efforts are underway on methods consolidation and what is going on, in general, in the EMMC and give you an overview of what has happened.

Thank you.

METHODS INTEGRATION IN EPA
THE ENVIRONMENTAL MONITORING MANAGEMENT COUNCIL

MR. RUNYON: The Environmental Monitoring Management Council came about in 1990 in response to several issues. In the late 1980s, EPA faced a situation where the credibility and the quality of the EPA scientific data used to make policy decisions came under criticism. Reports from the General Accounting Office and the Science Advisory Board questioned the credibility of the science used to support policy decisions in the Agency.

There was also Congressional interest, with all the money that had been spent in wastewater treatment facility construction, with improvements in the environmental area in general, in what a national scope assessment would tell them about whether the waters are getting better, the air is getting better, et cetera. They found that they were unable to make national environmental assessments that were meaningful.

EPA's approach to analytical methods development was fragmented, and it was on a program-by-program basis. To address contaminants of concern within each particular program, methods were developed independently. This led to the creation of a number of methods for the same analyte that may have been only slightly different.

There was a great deal of confusion in the regulated community, because they really were not sure which method they were supposed to use in a given situation. In addition to that, there was a great deal of difficulty for the production laboratories to continually shift from using one method today, another method tomorrow, analyzing for the same analyte.

So, in March of 1990, the Deputy Administrator from the previous administration, Hank Habicht, endorsed the formation of the Environmental Monitoring Management Council. The council was established to address all of the issues that I have just mentioned.

The EMMC is a four-tiered organization. It has a policy council that is made up of assistant administrators, regional administrators, chaired by the Region III regional administrator and the AA for the Office of Research and Development (ORD).

Under the Policy Council, there is a steering committee that is composed of office directors and division directors from programs, regions, and ORD.

Under the Steering Committee, there are ad hoc panels composed of scientific and engineering program and regional staff. In addition to the panel tri-chairs (program, region, ORD) each panel has work groups with representatives from the regions, the Office of Research and Development, and the program offices.

The next overhead illustrates the organizational chart for the EMMC. As you can see, under the steering committee, the four panels that are currently in place are the methods compendium panel which has led to the formation of EMMI, the methods integration panel, the lab accreditation panel, and the regulation development panel.

The methods compendium panel is charged with developing a readily available methods index for the Agency, and we are going to hear a little more about that later.

The regulatory development panel is charged with assuring that, as regulations are promulgated by the Agency either, in the development process or in the revision process, if environmental measurements are involved, the panel would ensure that there is an appropriate method and that there is appropriate quality assurance included in the method so that the Agency would not promulgate a regulation with no ability to analyze for the parameter that is being regulated.

The lab accreditation panel is charged with investigating the feasibility of a national lab accreditation program.

The methods integration panel has quite a large number of work groups. We have the water, solids, air, biological, radiation, field methods (a new one), performance-based methods (a new one), and a QA/QC work group.

The first action that EMMC took was to establish an infrastructure for addressing the issues that it was charged to address. EMMC focused on the cross-program issues, because they were the most critical areas within EPA.

The first accomplishment was the development of a common method format. The EMMC Format for presentation and documentation of methods is one of the major successes of EMMC (in addition to EMMI, of course).

All the new Agency methods are going into EMMC Format. EMSL-Cincinnati has, through the efforts of Tom Clark, started to incorporate every one of their new methods into the EMMC Format, and the integrated EMMC methods that have been completed are also in this format.

The EMMC Format allows for better assessment of comparability when you look at methods, because the documentation is consistent across all of the methods.

The EMMC Framework for Methods Development has also been completed. The Framework is a process for integrating methods development needs with the status of methods development within the Agency. It promotes joint methods development and funding, minimizes the overlap and the number of methods that are being developed for the same analyte, and ensures that the EMMC Format is going to be incorporated for each method.

EMMI, or the Environmental Monitoring Methods Index, is, as all of you know, the EPA compendium of methods. For those of you that are interested, outside on the table, there is some information as well as some demonstration disks. EMMI is available to the public through NTIS as well. That is my promotional spiel here.

This is a very good index of EPA methodology for anyone, and it is being updated this year.

The methods integration panel is charged with eliminating the unnecessary duplication of methods that are out there, and the EMMC provides a consensus forum for those methods that need integration. A priority list is developed for methods which should be integrated first, and the panel serves as a cross-program mechanism for methods and data documentation. Methods integration allows for the development of comparable data across programs.

Four methods, as of right now, have been integrated: graphite furnace-AA; ICP spectrometry; hot acid extraction for elemental analyses in those first two; and the fourth one is purgeable organics by capillary column GC.

There are four others that are in the process right now, semi-volatiles, dioxins, halogenated pesticides, and microwave digestion.

I will talk a little bit more about that integration effort in a minute, but the next steps will be to finish those methods that are in the process in terms of integration as well as then put them into the Federal Register in the EMMC format so that they can be officially adopted.

A discovery in the methods integration process has been that it is a very difficult process to go back and have people integrate existing methods that are different. There were many turf battles. Bill bears the scars of many of those battles.

It is felt that, once we finish those methods that are in process in terms of integration, the effort that would be required to integrate further methods may not be worth the return that we would get on it.

The current thinking is that we need to evaluate the performance-based method approach. There are advantages to the performance-based method approach, one being that it would definitely minimize the regulatory modification work that would be involved as technology and methods improve over time.

Currently, with the specific methods being regulated and identified in the regulations, to go back and modify a method based on new and innovative technology that has come on line may take a year and a half to two years to go through the regulatory revision process to get that new technology on line.

With the performance-based approach, changes would be much more rapidly accommodated.

The challenge is to encourage the technology, innovation, and method development while preserving data integrity. The issues currently being discussed involve what constitutes adequate documentation if you choose to take the performance-based approach, what do you use as your criteria for selecting the reference methods that would be utilized in any performance-based method approach, and what reference materials are going to be available for you to be able to demonstrate the performance of any alternative technology that someone would want to use aside from the reference method?

The Office of Ground Water and Drinking Water came up with a pilot approach for performance-based method implementation, and that currently is under internal review within the Agency. They have developed a draft documentation package that will lay out what the requirements would be in a laboratory for documentation in a performance-based methods system.

That particular documentation scheme has been distributed to all the members of the steering committee on EMMC, and their comments are coming in now. As you will see in a minute on one of these overheads, the Deputy Administrator of EPA has charged EMMC with presenting an option paper on the use of a performance-based methods approach by the end of this calendar year.

There are two other new work groups in the EMMC methods integration panel, the field methods work group (proposed to deal with new methodology as it comes on line for use in the field, i.e. portable in-the-field analytical methods), and due to the fact that we are

evaluating the performance-based method approach, we have adopted the performance-based methods work group that was not a part of EMMC as a work group now under the methods integration panel in EMMC.

The quality assurance regulatory development panel is charged with, as I mentioned before, ensuring that there are appropriate methods for any regulated analytes.

EPA is currently in the process of revising its regulatory development process into a tiered approach to try and speed up the regulation implementation process. EMMC is trying to ensure that we get the same level or better control over assuring that there are methods available, if there are environmental measurements included in the regulation, and that the quality assurance concerns are addressed in the regulation when it comes out under this new three-tiered process.

Another effort of this panel is to conduct an assessment of the use of performance evaluation materials across the Agency, how they are utilized by the different programs within EPA, and to try and establish what would be a stable source of funding to ensure that there will be a continuing source of performance evaluation materials.

Particularly, if we are going to a performance-based approach or we are going to be using that to a greater or lesser extent, performance evaluation materials are even more critical to the Agency.

The lab accreditation panel may, from the raising of hands the other day as to the people that were represented here, have the most impact on many of you. The national lab accreditation evaluation effort that is being put forth by EMMC resulted from the CNAEL report.

That report was submitted to the government and currently, there are State EPA focus groups that were formed that evaluated and analyzed the issues raised in the report, and have now prepared papers on each of the issues that were raised in terms of implementing a national lab accreditation program. They have also developed options under each of the issues in terms of the questions that would be needed to be answered.

That is where it stands right now. The next step is a national conference held on the national lab accreditation program. The EPA Administration has endorsed going forward with that conference.

The funding is being made available to develop that national conference which, the latest information I have, is intended to be held sometime next spring, early in 1995.

As Bill has said, we have not necessarily moved forward with the speed of light. The EPA Deputy Administrator, Bob Sussman, was briefed on EMMC to ensure recognition and,

I guess, the blessing of the current administration to go forward in the directions we were going.

That occurred in March of this year, and he essentially has approved EMMC progress made to date and endorsed the EMMC, the focal point for internal EPA and external contacts with EPA on monitoring management issues; has endorsed the EMMC methods format and the EMMC framework for methods development; and has indicated that he wishes us to continue on the national lab accreditation development process.

He directed EMMC to brief the Science Policy Council (which actually took place in April) on the lab accreditation activities that had come forth to date. At that point, it was decided that the conference will go forward and also that there will be funding to accomplish that.

The performance-based method approach evaluation has been scheduled to be completed by the end of this calendar year.

The EMMC has been identified as EPA's internal and external focal point on monitoring management issues, and one of the major activities we are involved with now is serving as the EPA contact point for the Intergovernmental Task Force on Monitoring Water Quality which Elizabeth Jester Fellows is going to talk about in the next talk.

We will be the focal point for interacting with ITFM on the issues of comparable methodology, lab accreditation, methods compendium issues; issues that the ITFM is addressing on an inter-agency level that EMMC is addressing within EPA itself.

I guess the question we have to ask ourselves is "Why EMMC?" Really, it is an effort to go across programs in trying to develop better scientific credibility and data comparability within the Agency, and that will also interact with the ITFM across agencies.

Essentially, with the watershed approach of EPA and the other geographically based initiatives that are taking place, data sharing is becoming more and more critical. So, when you make cross-media decisions, we need to have the integration capability across the Agency itself.

It is simplifying lab procedures. The integrated methods have reduced large numbers of methods into more consistent methods and in a format that everyone will be able to, I think, understand. Since all methods will be in the same format, it will allow you to make comparisons much more easily.

There will be cost reductions in methods development, because, hopefully, EMMC will result in more sharing of the efforts in developing methods and making the methods more comprehensive, beyond specific program needs.

It will avoid the duplication of field, lab, and QC efforts.

The national lab accreditation program, has a major focus to deal with the issue of the current lack of reciprocity and the amount of time that labs spend doing multiple proficiency analyses, going through multiple lab audits if they do business outside of one State, also EMMC is dealing with different criteria for accreditation across the nation.

Hopefully, there will be consistency, and there will be a savings not only to agencies but, as well, to the regulated community and the lab community.

That is all I have. Do you have questions?

QUESTION AND ANSWER SESSION

MR. TELLIARD: This gentleman?

MR. BOWDEN: My name is Brian Bowden. I am with Hach Company. I have two questions for you, Bob. The first is with regard to the EMMC format. As you might know, Hach Company is a vendor which supplies water quality testing analysis systems.

My question is, when we take our methods and transcribe our format and procedures into the EMMC method format...the procedures that we offer now, we feel and our users feel, are very simple, very easy to use, very easy to understand. When we transform them into the EMMC format, we get procedures that go from being two pages long to procedures that are 20 pages long, and we get feedback saying that they are not as useful.

So, my question for you is, is this EMMC format expected to be standardized and used by method suppliers?

MR. TELLIARD: You want me to take a shot at that?

MR. RUNYON: Yes, if you will.

MR. TELLIARD: As a non-supporter of the EMMC format, I would say right now that it is the one on the table, and it is the one we are using. We agreed to use this format, and we are converting all the 500, 600, and 1600 series methods into that format.

We have not put that format out for comment, and I would like to do that, and that is something that we probably ought to address if we are asking you, as a vendor, to use the format. We have not done that, but, then again, we have not asked you to do that.

So, right now, the answer is you can do what you want, and the second part is if we are going to ask you to do that, then it is only fair to put that format out for comment, and I think that there are better ways to write a lab format.

What you do with the EMMC format is you write an SOP, so you can take the 20 pages and reduce it down to what you have where you add the blue stuff and it turns green, count three minutes. Okay? We do not do that. We have a document.

MR. BOWDEN: Right now, the feedback we are getting from EPA-EMSL is that they are asking us to put our methods in the EMMC format procedure prior to submission for acceptance or approval review.

MR. TELLIARD: For ADP? Yes, right. If that is what they want, that is what you will have to do.

MR. BOWDEN: Okay. My second question is with regard to colorimetric chemistries and methodologies. I noticed on your method integration listing, you did not include colorimetry. I am wondering where colorimetry stands in the EMMC committee's mind.

MR. TELLIARD: I think the colorimetry tests are the same ones...you know, they are basically the oldest ones we have. They are impacted pretty much by matrix.

The ones we picked for integration, the volatile method, semi-volatiles, the metals methods, were ones that basically all the program offices were using anyhow, and if you can get them all in a room and lock the door, you could come out with a kind of consensus method that says yes, you will use these surrogates and, yes, we will use these internal standards, and we will run at such an such a rate.

That was easy, but when you get into a situation where you are doing solids versus water versus air where the matrix is a big player, we do not feel that it is economically practical to tackle colorimetry for those areas.

It is not to say we do not like it. It certainly has its place and its use, but as far as an effort to combine those methods, it is not afoot.

MR. BOWDEN: Thank you.

MR. GRIFFITHS: David Griffiths, Olver, Incorporated. I, too, have two quick questions, I think. I have a vested interest in a commercial laboratory, and as such, I strongly endorse the initiative towards consolidation of the various methods that we are obligated to use today. When can we see the first integrated methods published in the Federal Register? That is really my first question.

MR. TELLIARD: The metals method is probably ready to go out for comment. Bill, do you know? I think it is pretty close, isn't it?

MR. POTTER: We expect to publish... this summer. It is real close.

MR. TELLIARD: Yes, it has been badgered, beaten up, and flogged. It is ready to go, so it will probably be mid-summer.

1613, the dioxin integrated method, is due this summer, probably late summer. 524.2 which is the volatile method which is an abstract of the water method is due this summer. We have just generated the method specs, and we are looking at the tiered approach, drinking water, wastewater, solids. So, there will be different levels and the QC will be a little bit different, but that is ready for this summer, too.

That is the best I can do and I do not know where the digestion is. That is the one I have not kept track of, because it is... the microwave digestion. The last I saw, it was almost completed, and that was February. So, it would be amazing, but we could shoot to put all these methods in one notice, but we don't want you to stop reading the Federal Register, but I am not about to promise that.

MR. GRIFFITHS: I think I speak for many of us in saying we are looking forward to it.

MR. TELLIARD: Okay, thank you.

MR. GRIFFITHS: Secondly, there are some other issues worthy of consolidation, and I think we have heard two of them today or yesterday and today. One is clean metals, and the other is methods for dealing with uncertainly analytical data, namely, data at or near the method detection limit or below.

These cross over several programs, most notably, drinking water for clean metals and groundwater monitoring under the various solid waste programs. Is this a subject, consolidation of methods for clean analytical protocols and methods for statistically analyzing data that may be uncertain? Has this been brought up for discussion or consideration?

MR. TELLIARD: The metals issue certainly will. The ambient and drinking water methods certainly are applicable to be combined, and we will do that. Ivan Deloach from Drinking Water is floating around here someplace. He and I talked and we will make it fit. Both of us will use those methods.

The data integration issue is something that we are working with, at least in the Office of Water, with Drinking Water and Permits and Enforcement to come up with a strategy. We have a document floating around which we affectionately refer to as the pumpkin book which lays out data review, data requirements, data information, how you review data.

That is going to be updated this year, and it will hopefully have in it MDLs and MDL procedures.

So, hopefully, it is going to be a busy summer and fall, because a lot of these things, hopefully, will be coming to fruition. It is not a question now of resources; it is a question of time.

MR. GRIFFITHS: Is solid waste represented within the EMMC?

MR. TELLIARD: Yes, it is.

MR. RUNYON: Yes.

MR. GRIFFITHS: Thank you.

MR. THOMA: Jerry Thoma, Environmental Health Laboratories. A multi-part question. Number one, Bob, are you willing to speculate just a bit on what the content of the option report to the deputy administrator might be? Maybe more easily said, do you expect a pro position from the Agency on performance-based methods?

Secondly, how do you expect to integrate the criteria in the performance-based method guidelines into the existing methods?

Thirdly, is there a time frame when you expect, assuming that the Agency has a positive outlook, is there a time frame on when these criteria actually might be integrated into the Agency framework?

Then, I guess fourthly, in the performance-based method structure, are holding times and sample preservation issues considered sacred?

MR. TELLIARD: The last part is yes, unless we have data. Okay?

Performance-based methods are probably a positive position in the Office of Water, they have always written performance-based methods. All the 1600 series are performance-based.

The other thing is the application of 8.2.1 in the 600 series methods which says, you can change the column as long as you meet the method specs. In the new EMMC format, it is 9.1.2, if you are up on your sections.

Anyhow, if we really define this, and that is what this pumpkin book does, what you need to do under 8.2.1 or 9.1.2, it takes away probably 90 percent of the changes you want to make in the method anyhow. Now, it is not... that is to say, if you want to change the extraction procedure, if you want to change the temperature ramp, if you want to change the column, if you want to change the detector, pretty much...no, that won't go for a detector, but these changes are all covered, and it tells you what you need to do to document a change which is equivalent or better. We are not against better, either.

So, that is out there now, and we are pushing it.

Now, there are a lot of folks who are not real happy with performance-based methods. Don't let me misrepresent that. People who have to enforce this stuff do not like to have to spend many hours trying to figure out whether you cheated or you were honest.

Those people have the nasty part of working in the real world and dealing with real issues. We can sit here and proselytize all we want, because we do not have to do any of that hard stuff.

I think, the Agency's position is that probably performance-based methods are good and it makes our lives easier. To the working world, they may not be believers yet.

So, when we hear back from the States, municipalities, and people who have to actually work in the trenches, we may want to change our mind a little bit. I am not sure yet, but what I have heard in this meeting and other meetings is when you say performance-based methods and are waiting for the roar of thundering clapping, it is pretty quiet.

So, there are differing views. I think we are for it, but I am not sure that the working world is, and I am sure there will be some compromise.

MR. RUNYON: And it is consistent with the innovative technology initiative, trying to get technology up to speed and not two years down the road trying to change a specific method.

MS. ASHCRAFT: I am Merrill Ashcraft with the Navy Public Works Center in Norfolk. I would like to ask you to give us a little glimpse of what they are looking at in the national accreditation program, because that is a concern to us, many of us here. If you are going to hold a conference in the spring, will the attendees that were at this conference be invited? How are you going to get your mailing list?

MR. TELLIARD: The last I heard was that the attendees were primarily going to be the States and certain organizations. It was not going to be a, quote, public meeting. It was going to be an organizational meeting where the States and the regulated community, i.e., laboratories, would have representatives. That is the last I heard, and that is a year old.

MR. RUNYON: Right, and it is still in the formative process, but I am sure that everyone that is in the community, the laboratory community, will be aware that this is taking place. There will be adequate notice that this is going to be occurring.

MS. ASHCRAFT: And the glimpse of what you are seeing as part of that policy, what do you think it is going to involve?

MR. RUNYON: Well, the State EPA focus groups are picking up right where the CNAEL report left off. They have put together a proposal that was developed as to how they thought the CNAEL Report might be implemented and what the issues were, et cetera.

The EPA and State focus groups have now taken that and spent several meetings hammering out what the actual issues are that need to be developed, like proficiency materials and how will it be administered?

No final decisions have been made at this point, because EPA wanted to make sure all the players would have an opportunity to input into any decision. So, there have been a series of options that have been presented on how to administer it, what the scope would be, what reciprocity issues would be dealt with, and no decisions have been made in those areas.

The focus groups give options that range from one end of the spectrum to the other. So, it is really impossible for me to tell you what the final resolution will be.

I presented some of the issues that prompted this whole initiative to take place which are the lack of reciprocity, the inability to have consistent criteria across the country, et cetera. The national program is going to try to address some of those issues and minimize the impact on the lab community and the costs that are associated with it from a time and dollars aspect in trying to meet multiple requirements across the board.

So, there are issues with implementation that are going to be presented and grappled with. Just as with the performance-based methods issue, there are people on differing sides of how this should be handled, whether you use a third party accrediting body, whether the States are required to be the accreditors, and how will this be handled? Can they add extra criteria to a national lab accreditation program for their respective State accreditation?

Those are issues that are going to be addressed in the conference. They have not been resolved at this point in time.

Any other questions?

MR. TELLIARD: Thank you Bob.

The Environmental Monitoring Management Council (EMMC)

The EMMC was established in March of 1990 to:

- Coordinate Agency-wide policies concerning environmental monitoring issues especially in the areas of analytical methods integration, laboratory accreditation, and QA

- Address Congressional concern over our ability to make national environmental assessments, and

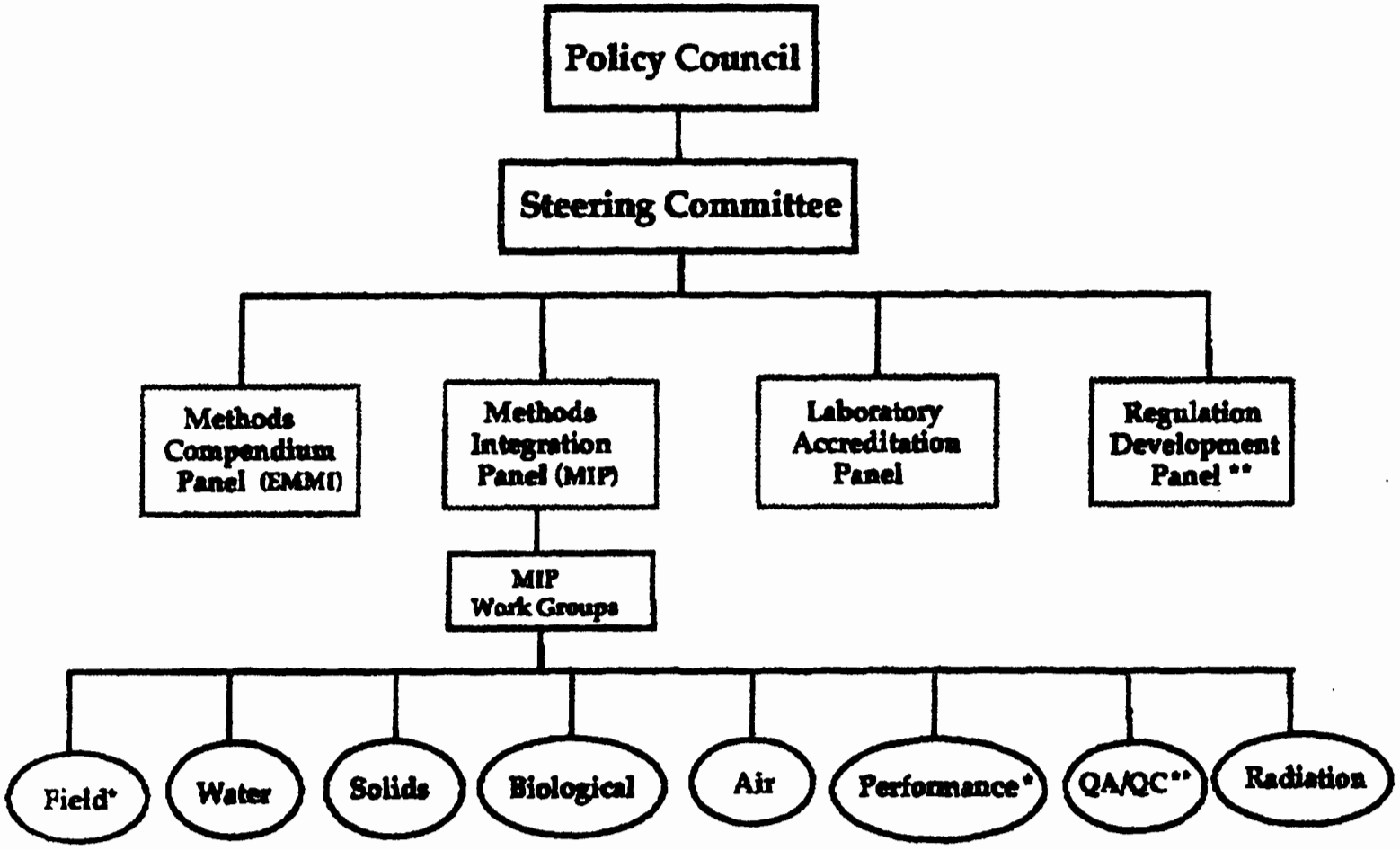
- Respond to needs of Administrator/Deputy Administrator to make decisions based on credible scientific data.

EMMC Organization:

- EMMC Policy Council is made up of AA/RA level and is chaired by ORD AA, and the Region III RA

- Steering Committee is comprised of Office Directors and Division Directors, with scientific and engineering program and regional staff providing direction to the panels and work groups

The Environmental Monitoring Management Council (EMMC)



*Proposed

** Activities may be combined to form a new QA Panel

4/28/94

EMMC PROCESS FOR ADDRESSING ISSUES - Focus on cross program issues to ensure real improvements:

- EMMC Infrastructure established

  - EMMC Format - For All New Agency Methods/builds consistency/comparability in documentation/facilitates assessment of methods

  - *Framework for Development of New Methods* - Uses *EMMC Format* for consistency; based on existing methods; promotes joint methods development/funding; facilitates geographic, multi-media assessment processes.

  - Environmental Monitoring Methods Index (EMMI) - Agency compendium/facilitates methods selection for specific purposes/about 800 Agency users/public purchase available through NTIS.

INTEGRATION OF MONITORING METHODS

The EMMC serves as a forum to determine which methods need integration; provides for consensus of all offices, serves as a cross-program vehicle for assuring documentation of methodology and data, and comparability of data.

- Integration of four monitoring methods completed:
  - Graphite furnace atomic absorption; Inductively coupled plasma atomic emissions spectrometry; Hot acid extraction for elemental analyses (as part of above); Determination of purgeable organic compounds by capillary column gas chromatography.
  - These four may account for half of all lab monitoring procedures
  - Others still in-process [Semi-volatiles; Dioxins; Halogenated pesticides; Microwave digestion]
  - Next step/publish integrated methods in the Federal Register.

■ PILOT OF PERFORMANCE-BASED (PMB) Approach to Methods

- EMMC to bring recommendations for an Agency-wide approach to the Science Policy Council by end of year

- The PBM approach minimizes regulatory modification workload as technologies change;

- Encourages technology development and innovation;

- Preserves data integrity through proper criteria and evaluation [Drinking Water Initiative]

QUALITY ASSURANCE/ REGULATORY DEVELOPMENT

- Currently working on assessment/design to ensure environmental measurement/quality assurance issues are built into the new three tier approach to regulatory process.

- Performance Evaluation samples/critical to enforcement of statutory requirements/ currently on ad hoc funding basis/should be part of cross-program budget process.

DEVELOPING THE NATIONAL LABORATORY ACCREDITATION PROGRAM PROPOSAL

- Voluntary national program to encourage reciprocity
- Simplifies standards for federal, state, and local laboratories
- Regulated laboratories receive better coverage for same costs
- Needs Agency resources to support National Environmental Laboratory Accreditation Conference (Issue to be presented to the Science Policy Council on April 15, 1994)

Deputy Administrator reviewed EMMC activities on March 4, 1994:

- Approved progress to date;
- Made the following decisions:
  - EMMC to be focal point for internal/ external policy on monitoring information activities;
  - Endorsed EMMC Methods Format and Framework for Methods Development;
  - Encouraged EMMC to continue developing a national program for laboratory accreditation;

DECISIONS (CONT)

- **EMMC to brief the Science Policy Council (SPC) on its activities including :**
  - **the laboratory accreditation activities and associated near term resource needs;**
  - **options and recommendations for an EPA-wide approach for applying performance-based methods to monitoring activities;**
- **Requested Assistant Administrators and Regional Administrators to continue support of EMMC activities.**

EMMC as Internal and External Focal Point for Policy on Monitoring Information Activities

Major External Activity: Intergovernmental Task Force on Monitoring Water Quality (ITFM) requested formal link with EMMC. [ITFM consists of all federal/state governments that monitor water quality]

- EMMC/ITFM will address issues of comparable and performance-based methods, laboratory accreditation, and government-wide compendiums of methods, and

- The EMMC to review specific products and provide formal EPA responses in the areas that are most important to achieving comparability nationwide.

WHY ARE EMMC ACTIVITIES IMPORTANT

- Better Science/Credibility
- Data Comparability for Sharing Information
- Required by Cross-media Decision Making (Cross Programs and Cross Agencies)
- Simplified Lab Procedures
- Cost Reductions from:
  - Eliminating duplication of methods development efforts
  - Avoiding duplication of field, laboratory and QC efforts
  - Fewer lab evaluation programs

MR. TELLIARD: Following along on this, our next speaker is Elizabeth Fellows. She is going to be talking about a nationwide strategy for improved water quality.

Elizabeth is Chief of the Monitoring Branch in the Assessment and Watershed Protection Division. Also, she is the Co-chair of the Intergovernmental Task Force on Monitoring Water Quality.

This kind of ties in, we thought, with what Bob has just said, and Elizabeth is going to give you an overview of what is going on in ITFM.

A NATIONWIDE STRATEGY TO IMPROVE WATER-QUALITY IN THE UNITED STATES

MS. FELLOWS: Can you hear me? Yes, I guess so.

As Bill Telliard said, I am the Chief of the Monitoring Branch for EPA's Office of Water. That is ambient water. As such, I have responsibility both for the computer systems that hold ambient water data and, on the other side, for the monitoring protocols, procedures, reports, et cetera that we do in EPA.

I have had the position about three years now, and in sitting down to do a game plan for what we wanted to do in the new Office of Water reorganization, we quickly realized EPA itself collects very little data. Our regional folks do a great job for certain kinds of data, but we rely enormously on the States and on other Federal agencies to give us data to answer questions that we are constantly asking. Such as:

"How clean is the water?" "How and why is water quality changing over time?" "Are our programs effective in improving or preserving water quality?"

So, the first thing we needed to do is go talk to our partners in the States and other Federal agencies to see if we can do a better job of combining our data to answer clearly identified questions. We went to USGS first, and they said yes, we confront that problem, too.

We then jointly went to other Federal agencies and to States, and all of them said yes, monitoring in this country is not working as well as it could. There are a number of reasons for that. Let's sit down and try to solve them.

So, what we did was, of course, form a task force. It is the Intergovernmental Task Force on Monitoring Water Quality and it is a three-year task force designed to recommend

solutions to solve the monitoring problem by specific deadlines and then sunset in favor of whatever was needed to implement the proposed solutions. We wanted to get in, we wanted to try and come up with solutions to solve the problem, and then sunset into whatever would need to be done to implement the solutions.

The major problem we all face is that we cannot answer well the most basic question about water quality, how clean is our water and how is it changing over time?

That is a simple question that Congress and everybody else asks us all the time. Obviously, it does not have a simple answer. What do you mean by clean? What kind of time period are you talking about?

But however you define the question, the key is better water quality monitoring, assessment, and reporting, and we do not have a system that is good enough at this point to answer nationwide questions at a specific site or in particular States. Specific questions can be answered , but on a national level, we cannot do it well enough.

One of the reasons we cannot at this point is that our water programs are changing. The Clean Water Act passed over 20 years ago. We have learned a lot more about our water resource, and many other things have considerably changed including a large population increase along the way.

EPA itself has changed. We are, of course, still a regulatory agency, but that is no longer our primary mission. We are really moving into more holistic geographic programs using risk reduction principles. New emphases, as Bob was talking about, include a watershed and ecosystem focus emphasizing biological, ecological, and habitat as opposed to a specific chemical focus.

Nonpoint sources, as we have solved our point source problems over the years, we have uncovered the major nonpoint source problems we have. Wetlands are disappearing at an alarming rate. Sediment, both clean and contaminated, is a problem. It is monitoring that shows us where and how grave our problems are.

Thousands of groups monitor, spending millions, even billions, of dollars annually in their monitoring for a variety of purposes, and the roles of partners contributing to a nationwide strategic look at monitoring have never been clearly defined.

Also different agencies use different methods to monitor the same parameter. Obviously, this is how this connects with this audience most directly. In spending three years thinking on a nationwide level about our monitoring programs and of all the problems we have to deal with, if I had to choose one, it would be the methods problem... inconsistent methods for the same parameters when collected for the same purpose.

There are obviously reasons to have different methods where monitoring purpose differ, but there are many cases where different methods are not necessary. You can have the best linked computer systems that you possibly can. You can talk all you want over a table. But if you have collected your data with inconsistent, incomparable methods and you have not documented how you have done it, you have lost already. You cannot combine your data.

So, I think what you are doing in dealing with methods is probably the most important thing in this whole complex monitoring picture.

As well as problems in the monitoring area, there are, of course, opportunities. First of all, the spotlight is shining on monitoring right now. It is shining on monitoring for a number of reasons.

The whole ecosystem/watershed approach, as Bob Runyon says, is targeting the need for integrated data and the need for a variety of data, not just, say, chemical water column data. And everyone is recognizing that. Congress is, OMB is, States are, Federal agencies, all the volunteer groups that are springing up to do their own kinds of monitoring.

We have many new scientific and computer techniques, including, obviously, GIS, ...geographic information systems... which allow you to easily portray your data in an integrated way and immediately points up if you are trying to portray apples and oranges together. This again, points out the need for comparability in methods and in data here.

EPA and USGS are modernizing our computer systems which are 20-plus years old. It would be stupid not to modernize them so they can talk to each other better, and we are using joint design features to ensure easy data sharing.

There is a lot of increased ancillary data that is being collected, that we can obtain once and share, rather than separately reinventing the wheel.

So, all of this led to the ITFM. The first meeting was in January of '92. The final recommendations are due in January of '95. We are working on those now.

It is a Federal-State partnership. Of the specific membership of 20 members, the Feds are the usual suspects, EPA, USGS, NOAA, USDA, Fish and Wildlife, et cetera. Of States and Tribes, we have ten of them. They are geographically dispersed and have expertise in various water resource areas across the country.

Over 140 Federal and State staff sit on various working groups working on the various problems, and we have an advisory committee which includes municipalities, industry, academia, and volunteer groups. We are trying to pull all the players together here.

I am the Chair of that group, and USGS is the Vice Chair and the Executive Secretariat.

We are not just talking, as I said, about traditional water column kinds of things. We are talking about a resource that includes surface and ground waters, coastal waters, associated aquatic communities, habitat, wetlands, and sediment. So, we have got the whole range here.

We are talking about protecting uses which gets back to State water quality standards of human health, ecological health, and then the uses that are designated through the State standards. We are talking about physical, chemical, and biological parameters here.

When we say monitoring, we do not, again, just mean traditional monitoring, either. We mean the whole range of activities that go from what is the program objective all the way up to giving the data to whomever needs it, which includes indicators, field data collection and methods, lab, QA, data storage, data analysis and reporting.

