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Table of Contents

March 16, 1983

Table of Contents

March 16, 1983

Table of Contents

March 17, 1983

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INTRODUCTION and WELCOME

William Telliard
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MR. TELLIARD: Good morning. There are a number of empty seats down here in front. I guess those were some of the people that are now in the Washington Post. So if you want to move down you can use those seats.

Welcome to Norfolk, our third visit here, subject the same, Priority Pollutant Analysis and their kindred. I would like this morning to introduce the Director of the Effluent Guidelines Division, Jeff Denit, who would like to say a few things to welcome you to this meeting. Jeff.

MR. DENIT: Thank you very much, Bill. It is a personal pleasure and a pleasure for the Division to once again be able to sponsor our conference on analytical methods, this being the 6th annual. We are looking forward to the exchange of ideas and the dialogue as we mutually work to advance the state of the art of analytical methods.

I am certainly looking forward to the conference. I wish you all well, and please, by all means if you have the opportunity, stop by and introduce yourself if I haven't had the chance to meet you of if you have any questions of me, and enjoy the time that we can spend together to discuss any of your ideas.

At this point I'll turn the program back over to Bill for our morning session and, once again, best of luck and thank you so much for coming.

MR. TELLIARD: Thank you, Jeff. A couple of announcements; one, as usual, concerning this evening. Right at the break Captain Whitescarver will announce some arrangements we've made for our usual soiree out to dinner tonight with a cast of thousands.

At this time I would like to introduce our first speaker, Bob Medz. Bob has addressed this group

on the same subject before and it's kind of a continuing saga. Bob has been developing a certain package now for a number of years, and it feels like trying to guideline out, doesn't it, Bob?

MR. MEDZ: It does.

MR. TELLIARD: Dr. Medz is Associate Director of Water and Waste Management, Monitoring Research Division, Office of Research and Development, EPA. Bob's subject this morning is the approved analytical methods, affectionately referred to as 304-H. Bob.

STATUS OF ANALYTICAL METHODS FOR WASTEWATER MEASUREMENT, CWA SUBSECTION 304(h)

Robert B. Medz
U.S. Environmental Protection Agency
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MR. MEDZ: I think the last time I addressed the group I said the regulations on analytical methods would probably come out within about three to six months and that was two years ago. They still haven't come out, but they'll be out, and again I'll say, in three to six months. But this time I think we're closer than that.

First of all, what are these analytical methods we're talking about? In Subsection 304(h) of the Clean Water Act (CWA) Congress said that the Administrator would develop and promulgate guidelines establishing test procedures for the analysis of pollutants. These test procedures are intended to be used in any certification made under Section 401 of the Act or any permit application under Section 402 of the Act. Now, those requirements

have quite a scope of application for these analytical methods. The analytical methods are to be used in any enforcement and compliance action that is dependent upon any of the regulations that go into permits.

The 304(h) regulations are promulgated at Part 136 of Title 40 of the Code of Federal Regulations. The first regulations under this Part 136 were published in the Federal Register on October 16th, 1973 (38 FR 17318). They were first amended on December 1st, 1976 (40 FR 52780). The basic thrust of this regulation is to look at the available analytical methodologies that have been developed by concensus organizations, that have been developed by industrial groups, or that have been reported in the analytical literature and to select these analytical methods that have been so described which meet the precision and accuracy requirements and other criteria of the agency.

In 1976 a new condition was placed on the agency. The regulations that were intended to implement the toxics regulations of Section 307 of the Act

had been floundering. The new condition was established in a lawsuit against the agency and in a subsequent consent settlement in 1976, which established the priority pollutants. I think you are all familiar with the priority pollutants. At that point, the analytical methods by which trace organic pollutants could be analyzed in industrial discharges just were not available in the reported literature or the consensus manuals. There were a few analytical procedures that had been developed by single laboratories relative to measurements of pesticides. EPA's Environmental Monitoring and Support Laboratory in Cincinnati had developed a few of these analytical methods based on gas chromatography (GC) and thin layer of chromatography, (TLC) but the wide testing of these test procedures was just not available. The type of validation that you would expect of a concensus method was not available for the priority pollutants. So the agency set out to develop these methods. On December 3, 1979, the agency

proposed these analytical methods (44 FR 69464) which had been developed to a point where, even though they hadn't been fully validated by multi-laboratory collaborative tests, the agency still felt were sufficiently reliable for use in enforcement and compliance measurements. The methods that were proposed included 12 methods based on gas chromatography or high pressure liquid chromatography (HPLC) and three methods based on gas chromatography with the mass spectrometric detection (GC/MS).

Methods 601 through 612 were the GC or HPLC methods. Method 613 was a high performance GC/MS method. Method 624 and Method 625 were based on the quadrupole GC/MS. The methods were proposed and the performance criteria that were included in the methods were based on single laboratory experience. The GC/MS test protocol that was proposed wasn't significantly different from the screening GC/MS test protocol that had been

used by the Effluent Guidelines Division (EGD) in their industrial survey work. So we had some information on the applicability of the GC/MS test procedures to industrial wastewaters. But the experience with the GC/HPLC methods was restricted to the experience of our contractors and some of the work done in house at EMSL-Cincinnati and some of EPA's regional laboratories.

Proposed at the same time with the trace organics pollutant test procedures was a test procedure for carbonaceous biochemical oxygen demand (CBOD). The CBOD test procedure was being proposed because it was becoming more and more apparent that in many instances the traditional five-day BOD might not be the most appropriate measure of performance of control technology for secondary treatment plants, i.e., the biological treatment plants. Nitrification was becoming a problem after treatment had been completed and was giving abnormally high BOD_5 readings because

of the oxygen demand of nitrifying bacteria. So the CBOD five-day test procedure was proposed in order that a nitrogen bacteria inhibitor could be used to prevent nitrification in the test that was being used to show that the proper control technology had been applied.

Additionally, the inductively coupled plasma optical emission spectroscopic test procedure (ICP) was proposed for trace metal analysis. ICP is probably one of the more powerful state-of-the-art instruments by which trace metals can be rapidly and reliably analyzed.

The final item that was included in the proposal was a table of mandatory requirements addressing sample container material, sample preservation, and maximum allowable sample holding times. The preservation requirements are for samples which are taken from industrial wastewaters to a laboratory for the measurement at some later time. The holding times are the length of time that such

samples can be held before analyses without losing their integrity.

Now, those were the things that were included in the proposed regulations. Everyone has been quite anxious to know exactly when the final regulations will come out. The multi-laboratory validation studies that were initiated in the 1979-1981 time frame for the GC and HPLC test procedures have been completed. These validation studies include Methods 601, 602, and 604 through 612. The validation of the GC/MS test procedure defined in Method 613 for dioxin is also completed. Incidentally, the raw data from these validation studies are available at Environmental Monitoring and Support Laboratory in Cincinnati in case anyone has occasion to want to see the raw data. The raw data has been reduced and has been used for calculating the mean recoveries of spikes, the standard deviation of recoveries of spikes for the overall study, and the standard

deviation for single analyst performance. The validation studies were conducted in six different matrices: distilled water, tap water, one surface water known to be prone to contamination by organic pollutants, and in three different industrial wastewaters in which it was highly likely priority pollutants in the particular categories covered by the methodolgy would be regulated.

The validation test procedures were designed after the procedure developed by Youden. Youden is a statistician and I think he still is at the National Bureau of Standards. In his approach samples of a given pollutant in closely matched concentrations are analyzed by the participants in the validation study. These particular tests were conducted under the auspices of EPA's Environmental Monitoring and Support Laboratory in Cincinnati (EMSL-Ci). Incidentally, the names that are critical in these studies are Jim Longbottom

and Jim Lichtenberg of that laboratory. They have been the principal investigators on these studies together with Bob Graves who is here sitting right next to me. The Youden test was designed to have the lowest concentration pair slightly above the detection limit. The second Youden pair was at a mid-range concentration and the third Youden concentration was at the upper end of the concentration range that was being tested.

These concentration weren't the same for each method and there were also some variations in concentration ranges depending on the analyte. The main conclusions of these tests was that the means and the standard deviations, i.e., the overall study standard deviations and the single analyst standard deviations over the concentration ranges studied could be expressed as linear regression equations. Another conclusion that came from these studies was that in the family of linear regression equations for a given compound

that were developed for the six different matrices, the statisticians couldn't find any statistically significant differences in the slopes and the intercepts of each of the regression lines applicable to the different matrices.

So the conclusion reached from these studies is that in the methods themselves (and the methods are being revised right now to include this new information) the performance data for distilled water is all that we need to require an analyst to meet in order to establish that the analyst can apply these methods within acceptable confidence levels to industrial wastewater matrices. Now, as chemists we feel or at least I feel uneasy with that. I feel there are going to be matrix effects. What the statisticians tell us from these studies is that if you wanted to see what these matrix effects really are, at least in the scope of these studies you would probably have to have many, many more data points in your

study population to establish the means and the standard deviations with a much higher degree of confidence; I guess what the statisticians call the central limits theoram. If you make a measurement a sufficient number of times regardless of whether it's being measured at two or more significant figures, if within the population that you are measuring, the number of observations you make is large enough, the statisticians tell us that there are equations by which you can calculate the means to many, many more significant figures for that particular population than any of its individual measurements. In other words, if your individual measurements have two significant figures, if you had sufficient numbers of measurements you could express the mean for that particular population to as many significant figures as you wanted to and it's statistically valid.

So for the number of data points that we have

in these studies and there were from 15 to 20 laboratories that participated in these studies, the general conclusion is that we can use the distilled water data to show that the analyst may be competent to apply the methods to more complicated matrices, such as treated industrial wastewater effluents. Now, this statement is only restricted to treated wastewater effluents. The statement does not apply to the raw influent wastewaters.

So now where are we within this particular regulation and when is it going to come out? Right now we are in the process of incorporating the texts of the analytical methods within the regulations by reference. Incorporation by reference is an administrative term that is placed on us by the Office of the Federal Register. When you incorporate any material into a regulation by reference it means that the material being incorporated has the full effect of regulation as though it had actually been

printed in the Federal Register. One of the restrictions that is placed on incorporating by reference is that the method is incorporated into the regulatory language in exactly the text which is submitted to the Federal Register. Any alterations in that text in the future requires that a new Federal Register notice be made to show the alteration.

If you will remember, I said that only methods 601, 602, and 604 through 613 had been fully validated and the performance criteria for those methods would be incorporated within the analytical method. Multi-laboratory performance criteria for Methods 603, 624 and 625, and Bob Graves will tell us more about the status of those validation studies, are not available right now and so the Methods 603, 624 and 625 will be incorporated with the best single analyst data that is currently available to the agency; which means at such a time as the data from the multi-laboratory

validation studies are completed for Methods 624 and 625, i.e., the GC/MS test procedures, we will have to go back with a Federal Register Notice to indicate that the criteria in those methods has been changed.

There are several reviews that have to be made on this regulation once it leaves the agency. The incorporation by reference by the Office of the Federal Register is one of them. There is another review which comes under the Paperwork Reduction Act which is performed by the Office of Management and Budget (OMB). Any regulation that requires information to be provided by the community which is affected by that regulation has to be reviewed by OMB under the provisions of the Paperwork Reduction Act. In Part 136 we have two provisions where we ask the affected community for information. One of these is in the equivalency program where an instrument manufacturer might have a new instrument system based on a principle

other than those that have been approved and wishes to have it added to the approved list. There we are asking for information that comes under the Paperwork Reduction Act. The amount of time that this request for information requires of the respondents has to be estimated and submitted for OMB review and approval.

Another provision in the regulation is that in the holding times and preservation techniques there might be industrial discharges that because they have limited interferents can have holding times and preservation requirements other than those that are being made mandatory in Table II. For such discharges, the permittees can apply for variances from the mandatorily prescribed holding times and preservation requirements. That also comes under the Paperwork Reduction Act. The Paperwork Reduction Act review takes two to three months, but it will not hold up the regulation. Only those parts of regulation

which require information to be furnished may be delayed.

Then, we have another 20 days of review by OMB for the regulatory reform review which every regulation now has to undergo.

So my best estimate for publication of the final regulation is based on the completion date of EPA's internal "Red Border Review" which should be finished in the next several weeks. We then submit this reviewed regulation to OMB where they will have 20 working days for the regulatory reform review which means (and I hate to make this prediction again), that in another two to three months we'll have the regulation published.

MR. TELLIARD: Thank you. Any questions?

QUESTIONS AND ANSWERS

MR. VINCENT: Frank Vincent. This has to do with the Table II in the regulation. If we can show that the sample arrives at our laboratory in sufficient time that preservation is not required, is it probably true that we could establish a variance on that situation?

MR. MEDZ: I would say the answer is affirmative on that. You would have to provide the data that shows that this is the case.

MR. VINCENT: Sure.

MR. MEDZ: I would say if your data bears this out, there would be a variance to the preservation requirement that you have demonstrated for your sample type. That's the intent of this provision of the regulation.

MR. VINCENT: Thank you.

MR. STANKO: George Stanko, Shell Development. Bob, could you identify the version

of Methods 624 and 625 that will come out in the regulation; is it the version that was in the document from Cincinnati dated July, 1982?

MR. MEDZ: There will be slight changes from that. Let me tell you where the changes will be.

Our general counsel tells us that regulations have to stand on the text which is to be incorporated by reference. The text that is incorporated by reference cannot include regulatory requirements which at some later time would automatically change the text of the method without further notice in the Federal Register. What I'm talking about right now is the provisions in Methods 624 and 625 that says, "Here are the single laboratory performance criteria which you will use until the Environmental Monitoring Support Laboratory establishes the multi-laboratory performance criteria, and when these are available

they will automatically be used in this method." Our general counsel tells us we can't do that; that is saying that there is going to be future automatic regulatory revision that is being predicted in the text right now. They say the text has to be binding as of the date of the promulgation. So that kind of language is going to be deleted.

MR. STANKO: Could you tell me, specifically, if Table 5 in the version published in July, 1982 shows up in the final version?

MR. MEDZ: Will you refresh my memory as to which Table 5 is; is that the performance criteria?

MR. STANKO: That is the performance criteria with respect to R and 5.

MR. MEDZ: That will remain the same, but Bob Graves will be able to tell you more about that.

Let me make the statement, myself. The performance criteria that was in the July 1982 release was the best single and multiple laboratory data we have right now and that will stay in.

MR. STANKO: Thank you, Bob, that's what I needed to know.

MR. TELLIARD: Any other questions?

Thank you, Bob, look forward to having you back next year to tell us when they're coming out.

Our next speaker is Robert, commonly known as Bob Graves from the Environmental Monitoring and Support Laboratory in Cincinnati. Bob is the project manager for the review and verification of the GC/MS procedure, affectionately referred to as 624 and 625. Bob is fortunate to be here today because he wouldn't have to stay home in Cincinnati for the EMSL program review. Bob.

VALIDATION STUDY OF EPA METHODS 624 AND 625

Robert Graves
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Abstract

The Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, is responsible for conducting interlaboratory method validation studies for EPA analytical methodologies as they pertain to measuring analytes in water media. The study design and data analysis scheme used in validating EPA's GC/MS Methods 624 (Purgeable) and 625 (Base/Neutrals, and Acids) will be discussed. General areas to be covered include: selection of participants, preparation of samples, selection of water-types, rejection of outliers, calculation of statistics, weighted linear least square regression equations, correlation between surrogates and analytes, false positives and false negatives, and comparison of method capability across water-types.

Introduction

The Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, is responsible for conducting interlaboratory method validation studies for EPA analytical methodologies as they pertain to measuring analytes in water media. The impetus that drives the Environmental Protection Agency to promulgate guidelines establishing test procedures for the analysis of pollutants are Sections 304(h) and 501(a) of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977. The document that delineated which organic pollutants were to be initially studied is the so-called "Consent Decree". On June 7, 1976, in the United States District Court for the District of Columbia, a settlement agreement was reached. The litigants were as follows: Natural Resources Defense Council, Inc., et al. versus Russell E. Train (Civil Action No. 2153-73); Environmental Defense Fund, et al. versus Russell E. Train (Civil Action

No. 75-0172); Citizens for a Better Environment, et al. versus Russell E. Train (Civil Action No. 75-1698); and the Natural Resources Defense Council, Inc. versus James I. Agee, et al. (Civil Action No. 75-1267).

METHOD VALIDATION STUDY

Conducting interlaboratory studies involve designing the studies and developing appropriate data analysis techniques to process the data. The study design and data analysis scheme specific to validating EPA's GC/MS Methods 624 (Purgeables) and 625 (Base/Neutrals and Acids) are presented.

STUDY DESIGN

Participants, prior to their acceptance for this study, were required to analyze a performance evaluation sample. The sample was designed so as to present an analytical challenge to the analyst. The purpose of this preliminary study was to ensure that the participants were familiar with the analytical

methods, the sample handling procedures, and that the analysts were competent. Previous studies have shown that a screening process such as this leads to more reliable data, and thus, the statistical evaluation of the method becomes more indicative of the method's true capability.

Samples were prepared to conform with Youden's plan for collaborative evaluation of analytical methods. The analytes were prepared as three Youden pairs, one pair just above the detection limit, one mid-level pair, and one pair near the upper limit for use of these methods. A Youden pair consists of two samples with analytes at similar, but distinctly different concentrations. Analytes were weighed out, dissolved in an organic solvent, and shipped to participants as liquid concentrates in sealed glass ampuls. As many analytes as possible, within any one group of compounds that are analyzed together, i.e., purgeables, base/neutrals, acids, and pesticides, were placed within the same

ampul. Methods 624 and 625 require that surrogates be dosed into each water sample prior to analysis. Surrogates were also supplied to each participant as liquid concentrates.

Caution was taken as to prevent problems with the simultaneous qualitative and quantitative measurement of any of the compounds dosed within a water-sample. Purgeables were analyzed simultaneously; base/neutrals and pesticides were divided into two sets, and acids were analyzed simultaneously.

Prior to distribution to participants, ampuls were analyzed to assure that the added constituents were present at the intended levels, and they were analyzed periodically thereafter to assure stability.

Various water-types were studied, namely, reagent water, drinking water, surface water, and industrial effluent. Reagent water represents the control; it represents the primary matrix, i.e., WATER. The other water-types were chosen because they effect the analytical procedures via other

impurities being present in the water causing matrix effects due to considerations other than water. Participants secured their own water samples, thus allowing each water-type to be tested by the methods on a myriad of individual waters each possessing varying interferences. The participants then prepared their own samples by dosing a specified aliquot of liquid concentrate from the supplied ampuls into their self-collected water-samples.

TREATMENT OF DATA

The primary purpose of conducting interlaboratory validation studies is to document the method's capability, i.e., precision and accuracy, when a competent analyst, practicing appropriate quality control techniques, uses it. The operative ideas here are competent analyst and appropriate quality control techniques; these two factors define what a laboratory, that will eventually conduct routine analyses via this methodology, must possess. The interlaboratory validation studies conducted by

EMSL-Cincinnati are intended to define the accuracy and precision of a method when in fact these two items are operational.

Spurious data points are always a part of any set of data collected. Some objective technique must be performed to identify and to rid the data set of these spurious data points. EPA, EMSL-Cincinnati applies Youden's laboratory ranking procedure (1) at the 5% level of significance to identify outlying laboratories. However, the Youden ranking procedure requires a complete set of data from each laboratory within each water-type. Therefore, missing data within a laboratory data set are replaced by taking the natural logarithms of the laboratory's available data and regressing it against the natural logarithms of the true concentration levels. The missing values are then estimated by ey where Y is the predicted value from the regression analysis corresponding to the missing value. (2)

After completing the laboratory ranking procedure, zero, missing, "less than", and "nondetect"

data are rejected as outliers (2). The data remaining are now checked for individual outliers at the 5% level of significance using the outlier rejection test constructed by Thompson (3), and recommended by the ASTM Committee D-19 on Water (4).

Summary statistics documenting the method's capability are calculated using the retained data.

Mean Recovery ($\bar{X}$): $$\bar{X} = \frac{1}{n} \sum_{i=i}^{n} X_i$$

Accuracy (% Relative Error):

$$\%RE = \frac{\bar{X} - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=i}^{n} (X_i - \bar{X})^2}$$

Percent Relative Overall Standard Deviation:

$$\%RSD = \frac{S}{(X)} \times 100$$

Single-Analyst Standard Deviation:

$$S_1 = \sqrt{\frac{1}{2(n-1)} \sum_{i=i}^{n} (D_i - \bar{D})^2}$$

Percent Relative Single-Analyst Standard Deviation:

$$\%RSD\text{-}SA = \frac{Sr}{\overline{X}*} \times 100$$

where:

n = number of retained data points;

X_i = value for the ith retained data point;

n = number of retained Youden paired observations;

D_i = difference between the observation in the ith Youdoun pair;

$\overline{D}$ = average of the D values; and

$\overline{X}*$ = average of the two mean recoveries corresponding to the two ampuls defining a particular Youden pair.

From the summary statistics EMSL-Cincinnati develops statements, in the form of linear equations, for each compound and each water-type delineating the method's accuracy and precision across concentration levels. Mathematical equations of the form y = ax + b are generated, where for precision y = overall or single-analyst standard deviation and x = mean recovery; for accuracy y = mean recovery and x = true value; and the constants a and b represent the slope and the intercept, respectively.

In order to get a good fit of the linear regressions to the low concentration points it was decided to minimize the sum of squares of the percent difference between each of the points and the line. To accomplish this the traditional least-squares algorithm was applied to a modified data set (y/x as the dependent data set and 1/x as the independent data set).

	Dependent	Independent
Accuracy:	mean recovery/ true value	1/true value
Single-Analyst Precision:	single-analyst std. dev./mean recovery	1/mean recovery
Overall Precision:	overall std. dev./mean recovery	1/mean recovery

The resulting regression is of the form $y/x = a + b\,(1/x)$ and can easily be converted to the desired relationship $y = ax + b$. The intercept (a) from the equation $y/x = a + b\,(1/x)$ becomes the slope (a) in the equation $y = ax + b$, and the slope (b) from the equation $y/x = a + b\,(1/x)$ becomes the intercept (b) in the equation $y = ax + b$.

The relationship (correlation) that exists between each surrogate and each priority pollutant will be established. The intent is to statistically establish which surrogates should be monitored to assure that the data submitted for the priority pollutants are of high quality.

The potential for these GC/MS methods to give false-positives and false-negatives is assessed in this study by requiring each analyst to analyze a real-world sample laden with priority pollutants and interfering compounds. The output from this will be a statement concerning the methods probability of producing false-positives and/or false negatives.

Comparison of method performance vis-a'-vis water-types tested is performed to determine if there are differences in the method's capability across water-types. A formal analysis of variance test for differences across water-types is performed. The test is based on a regression model that directly compares each water-type to reagent water, which serves as a control (5).

The basic model used to describe the data is given by the multiplicative form

$$X_{ijk} = B_j\, C_k\, Y_j\, L_i \bullet \varepsilon_{ijk} \qquad \begin{matrix} i = 1,2,\ldots, n \\ j = 1,2,\ldots, 6 \\ k = 1,2,\ldots, 6 \end{matrix}$$

where B_j and Y_j are the fixed effects due to water-types, C_k is the true concentration for ampul k, L_i is the systematic laboratory effect for lab i, and ε_{ijk} is the random within laboratory error. This model converts to a linear regression model on a ln - ln scale.

$$\ln(X_{ijk}) = \ln B_j + Y_j \ln C_k + \ln L_i + \ln \varepsilon_{ijk}$$

The random error terms, namely, (L_i) and (ε_{ijk}), are assumed to be mutually independent and to follow a lognormal distribution. Therefore, ln L_i and ln ε_{ijk} are normally distributed with constant variance. Now by transforming the data within each laboratory by a set of independent contrasts, the laboratory bias term L_i can be eliminated. The model now depends only upon the water-types through the parameters B_j and Y_j.

There is no differences across water-types if $\ln B_j - \ln B_1 = 0$ and $Y_j - Y_1 = 0$ for $j = 2,3,4,5,6$ where $j = 1$ refers to reagent water. In this case the parameters $B_1,\ldots, B_6$ are all equal and $Y_1,\ldots,Y_6$ are all equal.

The analysis of variance procedure tests at the 5% significance level the null versus alternative hypothesis

H_0: $\ln B_j - \ln B_1 = 0$ and $Y_j - Y_1 = 0$ for $j = 2,3,4,5,6$

versus

H_1: $\ln B_j - \ln B_1 \neq 0$ and/or $Y_j - Y_1 \neq 0$ for some $j = 2,3,4,5,6$

using a standard F-test.

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QUESTIONS AND ANSWERS

MR. STANKO: George Stanko, Shell Development. Bob, I have a couple of questions; one, deals with EMSL-Cincinnati criteria. Does Cincinnati have a criteria for the EPA standards priority pollutants that can be expressed in plus or minus a certain amount from the true value?

MR. GRAVES: For the standards themselves?

MR. STANKO: Yes.

MR. GRAVES: Not that I am aware of, no.

MR. STANKO: My second question is, you talked about calculating a standard deviation and also a mean value. Was the standard deviation an estimate from the inter 50 percent quartile of your data?

MR. GRAVES: Absolutely not.

MR. STANKO: Thank you, I

needed...

MR. GRAVES: What you're referring to Windsorization.

MR. STANKO: That was my third question. Thank you.

MR. GRAVES: That was not done in this case. The standard deviations, the overall, and the single laboratory standard deviation, were calculated with retained data in the normal fashion (see Youden's statistical manual of the AOAC).

MR. VINCENT: Frank Vincent. I perceive a conflict and maybe it's because I don't understand. I wonder if you would clarify it. You said that it's up to the analyst to decide if a method is applicable and I guess I was under the impression that the published methods are pretty much mandated and they are defined to be applicable. Is that...am I wrong somewhere?

MR. GRAVES: Well, I'm speaking strictly for myself, okay. The way I interpret it is that it's up to the analyst to show that the method works on the matrix to be analyzed.

Now, if one would pick a very messy matrix, then gas chromatography, even when coupled to something like an eletron capture detector, which is quasi-specific, may not allow you to identify or quantitate the analyte of interest. There may be other interferring compounds in that particular matrix that co-elute with te analyte. Now, if this is the case, then, obviously, the GC method is not applicable.

Hopefully, the precision and accuracy statements supplied in the method write-ups will help you in determining if, in fact, that's the case. You can do things such as standard addition to help determine that the wastewater under study is, in fact, applicable to the method then from that point on you have no problem. However, if

in fact, you find interferring substances, you do not go willy-nilly ahead. You, in fact, say, okay, let us try a different column or let us go to a more universal method such as GC/MS; namely, methods 624 and 625.

MR. VINCENT: What position would we then be in as far as complying with the regulations? I guess that's what I'm really wondering about in any kind of compliance enforcement situation. We have used a method which basically is not in the regulations. We can validate that the method is applicable, that it gives the right result. I guess that's part of where my confusion is right now.

MR. GRAVES: Dr. Medz seems to want to answer this one.

DR. MEDZ: Let me get him off of the hook on this one.

MR. VINCENT: Thank you.

DR. MEDZ: The methods as they

are written are the yardstick by which all discharges are being measured for compliance and enforcement. We recognize there will be situations where the methods because of interferring problems, even though it's a treated wastewater where the interferring problems may make the applicability method a little difficult.

We have, in Cincinnati, a program which we are funding at least through 1985 called the Correction of Deficiencies Program. This is designed to be an interactive program with the regulated community, wherein when the regulated community finds problems with the analytical method they get on the phone and then talk with people in Cincinnati. Jim Lichtenberg would be a point of contact on this one; Jim Longbottom.

MR. VINCENT: I didn't get the name, I'm sorry?

DR. MEDZ: Jim Lichtenberg or Jim Longbottom would be the people.

MR. VINCENT: Lichtenberg or Longbottom.

DR. MEDZ: Or Longbottom; and, the problem that is being encountered would be discussed, analytical chemist, to try to resolve where the difficulties were. If the difficulty can be resolved and if there are sufficiently important we would revise the method and repropose the method.

MR. VINCENT: Thank you. Let me congratulate you. I think that is an excellent idea because when the analytical chemists can talk to each other frequently the problems seem to evaporate. So I'm very glad to hear that. Jim Lichtenberg and Jim Longbottom are the two individuals?

DR. MEDZ: And Bob Graves for the GC/MS.

MR. VINCENT: All right. That name, I think, I can get; thank you.

MR. MADDALONE: Ray Maddalone from TRW. I'm interested about the 15 industrial wastewaters. Do you intend to test the variances from each one of the individual wastewaters, each one of the contractors wastewaters to see if there is any significant difference in the precision obtained from each of the waters?

MR. GRAVES: Right now we do not. The 15 wastewaters give you a broad selection of the type of effluents that are out in the real world. The precision and accuracy for these 15 wastewaters as a group will give you an idea of what other people performing these methods on industrial wastewater get - regardless of the water type that they are analyzing. But, to answer your question, no, there is no intent at this time to take each individual laboratory as they present their data and compare it to the other 14 laboratories.

MR. MADDALONE: So there will

be a single operator and overall standard deviation that will be pooled from those 15 different wastewaters?

MR. GRAVES: Yes. The thought right now, I think, is that GC/MS should be more free of major interferring affects than the non-GC/MS methods.

MR. TELLIARD: Anyone else?

MR. GRAVES: Well, thank you.

MR. TELLIARD: Thank you, Bob.

OVERVIEW OF EFFLUENT GUIDELINE'S ANALYSTICAL ACTIVITIES

William Telliard
U.S. Environmental Protection Agency
Effluent Guidelines Division

I just can't say enough about our next speaker. Most of you know Bill Telliard as a serious, studious, scientific chemist, but he can be a lot more than that, isn't that true, Tonie?

This morning we would like to talk a little bit about EGD's analytical program. It is changed a little bit. As you notice, I'm not as tall as I used to be and I don't wear a sheep's scowl. We have changed a number of personnel over the last couple of years and we have trimmed down. We're doing less with less and I would like to introduce the people that are now in the program. The first one is Lynn Beasley. Lynn, would you stand up to provide a picture for these folks when you talk on the telephone. Next to her is Susan Hancock, Sample Control Center - you know the one - you can

never get the numbers you want from her; and, my new Dean Neptune and Mike Carter all rolled into one, Tom Fielding over here (indicating). Tom is also the project officer in organic chemicals in his spare time.

This morning I think it's important that we look back to where we came from and where we're going. As you know, we were assigned the small task of writing regulations on a number of compounds, most of which the engineers couldn't even pronounce, and to come up with analytical methods that were "useable" to develop a data base to do that.

When we started out it was a kind of rough decision-making process, but through the efforts, really, of a few people in our Athens Laboratory, Ron Webb and Larry Keith, we sold the Agency on an idea of using GC Mass Spec for looking at garbage. We've taken the mass spectrometer out of the closet and only because of the work of Larry Keith and Ron Webb through the long term R&D

project were we able to do that. As Ron pointed out to his management, "We've were sitting down here for years and no one asked us what to do. Now they are actually going to use some of this stuff that we did."

We set out by using a mass spectrometer to look at garbage, and we took a number of efforts, realizing that we were on kind of a experimental path, and out of it came a group of industrial work groups, as we like to call them. Pulp and paper people had one, Chemical Manufacturers' Association, the iron and steel industry put forward one, the Amercian Petroleum Institute put one through. I remember our first meeting with them. We sat at this big round table, the kid in the crowd was about 68. He looked at us and said you all got a big problem here, boy. We said, yes, we have to be done in a year. Since then we have had numerous meetings like this, which I think are important, where all of us get together and lie to each other.

We set out by doing a number of different phases in this development. The first phase was the one which we affectionately called screening, which meant we didn't know enough to say how good we were. After that we went back and did some verification studies called precision and accuracy after the fact, using what is now basically 624 and 625 Method. What we found was that, basically, in treated effluents, we really didn't have too much of a problem. Now problem is defined by degree - I will preempt Stanko - realizing that by "degree" is meant varying degree.

Again, in an effort to get better quantification, we went to a phase called verification, which used surrogate spiking compounds to insure or try to do some recovery corrections. As we all know, recoveries on things like phenol, particularly in untreated or raw discharges, can vary somewhat, from 22 to 94 percent, which gives you a rather large window when you're trying to do some calculations.

In an effort to keep growing we initiated the use of stable labelled isotope dilution for GC/MS about two and one-half years ago...and we used this protocol particularly in looking at the petroleum industry, offshore oil and gas, and some work in the area of organic chemicals. That's kind of where we are today. There are some deficiencies in the program that we're going to try to correct. One was the...when we started out on the isotope dilution we were limited on the available compounds to use, and we had to go through the internal standard approach for those compounds that weren't available.

In addition we expanded the use of the protocol. For example, in the petroleum industry we did not only look for the 129 compound, but for another group of compounds affectionately referred to as Appendix C. For those of you who aren't familiar with Appendix C, there is another group of compounds that the Agency is committed to do something

about some day, and we incorporated those compounds, both through the development of their analogs and the procedure for identifying these compounds.

The third expansion was into an area which is now extinct, the Synfuel industry, where we picked out specific compounds, again, going through the same workups that we did for developing the 129 original; the same standard criteria for selection of compounds. The Appendix C compounds that I spoke about are available now as spiking material.

We have had this ongoing development program. What we're looking at here is a problem that keeps creeping up which was addressed a little earlier, the cookbook versus the protocol approach to analytical chemistry. Being that most of us here are chemists, no one likes to be handed the method and told, you don't deviate, you don't do it. It says shake it ten minutes by the clock and stand under the clock and shake for ten minutes, not nine, not seven; you do it that way. Of course,

this stifles creativeness. We know we can get by with five minutes under that clock; it stops creative thinking. Three degrees a minute is fine, 15 is better.

We have a small problem. We have a protocol and we have takers, tuners, tighteners, fixers, and we end up with some questions of what is the quality of the data we're generating with these protocols. Now, we have built-in quality assurance practices; that is to say, a written protocol that we all know you won't deviate from. We have check samples which we sneak in and you run over and say that's a check sample, watch it. You can tell that because they all look the same. We have lab visits and lab reviews; that's where we all show up and everybody has a new white lab coat, all of the samples are in a row, all of the extractors are clean, all of the people are smiling. Nowadays you even have some people in the lab, I think that's a new addition.

So I think in this growth process our next step is to try to quantitate and insure the quality of the data we're getting: in one, timeliness; and, in two, reproducibility or comparability, I guess is a better term. Our group is now reduced both in the engineering staff and in the analytical staff, and we have to look at ways in which we can expand this program under this handicap. That's what I really want to talk about today.

We want to talk about a new program. The reason we do this is so that when CMA catches up with one protocol we can come out with another; got to stay about six months ahead of them. Otherwise Stanko would have to stay in the lab and work. So what we're attempting to do here is to establish a basic performance over an area of prerogatives and we're going to take some prerogatives away; I think it's important that we do so.

The question is, what is this new gimmick? Presently, we have a system where the laboratories, for all of those out there who know, receive their samples and their small amount of paper work that goes with it, fill out these wonderful tracking forms, and mail them back to Susan who then makes copies of them and sends and mails them to the project engineer, who then makes copies of them and mails them to the engineering contractor. Meanwhile, the Sample Control Center punches up the data in its computer. The engineering contractor punches up the data in his computer; and, of course, we have a few transitions or errors.

Then, a year later, after the study is done, we do a statistical package of all of the data run on various industrial categories, Oyster and Other Shuckers, for example, and we'll tell you how wrong you were a year ago. Of course, we're all busy mailing in tracking forms.

So what we're proposing to do is to cut out the paperwork. Now, you know what that means in government, you just generate more. The first thing we're suggesting is a revision of 1624 and 1625 and update to it, which is going to require the laboratories to report their data on nine track mag tape. You would mail the tape to the Sample Control Center and they would punch up the data. We would call the engineering contractor and say that the data is in the machine along with the package we put together to give us real time statistics. Therefore, the statistics would be run on, say, an eight plant visit, or the affectionate term, episode, whatever the hell that is; and, at the same time, this would give us an understanding that this data that we received is acceptable. That is to say, you must report performance. In the new protocol there will be requirement of performance; no folks, if three degrees is in the protocol, you can't run 15.

If it says a 43 hold, you can't hold it 15. If the eluting time is 12 minutes, it better come out in 12 minutes because, guess what, if it doesn't the data is not acceptable and you get to do it over again. More importantly, you don't get paid; harsh.

Now, I know you're all interested in this new protocol and I think that what we're looking at here is a step towards somewhat automating the process; one, out of necessity, due to the lack of people; and, two, out of the fact that we can no longer wait and find out what we've done; and, three, so as not to wait until the development document is half written to find out that the data is no good.

In addition to the GC/MS workup, we are also looking at doing a similar effort for metals, realizing that nine track tape for metals is not

all that common right now. We have been talking to manufacturers and some of the laboratories on putting this program out. What we are trying to do is to come up with a system of generating quality assurance data for people to look at which is better than that in the presently available records, whether it of the courts or of our own people. Real time information to the project engineer then thereby generates some effort and real time statistics. We are looking at, also, some more flexibility. We would like somehow or other to automate the tracking forms, and we are not too sure how that will happen.

Now, all of this effort has been going on for a while, and I guess the question is where, when, and how. We are presently...no, we can't transpose the tape. As of yesterday we have made the final the revisions in the new protocol, which Dale Rushneck will address, and John Norris will

show you how the tape program is going to work. Barry Eynon will tell you what the statistics are going to look like. So all of the first three parts as they relate to GC/MS are almost in place, and we would hope that by the beginning of the month we could have enough information to have a number of laboratories try using the method, which means that the next SAS (Special Analytical Services) Contract will require that the laboratory be able to perform these functions, report on tape, and meet the statistical requirements. You will look for this in your new contracts.

Also in the contracts you will find an understanding that if these criteria are not met, a whistle goes off and a flare goes up and you are told that it definitely impacts you where you are most interested, in your pocket. The new contracts will also contain a penalty clause for late arrivals. Now, we all know that there are

instrument problems, deaths in the family, more expensive samples to come in -- therefore, I realize that while you're making it really fat on our dollar, here now and then you get an outside sample where you can make a few more bucks and my sample sits in the corner of the bench growing hair. I get a phone call that says you wouldn't believe what happened yesterday, that data all set to go out, and you know that plane crash -- did you see that in the paper this morning? Your data was in that plane crash, but don't worry, it will get out next week; no problem.

So there is going to be a penalty clause for time and for performance. I think we've come far enough in this process that we are able to do this. I don't think it's going to stifle the creative, but somewhat blunt the crooked. The sole purpose here is to give all of us a better handle on where the data is and where it is coming from. I

think it is important that we are the ones that are going to do this. I hope that some of the other programs in EPA might want to use a similar system; and, of course, it's open to them. Again, since we invented everything else, it's only right that it should start in EGD. If there are any questions on this methodology, I'll be glad to address them now. I'm off free; good.

A couple of announcements while I've got you. Out in the registration desk is a setup of former historical documents, former Norfolk, Savannah, Denver proceedings for those of you who have a gap in your lives or really need something. If you want any of these, there is a sign-up sheet and we will make them available to you.

In addition, on the back table are the proceedings from the Hershey meeting of a year and a half ago, which I did not attend, for anyone who didn't get them because there was restrictive printing on those copies.

(WHEREUPON, a coffee break was taken.)

MR. TELLIARD: Our next speaker is from Interface, Dale Rushneck, who has appeared on a number of these programs before. Dale is going to talk about the revised 1624, 1625. Those of you who don't know the jargon, 624/625 is the EMSL-Cincinnati GC/MS procedure. 1624/1625 is the EGD GC/MS procedure which is a thousand times better, hence the number. I just wanted to bring you up to speed.

At this time I would like to introduce Dale and point out when Dale started in this program he was only 5'1".

REVISIONS A OF METHODS 1624 AND 1625

Dale Rushneck
Interface, Inc.

ABSTRACT

Methods 1624 and 1625 are protocols for analysis of the volatiles and semi-volatiles fractions of the organic priority pollutants by isotope dilution gas chromatography-mass spectrometry (GCMS). This paper presents improvements in these protocols, directed mainly at quality assurance and quality control (QA/QC) of the data the methods produce. Copies of Revisions A of Methods 1624 and 1625 are available from the EPA Sample Control Center, P.O. Box 1407, Alexandria, Virginia 22313.

INTRODUCTION

Isotope dilution methods employ an isotopically labeled analog of each compound of interest to track that compound through the analytical process. Methods 1624 and 1625 employ stable isotopes of the organic pollutants for this purpose.

There are two major advantages to isotope dilution methods over conventional analytical methods: first, the labeled compound quantifies and compensates pollutant loss in the analytical process; second, a spike of the labeled compound into the sample obviates the need for a spike of the pollutant itself in order to determine compound recovery. The first advantage results in a more accurate analysis; the second effects a cost savings by reducing the number of analyses required.

The original versions of Methods 1624 and 1625 (1) were the first application of isotope dilution methods on a large scale for a large number of pollutants. Such application was possible because of the availability of labeled analogs of the priority pollutants, and the widespread use of GCMS for pollutant analysis. Revisions A of these methods incorporate more labeled compounds, not only of the organic priority pollutants, but also of the Appendix C and Synfuel pollutants. In addition,

Revisions A incorporate the experiences of several laboratories (2) in use of isotope dilution methods.

OVERVIEW OF METHODS IMPROVEMENTS

The major areas of methods improvement are listed below and detailed in the sections following.

1. Provisions for analysis of complex samples.
2. Allowance for computerized data reduction and reporting.
3. Use of fused silica capillary column for semi-volatiles.
4. Standarized QA/QC.
5. Improved criteria for qualitative determination.

These improvements are directed at obtaining more precise and accurate data and at providing well defined levels of data quality.

Analysis of Complex Samples. Many of the wastewater samples analyzed in support of effluent guidelines contain large quantities of dissolved minerals,

suspended solids, polymeric compounds, and other materials which can interfere with analysis of the pollutants. Spike recoveries of the pollutants range from zero to 400 percent in these samples because the spike can be dissolved irreversibly by the matrix, or the spike can liberate a pollutant from the matrix. Use of the labeled pollutants permits these effects to be quantified. The isotope dilution method works well when greater than ten percent of the labeled compound is recovered. In the revised methods, data are acceptable if recovery of the labeled compound is greater than 10 percent of its recovery from reagent water. If not, the volatiles fraction is diluted by successive factors of ten and analyzed; the semi-volatiles fraction is diluted by a factor of 100, then extracted and analyzed. As a result, pollutants are accurately quantified in an analytical range in which the method is known to work.

Further provisions in the revised methods for analysis of complex samples are use of an alternate quantitation mass or an internal standard method if an interference is present at the primary mass, use of a lower GC column temperature program rate as an option to resolve overlapped GC peaks, and dilution of the water or extract to bring high concentrations of pollutants within the calibration range of the GCMS.

Computerized Data Reduction and Reporting. The number of pollutants and labeled compounds in each sample ranges from approximately 100 to 214, with 13 discrete pieces of information required for rigorous quality assurance of each pollutant or labeled compound. Clearly, a computer is required for storage and tracking of this information. The methods were revised to permit maximum utilization of computerized GCMS data systems for repetitive operations, with the safeguard that all results

must be verified manually by a qualified spectrometrist.

Modern GCMS instruments use a calibration curve for those compounds which have a non-linear response, or use an averaged calibration or response factor for those compounds which respond linearly. The revised methods employ a five-point calibration (most methods use three) to better define the curve over the calibration range. Once the curve is defined, it is verified at a single point on each shift. Other information stored for each pollutant is the mass spectrum, retention time (absolute and relative), quantitation mass, and peak area. These data are used to search and locate each compound and to identify and quantify it properly.

Quality control charts (3) are generated by the GCMS computer to determine and assure a high level of data quality. These charts are updated each working shift.

Data can be reported on magnetic tape to eliminate transcription errors and reduce reporting times.

Fused Silica Capillary Column. The advantages of these columns for analysis of the semi-volatile priority pollutants have been demonstrated by Sauter, et al. (4). Method 1625A mandates the use of capillary columns for the acid and base/neutral fractions of the pollutants. The improved GC resolution provided by a capillary column is required for separation of the large number of compounds in these fractions when the labeled compounds are included.

Standarized QA/QC. The July 1982 Revisions of the 600 series EPA Methods for analysis of priority pollutants in waters (5) incorporate repetitive analyses of the pollutants spiked into reagent water for initial and on-going tests of laboratory performance. Methods 1624A and 1625A incorporate

these tests, also. Additional tests required by the revised Methods are summarized below:

1. Each working shift

    1.1 Mass spectrometer

        1.1.1 Spectrum validity and resolution

            1.1.1.1 Volatiles: p-bromofluorobenzene (BFB)

            1.1.1.2 Semi-volatiles: decafluorotriphenylphosphine (DFTPP)

        1.1.2 Absolute response (suggested)*

            1.1.2.1 Volatiles: 80,000 to 150,000 area for 100 ng toluene

            1.1.2.2 Semi-volatiles: 20,000 to 50,000 area for 20 ng phenanthrene

        1.1.3 Relative response (to isotopic diluent or internal standard)*

            1.1.3.1 Response ratios by isotope dilution: $\pm$ 10 percent of initial calibration

            1.1.3.2 Response factors by internal standard: $\pm$ 20 percent of initial calibration

    1.2 Gas chromatograph

        1.2.1 Resolution

            1.2.1.1 Volatiles: <10 percent valley height between toluene and toluene-d8

* variables to be investigated in inter- and intralaboratory studies

1.2.1.2 Semi-volatiles: <10 percent valley height between phenanthrene/anthracene

1.2.2 Absolute retention times*

1.2.2.1 Volatiles: chloromethane in 2-4 minutes; ethylbenzene in >30 minutes

1.2.2.2 Acids: phenol resolved from solvent: pentachlorophenol >20 minutes

1.2.2.3 Base/neutrals: N-nitrosodimethylamine resolved from solvent; benzo(ghi)-perylene >40 minutes

1.2.3 Difficult compound detection*

1.2.3.1 Volatiles: 100 ng 2-chloroethylvinyl ether, bromoform, and 1,1,2,2-tetrachloroethane

1.2.3.2 Acids: 50 ng pentachlorophenol; 100 ng 2-methyl-4,6-dinitrophenol; 250 ng hexanoic acid

1.2.3.3 Base/neutrals: 50 ng benzidine; 100 ng di-n-butylamine, 10 ng B-naphthylamine

2. Each sample

2.1 Internal standard peak area: $\pm$ factor of two of area in standard

2.2 Labeled compound recovery: >10 percent of recovery from reagent water

3. Each sample lot (samples analyzed on a given 8 hour shift for volatiles; samples started through the extraction process on a given shift for semi-volatiles, to a maximum of 20)

   3.1 Blank: all pollutants <10 ug/L

   3.2 Recovery of standards spiked into reagent water*

      3.2.1 Volatiles: 85-115 percent by isotope dilution; 60-140 percent by internal standard

      3.2.2 Semi-volatiles: 85-115 percent by isotope dilution; 40-160 percent by internal standard

4. Miscellaneous

   4.1 Sample carry-over (volatiles only): <5 ug/L

   4.2 Recording of extraction and concentration variables (semi-volatiles only): initial and final extraction and concentration volumes

   4.3 Manual examination of GC peaks greater than height of internal standard peak(s)

The specifications above are being revised based on inter- and intra-laboratory testing of the Methods, so that final specifications will reflect performance

actually achievable by analytical laboratories. Where possible, these specifications are performance based; i.e., they require that a laboratory repetitively demonstrate the ability to analyze the pollutants spiked into a reagent water matrix.

Improvements in Qualitative Determination. In the original versions, methods 1624 and 1625 specified ± 20 percent relative abundances of one to three spectral masses plus relative retention time for pollutant identification. Revisions A require ± a factor of two in relative abundances of 5 masses minimum, and all masses having abundances greater than 10 percent of the base peak plus relative retention time for pollutant identification. This change is directed at reducing the number of false positives reported and is based on the fact that the presence or absence of a given mass is of greater significance than its relative abundance. The disadvantage to use of 5 masses is that some

pollutants do not produce spectra with 5 masses with 10 percent or greater relative abundance. As a result, the detection limit for these pollutants will be proportionately raised by the reduction in relative abundance below 10 percent. (Ten percent was chosen based on experience with pollutant spectra.) But it is better to know that the actual pollutant was detected than achieve a low detection limit with high risk of a false positive. A further requirement by the revised methods is that a qualified spectrometrist must decide if the spectrum is that of the pollutant; therefore, an interference at one or two of the five minimum masses does not preclude identification. A subsequent revision of the methods will specify mass-relative abundance data for the pollutants and labeled compounds based on inter-laboratory studies, but the requirement shall remain that each laboratory must obtain authentic spectra of the pollutants on each instrument used for pollutant analysis

under BFB or DFTPP tuning conditions. Understanding these spectra is fundamental to pollutant identification.

With isotope dilution methods, one of the most important criteria for compound identification is the relative retention time between the pollutant and its labeled analog. This measurement is usually more accurate than the scan resolution specified for most GCMS methods. Revisions A specify a retention time tolerance of $\pm$ 6 seconds for volatiles, and $\pm$ 2 seconds for semi-volatiles, based on relative retention time computations. The exact tolerance in relative retention time will be specified on a per compound basis as a result of inter-laboratory studies in a subsequent revision to the methods. Relative time tolerances between internal standard(s) and the labeled compounds will also be specified as a result of inter-laboratory studies, but are typically $\pm$ 30 seconds.

Of concern in the identification of a pollutant by its relative retention time is the effect of column overloads by a large concentration of the pollutant or by other compounds, especially when capillary columns are employed. The use of a large window for the labeled compound, coupled with a small window for the pollutant relative to the labeled compound nearly precludes a false negative under these conditions. In addition, the spectrometrist is required to examine manually all GC peaks with heights greater than the internal standard(s).

SUMMARY

The A revisions to Methods 1624 and 1625 have been outlined above. Further revisions will be made based on advances in GCMS technology and on feedback from laboratories performing analyses using the revised methods. QA specifications will be revised to reflect performance obtainable

by analytical laboratories. Revisions A reflect the state-of-the-art in analysis of pollutants by isotope dilution GCMS.

REFERENCES

1. Methods 1624 and 1625, USEPA, Effluent Guidelines Division, WH-552, 401 M Street, S.W. Washington, D.C. 20460.

2. The laboratories participating in the original and/or revised methods were: Acurex, Environdyne, IT Analytical (Knoxville), Radian, S-CUBED, and TRW.

3. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EMSL, ORD, USEPA, Cincinnati, Ohio 45268, EPA-600/4-79-019.

4. Sauter, A. D., et al., "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants." "Journal of HRC & CC," 4 (1981) 366.

5. Longbottom, J. E., and Lichtenberg, J. J., Ed., "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EMSL, USEPA, Cincinnati, Ohio 45268, EPA-600/4-82-057.

QUESTIONS AND ANSWERS

MR. WALTERS: Gary Walters from Jordan Labs. The use of five masses for compound identification may increase the possibility of false positives in complex samples, because the greater the number of masses, the greater the chance of interference at one of these masses. Do you agree?

MR. RUSHNECK: I would not agree with that as a general statement. Under certain circumstances, what you say may be true, but these protocols address the broadest number of circumstances.

MR. WALTERS: Well, it is my contention that a limited number of masses might permit measuring compounds which have one main base peak with other peaks close to 10 percent relative abundance at lower levels. For example, The poly-nuclear aromatics.

MR. RUSHNECK: If you drive that to its logical conclusion, only one mass would be best.

MR. WALTERS: I see your point. You want to save time, but not make the mistake of not seeing something that is really there.

In using a dilute aliquot for semi-volatiles, is the decision to use the dilute aliquot based on prior experience with the sample?

MR. RUSHNECK: Yes. For example, if we know that untreated effluents from a given industrial category have caused extraction or concentration problems in the past, the dilute aliquot would be required.

MR. WALTERS: How do you handle complex samples? For example, a sample which contains free oil?

MR. RUSHNECK: I think a number of people here have been exposed to that type of sample. Several options are available: the sample

can be processed as if it were water to see if it can be extracted and concentrated; each phase can be processed as a separate sample; or it can be stirred vigorously while a representative aliquot is withdrawn.

MR. WALTERS: Thank you.

MR. DELLINGER: Bob Dellinger, Effluent Guideilnes Division. What was the lower end of acceptable recoveries for semi-volatiles?

MR. RUSHNECK: For the labeled compounds in any sample?

MR. DELLINGER: Yes.

MR. RUSHNECK: It was 10 percent for volatiles or semi-volatiles when compared to recovery from reagent water.

MR. TELLIARD: Thank you, Dale.

As you noticed, for those of you who were fortunate enough to be here yesterday we just had one hell of a good time. Anybody want to talk about how low we should scan.

Our next speaker is Bruce Colby. Bruce has also been a continuing appearing act on this road show. Bruce is from what we used to call S-CUBED, now named SCUBED, and is going to talk about something...what; see, I knew he was going to remember. Bruce.

OPTIMIZATION OF GC/MS ANALYSES

Bruce Colby
S-CUBED

DR. COLBY: The topic that I am going to be addressing was initially described as Optimization of GC/MS Analyses. For this presentation this will be a description of some of the kinds of information that has been developed and incorporated into the revision that Dale was just speaking about. Historically, we have called these acceptance criteria. The main thrust of these criteria has centered around the precision with which measurements should be made in a laboratory on a very routine basis.

The first topic I am going to address is the question 'when does a retention time for a compound detected in a data file agree with the retention time of a standard run previously.' The major issue in this apparently trivial question has to do with compound identification. If the

retention time is not in agreement, even though the mass spectrum is the same, it's improper to make a positive identification of a compound. Further, more precise the retention times result in narrower windows within which identification can be made, the less likely a false positive identification will be generated.

The second topic I'm going to address is the reproducibility of responses on a nominal one-month basis. The data I'll show were acquired over approximately a four-week continuous activity. The specific data are from standards analyzed on a daily basis. The rest of the acquisition time was devoted to analyses of samples from the Synfuel industry. The samples were particularly dirty. They were process waters, treated and untreated effluents, and they contained percentage quantities of some of the priority pollutants. The impact that samples had on the data was quite real and I'll try to point out some of

the manifestations of running these "dirty" samples on a routine basis as I go along.

The first thing, then, that we will look at a plot of the absolute retention time precision in terms of percent standard deviation as a functional retention time (top).

Below that is relative retention time precision, and finally the isotope dilution relative retention time precision. What we desire for predicting further retention times are the most precise retention times. In other words, we have run standards so we know the retention times. How we can predict what that retention times will be in a sample file when we inspect it. Clearly we can see some interesting things in this slide.

Initially, in the run retention times is considerably less precise than it is later on in the run. This is true both for relative and absolute retention times. I should point out that

this is fused silica data; we'll get to the packed-columns in a minute. We believe the thing that causes this is lack of precision in re-setting or reestablishing the initial chromatographic conditions, particularly oven temperature and carrier flow rate. We're near ambient temperature, and most GC ovens don't control well in that area unless they have a sub-ambient regulator. In this situation we did not have that.

With the relative retention times, where an internal standard present, we start to see one other thing; a significant dip right at the time that the internal standard is eluted. This is followed by a slow rise (decrease in precision) as we go out to longer retention times. This seems to say that if we put in more than one internal standard which is something that certainly could be done, we could improve relative retention time precision and consequently the ability to predict them.

This is consistent with short-term precision data that Drew Sauter has published and is something that the hazardous waste people are currently doing. The ultimate extention of using internal standards, if you will, would be isotope dilution where for each compound has a labeled analog present. The result is exactly what you would expect; it drops percent standard deviation right down onto the baseline pretty near.

The predictability of isotope dilution relative retention times, if you will, is extremely good. I have taken those points and expanded the scale a little bit. The scale here (Slide 2) instead of being 10 percent is now 1 percent and you can see that precision is essentially constant across the figure. Right in the beginning it's not quite as precise, and I think this probably has to do with the fact that the peaks are very narrow at that point and that it is very easy for a one scan difference to have a fairly signi-

ficant impact on the ability to calculate the relative retention times.

For packed-column work, this is the volatile methodology. I have created a similar set of plots (Slide 3). We see, roughly, the same behavior as with fused silica capillaries. That is initial poorer precision compared to the precision later on in the run where the chromatographic conditions become more reproducible. When we go to internal standards and I have only plotted data for two in order to keep it easy to see, again there is a dip where internal standards are eluded with best precision right at the internal standard elution point. This is true for both internal standards, although the second dip is much broader than the first. Again, with isotope dilution we have the best case situation, a closely eluted reference for each compound and the retention times are quite precise. The slight decrease in precision at short retention times

we suspect has to do with peak width, the peaks are more narrow in the beginning and a one scan difference at 200 scans has a more significant impact then a one scan difference in 1600.

Now if we take those precision data and use them to identify what we really want to know, that is the range of time within which we should look for a spectral pattern in the data file, we get a plot such as that in Slide 4. Here the search windows are plotted as plus or minus three standard deviations in seconds for each compound.

With the absolute retention times we have wider windows in the beginning. Then they become relatively constant somewhere around 35, 36 seconds. The times plotted are the total window width you would expect to find the spectral pattern in. When we go to relative retention times we see a very marked dip in the curve right at the elution point of the internal standard. Again, we could expand the internal

standard technique to improve the retention time or narrow the retention time windows down by adding more internal standards. The ultimate case, again, being isotope dilution where we have specific internal standards present for each compound.

The isotope dilution data plotted on a factor of 10 different scales so that you can see more closely what that looks like is shown in the fifth slide.

The windows for searching or accepting a spectral pattern for a postive identification in the volatile fraction looks something like what I have shown in these curves (Slide 6) with a 100 second full scale for the window width. Absolute retention times are not much of a problem initially. I'm showing a dip and a rise in the curve, but I may be overly optimistic in the shape and may be weighing this last point a little too heavily. Nominally, however, it's fairly constant

across the retention time scale. When we go to the internal standards, we see the dips at the elution points for the internal standards. Clearly, more than one internal standard improves, i.e., narrows, the windows. We can reference the early ones to correspond to the first internal standard and the later ones to the second internal standard. Historically, our lab had been using the internal standard which is eluted most closely to the compounds we are attempting to identify. Now we know the cross-over is not as straight forward as that, so we have moved the cross-over point down to here, decreased the windows slightly and believe we are doing a more credible job. With isotope dilution, again, very, very narrow windows can be used due to the highly reproducible relative retention times.

In tabular form the plotted data looks something like this (Slide 7) for fused silica precision. The absolute retention times came out to

be on the average about 2.27 percent deviation, but keep in mind that there is a distribution to these data which is not a normal random distribution. There are significant trends within the result so this is just a ballpark kind of number to fall back on. Relative retention times are roughly twice as precise using a single internal standard and somewhere around 20 times is precise using isotope dilution. The effect of precision on the search windows within which one would accept agreement of a spectral pattern results in a nominal 40 second window for absolute retention times, and about half that (20 seconds) for relative retention times. This means that we have cut down the quantity of data that must be processed by a factor of two by using one internal standard. We have also cut down the possibility that similar spectral pattern will exist in the window and result in a false positive identification. We cut the window down to a very, very small one by going

to isotope dilution. With a one second scan you are looking at a one standard deviations on the order of a third of the scan or a little less. Of course, we can't really make any technical sense out of a partial scan.

For the pack-column VOA data, precisions are nominally the same as they were with the fused silica capillary data for absolute retention time and relative retention time. Remember, however, we had a factor of 10 improvement with the fused silica data. With packed columns we're dealing with peaks which are much wider, we're scanning slower, and this results in somewhat lower precision.

The windows, again, are very similar to what we had with fused silica, nominally 40 and 20 seconds but not quite as narrow for the isotope dilution technique. We pretty much settled on the plus or minus three standard deviation numbers for acceptance criteria and, in a short term, we

would expect people to be able to do that. The windows are sufficiently small so that even a three sigma window is easy to work with from a data handling standpoint.

The second area that we get into now has to do with the response precision of the standards that were analyzed. The data we see first is for fused silica runs of the base/neutral and acid fractions. With an external standard situation we see precisions which are nominally the equivalent averaging about 34 or 35 percent standard deviation for either fraction.

When we go to a conventional internal standard, in this case the difluorobiphenyl Dale mentioned earlier, we see a considerable improvement, about a factor of two for the base neutrals and not quite that with the acids. I'll get into some of the difference that appears to exist here in a moment. This is sort of like the retention time precision improvement.

With isotope dilution we see roughly another factor of two improvement in terms of the response reproducibility. We expect standard analysis results to be this precise day-after-day-after-day; if it's not, something is wrong with the equipment, the standard, the analyst, or possibly all three.

The interesting thing to note is that there seems to be a fairly substantial difference in the internal standard precision for base/neutral and acid fraction compounds. The quick thing to note, of course, is that our internal standard is essentially a neutral compound and that perhaps there is a relationship here. Consequently, we took the data and re-normalized it to 2,4,6-tricholorophenol. This compound is eluted right next to difluorobiphenyl so its retention time is the same. Also, its quantitation mass is within a few masses of the mass used with difluorobiphenyl so we expect no major spectral impact of using the trichlorophenol. When we do that

renormalization the acid fraction precision improves markedly, roughly about a factor of 2.

In looking at these data it was pretty clear that there were several other compounds that seemed to behave more like the acids when we did this renormalization. When we took those compounds which are more precise with the trichlorophenol as the normalizing response then we have got, again, an improvement in the situation in both cases. Now, we've taken some previously so-called base/neutrals and treated them as if they were acids and picked up some improvement. The degree of improvement is shown here where all eight of the phenols present improved on the average 37 percent by going to the trichlorophenol reference. All of the phthalates present improved by 35 percent. Isophorone improved 40 percent and nitrobenzene improved 60 percent. These are all compounds that are somewhat more polar due to functional groups "hanging out" of them that

probably tend to behave differently from the difluorobiphenyl. So there appears to be some sort of a chemical consideration here and that is quite interesting. What it seems to say is that in dealing with retention times, one would like to use the reference most closely eluted in time as the reference but for quantitation, to use some other compound present in the run to do response normalization calculations.

We also looked for a correlation between response precision and the difference between quantitation mass of the reference compound and the target compound, for conventional internal standard situation. We found what may be a weak but not a very convincing correlation. We expected that even if DFTPP criteria are met, there is still room for a great deal of latitude in terms of the response factors one would expect to get and that as the difference in mass between target and internal standard increases, we would expect

response precision to become poorer.

From these data, it's not totally clear that this is the case, but it is easy to argue that it could. I was surprised that something much more dramatic didn't show up here, but I think it says is that tuning with DFTPP is useful.

Overall, the use of an internal standard improves precision, but you have to give up a piece of information in the process in that normalization takes place and if the instrument's performance is degrading in an absolute sense this might not be detected.

When we go to isotope dilution there is about a factor of three gain in precision and the precision for isotope dilution standards is extremely good.

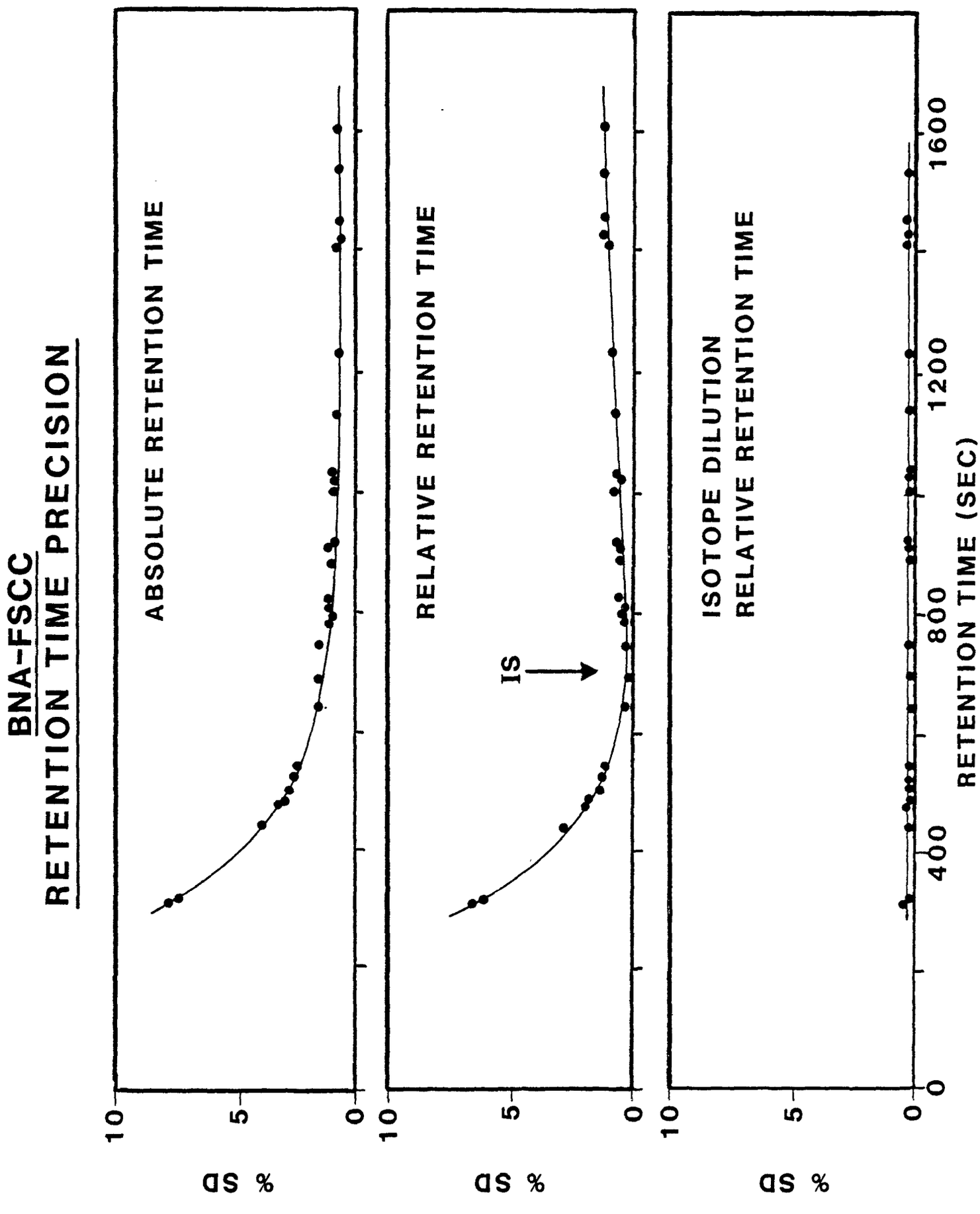
Finally, I took a quick look at the pack versus fused silica capillary column data. I'm not sure this is really valid owing to differences in method but I did it anyway.

When we look at the retention time windows it was rather striking to find them so close, both for absolute area or external standard and for internal standard. Isotope dilution was not nearly as comparable, perhaps because we are in an area where scan rate and peak shape become the limiting factors affecting precision. There was also fairly good agreement between external standards or raw area precision. The same is true for the internal standard data. I was surprised to see these data, but also encouraged to see them because I think what it's saying is that we are looking at numbers which represent what can be done with the methodology and not what a single operator or instrument is doing. With isotope dilution relatively the same kinds of precision again. It's interesting to see that an external standard, an internal standard, or an isotope dilution approach will yield results not highly dependent upon whether the approach is geared around pack columns or

fused silica capillary columns.

The general conclusion we come up to, and I brushed on these earlier, is that the data tend to support the conclusion that one should calculate relative retention times using the nearest eluted internal standard, and that the relative response, be it isotope dilution or internal standard be calculated using an internal standard which is chemically similar to the target compound. Naturally, in both of these cases the ultimate would be isotope dilution. One can also make use of this information with internal standard approaches and expect some improvements.

This brings me to the end of my data. I would be willing to address any questions that you may have at this time.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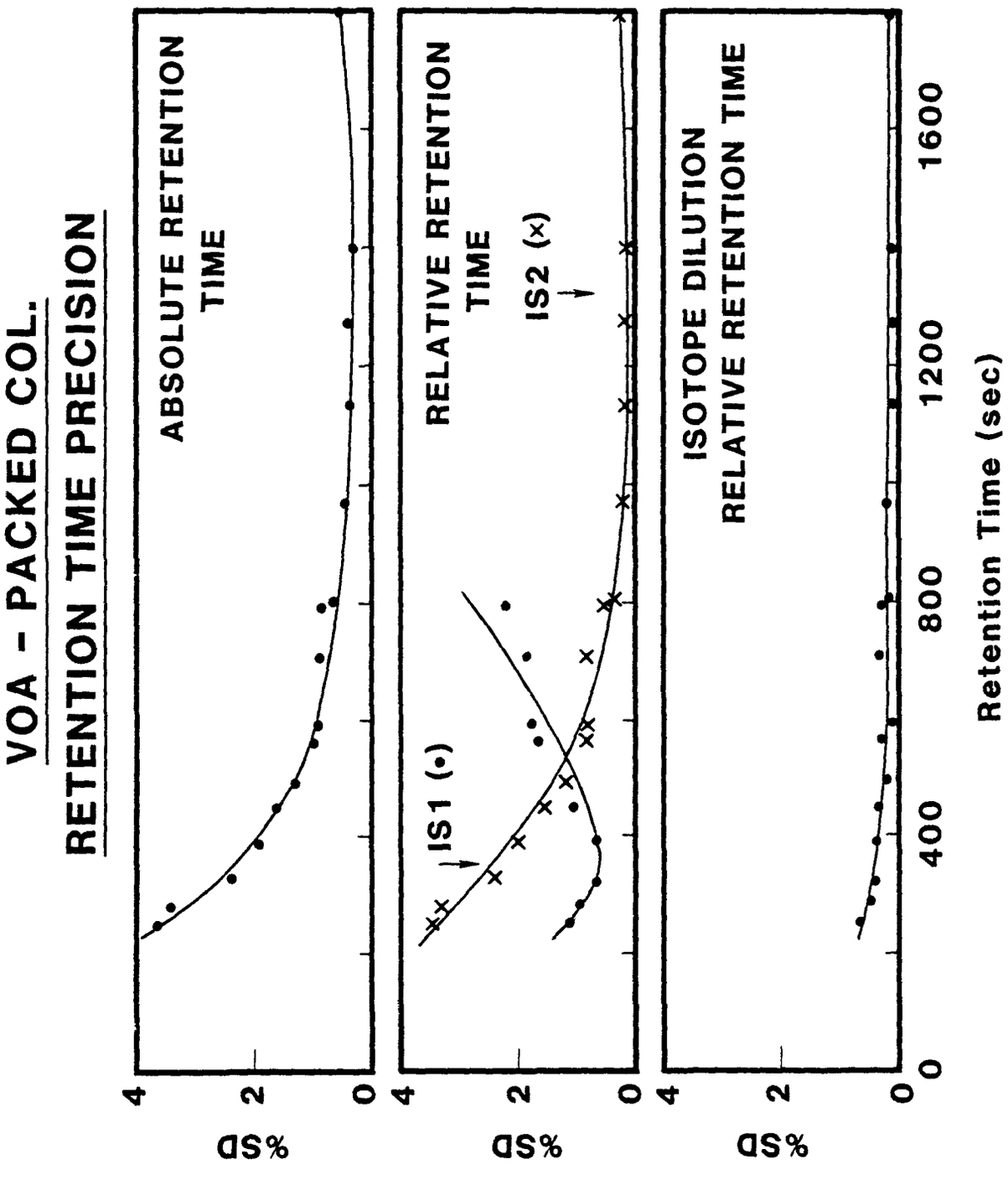
VOA - PACKED COL.
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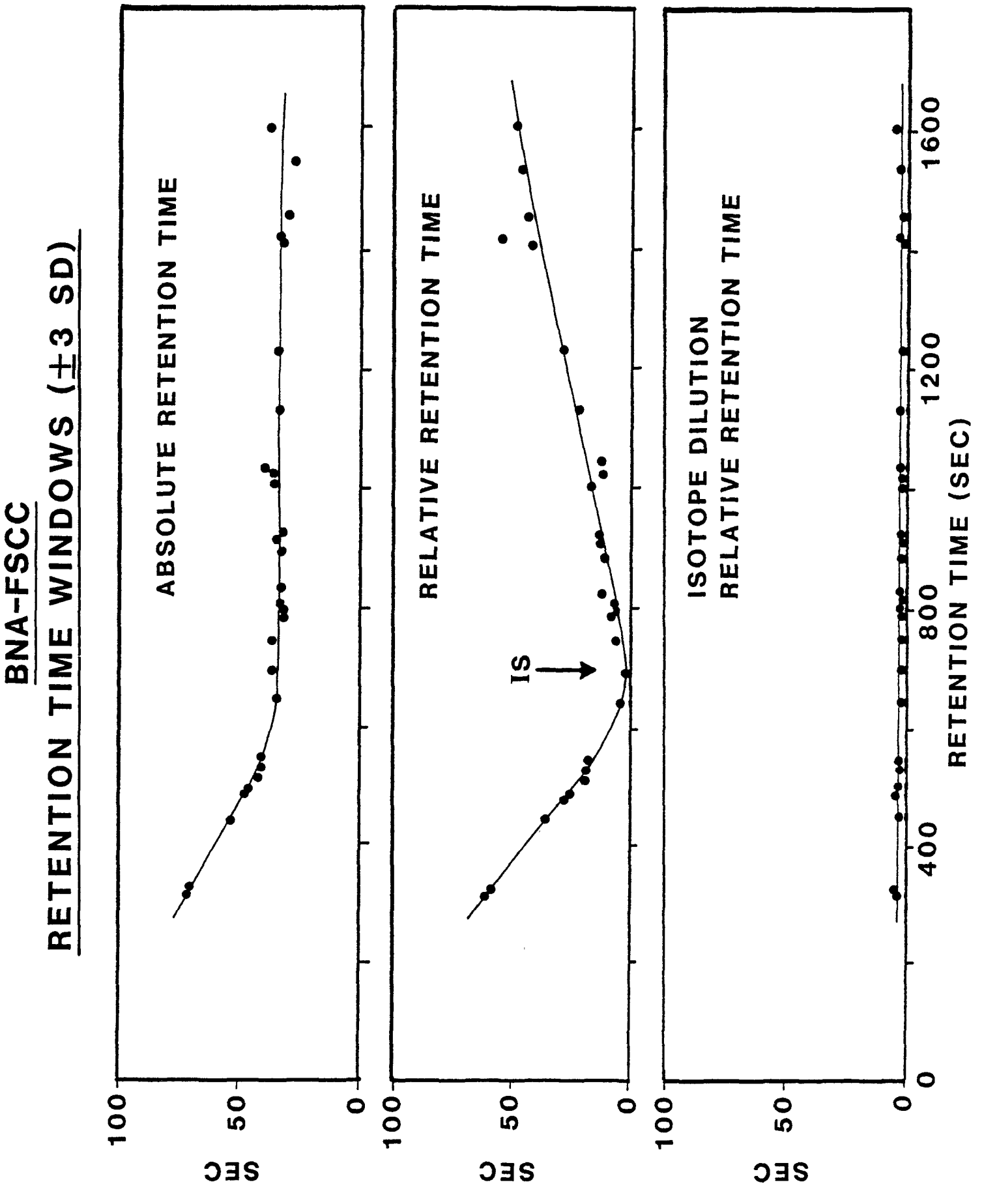
BNA-FSCC
RETENTION TIME WINDOWS (±3 SD)
ABSOLUTE RETENTION TIME
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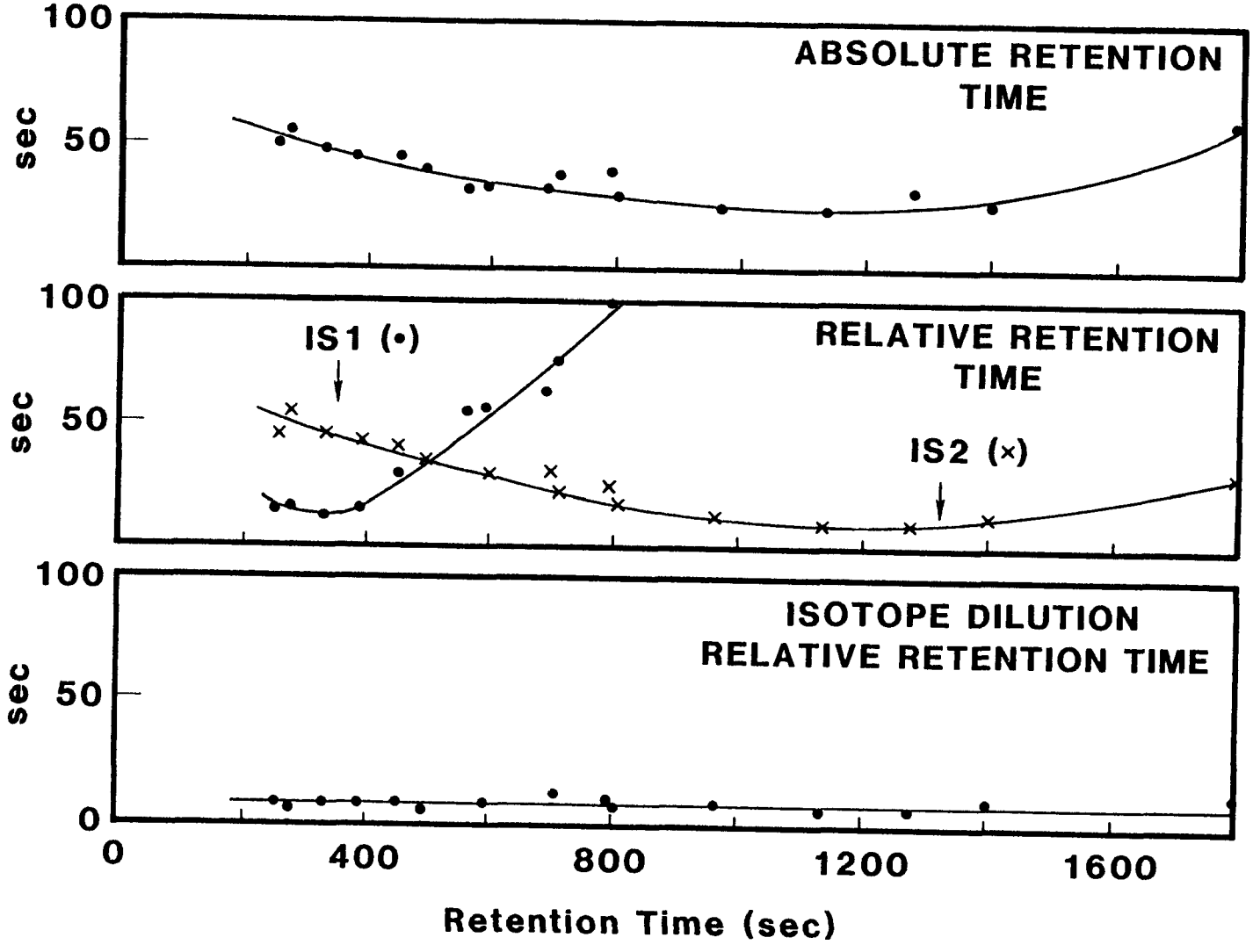
RETENTION TIME (SEC)

VOA - PACKED COL.
RETENTION TIME WINDOWS (±3SD)



BNA-FSCC
MEAN TARGET COMPOUND RETENTION TIME PRECISION

METHOD	PRECISION (% SD)	±3SD WINDOW (sec)
Absolute Retention Time	2.27	39.4
Relative Retention Time	1.21	23.9
Isotope Dilution Relative Retention Time	.085	1.8

VOA - PACKED COL.
MEAN TARGET COMPOUND
RETENTION TIME PRECISION

METHOD	PRECISION %SD	±3SD WINDOW (sec)
Absolute Retention Time	1.30	39.1
Relative Retention Time	0.60	20.0
Isotope Dilution Relative Retention Time	0.25	8.4

BNA-FSCC
MEAN MASS SPECTROMETER
RESPONSE PRECISION (% SD)

METHOD	BASE/ NEUTRAL	ACID	TOTAL
External Standard	30.4	41.5	34.4
Conventional Internal Standard*	15.0	29.1	17.2
Isotope Dilution	7.4	5.3	6.6

*difluorobiphenyl

MEAN INTERNAL STANDARD RESPONSE PRECISION (% SD)

INTERNAL STANDARD	BASE/ NEUTRAL	ACID	TOTAL
difluorobiphenyl	15.0	29.1	17.2
2,4,6-trichlorophenol	15.4	16.0	15.6
optimum	10.4	15.2	12.9

COMPOUNDS SHOWING IMPROVED RESPONSE PRECISION WITH 2,4,6-TRICHLOROPHENOL INTERNAL STANDARD

COMPOUNDS	IMPROVEMENT (%)
All 8 phenols	37
All 4 phthalates	35
isophorone	40
nitrobenzene	60

RESPONSE PRECISION vs Δ MASS

METHOD	FRACTION	CORRELATION COEFFICIENT	SLOPE
Conventional Internal Standard	Base/Neutral	.488	1.02
	Acid	-.264	-.399
	Total	.538	1.367
Isotope Dilution	Base/Neutral	-.079	-.102
	Acid	.040	.012
	Total	.139	.136

VOA - PACKED COL.
MEAN MASS SPECTROMETER
RESPOSE PRECISION

METHOD	%SD
External Standard	28.7
Internal Standard	10.6
Isotope Dilution	3.7

PACKED COL. vs FSCC PRECISIONS

METHOD	RT (±3SD in/sec)		RESPONSE (%SD)	
	PACKED	FSCC	PACKED	FSCC
Ext. Std.	39.1	39.4	28.7	34.4
Int. Std.	20.0	23.9	10.6	12.9
Iso. Dil.	8.4	1.8	3.7	6.6

CONCLUSIONS

- Calculate RELATIVE RETENTION TIMES using NEAREST INTERNAL STANDARD
- Calculate RELATIVE RESPONSE using MOST SIMILAR INTERNAL STANDARD

QUESTIONS AND ANSWERS

MR. SAUTER: Drew Sauter with the Environmental Monitoring Systems Lab in Las Vegas. The only thing I would like to point out, Bruce, when you talk for those others that are using multiple internal standards, your internal standard data which, you know, it was an interesting present on that, is somewhat biased towards the worst case of internal standardization. That is, there is only one multiple internal standard which approach isotopic dilution in infinite extrapolation would provide in many cases better relative retention time; I think that's really the gist of what you're saying.

So that internal standard quantification and relative retention time precision information that's been given should be considered as a worst case, internal standard comparison. Would that be accurate?

MR. COLBY: One internal standard is the worst case of an internal standard technique; yes, definitely.

MR. BEIMER: Bob Beimer, TRW. Did you try, in terms of the most similar chemically type of compound, to determine the effect of the difference, the absolute delta in mass from the quantitation mass of what you are analyzing to the quantitation mass of the standard and the internal standard to determine if the magnitude of that difference has an absolute effect on the ability to quantitate; did I make myself clear?

MR. COLBY: I think so. I think the answer is, yes, but that's a difficult question to address. Probably what we ought to do is sit down and I can describe in more detail what we really did.

We expected a large delta between the two masses used to calculate a relative response, and that large deltas would led to an equally large delta on

a day-after-day basis. The changes in them, slight changes in the tuning would yield measureable or noticeable changes in the relative response; is that what you're asking?

MR. BEIMER: Well, let me put it in terms of an example. If you used phenol as an internal standard for pentachlorophenol, would you get a better number than if you used a compound which had a mass more close to the pentachlorophenol quantitation massive 266?

MR. COLBY: The data that I have presented here supports the argument that you would be better to use phenol as a reference for pentachlorophenol even though the mass delta is very large. I think if you made a point of doing crummy DFTPP tunes so that you skewed in one direction one day and skewed in the other direction the next day, this would not hold.

MR. TAYLOR: Paul Taylor from California Labs. All of this is all in the recs

because you have polarity problems, chromatography problems and it's not simple to separate the example of phenol and pentachlorophenol is a particular example of that where you are not only dealing with difference in mass, difference in retention time and perhaps an affinity for the column.

So that's probably the reason you have a problem with the correlation co-efficient for whether there was a change in mass; precision response factor with delta mass.

MR. COLBY: In this particular instance we had data and we just went back and looked at them to see what we could do. If we set out to prove that delta mass can have an effect, certainly could establish it, but I agree with you completely, there are a lot of things that come to play in this and we're only trying to sort out the ones that seem to have enough impact

that we can clearly identify them as significant and try to make the best of that information.

MR. TAYLOR: So basically your most similar internal standard definition is empirical, whatever works?

MR. COLBY: It definitely is.

MR. TAYLOR: And that's reasonable.

MR. SAUTER: Drew Sauter, again, with EPA, Las Vegas. I think what your data shows, Bruce, is that effectively what it's saying and we've discussed this before is, that the instrument once tuned with some error.

