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

May 9 & 10, 1990

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF WATER
INDUSTRIAL TECHNOLOGY DIVISION

THIRTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

MAY 9 & 10, 1990

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MEMORANDUM

APR 26 1991

OFFICE OF WATER

TO: Attendees

FROM: William A. Telliard, Chief
Analytical Methods Staff
Engineering and Analysis Division

WITHDRAWN

SUBJECT: The Thirteenth Annual Analytical Symposium Proceedings

Enclosed please find a copy of the Proceedings of the Thirteenth Annual Analytical Symposium sponsored by the USEPA Office of Water, Industrial Technology Division (now known as the Engineering and Analysis Division), held in Norfolk, Virginia, May 9-10, 1990. We believe you will find these Proceedings to be an invaluable reference for the analytical methods discussed during the symposium.

Thank you for your continued interest and support in the Division's Analytical Symposium.

TD 175 E62 1990

FOREWORD

The Industrial Technology Division of the USEPA Office of Water Regulations and Standards sponsors an annual conference on the analysis of pollutants in the environment. This symposium is attended by laboratory and sampling personnel, data users, and regulatory agencies. It is intended to provide a forum for the discussion of current and proposed analytical methods for the analysis of priority pollutants.

These proceedings document the presentations and discussions from the Thirteenth Annual Analytical Symposium. Topics this year encompassed discussions of method validation, determination of volatile and semi-volatile compounds, and the effects of new regulations on laboratories. A special panel discussion was held by Federal, State, and industry representatives on laboratory certification and reciprocity.

This year's conference was very successful, with over 270 people in attendance. We look forward to the Fourteenth Symposium in May 1991.

W. A. Telliard

THIRTEENTH ANNUAL EPA CONFERENCE ON
ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

Office of Water Regulations and Standards
Industrial Technology Division

May 9-10, 1990
Norfolk, Virginia

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P R O C E E D I N G S

MR. TELLIARD: Good morning. My name is Bill Telliard. I am from EPA, and I am here to to help you. Welcome to the 13th, our lucky 13th, annual symposium on measurement of pollutants in the environment.

A couple of notes on housekeeping things before we get started. We have a substitution at 9:00 o'clock. Dr. Fielding will not be presenting. His paper has been dropped due to a lack of interest on Dr. Fielding's part. And for tomorrow's talk on the coastal marine environment by Gordon Wallace, Larry Keith will speaking in his place.

This morning and throughout the next couple of days, we are going to talk about a myriad of different problems in environmental measurement. Our people to our left are County Court Reporters, Inc., who take down your every single, dripping word that you might want to put forward. If for some reason you don't want your words on the record...and we all know what that means; it is like telling your wife where you are...we will be happy to tell them to stop recording and stop typing which they do real well. Stopping is one of the best things they do. And we will be glad to take it off the record.

Our first speaker this morning is Jim King from Viar & Company...which reminds me of a story. Has nothing to do with Viar & Company, but I had to lead in with something.

This lawyer has a parrot on his shoulder, walking down the street, walks into a bar, walks up to the bar, and the parrot says give this guy a beer. Bartender says wow, this is really kind of a neat bird, you know. So, he gives the guy a beer, goes down the bar, and he turns to this other guy and says that parrot is really kind of neat. So, he comes back up the bar and he turns to the lawyer and he says, where did you get him? And the parrot says Washington, there's thousands of them there.

Our first speaker is Jim King, and Jim is going to talk about one of my favorite subjects which is the list of lists.

Jim is going to talk about a program that ITD has come up with dealing with the use of a listing series to cover a catalog of analytical methods and also those listed compounds that appear on various agency lists throughout the agency.

Jim King from Viar and Company.

MR. KING: Thank you, Bill.

Hi. I am Jim King from Viar and Company. We operate the Sample Control Center for Bill Telliard and EPA's Industrial Technology Division (ITD).

In 1985, ITD project officers were faced with the prospect of regulating a wide variety of compounds, not only Priority Pollutants,but also this very strange list that appeared in the 1984 Hazardous and Solid Waste Amendments called the RCRA Appendix VIII list. There were a number of compounds on this list that were unanalyzeable by present methods. Bill Telliard decided to develop an automated catalog of these analytes and ideas and thoughts about the methods that might work for them.

Over the years, this system has grown into a compendium of all of the analytes of interest at the Agency contained in regulatory, as well as, office-based lists. When I say regulated, I am referring to environmentally significant regulations rather than product regulations such as the FIFR/TSCA rules and others like that.

Now, I'll demonstrate the current system. I will talk everyone through the system as we view it on the screen. If anyone has any questions, feel free to ask them at the end.

This is the main menu for the system. It does work with a Microsoft compatible mouse. When the device driver

for the mouse if installed, you will see a highlighted bar menu at the bottom of the screen.

The system runs on an IBM PC or compatible. It requires about 256K of memory. A hard disk is required. The database is indexed by these seven primary keys and a number of other alternate keys that once you become familiar with the system, you can utilize.

The primary key and the one on which we place the most significance is the CAS number. When entering data into the system, we go through and thoroughly research the CAS number either using Chemical Abstracts on line or two hard copy references in order to verify it, because we have found a number of regulations and other listings of compounds with CAS numbers that just were not correct.

The easiest way to view the data is by name, so we will take a look at it by name. Place the cursor in the lookup field and search for a compound. Here we have acenaphthene, CAS Number 83329. Here we have the CAS number, the regulatory origin and sequence, reportable quantities if there are any associated with the regulation, the analyte name as listed in the regulation, the International Union of Pure and Applied Chemists (IUPAC) name, and then any synonyms would appear after the IUPAC name.

The first screen is the original screen developed in 1985, so we had relatively few locations for apparatus, method, and a use code, but at that time, we were very interested in sources for standards. So, here we have a little catalog of sources of standards for true analytes.

We also have some physical properties data such as whether the compound hydrolyzes or decomposes in water, extracts or purges from water, whether it is possible to do by gas chromatography or whether you have to resort to liquid chromatography.

There is also a location for the EPA-NIH mass spectral library page number.

This is a relational data base, and if we place the cursor in one of these fields, we can scroll through these regions, and handle a relatively large number or regulations per compound.

If we flip over to page 2, we see the methods screen. This was developed in early 1988, and the objective here was to catalog as many methods as were available for a particular compound and some information about the method. We have the origin of the method here, the apparatus utilized, the method number if there is one, the suffix which is really a use code (the Contract Laboratory Program uses that for low soils, medium soils, water, et cetera).

We also have the detection limit appearing here, expressed in the identical terms that it was expressed in the method. In other words, we did not convert everything into some common detection limit or common unit.

Some fields that we will be updating in 1990 include precision expressed as standard deviation or coefficient of variation and other methods information. We are going to take the same approach that we took with the detection limits. However precision is expressed in the method, that is how it will appear here for that particular compound. And also bias expressed as percent recovery.

We are also talking about adding an additional screen, and we have a prototype of that. If you place the cursor on a method number and then hit PF key 5, it will take you into the Method Information Screen. This screen is in prototype form right now. We are still experimenting with what sort of data we want to display on this screen.

We often receive comments from people who say "well, why don't you just put the whole method in there". We are trying to keep the focus of the system very clear so that it doesn't become unwieldy and you need a monster 80386 PC to run it on. We have run this on an XT for a number of years with no problem. It works quite well.

On the Methods Information Screen, we look up by method number, the primary key. We have the revision, the date of

the method, the status, whether it is draft, final, proposed, or promulgated, the number of labs that participated in the validation study, the type of analysis, the matrix, the apparatus used, the appropriate concentration range, a citation for the method, and a short abstract of the method.

If we go back to the previous screen, one thing that is real interesting, is that we can actually switch indices here with the mouse just by clicking the right button on the actual fields. So, here we are in the name index, and we are viewing it by name. With a right click we will go over to the method index, organization index, etc.

Let's go back to the name index here. The name index contains a little over 10,000 entries. What appears in this window is the compound name as it appears in the reg, the UPAC name, and any synonyms. So, there are actually just under 1800 unambiguous analytes in the system, 150 methods for their analysis, compiled from 26 regulatory lists.

We can move from A to Z down through an index of 10,000 in less than one second. Here we see zectran, our first entry in the Z's, but let's look up...and basically what we have here is a byte by byte search of the data base. So, if we enter an "L", it will bring up the actual first occurrence of an "L" compound.

This particular index contains analytes names listed multiple times, as they appear in the regulation, by IUPAC name, and by synonym. We can look up lasso, and we can also look it up as alachlor or metachlor or by the IUPAC name which I won't even try to pronounce.

The 1990 revision of the system is scheduled to be complete by the end of the current fiscal year, and we expect at that time to publish a new List of Lists document, and it is probably going to be a little unwieldy at 200 pages to reduce this bulk, we are looking at is distributing the system, the system software and the data on diskette for a break-even cost, outside of the agency.

The diskette version is slated to start beta tests within the next 60 days, and we would hope to send it out to all current requesters. There were a number of people at the Water Pollution Control Federation conference last year that requested this system, and at that time, we were hoping to have it available sooner, but we have maintained their names on file, and they will be getting a copy of the system software in this first round of distribution.

If anyone has any questions at this time or has any favorite compounds that they would like to look up, feel free to ask, and I will do my best to answer them.

MR. TELLIARD: I should point out that these people who wanted a copy of this wonderful

system, we don't take green stamps, but we are going to use something that we feel the price will be probably about $70 on the first issuance.

We were talking about handling it through NTIS. I think, for the moment, we will handle it through Sample Control Center. I think it is faster, and I think the product is better if we can get it out to the folks.

We are putting it in all the EPA Regional libraries, permits office, and ESD laboratories, and Region III is the beta test area, so we will put it in all the State offices there to see how the thing works and what, if any, problems we have with it.

Since we have a working product, of course, the new EMMC, Environmental Methods and Management Committee, has put a work group together to figure a way that this can cost more. So, we are working on that now. It is your government in action: if it is working fine, let's fix it.

So, one of the areas that is totally lacking, as pointed out by Jim, is the fact that we don't have a lot of data on the precision and accuracy of the method, and we are just going to extract that from the existing method write-ups. Some of that is good, some of that is bad, some of that is indifferent, but we are going to put it in there at least as a starting point and see what type of feedback we

receive from the other users in the other laboratories that may have an interest in this particular program.

So, are there any questions? When you come to the microphone, please identify yourself and tell us who you are.

QUESTION AND ANSWER SESSION

MR. RICE: Jim Rice. I am a consulting engineer.

Bill, I have several questions. First, what is the data base management system you are using?

MR. KING: The software is written in system J. It is as relatively unknown system. However, in 1985...

MR. TELLIARD: Obscure is the word.

MR. KING: Yes, obscure.

MR. RICE: When you make it available on diskette, what will come with it is the license to the data base management system as well and the software?

MR. KING: No, it will not. It will be run-time only module. So, in other words, we will send you only a couple files that are required to run the system.

MR. RICE: Right. Well, that is what I meant.

And now the other question, Bill, and a comment. You mentioned about putting precision...I think it says precision and bias on those columns up there.

MR. KING: That is correct.

MR. RICE: But I would make a plea to you not to use and put up and, in effect, put into a data base for wide distribution data that you know is not worthy to reprint. I think I would only put that which is...that you consider really valid interlaboratory data on a method that has been checked out by a large suite of laboratories with it rather than put up junk, because other people than this group which are technically astute and can understand that get hold of that data, and then it causes all kinds of mischief.

MR. TELLIARD: Thank you, Jim. I agree with you, but, you know, there is a box to be filled in.

(Laughter.)

MR. TELLIARD: It is kind of like your census. Irrespective of how many live in the house, you have to fill in the box.

We are aware of the problem that some of the data is better than others, and I think for the first go-around, as we mentioned, for the beta test, we are going to try to put everything in and circulate it and have people pull it out or revamp it based on their experience or their information.

We haven't figured a way to flag what we call real good, not so good, and mediocre, but I agree with you. I think we ought to do that, but we haven't addressed that issue yet.

MR. FRAZIER: My name is Bill Frazier, City of High Point, Central Lab Services.

In the first screen, you had information about chemical and physical properties. Is that also going to have toxicology data available with it?

MR. KING: We have talked about it, but the problem is there is such a limited data base of toxicological information.

MR. FRAZIER: Is that a future plan for it?

MR. KING: That is currently in the plans.

The agency has a data base called IRIS. I believe there are only about 200 entries in the data base FOR mammalian toxicity.. So, that would be a very minor subset unless we wanted to extend it to different salmonella type toxicity tests or other toxicities that may or may not have relevance on mammalian toxicity.

MR. FRAZIER: Thank you.

MR. TELLIARD: TSCA has a similar list that they have generated for the Office of Toxic Substances. We are not trying to combine them, but

where their data interfaces with ours, what we are thinking of doing is having a reference arrow that says see block something or other.

This system will allow us to add additional screens where we could add a toxicity screen or one of the other things that we are interested in is a production screen. How much of 1,2-diphenol bat shit is made, exported, used internally, controlled and kind of from a permitting standpoint when the guy is writing the permit know how much he should be concerned about it.

That is an option that is probably a couple of years away if we wish to implement it, but right now, we are trying to get it out that says it is on somebody's list, somebody is concerned about it, and we are monitoring for it.

Now, when we say a list, it is not necessarily a regulatory list. It is a list whether you are in the Office of Solid Waste or you are CERCLA or you are inter-toxic where someone is going to have to make a measurement, either in a permit, in a monitoring mode, or somewhere. So, when we say list, it is not the narrow list of just those regulated compounds which, of course, is probably like 85 and we have, what, 1700 or something on here.

MR. KING: Right.

MR. TELLIARD: So, when we say list, our analogy is those compounds which you as a user or a producer or a manufacturer may have to monitor for.

MR. KING: In fact, if we look at the on-line help screen, you can see where are origins are derived, and these are the regulatory origins here. We have various lists on there from the Appendix C list, from the consent decree, California list of pollutants, CERCLA 302, Clean Water Act 116, the Michigan Petition list, the administrator's VTOX list which ultimately became the SARA Section 313 list.

Also, there are a couple of office-based lists on there. There is a list of fish tissue contaminants that are monitored by the Office of Water Regulations and Standards that we do have on here.

MR. TELLIARD: Good morning, George.

MR. STANKO: George Stanko, Shell Development Company.

I think I may have a solution to Jim Rice's problem and also would ask a question.

Could we replace that precision field with something on MSDS for these compounds, or was anything considered with respect to MSDS?

MR. KING: No.

MR. STANKO: Because a lot of us have to handle these, ship these, and do that, and that kind of information with this kind of a data base looks like it would be very useful.

MR. TELLIARD: Well, we certainly have the capability of adding that, George. Thank you.

Any other questions?

(No response.)

MR. TELLIARD: Again, if you will pick up this little blue card, we have had the format and the obscure...obscure was the term?...obscure language has been approved by the agency for circulation, and we are going to try to get this thing out by mid summer to the world.

There is also an issue in fact that we may rewrite the program into a different format, that is to say, a different language based on what our computer folks tell us in RTP, but right now, we are shooting to have the program available by mid summer. So, if you would like a copy...as I say, we are estimating $70 for the cost.

MR. TELLIARD: If you fill out the little blue card, when we figure out what the real price

is, we will send you a notice, and if you still want one, if you send the check to my sister...

(Laughter.)

MR. TELLIARD: We will be glad to send you a copy.

We would also like as you get this copy any feedback that you can send to us on ways of making it better or changing it or reformatting it. Since it is our first effort at it, we would be glad to have some feedback from you folks, particular the user community like you. Also, as was pointed out, you are probably more on top of this than a lot of the other people who are going to be using it. So, any information you can send back to us to make it better would certainly be appreciated.

Thank you, Jim.

MR. KING: Thank you.

THE ITD LIST OF LISTS SYSTEM

"*A Catalog of Analytes and Methods*"

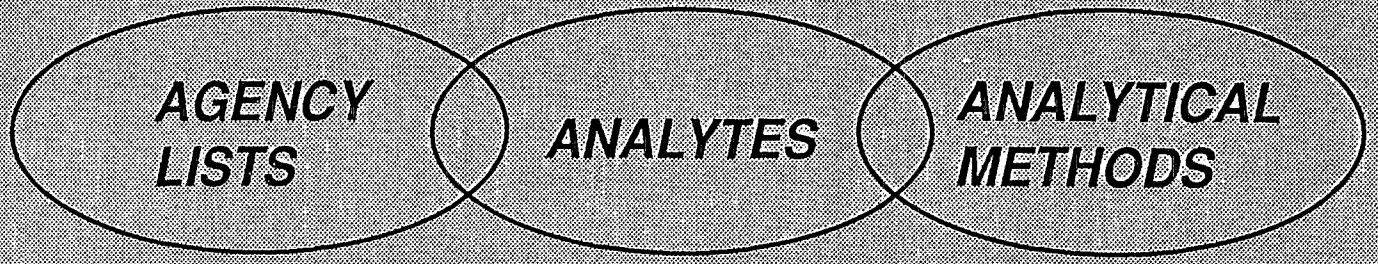
Analytical Methods Staff
USEPA Office of Water Regulations and Standards
Industrial Technology Division

OWRS ITD

WHAT IS THE LIST OF LISTS?

The Office of Water Regulations and Standards Industrial Technology Division has developed, maintained, and distributed, since October of 1985, an automated composite index of analytes listed by the Agency. This master database is known as the "List of Lists" (LISTS).

The List of Lists is a comprehensive cross-referencing tool for information on



WHY WAS THE LIST OF LISTS CREATED?

PROLIFERATION OF LISTS AND ANALYTES

By 1985, there were 15 Agency lists and over 1,000 analytes. Analyte lists could no longer be managed individually.

TO HELP ITD DESIGN MONITORING PROGRAMS

Tasked with promulgating industrial effluent limits for the Priority Pollutants, RCRA Appendix VIII list of 385 compounds and compound classes, as well as CERCLA's Hazardous Substances List, ITD created an automated composite list of pollutants of concern to EPA as a resource to support its monitoring programs.

WHY THE LIST OF LISTS IS IMPORTANT TODAY

METHODS STANDARDIZATION

With the proliferation of field and laboratory measurement methods, it is necessary to establish degree of standardization among methods.

STUDY DESIGN

EPA monitoring program designers need analyte and methods information to make correct choices:

- Addressing cross-media contamination
- Intersection of Regulatory lists
- Selection of appropriate methods

SECTION 518 REPORT TO CONGRESS

The 518 Report recommends "establishment of a computerized catalogue of the availability, applicability, and degree of standardization of methods currently in use in the Agency."

OWRS ITD

SYSTEM DESCRIPTION

- LISTS is a PC-based system developed using System J.
- The List of Lists is distributed in both hardcopy and computer-readable formats. Over 10,000 hardcopies and ASCII files have been distributed since 1985.
- Run-time (read-only) module created for system dstribution to user community.
- LISTS database contains information on:
  - 1,716 regulated analytes
  - 26 statutorily-mandated and Office-based lists
  - 150 analytical methods

OWRS ITD

THE LISTS SYSTEM

FEATURES

- Menu Driven
- Rapid Text Search Using Lookup Field
- Indexed on Key Fields
- Simultaneous Display of Key Data Elements
- Optional use of pointing device ("mouse")

CAPABILITIES

- Search, Retrieve, Display, and Print Data Sorted by Key Field
- Database Add, Delete, and Modify
- Output ASCII Text Files in PC or Mainframe Formats
- Generate Standard Reports by Nine Key Fields

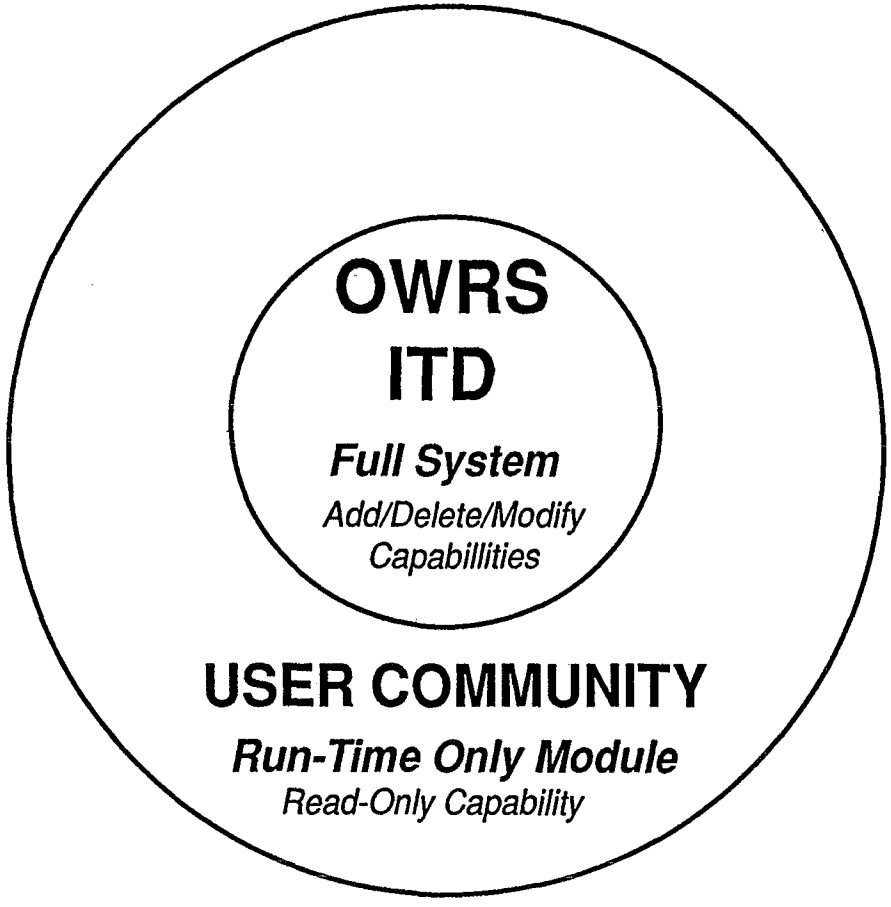
REQUIREMENTS

- IBM PC XT, AT, or Close Clone
- DOS Operating System
- System J Software
- Hard Disk and 256K RAM (640K RAM Recommended)

OWRS ITD

SYSTEM CHANGE CONTROL

OWRS MAINTAINS CENTRALIZED CHANGE CONTROL OVER LISTS SYSTEM CONFIGURATION AND DATABASE FILES.