When we sat down all together to figure out how we are supposed to think about the problem clearly and organize even a way to get our minds around an immensely complex problem with lots of players, we formed ourselves into eight task groups that are looking at the specific problems. One is institutional framework, obviously, who is doing what where and how can we do it better.

One is environmental indicators. If we can choose core indicators that will answer identified questions, and measure identified goals, then we can talk about commonality among methods and data and everything else for these indicators.

Methods, obviously, I will go into some more. Data management... how do we link our systems, store data with descriptors so we know the QA/QC used, and have data transfer standards so we can transfer the data better. Assessment and reporting... how can we tell identified audiences what they need to know about water quality.

Another working group concentrates on groundwater. Obviously, we are all aware of the difference between ground- and surface water, but much of our attention is devoted to the Clean Water Act kinds of programs, and we needed to have a separate group that was a groundwater expert to put the groundwater needs into the picture. So, we have a separate group looking at groundwater that will make sure that anything we come up with applies or is varied according to the needs of groundwater.

We are probably going to need to do that for coastal/marine waters and for wetlands as well.

Cost is obvious. How much money can we save by doing things better, and then do we need new money in addition to that.

Also, a pilot project, to do a nationwide aquatic biological integrity assessment of the flowing surface waters of the country. Can we actually take the recommendations the ITFM is making and see if they work on a particular project.

The overall recommendation we came up with was to develop an integrated nationwide voluntary strategy. As you may imagine, each of those words is freighted with significance here.

A strategy means an organized process using a range of monitoring approaches. We are way past needing only a fixed monitoring network across the country where you monitor all the same things with all the same methods. We need to include fixed stations, we need to include synoptic surveys, we need to include short-term studies, and a strategy has to incorporate all of those.

It needs to be nationwide, covering all the water resources I just mentioned.

It needs to be integrated with a unified process using common design guidelines, comparable methods, shared data, common reporting and training formats.

To top it all off, it needs to be voluntary. This is the only thing that has generated a lot of comment here, because with an issue of such complexity and so many people playing, people ask, quite legitimately, how can a voluntary system work.

Well, it can work because there are incentives and because there are benefits. I think this relates somewhat back to one of the questions that Bob Runyon discussed. Yes, a method, a format and a performance-based method is going to take more documentation and produce maybe a little more paper, but part of that additional work may be critical if a secondary user is going to use the data or the method that was thought up by somebody else.

So, we have got a tradeoff here, and that line of tradeoff is exceedingly difficult to arrive at, and it is at a different place for different kinds of problems. So, that is one of the things that we are in the middle of debating right now. Where is that line where voluntary works because it is beneficial to those who play?

The ITFM also recommends that there should be a permanent monitoring council, wherein all the public and private players sitting together to come up with guidelines, plans, and implementation approaches on all the things that I talked about before.

In particular, training is one of those, and methods training is, I think, a big part of that. Rather than trying to legislate or put out guidelines, if you train collaboratively among agencies and entities, you are way ahead of the game there.

ITFM spent their first year coming to consensus about what the problems, opportunities, and preferred strategy were. Actually, I was fairly amazed. The ITFM took very little time to become a cohesive working body and arrive at consensus on what the problem was and the ways we might approach it. There was very little turf protection and posturing which, I think, was indicative of the critical need we share to design a better way to get better water quality information.

The second year of the ITFM, we honed in and said okay, if we are really going to advance our recommendation, we need to produce building block products that would give us the foundations to implement our national strategy.

Those products are: a framework for monitoring programs... the steps that we recommend that any monitoring program should go through if it is really going to achieve its objective.

A charter for a permanent monitoring council to replace the ITFM, many parties have recognized the need for a permanent collaboration mechanism. It is in the Senate bill for the Clean Water Act that ITFM would just become a permanent body legislated under law.

We have done a matrix of monitoring activities of all the Federal agencies. We are beginning to do one for the States, and then there is the whole private sector as well.

We have got a selection criteria sheet for environmental indicators and also a matrix of environmental indicators that would best measure surface and groundwater so we have information on core parameters to measure our water quality.

Methods is what you are most interested in. Again, it was felt that there needed to be a very specific part of a national monitoring council which would be a national methods and standards comparability council. If you will, it is an interagency counterpart to EPA's Environmental Monitoring Management Council (EMMC).

I have to say... Bill Telliard is frank, and I will be frank, too... that it is kind of ironic being the EPA Chair of this national body when EPA, I think, is one of the biggest problems in terms of methods comparability and consistency. Right? I see some knowing smiles here.

Other agencies and, obviously, the private sector are very concerned about this. That is why we are so delighted to have an EMMC and, in particular, the strong backing of the new administration for EMMC, so we have a real EPA attempt to speak with a unified voice.

Obviously, if even on agency has a comparable methods problem internally, you can imagine the kinds of problems we have in trying to get methods comparability throughout the government. However, we <u>are</u> trying, and we do have some hopes here of success.

One of the things is a policy on performance-based monitoring methods.

The ITFM Methods Task Group began developing a performance-based methods policy with EMMC input, and the States and the other Federal agencies who sit on the ITFM methods group came to pretty much the same conclusion that EMMC did, and ITFM and EMMC will be working on this issue very closely together.

There was some previous discussion in this session about whether States really buy into performance-based methods. There are five States that sit on the ITFM methods group, and, it is Co-chaired by South Carolina... and those States really have bought into it, as have representatives of five or six Federal agencies as well.

Just to talk a little bit more about the task before the methods and standards comparability council, the first one is really to set the agenda, to agree upon those classes of methods which are priority to get methods comparability, another to sit down and try and figure out how to come to some commonality, again, much as EMMC did.

The task group is trying to produce guidelines for how you compare methods, develop a performance-based analytical system, establish some reference methods so the system can work, come up with a minimum data set of data qualifiers that would allow you to do intercomparison exercises, and support a lab accreditation program. The ITFM is not doing much on lab accreditation, but we are looking to the EMMC to have the lead on that.

The Task Group is also producing a glossary, and investigating the need for pre-laboratory certification. Certainly, as detection limits get more and more refined here, good laboratory procedures are becoming increasingly more important in this whole picture of data and data quality.

Biological methods... in thinking about what methods are a priority for us, what monitoring entity arena to work on together, biological methods come out as very important, number one, because we are going into a watershed-based ecological approach to environmental protection and need biological information in many cases, and number two, biological methods do not have so much historical baggage as the chemical methods do... indeed we are still developing procedures, and we figure if we can nip some of the confusion at the beginning, we will be far ahead.

Therefore, we held a workshop last June that had 12 Federal agencies as well as States and some other parties in it that looked at algal, benthic fish and habitat methods so far and tried to compare the differences, and we are looking at the report comparing the differences and figuring out where we can go from there in terms of negotiating how we might come closer before we get set in concrete on those methods.

Nutrients. There was a question about sample preservation time here. That is one of the specific areas that we have started working on already. USGS uses nutrient

preservation methods for ambient monitoring samples (not for regulatory monitoring) where evidence suggests that you can just use a cooling method rather than using some of the chemical preservatives.

EPA's Cincinnati lab has now looked at that, analyzed the information, and said well we may be able to agree on a common sample preservation method.

ITFM did not want to just theorize about how to solve our monitoring problems. So, we began a pilot project. We have four, actually, but the Wisconsin pilot project in particular is trying out a number of the recommendations, including, most importantly, a lot of methods comparison where EPA and USGS and the States and some other Federal agencies, where it is appropriate for the method, are going out into the field and sampling using their own methods to try and compare and see differences and opportunities for comparability.

This is the ITFM's third year. In the first year, we built consensus, launched our working groups, and made general recommendations. The second year we provided building blocks. The third year, we are really getting into the implementation aspects.

What do we mean by a national strategy? How will EPA's EMAP monitoring program, USGS' NAWGA program, USGS' fixed station design for NASQAN which they are redesigning, all the States with their comparability problems, all of the information from the private organizations, from the volunteer groups, how will it really fit together?

And finally, how do compliance monitoring and ambient monitoring fit together? Obviously, compliance monitoring is where a majority of monitoring money is spent, and it is kind of a chicken and egg situation. Good ambient monitoring is needed to set good compliance limits, and good compliance monitoring can produce information to augment the ambient data.

Indeed, a lot of ambient monitoring goes on in the compliance arena by sewage treatment plants, and by some industries, whether such monitoring is required in their permit or not. As good citizens, a lot of them have included some ambient monitoring... monitoring beyond the mixing zone.

Nobody is asking them to share that data so there is a rich wealth of data that we would benefit by capturing and sharing.

We have taken the steps to do that. We have had a couple of preliminary meetings with AMSA, the American Association of Metropolitan Sewage Authorities, the Water Environment Federation, and AMWA, the drinking water suppliers as well as some industrial associations such as NCASI. All of them are very interested in sitting down and really talking through this issue and what we might do.

It obviously has methodological parts to it as well, because if you are collecting compliance data differently than ambient data on the same parameters, you cannot put it together even if you manage to get it in the first place.

So, we are just starting to deal with all those issues. It is very important for us, and that is going to be a real focus for us in the next couple of months so we can have at least a good start on what part compliance monitoring should play in this strategy.

We will be holding a national conference on monitoring in the next year, and there will be specific components sitting down and talking about our recommendations for each one of these areas to which, obviously, you all would be invited. And at any time, we would love to have comments on our activities and recommendations to date.

Funding is an enormously big issue. Suffice it to say we are working hard on it. As usual, most of us are scientists, we are not economists, so we have linked with a series of economists who can help us.

We are doing a survey to try and capture the amount of money that is being spent on monitoring now, because nobody knows, except to say it is very large. What the Feds, States, and municipalities spend tends to be buried in the budget and not as a specific line item.

For instance, at EPA I may run the ambient water monitoring program, but my peers in the nonpoint source program and the combined sewer overflow program and the wetlands program all have monitoring portions as well, so trying to figure out how much money is spent is very difficult.

I would like to just take two minutes more and kind of shift to my EPA hat for a minute to show you again how important the EPA part of the national strategy is and how methods play into that. For the following overheads, you are not going to be able to read every word, but I just want to show you the principle, not the details.

This is basically a pyramid which shows that we in EPA, in doing our strategic planning for monitoring, realize that we need to have clearly identified goals, choose the indicators by which we can measure them, and then choose the methods by which we are going to measure those indicators.

So, what we have done is said our prime goal is human and ecosystem health. If you break that down, what do you mean by human health? We mean safe drinking water, safe fish consumption, et cetera. On the other side, you have the healthy ecosystem goal.

In order to get to those goals, you need to improve ambient conditions. How well is the water doing for both toxics and conventionals, from both point and nonpoint sources?

In order to improve ambient conditions, you have to reduce pollutant loads. In order to reduce pollutant loads, you have got to link it all to what your specific control programs are doing.

Take one of the goals of conserving and enhancing ecosystems. For each one subgoal, we are going to choose an indicator, such as is fish assemblage or benthic macro invertebrates or habitat or plankton or floral or faunal composition. For each one of those indicators, we show what the EPA data source is and what the other agencies' or private sector data source is.

So, we at EPA have got a scheme that tells us what our goal is, what the indicator is to measure it, who has got the data, and the next question is, what method are they using to get that data for that specific indicator?

So, both from an ITFM interagency point of view and a specific EPA point of view, we end up with the importance of the method that is being used to get the data. Since the data to measure our goals are coming from so many different agencies, how can the methods be comparable enough, to allow us to put the data together to come up with a specific answer to the question we have asked.

That is the quick overview of ITFM and of EPA's goals and indicators and how it relates to methods. I want to close by reiterating what I started out with. If I had to choose one thing that was of utmost importance in this entire monitoring, vastly complicated picture, it would be methods and a way to determine comparability and the known quality of it so you can figure out if you can use someone else's data.

I put a brochure on the ITFM out on the table, and on it there is an address there that you can write to in order to get a copy of the ITFM report with details on ITFM recommendations.

Any questions?

QUESTION AND ANSWER SESSION

MR. TELLIARD: Yes, sir?

MR. WINTERS: I am Dave Winters from the Arizona State Laboratory. I have a question, since we have just heard two talks about combining and being consistent with methods and getting consistent data, what is the movement within your Agency to get, for the laboratories, for us to get some consistency when we call, say, different Regions?

MS. FELLOWS: Right. There is a big laboratory study just going on in EPA now where that is one of the questions being asked. The study is part of the EPA effort to make our products easier for people to use.

There are other answers, and Bill might want to give them.

MR. TELLIARD: If you want an SW846 answer, there is an SW846 hotline. If you want a water answer, I generally get it or Cincinnati gets it, and we do the best we can. I don't get any air questions. That goes to RTB.

So, we have got it all covered, kind of like with a shotgun. One of the issues is how do you disseminate this. We now have a resource center that will mail out methods and all that sort of thing. So, it is starting to come together. Hopefully, within my lifetime, we will see that.

MR. WINTERS: As far as moving ahead on the methods, especially in performance-based methods, if you are allowing laboratories to make changes but then require certain documentation, it has been my experience that I have gotten differing answers even within a Region on what is necessary as far as documentation and what is acceptable.

MR. TELLIARD: I agree with you. That is true, and you can begin with the pumpkin book which will give you a starting point for documentation.

If, for some reason, the Region needs additional information for some purposes, enforcement, crucifixion, whatever, they will call you and let you know, but we can give you the bottom line.

I am going to put my name up here and phone number and a fax number, and you can send it to me, and I will send you a copy.

MR. WINTERS: Okay, thanks.

MR. TELLIARD: You are welcome.

MS. ALLEN: I am Linda Allen from the Minnesota Department of Health. My question was, what do you do when your methods are missing an analyte such as your Method 200.9 and 200.7 for metals do not contain titanium? We do ambient monitoring occasionally for titanium. I do not have an EPA method for that in your new methodologies.

What I am concerned about is when you do these metals methods, are you going to incorporate all the analytes or only a select few of the analytes and then we have to

scramble around finding other methods to cover these analytes that are not covered in your methods?

MR. TELLIARD: Yes, you have to scramble around and...yes, in the methods that we are looking at right now, titanium, lithium, and some of these others are going to be addressed. They are not on the high point. We are looking at what Billy Potter talked about, mercury, arsenic, selenium, thallium, the popular voices.

The less or secondary groups...molybdenum is a big one in sludge. We are working on that now. Titanium and some of these others are not something that we are moving on right now. So, basically, what we can give you is our best guess.

In your case, if you are going to use it, I would recommend all you do is keep documentation of it. We may say you were wrong, but we can't say you were dumb. What was it the guy said earlier today? We didn't care if it was right as long as it was reproducible. Somebody said that, but I think document the heck out of it. Okay?

INTERGOVERNMENTAL TASK FORCE ON MONITORING WATER QUALITY

(ITFM)

We cannot answer well the most basic question about water quality -- how clean is our water and how is it changing over time. This simple question, often asked of us by Congress, does not have a single simple answer and the multiple answers must come from many agencies and groups and cover many different parameters.

Better water quality monitoring, assessment, and reporting are essential to understanding and managing our resources.

WATER PROGRAMS ARE CHANGING MONITORING NEEDS ARE CHANGING TOO

The country is moving beyond single media command-and-control programs into holistic programs based on risk reduction. New emphases include:

- **Watershed, ecoregion, and geographically-based programs**
- **Biological, ecological, and habitat focus**
- **Nonpoint source remediation programs**
- **Wetlands**
- **Sediment**

OPPORTUNITIES

- Recognition of the need for better water resource information on the part of Congress, OMB, Federal agencies, States and Tribes, citizen groups

- New scientific and computer technologies, including GIS

- USGS and EPA modernization of NWIS and STORET computer systems; NBS and EMAP beginning theirs

- Increased ancillary data

PROBLEMS

- Many players spend millions annually monitoring water quality for a variety of purposes. Roles, objectives, and responsibilities are not always clearly defined and, until the ITFM, no clear leadership or intergovernmental strategy linked these efforts.

- Different agencies use different methods to measure the same parameter, often do not store information about the data that would enable others to use it with confidence, and keep the data in systems that other find hard to access.

- The resulting data are often not comparable and fall short of supporting effective management of water resources on a nationwide basis.

AUTHORITY

- In April 1991, EPA and USGS began discussion of the need for better water resources data. Together, they approached other Federal agencies and States, and all agreed the time was ripe to act.

- In January 1992, OMB Memorandum 92-01 replaced Circular A-67, reiterating the USGS lead in water data coordination, and setting up the Water Information Coordination Program (WICP) under which the ITFM then began to operate.

ITFM

- First meeting January 1992; final recommendations January 1995.

- Federal/State partnership of 20 members.

  Federal: USGS, EPA, NOAA, USDA, FWS/NBS, Corps, DOE, OMB, TVA, NPS

  State/Tribe: Arizona, Florida, New Jersey, Ohio, Potawatomi Community, South Carolina, Washington, Wisconsin, Delaware River Basin Commission.

- Over 140 Federal and State staff

- Advisory Committee on Water Data for Public Use; includes municipalities, industry, academia, volunteer groups

SCOPE OF RESOURCE

The Resource:	**Surface and ground waters, including coastal waters, associated aquatic communities and habitat, wetlands, and sediment.**
Uses to Protect:	**Human health** **Ecological health** **Uses designated through State Water Quality Standards**
Parameters to Measure:	**Physical** **Chemical/Toxicological** **Biological/Habitat**

MONITORING SCOPE

Activities:

- Selection of program objectives
- Selection of indicators
- Field data collection
- Laboratory analysis
- QA/QC
- Data storage, management And sharing
- Data analysis
- Data reporting

EIGHT TASK GROUPS

- Framework
- Environmental Indicators
- Data Collection Methods
- Data Management and Sharing
- Assessment and Reporting
- Groundwater
- Cost
- Nationwide aquatic biological integrity assessment

FIVE PURPOSES FOR MONITORING

- Status and Trends
- Emerging Problems
- Program Design
- Program Evaluation
- Emergency Response

ITFM VISION

Water quality monitoring will be fully successful when all levels of government and the private sector meet today's and tomorrow's priority information requirements, make the best use of available resources and institutional capabilities nationwide, and provide useful information for the future.

ITFM WATER QUALITY MONITORING PRINCIPLES

OBJECTIVES:
Clearly stated

COORDINATION:
Should be maximized

TIMELINESS:
Timely information available for decision making

METHODS:
Documented, scientifically accepted, and comparable

INFORMATION SHARING:
Easy access, use, and sharing

ASSESSMENT/PRESENTATION:
Information analyzed and provided in easily understandable and useable form

OVERALL RECOMMENDATION

Develop an integrated, nationwide, voluntary strategy

STRATEGY: An organized process using a range of monitoring design approaches

NATIONWIDE: Covering the country, including surface, ground, and coastal waters

INTEGRATED: Developed through a unified process using common design guidelines, comparable field and analytic methods, shared data, and common interpretive, reporting, and training formats

VOLUNTARY: Strategy will be built voluntarily from existing stations with modifications where needed

NATIONAL COMMITTEE

Would provide guidelines and support

- QA/QC
- Monitoring approaches
- Site selection guidelines
- Environmental indicators
- Comparable field and laboratory methods
- Data management/information sharing
- Ancillary data
- Interpretation techniques
- Reporting Formats
- Training
- Evaluation

REGIONAL STRUCTURE

Would implement data collection

- QA/QC
- Monitoring approaches
- Site selection
- Environmental indicators
- Sample collection and field analysis
- Evaluation

PILOT PROJECT

Pilot project in Wisconsin is applying the ITFM recommendations to test and refine them.

BUILDING BLOCKS

ITFM is producing "building block" products useful to itself and others in developing and reviewing monitoring programs. These include:

Institutional

- Monitoring program framework
- Charter for permanent National Monitoring Council
- Matrix of monitoring activities of Federal agencies

Indicators

- Environmental indicator selection criteria
- Matrix of environmental indicators to measure designated uses for both surface and groundwater

BUILDING BLOCKS (CONTINUED)

Methods

- Charter for a Standards and Methods Comparability Council
- Policy on performance based monitoring methods

NEXT STEPS

- Detailed national strategy out for public review in summer 1995. Will include a national and regional component of a strategy that recommends for the nation's waters:

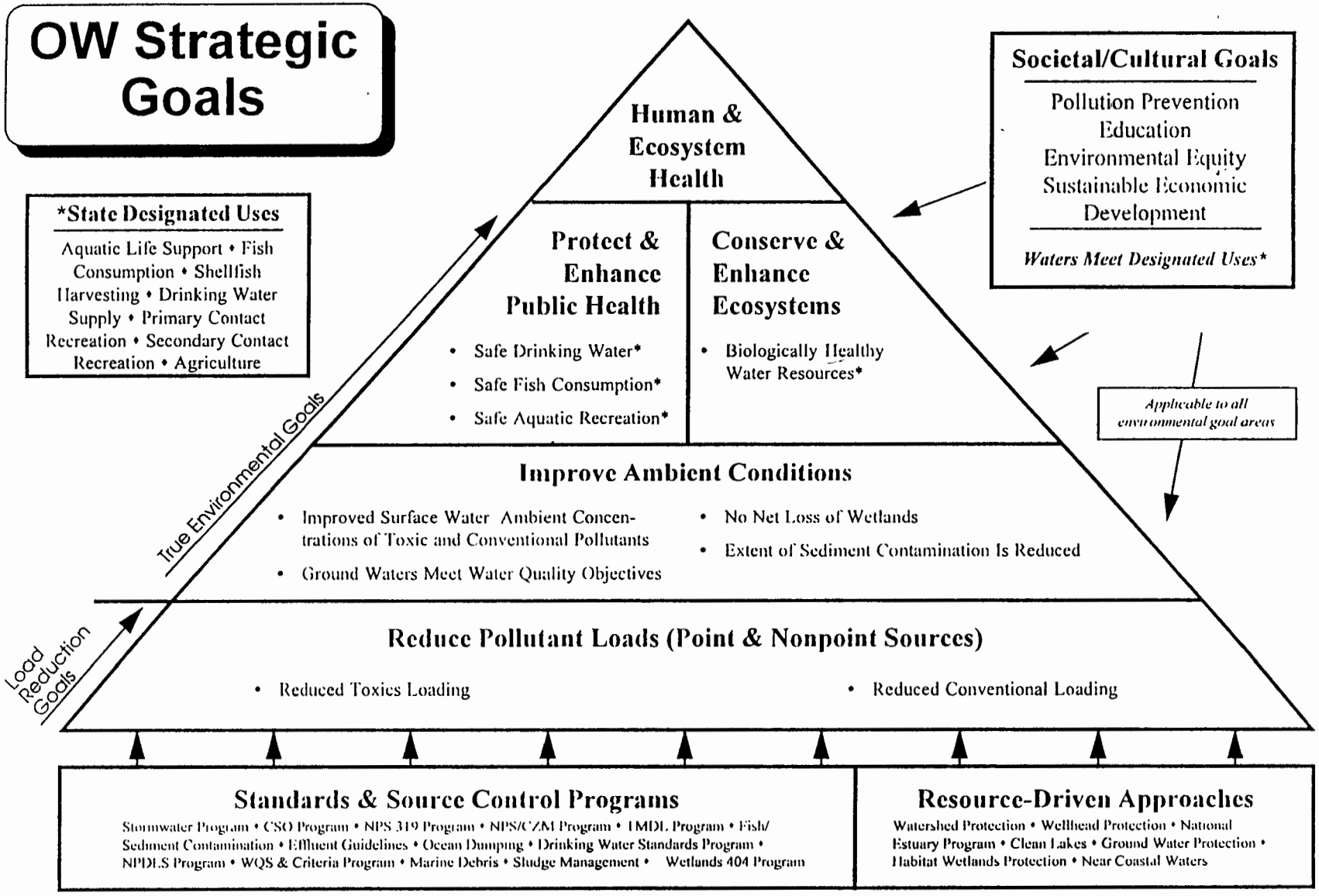
  - o collaboration of Federal and State monitoring agencies
  - o core indicators to answer national questions
  - o comparable methods
  - o ways to better share data, including common reference tables and linked systems
  - o integrated reporting of core data

FUNDING

ITFM recommendations will be initially refined and implemented within the base program funding of the agencies and groups involved.

Savings will be gained by better collaboration; new needs will be estimated.

OW Strategic Goals



CONSERVE AND ENHANCE ECOSYSTEMS

Biologically Healthy Water Resources Including Lakes, Rivers, Streams, Estuaries, Coastal Waters, Wetlands, and Ground Water

□□□■□□

Indicator
Waters Meet Aquatic Life Designated Uses (including ground water discharges to surface water)

EPA Data Sources
305 (b) ●
STORET/WBS ●

Other Sources
USGS: NAWQA ◗
USFWS ◗
State Water Programs ◗

□□□□□■

Indicator
Fish (assemblage) or IBI-like Index

EPA Data Sources
305 (b) 1
EMAP ◗
BIOS/STORET ◗

Other Sources
NOAA: ELMR ◗
NOAA: NS&T ◗
NOAA: FSP ◗
USFWS: NCBP ◗
USGS: NAWQA ◗
USFWS: BEST O
State Water Programs ◗

□□□□□■

Indicator
Benthic Macroinvertebrates (assemblage)

EPA Data Sources
EMAP ◗
BIOS/STORET ◗

Other Sources
NOAA: ELMR ◗
NOAA: NS&T ◗
MMS ◗
USGS: NAWQA ◗
State Water Programs ◗

□□□□□■

Indicator
Habitat (physical structure)

EPA Data Sources
EMAP ◗
BIOS/STORET ◗

Other Sources
USDA Forest Service ◗
USFWS: BEST m
USGS: NAWQA ◗
State Water Programs ◗

□□□□□■

Indicator
Plankton & Periphyton Assemblages

EPA Data Sources

Other Sources
Research Institutions ◗
State Water Programs ◗
USGS: NAWQA ◗

□□□□□■

Indicator
Floral Composition

EPA Data Sources
EMAP O

Other Sources
USFWS: BEST O
USGS: NAWQA ◗
States O

□□□□□■

Indicator
Faunal Composition

EPA Data Sources
EMAP O

Other Sources
USFWS: BEST O
States O

● data available now, needs improvement
◗ limited data available now
O no data available now

We can set baseline and begin to report in FY94 either nationally or for certain regions, specific geographic areas, or specific resource type.

□□□□□□ Hierarchy of indicators
1-2-3-4-5-6 ■ indicates level
1=Administrative; 6=True environmental

PROTECT AND ENHANCE PUBLIC HEALTH

Safe Drinking Water

Indicator Waters Meet Drinking Water Supply Designated Use
- *EPA Data Sources*: 305(b) ●; STORET/WBS ●
- *Other Sources*:

Indicator Population Served by PWSS with Wellhead Protection
- *EPA Data Sources*: Wellhead Protection Biennial Reports ◗
- *Other Sources*: State WHP programs ◗

Indicator Populations served by community water supply in violation.
- *EPA Data Sources*: FRDS ◗
- *Other Sources*:

Indicator Blood Lead Levels in Children
- *EPA Data Sources*:
- *Other Sources*: CDC ◗

Indicator Disease Outbreaks from Public Water Supplies
- *EPA Data Sources*:
- *Other Sources*: CDC ◗

Safe Aquatic Recreation

Indicator Waters Meet Swimming and Secondary Contact Designated Uses
- *EPA Data Sources*: 305(b) ●; STORET/WBS ●
- *Other Sources*: NOAA: NS&T ●; USFWS: NCBP ◗

Indicator Beach Closures: Miles Closed and Organism Levels
- *EPA Data Sources*: 305(b) ●; Regional
- *Other Sources*: State health depts. ◗; NRDC ◗

Indicator Disease Outbreaks from Swimming
- *EPA Data Sources*: Regional
- *Other Sources*: CDC ◗; State health depts. ◗

Safe Fish & Shellfish Consumption

Indicator Waters Meet Fish and Shellfish Consumption Designated Uses
- *EPA Data Sources*: 305(b) ●; STORET/WBS ●
- *Other Sources*:

Indicator Fish Advisories
- *EPA Data Sources*: 305(b) ●; STORET/WBS ●; EMAP ◗; OST: FAD ◗
- *Other Sources*: NOAA: NS&T ●; USFWS: NCBP ◗; USGS: NAWQA ◗

Indicator Waters with Fish Contaminant Levels of Concern to Human Health
- *EPA Data Sources*: 305(b) ●; STORET/WBS ●; ODES ●; EMAP ◗; OST: NFTD ○
- *Other Sources*: NOAA: NS&T ●; USGS: NAWQA ●; SFWS: NCBP ◗

Indicator Shellfish Bed Closures
- *EPA Data Sources*: 305(b) ●; STORET/WBS ●
- *Other Sources*: NOAA: NSR ●; NOAA: NS&T ●

Indicator Disease Outbreaks from Fish and Shellfish Consumption
- *EPA Data Sources*: ODES/STORET ◗
- *Other Sources*: CDC ●

● data available now, needs improvement
◗ limited data available now
○ no data available now

We can set baseline and begin to report in FY94 either nationally or for certain regions, specific geographic areas, or specific resource type.

Hierarchy of indicators
1-2-3-4-5-6 ■ indicates level
1=Administrative; 6=True environmental

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IMPROVE AMBIENT CONDITIONS

Ground Waters Meet Water Quality Objectives

□□□■□□

Indicator
Ground Waters Water Quality

EPA Data Sources
CWGWPP Biennial Report ●
OPTS: PGWDB ●
NPSurvey ◗
305 (b) ◗
STORET ◗
ERAMS ◗

Other Sources
WIDB ●
USGS ●
USGS: NAWQA ◗

Improved Surface Water Ambient Concentrations of Toxic & Conventional Pollutants

□□□■□□

Indicator
Selected Water Quality Parameters

EPA Data Sources
EMAP ◗
BIOS/STORET ◗

Other Sources
USGS NASQAN Stations ◗
USGS: NAWQA National Monitoring System Stations ○

□□□■□□

Indicator
Water Quality Standards Attainment

EPA Data Sources
305(b) ●
303(d) ◗
304(l) ◗
BIOS/STORET ◗

Other Sources
USGS: NAWQA ◗

Extent of Contaminated Sediments is Reduced

□□□■□□

Indicator
Extent of Contaminated Sediments

EPA Data Sources
305(b) ◗
Superfund ◗
BIOS/STORET ◗
CSSI ○

Other Sources
NOAA: NS&T ◗
USGS: NAWQA ◗

No Net Loss of Wetlands

□□□■□□

Indicator
Loss or Gain of Wetland Acreage

EPA Data Sources
Regional

Other Sources
USFWS: NWI ●
NOAA: NCWI ●
USGS: NAWQA ◗

● data available now, needs improvement
◗ limited data available now
○ no data available now

We can set baseline and begin to report in FY94 either nationally or for certain regions, specific geographic areas, or specific resource type.

□□□□□□ Hierarchy of indicators
1-2-3-4-5-6 ■ indicates level
1=Administrative; 6=True environmental

REDUCE POLLUTANT LOADINGS

Reduced Conventional Pollutant Loadings

Reduced Toxics Pollutant Loadings

□□■□□□

Indicator
Pollutant Loading to Ground Water from Underground Injection Wells

EPA Data Sources
TRI ●
STORET ◗

Other Sources

□□■□□□

Indicator
Point Source Toxics

EPA Data Sources
NPDES Permits ●
TRI ●
PCS ●
Needs Survey ●
STORET ◗

Other Sources

□□■□□□

Indicator
Selected Conventional Pollutants: TSS, BOD, Fecal Coliform & Nutrients

EPA Data Sources
Needs Survey ●
PCS ◗
EMAP ◗
STORET ◗
NPDES Permits ◗

Other Sources
NOAA: NCPDI ●
USGS: NAWQA ◗

□□■□□□

Indicator
Key Wetweather Conventionals from CSOs

EPA Data Sources
Needs Survey ●
PCS ◗
TRI ◗
NPDES Permits ◗

Other Sources

□■□□□□

Indicator
Number of State and Local Gov'ts Requiring Treatment of Stormwater Runoff from Rural, Suburban & Urban Land Uses

EPA Data Sources
RCW Program ◗
319 Program ○
NPDES Stormwater Permit Program ○

Other Sources
USGS: NAWQA ◗
NOAA: NCPDI ●

□■□□□□

Indicator
Number of BMPs Implemented at State and Local Level

EPA Data Sources
RCW Program ◗
319 Program ○
NPDES Stormwater Permit Program ○

Other Sources
USGS: NAWQA ◗
NOAA: NCPDI ●

□□■□□□

Indicator
Key Wetweather Conventional Pollutants from Nonpoint Sources and Stormwater

EPA Data Sources
EMAP ◗
RCW Program ◗
319 Program ○
NPDES Stormwater Permit Program ○

Other Sources
USGS: NAWQA ◗
NOAA: NCPDI ●
CZM Program ○

□□□□■□

Indicator
Marine Debris

EPA Data Sources
EMAP ◗

Other Sources
Center for Marine Conservation ●
NOAA ◗

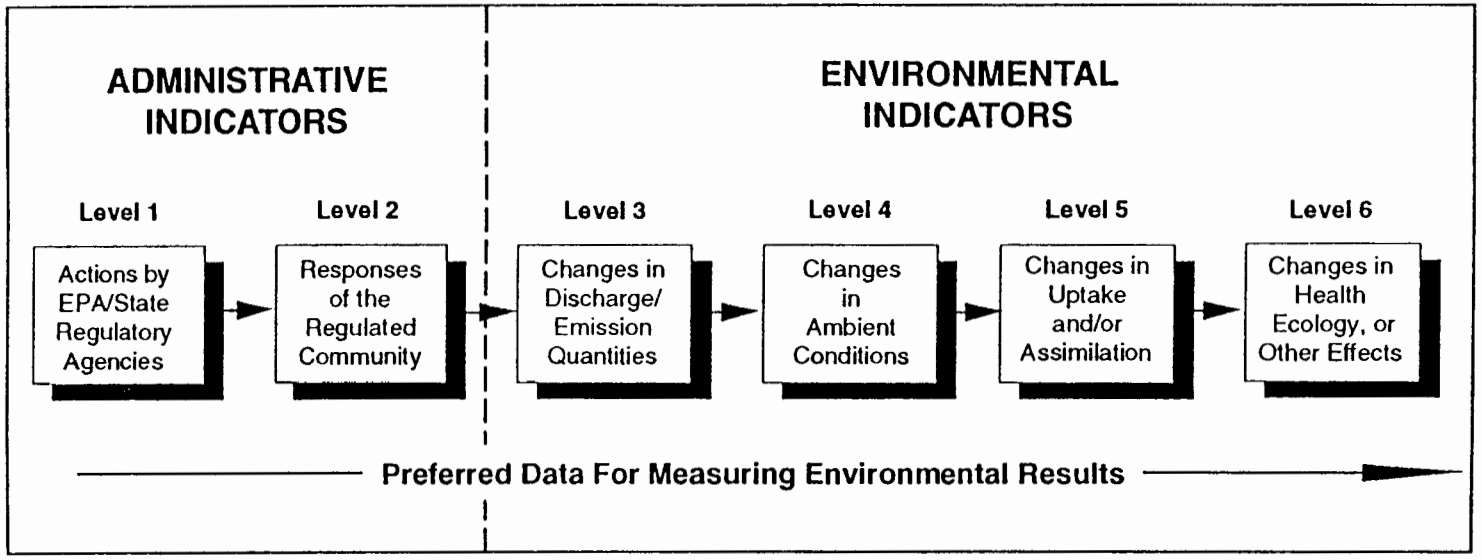
● data available now, needs improvement
◗ limited data available now
○ no data available now

We can set baseline and begin to report in FY94 either nationally or for certain regions, specific geographic areas, or specific resource type.