Another point, though, with respect...it all depends on how you want, I think how one wants to look at the data and whether you are looking at it through an inter and intra-laboratory perspective. I could see problems; and, other people have published this.

We approached GC/MS a long time ago on this where relative response factor precision does seem to expand away from the internal standard. I think if you were...I could see some chemical sense in some of the data that you give, obviously, supports that similar compound classes should be used as internal standards which is effectively isotopic dilution. One might find a response factor precision problem with phenol relative to pentachlorophenol, for example, strictly because the mass difference is large; but, within the limits of DFTPP tune, I think your data shows that that difference is not that great.

MR. RUSHNECK: Dale Rushneck, Interface. In those instances in which you have compared pack and fused silica capillary, were the labeled compounds present as well as the unlabeled compounds in all of the samples you analyzed; that is, was there a carrier effect?

MR. COLBY: I am not totally

sure I understand your question, but I don't expect much of a carrier effect with a few hundred nanograms of most labeled compounds. If we had put a microgram in, perhaps.

Can you rephrase the question if I didn't answer it?

MR. RUSHNECK: Yes. When you compare the capillary and the pack and you inject the samples, were the labeled compounds always present in those samples?

MR. COLBY: Always, yes.

MR. RUSHNECK: Well, I agree with you. The carrier effect is most pronounced at the higher levels, but even 100 nanograms is sufficient, I think, and that accounts for what surprises me is as to how good the pack column data are.

MR. COLBY: Well, it is volatiles data; if it were base/neutral fraction data, I expect it would be much worse.

MR. TELLIARD: Any other questions?

Thank you. We'll break for lunch and we are due to reconvene at 1:30.

(WHEREUPON, the lunch recess was taken.)

MR. TELLIARD: I would like to start the afternoon session of the continuing saga, fun in the labs. In the afternoon session, our first speaker is George Stanko from Shell Development. George is one of the rare people who have been with this ongoing scenario since the very beginning. There was water, darkness and George. Darkness didn't seem to bother George at all.

When we started in this program, George was one of the harder people to deal with because he had data. Most of the other members of the committee were your basic coffee cup chemists, but George went out and did some nasty things, he actually got some numbers. Therefore, it had

made it a little bit more difficult for me to deal with him. Today, George is also going to show us some of his new data on 624 and 1624 on the volatile fraction and the GC/MS procedure.

ROUND ROBIN STUDY OF EPA METHODS 624 and 1624 FOR VOLATILE ORGANIC POLLUTANTS

George H. Stanko
Shell Development Company

ABSTRACT

A round robin study of EPA Methods 624 and 1624 for volatile organic pollutants was conducted at eight laboratories. The study was designed to determine interlaboratory and intralaboratory precisions and accuracies of EPA Methods 624 and 1624: to evaluate laboratory performance for EPA Standard Samples; and to explore the use of methods of standard addition. The precision, accuracy, variability, and uncertainty in the resulting data for the methods studied are reported and discussed.

INTRODUCTION

Previous experience with Gas Chromatography/ Mass Spectrometry (GC/MS) analytical methods for priority pollutants in wastewater prompted a study to evaluate the performance of a selected number of industrial and contract laboratories that routinely employ GC/MS methodology for the analysis of priority pollutants in wastewater. The study was limited to EPA Methods 624 and 1624 for a selected number of volatile organic pollutants, and was designed to determine the precision and accuracy of the methodology, to compare Method 624 with Method 1624, and to explore the use of method of standard addition with GC/MS methodology. The prime focus of the study was directed toward the GC/MS methodology by holding other variables associated with sampling, sample preparation, preservation, and holding time constant. The resulting data and the statistical analysis of the data reflect only the variability and uncertainty associated with the GC/MS methodology.

Arrangements were made with eight industrial and contract laboratories to analyze identical samples within a specified time and report the data within 30 days. Each of the participating laboratories was furnished a set of nine samples, along with instructions which outlined procedures and goals of the study. Participants were advised that each sample had been spiked with nine deuterated compounds. The identities of the deuterated compounds and the theoretical concentrations for each of the components in a stock spiking solution were provided, as well as a portion of the stock spiking solution to facilitate calibration.

TEXT

Samples for Study

A total of nine samples were prepared for the study using an organic-free water (Super Q) or a chemical plant effluent. Three of the samples (1, 2, and 9) were prepared with Super Q water, and six of the samples (3-8) were prepared with portions of the same chemical plant effluent which was collected as a single grab sample. Table 1 lists the theoretical spike concentrations for the nine samples used for the round robin study.

Samples No. 1 and No. 2 were prepared in an organic-free water matrix using EPA Standard No. 2. The concentration range of the nine priority pollutants ranged from 22ug/l to 228ug/l. These samples also were spiked with the nine deuterated compounds, all at the 100 ug/l level. Samples Nos. 3-8 were prepared using the same chemical plant effluent. Sample No. 8 was the chemical plant effluent that was spiked only with the deuterated compounds. Samples Nos. 3-7 were prepared with the same chemical

plant effluent and by blind spiking with eight selected priority pollutants, at three concentration levels ranging from 50 ug/l to 200 ug/l. Samples Nos. 3 and 6 and Nos. 4 and 7 were blind duplicates. Sample No. 9 was prepared by spiking the eight priority pollutants into an organic-free water matrix at the 100-150ug/l level plus spiking with the nine deuterated compounds.

Purpose for Samples

Samples No. 1 and No. 2 were prepared to evaluate laboratory performance using an EPA standard (No. 2) and EPA Effluent Guidelines Division (EGD) criteria for acceptable performance. The data for Samples No. 1 and No. 2 were also included in the evaluation of between-laboratory (inter-laboratory) precision and accuracy. The blind duplicate pairs (Samples Nos. 3 and 6 and Samples Nos. 4 and 7) were prepared to assess within-laboratory (intra-laboratory) precision on an individual laboratory basis or on a pooled average basis. Samples Nos. 3, 4, 5, and 8 were used to evaluate the method of

standard addition. The primary purpose for Sample No. 9 was to identify any particular matrix problems with the chemical plant effluent. Sample No. 8 represented the chemical plant effluent and the resulting data were used to correct Samples Nos. 3-7 for background. All nine samples were used to compare the precision and accuracy of EPA Methods 624 and 1624.

Initiation of the Round Robin Study

A single grab sample of a chemical plant effluent was collected and all samples were prepared at Shell's Westhollow Research Center on July 19, 1981. After preparation, the sample vials were divided into sets of nine and each set was placed in one-pint bottles with bakelite tops and aluminum foil liners. The pint bottles were then packed in wet ice inside of foam ice chests and sent by Federal Air Express to the participating laboratories. The samples were received by all participants within 24 hours and were analyzed within 7 days of being shipped. All of the data were returned within 30 days. The

data obtained for the study are rather massive and have not been furnished in this report. Engineering-Science, Inc. (3109 North Interregional, Austin, Texas 78722) was retained to statistically analyze the resulting data and to prepare a technical report. The information and results from the study provided in this paper summarize the information from the Engineering Science Report.

Data Analysis Methods

Most of the calculations involved with the data analysis were performed on a WANG System 2200 computer. Statistical programs were written in BASIC to calculate accuracy, interlaboratory and intralaboratory precision, and to check for outliers in sample population distributions. Programs were also written to determine the points for plotting the method of standard addition, and to perform linear regressions.

Compounds reported by the laboratories only as "detected" in any sample were not given a quantitative value, and therefore were not included in any

of the statistical calculations.

The criterion for identification of outliers was set at the 90 percent confidence level. Checks for outliers were made for interlaboratory precision calculations with respect to the geometric mean concentration for a sample.

Outliers were not removed from the data sets in the calculation of mean accuracies and related precision estimates. It is believed the inclusion of any outliers would present a more representative picture of the average laboratory accuracy which could be expected for the volatile pollutants analyzed in this study.

Interlaboratory (between) precision with respect to the geometric mean concentration was calculated for each compound in a sample. The concentrations were assumed to follow a log-normal distribution, as was assumed in previous and similar studies. The pooled interlaboratory standard deviation (s_p) for each compound was calculated in the

following manner:

$$s_p = \left[\frac{\sum_{i=1}^{n} \nu_i (s_i)^2}{\sum_{i=1}^{n} \nu_i} \right]^{1/2}$$

where s_i = the standard deviation for sample i

ν_i = the degrees of freedom associated with the mean for sample i

n = number of samples

Interlaboratory (within) precision estimates were made for those samples having replicate analyses. Samples No. 3 and and No. 6 were replicates and Samples No. 4 and No. 7 were replicates. In addition, replicate analyses data were provided by one laboratory for Sample No. 8 for deuterated compounds, and in Sample No. 9 for both deuterated and nondeuterated compounds. The intralaboratory precision was calculated for each compound measured by a laboratory in a sample, assuming a log-normal distribution.

For any two replicate values (x_1, x_2) in a log-normal distribution, the standard deviation(s) ($\log_e$ base) is:

$$s = \left| \sqrt{\frac{1}{2}} \ln \ (x_1/x_2) \right|$$

The pooled intralaboratory precision (s_p) for n replicate pairs is:

$$s_p = \left[\frac{\sum_{i=1}^{n} s_i^2}{n} \right] 1/2$$

Where s_i = standard deviation of the replicate pair mean for a compound in sample i

Variability factors as used in this report define the 95 percent confidence limits in relation to a calculated mean from a data set. When the mean is a geometric mean calculated from a log-normal distribution, the variability factor is multiplicative rather than additive as with an arithmetic mean. The upper and lower variability factors (V_U, V_L, respectively) are defined for a geometric mean as follows:

$$V_U = \exp (t \cdot s)$$

$$V_L = \exp (-t \cdot s) = \frac{1}{\exp (t \cdot s)} = \frac{1}{Vu}$$

where t = value of Student's t distribution at the 2.5 percent probability level (two-tailed distribution for 95 percent confidence level) for the degrees of freedom associated with the sample mean.

s = sample standard deviation

The upper and lower 95 percent confidence limits (U, L) are then:

$$U = \bar{x}V_U$$

$$L = \bar{x}V_L$$

where $\bar{x}$ = sample geometric mean.

The meaning of upper and lower variability factors is best illustrated by an example. The upper interlaboratory variability for a sample with a known mean pollutant concentration of 100 ppb was determined to be 1.28. Based on this estimate of interlaboratory variability, 95 percent of analyses from all laboratories for this sample would fall

between 78 ppb $\left(\frac{1}{1.28} \times 100 \text{ ppb}\right)$, and 128 ppb (1.28 x 100 ppb).

The repeatability factors define the 95 percent confidence interval for the difference between two analyses when the mean of the sample is not known. The variance related to the difference between two values (x_1, x_2) with the same standard deviation(s) is:

$$V(x_1 - x_2) = 2s^2$$

Therefore, the standard deviation related to the average difference between two values is $\sqrt{2} \cdot s$. The repeatability factors for the upper and lower 95 percent confidence limits (R_U, R_L, respectively) relative to x as defined above are:

$$R_U = \exp\ (\sqrt{2} \cdot t \cdot s)$$

$$R_L = \exp\ (-\sqrt{2} \cdot t \cdot s)$$

To illustrate, a laboratory analyzes a sample and reports a concentration of 100 ppb. Based on an interlaboratory repeatability factor (R_U) of 1.42, 95 percent of the values of a second analysis per-

formed by any other laboratory would fall within 70 ppb ($\frac{1}{1.42}$ x 100 ppb) to 142 ppb (1.42 x 100 ppb). The 95 percent confidence range as defined by the repeatability factors is a good indication of the range of values that can be expected when only a single analysis is reported.

The recovery (accuracy) of each laboratory was calculated for each compound in Sample Nos. 1 through 9. Accuracy was reported as a percent of the known concentration. Interlaboratory and intralaboratory mean accuracies were calculated as simple arithmetic means. Standard deviations and pooled standard deviations were also calculated in the usual manner.

Deuterated analogs of nine compounds were spiked into all the sample solutions in order to compare Methods 624 and 1624 in the analysis of these volatile organic pollutants. Method 1624 is similar to Method 624, except that the recovered fraction of the deuterated analog spike of a compound is used to adjust the analytical value. Recovery correction incorporated in Method 1624 is illustrated

by the following equation:

$$C_{1624} = \frac{C_{624}}{CD_{624}/CD_S}$$

where C_{1624} = the recovery corrected concentration by Method 1624

C_{624} = the measured concentration of the compound by Method 624

CD_{624} = the measured concentration of the deuterated analog of the compound by Method 624

CD_S = the theoretical (spiked) concentration of the deuterated analog of the compound

Deuterated analogs were not spiked for six of the compounds analyzed in this study. Only Samples No. 1 and No. 2 contained these compounds; these samples were prepared from an EPA volatile pollutant standard. Deuterated analogs of all the compounds analyzed in the effluent matrix samples, however, were spiked into the sample solutions. Therefore, direct comparison of Methods 624 and 1624 relative to the effluent matrix samples could be easily made.

Spiking of the samples with nondeuterated compounds was designed so that three spiked concentrations of each compound were present in Samples Nos. 3, 4, and 5. This spiking arrangement allowed the interlaboratory mean concentration for each spike level of a particular compound to be plotted, versus interlaboratory mean measured concentrations in the manner of the method of standard addition. Linear regression was then performed on the data set.

The analysis of these plots can define: (1) the relative response to spike addition; (2) the expected range in measured values at a given confidence level for a given spike concentration; (3) the base level of the compound in the unspiked sample (extrapolation to zero spike addition); and (4) the expected range in values at very low concentrations for a given confidence level.

Samples Nos. 3, 4, and 5 also were spiked with deuterated analogs of the sample compounds so that Method 624 could be compared to Method 1624 relative to the method standard addition.

Eight compounds were analyzed in this manner. They were:

Benzene
1,1-dichloroethane
1,2-dichloroethane
1,2-dichloropropane
Ethylbenzene
1,1,2,2-tetrachloroethane
Toluene
1,1,1-trichloroethane

Laboratory Performance

There are a number of criteria that may be used to assess the performance of laboratories. The EPA EGD has considered a laboratory's performance acceptable for guideline development purposes when standards in organic-free water are found to be within the range of minus 50 percent and plus 100 percent of the true value. Samples Nos. 1 and 2 were prepared with EPA Standard Solution No. 2. The resulting data from all laboratories for Samples Nos. 1 and 2 easily met the EPA EGD criteria for volatile priority pollutants. All of the observations for Samples Nos. 1 and 2 fell within minus 40% to plus 25% of the true value. If one considers

only the lowest and highest reported values (extremes) from the eight laboratories for the nine components in Samples Nos. 1 and 2, the range of low values was from 9 - 40% with a mean of 23%, and the range of high values was from 0 - 25% with a mean of 12%. Sample No. 9 was similar to Samples Nos. 1 and 2, since it was composed of standard compounds in an organic-free water matrix. Again, all of the laboratories met the EPA EGD criteria for acceptable performance for Sample No. 9.

Precision of Method 624

The interlaboratory precision of Method 624 for this study with respect to each compound in this study is presented in Table 2. It should be noted that the data summarized in Table 2 assume that errors are independent of concentration. Table 2 also includes the calculated upper 95 percent confidence level factors for variability (V_U) and repeatability (R_U) on a compound specific basis. Average variability and repeatability factors were calculated

for the deuterated and nondeuterated compounds as independent groups. The assumption made in calculating such averages is that a homogeneous set of variance exists (i.e., all compounds have the same variabilities or errors).

The tabulated data show that the variability factors (V_U) for nondeutrated compounds ranged from 1.14 for bromoform to 1.76 for 1,2-dichloropropane. Variability factors (V_U) for the deuterated compounds ranged from 1.30 for both 1,2-dichloroethane-d_4 and 1,2-dichloropropane-d_6 to 1.49 for 1,1,2,2-tetrachloroethane-d_2. The 1.49 and 1.76 values both fall outside the calculated 95 percent confidence range, via the Student's t confidence interval for a normal distribution. The variabilities in the analyses of 1,2-dichloropropane and 1,1,2,3-tetrachloroethane-d_2, appear to be significantly larger than the rest of the compounds listed. The reason for this is not clearly understood. The mean interlaboratory variability factors (V_U's) for nondeuterated and deuterated compounds is the

same, 1.35, although the standard deviation for deuterated compounds (0.063) is less than half of the standard deviation for nondeuterated compounds (0.145).

The variability factors (V_U's) and repeatability factors (R_U's) listed in Table 2 define the interlaboratory precision of Method 624 for the compounds listed, with the matrix studied, and as practiced by the laboratories included in the study. For example, the average mean variability factor (V_U) listed in Table 2 for nondeuterated compounds is 1.35. If the known mean or true value of a component is 100 ppb, 95 percent of the results for the sample would fall in the range of 74 ppb ($\frac{1}{1.35}$ x 100 ppb) to 135 ppb (1.35 x 100 ppb). However, if the true or mean value is not known, the 95 percent confidence range to be expected relative to a single observation can be calculated using the average repeatability factor (R_U). Using the average repeatability factor listed in Table 2 of 1.54, if the first determination yielded a value of

100 ppb, 95 percent of the values for a second determination would fall in the range of 65 ppb ($\frac{1}{1.54}$ x 100 ppb) to 154 ppb (1.54 x 100).

The intralaboratory (within) precision of Method 624 with respect to each compound for which replicate analyses were available is presented in Table 3. Variability (V_U) and repeatability (R_U) factors for the upper 95 percent confidence limit are also included in the table.

The variability (V_U) factors for nondeuterated compounds ranged from 1.16 for 1,2-dichloroethane to 1.72 for 1,2-dichloropropane. As with the interlaboratory variability, 1,2-dichloropropane was found to be outside of the 95 percent confidence interval for the mean V_U for nondeuterated compounds (Student's t confidence interval for a normal distribution). Intralaboratory V_U for deuterated compounds ranged from 1.16 for chloroform-d_1, to 1.28 for toluene-d_8. All of the deuterated compounds are within the 95 percent confidence interval for the mean intralaboratory V_U. As

noted in Table 3, the variance associated with the average difference between mean V_U's for non-deuterated and deuterated compounds is 4.49×10^{-3}. The difference between mean V_U's is 1.31 minus 1.22, or 0.09. Based on a variance of 4.49×10^{-3}, a difference between mean V_U's as great as 0.09 can be expected to occur only 10 percent of the time. This indicates that the mean intralaboratory variability of deuterated compounds for Method 624 is noticeably lower than that for nondeuterated compounds.

Precision of Method 1624

The concentration values reported by all the laboratories using Method 624 were recovery corrected by the recovery percentages of the deuterated analogs to represent Method 1624. Precision calculations on the resulting values were then made. The interlaboratory precision for Method 1624 is summarized in Table 4, along with the upper 95 percent variability (V^U) and repeatability factors (R_U). The V_U range from 1.19 for

1,2-dichloroethane to 1.67 for 1,1,2,3-tetrachloroethane. The average V_U over all compounds for Method 1624 is 1.35, plus or minus 0.152. In comparison, the average V_U for the same nine compounds with Method 624 is 1.37, plus or minus 0.171, indicating that variation between laboratories is not reduced by recovery corrected with Method 1624. The largest difference between Method 624 and Method 1624 on variability within compounds is with 1,1,2,2-tetrachloroethane. With Method 624, V_U is 1.49; whereas, V_U is 1.67 for Method 1624. This increase in variability is due in part to the relatively high V_U for the deuterated analog, 1.49 (Table 2), as compared to the other deuterated compounds. Another source of increased variability in Method 1624 with respect to 1,1,2,2-tetrachloroethane results from the fact that the recoveries of 1,1,2,2-tetrachloroethane and its deuterated analog vary inversely. That is, when 1,1,2,2-tetrachloroethane is measured at a value higher than the true mean, its

deuterated analog is recovered at less than 100 percent.

As noted in Table 4 the variability (V_U) factor for 1,1,2,2-tetrachloroethane (1.67) falls outside the 95 percent confidence interval of the mean variability factor for all compounds for Method 1624. Again, this implies that this value is either an outlier (95 percent confidence) when compared to the mean value for all compounds, or that 1,1,2,2-tetrachloroethane may have a larger error when analyzed by the method under the experimental conditions used.

The intralaboratory precision of Method 1624 is presented in Table 5. The upper 95 percent confidence level variability and repeatability factors are included. The average V_U for eight compounds (chloroform had no replicates with Method 1624) is 1.27, plus or minus 0.215, not greatly different from the mean intralaboratory V_U for Method 624 for the same eight compounds (1.31, plus or minus 0.186). The lowest intra-

laboratory V_U with Method 1624 is 1.07 for benzene; the highest is with 1,2-dichloropropane at 1.69. This compound also exhibited the highest intralaboratory variability with Method 624. The 1.69 V_U for 1,2-dichloropropane lies near the upper limit of the 95 percent confidence for the mean intralaboratory V_U with Method 1624 (0.84 - 1.70).

Accuracy of Method 624

The accuracy of Method 624 for the individual compounds in this study is presented in Table 6. The average accuracy (recovery) for all nondeuterated compounds in this study was found to be 94 percent, plus or minus nine percent. The range of recovery was from 70 percent for 1,1,1-trichloroethane to 106 percent for 1,2-dichloroethane. The accuracies of all 15 nondeuterated compounds fall within the 95 percent confidence interval (77-111 percent) of the average mean accuracy and for nondeuterated compounds except for 1,1,1-trichloroethane (70 percent). The mean

accuracy for all deuterated compounds of Method 624 was found to be 95 percent, plus or minus six percent. The lowest mean recovery was 85 percent for ethylbenzene-d_{10}, and the highest mean recovery was 105 percent for 1,2-dichloroethane-d_4. All mean accuracy values fell within the 95 percent confidence interval of 83 to 107 percent.

The most recent version of EPA Method 624 (Ref. 1) includes a section identified as "8. Quality Control". In Section 8.2 one is directed "to establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations". The data summarized in Table 6 are virtually what one is directed to obtain in Section 8.2.3 except it represents an average of eight laboratories instead of a single laboratory. Section 8.2.4 directs one to compare their results with those expected for the method for each method parameter given in Table 5 for the method. If two specified criteria cannot

be met, one is directed to review potential problem areas and repeat the test. The data summarized in Table 6 were subjected to the criteria listed in 8.2.4. Criteria were not met for 8 of the 15 compounds included in the round robin study. The eight laboratories which participated in the study did not meet quality control conditions specified in EPA Method 624, although they were able to meet EPA EGD criteria.

Accuracy of Method 1624

The accuracy of Method 1624 for the individual compounds in the study is summarized in Table 7. The average accuracy (recovery) for the nine EPA organic pollutants included in the study was 100 percent, plus or minus 10 percent. The range of recovery was from 78 percent for 1,1,1-trichloroethane to 109 percent for benzene. The accuracies for all nine compounds fall within the 95 percent confidence interval (80-120 percent) of the average mean accuracy, except for 1,1,1-trichloroethane

(78 percent). Compared to the average mean accuracy for Method 624 (93 percent, plus or minus 11 percent) for the same nine compounds, the average mean accuracy for Method 1624 (100 percent, plus or minus 10 percent) represents an improvement in the determination of the true concentration on the average. The observed mean accuracy for Method 1624 was identical with the true mean, while the mean accuracy for Method 624 was 7 percent less than the true mean.

Method of Standard Addition

The EPA has proposed (46 Federal Register 3033, January 13, 1981) quality control procedures (Section 8) for Method 624 which call for the determination of actual recovery levels for priority pollutants from a sample matrix. This is accomplished by first determining the background level of a sample, then fortifying (spiking) the same at two times the background level and reanalyzing. After correcting for the background, the

percent recovery can be calculated. There also has been some indication that the EPA has considered recovery correcting observed values on the basis of the recovery data. This procedure was attempted by the EPA during the long-term study (Ref. 2) at Shell's Deer Park Chemical Plant, but the EPA data indicated some serious problems with the approach. The percent recovery was quite variable and ranged from 0-576% for treated effluent samples. Because of the Agency's interest in this area of analyses, one portion of the study was designed to allow for the calculation of eight priority pollutants by method of standard addition using a three-point plotted curve. Samples Nos. 3, 4, and 5 were fortified (spiked) at three different levels with the eight nondeuterated compounds in an attempt to quantify pollutants present in the background sample (Sample No. 8) by method of standard addition using both Methods 624 and 1624. This part of the study was only partially successful, primarily due to the

fact that Sample No. 8 contained virtually no measureable concentration of priority pollutants.

Plots were constructed in the method of standard addition for the eight compounds spiked into Samples Nos. 3, 4, and 5. Two plots were made for each compound; one for concentrations as measured by Method 624, and the other for concentrations as calculated by Method 1624. The actual plots are included in Figures 1-4. A summary table of the regression equations for each of the plotted lines is presented in Table 8. It should be noted that the plots, as well as the regression equations, were derived from average measured concentrations from all laboratories. Normally, the method of standard addition is done by a single laboratory, and individual plots and regression equations are prepared by the laboratory. Plots and regression equations were prepared for the data from each of the laboratories, and these were compared with the plots shown in Figures 1-4 and the regression equations in Table 8. The result-

ing plots and regression equations were found to be similar.

The regression equations resulting from the plotted data for Samples Nos. 3, 4, and 5 can be extrapolated to the point of zero spike addition ($x = 0$) in order to estimate the concentration level of the eight priority pollutants, or the concentration can be read directly from the y-axis intercept. Also included in Table 8 are the numerical uncertainties at one standard deviation associated with the various components of the regression equations. This information can be used to derive the range of uncertainty associated with the y-axis intercept value. For example, the regression equation for benzene by Method 624 is:

$$y = (1.02 \pm 0.21)x - (0.96 \pm 32.10),$$

where 0.21 is one standard deviation relative to the slope value, 1.02 and 32.10 is one standard deviation relative to the y-axis intercept, -0.96. When x is zero, y is equal to -0.96, plus or minus

32.10, and the range of values for a zero spiking concentration is from -33 to 31 ug/l. The calculated range of values for all of the regression equations are also included in Table 8. It is immediately apparent from Table 8 that there is a large uncertainty associated with measurements of zero or near zero concentrations of priority pollutants.

Using the method of standard addition for Sample No. 8, it was determined that most of the y-axis intercept values were negative. Negative concentration values have little meaning; however, they, along with zero, are well within the 95 percent confidence interval associated with the y intercept. The ranges listed in Table 8 also indicate that an analysis producing a positive value even as high as 31 ppb (benzene) can, in fact, likely have a true value of zero. For all practical purposes, there is a high probability that the compounds with negative intercept values are at zero concentration, or nearly so. If one assumes

that the observed negative values are indeed zero, the method standard addition indicates that Sample No. 8 contained virtually no measurable concentration of priority pollutants. These data are consistent with the resulting data from the eight laboratories for Sample No. 8 using Methods 624 and 1624. Only a few compounds were detected in the sample, and those that were found were not detected by every laboratory.

The range listed in Table 8 can be used to assess the relative precision of Methods 624 and 1624. The data indicate again that the overall precision of Method 1624 is not improved over Method 624.

The results from the limited study show that the method of standard addition has some promise as an alternate procedure for the EPA recovery correction by fortification. It should also be recognized that the technique is more time-consuming and costly, and might find utility for critical situations where the best estimate of true value is required.

The limited study demonstrated that the method of standard addition was capable of establishing that Sample 8 contained no measurable concentrations of priority pollutants. No data resulted from this study to show how well or how poorly the method of standard addition works when a sample actually contains measurable levels of a number of priority pollutants.

Additional Observations

Methylene chloride was detected in Samples Nos. 1 and 2 by some laboratories. This compound is often detected in samples or standards prepared in laboratories performing numerous extractions associated with EPA Method 625. It is very likely that the source of the methylene chloride was the EPA Standard Solution No. 2, which is common to both Samples Nos. 1 and 2. No values were reported for methylene chloride (methylene chloride was only reported as detected, "D"), and it was, therefore, not included in any of the data analyses.

Sample No. 8 was prepared as a matrix background for Samples Nos. 3 through 7, and was chemical plant effluent spiked only with the deuterated compounds. One of the laboratories detected the presence of five nondeuterated compounds. Four other laboratories detected the presence of one compound (1,2-dichloroethane), with three of these laboratories having values listed. Review of the data suggests that 1,2-dichloroethane was probably present at a nominal 10ug/l (ppb) level in Sample No. 8. Because only five of the eight laboratories were able to detect its presence, one might conclude that the minimum detection limit (99 percent confidence level) for this compound in the chemical plant effluent (matrix) is somewhat higher than 10 ppb.

It was very fortuitous that Sample No. 8, the background matrix for Samples Nos. 3 through 7, contained virtually no measurable concentration of the EPA volatile organic pollutants. This allowed the assessment of accuracy (recovery) for the

spiked nondeuterated compounds with no background correction. Because the values listed for 1,2-dichloroethane were so low (approximately 10 ppb), and came from only three of the eight laboratories, these data were not included in any other data analysis.

Sample No. 9 was prepared by spiking all of the deuterated and nondeuterated compounds in organic-free water. All of the laboratories detected the presence of 1,1,2-trichloroethylene even though the compound was not spiked into Sample No. 9. Seven of the laboratories were able to quantify the level present, which appeared to be a nominal 20ug/l (ppb) concentration. Because all of the laboratories were able to detect the presence of the compound, it was believed to be a true contaminant in the organic-free water. Also, one might conclude that 20 ppb is above the minimum detection limit (99 percent confidence level) for this compound in the organic-free water matrix. Because the values listed for 1,1,2-trichloroethylene were

much lower than the 50 to 200ug/l spiking level of the compounds of interest, the values were not included in any of the data analysis.

Two laboratories also reported the presence of chloroform in Sample No. 9. Chloroform was also detected ("D"), but not quantified, in several other samples. One laboratory reported a value of 3ug/l in replicate Samples Nos. 3 and 6. This value was considered not reliable, and was omitted from the data analysis. Review of the data from all laboratories did not reveal strong enough evidence to indicate that chloroform was present in any of the samples except Samples Nos. 1 and 2, in which case chloroform was an added component at measurable concentrations.

One of the major concerns with the analysis of priority pollutants at or near detection limits is false positive and negative identifications. These problems are difficult to define for a single laboratory, but become obvious when numerous laboratories analyze the same sample and in particular,

when known concentrations of compounds are spiked into samples. For this study, there was one case of a false negative; that is, the compound should have been detected but was not. This occurred with blind duplicate Samples Nos. 4 an 7. 1,2-dichloropropane was spiked into Samples Nos. 4 and 7 at a 50ug/l (ppb) level, and all laboratories except one quantified its presence. The reason that one laboratory was not able to detect the presence of the compound has not been determined.

CONCLUSIONS

All of the laboratories in the round robin study easily met the EPA EGD performance criteria for the two samples prepared with EPA Standard Solution No. 2 as well as the sample prepared using Shell's standards and organic-free water. This was not surprising since all of the participating laboratories were experienced in the GC/MS methodology studied.

The calculations revealed that the interlaboratory and intralaboratory precision for Method 1624 did not represent an improvement over the precisions observed for Method 624. This observation is consistent with the results from a previously reported study (Ref. 3). The study demonstrated the uncertainty in GC/MS data currently being generated by qualified laboratories. The resulting average interlaboratory variability factor (1.35) and repeatability factor (1.54) for the compounds included in the study define the actual level of uncertainty

for the GC/MS methodology exclusive of any variability associated with sampling. The range of values one can expect when the true value of a pollutant is 100 ppb is from 74 ppb to 135 ppb (95% confidence interval). When the first analysis of an unknown sample yields a value of 100 ppb, the range of values expected for a second analysis is from 65 ppb to 154 ppb (95% confidence interval). This degree of uncertainty associated with the GC/MS methodology as well as that for sampling and sample handling most certainly must be addressed in NPDES Permit limitations, as well as in compliance monitoring and enforcement action.

The results of the study indicated that the average mean recovery for Method 1624 (99.8% $\pm$ 9.9%) represented a small ($\simeq$ 7%) improvement in the determination of true concentration as compared with the average mean recovery for Method 624 (92.8% $\pm$ 10.8%). The study of recovery also revealed that the eight laboratories could meet EPA EGD performance criteria but could not meet recovery

criteria currently described in the July 1982 version of Method 624 for approximately one-half of the compounds studied.

The results from the limited study show that the method of standard addition has some promise as an alternative procedure for recovery correction by fortification, and might be useful for critical situations where the best estimate of true value is required. One important observation resulting from the method of standard addition study was the definition of uncertainty associated with measurements of priority pollutants at zero or near zero concentrations.

The problem of false positive and negative identifications still persists. It does not appear to be a major problem particularly if one totally ignores all data below a 10 ppb and considers these as unreliable. The documented case of a false negative at the 50 ppb was startling; however, the reasons could not be established.

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ROUND ROBIN STUDY OF EPA METHODS 624 AND 1624 FOR VOLATILE ORGANIC POLLUTANTS

BY
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TABLE 1.
THEORETICAL SPIKE CONCENTRATIONS (μg/ℓ) IN SAMPLE SOLUTIONS

	Sample Matrix								
	Super Q Water		OPMC Chemical Plant Effluent Sample Solution						Super Q Water
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Nondeuterated Compounds									
Benzene	-	-	200.0	150.0	100.0	200.0	150.0	-	100.0
Bromodichloromethane	34.4	43.0	-	-	-	-	-	-	-
Bromoform	41.6	52.0	-	-	-	-	-	-	-
Carbon Tetrachloride	37.6	47.0	-	-	-	-	-	-	-
Chloroform	182.4	228.0	-	-	-	-	-	-	-
Dibromochloromethane	48.0	60.0	-	-	-	-	-	-	-
1,1-dichloroethane	-	-	50.0	100.0	150.0	50.0	100.0	-	150.0
1,2-dichloroethane	80.0	100.0	100.0	50.0	150.0	100.0	50.0	-	150.0
1,2-dichloropropane	-	-	100.0	50.0	150.0	100.0	50.0	-	150.0
Ethylbenzene	-	-	200.0	150.0	100.0	200.0	150.0	-	100.0
1,1,2,2-tetrachloroethane	-	-	50.0	100.0	150.0	50.0	100.0	-	150.0
1,1,2,2-tetrachloroethylene	22.4	28.0	-	-	-	-	-	-	-
Toluene	-	-	200.0	150.0	100.0	200.0	150.0	-	100.0
1,1,1-trichloroethane	56.0	70.0	50.0	100.0	150.0	50.0	100.0	-	150.0
1,1,2-trichloroethylene	52.0	65.0	-	-	-	-	-	-	-
Deuterated Compounds									
Benzene-d_6	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Chloroform-d_1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1,1-dichloroethane-d_4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1,2-dichloroethane-d_4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1,2-dichloropropane-d_6	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ethylbenzene-d_{10}	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1,1,2,2-tetrachloroethane-d_2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Toluene-d_8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1,1,1-trichloroethane-d_3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

VARIABILITY FACTORS

$$V_U = \text{EXP}\ (T \cdot S)$$

$$V_L = \text{EXP}\ (-T \cdot S) = \frac{1}{\text{EXP}\ (T \cdot S)} = \frac{1}{V_U}$$

REPEATABILITY FACTORS

$$R_U = \text{EXP}\ (\sqrt{2} \cdot T \cdot S)$$

$$R_L = \text{EXP}\ (-\sqrt{2} \cdot T \cdot S) = \frac{1}{R_U}$$

RECOVERY SAMPLES NOS. 1 AND 2

ALL WITHIN MINUS 40% TO PLUS 25% OF TRUE VALUE

RANGE OF RECOVERY LESS THAN TRUE VALUE 9-40% WITH MEAN OF 23%

RANGE OF RECOVERY GREATER THAN TRUE VALUE 0-25% WITH MEAN OF 12%

TABLE 2.
INTERLABORATORY PRECISION OF METHOD 624 BY COMPOUND

Compound	Pooled Standard Deviation (Log Scale)	Upper 95 Percent Variability Factor	Upper 95 Percent Repeatability Factor
Nondeuterated Compounds			
Benzene	0.116	1.26	1.39
Bromodichloromethane	0.122	1.30	1.45
Bromoform	0.062	1.14	1.21
Carbon tetrachloride	0.152	1.38	1.58
Chloroform	0.139	1.35	1.53
Dibromochloromethane	0.149	1.38	1.57
1,1-dichloroethane	0.125	1.28	1.42
1,2-dichloroethane	0.079	1.17	1.25
1,2-dichloropropane	0.283	1.76*	2.23
Ethylbenzene	0.129	1.29	1.44
1,1,2,2-tetrachloroethane	0.198	1.49	1.75
Tetrachloroethylene	0.171	1.44	1.68
Toluene	0.141	1.32	1.49
1,1,1-trichloroethane	0.161	1.38	1.58
1,1,2-trichloroethylene	0.127	1.31	1.47
Average ± standard deviation	0.144 ± 0.051	1.35 ± 0.145	1.54 ± 0.239
Deuterated Compounds			
Benzene-d_6	0.134	1.31	1.46
Chloroform-d_1	0.140	1.32	1.49
1,1-dichloroethane-d_4	0.141	1.33	1.49
1,2-dichloroethane-d_4	0.132	1.30	1.45
1,2-dichloropropane-d_6	0.133	1.30	1.45
Ethylbenzene-d_{10}	0.142	1.33	1.49
1,1,2,2-tetrachloroethane-d_2	0.198	1.49*	1.75
Toluene-d_8	0.166	1.39	1.60
1,1,1-trichloroethane-d_3	0.170	1.40	1.62
Average ± standard deviation	0.151 ± 0.023	1.35 ± 0.0632	1.53 ± 0.102

*Outside 95 percent confidence interval for mean variability factor.

VARIABILITY FACTOR = 1.35

V_U = 100 PPB x 1.35 = 135 PPB

V_L = 100 PPB x $\frac{1}{1.35}$ = 74 PPB

REPEATABILITY FACTOR = 1.54

R_U = 100 PPB x 1.54 = 154 PPB

R_L = 100 PPB x $\frac{1}{1.54}$ = 65 PPB

TABLE 3.
INTRALABORATORY PRECISION OF METHOD 624 BY COMPOUND

	Pooled Standard Deviation (Log Scale)	Upper 95% Variability Factor	Upper 95% Repeatability Factor
Nondeuterated Compounds			
Benzene	0.111	1.26	1.39
1,1-dichloroethane	0.078	1.18	1.26
1,2-dichloroethane	0.072	1.16	1.24
1,2-dichloropropane	0.257	1.72*	2.16
Ethylbenzene	0.088	1.20	1.30
1,1,2,2-tetrachloroethane	0.103	1.24	1.36
Toluene	0.113	1.27	1.40
1,1,1-trichloroethane	0.170	1.43	1.66
Average ± Standard Deviation	0.124 ± 0.062	1.31 ± 0.186	1.47 ± 0.307
Deuterated Compounds			
Benzene-d_6	0.104	1.24	1.36
Chloroform-d_1	0.070	1.16	1.23
1,1-dichloroethane-d_4	0.075	1.17	1.25
1,2-dichloroethane-d_4	0.103	1.24	1.36
1,2-dichloropropane-d_6	0.091	1.21	1.31
Ethylbenzene-d_{10}	0.094	1.22	1.32
1,1,2,2-tetrachloroethane-d_2	0.109	1.26	1.38
Toluene-d_8	0.119	1.28	1.42
1,1,1-trichloroethane-d_3	0.091	1.21	1.31
Average ± Standard Deviation	.095 ± 0.015	1.22 ± 0.039	1.33 ± 0.061

NOTE: Variance of mean difference between mean V_u's for nondeuterated and deuterated compounds equals $[0.186^2/8 + 0.039^2/9] = 4.49 \times 10^{-3}$.

*Outside 95% confidence interval for mean variability factor.

TABLE 4.
INTERLABORATORY PRECISION OF METHOD 1624 BY COMPOUND

	Pooled Standard Deviation (Log Scale)	Upper 95% Variability Factor	Upper 95% Repeatability Factor
Benzene	0.116	1.26	1.39
Chloroform	0.114	1.28	1.41
1,1-dichloroethane	0.170	1.40	1.62
1,2-dichloroethane	0.088	1.19	1.28
1,2-dichloropropane	0.205	1.51	1.79
Ethylbenzene	0.149	1.35	1.52
1,1,2,2-tetrachloroethane	0.256	1.67*	2.06
Toluene	0.115	1.26	1.39
1,1,1-trichloroethane	0.117	1.26	1.38
Average + Standard Deviation	0.147 + 0.054	1.35 + 0.152	1.54 + 0.249

*Outside 95% confidence interval for mean variability factor.

COMPARISON OF PRECISION FOR METHODS 624 AND 1624 (Vu)

	624	1624
1,2-DICHLOROPROPANE	1.76 *	1.51
1,1,2,2-TETRACHLOROETHANE	1.49	1.67*

*OUTLIERS

TABLE 5.
INTRALABORATORY PRECISION OF METHOD 1624 BY COMPOUND

	Pooled Standard Deviation (Log Scale)	Upper 95% Variability Factor	Upper 95% Repeatability Factor
Benzene	0.034	1.07	1.11
1,1-dichloroethane	0.049	1.11	1.16
1,2-dichloroethane	0.080	1.18	1.27
1,2-dichloropropane	0.249	1.69	2.11
Ethylbenzene	0.103	1.24	1.36
1,1,2,2-tetrachloroethane	0.117	1.28	1.42
Toluene	0.046	1.10	1.15
1,1,1-trichloroethane	0.186	1.48	1.74
Average ± Standard Deviation	0.108 ± 0.075	1.27 ± 0.215	1.42 ± 0.347

COMPARISON OF PRECISION FOR METHODS 624 AND 1624 (Vu)

	INTERLABORATORY	INTRALABORATORY
METHOD 624	1.37 ± (0.171)	1.31 ± (0.186)
METHOD 1624	1.35 ± (0.152)	1.27 ± (0.215)

TABLE 6.
ACCURACY OF METHOD 624 BY COMPOUND

Compound Number		Mean Accuracy (percent)	Pooled Interlaboratory Standard Deviation	Number of Values
Nondeuterated Compounds				
1	Benzene	99	12	48
2	Chloroform	95	13	16
3	1,1-dichloroethane	84	10	48
4	1,2-dichloroethane	106	10	64
5	1,2-dichloropropane	101	33 *	46
6	Ethylbenzene	88	11	48
7	1,1,2,2-tetrachloroethane	98	19	48
8	Toluene	94	13	48
9	1,1,1-trichloroethane	70	9	64
10	Bromodichloromethane	96	12	16
11	Bromoform	99	12	16
12	Carbon tetrachloride	96	15	16
13	Dibromochloromethane	99	14	16
14	Tetrachloroethylene	91	15	16
15	1,1,2-trichloroethylene	92	7	16
	Average ± Standard Deviation			
	Compounds (1) - (9)*	92.8 ± 10.8	-	9
	Compounds (1) - (15)	93.9 ± 8.5	-	15
Deuterated Compounds				
	Benzene-d_6	93	14	72
	Chloroform-d_1	97	14	72
	1,1-dichloroethane-d_4	95	14	72
	1,2-dichloroethane-d_4	105	14	72
	1,2-dichloropropane-d_6	97	13	72
	Ethylbenzene-d_{10}	85	12	72
	1,1,2,2-tetrachloroethane-d_2	100	19	72
	Toluene-d_8	89	15	72
	1,1,1-trichloroethane-d_3	94	15	72
	Average ± Standard Deviation	95 ± 6		

*These compounds directly comparable to Method 1624.

TABLE 7.
ACCURACY OF METHOD 1624 BY COMPOUND

	Mean Accuracy (percent)	Pooled Interlaboratory Standard Deviation	Number of Values
Benzene	109	12	48
Chloroform	96	10.6	16
1,1-dichloroethane	92	15	48
1,2-dichloroethane	102	10	64
1,2-dichloropropane	107	31	46
Ethylbenzene	106	16	48
1,1,2,2-tetrachloroethane	101	24	48
Toluene	107	12	48
1,1,1-trichloroethane	78*	13	64
Average ± Standard Deviation	99.8 ± 9.9	-	9

*Outside 95% confidence range for average mean accuracy for all nine compounds.

COMPARISON OF ACCURACY FOR METHODS 624 AND 1624 (% RECOVERY)

METHOD 624	92.8% ± 10.8%
METHOD 1624	99.8% ± 9.9%

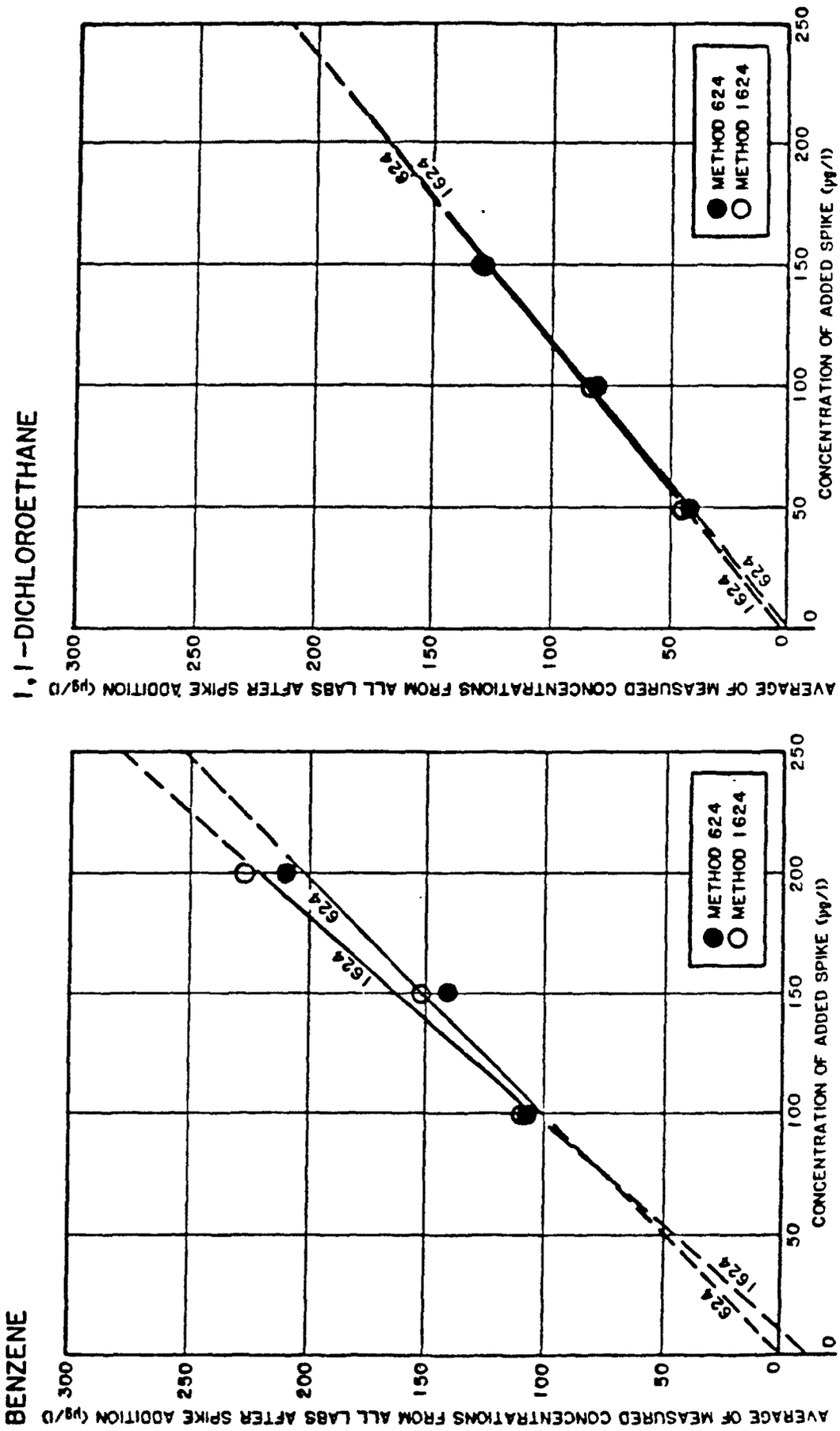

1,1-DICHLOROETHANE
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
METHOD 624
METHOD 1624
624
1624
BENZENE
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
METHOD 624
METHOD 1624
624
1624

FIGURE 1.

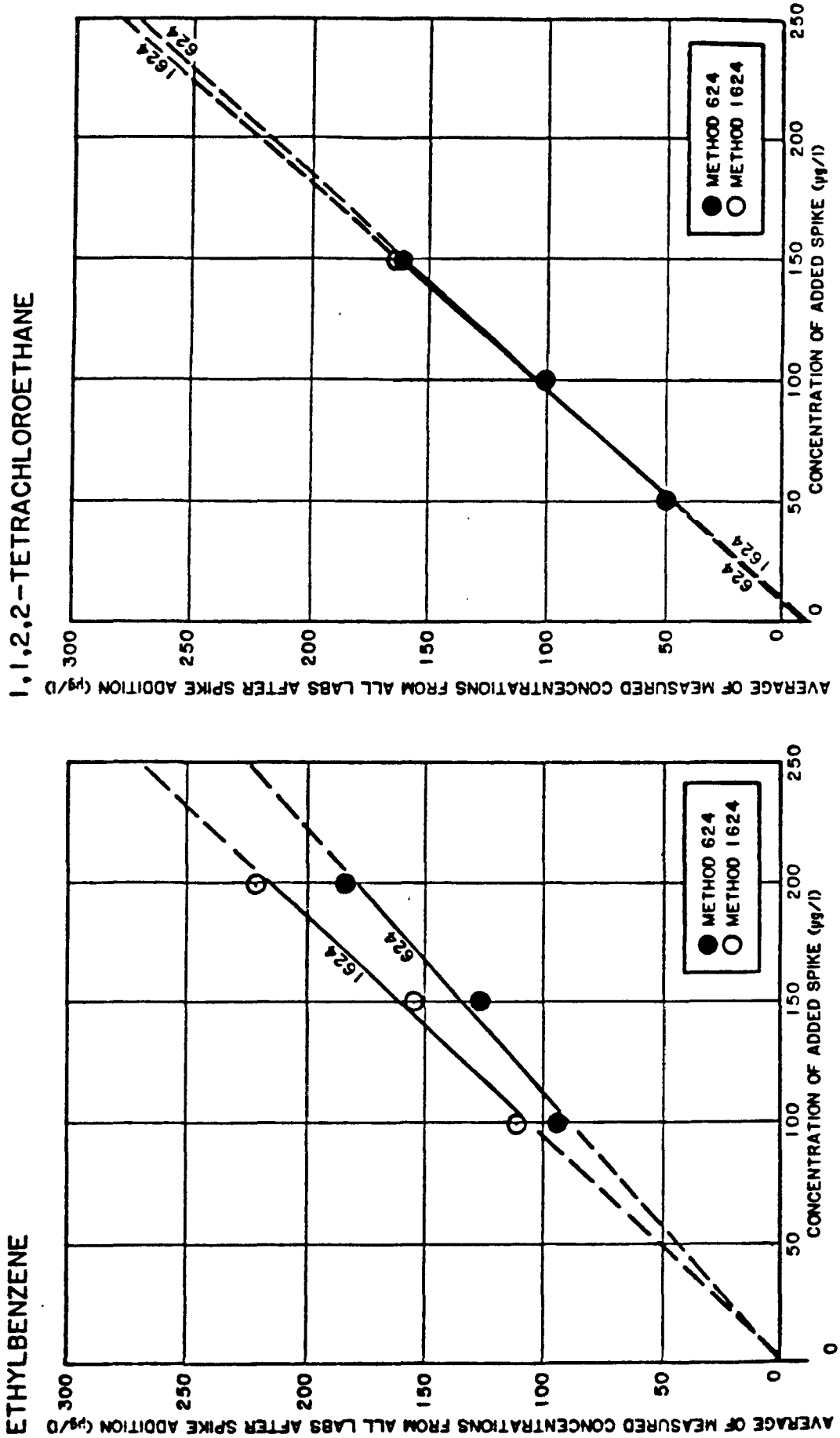

1,1,2,2-TETRACHLOROETHANE
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
METHOD 624
METHOD 1624
624
1624
ETHYLBENZENE
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
METHOD 624
METHOD 1624
624
1624

FIGURE 2.

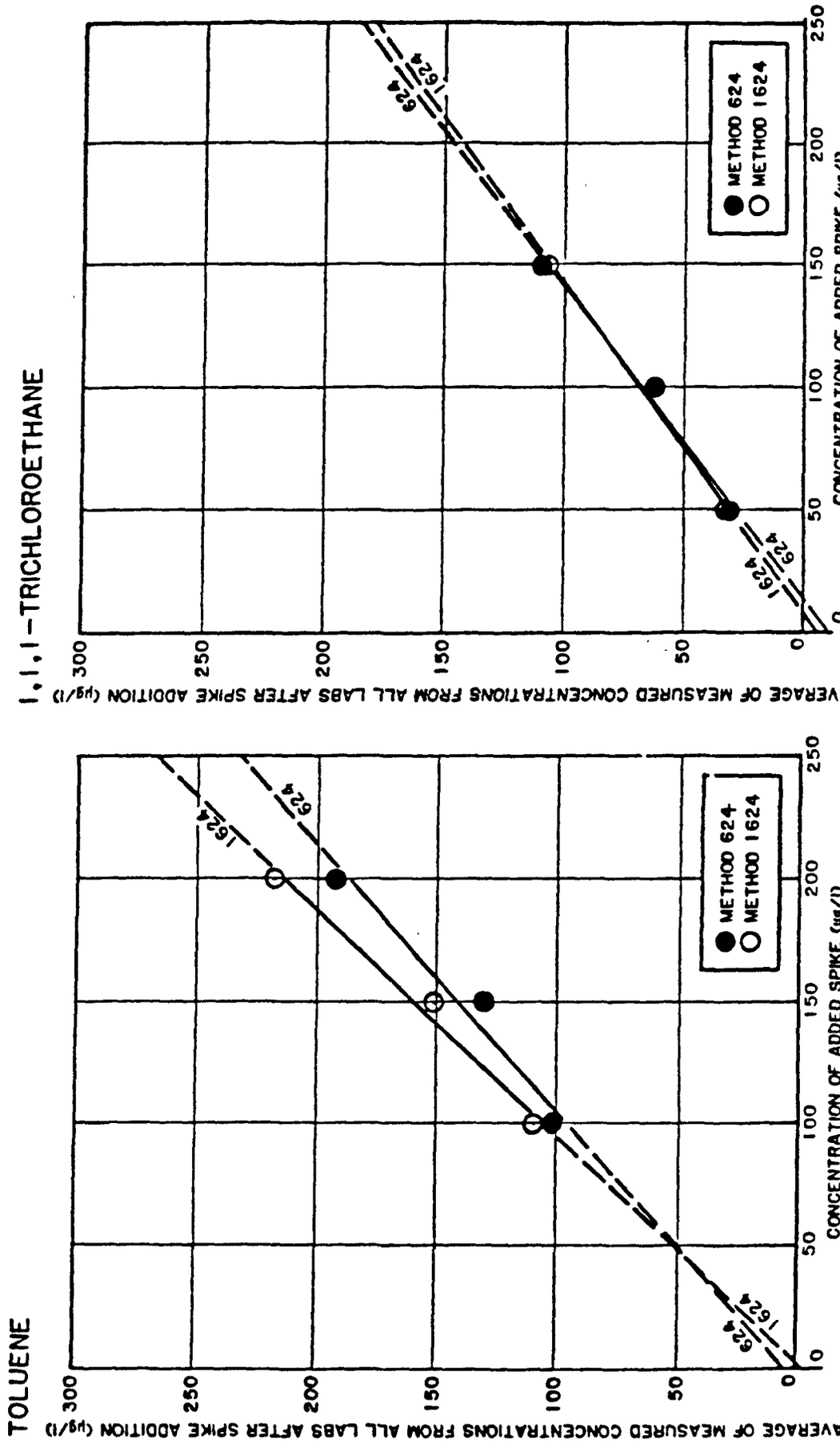

1,1,1-TRICHLOROETHANE
TOLUENE
METHOD 624
METHOD 1624
624
1624
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
0
50
100
150
200
250
300

FIGURE 3.

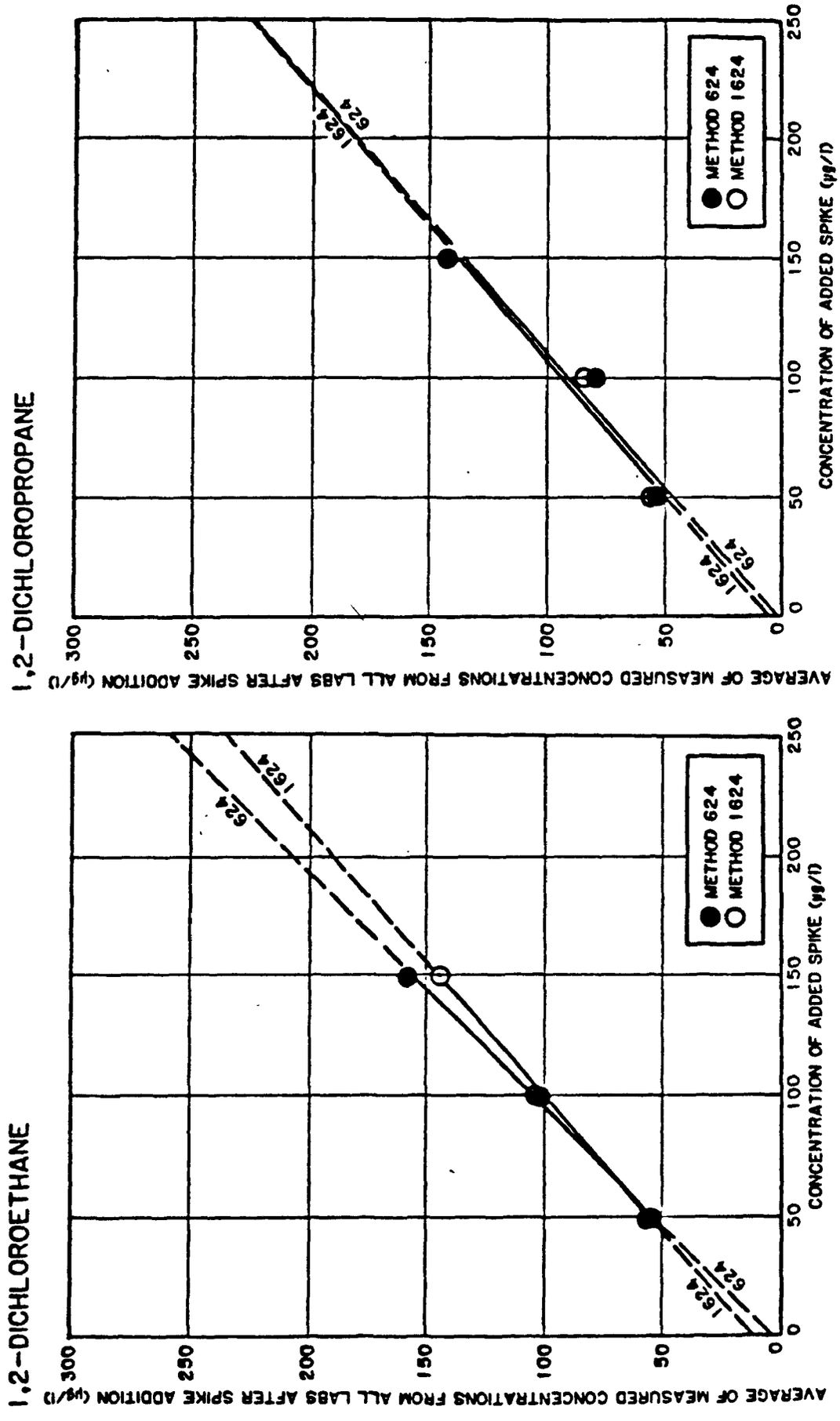

1,2-DICHLOROPROPANE
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
METHOD 624
METHOD 1624
624
1624
0
50
100
150
200
250
300
1,2-DICHLOROETHANE
AVERAGE OF MEASURED CONCENTRATIONS FROM ALL LABS AFTER SPIKE ADDITION (µg/l)
CONCENTRATION OF ADDED SPIKE (µg/l)
METHOD 624
METHOD 1624
624
1624

FIGURE 4.

TABLE 8.
COMPARISON OF METHODS 624 AND 1624 WITH METHOD OF STANDARD ADDITION

Compound	Regression Equation For Standard Addition		Extrapolated Range At x = 0(±1σ), ppb	
	Method 624	Method 1624	Method 624	Method 1624
Benzene	y=(1.02±0.21)x+(-0.96±32.10)	y=(1.17±0.20)x+(-12.76±30.47)	-33 to 31	-43 to 17
1,1-dichloroethane	y=(0.85±0.06)x+(-1.91±6.00)	y=(0.83±0.04)x+(2.37±3.92)	-8 to 4	-2 to 6
1,2-dichloroethane	y=(1.02±0.06)x+(3.37±6.32)	y=(0.89±0.07)x+(11.98±7.04)	-3 to 10	5 to 19
1,2-dichloropropane	y=(0.90±0.21)x+(1.97±22.67)	y=(0.89±0.16)x+(5.11±16.99)	-20 to 25	-12 to 22
Ethylbenzene	y=(0.91±0.15)x+(-1.99±22.78)	y=(1.11±0.15)x+(-4.51±22.71)	-25 to 21	-27 to 18
1,1,2,2-tetrachloroethane	y=(1.13±0.06)x+(-9.33±6.16)	y=(1.17±0.05)x+(-12.10±5.94)	-15 to -3	-18 to -6
Toluene	y=(0.91±0.20)x+(5.19±30.63)	y=(1.08±0.15)x+(-2.74±23.18)	-25 to 36	-26 to 20
1,1,1-trichloroethane	y=(0.78±0.08)x+(-10.71±8.74)	y=(0.74±0.07)x+(-6.29±7.89)	-19 to -2	-14 to 2
All Compounds	y=(0.97±0.06)x+(-4.99±8.10)	y=(1.10±0.07)x+(-13.24±9.16)	-13 to 3	-22 to -4

NOTE: Equation $y = mx + b$

where y = measured concentration, ppb
m = slope of equation
x = concentration added with spike, ppb
b = y-axis intercept when spike (x) is zero.

$$Y = (1.02 \pm 0.21)X - (0.96 \pm 32.10)$$

QUESTIONS AND ANSWERS

MR. SAUTER: Drew Sauter with EPA, Las Vegas. Did you allow...I was just snowed by the presentation, excellent presentation, but I was snowed with the numbers.

Did I understand you to say that you allowed the laboratories to utilize their own standards?

MR. STANKO: For the non-deuterated compound, yes. For the deuterated compounds we provided the stock solution that had been used to spike each one of the samples. Each one of the samples actually was spiked at 100 parts per billion level.

MR. SAUNTER: So in other words, then, is it possible that what you saw was the laboratories...in your isotopic dilution, saying that...see, it just strikes me fundamentally incorrect that isotopic dilution, GC/MS is not better than internal standard GC/MS.

I am wondering, could someone ask the

question that your study, while probably one of the best I have ever seen presented at a meeting, might have demonstrated that you can't trust laboratories to make up their own standards?

MR. STANKO: To answer your question, I think if you look at the variability factors that we saw in this particular study, in particular the relationship of the intralaboratory variability factors with the interlaboratory variability factors, it tells you that these laboratories are doing an excellent job. I don't think they could do any better. I think they have very good standards. They were probably not...

MR. SAUTER: But it was outside of your control, then?

MR. STANKO: It was outside of my control.

MR. SAUTER: I have done a few studies like this; I mean, in the area of organic

and analytical GC/MS and I have done probably 40 or 50 laboratory audits in regards to the hazardous waste program and it is my unequivocal experience that it is not preferred to allow the laboratories to make up their own standards.

It might be worthwhile looking at the data in that again; and, there are some other situations.

MR. STANKO: In this particular case, we were trying to study the methodology as applied by industrial and contract-type laboratories on samples of real world wastewaters.

MR. SAUTER: I understand that.

MR. STANKO: In that particular case, they do use their own calibration standards and curves to determine that and we thought it would be unfair for me to provide that portion of the standards as well.

The purpose for doing it with the deuterated compounds was to insure that all laboratories used the same source of deuterated material.

MR. SAUTER: I still think, although from the volume of the data you presented it's difficult for me; that that study might have shown that given the laboratory the freedom to essentially make up their own standards, 1624 and 624 will give you approximately the same results.

I'm really wondering if that's not a real... really what was presented and from the volume... like I said, it was an excellent presentation, but from the volume of the data I can't really digest it at this point.

MR. COLBY: Bruce Colby, S-CUBED. George, let me go back to the Table 1 you showed, I didn't have this when you were telling which samples were which. Is sample No. 8 your industrial wastewater?

MR. STANKO: That's correct.

MR. COLBY: Were there any of the priority pollutants in there?

MR. STANKO: To our knowledge,

there really was one compound that we think was there below what we call an operational limit of detection; that particular compound was 1, 2-dichloroethane. Four of the eight laboratories said they detected it; three tried to quantify it; four did not even see it. On that kind of a basis, I would say that it was below the method detection limit.

In one particular sample, sample No. 9, there was a contaminate that showed up that we don't know where it came from. All eight laboratories were able to detect it; seven of them were able to quantify it, and if you want to take the average, it is somewhere between 20 and 22 ppb. So here, again, I would say that's the limit of quantification, which is above the operational limit of detection.

MR. COLBY: Would it be fair to conclude, then, that your conclusions are based primarily on the analysis of reagent or very clean water samples, rather than on typical

industrial waste samples?

MR. STANKO: In this particular case, the chemical plant effluent that we had used was studied before by the EPA. In our data it didn't show that there was any difference with respect to precision or recovery with the matrix sample versus the distilled water sample.

MR. COLBY: There was nothing in that sample?

MR. STANKO: There was nothing? No, I am not saying that. There were no priority pollutants in that sample or volatile priority pollutants.

MR. COLBY: All right, I think my point has been made, George. Thank you.

MR. GRAVES: Bob Graves, EPA, Cincinnati. If I understood you correctly you did say...well, you used transform the data to log data.

MR. STANKO: That's correct.

MR. GRAVES: Can I ask you why you did that?

MR. STANKO: I have given several papers before. It has been a precident used by Radian in the report on the EPA screening phase (API), and the CMA report on the screening phase. In the paper I presented at Hershey on the five-plant study, it had also been used. In this particular study, we preferred to go that way.

If you looked at the data, in a number of cases and on a given sample, the data did look as if it were normally distributed. If you use log-normal statistics, and you can try this on a normal distribution, you will end up with a standard deviation that is somewhat less than if normal statistics were applied. So, using log-normal statistics on normally distributed data results in standard deviations that are conservative.

MR. GRAVES: Well, if they are less I would say they are standard deviations that are very...well, I guess you're right, okay,

because from what we found is, normally log-normal data comes from environmental samples.

If you are taking samples from a screen with respect to time they would normally vary log-normally to get them, you know, transform them back; but, if you take a standard and have 10 labs analyze where there's a set true value then that normally will follow a non-transformed with just random variation around the true value.

MR. STANKO: In this particular study, if you took a given sample that had nine compounds or 15 compounds and you looked at it on a compound specific basis, for one compound, the data were normally distributed. For several others, it would have been log-normally distributed. Even there, the difference was not all that great.

MR. GRAVES: Thank you.

MR. STANKO: I don't think we over-estimated the variability because of using log-normal statistics. If anything, we have slightly under-estimated it.

Any further questions? Thank you.

MR. TELLIARD: Thank you, George, up to your same old more data; I liked it better the other way.

Our next speaker...that was a very good presentation.

MR. STANKO: Thank you, Bill.

MR. TELLIARD: And I like the way you made it clear enough that we couldn't see the numbers.

MR. STANKO: They are definitely in the paper, though.

MR. TELLIARD: Yes, I understand, George.

Our next speaker is Phil Ryan from S-CUBED in La Jolla. Phil is a mass chrotomatogist with S-CUBED and is going to make his presentation now. Phil was fortunate enough to participate yesterday in that exciting review that we went over on all of the quality assurance stuff and I think he's recovered.

AUTOMATED IDENTIFICATION OF PRIORITY POLLUTANTS FROM GC/MS DATA

Philip W. Ryan, S-CUBED

I am going to address the topic of automation of data reduction from the point of view of a commercial laboratory which has for several years faced the necessity of automating in order to get its work done in a cost-effective manner. In response to that necessity, we have developed routines for automated processing that really do work well and have allowed us to operate with efficiency in a competitive field. So I'm going to spend most of my time discussing our particular routines, and also show a few comparisons with some of the other automated reduction routines that are available.

The first slide summarizes the problem we face in data reduction, one which is particularly severe in the case of isotope dilution work. The old needle-in-a-haystack analogy is sometimes used with this problem, but it really doesn't serve quite adequately. With isotope dilution, we typically

have more like 100 needles to find, and for each instrument being used, we have to do it a dozen or so times each day.

This slide is designed to emphasize the time constraints. The rate at which we need to process GC/MS data leaves us with only 18 seconds alloted for each target compound, and that rate can only be achieved with extensive automation. There is no chance of ever coming close to that rate with the traditional user-interactive routines that most of us learned in more research-oriented contexts.

There are a number of reasons for insisting on such short times. These are both scientific and economic, particularly as Bill Telliard tightens up his demands for timely reporting and quality control. The stringent time requirements are derived from the imperative of getting the greater part of the data reduction done in time for the operator to see his results before he has moved on too far to make good use of it. In practice, that means we need to get that part done during the succeeding GC/MS data

acquisition, and that is where these numbers come from: at 18 seconds per compound, the typical isotope dilution set of 100 or so target compounds can be handled in the 30 or so minutes available during the next acquistion.

The next slide lists the component parts of a GC/MS analysis. The first part, automated data acquisition, is something you always get done rather well when you spend $200,000 for a GC/MS/DS instrument. The last point, report preparation, is generally best done without too much reliance on computers. But the other three points, qualitative analysis, quantitative analysis and much of the quality control activity, all ought to be done at a rate which requires the kind of automated routine I am going to describe shortly, preferably within the 30 minutes available during the succeeding acquisition.

In order to provide the analyst the information he needs in a time which allows him to make use of it, we need to accomplish the steps detailed on the

next slide, and we need to complete them at the rate of 18 sec per compound. For each of the 100 or more compounds, we want to look through the GC/MS data file and select the appropriate portion of the file for more detailed inspection: in other words, choose a retention time window in which to search for the compound. Then we want to look at the selected portion of the file in more detail to decide whether the compound is present, is not present, or might be present. If it is, or might be there, we want to take a very close look at the mass spectrum to be sure we can make a positive identification of the compound.

Then we want to take the first steps toward quantitative analysis. This means we want to measure instrument response as peak area or peak height for the selected quantitation mass chromatogram. Finally, we want to present the analyst with all of the information he needs in order to know how his analysis is proceeding, what his results are and whether he needs to take care of some kind of instrumental problem or reanalyze a difficult sample.

The scheme I have just sketched is the traditional one used in semi-automated as well as in fully-automated approaches with differences primarily in the order of specific operations. The usual sequence of operations for automated reduction is depicted in this slide. The sequence describes the Finnigan/INCOS scheme as well as ours, and I am not aware of any system which makes significant deviation from it.

The program we use at S-CUBED follows the flow diagram shown on the next slide. As you can see, there are several decisions and selections to be made, and this is where the difficulty comes in reliably automating a data reduction. We must rely on a computer to make decisions and to recognize things which were formerly the responsibility of a human being, presumably one with extensive experience and training in the nuances of mass spectral data. For example, a computer will have to decide whether the data justifies concluding that a compound is, or is not, present, and we must come up

with much better defined criteria for the computer than we have available to characterize the user-interative approach.

To see what's involved in automation of such decisions, let's look more closely at the computer implementation of some of them. Specifically, let's look at the process of identifying a target compound on the basis of GC/MS data.

We get some guidance from Method 625. Everyone will probably recognize the contents of this slide, which are taken directly from the method. The corresponding criteria for Method 1625 are in a state of flux right now, but they will be similar when the revised method is published. These instructions are acceptable identification criteria from a scientific point of view, and they fulfill an important function in assuring that consistent criteria are applied among various labs. They were formulated in the earlier days of priority pollutant analysis when user-interactive software was all we had to work with, and they are best suited to that semi-automated approach.

The user is given a library of identification criteria, and displays data in such a way that he can see whether the criteria are met. For example, combining the instructions in this slide with library information of the type shown in the next (7th) slide (also from Method 625), and displaying the data as in the following (the 8th) slide, the operator can see quickly that the target compound probably was eluted at scan No. 925. This slide portrays a nearly ideal situation where the criteria are definitive and nothing in the data is likely to confuse the analyst's judgment. As we all know, not all data is so clean-cut. The next slide shows the same type of data display for less ideal data. A little more thought is demanded of the analyst in this case, and a little more chance of confusion is introduced. This less ideal case will be used as an example for the computer algorithm I'm going to discuss next.

The Method 625 criteria are actually a mechanism for keeping the intuition of an expert analyst within

defined bounds, particularly when poor data such as this introduces ambiguity and calls for exercise of judgment. As such, they can be inappropriate for other analytical endeavors and are not suitable for adaptation to fully automated identification algorithms.

More useful identification algorithms for target compound identification can be derived from the conclusions of pattern recognition theory by using computed similarity indices. These utilize most of the information contained in the spectrum and can be shown to be the best possible indicaters of similarity between reference mass spectra and sample spectra.

Library search routines almost always generate similarity indices and use them to rank possible matches. Within the INCOS system, the fundamental indices are called FIT and PURITY, and the strategy for target compound location involves locating the mass spectrum for which the index is a maximum. In this slide, we take the same data as in the previous one but we plot FIT and PURITY rather than char-

acteristic ion intensity.

While the similarity parameters alone do not seem to be strong indicators of compound presence, the parameter plotted at the bottom is a pretty clear marker of the correct elution time. That parameter is a product of FIT, PURITY and the quantitation mass intensity and is the parameter used in our software. It typically displays very sharp peaks with very good signal-to-noise even with data for which other indicators are ambiguous. The computer locates target compounds by locating peaks in this search parameter, and in our experience, that is the most reliable, least ambiguous identification criterion for automated GC/MS data processing.

Other criteria, based on other search parameters are used as well. The next slide shows some of the possibilities. This data is a case where benzene is eluted between two major interfering components so that it doesn't even produce a peak in the total ion chromatogram. The third and fourth plots are

the options provided by the INCOS search program, and the last trace is the one we use.

This case illustrates the special problems of isotope dilution GC/MS. In isotope dilution, there are always large peaks due to the labeled analogues, which are eluted very close to the target compounds. The failure of the INCOS options is due to their being weighted with total ion intensity, and that total ion intensity is dominated by labeled analogues and other interferences. The next slide summarizes some of the special considerations imposed by isotope dilution. The negative aspects of using total ion weighted criteria have been discussed. Another special problem with software which was not designed for isotope dilution is the inflexibility of the reference peak designation. Isotope dilution requires that the data system be able to use different peaks for retention time reference and for quantitation internal standard.

In the context of target compound location algorithms, I've shown some comparisons among our

software, the standard INCOS software and the traditional user-interactive approach. Now let's return to the consideration of data reduction pace and make similar comparisons there. The next slide summarizes the requirements for getting the reduction done in time for the analyst to make efficient use of the information. Also shown are the times required: 150 minutes and 50 minutes, respectively, for user-interactive techniques and for standard INCOS procedures. Only our SRCHMX approach, which takes only 5 minutes, allows any time for the operators to look at results and act on them during the succeeding run.

The last point I want to address is what kind of results the operator gets, and what happens to the data next. The diagnostic information shown in this slide is available to the operator after completion of the automated data processing. This happens to be data from a standard mixture, so it is unacceptable that the 11th compound, pentachlorophenol, is not found. This is the kind of feedback

the operator needs immediately because he has to correct whatever problem has occurred before going on. Remember, this diagnostic information is distilled from 2700 mass spectra, and only a fast automated data reduction could do this in time.

There is a lot of other diagnostic information here, too, including the pattern recognition parameters which are indicative of spectra quality, and retention time data which reflect chromatography performance. The operator using our software has 25 minutes to look at this reduced data and decide whether he has some problem to correct. With slower techniques, he may not know he has a problem until the next day.

My last slide indicates the next stage of data reduction as practiced in our laboratory. The problems identified by the diagnostic are reflected in the reduced data included in this upper quantitation report. We return to the user-interactive philosophy at this point and use our own data editing software to correct errors in the reduced data files. In

this case, a tailing peak required re-integration for compound No. 8 and an antiquated library was responsible for not finding entry No. 11.

Isotope Dilution
Priority Pollutant Analysis

- 45 minute FSCC GC/MS analysis
- 2700 spectra recorded
- 100 target compounds to be determined
- 30 minutes per analysis for data reduction to keep up with data acquisition
- 18 seconds per compound

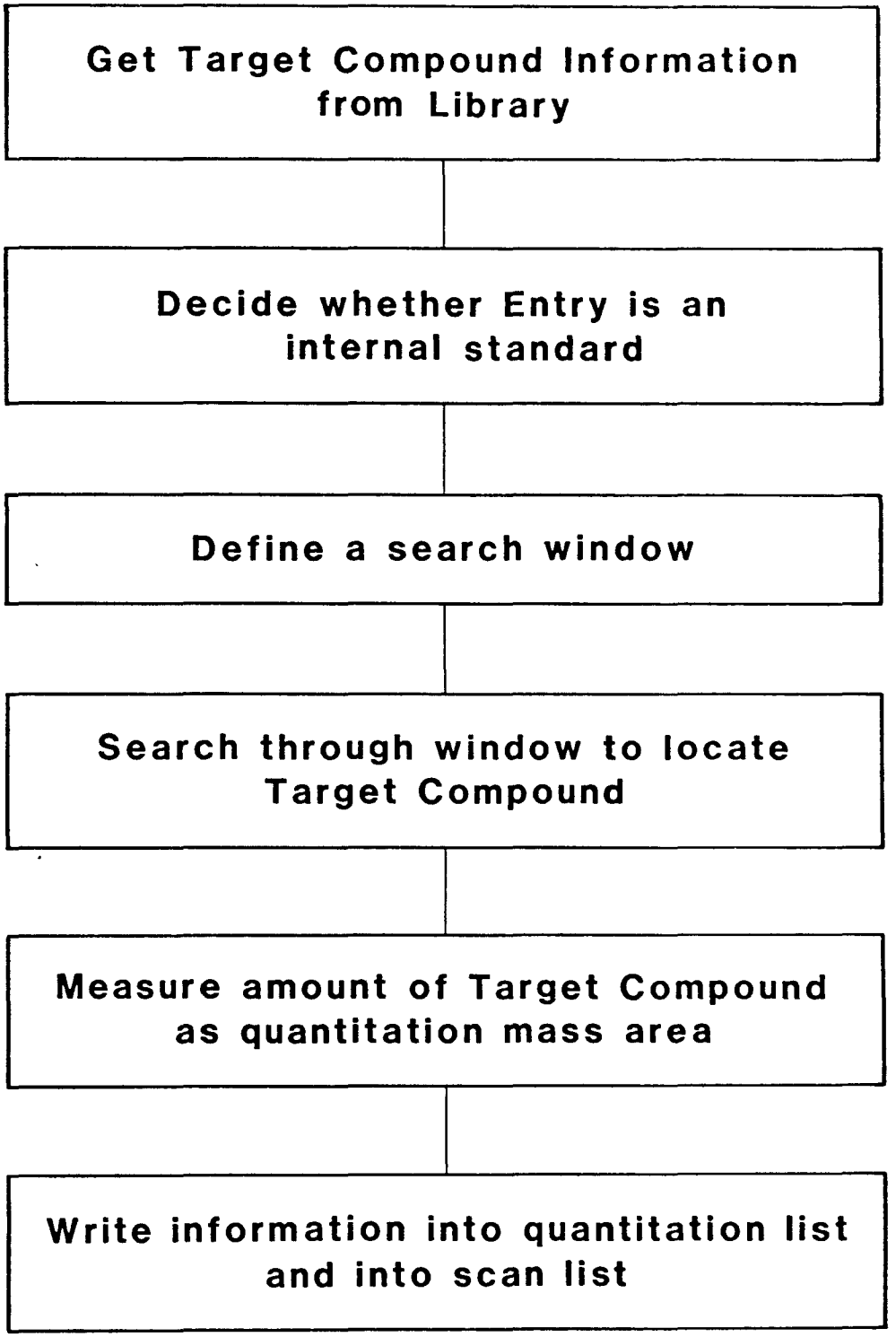
For Each Analysis

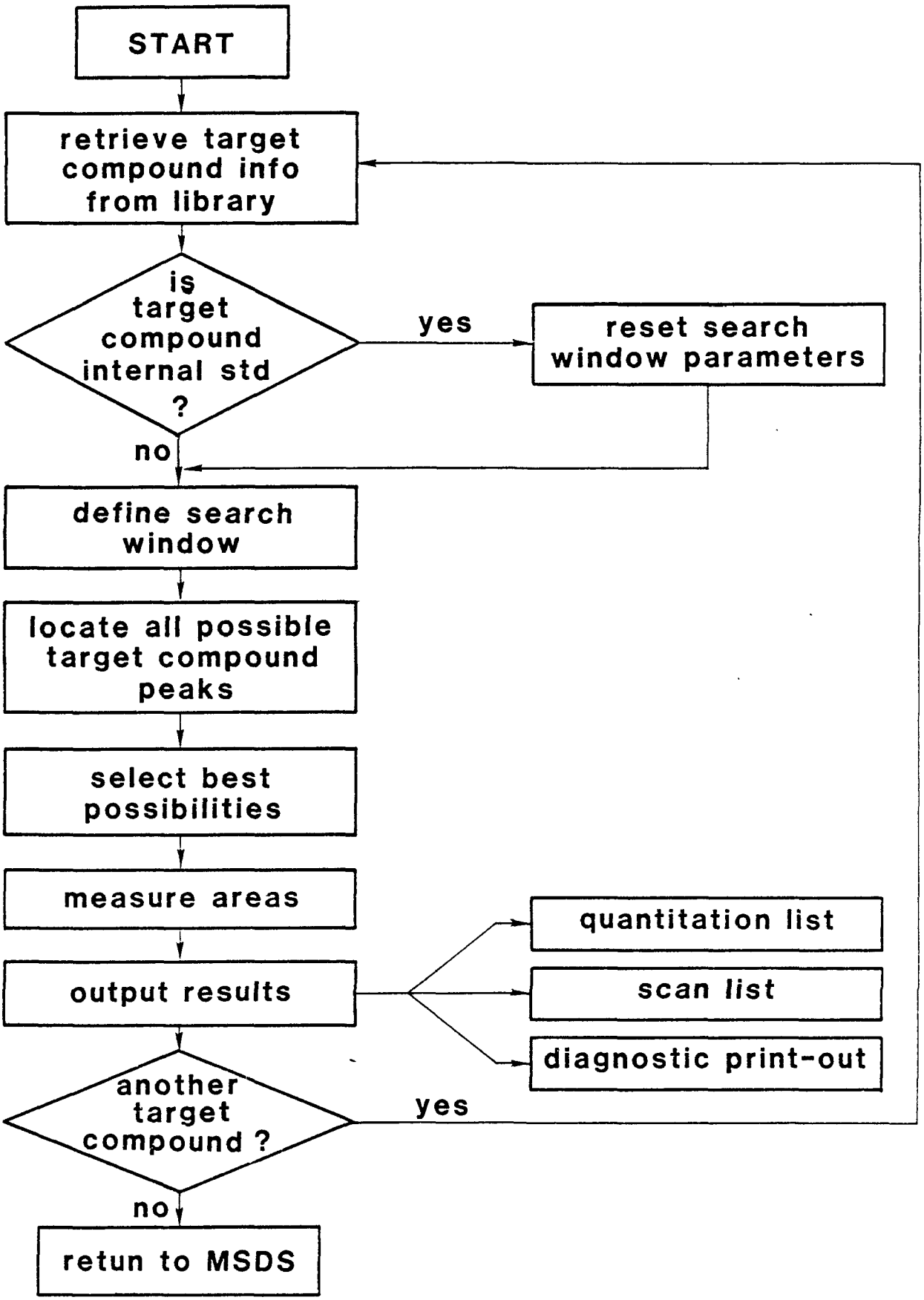
- Data acquisition and recording
- Qualitative analysis: Search through data file and identify target compounds
- Quantitative analysis: Calculate pollutant concentration in sample
- Quality Control and Quality Assurance
- Report generation

For Each Target Compound

- Select appropriate portion of data file
- Inspect selected portion to determine if target compound might be represented
- Analyze spectrum to make definitive identification
- Measure value of quantitation parameters
- Generate QC data (diagnostic information)

TARGET COMPOUND DATA REDUCTION




START
retrieve target compound info from library
is target compound internal std ?
yes
reset search window parameters
no
define search window
locate all possible target compound peaks
select best possibilities
measure areas
output results
quantitation list
scan list
diagnostic print-out
another target compound ?
yes
no
retun to MSDS

Qualitative Identification

14.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

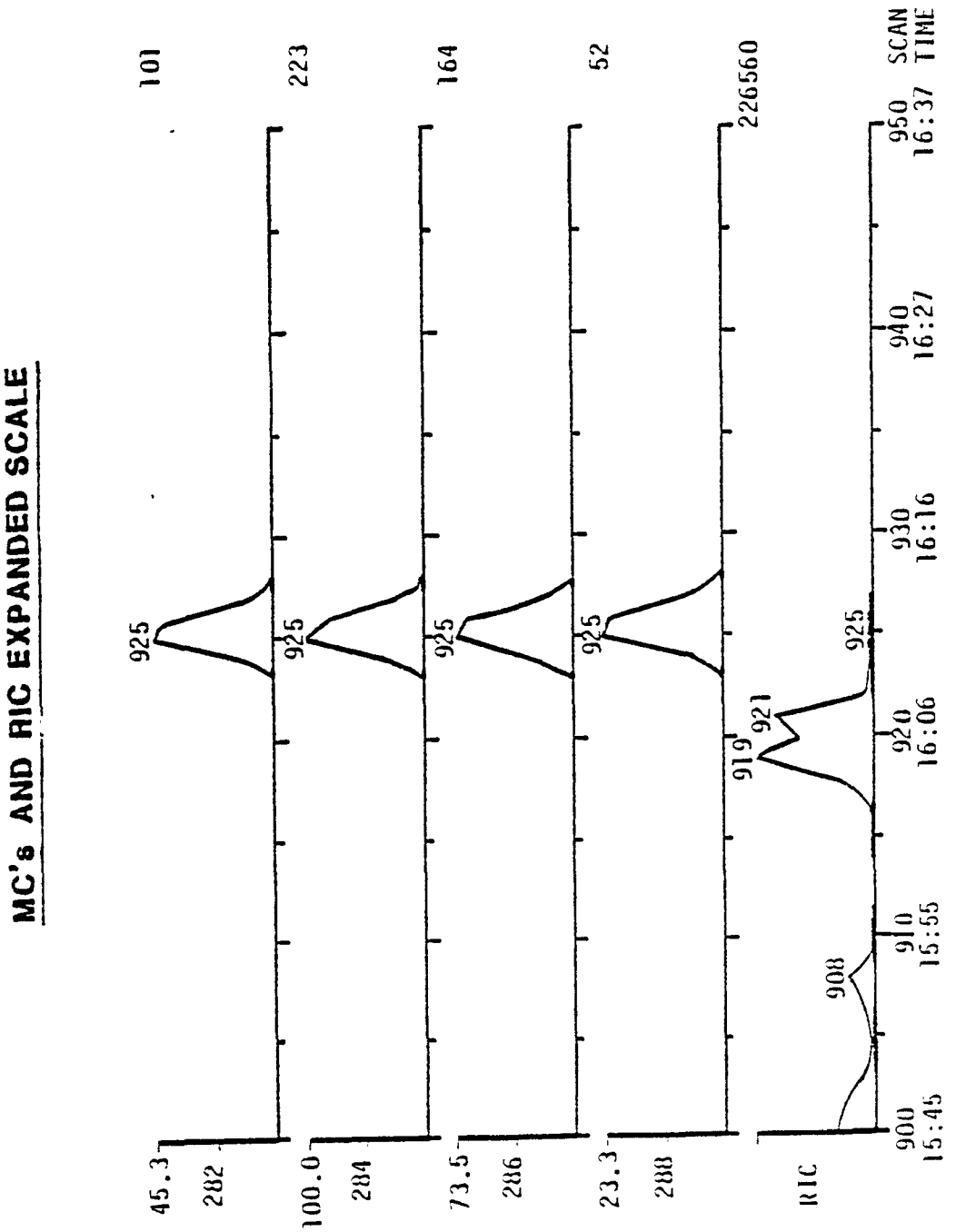
14.1.2 The retention time must fall within ±30 seconds of the retention time of the authentic compound.