WHAT DATA ARE IN THE LISTS SYSTEM?

ANALYTE DATA

- Analyte Name (as appears on Agency list)
- Common, trade, synonym, and IUPAC Names
- CAS Number and Base CAS Number
- Regulatory Origin/ Agency List
- Analytical Method(s)
- EPA/NIH Mass Spectral File Reference
- Physical Properties
- Source for Standard

METHOD DATA

- Method Number/ Identification
- Custodial Organization
- Instrumentation / Technique (Apparatus)
- Sample Matrix, Fraction, and Level (Suffix)
- Detection Limit by Analyte
- Precision and Bias by Analyte

LIST DATA

- Regulatory Origin or Name of Agency List
- Custodial Organization
- Reportable Quantity
- Analyte Names (as appear on Agency list)

OWRS ITD

DATA INTEGRITY

Integrity of LISTS system data is ensured by use of an unambiguous identifier (CAS number) as a primary key and stringent verification of each CAS number before entry into the system.

Each CAS number is checked to verify that it is an unambiguous identifier for a specific analyte.

- Check-sum algorithm applied to ensure that CAS number is valid.
- CAS number checked against two published sources or one published source and one on-line source to ensure that it accurately identifies the listed analyte. If necessary, the Agency office responsible for the list is contacted for confirmation.

KEY FIELDS

LISTS data can be retrieved, displayed, and printed by any of nine key fields:

- **CAS Number** *PRIMARY KEY*
- **Analyte Name**
- **Base CAS Number**
- **Apparatus and Method**
- **Method and Apparatus**
- **Regulatory Origin/Agency List and Analyte Sequence in List**
- **Custodial Organization**
- **Standard Source and Analyte Name**
- **Method, Suffix, Apparatus, and Analyte Name**

OWRS ITD

WHAT ANALYTICAL TOOLS ARE AVAILABLE TO LISTS USERS?

- Data search on key fields
- Data retrieval and display sorted by selected index (key field)
- Look up data for specific variable while in selected index
- Print data sorted by selected index
- Output data from selected index for loading to other computers (create print file)

WHAT SYSTEM REPORTS CAN BE GENERATED?

A user can print LISTS reports presenting data ordered by any of the nine key fields. Report data is presented in alphanumeric order by data element(s) in the key field.

- CAS Number
- Analyte Name
- Base CAS Number
- Apparatus and Method
- Method and Apparatus
- Regulatory Origin/Agency List and Analyte Sequence in List
- Custodial Organization
- Standard Source and Analyte Name
- Method, Suffix, Apparatus, and Analyte Name

SYSTEM ENHANCEMENTS

- **Addition of Analyte-Specific Precision and Bias Information**

  Data fields for precision and bias information have been created and entry of these data is ongoing.

- **Addition of Methods Abstract Screen**

  A methods abstract screen has been created to provide information on method standardization and validation. Entry of method abstract data is in process.

- **Development of User Documentation**

  A Draft User Manual has been written, which provides detailed information on how to install the LISTS system, retrieve and display data, and print standard reports. The Draft User Manual will be utilized in the upcoming beta test and user input will be incorporated in the final manual.

EXAMPLE SCREENS AND ON-LINE HELP FILE

1. Main Menu
2. Data Screen Indexed by Name - Pages 1 and 2
3. Methods Abstract Screen
4. Excerpt from On-line Help File

MAIN MENU

OW LIST OF LISTS MENU

The OW LISTS database contains environmentally significant analytes and information necessary to develop methods for their regulation.

DISPLAY ANALYTE DATA

F2 = By CAS number
F3 = By name (alphabetically)
F4 = By base CAS number
F5 = By apparatus and method
F6 = By method and apparatus
F7 = By origin and sequence
F8 = By organization

To PRINT ANALYTE DATA, use Alt with any of these function keys.

ORGANIZATION TO DISPLAY/PRINT
PRINT FILE

OTHER LIST OF LISTS FUNCTIONS

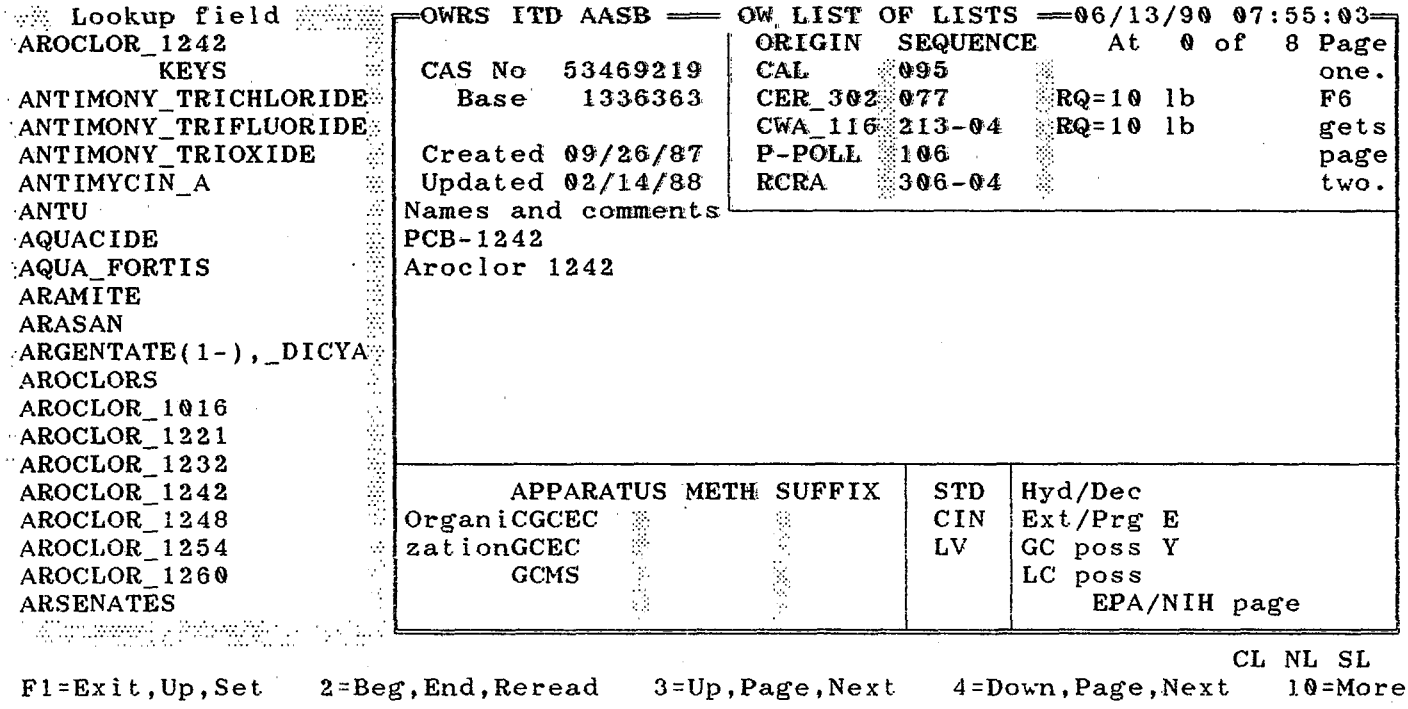
F10 = Help for this menu
Alt-F10 = Rebuild database indices

SYSTEM J ACCESS

F1 = Exit menu to J() prompt
Type I_HELP to get back
F9 = System J command menu

F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 | F10 | HELP

DATA SCREEN INDEXED BY NAME – Page 1



DATA SCREEN INDEXED BY NAME - Page 2

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   Lookup field
AROCLOR_1242
        KEYS
ANTIMONY_TRICHLORIDE
ANTIMONY_TRIFLUORIDE
ANTIMONY_TRIOXIDE
ANTIMYCIN_A
ANTU
AQUACIDE
AQUA_FORTIS
ARAMITE
ARASAN
ARGENTATE(1-),_DICYA
AROCLORS
AROCLOR_1016
AROCLOR_1221
AROCLOR_1232
AROCLOR_1242
AROCLOR_1248
AROCLOR_1254
AROCLOR_1260
ARSENATES
```

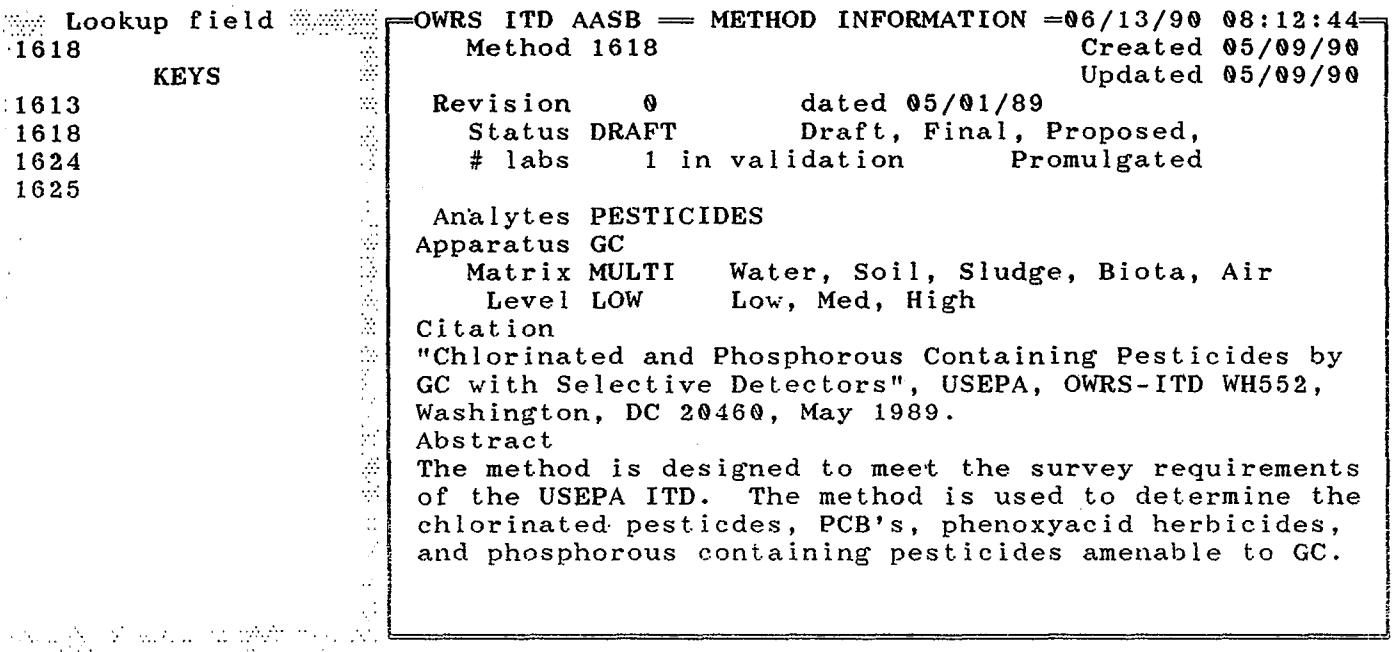
```
OWRS ITD AASB ═══ OW LIST OF LISTS ═══06/13/90 07:52:28

 CAS No  53469219          Page two.  F6 gets page one.
Names and comments
PCB-1242
Aroclor 1242

                                                                  At 0
ORG APPARATUS METH  SUFFIX  DETECT LIMIT  PREC BIAS of11
ASTM GCEC    D3534          EDL=1 ug/L
CIN  GCEC    608            MDL=0.065 ug/L
CIN  GCMS    625    BN
CLP  GCEC    PEST   LS      CRQL=80 ug/kg
CLP  GCEC    PEST   MS      CRQL=1200 ug/kg
CLP  GCEC    PEST   W       CRQL=0.5 ug/L
ITD  CGCEC   1618
ODW  GCEC    505            MDL=0.31 ug/L
OSW  GCEC    8080           PQL=50 ug/L
OSW  GCMS    8250           PQL=100 ug/L
USGS GCEC    O-3104         EDL=0.01 ug/L