□□□□□□ Hierarchy of indicators
1-2-3-4-5-6 ■ indicates level
1=Administrative; 6=True environmental

735

Hierarchy of Indicators



Acronym List

AWWA	American Water Works Association
BEST	Biomonitoring and Environmental Status and Trends, USFWS (Update of NCBP)
BIOS	Biological System Component of STORET, OWOW/OW
CDC	Center for Disease Control
CSGWPP	Comprehensive State Ground Water Protection Programs
CSSI	Contaminated Sediment Sites Inventory
ELMR	Estuarine Living Marine Resource, NOAA
EMAP	Environmental Monitoring and Assessment Program, ORD
ERAMS	Environmental Radiation Ambient Monitoring System, Office of Radiation Programs
FAD	Fish Advisory Data Base, OST/OW
FRDS	Federal Reporting System, OGWDW/OW
FSP	Fisheries Statistics Program, NOAA
HWIW	Hazardous Waste Injection Well Database, OGWDW/OW
IBI	Index of Biological Integrity
ITFM	Intergovernmental Task Force of Monitoring Water Quality
LMR	Living Marine Resource, NOAA
MMS	Minerals Management Service
NAWQA	National Water Quality Assessment Program, USGS
NASQAN	National Stream Quality Accounting Network, USGS
NCBP	National Contaminant Biomonitoring Program, USGS
NCPDI	National Coastal Pollutant Discharge Inventory, NOAA
NCWI	National Coastal Wetlands Inventory, NOAA
NEP	National Estuary Program, OWOW
NFTD	National Fish Tissue Data Base, OST (does not yet exist)
NPDES	National Pollutant Discharge Elimination System, OWEC
NPSurvey	National Pesticide Survey, OPP
NRDC	National Resources Defense Council.
NRI	National Resources Inventory, SCS/USDA
NSR	National Shellfish Register, NOAA
NS&T	National Status & Trends, NOAA
NWI	National Wetlands Inventory, USFWS
ODES	Ocean Data Evaluation System
PCS	Permit Compliance System, OWEC
PGWDB	Pesticides in Ground Water Data Base, OPP
PWSS	Public Water Supply Systems
RBP	Rapid Bioassessment Protocols, OWOW
STORET	STOrage and RETrieval System, OWOW
TRI	Toxic Chemical Release Inventory System, Office of Toxic Substances
WBS	Waterbody System (for 305(b) Reports), OWOW
WIDB	Water Industry Data Base, AWWA

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MR. TELLIARD: David Kimbrough is going to be speaking on quality control levels, alternatives to detection limits. David is with the California Environmental Protection Agency, Department of Toxic Substances Control, and Hazardous Materials Laboratory - Southern California, and he is with us from southern California to come out here and enjoy the rain.

QUALITY CONTROL, AN ALTERNATIVE TO DETECTION LEVELS

MR. KIMBROUGH: The title of my presentation is the Quality Control Level, An Alternative to Detection Levels by myself and my supervisor, Janice Wakakuwa. The experimental data that this is presentation is based on is derived from our work in the analysis of soils (1-2) but the principles that will be presented here are general to all matrices.

The first part of this presentation will be a critical examination of the Method Detection Limit (MDL), the official method of USEPA (3-5). The basic question the MDL asks is what is the lowest concentration of analyte in a sample matrix that is not zero with 99 percent confidence (or that a particular reading has 99% confidence of not being a false positive. Using this procedure an individual reading has a 50% confidence of not being a false negative). The theoretical assumptions of MDL are 1) that you have an interference-free matrix, 2) that your sample preparation procedure is 100% effective for all concentrations, 3) and that you have a blank material with zero concentration of an analyte. There is a considerable body of literature that has examined the theoretical (i.e. statistical) validity of these assumptions (6-8). I will leave statistical theory to the statisticians. Rather, our goal was to examine the MDL from an empirical perspective. From an experimental point of view, there are no matrices or analytical methods that meet all four of these assumptions very few that meet any, especially in solids analysis. So right from the start, the MDL does not seem to be a very sound theory for empirical work.

The approach we adopted was to apply the MDL to some real analyses, which in our case was soils, and see if it worked. Our criteria for assessing whether the MDL "worked" was follow the MDL method for five analytes and three instruments and determine the frequency of false positives and negatives as well as the accuracy and precision of the results determined.

It will be useful to review the MDL procedure which is summarized on Table I. The term "MDL" is used a great deal to mean many different things by many different people. Not only do most people not realize that the MDL has a detailed set of the theoretical assumptions, they also do not realize that it has a very specific empirical procedure for its calculation. It is actually a rather complicated procedure. The first step is to make an estimated MDL, and there are four different procedures as to how to estimate an MDL. Depending on which one of these you choose, you will get a different estimated MDL.

Then, having chosen one of these methods, you make an estimated MDL. Then you choose or make a material in matrix of interest with one to five times the concentration of the estimated MDL of the analyte of interest. This material is analyzed seven times, the standard deviation of the mean measurement of the analyte is taken. The calculated MDL is equal to the Student's t value, which is about three, times the standard deviation. You have an option at the end of reiterating this procedure to validate your choice. It is important to note, there is no place for the accuracy of method in this calculation. The MDL is entirely based on a standard deviation, the precision, irrespective of how accurate the measurement ends up being.

It must be emphasized that it can only be calculated on a matrix by matrix, method by method, and instrument by instrument basis. There are very few laboratories that actually go through this entire procedure. Most of the "MDLs" that one sees on reports are actually determined on a "representative matrix" such as Ottawa sand for solid waste analysis and deionized water for any aqueous sample. These "canned" general purpose MDLs are at best Instrument Detection Levels (IDLs) and are not matrix specific.

For our study we chose five regulated toxic elements to study, arsenic, cadmium, molybdenum, selenium, and thallium and analyzed them on three different instruments, a sequential ICP- AES, a simultaneous ICP-AES, and a Flame Atomic Absorbence Spectroscopy (FAAS). I am only going to show you just one small set of that data which is representative of all the results. Table II shows the results for thallium in soil by simultaneous ICP-AES.

The first step is to make an estimated MDL for thallium when analyzed by ICP-AES. We determined four different estimated MDLs, one for each method and there is quite a range of estimates. We prepared a samples in the matrix of interest with a concentration of one to five (1-5) times the concentration of each of these estimated MDLs. The soil samples had concentrations with 500, 50, and 5 mg/kg of thallium which covered all of the estimated MDLs. These soils were each digested seven times, the mean values and standard deviations were calculated. The calculated MDL was determined for each soil.

All of these results are shown on Table III. If you use the 500 mg/kg soil, you get a calculated MDL of 23. Using the 50 mg/kg soil, you get a calculated MDL of 11. Finally, If you use the 5 mg/kg, you cannot get a calculated MDL because you can not get a signal at all; all you get are interferences. Judging from these results the actual MDL is somewhere between 23 and 11. It must be noted that determining MDLs in parallel at three different concentrations is not required. Technically, either of these MDLs is acceptable as the procedure is complete and the two results are not far apart.

To check the usefulness of these calculated MDLs we prepared a sample with 20 mg/kg thallium in the same soil used for the other samples. As can be seen, it does not even give a signal on this with the ICP-AES. Both of the calculated MDLs were completely unrealistic in the soil matrix for ICP-AES. The MDL procedure gives you an unrealistically low number, because underlying theoretical assumptions are not met.

Similar results were obtained for arsenic, cadmium, molybdenum, and selenium by ICP-AES, both simultaneous and sequential. ICP-AESs of course have no interference-free wavelengths. Every wavelength has some sort of interference on it, especially in solids analysis. FAAS has fewer interferences, so it tended to have better results. However, arsenic and selenium are very difficult to analyze by FAAS and so long as you are looking only at precision and not accuracy, you are going to have problems like this. We can conclude that the assumption of an interference free matrix is not met in soil samples for this analysis.

These results are from a single laboratory and may represent the limitations of the personnel or instruments of that laboratory (as much as we may not like to think this so). In order to determine how generalized a phenomenon this is, an inter- laboratory study was designed in conjunction with the Environmental Laboratory Accreditation Program in California, ELAP. As such, it was decided that this study would take the form of performance evaluation (PE) sample study. We prepared 10 soil samples, five soils spiked in these various combinations of the same regulated toxic elements used in the above single laboratory study and five more soils spiked with PCBs as Aroclor 1260 as shown in Table III. As can be seen, for each analyte, except arsenic, there is a sample that is unspiked and has a value significantly less than 1 mg/kg. These samples were validated first in-house and then by thirty reference laboratories. They were then sent out to 200 environmental laboratories.

All these laboratories selected were accredited by ELAP to perform these analyses in solids. Under California regulations there is separate accreditation for drinking water, wastewater, and solid waste. So, all these laboratories are accredited to analyze these for these compounds in this matrix.

Figure I summarizes the data we got back for thallium. Four measures are presented. It is important to note that the X axis is a logarithmic scale in mg/kg while the Y axis in not logarithmic and has the units percent. The first measure is the percent bias of the mean result where percent bias is defined as the measured mean value minus the true value divided by the true value times 100, so it comes up in units of percent. The second measure is the inter-laboratory percent relative standard deviation (%RSD) which is the standard deviation divided by the mean times 100 so the units are also in percent. The third measure is percent quantitative errors, that is, the number of laboratories were able to correctly identify the presence or absence of analyte but assigned a value that was beyond the control limits for that particular sample divided by the number of laboratories that turned in positive results for that sample, times 100. For the purposes of this study we established the control limits as $\pm$ 50% of the spiked value. Finally, the percentage of qualitative errors, false positives and false negatives are also presented.

It is important to note that we used a different definition of false positive and negative than is normally used. We defined a false positive as a result above the MDL of the laboratory when in fact the sample had a concentration less than that. Conversely, a false

negative is a result that is reported as less than the laboratories MDL when the actual concentration is larger than their reported MDL.

The first thing you notice which should not be a big surprise to anybody is that at high concentrations, you have relatively few problems. You get good precision, good accuracy, and relatively few numbers of errors of qualitative and quantitative types. At lower concentrations the percentage of errors increases and the precision deteriorates and the accuracy deteriorates. It can be seen that accuracy, precision, and number of errors and types of errors are concentration-dependent. The thallium results presented here are typical of the results for the other analytes.

What this study allows us to do is compare the claimed detection limits of the laboratories with what they were actually able to perform in a real sample. Consider a laboratory with a claimed MDL of 1 mg/kg for selenium. The laboratory analyzes a sample with 5 mg/kg selenium in it but reports a value of 2 mg/kg. It is not hard to see that if that same laboratory were to analyze a sample with 2 mg/kg selenium, it would be reported as less than 1 mg/kg, a false negative. Such an MDL would be quite meaningless. Obviously a similar problem could occur with positive biases and false positives.

Figure II, a log/log chart, shows some common spike recovery curves we got from a number of laboratories for PCBs. There are other types of spike recovery curves, but these are the ones we want to look at right now. If you did an MDL study at 10 mg/kg, you would come up with a detection limit of around 0.01 mg/kg. So using the assumptions of the MDL procedure, you would expect a straight line recovery as shown in the figure.

Unfortunately, using real samples, using real extractions, you get curves like this. You can have positive interferences. You can have linear range effects. You can have extraction inefficiencies. As you can see, if a laboratory generated either one of these other curves with the circles or the triangles, their MDL would be completely useless. They would either be high biased or low biased or have some other problem. Their reporting of them would be inaccurate based on their method detection study at 10 mg/kg.

We went through and looked at all the data from a total of 177 laboratories that returned data. We calculated from the results like this that about two-thirds of the reported MDLs were inaccurate. Either they were having problems with interferences or they were having extraction inefficiency. This study shows that the linearity assumptions of the MDL procedure are not realized in the field and that the results obtained from the first single laboratory study were not unique to that laboratory. Further, not only are interferences usually most significant at lower concentrations, but they are not predictable and must be determined empirically on a matrix by matrix basis.

One of questions that these first two studies raised for us was, is the MDL even asking the right question? The MDL theoretically can only answer the question what number is not zero with identifying the quality of that number. Quality assurance and

quality improvement have become the rallying cry in the USEPA, which presumably includes the quality of laboratory results. The MDL however is completely blind the issues of data quality. The precision and accuracy of results near the MDL, the two most important measures of data quality, are never determined so the quality of these results in never known. Of what use is a laboratory result if all that is known about is that it is not zero?

So we decided to take a closer look at the relationship between the quality control parameters of precision and accuracy versus concentration. Since our main area of work is with solids and toxic elements, this was the medium in which we decided to work. We prepared a series of spiked soils with a range of concentrations form 100 mg/kg to less than 0.5 mg/kg for sixteen toxic regulated elements as shown on Table IV. The elements were silver, arsenic, barium, beryllium, cadmium, cobalt, copper, molybdenum, nickel, lead, antimony, selenium, thallium, vanadium, and zinc. As most of you know, almost any soil will have most of these elements at concentrations in the range described. So we prepared an artificial soil from reagent grade chemicals which would have concentrations of aluminum, calcium, magnesium, manganese, and other soil matrix elements in the same proportions as the soils used in the first two studies.

Using an acid digestion (Draft Method 3055) which uses 2 grams and a final volume of 100 ml gives a 50-fold dilution from solid to liquid. Each of these soils was digested and analyzed in eight replicates. You can see if you divide all the values in mg/kg by 50, you get the equivalent concentration in mg/L, also shown on Table IV. For comparison we also prepared a series of aqueous standards was prepared, a 5 percent nitric acid aqueous solution over a range of concentrations from 2 mg/L down to 0.001 mg/L and double deionized blank all of which were also analyzed with eight replicates.

Figure III shows the results for cobalt which is representative for all of the elements. This is from a simultaneous ICP-AES, a Jobin-Yvon 50 P. Each point represent the mean result from the eight replicates. The X axis is logarithmic with units of ug/mL (ppm w/w) showing the results both the aqueous standards and the acid digestates. The Y axis has a linear scale with units of percent for percent bias of the mean result and the %RSD from the eight replicates.

Both the digestates and standards have the same pattern. Over about two orders of magnitude, you have very reproducible results, very accurate results. All of a sudden, at around 0.01 ug/mL, you have a sudden increase in bias and sudden increases in imprecision. The mean values become very inaccurate and very unreproducible. This is using baseline correction, so you are correcting for some of the interference of other elements. As you can see, the curves for both liquid and the solid are very similar. One thing we did on both of these graphs was we had it normalized for the fact that the most negative bias you can have is 100 percent but there is an infinite possible positive bias. So, just for the purposes of presentation here, we had a maximum bias of 100 percent, positive or negative, to normalize for this effect.

There is a general relationship between precision, accuracy, and concentration. There is a range of concentrations over which precision and accuracy are constant. At some concentration the both of these parameters deteriorate rapidly. In Figure III this happens for cobalt around 0.05 mg/L (or 2.50 mg/kg) for both the liquid standards and the acid digestates. As it happens the MDL for the aqueous standards is 0.05 mg/L and for the acid digestates it is 0.02 mg/L (1 mg/kg). Let us ignore the problems with the MDL already discussed and suppose that we can take the MDL at face value and say that these two concentrations have a 99 percent confidence of not being zero. These results, although not zero, have 100 percent bias and 300 %RSD.

So results near the MDL, whatever that may be, are going to be very imprecise and very inaccurate. One of the questions that comes up when this graph is presented is, how much of this is an artifact of the way you determine relative standard deviation? After all, the relative standard deviation is a ratio of the standard deviation to the mean, the numerator to the denominator, and if your denominator is constantly decreasing and your numerator stays constant, you expect the ratio to increase at lower concentrations solely as an artifact of how the precision is being measured.

On Figure IV we have plotted the standard deviation and the %RSD. Let us suppose, just for the sake of argument, that we really did have an interference-free matrix and an instrument that had a linear dynamic range through "zero" and an acid digestion that was 100% efficient at all a concentrations. Then the %RSD would be the standard deviation divided by the true value. So for comparison, we created a curve with this artificial %RSD. As you can see, all three curves look pretty much the same. However you chose to measure variance, the same pattern can be seen. A range of concentrations with constant precision and a range where the precision deteriorates rapidly. Sometimes there may be an even lower range of constant precision due to reproducible interference from the matrix.

It might be tempting to conclude that this was some artifact of elemental analysis of solid wastes. Figure V however is derived from data from a 1992 paper presented by Charles Hertz et al. of the Philadelphia Suburban Water Company presented in Montreal at the Water Quality & Technology Conference (9). Here you are seeing the same general relationship between concentration, precision, and accuracy in lead in drinking water. At high concentrations the results highly reproducible and very accurate. The lower the concentration becomes, the greater the imprecision, the greater the inaccuracy.

Now, just in case anyone thinks this pattern is only associated with inorganics, Figure VI is based on results from a 1991 paper presented by Yohe and Hertz presented in Orlando also at the Water Quality & Technology Conference (10). Here you see the concentration versus precision results for five carbamates. At ten times the MDL, you are getting very reproducible numbers. At the MDL of all five of these carbamates, the results are not reproducible. Similar results were obtained by Dr. William Horwitz of the Food & Drug Administration from inter-laboratory studies of food residues (11).

Why do we analyze environmental samples? We want to learn enough about some environmental situation so that useful decisions can be made, either to leave a situation alone or to improve it. In order to do this we need to have a certain level of confidence in the quality of the data. Different situations will require different levels of quality. This is, I suppose, what is meant by data quality objectives.

Two of the most important measures of data quality are precision and accuracy, so for any given situation the acceptable percentages of bias and %RSD will vary. What is the highest level of bias that will give you the confidence that you need to make a decision? What is the largest %RSD that tells you what you want to know? If you are a data user and your results have a 100 percent bias and 300 %RSD, of what use is that result to you? There may be situations where that is useful, but not many. In most situations, you are going to want to know what is the lowest precision and lowest accuracy that meets your data quality objectives.

That is really what I am trying to argue for here is that instead of looking at MDLs or other statistical measures, let's determine what is the lowest concentration in your matrix by your method that meets your data quality objectives. If 50 percent bias and 50% RSD is acceptable to you, then find the lowest concentration that gives you 50 percent bias and RSD or less and we will know that any higher concentration will have lower levels of both. This concentration is what we call the Quality Control Level (the QCL).

How would this be done on a routine basis? The first step would to determine the instrument QCL (IQCL) which should be constant barring instrument deterioration. In this case, the IQCL for cobalt in the aqueous standard with baseline correction is about 0.5 mg/L. From the IQCL, a good estimate of a method QCL (MQCL) would be 2.5 mg/kg, or 0.5 mg/L times 2 gram divided by 100 mL for the dilution correction of the acid digestion. Then you select the sample which you wish to know the MQCL, spike on enough cobalt to make a 2.5 mg/kg concentration, analyze that soil at least three times (although seven times would be best), and determine the precision and accuracy at that concentration. As it turns out the % bias is 4 and the %RSD is 15. If this is too high, the process would be repeated at higher concentrations until a the quality control is acceptable. Likewise, if 2.5 mg/kg is not a low enough concentration for other reasons, the process can be repeated at still lower concentrations.

I would argue that for values less than the QCL, the results should read, "Analyte not present in concentrations greater than QCL". If a positive value is measured but it is less than the QCL then it should either read the same as above or "Analyte detected but with unknown precision and accuracy". It would also be very useful to know if this less than QCL determination could be confirmed by another method.

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QUESTION AND ANSWER SESSION

MR. MADELONE: Ray Madelone, TRW. The data that you showed on your study that you ran in California, how was that pooled? Was that a single operator within the laboratory pooled, or was it all the laboratories?

MR. KIMBROUGH: It was all the laboratories using all the instruments.

MR. MADELONE: But did you use it as a single operator pooled, or did you take all the data at separate data points and pool it as an inter-laboratory?

MR. KIMBROUGH: As an inter-laboratory. We have an intra- laboratory, the very first one I showed, and then the second one was inter-laboratory, and the third one is intra again.

MR. STANKO: George Stanko, Shell Development Company. Could you go to the slide before this last one?

MR. KIMBROUGH: Sure. This is the carbamates from Charles Hertz' paper.

MR. STANKO: If there was ever a slide that made my day, that is the one. Industry has had the gospel all along that we should not be regulated nor measured at the MDL level. Your data says ten times MDL is the level where the precision and accuracy is acceptable.

That equals PQL. I have been sounding like John the Baptist,a voice crying out in a desert. I concur with your observations, and I appreciate your paper.

MR. KIMBROUGH: Well, thank you very much. Although I would argue not necessarily assigning ten as being the magic number. That is what it is here, but there should...and I would not even argue that it should be some multiple of MDL but that it should be done from the other end in terms of precision and accuracy, but yes, I understand what you are saying.

More questions? (No response.)

MR. TELLIARD: Thanks, David.

MR. KIMBROUGH: Sure.

Table I

1) ESTIMATE THE MDL:

a) The concentration that corresponds to an instrument signal to noise ratio of 2.5 to 5.

b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.

c) The concentration value that corresponds to the region where there is significant change in sensitivity at low analyte concentrations.

d) the concentration value that corresponds to the known instrument limitations.

2) SAMPLE WITH 1 TO 5 TIMES (BUT NOT MORE THAN 10)
ESTIMATED MDL

3) ANALYZE SAMPLE SEVEN TIMES

4) CALCULATE THE STANDARD DEVIAITON (S)

5) CALCULATE THE MDL BY USING THIS EQUATION

$$MDL = t * S$$

6) REPEAT STEPS 2 - 5 USING THE CALCULATED MDL

* IF THE S1 IS 3.05 TIMES GREATER THEN S2, START AGAIN.

* IF THE S1 IS LESS THAN 3.05 TIMES S2, POOL THE RESULTS.

$$S_{pooled} = [(6S_a)^2 + (6S_b)^2/12]^{1/2}$$

$$MDL = 2.681\ (S_{pooled})$$

Table II

The MDL for Thallium in ug/g for Simultaneous ICP-AES

STEP 1: ESTIMATE THE MDL

Procedure	Estimated MDL
a)	120
b)	110
c)	5.0
d)	5.0

STEPS 2-5: CALCULATE THE MDL

Calculated or Recalculated MDL

Spiked Value	Mean Value	Standard Deviation	MDL
500	452	7.4	23
50	42	3.6	11
5	<1	0	NONE

REALITY CHECK

Spiked Value	Mean Value	Standard Deviation	MDL
20	<1	0	NONE

Table III

Spike Concentrations of Analytes in Perfromance Evaluation Samples in ug/g

Sample ID	A	B	C	D	E
Arsenic	4,000	500	55	10	5
Cadmium	500	50	5	-	5,000
Molybdenum	30	5	-	5,000	500
Selenium	5	-	5,000	500	50
Thallium	-	4,400	500	50	5

Sample ID	F	G	H	I	J
PCBs	100	10	1.0	0.1	<0.01

Table IV

STUDY DESIGN

LIQUID CONCENTRATION mg/L	SOLID CONCENTRATION mg/kg
2.00	100
1.50	75
1.00	50
0.50	25
0.20	10
0.15	7.5
0.10	5.0
0.05	2.5
0.02	1.0
0.015	0.75
0.010	0.50
0.005	0.25
0.002	0.10
0.001	0.05
<0.001	<0.05

FIGURE I

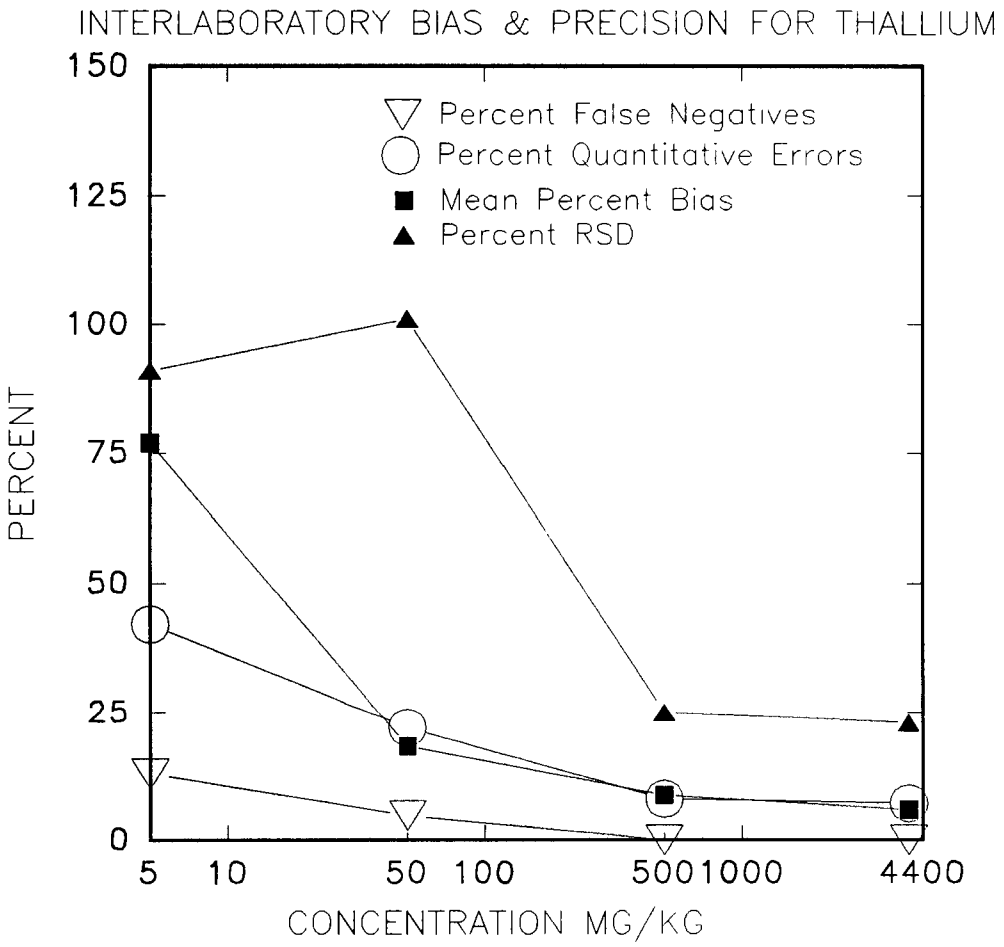

INTERLABORATORY BIAS & PRECISION FOR THALLIUM
Percent False Negatives
Percent Quantitative Errors
Mean Percent Bias
Percent RSD
PERCENT
150
125
100
75
50
25
0
5
10
50
100
500
1000
4400
CONCENTRATION MG/KG

FIGURE II

Common Measured Recovery Curves

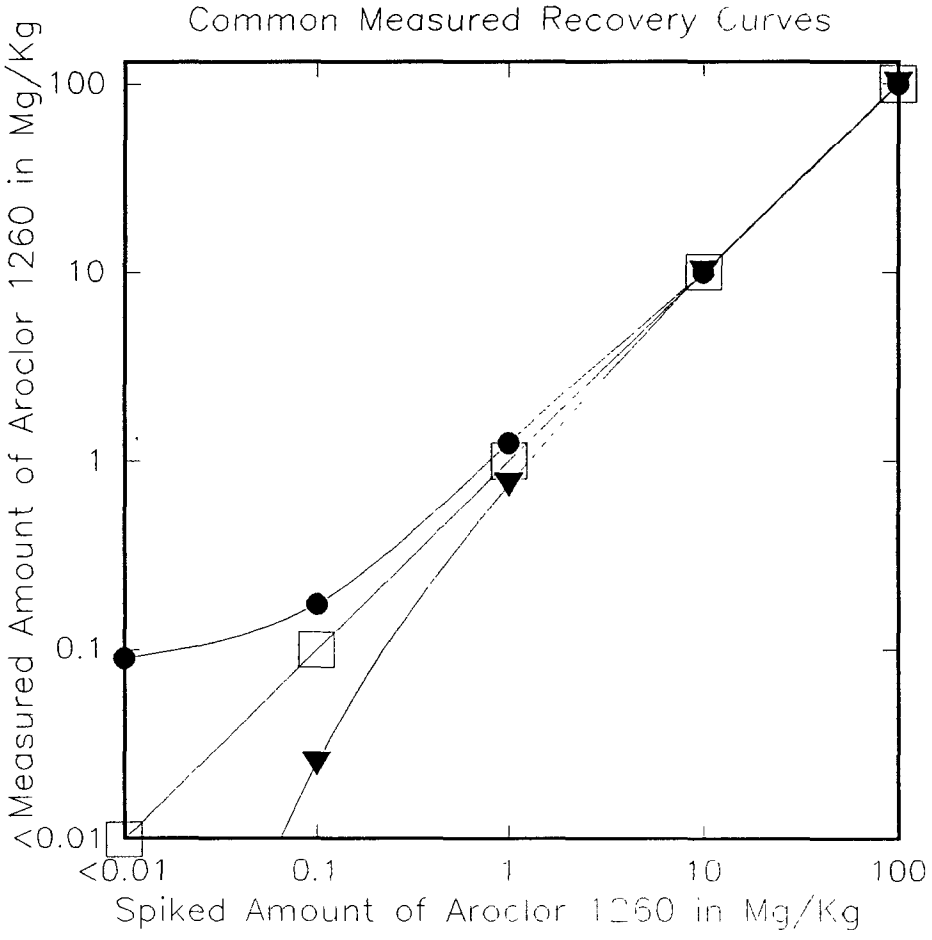


FIGURE III

BIAS & PRECISION FOR COBALT

Using Baseline Correction

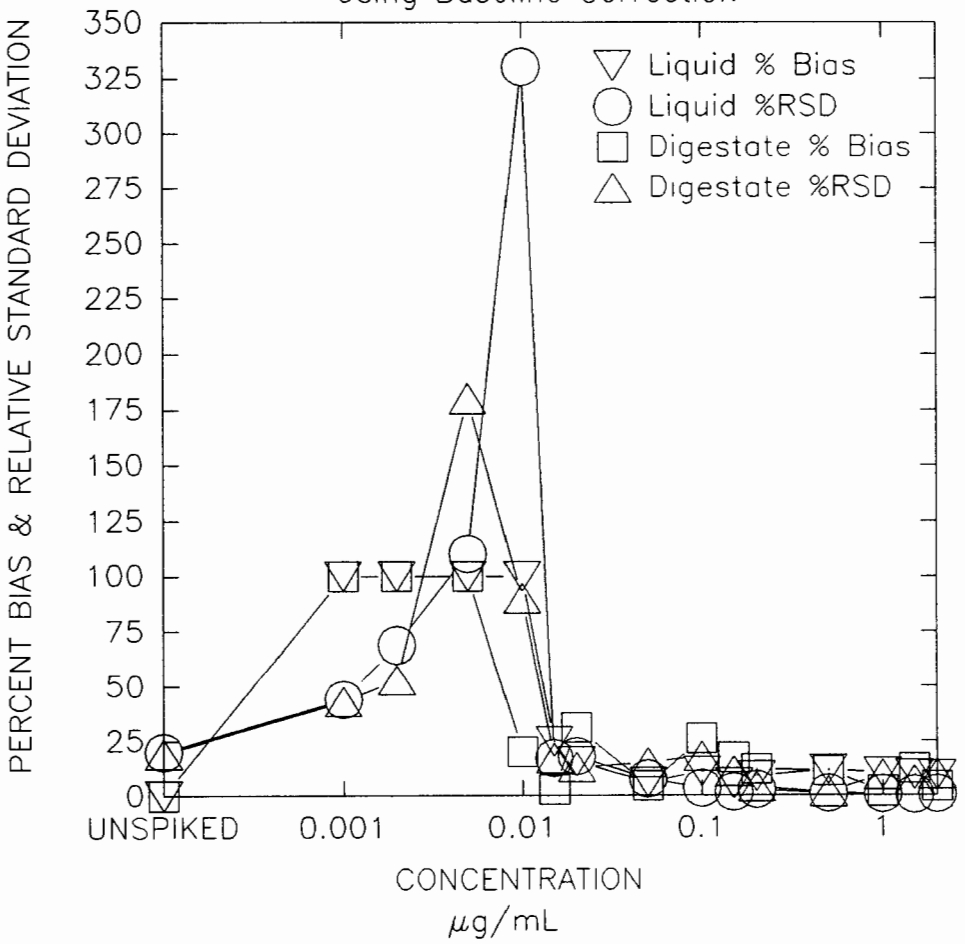


FIGURE IV

PRECISION AND ACCURACY FOR LEAD IN DRINKING WATER

Hertz et al.1992

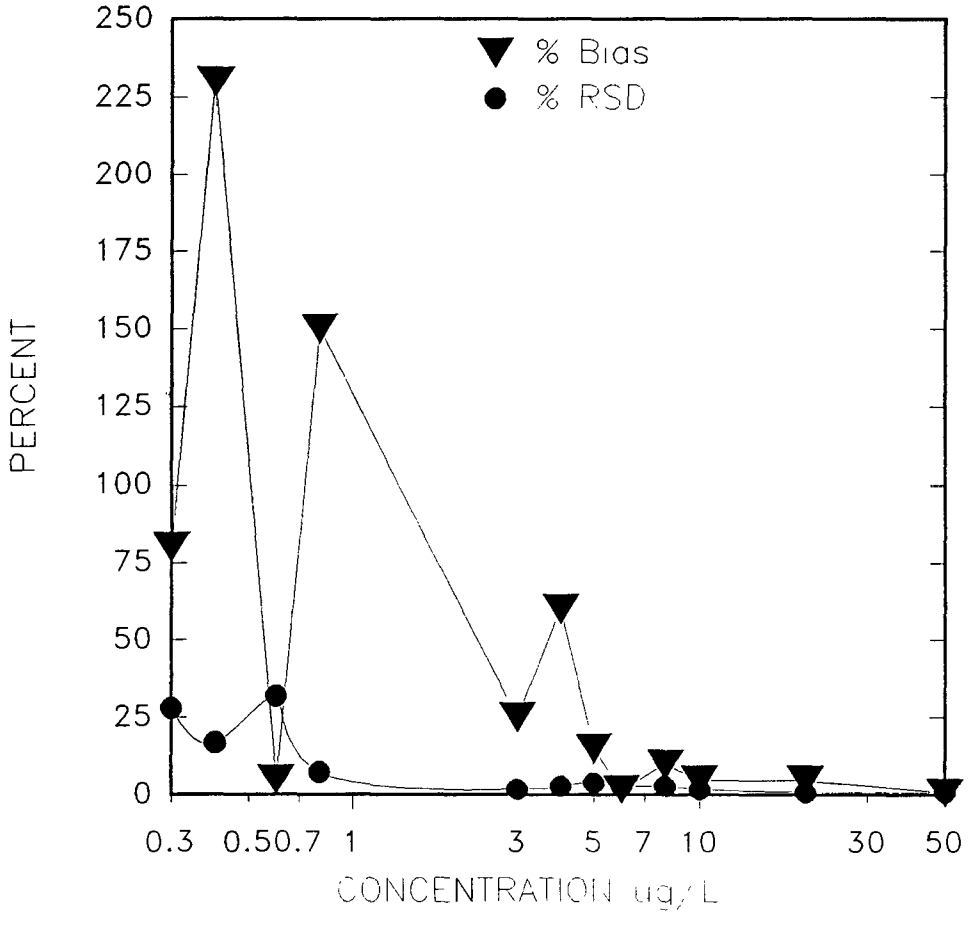
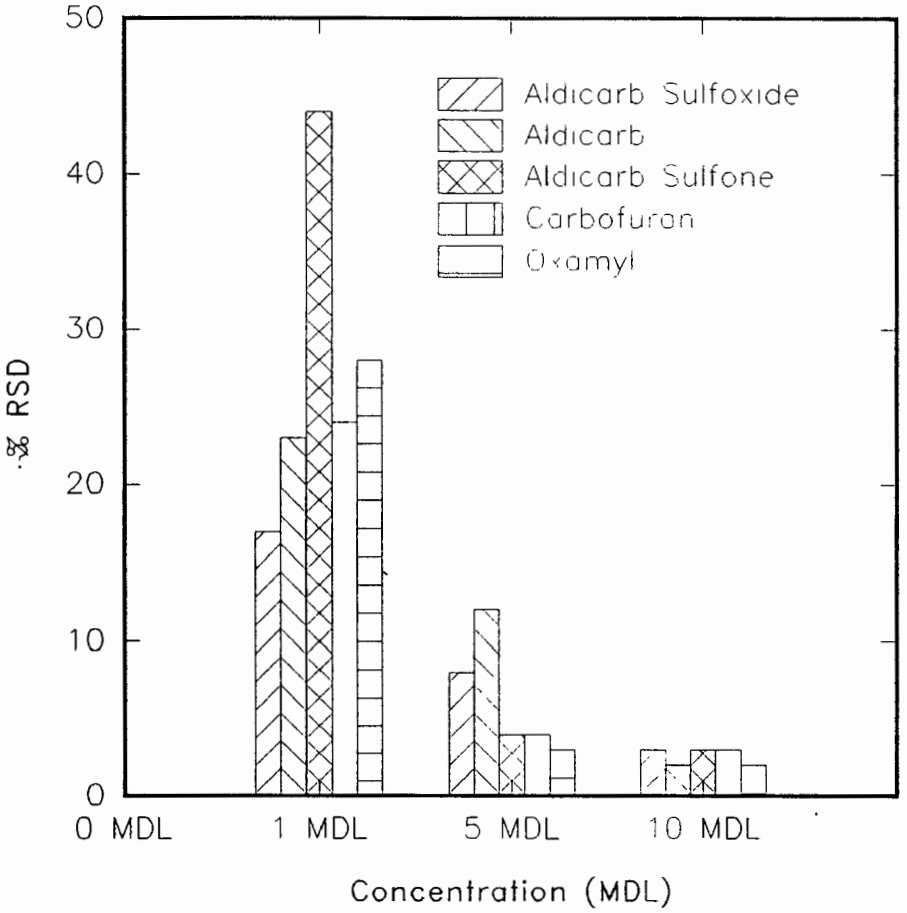


FIGURE V

VARIANCE FOR CARBAMATES IN DRINKING WATER

Yohe and Hertz 1991



MR. TELLIARD: Our next speaker is Dr. Paul Berthouex who is a Professor in the Department of Civil and Environmental Engineering at the University of Wisconsin.