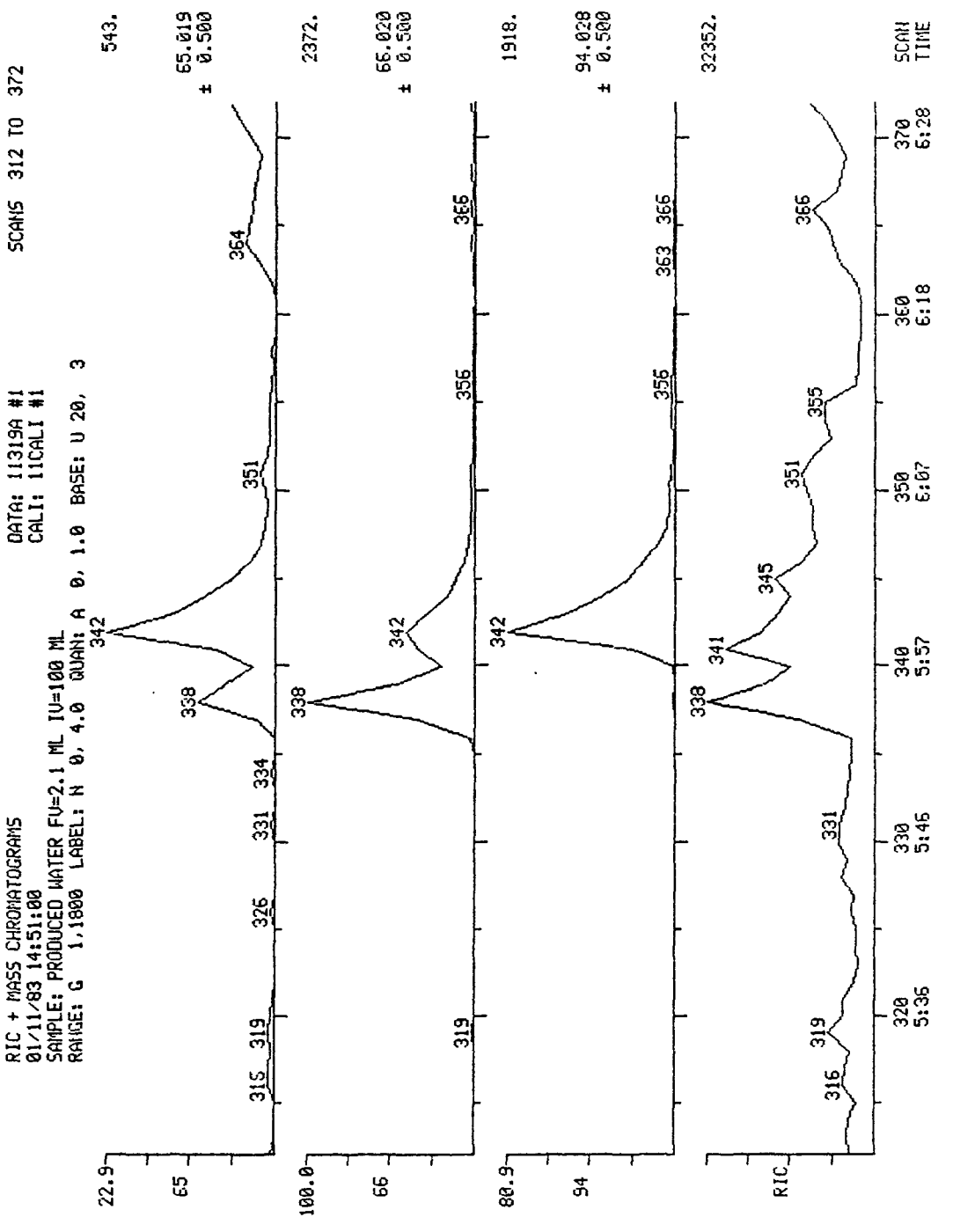
14.1.3 The relative peak heights of the three ions in the EICP's must fall within ±20% of the relative intensities of these ions in a reference mass spectrum. The reference mass spectrum can be obtained by a standard analyzed in the GC/MS system or from a reference library.

EPA Method 625

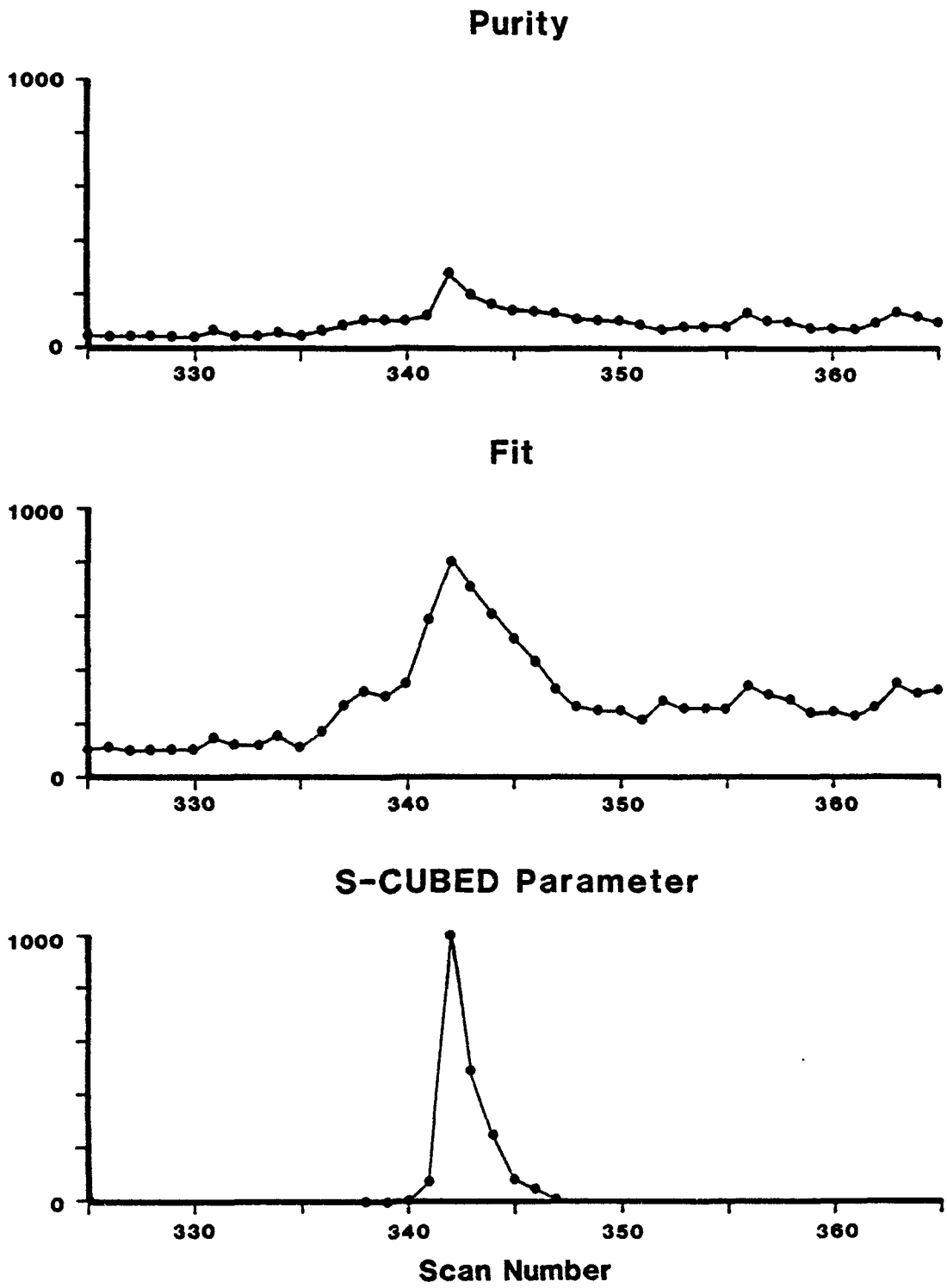
3-Peak Library

Parameter	Retention Time (min.)	Method Detection Limit (µg/L)	Characteristic Ions		
			Primary	Secondary	
2-Chlorophenol	5.5	3.3	128	64	130
2-Nitrophenol	6.5	3.6	139	65	109
Phenol	8.0	1.5	94	65	66
2,4-Dimethylphenol	9.4	2.7	122	107	121
2,4-Dichlorophenol	9.8	2.7	162	164	98
2,4,6-Trichlorophenol	11.8	2.7	196	198	200
4-Chloro-3-methylphenol	13.2	3.0	142	107	144
2,4-Dinitrophenol	15.9	42	184	63	154
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77
Pentachlorophenol	17.5	3.6	266	264	268
4-Nitrophenol	20.3	2.4	65	139	109

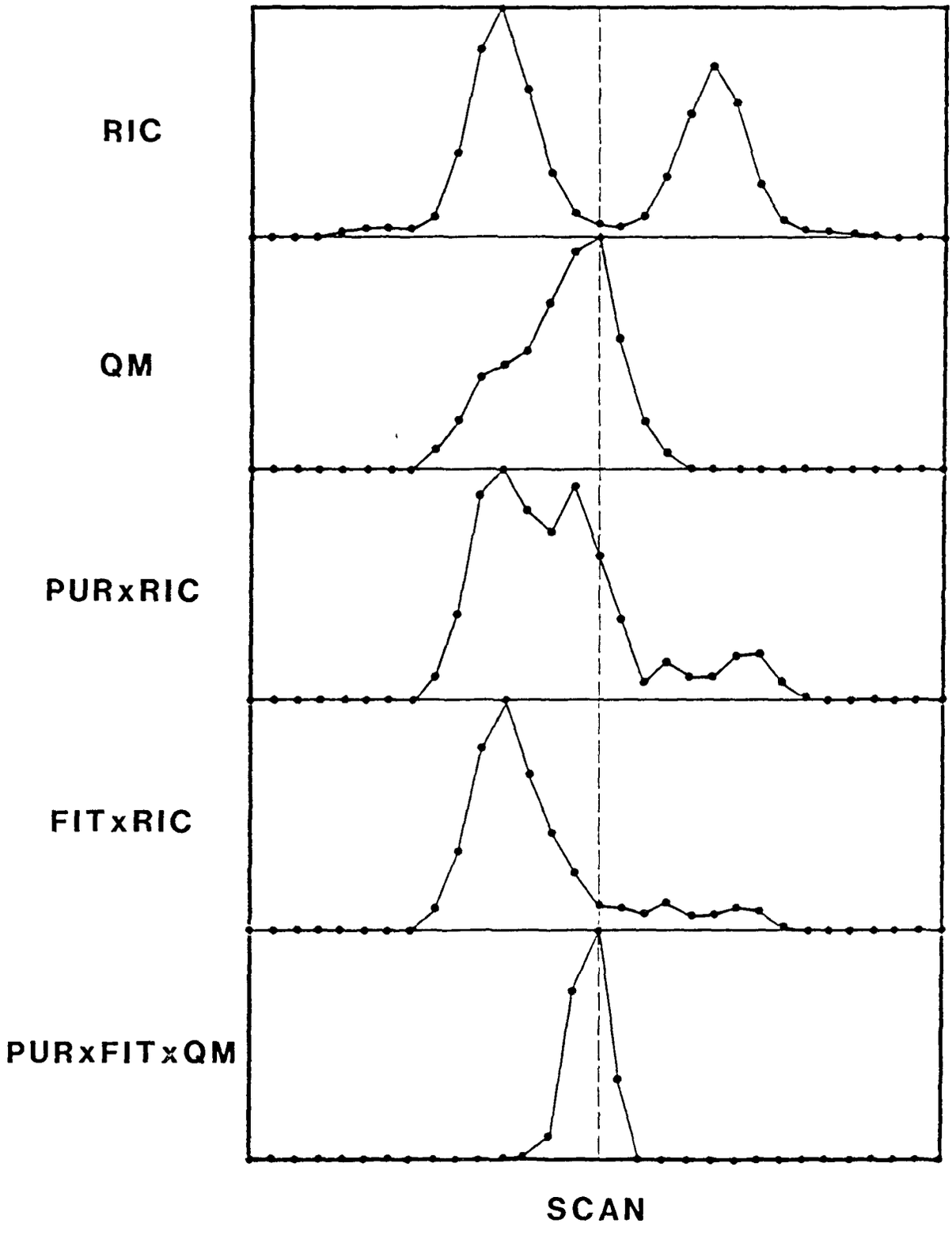

MC's AND RIC EXPANDED SCALE
101
223
164
52
226560
925
925
925
925
925
908
919
921
45.3
282
100.0
284
73.5
286
23.3
288
RIC
900
15:45
910
15:55
920
16:06
930
16:16
940
16:27
950
16:37
SCAN
TIME


RIC + MASS CHROMATOGRAMS
01/11/83 14:51:00
SAMPLE: PRODUCED WATER FU=2.1 ML IU=100 ML
RANGE: G 1,1800 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3
DATA: 11319A #1
CALI: 11CALI #1
SCANS 312 TO 372
543.
65.019
± 0.500
2372.
66.020
± 0.500
1918.
94.028
± 0.500
32352.
RIC
SCAN
TIME

Identification Parameters



The Search Parameter



Special Considerations For Isotope Dilution

- TIC is always too complex to be a useful search parameter factor
- Multiple internal standards in a single library are desirable
- Different references for retention time and for internal standard quantitation in a single library are desirable

Data Processing Pace

- Data system must have the capability to process one data file while another is being acquired
- 30 minutes are available to process a file for 100 target compounds
- SRCHMX requires 5 minutes
- INCOS procedures require 50 minutes
- User-interactive technique requires 150 minutes

SRCHMX Diagnostic

1U1LSTD6
6CALI
01/06/83
83.5 PPM LABELED + UNLABELED COMPOUNDS
OWA

NO	LIB	ID	M/E	SCAN	PRED	DELTA	FIT	PUR	MATCH	AREA
1	JA	**IS	188	961	961	0	971	858	99.	67201.
				-969		-8	973	852	84.	
2	JA	21A-	196	656	656	0	933	633	99.	11075.
3	JA	22A-	142	609	609	0	913	582	99.	16775.
4	JA	24A-	128	339	324	-15	672	272	27.	7755.
5	JA	31A	162	501	501	0	965	696	99.	22779.
6	JA	34A	122	487	487	0	971	582	99.	27388.
7	JA	57A	139	464	464	0	962	572	99.	17333.
8	JA	58A	65	812	810	-2	710	459	76.	1165.
	*****	WARNING:		QUESTIONABLE	AREA	MEASUREMENT #		8	*****	
				-807		3	665	50	48.	
9	JA	59A	184	775	775	0	825	163	71.	1446.
10	JA	60A	198	855	855	0	944	531	99.	4305.
11	JA	64A	266	----	932	NO PEAKS FOUND				

Original Quan List

NO	M/E	SCAN	TIME	REF	RRT	METH	AREA(HGHT)	AMOUNT		%TOT
1	188	961	16:49	1	1.000	A VV	67201.	83.500	PPM	7.45
2	196	656	11:29	1	0.683	A BB	11075.	54.281	PPM	4.84
3	142	609	10:39	1	0.634	A VV	16775.	73.459	PPM	6.55
4	128	339	5:56	1	0.353	A BB	7755.	37.825	PPM	3.37
5	162	501	8:46	1	0.521	A BB	22724.	114.566	PPM	10.22
6	122	487	8:31	1	0.507	A BB	27388.	136.263	PPM	12.15
7	139	464	8:07	1	0.483	A VB	17333.	139.932	PPM	12.48
8	65	812	14:13	1	0.845	A VB	1165.	42.501	PPM	3.79
9	184	775	13:34	1	0.806	A BB	1446.	36.127	PPM	3.22
10	198	855	14:58	1	0.890	A VB	4305.	39.007	PPM	3.48
11	NOT FOUND									

Corrected Quan List

NO	M/E	SCAN	TIME	REF	RRT	METH	AREA(HGHT)	AMOUNT		%TOT
1	188	961	16:49	1	1.000	A VV	67201.	83.500	PPM	7.20
2	196	656	11:29	1	0.683	A BB	11075.	54.281	PPM	4.68
3	142	609	10:39	1	0.634	A VV	16775.	73.459	PPM	6.33
4	128	339	5:56	1	0.353	A BB	7755.	37.825	PPM	3.26
5	162	501	8:46	1	0.521	A BB	22724.	114.566	PPM	9.87
6	122	487	8:31	1	0.507	A BB	27388.	136.263	PPM	11.74
7	139	464	8:07	1	0.483	A VB	17333.	139.932	PPM	12.06
8	65	812	14:13	1	0.845	GEDT	1716.	62.015	PPM	5.35
9	184	775	13:34	1	0.806	A BB	1446.	36.127	PPM	3.11
10	198	855	14:58	1	0.890	A VB	4305.	39.007	PPM	3.36
11	266	953	16:41	1	0.992	GEDT	2683.	19.312	PPM	1.66

MR. RYAN: I'll be glad to answer questions if anybody has some questions on this automated procedure.

MR. TELLIARD: Questions? Anyone; last chance, he gets off free?

Thank you, Bill.

Our next speaker is John Norris from Viar and Company. John is going to explain step two of what we had discussed this morning about the automated data system. He will carry on from where Dale left off and John has been the project manager on this project for about the last year; John.

RECEIPT AND TRANSCRIPTION OF QUANTITATIVE DATA ON MAGNETIC TAPE AT THE EPA SAMPLE CONTROL CENTER

John Norris, Viar and Company

MR. NORRIS: Good afternoon ladies and gentlemen. I would like to take this opportunity to briefly describe the Effluent Guidelines Division's Program for the receipt of quantitative data on magnetic tape. I kind of feel like one of Bruce Colby's outliers standing up here today because all of the previous speakers have been pretty much chemically or lab oriented. My area of expertise is the data processing field and in this case I guess I'm representative of Bruce's slide with its single outlier.

During this presentation I'll be covering the topics as shown on this slide. First, we'll start off the session with a quick overview of the EGD's analytic process and briefly describe the role that the Sample Control Center plays in it. Next, we'll look at the actual collection and reporting of quantitative data by the laboratorys, how it has been done in the past and more importantly how it

will be accomplished in the future. Since the new media will be magnetic tape we'll look at the elements of information that would be on the tape and the formats that this data will be recorded in. First let us look at the overall analytical process that transpires prior to the institution of effluent regulations.

The key players in this process are shown in this slide. The EPA Project Officer for the specific industry being regulated has overall responsibility for developing the effluent regulation. The Effluent Guidelines Division, Office of Analytic Support has overall responsibility for the analytical process. The Sample Control Center assists the EGD's Office of Analytical Support in carrying out its responsibilities. We'll look at the role that the Sample Control Center plays in this process in detail later. The laboratories provide the staff and equipment necessary for sample analysis and generally perform under contract with the EGD.

As can been seen in this slide, the analytical process is initiated by the EPA Project Officer

when specific analyses are requested to be performed. These requests are forwarded to the EGD's Office of Analytical Support for processing.

The Office of Analytical Support in conjunction with the Sample Control Center defines appropriate tests and selects the particular laboratory best suited to perform them. Samples are then collected by field sampling teams. These field sampling teams are frequently agency contractors. The samples they collect are shipped to the appropriate laboratory for analysis. Once the laboratory has completed its analysis of the samples, it assembles its findings into data packages and forwards them to the EGD Sample Control Center. The quantitative results from from the data packages are in turn presented to the EPA Project Officer for review.

What I have just described is a very simplistic view of the actual process that transpires prior to regulation implementation. To reiterate, the EGD's Office of Analytical Support has primary responsibility for this process.

The Sample Control Center assists the Office of Analytical Support in this process and is their primary arm for insuring that the process works. The current slide shows some of the major functions that this Center performs for them. It is through the Sample Control Center that actual samples are scheduled for analysis at the specific laboratories; sampling progress is monitored; and sample scheduling problems are resolved.

Also, the Sample Control Center monitors laboratory progress and directs any technical and/or scientific problems to appropriate EGD personnel for resolution. The Center also maintains an inventory of chemical standards and spiking cocktails for use by the laboratories in the sample analysis. The Sample Control Center also functions as the EGD's focal point for the receipt and management of data packages from the laboratories. They are responsible

for entering the majority of this quantitative data into the EGD's data base. They are also responsible for maintaining the data base itself and using it to derive management information for the EPA Project Officer. It is the last three bullets on this slide, what I'll call the collection and reporting of quantitative data that I would like to focus attention on at this time. Let's look at how this process was performed in the past.

Collection and reporting of quantitative data begins at the laboratory during sample analysis. The laboratories are responsible for transcribing all quantitative results onto data sheets once sample analysis is completed. This is a very time-consuming and exacting process for the labs to perform. The laboratories then assemble these data sheets into data package organized by sampling visit or episode and forward them to the Sample Control Center. Upon receipt of

the data packages, the Sample Control Center performs initial receipt and control procedures to insure completeness of the data. If the data sheets are missing the laboratory is contacted and asked to supply the missing data.

Once receipt problems are resolved, the hard copy data is keyed into machine-readable format. The data thus keyed is edited and verified to insure exactness of the entry function. Next, quality control checks are applied to the data and any discrepancies that are found are resolved with the laboratory. Finally, the data is summarized using various statistical routines and presented to the EPA Project Officer for review.

The overall process of transcribing data onto hard copy data sheets and eventually entering this data into machine-readable format has been at times a very costly, time-consuming and labor intensive method for data collection. The

process is costly, not only in terms of the additional dollars required to transcribe the data and key it, but also in terms of the additional time that these steps add to the process. In addition, this methodology presents a high potential for injecting error into the data that is being collected. Each time a laboratory copies data for a report onto a data sheet or a data entry person keys the results from the data sheet there is a chance that error could be made. Realizing these deficiencies, the EGD looked at alternate approaches for collecting and reporting of this data. I would like to now describe the methodology that's been adopted by the EGD for collecting this quantitative data. This slide shows what I call the analysis and confirmation portion of the collection and reporting process.

It depicts the actual steps that are performed during the process, the center portion of the slide; and, the actual flow of data represented by the right-most portion of the slide.

This process is performed by the laboratory for each blank, standard or sample fraction it is required to analyze. The process begins with the analysis of the sample fraction by the laboratory. The raw data generated by the GC/MS with computer interface is used to produce a quantitation report, or quantitation list as I have heard it called here today, for each sample fraction analyzed. This quantitation report is then subjected to a compound verification process where the report should be reviewed by a chemist. This review is necessary to insure that appropriate compounds were determined and to compare the mass spectrum for each compound

against the standard. Once the quantitation report is reviewed and approved by the chemist, then a final report is produced. At this point, the lab should have a quality assurance inspector review and verify the results on the quantitation report. The QA Inspector verifies that the appropriate method protocol was followed and that the quality assurance specifications were met during the analysis. The quality insurance inspector then certifies the analysis by a formal signoff procedure. Once the sample analysis has been certified then a magnetic tape copy of the Quantitation report is made and sent to the Sample Control Center for processing.

This slide depicts the SCC validation portion of the collection and reporting process. It begins when the data tape is received at the Sample Control Center. Each tape received is logged in and several checks are made against the tape to ensure all data is present. First,

the files contained on the tape are verified against a transmittal received with the tape. A file in this case is the same as a single quantitation report. Second, the actual compound data within a file is read from the tape and edited for completeness. If the data on the tape passes these checks, it is then subjected to the same quality control checks that were applied at the laboratory. Any problems noted in processing of the tapes results in a discrepancy report as shown down on the bottom right of the slide. This discrepancy report becomes the basis for requesting the laboratory to reanalyze and/or resubmit the quantitative data. All data that passes these checks is then merged with sample information derived from other sources and loaded into an EGD data base for subsequent statistical analysis and reporting. Once that is completed, it is then summarized and presented to the

to the Project Officer for his or her review as was done in the previous method.

Submission of data by magnetic tape has several advantages over the previous hardcopy method of data collection. Some of the more significant ones I have shown here (indicating).

First, the method streamlines the reporting and collection process by eliminating the transcription and data keying steps. This elimination significantly decreases the time required to place results into the hands of the Project Officer and, more importantly, decreases the overall cost of the collection process.

Second, quality assurance is improved with the certification process at the laboratory and the automated quality control review of the data at the Sample Control Center.

Third, the accuracy of the data is improved with the automation of the collection function

Automation also allows additional elements of information about the sample fraction analysis to be collected at no additional cost.

Let's now look at the types of information that will be captured by this process. This slide gives a general idea of the categories of data that will be captured on the quantitation tapes that are submitted. Sample number and EGD compound numbers are some examples of the types of data fields that we found in the identification category. Extraction date and date of analysis are examples of the date information that will be captured. Fraction type, that is, acid, base neutral, or volatile and dilution or concentration factors are some examples of those that we included under the fraction category.

The next category, analytic conditions, would include information about the column that was used, the temperature information, and flow

or velocity rates. Results such as retention time, mass to charge ratio, or scan time would be examples of the data fields that would be reported for each compound under the results by compound heading.

The library information that you use during your analysis for the reference amount, response factor, or reference peak would be examples of data included under the QA category.

In summary, 26 unique elements of information or data fields have been identified for collection purposes. Some of these data fields will be presented only once on the quantitation report while some will be represented for each compound that is determined.

The last topic that I would like to cover is the actual format of the quantitative data on magnetic tape. The format that has been adopted by the EGD Division is the quantitation report that is produced by the GC/MS now. This format

is being developed for a variety of the GC/MS machines. For purposes of discussion, the report has been broken down into three main parts as shown on the current slide.

Let us now look at the format of each of these parts. The first part is the header segment. The top portion of the slide gives you a visual of what the data looks like on the tape and also what the report looks like. The circled numbers identify the data fields that are used from this segment of the report. The names of the data fields are identified at the bottom of the slide.

This slide gives a visual of the data segment of the tape. The segment contains the analysis results for each compound that was determined. Notice item number 13 up there, it points to something new (indicating). What we're asking each lab to do is to precede the compound name in the library with the EGD

compound number for identification purposes. The number beside the EGD number on the slide is called a reference number and is used to tie the data portion back to the actual name and compound number identification. The compound number is required to insure proper compound identification and eliminate variances in spelling.

This is the third portion of the report. It is called the F-2 segment. This segment basically provides library information from the analysis. It is presented for each compound analyzed.

This concludes my discussion. Are there any questions?

Thank you.

MR. TELLIARD: Thank you, John.

(WHEREUPON, a recess was taken.)

RECEIPT AND TRANSCRIPTION OF QUANTITATIVE DATA ON MAGNETIC TAPE AT THE EPA/EGD SAMPLE CONTROL CENTER

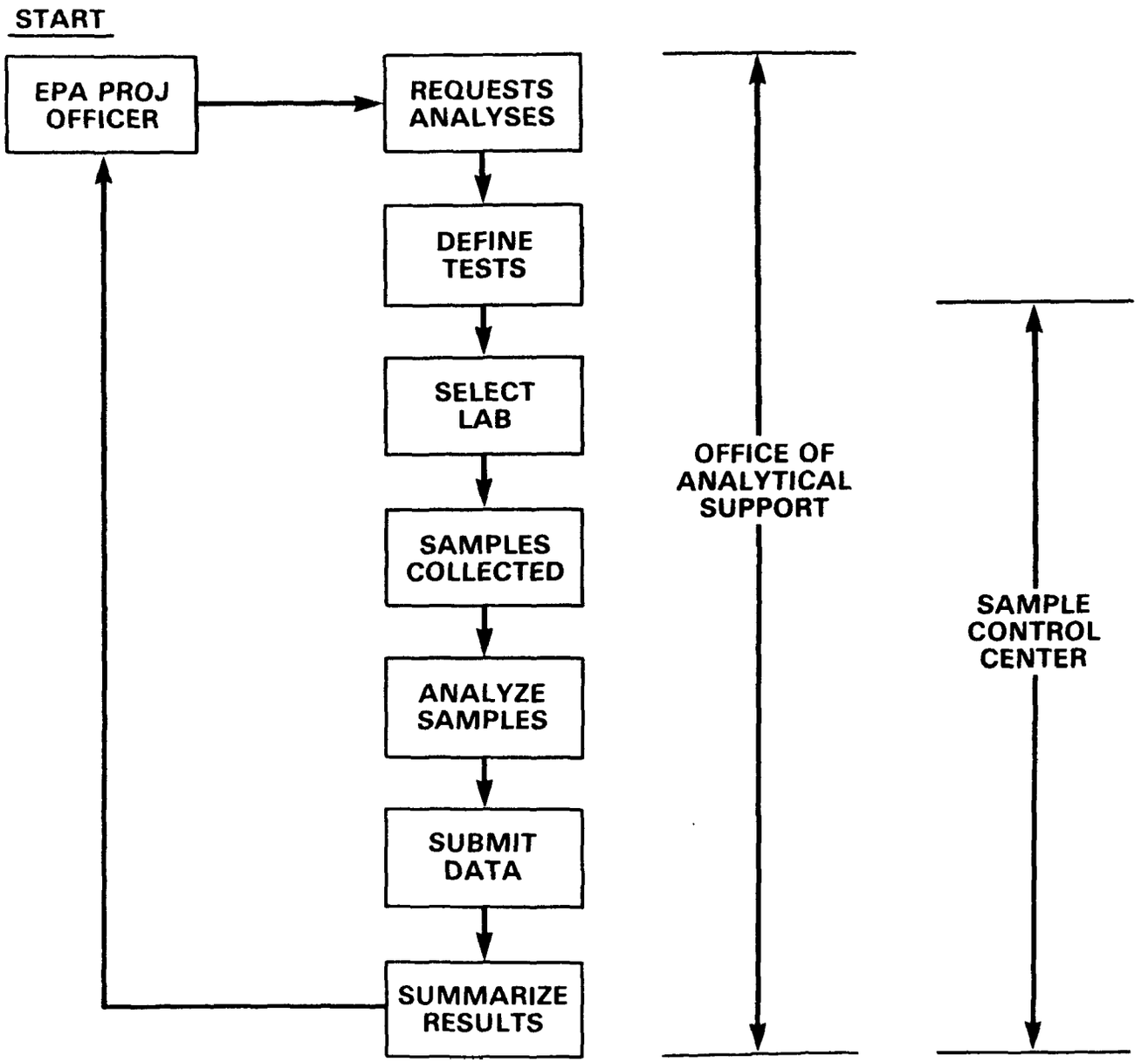
DISCUSSION OUTLINE

- OVERVIEW OF EPA/EGD ANALYTIC PROCESS
- SAMPLE CONTROL CENTER
- QUANTITATIVE DATA COLLECTION/REPORTING
- MAGNETIC TAPE DATA
- TAPE DATA REPORTING FORMATS

ANALYTIC PROCESS KEY PLAYERS

- EPA PROJECT OFFICER
- EGD OFFICE OF ANALYTICAL SUPPORT
- SAMPLE CONTROL CENTER
- ANALYTICAL LABORATORIES

OVERVIEW OF EPA/EGD ANALYTIC PROCESS



SAMPLE CONTROL CENTER FUNCTIONS

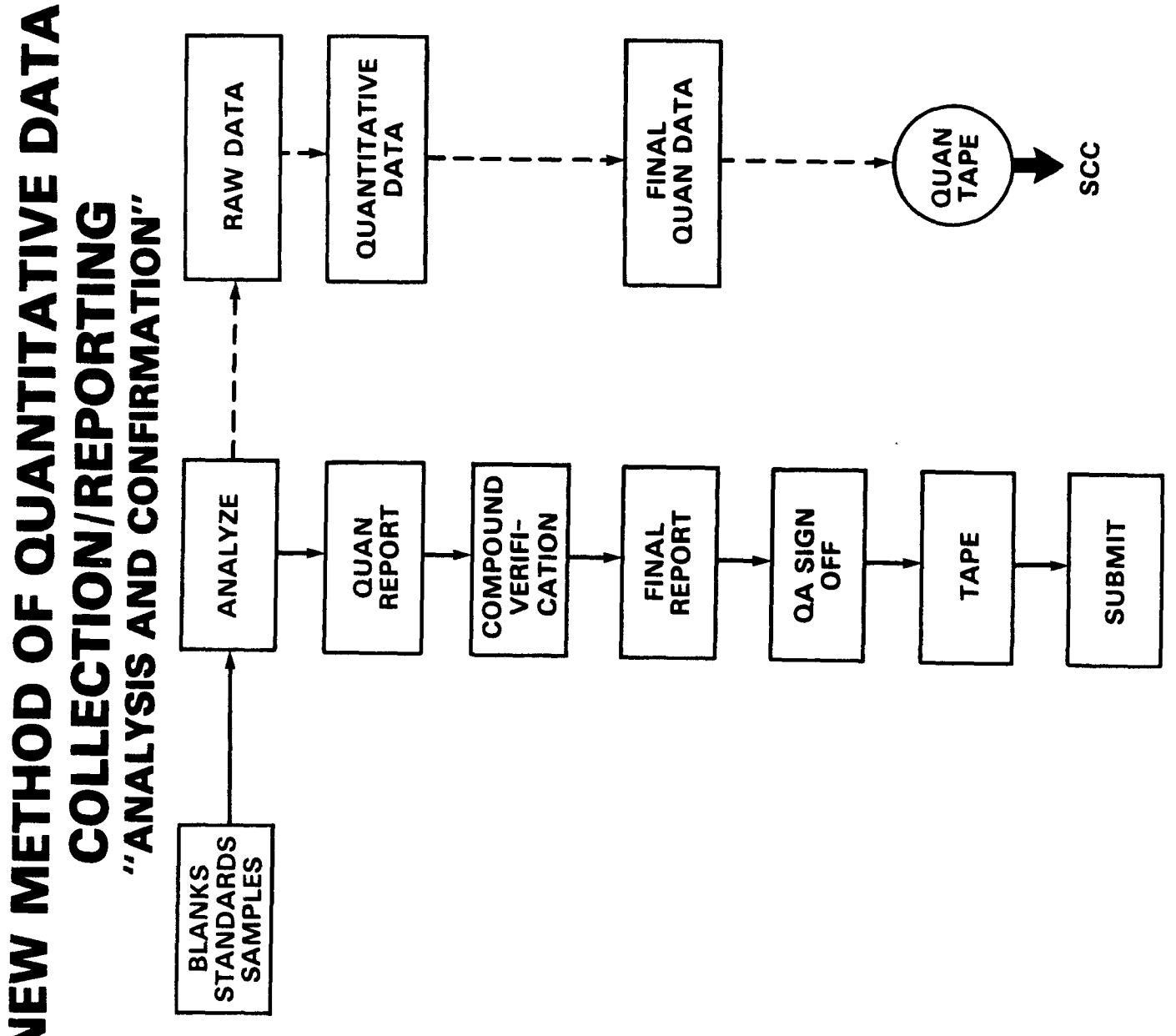
- SCHEDULE AND TRACK SAMPLES
- PROVIDE SCIENTIFIC AND TECHNICAL ASSISTANCE
- MAINTAIN AND DISTRIBUTE STANDARDS/ SPIKING MATERIALS
- PERFORM ENTRY OF QUANTITATIVE DATA
- DEVELOP AND MAINTAIN EGD DATA BASE
- FORMULATE MANAGEMENT INFORMATION

PREVIOUS METHOD OF QUANTITATIVE DATA COLLECTION/REPORTING

- SAMPLE ANALYSIS PERFORMED
- RESULTS TRANSCRIBED ONTO DATA SHEETS
- DATA PACKAGES SUBMITTED TO SCC
- RECEIPT AND CONTROL
- QUANTITATIVE RESULTS ENTERED INTO MACHINE READABLE FORMAT
- QUALITY CONTROL CHECKS APPLIED
- DISCREPANCIES RESOLVED
- STATISTICAL ANALYSIS AND REPORTING PERFORMED

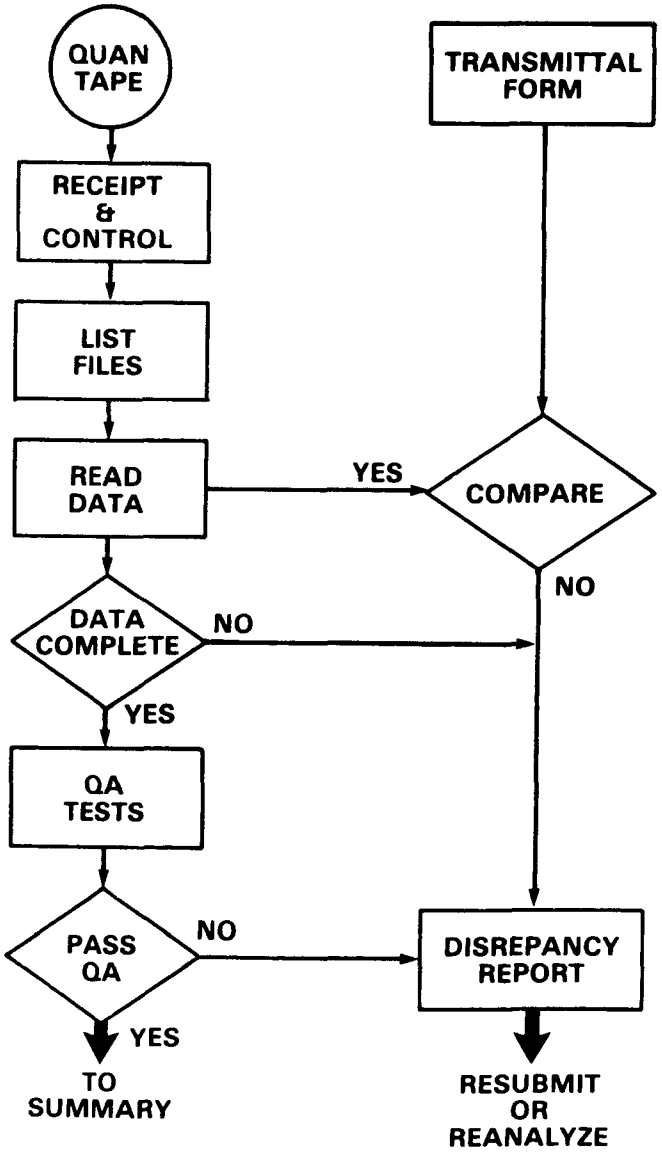
DISADVANTAGES OF PREVIOUS METHOD

- COSTLY
- TIME CONSUMING
- LABOR INTENSIVE
- HIGH POTENTIAL FOR INTERJECTING ERRORS


NEW METHOD OF QUANTITATIVE DATA COLLECTION/REPORTING
"ANALYSIS AND CONFIRMATION"
BLANKS STANDARDS SAMPLES
ANALYZE
RAW DATA
QUANTITATIVE DATA
FINAL QUAN DATA
QUAN TAPE
SCC
QUAN REPORT
COMPOUND VERIFI-CATION
FINAL REPORT
QA SIGN OFF
TAPE
SUBMIT

NEW METHOD OF QUANTITATIVE DATA COLLECTION/REPORTING

"SCC DATA VALIDATION"



ADVANTAGES OF TAPE SUBMISSION

- MORE TIMELY REPORTING
- LESS COSTLY
- ELIMINATES TRANSCRIPTION OF DATA
- PROVIDES FOR QA REVIEW AND SIGN-OFF AT LAB
- ELIMINATES HARD COPY DATA ENTRY
- PROVIDES MORE ACCURATE INFORMATION
- EXPANDS ELEMENTS OF INFORMATION COLLECTED
- AUTOMATES THE QA REVIEW OF DATA

EGD MAGNETIC TAPE DATA

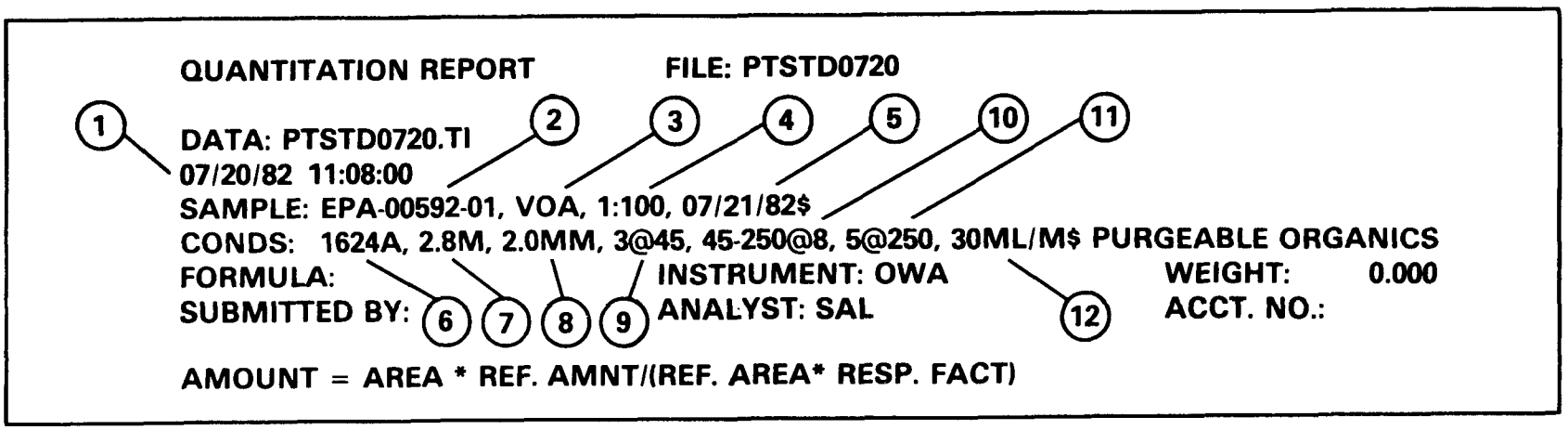
- IDENTIFICATION INFORMATION
- DATES
- FRACTION INFORMATION
- ANALYTIC CONDITIONS
- RESULTS BY COMPOUND
- QA INFORMATION

MAGNETIC TAPE DATA FORMAT

QUANTIFICATION REPORT

- HEADER SEGMENT
- DATA SEGMENT
- F2 SEGMENT

HEADER SEGMENT



1. DATE ANALYZED
2. SAMPLE NUMBER
3. COMPOUND FRACTION
4. CONCENTRATION/DILUTION FACTOR
5. DATE EXTRACTED
6. METHOD
7. COLUMN LENGTH
8. COLUMN DIAMETER
9. COLUMN INITIAL TEMP
10. TEMPERATURE PROGRAM
11. FINAL HOLD TEMP
12. CARRIER GAS FLOW RATE

DATA SEGMENT

NO	NAME (13)
1	088 VINYL CHLORIDE
2	016 CHLOROETHANE
3	055 METHYLENE CHLORIDE
4	049 TRICHLOROFLUOROMETHANE
5	029 1,1-DICHLOROETHYLENE

NO	M/E (14)	SCAN (15)	TIME (16)	RFF (17)	RRT (18)	METH	AREA (19)	AMOUNT (20) (21)	%TOT
1	62	112	3:44	8	0.347	A BB	27094.	40.000 UG/L	9.5
2	64	143	4:46	8	0.443	A BB	18898.	40.000 UG/L	9.5
3	84	217	7:14	8	0.672	A BB	12810.	10.000 UG/L	2.3
4	101	284	9:28	8	0.879	A BB	8577.	10.000 UG/L	2.3
5	96	306	10:12	8	0.947	A BV	8978.	10.000 UG/L	2.3

(13) EGD COMPOUND NUMBER

(14) MASS TO CHARGE RATIO

(15) SCAN NUMBER

(16) ABSOLUTE RETENTION TIME

(17) REFERENCE COMPOUND

(18) RELATIVE RETENTION TIME

(19) PEAK AREA

(20) MEASURED AMOUNT

(21) UNIT OF MEASURE

F2 SEGMENT

NO	RET (L) ㉒	RATIO	RRT (L) ㉓	RATIO	AMNT	AMNT (L) ㉔	R. FAC ㉕	R. FAC (L) ㉖	RATIO
1	6:43	0.98	1.000	1.00	60.00	60.00	1.000	1.000	1.00
2	1:43	0.95	0.255	0.98	45.48	100.00	0.194	0.426	0.45
3	1:14	1.40	0.184	1.43	73.92	100.00	0.197	0.266	0.74
4	2:02	0.95	0.303	0.97	63.39	100.00	0.177	0.279	0.63
5	1:58	0.98	0.294	1.00	100.44	100.00	0.285	0.284	1.00

㉒ LIBRARY RETENTION TIME

㉓ LIBRARY RELATIVE RETENTION TIME

㉔ LIBRARY AMOUNT

㉕ RESPONSE FACTOR

㉖ LIBRARY RESPONSE FACTOR

MR. TELLIARD: Our next speaker is from our Office of Research and Development, our Athens Laboratory, Walt Shackelford. Walt has been involved in a number of parts of this program for the few years, and, in particular, the tape program we have been carrying out on spectral matching; and, which is what Walter is going to speak about today. I hope you can understand him, he has a funny sound in his voice, I understand, but...Walt.

INCREASED CONFIDENCE IN SPECTRUM MATCHING BY USE OF A RETENTION TIME LIBRARY

Walter M. Shackelford
U.S. Environmental Protection Agency
Athens Laboratory

ABSTRACT

To successfully extract the maximum amount of information, all dimensions of the gas chromatography/mass spectrometry (GC/MS) data from a sample run must be used. In this work, retention data were combined with reference mass spectra for computer-aided identification of organics in industrial effluent. Use of retention data proved to be a great help in increasing the analyst's confidence in compound identifications from low quality spectrum matches. Even greater confidence will be achieved when libraries that include capillary column retention data and gas phase infra-red spectra are available.

Increased Confidence in Spectrum Matching by Use of a Retention Data Library

Introduction. The data acquired in a scanned gas chromatography/mass spectrometry (GC/MS) analysis has three dimensions of qualitative information (Figure 1). Each dimension can provide the chemist with varying degrees of confidence in identification, but it is when these parameters are combined that the power of GC/MS is evidenced. The elution time of a component taken by itself provides useful qualitative information only if the sample has no interferences. Likewise, the masses recorded in a given scan, while providing more qualitative information than elution time, are of little value unless coupled with intensities. The detector's response to a compound without elution time or specific mass data provides little in the way of qualitative information.

Even if two dimensions are combined, the resulting qualitative information falls far short of the total capabilities of GC/MS in qualitative analysis.

For instance, an extracted ion current profile (EICP), which combines mass and retention data, while narrowing a chemist's search for compounds having a certain characteristic mass, still requires manual search of each occurrence of that mass for compound identification. Use of the full mass spectrum, which includes mass and intensity for all masses recorded, eliminates many of the ambiguities found in using characteristic ions or retention times alone, but requires that probability based matching (PBM), an automated library search system, be used for acceptable efficiency.

The use of automated spectrum search and retrieval systems is a great aid to qualitative analysis of large numbers of unknowns, but the reliability of such systems is suspect. For example, it is well known that mass spectra, while highly characteristic of a molecule, are not always unique. Also, when dealing with real world data, one often finds contaminated spectra and spectra skewed from instrumental problems.

In this work, elution time information was added to full-scan mass spectra to increase the reliability of automated spectrum matching. In this way, mass spectrum ambiguities were alleviated by requiring retention data matching. Retention data overlaps were overcome by use of mass spectral data. A dynamic historical library was managed that increased in size as compounds were authenticated and more retention data were added. The increase in confidence of automated spectrum matching gained through the use of retention data was measured. In Figure 2 the use of mass, intensity and retention data to narrow the choices for identification is depicted as a set of filters.

Experimental. This work is the result of a study of wastewater from 21 industrial categories and finished water from publicly owned treatment works (POTW). The study encompassed some 4000 samples that were analyzed at 14 contract laboratories and EPA regional laboratories. Details of the study, computer system, and data reduction systems can be found elsewhere.[1]

To create the historical library, several homologous series standards were analyzed to provide retention data. The classes of compounds used are shown in Table 1.

The logic of spectrum analysis is shown in Figure 3. The library2 of reference mass spectra, which contained more than 40,000 spectra, was searched first. In this way, compounds for which no retention data existed in this historical library were not prematurely eliminated from the search procedure.

As compounds are tentatively identified using spectra from different GC columns from different laboratories, provision in the library must be made to differentiate among retention data from different columns. In addition, care must be exercised to differentiate among the internal standards used for reference in retention data.

A search was conducted in three steps:

1. The Chemical Abstracts Service (CAS) number of the best acceptable spectrum match for

the unknown was recorded, along with the GC column identification number, relative retention time and internal standard.

2. The historical library (ordered on CAS number) was searched for the candidate's CAS number. If the numbers matched, the GC column and internal standard had to match as well.

3. The relative retention time of the candidate compound and the retention window allowed for the library entry were compared. If these two were in accord a match was recorded. If the two did not match, the next best acceptable spectrum match was carried through. If no other spectrum matches were acceptable, the computer program flagged the spectrum so that a chemist could make an appropriate decision on its identification.

The Probability Based Matching (PBM) system has been reported by Pesyna and coworkers.[3] Figure 4 depicts the matching parameters used in this study. The measure of match overall quality, K, is theoretically unbounded, but, in practice depends on the

number of peaks available for matching in a spectrum. Thus, K_{max}, the K for a perfect match, varies with the number of fragments. This means that rather than relying on K alone, Δ K, the algebraic difference between K_{max} and K, should be considered. To consider K and Δ K simultaneously, the ratio $\Delta K/K_{max}$ can be used as a matching parameter that reflects both positive and negative match qualities.

Confirmation of computer matches was accomplished by reanalysis of sample extracts using capillary column GC/MS[4]. More than 3000 computer-matched identifications were studied in the confirmation process.

Results and discussion. In Table 2 are shown the relations between the match parameters K and K/K_{max} and the precision of relative retention data. The standard deviation of the relative retention data is expressed in relative retention units and is calculated using data from the 14 participating laboratories. The compounds shown here are representative of commonly found compound classes for each fraction or column. The fused silica capillary

column data are from compounds not commonly found on the acid or base/neutral packed columns.

In comparing the relative retention times with K values for each compound, one can see that whereas retention data variance is very small, the K value range is a factor of 2-5. The narrow retention time windows allow greater confidence in poor spectrum match parameters as will be shown below.

Note that the standard deviations of the fused silica capillary column data are much smaller than those of the other columns. Although a smaller number of laboratories is represented in the fused silica data (only 2 compared to 14 with the packed column data), later work[5] has shown the interlab precision of retention data using fused silica columns to be excellent also.

In Figure 5, the effect that retention data has on matching confidence when using K as the deciding match parameter is seen. The upper curves refer to data collected in this work, where the lower curve refers to Atwater's previous study[5]

using spectrum data alone. As can be seen, although the curves merge at high K, much higher confidence can be placed in the matches from the present study that have retention time corroboration at low K values.

An anomaly can be seen in the two uppermost curves. Whereas the confirmation rate should increase with increasing K, one of the curves shows a decrease in confirmation rate at high K. Examination of the data revealed that, although aliphatic carboxylic acids were the largest group of compounds at K>100, only 32 percent were confirmed. Likewise, aromatic acids had a confirmation rate of only 37 percent. Results of the carboxylic acids were deleted from the data set and replotted to obtain the topmost curve, which follows closely that of Atwater5 at high K.

Poor confirmation rates for the carboxylic acid matches can be attributed to degradation of sample extracts used for confirmation studies during storage. To examine the confirmation characteristics of other

compound classes, note Table 3. Even though the ambiguity of matching results among hydrocarbons should be high, hydrocarbons evidence the highest confirmation rates. Perhaps storage stability explains this fact as well. Note that carboxylic acid esters had a much greater confirmation rate than the acids.

The data of Figure 5 show the fallacy of using K value alone. Since K is unbounded (Figure 4), a molecule with many fragments will have a higher K value in matching than a molecule with fewer fragments. Thus, the carboxylic acids of carbon length >12 have a high K value even when the match is not good simply because of the number of fragments matched. One must also look at the negative points of the match.

In Figure 6 the relation between Δ K and confirmation can be seen. Note that again the use of retention data improves match confidence greatly at low match quality (high Δ K in this case). Note also that there is no anomalous behavior due to the carboxylic acids. In this case, since the dif-

ference between the calculated match and a perfect match is represented, the effect of increased fragmentation due to increased molecular weight is not seen.

Observations such as this led to the use of K/K_{max} as the deciding match parameter. In this way, both positive and negative match parameters can be viewed in one term. In Figure 7, the relation of this parameter to match confirmation rate is shown to be a function of the size of K/K_{max}.

Conclusions. This study shows that the confidence of poor spectra matches can be greatly increased by using retention data as a match parameter. The confidence of excellent spectra matches is not affected by retention data -- probably because closely eluting compounds with very similar spectra begin to interfere at this level of confidence. The building of larger retention data libraries and the construction of an FT/IR segment to the historical library management program (Figure 8) are the next steps in improving the analyst's confidence in automated identifications.

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4. EPA Contract Number 68-03-2867, Research Triangle Institute, Research Triangle Park, NC.

5. A. D. Sauter and D. Betowski, HRC&CC, 4, 1981, 366.

6. B. L. Atwater, Ph.D. Thesis, Cornell University, Ithaca, NY, 1980.

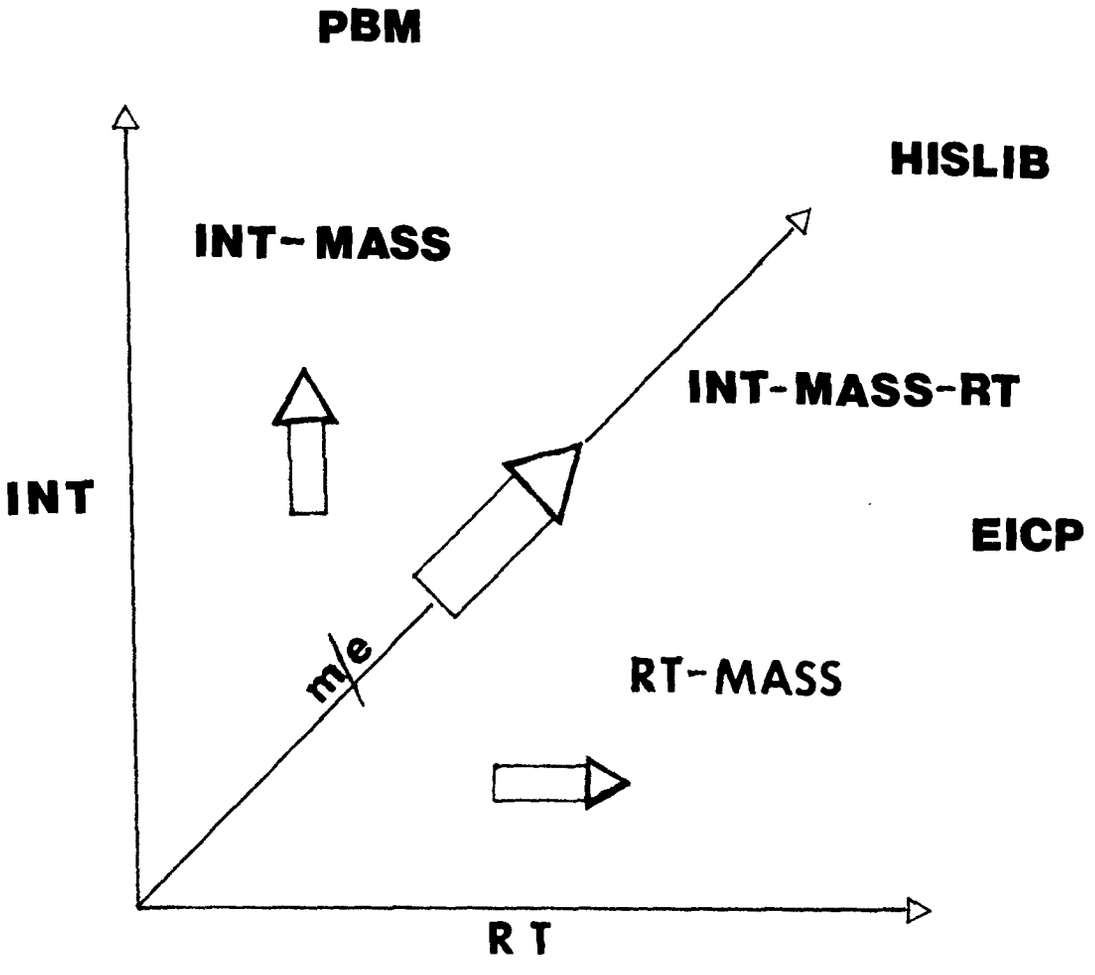


Figure 1. The three dimensions of GC/MS data.

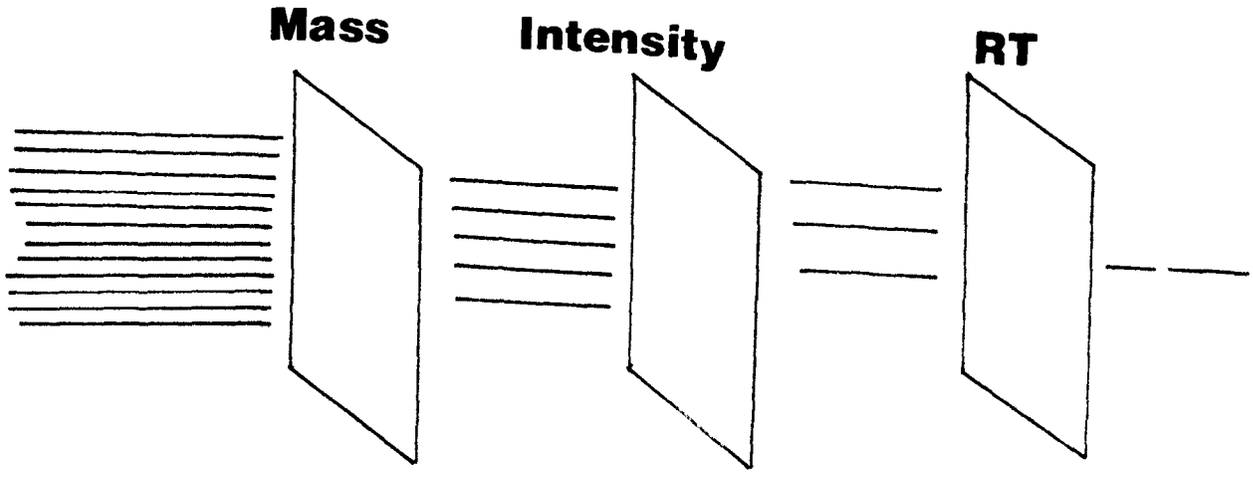


Figure 2. Mass, Intensity and Retention Time Filters for spectrum matching.

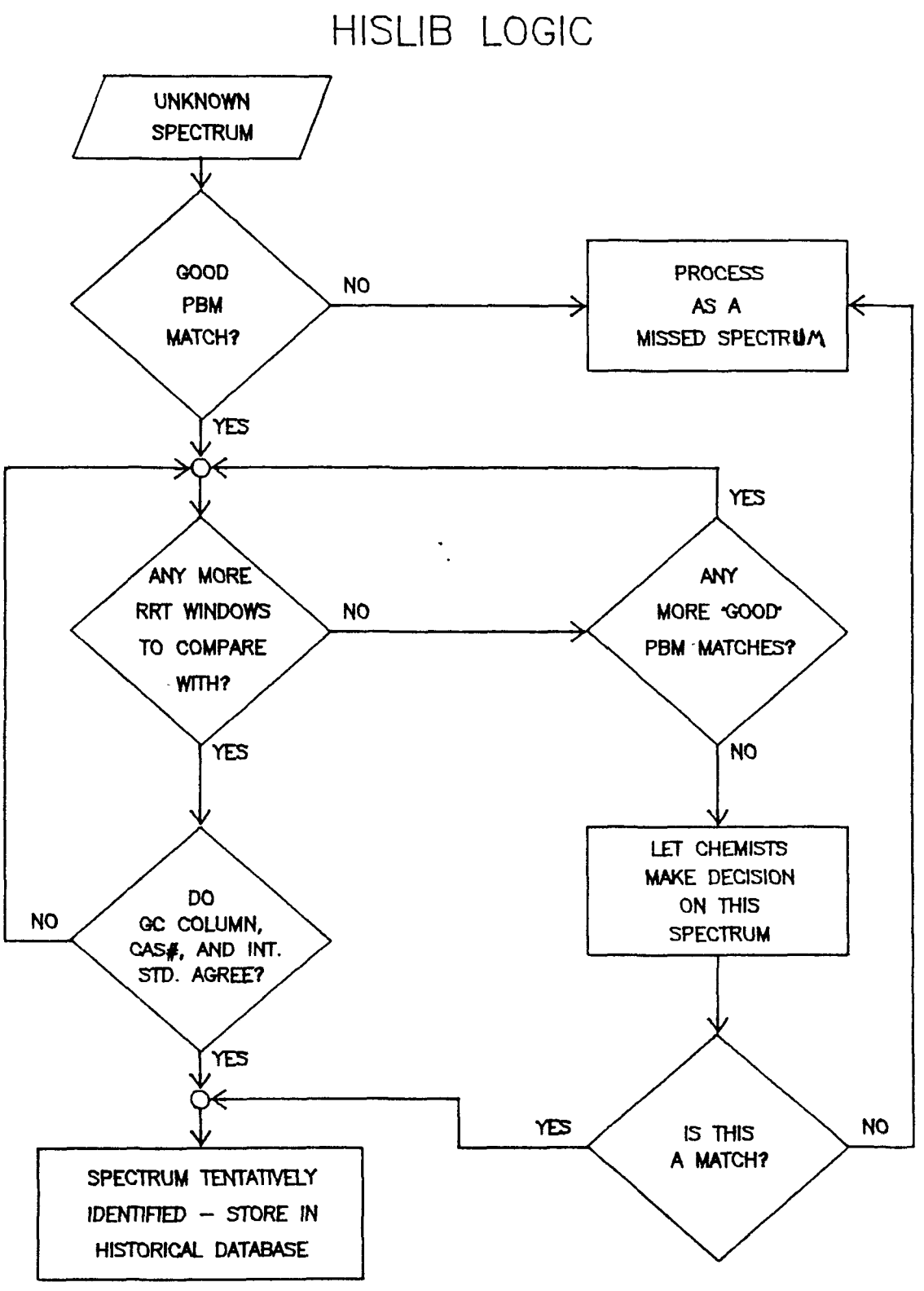


Figure 3. Logic of spectrum analysis in the historical library.

MATCHING SYSTEM PARAMETERS

PBM

- $K = \Sigma (U_i + A_i - D - W_i)$

  THEORETICALLY HAS NO LIMIT

- $\Delta K = K_{max} - K$

- $\frac{K}{K_{max}}$ MINIMIZES BIAS TOWARD COMPOUNDS WITH MANY FRAGMENTS

Figure 4. Probability based matching parameters. U_i = empirically derived uniqueness; A_i = empirically derived abundance value; D = dilution of spectrum by impurity; W = the tolerance allowed for abundance match.

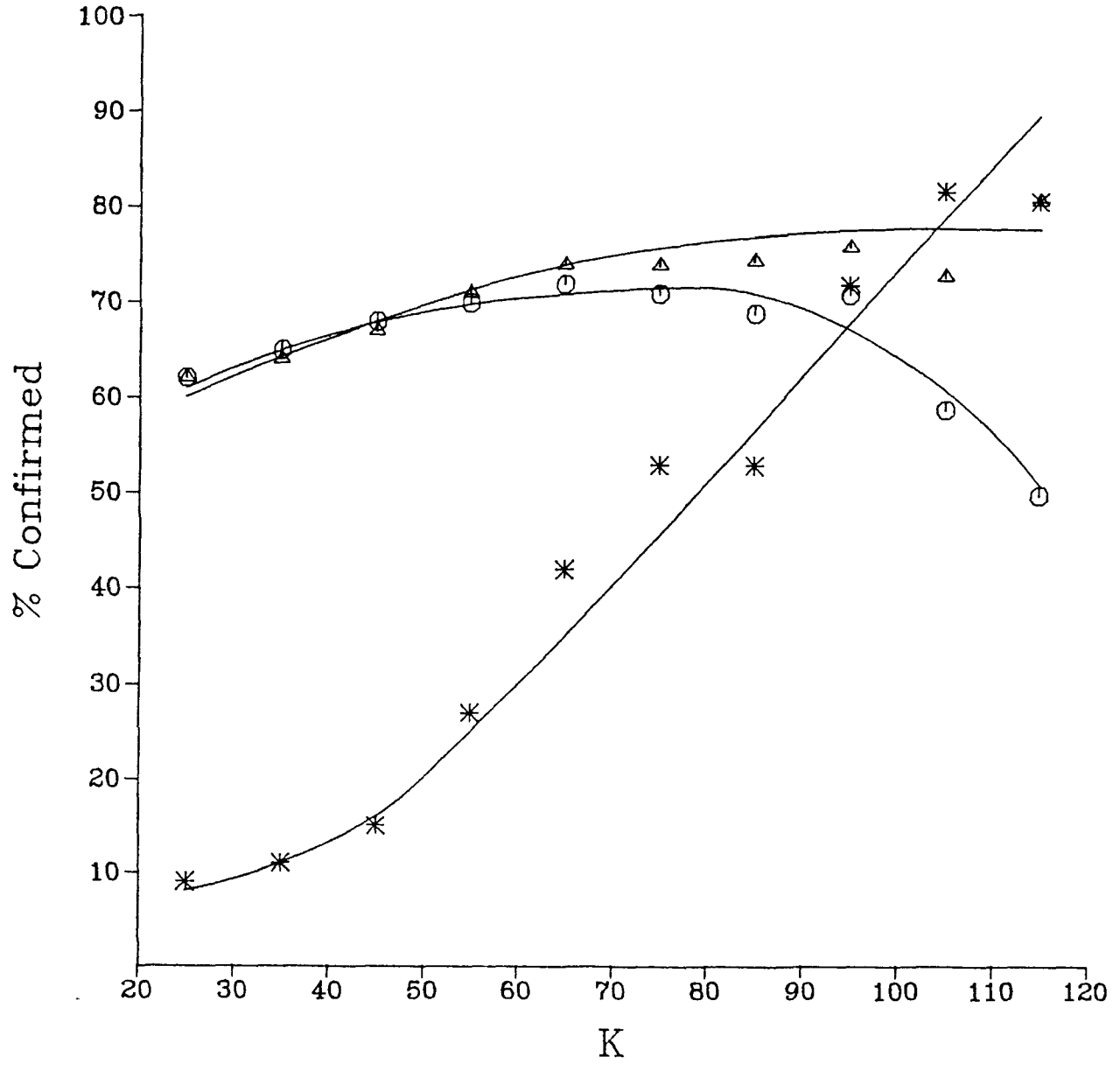
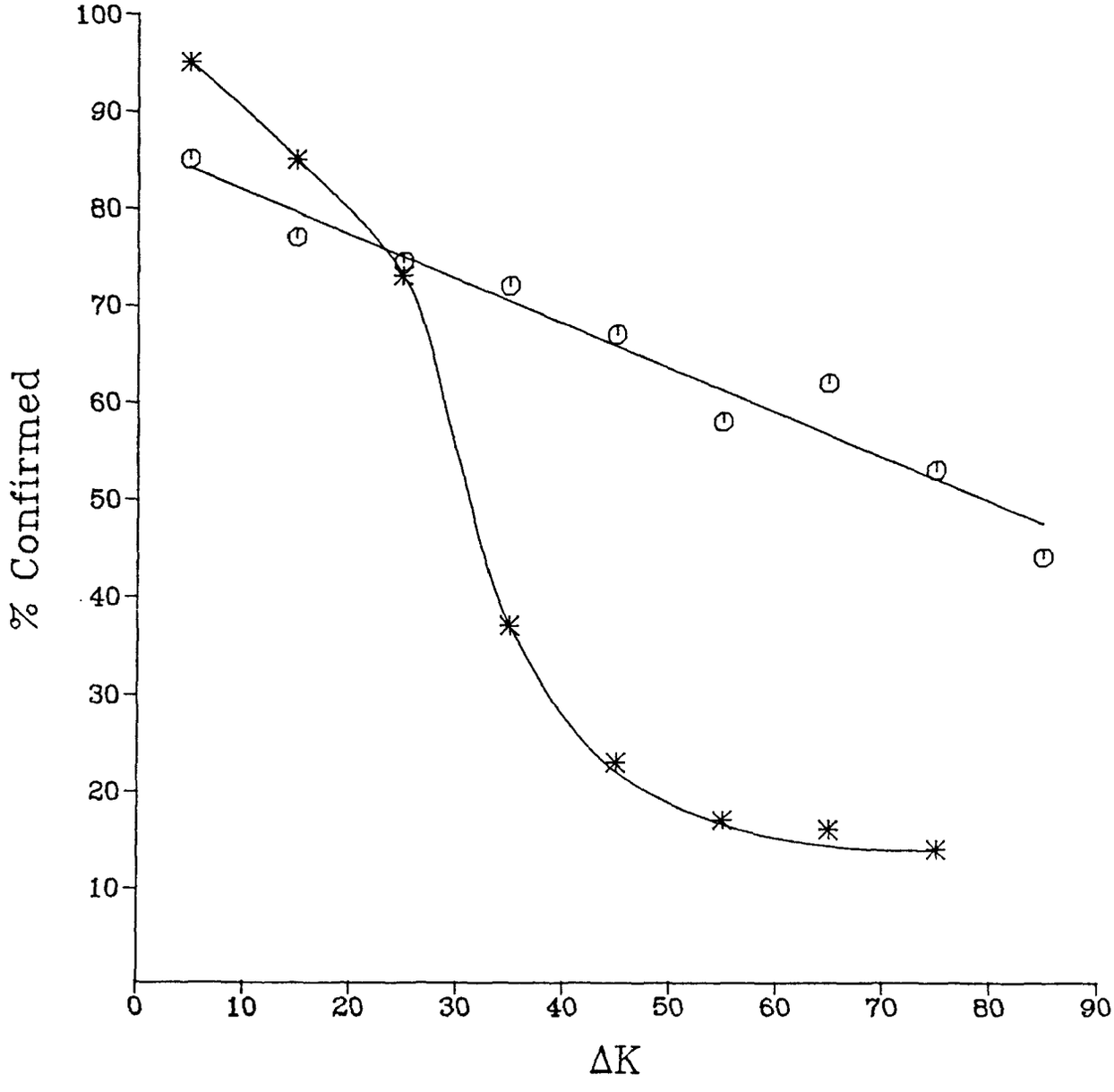


Figure 5. Plot of K versus confirmation rate for this study and that of Atwater (5).



O - All compounds
* - Data of Atwater (5)

Figure 6. Plot of ΔK versus confirmation rate comparing this study with that of Atwater (5).

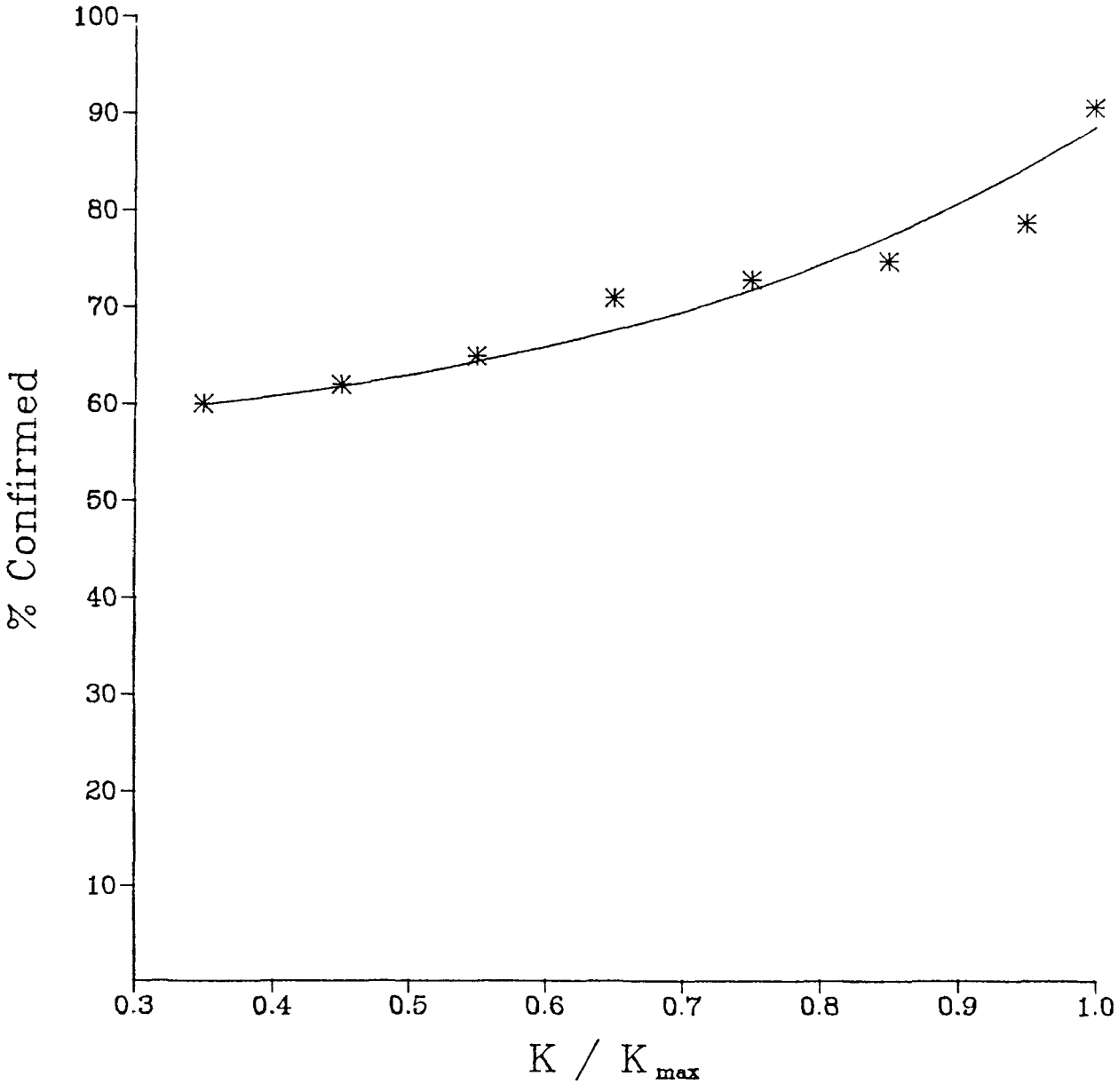


Figure 7. Relation of $\frac{K}{K_{max}}$ to confirmation rate with all compounds included.

FUTURE STUDIES

- BUILD RT LIBRARY WITH CAPILLARY COLUMN DATA
- ADD IR SPECTRA
- ADD SITE SPECIFIC DATA

Figure 8. Planned improvements to the historical library for further selectivity.

HOMOLOGOUS SERIES STANDARDS

C_6 - C_{19} N-ALKANES

C_{19} - C_{40} N-ALKANES

C_6 - C_{10} ALKENES

C_8 - C_{22} ALKENES

C_4 - C_{22} N-ALCOHOLS

C_3 - C_{16} ALDEHYDES

C_4 - C_{14} PRIMARY AMINES

C_4 - C_{18} SECONDARY AND TERTIARY AMINES

BENZENOID HYDROCARBONS

DICARBOXYLIC ACIDS

DIMETHYL ESTERS OF DICARBOXYLIC ACIDS

C_3 - C_{18} FATTY ACIDS

C_3 - C_{12} GLYCOLS

C_3 - C_{10} GLYCOL ETHERS

LOW BOILING ESTERS

C_3 - C_{19} METHYL KETONES

PHENOLS

PHTHALATE ESTERS

Table 1. Compound families used to initialize the historical library.

Table 2. Comparison of Retention Data with K and $\frac{K}{K_{max}}$ for Selected Compounds

Compound [CASRN]	Number of Occurrences	GC Column	Relative Retention Time Std. Dev.	K Median	K Range	$\frac{K}{K_{max}}$ Median	$\frac{K}{K_{max}}$ Range
2-butanone [78-99-3]	67	0.2% Carbowax 1500	± 0.062	36	62-20	0.57	0.86-0.41
1,1,2,2-tetrachloroethane [79-34-5]	93	0.2% Carbowax 1500	± 0.007	65	99-25	0.65	1.00-0.26
α-pinene [80-56-8]	82	0.2% Carbowax 1500	± 0.067	67	89-42	0.74	1.00-0.48
2-chlorophenol [95-57-8]	18	SP-1240 DA	± 0.043	52	78-38	0.56	0.79-0.41
benzoic acid [65-85-0]	298	SP-1240 DA	± 0.035	66	100-22	0.74	1.00-0.38
stearic acid [57-11-4]	66	SP-1240 DA	± 0.053	88	138-44	0.63	0.95-0.30
α-terpineol [98-55-5]	224	3% SP-2250	± 0.041	72	97-38	0.74	1.00-0.38
diethylphthalate [84-66-2]	222	3% SP-2250	± 0.012	75	113-36	0.66	1.00-0.32
cholesterol [57-88-6]	79	3% SP-2250	± 0.055	111	193-41	0.54	1.00-0.19
α-picoline [108-89-4]	21	SE-54 FSCC	± 0.007	59	74-43	0.64	0.80-0.46
nitrobenzene [98-95-3]	20	SE-54 FSCC	± 0.004	73	83-45	0.82	0.89-0.47
fluorenone [486-25-9]	10	SE-54 FSCC	± 0.001	87	95-55	0.92	1.00-0.58

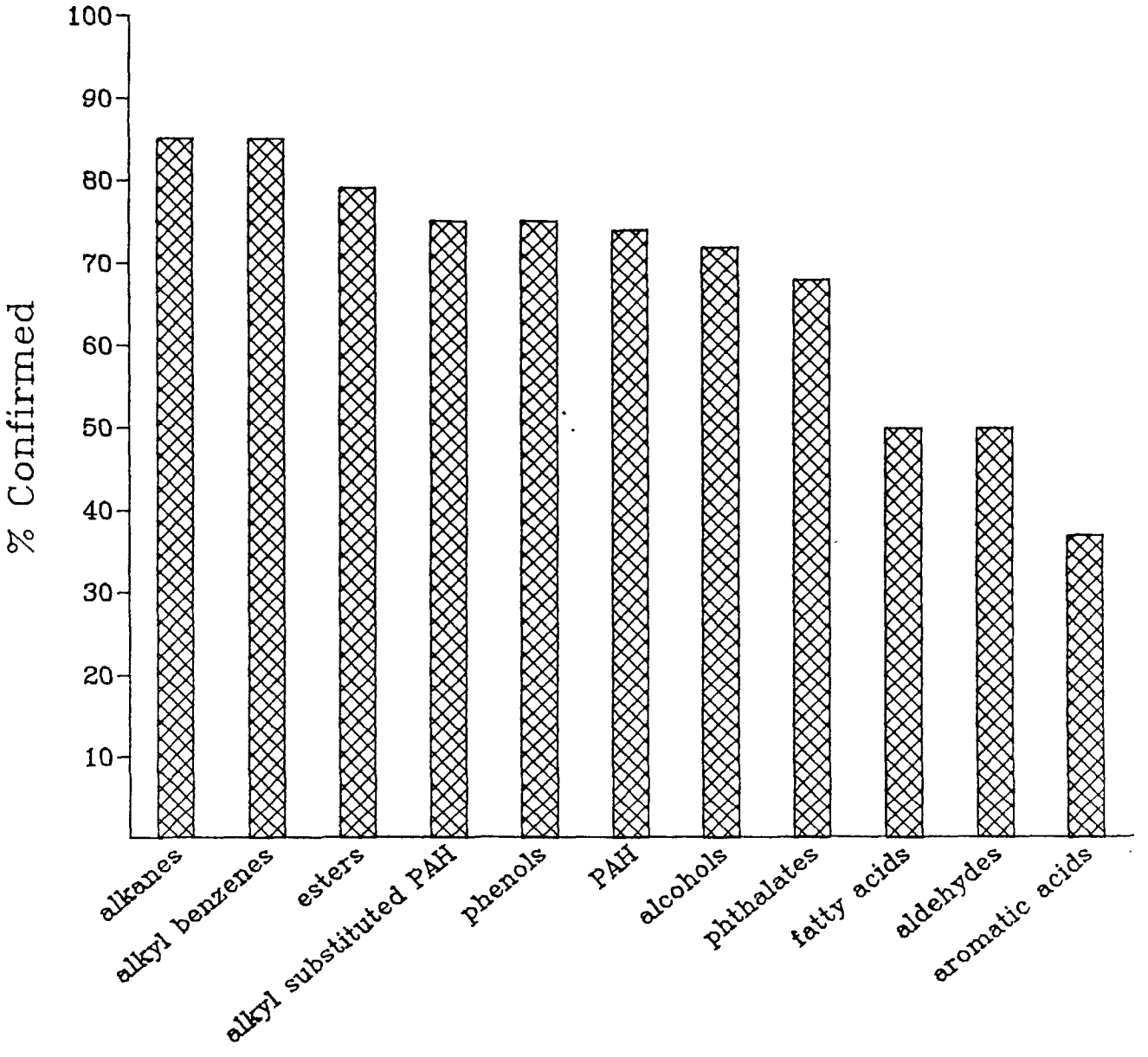


Table 3. Rate of confirmation for selected chemical classes.