                                                  CL NL SL
 5=Method,Swap/Dup   6=Page,Ed   F10=More   Shft-Fn=Fn Help
```

METHODS ABSTRACT SCREEN



EXCERPT FROM ON-LINE HELP FILE

I_RCRA.DSC
02/27/89

ITD LIST OF LISTS DATABASE
Legend for Information in Data Fields.

The Industrial Technology Division's List of Lists system is an automated catalog of analytes of environmental concern and methods for their analysis.

CAS NO The Chemical Abstracts Service (CAS) Registry Number for the analyte. In certain instances, CAS has assigned a number to a compound class and this number is used.
Note: where CAS has not assigned a number to an analyte or class, a synthetic numbering system has been used. This number begins with a digit(s) followed by an underscore or hyphen followed by three digits (e.g., 1_001) and assures that an analyte can be unambiguously identified in relationship to the class from which it is derived. The three digits following the underscore identify its position on the parent list and match the ORIGIN SEQUENCE number. At present, the following leading digits are used (definitions of acronymns and abbreviations are listed under ORIGIN below):

0- identifies the Drinking Water Priority List
0_ identifies the RQ List
1- identifies analytes on ITD's List
1_ identifies the RCRA Appendix VIII List
2- identifies the AIR List
2_ identifies the RPAR List
3- identifies the SWDA List
3_ identifies the VTOX List
4- identifies the SEC_313 List
4_ identifies the OAG_SRB List
5- identifies the SEC_112 List
10- identifies the FTC List

CAS Number Error Checking on the PC: When a CAS number is entered in the CAS NO or BASE CAS NO field, the CAS error checking algorithm is run at the instant the cursor leaves the field. If the CAS number is incorrect, the message "CKSUM" will appear immediately above the CAS number or below the BASE CAS number, indicating that an incorrect number has been entered.

BASE The "base" CAS NO. If the analyte is derived from a compound class (e.g., "Chlorobenzenes"; "Silver and Compounds, NOS"), and the analyte can be traced to the class, the CAS NO of the class from which the analyte is derived will appear in this field.

ORIGIN An acronym or abbreviation for the list from which the analyte is derived. The following lists are used:

AIR Analytes of the air "List of 37"
APP-C Analytes listed in Appendix C of the Consent Decree.
APRIL Analytes added to the RCRA groundwater monitoring list by Bob April of EPA.
CAL California List pollutants [40 CFR Part 268, Appendix III; 52 FR 25791].

EXCERPT FROM ON-LINE HELP FILE (cont.)

CER_302 CERCLA Reportable Quantities List [40 CFR 302.4, Table 302.4].

CWA_116 Hazardous substances under Section 311(b)(2)(A) of the Federal Water Pollution Control Act [40 CFR 116, Table 116.4A] and Reportable Quantities [40 CFR 117, Table 117.3].

CWS_DIS List of analytes for which Community Water Systems and non-transient, non-community water systems shall monitor at the discretion of the State [52 FR 25715, 08 Jul 87].

CWS_REQ List of analytes for which Community Water Systems and non-transient, non-community water systems shall monitor [52 FR 25715, 08 Jul 87].

DWPL Draft Priority List of Drinking Water Contaminants [52 FR 25720]

FTC ITD's list of Fish Tissue Contaminants

ITD Additional metals, classical analytes, and dioxins that the Industrial Technology Division monitors in its sampling and analysis programs.

MICH The list of analytes proposed to be added to the RCRA Appendix VIII List by the Michigan Petition [49 FR 49793, 21 Dec 84].

OAG_SRB Oil and gas, secondary recovery biocides: biocides, slimicides, and molluscides used on oil platforms.

P-POLL The priority pollutant list [NRDC vs Train, 8 ERC 2120 (DDC 1976)] as expanded to the 129 "Priority Pollutants", Appendix C Pollutants, and High Priority Paragraph 4(c) Pollutants. (The specific compounds on this combined list are given in Methods 1624, 1625, plus the original Priority Pollutant list of pesticides, metals, cyanide, and asbestos).

PARA-4C The list of 56 compounds detected in the 4(c) study.

PARA_4C The remaining 367 compounds detected in the 4(c) study.

RCRA RCRA Appendix VIII list [51 FR 28305, 06 Aug 86].

RCRA_IX The RCRA Appendix IX Groundwater Monitoring List [51 FR 26632, 24 Jul 86].

RPAR "Rebutable Presumption Against Registration" - compounds EPA is considering removing from registration as pesticides.

SARA110 Hazardous substances most commonly found at facilities on the CERCLA National Priorities List [52 FR 12866] under Section 110 of the Superfund Amendments and Reauthorization Act (SARA).

SDWA Safe Drinking Water Act Amendments of 1986 [House Report 99-575]

SEC_112 Pollutants listed as hazardous under the Clean Air Act.

SEC_313 The toxic chemicals subject to the provisions of Section 313 of the Emergency Planning and Community Right to Know Act of 1986

TCL Superfund Target Compound List (current as of August 1987).

VTOX Compounds on the "Acutely Toxic Chemicals" List in EPA's Chemical Emergency Preparedness Program [EPA OPTS-00066, November 1985; 52 FR 13378], mandated under Section 302 of the Superfund Amendments and Reauthorization Act (SARA).

SEQUENCE The sequence number on the respective list. In those instances in which the list was unnumbered, a sequential number starting with 001 was assigned to each analyte, except for the HSL in which the number used by the QA Formaster data base was used (because a sequential reference number would change every time the HSL is revised), and numbers beginning with Z to represent the atomic number of a given

element (e.g., boron is Z05).

REGULATORY NOTES (Column heading not given; found next to "SEQUENCE" field)
Location for encoding information pertinent to a given regulation.
RQ Reportable quantities under CERCLA and FWPCA (CWA).

NAMES AND COMMENTS Various names for this analyte and other unrestricted comments. Names are listed in approximate order of common usage. Each distinct name starts on a new line and has no leading spaces. Continuation lines for this name should have four leading spaces. Blank lines and comments can be entered anywhere between names. Comment lines should have two leading spaces.

The I_EXPORT program assumes the following about names:

1. The longest name is 168 characters -- not counting leading spaces.
2. When making a continuation line back into a full name, a space should be inserted if the previous line ends in a letter, digit, colon, semicolon, close parenthesis, close bracket, or a comma preceded by a dash.

ORGANIZATION The organization originating the method, as follows:

ASTM	American Society for Testing Materials
CIN	EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio
CLP	EPA's Office of Emergency Response Contract Laboratory Program
ITD	EPA's Industrial Technology Division
ODW	EPA's Office of Drinking Water
OSW	EPA's Office of Solid Waste
STD	"Standard Methods" published by the American Public Health Association
USGS	US Geological Survey Techniques of Water Resources Investigations

APPARATUS As derived from the METHOD. The following apparata are encoded:

BRIDGE	Conductivity bridge.
CGCEC	Combination method using gas chromatography with electron capture detector.
CGCFPD	Combination method using gas chromatography with flame photometric detector.
COLOR	Colorimetric determination
COUL	Coulometric detector
CS2	Analysis of a carbamate by liberation of carbon disulfide.
CVAA	Cold vapor Atomic Absorption Spectrometry
DICHROM	Dichromate oxidation
EVAP	Evaporation
FID	Flame ionization detector
FILTER	Filtration
FLAA	Flame atomic absorption spectrometry
FURNAA	Furnace atomic absorption spectrometry
GCAFD	Gas chromatography with alkali flame detector
GCEC	Gas chromatography with electron capture detector

GCFID	Gas chromatography with flame ionization detector
GCFPD	Gas chromatography with flame photometric detector
GCHRMS	Gas chromatography with high resolution mass spectrometry
GCHSD	Gas chromatography with halogen specific detector (Hall, O.I., microcoulometric, electrolytic conductivity)
GCMS	Gas chromatography/mass spectrometry
GCNPD	Gas chromatography with nitrogen-phosphorus detector
GCPID	Gas chromatography with photoionization detector
GRAV	Gravimetric
HPLC	High performance liquid chromatography
HPLCUV	HPLC with an ultra-violet detector
HYDAA	Hydride atomic absorption spectrometry
ICP	Inductively coupled plasma spectrometry
MICRODF	Micro diffusion
NEPHELO	Nephelometer
OXY-FID	Oxidation/reduction followed by flame ionization detection
OXY-IR	Oxidation followed by infra-red detection
PHMETER	pH meter
RETORT	Oil platform operator's apparatus for determining oil content of a drilling fluid
SCINT	Scintillation counter
SPECTRO	Spectrophotometer
TITR	Titration
WET	Analysis by a classical wet method
WINKLER	Incubation in airtight bottle

METHOD The Method number where it is known. Methods and method numbers are associated with an ORGANIZATION.

SUFFIX The suffix to the METHOD. The suffix is specific to the sample fraction, matrix, and level. Suffixes are as follows:

Suffix	Frac	Matrix	Level
AW	Acid	Water	
BN	B/N		
BNW	B/N	Water	
CHS	Combine	Solids	High
HS		Solids	High
LS		Solids	Low
MS		Solids	Medium
S		Solids	
W		Water	

STD Sources for a standard for the analyte. Acronyms and abbreviations are defined as follows:

ALD	Aldrich, Milwaukee, WI
ALF	Alpha
ATH	Athens ERL
CIL	Cambridge Isotope Laboratories
CIN	EMSL Cincinnati
DUP	DuPont
EPA	EPA repository at RTP
EXX	Exxon

 EXCERPT FROM ON-LINE HELP FILE (cont.)

LV	EMSL Las Vegas
NAN	Nanogens, Watsonville, CA
NCI	National Cancer Institute
PAB	Pfaltz & Bauer
SCC	Sample Control Center
SIG	Signal
SUP	Supelco
SYN	Must be synthesized in the lab
ULT	Ultrex

HYD/DEC The analyte hydrolyzes (H) as estimated by Athens-ERL, or decomposes (D) as determined by Dr Beimer of S-CUBED.

EXT/PUR The analyte can be extracted from water as determined by Athens-ERL or by S-CUBED. E=can be extracted; P=can be purged; N=can neither be extracted nor purged.

GC POSS The analyte can be gas chromatographed as determined by Athen-ERL or S-CUBED.

LC POSS W Roy Day of Waters Associates believes that the analyte can be determined by LC.

EPA NIH PAGE The page number in the EPA/NIH mass spectral file where the reference mass spectrum for the analyte can be found.

*** Information Specific to Screen 2 ***

DETECTION LIMIT

EDL	Estimated Detection Limit
MDL	Method Detection Limit [49 FR 43234, (Appendix B)]
ML	Minimum Level-ITD's definition of the minimum level that must give recognizable mass spectra and acceptable calibration points (see footnote 2 to Table 2 of Method 1624, Revision B [49 FR 43234].
PQL	Practical Quantitation Limit-EPA Office of Drinking Water definition of the lowest level that can reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions [52 FR 25699], or the Office of Solid Waste definition of EPA's current best estimate of the practical sensitivity of the applicable method for RCRA groundwater monitoring purposes [52 FR 25945].

NOTES (Column heading not given; found next to "DETECTION LIMIT" field)
Notes pertaining to a given method for the analyte.

MR. TELLIARD: Our next speaker is Dave Mount who is going to talk about the joys of a toxicity-based approach to pollutant identification.

MR. MOUNT: Thank you, Bill.

I want to start with two disclaimers which should make you all nervous. Could I have the first slide, please?

For those of you who are astute, you will notice that I have made a one-word change in my title from "A Toxicity-based Approach" to "The Toxicity-based Approach." The reason I did this has to do with my first disclaimer. Although I am presenting this information today, it is by no means a lone effort on the part of our laboratory. It really represents the efforts of a great many laboratories. In particular, the EPA lab in Duluth, Minnesota, was heavily involved in the development of some of the techniques I will discuss today.

The other disclaimer I want to make is that I am not a chemist. I am an aquatic toxicologist, and I think that is an interesting point to make prior to this talk. As we have entered the world of toxicity-based toxics identification, it has become apparent the need for interdisciplinary communication and effort in order to most effectively deal with these problems, because the knowledge that is needed really far exceeds the knowledge of any one person.

I need to provide information as a toxicologist. Analytical chemists and other types of chemists as well have to provide me information from their disciplines. Engineers

and all kinds of people have to become involved in order to make this effective.

As many of you are aware, toxicity, as measured in toxicity tests, is gaining fairly wide acceptance, at least in some areas of environmental regulation. The most notable of these is the NPDES effluent discharge program, but there are other areas in which toxicity as a unit of measure is becoming favored as well. The hazardous waste classification system is using it some places. EPA has recently issued guidance on using biological assessment techniques to look at hazardous waste sites.

And there are a lot of reasons why. There are several advantages to using toxicity testing for environmental monitoring. One is that measuring toxicity addresses a lot of questions that aren't addressed by general analytical techniques, such as are questions of bioavailability. A chemical analysis can tell you if a contaminant is present, but it can't tell you whether it is in a form that will cause adverse effect to organisms out in the environment.

Another consideration is matrix effects. Of course, all analytical chemists are familiar with matrix effects, but the same things happen in toxicity testing. A common one we are probably all familiar with is the effect of hardness on metal toxicity. There are considerations relating to the physical/chemical environment in which a

contaminant exists in the environment that will heavily influence its toxicity.

Finally, there are interactions among toxicants. We can study a single compound to death and know exactly how toxic it is in and of itself, but when it is present with other contaminants, how toxic will it be?

All of these considerations are addressed by toxicity testing. As some of us are fond of saying, an organism knows more than we do.

Another feature of toxicity testing is that it will detect the presence of all toxic chemicals that are there, if they are present in toxic amounts; and that beats any analytical chemistry technique known. Every last one is detected if it is present in toxic amounts. An interesting sidebar to that quote is the toxic materials in toxic amounts reference, which is in the Clean Water Act, and is encompassed by toxicity testing as a monitoring approach.