Mac is back. Mac has been here before and is going to talk to us today about reporting and interpreting data near the limits of detection. It sounds like we have a roll going on here.

Mac?

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REPORTING

AND

INTERPRETING DATA

NEAR

THE LIMIT OF DETECTION

P. M. Berthouex
Department of Civil and Environmental Engineering
The University of Wisconsin-Madison

I believe most of you here are chemists. I am an engineer and I am going to view this problem as an engineer, which is a little different from that of many chemists.

The limit of detection is a very shaky number on which to base any kind of important decisions. However, the concept has been around a long time is widely accepted. It seems that chemists like this concept, or at least accept it willingly. I have never quite understood why. If I were expertly operating a tremendously expensive piece of equipment, I would not be happy if somebody declared most of the numbers being produced as rubbish and said they should be discarded and treated as if they are unknown.

The process of disregarding certain measurements and recording the data values as "unknown" is called data censoring. Censored data sets are a shaky basis for making important decisions. Statisticians would prefer not to see data censored, but it must be admitted that censored data sets provide them with a good deal of work. A little while ago you heard about some complicated calculations that can be done on censored data sets. What those calculations amount to is trying to replace values that existed at one time but were thrown away. These calculations do not replace the lost information.

Engineers tend to agree with the statisticians. We would prefer to see a number.

THE MDL, ML, AND REGULATORY DECISIONS

We need to make a distinction between bias (sometimes called accuracy) and precision. The method limit of detection (MDL) deals only with precision. It gives no information about bias. Often bias in measurements, including measurements on trace quantities, is more a problem than poor precision.

Figure 1 shows the hypothetical distribution of differences between a control blank and some reference sample. If one makes seven replicate measurements (the minimum recommended by the USEPA), the MDL will be equal to 3.14 times the standard deviation of the replicate specimens. The MDL is supposed to be the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero.

The latest proposal is to use the minimum limit (ML) for purposes of judging compliance with water quality and effluent standards. The ML is 3.18 times the MDL, or about 10 times the standard deviation used to estimate the MDL.

Since both the MDL and ML are estimated from the standard deviation of measurements on replicate specimens, both depend on how the operational definition of this standard deviation. There are different definitions and different ways to estimate the standard deviation and the MDL (or ML) obtained will depend on the number of replicates, the analyte concentration of the test specimens, the background sample matrix, and perhaps many other factors. When all is said and done we don't know that we have established 99 percent confidence in anything. The chance of the true analyte concentration being greater than zero might be 90 or 99.9 percent. In short, our ability to estimate the standard deviation of a blank sample is so weak, that we do not know what the confidence level really is.

Wisconsin has fifteen water quality limits that are currently set below the MDL of our analytical procedures. One of the first proposals in Wisconsin was to call a discharger in compliance so long as the analyte was "not detected" MDL" and to declare non-compliance on any occasion when the analyte was detected. That would have been an extremely unfair policy. It guarantees that every discharger eventually will be found in violation, even those discharges whose effluent may truly be blank. The only question is how how long your luck will hold until the inevitable mathematical laws of probability will wrongly declare an innocent man guilty.

The proposal to use the ML to judge compliance has some tremendously appealing features as an administrative structure. All measured values below the ML are to be treated as zeros for the purposes of calculating averages and judging compliance. This does give relief to permittees who seek to avoid being falsely accused of violations. It also accomplishes the EPA's stated second objective of providing a great deal of certainty to the regulatory agency that a violation has indeed occurred when a measurement above the ML is reported.

SCIENTIFIC PROBLEMS WITH THE MDL AND ML

Since many of us are engaged in investigating scientific problems rather than in making

regulatory decisions, it is worth reviewing some scientific problems with the MDL.

Our business is trying to learn the truth about waste treatment systems. Is performance getting better or worse? Have our interventions in the process been effective? What are the trends? What is the level of performance? To know only that we are above or below a numerical specification like the MDL or ML does not help in making these kinds of decisions. We need numbers. Numbers that are useful for judging these kinds of questions may be attractive for making regulatory decisions. The corollary is that disregarding certain values in one decision-making setting does not require us to disregard them is all other settings. The problem with censoring at the point of data generation (the laboratory) is that the decision maker is prohibited from deciding the utility of the data for his specific purpose.

The "detection limit" is a misnomer. What does it limit? It addresses only the probability of false positives, and not false negatives. If an analyte is not detected, it does mean that the analyte is absent. It may just be hidden in the sample matrix. Not detected does not even mean that the true concentration is below the MDL.

The MDL is an elusive and fuzzy value to estimate and we cannot estimate it very precisely. Its value may depend more on the statistical definition and the operational procedure used to estimate the standard deviation than it depends on the intrinsic properties of the analytical method.

The MDL considers only measurement precision. Bias may be a more important measurement problem.

With all these weaknesses, why has the use of the MDL survived so long? (There were papers published in the MDL at least as far back as 1968). A common answer is that we want to avoid reporting a positive concentration for a specimen that may be blank. But, is this really a problem? As a scientist, have you ever expected that a specimen truly would be blank? Isn't the MDL based on a statistical hypothesis that few of us really believe? Many hypotheses we construct in statistics is like that. We hypothesize, for example, that the mean level of two procedures are the same and we set of a t-test to examine the hypothesis even while know in our heart that the two things are not the same. What we may be prepared to believe is that the difference between the two

procedures is small enough to have no practical importance, just as we may be prepared to believe that the concentration of an analyte is so low that we are indifferent to its presence or absence.

The MDL is determined from replicate analyses, but it is intended to be applied to a single routine measurement. Engineers, as I think most scientists should, object to having any important decisions made on the basis of a single measurement. Standards based on such measurements are flawed and serve no proper scientific purpose. Such judgments should be based on a collection of measurements, and based on trends and levels over a period of time.

RESULTS OF SOME LEAD MEASUREMENTS ON WASTEWATER

We did a study in order to get some data on measurements at and below the MDL. We chose to do the study on lead because we had friends in laboratories who could measure lead without too much extra trouble. We made fifty test specimens for each participating laboratory.

These were prepared by filtering effluent from an activated sludge treatment plant that routinely produced 5-day BOD below 10 mg/L and received virtually no industrial wastewater. A large volume of this background matrix was subdivided to give five bulk portions of identical matrix. One subsample was the unspiked background matrix; four of the large subsamples were spiked with 1.25 μg/L, 2.5 μg/L, 5 μg/L and 10 μg/L. The spikes were in addition to the background concentration of lead in the effluent.

These test levels were determined after asking each participating laboratory their MDL for lead. Most of them told us their MDL was 5 μg/L; all were between 2.5 μg/L and 10 μg/L. In order to be sure of having a lot of measurements at or below the labs stated MDLs, most test specimens were at the 1.25 and 2.5 μg/L spike concentrations, and some were unspiked. The laboratories were not told that there were five different lead levels, or that the highest spike concentration was 10 μg/L. They were told the matrix was activated sludge effluent and that the lead concentrations were "low".

The labs were told to report a numerical value for each test specimen. We did not want any results report as "not detected" or "below the limit of detection." All the labs satisfied this request but one. Fortunately this lab still had the raw instrument readings in computer files and could later

provide the wanted numbers. Ironically this laboratory, which was originally willing to discard about 85 percent of their measurements, turned out to perform the best.

Figure 2 shows the data obtained from two of the laboratories. The x-axis is the amount of lead spike that was added and the y-axis is the measured concentration. The solid line is the true concentration for a background matrix that contained zero lead (the concentration in this matrix was non-zero). These laboratories had told us their MDL was 5 μg/L. The true lead concentration in the unspiked, 1.25 and 2.5 μg/L spikes were below the level these labs thought were their MDL. In their normal course of work, these laboratories would have disregarded all measured values that were below 5 μg/L.

It is my opinion that the measurements on these specimens contain much useful information. There is good consistency and the precision (variation) is good, even at these low levels. It would be wasteful not to use these data. Censoring at the MDL would distort, rather than clarify, our knowledge about the set of test specimens.

We need to be careful how we think and talk about precision. I do not like to think about precision as a percentage (i.e. as a relative standard deviation). I prefer to view precision as an interval on the original metric scale of the measurement process. Viewed this way, the precision (the spread or variation) is about the same at all five levels of lead. Precision has not deteriorated with a decrease in concentration even down to the unspiked (background) concentration.

On the other hand, it would be true that the relative standard deviation (RSD) of the low concentration specimens is larger than the RSD at the higher concentrations. But, note that this is entirely due to the change in concentration level and not because the absolute measurement errors have increased.

Figure 3 compares the low level measurements from six laboratories (three municipal wastewater treatment plants, two commercial, and one state lab). The true lead concentration of all the represented test specimens were less than 5 μg/L. The values measured on unspiked specimens are the open boxes, the 1.25 μg/L spikes are the solid boxes, and the 2.5 μg/L spikes are the open circles. You will note differences between the laboratories, but the differences are notably in respect to measurement bias and not to precision. The range of variation is remarkably

similar at the three levels for all six laboratories. The differences in average concentration between the three concentration levels are also remarkably consistent at just about the magnitude of the true differences between the added spikes. I find this consistency impressive in view of the fact that these laboratories ordinarily would have censored a great deal of useful data. Figure 4 is another way to look at the data. It shows that there is consistency when the data are considered collectively.

The MDL for each laboratory could be estimated using the values measured on the unspiked specimens, or on the 1.25 or 2.5 μg/L spiked specimens, or on these results pooled together. Any of the estimated MDLs would be legitimate under the EPA definition and procedure. Depending on the choice that is made, we get estimates of the MDL ranging from 0.4 μg/L up to about 6 μg/L. (Note that these MDL results are independent of any bias in the measurements because the MDL reflects only measurement precision.) This is quite a range of MDL values. We do not know which value in this range to pick. This is why I agree with the previous speaker that the MDL is an imprecise number, perhaps so imprecise as to have little scientific merit. The notion that we can determine an MDL that gives 99 percent certainty of making correct decisions regarding presence or absence of an analyte is clearly not well supported by real data.

COMMENTS

What should be concluded about the limit of detection? Is it helpful? In this particular case of lead in wastewater effluent much useful data would have been thrown away if the measurements were censored at some MDL. Using a laboratory's *a priori* MDL would have discarded about 85 percent of the measurements, with the remaining values including the most suspicious measurements and large outliers.

To illustrate how severe this would have been, I have used the data from laboratories E and F at the unspiked, 1.25, and 2.5 μg/L spike levels to construct the series of 100 values shown in Figure 5. Imagine this is a record of effluent quality for a treatment plant. Censoring the data at 5 mg/L gives the picture shown in Figure 6. Eighty percent of the values are disregarded. Now,

suppose this censored data record were given to a discharger or statistician who wanted to figure out what to do about the data hidden under the grey bar. No matter what they do, they are not going to get the right answer.

This censored data presentation gives a sadly distorted view of effluent quality. You are left with the impression that effluent quality was not very good, when in fact it was almost always at a low level, about 2 μg/L. This will only be apparent if the chemist reports all the values measured. As an engineer who designs and evaluates the efficiency of treatment plants, this is the impression I want to convey because this is the impression that is relevant to judging the efficiency of the process.

Let us rearrange the data and look at it in a slightly different way. Suppose that I had a treatment plant or an industrial discharge, and that from time to time I made improvements to it. I have reordered the data to construct Figure 6, which will represent these imaginary improvements of the imaginary process. (The solid line in Figure 6 is the moving average.) At the beginning of the record are samples that were spiked with 5 μg/L, followed sequentially by those with spikes at lower levels. If the data were censored at 10 μg/L (one possible value for the ML), or at 5 μg/L (a possible MDL), the substantial improvements would not be revealed. All the discharger's good work is hidden. This should not be done.

SUMMARY

In summary, analyses at and below the limit of detection can produce useful numerical data. It is not necessarily true that measurements at low concentrations are less precise than those at high concentrations. If, however, such properties exist in the data, they should be handled statistically by the data user. It should not be handled by censoring the data at the point of data generation. Chemists should be encourage to keep and report all measured numerical values. The ultimate data user can make the appropriate manipulations to account for differences in precision, or to compute statistics that are used for administrative purposes.

The detection limit really is a troublesome invention. It causes a lot of problems, but I do not see that it solves many. It is a statistical (not a chemical) concept based on a hypothesis that many

of us do not believe. The MDL itself is a statistic (i.e. a value estimated from data) that cannot be estimated precisely. It is defined only in terms of precision of measurements at low concentration. Bias in these measurements is likely to be a more important problem.

The Method Limit (ML) is a beneficial administrative tool. It will accomplish its stated objectives. But, as a scientific tool it has all of the disadvantages of the MDL, some of which are exaggerated when we are trying to generate and interpret data for the purpose of judging trends, interventions, and process efficiencies. In fact applying an MDL or ML at the point of data generation may make it impossible to do these things.

A final reason for not censoring data is that chemists may be better than they admit and are producing a lot of numbers that do not deserve to be thrown away.

QUESTION AND ANSWER SESSION

MR. AUSES: Jay Auses from Alcoa. It is not really a question; it is just a comment. Paul, I am a chemist, but I disagree with you on one part, and I agree on the other. My disagreement is in that chemists, as a whole, agree with and accept the MDL.

I do not think that is necessarily the case in all cases. I do agree with you, on the other hand, that most of what you presented are very valid issues that need to be dealt with, and thank you.

MR. BERTHOUEX: Thank you.

MS. KNOX: I am Robin Knox with Geraghty and Miller. I would like to make a comment about a similar type of approach where data below MDLs could be useful. You gave the example of looking at a wastewater treatment process. It is also useful when you are looking at natural processes in streams.

It is very difficult when you are trying to develope permit limits that address the differences between dissolved and total metals concentrations when most of your data is getting discarded because it is below the detection limit. I think, in these cases, that data that is being obliterated by the way the laboratories are reporting could be very useful to the permittees and the agencies.

I think, you know, that the reason the MDLs are so important and the labs are hesitant to report that on a lab report is because of all the legal concerns and the fact that all these permits are in administrative processes where, you know, a lot of questions are asked about the validity of the data.

That is something the agency has a role in doing, is to allow data to be discussed and used in determining what is going on in natural processes without turning around and using it against the permittee that collected it for compliance purposes.

So, I think those are some very valid things, and looking at that data could help solve a lot of the real world problems.

Thank you.

MS. ASHCRAFT: Merrill Ashcraft from the Navy Public Works Center. I have a comment also. I want you to know that we are one of the labs that do not throw out that data. We had some problems initially, and we did go back to reporting non-detect, because our customers were so confused when we reported the real numbers.

I wanted to report the real numbers to give that valuable information to our customers to use as a statistical data base. I reported also our method detection limit, and they were just totally confused.

So, I resorted to putting less than, but the actual data is in our data base and can be gotten out.

MS. ROMNEY: I just wanted to make one point. To address the issue of not having actual data for trend analysis, we have recommended in the draft document that in the comment part of the DMR (discharge monitoring report) you at least list or note the number of non-detect/non-quantifiable data that you actually have.

We do not ask that you record all the non-detect/non-quantified values, but we do try to account for this data by keeping a record of the number of non-detects/quantifiables that were observed. The fact that you have a record of the non-detect/quantifiable data allows you to explain the basis for the trend analysis.

MR. TELLIARD: Who said so? You did not tell us who you were.

MS. ROMNEY: Jackie Romney from EPA.

MR. TELLIARD: Those people over there are going to get you, Jackie. Thank you.

MS. ROMNEY: I really agree with what you are saying in terms of censoring data. I do not think a lab should ever censor data. It should provide the data to the user with the proper information in terms of the detection limit.

I have a little concern with some of the statements you made about the data, particularly at the zero, 1.25, and 2.5. On one of your charts, you showed the variability associated with each one of those data points in a real sense in terms of the standard deviations, and earlier, you stated that your interest as an engineer was to determine whether one process was better than another process.

Typically, how you do that is you do a comparison of means based on the variability. Using the data that you have there, if you try to determine that 1.25 is better than 2.5, I do not think it would pass the standard t-test.

So, in fact...

MR. BERTHOUEX: Oh, it will.

MS. ROMNEY: The trends that you are pointing out there may not be trends that you can prove in any statistical or even engineering sense.

MR. BERTHOUEX: I have done the statistics on it, and I can assure you that lab after lab, the difference between the levels at 1.25 and 2.5 are different. Furthermore, that difference, which should be 1.25, is, within statistical limits, 1.25.

MS. ROMNEY: But your data showed that the...at least the range of data points that you had there were on the order of almost 2 plus or minus 1 it looked like.

MR. BERTHOUEX: That is right, but when you average them together and do the t-test, it is very clearly different.

MS. ROMNEY: All right.

MR. TELLIARD: I would like to cut it off now. Could you talk to Dr. Mac at the break? I am trying to get people out of here on time so they do not miss airplanes.

If you could take a 10-minute break so we can kind of get back on schedule so folks can get out of here on time, we would appreciate it.

Thank you very much, Dr. Mac.

(A brief recess was taken.)

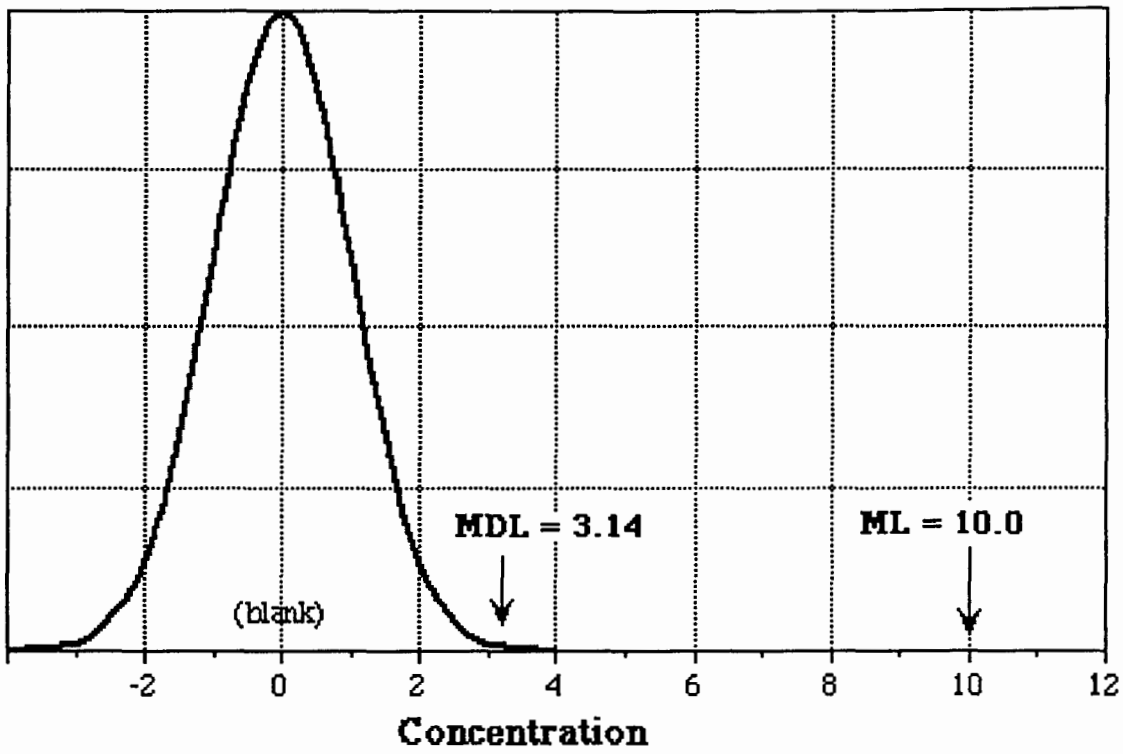


Figure 1. Graphical definition of the Method Detection Limit (MDL) and the Method Limit (ML)

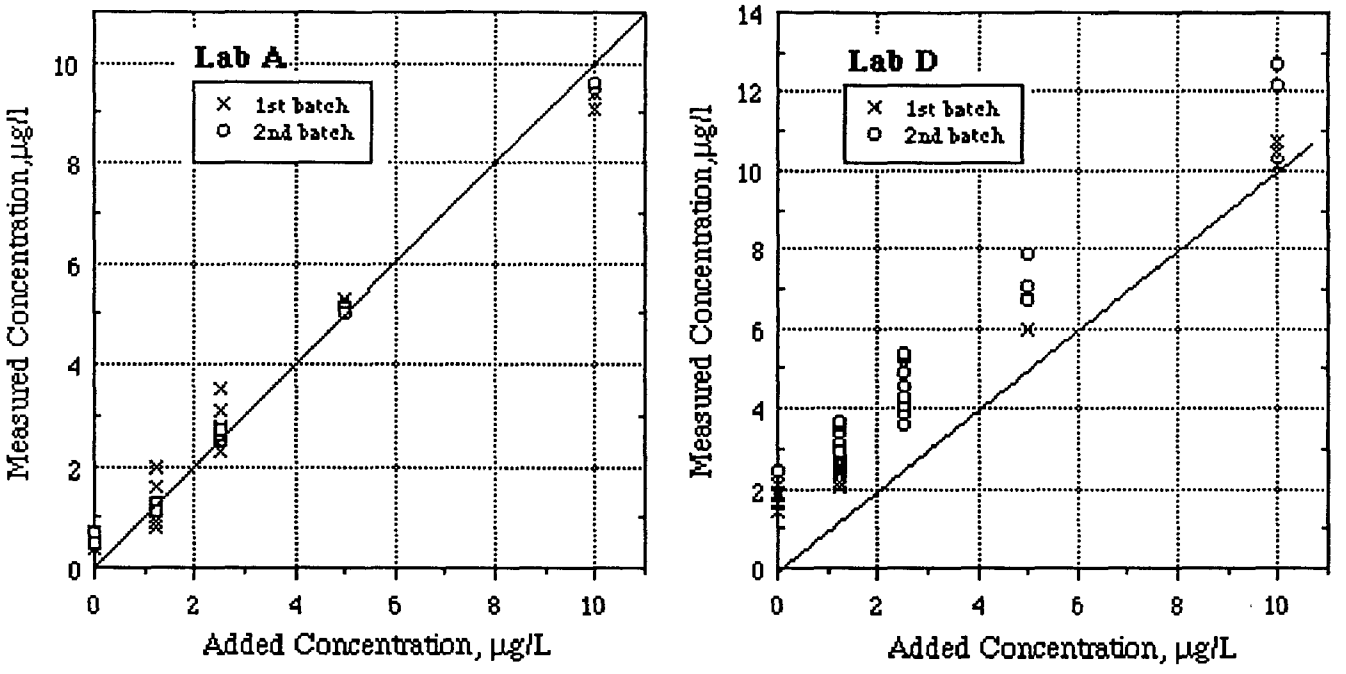


Figure 2. Lead data produced by Laboratories A and D. The solid line is the true concentration that would exist if the background matrix concentration were zero.

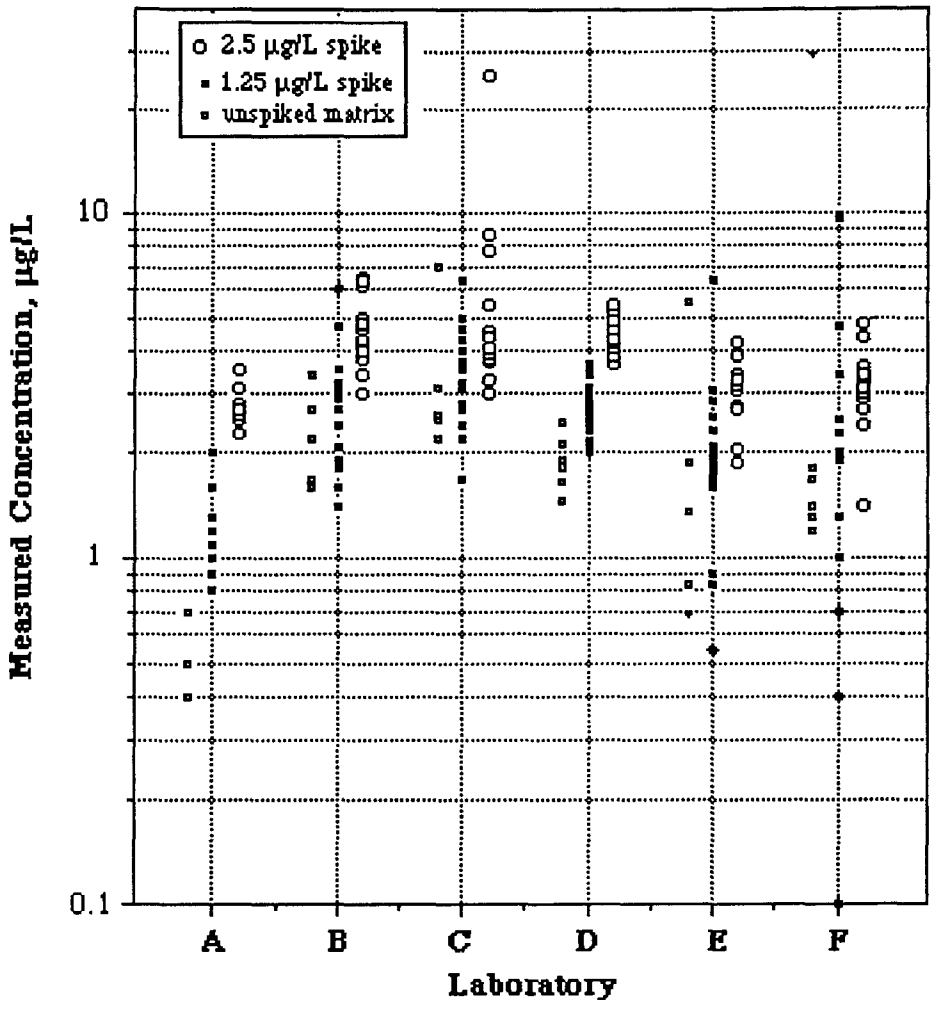


Figure 3. Comparison of measurements from six laboratories at the three lowest lead levels (spikes of 0.00, 1.25 and 2.50 µg/L Pb added to a matrix of filtered activated sludge effluent)

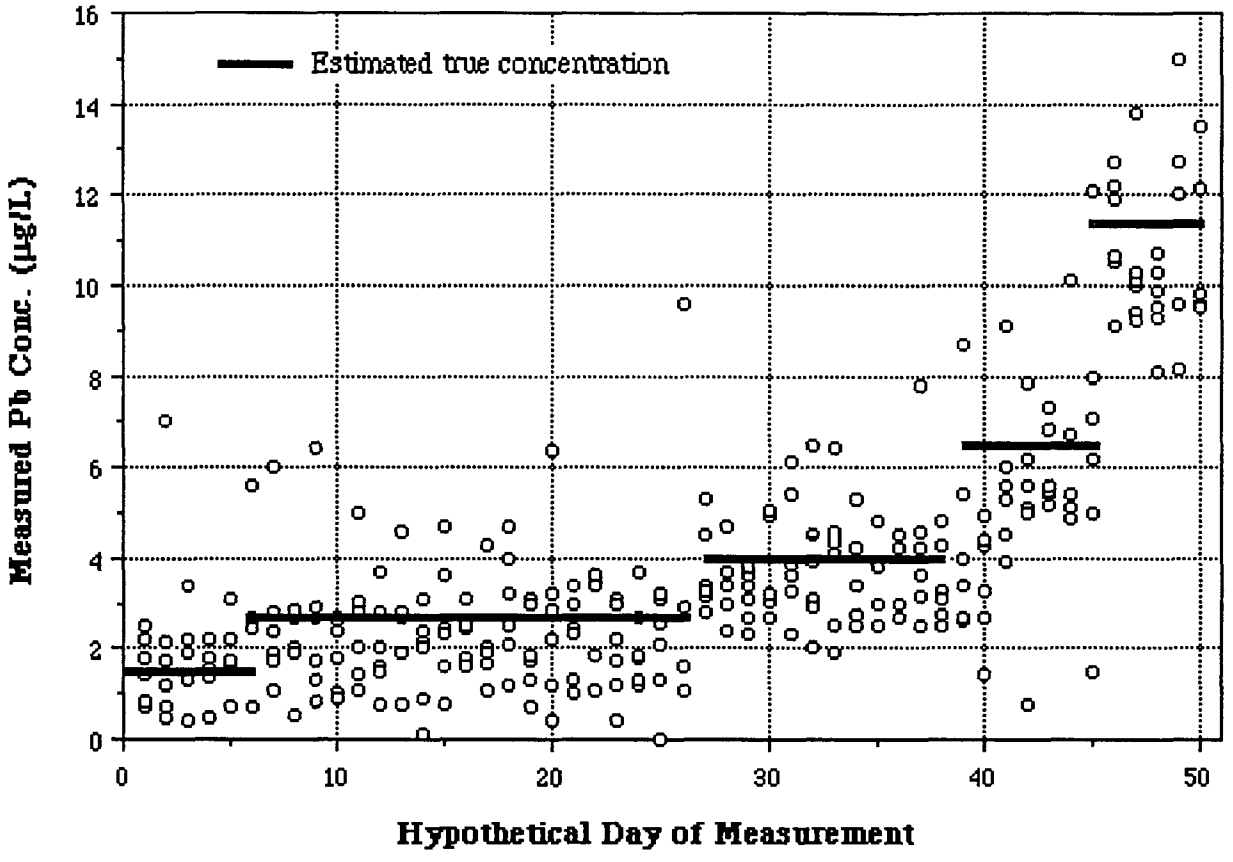


Figure 4. Collective view of the data at all five lead levels from the six laboratories. The measurements on the unspiked matrix are at the left-hand side of the graph, followed by the 1.25 µg/L spikes, and so on. The six values plotted for each hypothetical day are the results from six laboratories.