QUESTIONS AND ANSWERS

MR. STANKO: George Stanko, Shell Development. Walt, obviously, this work was done with some of the data and some of the extracts that had been sent to Athens as part of the screening phase.

MR. SHACKELFORD: That's correct.

MR. STANKO: Could you tell us what has happened with that program; where are you in that particular program now?

MR. SHACKELFORD: Well, as far as Athens is concerned, we have finished all of the computer matching tests that we are going to do. We have done the confirmation study and we were able to confirm 435 compounds.

These are compounds that were found at a high frequency. We also tried to confirm each compound at least once in every industrial effluent in which it was found. The library of unknowns is presently being evaluated right now. We have

some 55 or 60 candidates presently being studied whose spectrum does not exist in our reference library. For the final end of the data you have to refer to the Effluent Guidelines Division.

MR. TELLIARD: I want to add some toxics to the list, George, only in petroleum.

Thank you, Walter. We are going to try to continue this program with the additional industries of offshore oil and gas and organic chemicals that will be coming up this year. We will continue to use the tape program and the extracts, with the new quality assurance built into the data set, which will make Walter's life easier. Of course, Walter is saying, "who's going to pay me to do this".

Our next speaker is Paul Mills from Mead CompuChem. Mead has spent some time in developing a quality assurance decision tree I guess is the best way to describe it for real time quality

assurance. This was developed primarily for the garbage people, the solid waste people, but I think a lot of these measurements decision can be made applicable to the work we are doing. So we have invited Paul to come today and explain the system.

QUALITY ASSURANCE DECISION MODELS FOR HAZARDOUS WASTE ANALYSIS

Paul Mills, Mead CompuChem

MR. MILLS: Thank you. I have asked Nancy to handle some transparencies for me.

Now, this will be a multi-media show because it deals not only with transparencies and slides, but because it will also deal with soils, sludges, solid and hazard waste as well as water that you are primarily interested in.

Earlier in the program we have heard several speakers talking about quality assurance and what you do, for example, at the instrument, how can an operator make decisions as to the quality of the data that has been produced. I thought for those people who may or may not have some familiarity with quality assurance I would put the obligatory quality assurance and quality assurance definition up there; is that focused

well? (Indicating.)

CompuChem is one of the largest analytical facilities in the country. We have quite a few GC/MS instruments and it poses some unique problems for me as Director, Quality Assurance, some of which we will get into which led me to help develop the model that I will be talking about. Some of the things down here that I would like to point out (indicating). We do hundreds of samples a month, by a variety of methods, both EPA and commercial methods for a variety of customers and industries. We have three shifts, 24-hours a day, we never close. We have significant computer capability so that we can process the data that is generated and turn it around quickly. We have a laboratory at Research Triangle Park, North Carolina, and one in Cary, Illinois, near Chicago. We have 24 GC/MS instruments and trying to keep track of the data from all of those can be time-consuming.

The manner and the size, the scope of CompuChem is set up so that samples come in on what amounts to an assembly line; no one person sees the entire job on the sample from extraction to concentration through clean-up, through GC/MS analysis through data reporting. So we found that it is critical that each person who does a piece of that sample as it is passed along knows how well that that job has been done because they get immediate feedback as to "Did I do my job correctly, or did I screw it up, does it have to be done again?" The person next in line that gets that sample to be able to do his part of the job with it, like an auto assembly plant, needs to know that that job was done correctly so that his piece will have value when it is added as the product goes down the line.

So we must make sure that the quality of the product that went out the door to the

customer meets the standards that are demanded, whether it is by contract or purchase agreement. Also, to facilitate intralaboratory transfers between departments and between people of products of known quality, we started by implementing a system so that each person, each product, each lab area was defined as to the type of quality that was required.

May I have the next transparency, please, Nancy. This you should have seen before, the elements of quality assurance that are listed in the EPA quality assurance guidelines. We started to look at how are we organized and who are responsible for what aspects of quality in the laboratory, what are the quality assurance objectives for the data in terms of these parameters.

In EPA contracts these are very well spelled out in some regards with the number of definitive criteria that are supposed to be applied:

Surrogate recoveries, internal standard areas, how well your spikes and duplicates are supposed to be recovered and duplicated, things like that. However, there are sections in the contracts which read such as, '...If these criteria are not met it is left up to the judgment of the anlyst in order to take corrective actions'; it's not spelled out clearly what those should be or how those should be implemented.

There are also procedures spelled out for how sample custody should be handled, how do you calibrate, how do you tell if your instruments are properly calibrated, the methods that are to be used. Some of the methods in the hazardous waste program that we found have been developed in advance of validation data because of the urgencies for some of the data to be produced. We find, not surprisingly, that the methods don't work for all kinds of samples very well.

Some they will work for very well, but some they won't. Then, how do you produce and validate your data, what checks are performed within the laboratory on how well that data has been produced, and the procedures that are used; in particular, corrective actions and reports to the management on the corrective actions.

May I have the next slide, please. I went up to the mountain one day and came down with a stone tablet with the Four Laws of Quality Assurance engraved on it, which are not my invention but they seem to make some kind of a sense and at least the people that I work with understand them. The first law, the most important one is, 'Do it right the first time'. If you are going to take the time to process a sample and report it out, do it right the first time so there are no mistakes. Secondly, 'Detect errors as soon as possible'. If you know that there was a mistake made in the

laboratory try and get that mistake rectified or start the reprocessing of the sample; don't wait until it is ready to be reported out the door to say there was a problem. You have lost time and you have wasted a lot of energy. Again, this gets back to one of the things Phil Ryan said earlier, you want to correct the error as close as possible to its source. If an instrument operator can detect that there is a problem with the surrogate recovery, that's the time that something could be done about it. It is also cheapest and quickest to do it that way; and, from a quality assurance standpoint I demand that all of the actions that have been taken for problem data be documented. I want to know what the corrective actions were, who did them, what was their rationale, what was the result.

On the next transparency, we started to build an example criteria for building a decision

model. How do you apply those four laws of quality assurance so that you would apply some sort of a logical or hierarchical framework for making decisions based on problems that you might see?

So we looked at, first, what data can be examined by the analyst or someone who detects the error. For example, you could look at it as a GC/MS operator: Was the tune correct? Was the blank run okay? Was the standard within the criteria for calibration? Did all of the pieces of information that were passed to him concerning the preparation of that sample match what it was supposed to be for that procedure? Were there other samples in that data set, say if they came from a particular case, that have similar problems that could account for the problems that are being seen? Essentially, what was the quality criteria for the product and were they met?

If some of these things are not correct then in what order should you examine the possible causes? You could look and say certain things like the tune, the blank, the standard must have been acceptable or the analyst would not have run the sample. You can check internal standard areas, you can check the worksheets, you can check response factors, things like that, and check to see whether there was anything special about those samples. Was there any additional data that may be necessary to determine the source of the error? For example, the data from other sets of samples.

In our set up, a particular operator may not have analyzed all of these samples from a particular case. They may have been prepared at different times, they may have been done by a different instrument, a different operator, a different shift; but, the laboratory manager in charge of that area can go back and

determine they get similar samples from the same set of samples to have the same problems. Are there additional people outside of that laboratory that it may be necessary to determine the source of the error, like the lab manager or the QC Department? And what are the options for taking corrective action? What are the ones that are most prompt, likely to lead to the solution and elimination of the errors and saving costs, especially saving time in identifying and correcting the problems?

It may be possible that a calculation error was made in the information that was provided to the analyst. If that is detected a calculation correction can be made; that is quick, that is simple, that does not effect the quality of the data except to correct the mistake. You may be able to reinject the sample, in the worst case you may have to go back and reanalyze an entire lot of samples. Then, how are the corrective

actions documented? They are supposed to be documented on the worksheet associated with the sample in the laboratory files by a personal memo to me, to the files, and in the report to the customer.

The next slide, please. These are some of the advantages and disadvantages of the implementation of this system, at least as it applies within CompuChem. It has shown an improvement in the turn around time because it will detect and correct problems earlier and, I'm sure, avoid repetition. It has improved the laboratory working relationships. If you have established with each part of the laboratory that you expect a certain quality of product from them, all of the little pieces of paper completely filled out, and you don't get it, then you turn it back to them or don't accept it, they tend to get the message very

quickly when things pile up on them, that it's got to be right or it won't be passed along.

To reduce rework and the associated cost with the rework because people are starting to do things right more often, it has improved our good will and our prestige to the customers because you have decreased the turn-around time and it improved the quality of the product to the customer. It tends to free higher level staff for planning instead of problem-solving if things can get solved at lower levels. You can document the accountability for quality, something I am particularly interested in. I am always trying to establish that quality control and quality assurance are really profit centers, they are not cost centers or overhead; they contribute to the value of the products. If you can document what corrective actions were made and taken

and that you can reduce costs, you can show that the quality departments are paying their way.

The detailed logic that goes into the corrective actions for each area can be put into the computer so that eventually there will be no human intervention. Data can go directly from the GC/MS instrument to a main-frame computer that has the logic of the corrective actions and decisions built into it so that those data can be rejected or accepted right there. You save a lot of manual intervention. We have this currently in force for our biomedical area which deals with much less complex samples than the environmental ones. We are a few months away from implementing it entirely for the environmental, but the concepts in what we have learned in biomedical will apply in environmental samples. Having the defined criteria we found makes training of new staff quicker and more effective. They know what is expected of them

and they know what they have to do.

The system for documentation as required by the customer for this product is on the computer that allows ready access by managers, so if there is a question: "How good does this piece of information have to be?," it is spelled out and it is readily accessible. It's nice to be able to know how much things cost so that you can bid on some of the new work, for example. It is an excellent management tool for measuring performance.

Some of the disadvantages are there are some costs associated with implementation because you have to make changes in how the laboratory does some things. In the past, it has been the policy of CompuChem to use code numbers so that the analysts working in the laboratory do not know which samples are duplicates, blanks, or spiked samples. This is so that we can

identify how well the laboratory does on all kinds of samples. In order to make sure certain kinds of information are detected at the earliest possible level, the analysts need to know the identities of those samples. If someone thinks that that may distort the performance, that if they know it is a QC sample they are going to do even better than normal on regular samples, there are still periodic blind samples submitted that are doctored by our quality control and quality assurance department which come in as true "blinds" and will test how well people are doing. Those are submitted for each of the analysts and operators every month. As you will see later in the presentation that data is available for their managers to review, comment on, and correct if performance is under par.

May I have the next slide, please. This is just a brief summary of the decision model

steps as applied to, for example, if you are looking for contamination in a blank associated with a set of soil samples that has been prepared. You have to define the product; usually that's defined by the customer or in the contract. What are the attributes that you want to be determined? How much contamination do you want or how little? How is the report to be delivered? How do you make that product? Is it on the GC/MS or do you want it on the GC? It is usually defined by the contract for that product. What quality of performance is desired? For example, if something has failed the criteria. How do you measure the product quality? How often do you measure it? Who is responsible for measuring it? Then, this is where the managers and the actual technical staff have to get heavily involved, listing in detail all of the possible

reasons why you might not be able to meet that criteria; such as, contamination in various parts of the laboratory. Then, how would you test and document those...or eliminate those sources of problems in a logical manner. Describe the documentation, corrective actions, train the staff, report it, and then notify the customer if it is necessary.

Some of the changes that we have come up with, now, for example in the processing of blanks for the volatiles we have changed hoods, we have changed types of inpingers, we have changed the location of sample preparation based on the results of some studies indicating there is some volatile contamination in certain parts of the laboratory. We have changed certain times when we do things to limit the contamination and have seen an overall improvement,

for example, in the quality of the volatile blanks.

Next slide, please. This is a listing of the desired product quality; for example, from the previous slide, our example of the volatile soil blank. Most of this is taken straight from the contracts that come from the Hazardous Waste Program office, but it is translated into saying "This for our laboratory is what has to be produced." You have to say the RIC of the sample doesn't end on an eluting peak, for example. You have to have certain kinds of information, document control number, you have to label certain peaks, identify who did it, when, how, what standards they used; all of these kinds of things go into making up the attributes of an acceptable product. If there is any qualifying data it is important to put footnotes in there so people understand it.

Next slide, please. This is the example for the volatile blank of what happens. There are three different blanks made up to be able to determine for a particular set of 20 samples where a contaminant might occur. If you check the first blank and it is clean then you move to check the second blank. If that is clean you check the third blank. If any of the blanks have a contamination problem in them you can then narrow down where the source of the contamination might be coming from, go back and correct it; or, you prepare the sample and do it until you have gotten a clean blank and clean samples associated with it. This is the kind of logic that is being applied for other types of samples in spikes, the duplicates, as long as the blanks are in addition across the laboratory.

Now, I would like to switch, if possible,

back to the 35 millimeter slides and then at the end of that I'll have about three more transparencies.

Could someone turn on that slide projector, please. In case you haven't seen a GC/MS laboratory with a lot of instruments in it that's what it looks like (indicating). This is, for the example that I was using, the volatile bottles are on the top and packed in nice little Styrofoam containers so that they don't break. There are four there, they are contained in four volatile bottles. That's CompuChem's...our EPA samples don't come in nice containers like this. If they did we wouldn't have as much breakage problems as we see with them; in these we don't lose samples for our commercial customers, they come in like this (indicating).

As part of the laboratory quality control some of these things...well, all of these

things have to be met. These are pieces of information that are reported to the customer; for this instance, in the Hazardous Waste Program of EPA. I certainly echo, I nearly stood up and applauded when I heard that the Effluent Guidelines is trying to reduce the amount of paper that is produced, they can get more on tape because for several years we have been trying to get the Hazardous Waste Program to do that. All of our customers are the regions so they are demanding additional paperwork. Some of the tests that are done in order to insure that there is no contamination in the glassware, for example, for every set of samples, say, for sample containers that are prepared, a portion of them are prepared for tests to determine if they look clean before they are used. We have storage stability tests in order to monitor the atmosphere in which...you walk in a

refrigerator in which the volatiles that are prepared are stored to make sure that there is no contamination occurring from the storage of the samples.

This is the purged water that is used for the preparation of the samples so that we can demonstrate that we are not contaminating the samples with the water. The purge and trap, GC/MS, is where they get analyzed. Some of the reports that we put out to the managers to document how well the decision models are being followed, how well the people that they have for their work are performing. We have computer-generated reports which will show surrogate recoveries by matrix, by level, by individual extraction person, by GC/MS instrument, by operater, by shifts; all of the different ways so that the manager can actually determine if somebody is out of line and

what needs to be done about that. You have this kind of information that is also useful to determine how well the laboratory is performing and all of that. Quarterly we will take a look at our recoveries and determine whether or not they need to be tightened based on what we are seeing on the results.

The thrust of what we are trying to do is to establish if we find a problem is it a problem with the laboratory in technique? Is it a problem with the method and its applicability for those samples so that we can document for our customer it's our fault, we screwed up, don't pay us for our mistakes? Or, if it is not our fault we can present that to the customer and say it is a problem that either the method or the matrix causes the data not to be acceptable to meet the criteria as has been specified.

This is the main frame of the computer or it is back behind there that we use for processing some of the reports (indicating). I'll turn up the lights again. There are just a few more transparencies that I wanted to show which will show the form of some of the reports that we get.

This is an example of a pie chart that essentially tells the managers, the people that I work with how many repeat requests for sample repreparation or, for an example, reinjection that were done during February. The pie chart is divided into different sections depending on the type of fraction which is analyzed. The volatiles over here, acid, base neutrals, semi-volatiles is part of the chart and that seemed to be where a large number of the problems were.

If you are interested to know how big a problem this represents, this is less than

four percent of the total number of samples that we processed for the month that represented things that had to be reprepared.

The next one, please. An example of some of the information, say, for surrogate recoveries for volatile samples. A target range is based or set up based on the criteria that are in the EPA contracts that we have saying, assuming a normal distribution of the surrogate recoveries you would want to see the same distribution up here (indicating). This is the actual distribution that we are seeing, to be able to see for the kinds of samples that we are getting in, if we are within the control limits for those types of samples and on that particular indicator.

The last one, please. Here is an example of tracking internal standard response verifications. Here is an instance in which suddenly something went way out of control

down here, the instrument stopped, maintenance was performed on the instrument and brought back up (indicating); and, it's within the criteria. That kind of information is available promptly at the instrument, although the graph was not made until later. The operator at the instrument has to make decisions if he sees that happen; that's it.

Thank you. I would like to thank Nancy. I'm sorry you only got to see the back of her head while she was doing that; the rest of her is nice, too. That's the end of my presentation. I would be glad to answer any questions that you may have.

MR. TELLIARD: Thank you, Paul.

A couple of announcements.

* * * * * *

QUALITY ASSURANCE DECISION MODEL FOR HAZARDOUS WASTE ANALYSIS

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ABSTRACT:

Adopting a customer and service-orientation within a laboratory Quality Assurance program provides better-defined product quality within laboratory areas, and ultimately for the laboratory's customers. This presentation describes a quality assurance decision model which is being installed at Mead CompuChem. The model defines the various products of the laboratory as "analytical results" which are conveyed via paper or magnetic tape to each part of the laboratory or to customers. Each product must meet a pre-defined set of criteria; for EPA hazardous waste analyses, these are based on contract-specified deliverable documentation. Each laboratory area is responsible for the quality of its products. The Quality Control and Quality Assurance Departments monitor product quality, and check that documentation of corrective actions is complete and consistent with the model. The second generation of the model will extend the concept to allow "quality-costing" to be applied to finished and reworked products. The advantages of this decision model are: 1) It is accessible to each manager through a common file; 2) Corrective actions are made consistently the same for similar problems; 3) Logic applied can be used for automating review systems, and ultimately "networking" to eliminate the need for manual interventions; 4) Cost of producing products of defined quality can be determined and used in assessing laboratory performance.

INTRODUCTION:

This paper provides a description of a management concept for improved product quality from an analytical chemistry laboratory. I have provided a summary of its development, and a description of the advantages of the system. Some examples are provided of the logic applied, and the system performance data on portions installed and currently operating.

Because of the size of Mead CompuChem (24 GC/MS instruments at 2 locations) and the scope of the company's business, the concept of manufacturing centers has been used in planning and production. Productivity is essential to warrant capital investment. Specialization is applied to tasks such as sample receipt, extractions, analysis, and data reporting. No one person does the "whole job" on a sample. Therefore, it is critical that information accompany the sample in process down the "assembly line". Each lab area must check its products' quality prior to transferring samples to another lab area.

The original concept for this paper developed from attempts to quantitate the contribution of QA and QC to profits. Several references are included which provided assistance in this effort.

The productivity of a quality system can be measured by its contribution to business profits. It is desirable to develop a quality system to achieve and maintain product quality and decrease variability. To accomplish this, it is necessary to define the product, its quality, and the quality of the performance necessary to make the product. The procedures or methods used in production place constraints on the quality by specifying: Limits of detection, sensitivity, safety, cost measurability, precision, accuracy, selectivity, and specificity. It is important to identify areas of responsibility to be effectively managed to obtain control of product quality. It is also important to measure the performance of procedures and analysts for the samples being analyzed.

The objective of CompuChem's system is to improve product quality for the laboratory's customers. I have suggested the definition that the lab's products are "analytical results". These products consist of information packaged in customer-requested formats such as EPA deliverable paper, GC/MS magnetic tapes, etc. A sub-objective is to improve the quality of information exchanged within the laboratory used to produce the customer-reportable data; i.e., each area of the laboratory is a customer for intra-lab data; QA uses it to determine how well those areas are performing.

To attain the objective, at least the following goals must be met; they are stated in the form of Quality Assurance Laws for impact and for easy remembering. The First Law of Quality Assurance is "Do it right the first time!" The Second Law is "Detect errors as soon as possible!" The Third Law is "Correct the error as close as possible to its source!" The Fourth Law is "Document all actions taken!"

The objectives and goals can be met if the following concepts are adopted for the laboratory: 1) Each product of the laboratory must be a defined quality. 2) Criteria are established by Marketing and the customer for the products to be delivered; criteria are established by QA for those products remaining inhouse. Specifications for finished products must define the desired attributes and subcomponents. They must specify the inspection methods and frequencies and who is responsible for inspections. Specifications must be expressed as "targets" and "ranges". 3) Each lab area is responsible for the quality of its products, or the product is returned for rework or explanation. Specifications for the disposition of rejects (rework or scrap) must be made. No one should have to look at bad data from another part of the lab! Each lab area should be viewed as a "customer" for the products of the other lab areas. Each lab area has the right as a customer to demand that the quality levels be met and maintained. 4) Make QC samples, such as blanks, spikes, and duplicates, known to the analysts, in the laboratory, to allow for prompt detection of problems. 5) Before changes in product specifications or procedures are made, the approval of the Director, Quality Assurance, is necessary. 6) Training and documentation are critical steps to ensure quality. Figure 1 shows an example which summarizes the steps in establishing the decision model.

While these system concepts were being developed for application at Mead CompuChem, several EPA customers began requesting that the current set of hazardous waste analytical contracts be modified to define more specifically the data quality desired and corrective actions to be taken if acceptance criteria were not met. EPA contract requirements would seem to imply that, by using the required procedures for analyzing hazardous waste samples, it is possible to produce data of acceptable quality on most samples, as determined by specified

quality indicators. Unfortunately, insufficient data is available to prove this is true for all samples to which the methods are being applied. For the contracts, the nature of corrective actions has been left to the "judgment of the analyst" without specifying that the same problems (i.e., exceeding acceptance criteria) should be treated in a standardized fashion for all who experience the same problems. However, there may in fact be samples for which the methods and therefore the quality criteria do not apply. The lab must therefore demonstrate that the analytical procedure and the techniques of analysts are in control, or that the problems are inherent in the method or the nature of the sample. This can be established, for example, by using duplicates, spikes, blanks, and other test samples to evaluate lab performance.

Using the EPA contract-specified deliverables list, I have produced a document which defines the desired quality of the products (pieces of paper) which make up the EPA data package. The criteria applied are either specified in the EPA contract, or have been established by CompuChem in their absence in the contract. It is the responsibility of the manager of each lab area that his products meet the quality criteria. An example is provided in Figure 2 of the criteria used in building the model. Each manager is responsible for rework until the product is acceptable. The system for detection and correction of such problems are established within a lab area by its manager, who presumably knows its capabilities and resources best. Each manager goes through the logic required to produced acceptable quality products. Quality of product should be considered as well as the constraints of productivity and resources. Where there are conflicts, top management must resolve them. This will give some options to management in producing certain products. For example, if the product is a "screening analysis" to determine approximate amounts of organics in a sample, it may be that the screening data can be acceptably produced either by GC or GC/MS. The system must define how many and what types of errors are to be monitored and corrected, the frequency of testing, and what kinds of corrective actions are appropriate. In addition, quality measures of performance are required. An example of the product quality, procedure for production, and flow chart of the decision model is shown in Figures 3, 4, and 5.

It is the responsibility of each lab manager to monitor for errors within his area, to implement corrective actions, and to report the problem, its extent, and the effectiveness of remedies, to QC and QA. If quality control samples are outside control limits, the manager is informed by the QC Department, so that the manager can correct the problems. QC and QA can assist and advise on the appropriate actions. QC monitors the effectiveness of these actions, and reports this to QA. Documentation of problems and actions must be made, either by footnotes or written explanations within the body of the report. This documentation should provide adequate detail to state the problem, actions taken, and their effectiveness, what data was affected, what dates these things occurred, and the names of parties responsible, should there be questions. In Figure 6 I have listed advantages and disadvantages of conversion to this system.

The system described has demonstrated improved product quality and lowered costs for those areas in which it has been installed. The system is being expanded into other lab areas, and its operation continues to be refined with experience. Figures 7, 8, and 9 show the type of management information generated.

Appraisal of the effectiveness of the system will eventually be handled by acceptance sampling at CompuChem during review processes. Currently, several levels evaluate all the data prior to release to other lab areas and to customers. Acceptance sampling will be instituted as observed error rates fall.

I would like to acknowledge my colleagues who contributed their time effort and study results to developing parts of the system: Mrs. Patty Ragsdale; Mr. Robert Meierer; Mr. Robert Whitehead.

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Managing Quality for Higher Profits, Robert A. Broh, McGraw-hill, 1982.

Quality Control in Analytical Chemistry, G. Kateman & F. W. Pijpers, Wiley-Interscience, 1981.

FIGURE 1:

SUMMARY OF QA DECISION MODEL STEPS EXAMPLE OF VOA BLANK, SOIL SAMPLE

1) Define product (VOA blank)
2) Describe attributes to be determined (extent of contamination, form and content of report to be delivered)
3) Define how product is to be made (GC/MS output, contract method)
4) Define quality of performance desired (no blanks fail criteria)
5) Define product quality criteria (specified in contract, priority pollutants less than half detection limits)
6) Determine measurements of product quality, frequency of measurement, and responsibilities (each set of samples prepared, analyzed by GC/MS operator, within acceptance criteria)
7) List in detail all possible problems which could cause unacceptable product quality (contaminated standards, glassware, water, etc.)
8) For all problems, list tests to determine source of problem in a logical, heirarchical order (operator, manager check, reanalysis).
9) Describe documentation of corrective actions to be reported (reanalysis)
10) Implement system with training for staff responsible
11) Monitor and report on system effectiveness
12) Modify as necessary, and document changes (eg., change type of impinger, change location of sample preparation).

FIGURE 2:

EXAMPLE CRITERIA APPLIED TO BUILD A DECISION MODEL

What data can be examined by analyst who detects error? (For example, instrument performance Tune, blank, standard data, worksheet, vials are all available for inspection at the bench, as well as results of previous, related, samples, and the quality criteria for the product)

In what order should it be examined? (Tune, blank, and standard must have been acceptable, or no samples could be run; check internal standard areas, check internal standard areas; check worksheets for amount of sample used, volume of concentrates, surrogate and spike standards used, any nonroutine actions taken or problems encountered in prep.)

What additional data may be necessary to determine the source of error? (Other data from same set of samples)

What additional people may be necessary to determine the source of error? (Lab manager, QC, etc.)

What options for corrective actions are most prompt, likely to lead to elimination of errors, save costs? (From least to most costly, identify and correct calculation errors; reinject sample; reprepare and reanalyze samples.)

How are corrective actions documented? (In report, in lab files, by memo, etc.)

FIGURE 3

DESIRED PRODUCT QUALITY: VOA SOIL BLANK

Desired Product:

The RIC must be normalized to the largest, non-solvent peak.

The RIC must cover the range of Hazardous Substances List compounds.

Internal and surrogate standards must be labelled on the RIC.

There should be no tailing or elevated baselines (the latter portion of the baseline should not rise by more than 4X the midrange level).

The RIC must not end on an eluting peak; peaks must not be cut off by the end of a page.

Contaminants must be less than 1/2 the detection limits for HSL compounds, and less than 25% the peak height of the nearest internal standard for others. Contaminants must be accounted for.

There must be a document control number of the RIC, representing the EPA case and sample numbers.

The RIC scan starts before the firt eluting HSL compound, and ends no sooner than the latest eluting HSL compound.

File header information is included to identify the ID number, standards used, operator, shift, instrument, and time.

Tabulated results (identification, quantity, scan number of retention time) of the specified HSL compounds must be submitted, validated and signed in original signature by the Laboratory Manager.

On the EPA reporting form, the appropriate units and detection limit factors must be circled and/or adjusted.

Appropiate footnotes for qualifying data must be included.

FIGURE 4

VOA SOLID SAMPLE PREPARATION

Three different laboratory areas are involved in preparation and analysis of VOA solid samples: Glassware preparation; Inorganics lab hood for sample preparation; GC/MS lab for addition of water, sample storage, and analysis.

Glass impingers are taken from the oven in Glassware preparation area and transported to the Inorganics lab hood. Samples are transported to the lab area for preparation, but kept outside the hood until each one's turn for preparation. Only one impinger and one sample at a time are in the hood during preparation.

Water from the GC/MS lab (purged organic-free water) is taken into the hood for filling the designated "A" and "B" blanks. A "C" blank is filled in the GC/MS lab and makes the trip with the other samples, but is not opened in the hood; it is similar to a trip blank.

The "A" blank is prepared first, by filling the impinger with the GC/MS water. (This tests the hood area, to demonstrate it is clean before preparing other samples).

20 samples are prepared, one at a time. Weighed quantities of samples are transferred from jars into impingers with appropriate utensils, then capped.

After the 20th samples is prepared, the "B" blank is made, similarly to the "A" blank. (This tests that there has been no contamination introduced into the hood during sample preparation).

Prepared samples are taken into the GC/MS lab, filled with aliquots of GC/MS water, and stored in the GC/MS lab refrigerator for VOA's only. It is equipped with a charcoal scrubber.

The order of analysis for these samples and blanks is described on the following flow chart.

LOGIC: The instrument blank shows that the internal surrogate standards were not contaminated, and that the GC/MS lab air and water are clean, and that the instrument is not contaminated.

The "A" blank will show is the hood area was contaminated prior to sample preparation.

The "B" blank will show if there has been "cross-contamination during transit or staorage due to faulty impinger seals, lab air, etc.

The latter three blanks will also show if there is contamination of syringes or glassware.

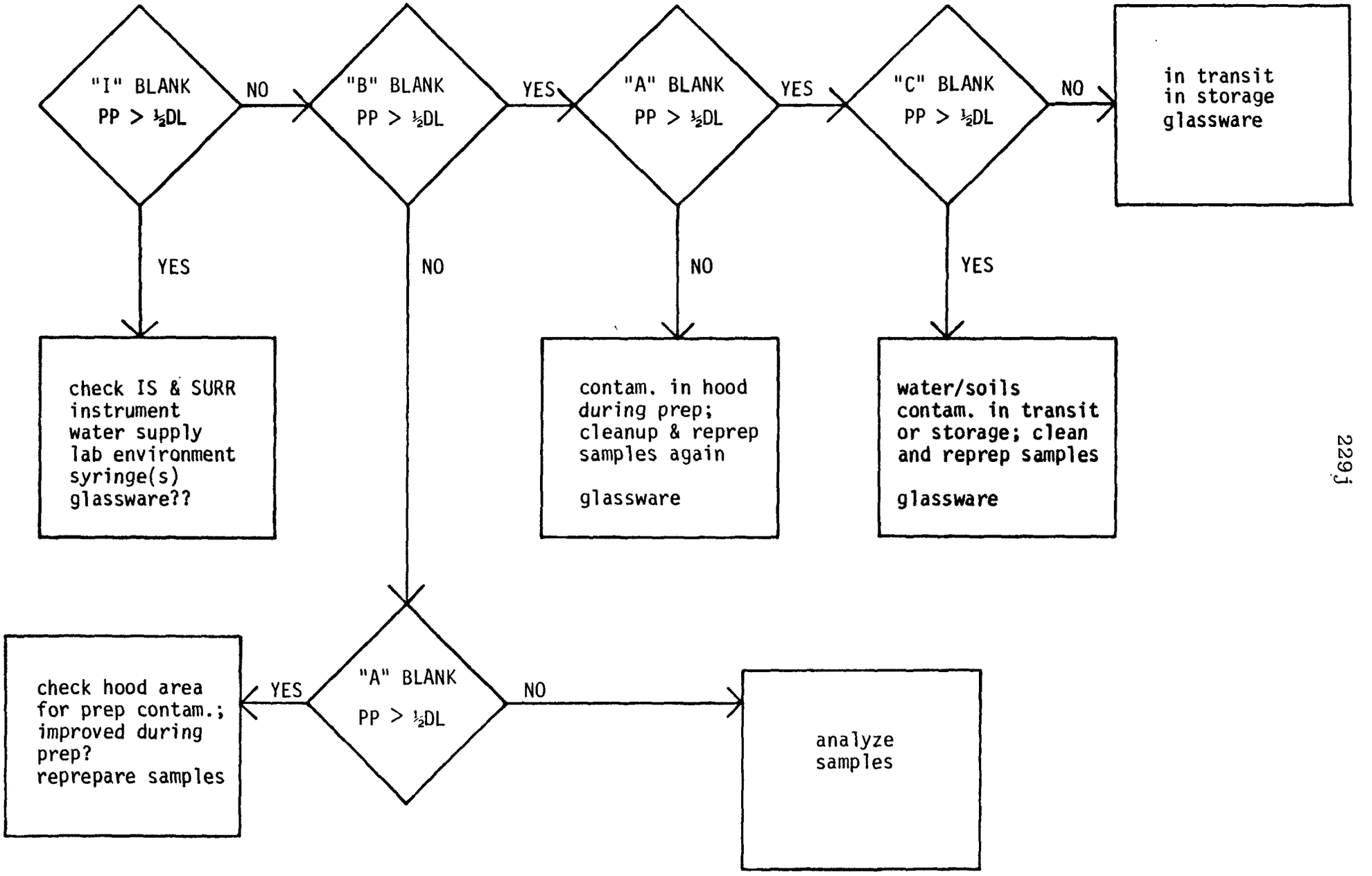

"I" BLANK
PP > ½DL
NO
"B" BLANK
PP > ½DL
YES
"A" BLANK
PP > ½DL
YES
"C" BLANK
PP > ½DL
NO
in transit
in storage
glassware
YES
NO
NO
YES
check IS & SURR
instrument
water supply
lab environment
syringe(s)
glassware??
contam. in hood
during prep;
cleanup & reprep
samples again
glassware
water/soils
contam. in transit
or storage; clean
and reprep samples
glassware
check hood area
for prep contam.;
improved during
prep?
reprepare samples
YES
"A" BLANK
PP > ½DL
NO
analyze
samples

FIGURE 5

FIGURE 6

ADVANTAGES AND DISADVANTAGES

ADVANTAGES:

- Improvements in turnaround time
- Improved intralab working relationships
- Reduced rework and associated costs
- Improved goodwill and prestige with customers
- Correction of problems at earliest stages
- Higher-level staff are freed for planning, not problem-solving
- Accountability for quality can be well-established
- Detailed logic of corrective actions can be automated, "networked"
- Defined criteria makes training quicker, more effective
- Automated system allows prompt access, consistent responses
- Costs of errors can be documented
- Costs of corrective actions can be documented
- Costs data assist in bidding new work, measuring performance, etc.

DISADVANTAGES:

- Minor costs of implementation: Changes in paperwork, work flow, training
- Allowing analysts to know identities of QC samples may distort true performance; can be corrected by submitting true "blinds"

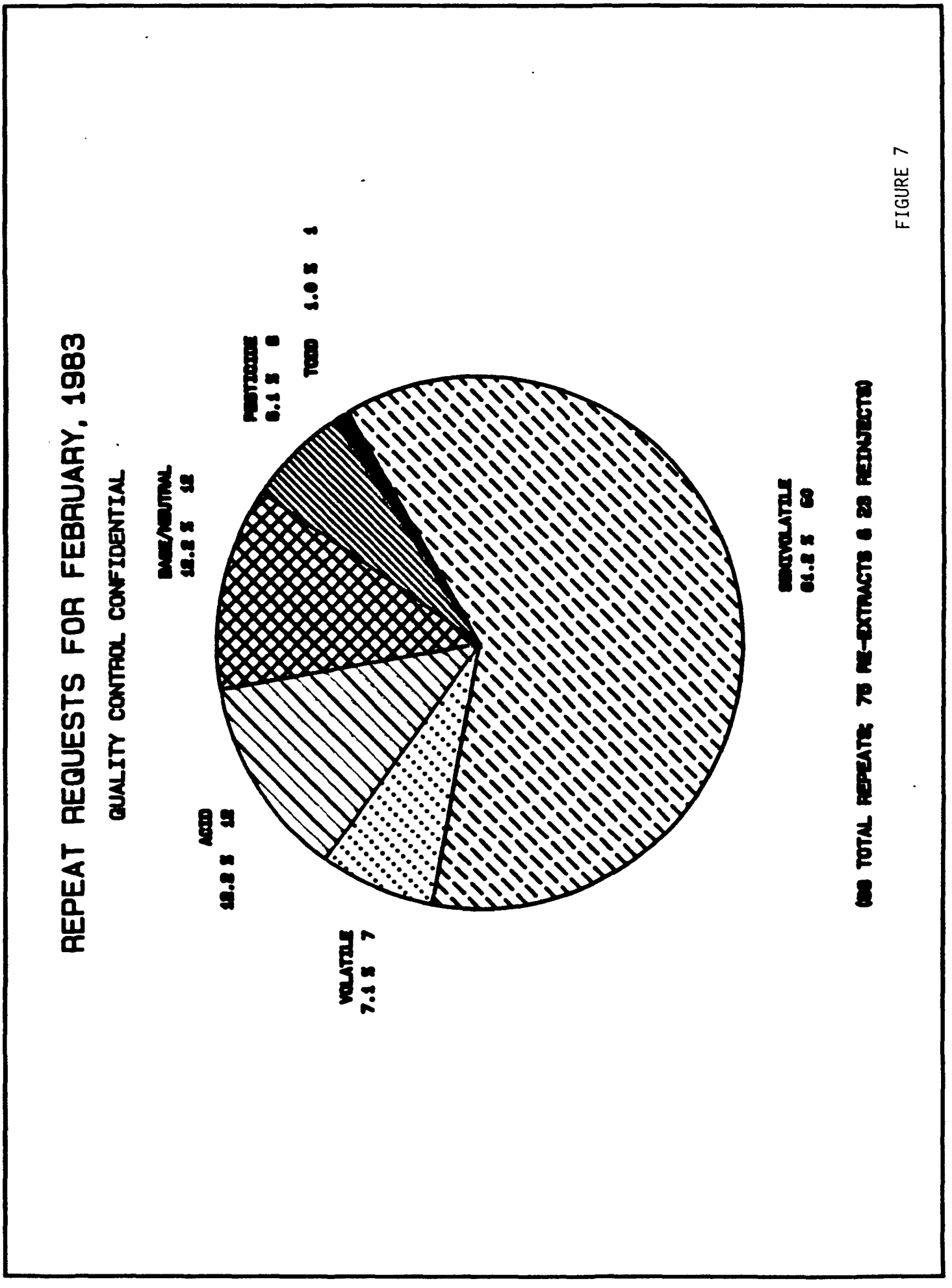

REPEAT REQUESTS FOR FEBRUARY, 1983
QUALITY CONTROL CONFIDENTIAL
BASE/NEUTRAL
ACID
VOLATILE
TOTAL
NONVOLATILE
TOTAL REPEATS: 70 PRE-EXTRACTS 0 23 REINJECTION

FIGURE 7

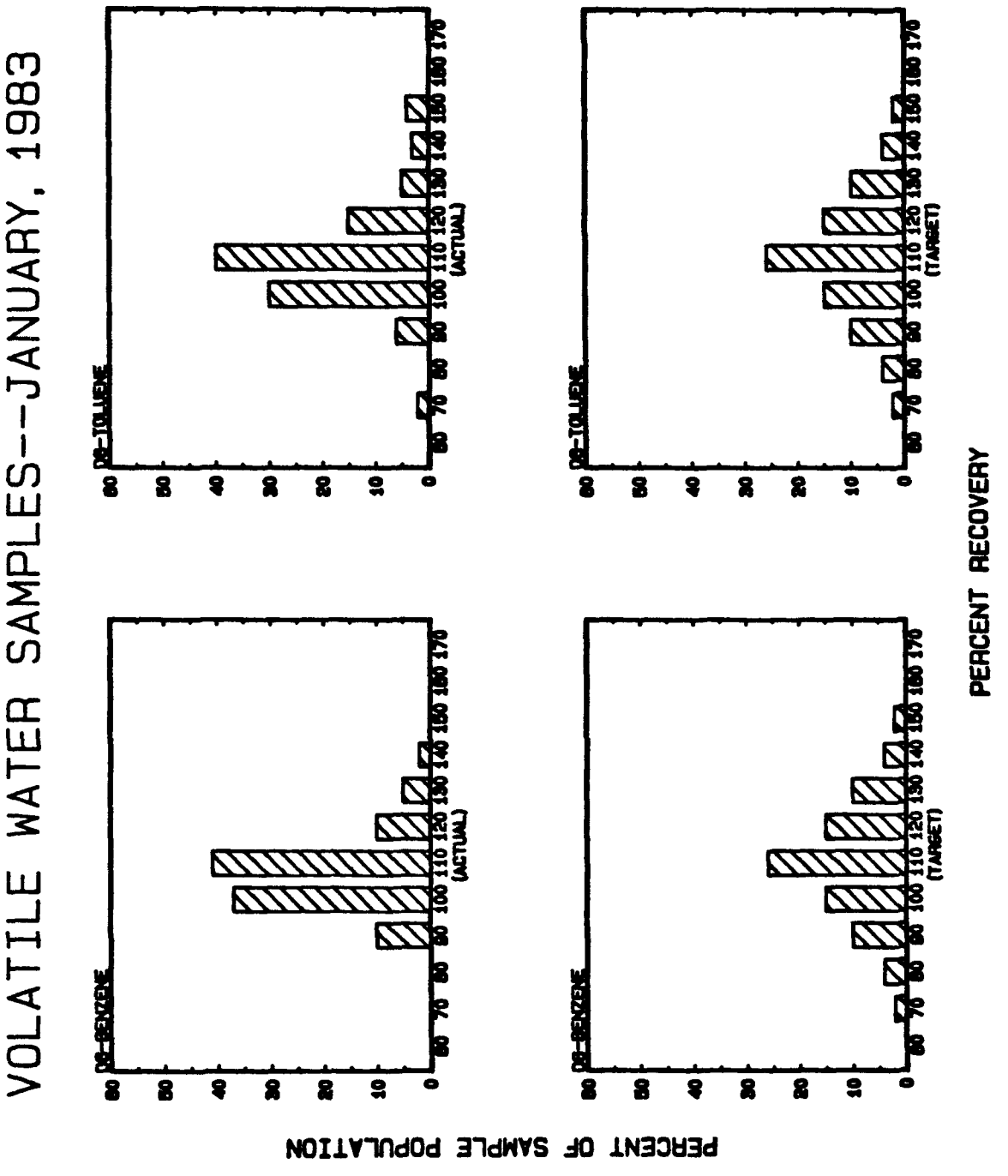
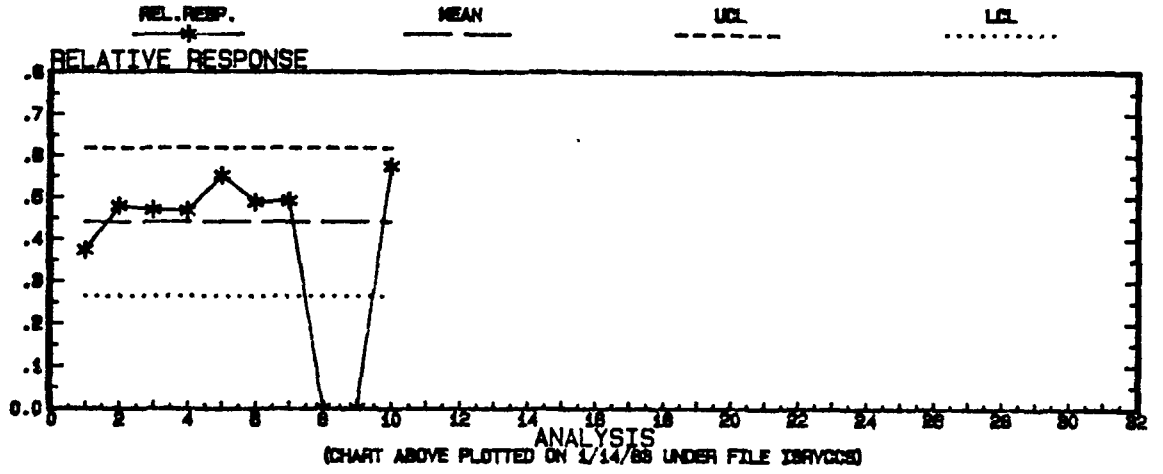

VOLATILE WATER SAMPLES--JANUARY, 1983
DB-TOLUENE
DB-BENZENE
(ACTUAL)
(TARGET)
PERCENT OF SAMPLE POPULATION
PERCENT RECOVERY

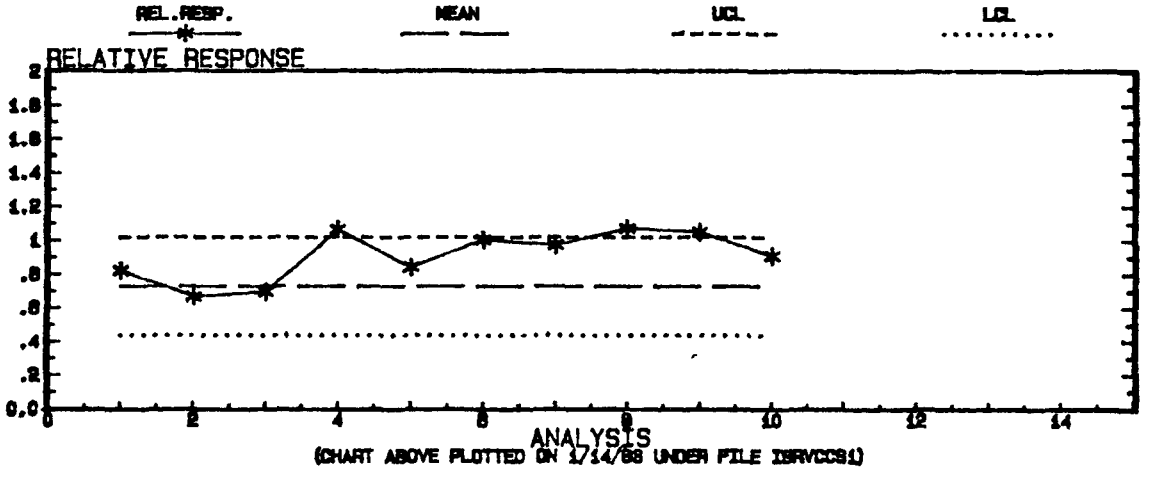
FIGURE 8

INT.STD.RESP.VERIFICATION CONTROL CHART

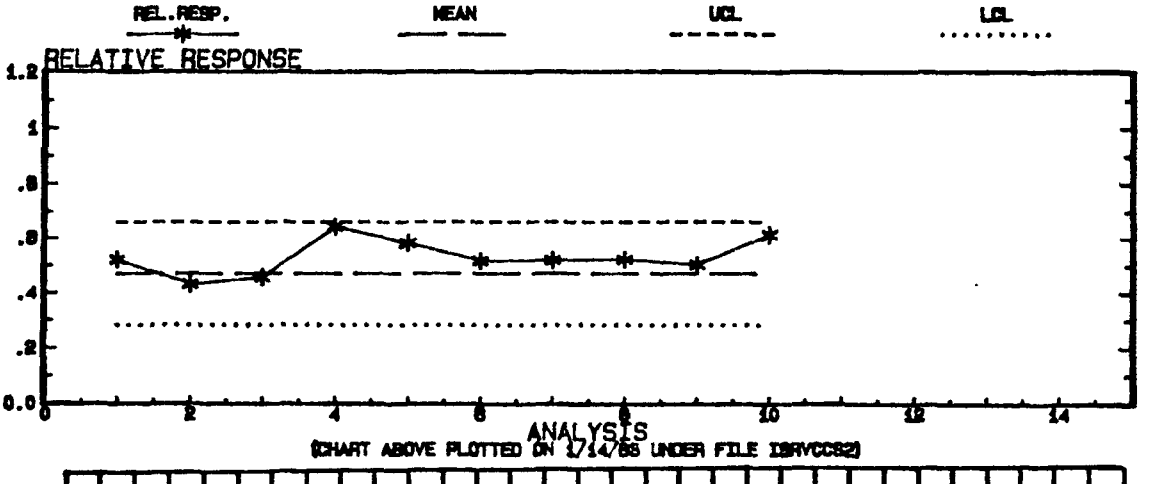
SEMIVOLATILE: D3-PHENOL/D8-NAPHTHALENE



SEMIVOLATILE: D8-NAPHTHALENE/D10-PHENANTHRENE



SEMIVOLATILE: D10-PHENANTHRENE/D12-CHRYSENE



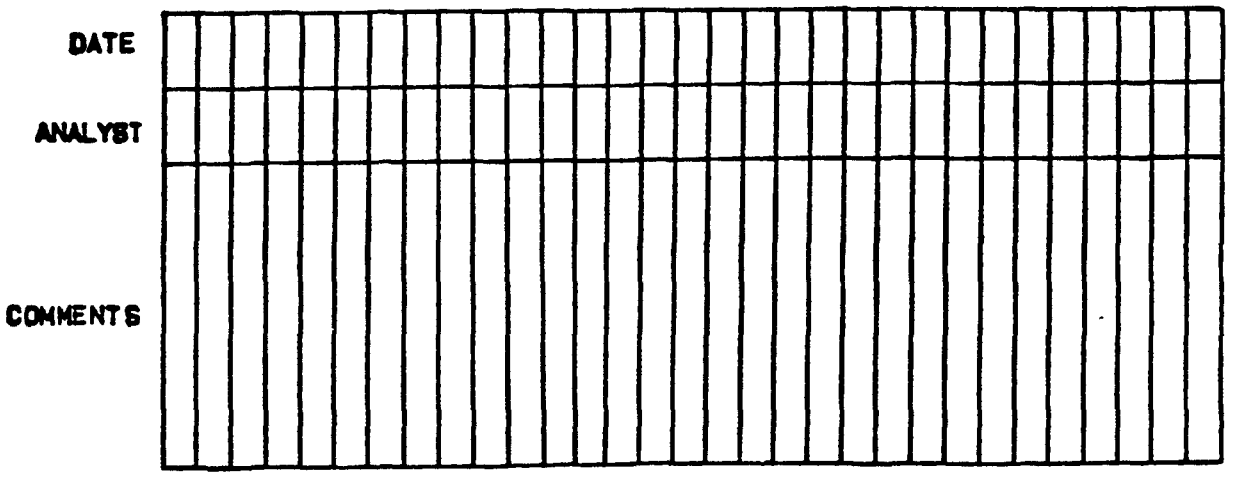


FIGURE 9

P R O C E E D I N G S

MR. TELLIARD: Good morning. Contrary to the program, we have made a few minor changes, there is no break this morning so that we can stop about 11:30 for lunch and people can check out.

Our first speaker this morning is Barry Eynon from SRI. Barry is part three of the continuing saga of the new procedure that we are trying to enact and which we discussed all day yesterday and which we will touch on again today. Barry is going to discuss this morning something we all want to listen to at about quarter to 10, statistics; the joy and fun of numbers.

STATISTICAL METHODS FOR EFFLUENT GUIDELINES

Barrett P. Eynon
SRI International

MR. EYNON: Good morning, I am glad to see we are all still here or at least partly. Bill asked me to come down and talk to you a little bit about what we at SRI and other groups working with effluent guidelines have been doing as far as the statistical analysis of pollutant data for setting effluent guidelines.

The statistical analysis of industrial waste pollution data is an important step in the determination of effluent water guidelines. A number of different statistical techniques are used to address the information needs of the technical staff at EPA in setting limitations guidelines. There is not time today to talk about all of the different methodologies, but what I will try to do is give a general review

of the circumstances, methods, and objectives of some of these analyses.

SRI and myself, personally, have been involved in three major industrial categories over the past three years on both conventionals and priority pollutants: pharmaceutical, petroleum refining, and organic chemicals manufacturing. This work has been in cooperation with Effluent Guidelines and the Office of Analysis and Evalution.

The data that we use in these analyses is usually voluntary data submitted by the plants and will consist of influent and effluent treatment concentrations of pollutants. The plants are selected from among the voluntary participants to be those which have well-designed and operating treatment systems of the appropriate type for the regulatory package. For instance, of the set of 22 pharamaceutical plants which submitted data, 13 were judged to

have well-designed and operating biological treatment systems and were designated as BAT/BCT plants for the purposes of constructing regulations. A further subset of 10 plants among the 13 were designed as NSPS plants for setting NSPS limits. The characterization of these plants represents the engineering and technical evaluations of the plants by EPA.

The sampling and data handling for each study proceeds through several stages to insure high data quality. The samples are usually taken by the plant according to a pre-determined sampling plan. The sampling plan can be as straightforward as one sample taken each day or each week at each sampling point; or, as extensive as that in the first slide which is the sampling design for the Organic Chemicals 5-Plant Study.

In this study at each of the participant plants approximately 30 days of sampling were performed. On each sampling day, one sample was taken at the

pre-treatment and the post-treatment sampling points. Each sample was analyzed by an EPA contract laboratory for a specific set of priority pollutants and the samples were also analyzed by a Chemical Manufacturers Association contract laboratory and also by the participant plants.

The pollutants that were analyzed for were chosen from one or more of the analytical fractions of the organic priority pollutants so as to reduce the number of analyses needed on each sample and also to satisfy the confidentiality restrictions of each of the plants. In order to evaluate the accuracy and precision of the priority pollutant measurements several quality control measures were included in the sampling design.

Approximately two-thirds of the samples were spiked with known concentrations of priority pollutants after their analysis and reanalyzed

in order to measure the percent recovery of the analytical methods. The remaining one-third of the samples were analyzed in duplicate in order to measure laboratory precision. The samples were also spiked with known amounts of "surrogate" chemicals known not to be present in the waste stream, in order to aid in measuring the recovery of the analytical methods. Measurements were also made on blank samples of distilled water, some of which were shipped with the waste samples to check for contamination.

Upon receipt of the laboratory reports on the chemical analyses, the data from such studies are coded and entered into the computer data base. As we have heard today, hopefully some of this stuff will be obviated in the future, but the current work on this study we coded the data and checked the data and then reviewed the data.

The data base that we have found to be very effective for setting up data bases to handle

complicated studies like this is the Statistical Analysis System package, SAS, which we have available on EPA's IBM computer and it runs on IBM main frames. A very powerful and flexible package for data processing that has data management and reporting facilities and also has the capabilities for sophisticated statistical analyses.

Once the data is stored in the computer, data listings and plots of the data can be generated. These are checked for unusual or extreme values which may indicate coding or transcription errors. The values are reviewed with the laboratory reports and with the laboratory to correct any errors. In addition, concentrations which are confirmed by the laboratory, but which are attributable to known plant treatment upsets, or deemed to show variation beyond that associated with well-operated treatment systems, can be removed from the analysis, in order to

focus on the behavior of well-operating treatment systems.

Figure 2 shows plots of the Effluent Total Suspended Solids concentration versus time for one of the plants in the pharmaceutical data base before and after removal of an extreme value. In the top picture we can see that one point just sticks out like a sore thumb and we went back and checked it out. I'm not sure exactly what was going on in this one, it could have been a typo or it was a value that just was an upset. We reviewed the plant records and removed that value from the data set and then we get...when we replot the data and rescale it we get a much more reasonable looking view of the situation at that plant.

So this is done for the set of data and the final data set or edited data set is then available for analysis by statistical methods. So now we go into what is it that we are

trying to determine from this data once it is in the computer. There are two major quantities of interest in all of these studies. The first is to measure the average concentration of each pollutant in the wastewater of each plant, before and after treatment.

Why don't we put up the next slide. This can be directly estimated from the data, using the arithmetic averages of the measured concentrations for each sample. If the set of plants for which the data is available is deemed to be a representative set of the set of all plants with well-operating treatment systems for the industry, then the average pollutant concentrations can be taken across plants to estimate the average effluent concentrations for the industry. So we will start with an averaging, if we have multiple analyses per sample we will start with an average and come up with a number for each sample. Then, we would take an average across

those samples to come up with a value for the plant and then an average across the plants to come up with an overall concentration value.

In other situations similar to the organics five-plant study where the plants were more on the order of case studies with specific pollutants of interest there we want to actually review the pollutants on a pollutant-by-pollutant basis on a plant-by-plant basis to look for pollutants in each different kind of effluent.

If both influent and effluent data are available on a particular data base, a second quantity which can be calculated is the percentage reduction of the pollutant; and, that is given in the format up there, influent minus effluent divided by influent and corrected by 100 to turn into a percentage. This is used to quantify the effectiveness of the treatment system by the plant.

The second main quantity of interest is to characterize the day-to-day variability in the concentrations of a pollutant in a waste stream. For regulatory purposes, the quantity of interest known as the variability factor is defined to be the 99th percentile of the distribution of daily concentrations divided by their long term mean. This quantity which is similar in concept to the usual coefficient of variation, except we are aiming at a different percentile; this is found to be a reasonable stable measure of the amount of day-to-day variation in a pollutant independent of the overall level of the pollutant in the effluent.

If the appropriate variability for a pollutant is determined, then it could be multiplied by a designated long-term plant mean concentration for that pollutant such that if the plant is discharging overall at the designated long-term

mean concentration, then the rate of exceedance of the limitation will be one day in 100. Long-term mean effluent concentrations above the designated mean level will show an exceedance rate in excess of one in 100.

In order to calculate the variability factor from a set of data, an estimate of the 99th percentile of the distribution is necessary. This is a more complex problem than the estimation of mean concentrations, since the data at hand often only consist of 30 to 50 points, or less. Several statistical methods of estimating the 99th percentile have been examined in the course of these studies. Figure 3 shows the models used in the three main methods, superimposed on a hypothetical data histogram.

If sufficient numbers of points are available, nonparametric estimates of the 99th percentile can be calculated directly by looking at the histogram. These estimates make no parametric

assumption about the shape of the distribution. In particular, the specific which was used in work where we have sufficient data is 50 percent non-parametric tolerance estimator. I have the reference in the paper when it comes out. This requires at least 69 data points to be calculated.

There is also another form of estimator known as the tail-exponential estimator which makes a parameteric assumption about the upper tail of the distribution. That's the dotted curve up there, and it assumes that beyond a certain percentile, usually we take like a base 90 of the percentile, that the tail of the distribution falls off like an exponential distribution (indicating). Taking only the data in the tail we can construct a smooth...we smooth that out and use that to estimate the 99th percentile. Again, this requires about 70 data points to be an effective method of calculation.

For cases with fewer data points, distributional

models are necessary. The best general distributional model that we have found for low concentration pollutant data is the log-normal distribution. The log-normal distribution is the distribution of the variable whose logarithm has a normal distribution. Log-normal distribution is appropriate for this type of data because it does not assign any probability to negative concentrations, and it has an appropriate frequency distribution which accords with the actual distributions observed in the sample data.

The next figure shows a sample cumulative distribution for an actual set of data along with a fitted cumulative distribution of log-normal. As you can see, they fit each very well...I'm afraid that's a little light, but the jagged line is the frequency distribution of the actual data. It's a rather large data

set in this case. The smooth line is the fitted log-normal distribution (indicating). So they do appear to fit each other very well and have the appropriate type of behavior. To estimate the 99th percentile, the log-normal distribution is fitted to the data and then we obtain the 99th percentile from tables of the fitted distribution.

The concept of variability factor is also applied to the situation of determining limitations for average concentrations over longer time periods. For instance, for the pharmaceutical and petroleum studies, variability factors were calculated for averages over 30 consecutive measuring days. The long-term mean of 30-day averages is equal to that of the daily values, but the averaging decreases the variability in the resulting measure. Therefore, the appropriate variability factor for 30-day average concentrations will be

smaller than that for daily concentrations. If the concentrations on each day were completely independent, the appropriate formula for a variability factor for these averages would be as given in the first figure there. This comes about through the central limit theory of statistics which says that if we take X bar here is the mean of the data from which we are investing and S of X is the sample standard deviation, that if we take averages of size 30 from a process with this mean in standard deviation they will tend to have the same mean and a standard deviation which reduces by root 30.

Actually, in practice, we find that the concentration values on successive days tend to be more similar than that which would be suggested by independents. This is presumably due to dependencies in the effluent discharge from the plant and mixing and

holding systems in the treatment process.

Figure 5 shows some sample graphs of the autocorrelation functions which we calculate at...it doesn't...we can take either half. These were calculated on some pharmaceutical data where we had long-term data and we could calculate the autocorrelation which is the correlation between values, a particular fixed number of days apart. So the autocorrelation of lag one is the correlation between concentrations one day apart, an autocorrelation of lag 30 is the correlation between values 30 days apart. If we plot those as a function of the lag going down, correlations running between minus one and one, we see that we have for each of these situations we have positive autocorrelations and their positive and tail-off get smaller and smaller as we get a longer and longer lag. Of course, we would expect as the distance

between any two measurements goes towards infinity, that the correlation between those measurements would tend to go to zero. The effect of this is that the averaging process on consecutive days reduces the variability, but not by as much as would be suggested by independents.

Could we back up one slide; that's the one. The calculated autocorrelation for lags up... I guess we need lags 1 to 29 in order to calculate a 30-day variability factor, then the formula for the appropriate variability factor is similar, but it has another term in it which depends on the autocorrelation. This can be used to calculate appropriate variability factors for 30-day averages for consecutive days. For 4-day averages such as have been suggested for priority pollutant limitations, the appropriate variability factor would be what we have got on the bottom because those

are being suggested for non-consecutive days of measurement. Also because when we look at the priority pollutants we see less auto-correlation than in the conventional pollutants. This could be due to the effect of analysis variability or just that priority pollutants work differently, but our preliminary look at priority pollutants shows that there is less evidence of autocorrelation present.

So that's really where we're coming from on objectives and how we would calculate these numbers if data were perfect, perfect in the sense of no reporting problems and no other external considerations. Data, of course, all laboratory data always, of course, are expected to have some variability in them.

There are some special topics I would like to mention. On things that are particularly applicable to priority pollutants and the way that they effect our statistical analysis. In

particular, there is the reporting and handling of detection limit values. When the concentration of the sample is too small to measure, the laboratory will report not detected. This is fine and very appropriate as an analytical tool, but just drives the statisticians nuts because it is not a numerical value. Somehow in order to do a calculation with these values we have to come up with some sort of numerical value to use. The first cut on this would be to stick these values in at a concentration of zero. This is not bad, but it may under-estimate the concentration of the pollutant.

So what we want to do is, we would also like to explore the sensitivity of our analyses to the assignment of these values by also assigning them to an upper value for the concentration. This works best if we know

the detection limit for the methodolgy; and, that's not always true in the data that we see. If we calculate a statistic with the data assigned at zero and then assigned to the detection limit, we get a sensitivity type of analysis which will tell us how much the means, for instance, could change between these two values.

There are also other more sophisticated techniques for handling these quantities that deal with the detection limit data as missing information or sensored data, not in any majority of sense; simply, that the concentration would be known to be below a certain low but would not be known quantitatively further than that and that that would be the kind of model.

The appropriate handling of detection limit data is a question that has to be approached for each different technique,

statistical technique that we are going to use. For the calculation of variability, simply assigning the values to a particular numerical concentration is not quite the right thing to do. We have done a lot of work with what is called the Delta log-normal model where we explicitly give these concentrations their own probability mass at zero and this allows... and then we model the data above the detection limit by a log-normal distribution. This seems to work fairly well.

For other types of considerations and situations, has to be a continuing factor in the statistician's mind as to how he is going to handle these detection limit values. What I would also like to say is that continued attention by analytical chemists to the definition of reporting of detection limits will be an important step in clarifying how

these values should be used. I have seen some American Chemical Society publications and some of the things that we talked about in these conferences on clarifying detection limits and defining them. I would like to suggest that that always can be carried further in terms of standards and reporting practices for all of the laboratories.

Another issue in the analysis of priority pollutant data is inter-laboratory and intra-laboratory variation. The analysis replication in the organic 5-plant study allows an investigation of the sources of variation in the concentration measurements because the study includes multiple samples, multiple laboratories analyzing each sample and replicate analyses by laboratories on at least a portion of the samples. Using statistical variance components estimation

techniques, the variability in these samples can be broken down into four components.

There is the inter-sample variability which would be the natural variability of the true concentrations in each sample which we would see if there were no analytical errors. This would be representative of time or sampling variation in these samples. The second factor is the consistent inter-laboratory variability which is, if we take a set of samples and give them to a set of laboratories and look at the mean concentration that each laboratory gives, each laboratory will vary slightly and the variation between laboratories on that is another factor that can come out. This could be called the inter-laboratory accuracy or lab bias. The third factor is, within-sample inter-laboratory variability which has to do with the individual handling of each sample by the laboratory; and, if we

took one sample and gave it to a bunch of laboratories they would also vary. This could be thought of as the inter-laboratory precision. The fourth factor is the intra-laboratory variability which would be the variability between pairs of replicates run at the same laboratory. So this would be the intra-laboratory precision.

These four components were estimated in the organic study for each pollutant for which there was sufficient data and the model we used was a slight modification on the ordinary variance components model in that we applied this to the log-normal model effectively analyzing the logarithm to the concentrations and what we end up with is a multiplicative model rather than the ordinary additive model. It seems to work fairly well with the log-normal distribution and all of our other assumptions in the analysis.

We did run into some problems with lots of detection limit data on some of this data. A lot of the effluent data was consistently down to detection limit. We can't really say much about these sources of variability in such cases. That's why it's nice to have studies like George's study with designed levels of pollutant concentrations so you can actually see what's going on there. So these kinds of factors can be quantified in cases where we have sufficient data.

The last issue that I wanted to mention was spike sample analysis. We had data in the organic study for both priority pollutant spiking and also surrogate chemicals, deuterated or halogen substituted pollutants which were added to the sample after the original analysis and measured for their concentration.

The last slide here shows...just gives the ordinary formula for percent recovery and here we have the spike...we take the raw sample

concentration, C, the spike level as L and the spike sample concentration as S; we calculate the percent recovery this way. For the surrogate chemicals, C would be fixed at zero because we know these chemicals would not be present in the sample and we can calculate the recovery.

Now, the important point here from a statistician's point of view is that we can assume fairly well that we know L because it is a laboratory standard, but S and C are both subject to analytical variation and, therefore, for a single sample the estimate of the recovery is subject to analytical variation. Therefore, when we calculate these recoveries we like to take an average over many samples in order to evaluate the overall recovery of the method; and, that's fine. The other issue which comes up is the question of correcting individual sample values. We decided that it was probably better not to do

that because while you are increasing the accuracy, you are also decreasing the precision of the concentration measurement. So we decided it was better in this case not to do this on these samples.

There was also an additional consideration in that not all samples were spiked and so we couldn't...we wanted to make sure we were doing everything the same on all samples. So we evaluated that for each method, for each chemical. We evaluated recovery and that's part of our summary that we will be presenting to the agency.

Hopefully, this has given an idea of some of the types of techniques and issues in the statistical analysis of the data for effluent guidelines, and I hope that continued cooperation between statisticians and analytical chemists, I hope that will continue. I think it is important in exploring all of the facets of this complex subject. Thank you.

Statistical Methods for Effluent Guidelines

Barrett P. Eynon

SRI International

I. Introduction

The statistical analysis of industrial waste pollution data is an important step in the determination of effluent water quality guidelines. A number of different statistical techniques are used to address the information needs of the technical staff at EPA in setting limitations guidelines. There is insufficient time today for a detailed discussion of all of these methodologies; what will be aimed for in this talk is a general overview of the circumstances, methods, and objectives of some of these statistical analyses. SRI has been involved in the data analysis for three major industrial categories over the past three years: pharmaceutical manufacturing (1), petroleum refining (2) , and organic chemicals manufacturing industries (3). This work has been performed under the auspices of the EPA Office of Analysis and Evaluation. The topics presented here are drawn from our work on these projects, and are intended to indicate some of the important concepts and methods in this

work.

II. Description of Data

The basic data used in these projects consists of measurements of pollutant concentrations in water samples taken at the treatment influent and effluent points, at a set of representative plants from the industrial category in question. The plants involved in the study are generally voluntary participants from among the set of plants having well-designed and operating treatment systems of the appropriate type for the regulatory package. For instance, of the set of 22 pharmaceutical plants which submitted data, 13 were judged to have well-designed and operating biological treatment systems, and were designated as BAT/BCT (Best Available Technology/Best Conventional Technology) plants for the purposes of constructing regulations. A further subset of ten plants from among the 13 were designated as NSPS (New Source Performance Standards) plants for setting NSPS limits. The characterization of the plants represents engineeering and technical evaluations of the plants by EPA.

The sampling and data handling for each study proceeds through several stages, to insure high data quality. The samples are usually taken by the plant according to a predetermined sampling plan. The sampling plan can be as

straightforward as one sample taken each day or each week at each sampling point over the sampling period, or as extensive as that shown in Figure 1, the sampling design for the Organic Chemicals 5-Plant Study.

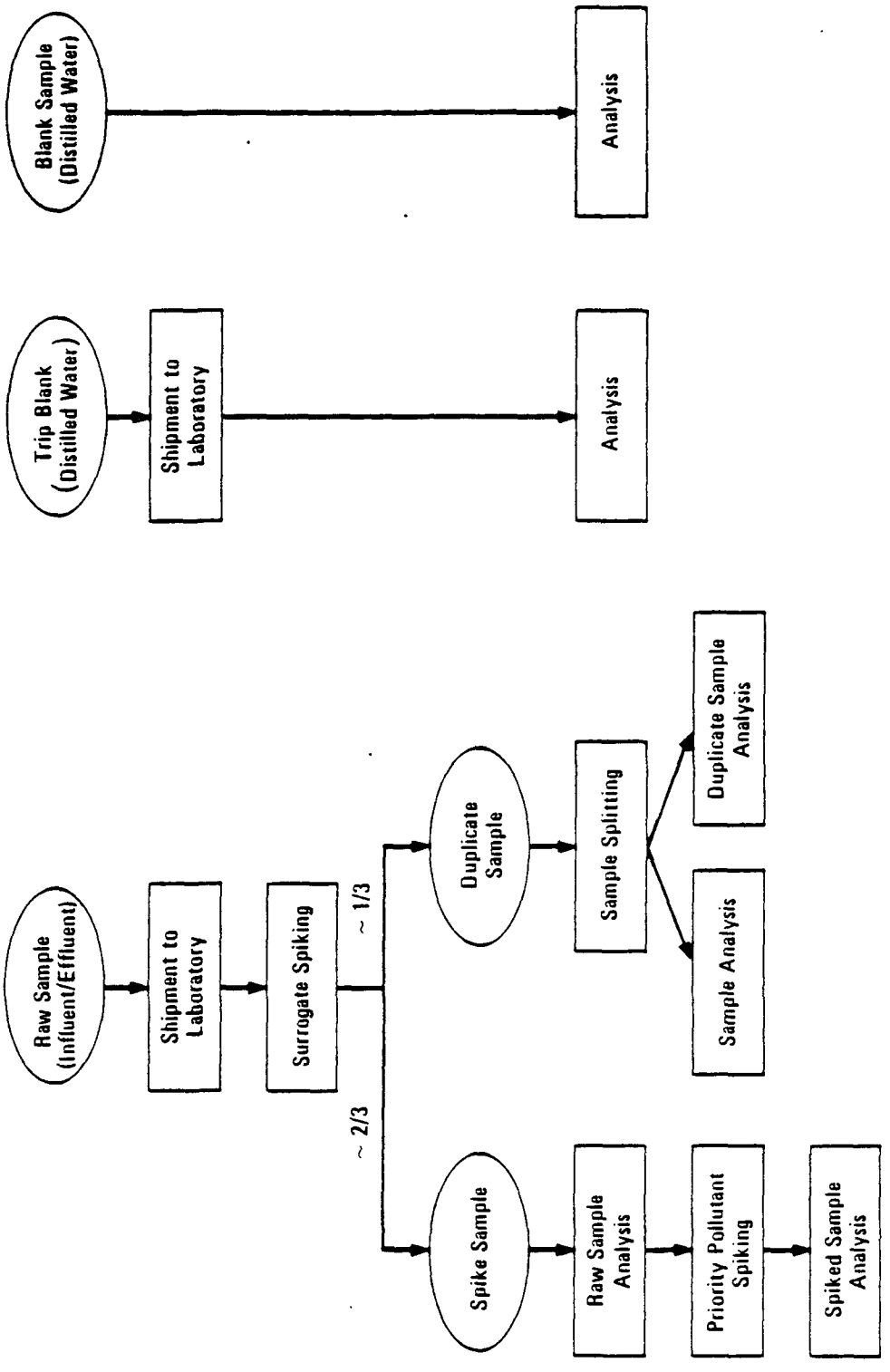


Figure 1. Schematic Diagram of Sampling Design for Organic Long-Term (5-Plant) Study.

In this study, at each of the participant plants, approximately 30 days of sampling were performed. On each sampling day, one sample was taken at the pre-treatment and the post-treatment sampling points. Each sample was analyzed by an EPA contract laboratory for a specific set of priority pollutants. The pollutants analyzed for were chosen from one or more of the analytical subsets of the organic priority pollutants, so as to reduce the number of analyses needed on each sample, and to satisfy the confidentiality restrictions of each of the participant plants. Approximately one-fourth of the samples were also analysed by a Chemical Manufacturers Association (CMA) contract laboratory, and the participant plants were also encouraged to conduct their own analyses of the samples.

In order to evaluate the accuracy and precision of the priority pollutant measurements, several quality control measures were included in the sampling design. Approximately two-thirds of the samples were spiked with known concentrations of priority pollutants after their analysis, then reanalyzed, in order to measure the percentage recovery of the analytical methods. The remaining one-third of the samples were analyzed in duplicate, in order to measure laboratory precision. Samples were also spiked with known amounts of "surrogate" chemicals known not to be present in the waste stream, in order to aid in measuring the recovery of the analytical methods. Measurements were also made on

blank samples of distilled water, some of which were shipped with the waste samples to check for contamination.

Upon receipt of the laboratory reports on the chemical analyses, the data are coded and entered into a computer data base for processing. An appropriate data base structure is set up to incorporate the elements of the study design. In our work at SRI, we have found the Statistical Analysis System (SAS) computer package (4), which is available on EPA's NCC-IBM system, to be the most effective system for flexible and efficient data processing, because it both provides data management and reporting facilities, and has the capabilities for sophisticated statistical analyses.

Once the data is stored in the computer, data listings and plots can be generated. These are checked for unusual or extreme values, which may indicate coding or transcription errors. These values are reviewed with the laboratory reports and with the laboratory to correct any errors. In addition, concentrations which are confirmed by the laboratory, but which are attributable to known plant treatment upsets, or deemed to show variation beyond that associated with well-operated treatment systems, can be removed from the analysis, in order to focus on the behavior of well-operating systems. Figure 2 shows plots of the Effluent Total Suspended Solids (EFTSS) concentration versus

time for one of the plants in the pharmaceutical data base, before and after removal of an extreme value. Note that the plots of the data after correction have been rescaled, and the data now exhibits much more homogenous behavior.

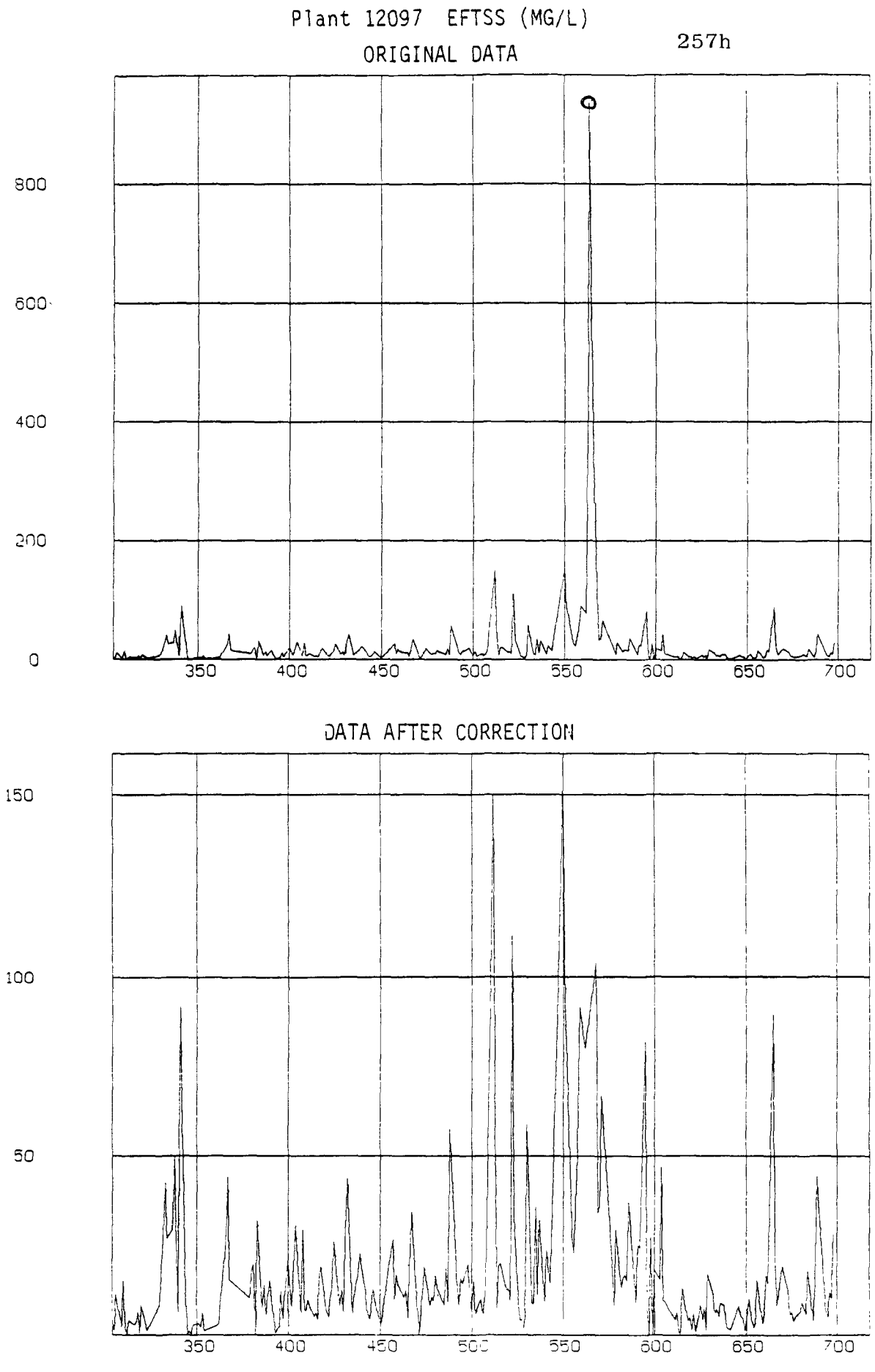


Figure 2. Plot of Effluent Total Suspended Solids for a pharmaceutical plant, before and after correction of an outlier.

III. Statistical Analysis

After the data set is cleaned and checked, statistical analyses are performed. There are two major quantities of interest in all of these studies. The first is to measure the average concentration of each pollutant in the wastewater of each plant, before and after treatment. This can be directly estimated from the data, using the arithmetic average of the measured concentrations for each sample. If the set of plants for which data is available is deemed to be representative of the set of all plants with well-operated treatment systems in the industry, then the average pollutant concentrations for the industry can be estimated by taking the average across plants of the average concentrations for each plant. In other situations, such as the organics study, where there are only a few plants, each analyzed for a different set of pollutants, a case-by-case analysis can be prepared for each plant, focusing on the pollutants found to be present in large concentrations in the effluent streams of specific plants.

If both influent and effluent data are available for a pollutant at a plant, the percentage reduction of the pollutant can be calculated by:

$$100 \times \frac{\text{(influent concentration - effluent concentration)}}{\text{influent concentration}} .$$

The second main quantity of interest is a characterization of the day-to-day variability in the concentrations of a pollutant in a waste stream. For regulatory purposes, the quantity of interest, known as the variability factor, is defined to be the 99th percentile of the distribution of daily concentrations, divided by their long term mean. This quantity, (which is similar in concept to the usual coefficient of variation, the ratio of the standard deviation to the mean), is found to be a reasonably stable measure of the amount of day-to-day variation of a pollutant, independant of overall level of the pollutant concentration. If the appropriate variability factor for a pollutant is determined, then it can be multiplied by a designated long-term plant mean concentration for that pollutant at that plant, such that if the plant is discharging overall at the designated long-term mean concentration, then the rate of exceedance of the limitation will be 1 day in 100. Long-term mean effluent concentrations above the designated mean level will show an

exceedance rate in excess of 1 in 100.

In order to calculate the variability factor from a set of data, an estimate of the 99th percentile of the distribution of daily values is necessary. This is a more complex problem than the estimation of the mean concentrations, since the data at hand often only consist of 30-50 points, or less. Several statistical methods of estimating the 99th percentile have been examined in the course of these studies. Figure 3 shows the models used in the three main methods, superimposed on a hypothetical data histogram.

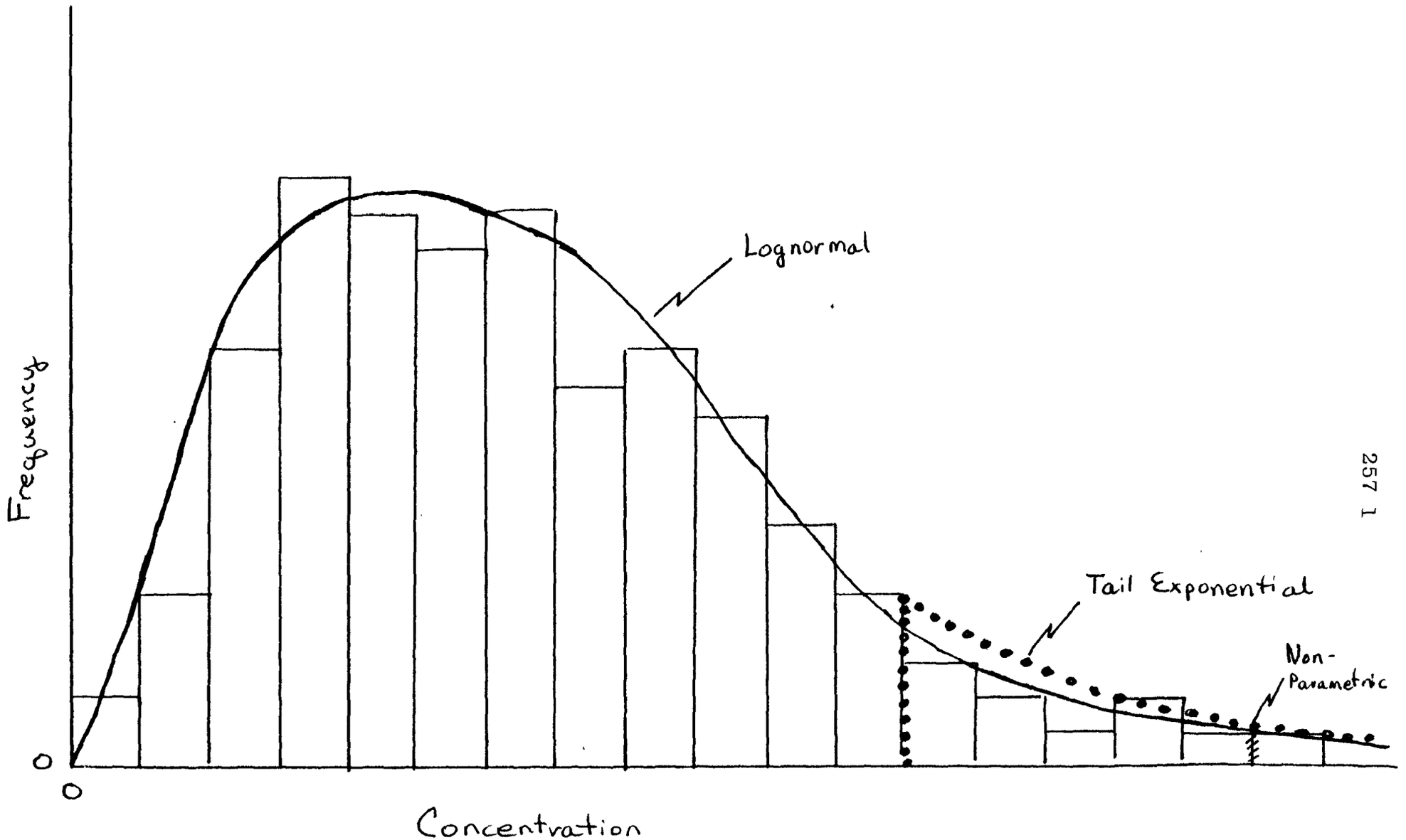


Figure 3. Three methods of estimation of the 99th percentile of the distribution of daily concentrations

If sufficient numbers of points are available, nonparametric estimates of the 99th percentile can be calculated. These make no parametric assumption about the shape of the distribution. In particular, the 50% nonparametric tolerance estimator (5, pp 40-43), is a useful estimator, but requires at least 69 data points to be calculated. Also, tail-exponential estimators(5), which make assumptions about only the shape of the upper tail of the distribution, have been found to be effective, but require about 70 points to be effectively calculated. In cases with fewer data points available, distributional models are necessary. The best general distributional model we have found for low concentration pollutant data is the lognormal distribution. The lognormal distribution is the distribution of a variable whose logarithm has a normal, or Gaussian distribution. The lognormal distribution is appropriate for this type of data, because it does not assign any probability to negative concentrations, and it has a skewed frequency distribution, which accords with the actual distributions observed in the sample data. Figure 4 shows a sample cumulative distribution, along with the cumulative distribution of a fitted lognormal . To estimate the 99th percentile, the lognormal distribution is fitted to the data, and the 99th percentile of the fitted distribution, obtained from tables of the lognormal distribution, is used to calculate the variability factor.