However, if we are to regulate on the basis of toxicity, we have an obligation, to develop means to determine sources of toxicity, so that control strategies can be implemented. This gets into the focus of what I am going to talk about today. This led to the buzz words, the "toxicity reduction evaluation," or TRE as it is commonly referred to. In the case of effluents, a TRE is a systematic evaluation, of both plant and effluent to

identify sources of toxicity and, ultimately, to control toxicity.

Now, people have been trying to do things like this for a long time, and the traditional approach has been analytically-based, using tools like a priority pollutant analysis. If you have something toxic, what do you do? You do a priority pollutant analysis and find out what is in there. The problem is that in order for this to be effective, you have to be measuring whatever it is that it toxic. Another problem is that analytical approaches, at least most of them, don't account for the questions I spoke of earlier, bio-availability matrix effects, and interactions among toxicants. Hence, this analytical approach generally falls short, in our experience, of identifying toxicants in a complex matrix such as an industrial effluent.

The other approach that has been used is the engineering and treatability approach. Basically, you don't worry about what is causing toxicity, you just find some treatment strategy that will remove it.

There are some real disadvantages to this approach also. First of all, you run a large risk of having your treatment remove toxicity, but doing it in a way that you didn't expect or that does not lie along the usual means of that treatment technology. Another is that if you don't

know what it is and you are just going to treat it, things like source control aren't an option. If you don't know what it is, you can't figure out how to stop putting it in.

This is a very simple schematic example I will use to talk about a couple concepts (Fig. 1). Let's imagine that the center box is a waste water treatment plant. We have two influent waste streams in our waste water treatment plant. If we were to measure the toxicity of Influent 1, it would be moderately toxic, and it would have a toxicity due to compound A, although we don't know what compound A is at this point. Influent 2 would be extremely toxic. It has toxicity due to compound B.

Both influents enter the waste water treatment plant. Compound B is effectively treated. Compound A is resistant to treatment, and we end up with a final effluent that is moderately toxic, and it is toxic due to compound A.

Now, if we were to go and look for toxicity back up through this system, we would say it looks like Influent 2 is the source of our toxicity when, in fact, it has nothing to do with it.

If we were to take the analytical approach, we would analyze the final effluent. Well, if compound A is a priority pollutant or other commonly analyzed parameter, we might pick it up. On the other hand, I have had lots of people come up to me with a list of tentatively identified

GC/MS compounds and say, "are any of these toxic?" And I say, " yes, they are all toxic". But the question is, how much? Furthermore, with all the other matrix effects and interactions, you simply can't take a list like that, compare it to toxicological benchmarks, and know whether or not any of those compounds are causing your problem.

So, the goal of the procedures that I am going to talk about today is to work on that final effluent, and using toxicity-based procedures, find the identity of compound A. Once we know what compound A is, then we can take analytical approaches, go back through the system, and find out exactly where compound A comes from. And with that all kinds of control options become possible. In addition to just treating the final effluent for compound A, we can treat just that influent line, we can modify the source, we can do all kinds of things that we couldn't do before.

So, the strategy for the toxicity-based approach is to use simple separation chemistry techniques to separate toxic components of the effluent from other components of the effluent. In all cases, we use toxicity tests as our analytical detector, rather than flame ionization or some other standard analytical detector. We use a toxicity test to find out, for that separation technique, where did the toxicity go?

This has led to the development of a subset of studies under the TRE, the Toxicity Identification Evaluation or TIE. As you might have guessed from my discussion earlier, the objective of the TIE is to relate observed toxicity to a parameter that has application to engineering solutions.

A lot of what I'll talk about today is heavily geared toward effluent toxicology, because that is where the majority of the toxicity limits have been placed. In the case of hazardous waste sites, a toxicity test can also be a very useful tool for determining whether or not a hazardous waste presents a potential toxicological effect. But more than just that, we then need to know what the toxic compound is. And if we know what it is, then we can go about setting cleanup criteria. So, there are all sorts of other applications of this approach.

The phased approach to the TIE was developed largely by the EPA Duluth lab and consists of three phases. I am not going to go through each phase indepth, except to tell you that they exist. There are guidance manuals that have been issued by EPA that explain each in great detail. I am going to talk specifically about some of the tests, some of the information that you get out of and these tests, and how this information is applied.

The approach for a Phase I TIE may not seem very unusual (Fig. 2). It is a lot like a traditional

engineering treatability approach. We have a whole effluent sample or any other sort of environmental sample, that can be used in a toxicity test, a sediment, anything. We split it. On the left side, we do a toxicity test on it. Down the right side, we do some sort of physical/chemical manipulation, and as you will see in a minute, there are a great many of them that are done in parallel. We conduct a toxicity test on the manipulated sample and then compare the toxicity in both of the tests to determine whether or not that physical or chemical manipulation had any effect on the causative toxicant in the matrix.

I hate to get into methodological detail, but I want to make sure we are on the same wavelength as we go through some example data. These are some of the tests that are used in this procedure. (Fig. 3). At the top, we have the whole effluent test which is simply a standard toxicity test. The whole effluent or other sample, is diluted and tested for toxicity along a concentration series to determine just how toxic that material is. This serves as the comparison for all the other tests.

There are two pH adjustment tests, pH 3 and pH 11. The sample is simply adjusted to that pH, left there for three hours and then returned to the original pH. Then the toxicity of the manipulated samples is measured using toxicity tests.

The pH adjustment tests primarily address compounds that undergo some sort of physical transformation at those pH's, an irreversible transformation like hydrolysis. They also serve as the procedural blank for other tests that use pH adjustment.

We also use aeration tests. In these, we use aliquots of sample at the initial pH, and also at acidic and basic conditions. These aliquots are aerated for 30 minutes, returned it to the original pH, and then tested it for toxicity. These tests obviously address volatile or easily oxidizable compounds.

The filtration tests have a similar structure to the aeration tests except that we filter the sample instead of aerating at those three pH levels. This gets at materials whose toxicity is associated with filterable solids or toxicants whose solubility is affected at extremes of pH. For example, a lot of heavy metals will precipitate at pH 11, and we can filter them out. If they were the cause of toxicity, the sample will lose its toxicity.

Solid phase extraction is a very simple technique using $_{s}$ep-Pak C18 columns. We run the effluent through the column, and it removes a great many non-polar organic compounds. Like the aeration and filtration tests, this is done at acidic, basic, and neutral conditions.

We use an EDTA test in which we add EDTA over a range of concentrations to determine if that has any effect on toxicity. EDTA will reduce the bioavailability of many heavy metals. Therefore, if those are the source of toxicity, we will see a reduction in toxicity when we add an appropriate amount of EDTA.

There is an oxidant reduction test using sodium thiosulfate. This test has the same structure as the EDTA test, except use sodium thiosulfate to reduce residual chlorine and other oxidants.

Finally, there is a graduated pH test where we adjust the pH to 6, 7, and 8, test the toxicity, and see if there is a marked difference in toxicity at those different pH's. Toxicity of many materials is greatly affected by pH. Ammonia is a good and common example of a pH-sensitive toxicant.

So, what kind of information do we get out of this? I am going to show you some specific data in a moment, but this is conceptually what we find out. These are results from a wire coating facility in the Northeast, showing the information from a Phase I characterization. (Fig. 4).

The solid phase extraction test, which is geared toward non-polar organics, did not remove toxicity. EDTA chelation did remove toxicity. With that, we begin to think metals may be the cause in this case. Aeration did nothing at any

pH. Acid and neutral filtration did nothing. However, filtration at pH 11 did remove the toxicity.

So, we can say at this point we feel pretty confident we are zeroing in on heavy metals. We did some more tests to confirm that heavy metals were, in fact, the cause. I am not going to go through those, but once we knew that it was a metal, we turned to analytical approaches to determine which metal it actually was.

These are actual data from a municipal wastewater treatment plant effluent (Fig. 5). Listed on the left are the Phase I characterization tests; on the right is the 48-hour survival observed in each of those tests.

There was 20 percent survival in the whole effluent after 48 hours, which made it toxic by the regulatory standard that had been applied. Without going through all the tests individually, you can see by the 100 percent valves in bold that aeration and solid phase extraction removed toxicity at all three pH's. Based on this we suspected the causative toxicant was a non-polar organic. It may also be volatile.

Where do we go with that? Well, we move into what is called a Phase II study, geared toward toxicant identification (Fig. 6). We know from Phase I studies that solid phase extraction will take out the toxicity. So, we take a liter of effluent, pump it through the SPE column,

and test the toxicity of the post-column effluent. It is not toxic. We assume, therefore, that whatever is toxic is on that column.

Next we do a very simple elution of that column, using a series of methanol concentrations. We use methanol because methanol is not very toxic to the organisms, so we can do toxicity tests with samples that are in a methanol matrix, as long as they are appropriately diluted. Other solvents like hexane, more common analytical solvents, are too toxic to be of much use in this procedure.

At any rate, we elute the column with a series of methanol fractions, ranging from 25 to 100 percent. Then we test each one these eight functions for toxicity.

The resulting 48-hour LC_50 valves are shown here in percent (Fig. 7). The LC_50, again, is the theoretical concentration of that sample that would cause 50 percent mortality of the test organisms.

Of the eight methanol fractions, only two showed toxicity, the 85 and 90 percent fractions. The recovery of this toxicity shows that we have the causative toxicant out of the effluent matrix and have begun to separate what is toxic from what is not toxic.

We can extend these results by conducting additional separation procedures. And at every step along the way, we

do toxicity tests to confirm that we still have the causative toxicant isolated.

We combine the toxic fractions, concentrate them on a C_{18} column, inject the concentrate into the HPLC, and split those toxic fractions into 25 fractions. For illustration purposes, we'll assume that compounds distribute themselves randomly among all functions. We took the original sample, split it in 8 fractions, then threw out 6 and kept 2. Based on this, we would be down to a quarter of the original compounds in the sample. Then, we split the remaining compounds into 25 more fractions. In theory, then, each of these fractions contain only 1 percent of the compounds that were in the original sample, if you will forgive the simplistic assumptions.

After the HPLC separation, we test each of the 25 fractions for toxicity. In this particular case, we found that fractions 21 and 22 were toxic. We then combined those two fractions, concentrated them, and submitted them for GC/MS analysis. This analysis turned up diazinon in sufficient concentration to explain the toxicity of the sample.

There are some analytical wrinkles that can arise from this process. First, the question being asked of the analytical chemist is not "How much of compound X is in this sample?" Instead, we are asking "There is an unknown toxic

compound in here; what is it?" As you no doubt realize, those two questions are quite different, and require different analytical thinking.

Another potential analytical difficulty is that not all organic compounds are amenable to GC/MS analysis. Knowing whether this is the case is impossible, a priori, since we don't know what it is we are analyzing for. This kind of problem also requires some innovative thinking, and sometimes some innovative techniques. HPLC-MS and super-critical fluid extraction are some alternative procedures that are showing some promise for these situations. This diagram illustrates some ongoing research that we are doing in our laboratory (Fig. 8). One of the big problems we run into is heavy metal toxicity, because the bioavailability of heavy metals varies widely. Even if you measure total, total recoverable, and dissolved concentrations, toxicity will not necessarily relate to any one of those. If you have a concentration below the toxicological benchmark, you can feel confident that it is not a source of toxicity. But, for example, a great many effluents in this country have potentially toxic amounts of zinc in them, yet they aren't toxic. The reason is that the zinc is not in a bioavailable form.