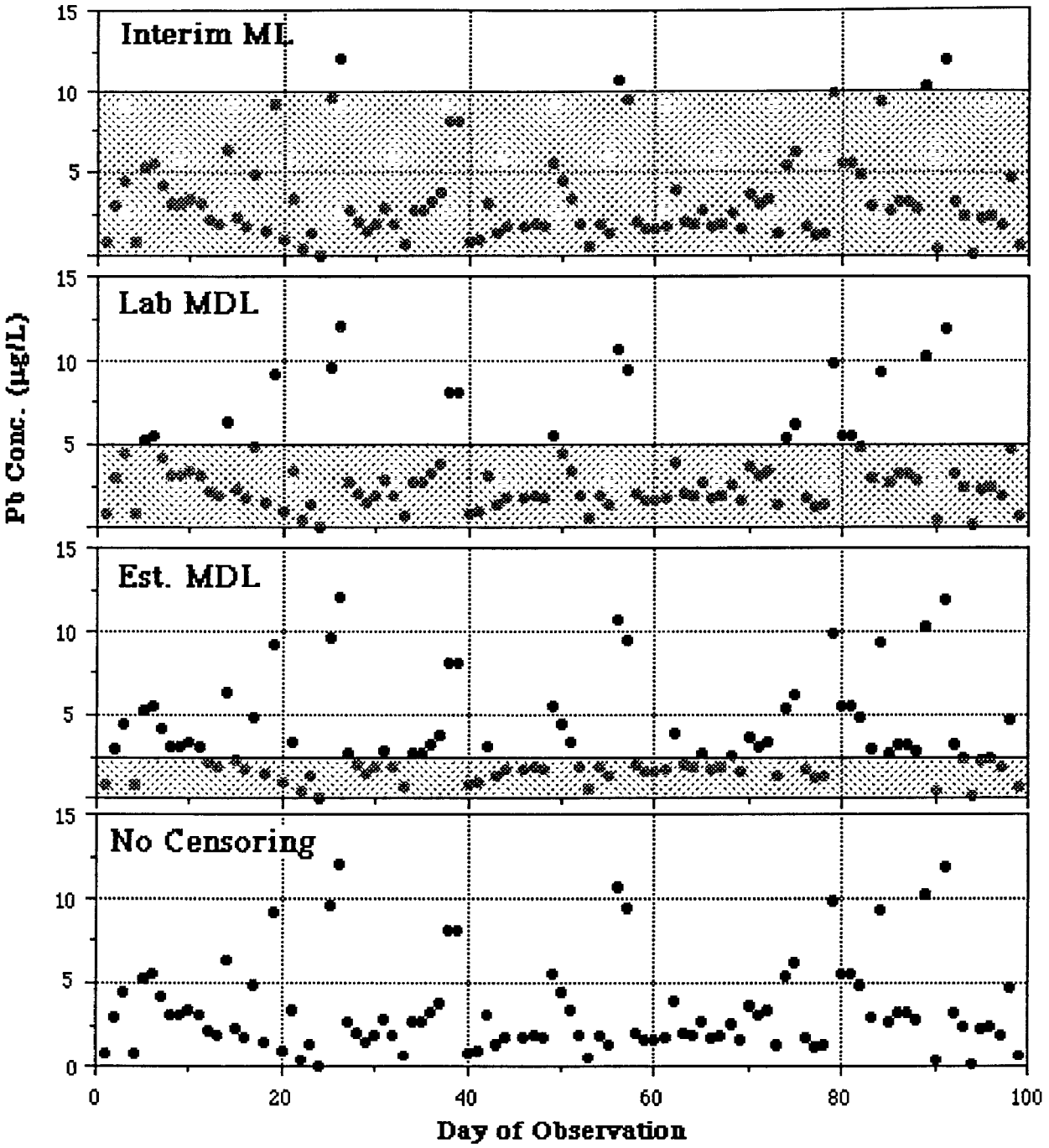
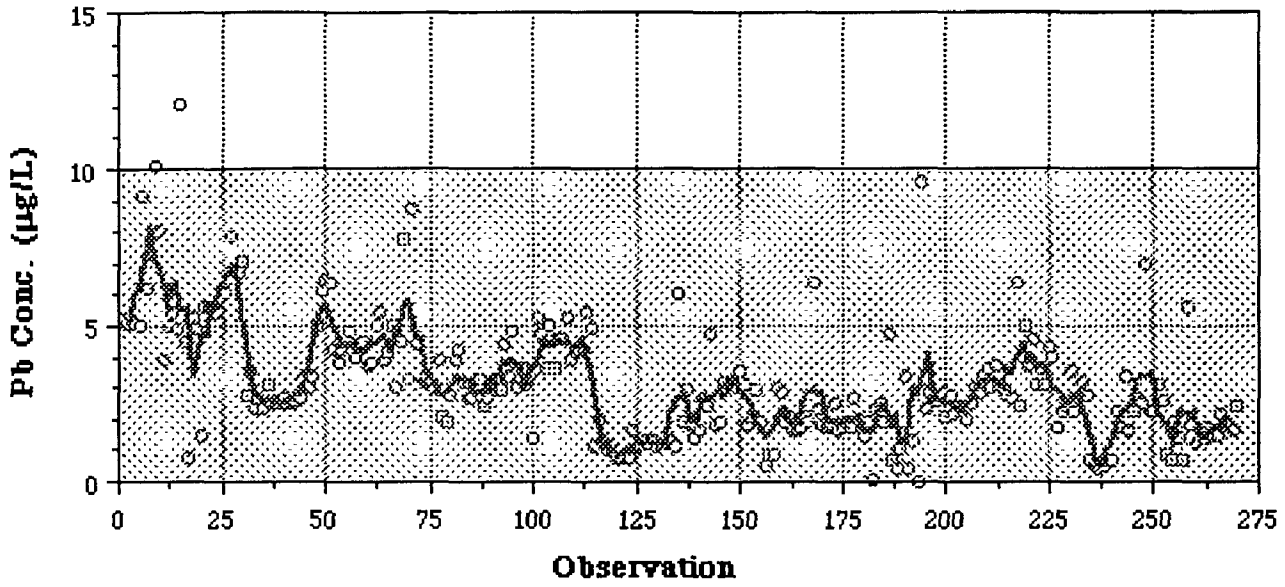


Figure 5. Plots of the data from laboratories E and F at the unspiked, 1.25, and 2.5 µg/L spike levels showing how many values are discraded by different levels of censoring. The true concentrations of all test specimens represented were less than 5 µg/L.



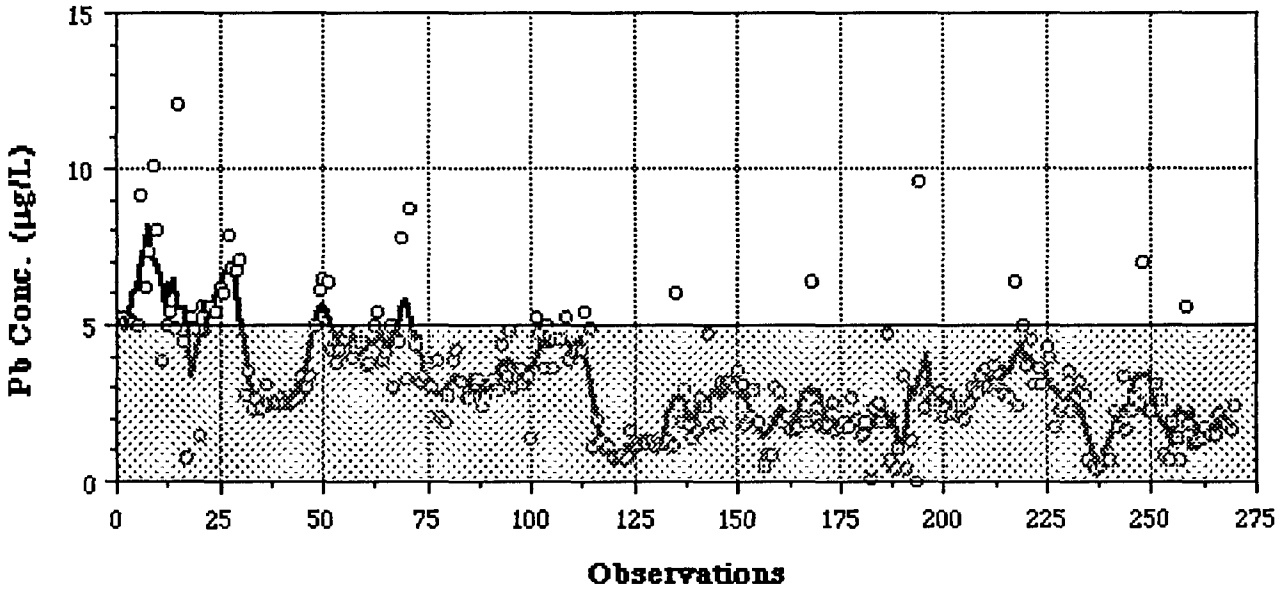


Figure 6. Series of measurements constructed from the lead data representing a hypothetical effluent that has improved over time.

MR. TELLIARD: If you could sit down, we would like to get started again.

Our next speaker is a constant companion to this meeting, thank heavens. George Stanko from Shell has been with us for, I think, maybe all but one or two meetings, all of them here at Norfolk.

As you know, there are those reviews in your forms. Please fill them out on ranking the papers. We have done this for a number of years, and out of 17 years, by the way, George was selected as the best presenter. So, with that in mind, I will introduce George.

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SHELL PERFORMANCE EVALUATION STUDY OF EPA METHODS 8270, 8020, and MODIFIED 8015 (TPH)

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ABSTRACT

A performance evaluation (PE) study of contract environmental analytical laboratories currently being used by Shell was conducted. The study was designed to establish the level of performance for 29 laboratories and the methods selected by Shell for the study were EPA Methods 8270, 8020, and Modified 8015. The study was limited to selected polynuclear aromatics and phenols by Method 8270, BTEX plus MTBE by Method 8020, and total petroleum hydrocarbons (TPH) by Modified Method 8015. A contractor, Analytical Standards Inc. (ASI), was hired to prepare the whole-volume water samples and to perform statistical analysis of the resulting data. Participation in the PE study was voluntary and each of the participants received a report of their performance from ASI. The results for the PE study are presented in the paper.

SHELL PERFORMANCE EVALUATION STUDY OF EPA METHODS 8270, 8020, and MODIFIED 8015 (TPH)

INTRODUCTION

A performance evaluation (PE) study of 29 contract environmental analytical laboratories that are currently in the Shell Laboratory Accreditation Program (SLAP) was conducted in late 1993. The authors selected the methods for the PE study as well as the limited list of target analytes. These selections were based on the nature and volume of work being performed at SLAP laboratories. A contract was negotiated with Analytical Standards Inc. to prepare the whole-volume water samples, to collect all the resulting data, to statistically analyze these data, and to prepare a report for each of the laboratories which showed their performance for the study. ASI also prepared a summary report for Shell. All the laboratories that participated in the PE study were initially contacted by Shell and were asked to participate at their expense. All laboratories did volunteer for the study.

The study was initiated in late November and samples arrived at laboratories in early December. Results from laboratories were reported directly to ASI in late December and ASI reports were sent directly to laboratories in early January. ASI also prepared a report for Shell which summarized the results for the PE study. This paper includes much of the material in the ASI format and from the ASI report for the PE study as well as Shell's interpretation of these results.

SLAP PERFORMANCE EVALUATION STUDY

The most recent Shell SLAP PE study(1) evaluated laboratory performance for volatiles by EPA Method 8240 (GC/MS), metals by ICP, and five general parameters – oil and grease, BOD, pH, COD, and TOC. The study was done blindly and represented the level of performance one could expect from commercial laboratories for routine samples. Such a study required considerable effort, time, and was quite costly. Since the study, the list of contract laboratories being used by Shell changed considerably and it appeared timely to conduct another PE study of SLAP laboratories to assess the performance for the current list of laboratories.

Due to cost constraints, it was decided the current study had to be more limited and focused. The costs associated with a blind study were too prohibitive. While Youden pairs were initially considered, it was decided not to use pairs of samples because of costs and the fact that laboratories knew they were participating in a PE study and resulting data might not be truly representative of routine operations. However, it was decided to use whole-volume water samples rather than concentrates to eliminate the possibility of laboratories analyzing concentrates.

Study Design

A number of factors were considered in developing the study design. Review of the nature of the work being done for Shell at SLAP laboratories was the main criteria used for selecting the methods to be studied. It was also decided not to include any of the methods previously studied. After EPA Methods 8270, 8020, and Modified 8015 were selected, the lists of target analytes were selected. Methyl tertiary butyl ether (MTBE) was included in the list for Method 8020 because it is a component of most commercial gasolines and has been found in environmental samples. To make the PE samples more realistic, small amounts of commercial gasoline were added to the Method 8020 sample and small amounts of turbine fuel (Jet A) were added to the Method 8270 sample.

The PE study was also limited with respect to the concentration levels selected for target analytes. The current study was not designed to assess performance at or near detection limits, but to assess laboratory performance well above quantification (PQL) levels. Basically, good laboratories should not have had any problems with any of the samples or target analytes with the possible exception of MTBE. All laboratories may not have had much experience with MTBE. Table 1. identifies the lists of target analytes and concentrations used for the PE study.

TABLE 1.

	Parameter	"True Value"(ug/L)
Method 8270		
	Acenaphthene	3.028
	Acenaphthylene	33.865
	Anthracene	71.000
	2,4-Dimethyl Phenol	46.950
	2-Methylnaphthalene	88.990
	Naphthalene	24.950
	Phenanthrene	42.900
	Phenol	65.070
Method 8020		
	Benzene	20.000
	Ethyl Benzene	35.000
	Toluene	42.000
	Xylenes	55.000
	MTBE	85.000
Mod. Method 8015		
	Gasoline Range Organics	500.000

It should be noted that acenaphthene was not one of the initial target analytes, but resulted as an impurity in the acenaphthylene standard used to prepare the sample. A number of laboratories reported the presence and concentration of acenaphthene so it was decided to include and list the compound as a target analyte.

Contractor

A contract was negotiated with Analytical Standards, Inc. (ASI) to do most of the work for the PE study. Shell provided ASI with the list of laboratories to be included in the study and ASI prepared and shipped the whole-volume water samples directly to the laboratories. Laboratories were directed to report results for the study to ASI who would be doing their usual statistics and who would return an individual report to each laboratory which showed their performance. In addition, ASI would prepare a summary report for Shell which showed the performance of all SLAP laboratories on an individual and combined basis. Most of the information included in this paper was taken from the ASI summary report to Shell and is shown in the ASI format.

Performance Evaluation Results

The statistical summary report from ASI for the SLAP PE study is shown in Table 2 (attached). Table 2. lists the "true" values; the statistical means for the study; the standard deviations for the means; the highest/lowest reported values; and the upper/lower "warning" and "control" limits for each of the parameters. Table 2. provides a general overview for the performances of all the laboratories for the methods/analytes included in the study.

ASI prepared control (Shewhart) charts for the PE study which illustrates laboratory performance for each individual analyte. The control charts are shown in Figures 1 to 14. Whenever possible, the outliers were left on the charts for identification of poor performance. However, if they greatly distorted the graphing scale, they were removed.

The bottom line is that the performance for this group of laboratories was quite good. One has to look at the performance for each laboratory to identify specific problems and/or corrective action. If one chooses to assess overall performance using the EPA and ASI "acceptable", "check for errors" and "not acceptable" categories for all laboratories, most laboratories performed very well. In addition, where the statistical mean and corresponding control limits indicated significant method bias, laboratories were not penalized in this assessment for being closer to the "true" value. Table 3. shows such an assessment. It should be noted that not all laboratories reported results for all parameters.

TABLE 3.

	Method 8270	Method 8020	Method 8015
Acceptable	22	25	25
Check for Errors	1	2	0
Not Acceptable	3	2	0

Specific Observations from SLAP PE Study Results

Lab #33 reported their result for TPH (Method 8015) as <1,000 ppb. One wonders why their quantification level is so high. This problem requires some kind of explanation and perhaps corrective action.

Lab #8 did poorly on both benzene and ethyl benzene. Both values were very low. Lab #8 needs to review their raw data and take corrective action. They also need to demonstrate they can run Method 8020.

Lab #59 was acceptable for all parameters except for 2-methylnaphthalene where it was a factor of 2X high. A bad standard or dilution error are possible causes. Corrective action is in order to establish the cause for the problem.

Lab #159 missed all target analytes for Method 8270. They need to correct the problem then demonstrate they can run Method 8270.

Lab #162 missed phenol. They need to correct the problem then demonstrate they can run Method 8270.

Lab #166 had an accuracy problem. They have a low bias problem of approximately 1.5. Corrective action is in order.

Lab #167 was low by a 2X factor for toluene by Method 8020. Corrective action is needed for the problem.

Lab #168 has a major problem with Method 8020 and corrective action is needed. They need to correct the problem then demonstrate they can run Method 8020.

Modified Method 8015

Some general observations resulted for Modified Method 8015. These observations apply more to the TPH method rather than any or all laboratories. The sample was prepared to have a "true" value of 500 ug/L and was prepared using a commercial unleaded gasoline purchased in ASI's local area. Review of the statistical data showed there were both

precision and accuracy problems. The precision expressed as the standard deviation was 77 ug/L (S) which indicated a lot of analytical variability. Statistically, there were no outliers because of the large variability. The mean for all laboratories was 268 ug/L which showed poor accuracy (low bias). Even the highest reported value 440 ug/L represents a low bias.

Some follow-up contact with laboratories revealed that there really is a method problem with Modified 8015. For example, laboratories that used a synthetic mixture of compounds as a standard exhibited the lowest bias. Current plans are to attempt to standardize the method for all SLAP laboratories in an effort to improve both precision and accuracy for TPH. Shell will prepare an SOP for SLAP laboratories to use for future Shell samples. Some additional PE studies are planned for the immediate future and will probably be the subject of a future paper.

Acenaphthene

Acenaphthene was not added to the samples on purpose, but was an impurity in one of the other analytes. Ten out of twenty-six laboratories reported values from 2 to 3 ug/L for the compound. The actual concentration of acenaphthene in the sample was below the EPA listed PQL for the analyte in Method 8270 (PQL = 10 ppb). Ten laboratories reported values from 2 to 3 ug/L for the compound. 15 laboratories reported the observation as <10 ppb. One laboratory reported the observation as <11 ppb; another laboratory reported <50 ppb; and two laboratories reported <5 ppb. There was just too much good data for acenaphthene to ignore it. No attempt was made to contact laboratories to establish whether the raw data indicated the presence or absence of acenaphthene. It is obvious that laboratories will report such observations differently.

CONCLUSIONS

The results from the PE study indicated that most of the laboratories currently being used by Shell perform quite well for the three methods evaluated.

Unfortunately, there were some laboratories that did not adequately perform Methods 8020 or 8270. There appeared to be other possible and known causes which resulted in data that were not acceptable. There is concern for this observation since all laboratories knew they were participating in a PE study. One would expect that bad standards and/or dilutions or transcription errors would (should) have been caught if appropriate levels of QA/QC were in place. Corrective action is needed at a few of the laboratories and, in some instances, a demonstration that the laboratory is now in control and has the capability to run the methods is required.

The results from the SLAP PE study of Modified Method 8015 revealed there is a problem with lack of standardization of the procedure. The results indicated that the most obvious source of method bias was the type of standard used.

The prime goal for the PE study, to assess the performance of the current list of contract laboratories used by Shell, was met in a cost-effective manner.

REFERENCES

1. G. H. Stanko, "Performance Evaluation Study of Environmental Analytical Contract Laboratories," 14TH Annual EPA Conference on Analysis of Pollutants in the Environment, Norfolk, Virginia, May 8-9, 1991.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Are there any questions? (No response.)

Thank you George.

SHELL PERFORMANCE EVALUATION STUDY

OF

EPA METHODS 8270, 8020, AND MODIFIED 8015 (TPH)

G. H. STANKO
T. L. NORTON
R. A. POOLE

17TH ANNUAL EPA CONFERENCE
ANALYSIS OF POLLUTANTS
IN THE ENVIRONMENT

NORFOLK, VIRGINIA
MAY 4-5, 1994

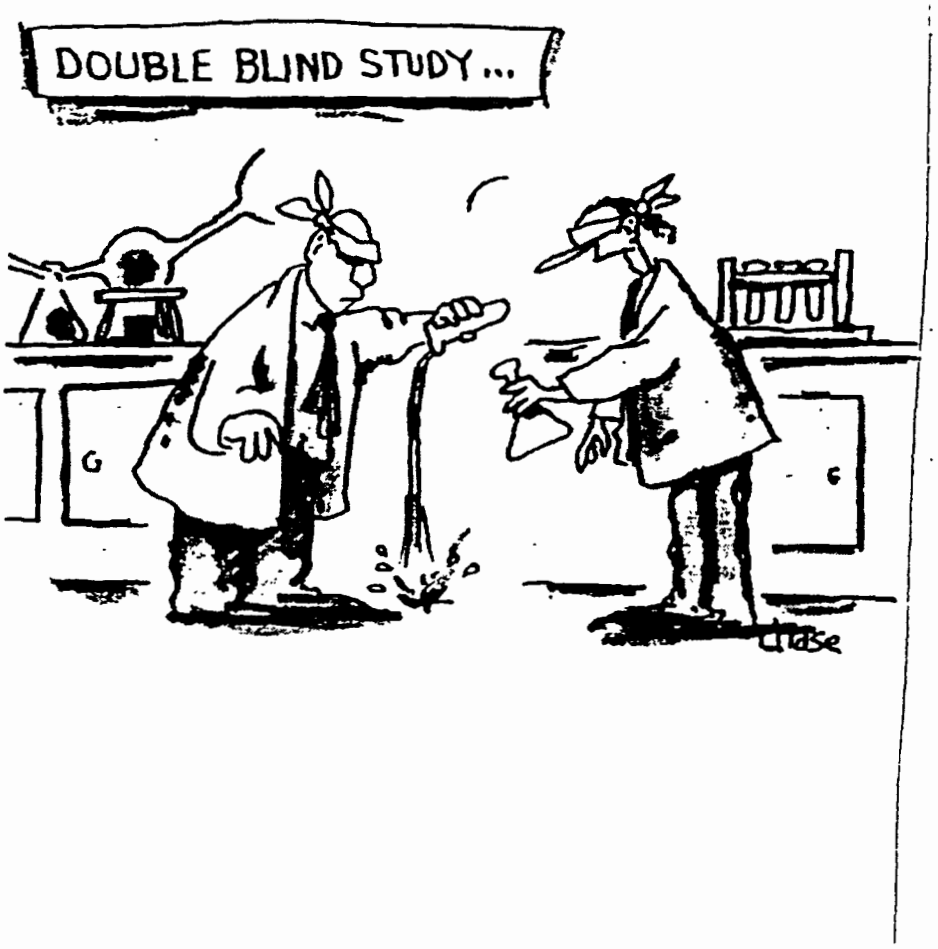
DOUBLE BLIND STUDY...
chase

Table 2

Shell Development Company SLAP Audit

Statistical Summary Report

PARAMETER	Calculated "True" Value	Statistical Mean	Standard Deviation	Upper Warning Limit	Lower Warning Limit	Upper Control Limit	Lower Control Limit	Highest Reported	Lowest Reported
Gasoline Range Organics	500.000	268.037	77.458	419.855	116.219	467.879	68.195	440.000	110.000
Benzene	20.000	17.889	2.373	22.540	13.238	24.011	11.767	23.900	5.900
Ethyl Benzene	35.000	30.507	5.261	40.819	20.195	44.080	16.934	42.500	5.300
Toluene	42.000	38.846	5.654	49.928	27.764	53.433	24.259	53.200	17.000
Xylenes	55.000	45.314	6.998	59.030	31.598	63.369	27.259	62.100	11.000
MTBE	85.000	86.904	18.608	123.376	50.432	134.913	38.895	123.000	50.000
Acenaphthene	3.028	2.479	0.388	3.239	1.719	3.480	1.478	3.000	2.000
Acenaphthylene	33.865	30.768	4.544	39.674	21.862	42.492	19.044	47.000	19.000
Anthracene	71.000	58.504	7.859	73.908	43.100	78.780	38.228	77.000	45.000
2,4-Dimethyl Phenol	46.950	36.864	5.891	48.410	25.318	52.063	21.665	50.000	18.000
2-Methylnaphthalene	88.990	66.252	13.031	91.793	40.711	99.872	32.632	130.000	40.000
Naphthalene	24.950	20.240	3.612	27.320	13.160	29.559	10.921	28.000	13.000
Phenanthrene	42.900	33.580	4.685	42.763	24.397	45.667	21.493	95.000	24.000
Phenol	65.070	35.009	13.315	61.106	8.912	69.362	0.656	55.000	15.000

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Shell Development Company SLAP Audit

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Figure 1

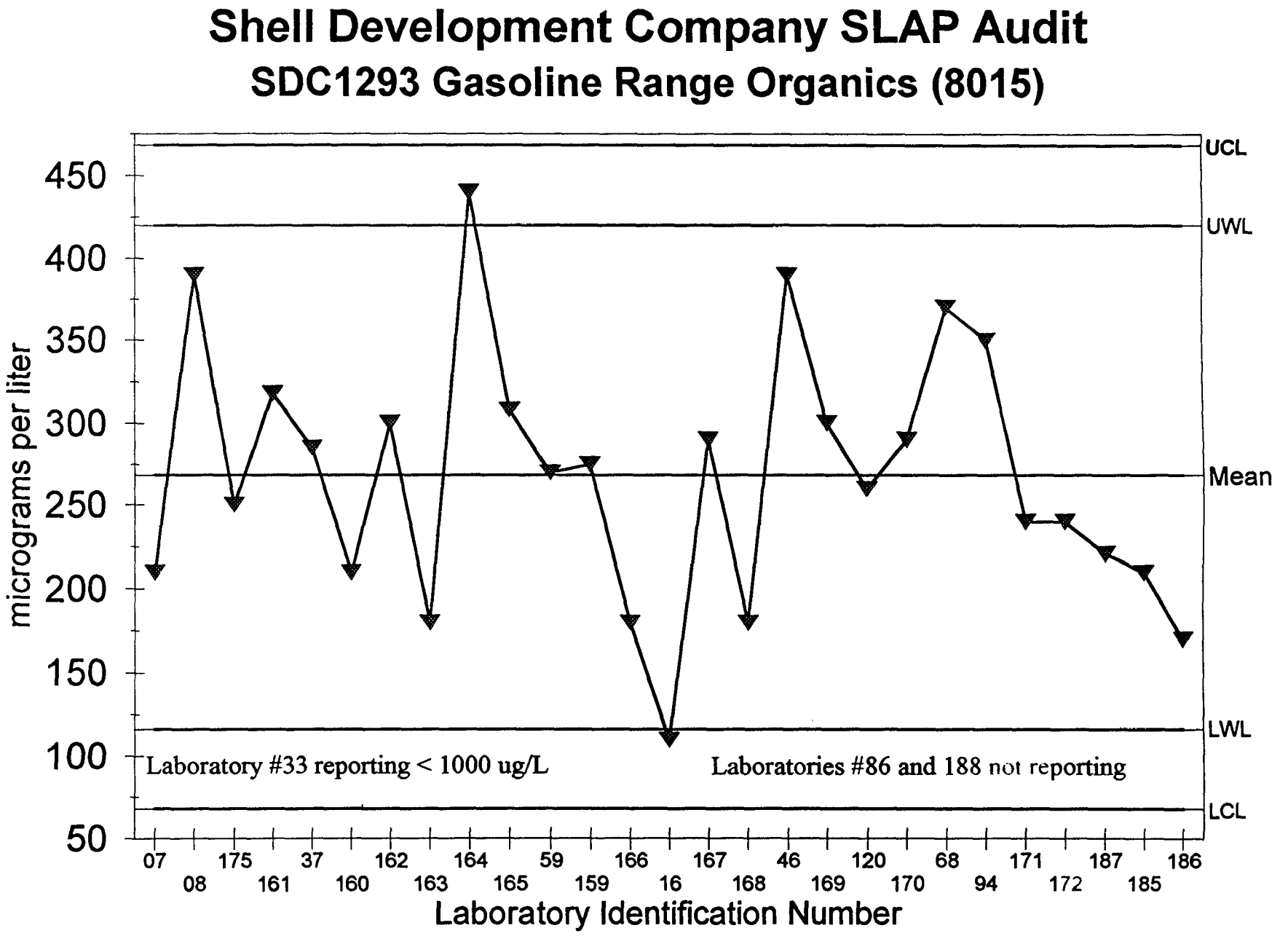

Shell Development Company SLAP Audit
SDC1293 Gasoline Range Organics (8015)
micrograms per liter
450
400
350
300
250
200
150
100
50
UCL
UWL
Mean
LWL
LCL
Laboratory #33 reporting < 1000 ug/L
Laboratories #86 and 188 not reporting
07
08
175
161
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
171
172
187
185
186
Laboratory Identification Number

Figure 2

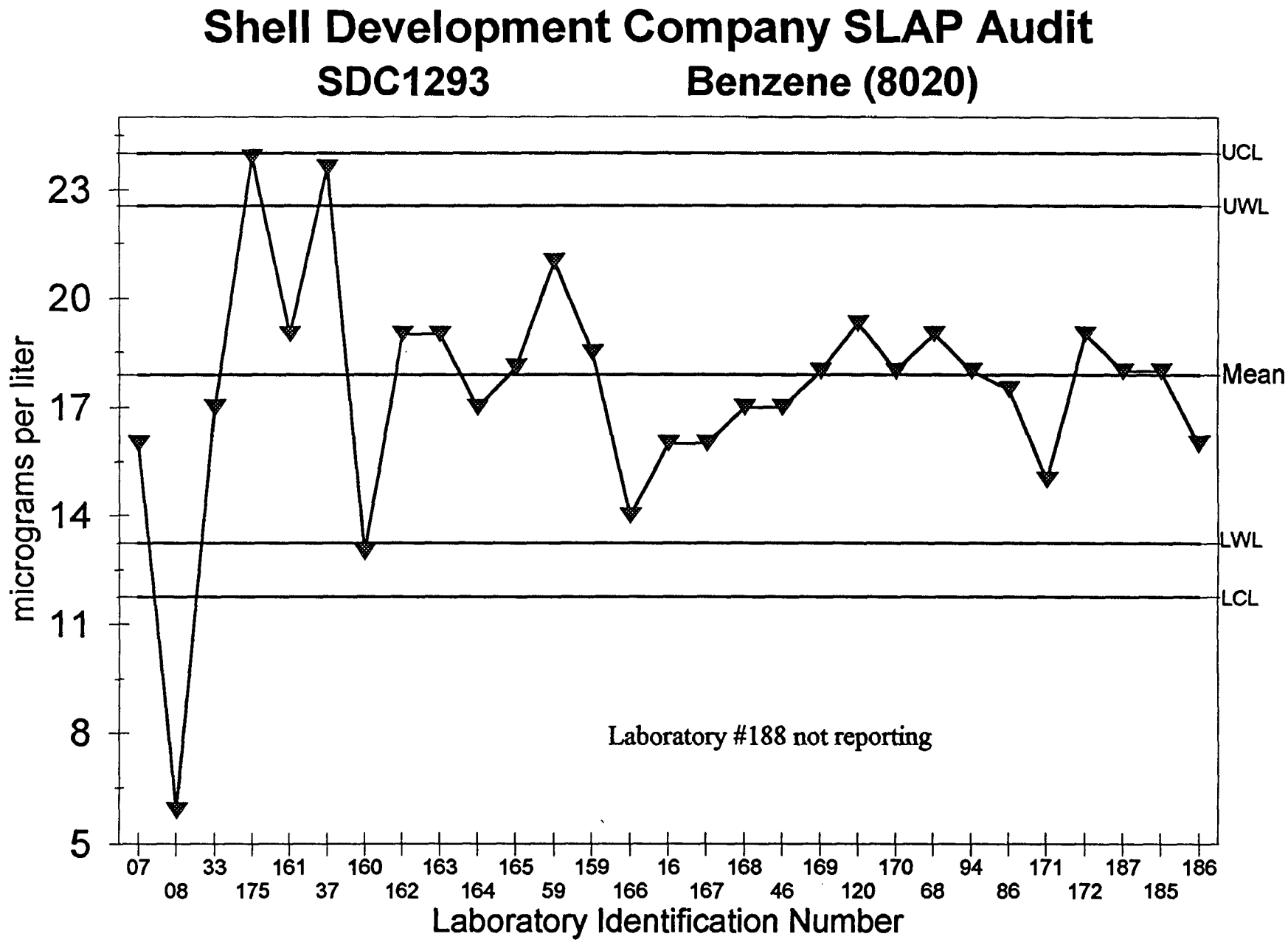

Shell Development Company SLAP Audit
SDC1293
Benzene (8020)
UCL
UWL
Mean
LWL
LCL
23
20
17
14
11
8
5
micrograms per liter
Laboratory #188 not reporting
07
08
33
175
161
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
172
187
185
186
Laboratory Identification Number

Figure 3

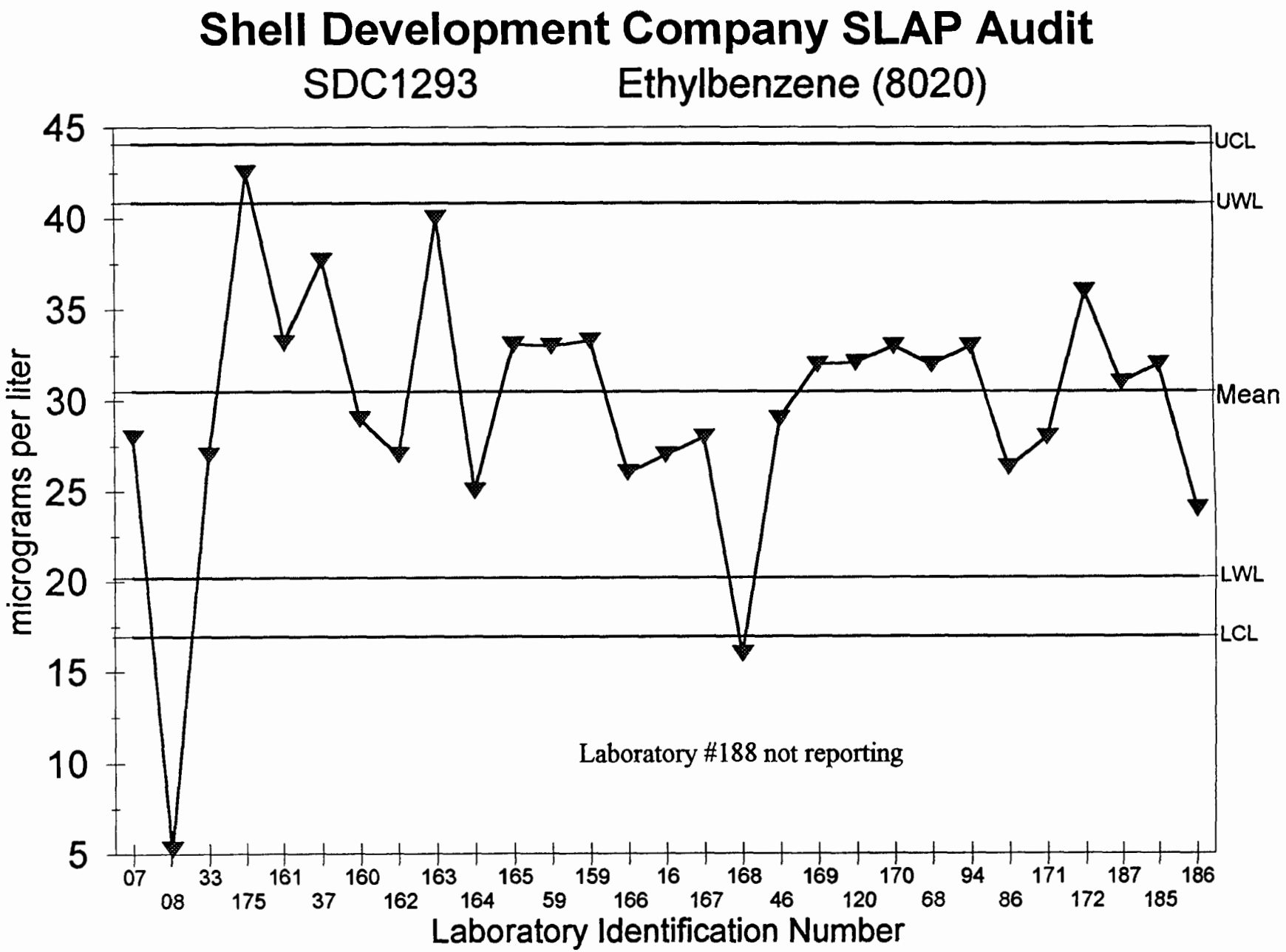

Shell Development Company SLAP Audit
SDC1293
Ethylbenzene (8020)
45
40
35
30
25
20
15
10
5
micrograms per liter
UCL
UWL
Mean
LWL
LCL
Laboratory #188 not reporting
07
08
33
175
161
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
172
187
185
186
Laboratory Identification Number