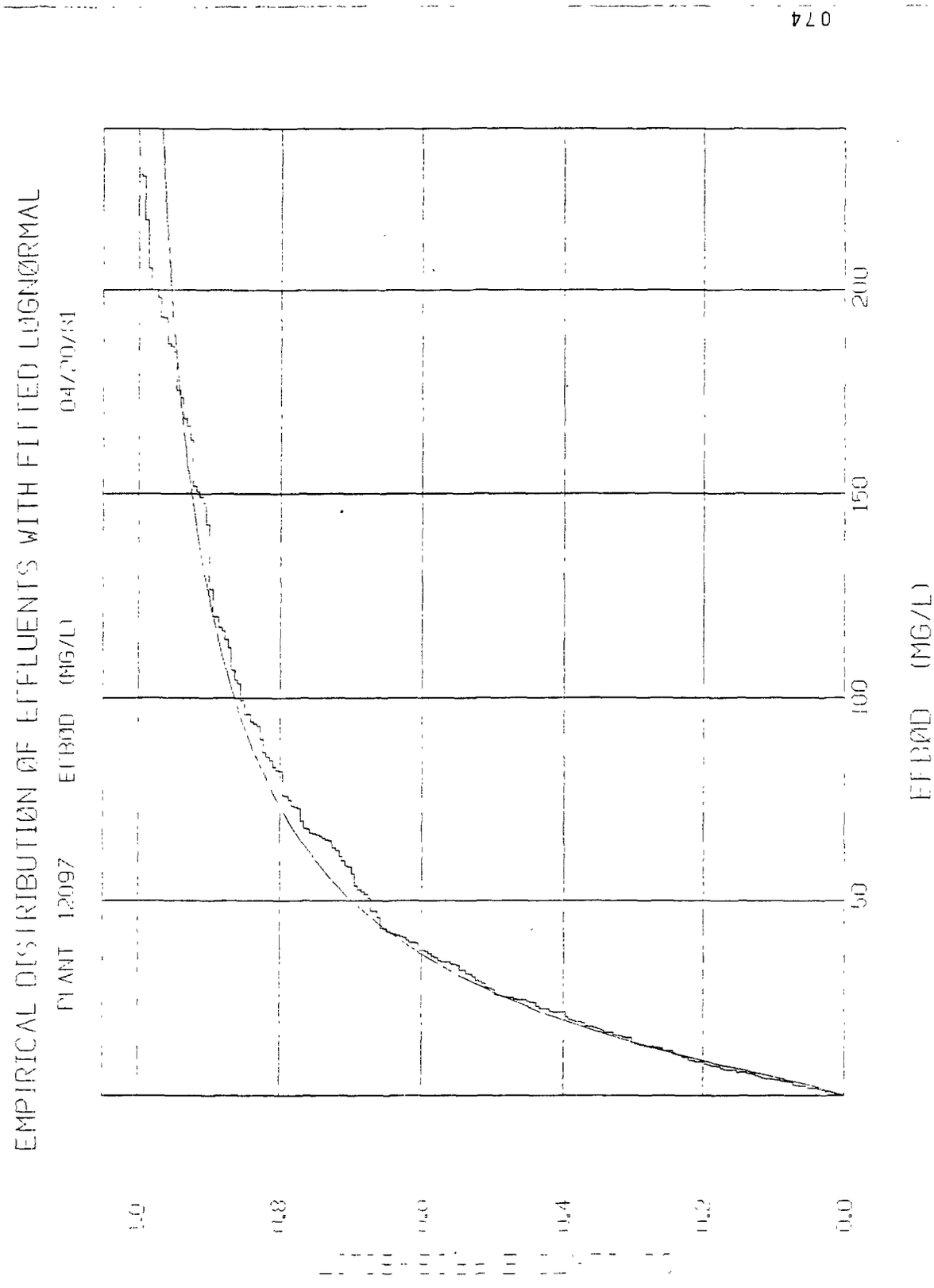


Figure 4. Sample cumulative distribution function with fitted lognormal

The concept of the variability factor is also applied to the determination of limitations for average concentrations over longer time periods. For instance, for the pharmaceutical and petroleum studies, variability factors were calculated for averages over 30 consecutive measuring days. The long-term mean of 30-day averages is equal to that of the daily values, but the averaging will decrease the variability of the result. Therefore the appropriate variability factor for 30-day average concentrations will be smaller than that for daily concentrations. If the concentrations on each day were completely independent, the appropriate formula for the variability factor would be

$$\frac{\overline{X} + 2.326\, S_x / \sqrt{30}}{\overline{X}}$$

where X and S are the sample mean and standard deviation of the daily concentrations. (The numerator is the 99th percentile of the asymptotic distribution of 30-day averages according to the Central Limit Theorem of statistics). However, examination of the data reveals that concentration values on successive days tend to be similar, presumably due to dependencies in the effluent discharge from the plant, and mixing and holding systems in the treatment process. Figure 5 shows sample graphs of autocorrelation functions for effluent Biological Oxygen Demand (BOD) and Total Suspended Solids (TSS), measured in concentration and mass discharge units, at a representative pharmaceutical plant.

The autocorrelation a_ℓ , $\ell = 1,\ldots,30$, represents the correlation between concentration values measured ℓ days apart. Note that, in the figure, the calculated autocorrelations are all positive and decrease with increasing time lag, which is consistent with the physical model proposed above. If a_ℓ is calculated for a plant, then the appropriate formula for the variability factor for 30-day averages is

$$\frac{\overline{X} + 2.326\, S_x \sqrt{\left(1 + 2\sum_{\ell=1}^{29}\left(1 - \frac{\ell}{30}\right) a_\ell\right)/30}}{\overline{X}}$$

See, for instance, Switzer (7).

For 4-day averages, as are under consideration for priority pollutant limitations, the appropriate variability factor would be

$$\frac{\overline{X} + 2.326\, S_x / \sqrt{4}}{\overline{X}}$$

No autocorrelation correction would be used, because the sets of four days are not consecutive. In addition, preliminary analysis of priority pollutant data shows much less autocorrelation than the conventional pollutants.

ESTIMATED AUTOCORRELATION FUNCTIONS

PLANT 12022.
VARIABLE - TSS MG/L
NOBS0 - 395 NXNM - 395
MEAN - 84.846 NOBS - 396
MAXLAG - 30 VARIANCE - 2849.1

L	NLAG	COVAR	ACF	-1 0 +1
1	391	.190E+04	0.6670	XXXXXXXXXXXXX
2	390	.147E+04	0.5144	XXXXXXXXXX
3	389	.121E+04	0.4247	XXXXXXXX
4	388	.109E+04	0.3827	XXXXXXX
5	387	.101E+04	0.3532	XXXXXXX
6	386	962.	0.3376	XXXXXX
7	385	.110E+04	0.3857	XXXXXXX
8	384	.111E+04	0.3899	XXXXXXX
9	383	.104E+04	0.3668	XXXXXXX
10	382	.105E+04	0.3692	XXXXXXX
11	381	.106E+04	0.3730	XXXXXXX
12	380	972.	0.3412	XXXXXX
13	379	852.	0.2991	XXXXX
14	378	837.	0.2939	XXXXX
15	377	807.	0.2833	XXXXX
16	376	.100E+04	0.3523	XXXXXXX
17	375	.119E+04	0.4171	XXXXXXXX
18	374	.118E+04	0.4133	XXXXXXXX
19	373	.116E+04	0.4072	XXXXXXXX
20	372	.112E+04	0.3929	XXXXXXX
21	371	.100E+04	0.3526	XXXXXXX
22	370	873.	0.3066	XXXXXX
23	369	847.	0.2973	XXXXXX
24	368	962.	0.3378	XXXXXX
25	367	.106E+04	0.3714	XXXXXXX
26	366	.105E+04	0.3679	XXXXXXX
27	365	.111E+04	0.3906	XXXXXXX
28	364	.113E+04	0.3964	XXXXXXX
29	363	.110E+04	0.3877	XXXXXXX
30	362	.107E+04	0.3741	XXXXXXX

PLANT 12022.
VARIABLE - TSS LB/DAY
NOBS0 - 395 NXNM - 394
MEAN - 990.97 NOBS - 396
MAXLAG - 30 VARIANCE - .32852E+06

L	NLAG	COVAR	ACF	-1 0 +1
1	390	.213E+06	0.6477	XXXXXXXXXXX
2	389	.158E+06	0.4821	XXXXXXXXX
3	388	.133E+06	0.4058	XXXXXXXX
4	387	.122E+06	0.3709	XXXXXXX
5	386	.110E+06	0.3347	XXXXXX
6	385	.109E+06	0.3327	XXXXXX
7	384	.129E+06	0.3932	XXXXXXX
8	383	.132E+06	0.4032	XXXXXXXX
9	382	.122E+06	0.3712	XXXXXXX
10	381	.120E+06	0.3665	XXXXXXX
11	380	.121E+06	0.3697	XXXXXXX
12	379	.113E+06	0.3440	XXXXXX
13	378	.974E+05	0.2966	XXXXX
14	377	.924E+05	0.2814	XXXXX
15	376	.848E+05	0.2580	XXXXX
16	375	.104E+06	0.3178	XXXXXX
17	374	.124E+06	0.3763	XXXXXXX
18	373	.125E+06	0.3796	XXXXXXX
19	372	.128E+06	0.3896	XXXXXXX
20	371	.126E+06	0.3835	XXXXXXX
21	370	.112E+06	0.3416	XXXXXXX
22	369	.894E+05	0.2720	XXXXXX
23	368	.848E+05	0.2580	XXXXXX
24	367	.975E+05	0.2969	XXXXXX
25	366	.110E+06	0.3356	XXXXXX
26	365	.113E+06	0.3426	XXXXXX
27	364	.120E+06	0.3641	XXXXXXX
28	363	.125E+06	0.3817	XXXXXXX
29	362	.123E+06	0.3735	XXXXXXX
30	361	.117E+06	0.3560	XXXXXXX

ESTIMATED AUTOCORRELATION FUNCTIONS

PLANT 12036.
VARIABLE - BOD MG/L
NOBS0 - 366 NXNM - 366
MEAN - 33.041 NOBS - 366
MAXLAG - 30 VARIANCE - 604.25

L	NLAG	COVAR	ACF	-1 0 +1
1	365	274.	0.4529	XXXXXXXXXX
2	364	183.	0.3035	XXXXXXX
3	363	134.	0.2224	XXXXX
4	362	132.	0.2177	XXXXX
5	361	93.3	0.1544	XXXX
6	360	57.4	0.0950	XX
7	359	45.0	0.0744	XX
8	358	60.0	0.0994	XX
9	357	58.7	0.0971	XX
10	356	96.7	0.1601	XXXX
11	355	121.	0.2007	XXXXX
12	354	166.	0.2748	XXXXXX
13	353	141.	0.2327	XXXXX
14	352	131.	0.2160	XXXXX
15	351	128.	0.2127	XXXXX
16	350	111.	0.1843	XXXX
17	349	94.5	0.1564	XXXX
18	348	62.2	0.1029	XXX
19	347	27.4	0.0453	X
20	346	31.0	0.0512	XX
21	345	22.1	0.0366	X
22	344	52.0	0.0861	XX
23	343	13.8	0.0229	
24	342	19.3	0.0319	X
25	341	5.27	0.0087	
26	340	30.5	0.0505	XX
27	339	44.9	0.0743	XX
28	338	27.6	0.0457	X
29	337	19.1	0.0316	X
30	336	17.0	0.0282	X

PLANT 12036.
VARIABLE - BOD LB/DAY
NOBS0 - 366 NXNM - 365
MEAN - 293.70 NOBS - 366
MAXLAG - 30 VARIANCE - 44255.

L	NLAG	COVAR	ACF	-1 0 +1
1	364	.218E+05	0.4922	XXXXXXXXXX
2	363	.154E+05	0.3488	XXXXXXX
3	362	.111E+05	0.2519	XXXXXX
4	361	.868E+04	0.1962	XXXX
5	360	.391E+04	0.0883	XX
6	359	.304E+04	0.0688	XX
7	358	.200E+04	0.0453	X
8	357	.414E+04	0.0936	XX
9	356	.392E+04	0.0886	XX
10	355	.828E+04	0.1872	XXXX
11	354	.822E+04	0.1858	XXXX
12	353	.106E+05	0.2336	XXXXX
13	352	.732E+04	0.1654	XXXX
14	351	.680E+04	0.1536	XXXX
15	350	.640E+04	0.1446	XXX
16	349	.661E+04	0.1493	XXX
17	348	.521E+04	0.1178	XXX
18	347	.263E+04	0.0595	XX
19	346	267.	0.0060	
20	345	.172E+04	0.0390	X
21	344	.102E+04	0.0231	
22	343	.116E+04	0.0263	X
23	342	-809.	-0.0183	
24	341	677.	0.0153	
25	340	-310.	-0.0070	
26	339	317.	0.0072	
27	338	.185E+04	0.0419	X
28	337	.262E+04	0.0592	XX
29	336	.139E+04	0.0313	X
30	335	-56.4	-0.0013	

Figure 5. Estimated autocorrelation functions for BOD and TSS in mg/l and lb/day at a pharmaceutical plant.

IV. EXCEPTIONS AND SPECIAL TOPICS

The objective of calculating means and variability factors can be accomplished as described above, for any set of standard data. However, in many cases, there are side issues and complications which affect the data analysis. Some of them are particularly prevalent in the analysis of priority pollutant data, due to the necessity of measuring concentrations very near the limits of the measurement technique.

One issue in particular is the reporting and handling of detection limit values. When the concentration in a sample is too small to measure, the concentration is reported as "not detected" (ND). This is fine as a descriptive statement, but causes problems for the statistician, because statistical procedures must work with numerical concentration values, and these measurements still reflect valid samples and must be accounted for in calculations. For even the usually straightforward process of calculating mean concentrations, the handling of these values can be approached in several ways. Using a zero concentration is a reasonable first approximation, but may understate the actual average concentration. If the analytical detection limit for the particular method was supplied by the laboratory, or can be assumed to be known, a sensitivity analysis can be performed by also calculating statistics

with ND values set to the detection limit, giving an upper and lower limit to the "true" value. Compromise solutions, with ND values set to 1/2 the detection limit are also often used. However, all of these methods produce a somewhat distorted estimate of variability, because all of the detection limit values are being placed at the same point. In our work, we have made extensive use of an extention of the lognormal distribution, known as the delta-lognormal distribution, in which the detection limit data are placed in a separate probability spike at zero, or the detection limit value, and the concentrations above the detection limit are modeled with the lognormal distribution. This allows calculation of appropriate variability factors.

However, the appropriate statistical handling of detection limit data has to be addressed for each statistical technique. Continued attention by analytical chemists to the definition and reporting of detection limits, and standardization of reporting formats and notation would be of great aid in this task. Various recent American Chemical Society papers and talks have addressed these questions (8,9), but more needs to be done to implement standards in practice.

Another issue in the analysis of priority pollutant data is inter- and intra-laboratory variation. The analysis replication in the organics 5-plant study allows an

investigation into the sources of variation in the concentration measurements, because the study includes multiple samples, multiple laboratories analyzing each sample, and replicate analyses by laboratories on some samples. Using statistical variance components techniques, the variability can be broken down into four components:

- Inter-sample variability. Variation in the true concentration of each sample (time and sampling variation).

- Consistent inter-laboratory variability. Variation between the average concentrations measurements from each laboratory (laboratory bias, or inter-laboratory accuracy).

- Within-sample interlaboratory variability. Variation between laboratories in the analysis of each sample. (inter-laboratory precision).

- Intra-laboratory variability. Variation between repeated measurements at the same laboratory (intra-laboratory precision).

For the organics study, these analyses were performed in terms of a multiplicative effects model consistent with the

lognormal distribution. These analyses were done for each pollutant, at each samling point at each plant, for all situations having sufficient data above the detection limit.

The final issue I will mention is that of spiked sample analyses. The organics study included both priority pollutant and surrogate chemical spiking of samples. The calculated percent recovery for a sample is:

$$100 \times \frac{S-C}{L}$$

where C is the raw concentration measurement, L is the spike level, and S is the spiked concentration measurement. for surrogate chemicals C is zero. these quantities can be computed, and then averaged across samples, to give a measure of the average recovery for each chemical by each method.

Some consideration was given to the correction of individual sample measurements according to the measured recovery in that sample (10). While this method generally increases the accuracy of the measurements, it also decreases the precision of the measurements substantially. Because of this, and because not all samples were spiked in the study, it was decided to do all statistical analyses on the uncorrected data.

V. CONCLUSIONS

Hopefully, this has given an idea of the types of techniques and issues in the statistical analysis of data for effluent guidelines. Continues cooperation between the statistican and the analytical chemist is important in exploring all aspects of this complex subject.

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QUESTIONS AND ANSWERS

MR. MADDALONE: Ray Maddalone, TRW. I actually have a comment and a question.

MR. EYNON: Sure.

MR. MADDALONE: We run into the problem of detection limits and the problem of trying to determine what value to put into the data base, and some of the reports have not detected value. I don't think there's any really good solutions when you don't have a base of data to go back on.

My question is, when you don't have a base of data, a historical base of data just a single number without a detection limit reported, what do you recommend? Is it a zero, is it one-half of the value that the report has the less than or non-detected?

MR. EYNON: I'll tell you what

we did in the organics data base and that is, we stored the number as a zero, but we also kept a comment field associated with each entry. Part of that comment field was the fact that this was really a non-detected value. Now, that was actually the only way you could get an actual zero concentration was to have a not detect or a less than 10 or something like that as the statement by the laboratory; but, we kept the detection limit. If it was present we knew the fact that these were not detected values and there is no easy answer to this question. I don't think there is any single numerical value which is the correct value to put in. If we knew the correct value we would have detected, you know, we wouldn't be worried about this detection question. I think that what has to be done is, you have to do some exploratory statistics on the effect of these values on your overall statistical

analysis.

MR. MADDALONE: What about less than numbers? I asked, actually, a two part question. Less than, you have a number and that really can't...

MR. EYNON: Well, let's say you have a number; I found that the difference between saying less than 10 and saying not detected seems to be more of a phenomenon of the laboratory reporting criteria than anything else which is really going on with the data,. So I think it would be unfair to treat those any particularly differently.

It would be nice to always have the detection limit; and, if you have a not detect and you have no other information about the upper limit and you have to calculate a mean, I don't see that you can have any argument for anything other than this real value to put in. You simply have to caveat your result and say, look,

this is all we could do, we have no further information about this value, we're going to have to stick it into zero. The thing you can't do is, you can't ignore that value because you are told something positive, although not exact about the concentration. You can't leave it out of the calculation, you can't ignore it, you can't put it as missing; so, you know, it's a total lack of any sort of information about the level of that pollutant, or about the detection limit I would say, yes, you would have to put a zero.

MR. MADDALONE: My comment is, is that as part of the effort that we did we reviewed the various definitions of limit of detection. I think one definition has been grossly overlooked by agencies and the people using or setting definitions for the limit of detection is, are the ACS guidelines that were published in Analytical Chemistry in 1980;

it was Volume 52, page 2252. Those are extremely good because they set three different levels. They chose a three sigma detection limit and they said if the values are less than your three sigma detection limit you report them as not detected with the LOD. Now, that would solve part of the problem that you get with these not detected values.

Then if you have a value above your three sigma you report it as a real value, but you also, again, put the limit of detection in parenthesis so you know where you are in relationship to that. I think that some sort of consistent use of a definition ought to be assigned; and, then, some explanation of what the risk is associated with that definition because it really varies and whether you consider false positive or false negative errors.

MR. EYNON: I couldn't agree with you more. In fact, I think I'm talking about the...when I mentioned ACS I think I'm thinking of the exact same paper you are talking about. So, yes, I think that that's an important question to standardize the laboratory reporting practices on these issues.

MR. DELLINGER: Bob Dellinger, Effluent Guidelines Division. My questions on the use of autocorrelation in establishing 30 day variability factors. I was wondering if you checked your 30-day, 99th percentile estimates on the data sets from which they were derived to see if they were good estimators of the 99th percentile?

MR. EYNON: We have in cases where that's possible. Sometimes we can't because we don't have complete sample information on every day. Therefore, we cannot construct 30-day running averages from the

daily data that we are given. There are many cases in which we could estimate the autocorrelation function and come up with the variability factor without being able to go back and check that.

However, there are a few cases that we have, we have looked at some other smaller data sets on...I think we looked at the leather tanning and the iron industry and the cases we have checked out, yes, much better agreement than the central limit theory in value would give, much more...much closer agreement with the actual empirical.

I mean, if we had years and years and years of data we could even think about constructing the 30 days, then actually using some sort of non-parametric estimate or model the 30-day averages directly, but that's well beyond any scope of any data set we have.

MR. DELLINGER: Okay, because we have checked the central limit theory as a predictor with biological treatment and it is not very good at all. We get something like 20 percent of the values from the data set from which the number was derived at higher than the 99th percentile.

MR. EYNON: I'm not surprised. The correction for autocorrelation can actually make a noticeable difference in the variability factor that you would get and, indeed, they have used the central limit theory that assumes independence; actually central limit theory underlies both these. The ordinary central limit theory which is the independent one would, indeed, give too small a variability factor. If you went back and checked it, you would get exactly what you're saying; which is, you would get too many exceedances even in the data set that you calculated it.

MR. DELLINGER: Now, we have used things like taking the 30-day averages. Let's say we had 12 or 14 or 16 30-days averages on a set.

MR. EYNON: That's a different question because there if you are calculating your 30 day averages on less than 30 days data, you are also going to get a larger variation because...

MR. DELLINGER: No, these would be straight 30 day values.

MR. EYNON: See, I mean, if you only measure 12 days out of the 30.

MR. DELLINGER: No, that's not what I am...what I am saying is, we have used... let's say we have had 12 sets of 30 day averages.

MR. EYNON: Right, okay, that gives you 12 numbers.

MR. DELLINGER: That's right

and we have checked for...

MR. EYNON: Just enough to look at, to examine how many are exceedance.

MR. DELLINGER: And then we have just checked for using parametric procedures and establish variability factors that way.

MR. EYNON: You could do that also, although I think that this method will be stronger because you are using more of the information in the data to actually calculate the autocorrelation.

MR. DELLINGER: You are using each individual data point as opposed to using...

MR. EYNON: Right, rather than combining each...

MR. DELLINGER: ...30 day average.

MR. EYNON: That's a tough question; I think that's true. Yes, we have done...we have our program that does this.

I have been working...if you would like to catch me later and you have your data set on the PA System I can talk to you about maybe our stuff through if you are interested in seeing 30 day numbers based on the stuff; it's not too hard to do.

MR. DELLINGER: Sure.

MR. TELLIARD: Anyone else?

Thank you, Barry.

Our next speaker is from Battelle, Columbus. Jim Brasch is going to talk about something that we haven't utilized too much in this program, but we have skirt it; that is, the Utilization of GC/FT as it relates to Analysis Priority Pollutant.

GC/FT-IR and GCMS: WHICH, WHEN and WHY?

Jim Brasch
Battelle's Columbus Laboratory

MR. BRASCH: Have you ever heard the expression, as confused as the little farm boy who dropped his chewing gum on the floor of the chicken house and didn't know which one to pick up?

I know why I am here; why I, personally, am here. It's because Dale Rushneck called Battelle and he started talking to people and filtered down through the hierarchy. By the time he got down to my level to talk to me, I had been told that I would give a talk on GC/FT-IR if he asked me to. I did respond positively to his request. Let me assure you, if I had had any idea how big he was when I was talking to him, I would have responded much faster.

Now, what continued to puzzle me was, why one GC/FT-IR talk in a GC/MS Symposium? Those

of you attending the Hershey meeting in 1981 saw the same phenomenon; one GC/FT-IR talk in a GC Mass Spec Symposium. It was only last night after an exquisite meal and a delightful glass of wine that it became smashingly clear to me; mass spec ceremonies require the periodic sacrifice of a pristine virgin. Obviously, these qualities require they go outside the mass spec community for their victim. I am complimented by Battelle's recognition that I have these qualities. This is mitigated by the fact that they also, obviously, consider me totally expendable.

Nevertheless, I am here and I want to give you a state of the art status report of GC/FT-IR stressing its complementary nature with GC/MS. How do you do GC/FT-IR? You can obtain one of the earlier generations of the system, such as the DIGILAB instrument, shown in Figure 1, first produced three or four years ago. You can get

one of the later generation, shown in Figure 2, again, a DIGILAB system which is much more cosmetically nice and is configured so the instrument is free for normal operation. All of the major manufacturers produce these now; Nicollet, IBM and Analect. Beckmann and Bowmen are very hard at work on their systems.

You can also do like we did at Battelle where we are faced with two problems; one, the equipment is expensive and sometimes we can't buy it; secondly, we are concerned only with selling the output, we don't have to sell the instrument. So we are somewhat less concerned with aesthetics and cosmetics and you can do as in Figure 3, which shows our interface, the chromatograph and our instrument. What else is required? Nothing particularly profound as diagramed in Figure 4. What you do is just take the infrared beam from your

instrument through the light pipe through which the GC effluent is going. Take the output from an MCT detector and you can get the spectrum that way; nothing particuarly profound. There is a little technology in the light pipe, but it is also not difficult as shown in Figure 5. You just have some way to get the effluent in, traverse it down the pipe and back out. For mid infrared spectroscopy, one generally uses KBR windows. There is a little technology effecting a good seal at the windows and the transfer lines so that you don't lose the sample. You also need to heat the light pipe. This can be done relatively simply as I'll show you in just a moment, but the only other requirement then is some technology in the light pipe coating. I really hesitate to use the word technology; it's absolutely a black art. We make our own light pipes. They are simply precision bore glass tubes that we put a gold coating on

ourselves. Most of the manufacturers are doing the same thing or else they have a sole source of supply. Nothing really profound. It is just difficult to get a really good gold coating on it.

The only other problem then is, how do you heat it? Again, in our system we enclose it with a very simple aluminum block as shown in Figure 6. This is the end of the light pipe here; ours is only about four inches long. So this is relatively compact. We have a heated transfer line here through which we are actually bringing the fused capillary from the GC, routing it over to here so you can get the effluents into the light pipe, traverse it down here, it comes right back through the heated transfer line back over to the FID of the GC. So we get infrared data, and FID traces after it has been through the light pipe; really rather simple.

What do you do with it then and why would I

want to give you a comparision to mass spec? (Figure 7). I want to compare the information content, the speed and ease of operation, the sensitivity, and the chromatographic resolution. I can actually dismiss the last one because when that slide was made the first approaches to doing capillary column work were being made. There was considerable necessity to justify all of the additional work and complexities for the capillary work to show that you did get an improvement in data that was worth the extra trouble.

Now, with the capillary ability, the chromatography is the same. So that has become quite irrelevant. The other three I do want to talk about some more. I will demonstrate this to you by using what I will define only as a "hazardous waste sample." What happened with this was that in our laboratory we did GC/FT-IR on the sample using a packed column.

We also did the capillary column work and this is where we first demonstrated that the additional difficulty was well worth it. A second laboratory was also running capillary GC/FT-IR. At Battelle we also were doing the mass spec on it. Another laboratory, completely independent of all of these was also doing mass spec on it. So we had an excellent cross-check here; from laboratories using mass spec and giving, for all practical purposes, absolutely identical results, and two different laboratories using GC/FT-IR and, while they were not absolutely identical because they did not use exactly the same column, there was no difficulty in correlating the two and seeing that they reproduced each other extremely well.

So we had a very nice cross-check here, not only of the two different techniques,

but the validity of the technique in our laboratory, and outside of our laboratory. What do you get, then? As I mentioned, as the sample traverses the light pipe, in addition to transforming the data and producing a spectrum every second, if there is any absorption above the baseline, the computer also takes a point and stores it to reconstruct a gas chromatograph; a Gram-Schmidt reconstructed gas chromatograph. Then, the effluent goes on to the FID. So, as shown in Figure 8, we have an FID trace where we can check the chromatographic resolution and make sure we haven't degraded that. We also have a reconstructed gas chromatograph based on the infrared data so we can correlate those. I don't know if it is apparent from that slide, but there is very nice correlation there. You have no trouble whatsoever in correlating a GC/FID peak with its corresponding infrared

peak in the data bank.

How does that stack up with the mass spec data? Well, Figure 9 shows the RGC from mass spec (a total ion count RGC) and what you just saw, the RGC from the infrared. Now, there are differences here, but there are also great similarities. The differences are sensitivity differences and I can point out instances where, for example, mass spec saw a rather intense peak that was missing in the infrared. On the other hand there are instances where the converse is true. I don't want to spend too much time on the whys of that; it has to do with the absorbtivity in the infrared which determines whether it is going to see it or not. The major point I want to make is that their differences are complementary.

Again, on that slide I want to make the point that we can correlate these data very well. We have no difficulty in correlating an infrared

peak to a mass spec peak. What sort of data do we get in the infrared? Well, Figure 10 shows three spectra that are pulled out almost at random showing one of the stong peaks, a medium peak, and a very weak peak. The middle region includes strong absorption from CO2, which we do not purge out of our instrument and, indeed, all of the search programs completely obliterate this region in their searches; you do not use this region. You can see that as we get to the very weak peaks we have a much lower signal noise level and this is where we ultimately lose out. If we do not have the discrimination of the signal there we can't get any useful spectrum information. The lower example is an excellent spectrum and this is from one of the very weak peaks in that RGC. What else do we see? We see a lot of structural information, functional group information. I'll mention that one again later.

The software programs that are available are nice, getting nicer, getting faster, getting better all of the time. Figure 11 illustrates some software features. This is a DIGILAB slide, it is not of the data from this hazardous waste sample. I just wanted to show you what you can do with this. The lower trace is a spectrum from a GC run; the other spectra are the results of their search program through their catalog of spectra. They have a HIT index listed.

Now, another thing I wanted to point out; if you get a very low number here, it's an excellent identification, particularly if there is a low first number here and then a wide gap between the others; that is what you call a positive ID. Actually, what I have chosen here, I don't know if you can read that number, but the HIT index ranges from .61 here to .69; this means that the search really wasn't sure what this compound was. It couldn't

discriminate between these four or five candidates. One of the flexibilities you have, you can tell it to look for the top ten, the top five, or another number of your choice. The other point I wanted to make here, that they are all chemically similar. This particular one is an ester; and, while it couldn't identify the particular ester this was, the search program picked out all esters. That is because of the nature of the infrared information that's here; this carbonyl group absorption is specifically characteristic of esters. From this you also could tell that it is not terribly complicated. So all of this information is inherent in the infrared spectrum and even if it doesn't come out positively identified, you will get excellent chemical type information.

Some of the results, now, from the hazardous

waste sample are shown in Figure 12, again, to talk about this complementary nature. Here an X means the compound was positively identified, and zero means the compound type was identified, but not specifically. The mass spec did not see the fluorinated alcohol; the infrared not only saw it, it identified it. Why? Carbon-fluorine stretching vibration is one of the most intense infrared absorbers. So if there is much there, the infrared is going to see it. Other things you might expect: mass spec, certainly cannot discriminate ortho- and para-chlorotoluene; infrared did.

Similar things here are seen in Figure 13. Another isomer, mass spec typed it, infrared identified it. A case where mass spec gave an indentification and infrared didn't even see it; a very weak infrared absorber with very few bands for the infrared to key on. So, again, the complementary nature of the two techniques.

Now, I want to very quickly show Figure 14 where I have more recent tabulations of this data. This summarizes where we are with this particular sample. There were 44 components in the GC FID trace. By the infrared data, we identified specifically 28 of them, and we got information on 15 types. By infrared alone we got good chemical evidence on 43 of the 44 components. Mass spec gave a positive IDS on 13; and good information on 23 compound types; a total of 36.

At this point, now, I want to say something with great caution. This sample was probably optimum to show the value of infrared. We did not chose the sample, however, to demonstrate this point. The sample came in totally blind. We had no idea what is was. It worked out that infrared gave a lot more data than mass spec on this sample. I can suggest some other

samples where the converse would be completely true, namely, long chain hydrocarbons; then, mass spec would shine, infrared would tell you it was hydrocarbons, but it would not give great definitive information. This one happened to work out to show the power of infrared.

Another point I want to make and I cannot emphasize too much. If we combine the two sets of data we see the complementarity even greater; of the 23 compound types identified by mass spec, 19 of them are positively identified by infrared. There were only seven overlaps in here; five of these, GC mass specs identified that infrared did not identify. If we combine these two sets of data, we get useful information on all 44 of them. We would have specific identifications on 33 of the 44. This impresses me. I

think this demonstrates beyond any question that the two together are best. What if you can't do that?

Let's compare them in Figure 15. Sensitivity: the gap is not as great as in the past, and it is getting smaller. But there is no question, if you know what compound you are looking for and where to look for it, infrared will never compete with mass spec on sensitivity. The gap now is certainly one, perhaps as much as three orders of magnitude. Infrared is going to improve and I expect mass spec will also. So I think that ultimate gap is going to remain there.

Ease of operation: the mass spec is better. That gap is closing also, but there is one very important difference. At our laboratories, and I'm sure this is common with other laboratories also, we can bring

a kid with a decent high school education into our mass spec lab and we can have him getting reliable, useful data in a day or two. It is just so well automated, so well software that that is no problem. Infrared GC software is very nice, but it presently requires an experienced spectroscopist to utilize the system and to make sure it is doing what it should be doing. That will obtain for quite awhile because of the different nature of the data, the information that is coming out.

The time element is not that much different now. The software programs for the GC/FT-IR are becoming very fast now and just last week at a Pittsburgh Conference there was some very exciting new developments that are going to make it even faster. So I think that's going to be quite comparable. I've mentioned the chromatography is identical (capillary

column). In fact, there have been several laboratories, including ours that have successfully coupled a GC to an infrared and then onto a mass spec; that is super powerful, but it is going to be a few years before that is routine. Information Content: infrared is the best; no question.

Anaylsis time. Again, they are just about equal now; with the exception, again, that the infrared requires an experienced spectroscopist and there are some manual operations that help you out.

In a pseudo-summary, on Figure 16, if your problem is to detect a specific component and you know exactly where it is, GC mass spec is the way to go. If you want to identify components in an unknown sample, far and away the best thing to do is use both. If you can only use one, you will get more information by GC infrared.

Now, at considerable risk I am going to completely change subjects. The risk is that neither Bill nor Dale knew I would do this and by so doing, I am following a philosophy expressed by a colleague, that if you want to do something, it is almost always easier to obtain forgiveness than it is permission. In a very few minutes I want to give you an abbreviated version of a development first announced publicly only a week ago yesterday at the Pittsburgh Conference.

Ken Shafer has added another important member to the analytical alphabet soup; SFC/FT-IR. He has successfully coupled an FT-IR system to the effluent of a supercritical fluid chromatograph. Why do you want to do that? What is a supercritical fluid? (Figure 17) It is one that is above its critical temperature and pressure. It is neither liquid nor gas. It has properties intermediate. The

one I want to talk about is CO_2 which has a critical temperature of 31 centigrade and at a pressure of about 73 atmospheres.

Why is this important or useful to anybody? (Figure 18) In normal GC you have lots of stationary phases, one mobile phase. In HPLC you have a few stationary phases and many mobile phases. SFC has those intermediate properties. It can use all GLC and HPLC columns. It can use a variety of mobile phases. The one I'll talk about today is CO_2, but pentane, N_2O and the Freons have also been used.

(Figure 19) Common detectors, GC uses, FIDs, HPLC uses UV; SFC can use both of them. I'll show you data to support that. (Figure 20) GC uses temperature programming to get your separation; in HPLC you use solvent programming; SFC you use pressure programming. This is the major difficulty of it, but it's not that hard to do. Figure 21 shows some

separations and the use of two detectors. This is a mixture...of biphenyl, isomers of terphenyl, another phenyl, a triphenyl benzene, and two quaterphenyls. These are highly condensed ring compounds. The separation here is very good and what you see slightly displaced here is a UV trace followed then later on by an FID trace (indicating). So you have both detectors it's possible to use and you see here the separation of these isomers and some condensed ring compounds of relatively high molecular weight.

This is one of the more exciting avenues for this is, in the separation of higher molecular weight compounds. But I want to show you today that it can also be used for low molecular weight materials that you would be interested in. Some other considerations in interfacing FT-IR with various chromatographies are shown in Figure 22.

In GC/FT-IR, you use a light pipe with a volume as you would like to have it, the exact volume of the peak that is coming out. In HPLC you either have to get rid of the solvent or you have to use a flow through cell that is much, much less than the volume of the peak; and, one of the major handicaps of HPLC/FT-IR is this problem right here (indicating). With SFC you can use a flow cell with the volume equal to or greater than the peak width. What I'll talk about is using CO_2 as the mobile phase. You can eliminate the solvent much more easily than you can with HPLC, but with infrared you don't need to. CO_2 is a beautiful infrared solvent.

Figure 23 is the spectrum, a transmission single beam spectrum of CO_2; this band about 2400 wave numbers. There is another strong bend out here about 3600; this is a

little unfortunate because you would like to look at some alcohols out here, but the only thing that ever shows up in the 2400cm-1 region is a few nitriles, C=N compounds, and you don't see those very often; otherwise, it is an absolutely beautiful solvent. This cut off here was caused by the C_2F_2 window of the cell, the only one that he had at this moment that would take this pressure. CO_2 remains a very good solvent on for several hundred wavenumbers.

Now, the only problem with it, it shows changes with pressure as shown in Figure 24. This is a relatively low pressure and at a higher pressure you see some other bands coming out here because of a Fermi resonance interaction. This is very easy, you can just program your computer to use a particular background of whatever pressure you are at

and these will substract out. It handicaps your sensitivity here a little bit, but that can be handled by the software quite nicely. So it is a very good infrared solvent.

How do you do it? (Figure 25) You have a Varian syringe pump for HPLC that nobody wanted. Hooked up the CO_2 tank to it, a simple pressure controler, through a preheating coil and a valve loop injector into the conventional gas chromatograph with a conventional capillary column, went through the UV detector; and, that's another neat thing. All he did was run the capillary all of the way through here and just scratch off the outer coating and actually do the UV detection directly in the capillary. Then went to this FT-IR (in this case it was one of the small, low cost Analect systems) and on beyond that to the FID. So you had the UV detection here, the IR detection here, and the FID detection

here (indicating); a very powerful combination.

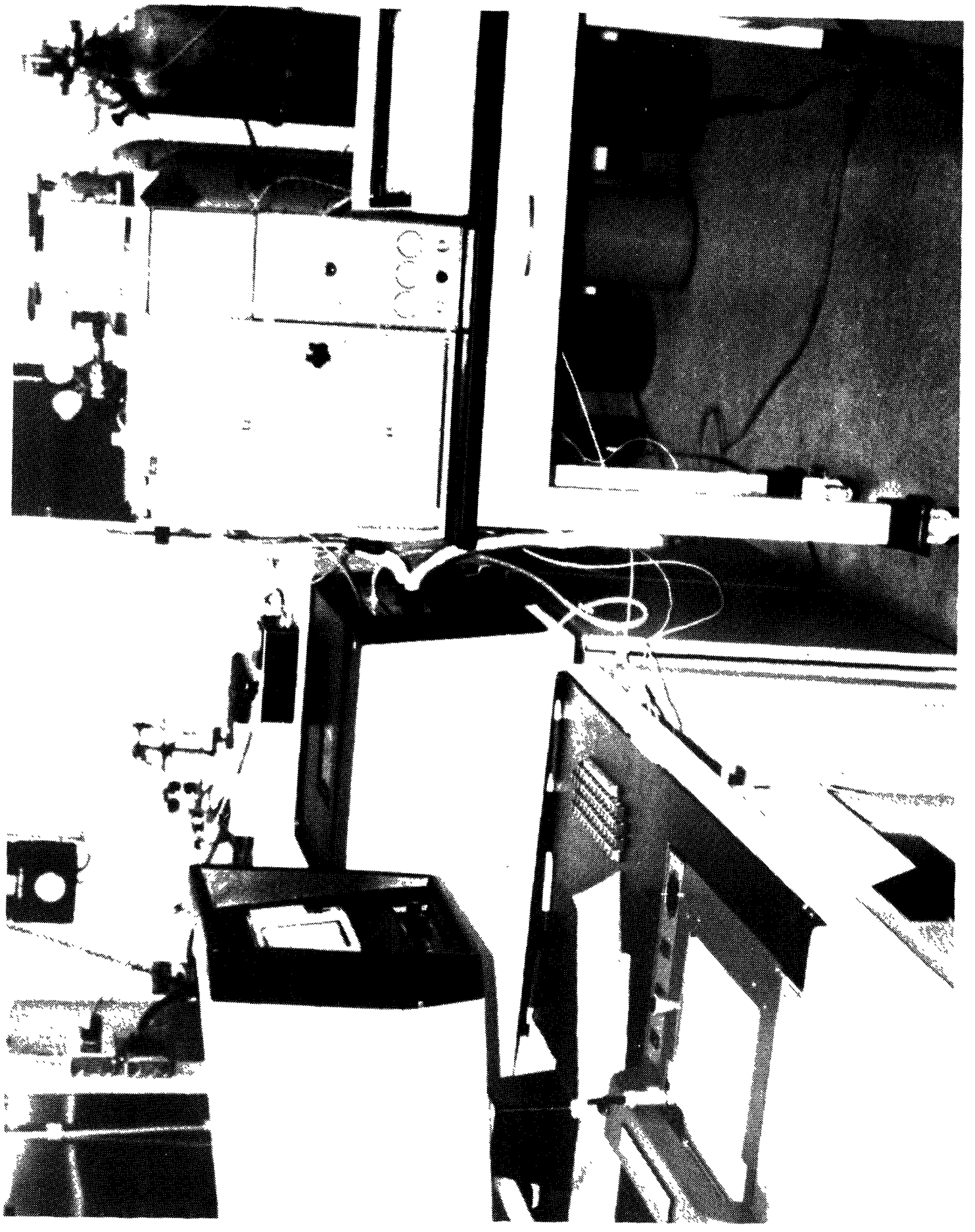
Did he get data? Well, Figure 26 shows the chromatography on it. This is a mixture of anisole, acetophenone and nitrobenzene. You see the differing sensitivities of the two different detectors, the UV detector here, the FID here, the solvent peak from the chloroform and the separation of those three materials. Figure 27 shows the spectra he obtained, anisole, acetophenone and nitrobenzene (indicating).

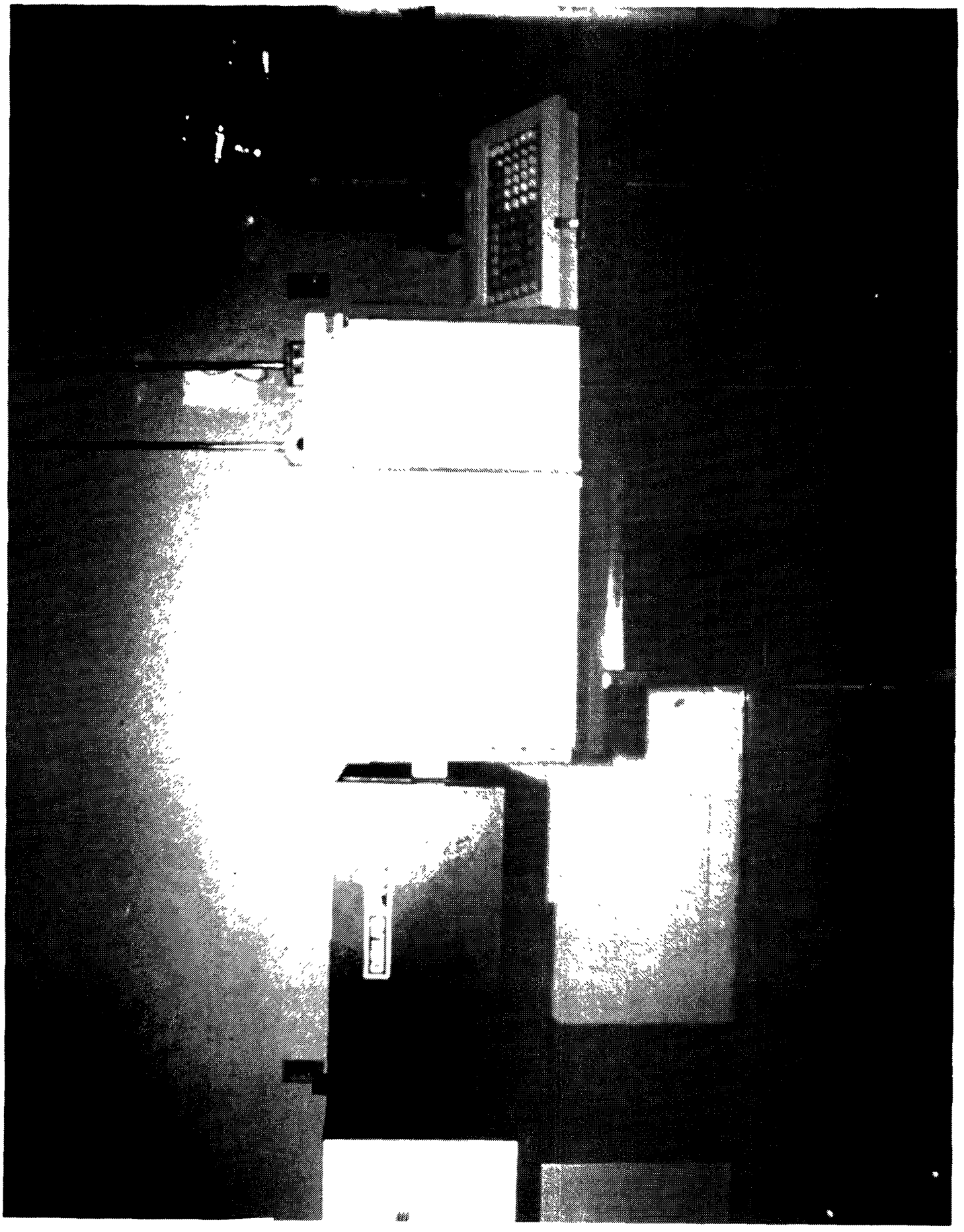
This is brand new. The slides were still wet when Ken reported it at the Pittsburgh meeting last week. So these data are about two weeks old. The first public report is a week and one day old; it is very exciting. So in overall summary, then, GC/MS or GC/FT-IR. Which and when are a matrix into which are factored the nature of the sample, the information you need, and the differing selectivities, specificities, and sensitivities of the two

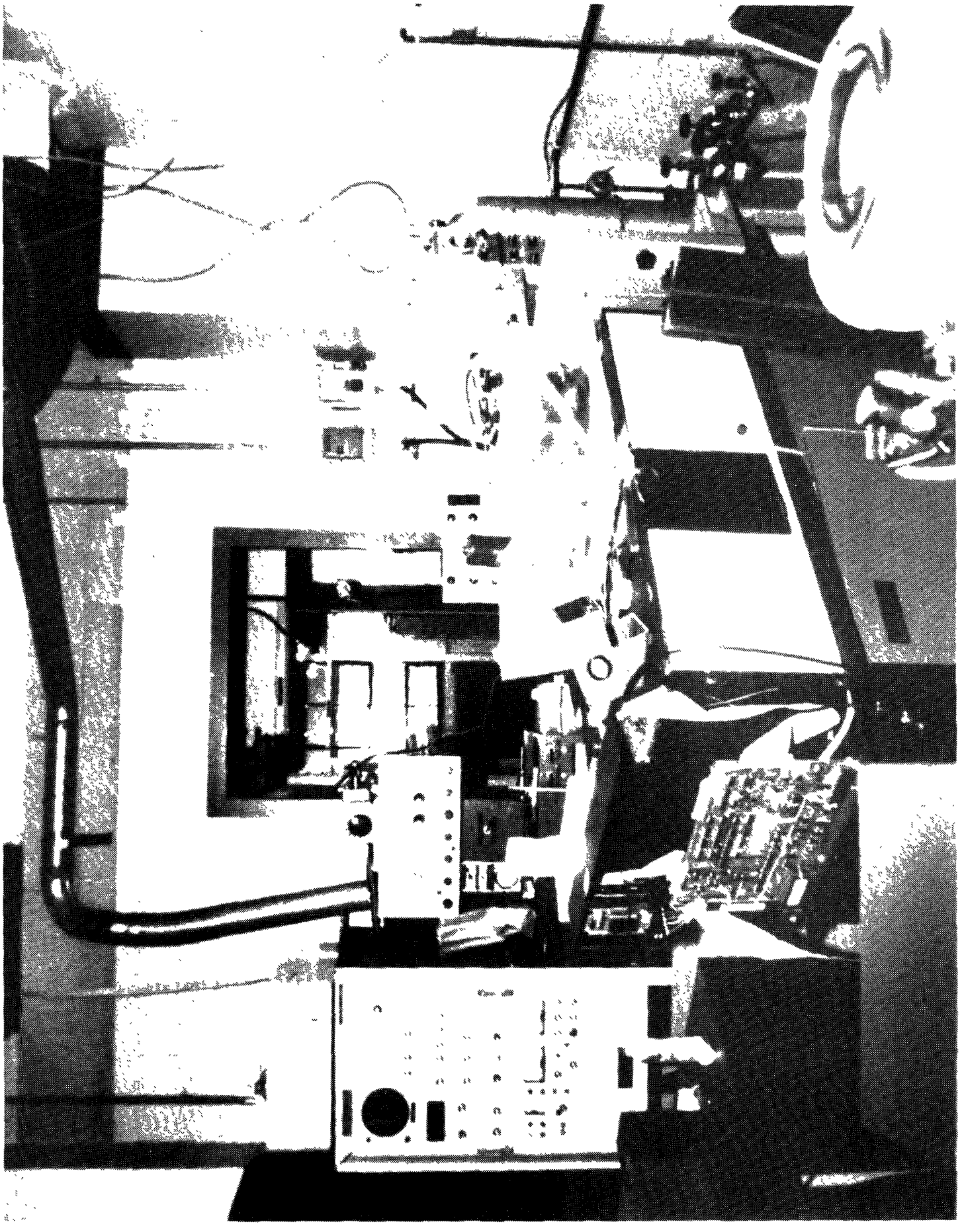
techniques. Why? Because the complementary nature of these techniques effects a synergism such that the whole is substantially greater than the sum of the parts.

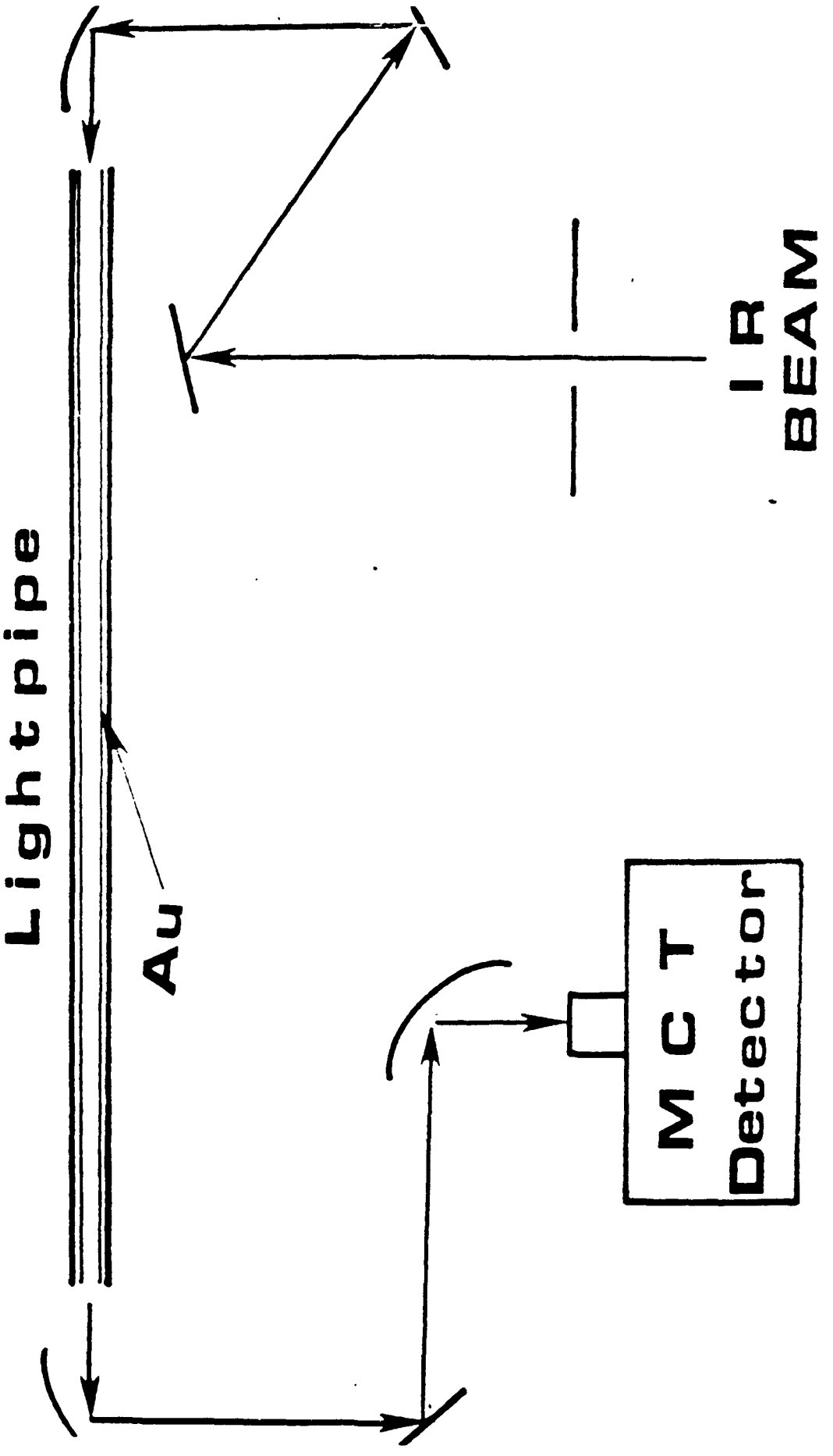
Last, but very far from least, SFC/FT-IR has been accomplished. Its potential is truly exciting because the chromatography is exceptionally versatile and the spectroscopy is relatively simple. That potential is further enhanced by earlier but still recent demonstrations of SFC/MS. The very same complementary nature I have stressed today will be evidenced in this new field. With this I have now fulfilled my commitment to Battelle and I dutifully submit myself to the remainder of the ceremony, whether this be the leap into the flaming volcano; or maybe questions. Thank you.

MR. TELLIARD: Any questions?





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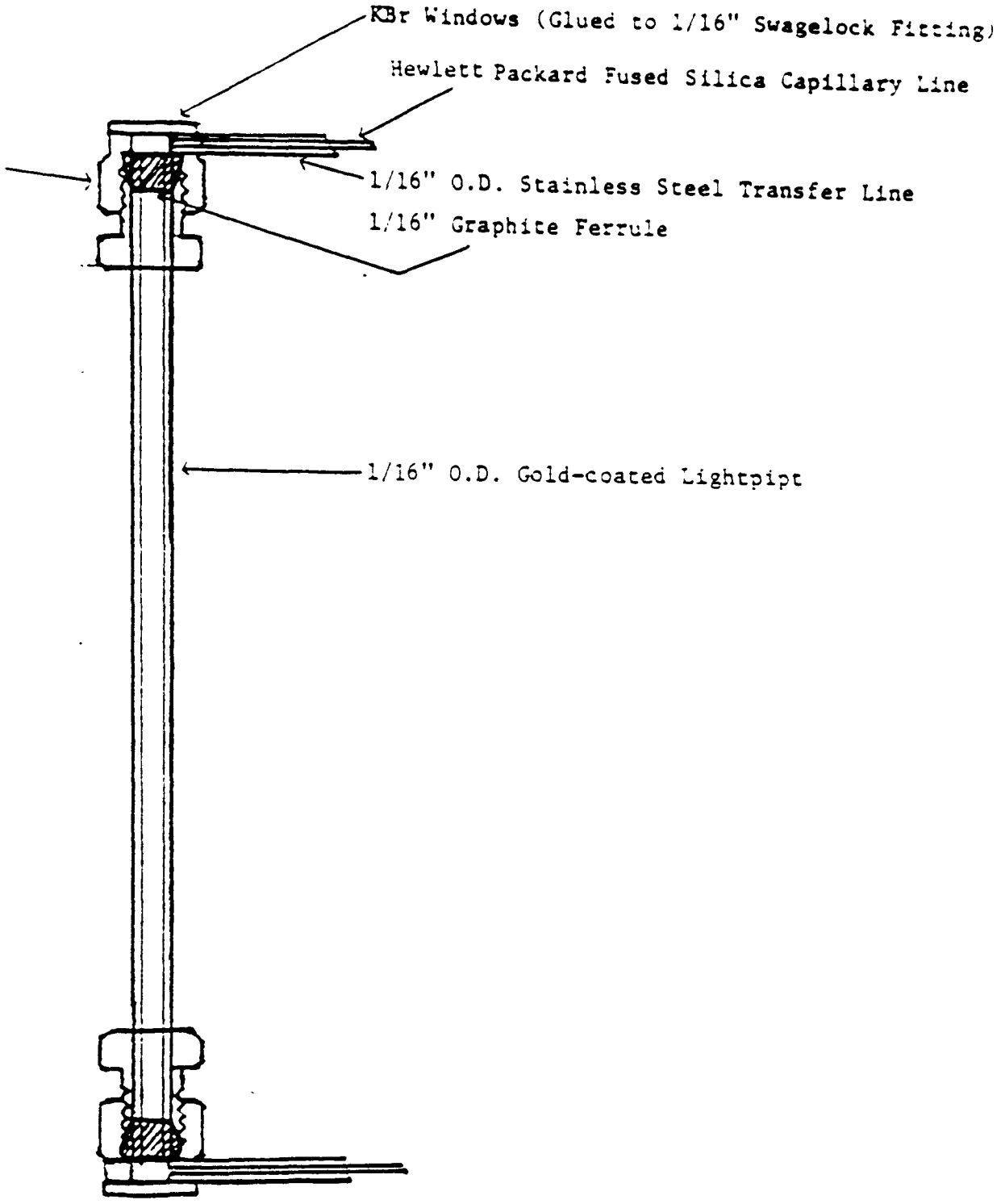
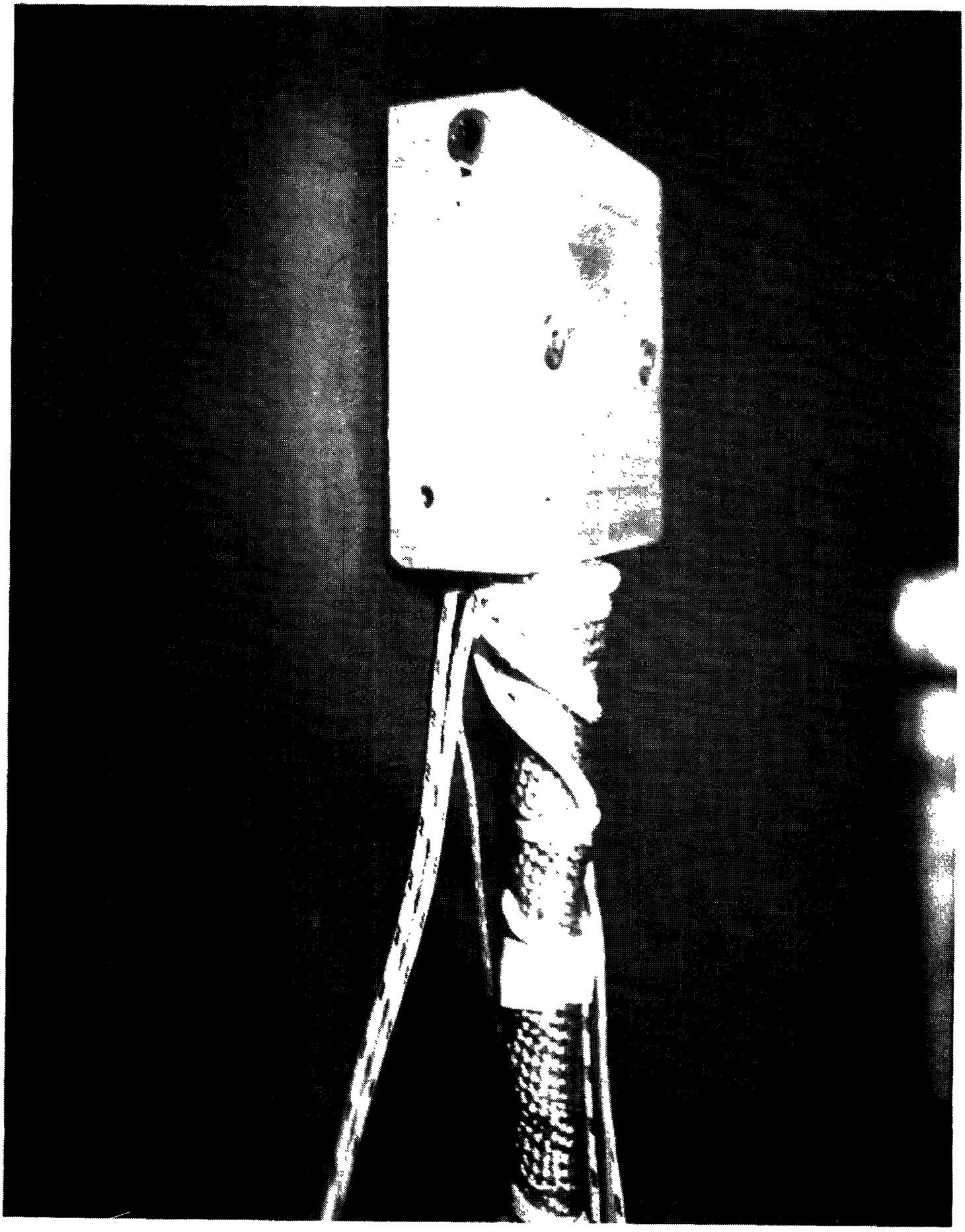
IR
BEAM
MCT
Detector



IGURE 1. DIAGRAM OF 1/16' LIGHTPIPE AND FITTINGS



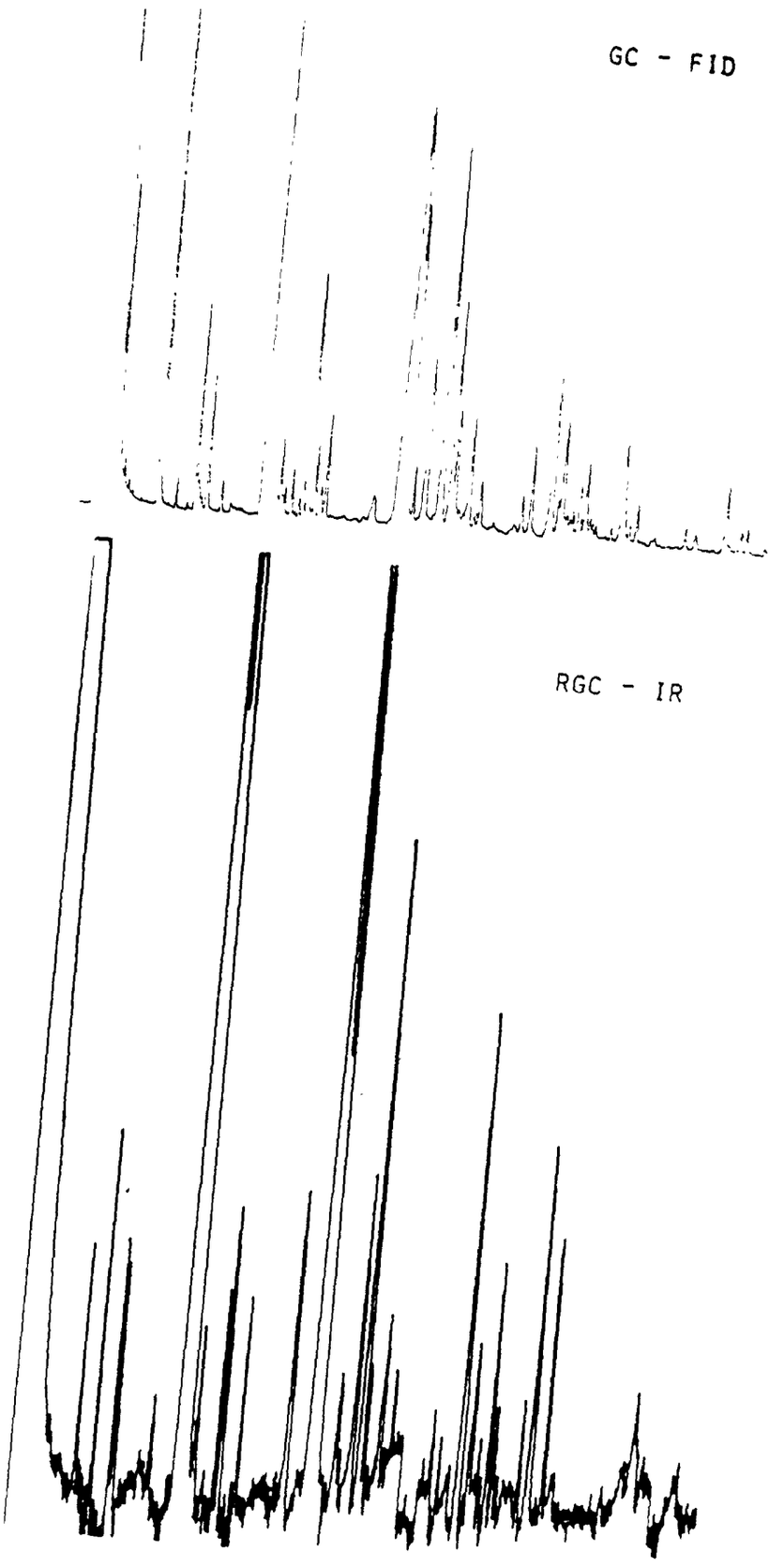
POINTS OF COMPARISON

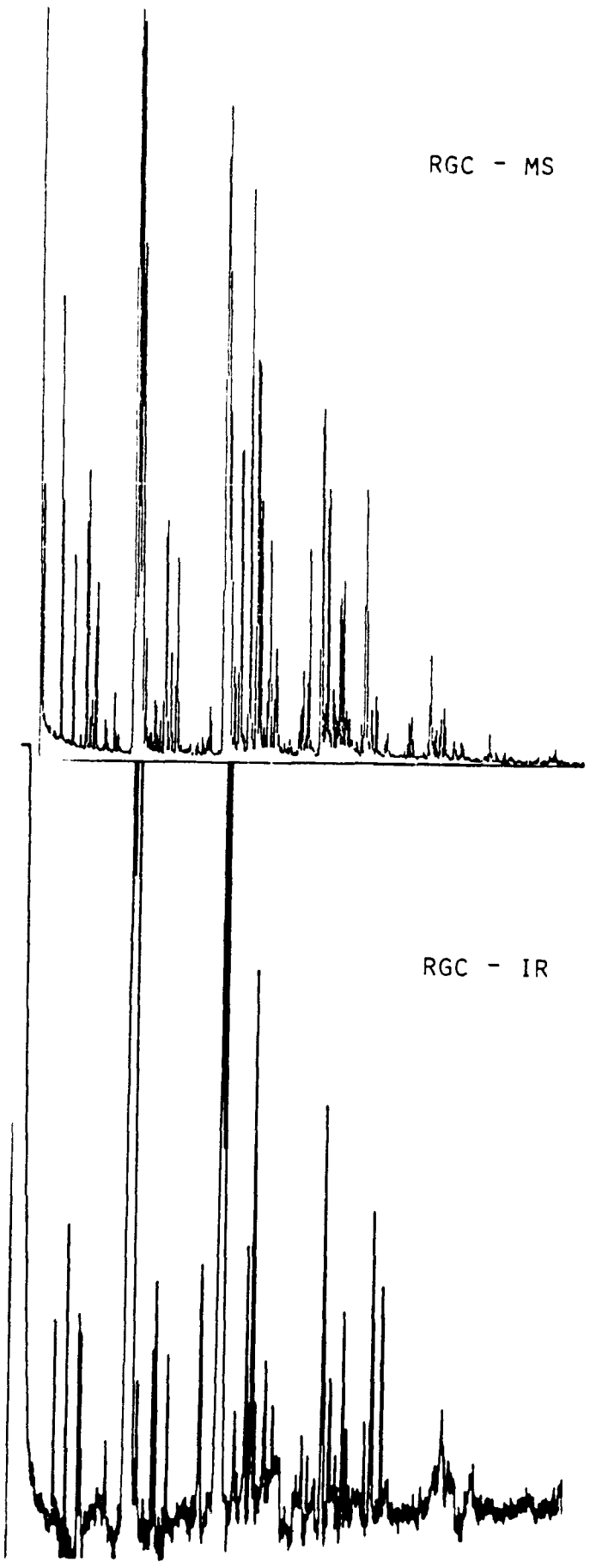
INFORMATION CONTENT

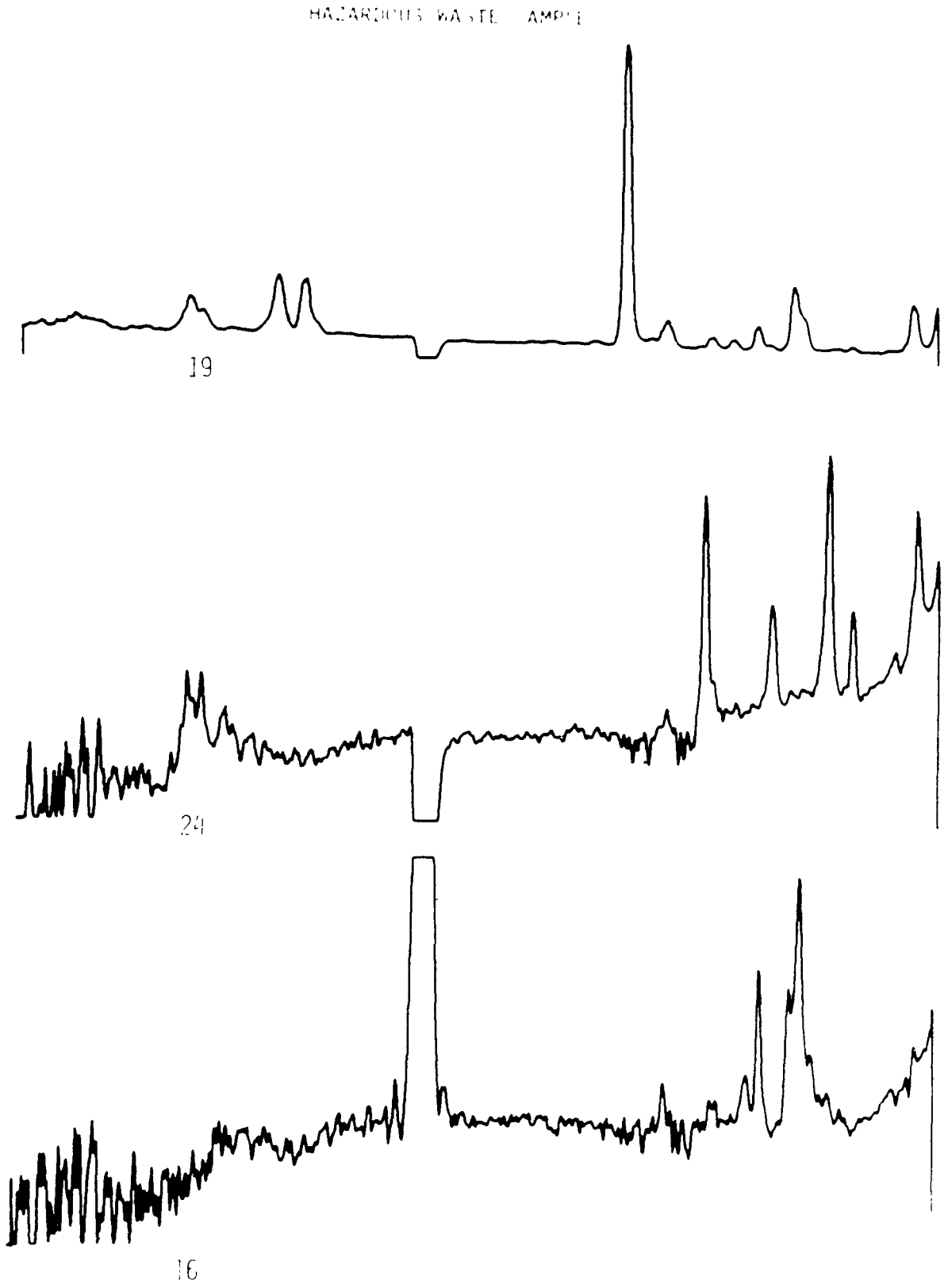
SPEED AND EASE OF OPERATION

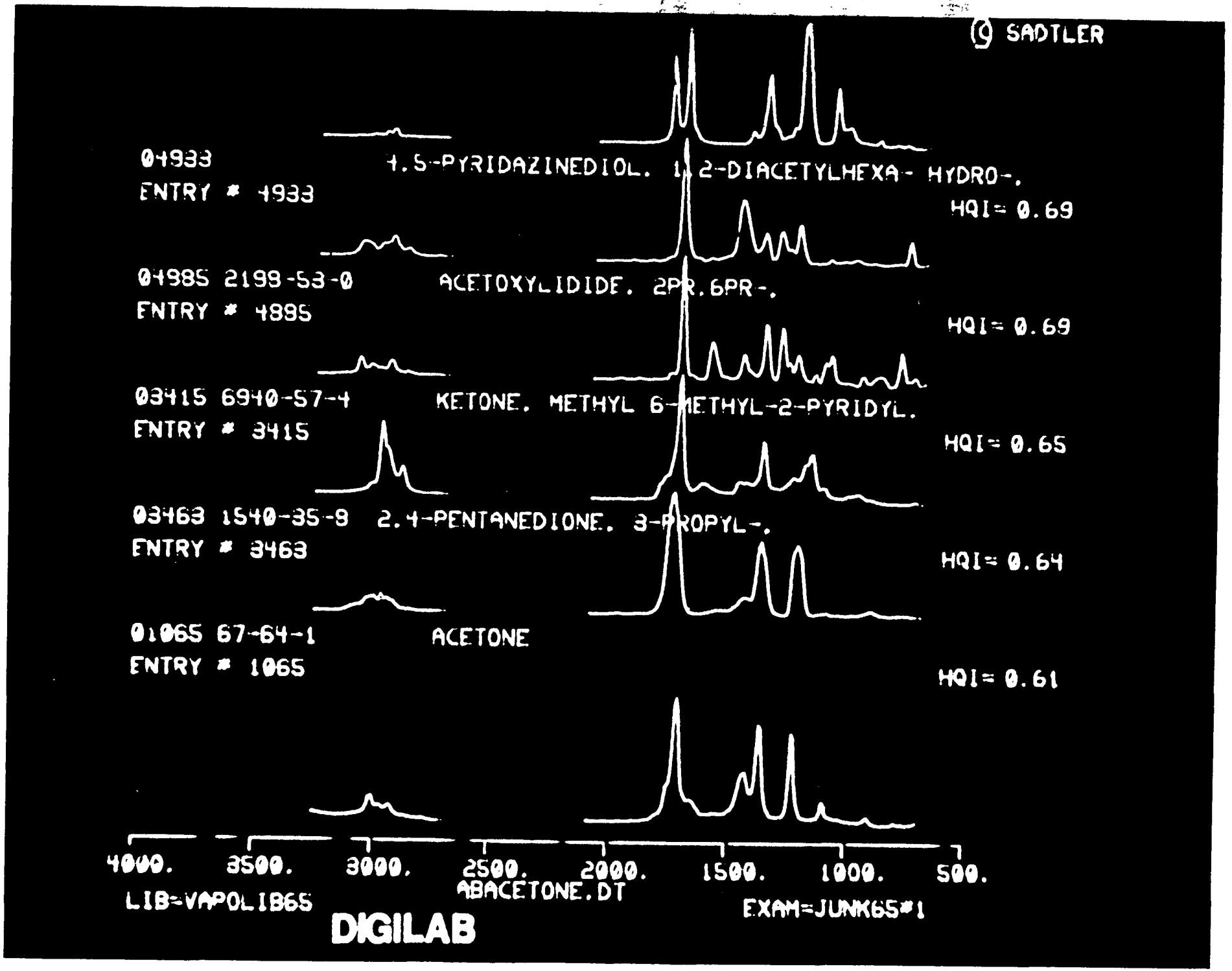
SENSITIVITY

CHROMATOGRAPHIC RESOLUTION


GC - FID
RGC - IR


RGC - MS
RGC - IR


HAZARDOUS WASTE AMPLE
19
24
16


© SADTLER
04933
ENTRY # 4933
4,5-PYRIDAZINEDIOL, 1,2-DIACETYLHEXA- HYDRO-.
HQI= 0.69
04985 2198-53-0
ENTRY # 4895
ACETOXYLIDIDE, 2PR.6PR-.
HQI= 0.69
03415 6940-57-4
ENTRY # 3415
KETONE, METHYL 6-METHYL-2-PYRIDYL.
HQI= 0.65
03463 1540-35-9
ENTRY # 3463
2,4-PENTANEDIONE, 3-PROPYL-.
HQI= 0.64
01065 67-64-1
ENTRY # 1065
ACETONE
HQI= 0.61
4000. 3500. 3000. 2500. 2000. 1500. 1000. 500.
LIB=VAPOLIB65
ABACETONE.DT
EXAM=JUNK65#1
DIGILAB

HAZARDOUS WASTE SAMPLE
CAPILLARY GC/IR AND GC/MS

COMPOUND	GC/IR	GC/MS
TETRACHLOROETHYLENE	X	X
CHLOROBENZENE	X	X
M-XYLENE, HEXAFLUORO	X	X
M-XYLENE	X	X
FLUORINATED ALCOHOL	X	
O-CHLOROTOLUENE	X	O
P-CHLOROTOLUENE	X	O
CYCLOALKANE	X	
α-CHLOROTOLUENE	X	O

X = COMPOUND IDENTIFIED ; O = COMPOUND TYPE IDENTIFIED

HAZARDOUS WASTE SAMPLE
CAPILLARY GC/IR AND GC/MS

COMPOUND	GC/IR	GC/MS
P-CHLOROBENZALDEHYDE	X	O
P-SUBSTITUTED ALDEHYDE	X	
2,4-DICHLOROTOLUENE	X	O
2,6-DICHLOROTOLUENE	X	O
CYCLOPENTANE	X	
3,4-DICHLOROTOLUENE	X	O
BICYCLOHEPTANE		X
1,2,4-TRICHLOROBENZENE	X	O

X = COMPOUND IDENTIFIED ; O = COMPOUND TYPE IDENTIFIED

RESULTS WITH
HAZARDOUS WASTE SAMPLE

44 COMPONENTS (GC-FID)

METHOD USED	SPECIFIC ID'S	COMPOUND TYPES
GC/IR	28	15
GC/MS	13	23

COMBINED DATA SETS
33 SPECIFIC ID'S

11 COMPOUND TYPES

COMPARISON OF GC/IR AND GC/MS

Comparison Point	GC/IR	GC/MS
Sensitivity		+
Ease of operation		+
Chromatography	=	=
Information content	+	
Analysis time	=	=

COMPARISON OF GC/IR AND GC/MS BY TYPE OF ANALYSIS

	GC/IR	GC/MS
DETECTION OF SPECIFIC COMPONENTS		+
IDENTIFICATION OF COMPONENTS OF UNKNOWN SAMPLE	++	+

SUPERCRITICAL FLUID: SUBSTANCE ABOVE CRITICAL TEMPERATURE AND PRESSURE

PROPERTIES INTERMEDIATE BETWEEN GAS AND LIQUID

LOW VISCOSITY, HIGH DIFFUSIVITY

GOOD SOLVENT FOR HIGH M.W. MATERIALS

FOR CO_2 $T_c = 31.3°C$

$P_c = 72.9$ ATM

SELECTIVITY

	Stationary Phases	Mobile Phases
GC	MANY	ONE
HPLC	A FEW	MANY
SFC	ALL GC & HPLC Columns	CO_2 Pentane N_2O Freons

COMMON DETECTORS

GC : FLAME IONIZATION (FID)

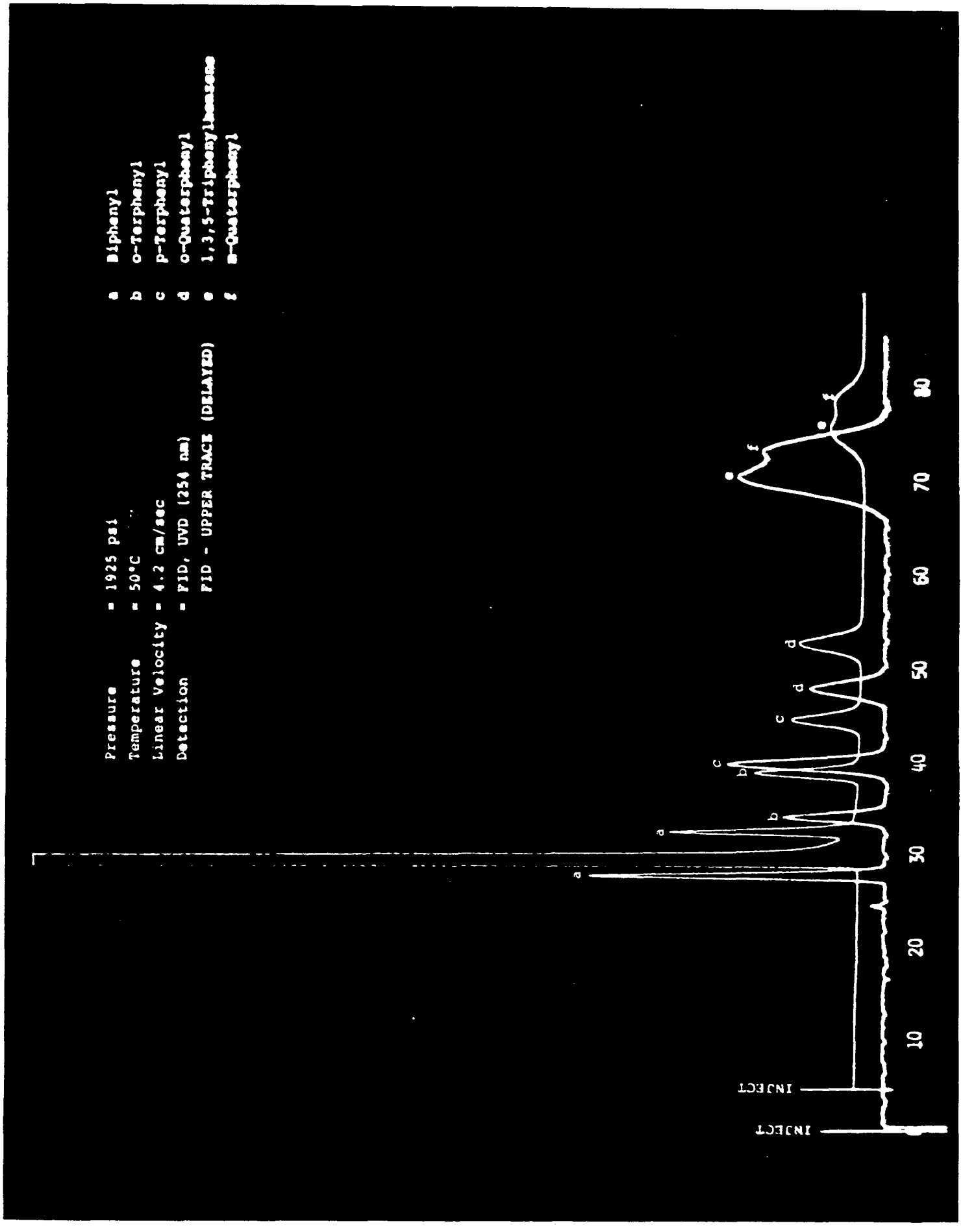
HPLC : ULTRAVIOLET (UVD)