To identify the heavy metal responsible for toxicity, we need to give the analytical chemist a boost. What we have done is to combine tests using two different metal ligands.

Although the sodium thiosulfate test is intended to remove toxicity due to oxidants, we discovered during the course of one TIE that the sodium thiosulfate test would remove copper toxicity. When we went back and asked the chemists about this, they weren't surprised, as sodium thiosulfate will chelate copper.

We decided to explore this further, by conducting both EDTA and thiosulfate tests on a range of metals.
The results are presented here (Fig. 8) in a simple 2 by 2 contingency table, with toxicity removal by EDTA in the left column, and no removal by EDTA in the right column. The same applies to results of the thiosulfate test, positive results in the upper row and negative in the lower. So, for example, in the case of that original effluent, we noticed that both the EDTA test and the thiosulfate test took out toxicity. At the time we did that study, we didn't have this table to look at. But if we had, we could have pointed to the yes/yes box in the upper left, and would have suspected that the toxicant was either copper, cadmium, or inorganic mercury.

As another example. we recently completed some work on a drain water from an historic mining operation. It was

quite toxic and had a myriad of heavy metals in it. We conducted both tests on the sample and found that EDTA the removed the toxicity and sodium thiosulfate didn't. By using this table, we then removed the range of metals that might be responsible for toxicity. So, even though there were a tremendous number of heavy metals in the effluent, we zeroed in on zinc as being the only metal in this category that was present at potentially toxic concentrations.

I have a final example TIE, to illustrate that it is not always as simple as I have been showing. this effluent had an LC_50 of about 33 percent, and solid phase extraction removed this toxicity.

In order to get you to discuss the fine points of this example, I have to introduce one more term, the toxic unit. A toxic unit is 100 percent divided by the LC-50 of the solution. An effluent with LC-50 of 50 percent, has 2 toxic units. One with an LC50 of 25 percent would have 4 toxic units. The number of toxic units also indicates the number of times you need to dilute that sample to reach 50 percent survival in a 100 percent sample.

As I said, the toxicity of this effluent was removed by solid phase extraction. We then conducted the solid phase (Fig. 9) extraction and elution that I showed you earlier, with the following results. The whole effluent had an LC50 of 33 percent, corresponding to 3 toxic units. The toxicity

tests on the fractions showed toxicity in the 75, 80, 85, and 90 percent fractions. There is a concentration step involved with the SPE dilution, which is 5x with the methodology that we use. Calculating toxic units and dividing by 5 we have these toxic units listed on the right, corrected to the whole effluent concentration. Adding the four toxic fractions together, we had 1.3 toxic units, but we had removed 3 from the whole effluent.

Well, this kind of disturbed us, because it meant either that something was still stuck on that column or that we had very, very poor recovery for some reason. In this case, it is hard just to live with poor recovery, because of the risk that it actually indicates the presence of a second toxicant.

The clue to this problem came in another sample (Fig. 10). We did a graduated pH test on this other sample, and found no survival at pH 6, 100 percent survival at pH 7, and no survival again at pH 8.

Now, there was ammonia in this sample, and ammonia is more toxic at high pH, so we were expecting and could explain the toxicity at pH 8. But we couldn't explain the toxicity at pH 6. Because we had seen non-polar organic toxicity in this effluent before, we did a solid phase extraction on that sample and then did the graduated pH test. This manipulation took out the toxicity at pH 6. We

assumed, therefore, that the toxicant responsible for the toxicity at pH6 was now on the C18 column. Since ammonia isn't affected by the column, there was still toxicity at pH8.

Having found that out, we did the solid phase elution (Fig. 11).

As background information, the effluent pH was in the high 7's, while the pH of the dilution water that was originally used for testing fractions was about 8.5. When we tested the toxicity of these fractions at pH 8, we saw no toxicity at all. But when we tested them at pH 6, we saw toxicity in the 75 and 80 percent fractions, and the pieces began to fall together.

What had happened in the first sample was that the effluent fractions were tested in dilution water with pH just a few tenths higher than the whole effluent. Because this material appears to be more toxic at lower pH than at higher pH, we could thereby account for the difference in toxicity that we observed originally.

With that, I would be happy to open it up for any questions you might have.

QUESTION AND ANSWER SESSION

MR. HACHIGIAN: Lee Hachigian of General Motors.

Have you tried the guidance manual with regard to chronic toxicity applying the same types of methodologies?

MR. MOUNT: Yes, we have. For those of you who aren't familiar with toxicity testing, there are two general types of toxicity tests, acute and chronic. I have been talking about acute toxicity, which generally deals with survival. Chronic toxicity a longer term test, and deals not only with survival but with more subtle and points.

Yes, we have worked on applying the TIE methods to chronic toxicity. That is certainly an area of heavy methods development right now. EPA Duluth is working on it. We are working with a couple of dischargers who are being regulated on chronic toxicity, and have to find ways to control it.

It is definitely a trickier situation. There are a lot of shortcuts that can be taken with acute toxicity that are more difficult with chronic toxicity, but some of the methods still apply. One of the problems is simply that the chronic tolerance of organisms for substances like EDTA and thiosulfate haven't been worked out thoroughly yet. But that information is coming, and I would imagine...well, I am

not going to speak for when EPA will issue guidance, but they will probably be technically ready to issue guidance within the very near future.

Yes?

MR. HOWE: Stavros Howe with the Molecular Ecology Institute.

I think there is a whole suite of assays that currently exist that would compliment your scheme there very well and perhaps would be more sensitive in addressing some of the chronic toxicity issues. Specifically, I am thinking about stress protein assays, metal binding ligand assays, various enzyme assays that would correlate much closer with the mechanism of toxicity and give you a better handle on what is causing the problem, basically.

I think the screening approach would be far more rapid and much more cost effective.

MR. MOUNT: A lot of other assays have been suggested. There are a couple comments I might make on the choice that is made.

For those of you who are familiar with toxicity testing as a monitoring tool, you will know that they cost from several hundred to a thousand dollars each test. When they are done in the context of a TIE, however, they are much, much less expensive, down on the order of $50 per test. So, the cost effectiveness issue starts to go away.

People get into this situation as the result of compliance monitoring, which is whole organism monitoring. Therefore, whole organism testing is a very appropriate measure to use, because it is the measure by which the problem is defined.

The danger in using other assays is that they may respond to things other than what is causing the toxicity to the original organism, other things that are present in the effluent. For example, the Microtox assay has been suggested for use, and it is an effective tool if it is responding to the same material as is the original test organism.

If you use something other than the original organism, you need to do some background work to establish for certain that there is a correlation between the alternate assay and the tests that is of regulatory concern.

Finally, I'll admit that this is a regulatory policy constraint on the scientific process, and what you are doing the study for depends on how you might approach that problem.

MR. YOCKLOVICH: Steve Yocklovich from Burlington Research.

While we use this type of analysis ourselves, I was wondering what you would see if this was implemented nationwide. What kind of cost of analysis could you see if

it were put into regulation, and how many labs in the country are equipped to do it?

MR. MOUNT: Let me get all the parts of your question here. As far as implementation, it has been implemented in many, many parts of the country. In our region, Region VIII, and in most of the EPA regions in the East, it is in place, and we are working with several clients who are doing it not as a proactive stance, but who are in it as a result of their permit monitoring.

In terms of cost, we have solved problems for a few hundred dollars if it is real obvious. It can also cost a lot more than that. But I would venture to say some of the horror stories that are floating around about the potential cost aren't realistic, if the studies are properly done. There are stories running around about expenditures of $200,000 or $250,000. We certainly haven't run up any bills like that, and I don't think that it is necessary.

This is an emerging area, so there is varying expertise out in the world regarding how effective labs are.

In terms of equipment, there is really very little equipment needed aside from the analytical capabilities. Of course, what analytical equipment you need depends on what direction you end up going, metals, non-polars, or some other compound. But in terms of the laboratory equipment to do the separations and the toxicity tests, there really

isn't much. A couple thousand dollars in equipment is all that is required. Obviously, the analytical situation is different.

Within our company, we have the full range of analytical equipment. On-site, we have GC, HPLC, and AA. If we run into GC/MS work, we often contract with a laboratory that happens to be right across the street from us.

Is there anything I didn't touch on you want to follow up with?

MR. YOCKLOVICH: Thank you.

MR. MOUNT: Thank you.

MR. TELLIARD: Any more questions?

MR. FRAZIER: In the TRE/TIE approach, there is not anything specifically addressing the diseases of organisms. Are you all aware of any body of knowledge of this either affected by effluents or once you get them in the laboratory?

MR. MOUNT: There are diseases of organisms that definitely influence test results. In terms of diseases inherent to the laboratory, the laboratory culturing and quality assurance practices should address the presence of pathogens in the laboratory in general.

As far as pathogens in the effluent, we have never had any experience with that. I do know of one example, but I

haven't reviewed the data to know if I feel their conclusions are accurate. But I do know of one example where a municipal plant had an experience where they were convinced that a bacterium growing inside their sampler was causing disease in the toxicity tests.

And there are some things as a toxicologist you can do to spot that kind of problem. For example, if you have toxicity due to a pathogen, you essentially have a toxicant that can multiply.

As a result, things like concentration response relationships will likely fall apart. Frequently, you will see higher mortality at lower concentrations, or other irregularities that lead you to suspect that something else may be involved.

Another option if you suspect that, of course, is to use ultrafiltration to try to physically sterilize the sample, and remove at least bacterial pathogens from the matrix.

MR. TELLIARD: Thank you, Dave.

MR. MOUNT: Thank you.

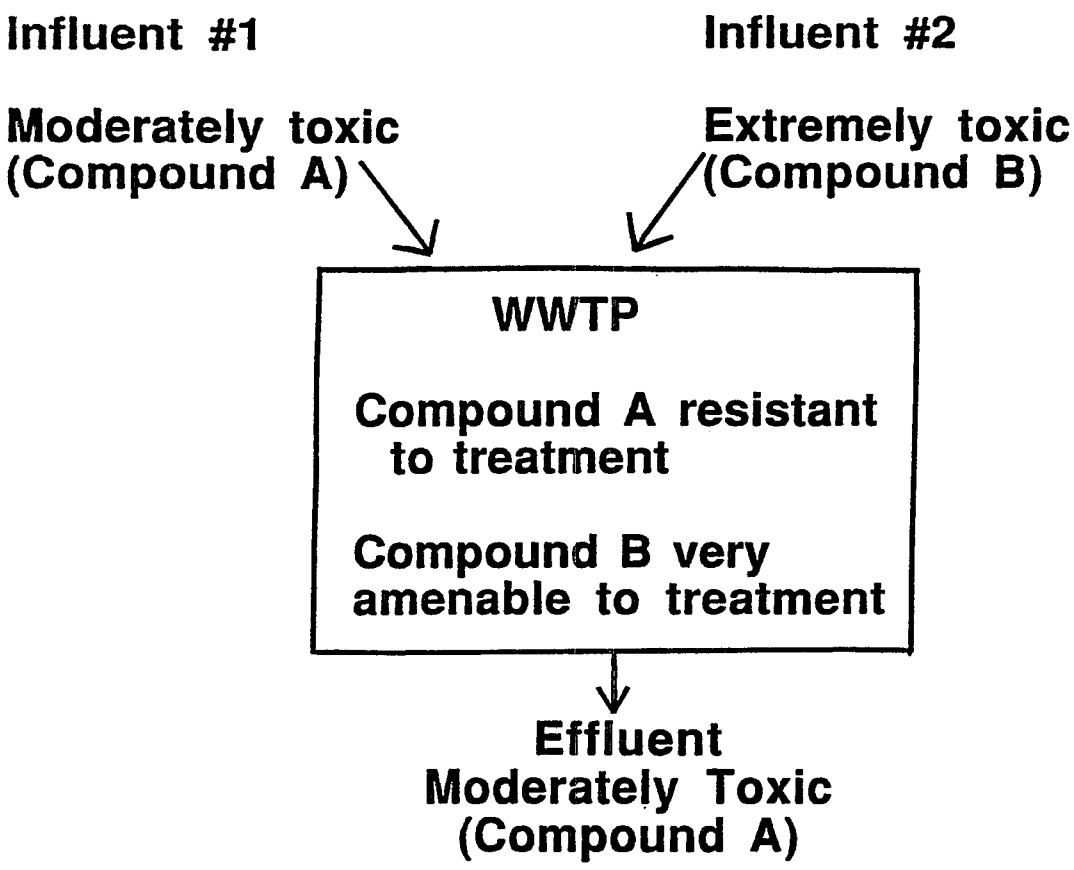

Influent #1
Moderately toxic
(Compound A)
Influent #2
Extremely toxic
(Compound B)
WWTP
Compound A resistant to treatment
Compound B very amenable to treatment
Effluent
Moderately Toxic
(Compound A)

Figure 1

APPROACH FOR A PHASE I TIE

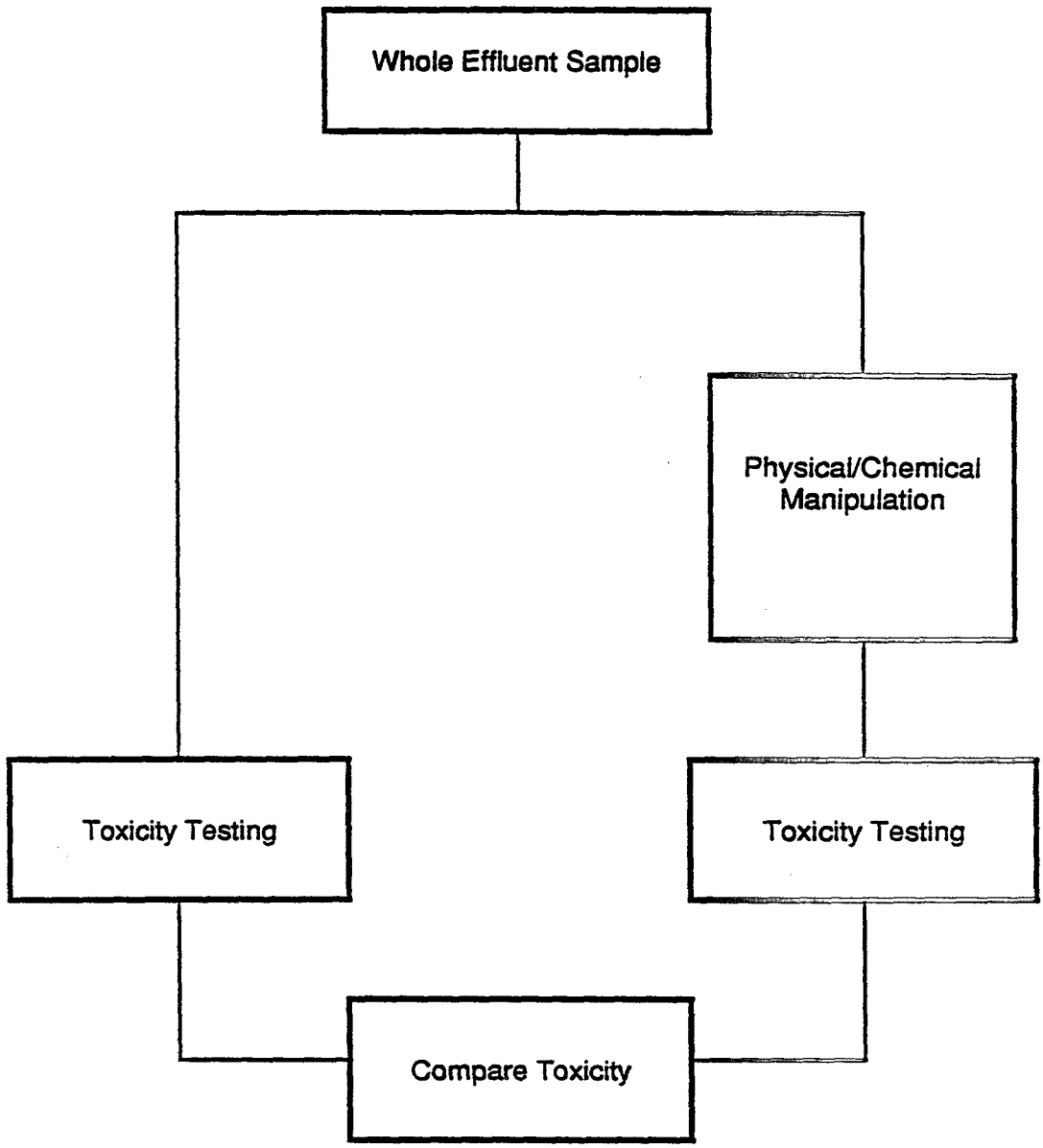


Figure 2

ENSR

Phase I -- Toxicity Characterization

- Physical/Chemical Manipulations
  - Baseline Toxicity
  - pH 3 Adjustment
  - pH 11 Adjustment
  - pH 3 Aeration
  - Initial pH Aeration
  - pH 11 Aeration
  - pH 3 Filtration
  - Initial pH Filtration
  - pH 11 Filtration
  - pH 3 Solid-Phase Extraction
  - Initial pH Solid-Phase Extraction
  - pH 9 Solid-Phase Extraction
  - EDTA Chelation
  - Oxidant Reduction
  - Graduated pH
- Toxicity Testing
  - Compare toxicity of manipulated effluent samples with toxicity of whole effluent

Figure 3

Phase I TIE

Manipulation	Reduce Toxicity? Yes	No
Solid-Phase Extraction (non-polar organics)		X
EDTA Chelation	X	
Aeration (any pH)		X
Acid or Neutral Filtration		X
pH 11 Filtration	X	

Figure 4

Municipal WWTP

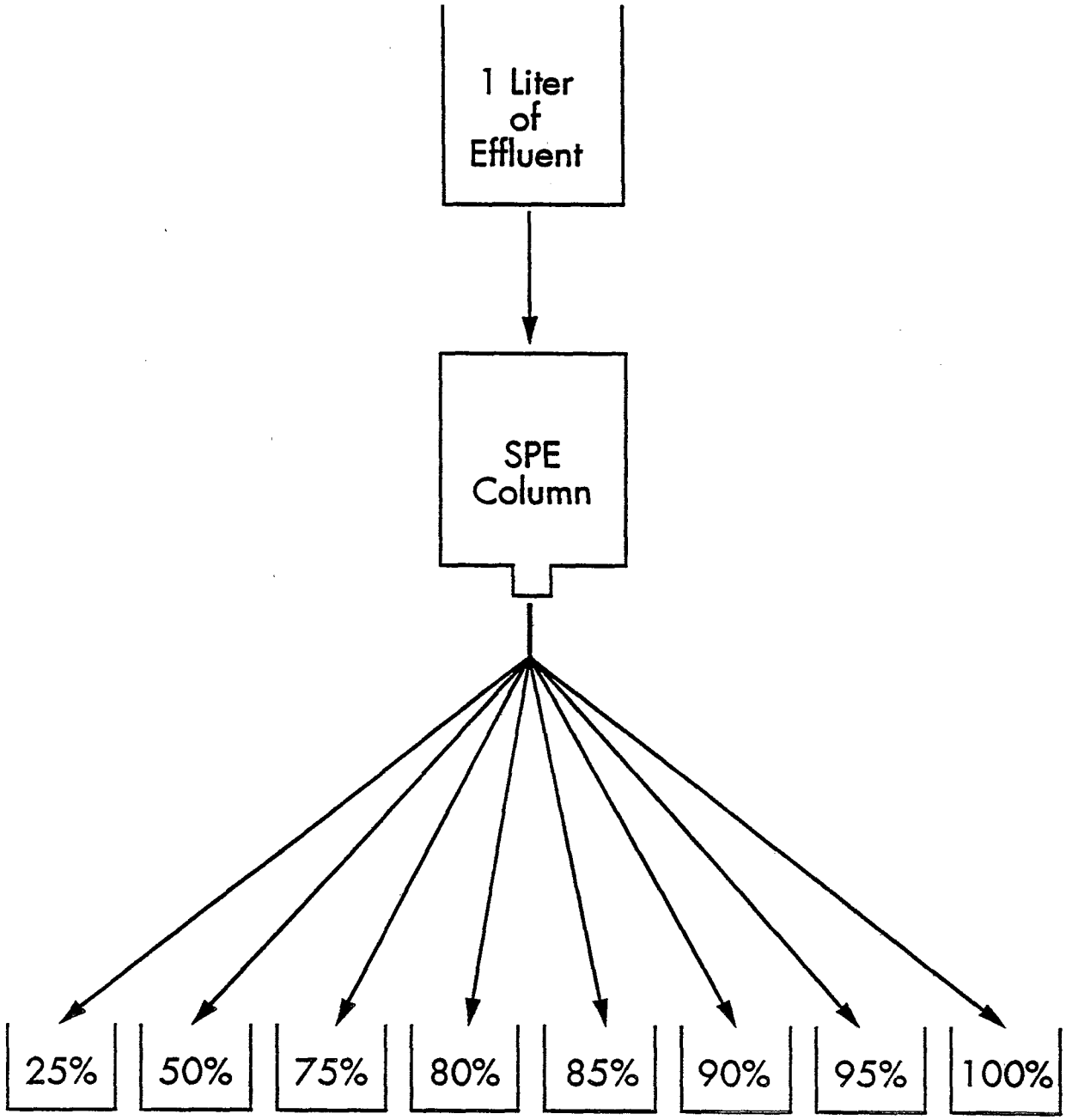
Phase I Results

Manipulation	48-hour Survival (%)
Whole Effluent	20
pH 3 Adjustment	60
pH 3 Filtration	20
pH 3 Aeration	**100**
pH 3 SPE	**100**
Initial pH Filtration	0
Initial pH Aeration	**100**
Initial pH SPE	**100**
pH 11 Adjustment	20
pH 11 Filtration	0
pH 11 Aeration	**100**
pH 9 SPE	**100**
EDTA Chelation	0-80
Oxidant Reduction	0-20

Figure 5

ENSR

SPE Elution



Test Each Methanol Fraction for Toxicity (5x)

Figure 6

ENSR

SPE Elution Results

Fraction	Survival (%)
25%	100
50%	100
75%	100
80%	100
85%	0
90%	0
95%	100
100%	100

Figure 7

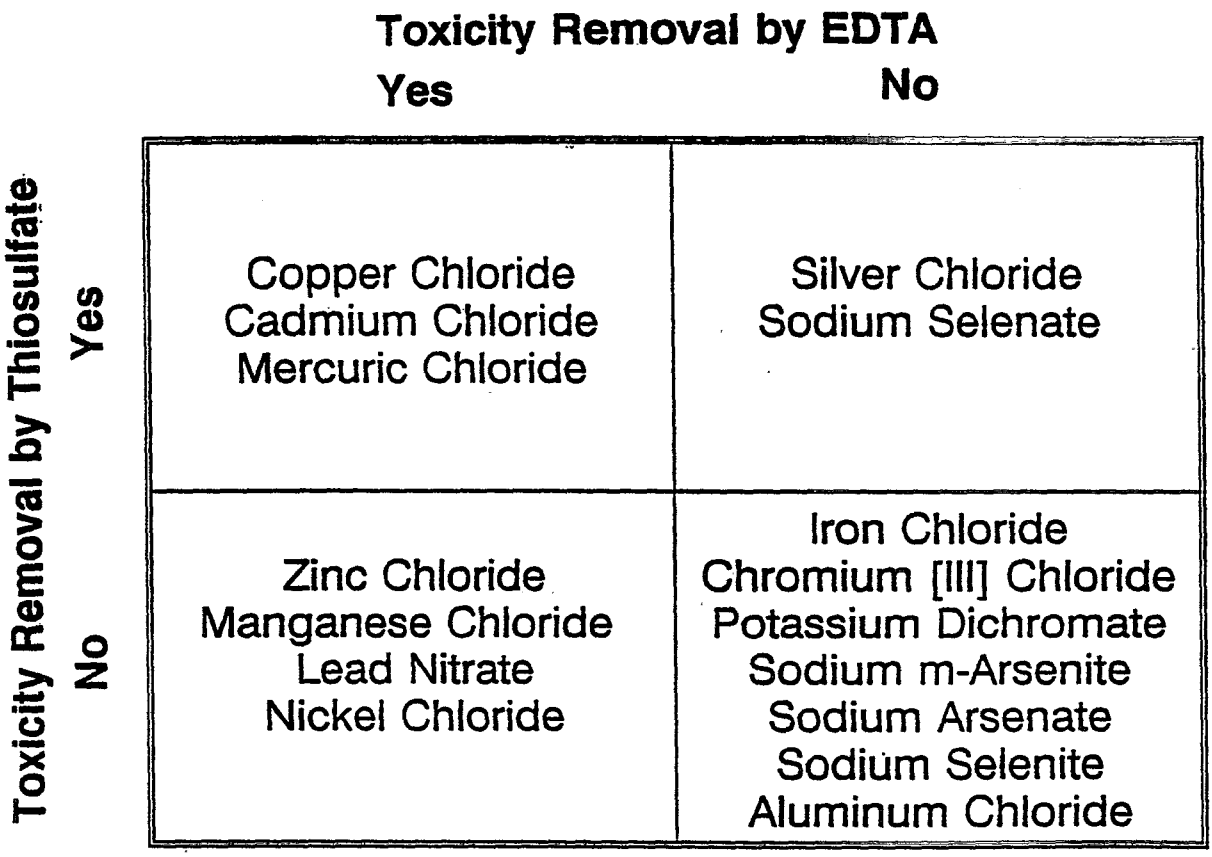

Toxicity Removal by EDTA
Yes
No
Toxicity Removal by Thiosulfate
Yes
No
Copper Chloride
Cadmium Chloride
Mercuric Chloride
Silver Chloride
Sodium Selenate
Zinc Chloride
Manganese Chloride
Lead Nitrate
Nickel Chloride
Iron Chloride
Chromium [III] Chloride
Potassium Dichromate
Sodium m-Arsenite
Sodium Arsenate
Sodium Selenite
Aluminum Chloride

Figure 8

Refinery Effluent
SPE Elution

Test	48-h LC_{50}	Concentration	Toxic Units
Whole Effluent	33	1x	3
25%	>100	5x	-
50%	>100	5x	-
75%	71	5x	0.3
80%	55	5x	0.4