Figure 4

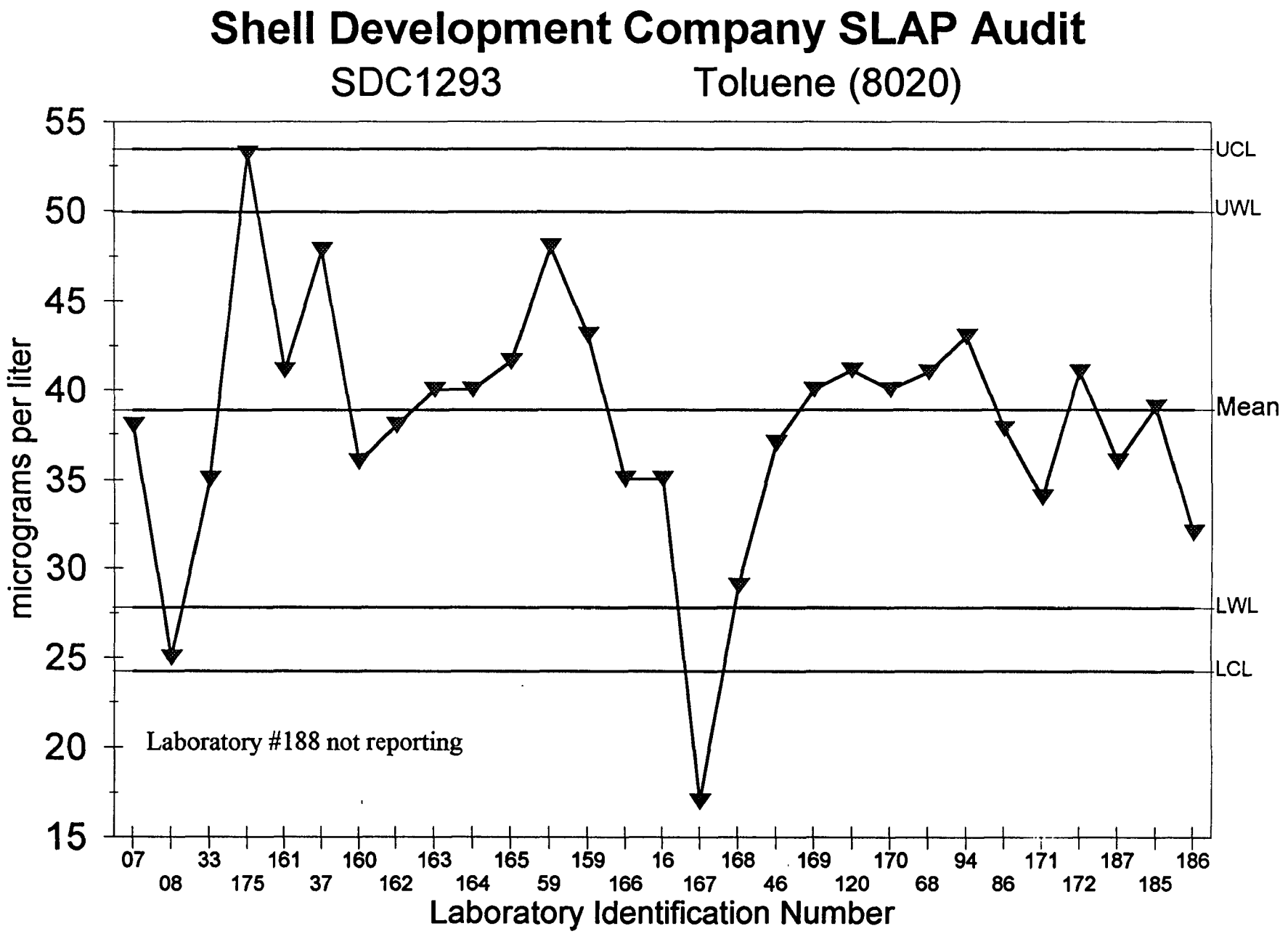

Shell Development Company SLAP Audit
SDC1293
Toluene (8020)
55
50
45
40
35
30
25
20
15
micrograms per liter
UCL
UWL
Mean
LWL
LCL
Laboratory #188 not reporting
07
08
33
175
161
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
172
187
185
186
Laboratory Identification Number

Figure 5

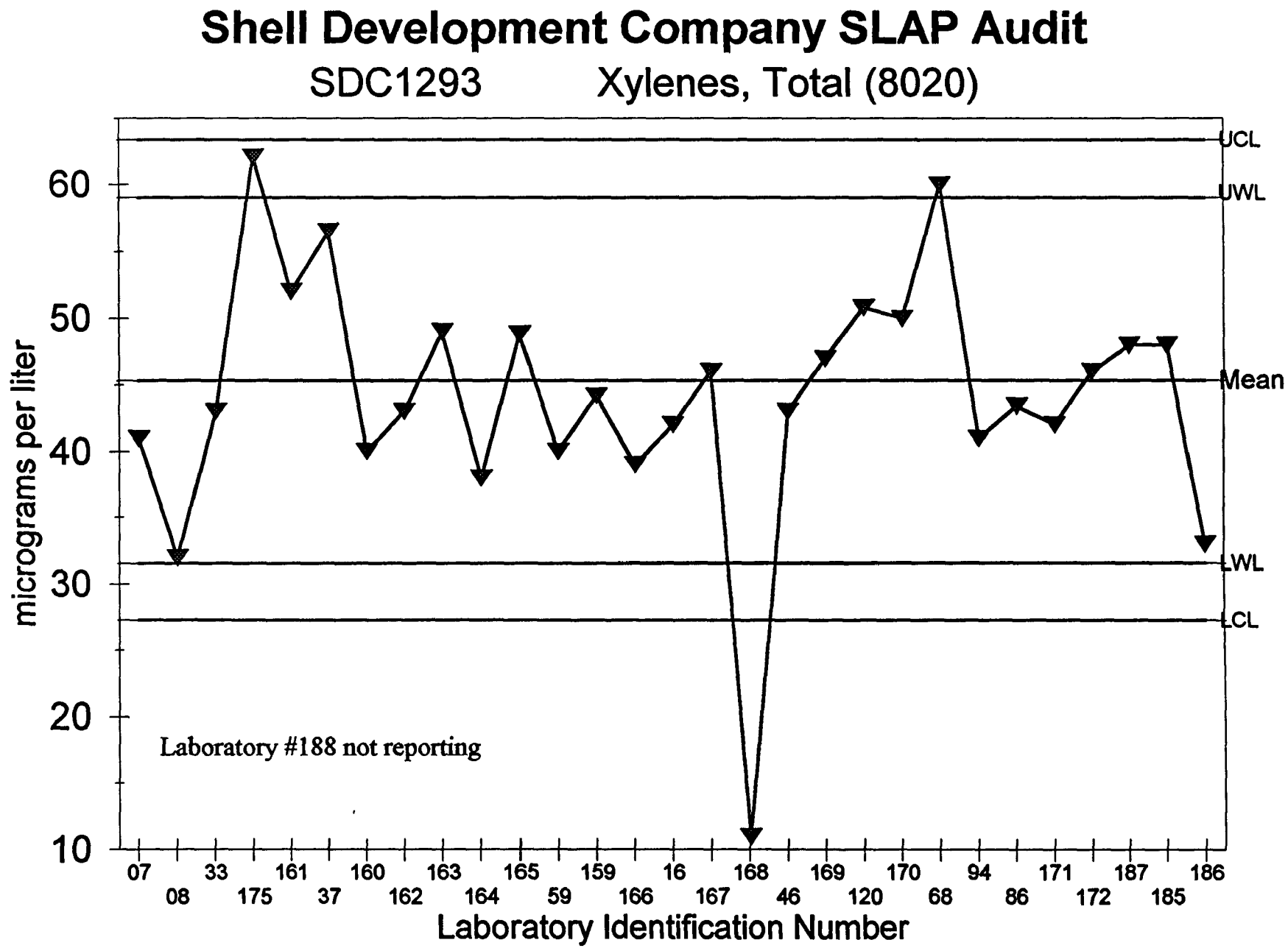

Shell Development Company SLAP Audit
SDC1293 Xylenes, Total (8020)
UCL
UWL
Mean
LWL
LCL
60
50
40
30
20
10
micrograms per liter
Laboratory #188 not reporting
07 08 33 175 161 37 160 162 163 164 165 59 159 166 16 167 168 46 169 120 170 68 94 86 171 172 187 185 186
Laboratory Identification Number

Figure 6

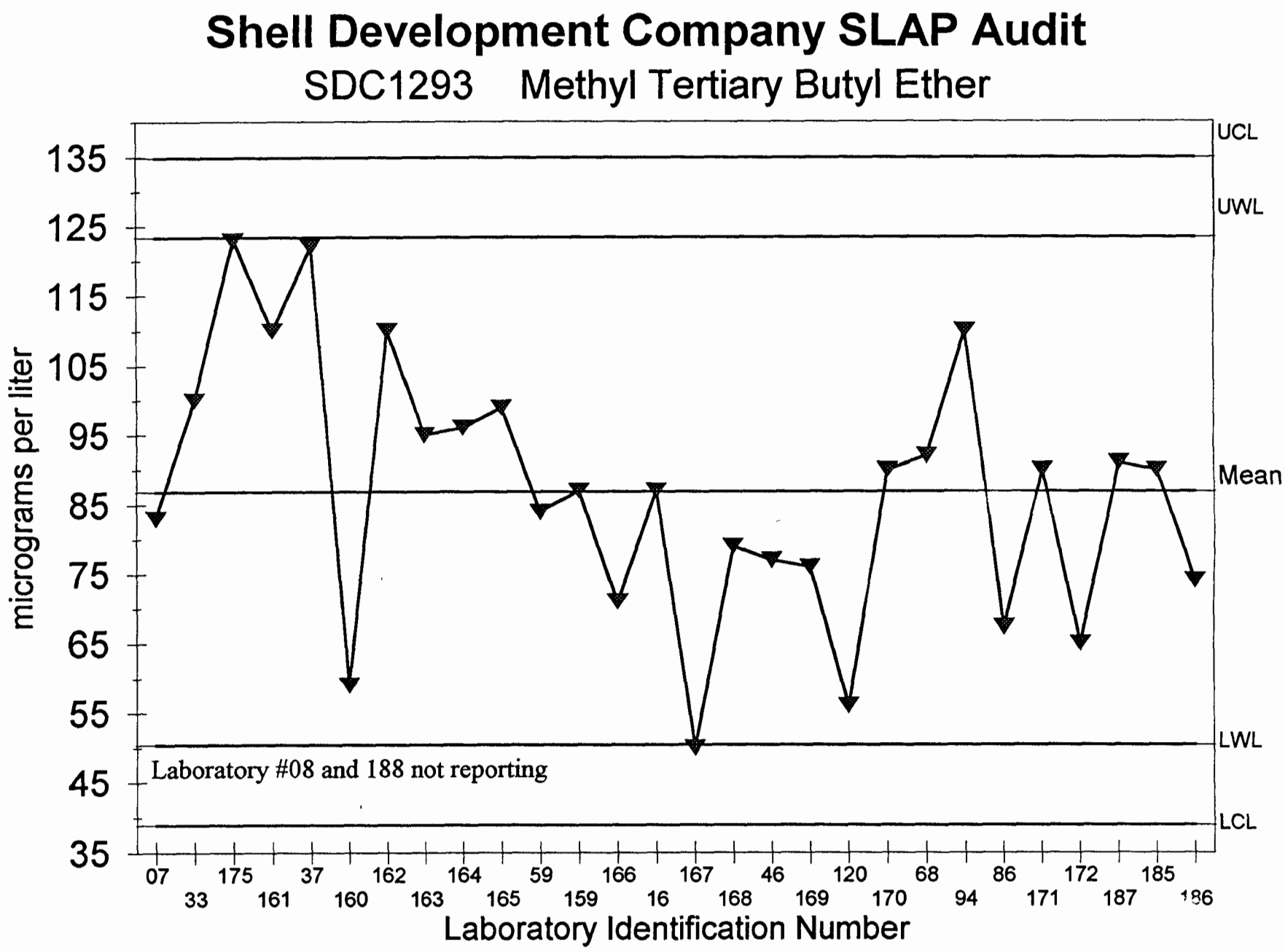

Shell Development Company SLAP Audit
SDC1293 Methyl Tertiary Butyl Ether
micrograms per liter
135
125
115
105
95
85
75
65
55
45
35
UCL
UWL
Mean
LWL
LCL
Laboratory #08 and 188 not reporting
07
33
175
161
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
172
187
185
186
Laboratory Identification Number

Figure 7

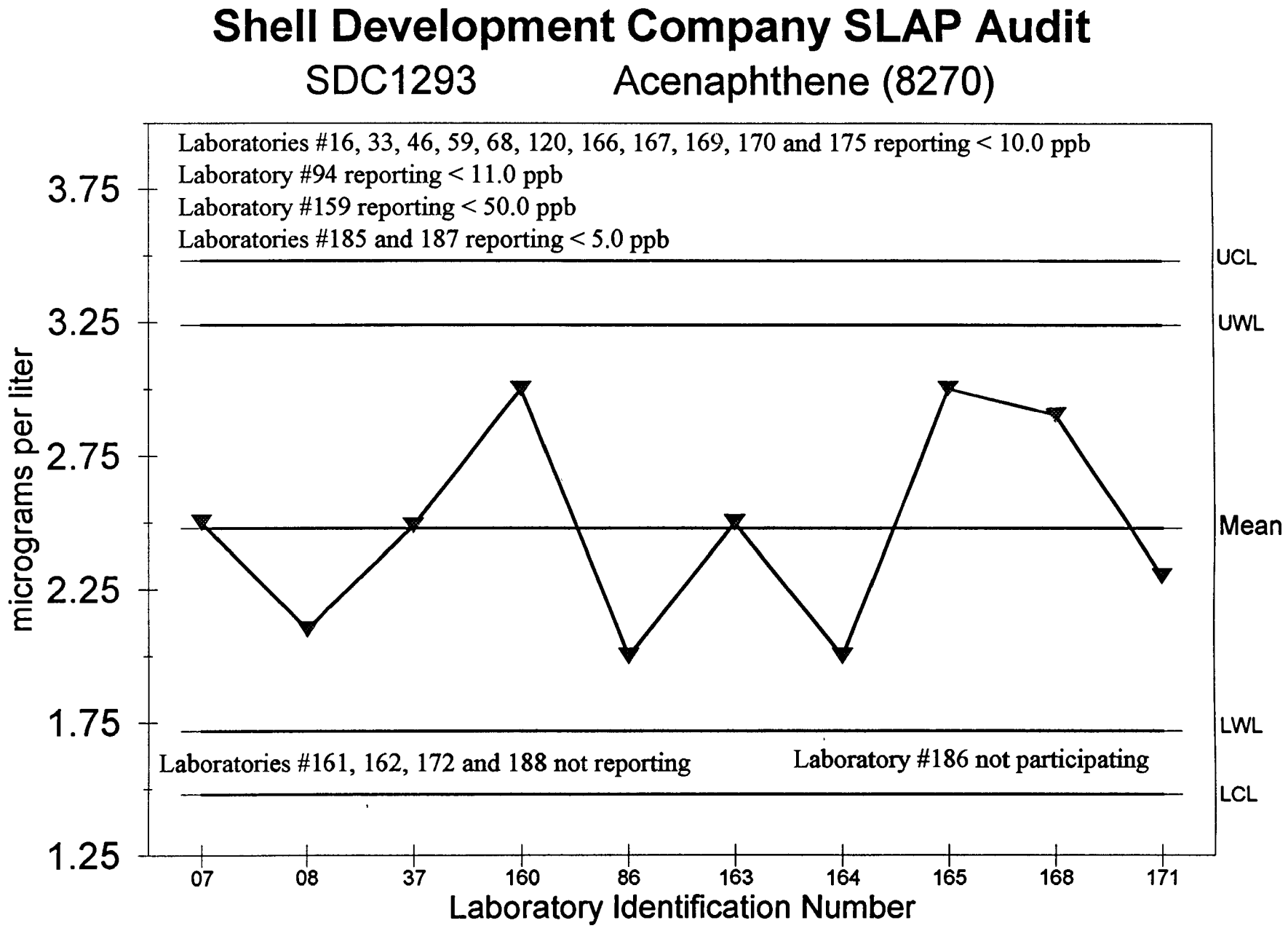

Shell Development Company SLAP Audit
SDC1293 Acenaphthene (8270)
Laboratories #16, 33, 46, 59, 68, 120, 166, 167, 169, 170 and 175 reporting < 10.0 ppb
Laboratory #94 reporting < 11.0 ppb
Laboratory #159 reporting < 50.0 ppb
Laboratories #185 and 187 reporting < 5.0 ppb
Laboratories #161, 162, 172 and 188 not reporting
Laboratory #186 not participating
UCL
UWL
Mean
LWL
LCL
3.75
3.25
2.75
2.25
1.75
1.25
micrograms per liter
07
08
37
160
86
163
164
165
168
171
Laboratory Identification Number

Figure 8

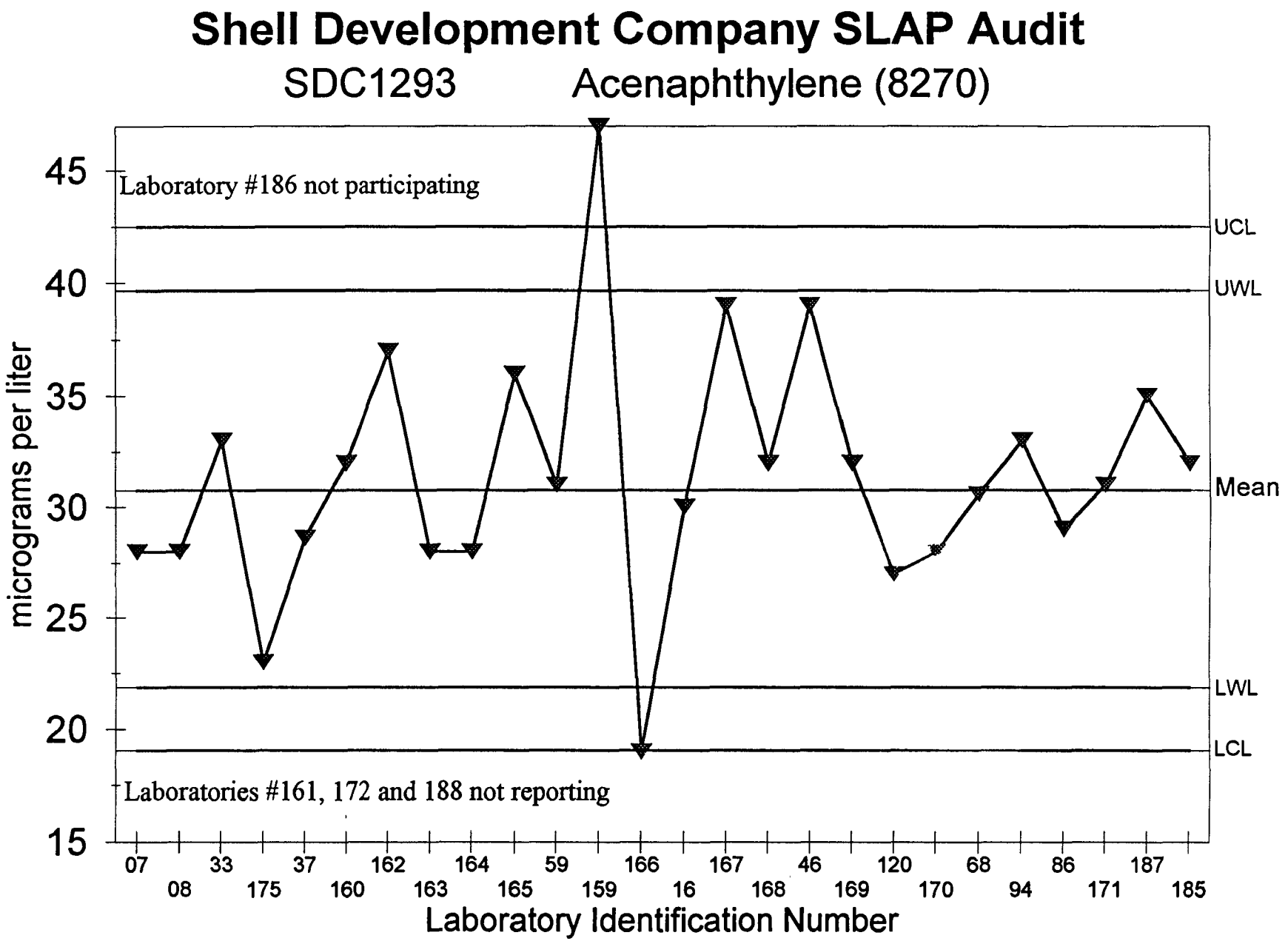

Shell Development Company SLAP Audit
SDC1293 Acenaphthylene (8270)
Laboratory #186 not participating
Laboratories #161, 172 and 188 not reporting
UCL
UWL
Mean
LWL
LCL
45
40
35
30
25
20
15
micrograms per liter
07
08
33
175
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

Figure 9

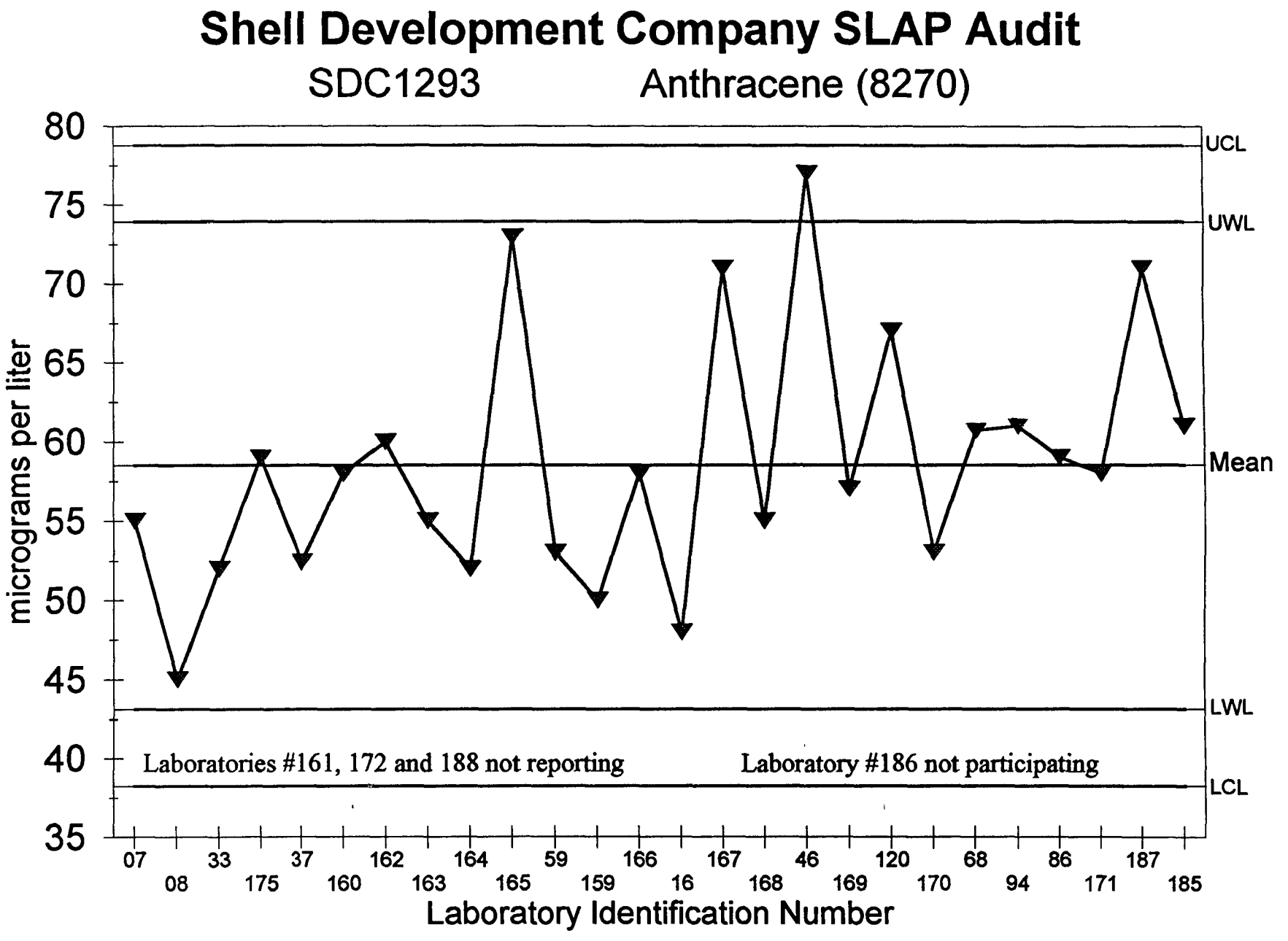

Shell Development Company SLAP Audit
SDC1293
Anthracene (8270)
micrograms per liter
80
75
70
65
60
55
50
45
40
35
UCL
UWL
Mean
LWL
LCL
Laboratories #161, 172 and 188 not reporting
Laboratory #186 not participating
07
08
33
175
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

Figure 10

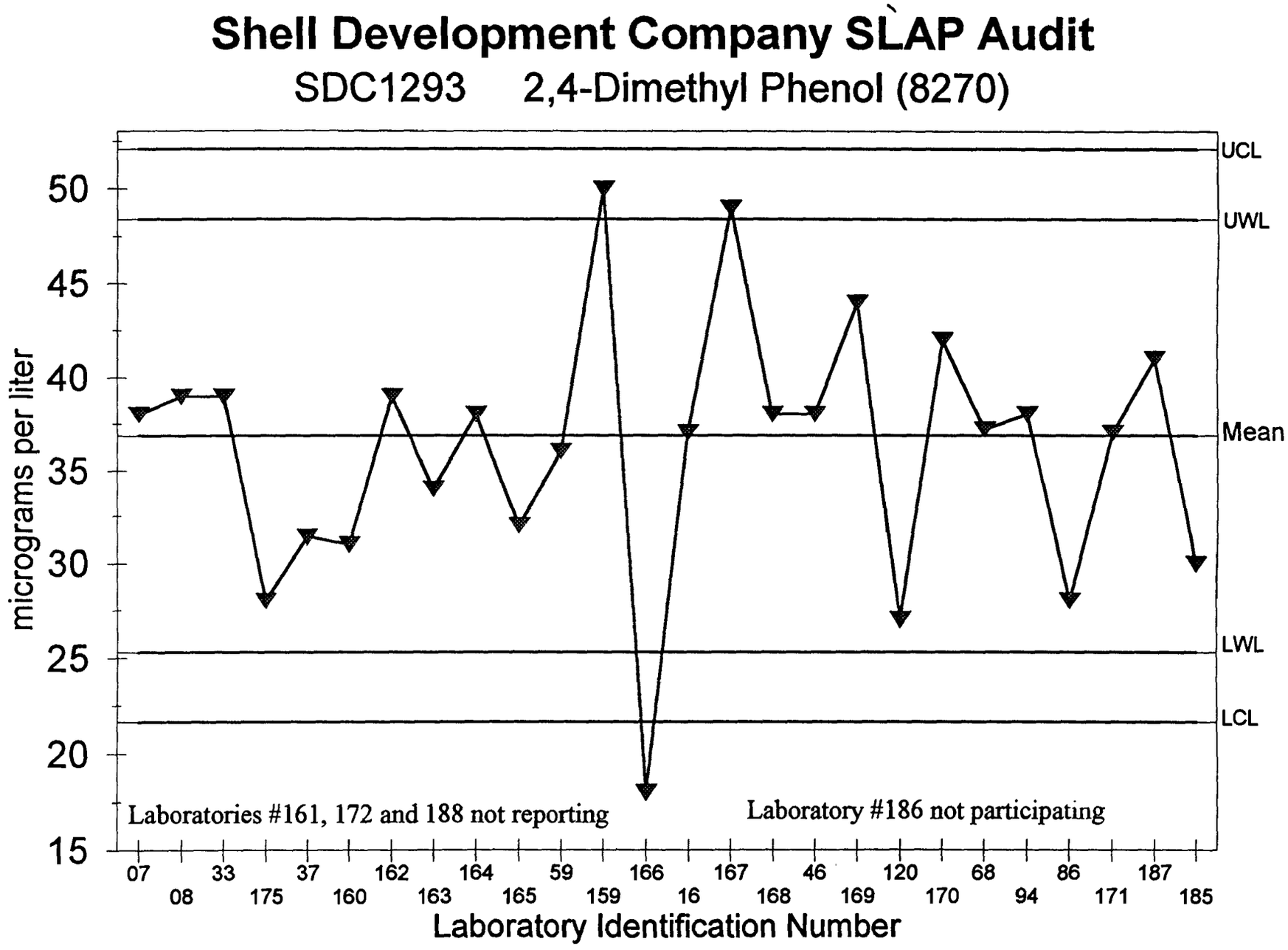

Shell Development Company SLAP Audit
SDC1293 2,4-Dimethyl Phenol (8270)
micrograms per liter
50
45
40
35
30
25
20
15
UCL
UWL
Mean
LWL
LCL
Laboratories #161, 172 and 188 not reporting
Laboratory #186 not participating
07
08
33
175
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

Figure 11

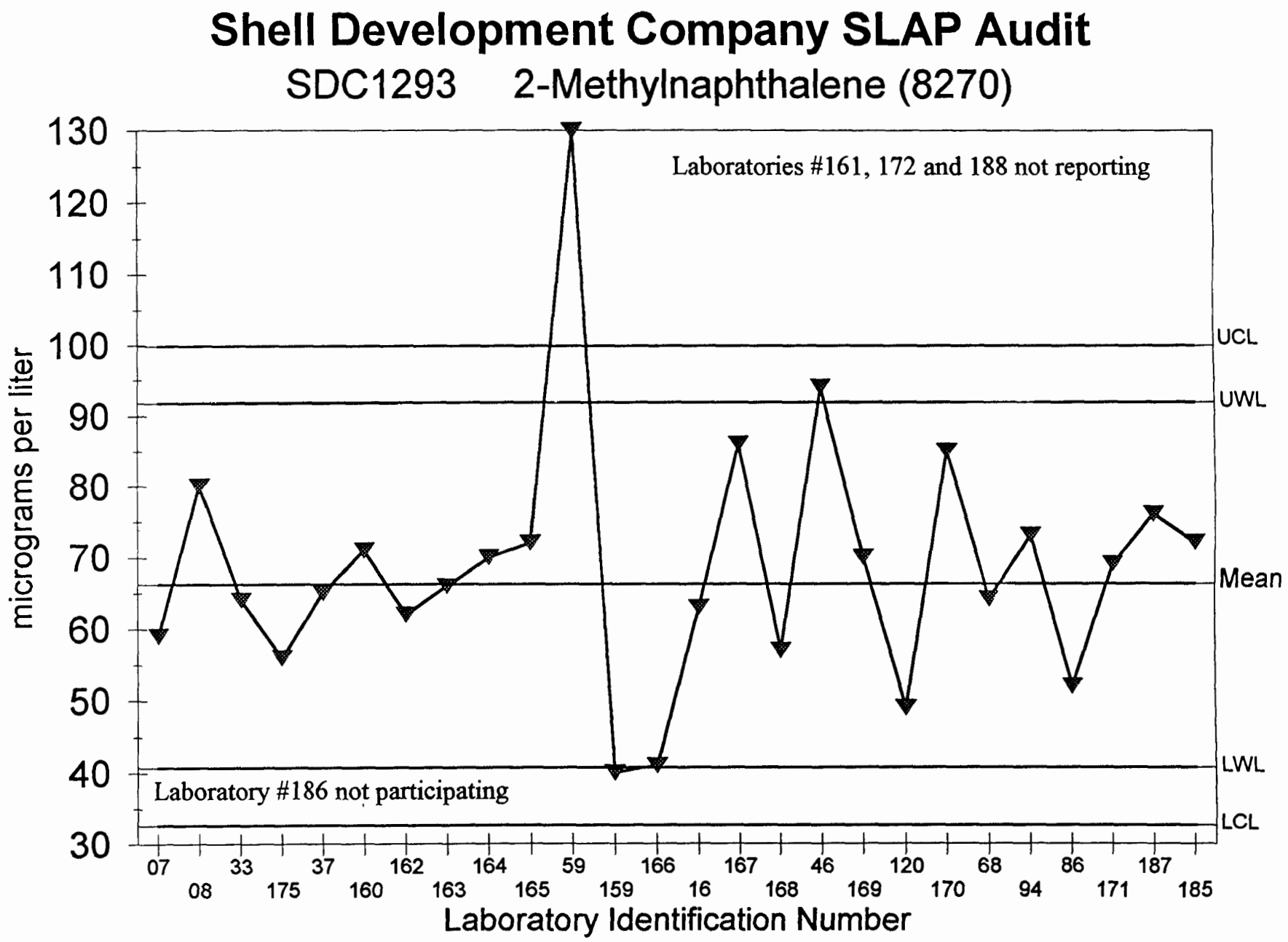

Shell Development Company SLAP Audit
SDC1293 2-Methylnaphthalene (8270)
Laboratories #161, 172 and 188 not reporting
Laboratory #186 not participating
UCL
UWL
Mean
LWL
LCL
130
120
110
100
90
80
70
60
50
40
30
micrograms per liter
07
08
33
175
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