SFC : FID AND UVD

GC : TEMPERATURE PROGRAMMING

HPLC : SOLVENT PROGRAMMING

SFC : PRESSURE PROGRAMMING

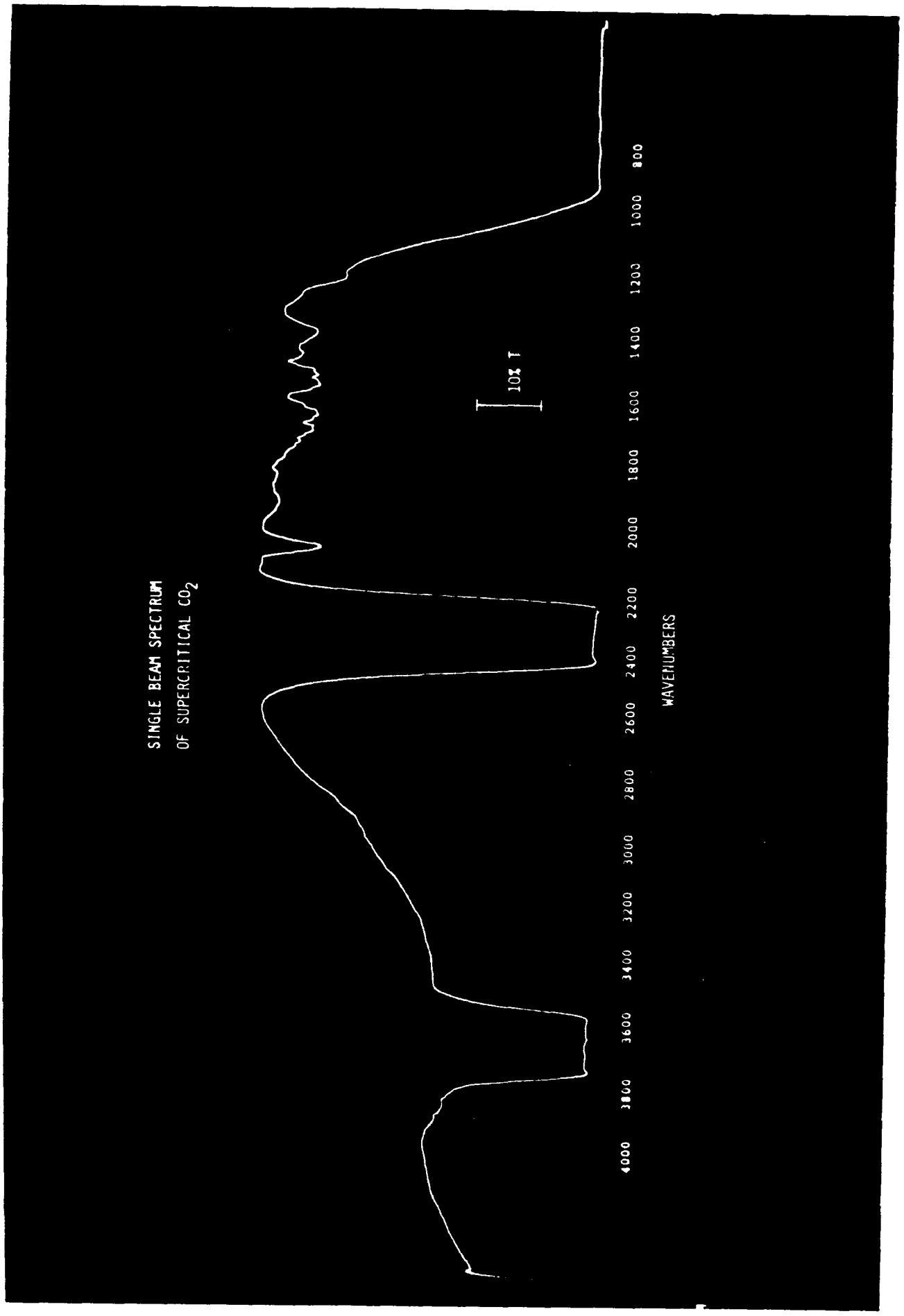

Pressure = 1925 psi
Temperature = 50°C
Linear Velocity = 4.2 cm/sec
Detection = FID, UVD (254 nm)
FID - UPPER TRACE (DELAYED)
a Biphenyl
b o-Terphenyl
c p-Terphenyl
d o-Quaterphenyl
e 1,3,5-Triphenylbenzene
f p-Quaterphenyl
INJECT
INJECT
10
20
30
40
50
60
70
80

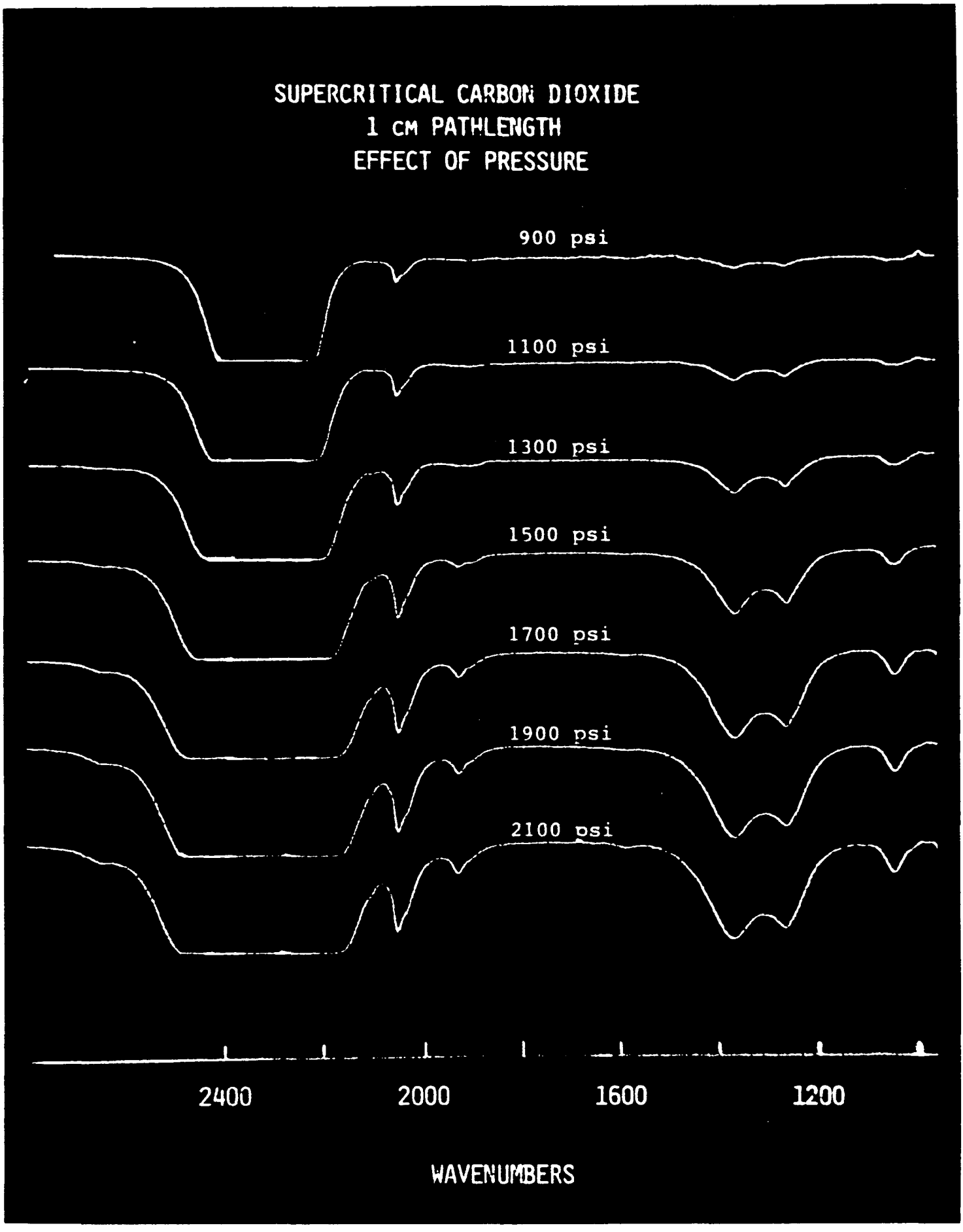
CHROMATOGRAPHY/FT-IR

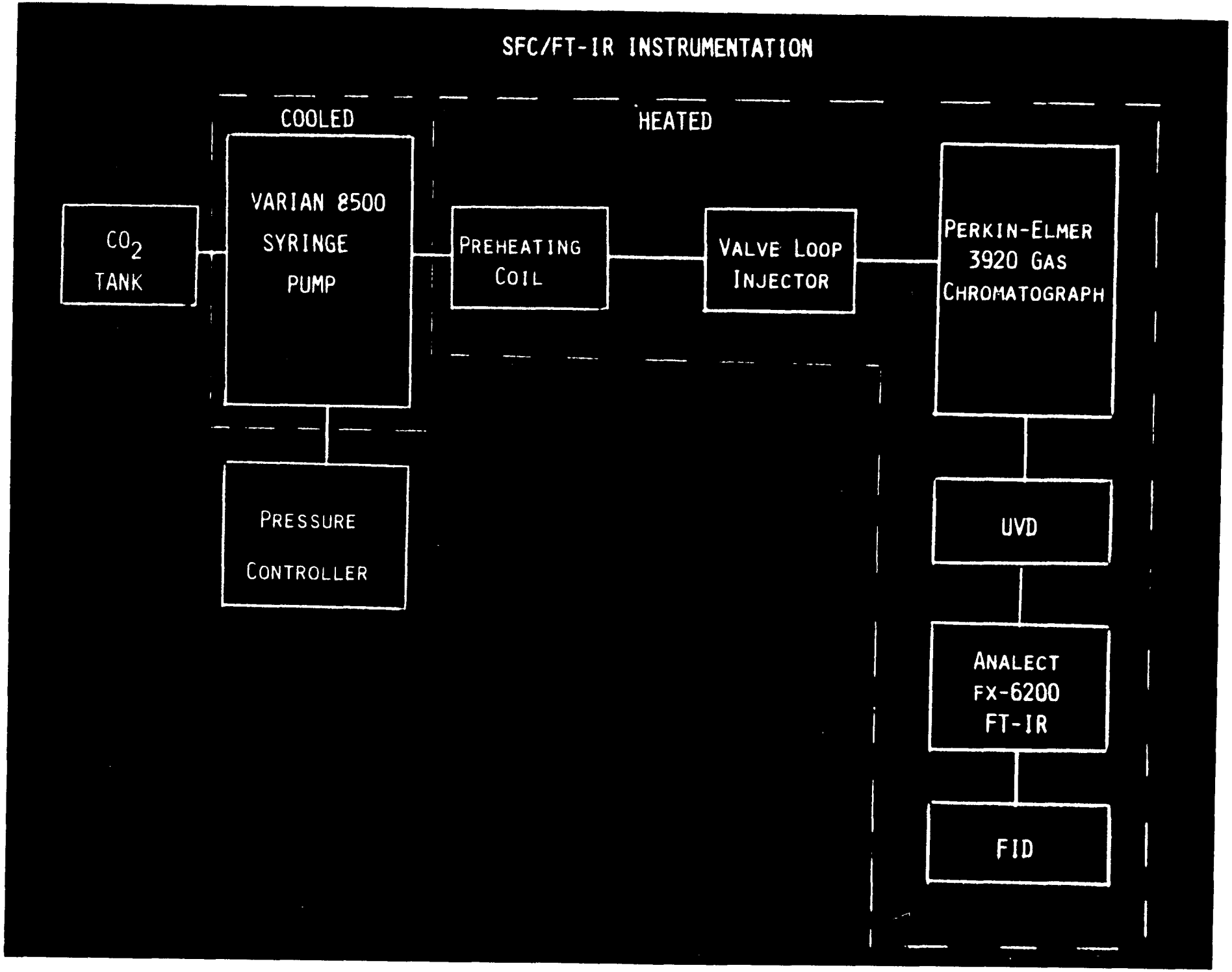
GC : LIGHTPIPE WITH $V_{CELL} \sim$ FWHH

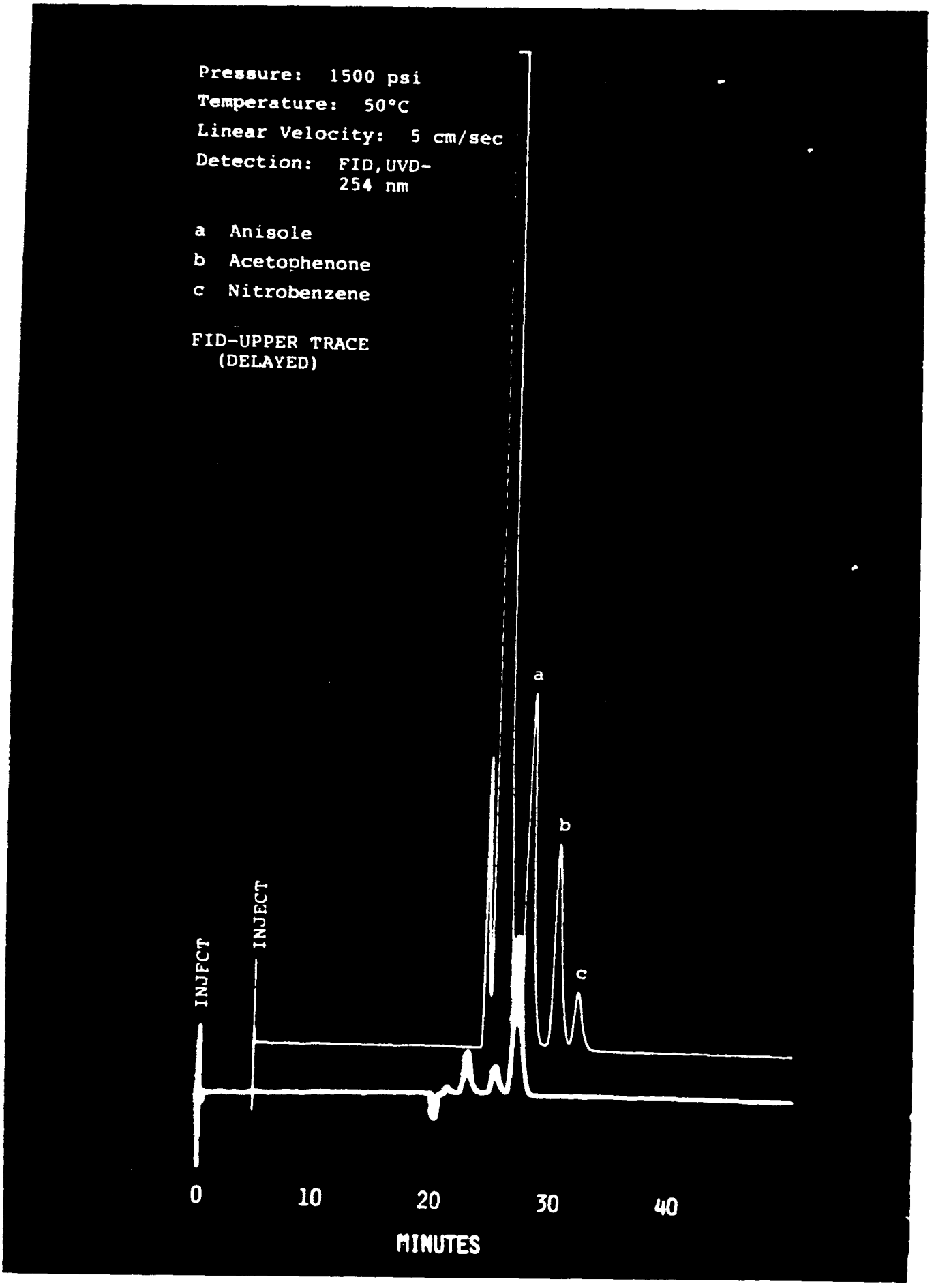
HPLC : FLOW CELL WITH $V_{CELL} << FWHH$
SOLVENT ELIMINATION

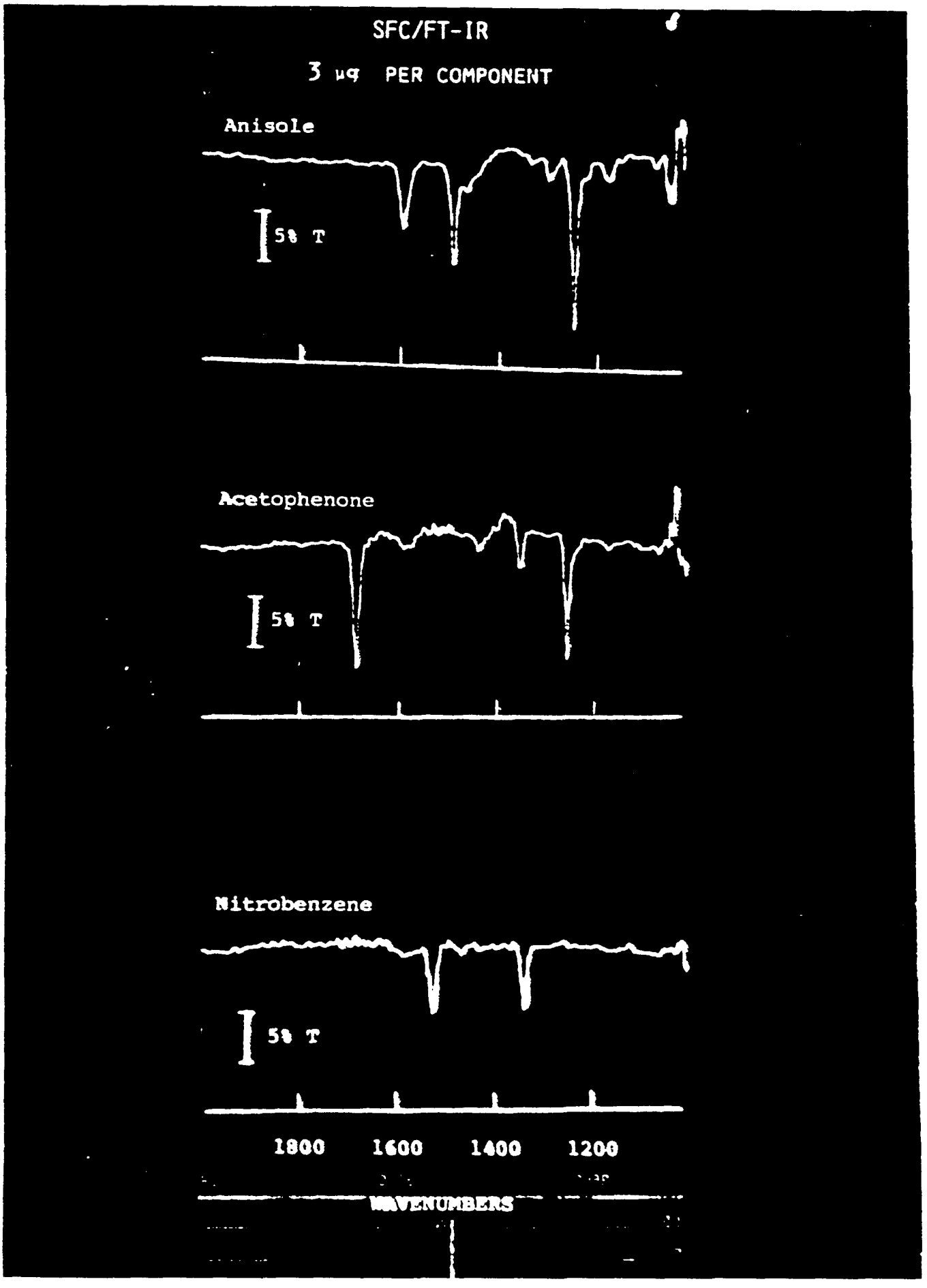
SFC : FLOW CELL WITH $V_{CELL} \leq$ FWHH WITH CO_2
SOLVENT ELIMINATION


SINGLE BEAM SPECTRUM
OF SUPERCRITICAL CO_2
10% T
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
WAVENUMBERS


SUPERCRITICAL CARBON DIOXIDE
1 cm PATHLENGTH
EFFECT OF PRESSURE
900 psi
1100 psi
1300 psi
1500 psi
1700 psi
1900 psi
2100 psi
2400
2000
1600
1200
WAVENUMBERS


SFC/FT-IR INSTRUMENTATION
COOLED
HEATED
CO_2 TANK
VARIAN 8500 SYRINGE PUMP
PREHEATING COIL
VALVE LOOP INJECTOR
PERKIN-ELMER 3920 GAS CHROMATOGRAPH
PRESSURE CONTROLLER
UVD
ANALECT FX-6200 FT-IR
FID


Pressure: 1500 psi
Temperature: 50°C
Linear Velocity: 5 cm/sec
Detection: FID, UVD-254 nm
a Anisole
b Acetophenone
c Nitrobenzene
FID-UPPER TRACE (DELAYED)
INJECT
INJECT
a
b
c
0
10
20
30
40
MINUTES


SFC/FT-IR
3 µg PER COMPONENT
Anisole
5% T
Acetophenone
5% T
Nitrobenzene
5% T
1800
1600
1400
1200
WAVENUMBERS

QUESTIONS AND ANSWERS

DR. VINCENT: Frank Vincent, James River Corporation. That was a fasinating presentation. I never heard of either one of these methods before. Are you talking about a precision bore glass tube, gold coated? I would assume that the interior surface has to be pretty smooth or you get so much breakup of the beam that you don't really get much energy out the other end.

Also, I was wondering about the gold coating. Is this something that is relatively simple to get done?

MR. BRASCH: The answer to the first is, yes, it must be quite smooth; and, the answer to the second is, yes, in the sense that the procedure itself is quite simple. It simple. It is just a solution that is poured into the tube to coat it and then it is heated.

The technology, or the "black art," comes in how to get the right thickness and the heating rate, to get uniformity of the coating. And that is, just from my point of view, a black art. There is nothing profound or difficult to it at all. It is used in many laboratories; but, it is just that there is an art to it.

DR. VINCENT: This was done at Battelle rather than some...

MR. BRASCH: Yes.

DR. VINCENT: So it is basically...it is something like silvering a doer flask, except, apparently, somewhat more critical in the way you handle it?

MR. BRASCH: Yes, very much so.

DR. VINCENT: Is the coating critical? The amount of coating and the amount of gold on the tube?

MR. BRASCH: I cannot give you an answer, only that there is a lot of work

going on on geometries and different coatings. If there is a critical thickness, it must not be too thick; an interesting phenomenon that the physicist understands, but I don't. It must be relatively thin, but not transparent.

DR. VINCENT: Thank you.

MR. TELLIARD: Anyone else?

For the presenters, for the proceedings we would like to have copies of your slides or your overheads; if you could supply us with xeroxes of them so that we can incorporate them. Otherwise, these two ladies up front here will come after you, that may not be bad. It wasn't a very good threat; sorry.

Our next speaker is Drew Sauter from EMSIL-Las Vegas. Now, that we have all mastered the use of a mass spectrometer, why not put them in tandem. If one is good probably more is better, is that true; you will see. Drew, come on up.

RAPID ORGANIC ANALYTICAL METHODS DEVELOPMENT, THE TRIPLE QUADRUPOLE MASS SPECTROMETRY POTENTIAL

Andrew Sauter
U.S. Environmental Protection Agency
EMSIL-Las Vegas

MR. SAUTER: May I have the first slide, please. The original work for Triple Quadrupole Mass Spectrometry that was funded within the agency was done out of the Athens Laboratory.

The Triple Quadrupole, was sold to the agency because supposedly one could reduce sample work-up. What I hope to do today is give some idea of the analytical utility of the instrument, hitting probably too many areas and to demonstrate why we feel that it does have great utility to the hazardous waste programs and I think in many specific areas to Effluent Guidelines or Priority Pollutant type programs.

Just last year in Analytical Chemistry, Burlingame said what is on that particular slide

and I think that's effectively true. Hopefully, what we will do today is give you an idea from about five or six areas why we think the Triple Quadrupole does have some great potential and, hopefully, demonstrate a little bit about it.

The ion optical train of a Triple Quadrupole is shown on this slide. There are three Quadrupoles, you might focus on that. The first one can be used to select and/or scan. The second Quadrupole is the collision chamber where the ions can be made to undergo collision-induced dissociation, generally in the range of a few volts. The instrument that we currently have, which, by the way, is a Finnigan Triple Quadrupole Mass Spectrometer. The third mass filter can be scanned and/or set at a given mass depending on the configuration. Alternatively, quadrupole one and quadrupole three can be offset...both scaned and offset, give characteristic neutral loss or gain.

So we have a variety of options with the instrument. Now, one of the things that most people did when they discussed the analytical utility, the potential of the Triple Quadrupole, they resolutely ignored both source introduction problems and problems which might occur from introductions of large volumes of material due to...for example, problems with source saturation which are found in all types of mass spectroscopy. So you can see that there is a fairly complex set of choices that one could have and what I'll do is take a few of these configurations today and try to give you an example of why we think the instrument is useful.

We have published in analytical chemistry in January a comparison of response factors from GC/MS, GC/MS/MS and compared those values. This comparison I think firmly establishes that one should be able to attain quantitative data out of such instruments which is effectively

identical to good GC/MS work. Peter Dawson, who is probably the most well-known gentleman in ion optics of Quadrupoles has described the ion optics of Triple Quadrupoles as complex. I submit that we should take his word there. So such observations are not trivial and are of some practical utility.

One does not buy a Triple Quadrupole to do GC/MS. One would like to be able to do other things and because the instrument costs approximately $350,000, one would like to be able to do a lot of other things.

This is a view of the Triple Quadrupole and you will note that in the front of the instrument is a moving belt, LC/MS interface. While this is a mechanically crude device, one can use this device to rapidly introduce samples into the ionization region and then perform a variety of different experiments. We have been doing this with a variety of samples and mixtures

and we believe that it will find great utility, perhaps in screening analysis.

Let me move on. By simply placing in this crude fashion, an extract on the belt, for example, neat transformer oils; One can screen for a variety of different compounds. One can also do that fairly quickly. This slide shows 25 determinations of Aroclor 1260; it is essentially a single level precision study that was done in slightly over 1,000 seconds. There are 25 measurements of Aroclor 1260 at 50 nanograms.

The precision, including all data there, was approximately...16 percent relative standard deviation and if you will allow me to throw three outliers, the RSD improves to 12 percent. This is a total ion current plot of a negative daughter ion experiment introducing standards of Aroclor 1260 into the ion source.

The next slide shows triplicate analyses of Aroclor 1260 from five to 100 nanograms per microliter and with the subsequent analyses of eight transformer oils in triplicate. These particular transformer oils were diluted by, I believe, a factor of two because the chlorinated biphenyls identified in these samples were found in the relatively high concentrations. In 27 minutes there were three times eight plus five times three determinations of Aroclor 1260. The ionization mode was methane chemical ionization at approximately one turn. We were doing negative parent ion scanning and it's obvious that analyses at this rate, is of considerable utility for a couple of reasons.

Most of the environmental measurements that are made, are made on one sample. They are not made in triplicate. It would be nice to have triplicate measurements to examine sample related precision. This is a multi-level calibration

curve of Arocolor 1260 using negative parent ion with methane at .94 in argon of approximately .5 millitons.

Again, the methane is utilized to create negative ion which are, in this case, then selected and undergo induced dissociation in Q2 creating ion current which is sensed at the multiplier. This is an example of a calibration curve that we can currently get now and such determinations can be done in the order of minutes. We think that is also useful.

This is a complex sample workup scheme that was utilized to obtain the data in the previous slide. Essentially, the transformer oils have been taken out of the vial and placed directly on the belt. We have done this probably eight or nine different times for the course of approximately an hour, demonstrating that, in fact, the system can take the abuse of direct complex, mixture analyses of chlorinated

biphenyls in transformer oils. The fact that the LC/MS Interface tends to throw away quite a bit of the material itself is the reason this system works. We gain back the sensitivity lost in that we are using negative ions.

So using this introduction technique one would take transformer oil and place it directly on the belt. A normal negative ion Q3 mass spectra produces a complex mass spectrum. Taking the same sample under the same ionization and introduction conditions and doing a negative parent ion scanning for the same sample, this is the resulting spectrum.

Most of the ion clusters are related to the formation of molecular anions of chlorinated biphenyls. The nice thing about this type of detection technique is, it takes a complex mixture, chlorinated biphenyls, and makes it simple. That is, I believe, of regulatory interest. One would not want to use this type of technique

if one was trying to study metabolism of given isomers, but for making regulatory decisions I think it is a valuable approach. Aroclor 1260 standard run under the identical conditions there are shown. So they are quite similar; in fact, Aroclor 1260, 1254, 1248 and 1242 and perhaps 1232 can be differentiated. The mixture mass spectra of negative parent ion scanning mode is unique. That is not to say that we could differentiate mixtures of those given mixtures, but under such analyses conditions we seem to be able to unequivocally determine that there are, in fact, molecular anions containing chlorine of the molecular weight which coincides with chlorinated biphenyls. One can do this quite rapidly, with effectively no sample workup.

We are interested, in our programs, in hazardous waste areas. In our particular aspect of the MS/MS Program we are particularly inter-

ested in compounds which cannot be done by Gas Chromatography, Mass Spectroscopy. This slide shows a variety of compounds, many of which cannot be done by Gas Chromatography, Mass Spectroscopy, but can be directly introduced in the fashion discussed previously.

We expect from our work that, in fact, methods for these given compounds of regulatory interest to RCRA could be rapidly developed. One, in fact, does need quite a bit of manpower to develop methods for many different molecules and while this is a major problem with rapid analytical method development, we feel quite certain that for a variety of molecules MS/MS coupled with this crude introduction technique can be exploited to develop methods rapidly.

This is an example of a positive daughter ion spectra of diethylstibesterol. This slide presents an indication of the information content available in daughter ion spectra acquired

in this nature. We have noticed that for many molecules the information content is sufficient to identify polar molecules in hazardous waste extracts.

Professor Hunt at the University of Virginia is developing priority pollutant methods. This slide presents a direct comparison of results done independently by GC/MS and MS/MS. A general summary of the work to date by Professor Hunt is that the results based on performance evaluation samples and a variety of hazardous waste samples, very complex mixtures, is that qualitatively the MS/MS scheme that he has developed is quite promising. In many cases, quantitatively, the data is excellent; in a quantitative sense it requires improvement.

The interesting thing about Professor Hunt's work is that sample workup for the priority pollutants and analyses and acquisition requires on the order of 25 minutes, total. Will that

type of methodology apply to every sample in the universe? I could probably say unequivocally, no. Will it have great analytical utility for certain industries and for certain waste industrial effluents? I believe it will. In fact, I had thought that his mission to develop analytical methods which would compete with the economics of fused-silica capillary column, GC/MS was a particularly difficult one. Both the qualititative and quantitative reliability of the data that has been provided to date has been good, but we anticipate further improvements. He is working under a cooperative agreement with EMSL-Las Vegas and Dr. Don Betowski at our laboratory is monitoring that program.

We are not concentrating on MS/MS analysis of priority pollutants at our lab, but as Bill invited us to talk here about MS/MS and as we were analyzing hazardous waste extracts and I thought we should examine some priority pollutant

data by MS/MS. What you are looking at right now is a positive ion Q1MS of an actual extract provided by Dr. Larry Straton at NEIC. This is a particularly clean hazardous waste extract. This is positive ion methane CI with a full scan. This is as if one would introduce a sample on the LC belt directly into a single Quadrupole Mass Spectrometer. You will note that in many cases fragments corresponding to molecular ions of the priority pollutants which were spiked into this mixture are obvious. This sample was spiked at approximately 100 nanograms per microliter.

It is interesting to look at the region... where the pointer is (indicating). The power of MS/MS becomes apparent when one looks, for example, at this region. At mass 139 and mass 140, the pronated positive molecular ions for isophrone and two nitrophenol. What one can do is introduce this sample in the same fashion

and instead of doing a full Q1 scan, one can ask for daughters of 139 or 140. This is a positive daughter ion spectra of 140 and you can see the pronated molecular ion and you can also see loss of water and phenol and a variety of other peaks which are quite characteristic of nitrophenols. In fact, the CID spectra of positive ions are, in fact, very similar to, in many cases, low energy electron impact mass spectra. I guess in retrospect that really shouldn't surprise anyone, but it is nice to know that if you can interpret electron impact mass spectra it is fairly easy to interpret CID spectra.

Taking M/Z 140 in the next few milliseconds of a scan for the positive daughters of 139, alternative identification of isophrone is mode. So going back again, selecting these peaks and doing daughter ion analysis allows one, despite the fact that their proximity is

1 amu apart, to identify these compounds in hazardous waste sample extracts.

Other things can be done. This is a negative Q3, CI mass spectra, full scan of another complex hazardous waste extract. Chlorinated materials are present, someone will say maybe that's a polynuclear. In selecting the daughter ion, M/Z 182, from this sample, just with the electronics of the instrument one gets a very characteristic and clean spectrum for that molecular anion of a dinitrotoluene. It amazed us that in many cases the instrument selects ions out of incredible garbage and provide one with reasonably clean spectra. We have been able to qualitatively verify a variety of priority pollutants in hazardous waste extracts via this approach. With proper quality control, we expect to attain good qualitative results. We had done some work with fused silica capillary column along with a lot of

other people here and the acquisition time for priority pollutant analysis was reduced to approximately 30 minutes. What would happen if we put all of the priority pollutants on the belt at one time and performed a full scan Q1 mass spectra. What one observes is 95 for phenol, 124 for nitrobenezene...let's see, 185...anyone that will give me help with that? I believe that's benzidine. And a variety of other compounds can be identified through appropriate daughter or parent ion scanning techniques. The information content in many respect to the priority pollutants daughter ions and other scanning modes are quite adequate for qualitative identification.

This is the negative ion CI Q1MS acquistion for the priority pollutant standard. So that half a half a second later taking negative ion Q1MS data from the same sample that you saw previously and you will note that where the

sensitivity is low in positive ion spectra, the negative ion CI is more sensitive. You see hexachlorobenezene, benzeneapyrene D-12 or benzapyrene or a molecular anion with that weight, trichlorophenol and a variety of other molecules at 25 nanograms are observed. Doing daughter ion experiments we have repeated this at one nanogram and using the belt introduction technique. You are able to observe signals for most of the priority pollutants, including some very low molecular weight compounds which surprised us, like dipropylnitrosamine and dimethylnitrosamine also. So MS/MS offers the possibility of a rapid screening procedure (MS/MS) for priority pollutants. One could analyze, at least theoretically, on the order of 150 to 200 samples an hour. It's not clear whether one could do 800 a day; it's not clear that one would want to do 800 day, but one could surely do in triplicate analysis of the samples

of interest. One might be able, then, to screen extracts for selected priority pollutants and other compounds of interest which can be done by GC/MS and in this fashion determine whether one needs to do GC/MS analysis.

A perfect example of this is the Missouri dioxin problem. The information that I have indicates that approximately 80 percent times 4,000 times $400 per sample minus the cost of a Triple Quadrupole screening scheme could be saved in that program by a MS/MS dioxin screening scheme. One of the reasons that we work with the chlorinated biphenyls was related to the interest in dioxin. In fact, it appears... there is every reason to believe that in actual extracts one will be able to have a very rapid screening technique for this molecule. The reason for this talk, is to present an idea which has become obvious to me, that it is still just an idea, that analytical methods

development can be structured such that methods with people and perhaps a few automated instruments can rapidly develop analytical methods in crash problems.

The Effluent Guidelines Division program has evolved over a number of years now, but it is still saddled in many cases with the matrix problems. When we were first told to write methods for priority pollutants I remember a lot of analytical organic chemists standing up and saying you can't write methods for everything in anything. The progress that has been made is really amazing, but there are reasons why one might want to have a matrix specific approach or a structured approach to methods development using, for example, the 1600 methods as the quality control check. Using that as a model and knowing a little bit about scanning options and ionization processes at MS/MS, it is not too difficult to say how one could go about making

the development of a method routine. Methods Development costs quite a lot and I think it is worthwhile for us to look into Rapid Analytical Methods Development.

To give you another idea what you can do with a MS/MS. We have a program to develop methods for dyes. There is a gentleman by the name of Professor McGovern at the University of Pennsylvania. If you have read C&E News last February, there was an article discussing instrumental applications to archeology. A dye that was discussed in that article called 6 of 6' dibromoindigo was of particular interest to Professor McGovern. The dye apparently at one time was used by the Greeks, Egyptians, Phonecians and Romans. Work to date has not been able to confirm that this dye is present in samples of archeological interest. We have contacted Professor McGovern and suggested another introduction technique which is a FAB-like technique where

one bombards a sample on a platform with ions. This mass spectrum is full negative ion scan of a polar dye, bromocresol purple. The structure of 6 of 6' dibromoindigo does have some structural similarity to this molecule and we sent him the spectra and asked if he would like to send us some sample. He appears to be interested in this application of MS/MS to his problem. We are going up to Philadelphia tomorrow and probably take a sample back from this artifact, but based on the structure of the molecule an MS/MS approach has become obvious. If the dye is present and if there are not ionization suppression problems with the matrix we should be able to unequivocally conclude...if the Phoenicians practice unregulated dye dumping in the year 1300 B.C. using DISIMS ionization and negative ion daughter scanning techniques.

Is screening important enough to warrant purchase of an MS/MS? The work of Dr. Shackelford

at Athens in creating the data base on the industrial effluents has indicated that, in fact, in industrial effluents the occurrence of priority pollutants is relatively rare. I believe the highest compound that was found was phenol and the frequency was 5 percent; that would indicate, then, that priority pollutant screening methods via MS/MS, would seem to be viable. It would seem to be economical to screen samples by MS/MS and the data could be produced for project officers in a more timely fashion.

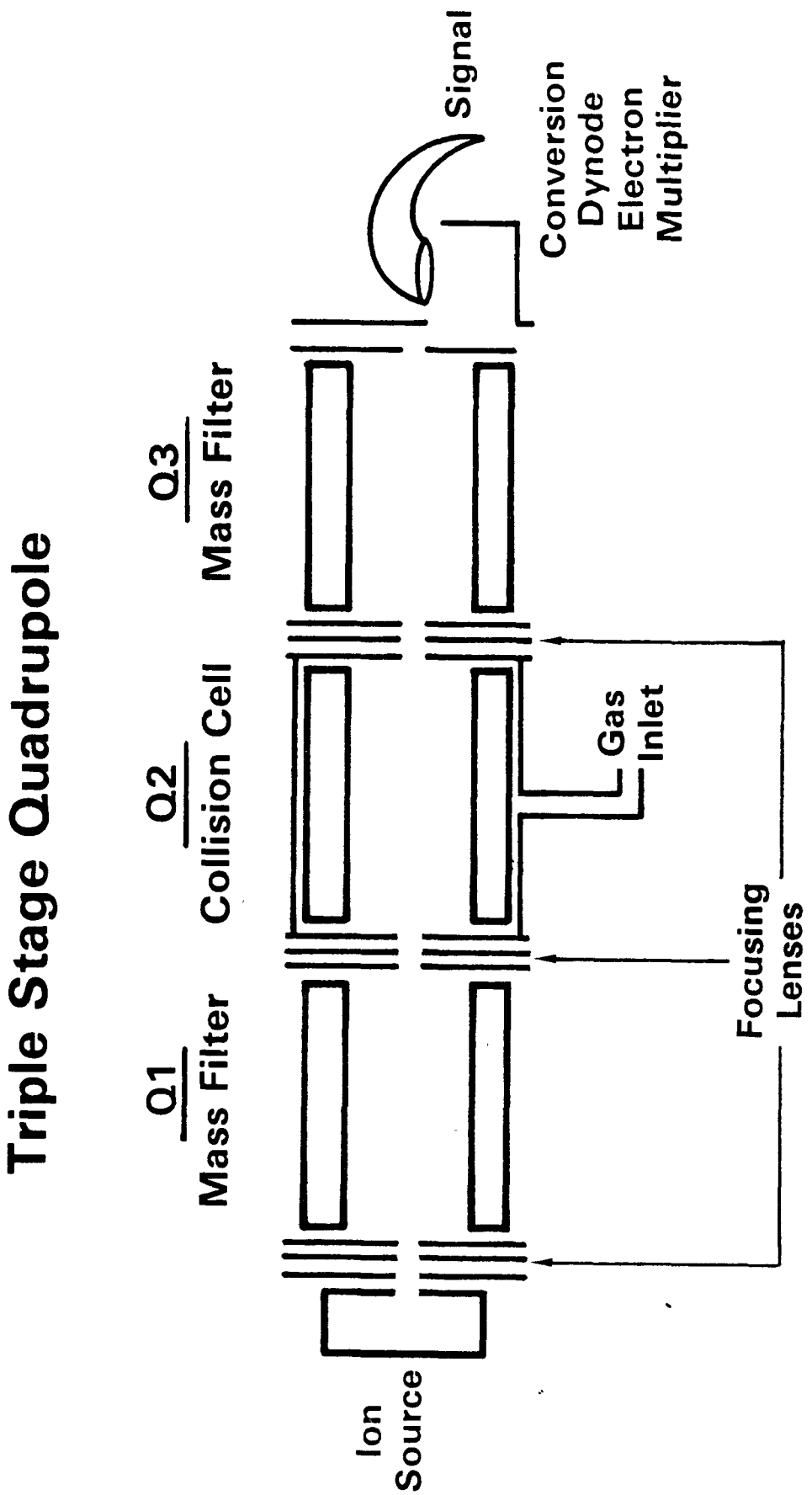
For dioxin, let me repeat 80 percent of 4,000 times $400 could be saved minus the cost of a TSQ mixture screening scheme. Is a method ready to go right now off of the shelf; it isn't. Should you go out and immediately purchase a Triple Quadrupole at $350K, I would probably wait. However, I believe you can see why we are excited about the technique and why

we think it has advantages. I think it will eventually find its way into the programs for programmatic as well as technical reasons.

Any questions?

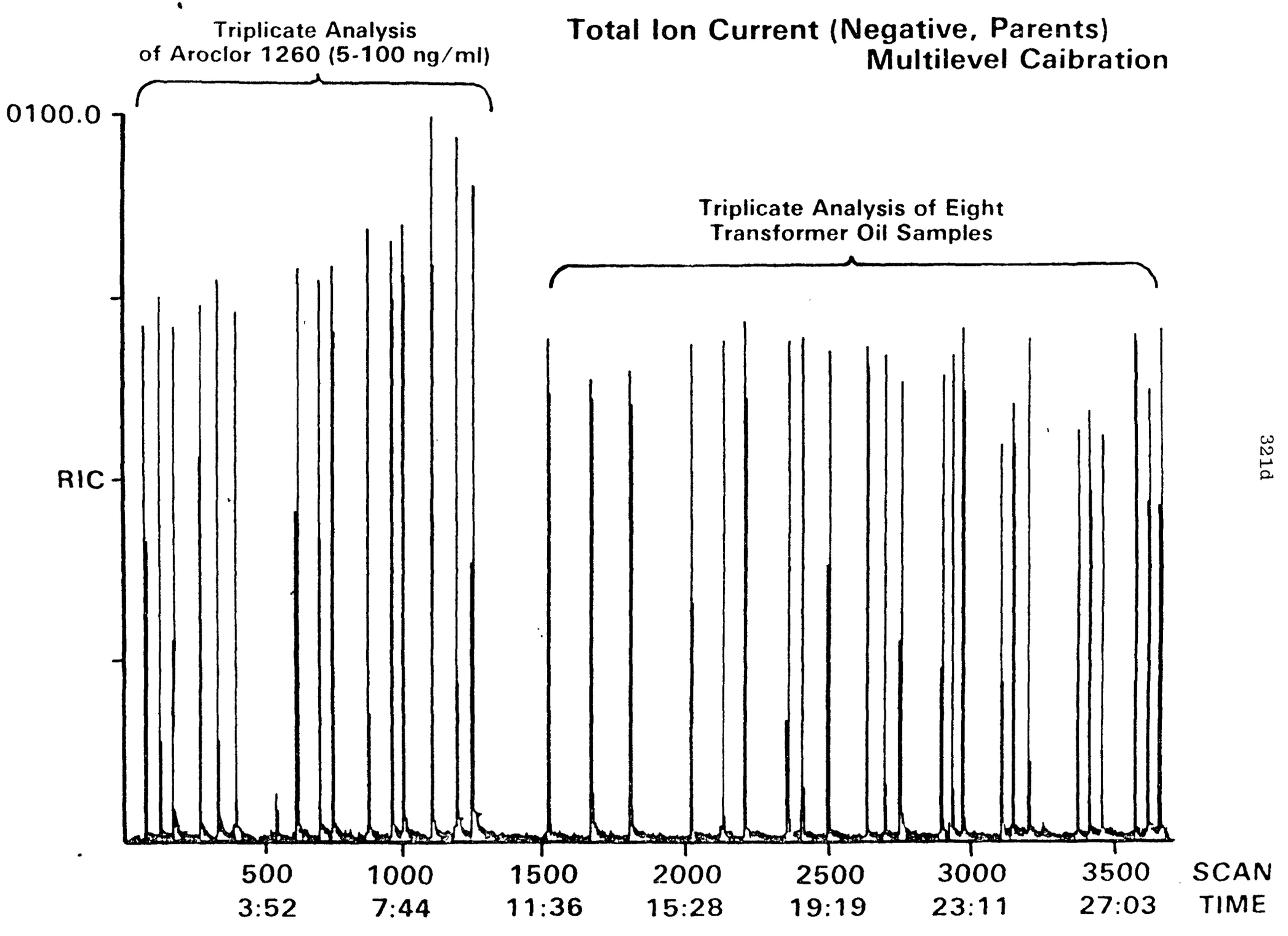
"There are insufficient experimental data available to establish exactly where the quadrupole MS/MS instruments performance fits into analytical picture."

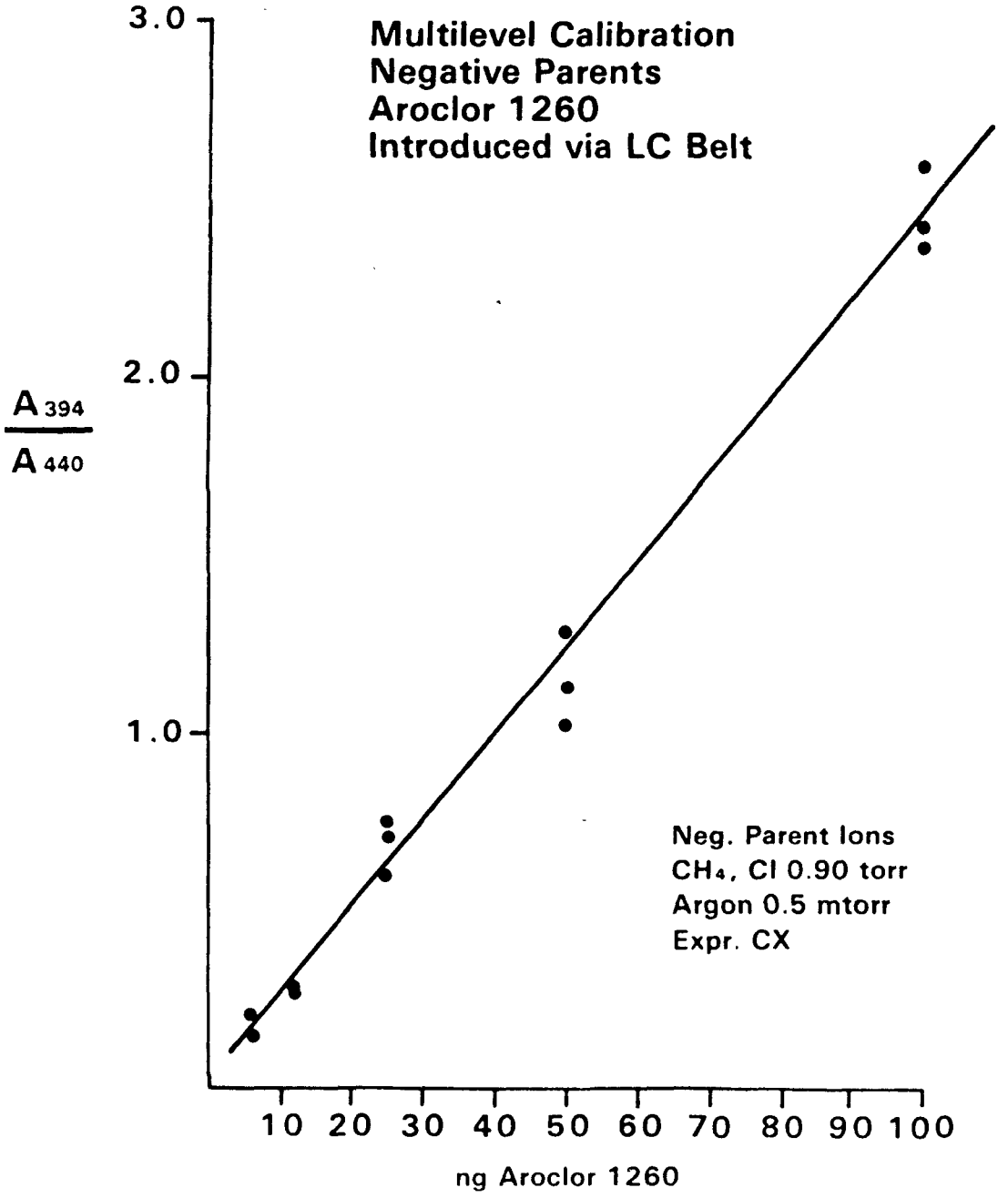
Burlingame, A.L.,; Dell, A.; Russell, D.H.,Analytical Chemistry, Vol 54. No. 5, April 1982 371pp.

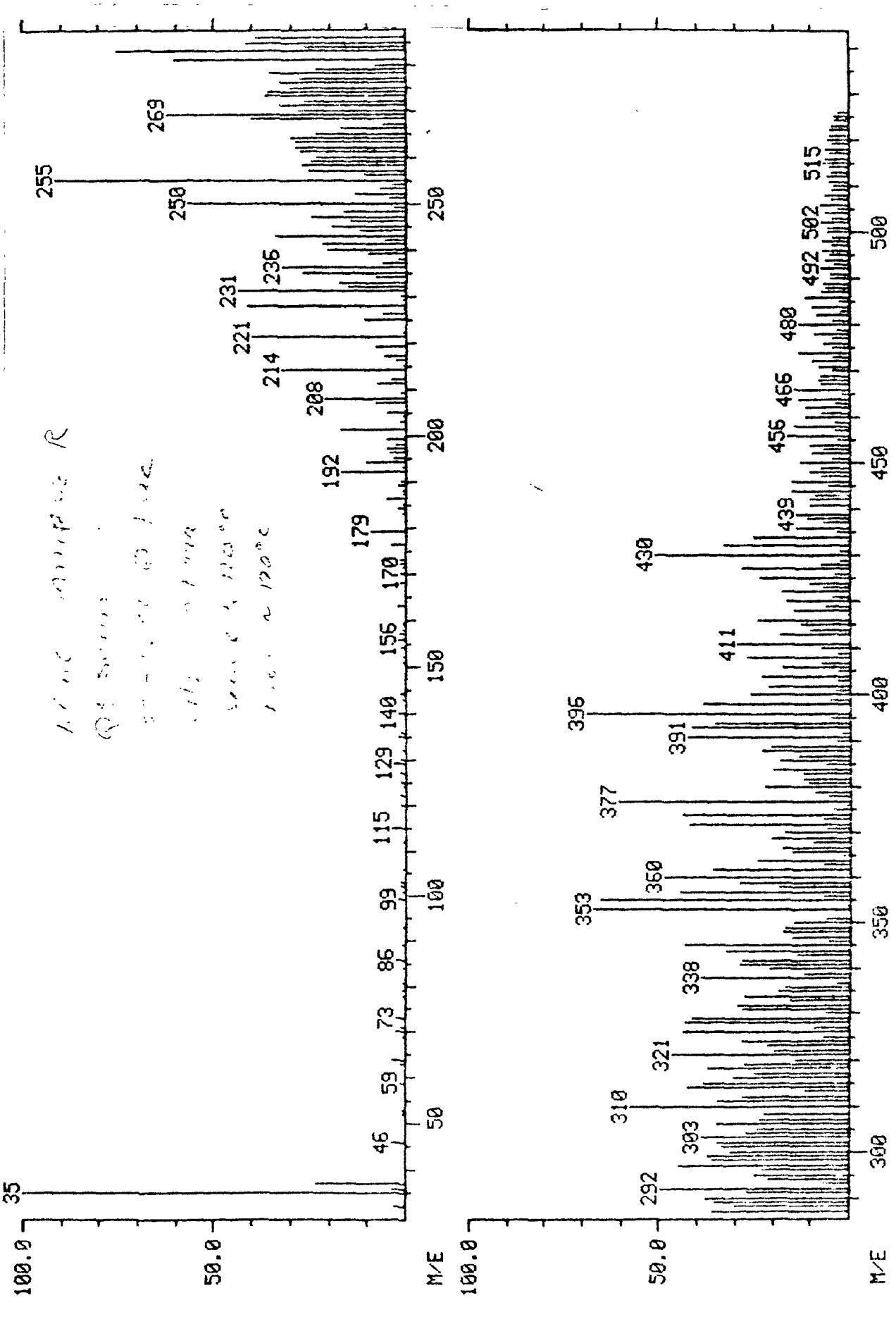

Triple Stage Quadrupole
Q1
Mass Filter
Q2
Collision Cell
Q3
Mass Filter
Signal
Conversion
Dynode
Electron
Multiplier
Gas
Inlet
Focusing
Lenses
Ion
Source

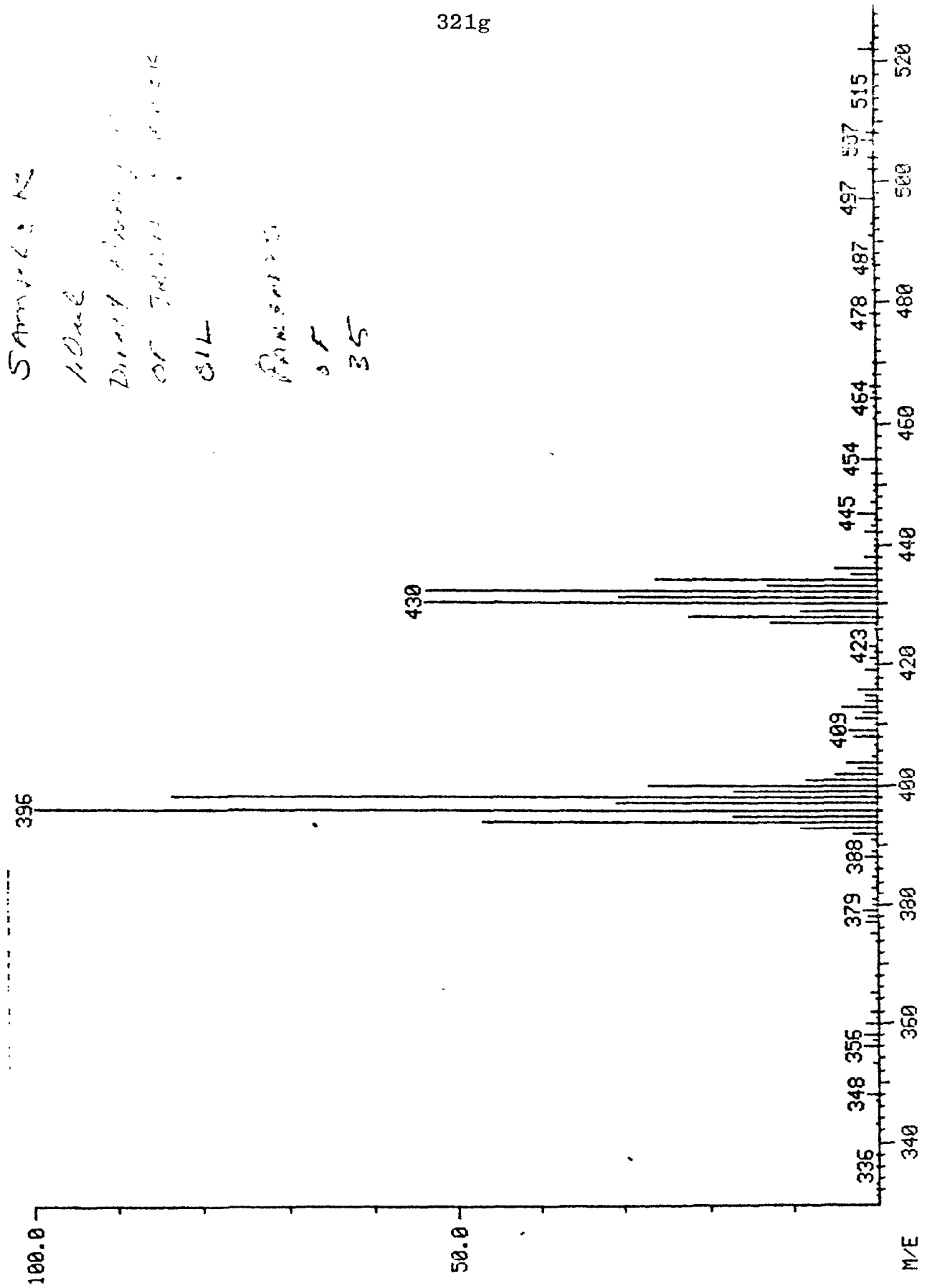
Partial MS/MS Experimental Menu

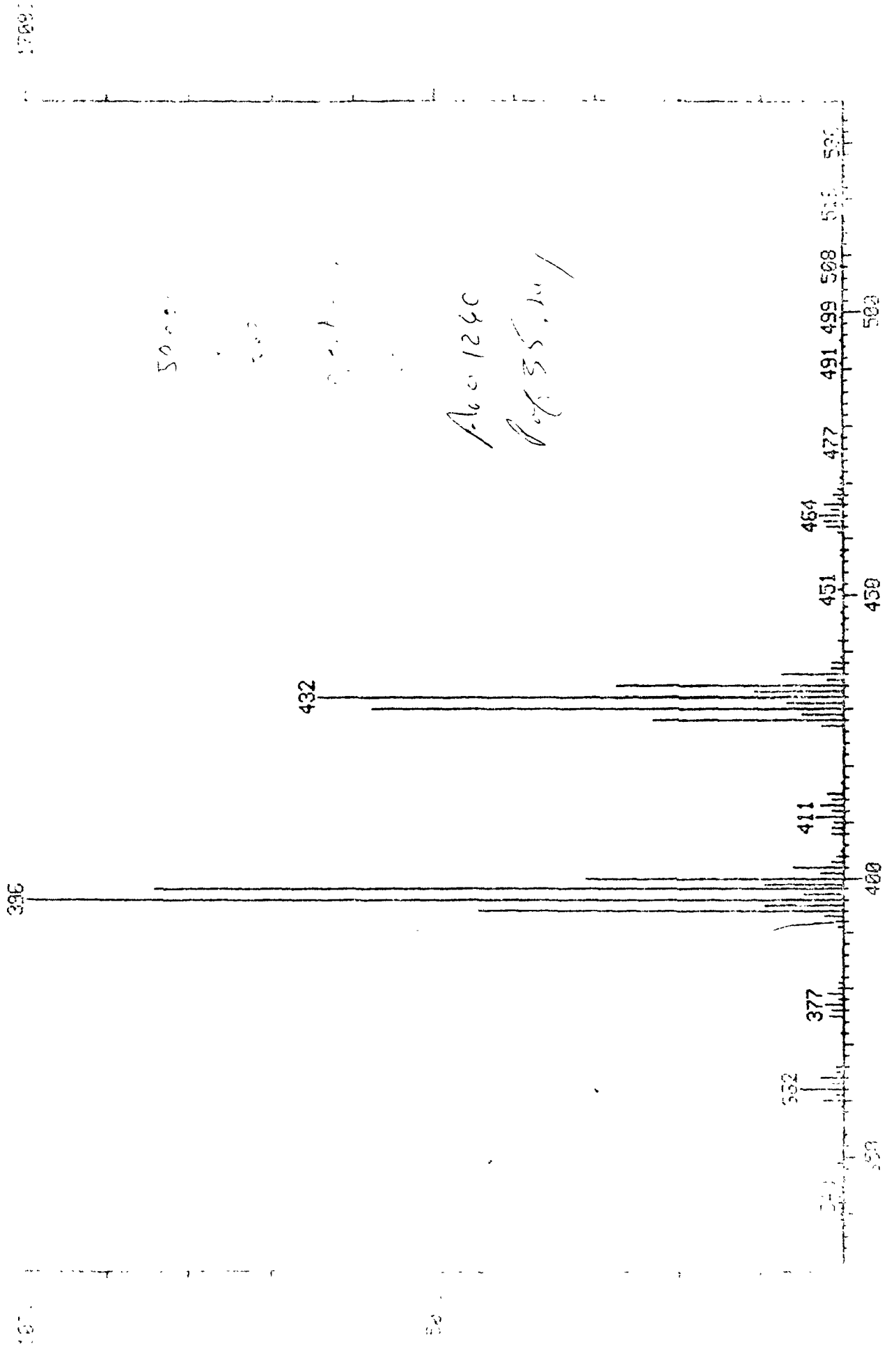
Source Introduction	**GC** **LC** **Probe** **Platform**
Sample Ionization	**EI** **CI (+/-)** **FAB or SIMS**
	CAD
Scanning Options	**MS (Q3 or Q1 scanned)** **Daughter (Q1 fixed, Q3 scanned)** **Parent (Q1 scanned, Q3 fixed)** **Neutral (Q1 & Q3 scanned, but offset)**
Other Options	**Collision Gas** **Collision Energy** **CI gas and Pressure**


Triplicate Analysis
of Aroclor 1260 (5-100 ng/ml)
Total Ion Current (Negative, Parents)
Multilevel Caibration
0100.0
RIC
Triplicate Analysis of Eight
Transformer Oil Samples
321d
500
3:52
1000
7:44
1500
11:36
2000
15:28
2500
19:19
3000
23:11
3500
27:03
SCAN
TIME


Multilevel Calibration
Negative Parents
Aroclor 1260
Introduced via LC Belt
3.0
2.0
1.0
A394 / A440
10 20 30 40 50 60 70 80 90 100
ng Aroclor 1260
Neg. Parent Ions
CH4, CI 0.90 torr
Argon 0.5 mtorr
Expr. CX


100.0
50.0
M/E
35
46
59
73
86
99
115
129
140
156
170
179
192
208
214
221
231
236
250
255
269
50
100
150
200
250
100.0
50.0
M/E
292
303
310
321
338
353
360
377
391
396
411
430
439
456
466
480
492
502
515
300
350
400
450
500


100.0
50.0
M/E
336
340
348
356
350
379
388
396
400
409
420
423
430
440
445
454
460
464
478
480
487
497
500
515
520

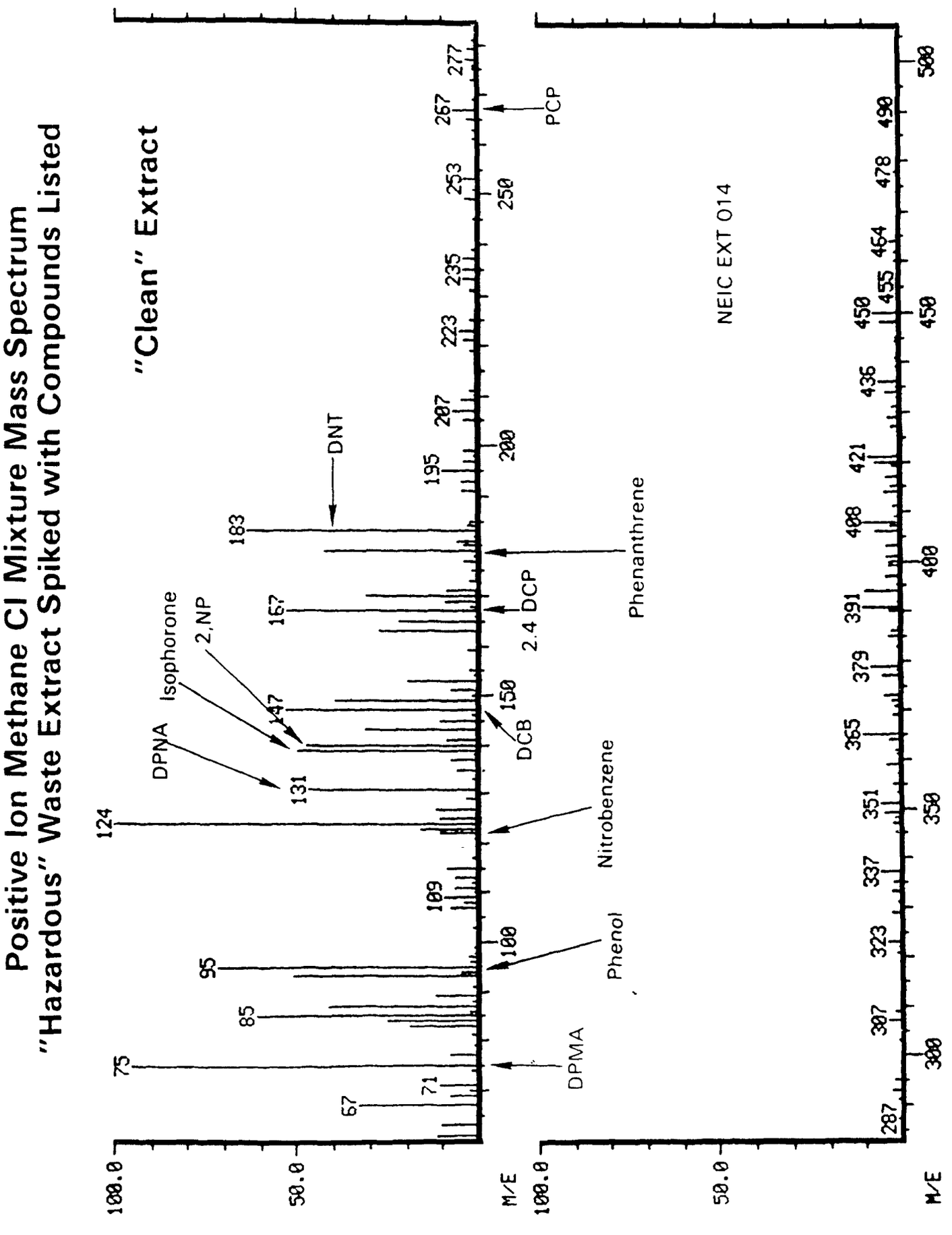

396
411
432
377
451
464
477
491
499
508

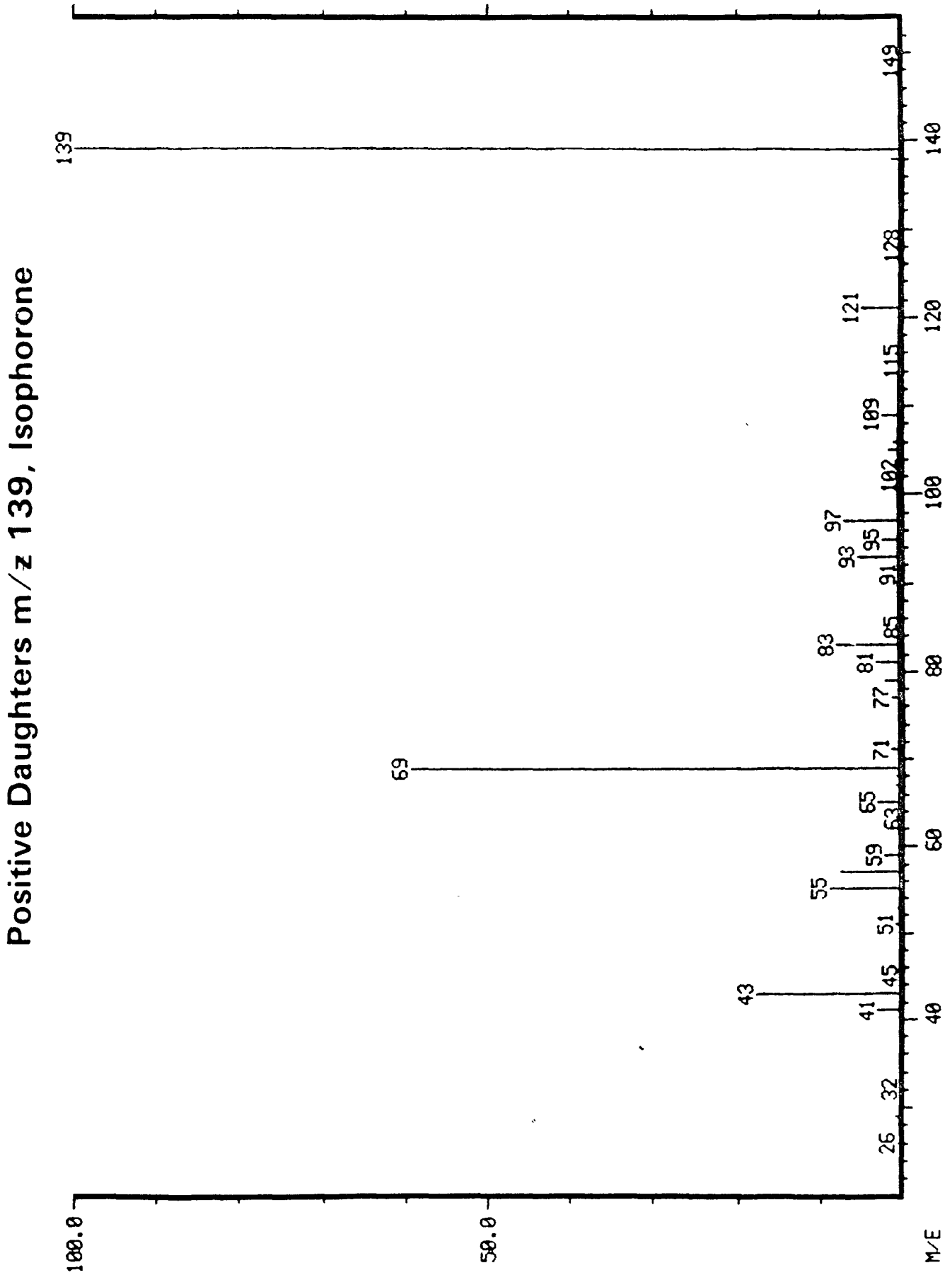
Appendix XIII Listed Compounds Which can be Directly Introduced to MS/MS via LC/MS Interface

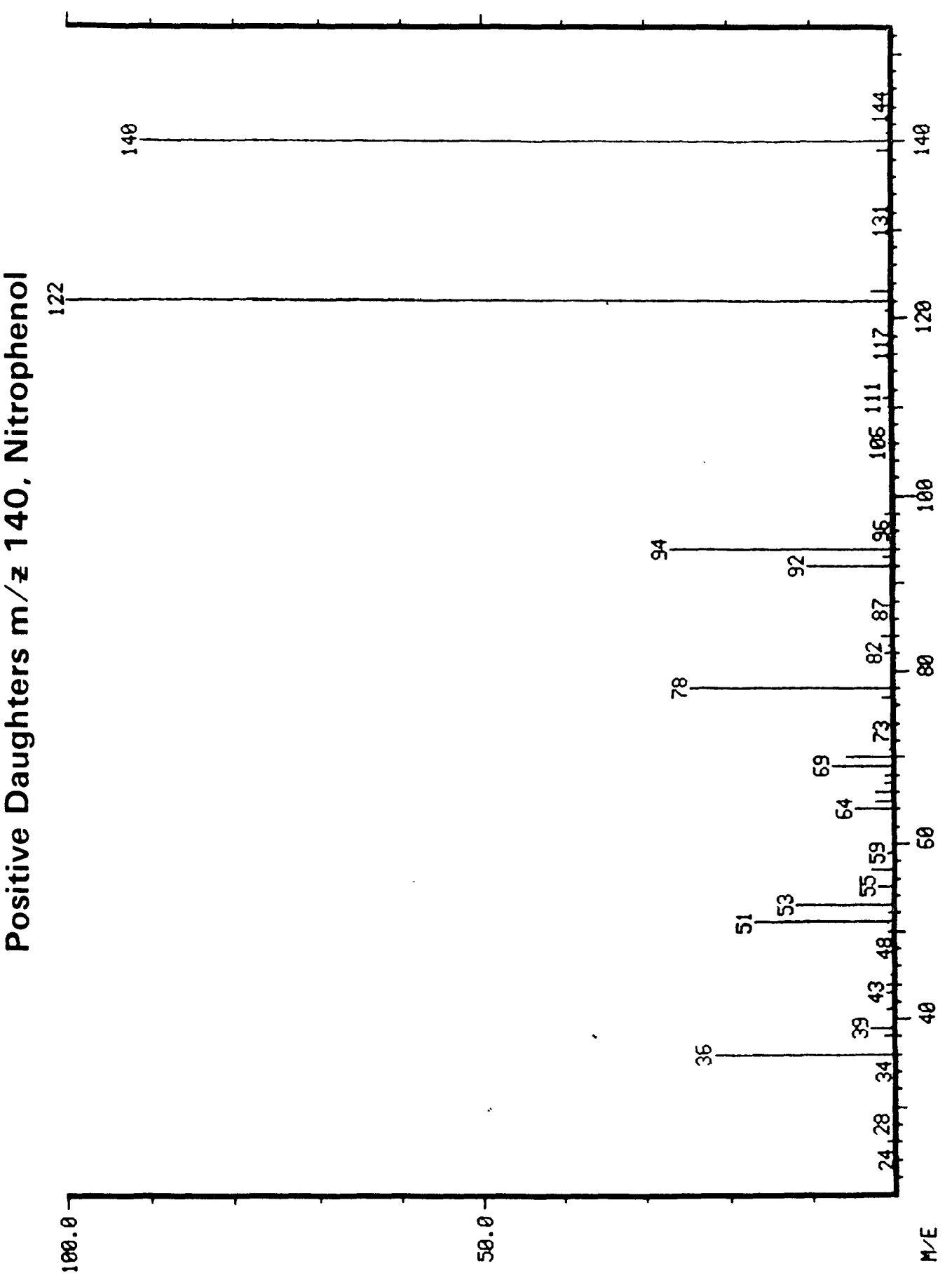
M. WT.	Compound
334	Strychnine
268	Diethylstilbestrol
77	Fluoroacetamide
338	Phenylmercuricacetate
254	2,4,5-Trichlorophenoxyacetic Acid
220	2,3-Dichlorophenoxyacetic Acid
220	2,4-Dichlorophenoxyacetic Acid
94	4-Aminopyridine
162	Safrole
169	o-Aminobiphenyl
75	Thioacetamide
195	2,4,6-Trichloroaniline
225	N-Iodosuccinimide
141	2-Chloro-6-methylaniline
141	4-Chloro-2-methylaniline
184	Benzidine-HCl
252	3,3'-Dichlorobenzidine-HCl
184	2,4-Dinitrophenol
198	4,6-Dinitro-o-cresol
404	Alpha Endosulfan

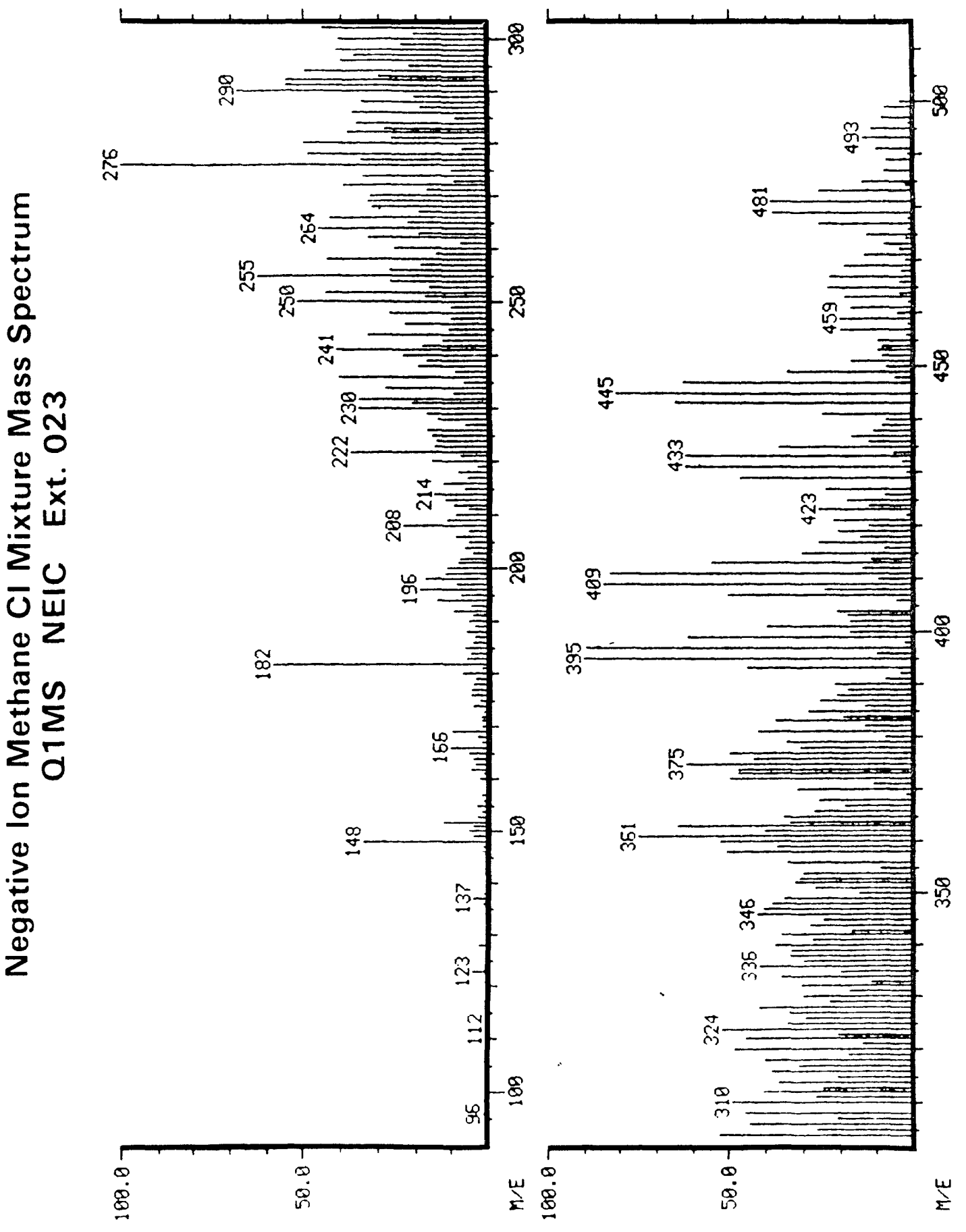
Summary of Results Obtained by the University of Virginia on an EPA "Rag Oil" Sample

Compound	Radian GC/MS (ug/mg)	MS/MS (ug/mg)
C2-benzenes	14	12.4
toluene	6	3.7
C1-dibenzothiophenes	3.4	8.0
C1-phenanthrenes	3.2	0.9
C3-benzenes	3.1	8.6
phenanthrene	2.0	1.0
dibenzothiophene	1.5	4.0
C1-naphthalenes	1.5	0.5
C4-benzenes	1.2	4.3
C2-phenanthrenes	1.1	0.3
C2-dibenzothiophenes	1.1	4.8
benzene	1.0	2.0
C2-naphthalenes	0.9	0.2


Positive Ion Methane CI Mixture Mass Spectrum
"Hazardous" Waste Extract Spiked with Compounds Listed
"Clean" Extract
NEIC EXT 014
DPNA
Isophorone
2,NP
DNT
DCB
2.4 DCP
Phenanthrene
PCP
Nitrobenzene
Phenol
DPMA
M/E
100.0
50.0


Positive Daughters m/z 139, Isophorone
100.0
50.0
M/E
26
32
40
41
43
45
51
55
59
60
63
65
69
71
77
80
81
83
85
91
93
95
97
100
102
109
115
120
121
128
139
140
149


Positive Daughters m/z 140, Nitrophenol
100.0
50.0
M/E
140
122
94
92
78
36
51
53
55
59
64
69
73
82
87
96
105
111
117
120
131
144
24
28
34
39
43
48
40
60
80
100
140


Negative Ion Methane CI Mixture Mass Spectrum
Q1MS NEIC Ext. 023
100.0
50.0
M/E
96
100
112
123
137
148
150
166
182
196
200
208
214
222
230
241
250
255
264
276
290
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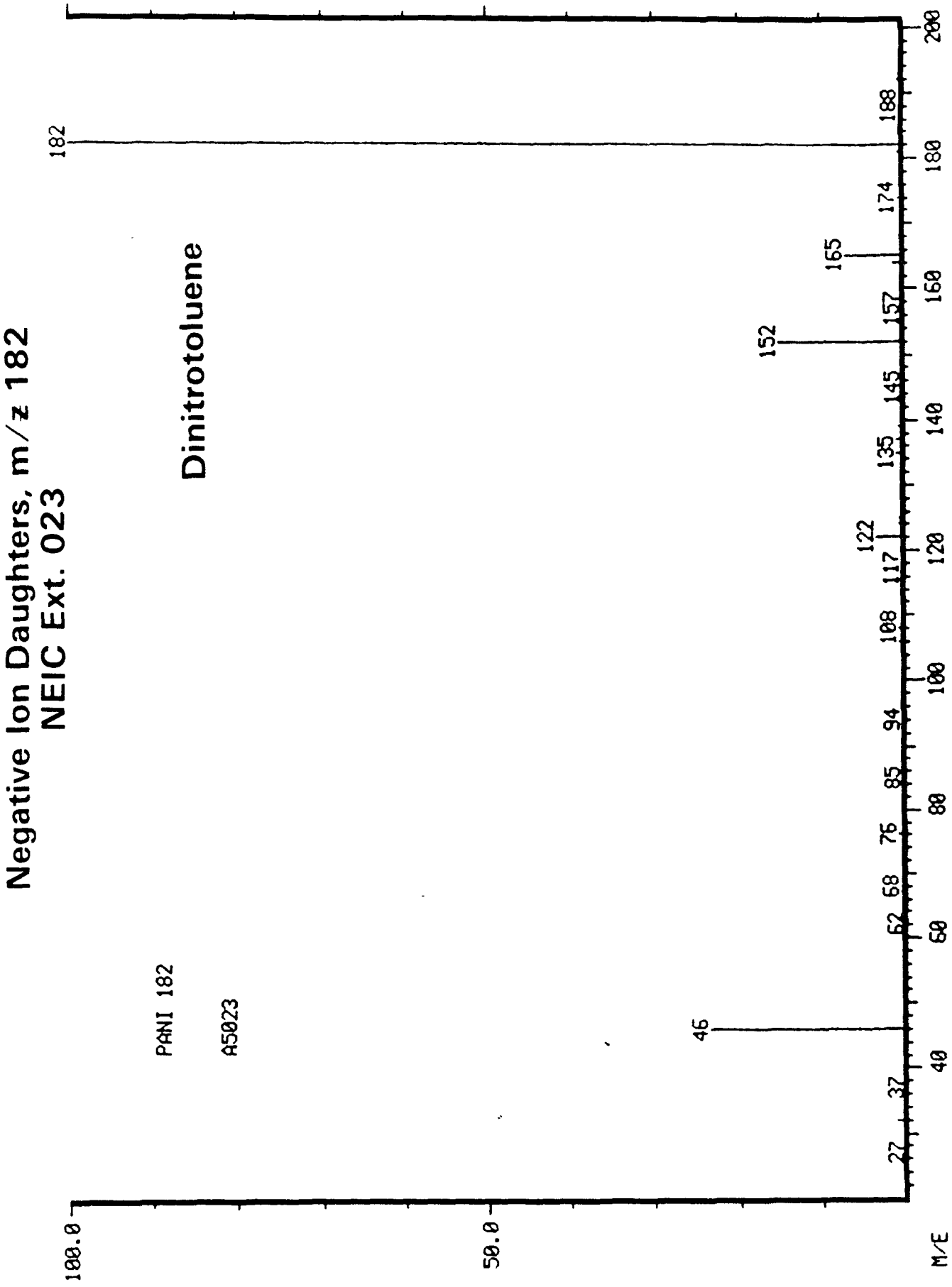
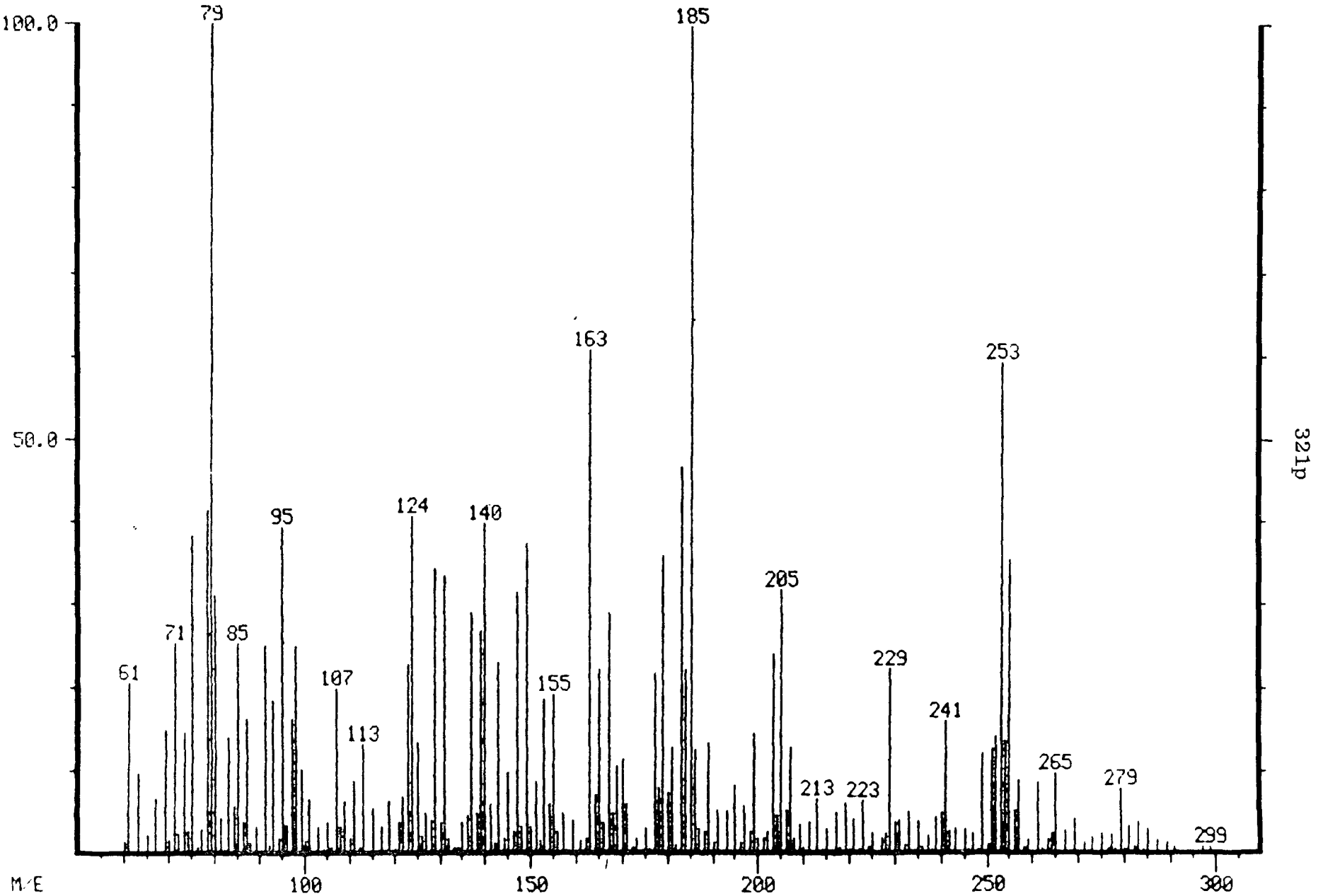
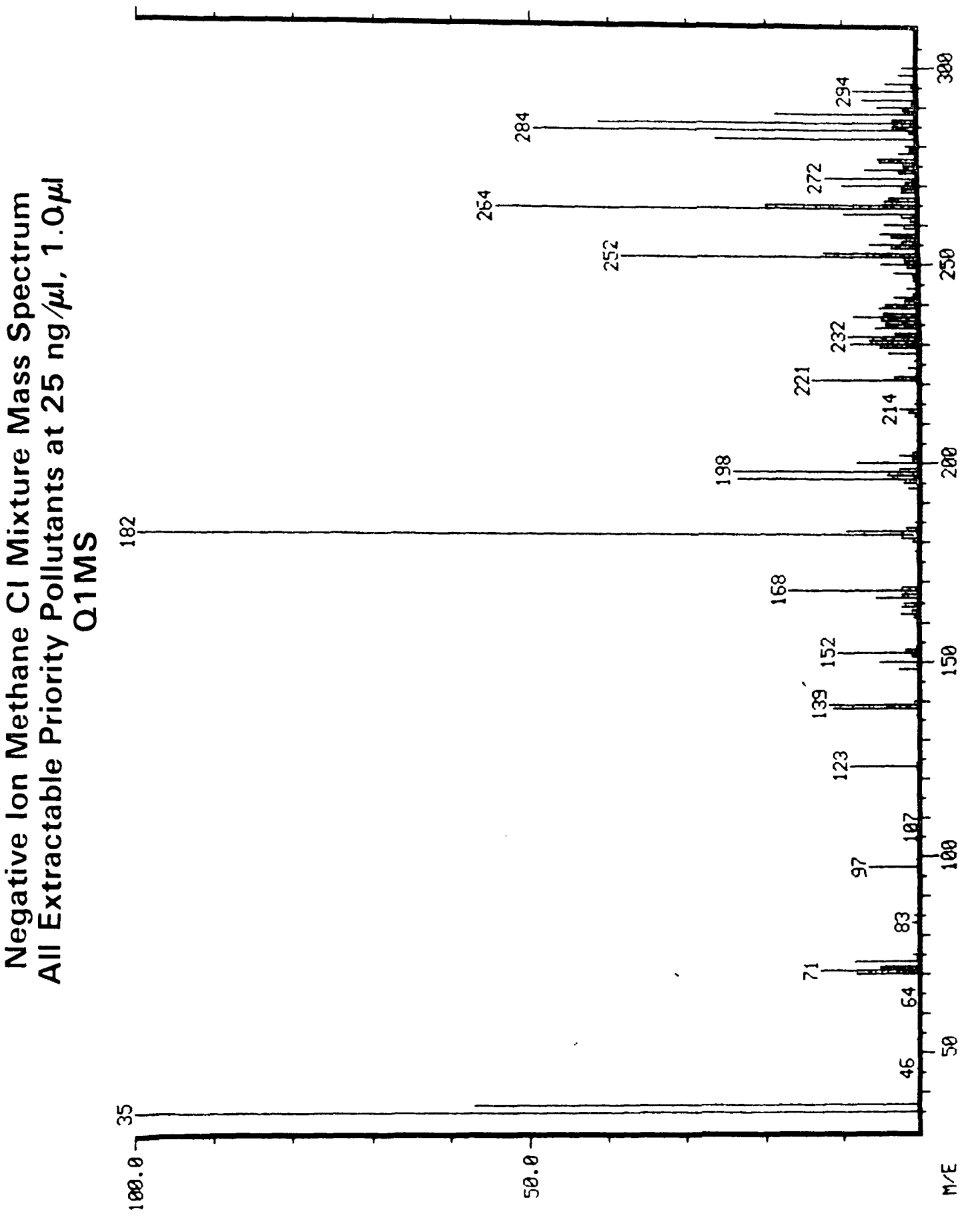
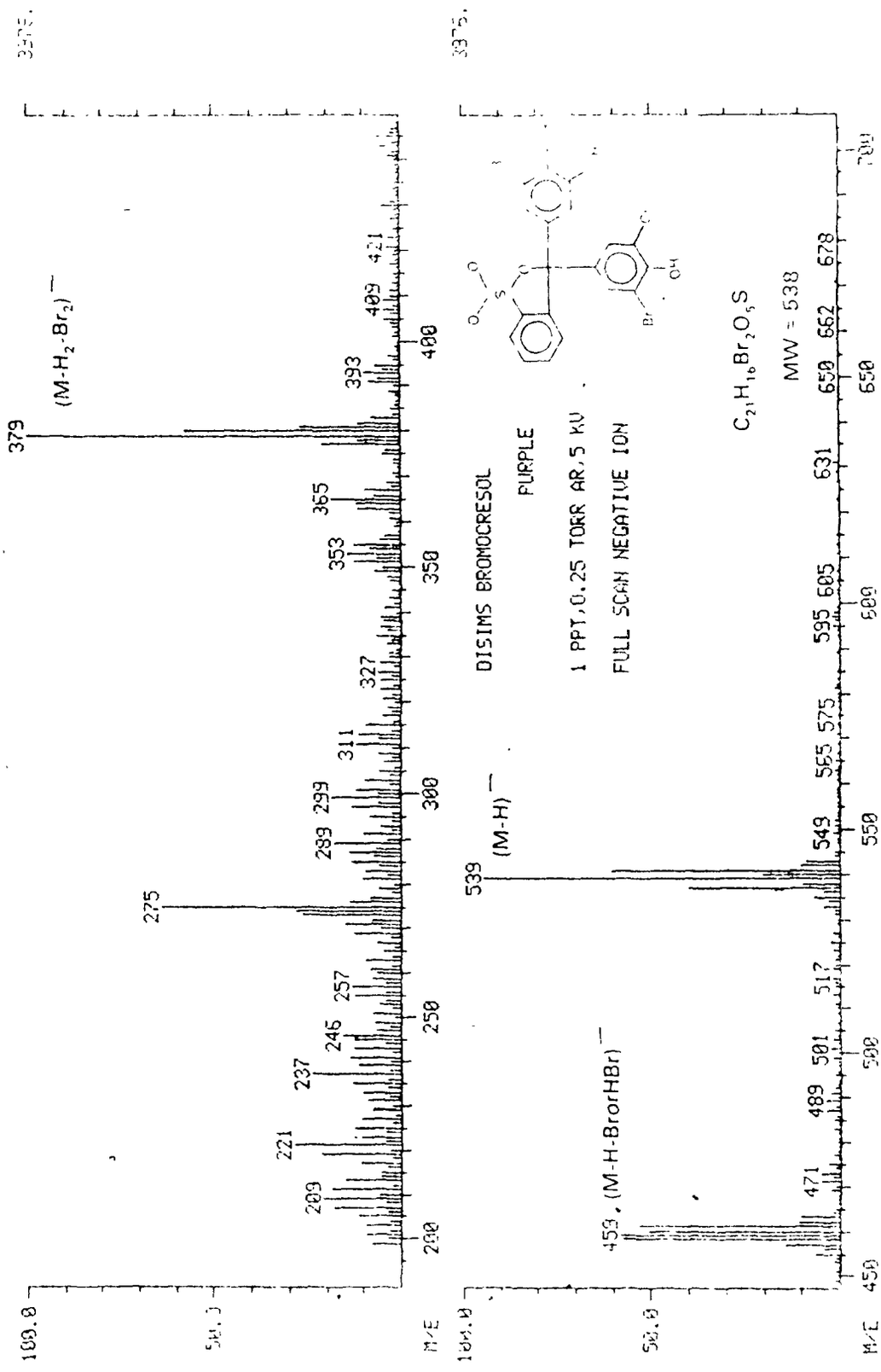
350
351
375
395
400
409
423
433
445
450
459
481
493
500


Negative Ion Daughters, m/z 182
NEIC Ext. 023
Dinitrotoluene
PANI 182
A5023
182
165
152
122
46
100.0
50.0
M/E
27
37
40
52
58
60
76
80
85
94
100
108
117
120
135
140
145
157
160
174
180
188
200

Positive Ion Methane CI Mixture Mass Spectrum
All Extractable Priority Pollutants at 25 ng/µl, 1.0µl
Q1MS




Negative Ion Methane CI Mixture Mass Spectrum
All Extractable Priority Pollutants at 25 ng/µl, 1.0µl
Q1MS
100.0
50.0
35
46
50
64
71
83
97
100
107
123
139
150
152
168
182
198
200
214
221
232
250
252
264
272
284
294
300
M/E


DISIMS BROMOCRESOL
PURPLE
1 PPT,0.25 TORR AR,5 KV
FULL SCAN NEGATIVE ION
$C_{21}H_{16}Br_2O_5S$
MW = 538
$(M-H_2-Br_2)^-$
$(M-H)^-$
$(M-H-BrorHBr)^-$
M/E

QUESTIONS AND ANSWERS

DR. COLBY: Bruce Colby, S-CUBED. Drew, I did a quick calculation here based on your 200 sample per hour estimate as a through put. If there were 90 compounds per sample that you were interested in, you would ultimately require or have available for any single compound identification, quantification, whatever you are going to do; one-fifth of one second in terms of data reduction.