85%	62	5x	0.3
90%	71	5x	0.3
95%	>100	5x	-
100%	>100	5x	-
Total of Fractions	-	-	1.3

Figure 9

Refinery Effluent

- Graduated pH Test (24-hour survival)

pH 6	pH 7	pH 8
0%	100%	0%

- After Solid-Phase Extraction

pH 6	pH 7	pH 8
100%	100%	0%

Figure 10

ENSR

Refinery Effluent

SPE Elution

Fraction	24-hour Survival (%) pH 6	pH 8
25%	100	100
50%	100	100
75%	0	100
80%	40	100
85%	100	100
90%	100	100
95%	100	100
100%	100	100

Figure 11

MR. TELLIARD: Is the coffee out back? Yes? Okay. We are going to take a 15-minute break, 15, that is, a 10 and a 5...a 15-minute break to get a cup of coffee, come on back in, and you can listen to Dow tell us about dirty, dangerous, and deadly dioxin.

(WHEREUPON, a brief recess was taken.)

MR. TELLIARD: Our next speaker this morning is Les Lamparski from Dow Chemical. The agency at the present time is spending $1.7 trigabucks looking at the impact of dioxins and furans in the environment, in particular, as it relates to the pulp and paper industry but also in refining, centralized waste treaters, and so forth.

This morning, we have two people speaking on dioxin analysis. Les is probably one of the more formal speakers in the sense that he has been at it longer than most of the average bears dealing with the analysis of dioxin and furans, and we are very fortunate to have him this morning.

So, with no further ado, Les?

MR. LAMPARSKI: Thanks, Bill.

Probably one of the few people who have, as Bill said, who has been involved in this longer than I have is the other speaker this morning. Tom Tiernan. So, I haven't been involved the longest.

This morning, Terry and I were sitting in the bar having a cup of coffee, and we decided that this talk was a little bit too boring the way I had it originally been configured. So, we took the slides from two talks and combined them, just sort of shuffled them up and put them together. So, I am going to try to go through these slides. Don't look at the numbers at the bottom of the slides, because they jump all over. Basically, what I am trying to do is describe the instrument and show some applications at the same time, so it may be a little bit jumbled around.

Our work in the measurement of chlorinated dioxins is driven by the fact that our laboratory at Dow has responsibility basically for the analysis of chlorinated dioxins and furans for all of Dow U.S.A. So, there are a number of sites across the country that we are responsible for answering to the various State and EPA regional regulations.

So, we have a wide variety of samples that have to be analyzed for these types of compounds, and we are always

looking for ways to make the analysis a little bit easier. And by being easier, we mean faster and cheaper.

Currently, chlorinated dioxins require quite a sophisticated cleanup procedure prior to the measurement, generally by GC mass spec. These cleanup restrictions tend to limit the size of studies that can be realistically performed in an environmental survey. If you have to spend a week to clean up a series of 5 or 10 samples, you are naturally not going to want to invest the time to analyze or to conduct a survey that would contain 1000 samples. So, this is a very strong limitation that is placed on environmental studies that are undertaken to analyze for these compounds.

Because of this, there is always possibility that any data that is generated in an environmental study...the data has been compromised in some fashion. If the samples have not been homogenized properly, if homogenization is the method that is chosen to reduce the number of samples that are analyzed, possibly we could collect 1000 samples and combine them in sets of 10 in some fashion and only analyze 100.

Well, if this combination procedure is not truly indicative of the samples in the environment, we may have compromised the integrity of the final data.

This type of approach may have a very serious effect on any risk assessment that comes out of a study, whether it is in a positive fashion and the risk is determined to be greater than it is or if the risk is falsely determined to be too low. Either of those possibilities can cause a problem.

We decided that it might be an interesting approach for an environmental study to focus on specific types of compounds. Rather than looking for all of the chlorinated dioxins and chlorinated furans that are possible, all 210 isomers, let's look specifically at only a couple of the key...let's call them the most toxic isomers.

In this case, we could say 2,3,7,8-TCDD and 2,3,7,8-TCDF. I will show this structure on a later slide for those of you who aren't familiar with them.

By limiting the amount of analytes and limiting the sensitivity that we are going to look for these compounds, let's not go down to 1 part per quadrillion or whatever in a soil sample. Let's set a realistic limit. If it is 10 parts per trillion or 1 part per billion, that limit will determine how large a sample is going to be analyzed to begin with.

Naturally, if you have a smaller sample to begin with, you can use a cleanup...the cleanup procedure will be much more effective, generally, if it only has to be applied to

10 mg of sample rather than to 100 grams. So, it will allow us to use more efficient methodology and simpler equipment.

What kind of simpler equipment are we talking about? We decided to investigate the use of 2-dimensional gas chromatography followed by a low resolution mass spectrometer as a detection system. There were a number of potential advantages that we saw when we decided to try to construct this instrument, and they are shown here on this slide.

Basically, they allow us to automate the system, and the changes that had to be made to the system were compatible with the instrumentation that we currently had in-house. Naturally, if somebody has a low resolution mass spectrometer and all of a sudden the EPA mandates that high resolution mass spectrometry is the only way that a sample can be analyzed, you are stuck with a $200,000 boat anchor.

So, we were looking for ways to extend the capability of low resolution mass spectrometry and, in fact, in some cases, to try to use low resolution mass spectrometry as an alternative to the high resolution mass spectrometers that are currently in vogue.

The system that we constructed shown here consists of a 5987 Hewlett-Packard low resolution quadruple mass spectrometer. It is a 7-year-old instrument, so it is a well run instrument.

The 2-dimensional system is contained in a 5890 GC shown here. It was purchased from a company called Analytical Controls, Incorporated.(ACI), and the 5890 contains a Dean switch and a cryogenic trap for collecting the analytes. It is configured presently with an FID and an electron capture detector for monitoring pre-column effluents.

The whole system is controlled by a single controller provided by ACI which monitors all of the components. It basically monitors all the components in the 5890. The only electronic link between the 5890 and the 5880, the GC/MS portion of the instrument, is by a remote start cable. That is the only connection except for the analyte transfer line which is that large black line going across the top of the two instruments.

The analyte transfer connection is an approximately 40-inch heated line. The transfer is through a fused silica tube which can be changed to match the characteristics of your analyte. So, if you want to have a coated fused silica column containing DB-5 or Supelco 2330 or whatever, you can change that. Presently, we are using DB-5 because it is very rugged, and that is also the column that we have on the pre-column instrument.

As you can see, the system is also automatable. We have an autosampler which can be and is routinely used, but it can be removed for manual injections.

This is the slide that we showed to management to try to sell them on the subject. It is very crude, and it is totally non-scientific, but management bought it, so they bought the instrument for us. But basically what happens is the sample is injected into the prep GC, goes through the capillary column, a switch is effected, and the analyte can either go to the detector or the cryo trap where it is collected by the CO_2-cooled trap, and then it can be heated, transferred into the second chromatographic column, and finally into the mass spectrometer for detection.

As I said, that was for management. What really happens looks something like this. This is the flow schematic for a Dean switch that is used by the ACI controller. I am going to show you four of these slides that are essentially the same, and what we are doing is looking at where the analyte goes during the various stages of the separation.

In the initial pre-column separation, the analyte is injected into the preparatory capillary column, and separation is achieved in this column. Generally, the analyte goes into the EC detector for detection and monitoring of effluent.

The system contains two basic carrier gas systems. The flow controlled system controls the preparatory GC column, and the pressure controlled system controls the Dean switch which is the method of switching the analyte flow between the monitor detector and the analytical column.

So, at the appropriate time when the analyte is eluting from the prep column, the Dean switch is switched. Valve 3 is switched so that flow goes in the opposite direction and essentially pushes the analytes onto the cryogenic trap which is being cooled by the CO_2.

The analyte is trapped out for a given period of time, and that is pre-determined by analyses of standards. The analyte can then be reinjected by stopping the cooling CO_2 onto the cryogenic trap, and it is resistively heated in roughly one minute from -50 to 250 degrees, and the analyte is deposited into the heated zone through the transfer line and onto the analytical column where separation can then be made under the types of conditions that are best for the analyte and the column that is used for the final separation.

At this time during the reinjection onto the analytical column, the flow on the prep column has stopped. So, if we want to collect multiple fractions, it is possible to then go back, start the flow again on the column, and collect

another fraction for a second analyte or any number of analytes.

After the analyte is injected into the analytical column, separation is made in the normal fashion, and the flow on the preparatory column is reversed. What this does is elutes off the very heavy boiling garbage that normally would stick on the front end of the column and cause problems.

This is a very real advantage for this type of system. I will show you later that we are looking at crude extracts of waste treatment sludge, let's say. We have analyzed through the single preparatory column which is a DB-5 column over 800 injections. We have made over 800 analyses on this column without having to change the column, and part of that advantage comes from the fact that the high boiling components are eluted backwards off the column during this phase of the analysis scheme.

If we look very briefly at the types of control sequences for various components of the system, basically, the prep controller...that is the ACI controller that is the dominant computer in the whole system...it looks for ready signals from the various other components in the system, the autoinjector, the prep GC, the mass spec computer, the mass spec GC, and the mass spectrometer itself.

When it gets ready signals from all of those components, it initiates the start of the run by telling the autoinjector to make the injection. Prep GC does the separation, and, as you can see, over a period of time, all of these control sequences are brought into play by the prep computer. All of this is done. There is no operator intervention at all. Once you load the samples into the autosampler rack, you can just walk away and forget about it.

If we look at some of the data that we have gotten out of this system, this is 2,3,7,8-TCDD. We have analyzed this on the top trace by GC/MS, and this is 40 picograms injected onto a DB-5 column running under conditions optimum for detection of that component. You see the retention time is about 6.5 minutes.

The bottom trace is the GC/GC/MS separation on a Lee SB smectic column which we have chosen at this time to be useful for determination of 2,3,7,8-TCDD isomer-specifically. We have yet to hear Tom's talk, so I can't really say that we want to use that column, but I am sure that is one that we are going to be investigating in the future.

I didn't want to steal any of his thunder, but I couldn't resist.

As you can see here, the sensitivity of the two traces, the signal to noise ratio for 40 picograms injected onto the column are virtually identical. Now, what this tells us is that we are getting good transfer through the Dean switch which is just a series of T's in the gas flow stream, and also, we are not seeing very drastic effects, if any, of adsorption onto various components in the switch itself.

It is predominantly a fused silica system, but there are places where, if the system is not put together properly, there could be some stainless steel active sites which would cause adsorption of TCDD, but we don't see any of that as evidenced by this chromatograph.

We then looked at the reproducibility of the system compared to GC/MS, and using a manual injection without the autosampler, you can see that the reproducibility over a period of time...this was 9 runs that were run over a period of 2 days...is certainly comparable to anything that can be done by GC/MS for a similar type compound.

Using the autoinjector where 10 runs were run over a period of about 20 hours total time, you can see that the reproducibility is essentially the same. There is some evidence that there was a little bit of gradual drift of the instrument sensitivity which is causing this number to be probably a little bit larger than it would be if it were a very short-term experiment, but each analysis takes roughly

38 minutes, and when we put in blank runs in between, it took quite a long time to do that precision study.

We looked at the linearity over a small range of concentrations for TCDD again, and these are injections from 5 picograms on column to 200 picograms on the first column. As you can see, the linearity is very good.

If we increase the concentration range up by a factor of 10 up to 2000 picograms on column, the linearity does skew a little bit. It is biased somewhat high at the higher concentrations, but this is certainly usable for most applications.