Figure 12

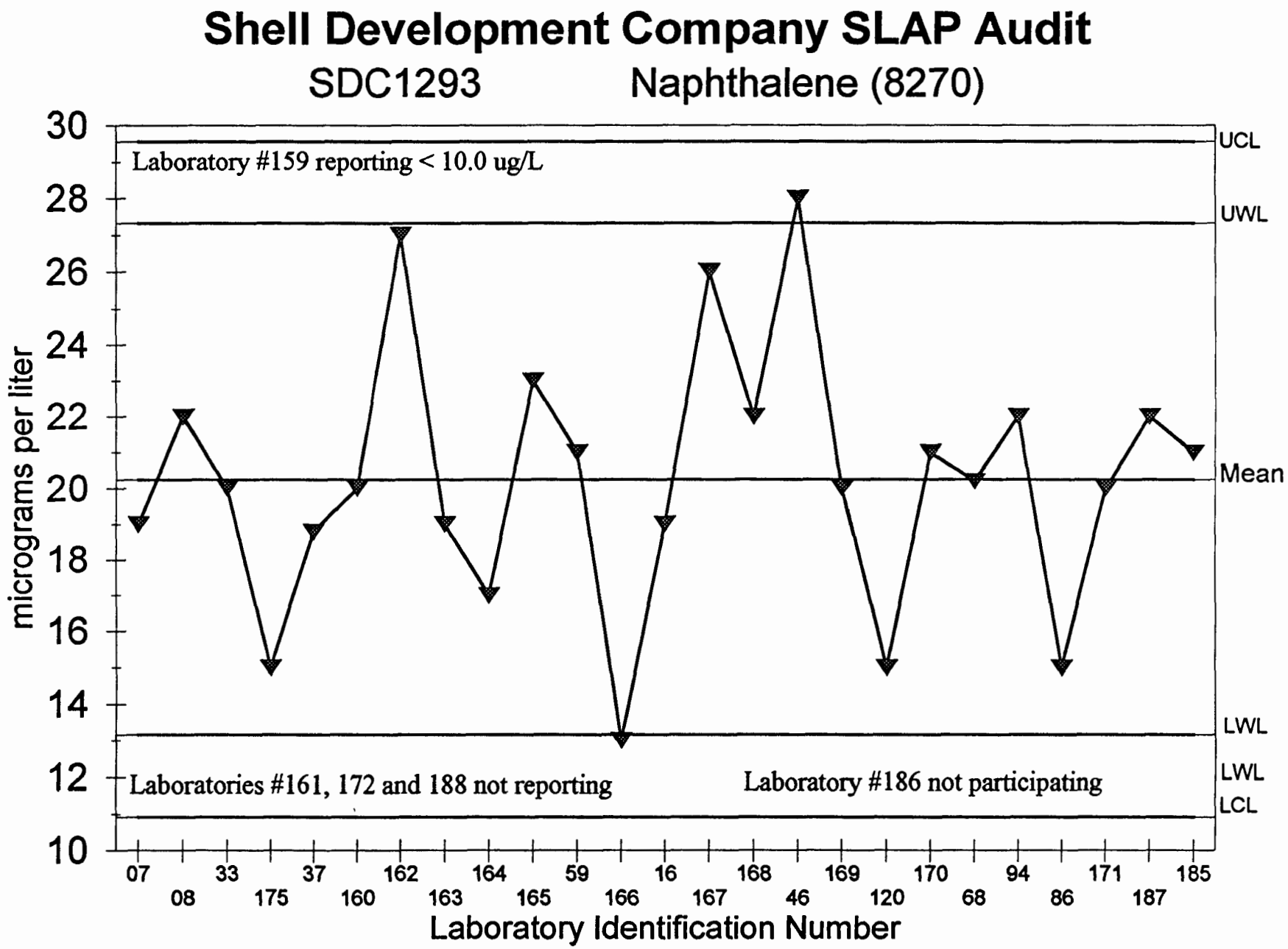

Shell Development Company SLAP Audit
SDC1293
Naphthalene (8270)
Laboratory #159 reporting < 10.0 ug/L
Laboratories #161, 172 and 188 not reporting
Laboratory #186 not participating
UCL
UWL
Mean
LWL
LWL
LCL
micrograms per liter
30
28
26
24
22
20
18
16
14
12
10
07
08
33
175
37
160
162
163
164
165
59
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

Figure 13

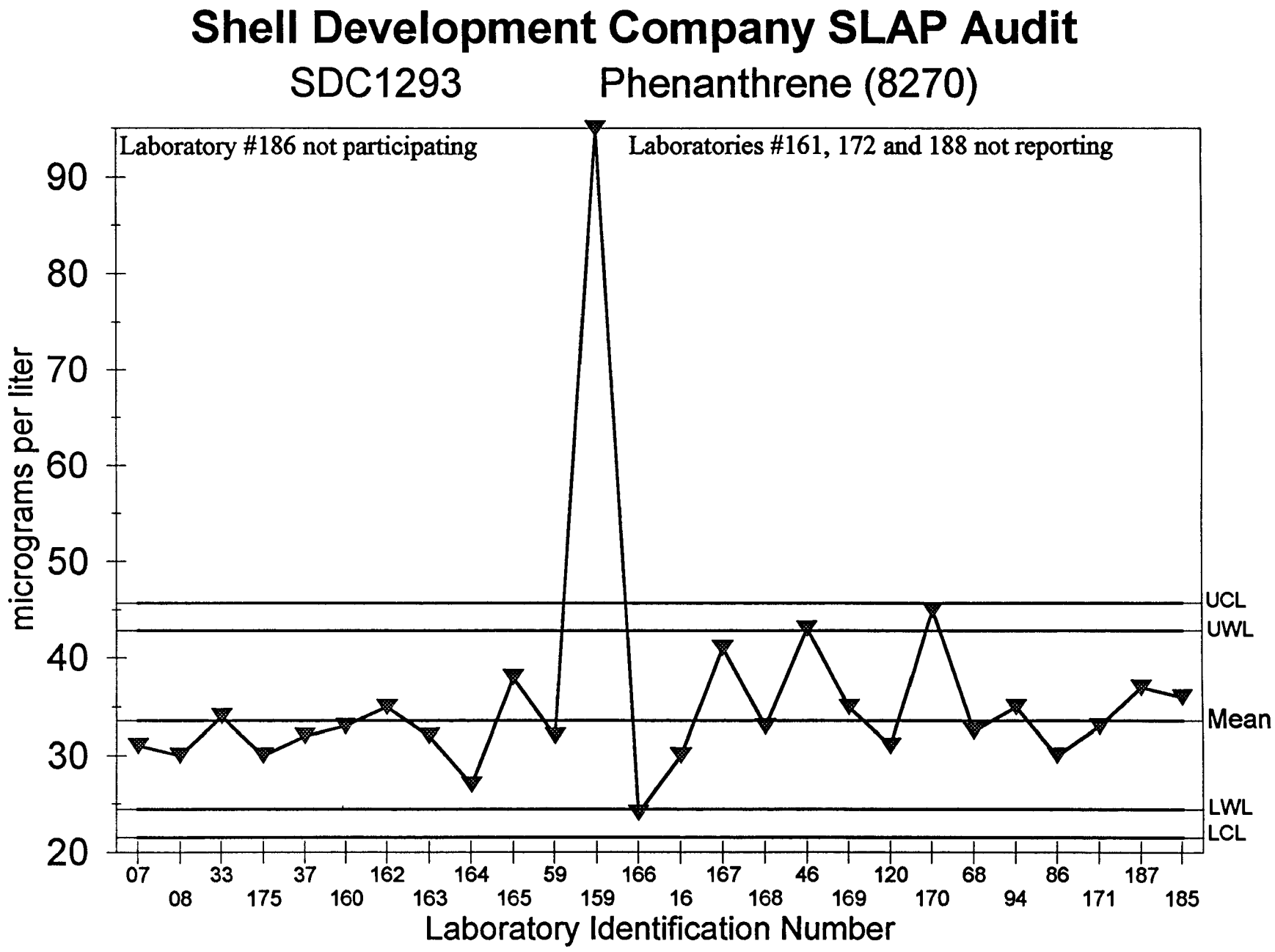
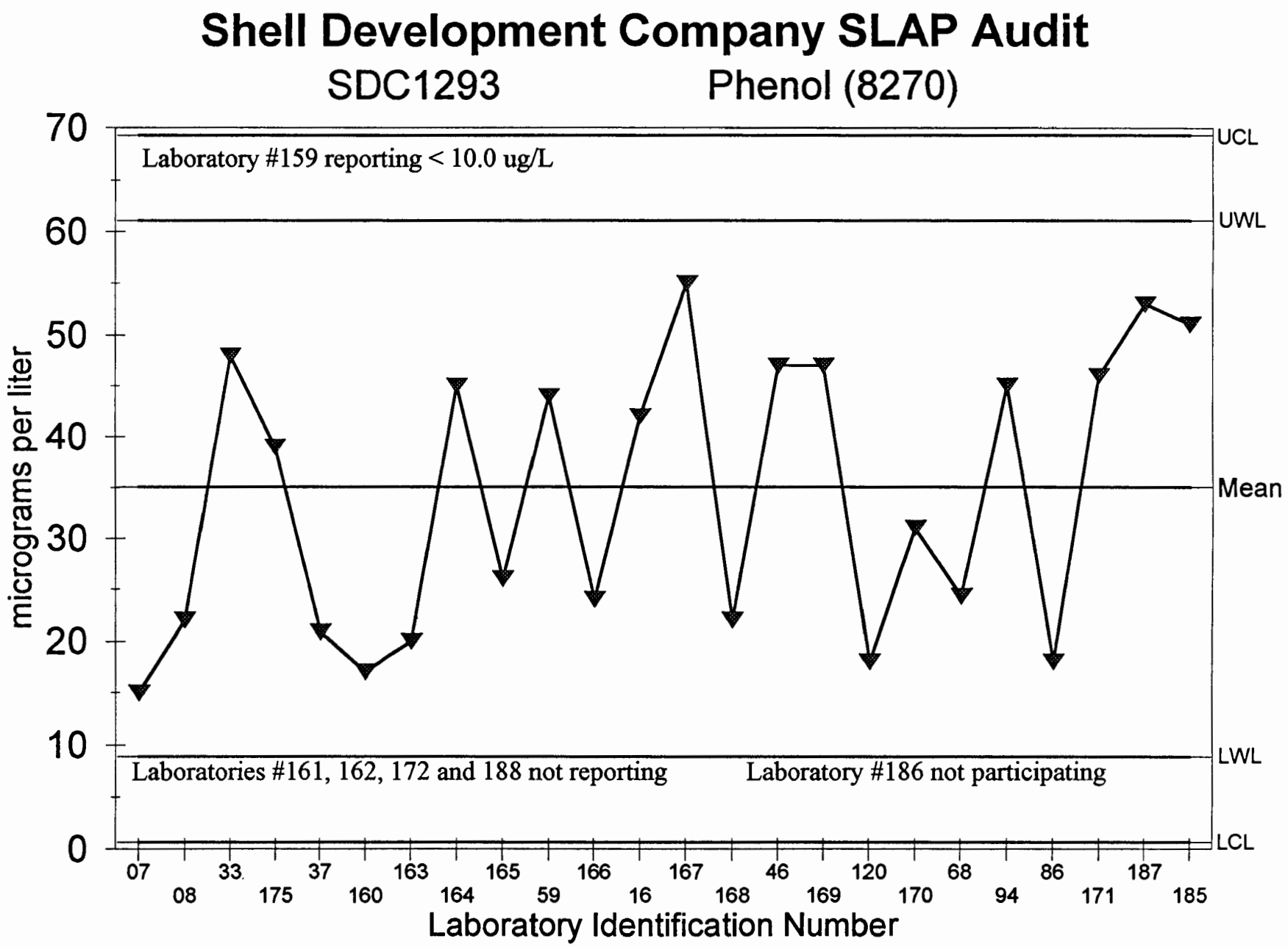

Shell Development Company SLAP Audit
SDC1293
Phenanthrene (8270)
Laboratory #186 not participating
Laboratories #161, 172 and 188 not reporting
micrograms per liter
90
80
70
60
50
40
30
20
UCL
UWL
Mean
LWL
LCL
07
08
33
175
37
160
162
163
164
165
59
159
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

Figure 14


Shell Development Company SLAP Audit
SDC1293
Phenol (8270)
Laboratory #159 reporting < 10.0 ug/L
Laboratories #161, 162, 172 and 188 not reporting
Laboratory #186 not participating
UCL
UWL
Mean
LWL
LCL
micrograms per liter
70
60
50
40
30
20
10
0
07
08
33
175
37
160
163
164
165
59
166
16
167
168
46
169
120
170
68
94
86
171
187
185
Laboratory Identification Number

MR. TELLIARD: Our final speaker of this meeting is Craig Markell from 3M. Craig is going to be talking about an evaluation that they have been running on the use of SPE, solid phase extraction, on the application of Method 608 and the results thereof.

AN EXTENSIVE EVALUATION OF AN SPE SAMPLE PREP FOR METHOD 608

MR. MARKELL: Thank you, Bill.

You know, normally, I would be really ticked off at being placed as the last speaker on the last day, but any time you get to share the podium with professors Stanko and Telliard, it is a great day, and I am highly honored. Also, thanks to all of you for staying.

We first introduced the mighty Empore disk in 1989. At that time, we got initial interest from the drinking water folks in Cincinnati who were having some problems getting solid phase extraction to work on some of the waters and thought they worked pretty well.

However, it has been five years now, and, still, on wastewater, I do not believe we have too many approved methods. There are some that were sort of slipped under the door which I will tell you about in a minute, but there is a huge energy barrier to getting wastewaters approved using solid phase extraction.

So, what I want to do today is tell you a little story about some of the efforts that have gone on and also the latest effort we have.

We were telling people this five years ago. We will still tell you it, we think, not only for drinking water, but, certainly, for wastewaters, especially the finished effluents that are the things you are regulated in your permits for, the 600 series types of analytes.

Now, you all know what a disk is, I think, by now. Hopefully, you do. If not, tell me, and our marketing people will get their hands slapped.

The method is fairly straightforward. There are a few little things you have to know, but, basically, you filter your water sample through it, and then you elute it. You have got the analytes now in organic solvent in concentrated form.

Then there are some advantages in using disks, and I will not go through all these, especially in view of the lateness of the day and the surely nature of the attendees.

Now, drinking water. Lots of drinking water approvals. There is no problem there whatsoever. We are looking here at 1991, we got some approvals already in some of the methods for semi-volatiles, 525.1, and so on and so forth.

Supplement II was written in 1992. That is right now in the approval process, and we expect Supplement II perhaps to go final later this year.

Finally, this is the one they slipped under the door. I am not sure who did this, but I think I know. In 1993 for the pesticide manufacture effluent guidelines, we actually saw some of the drinking water methods approved for wastewaters which was rather historic, considering that the drinking water folks wrote these methods, but the wastewater people actually approved them first. How did that ever happen, Bill?

MR. TELLIARD: We had to use them first.

MR. MARKELL: Now, drinking water is a no-brainer for most people. There are no problems with drinking water. It tends to be a pretty clean matrix.

What is the objection to the dirty water samples? Well, there are a couple of objections. One is very legitimate that if you have suspended solids in your water sample and you filter it through any sort of bed of particulates, whether it is in a tube or a disk form, you will wind up plugging the matrix.

The plugging depends on the number of particulates you have, the size of the particulates, the physical nature of the particulates, and the pore size of your matrix. That is really about all there is to it. Fairly straightforward, but if you have got a liter of water you have got to filter, and you can only get 250 ml through, you have got a problem there.

So, that is one objection. The second is some chemical interactions of the analytes with the matrix and also the solid phase. For example, suppose you have got an analyte that somehow complexes with humic materials made into a water soluble complex that can go sailing right on by the reverse phase/solid phase matrix. People are objecting on the grounds that maybe that can happen.

It is something we have never actually seen good data on. In fact, the papers that have been published do not have compelling data. They show a slight drop in recovery, but there has never been a good paper published on that that I have seen.

The other thing that perhaps is a little more real is if you have hydrophobic analytes that are stuck to hydrophobic particles, organic particles in your sample, what is going to happen to the analytes stuck to that particle? That is a legitimate concern.

At any rate, what I want to do now is tell you a little about some of the studies that have been done on Method 608 and the analytes. These have been done ever since 1990, '91, and have some really excellent results.

These are just some of the things you can do to counteract the plugging. I guess the things I would really recommend is you can always go to a larger disk, use a little bit more horsepower. You can let the sample settle and decant most of it before you throw the sediment on the disk. That helps a lot. That is something we always do.

A filter aid is nice. So on and so forth. You will see these slide copies in the proceedings.

MR. TELLIARD: And multiple disks.

MR. MARKELL: And multiple disks. Good point. If you get to the point where you just cannot filter any more through a single disk, save the water sample and put a new disk on, and you can finish up. That is a legitimate strategy, especially with large volume samples.

In fact, one guy just reported using five disks to do 100 liters of water. It is the only way you can legitimately do 100 liters of water.

Now, here are the analytes stuck to particles, and symbolizing the analytes are As that you can see on the red particulates. Okay, you are doing this in a liquid-liquid extraction, separatory funnel. You are shaking these particles up with the analytes on them, and you have got a micro-emulsion of methylene chloride. You have got water-saturated particles with the analytes on them, and you have got methylene chloride with which you are expecting to hit those particles, wet them out, and extract the analytes off.

It just is not going to happen. We have seen evidence of this. In fact, the last study I am going to show you proves that this is, indeed, a problem. So, you cannot expect liquid-liquid to work all the time in this type of format.

If you catch these particles on the disk and elute them, you can let them soak for a while. The water is all gone. You can actually let it dry if you like. You may well have a better crack at getting those analytes off of the particles than you will in a liquid-liquid extraction.

So, here is the traditional Method 608. You all know it, but, basically, you take a sample of water, you extract it with methylene chloride, shake it up, combine and dry them, take it down to 1 ml, and take it up in hexane to get rid of the methylene chloride for your electron capture detector.

Here is the first study that was done. This was really a good study. It was done by some of the folks at Waste Management. Anne O'Donnell was the one in particular. This was presented at the 1991 Pittsburgh conference.

Here is the way she did it. She took a disk. This was a 47 mm C_{18} disk. Conditioned it, ran the water sample through, added a little methanol...probably not necessary but she did...extracted with a little ethyl acetate which is a nice solvent to use, and I will tell you why in a minute, took it up with ethyl acetate, dried it, and ran it by electron capture detector.

That is the method, fairly straightforward.

The samples she did were RCRA types of samples. Can I use that word, RCRA? They were from ground water monitoring wells around their dump sites.

For those of you who do not know Waste Management, it is the biggest garbage company in the world.

At any rate, here are the recoveries and RSDs of the samples. Really nice recoveries. I will not spend a lot of time on them, but these are for the single component analytes. Nice looking RSDs, mostly single digit, and when they went down to the MDL level, still very nice data. There are a lot of data points in this study, and if anybody wants it, by the way, I can send you a copy.

I am afraid to use this slide. These are the MDLs, and what I will tell you is they compare very nicely to the standard liquid-liquid extraction method.

I will let you read these conclusions, but to make a long story short, she was convinced it worked very nicely for their types of samples and actually recommended that they approve the method. They never did, because it never became EPA approved.

Now, here is another method. I have got a couple of slides. These are the folks at Twin City Testing. This was actually reported here a couple of years ago by Merlin Bicking.

What they looked at was a 90 mm disk. Now, all of a sudden, they were looking at wastewaters, and there were problems with plugging. So, they used the larger disk, and it worked very nicely.

They also used a little glass fiber prefilter on top to catch some of the chunks and prevent some of the plugging. They did a 1 liter sample in this case, eluted with 3 x 15 ml dichloromethane.

Remember, the last study used ethyl acetate. This one uses dichloromethane. Then they dried it and concentrated it.

Here are the results. There were four authentic wastewaters here. What they did was a pesticide manufacturer's effluent, a POTW, a pulp and paper mill which was the worst matrix of all, had all kinds of cellulosic material floating around in it, and petroleum refinery effluent.

Now, they took the samples, spiked them, shook them up, and let them sit overnight so that these hydrophobic analytes can come to equilibrium with the particles in the sample, and that is an important point. If you ran it right away, it probably would not all adsorb to the particulate in the sample, and we wanted that to happen.

So, great recoveries for the most part, and great RSDs for the most part. I am going to point out a problem here, and it is the pulp and paper matrix. 68 percent recovery which is not a disaster, but it is a little lower than you would like to see, and the RSD is correspondingly higher than you would like to see.

That is a problem, and what the problem was is that the pulp and paper matrix had this cellulosic garbage saturated with water onto which the analytes had equilibrated. So, a lot of the organochlorine pesticides were stuck to the cellulosic material which was, in turn, saturated with water.

Well, here is the point. This is a simplistic diagram of what is happening at the molecular level. You have got our base sorbent particle. You have got the C_{18} chains here. The analyte comes in and sticks to the C_{18} chain through a hydrophobic interaction.

Obviously, when you are done with the extraction, you have got water everywhere. It is saturating the internal pores of the sorbent. So, you have got water covering up that site where the analyte is stuck.

You come in with something immiscible with water like dichloromethane. Hexane is even worse. It just cannot get through that water layer and get the analytes off efficiently. You have to use large volumes of elution solvent, and it still may not work.

Here is just an idea of some of the solubilities of water. Hexane, of course, will dissolve almost no water. You get up to methylene chloride, a little bit, but, really, you have got to get up to things like methyl t-butyl ether or ethyl acetate to really get that water out of the way. Acetone, of course, is miscible with water and a pretty good solvent, too.

Well, here is the latest work I really wanted to show you. This was presented at PittCon this year. It is the latest and, certainly, the most extensive study in Method 608 using solid phase extraction.

What they did here was a little different from the other two studies. They conditioned, took a liter sample through the disk. These are 90 mm C_{18} disks. They eluted

first by wetting the disk with 5 ml of acetone. This gets all the water out of the way, and it is no longer a problem even if you have some saturated particulate on top of your filter.

Then they eluted with dichloromethane a couple of times with 15 ml, dried it, took it down to volume, and shot it in the ECD. So, the difference here is the acetone, really.

You know what the disks are. Here is what a 90 looks like if you have not seen one.

What they did also was use some supplemental filter materials, glass fiber filter and/or some filter aid. They did not have to use this in all samples. I just wanted to show you what the scheme is.

You put a little in situ prefilter on top of the disk, and that can help you in a number of ways. There is one fellow I talked to, Paul Marsden from SAIC, who claims that they have been experimenting with a filter aid material. Not only does it make the filtration faster, but it helps recoveries in most cases simply because it is spreading the suspended solids out on a larger surface area, and it is easier to elute the analytes in there.

It is hard to read this. Basically, these organochlorine pesticides were spiked in at about 0.2, about 1.0, and about 5 ppb in the sample. Again, it was shaken and allowed to equilibrate with the sample.

Here is what the samples looked like. We had 10 samples which represented 5 SIC codes. There were some from the chemical industry, pulp and paper people, pharmaceutical, refuse, and sewerage.

What we are seeing here is a range of pHs, a range of suspended solids, a heck of a range in dissolved solids, and that is the characteristic of these samples. Obviously, authentic samples.

Now, you cannot tell much from this. The yellow bars show you the percent recovery of the disks. The blue bar is a side-by-side done on the same samples using a liquid-liquid extraction and separatory funnel, Method 608 in other words.

What you are seeing is that, with a couple of exceptions which I am going to focus in on and point out in a minute, the results are comparable. They look very good. We are getting results usually above 80 percent recovery, even at those low levels. It is something any reasonable analytical chemist would be proud to have.

Standard deviation, these are scattergrams, but what you are seeing is the standard deviation of the disk plotted against the standard deviation of Method 608, and, in fact, there is certainly no trend here. There is a bit of scatter but nothing consistent. Both had about the same RSDs.

The MDLs, again, I am afraid to use this slide, but the MDLs are reasonably equivalent. Certainly, there is no high or low trend here.

Now, everybody is afraid that if you use a new technique, there will be that nightmare matrix out there waiting to come into your lab, and your new method is not going to work on it. Well, there was a nightmare matrix, and it was the pulp and paper.

What you are seeing here is, in the yellow, the traditional Method 608 result. The blue is the disk result.

It turns out, if you notice, the nightmare matrices, 40 percent recovery or so, were actually on the Method 608. The separatory funnel method simply did not work on these samples. We were getting about a 40 or 50 percent recovery, and I suspect the reason is because the analytes had equilibrated with the water saturated suspended solids, and the methylene chloride just could not get in there and pull them off the particulate.

Maybe continuous would have been better. We did not try it, but the nightmare matrix in this case was for Method 608, not the disk modification which actually worked reasonably well. We are looking at about 80 percent recoveries here.

Again, there what you can do is actually let the methylene chloride soak into those suspended solids and dig off the analytes.

So, I will let you read these comparisons. The bottom line is this is the most extensive study that has been done yet.

What we have done is submitted this to the EPA as an alternate test procedure. We are fairly confident that it will pass the review of procedure and we will see some equivalent results. That is really the key, is equivalency here, and we certainly hope to see something by perhaps the end of the year, maybe early next year.

So, that concludes what I have. Thanks again for staying.

SPE Disks *Will* Replace LLE for Water Extractions

Method for Using Empore Disks

1) Pre-Wash Disk With the Final Eluting Solvent
2) Pre-Wet Disk with Methanol
3) Pass Water Sample Through Disk
4) Elute Disk using an Appropriate Solvent
5) Dry and Concentrate Elutant, if Necessary

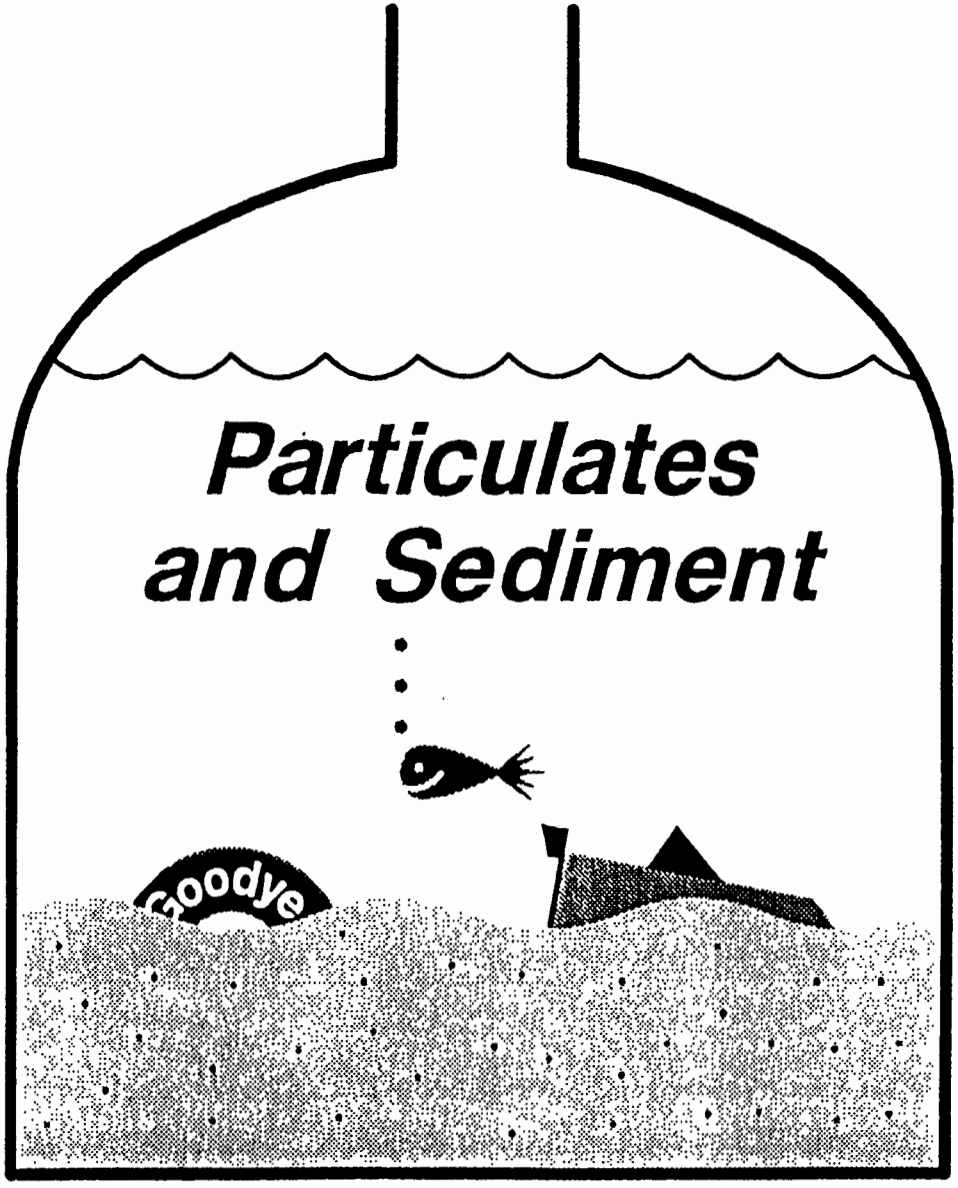
Why Disks?

- Higher Flow Rates Through a Large Diameter Bed (πr^2)
- Lower Back Pressure Through a Thinner Bed
- Smaller, More Efficient Particles (8 μm)
- Uniform Flow - No Channeling
- Inert, Clean

SPE Incorporation Into EPA Methods

1991	Drinking Water		
	506	Phthalates	
	525.1	SOCs	APPROVED
	550.1	PAHs	
1992	Supplement II		
	7 SPE Mtds or Options		Published
1993	Wastewater, Pesticide Mfg. Effluent		
	515.2	Acid Herbs	
	525.1	SOCs (Plus Cmpds)	APPROVED for Effluent
	548.1	Endothall	
	553	Benzidines, ONPs	
	555	Acid Herbs	
	Drinking Water		
	515.2	Acid Herbs	
	548.1	Endothall	Proposed Approval
	549.1	Diquat/Paraquat	
	552.1	Haloacetics/Dalapon	
	555	Acid Herbs	
	525.2	SOCs, Expanded	

Footnote: Allow Use of SPE for 507/508


Particulates
and Sediment
Goodye

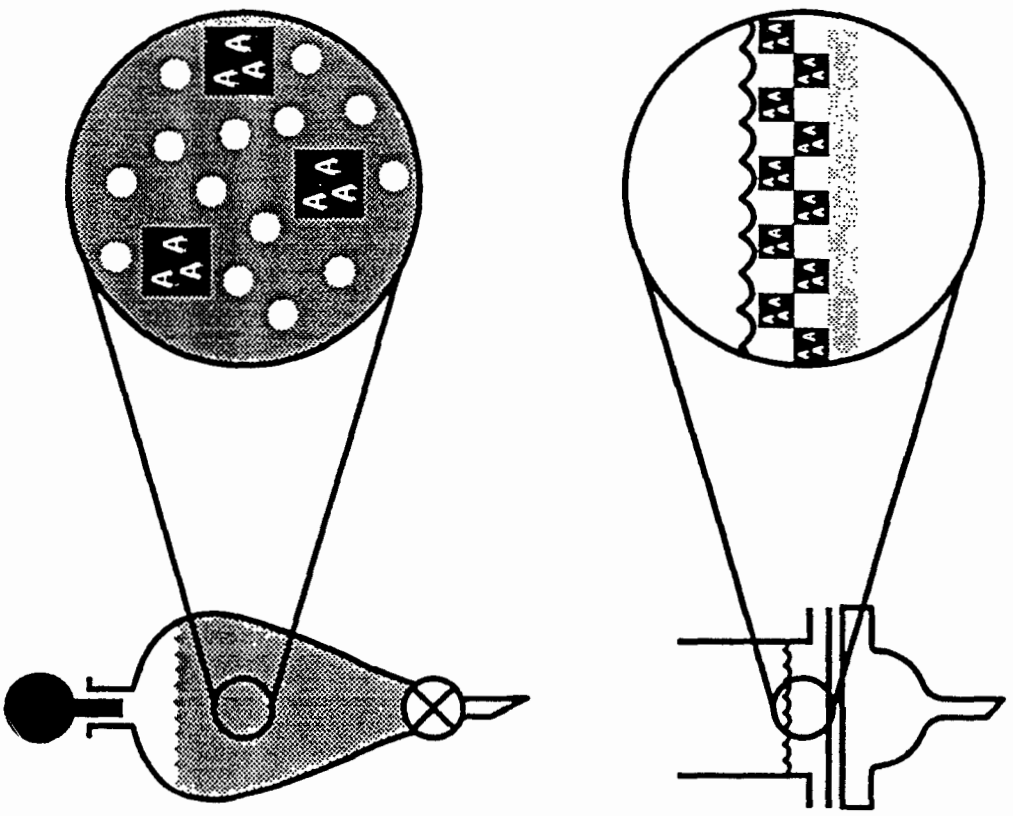
Slow Flows With "Dirty Water"

Suspended Solids Can Plug Pores in Disk - Severity of Problem Depends on Size and Concentration of Solids

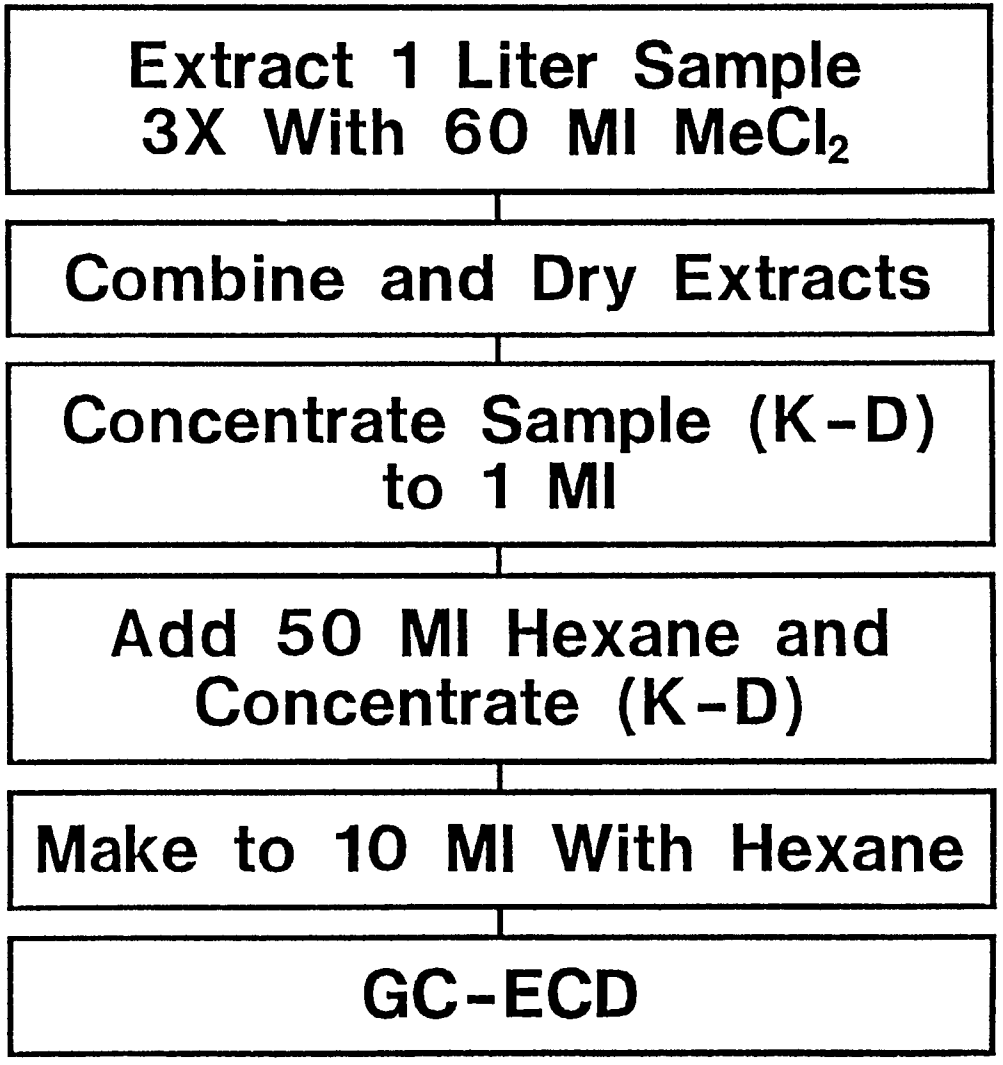
Worst Problems Are Often With Water High in Biological Activity (Ponds) or Fine Clay

Symptoms
- Flow Rate Drops Off Rapidly With Time

Remedies
- 90 mm Disk
- Smaller Volume
- In Situ Prefilter
- Filter Aid
- Settle and Decant Sample
- Good Vacuum
- Split Sample, Combine Eluates



Method 608

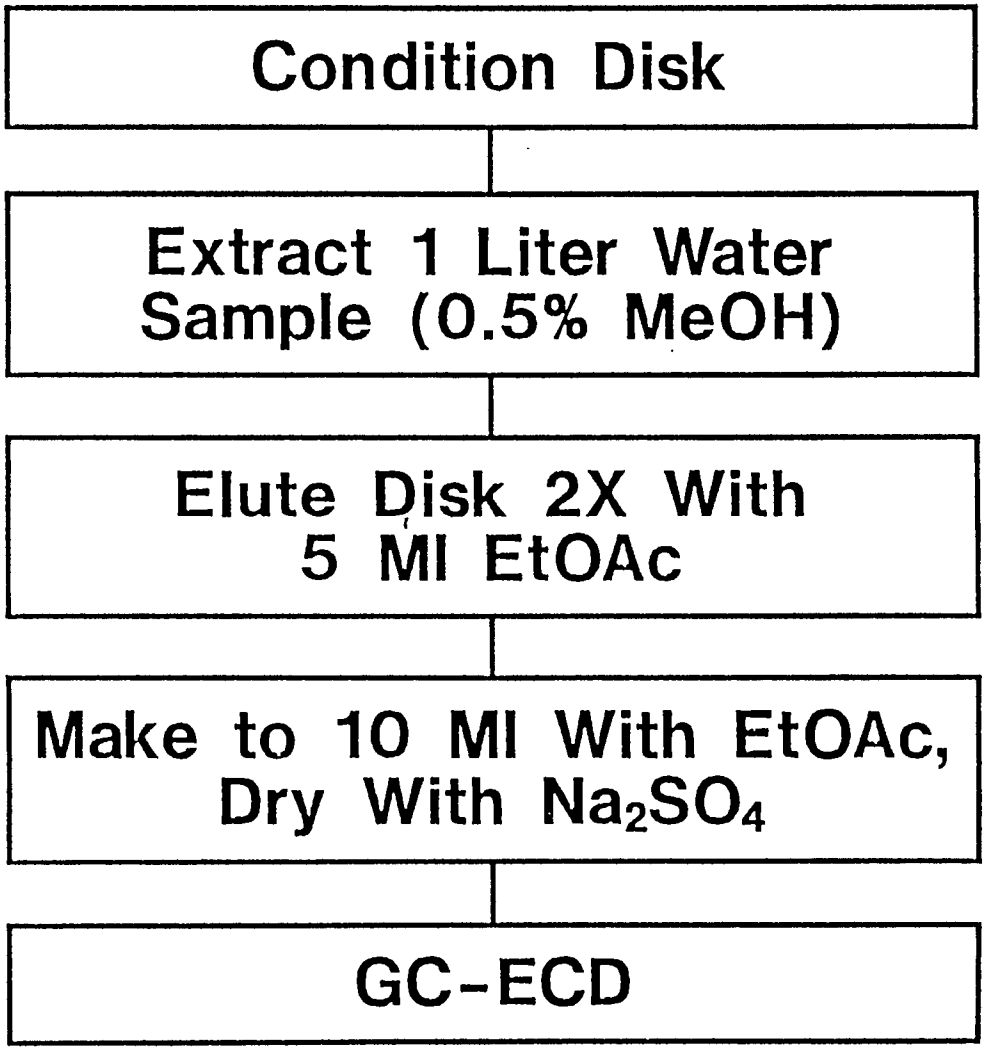

Extract 1 Liter Sample 3X With 60 Ml $MeCl_2$
Combine and Dry Extracts
Concentrate Sample (K-D) to 1 Ml
Add 50 Ml Hexane and Concentrate (K-D)
Make to 10 Ml With Hexane
GC-ECD

Evaluation of Solid Phase Extraction Disks as a Replacement for Liquid/Liquid Extraction in the Determination of Organo-chlorine Pesticides and PCB's in Water

Anne D. O'Donnell, Denise R. Anderson,
Laura Bartoszek and John T. Bychowski
WMI Environmental Monitoring Labs, Inc.