How is the agency addressing the data manipulation problem that would appear to be generated here?

MR. SAUTER: I think one of the ways that we would address that is not to address it, frankly. The problem...what I see in this meeting, for example, George Stanko's talk I thought was particularly interesting. Earlier on, what people have done in these methods

and programs is, they have come in and have said we can do anything in anything and a whole lot of that.

What you see now in the analytical community, I think, is a concentration on very specific issues. I feel quite confident from data with standards and samples to indicate that this type of screening techniques would be of great interest to people worried about the polynuclears at given levels. In the type of workup that I am talking about for parts per billion analysis, one does not gain the minimal sample workup; one still needs the concentration factor.

There is no reason to think on an average that MS/MS will be more sensitive than a single Quadrupole instrument. So that I don't think one would, in fact, want to look for every priority pollutant in a sample by the method that we have discussed. One might want to screen samples that way. Based on Dr. Shackelford's

work and on other areas of our work it strikes me that screening in such a fashion has interesting properties.

This is a potential approach for limited objective analytical strategies. For example, chlorinated biphenyls in transformer oils, dioxins in extracts, which have gone through some workup, polynuclear aromatics in a variety of different samples and one could go on and on. To me, the analytical applications are obvious. We have given a few examples of applications. We have not shown that it is an equivocal method to supplant GC/MS. It will augment GC/MS. It will not supplant GC/MS.

MR. RUSHNECK: Dale Rushneck, Interface, Inc. Well, the answer to Bruce's question seems pretty obvious, in addition to the Triple-stage Quadrupole you need a Triple-stage computer.

My question is one concerning isotope dilution. I noticed this belt technique in having worked with detectors of that nature myself. There is, of course, a lot of variability in getting reproducibility; that didn't play together. There is a lot of variability in that technique from the standpoint of getting the sample on the belt precisely the same way; and, I have wondered if you've tried isotope dilution in terms of the...

MR. SAUTER: That data that was presented was isotopic dilution.

MR. RUSHNECK: Pardon?

MR. SAUTER: The data that was presented, that multiple level concentration curve was effectively isotopic dilution.

We were using the C13 label chlorinated biphenyl standards which are now being used in the interlaboratory PCB study. We used the per C-13 CL-8 molecular anion relative to the

most intense molecular ion in the negative parent ion scan of Aroclor 1260 which was from the molecular anion of the heptachloro isomer, of all heptachloro isomers. So it was almost isoptic dilution. I think, your point is well taken; because of your work, Bruce's, Bill's, the labeled materials for priority pollutants are available. It would not take much ingenuity to take the 1600 methods and that's what I meant before, take the material available because of the work on the 1600 methods and lace that into some sort of screening scheme.

Your point about the belt is well taken, it is mechanically crude. I do not personally believe that the way we put material on the belt was, in fact, the best introduction method; but, I think in many cases it can work.

MR. RUSHNECK: Sure.

MR. SAUTER: I do believe very strongly that if, for example, newer developments

of the thermospray LC/MS interface may provide a superior introduction technique. I think the speed of the belt is worth considering and I think if one could demonstrate, unequivocally, the analytical utility of that approach then someone would figure out a damn precise way to put it on that belt or some other type of LC/MS interface.

MR. RUSHNECK: The second question I had was concerning the analysis of PCB's and transformer oils. Do you think with negative ion CI you could get sufficient results from a single stage instrument to be unequivocal.

MR. SAUTER: In many cases you can't. It depends on which regulation and probably which transformer oil. The OTS regulations are worried about 50 PPM, I believe, whether to incinerate or not.

Many of the samples that were provided to us could have been done in that fashion. How

well quantitatively and qualitatively it could have been done, I can't really say; but, at levels above 100 PPM, 75 PPM, one could use a 4,000 in theory to do this. One would like to have, I can tell you from a certain amount of experience; one would like to have the selectivity of a triple-stage instrument.

Thank you.

MR. TELLIARD: Thank you, Drew.

MR. KEEN: Gary Keen with Conoco. I may make one comment, Dale, we do use a single stage instrument for PCBs and negative CIs, but we use a mass 35 and 37 and not molecular ion and it works very well.

MR. RUSHNECK: And no GC; it is just a production sample?

MR. KEEN: No, we do have capillary GC on it. We find it works extremely well, better than, then, the specific GC techniques.

MR. TELLIARD: Our last speaker for this morning's session is Bob Beimer from TRW. Bob, as you know, has been on this program before and as we know Bob can't speak to metals analyses, but he is here to talk about some organic analyses which is, perhaps, more in his area of expertise.

Bob is going to talk about a direct injection technique that EDG has been working on, on and off, for the last year and a half. It, basically, is a selective little tubing. So Bob, now, is going to talk to you about a hose job; Bob.

EVALUATION OF A NEW GC/MS DIRECT AQUEOUS INJECTION INTERFACE FOR VOLATILE ORGANIC ANALYSES

Robert G. Beimer
TRW, Inc.

MR. BEIMER: There have been a lot of comments out there about the length of this morning's session. I'm going to try to run along pretty fast so that you won't miss the rubber chicken and peas.

At the request of Bill Telliard and others, we have done some work on evaluating a DuPont polymer called Nafion. We evaluated this material as a concentrator technique for the determination of volatile organic compounds in water. The analysis is conducted by directly injecting the water without any previous separation. The sample passes through the Nafion tube and right onto the GC column where the analysis is conducted.

The interface consists of an injector block that's the injector (indicating). Were were

using an all-glass system in order to minimize contamination problems. The carrier gas is pre-heated by winding through coils within that injector block, which is maintained at 150 degress centrigrade, passed into the injector port itself, and then the water sample is injected through the septum and is flashed in this zone in the glass injector. The material is carried from the injector in a vapor state into a six foot length of Nafion tubing. I have no idea of the chemical structure of this stuff; but, basically, it is a material which is at least permeable to water and at the most permeable to all polar organic compounds while being impermeable to non-volatile species.

The tube itself is this inner line here on the drawing, you can see that there are two lines there and the inner line is the Nafion tubing (indicating). The outer sheath is just

a nylon tube through which one passes a dry gas in a countercurrent direction to the flow of the helium. The countercurrent flow of dry gas around the Nafion tubing is flowing in the reverse direction carrying away the water that is permeating through the Nafion tube.

The reduction in relative humidity here is substantial as shown by work that has been done by Peter Simmons of International Science Consultants in England, the person who came up with this technique to begin with. Basically, the sample once injected at this point enters the GC column as a dry gas. There is no problem with water buildup in the system. We studied how much water could be injected into this system on a routine basis without deterimental effects on the mass spectrometer system and/

or the GC column.

Originally, it had been reported that seven microliters was the maximum water injection which could be tolerated when an electron capture detector was used. We felt that the mass spectrometer might be a little more tolerant of water than the electron capture detector system, so we started at seven microliters and worked our way up. Our determination was that 250 microliters or a quarter of a milliliter of water could be injected into this system on a routine basis. You could do that for at least eight hours at one sample each 45 minutes and not get an increase in the water background in the mass spectrometer and you could maintain your vacuum.

We did, however, find that when you inject in a half a milliliter of water, the system

self-destructs. If you will notice, we have got connectors here connecting the Nafion to the injector; and, then, there is another connector down here where the Nafion is connected to the GC column. We blew them both apart. There is quite a column change when you go from a half a ml of water in liquid to its equivalent vapor state. We ended with most of that half a ml of water on the end of the GC column which we ruined. It took the better part of the day to get the mass spectrometer vacuum back; but, basically, a quarter of a ml was not a problem. If injected in a reasonable way I think a half a ml could be done as well. In other words, you would have to inject it slowly, not trying to slug it in at a given instant because the way the technique works is, you are maintaining the GC column at room temperature or below. While you are making the injection, at this

point, and if you made it slowly you could hold the GC for just a little longer at room temperature before you programed it up to do your analyses. Effectively, your samples will be concentrating on the head of the GC column anyway.

The whole idea of this was to be able to run particularly nasty samples without going through the purging operation and the secondary traping operation. Before we did that we had to determine whether or not this technique was compatible, reasonable and similar to the purge and trap operation. In order to do that, we ran a rather significant number of standards by both the purge and trap technique and by the Nafion interface technique using similar concentrations of materials.

This is just a reconstructed ion trace of a 100 nanogram standard run, using the purge and trap technique. A number of the peaks are identified,

but that is really not important; more important is the shape of what you see here and then compared to the same standard run using the Nafion (indicating). Down at this end, you will notice the typical starting end of the GC trace for a volatiles analysis, the peaks are broad and unresolved; maybe that's only me, maybe the rest of you do better. If you will notice, with the Nafion injection a much better resolution at the low end (indicating). A reason, of course, that you have this is that you don't hold the GC for a significant period of time using the Nafion system like you do with the purge and trap. With the purge and trap you are holding the GC at the low end while you desorb the materials from the trapping column. Here, of course, you start the GC at room temperature and you inject through the Nafion and then you program the gas chromatograph. So there isn't that lag time, the material

doesn't have a chance to defuse at the head of the column at low temperature, and you get a much sharper chromatogram.

Well, that's fine for the beginning peaks, but one might expect that the later peaks could be a problem in that we are introducing a significant amount of volume before the GC column itself by having this six feet of tubing. This is a comparative trace, mass 78, I hope; I can't see all of the way over there, for benzene (indicating). The top trace is the Nafion direct injection interface, the bottom trace is the purge and trap; and, I think to anyone's satisfaction the GC resolution is virtually identical in both cases.

Now, this is all well and good, but assuming that you can only inject 250 microliters of water into this system, you are limited to a factor of 20 loss in sensitivity, assuming that five milliliters would normally be used in a

purge and trap operation. Therefore, we are not proposing this technique, supplant purge and trap. We are only saying that in those samples where you have a very high concentration of material this may offer a solution to diluting and rediluting your sample with water and purging it, you can just inject different volumes of it into the system using this technique and get some pretty good analytical results.

On this slide we have a response plot. The bottom axis is the amount injected in nanograms and up this side is an arbitrary uncorrected area count measurement. The idea here is to show you that although there is a displacement in the slope of the direct aqueous injection response curve which is this bottom line; I took some liberaties and dotted it down here at the low end where it didn't have any sensi-

tivity (indicating). The purge and trap line is the top one and basically they are the same, in the sense that you can get good linear response over a broad range of concentration. This concentration out here is about 1200; 1200 nanograms is this last data point injected into the system (indicating).

On this slide we have determined the limit of detection based on a 250 microliter injection volume into the Nafion system. What I want to point here is that there are some compounds that have poorer detection than others. Simply put, 1,2-dichloroethane at a 2,000 nanogram detection limit which is rather poor. The bromodichloromethane also had a 2,000 nanogram detection limit. I have no real good explanation for this since a lot of this work is preliminary. It may be that those materials have some significant affinity for the Nafion and, therefore, they are not transmitted effectively at low concentration.

However, benzene down here at 80 nanograms in a 250 microliter injection...or excuse me, this 80 micrograms per liter based on a 250 microliter injection. Toluene at 40. Aromatic hydrocarbons give very good transmission through the Nafion.

In order to try to nail down what the mechanism of some compounds being better performers than others, we calculated the recovery, if you will, of various different levels of standards injected through the Nafion interface and run by the purge and trap technique. We assumed the purge and trap technique was perfect; and, therefore, we ratioed everything to the purge and trap data at the same concentration. This chart shows the recovery of the materials that we studied. At the top is chloromethane and needless to say, a highly volatile gas which is not trapped all that well on the tenax trap

and lost somewhat through the GC column by migration. Performs much better by the Nafion technique. In fact, the ratio of the concentrations of the same material injected was 360. So we are getting almost a four-fold increase in sensitivity of chloromethane by this technique; but, down the list the rest of them, for the most part, are less than 100 which says that the Nafion is not transmitting quite as well as the purge and trap. With a couple of exceptions. The benzene, for example, is 160.

To get some idea of what effect the Nafion has on this transmission, I have also put on this chart boiling point. We are dealing with a 150 degree injector, we are taking that down to room temperature, presumably the injection has allowed the organic materials to move quickly through the Nafion before the water itself condensences. So let's think about boiling point as being the mechanism by which

materials are transmitted or lost. Well, that didn't work because you go down this list and you look at the boiling points and in some cases the higher boiling points have higher transmission efficiencies; in other cases they don't. So I think the mechanism or the thing to describe, the transmission efficiency probably has more to do with the polarity of the molecule than the boiling point. However, when you deal with similar molecules (i.e., benzene, toluene and xylene) with similar polarities, the transmission efficiency drops off as the boiling point increases.

The same is true for the chlorinated organic molecules, chloromethane, methylene chloride, chloroform and carbon tetrachloride which have the same trend as the boiling point increases, the transmission efficiency drops off;

which says that there is some condensation taking place in the Nafion tube. The idea here was also to determine how one can do the analyses on complex or nasty samples. We had a bunch of really nasty samples with water from a low BTU gasifier and if any of you have done any synfuel wastewater work you know that it may only be about half water and the rest of it is suspended garbage.

This is a sample run through the Nafion of the synfuel wastewater from a low BTU gasifier. The movements in the baseline down here are benzene and toluene; the two constituents of the priority pollutants that were actually observed in this sample. If you can notice these peaks, that's phenol and those are methyl phenols. The phenol and the methyl phenols injected by this technique not only passed the Nafion onto the GC column, but those

rascals can actually be chromatographed very nicely with the Carbowax on Carbopack column; something I didn't realize would be the case.

A sample was also run by purge and trap, the phenols, obviously, were not observed under those circumstances because phenol itself is not purged. We compared the two pieces of data and there was a reasonable correlation between the direct aqueous injection analysis of the sample and the purge and trap analysis of the sample. If one assumed that the low concentration materials would not be seen by the Nafion injection which was the case because we have a higher sensitivity cutoff of about 20 fold.

This is a standard which we ran three days after we finished the low BTU gasification study and surprise, surprise, we got phenols coming out in our standard. Well, obviously, we didn't have any phenols in our standard

to begin with, so it became very obvious to us that one of the problems we would have in running nasty samples through this Nafion interface is a carryover or contamination within the tube itself. When subsequent injections are we made we get a steam distillation effect and the phenols come off in the next sample. Well, that's not very good.

So we bake the Nafion tube 100 degrees centigrade overnight and put it back in the system and ran the standard again. Now all of the phenol materials are gone. So we learned something about the interface; in that when one is running dirty samples they are going to have clean it up and you can clean it up by thermally desorbing it and purging it with an inerx gas. That's all I have on the interface itself. I would like to talk to you just a little bit about where we are going from here.

It's obvious that the loss in sensitivity of a factor of 20 can be debilitating. It's obvious that the contamination problem that one has when you inject dirty samples onto the interface is a shortcoming; but, if one assumes that the Nafion is a good system for reducing the relative humidity of a gas and based on what we have seen that the Nafion can transmit non-polar halogenated organics or non-halogenated organics, non-water soluable species very well, then the thought that comes to mind is, why not use the purging apparatus, purge the volatile organics from the water, and then rather than trapping them secondarily on a tenax trap which is essentially is a water removing system, why not trap them directly on the end of the GC column, but remove the water by running this effluent through the Nafion tube.

Hopefully, within the next few months we

will have some data to show that this technique works and we can remove the trap part of the purge and trap and still maintain the sensitivity that one gets using this technique. If this works then we can go from there because there are many other applications that we are looking at in terms of removing moisture prior to analyses by GC/MS especially when one is dealing with capillary columns where even small amounts of water frozen on the end of the column using subambient conditions will cause the analyses to be totally useless. Thank you very much.

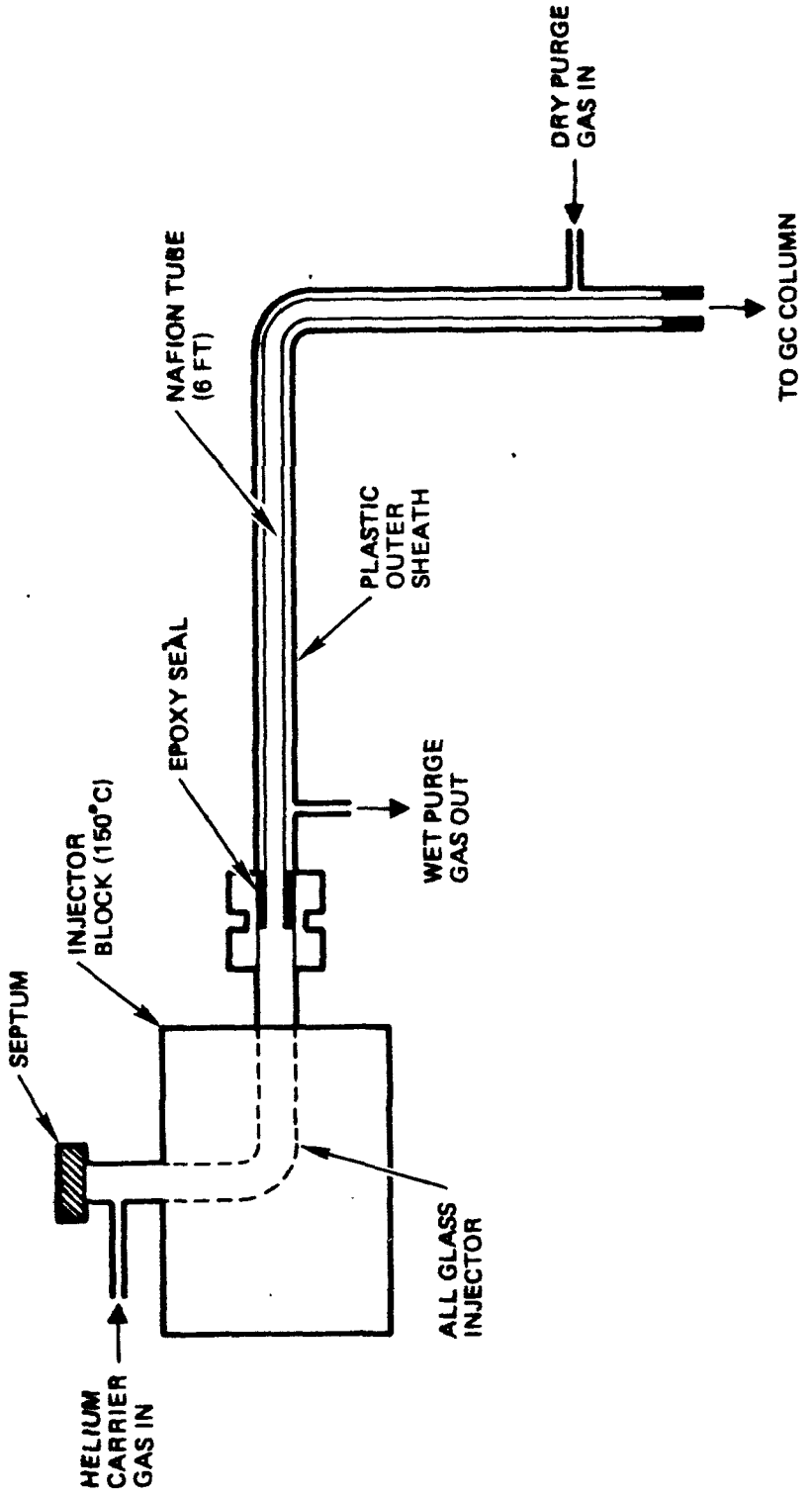
MR. TELLIARD: Any questions; none?

Thank you, Bob; and, that does it for our morning session. Checkout time is 1 o'clock. For those of you who want go up and bring your bags down and put them along the

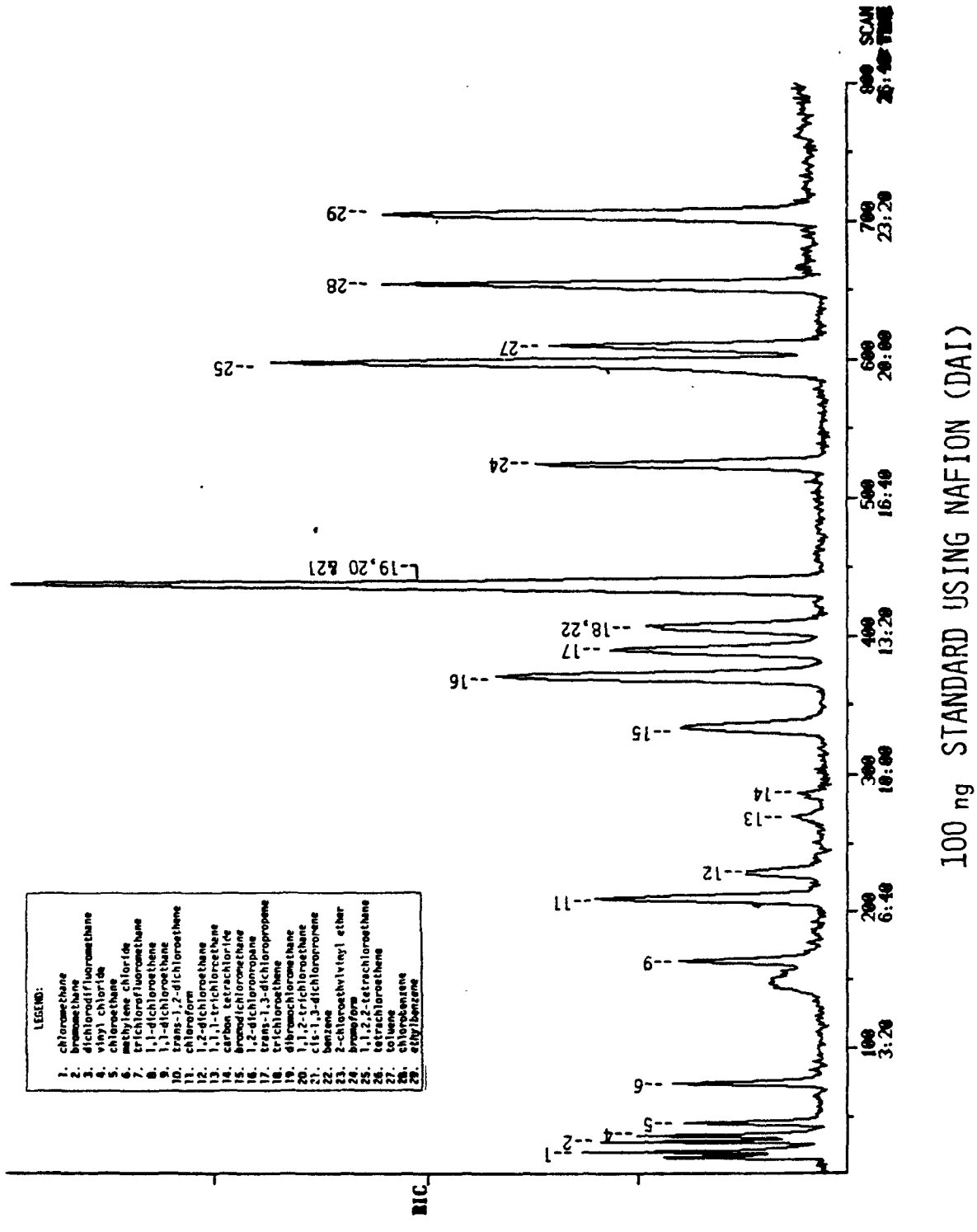
back. If the government people will put their bags on one side and not mingle with the industry bags.

Lunch is next door. So we will break until this afternoon.

(WHEREUPON, the lunch recess was taken.)



CONFIGURATION OF NAFION (DAI) INJECTION SYSTEM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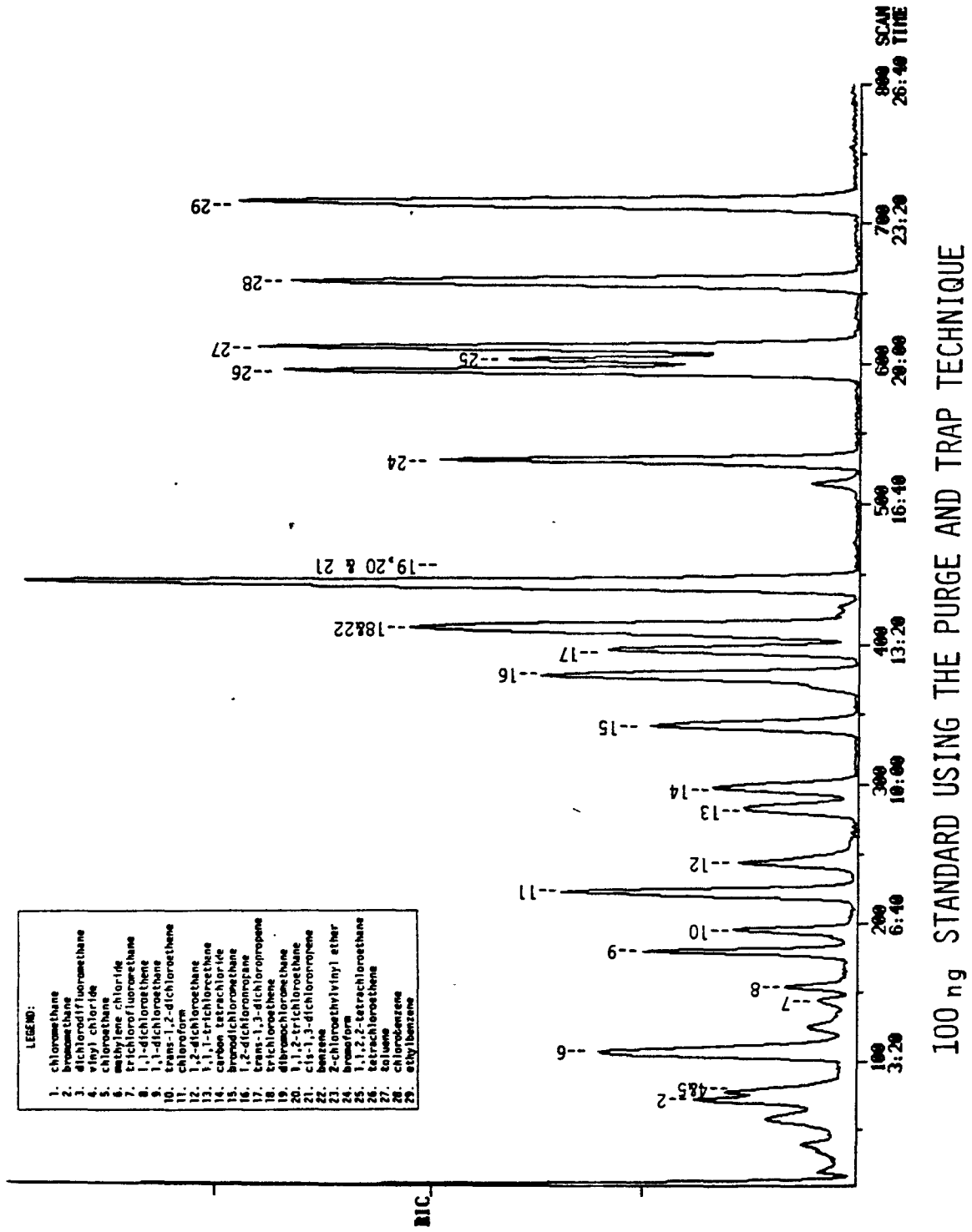
4. vinyl chloride
5. chloroethane
6. methylene chloride
7. trichlorofluoromethane
8. 1,1-dichloroethene
9. 1,1-dichloroethane
10. trans-1,2-dichloroethene
11. chloroform
12. 1,2-dichloroethane
13. 1,1,1-trichloroethane
14. carbon tetrachloride
15. bromodichloromethane
16. 1,2-dichloropropane
17. trans-1,3-dichloropropene
18. trichloroethene
19. dibromochloromethane
20. 1,1,2-trichloroethane
21. cis-1,3-dichloropropene
22. benzene
23. 2-chloroethylvinyl ether
24. bromoform
25. 1,1,2,2-tetrachloroethane
26. tetrachloroethene
27. toluene
28. chlorobenzene
29. ethylbenzene
TIC
SCAN
100 ng STANDARD USING NAFION (DAI)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4. vinyl chloride
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6. methylene chloride
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9. 1,1-dichloroethane
10. trans-1,2-dichloroethene
11. chloroform
12. 1,2-dichloroethane
13. 1,1,1-trichloroethane
14. carbon tetrachloride
15. bromodichloromethane
16. 1,2-dichloropropane
17. trans-1,3-dichloropropene
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19. dibromochloromethane
20. 1,1,2-trichloroethane
21. cis-1,3-dichloropropene
22. benzene
23. 2-chloroethylvinyl ether
24. bromoform
25. 1,1,2,2-tetrachloroethane
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27. toluene
28. chlorobenzene
29. ethylbenzene
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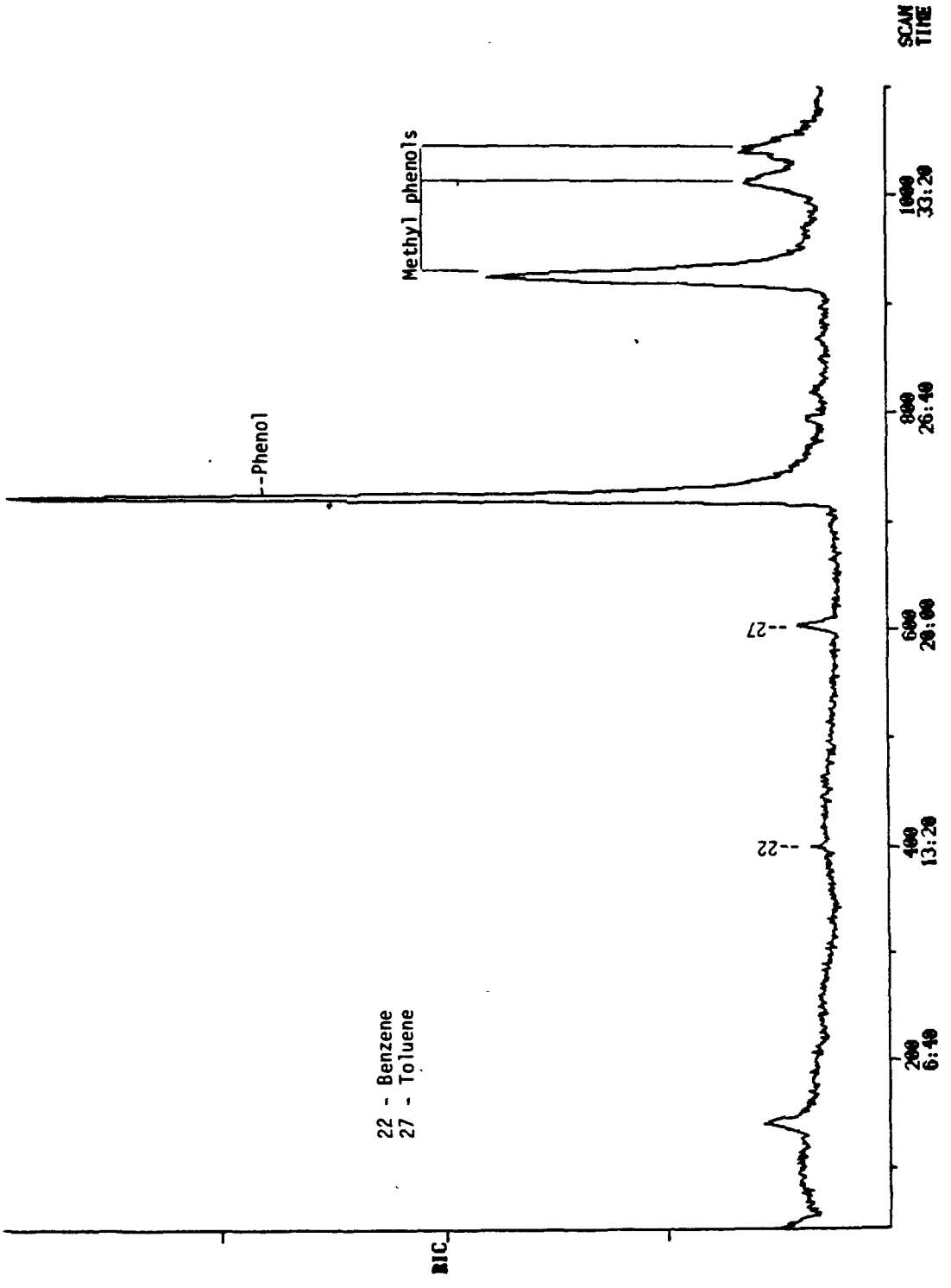
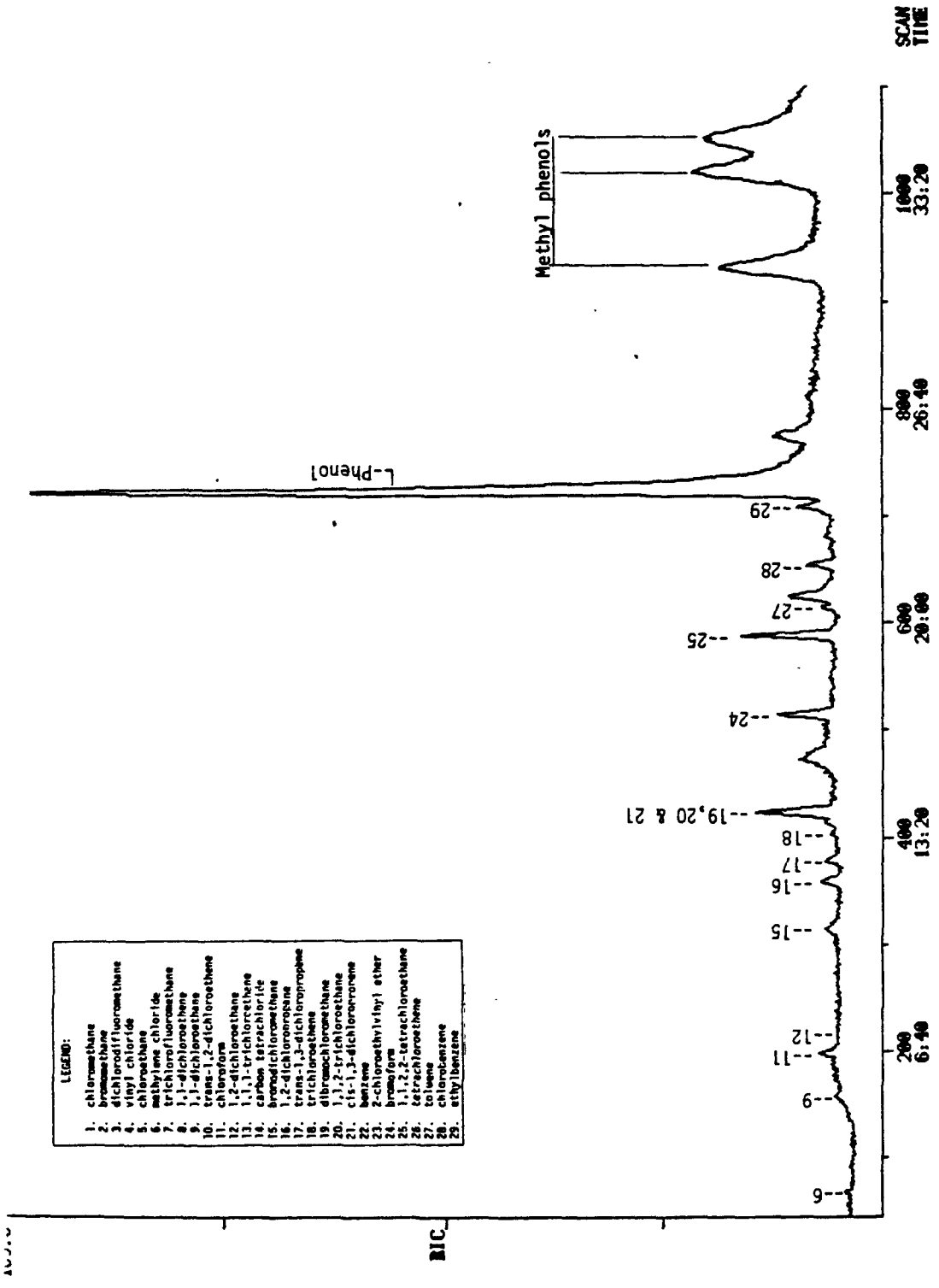
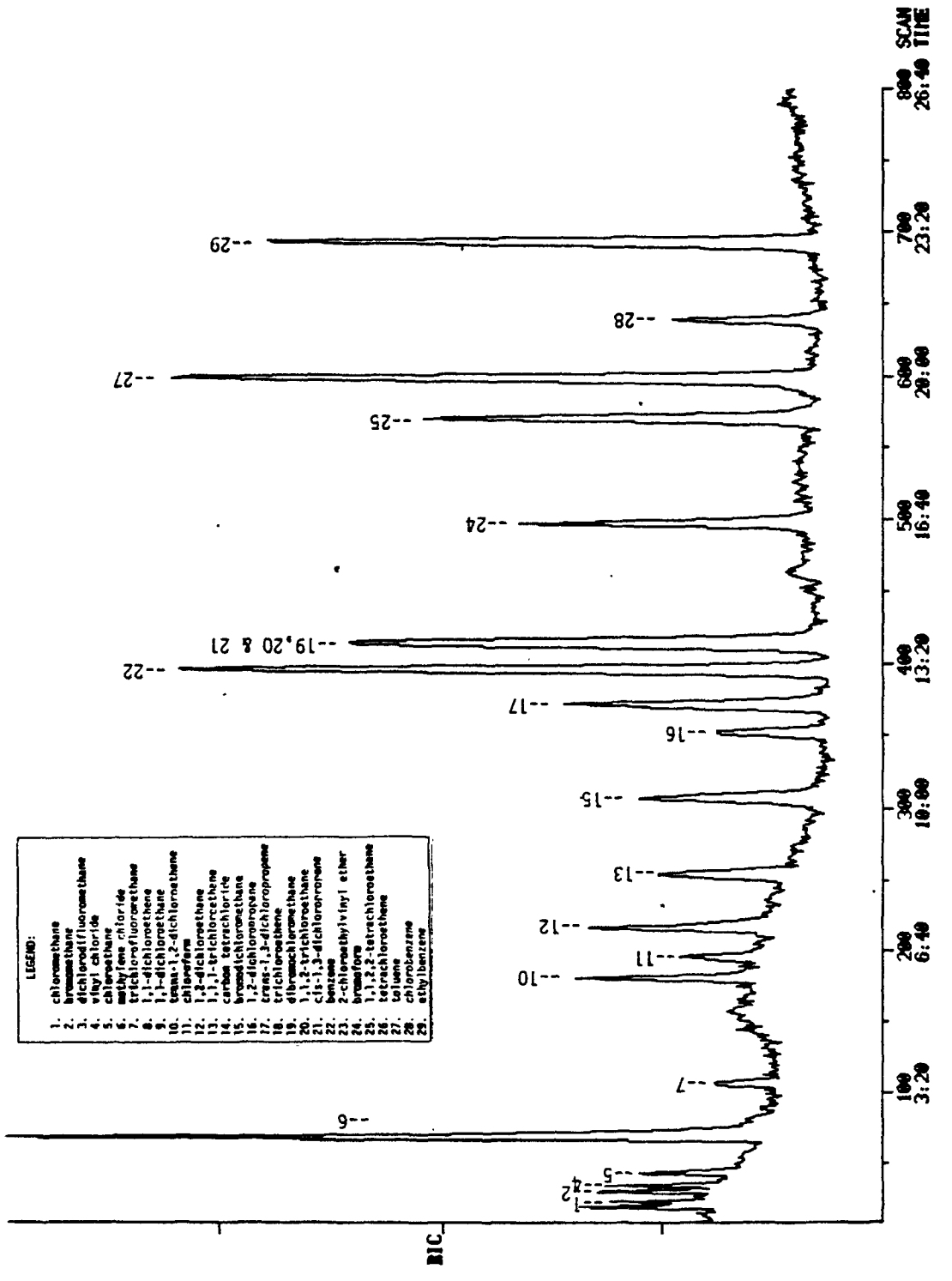
SCAN TIME
100 ng STANDARD USING THE PURGE AND TRAP TECHNIQUE



SYNFUEL WASTEWATER SAMPLE RUN BY DIRECT AQUEOUS INJECTION



100 ng VOA STANDARD RUN USING DIRECT AQUEOUS INJECTION,
3 DAYS AFTER SYNFUEL WASTEWATER SAMPLES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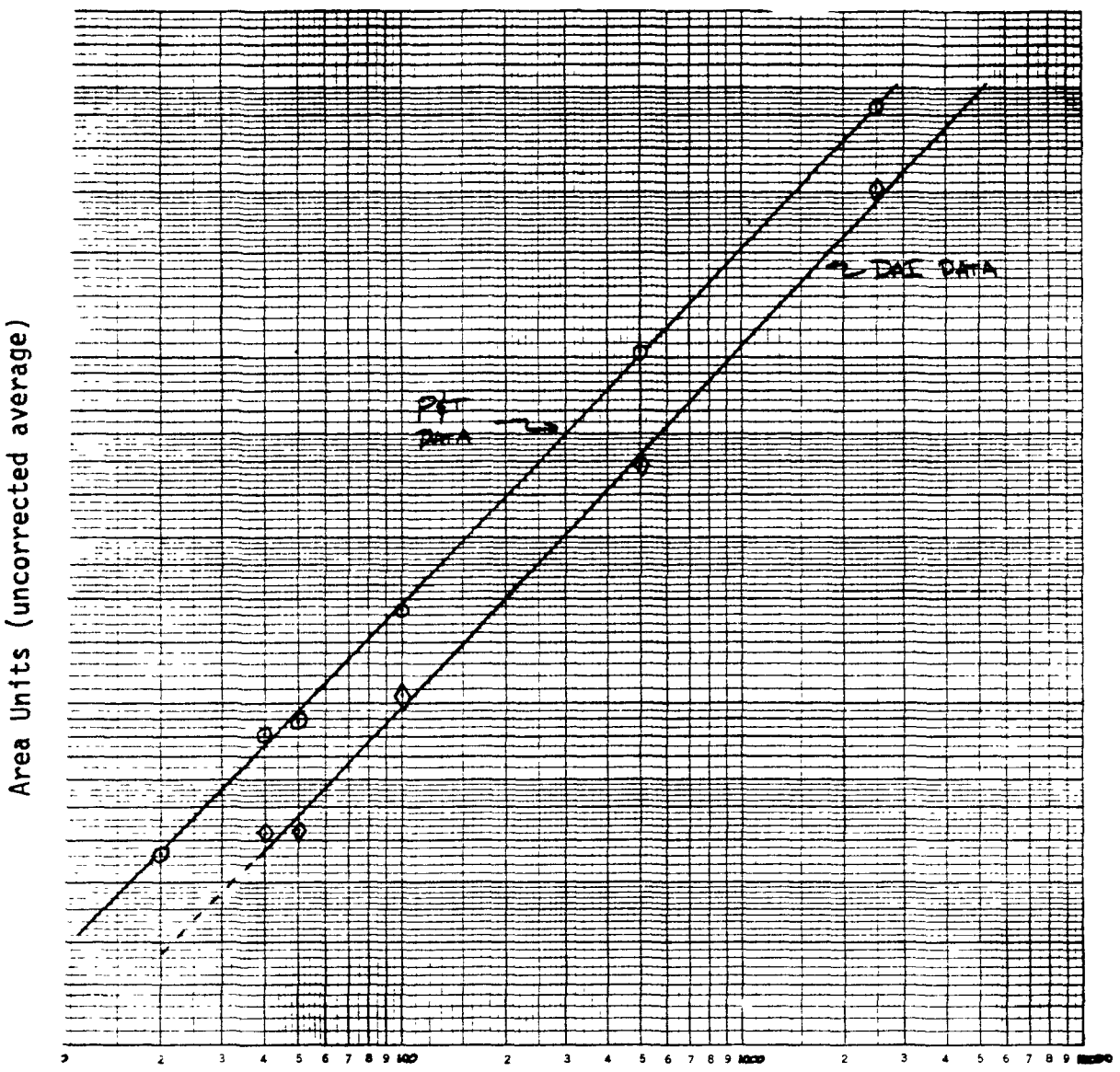
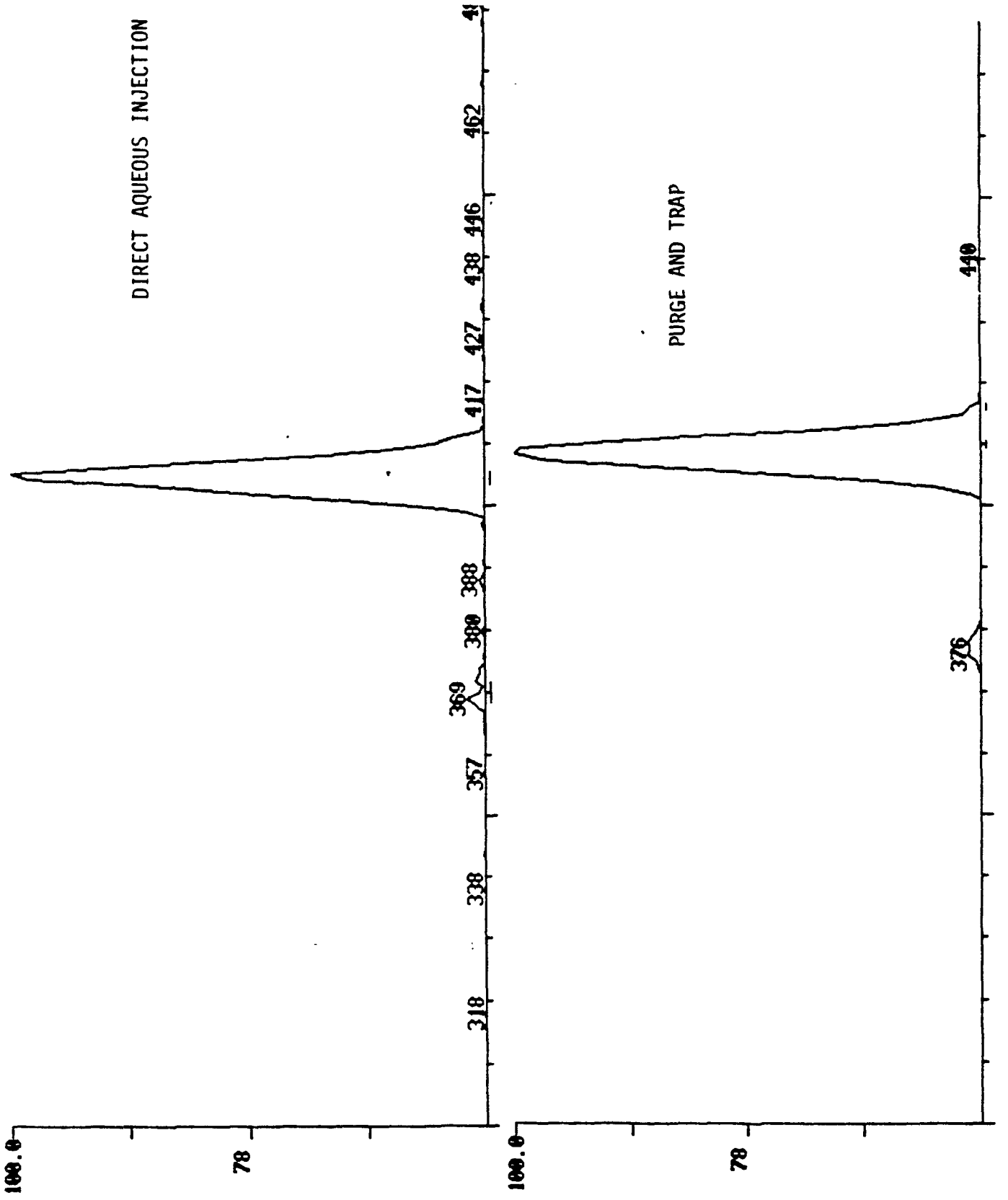
3. dichlorodifluoromethane
4. vinyl chloride
5. chloroethane
6. methylene chloride
7. trichlorofluoromethane
8. 1,1-dichloroethene
9. 1,1-dichloroethane
10. trans-1,2-dichloroethene
11. chloroform
12. 1,2-dichloroethane
13. 1,1,1-trichloroethene
14. carbon tetrachloride
15. bromodichloromethane
16. 1,2-dichloropropene
17. trans-1,3-dichloropropene
18. trichloroethene
19. dibromochloromethane
20. 1,1,2-trichloroethane
21. cis-1,3-dichloropropene
22. benzene
23. 2-chloroethylvinyl ether
24. bromoform
25. 1,1,2,2-tetrachloroethane
26. tetrachloroethene
27. toluene
28. chlorobenzene
29. ethylbenzene
BIC
SCAN TIME
100 ng VOA STANDARD RUN USING DIRECT AQUEOUS INJECTION
AFTER OVERNIGHT BAKE-OUT AT 100°C

CHLOROFORM RESPONSE CURVE





COMPARISON OF BENZENE PEAK WIDTH ANALYZED BY PURGE AND TRAP, AND DIRECT AQUEOUS INJECTION

OBSERVED DETECTION LIMITS FOR NAFION DIRECT AQUEOUS INJECTION

Reference Number	Compound	Limit of Detection (ug/L)*
1.	chloromethane	40
2.	bromomethane	120
3.	dichlorodifluoromethane	400
4.	vinyl chloride	120
5.	chloroethane	200
6.	methylene chloride	160
7.	trichlorofluoromethane	160
8.	1,1-dichloroethene	200
9.	1,1-dichloroethane	120
10.	trans-1,2-dichloroethene	160
11.	chloroform	160
12.	1,2-dichloroethane	2000
13.	1,1,1-trichloroethane	160
14.	carbon tetrachloride	200
15.	bromodichlororomethane	2000
16.	1,2-dichloropropane	200
17.	trans-1,3-dichloropropene	120
18.	trichloroethene	160
19.	dibromochloromethane	160
20.	1,1,2-trichloroethane	160
21.	cis-1,3-dichloropropene	120
22.	benzene	80
23.	2-chloroethylvinyl ether	N/A
24.	bromoform	120
25.	1,1,2,2-tetrachloroethane	160
26.	tetrachloroethene	160
27.	toluene	40
28.	chlorobenzene	80
29.	ethylbenzene	160

* Based on 250 uL Injection Volume

DIRECT AQUEOUS INJECTION RECOVERY EXPRESSED RELATIVE TO PURGE AND TRAP DATA FOR THE SAME STANDARDS OF VARYING CONCENTRATION

Reference Number	Compound	Direct Aqueous Recovery Relative to Purge and Trap (%)	B.P. (°C)
1.	chloromethane	360	-24
2.	bromomethane	62	4
3.	dichlorodifluoromethane	--	--
4.	vinyl chloride	81	-14
5.	chloroethane	45	12
6.	methylene chloride	--	--
7.	trichlorofluoromethane	--	--
8.	1,1-dichloroethene	--	--
9.	1,1-dichloroethane	39	57
10.	trans-1,2-dichloroethene	110	47
11.	chloroform	53	62
12.	1,2-dichloroethane	--	--
13.	1,1,1-trichloroethane	81	74
14.	carbon tetrachloride	33	77
15.	bromodichloromethane	--	--
16.	1,2-dichloropropane	--	--
17.	trans-1,3-dichloropropene	71	104
18.	trichloroethene	38	87
19.	dibromochloromethane	--	--
20.	1,1,2-trichloroethane	--	--
21.	cis-1,3-dichloropropene	67	112
22.	benzene	160	80
23.	2-chloroethylvinyl ether	--	--
24.	bromoform	61	150
25.	1,1,2,2-tetrachloroethane	42	146
26.	tetrachloroethane	36	121
27.	toluene	84	111
28.	chlorobenzene	38	132
29.	ethylbenzene	64	136

A F T E R N O O N S E S S I O N

MR. TELLIARD: Bob Maxfield is from Versar. About two years ago we had some concern in two particular areas in the mining industries, where we looked at some comparability between ICAP and AA. Versar, i.e., Bob, spent a lot of time and effort putting together a study which looked at the comparability, in a small sense, within the maxtrix of a mining sample; and, since then they have done the national validation study for ICAP and Bob is here today to tell us a little bit about it.

RESULTS OF THE U.S. EPA NATIONAL VALIDATION STUDY OF THE INDUCTIVELY COUPLED PLASMA METHOD

Robert Maxfield, Versar, Inc.

MR. MAXFIELD: Good afternoon. This afternoon I would like to briefly discuss the Inductively Coupled Plasma Method and the validation study that Versar is currently conducting on this method for EMSL-Cincinnati.

The method was originally published on December 3rd, 1979 in the Federal Register and has since been revised. The method that we are validating is method 200.7 which, as I said, is a revised method based upon the December 3rd, 1979 Federal Register version.

The method describes the requirements for ICP in the analyses of water and wastewater and details analytical procedures such as the sample preparation, interference testing, operating conditions, and quality control procedures that are required for the analyses

of water and waste by Inductively Coupled Plasma Emission Spectroscopy, or ICP. The objective of the validation study is to define the precision and accuracy of the ICP method. As we heard yesterday, EMSL has come up with a standard validation procedure which they have used on the 600 methods as well as the 624, 625 GC/MS methods. This is, in fact, the same sort of validation procedure that is being used on the ICP method.

My objective this afternoon will be to give you an idea of the study design and also to discuss some preliminary results of the study. The study is not complete at this point and a final report is not expected until sometime this spring. So, therefore, any comments I have with regard to the data are subject to further review and the EPA has not yet reviewed any data at this point.

The overall study design defined by EPA at the outset is shown on this slide and is also in a handout that you have in front of you. I will be discussing the various points of the overall design in some detail as I go along. This study design uses aspects of Youden's unit block approach as well as the ASTM method, Standard Practice for Determination of Precision and Accuracy. This approach has been used, as I said, to validate other methods and is currently being used by us, again, to validate the ICP method.

The first parameter that is included in the study design, is the elements, 27 were studied. All of the priority pollutants are included with the exception of mercury. I have put an asterisk next to the metals which are the priority pollutants.

The second aspect of the study design is the water types, there were six water types;

laboratory pure water, drinking water, surface water and three treated effluents from the chemical manufacturing industry, copper sulphate, sodium hydrosulphate and crome pigments manufacturing. These particular effluents were selected to present an analytical challenge and, indeed, were rather difficult samples to handle with the ICP instrumentation.

The two digestion types that we studied are termed the hard or total metal digestion, and the soft or total recoverable metals digestion. As the names imply, the hard digestion is a more rigorous procedure requiring a greater degree of refluxing and a greater degree of evaporation during the process. It is a somewhat longer procedure than is the soft digestion. These procedures are similar, although not identical to the methods that are included for the atomic absorption procedures in "Methods for Chemical Analyses of Water and Waste," the EMSL method book.

Another variable that we have in our study is the sample spikes. All of the samples were analyzed without any spike, that would be the background analyses. Then, we looked at three concentration levels, at each concentration level we had a Youden pair of spikes; that is, two spikes of similar concentration. That would total seven analyses per sample, background, plus six individual spikes.

The spike solutions were prepared in sealed glass ampules. All of the 27 elements were included in three individual spiked solutions. Very specific instructions were provided to the participating laboratories on how to go about spiking the water types with the elements of interest.

Again, the overall design included 27 elements, six water types, two digestion procedures, six spike samples, plus the background analyses and 12 participating laboratories.

That totals approximately 30,000 data points for 12 participating laboratories. The participating laboratories involved are listed on the slide, there are 12 of them. One is EMSL-Cincinnati. The other 11 were selected by Versar through a selection process whereby we collected bids, these bids were evaluated, the bidders deemed responsive were then included in a preliminary performance evaluation study where they received one sample which was treated in a manner similar to that which would be used in the study later on. They analyzed the sample, provided data to Versar and based upon this data Versar selected the 11 participants that would be included in the study.

The 30,000 data points were then evaluated using a software program developed by EMSL, termed IMVS, and this data is treated such that we produce measures of precision and accuracy for each of the various permutations of water

type, element, and digestion procedure. As you may well imagine, to digest the information generated from this program is very difficult; therefore, the summary plots are generated as an easier way to visualize this vast amount of data. The plots that we have generated summarize precision and accuracy under different conditions. Another plot we use is called the scatter plot which is also termed a Youden plot. These various plots allow one to visualize the vast amount of data and make some interpretations and comparisons between water types, digestion procedures and the like.

This is an example of a precision plot for lab pure water for copper using a hard digestion. Mean recovery is along the horizontal axis in micrograms per liter; and, on the vertical I have precision as S or overall precision, and Sr, single operator precision. The lower line represents a linear regression of the individual

operator precision. The upper, the regression analysis of the overall precision for the 12 laboratories. As is the case in most of my plots, the individual laboratory precision, the single operator precision is better than the overall laboratory precision. There are some 300 of these precision plots.

This next plot is an accuracy plot and what we have along the horizontal access is the true concentration of the spiked samples and on the vertical the mean concentration for the 12 laboratories. This slide also represents data for copper, laboratory pure water and the hard digestion. There are also 300 of these plots.

The third type of plot I call a scatter plot or a Youden plot, allows me to look at both precision and accuracy in one diagram. This plot has concentration plotted along the horizontal access and along the vertical. On the horizontal access we have one ampule from a Youden

pair, on the vertical a second spike of the Youden pair. The crossed lines in the upper right-hand portion of the plot are the true values. If we were to analyze these vials and get exactly the true value in the vial the data point should fall squarely in the center of that crossed area. As you can see, the plots are somewhat scattered about that point. The Xs I have on the diagram indicate one laboratory's data; a "Z" indicates that two laboratory's data fall on top of one another (indicating). This particular data is for chromium in drinking water for the hard digestion. If I show the next slide, I have an elipse drawn around the same set of data. This elipse is at a 45-degree angle to the plot and this is indicative of the larger systematic error involved in the analyses relative to the random error. The random error being made up of two possibilities; that is, random error within the laboratory,

or random error that may be a result of non-uniform samples. If the systematic error is dominate, this eliptical pattern is the pattern that one will get on a Youden or scatter plot. This appears to be the general case at this point in the study; most of the plots seem to form this sort of eliptical pattern.

I would now like to go into a few examples showing you some of the comparisons that we can make using the precision accuracy and scatter type plots. In my first comparison I have aluminum in laboratory pure water on your left and aluminum in effluent number one on the right. We are looking at precision; again, mean recovery for all laboratories on the horizontal axis, and precision on the vertical axis. The axis are identical on both plots. So, therefore, the regression lines are comparable. It would appear, then, that the laboratory pure water, as one might expect, exhibits better precision than

in the case of the effluent; the effluent being the more difficult matrix.

In my next example, we're looking at the same water types. Again, aluminum for laboratory pure water on the left, and aluminum for effluent number one on the right (indicating). These are accuracy plots, true concentration on the horizontal axis and mean recovery for all laboratories on the vertical axis. If the slope of the line approaches 1.0 that would indicate 100 percent recovery or perfect agreement between the true value of the sample and the mean observed value by the laboratories. As you can see, the laboratory pure water, the easier solution to analyze, has a slope of .93 approaching 1.0 which would indicate good recovery. In the case of the effluent, .78 indicates somewhat poorer recovery. This is the general case one would expect when analyzing a more difficult sample, that is, a poor recovery,

poorer precision than would be achieved with the lab pure water. Indeed, these plots for this particular example do point that out.

My next comparison is between digestion types. Again, we had the hard digestion, a more rigorous procedure, and the soft digestion, a less rigorous procedure. These are precision plots, mean recovery along the horizontal and precision along the vertical again. In this particular case, the scatter of points and the linear regressions that result from these points are inconclusive and I wouldn't like to say too much about the differences in precision between the hard and soft digestion. If we look at the accuracy plots for the same data, chromium in effluent number one, hard digestion on the left; chromium effluent number one, soft digestion on the right. The accuracy of the two methods appear to be very similar; that is, the recovery for the hard digestion and the soft digestion

appear to be about the same. Now, if the hard digestion is a more rigorous procedure and we are having some recovery problems with this effluent, one would think that the hard digestion might produce better data. In fact, that doesn't appear to be the case. The soft digestion, a simple or more economical procedure to use appears to be producing for this particular example data with similar recovery.

In is my last example I have a pair of Youden plots. Again, for chromium on the left in the lab pure water, the control; and, chromium for effluent number one on the right. These are scatter plots and the scatter of the points are indicative of the precision with which these laboratories were able to analyze the sample. Note the obvious better precision that one has with the laboratory pure water. The scatter is much tighter, the eliptical pattern again is there in both cases. It does appear, however,

that the chromium data for the effluent is skewed toward the lower left-hand quadrant of the Youden plot. This would be indicative of low recovery, poor recovery than in the case of the laboratory pure water. If the data points were skewed toward the upper right quadrant, this would indicate high recovery; and, again, if the pattern were not eliptical but more circular in nature one would expect that the random error is more dominant than the systematic error or, at least, the errors are somewhat equivalent.

In conclusion I would like to say that the ICP Validation Program is ongoing. The data has not been totally analyzed at this point. We are in the processing of analyzing the data and the report is not due until sometime in the spring. What this report should do is, allow us to quantitate the precision and accuracy for the Inductively Coupled Plasma

Method under a variety of conditions. Specifically with six different water types, realizing that that is not the universe, 27 elements and the two digestion procedures that were used in the study. I thank you for your attention and if there are any questions I would more than happy to try and answer them.