If we examined what does a real sample looks like on this system: here we have a complete electron capture gas chromatogram of an extract of waste solid from a waste treatment plant in our company. This is the crude extract, a benzene extract, of the sludge out of the treatment plant. As you can see, by electron capture, there are a lot of compounds eluting off of this column.

This is a 30-meter DB-5 column programmed from 135 to roughly 280. The fraction of interest...this is supposed to be highlighted in grey, and I don't know if you can see it in the back of the room...but we are looking at a roughly half-minute wide window between 9.5 and 10 minutes.

A 1-nanogram response with TCDD is shown on the upper right of the chromatogram. So, as you can see, some of

these components that are eluting off are very large compared to the TCDD that we are supposedly looking for.

We collected the 9.6-10.1 minute fraction and then put it onto our analytical column, the Lee smectic column, and what comes out by GC/MS...by the second GC/MS...is a single peak with no interfering components. The amount observed is 5.3 ppb. The detection limit was set up in this study to be of the order of .5 ppb. The regulatory level for this compound in this matrix was 1 ppb.

So, we set up the analysis by using a 10 mg sample to begin with. We extracted a large sample, took an aloquat corresponding to 10 mg and injected that directly into the GC/GC/MS, and we were able to determine the TCDD as shown there.

The bottom trace is the internal standard that is added prior to the analysis. We use this to monitor recovery through any cleanup procedures that could be used. In this case, we used the internal standard in a typical response factor calculation. The internal standard is used to determine the amount of analyte that is present.

What does all of this mean? Why would anybody want to invest the time? This instrument costs roughly...the 5890 GC and the controllers cost about $50,000. This is if you have a mass spectrometer that you are willing to devote to

this type of system. Why would I want to spend $50,000 for a single type of analysis like this?

First of all, we should make the point that this isn't a single type of analysis. This is a very broad...there are a lot of applications that are potential for this type of instrument, not only in the field of trace analysis but also in product analysis. If you are looking for a very minor component in a mixed product or a waste stream from a product, there is a very good likelihood that this type of instrument would be applicable for that type of analysis.

But let's stick to the original topic, determination of chlorinated dioxins and furans in environmental samples. We currently have an environmental study which is being mandated by the State of Michigan in which we are going to look at a variety of sediment samples from nearby the plant.

At present, this study is slated to be 100 samples large. Now, if we were to only look for 2,3,7,8-TCDD and TCDF by our current method which involves a significant amount of sample preparation prior to GC/MS measurement, we are looking at a time period of 24 weeks for two people to do the analysis, and that breaks down to a cost of roughly $2400 per sample.

Now, I am sure a lot of you contract labs say that you can analyze the samples for significantly less than that,

but let's just look at the relative amounts that we re talking about.

Using the 2-dimensional LRMS system, we project that these 100 samples can be done in 3 weeks. This breaks down into $240 per sample. Well, obviously, it won't take too many studies of this size to pay for that instrument many times over.

So, that is why we feel that it will be a useful tool in an general analytical laboratory in the future. As I say...this is the commercial...Analytical Controls is the company that sells this GC instrument and controller, and they will be more than happy to take your money.

MR. TELLIARD: Thank you, Les. Any questions?

QUESTION AND ANSWER SESSION

MS. KLATT: I am Kelly Klatt with J&W Scientific.

The question I do have is, you evidently showed first the GC ECD slide, the extract, and you had evidently spiked in the 2,3,7,8-TCDD. Right?

MR. LAMPARSKI: In the extract of the sample?

MS. KLATT: Right, right.

MR. LAMPARSKI: Yes.

MS. KLATT: And then you showed the...

MR. LAMPARSKI: No, that is not spiked in. This is naturally occurring TCDD.

MS. KLATT: Okay, right. And then you showed this. Was this sample that you extracted this from, did it also have the other tetra isomers?

MR. LAMPARSKI: Yes, it does.

MS. KLATT: It does. So, this does separate all the other tetra isomers?

MR. LAMPARSKI: Yes. The Lee column does separate 2,3,7,8-TCDD from the other TCDD's. It doesn't separate the furans.

MS. KLATT: Oh, okay.

MR. LAMPARSKI: And, to be truthful, when we started this study, Tom's column wasn't available yet.

MS. KLATT: Okay, thank you.

MR. TELLIARD: Any other questions?

DR. SCHULTZ: Bill Schultz from Eastern Kentucky University.

I don't suppose you have a trace of what it looks like with selected ion monitoring from a single column separation that compares to your ECD?

MR. LAMPARSKI: I don't have it on an overhead, but I can show you a similar comparison.

DR. SCHULTZ: It seems to me that the selected ion would give you some separation.

MR. LAMPARSKI: No, it is worse than a picket fence. It goes up, and it is just humpy.

MR. TELLIARD: A humpogram?

MR. LAMPARSKI: Yes. Well, this is the saturated one. It is humptane.

(Laughter.)

MR. TELLIARD: Good morning, John.

MR. MCQUIRE: John McQuire from EPA.

Have you, in the interest of trying to come up with low cost...lower cost...low resolution mass spec investigated any of the work that Don Hunt did a few years back, maybe 10, on negative oxygen CI? He claimed that you could get isomer-specific breakdowns and all sorts of things. I was wondering if you had done anything with that.

MR. LAMPARSKI: We haven't done anything with that, but in review of his work, the separation is not really that clear cut. You are looking at fragment ions that are potentially formed in one case and not in the other case. If the separation is not such that the appropriate isomer is separated, then you effect very little advantage.

Also, there are generally very real problems with matrix effects for NCI analyses. So, if you inject a standard, you get one response, and if you inject a dirty sample matrix, you will get something totally different.

For that reason, we felt that the reliability of that type of system was not what we were looking for. Basically, what we tried to do is, by selling the EPA the concept of running fewer samples, what we also try to say is we are going to run fewer samples, but we are going to give you more reliable data on those fewer samples.

MR. MCQUIRE: Okay, understood. Thank you.

MR. LAMPARSKI: So, we are trying to balance things out that way.

I might add that we have run a number of comparison studies between the 2-dimensional analysis and the GC/MS analysis using our full 3-day-long cleanup procedure, and the results are very comparable. So, the agreement between the two systems is very good. The only difference is the amount of time that it takes to do the analyses.

MR. MCQUIRE: Okay, thank you.

MR. TELLIARD: Anyone else?

I certainly like that $240 price, Les.

MR. LAMPARSKI: For you, it will be a little bit different.

MR. TELLIARD: Yes, Iknow, you are going to deal. Right.

Thank you very much.

DEVELOPMENT OF AN HRGC-HRGC-LRMS SYSTEM: INSTRUMENT DESIGN AND PERFORMANCE DATA

L. L. Lamparski and T. J. Nestrick

The Dow Chemical Company
Michigan Research and Development
Analytical Sciences, Special Analysis, 1602 Building
Midland, Michigan 48674 USA

Analytical Controls, Inc., can supply a Hewlett Packard Model 5890 high resolution gas chromatograph that is appropriately configured to accomplish fully automated, single-oven, 2-dimensional gas chromatography. As a portion of an extended research program dedicated to improving the capabilities of conventional instrumentation, we have developed and assembled the necessary components to permit the linkage of such a unit to a Hewlett Packard Model 5987A high resolution gas chromatograph–low resolution mass spectrometer (HRGC-LRMS). The results of this project have produced an instrument that can routinely conduct fully automated, dual-oven, 2-dimensional HRGC separations in conjunction with LRMS identification and detection for solutes eluting from the secondary analytical gas chromatograph. A description of this new analytical instrument and the techniques required to assemble it from commercially available resources will be the subject of our presentation. Preliminary evaluation and testing of the operational characteristics of the unit indicate that it may be a valuable tool for measuring a variety of compounds at trace concentrations in extremely complex matrices.

Development of HRGC-HRGC-LRMS

Instrument Design & Perfomance Data

Lester L. Lamparski & Terry J. Nestrick

The Dow Chemical Company
Michigan Research and Development
Analytical Sciences, Special Analysis Group, 1602 Building
Midland, Michigan 48674 USA

Current Situation for CDD/CDF Surveys

- Prelim matrix preparations often required.
- Variable extraction procedures for different matrices.
- Specialized cleanup often required for analytes.
- Cleanup simplification = Sophisticated instruments.
- Expensive & time consuming projects.

END RESULT for Current Situation

- Limited number of surveys actually performed.
- Limited number of samples examined in a survey.
- Often necessitates sample compositing.
- Sample *representativeness* often questionable.
- Statistics on resultant survey data less reliable.

Impact on Risk Assessment policies?

New Approach for Regulatory Surveys

- Limit analytes (*e.g.*, toxicological significance).
- Limit sensitivity (*e.g.*, ≥10 PPT).
- Use larger sample cohorts to improve reliability.
- Use efficient methodology & simpler equipment.

Why GC - GC - MS ?

- Affords increased chromatographic efficiency.
- Automation capability.
- Compatible with current GC-MS equipment.
- Extension of current cleanup capabilities.
- Potential means to reduce / eliminate cleanup.
- Broad applicability.

POTENTIAL

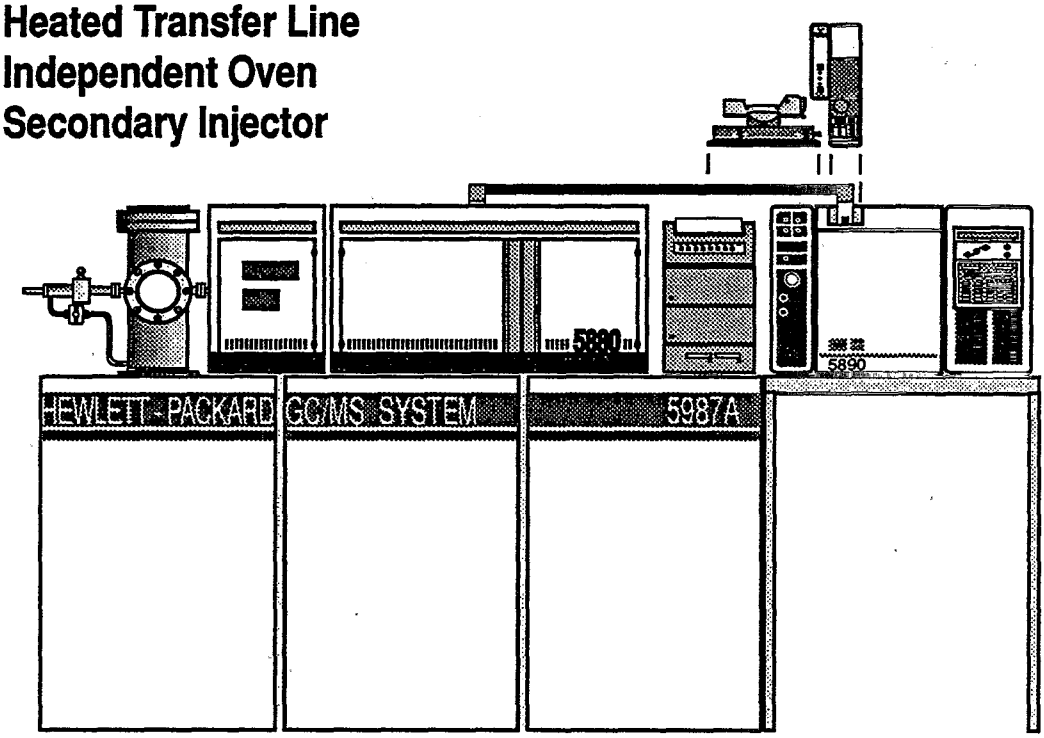
to extend capability of LRMS ?

ALTERNATIVE

to HRMS for trace analysis ?

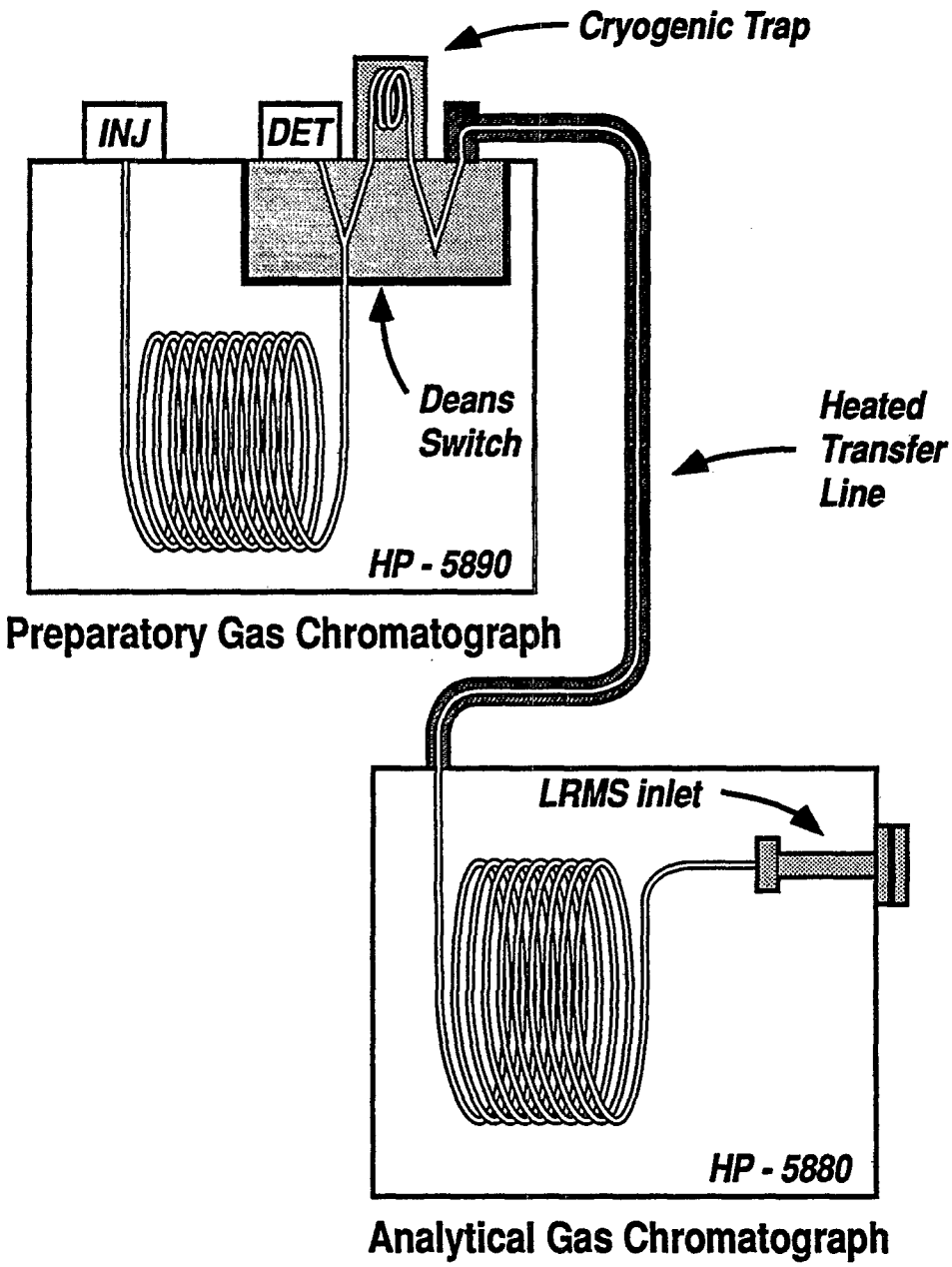
GC – ANALYTICAL

HP-5880 (LRMS)
Heated Transfer Line
Independent Oven
Secondary Injector

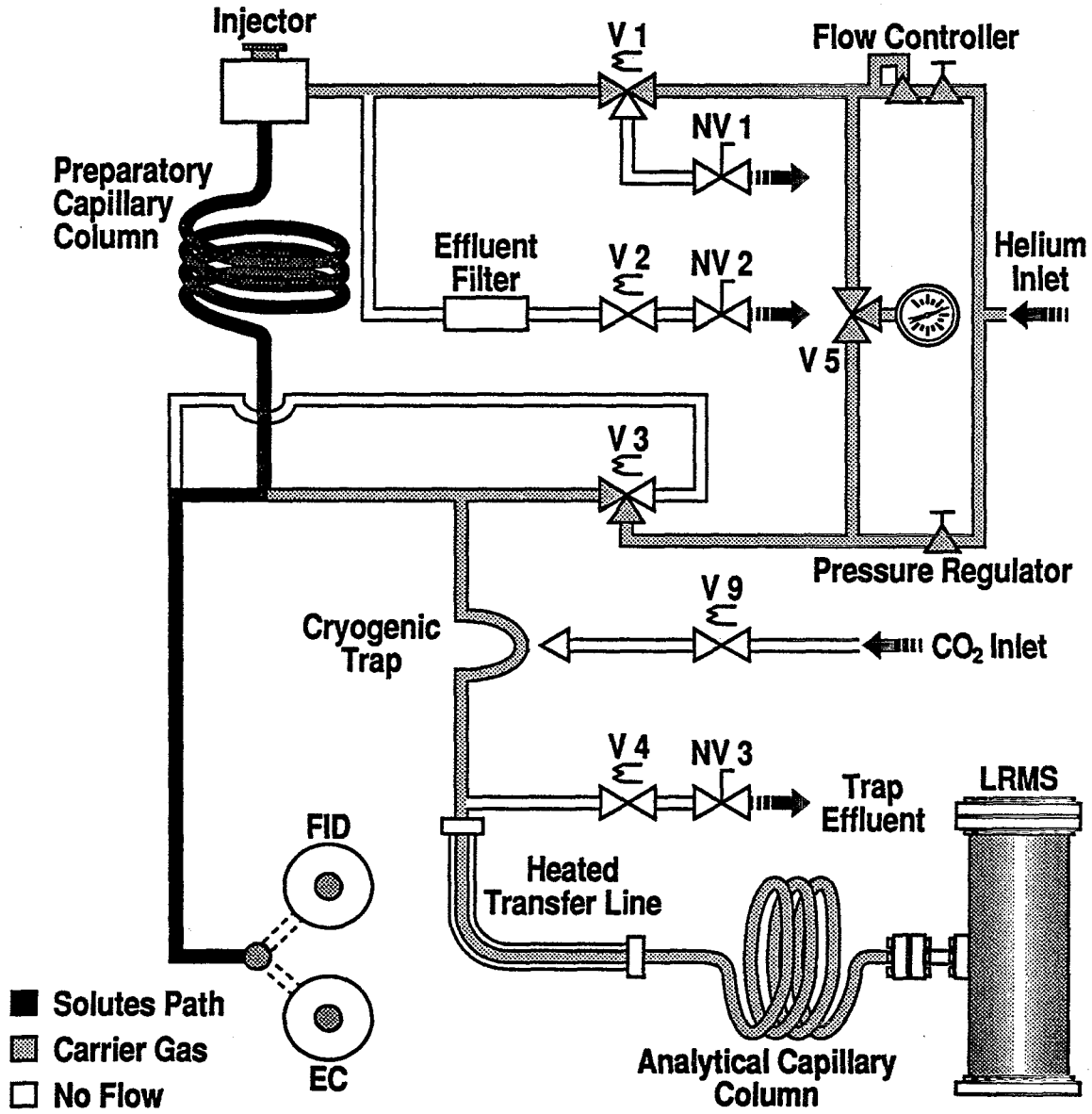


GC – PREPARATIVE

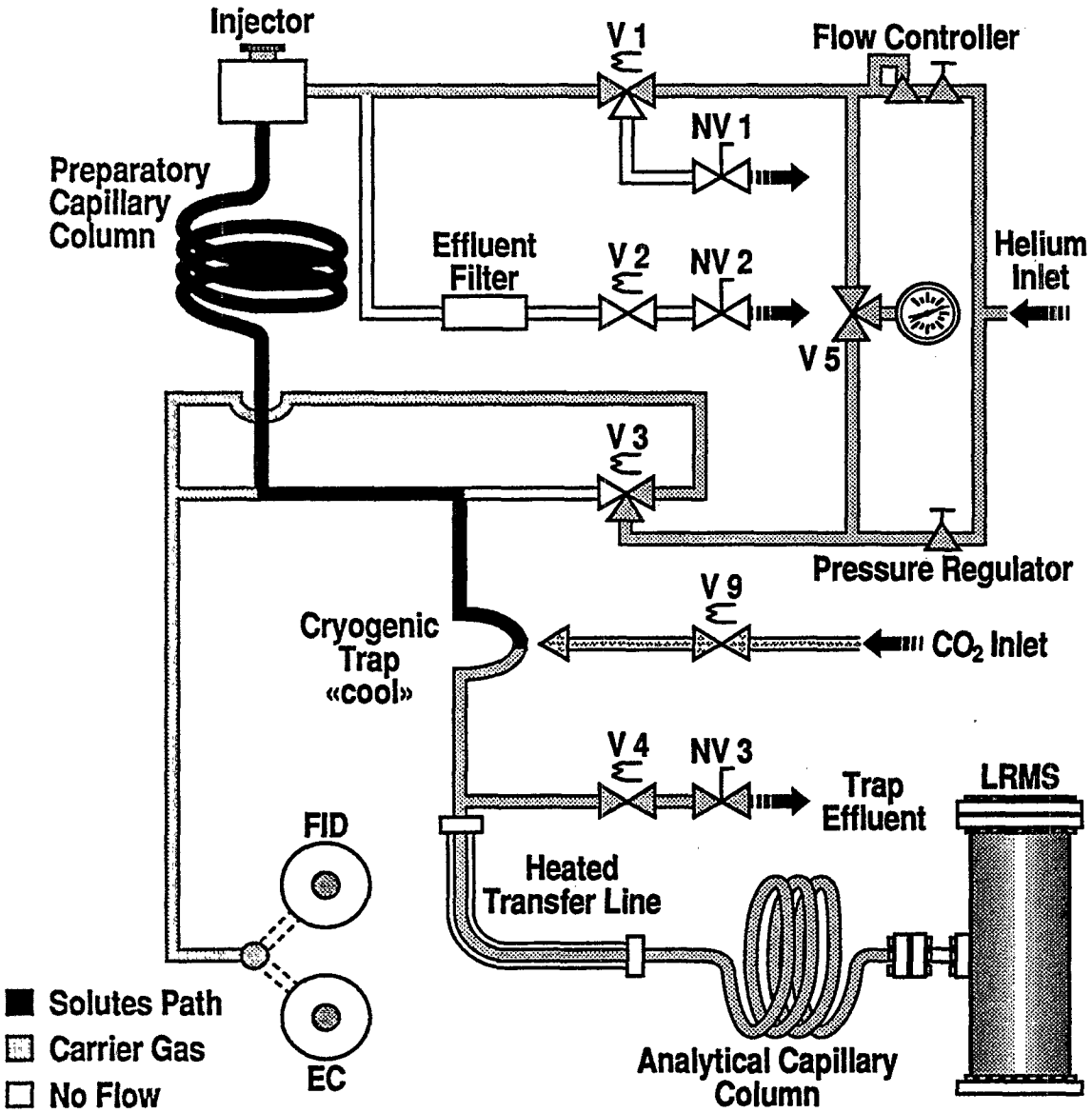
HP-5890 (FID & EC)
Deans Switching
Cryogenic Trap
ACI Controller
HP-7673A Autoinjector


Cryogenic Trap
INJ
DET
Deans Switch
Heated Transfer Line
HP - 5890
Preparatory Gas Chromatograph
LRMS inlet
HP - 5880
Analytical Gas Chromatograph

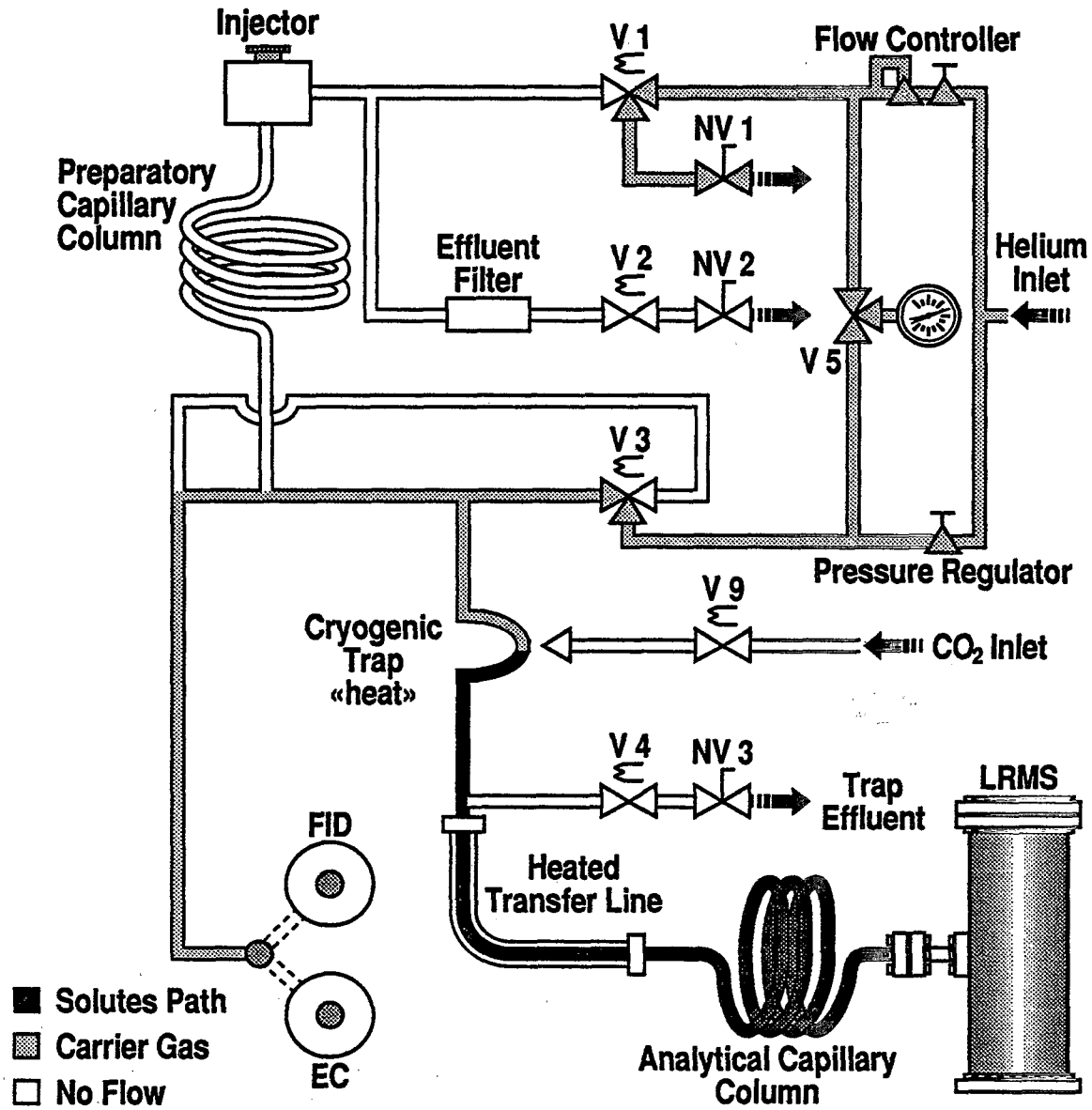
Precolumn Separation



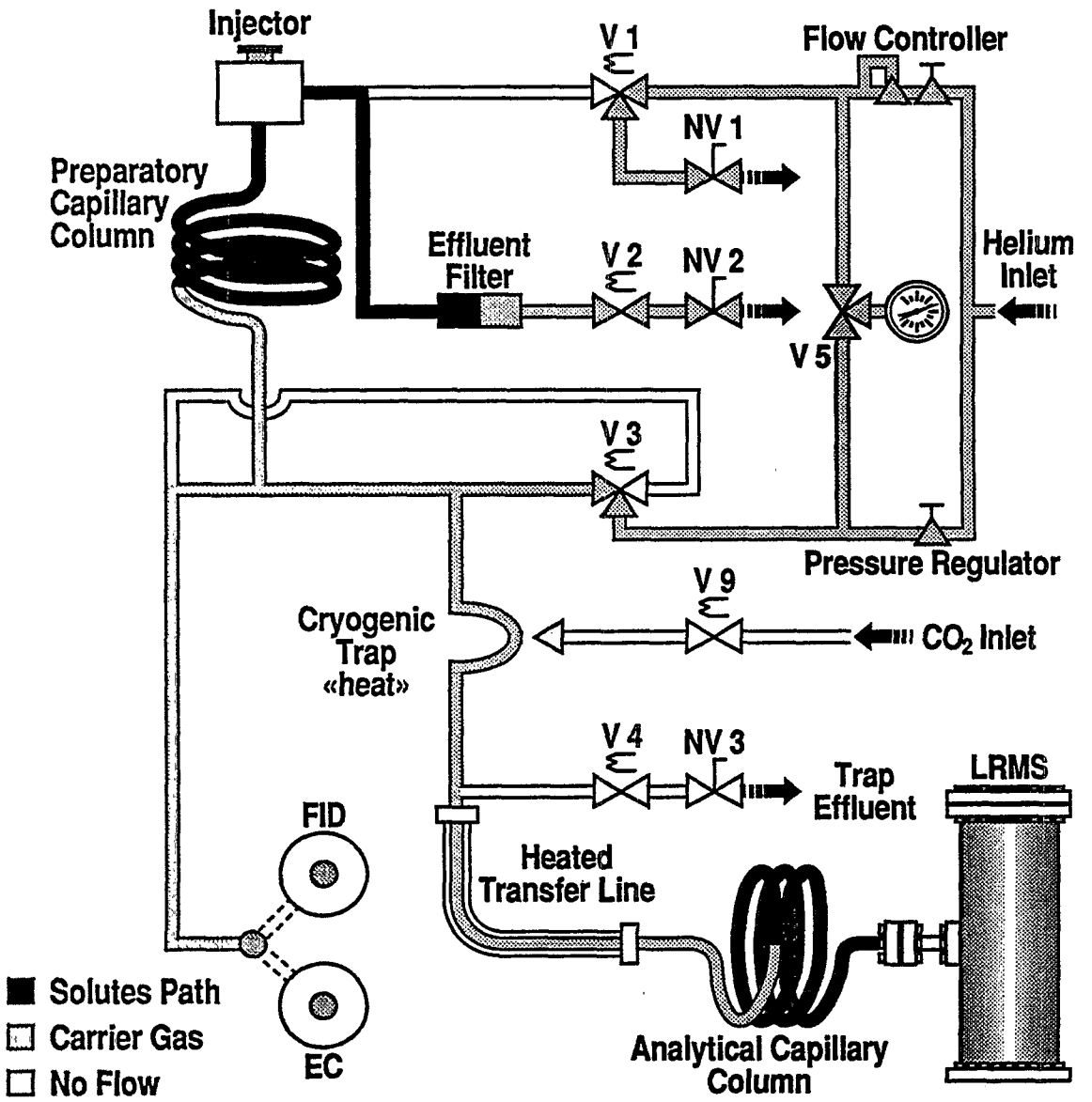
Analyte Trapping



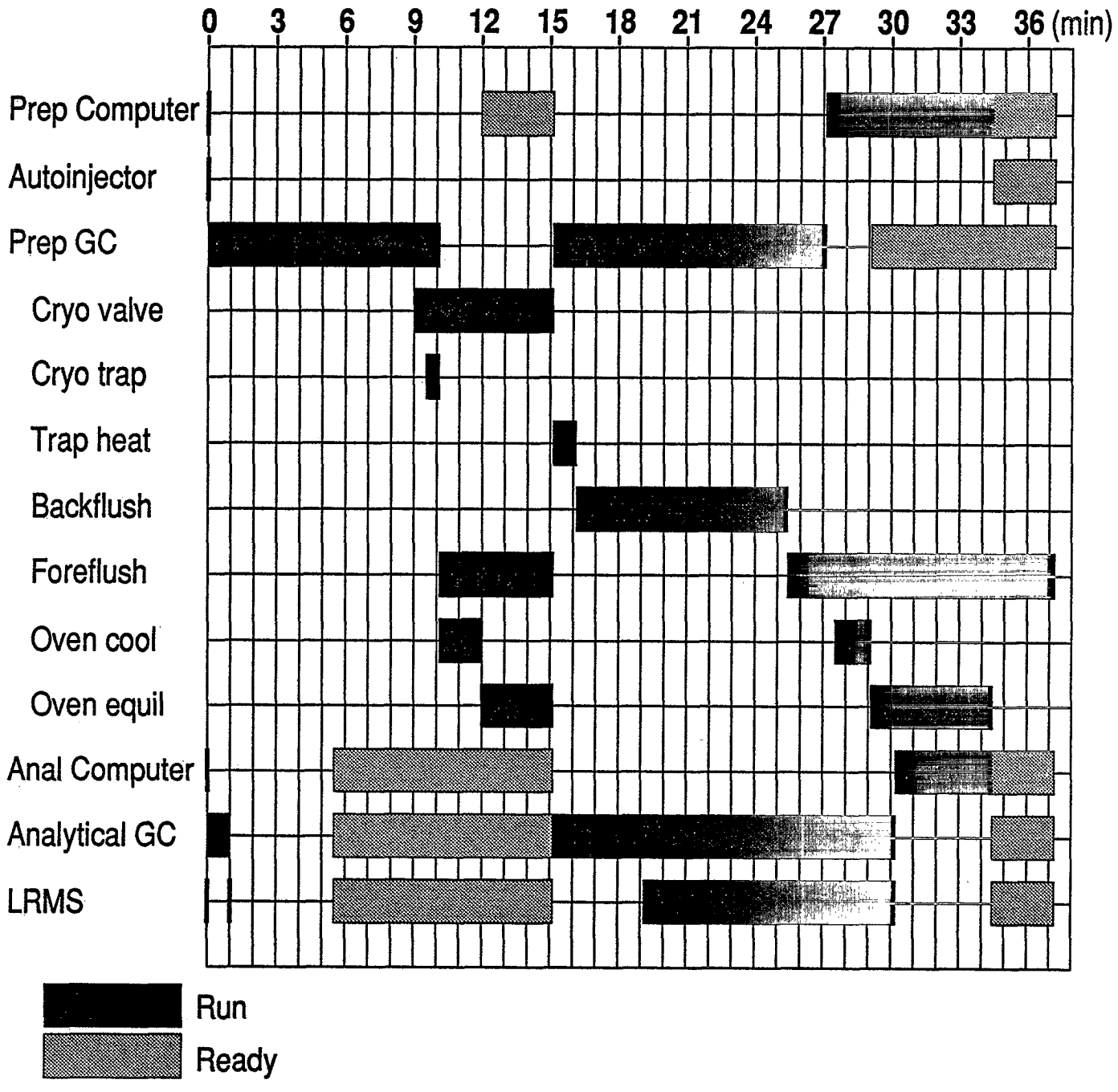
Analyte Reinjection



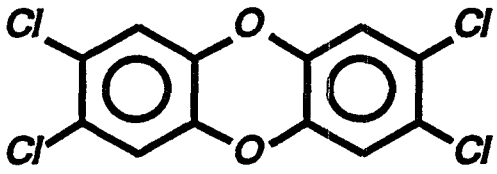
Analytical Separation & Precolumn Backflush



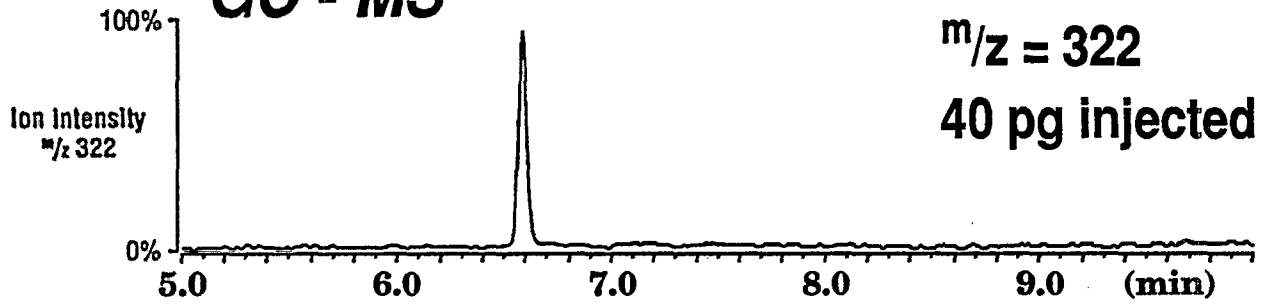
GC-GC-MS Control Sequence for TCDD



Chromatographic comparison...



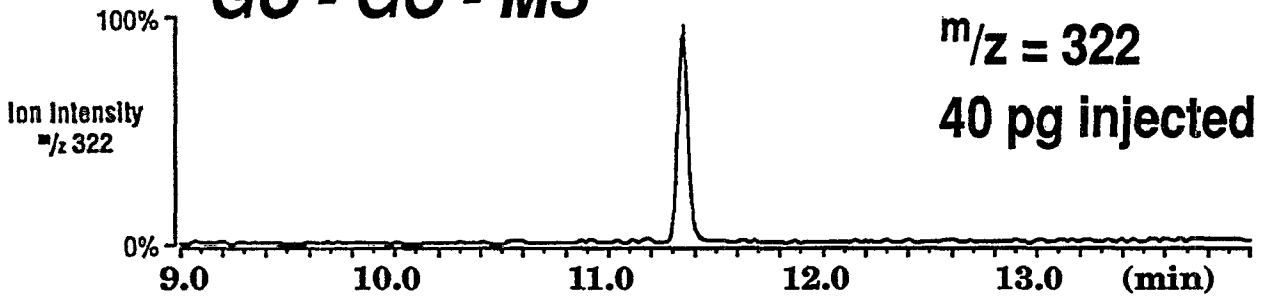
GC - MS



m/z = 322

40 pg injected

GC - GC - MS



m/z = 322

40 pg injected

Manual Injection GC - GC - MS

TCDD Reproducibility Data for 40pg

	$^{m}/_{z}$ 320	$^{m}/_{z}$ 322
n (number of runs)	9	9
$\bar{x}_g$ (avg response)	23 489	29 188
σ_{Rel} (relative S. D.)	3.5 %	4.6 %

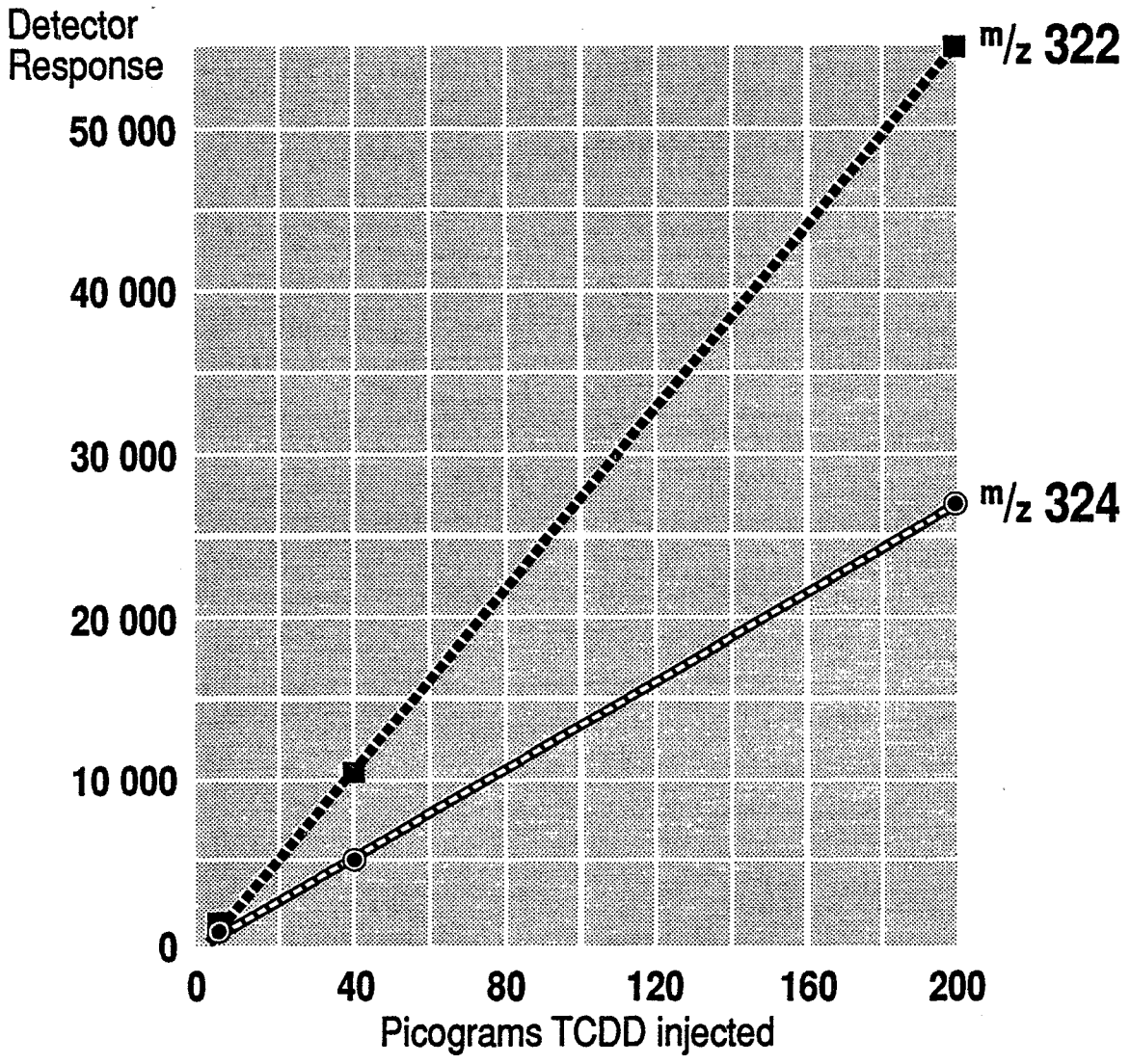
Autoinjector GC - GC - MS

TCDD Reproducibility Data for 40pg

	$^{m}/_{z}$ 322	$^{m}/_{z}$ 324
n (number of runs)	10	10
$\bar{x}_{10}$ (avg response)	7 784	3 774
σ_{Rel} (relative S. D.)	5.5 %	3.8 %

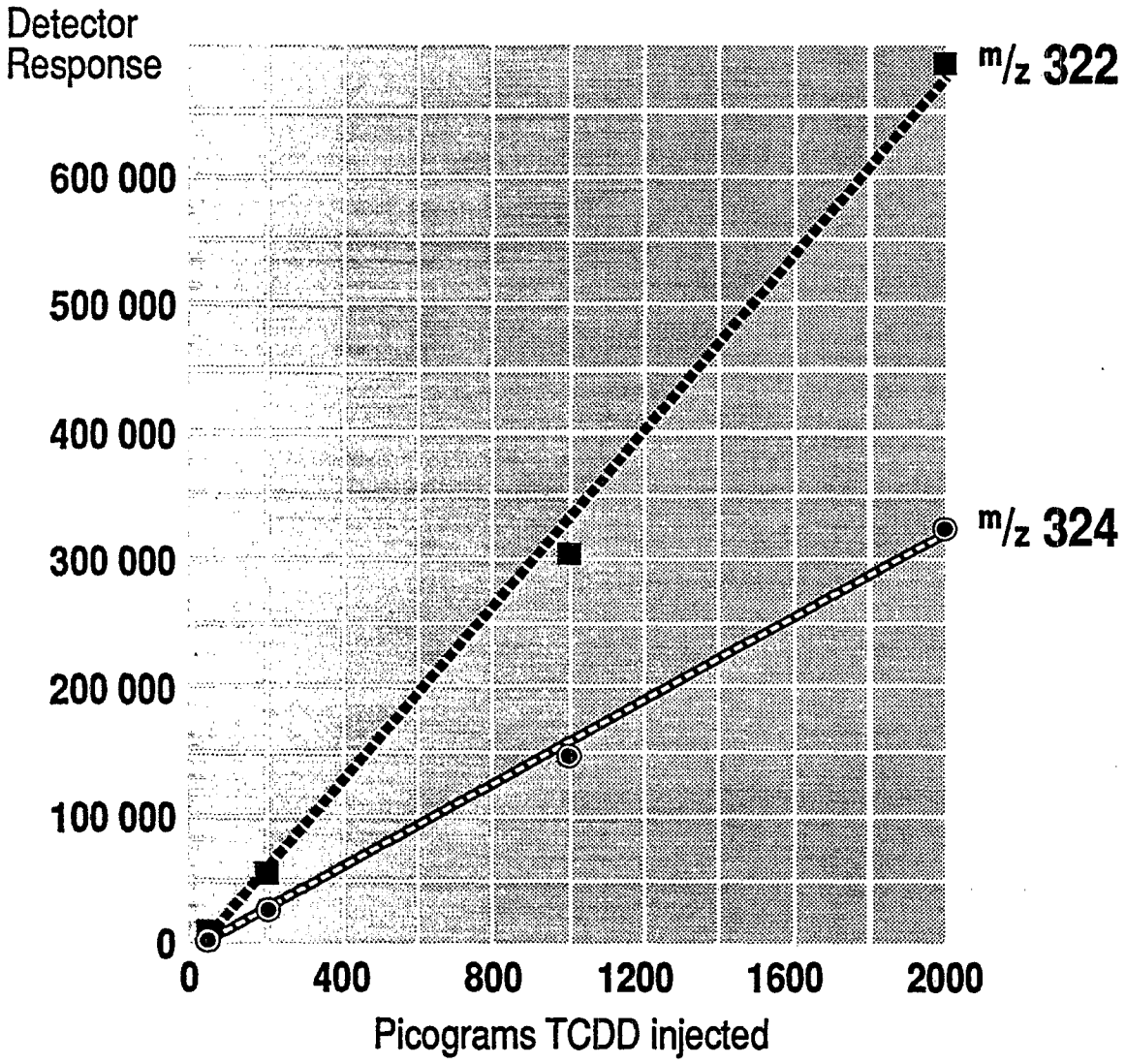
Autoinjector GC - GC - MS

Detector Linearity for TCDD (normal range)

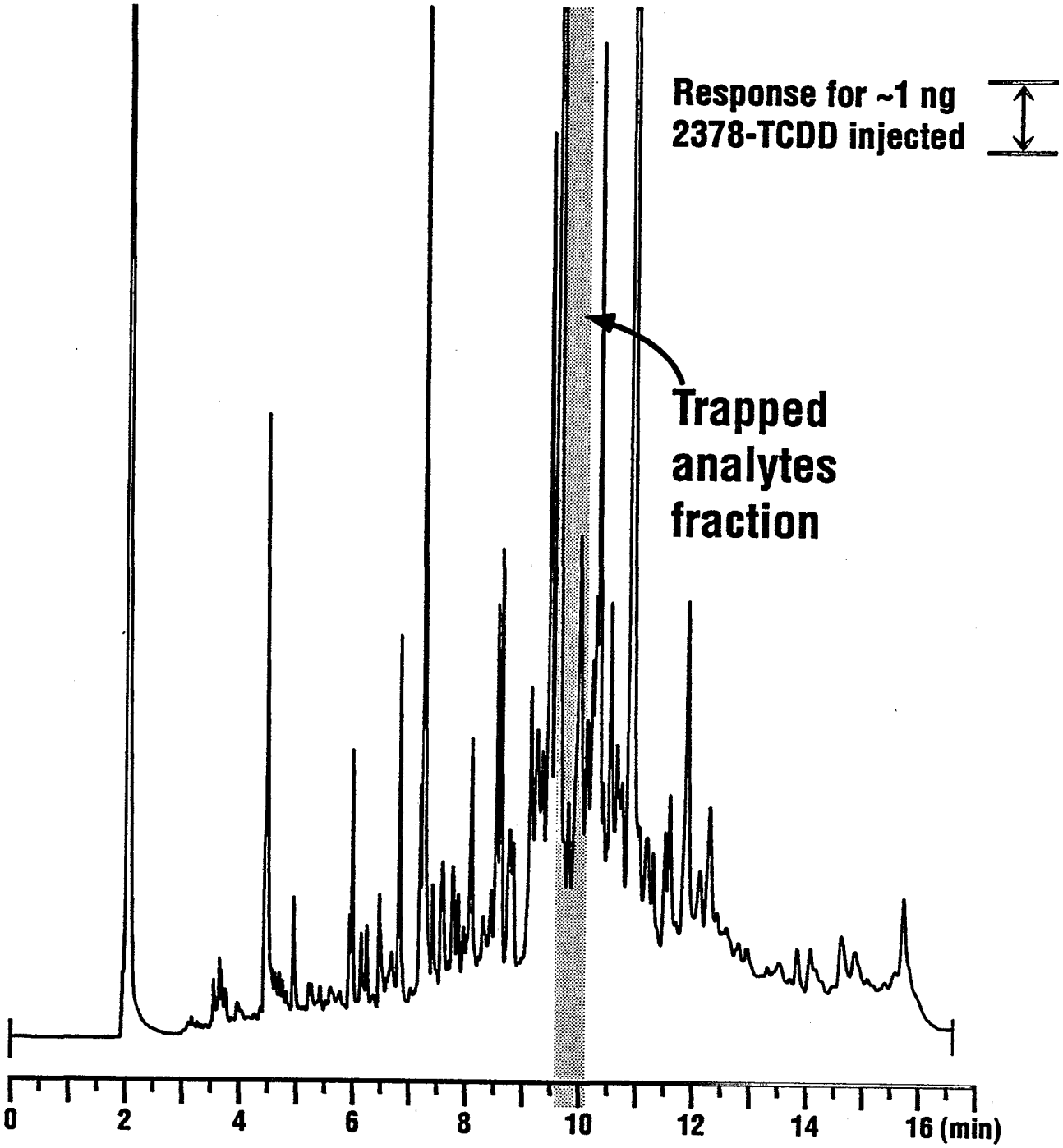


Autoinjector GC - GC - MS

Detector Linearity for TCDD (extended range)

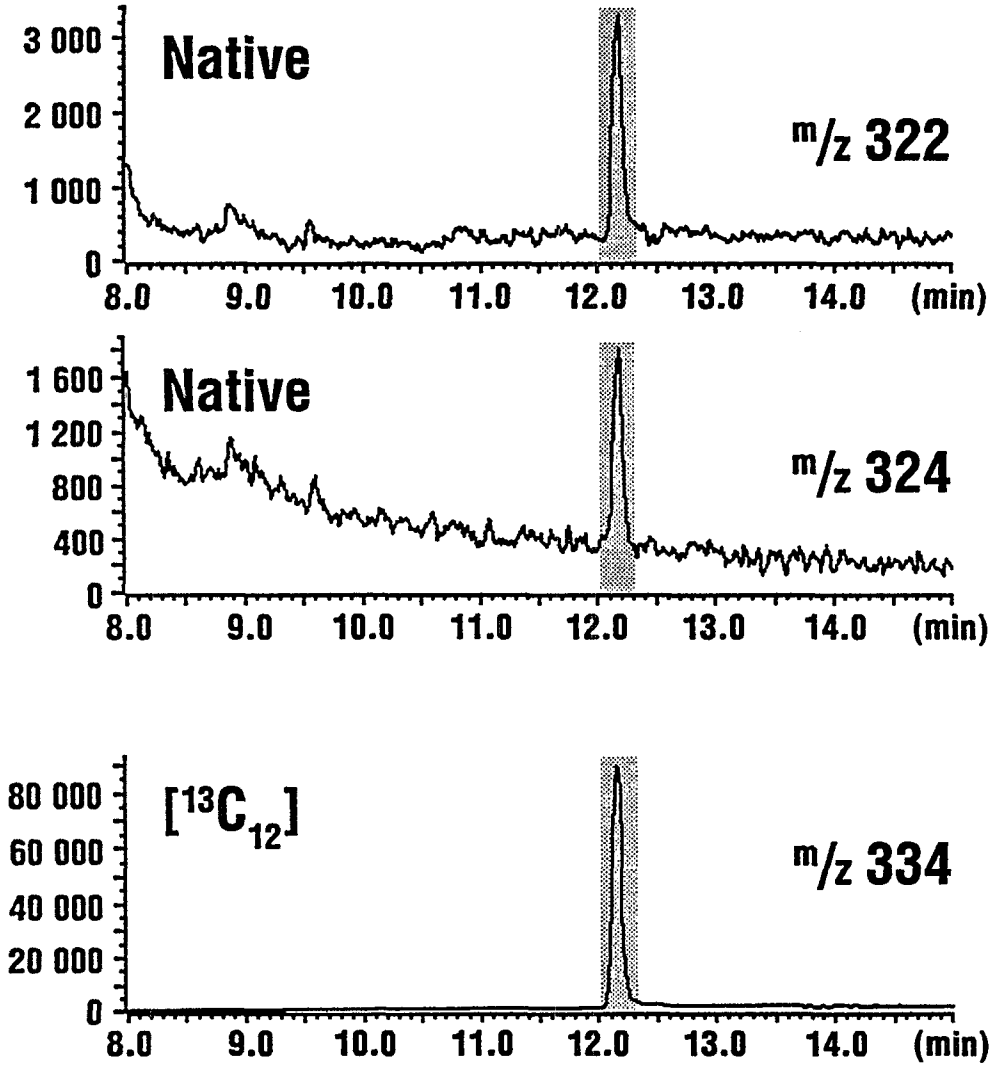


Prep HRGC (ECD) for Waste Solids



Analytical HRGC-LRMS for Waste Solids

2378-TCDD = 5.3 PPB



Why should I bother with HRGC-HRGC-LRMS?

Dow perspective: 100 samples
2378-TCDD & 2378-TCDF

Analytical Method	Analysis Time	~Cost per Sample
Full Cleanup	~ 24 weeks	$2,400.00
HRGC-HRGC-LRMS	~ 3 weeks	$240.00

MR. TELLIARD: The next speaker is going to talk about MAGIC. I always like that.

Jim de Haseth is with the University of Georgia. We heard about MAGIC four years ago when Dr. Browner talked about MAGIC as it related to particle beam, and today we are going to talk about HPLC/FT-IR MAGIC. Anytime we get MAGIC, it is fun.

DEVELOPMENT OF A MAGIC INTERFACE

FOR HPLC/FT-IR

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Atlanta, GA 30332

ABSTRACT

The interfacing of separation methods with selective detectors has been a long sought after goal. In some instances, such as gas chromatography (GC) interfaced with spectrometric methods such as mass spectrometry (MS) or Fourier transform infrared (FT-IR) spectrometry, considerable success has been achieved. Interfaces with liquid chromatography have been far less successful due to the difficulty in eliminating the mobile phase. In the infrared, liquid mobile phases must be eliminated as they are opaque at all wavelengths at even short pathlengths. The solutes are generally in such low concentration that long pathlengths must be used to record their spectra in the presence of the solvent. Nonetheless, the solvent opacity precludes this option. Solvent elimination has been possible for high volatility nonpolar mobile phases, yet the majority of liquid chromatography is accomplished with polar (reverse phase) solvents. An interface has been developed that can accommodate both normal and reverse phase solvent systems, as well as gradient elution systems. This interface is the Monodisperse Aerosol Generation Interface for Combining (MAGIC) liquid chromatography (LC) with Fourier transform infrared (FT-IR) spectrometry. This method provides a sensitive interface between HPLC and FT-IR spectrometry. Detection limits below 1 ng are possible, and the use of buffered solvent systems with the HPLC does not impair the performance of the interface.

INTRODUCTION

The increased identifying power that results from coupling separations techniques with selective detectors has been dramatic. The value of such procedures arises because the process of separation of a mixture into its components does not in itself identify the chemical or structural nature of the compounds present. Such vital information is only provided by a detector that is capable of responding in some unique manner to the chemical nature of the separated compounds.