Craig Markell and Donald F. Hagen
3M Corporate Research Laboratories

Method 608 - Disk Modification



Recovery and RSD (%)

Validation Level (∿1ug/L)	Ave. Recovery	Ave. RSD
Reagent Water	92	3.1
Average Groundwater	93	4.4
High SS Groundwater - Best Case	86	11.7
High SS Groundwater - Worst Case	63	8.6
MDL Level (∿0.02 ug/L)		
Reagent Water	93	5.7
Average Groundwater	81	7.1

Method Detection Limits (ug/L)

Analyte	Reagent LLE	Reagent LSE	Groundwater LSE
Aldrin	0.011	0.004	0.004
a-BHC	0.009	0.001	0.002
b-BHC	0.013	0.002	0.003
d-BHC	0.006	0.002	0.002
g-BHC (Lindane)	0.004	0.002	0.002
4,4′-DDD	0.006	0.003	0.002
4,4′-DDE	0.007	0.002	0.002
4,4′-DDT	0.006	0.004	0.003
Dieldrin	0.007	0.006	0.007
Endosulfan I	0.005	0.002	0.016
Endosulfan II	0.006	0.004	0.006
Endosulfan Sulfate	0.020	0.006	0.017
Endrin	0.006	0.003	0.003
Endrin Aldehyde	0.011	0.017	0.008
Endrin Ketone	0.015	0.002	0.016
Heptachlor	0.005	0.004	0.004
Heptachlor Epoxide	0.004	0.002	0.003
Methoxychlor	0.036	0.011	0.012

Conclusions

- 200-500 Ml $MeCl_2$ Replaced With 20 Ml EtOAc
- Significant Time/Labor Savings
- MDL´s Lower
- Recoveries and RSD´s Equivalent to LLE
- Suspended Solids Not a Problem in Average Groundwaters
- Worst Case Suspended Solids Needed Pre-Filtration and Affected Recoveries

Method 608/8080

- 90 mm C18 Disk + GF/A Prefilter
- Extract 1 Liter Sample
- Elute With 3 x 15 ml $MeCl_2$
- Dry and Concentrate

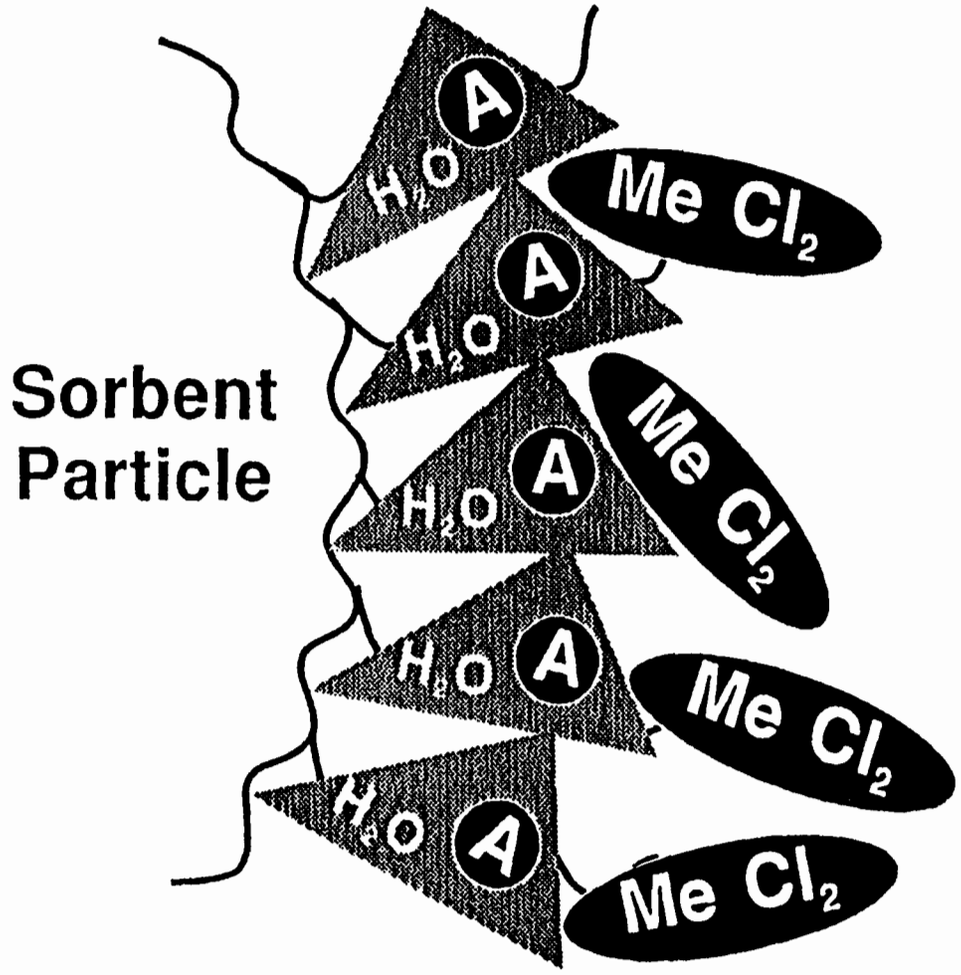
Method 608/8080

Waste Water Type	Average Recovery, % (Avg. RSD)*
Pesticide Manufacturer	91 (5.3)
POTW	86 (7.4)
Pulp/Paper Mill	68 (12.0)
Petroleum Refinery	80 (2.4)

*Average of 18 Single Component Analytes, n=5

3M

Elution Solvent/Water Miscibility



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*Solubility of Water in Solvents**
(% By Weight)

Hexane	0.01
Toluene	0.03
Methylene Chloride	0.24
Ethyl Ether	1.26
Methyl t-Butyl Ether	1.50
Ethyl Acetate	3.30
Acetone	Miscible
Methanol	Miscible

*Burdick and Jackson "High Purity Solvent Guide"

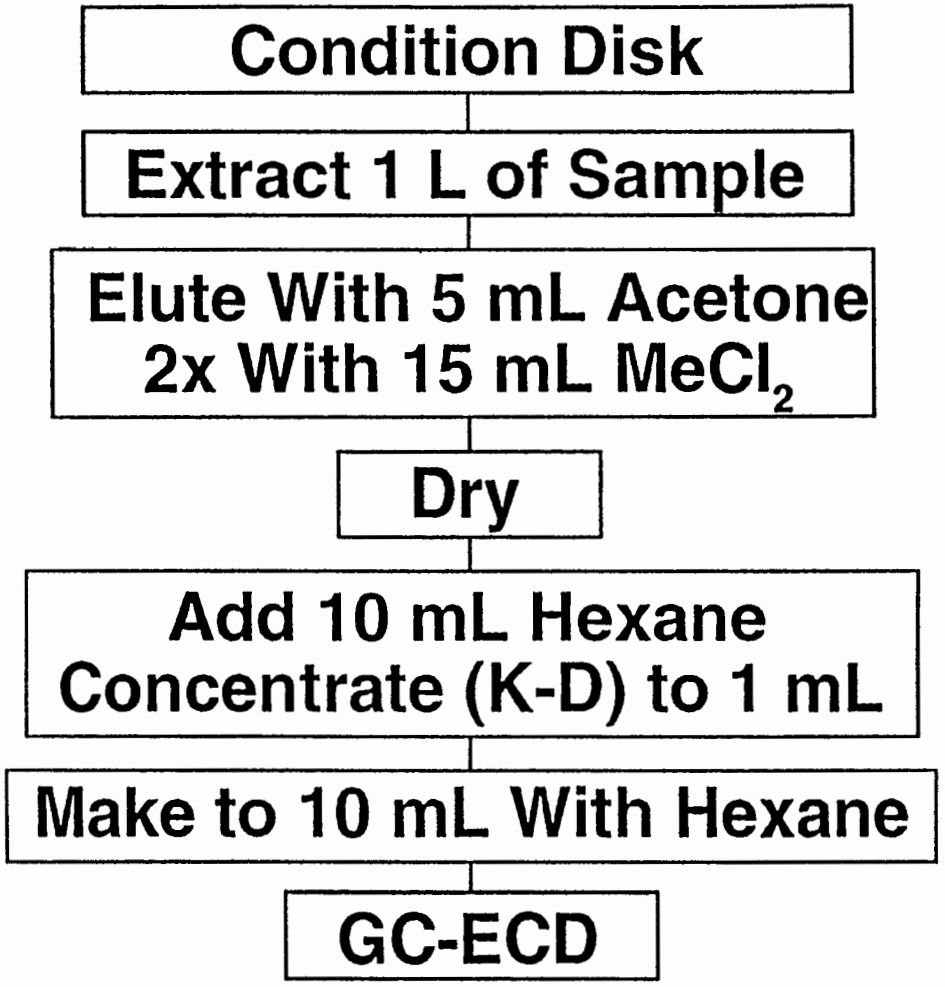
3M

PittCon® 94

Validation Study of Liquid/Solid Extraction for the Analysis of Organochlorine Pesticides and PCBs in Ground and Wastewaters

A.D. Vo., S.T. Rodriguez, K.M. Hoffmann
3M Environmental Laboratory
C.G. Markell
3M I&C New Product Dept.

Method 608 Using 3M Empore



3M

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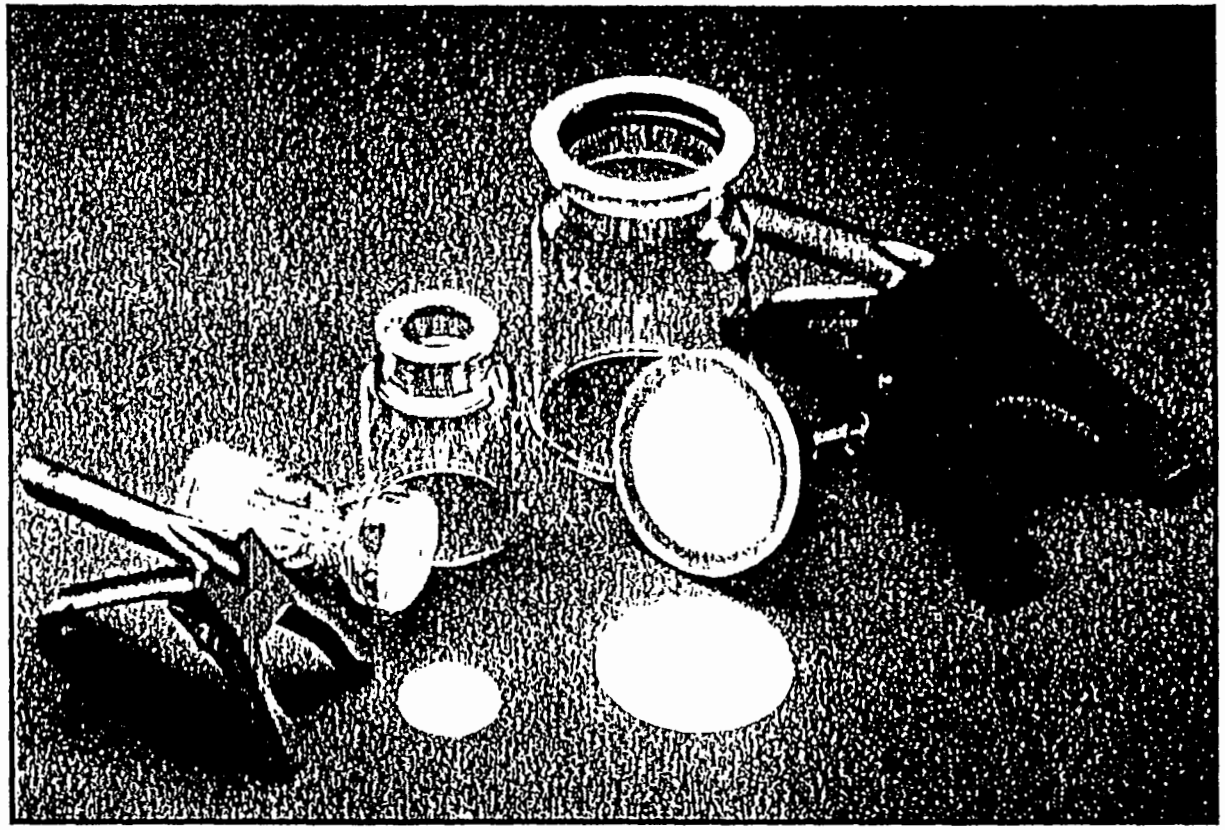
3M Empore™ Disks with Standard Apparatus



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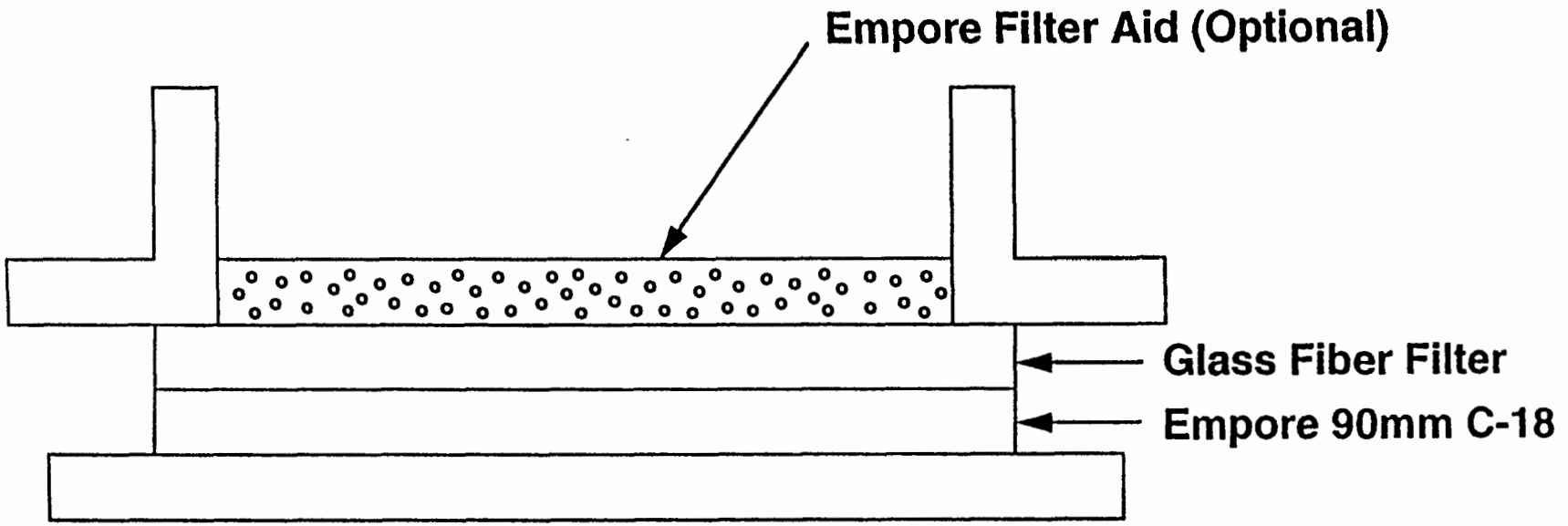
3M Empore™ Set-Up Schematic



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Analyte Groups and Concentrations

Analyte	µg/L Baseline (FLB)	Fortification 1 (FL1)	Fortification 2 (FL2)
4,4'-DDE	0.2	1.0	5.0
Aldrin	0.2	1.0	5.0
Alpha-BHC	0.2	1.0	5.0
Beta-BHC	0.2	1.0	5.0
Delta-BHC	0.2	1.0	5.0
Dieldrin	0.2	1.0	5.0
Endosulfan I	0.2	1.0	5.0
Endrin Aldehyde	0.2	1.0	5.0
Gamma-BHC	0.2	1.0	5.0
Heptachlor	0.2	1.0	5.0
Heptachlor Epoxide	0.2	1.0	5.0
Methoxychlor	0.2	1.0	5.0
4,4'-DDD	1.0	5.0	15.0
4,4'-DDT	1.0	5.0	15.0
Endosulfan II	1.0	5.0	15.0
Endosulfan Sulfate	1.0	5.0	15.0
Endrin	1.0	5.0	15.0
* Chlordane	2.0	10.0	50.0
* PCB 1254	2.0	10.0	100.0
* Toxaphene	10.0	50.0	250.0

* Multicomponents

3M

Physical Data on Samples as Collected

SIC	Industry	pH	mg/L TSS	mg/L TDS	mg/L TS
2869A	Chemical	7.8	3	2100	3100
2869B	Chemical	12.0	12	9100	9600
2621A	Paper	6.7	48	1300	1500
2621B	Paper	7.9	3	630	650
2833A	Pharmaceutical	6.5	18	1700	1800
2833B	Pharmaceutical	8.0	10	570	580
4953A	Refuse	3.1	14	360	560
4953B	Refuse	3.7	120	48300	50500
4952A	Sewerage	7.0	23	780	N/A
4952B	Sewerage	7.9	11	1000	1200

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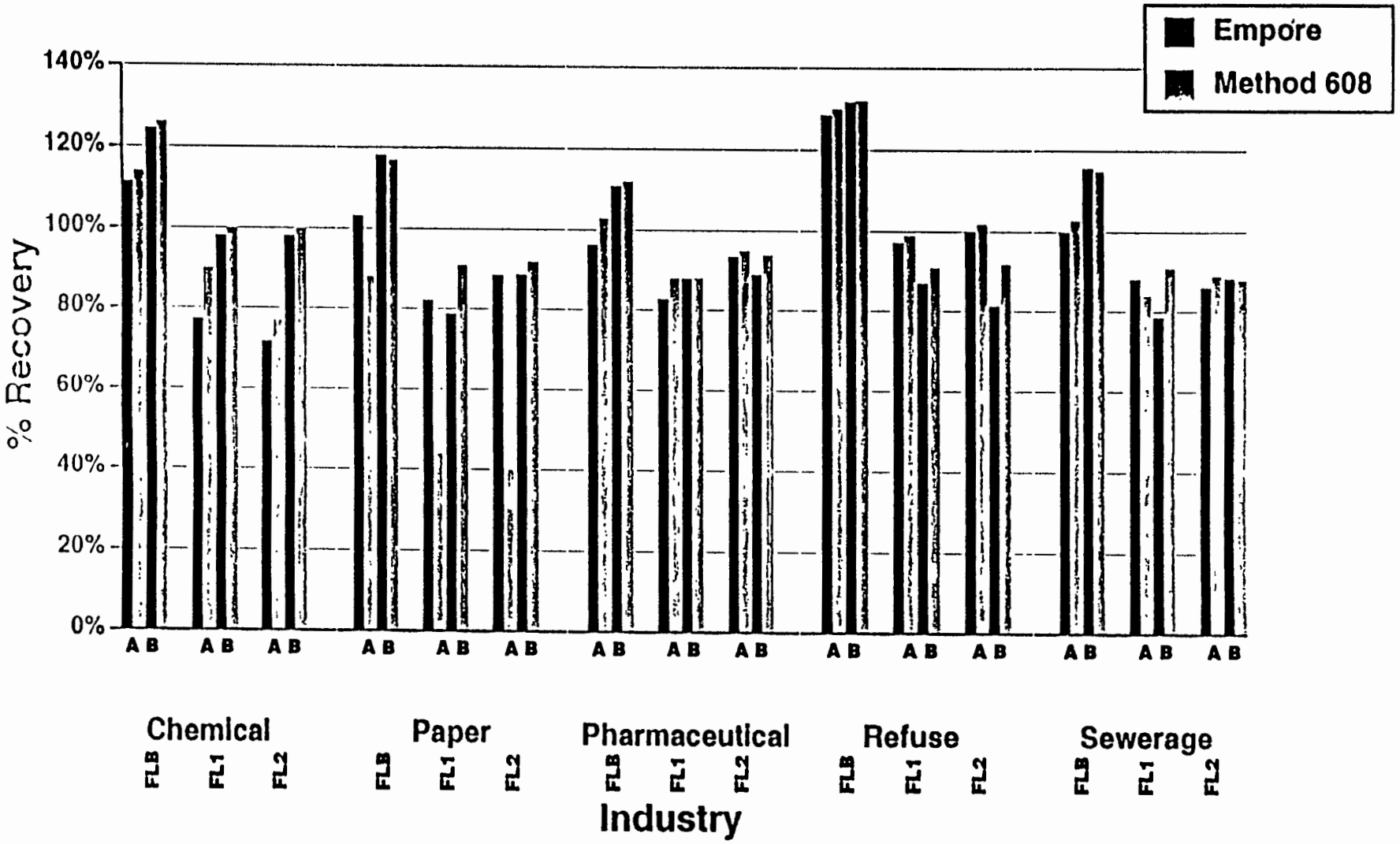
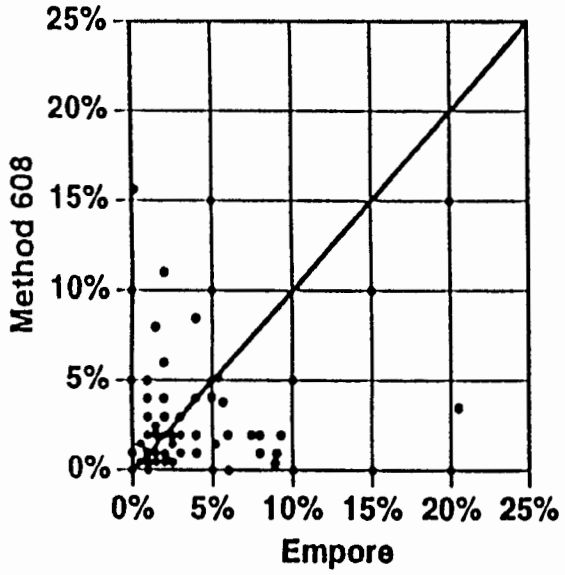
Average Recoveries for all Analytes by Industry



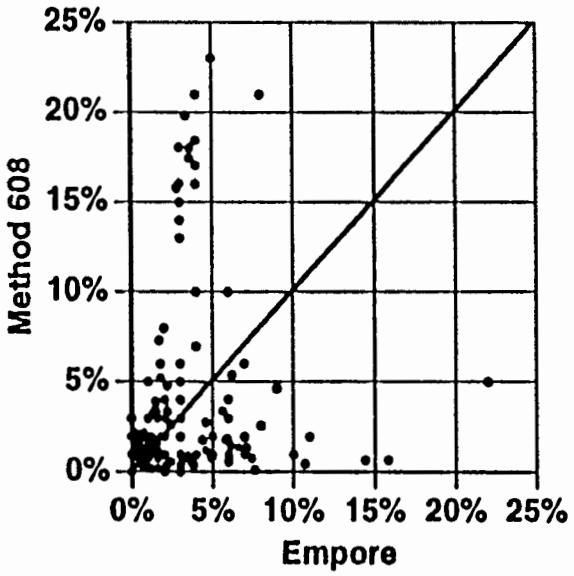
FLB, FL1 & FL2 levels all analytes and replicates

3M

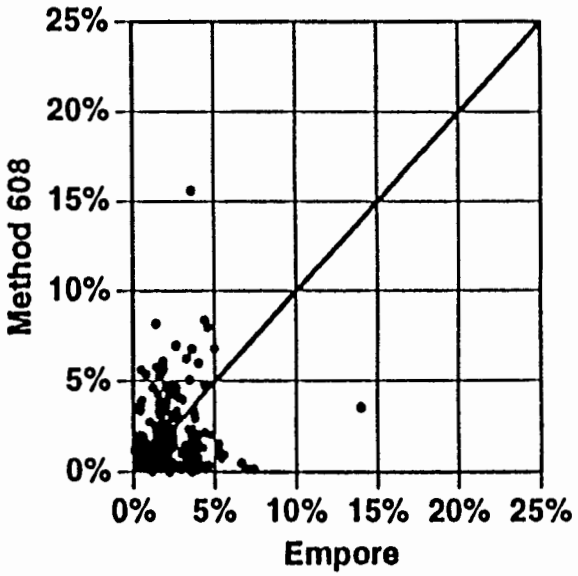
Relative % Standard Deviations by Level



Relative Std Deviation for FLB



Relative Std Deviation for FL1



Relative Std Deviation for FL2

3M

Statistical MDL - μg/L

Analyte	Empore	608
Alpha-BHC	0.005	0.006
Gamma-BHC	0.004	0.006
Beta-BHC	0.021	0.015
Heptachlor	0.020	0.015
Delta-BHC	0.011	0.006
Aldrin	0.008	0.011
Heptachlor Epoxide	0.010	0.008
Endosulfan I	0.008	0.005
4-4-DDE	0.022	0.013
Dieldrin	0.008	0.006
Endrin	0.068	0.028
4-4-DDD	0.083	0.071
Endosulfan II	0.043	0.032
4-4-DDT	0.071	0.039
Endrin Aldehyde	0.015	0.023
Endosulfan Sulfate	0.048	0.030
Methoxychlor	0.027	0.026
* PCB 1254	0.26	0.21
* Chlordane	0.07	0.08
* Toxaphene	0.61	0.88

MDL = 3.143 X Std Dev

3M

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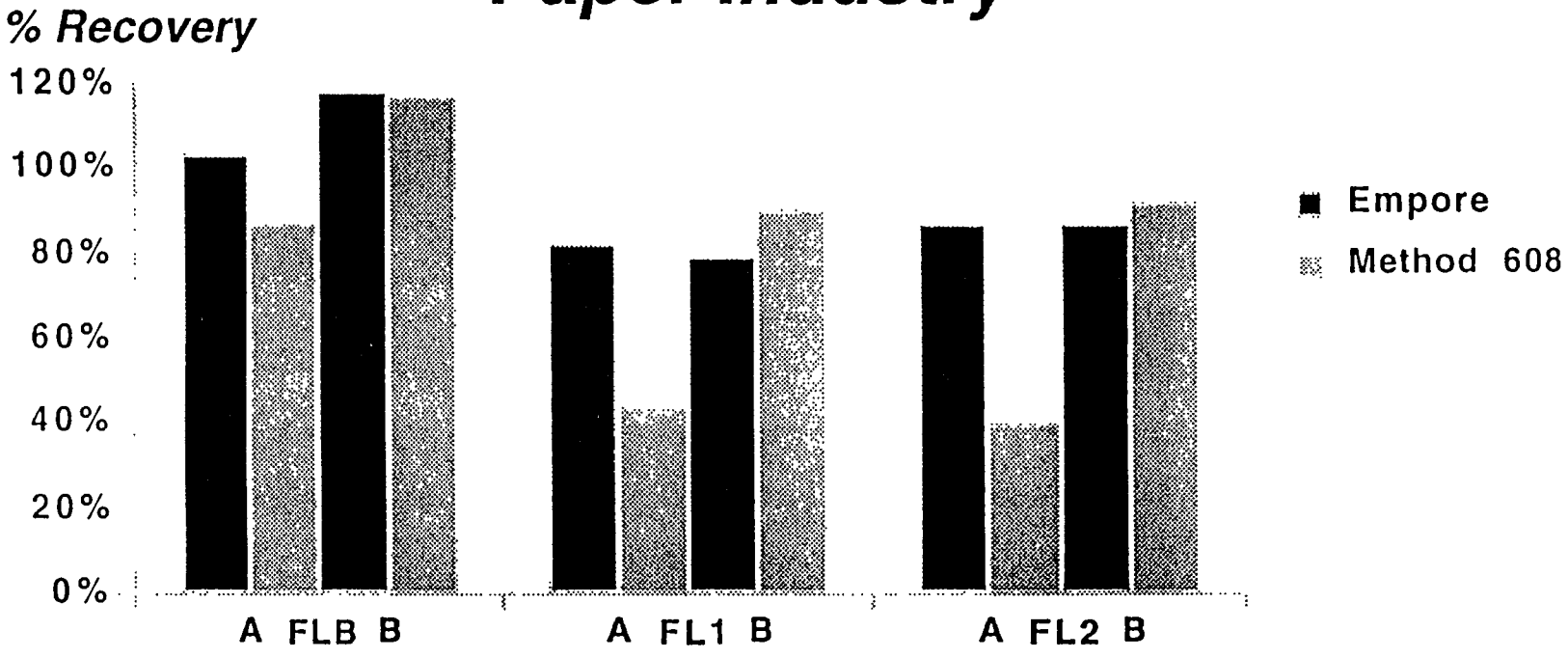
Average Recoveries for All Analytes in Paper Industry



SIC	Industry	pH	mg/L TSS	TDS	TS
2621A	Paper	6.7	48	1300	1500
2621B	Paper	7.9	3	630	650

3M

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Comparison of Empore™ & LLE

- **Less Solvent**
  - 1/3 Use in Extraction & Concentration
  - Less Contamination of Sample
  - Less Cost
  - Less Hazard to Personnel
  - Less Disposal and Emission = More Pollution Prevention
- **Less Time**
  - 2x the Samples
- **Less Space Required**
- **Less Labor Intensive**
- **Better Recovery Without Emulsion**

3M

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CLOSING

MR. TELLIARD: I would also like to thank you for staying. I would also like to thank a few other people.

This is our first effort at joint sponsorship with the WEF. I think it has gone well. We had a few glitches, but, you know, marriages have that, too. We are looking forward to coming back next year, and we are looking forward to having another joint session.

I would like to thank Bill Nivens and Suzanne Shutty for their help here. I would like to thank Dale Rushneck, particularly, for working on the technical program which is, I think, one of the strongest we have had in quite a few years. Now, we did have some hot topics that made it easy for him, but Dale certainly did a heck of a good job.

I would like to thank Cindy Simbanin from Viar who did a lot of helping with the registration, and Jan Kourmadas who ran around and worked with the hotel people, and Marion Thompson from my staff who answered all the phone calls when you called and said what time does it start. Another small glitch.

We are hoping to be back here same time, maybe same station, but general area. If you have any suggestions on things you would like to see or hear about, we would appreciate your giving me a call or dropping us a line.

We have asked you to sign and evaluate, for our purposes and everyone else's, the papers so that we can basically see how things are going.

I appreciate your time, patience, and hope to see you next year. Thank you so much for coming.

(The conference was concluded at 4:30 p.m.)

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SPEAKERS

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