VALIDATION
of ICP for
27 ELEMENTS
in
WATER and WASTES

METHOD 200.7

SPONSORED BY:

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO

ELEMENTS

Al	Co	K
Sb*	Cu*	Si
As*	Fe	Ag*
Ba	Pb*	Se*
B	Li	Na
Be*	Mg	Sr
Cd*	Mn	Tl*
Ca	Mo	V
Cr*	Ni*	Zn*

S3

WATER TYPES

1. LAB PURE WATER
2. DRINKING WATER
3. SURFACE WATER

TREATED EFFLUENTS FROM CHEMICAL MANUFACTURING INDUSTRY

4. COPPER SULFATE
5. SODIUM HYDROSULFATE
6. CHROME PIGMENTS

DIGESTION TYPES

HARD DIGESTION

"TOTAL METALS"

SOFT DIGESTION

"TOTAL RECOVERABLE METALS"

SAMPLE SPIKES

BACKGROUND

CONCENTRATION LEVEL 1	YOUDEN PAIR OF SPIKES	SPIKE 1 SPIKE 2
CONCENTRATION LEVEL 2	YOUDEN PAIR OF SPIKES	SPIKE 3 SPIKE 4
CONCENTRATION LEVEL 3	YOUDEN PAIR OF SPIKES	SPIKE 5 SPIKE 6

OVERALL DESIGN

27 ELEMENTS

6 WATER TYPES

2 DIGESTION PROCEDURES

6 SPIKED SAMPLES + BACKGROUND SAMPLE

12 PARTICIPATING LABS

TOTAL OF ~ 30,000 DATA POINTS

PARTICIPATING LABORATORIES

WEYERHAUSER TECHNOLOGY CENTER

HARRIS LABORATORIES

RALTECH

MONSANTO RESEARCH CORPORATION

ANALYTICS

ERCO

VETTER RESEARCH INCORPORATED

BATTELLE COLUMBUS LABORATORY

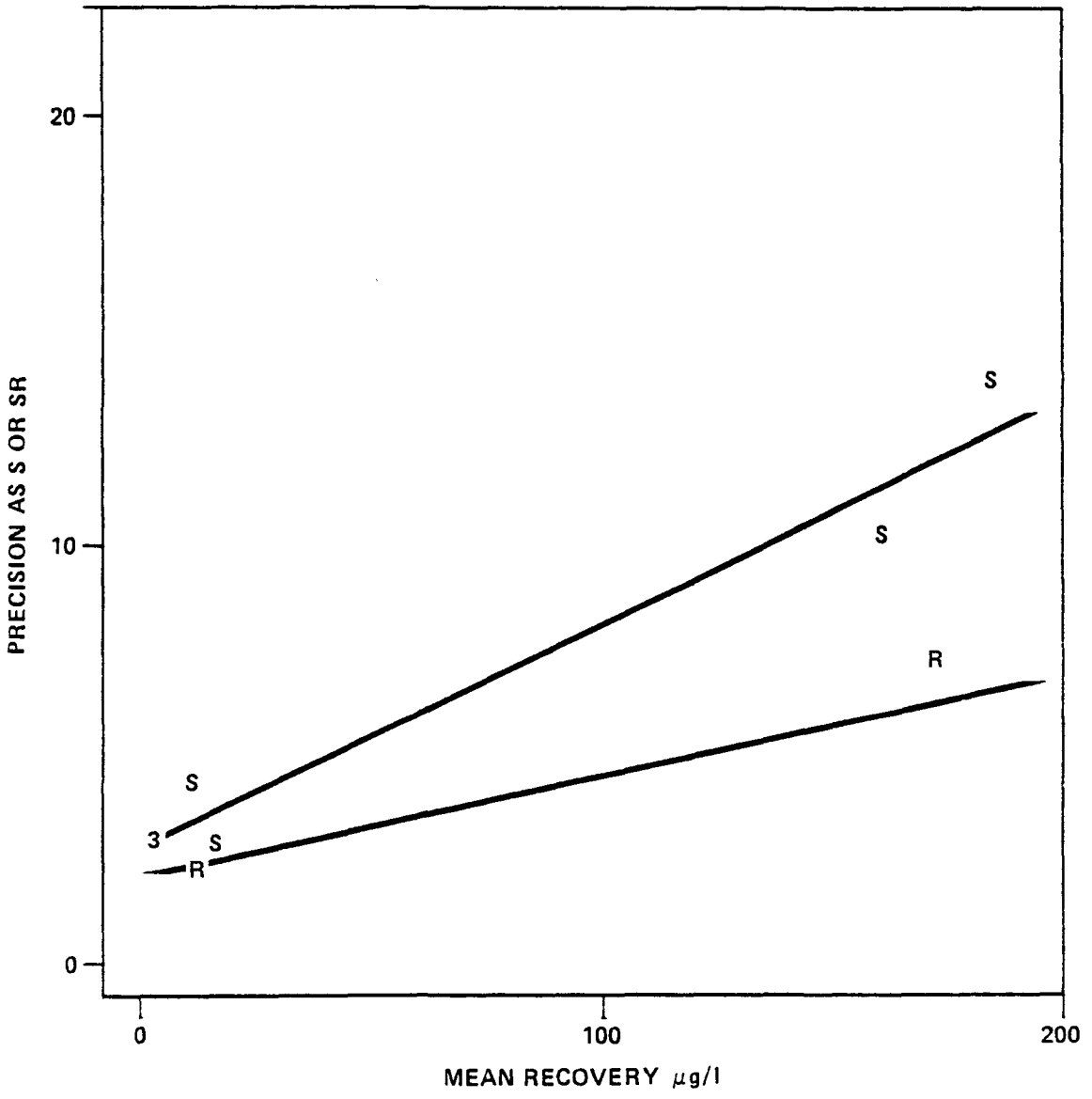
JOHNSON CONTROLS

RADIAN CORPORATION

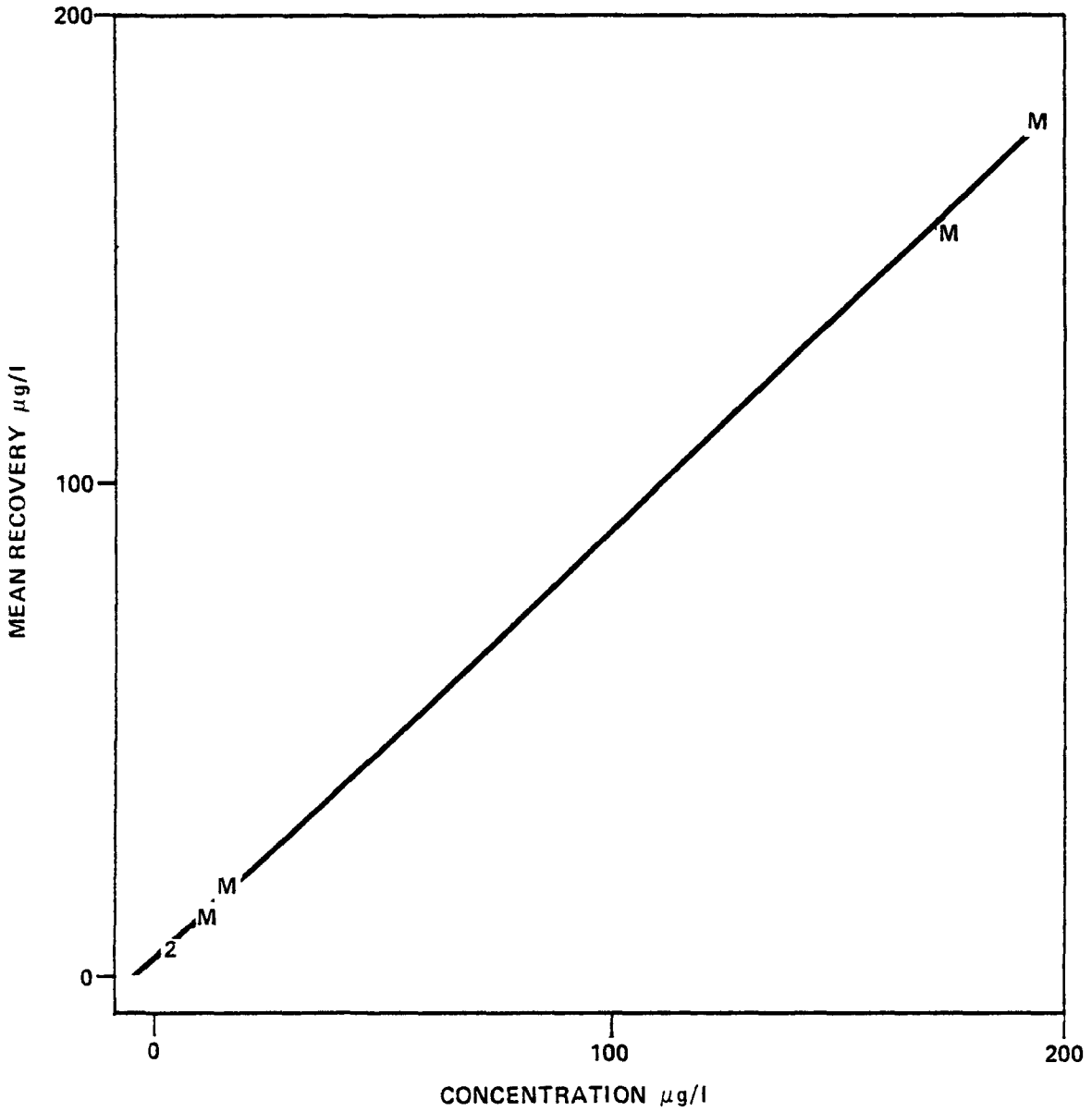
GCA TECHNOLOGY DIVISION

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY

COPPER – LAB PURE, HARD DIGESTION

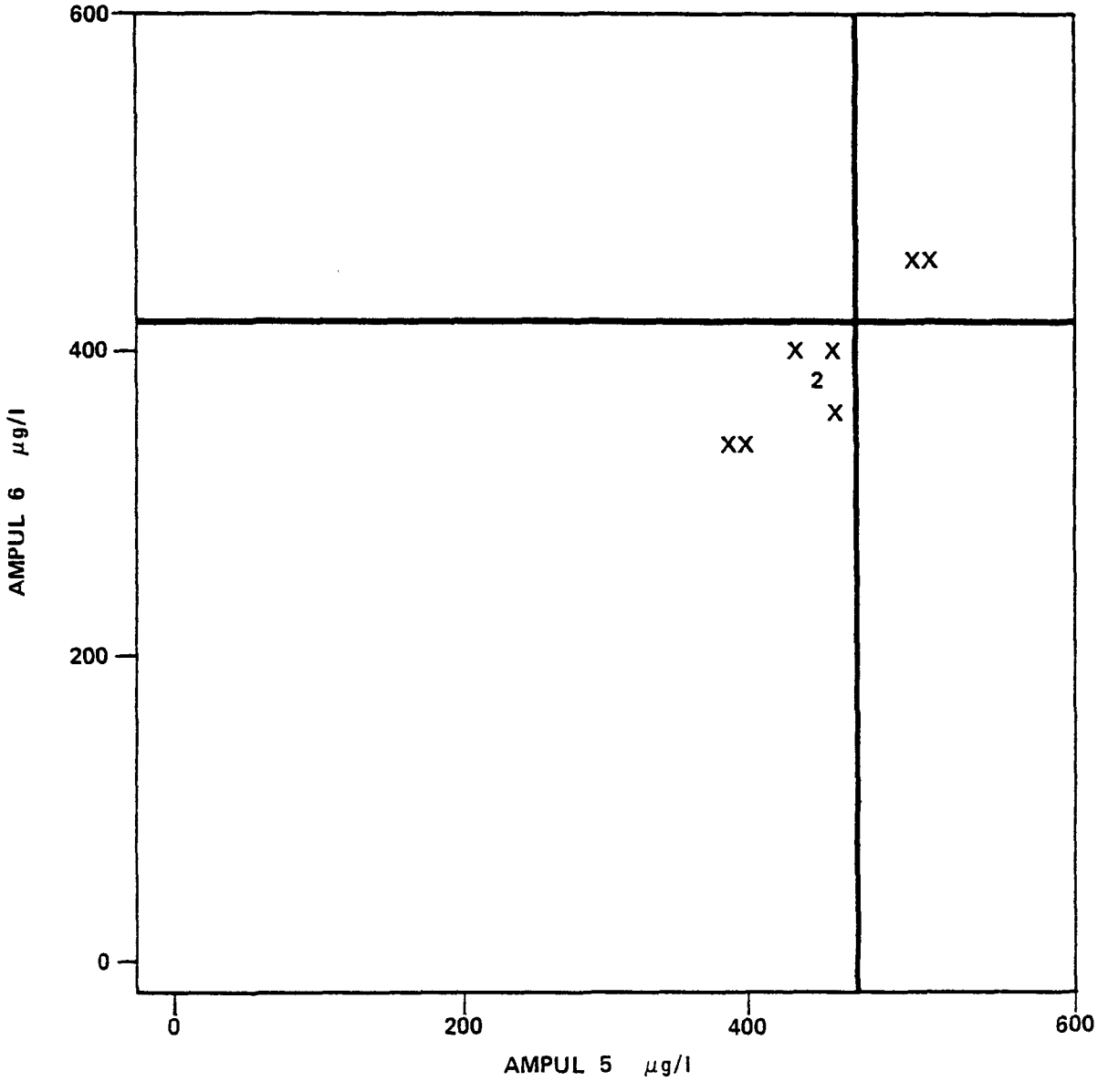


COPPER – LAB PURE, HARD DIGESTION



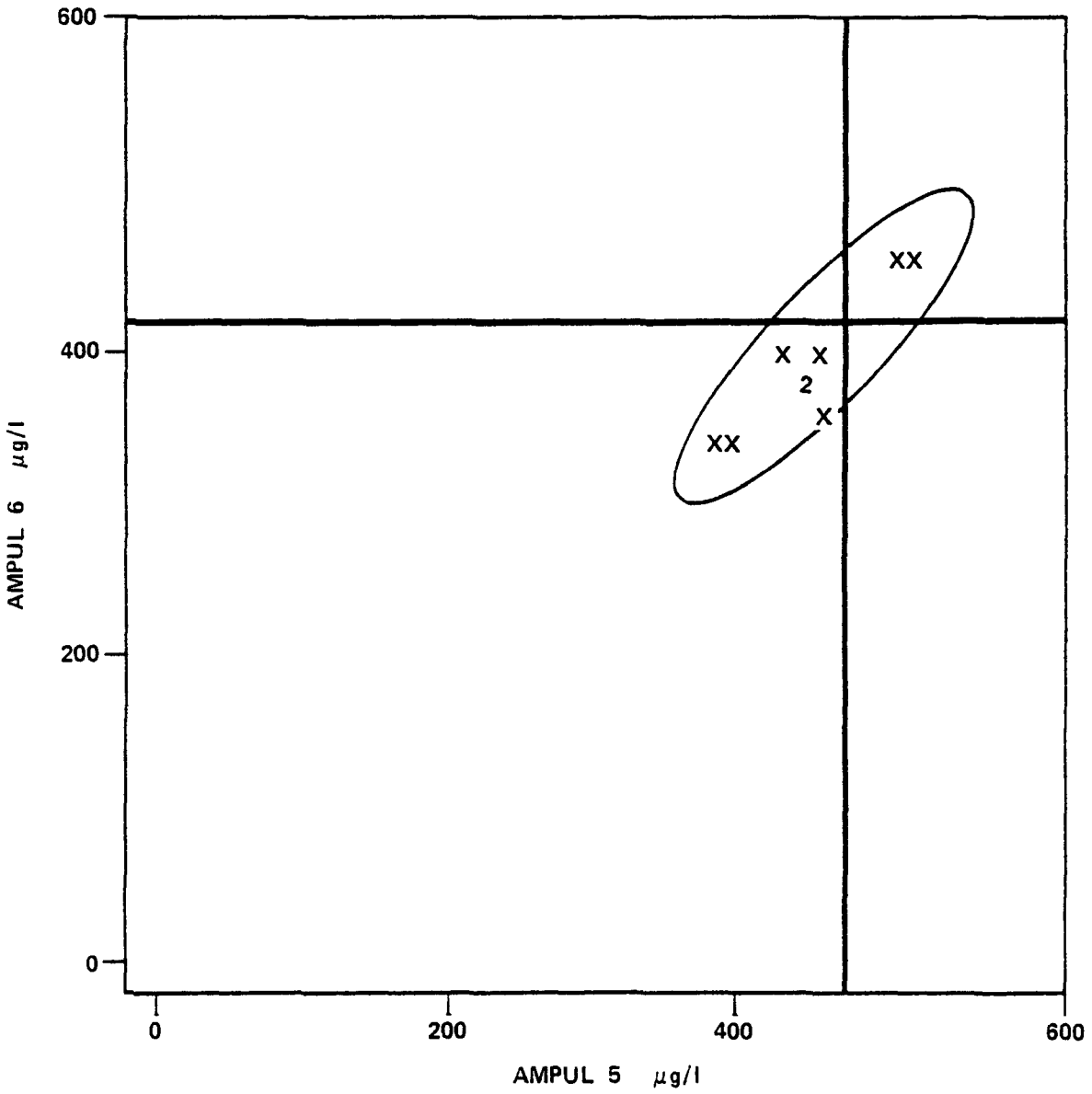
S10

CHROMIUM – DRINKING WATER, HARD DIGESTION

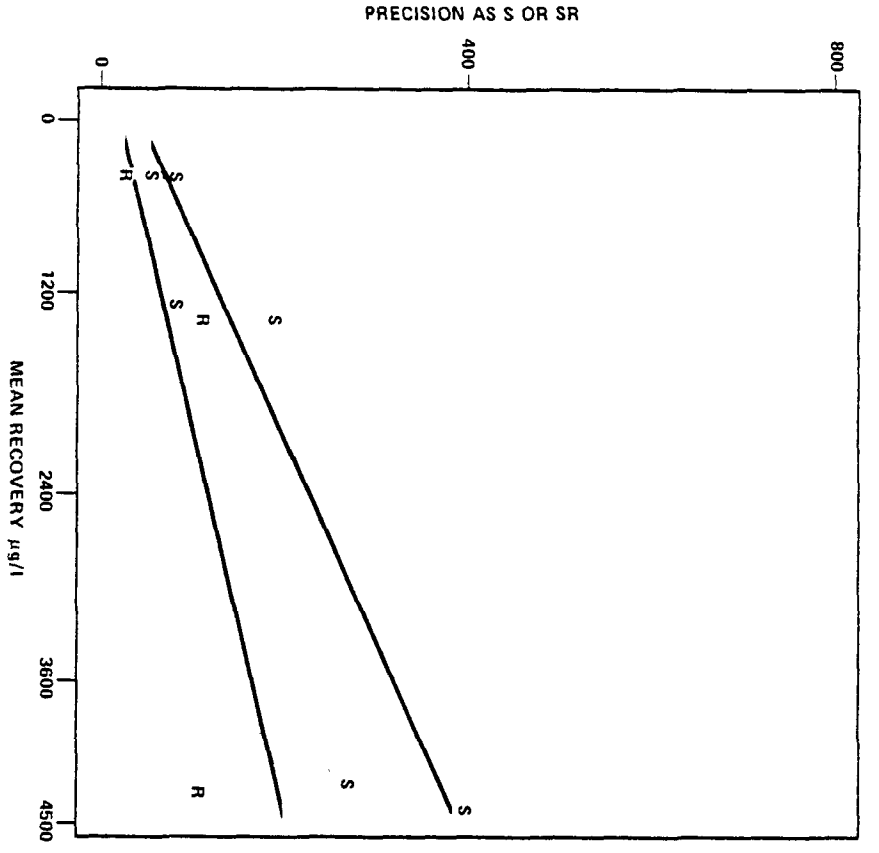


S11

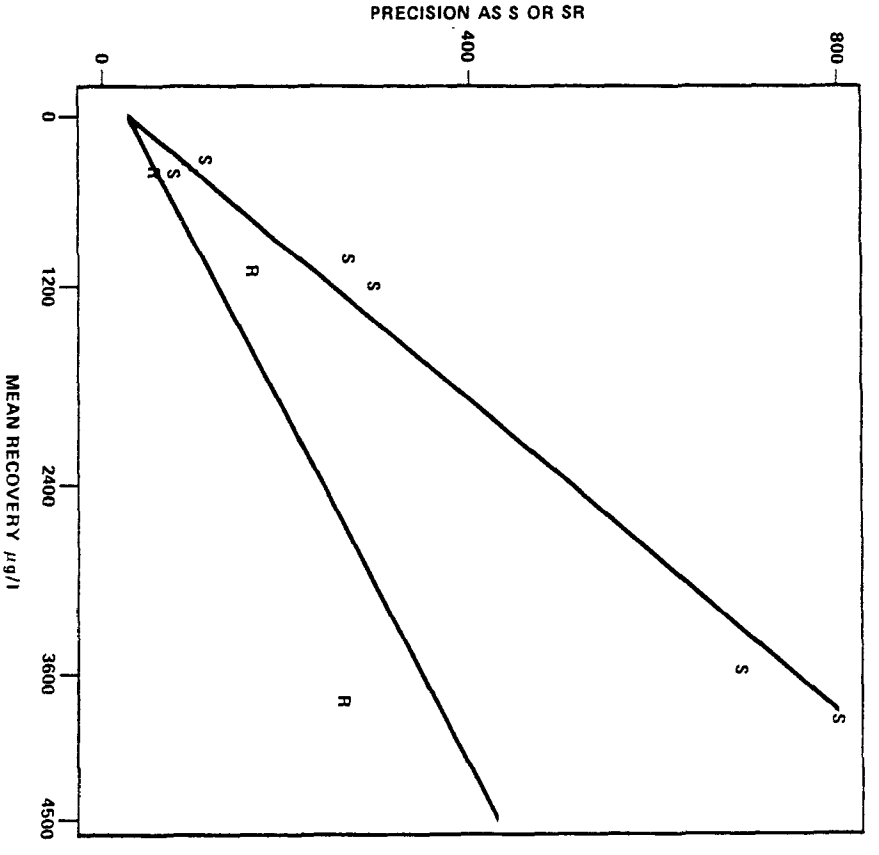
CHROMIUM – DRINKING WATER, HARD DIGESTION



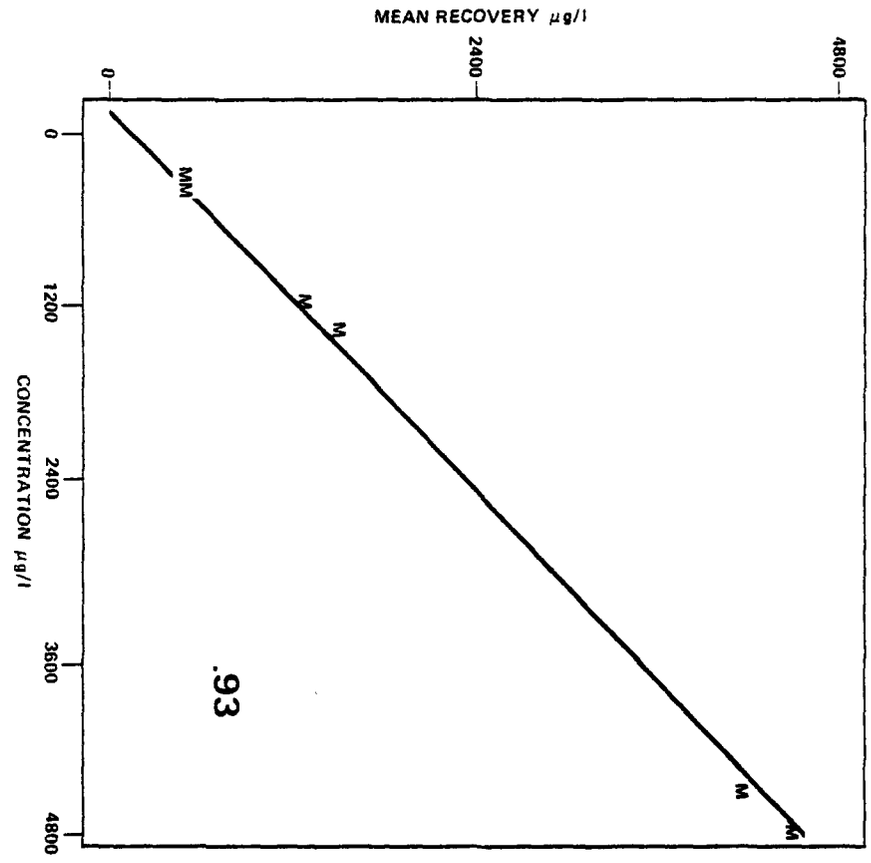
S12



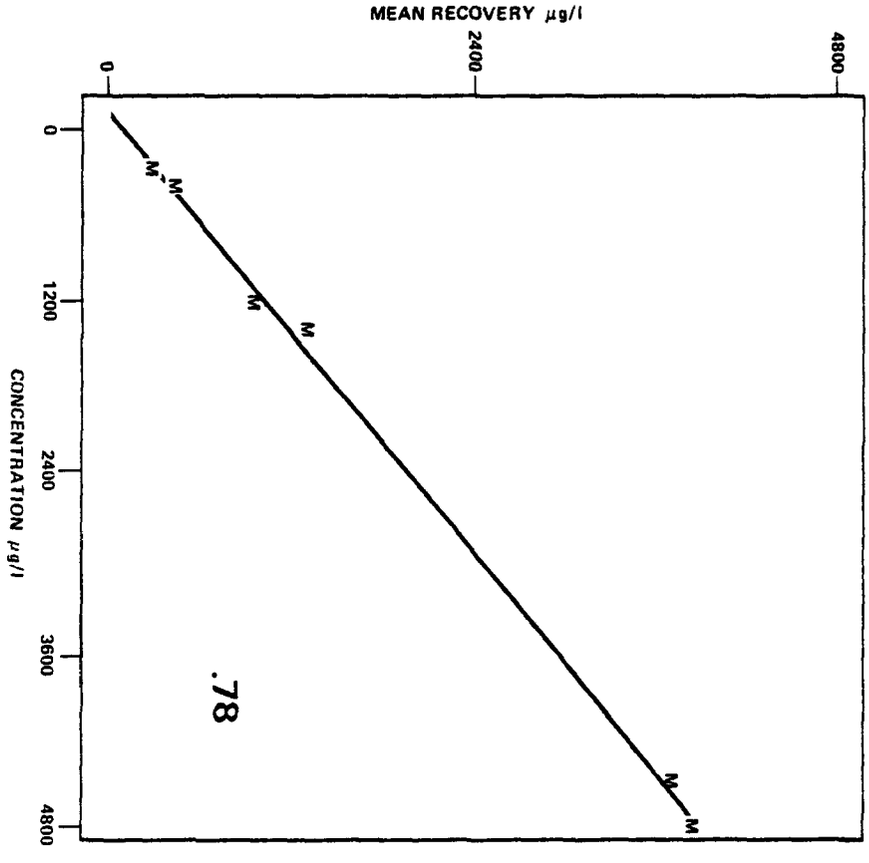
ALUMINUM – LAB PURE, SOFT DIGESTION



ALUMINUM – EFFLUENT 1, SOFT DIGESTION

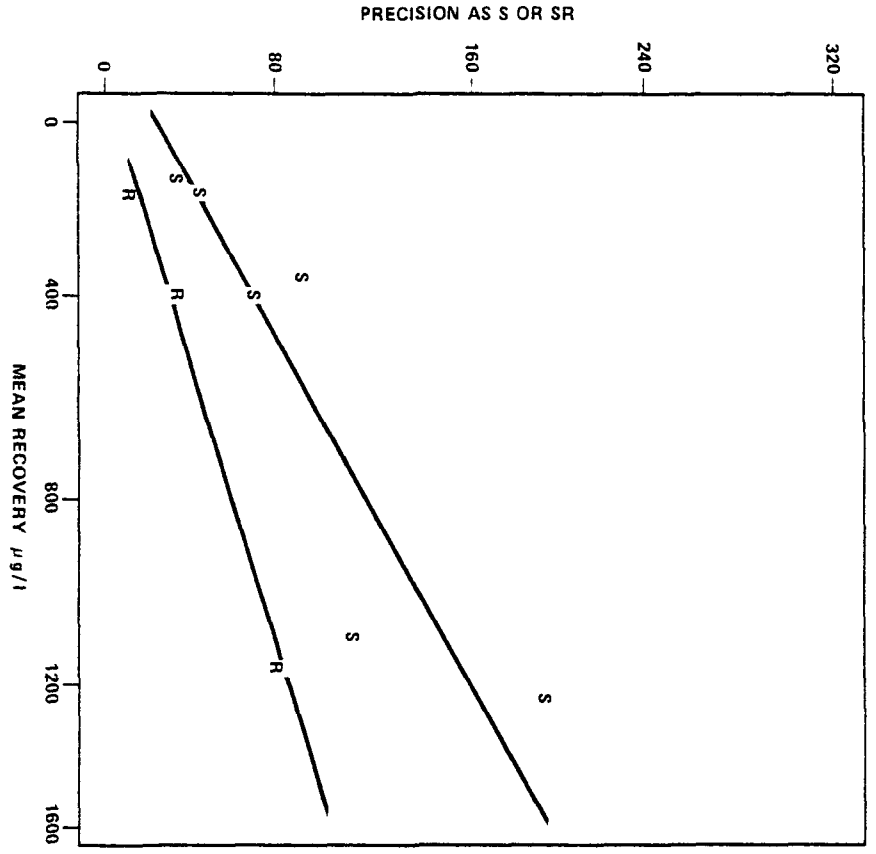


ALUMINUM – LAB PURE, SOFT DIGESTION

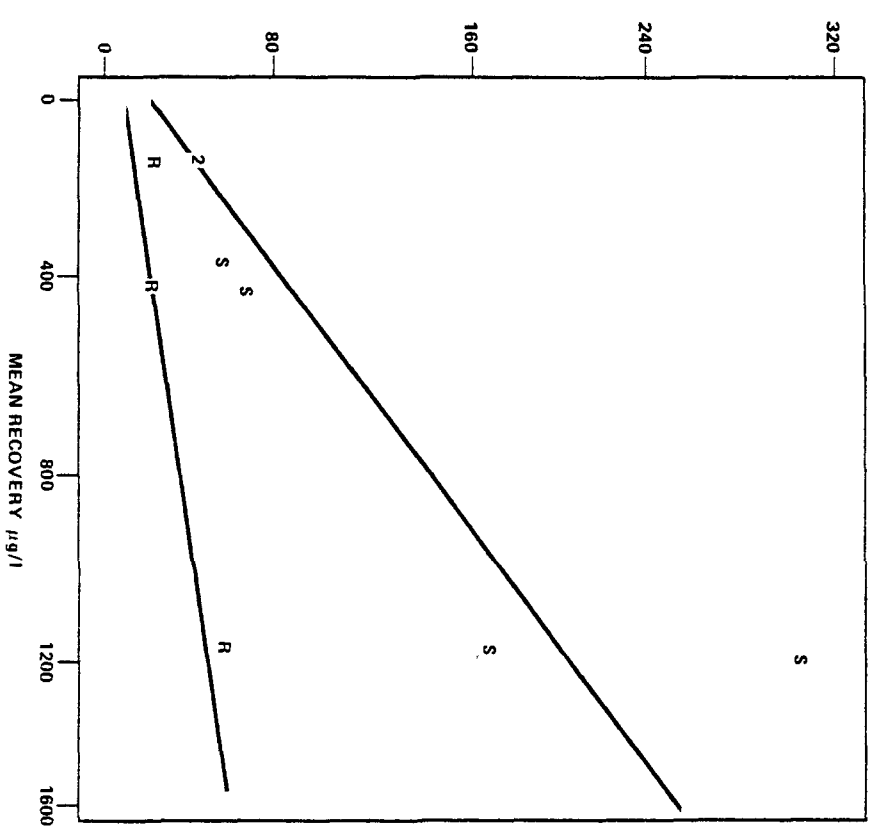


ALUMINUM – EFFLUENT 1, SOFT DIGESTION

S14

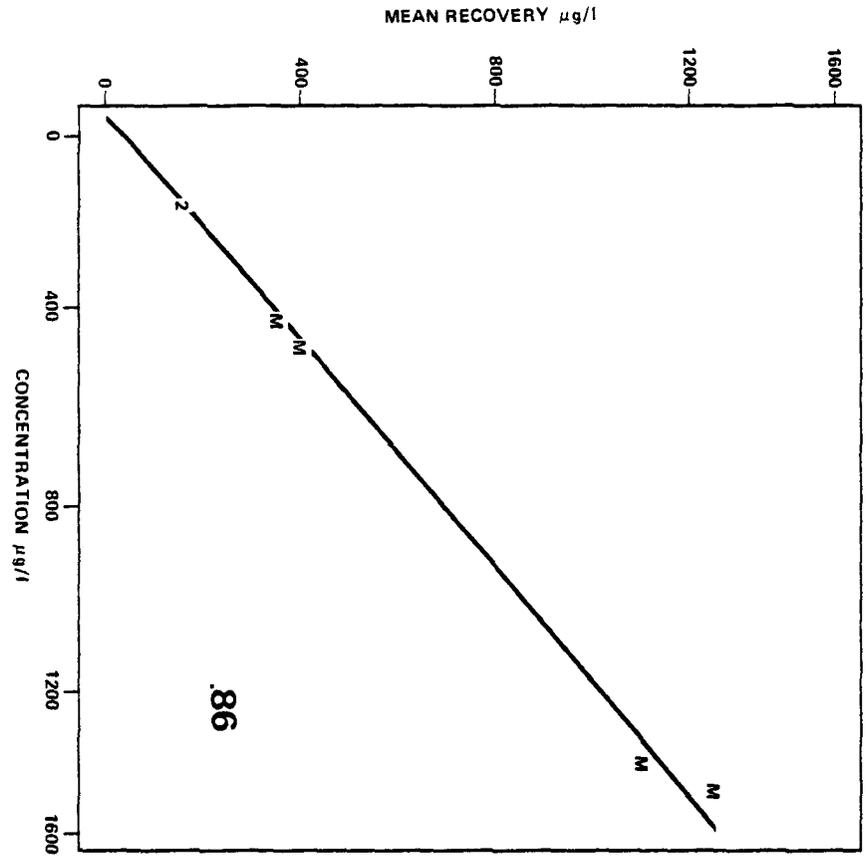


CHROMIUM – EFFLUENT 1, HARD DIGESTION

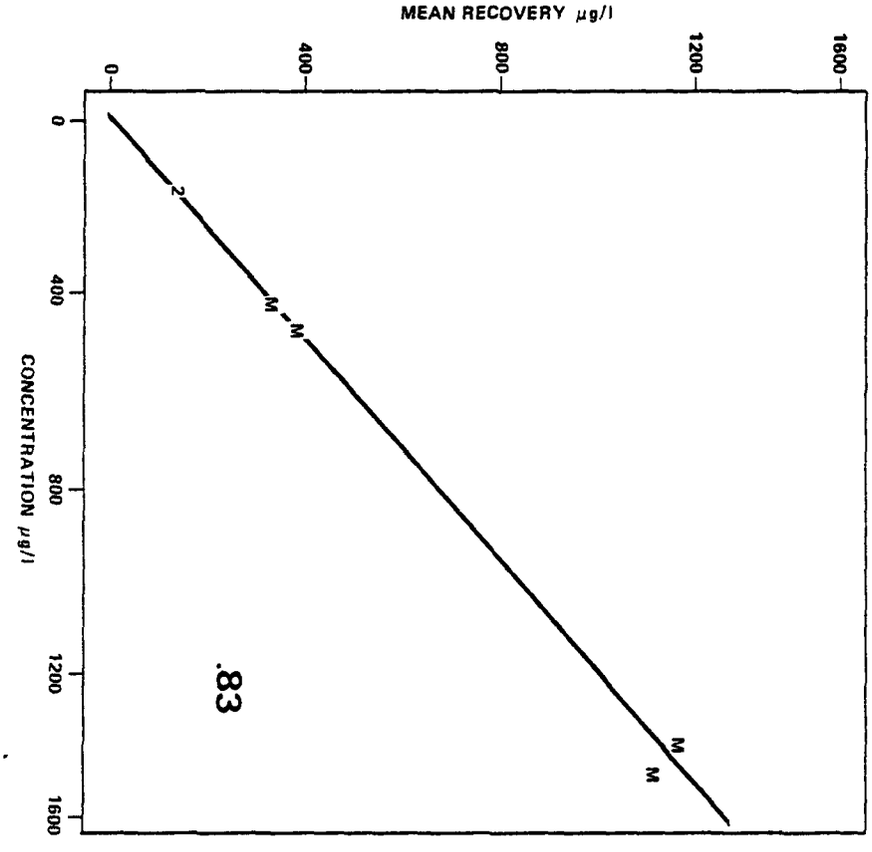


CHROMIUM – EFFLUENT 1, SOFT DIGESTION

S15

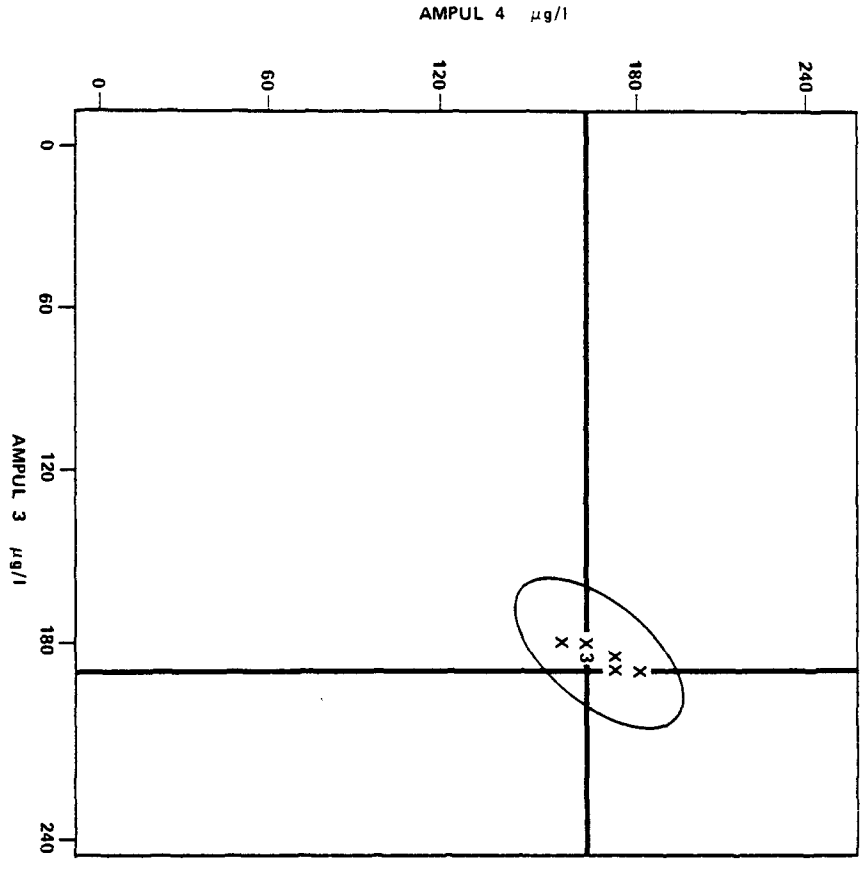


CHROMIUM, EFFLUENT 1, HARD DIGESTION

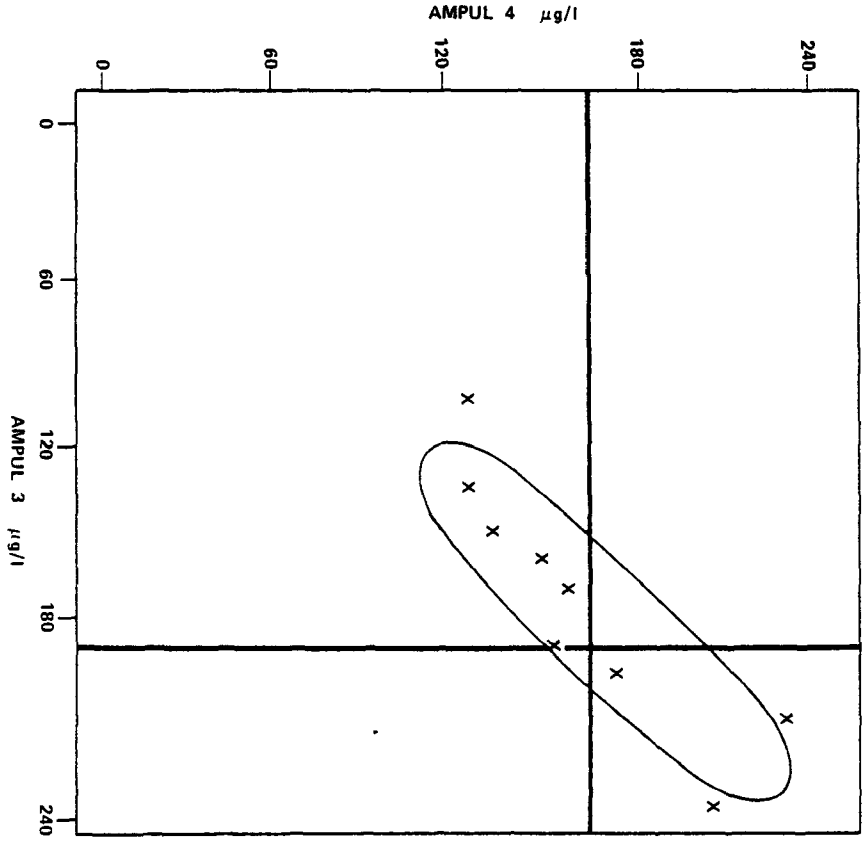


CHROMIUM – EFFLUENT 1, SOFT DIGESTION

S16



CHROMIUM – LAB PURE, HARD DIGESTION



CHROMIUM – EFFLUENT 1, HARD DIGESTION

QUESTIONS AND ANSWERS

FROM THE AUDIENCE: I have one for you. It's my understanding and recollection, and Bill you correct me if I am wrong, that the original ICP, Effluent Guidelines Study on Mining waste was conducted on field samples, spiked and shipped.

MR. MAXFIELD: That is correct.

MR. TELLIARD: That's right.

FROM AUDIENCE: I notice that this study was conducted on ampules split and received and diluted.

MR. MAXFIELD: In fact, it's a little bit more complicated than that. Could I explain.

FROM AUDIENCE: Well, then, my question is and you can maybe cover that in your explanation, then, too, is, did you evaluate the differences in errors that are introduced by those two processes?

MR. MAXFIELD: The answer to that question is no. In fact, what was done is, effluent samples were collected by Versar and tested, split and sent to the participating laboratories. Spiking solutions for all six water types were prepared by Versar and sent to all participating laboratories. The three other water types, the laboratory pure water, surface water and the drinking water were, in fact, collected at each of the participating laboratories in the study. So they are not the same waters.

MR. TELLIARD: The industrial samples, were those treated or untreated?

MR. MAXFIELD: Those were treated wastes.

MR. PRESCOTT: I am Bill Prescott, American Cyanamid Company. I have a question about the spiking solutions. You had obviously Youden pairs at each level, was that correct?

MR. MAXFIELD: That is correct.

MR. PRESCOTT: This implied...I guess I'm having difficulty saying what I want to say; 27 metals, the two Youden pairs that were high for one metal were the same spikes for all 27 metals?

MR. MAXFIELD: Do you mean the same spiked concentrations?

MR. PRESCOTT: In spike concentration.

MR. MAXFIELD: No.

MR. PRESCOTT: Let's say you have got vials A, B, C, D and E. And vials A and B for aluminum were the two low concentrations.

MR. MAXFIELD: That's right.

MR. PRESCOTT: Were those vials also the low concentrations for the other 26 metals?

MR. MAXFIELD: Not necessarily.

There was some mixing involved. For some metals it would not have been the same.

MR. PRESCOTT: Thank you.

MR. MAXFIELD: In fact, there were more than six spiking solutions because of the various matrices involved we had some effluent that had very high background concetrations for many of the metals. So, therefore, if we took something that would be an effective spike in, say, drinking water and attempted to put that into an effluent it would not be a reasonable spike level. There were, in fact, ten sets of spiking solutions; or, ten spiking solutions, five sets. Five sets of Youden pairs.

MR. TONKIN: Dave Tonkin, Centec. I missed the beginning of your talk so maybe you already addressed this, but were all of the instruments used in the study simultaneous or were there any sequential?

MR. MAXFIELD: There were 11

direct readers and one sequential device.

MR. TONKIN: Is there any conclusion about the precision accuracy, one versus the other at this point?

MR. MAXFIELD: There is none at this point and I doubt seriously whether we will be able to draw any conclusion with regard to direct reader versus sequential device with only one sequential device included in the study.

MR. TONKIN: Would you anticipate a need for this in the future? It seems like the instrumentation industry as in terms of ICAP is going towards the sequential.

MR. MAXFIELD: It would seem like a very reasonable thing to do. The problem I see with that is the sequential devices operate very differently and the operator of the sequential device can operate his particular device in so many different ways, using so many different lines and different procedures for background correction, et cetera.

Any other questions?

MR. MEDZ: In the regulations or in the write up of the procedure, are there going to be any changes to reflect that fact, that you have more latitude with sequential instruments in chosing your background correction or moving to another line when there are inferences?

MR. MAXFIELD: The method as it is currently written, I don't believe addresses the sequential device to any great degree. In fact, the lines are not specified at this point. There are some lines that are referred to in the method, but lines are not specified for individual elements; at least that's my understanding at this point.

MR. TELLIARD: Thank you, Bob. When did you say that report was going to be?

MR. MAXFIELD: The spring.

MR. TELLIARD: Direct draft, interim draft; you and Bob Medz, I'm sorry, Bob.

MR. TELLIARD: Our next speaker is from TRW and Ray is going to talk about precision. I won't address the rest of his title because bias is in the eye of the beholder.

A SURVEY OF PRECISION AND BIAS DATA FOR METHODS OF ANALYSIS FOR PRIORITY POLLUTANT ELEMENTS

Ray F. Maddalone, TRW, Inc.

MR. MADDALONE: Having sat through a few days worth of GC/Mass Spec and being a person who is more attuned to the inorganic analysis, I'm going to try to prove that there are other elements than carbon, hydrogen, oxygen, chlorine, and fluorine. I am going to talk about the other parts of the periodic table, in particular the 13 priority pollutant metals.

What we have been listening to is what has been going on with the forefront of technology. What TRW has tried to do in a study for the Electric Power Research Institute (EPRI) is to develop a picture of what the people in the trenches are actually doing and what they are capable of doing. What we have found in this study is that the analysts in the field are not

performing as well as the people on the forefront of technology expect them to.

Before I get into the actual presentation, I want to give you a brief outline of the program that TRW has with the Electric Power Research Institute. It is RP1851-1 and the EPRI program manager is Winston Chow. The project consists of four primary tasks. The first task is one on data base development. In this data, we took data from a number of sources, in particular 100 of the most recent NPDES 2C permit forms which were coded and then put into our computer system at TRW. In addition, all of EPA/EGD's data and information from open sources were included. All of this data was then computerized and statistically evaluated for outlines, and used to calculate the aqueous discharge concentrations for the steam electric power industry. We wrote a data base report which is now in the hands of the Project Manager and should be published this spring.

The second task, which is the main focus of the program, concerns the review of the sampling and analysis methods. This task had two major components, one of which was a precision and bias data compilation effort which I will talk about today. The second subtask is the literature review effort, which consists of reviewing the chemical literature for the last ten years with the intent of identifying interferences and finding solutions for the problems that exist with the NPDES approved methods for priority pollutant metal analysis.

The third task is a small effort to plan for Phase II, which we believe will be a validation study of the methods used for NPDES priority pollutant metal analysis. The fourth task was a workshop. At this workshop utility chemists came to Los Angeles for formal presentations and then broke up into working groups to discuss sampling and analysis problems related to the

utility industry. There will be a proceedings document from the workshop containing the formal presentations and the concensus R&D development ideas that were recommended by the utility chemists.

Today I am going to discuss the findings from two major sources of precision data on the priority pollutant metals analysis methods. The first source was the data tape from the DMR-QA-I study, which was obtained through the good offices of Bob Medz and Wayne Gueder in Washington, and John Winters and Paul Britton of EMSL-Cincinnati. DMR-QA stands for Discharge Monitoring Report, Quality Assurance program. The second source or rather sources of precision and bias data was compiled from the validation studies that we could find in the open or governmental literature.

The DMR-QA study we evaluated was conducted in 1980 and consisted of distilled water ampules containing 26 parameters, including 10 of the

13 priority pollutant metals. There were two concentration levels for each parameter which varied depending on the element and parameter. For the sake of this presentation I will simply refer to them by their code names: red and white. The data tape obtained from EMSL was coded in a manner which permitted us to make various data evaluations. For example, we could break out the EPA State results and compare them to the Permittee laboratory results. The data tape contained results from all the NPDES Permittees responding, so it wasn't specific to the utility industry. I want to define two words. When I say method, I'm referring to a generic title such as Graphite Furnace Spectroscopy (GFAAS), ICP, Flame Atomic Absorption Spectroscopy (Flame AAS). When I mention procedure, I'm referring to the protocol, such as ASTM, or Standard Methods that were used to perform the GFAAS or Flame AAS analyses.

The DMR-QA data reduction was done with software developed by TRW and using our CDC computer system. Without going into great detail, the first steps in the data reduction effort consisted of an outlier test, at the suggestion of Paul Britton, we used screening test to get rid of the decimal point errors or obvious recording errors. We did that by excluding any data point that was a factor of 5, higher or lower than the true value. The data that passed through this initial screening test was then tested with the ASTM D-2777-77 (a one percent double tail test). The data that failed either test were omitted from the final compilation. We calculated the mean, the standard deviation, and the relative standard deviation. We also calculated biases and differences. Biases being the mean of the EPA/State or the Permittees as compared to the true value. By differences, I am referring to the EPA/State mean compared

to the Permittee mean. All of this was placed with other details on a single page format for each parameter. If you are interested, I have a copy of the report here in the draft form and I can show you the type of format that was outputed. Incidentally, all the data for the 26 parameters were reduced.

This whole exercise was completed for the individual method procedures. The procedure data was also compiled so that all of the procedures for a given method were placed into one data set. We did that by taking the equivalent, alternate procedures listed under 40 CFR 136.

First, some general observations about the DMR-QA data set. The DMR-QA test concentrations were compound to the non-cooling water discharge (NCWD) concentrations calculated from the Task 1 data base. The non-cooling water discharge streams are all the power plant discharge streams except the cooling water streams.

Had we added the cooling water streams and computed the average, it would have given us an arbitrarily low number. So we sequestered the once through cooling water data into a separate group. The NCWD concentrations represent the nominal concentrations a plant chemist would monitor.

We found that the red sample set was approximately five times higher than the non-cooling water discharge concentration and the white set was generally greater than a factor of 15. As a result, we are not sure that the precision data that we saw in the DMR-QA data set is representative of the actual samples that the utility industry has to monitor.

The methods that were used by the EPA/State laboratories and the Permittees were primarily the same. The biggest difference was that the Permittees used wet chemical analyses (WCA) somewhere between two to nine percent of the time;

whereas, the EPA/State laboratories never used it at all. The biggest difference in Atomic absorption usage was for the Graphite Furnace AAS analyses of arsenic and selenium. As you can see by the data in the slide, the EPA/State laboratories primarily used GFAAS for those two elements; whereas, the Permittees used the combination of gaseous hydride, wet chemical methods, and GFAAS.

The procedure selection was also very interesting. The EPA/State laboratories, as you would expect, used the "Methods of Chemical Analysis for Water and Wastewaters" (MCAW) most of the time. The Permittees only used it 57 percent of the time and very surprisingly, at least as far as I was concerned, is that they used "Standard Methods" as their second choice. I think it's very important that we, as a group, try to get the message across to the users that the ASTM

procedures are far better written than "Standard Methods" on the MCAW. There are no precision and bias statements in the "Standard Methods"; whereas, the ASTM methods have precision and bias statements for each procedure. Also, each ASTM procedure is written from start to finish for each metal and not grouped under a general method as they are in "Standard Methods".

One final general observation about the DMR-QA data is that the EPA/State data set had far fewer outliers than the Permittee's. Many of the data points were removed by the initial screening test.

The next two slides are histographs summarizing the relative standard deviation data for flame and graphite atomic absorption. The relative standard deviation is plotted on the X axis with the number of elements falling in a given range of relative standard deviation plotted

on the Y axis. The top two histograms are for the Permittees red and the white concentration test sets. The bottom two are for the EPA/State data for the red and white test concentrations. So if you look at it in the vertical sense, you can compare the two histograms for data distributions. For Flame AAS both distributions are similar. The EPA/State RSD's tend to cluster in the 10 to 20 percent bracket. The Permittee Flame AAS data is slightly higher compared to the EPA/State laboratory data. In particular, there are three bad elements (As, Se, Hg) probably because they were determined by the Permittees using gaseous hydride absorption.

The next slide shows the same type of histograms for GFAAS. There is a much bigger difference in RSD's between the two different organizations when you look at the GFAAS data. In this case, you can see that the Permittees had a much wider spread in their relative standard

deviation versus the EPA/State, which was clustered, around or less than plus or minus 20 percent. Clearly, there is a difference in how these two groups are able to apply the methods methodology.

In addition to the DMR-QA data, we collated precision data from a number of sources. This next slide shows a list of the documents that we collected, and reviewed. During the course of this review we found that the 1975 AOAC Manual and "Standard Methods" used the same precision and bias data. The source for this precision and bias data was a 1968 Public Health Service study. This fact re-enforces my concern about using "Standard Methods" as a procedure manual. The best source for precision and bias data is the ASTM, Part 31, Water. In many cases we were able to obtain the original research reports used in ASTM, Part 31, Water.

We also collated data from Bill Telliard's study on Mining Effluents and the Utility Water Act Group (UWAG) inorganic analysis round robin study. These are the only two studies that used samples that were collected, spiked, and split in the field, and then sent to the participants.

Even with all of these studies that were performed, we found a lack of high quality data for matrices that might be considered challenging. If you look at this next slide which shows the matrices that were tested and the various methods that were used, you can see the limited extent validation data. If you look upward from the Ohio River water, you will see that there is a lot of data collected for standards either in distilled tap, or surface waters. Whereas you go down from there, you find the same elements are being done and only a few, maybe six or seven of the priority pollutant metals have been tested in matrices that are challenging

or representable of common SIC matrices.

Now, what do we do when we collect this precision data. The idea was to have precision data at three concentrations, so we could calculate a regression equation of the single operator and overall standard deviation obtained at the mean concentration tested. With these equations, we could go back and calculate what the relative standard deviation is at the specific non-cooling water discharge concentration. We could also calculate the limit of detection using the intercept of this equation. Finally, we could use this equation to calculate the limit of quantitation using a specific relative standard deviation.

Now, the idea with using the regression equation to calculate the limit of detection (LOD) is based on the idea that if you have a plot of standard deviation versus the test concentration, you then can extrapolate to the standard deviation at zero concentration. Some factor times the

standard deviation at zero concentration is defined as the LOD of a method. In most cases it is obtained by taking a distilled water blank or your blank reagent sample and analyzing it a number of times. In this case, we are using the actual data generated from these validation data to extrapolate to the standard deviation at zero concentration. LODs calculated in this manner are fairly conservative (i.e., low) estimates since as you approach the limit of detection, the absolute standard deviation tends to reach a limiting value and not linearly decrease.

This next slide shows the approach that we took in calculating the limit of detection. Generally, you can define the limit of detection as the minimum concentration that produces a specific relative standard deviation. This is pretty much what the ACS guidelines are and the general approach that Lloyd Curie took in his article on limits of detection quantitation.

Based on the RSDs calculated at NCWD concentrations, the relative standard deviation for routine analyses should be near plus or minus 20 percent. As this slide shows, you can use the linear regression equation to calculate a concentration that would give you a relative standard deviation of 0.2 (20 percent relative standard deviation). Taking this approach, we calculated both the extrapolated three signal limit of detection and the calculated limit of quantitation.

Before I show you a table which compares those numbers to the NCWD concentrations, I want to give you an overview of the precision and bias data that was obtained from these validation studies. We generally found that at the non-cooling water discharge concentrations that Flame AAS produced poor precision. This was not totally unexpected because NCWD concentrations are generally below its limit of detection.

We also couldn't see any trends with precision based on matrix effects, but this correlation may have been obscured because we didn't have the exact composition of a matrix to rank the matrices. Future validation studies should have a spark source mass spectroscopic analysis and an anion analyses of the matrix, so you have some idea of why one matrix's precision is different from another. There is another problem that there was no single study that covered all of the matrices, so we were trying to compare different groups of people doing different matrices.

The biggest single finding was that the overall precision was two times higher than the single operator precision for all the methods that we studied (Flame AAS, GFAAS, and ICP). This has a major impact when you calculate the limit of detection. It will make a factor of two difference when you use either the overall precision or the single operator precision.

To illustrate calculation of precision based on limits of detection, I took the data presented by George Stanko using the standard addition technique with Method 624 and compared it to the detection listed in Method 1624. I assume that in Method 1624 two sigma detection limits are reported though I may be wrong, but just for the purposes of discussion let's assume that that is the case. If a LOD was listed as 10, we converted that to a three sigma so it would be 15. If you compare that to a three sigma detection limit calculated from the data that George presented, you find that in some cases you have reasonably good agreement, but in other cases you have very poor agreement. This is the same sort of thing that we found with the trace metal data.

On this slide there is a listing of the non-cooling water discharge concentrations. I set a criteria that a method could detect or quantitate the method if its limit of detection or

limit of quantitation, based on overall precision was below the non-cooling water discharge concentration. This slide shows that ICP could not detect no more than six of the elements at their non-cooling water discharge concentration. GFAAS did a bit better. They were able to detect 10 of the 13, but unfortunately five of the data points were actually based on single operator precision.

When we get to quantitating; that is, being able to measure the element at plus or minus 20 percent relative standard deviation, we found that ICP can quantitate only a few elements at NCWD concentrations. Only two of the metals (cadmium and zinc) could be quantitated at the non-cooling water discharge concentration. GFAAS dropped down to five elements out of the 13, but four of those elements are based on single operator precision. As we mentioned earlier, the single operator precision is approxi-

mately a factor of two less than the overall precision. As a result, we are not exactly sure whether the data that we have really does indicate that the graphite furnace can be used to detect priority pollutant metals at non-cooling water discharge concentrations.

So what we have done in this EPRI program is to establish what the state of the art is for the methods being used to analyze the 13 priority pollutant metals. What we expect to do in the future is to extend the study to other parameters. In fact, we have a recent add-on to the project to do six more conventional and non-conventional parameters. We also hope to validate the methods used to monitor these metals using power plant discharge streams.

If you have any questions, I would be happy to answer them at this time.

SAMPLING AND ANALYSIS OF UTILITY POLLUTANTS
EPRI RP 1851-1

MAJOR TASKS AND OUTPUTS

TASK 1 - DATA BASE DEVELOPMENT

- COMPUTERIZED DATA BASE (NPDES, EPA, AND OPEN SOURCES)
- DATA BASE REPORT

TASK 2 - SAMPLING AND ANALYSIS REVIEW

- REFERENCE GUIDE
  - PRECISION AND BIAS ANALYSIS
  - LITERATURE REVIEW

TASK 3 - PHASE II PLANNING

- R/D PLAN

TASK 4 - WORKSHOP

- PROCEEDINGS DOCUMENT
  - CONSENSUS R/D RECOMMENDATIONS

DMR-QA PROGRAM

- DMR-QA PROGRAM
  - CONDUCTED IN 1980
  - 26 PARAMETERS (10 OF 13 PRIORITY POLLUTANT METALS)
  - KNOWN CONCENTRATIONS IN VIALS
  - TWO CONCENTRATION LEVELS (RED/WHITE)
- TAPE OBTAINED FROM EMSL/CINCINNATI
- CONTENTS OF DMR-QA DATA SET
  - EPA/STATE AND PERMITTEE (ALL SICs) DATA SEPARATE
  - TEST CONCENTRATIONS SEPARATE
  - PROCEDURES CODED (ASTM, EPA, MCAW, STANDARD METHODS)

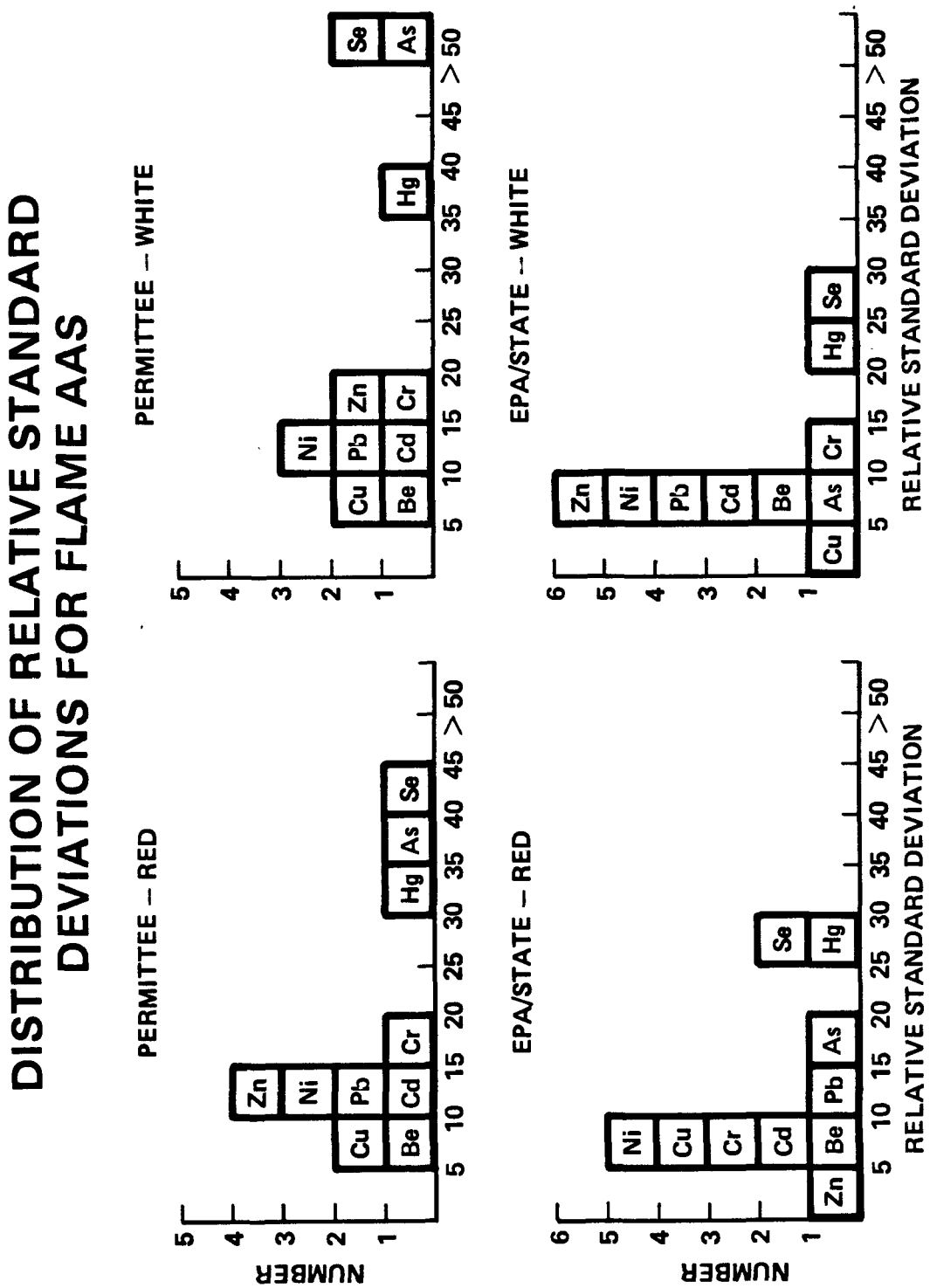
DMR-QA DATA REDUCTION

- DATA ANALYSIS SCHEME
  - OUTLIER TESTS
    1. TRUE/5 > X > 5·TRUE
    2. ASTM D2777-77, 1% DOUBLE TAIL
  - $\bar{X}$, RSD, NUMBER OF POINTS ACCEPTED/REJECTED
  - BIAS ($\bar{X}$ TO TRUE VALUE)
    - 1% DOUBLE TAIL
  - DIFFERENCES (EPA/STATE $\bar{X}$ TO PERMITTEE $\bar{X}$)
    - 1% DOUBLE TAIL

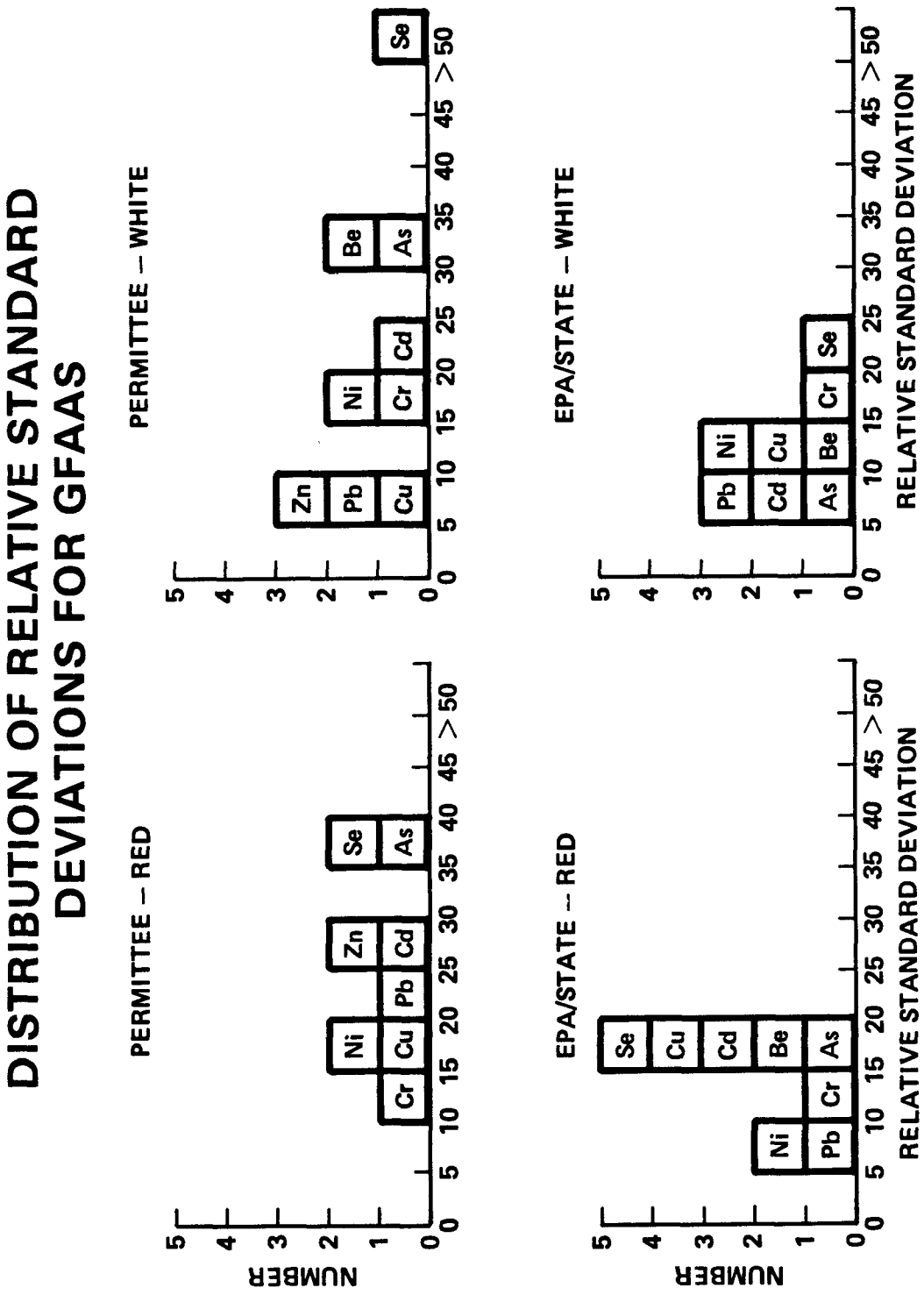
- EXERCISE REPEATED FOR EQUIVALENT METHODS
  - METHODS (FAAS, GFAAS, GHAAS, CVAAS, WCA)
  - ALTERNATE PROCEDURES COLLECTED UNDER METHOD (41 FR 52780)

DMR-QA GENERAL OBSERVATIONS

- REPRESENTATIVENESS OF THE TEST CONCENTRATIONS
  - DMR-QA TEST CONCENTRATIONS COMPARED TO NCWD LEVELS
  - RED (LOW) ~5 TIMES NCWD
  - WHITE (HIGH) >15 TIMES NCWD
  - PRECISION MAY NOT BE REPRESENTATIVE OF ACTUAL FIELD ANALYSES
- METHODS SELECTION
  - FAAS SIMILAR USAGE
  - PERMITTEES USED WCA ~2-9%
  - EPA/STATE USED GFAAS FOR As (73%) AND Se (87%)
  - PERMITTEES ANALYZED As BY GHAAS (31%), GFAAS (35%), WCA (34%)
  - PERMITTEES ANALYZED Se BY GHAAS (67%)
- PROCEDURE SELECTION
  - EPA/STATE 87% OF TIME USED MCAW
  - PERMITTEE 57% OF TIME USED MCAW
  - STANDARD METHODS SECOND CHOICE
- OUTLIERS
  - EPA/STATE <2.5% OVERALL
  - PERMITTEES ~14% OVERALL


DISTRIBUTION OF RELATIVE STANDARD DEVIATIONS FOR FLAME AAS
PERMITTEE – RED
PERMITTEE – WHITE
EPA/STATE – RED
EPA/STATE – WHITE
NUMBER
RELATIVE STANDARD DEVIATION
5 10 15 20 25 30 35 40 45 >50
Zn Ni Cu Pb Be Cd Cr Hg As Se

DISTRIBUTION OF RELATIVE STANDARD DEVIATIONS FOR GFAAS



COMPARISON OF BIASES/DIFFERENCES

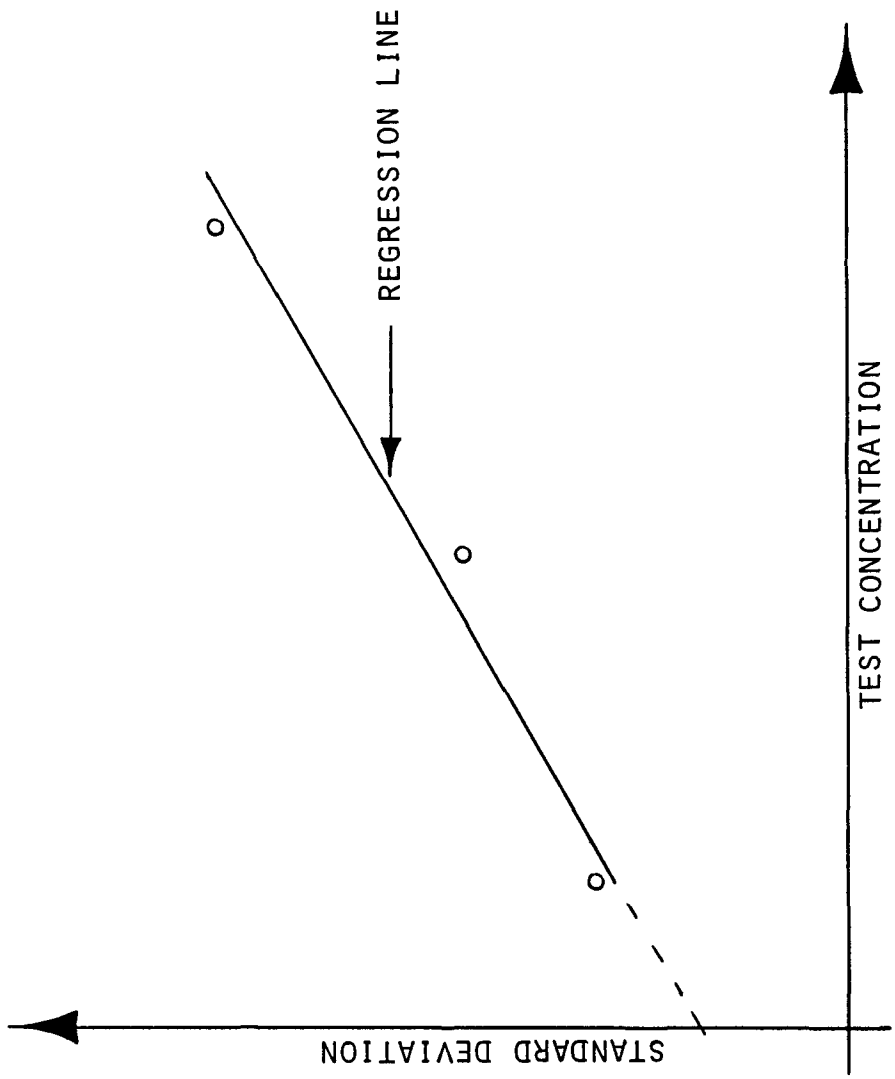
- EPA/TRUE, PERMITTEE/ TRUE, EPA/PERMITTEE
- HIGH RSD'S REDUCE SIGNIFICANCE OF BIASES/DIFFERENCES
- PERMITTEES HAD 7 SIGNIFICANT FAAS/GHAAS BIASES
  - ONLY FOUR $>-5\%$
- PERMITTEES HAD -17.5% SIGNIFICANT DIFFERENCE COMPARED TO EPA/STATE FOR Hg ANALYSIS
  - BOTH HAVE -10 TO -25% SIGNIFICANT BIAS
- WCA ALWAYS WORSE THAN INSTRUMENTAL METHODS
  - PERMITTEE DATA ONLY
  - As, Cd, Cr, Cu, Ni, Zn
- PERMITTEE DATA FOR GHAAS
  - As -29% AT 440 PPB
  - Se -24% AT 50.4 PPB

SOURCES OF PRECISION DATA

ORGANIZATION	SOURCE DOCUMENT
EPA/EMSL	"METHODS OF CHEMICAL ANALYSES OF WATER AND WASTES" (1979)
EPA/EMSL	DMR-QA STUDY (1980)
EPA/EGD	"METALS METHOD EVALUATION: ICP AND ATOMIC ABSORPTION ANALYSIS IN MINING EFFLUENTS" (1981)
EPA/EMSL	PERFORMANCE EVALUATION STUDIES (1980)
EPA/EMSL	FEDERAL REGISTER (DECEMBER 3, 1979)
AOAC	1975 AOAC MANUAL
USGS	"METHODS FOR THE DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS" (1982)
ASTM	PART 31, WATER (1981)
APHA	"STANDARD METHODS" (15TH EDITION)

PRECISION DATA ANALYSIS

- CALCULATE REGRESSION EQUATIONS ($SD = M\bar{X}_T + B$)
  - SINGLE OPERATOR/OVERALL PRECISION
- USES OF S_0/S_T REGRESSION EQUATIONS
  - CALCULATE RSD AT SPECIFIC NCWD CONCENTRATION
  - CLACULATE LOD FROM INTERCEPT
  - CALCULATE LOQ USING SPECIFIC RSD


REGRESSION LINE
TEST CONCENTRATION
STANDARD DEVIATION

MATRICES USED IN EPA OR UWAG SPONSORED RECOVERY OR VALIDATION STUDIES

MATRIX	ELEMENTS TESTED BY TECHNIQUE		
	FLAME AAS	GFAAS	ICP
STANDARDS, REAGENT WATER[4]	As[1],Ag,Se	Se	As,Be,Cd,Cr,Cu, Ni,Pb,Se,Zn
STANDARDS, NATURAL WATERS	Hg[2]		
MIXED STANDARDS, NATURAL WATER	Cd,Cr,Cu,Pb,Zn		
CINCINNATI, OHIO, TAP WATER (SPIKED)		As,Cd,Cr,Pb,Ag,Se	
OHIO RIVER WATER (SPIKED)	Hg[2]	As,Cr,Cu,Ni,Zn	
INDUSTRIAL WASTE EFFLUENT (SPIKED[3])		Se	
SEWAGE TREATMENT PLANT (SPIKED[3])		Se	
MIXED INDUSTRIAL/DOMESTIC WASTE (SPIKED)	Sb,Be,Ni,Tl	As	
COAL PROCESSING & ORE MINING WASTEWATER (SPIKED)	Cr,Cu,Pb,Ni,Zn	As,Sb	As,Cr,Cu,Ni,Pb,Sb,Zn
ASH (COAL) POND OVERFLOW (SPIKED)		As,Cr,Cu,Ni,Zn	

[1]GASEOUS HYDRIDE AAS, [2]COLD VAPOR AAS, [3]SINGLE SPIKE VALUE ONLY

[4]ALL THE DMR-QA DATA FOR As, Be, Cd, Cr, Cu, Hg, Ni, Se AND Zn ARE INCLUDED IN THIS MATRIX FOR A VARIETY OF EPA AND EPA APPROVED ALTERNATIVE METHODS.

SUMMARY OF PRECISION DATA

- AT NCWD CONCENTRATIONS FAAS HAS MUCH POORER PRECISION THAN GFAAS OR ICP

- MATRIX AFFECTS ON PRECISION DIFFICULT TO ESTABLISH
  - NO DATA ON MATRIX CHEMICAL MAKE-UP
  - NO SINGLE STUDY OVER ALL MATRICES
  - SKILL LEVEL OF PARTICIPANTS ADDS VARIABLE PRECISION

- OVERALL PRECISION TWO TIMES SINGLE OPERATOR PRECISION FOR FAAS, GFAAS, ICP
  - HAS MAJOR IMPACT ON LOD/LOQ

CALCULATION OF LOQ

- LOQ: THE MINIMUM CONCENTRATION THAT PRODUCES A SPECIFIED RELATIVE STANDARD DEVIATION (RSD)
- BASED ON PRECISION DATA AT NCWD, THE RSD SHOULD BE ± 20%
- CALCULATION PROCESS:

$$SD = M\bar{X} + B \quad (1)$$

$$SD/\bar{X} = M + B/\bar{X} \quad (2)$$

LET $SD/\bar{X} = 0.2$ (20% RSD)

$$\bar{X} = \frac{B}{0.2 - M} \quad (3)$$

SUMMARY OF METHODS CAPABLE OF DETECTING AND QUANTITATING PRIORITY POLLUTANT ELEMENTS

ELEMENTS	NCWD CONCEN-TRATION (ppb)	DETECT			QUANTITATE		
		GFAAS	FLAME AAS	ICP	GFAAS	FLAME AAS	ICP
ANTIMONY	37	Y	Y[1]			Y[1]	–
ARSENIC	41	Y	Y[1]		Y	Y[1]	
BERYLLIUM	5.2	–	Y		–		
CADMIUM	4.6	(Y)		Y	(Y)		Y
CHROMIUM	19	Y		Y			
COPPER	45	Y		Y			
LEAD	35	(Y)		Y	(Y)		
MERCURY	1.3	–	Y[2]	–	–		
NICKEL	39	Y					
SELENIUM	16	(Y)	Y[1]	Y	(Y)	Y[1]	
SILVER	7.7	(Y)		–	(Y)		–
THALLIUM	25	–		–	–		–
ZINC	76	(Y)	Y	Y			Y

[1] GASEOUS HYDRIDE AAS [2] COLD VAPOR AAS

Y MEETS CRITERIA (Y) MEETS CRITERIA, BUT ONLY SINGLE OPERATOR DATA AVAILABLE

– NO DATA

QUESTION AND ANSWER SESSION

MR. RICE: You might point out the number of participants and the composition in the DMR-QA1.

MR. MADDALONE: Generally, for the metals the number was about 200. I think the maximum number that I saw was on the order of 200 reporting in respondents for a given metal. Most metals on the order of 40 or 50 people reporting. There is a correlation. Since the DMR-QA study allowed them to monitor all or none of the parameters that were in the vials, depending on what elements are required by their permits, the number in the DMR-QA study related to the number of people required to monitor a pollutant.

MR. MEDZ: Ray, the 1980 DMR-QA program, was entitled program and we only had two states participating in the 1980

program. We had one state that had the primacy, that was Minnesota, and we had one state that did not have the primacy, that was New Jersey. The study on which we based the number two study, which is completed now, had almost a full 8,000 dischargers.

MR. MADDALONE: We would really like to get a copy of that information for our program.

MR. RICE: Bob, I had a question. As far as I was concerned we were led to believe that the DMR-QA tape that was made available to EPRY covered the round of the five or six major SIC category industries and that this represented all responses. It wasn't just a two-state affair.

MR. MEDZ: I remember, in 1980 we had a pilot program.

MR. RICE: Well, there was a pilot program prior to this, as far as I know, but that was New Jersey; wasn't it?

MR. MADDALONE: One problem with the DMR-QA1 study was the number of procedure codes available. There was a large number of procedures that were used that weren't expected to be used. There was a code "99" that lumps all those responses together. We would like to recover that information. I understand there's more codes in the second study based on the results from the first.

MR. STANKO: George Stanko, Shell Development. I think if you will check you will find that there was a DMR-QA study 1 with approximately 7,000 permit holders and that DMR-QA Study 2 with approximately 7,000 to 8,000. There was also a pilot program before Study 1 or Study 2. So there should have been a lot more data for Study 1 than what you show.

MR. MADDALONE: Well, it depends on the parameter. If you look at the pH, we had something like 2,000 respondents; but, then, in

the metals you would end up with 40, 50, to 200 people responding on that particular element.

MR. STANKO: I would have thought for zinc you would have had a lot more than what you did.

MR. MADDALONE: I'll have to look through...I don't have that data with me.

MR. RICE: I do, you will see it on the slide I have, George.

MR. STANKO: Thank you.

MR. MADDALONE: Bob, one question about that. The tape that we received, was that the pilot study?

MR. MEDZ: Well, when you said that you only had 40 or 50 respondents...

MR. RICE: No, Bob, I'm almost, answering for Ray, and that's what George says is true. Our understanding was that this was the first major round, it wasn't the pilot study, that on pH and total suspended solids and common

parameters such as that there were thousands of respondings on that data tape. The numbers that I will show on the slide I have are for those who had to run these elements.

MR. TELLIARD: Our next speaker, now speaking, is Jim Rice. Jim is a consultant to the utility industry. He and I have been jousting over monitoring questions for the last seven years and today he would like to talk a little bit about compliance monitoring and the poisons being discharged from public utilities.

COMPLIANCE MONITORING METHODS FOR PRIORITY POLLUTANT ELEMENTS IN THE DISCHARGES FROM STEAM ELECTRIC POWER PLANTS

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ABSTRACT

The data presented in the report by the Electric Power Research Institute, "Aqueous Discharges from Steam Electric Power Plants: Analytical Methods Precision and Bias," November 1982, clearly supports a concern of the Steam Electric Power Generating Industry that insufficient interlaboratory precision data exists for the compliance monitoring methods for priority pollutant elements associated with power plant discharges. In addition, the potential for greatly lowered NPDES permit limitations based on water quality standards emphasizes the need for validation at these concentrations in effluent matrices as well as in fresh, estuarine and ocean water.

In the absence of a national program for consensus validation of environmental monitoring methods

at appropriate concentrations and in representative matrices, the Electric Power Research Institute has been urged to undertake in cooperation with ASTM the task of validating existing and future EPA methods relevant to the power industry's discharges.

POLLUTANT PARAMETERS OF CONCERN

Pollutants derived from the fuel being burned, chemicals added for cleaning or for corrosion and deposit control, as well as pollutants present in the intake may appear in the process discharges from the steam electric power industry. The average concentration of the priority pollutant elements in such discharges is presented in a recent study of one hundred steam electric power plant NPDES Application Form 2C's by the Electric Power Research Institute (1). In a parallel study, EPRI determined the available precision and bias data for the approved analytical methods for the priority pollutant elements (2)(3). This latter study included an analysis of the results of the performance sample program con-

ducted by EPA in 1980 under Sec. 308 of the Clean Water Act (DMR/QA-1).

Table I summarizes the data on the major pollutants in coal-fired power plant process discharges. The parameters are shown ranked by mass discharge rate normalized by plant name plate capacity. It is important to note that the priority pollutant elements are present in the lowest two of the four order of magnitude range of the mass discharges of all of the pollutants. The average concentration of the priority pollutant elements in coal-fired plant discharges is used herein as the basis for examining the adequacy of the compliance monitoring methods approved for these elements.

REQUIREMENTS FOR COMPLIANCE MONITORING

As per Sec. 304(h) of the Clean Water Act, EPA has published analytical methods for use by permittees to determine whether their aqueous discharges comply with the terms of their NPDES permit. Any determination of the compliance of that result with the

limitations in the permit must take into account the precision of the method employed. Since the result is always subject to verification by the regulatory agency, a minimum of two laboratories are involved, expressly or implied, in making any compliance determination. Thus, determinations of compliance with a permit limitation can be made properly only in terms of the interlaboratory precision of the method employed on the matrix in question.

AVAILABILITY AND QUALITY OF PRECISION DATA

In view of the foregoing, the methods for the priority pollutant elements, as contained in 40 CFR Part 136, were examined by the EPRI study (2) to determine both the single operator and the inter-laboratory precision.

It is important to note that very little of the interlaboratory precision data was found by the study to have been collected in a manner that reflected the errors introduced by the sample container, by preservation, shipping and storage. ASTM Committee

D-19 has recently adopted a definition for a multi-laboratory operational precision that encompasses all of these errors as well as the more common within-the-laboratory errors.

An additional point revealed by the study is that the very largest portion of the precision data available on the Part 136 methods was developed on reagent water, or on fresh natural water, by employing vials of concentrated standards that were diluted by the recipient. Only a few studies determined precision data on specified effluent water samples, none separately on estuarine or seawater.

For the average concentrations in power plant process discharges Table II shows the relative standard deviation (RSD) as reported in the different flame AAS procedures approved by EPA in Part 136. It should be pointed out that the RSD's for the ASTM procedures may be not be applicable to the concentrations shown since, except for Se and As, they were developed over a concentration range much higher than those in Table II. Note that the mining indus-

try's effluents are the only ones for which the priority pollutant elements by flame AAS are specifically validated. In view of the many important and varied matrices for which these methods are approved, the amount of precision data available is clearly inadequate.

Table III shows data similar to that in Table II except for furnace AAS. Here there is even less interlaboratory precision data than for flame AAS. Even the 1979 MCAW does not contain any interlaboratory precision statements for furnace AAS. The only study available, with one exception, on the furnace AAS procedures for As, Cr, Cu, Ni and Zn as they appear in the 1979 MCAW was performed by the power industry on one ash pond effluent and on one river water (4).

APPROVED ALTERNATIVE METHODS

EPA faces numerous problems with validating the Part 136 methods. One underlying problem stems from 1973 when EPA accepted, a priori, that the differently

written procedures for a given method, such as flame AAS, for a given element as they appeared in several widely employed standards publications produced equivalent results. That is, the same level of confidence could be placed in the results produced by any of these several procedures when used by qualified operators. Subsequent experience with the methods concerned shows in hind-sight that this conclusion was incorrect. The clarity, the preciseness and the detail with which a method is written greatly influences the manner in which that method is carried out by different skilled, or unskillled, operators. Thus, the skill and care with which a method is written greatly influences the closeness with which one laboratory can verify the results of another (one measure of which is interlaboratory precision).

Table IV illustrates the varying degree of equivalence of two of the most widely used of the alternative procedures sources, 1974 METHODS FOR THE CHEMICAL ANALYSIS OF WATER AND WASTES (5) (MCAW) and

the 14th Edition of STANDARD METHODS (6) (SM). The relative standard deviations (RSD) were obtained from EPRI's analysis of the results for one of the two sample sets furnished by EPA/EMSL on the DMR/QA-1 program. In the foregoing program, each of the several thousand permit holders who received the samples (vials), diluted them with reagent water and then analyzed them for selected parameters (those required by their permits plus any others they chose) by employing the procedures they normally used for obtaining their compliance monitoring data. In addition to the results of their analyses, each permittee reported, according to a prescribed code, the specific procedure that they employed. EPRI examined the data using this code. It must be cautioned that there is no way of knowing if each respondent employed the procedures exactly as written. Nonetheless, the data in Table IV are very informative.

Of the nine elements studied, six have RSD's for the MCAW and the SM procedures that are significantly different at the 99% level of confidence.

Of these six elements, four (Cr, Cu, Ni, and Zn) have RSD's that are significantly higher for results determined using the procedure as it appears in STANDARD METHODS than if the results were determined following the procedure as written in the 1974 MCAW; two, Cd and Se, have lower RSD's following the SM rather than the MCAW procedures. It is well to remember that these significant differences in the performances of two widely used procedures sources arose on reagent water. What the performance differences would be on actual effluent matrices is not known.

EXISTING VALIDATION REQUIREMENTS

In 1978 EPA/EMSL made known a formal requirement for applicants who proposed test procedures as alternatives to the procedures approved in 40 CFR Part 136. These requirements for nationwide approval of equivalency specified comparative testing of representative samples of the point source discharges from five Standard Industrial Classification codes or subcate-

gories. It would appear from the EPRI study that none of the Part 136 methods for the nine priority pollutant elements discussed here has been so tested.

Table V summarizes the applicability of approved methods for the nine priority pollutant elements when these methods are evaluated by comparing their detection and quantitation limits with the average concentrations in power plant process discharges. By this criterion, approved methods are available to detect six of the nine for compliance purposes, but to quantify only two, As and Se.

POWER INDUSTRY CONCERNS

The absence of interlaboratory precision data for all of the matrices for each of the alternative procedures discussed herein would probably not be of great concern to the power industry if compliance with effluent limitations was to be enforced on only an order-of-magnitude basis at technology based effluent concentrations. The Part 136 methods precision data allows adequate confidence to be placed

in results under such circumstances. However, EPA's major effort under the Clean Water Act has now shifted from technology based effluent limitations to limitations based upon water quality standards. The changes proposed in October 1982 in the Water Quality Standards regulations (7) are a major step toward implementing that shift.

The concentrations for the priority pollutant elements in the present National Water Quality Criteria (8) are significantly lower than those discharge concentrations shown in Table I for power plant effluents. The latest draft revisions of the National Guidelines for Deriving Water Quality Criteria (9) will lower many of these concentrations still further. If future permits are likely to contain effluent limitations for the priority pollutant elements that result from more strict water quality standards, or from the waste load allocation systems that may be emplaced, a major effort to correct the situation evident in Table V must begin soon.

VOLUNTARY VALIDATION

The Electric Power Research Institute has been urged to begin a program whereby it will conduct in cooperation with ASTM and, hopefully with EPA, validation studies of selected EPA approved methods of concern to the power industry (10). These studies would be carried out on matrices representative of the industry's process discharges and of the major receiving waters, fresh, estuarine and sea. Power plant and selected state and federal laboratories would be the participants in the round robin studies. The result of the program would be precision and bias data that would be acceptable to the EPA, to the industry and to the courts as representative of the expected performance of the EPA approved methods on power plant discharges and associated receiving waters. It is possible that this effort could begin before the end of 1983.

Other industry associations may be interested in considering conducting methods validation programs for their own members. It is essential that a solution be found to the present impasse.

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7. "Water Quality Standards Regulation," Proposed Rule, Federal Register, 47, 49234 et seq., October 1982.

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9. Stephan, C.E., et al, "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Life and Its Uses," Draft, U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN, February 1983.

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TABLE I

NORMAL CHARACTERISTICS OF
COAL-FIRED PLANT
PROCESS WASTE DISCHARGES

Parameter	Mass Kg/day/GW	RSD %	Conc. mg/L	RSD %
TSS	1870	87	32	96
O&G	172	70	3.3	68
Mn	53	183	1.1	173
Fe	45	77	0.71	83
P	18	295	0.22	246
NH_3	12	118	0.28	109
Zn	4.4	68	0.075	76
Cu	3.2	118	0.043	147
As	2.8	130	0.050	112
Pb	2.6	94	0.034	87
Ni	2.2	84	0.041	88
Cr	1.0	128	0.017	108
Se	0.58	130	0.012	123
Be	0.35	65	0.005	71
Cd	0.34	156	0.005	147

Source: Table 4-11 and 4-17, (1)

TABLE II

REPORTED FLAME AAS RELATIVE STANDARD DEVIATIONS
BASED ON INTERLABORATORY PRECISION AT
PROCESS WASTE DISCHARGE AVERAGE CONCENTRATIONS

RSD(%)

Data Source		ASTM 1981	AOAC	USGS	MCAW 1979	EPA/EGD
Element	Conc. ug/L	Reagent Water	Reagent Water	River Water	Natural Water	Mining Effl.
As	41	8.5	-	-	41.2	-
Be	5.2	41.1	-	-	-	-
Cd	4.6	1134	121	-	128	-
Cr	19	62.3	67.5	26.5	66.3	86.6
Cu	45	274	38.9	27.1	34.6	27.6
Pb	35	169	120	-	69.4	157
Ni	39	240	-	-	-	70.1
Se	16	16.9	-	26.7	50.4	-
Zn	76	58.1	20.2	25.2	46.6	18.9

Source: Table 4-2 and 4-3, (2)

TABLE III

REPORTED FURNACE AAS RELATIVE STANDARD DEVIATIONS BASED ON INTERLABORATORY PRECISION AT PROCESS WASTE DISCHARGE AVERAGE CONCENTRATIONS

		RSD(%)				
Element	Conc. ug/L	ASTM 1981 Reagent Water	UWAG River Water	UWAG Ash Pond Efflu.	MCAW 1979 Natural Water	EPA/EGD Mining Effl.
As	41	-	47.1	9.1	-	53.8
Be	5.2	-	-	-	-	-
Cd	4.6	-	-	-	-	-
Cr	19	-	21.0	38.1	-	-
Cu	45	-	17.9	13.4	-	-
Pb	35	-	-	-	-	-
Ni	39	-	19.1	25.6	-	-
Se	16	-	-	-	-	-
Zn	76	-	24.5	42.3	-	-

Source: Table 4-2 and 4-3. (2)

TABLE IV

COMPARISON OF RELATIVE STANDARD DEVIATIONS BETWEEN ALTERNATIVE PROCEDURES FOR FLAME AAS BASED UPON EPA DMR/QA-1 PERMITTEE RESULTS

Element	Conc. ug/L	MCAW 1974 RSD%	n	STANDARD METHODS RSD%	n	R^2	F [.01]
As	235	28.5	(39)	35.3	(36)	1.54	No
Be	235	6.95	(34)	7.94	(16)	1.30	No
Cd	39	19.4	(171)	14.2	(111)	0.53	Yes
Cr	261	13.9	(265)	18.2	(204)	1.72	Yes
Cu	339	6.74	(310)	8.63	(177)	1.64	Yes
Pb	435	15.0	(238)	13.5	(135)	0.81	No
Ni	207	11.5	(210)	15.0	(128)	1.69	Yes
Se	50.4	94.6	(27)	37.3	(34)	0.16	Yes
Zn	418	7.95	(317)	12.4	(208)	2.43	Yes

R = (RSD STANDARD METHODS) ÷ (RSD MCAW)

Source: Table 2-16, (2)

TABLE V

CAPABILITY TO DETECT OR
TO QUANTIFY AT LOWEST REQUIRED
CONCENTRATION(1)

Element	WQS ug/L	Proc. Waste ug/L	Detect GF/AAS	Detect F/AAS	Quantify GF/AAS	Quantify F/AAS
As	50	41	Y	Y(2)	Y	Y(2)
Be	5.3	5.2	-	Y	-	N
Cd	10	4.6	N	N	N	N
Cr	50	19	Y	N	N	N
Cu	72	45	Y	N	N	N
Pb	50	35	N	N	N	N
Ni	13	39	Y	N	N	N
Se	10	16	N	Y(2)	N	Y(2)
Zn	47	76	N	N	N	N

(1) (Y) means that method LOD or LOQ is lower than either concentration shown; (N) means not lower than the lowest of the concentrations shown.

(2) Gaseous hydride method

Source: Tables 5-19 and 5-20 (2).

QUESTION AND ANSWER SESSION

MR. TELLIARD: And you say you looked at coal-fired and gas-fired?

MR. RICE: Maddalone separated the effluent data on steam electric plants into three categories: coal-fired, oil-fired, and gas-fired.

MR. TELLIARD: Any difference... you didn't sample any hydro?

MR. RICE: We decided that the question of potential pollution from hydro-power dams was better left to the courts.

MR. TELLIARD: That concludes this year's presentation. Thank you for coming, I hope you enjoyed it; hope to see you next March, same time, same station, same players, maybe a few more. Thanks a lot.

(WHEREUPON, the hearing was concluded.)