Depending on the perspective of the researcher, the development of such analytical techniques, loosely known as "*hybridized techniques*", may be seen either as a means of improving the quality of analytical detectors for chromatography, or of simplifying clean-up procedures for sample introduction to the detector of choice. In the recent past, when many of the selective detectors available commercially were extremely expensive, the second approach was prevalent. The advent of powerful but inexpensive detectors for mass spectrometry (MS) and Fourier transform infrared (FT-IR) spectrometry, for example, has radically changed the situation.

GC VERSUS LC SEPARATIONS

The separation and identification of volatile components of materials is generally accomplished by interfacing gas chromatography (GC) with sophisticated and highly selective

physical analysis detectors. The most notable physical analysis techniques used for this purpose are mass spectrometry (MS) and more recently, Fourier transform infrared (FT-IR) spectrometry. Both of these techniques provide information about an analyte's molecular structure; mass spectrometry provides structural information based on molecular fragmentation patterns, whereas FT-IR spectrometry provides characteristic functional group and isomeric information. A key factor is that the two techniques provide information that is very complementary in nature. By interfacing MS or FT-IR spectrometry with GC, either individually (i.e. GC/MS or GC/FT-IR spectrometry), or in combination (GC/FT-IR/MS), a wealth of information for the identification of gas chromatographic eluites results. Appropriate combination of the data from both techniques can give rise to a substantial increase in the identifying power available for unknown compounds. For example, work with combined systems has shown that a much greater success rate is obtained when spectral data from FT-IR and MS are used jointly, than when either technique is used alone (1).

The types of molecules that may be successfully separated by gas chromatography, while extensive, is nevertheless severely limited by the dual problems of compound volatility and thermal lability. While many procedures, such as derivitization, may help to circumvent these problems, there is clearly a limit to the molecular weight and the polarity of molecules that may be separated by gas chromatography. The only practical alternatives currently available for separation of high molecular weight and high polarity molecules are liquid chromatography (LC) and supercritical fluid chromatography (SFC). While SFC clearly has great potential for a large class of compounds of intermediate molecular weight and low or intermediate polarity, effective separation procedures are not yet available using SFC for either very large molecules (e.g. > 2000 daltons) or very polar molecules. Many compounds of great biological and environmental importance are therefore not presently amenable to SFC separation. SFC has an additional problem resulting from the limited

sample mass that can be injected on-column. Consequently, while absolute detection limits may be in the picogram range, concentration detection limits may be inadequate for trace analysis.

Interfacing liquid chromatography with MS and FT-IR detectors is a much more demanding problem than that experienced with interfacing GC with these detectors. This results from the much greater difficulty involved with removing the LC mobile phase. With GC separations, the mobile phase, which is often helium, presents little difficulty for the detector. For example, in GC/MS analysis with packed columns an enrichment device, such as a jet separator, is used. With low-flow capillary columns, the pumping capacity of the mass spectrometer itself provides sufficient enrichment. By these means, the carrier gas is reduced to a level that does not influence the operation of the mass spectrometer. In GC/FT-IR spectrometry, no mobile phase elimination is necessary, as the carrier gases typically used are optically transparent in this region of the electromagnetic spectrum. On the other hand, liquid chromatographic mobile phases are neither so readily eliminated nor are they optically transparent in the infrared region. As a consequence, there are currently no commercially available or widely accepted methods for directly interfacing LC and FT-IR spectrometry.

Two basic research approaches to LC/FT-IR interfacing have been followed to date: (1) effluent flow-through systems and (2) solvent elimination procedures.

SOLVENT CONSIDERATIONS FOR DIRECT LC/FT-IR MEASUREMENTS

If a liquid chromatographic eluite is sufficiently concentrated, its infrared spectrum can still be measured even in the presence of LC solvent. No solvent is totally infrared transparent, however, even in the regions where there is no apparent infrared absorption band. The object of the LC/FT-IR spectrometric experiment is therefore to record the spectrum of the eluite and ignore

or eliminate the spectrum of the solvent. In infrared spectrometry, as well as in many other absorption spectrometries, the spectrum of a solute is recorded by ratioing a solution spectrum against the spectrum of the pure solvent. This operation is valid only when the absorbance of the solute is relatively high and the absorbance of the solvent low. If the solvent absorbance becomes sufficiently great, the spectrum is opaque in the region of the absorption band and no solute absorbance can be measured. If the concentration of the solute is too low, the absorbance due to the solute will be in the noise level of the measurement, and again a spectrum cannot be recorded. In normal practice, spectrometric absorbance can be controlled by pathlength. In an ideal situation the solvent should absorb no more than approximately 37% of the infrared radiation. In this case an optimum signal-to-noise ratio can be attained (2).

Unfortunately typical liquid chromatographic solvents do not absorb uniformly across the infrared region, and it is impossible to design an ideal cell for a complex absorber. A compromise must thus be made, and generally pathlengths are chosen so that only a few bands are opaque and most of the spectrum is transparent. The relatively transparent regions of the solvent spectrum form windows in which the signal-to-noise ratio (SNR) is sufficiently high that a spectrum of the solute can be recorded. The pathlengths vary depending upon the solvent (3). For example, a weak infrared absorber such as carbon tetrachloride can be used with pathlengths of up to 1 mm. Very strong absorbers, such as water, permit only very short pathlengths, up to about 0.1 mm. Other solvents may fall into intermediate regions.

In a dynamic system, such as in LC/FT-IR spectrometry, the interface cell should be designed for the maximum SNR of the eluite. At a first approximation this is when the entire analyte band is trapped momentarily in the interface cell. In this situation, the maximum possible analyte mass is measured spectrometrically, and so highest sensitivity will be achieved. The practical problem this approach gives rise to is that of ensuring the chromatographic resolution is

not compromised. If the volume of the interface cell is too great, it is possible for two chromatographically resolved eluites to be in the cell at same time. To avoid this problem, the volume of the interface cell must be the full width at half height volume of the eluite peak (4). An appropriate diameter for an LC/FT-IR cell is on the order of about 4 mm, based on optical and chromatographic flow considerations. In a conventional HPLC experiment (column i.d. of 4.6 mm) a typical narrow peak is on the order of 250 μL. An ideal cell of 4 mm diameter (12.5 mm^2 area) would then have a pathlength of 20 mm. This is more than an order of magnitude longer than the maximum cell pathlength for the weakest infrared absorbing solvent. Cells of larger diameter provide an ideal shorter pathlength at the cost of sensitivity; smaller diameter cells are more sensitive because the ideal pathlength is longer, but the discrepancy between ideality and practice is greater.

LC/FT-IR spectrometry, therefore, presents the researcher with an interesting dichotomy: cell pathlength must be long for maximum sensitivity, but it must be short to provide adequate solvent windows to record solute spectra. As long as the chromatographic eluite is sufficiently concentrated, then short pathlength cells can be employed successfully. Where solute concentrations are extremely low, cell pathlengths are in practice too short to record spectra at useful signal-to-noise ratios.

FLOW-THROUGH LC/FT-IR SYSTEMS

The earliest LC/FT-IR spectrometry systems used flow-through cells (5-8). These prototype systems suffered from severe problems, and were not really practical. Two related areas where flow-through cells have proved to be of value, though, are those of gel-permeation chromatography (GPC) and size-exclusion chromatography (SEC). In these chromatographic techniques, where

components are separated on the basis of molecular size rather than by polarity or adsorption characteristics, chlorinated solvents can be used, that makes GPC/FT-IR spectrometry into a powerful technique. Chlorinated solvents, for the most part, do not absorb strongly across the infrared spectrum except in the C-Cl stretch region and possibly in the C-H stretch region. These regions are opaque even at short pathlengths. Vidrine (3) compiled a series of spectra of common LC solvents at various pathlengths and showed that many of the solvents that are useful for GPC can be used with reasonable pathlengths. Vidrine showed GPC/FT-IR spectra of the separation of poly(butyl acrylate) and polystyrene on a 100 Å μ-Styragel column using THF (tetrahydrofuran) as the solvent. Although THF is far from an ideal solvent because it is not transparent, some spectral information was still recorded in the flow-through system. The regions 3000 to 2800 cm^{-1} and 1300 to 800 cm^{-1} are obliterated due to THF absorptions. Had a more polar solvent been used, however, much less spectral information would have been recovered.

Flow-through systems are not restricted solely to GPC, and this technology has been applied to both normal-phase (NP-) and reverse-phase (RP-) HPLC. Most of the solvents used in NP-HPLC are less polar, and hence absorb IR radiation less strongly than THF, but overall performance is often not as good as in GPC/FT-IR spectrometry. In GPC, chromatographic sample loadings can be quite high, on the order of mg, but typical HPLC 4.6 mm i.d. silica gel columns have capacities of only 2 to 50 μg. The concentration of most NP-HPLC eluites is on the order of 200 ppm. These low sample loadings therefore require long cell pathlengths in order to record spectra with good SNR, but this contradicts the requirement for short pathlengths dictated by the solvent system.

A series of fine studies involving flow cells with NP-HPLC has been completed under the direction of Taylor (9-16). In the earliest of these studies Johnson and Taylor (9) compared the use of semi-preparative, analytical and microbore columns for NP-HPLC/FT-IR spectrometry. In order

to improve the transmission of the cell and reduce the number of opaque regions, Freon-113 was used as the mobile phase. Even so, it was necessary to use a 0.2 mm pathlength cell to minimize the number of opaque regions. These workers showed that microbore HPLC (μHPLC) columns were practical for flow-through cell FT-IR spectrometry. This was a consequence of the smaller volumes of the microbore eluite peaks compared to the analytical or semi-preparative peaks.

In an analytical column the typical eluite peak volume is at least 250 μL, and a 0.2 mm x 4 mm diameter cell has a volume of only 2.5 μL. This means that no more than 1% of the eluite peak will be in the cell at any given time. As the volume of the eluite peak decreases, a higher percentage of the eluite will be present in the cell; but this is offset by the reduced sample loading. Nevertheless, the tradeoff is in favor of the microbore column, hence, high SNR spectra can be measured in the transparent regions of the solvent. In later studies, Brown and Taylor studied material of intermediate polarity in coal-derived process solvents, using analytical NP-HPLC columns (10) and also compared analytical and microbore columns (11). Both studies used deuterated chloroform as the mobile phase. $CDCl_3$ is transparent in the C-H stretch region of the infrared spectrum, and hence has more useful windows than chloroform.

Taylor and coworkers have investigated many other aspects of NP-HPLC/FT-IR spectrometry (12-15). Coal derived products have been investigated: on a polar amino cyano (PAC) analytical column using a 98:2 $CDCl_3$:CH_3CN mobile phase (12), and, on an amino (NH_2) bonded microbore column using a 70:30 $CDCl_3$:CCl_4 + 0.02% triethylamine mobile phase. Amateis and Taylor (14) investigated the optimum experimental conditions for NP-HPLC/FT-IR spectrometry, including spectrometric signal-averaging and flow cell pathlength. Column overload and system detection limits were also investigated. Brown, Amateis and Taylor (15) determined detection limits for phenols and amines in NP-μHPLC/FT-IR spectrometric systems. These detection limits ranged from 300 ng to 12 μg, depending upon the eluite. These figures reflect injected quantities, not the quantities in the cell. One interesting development was a cylindrical bore cell for flow cell

μHPLC/FT-IR spectrometry. This has been named a zero dead volume (ZDV) cell (16). This cell provided a detection limit of less than 50 ng for 2,6-ditert-butylphenol measured at the O-H stretching frequency.

This cell, which is cylindrical, was designed to give a wide dynamic range of solvent:solute ratios. Unfortunately, the absorbance across the spectrum is then, by necessity, nonlinear, although some bands will exhibit linear behavior. Other workers have investigated flow cells for LC/FT-IR spectrometry involving normal phase systems (17-19). An unusual set of studies has involved interfacing a high speed planet coil countercurrent chromatograph (CCC) to an FT-IR spectrometer (19,20). The CCC is a liquid-liquid chromatograph that has no stationary support, and hence is able to operate at very high sample loadings. The eluites are then present in the system at high solute-to-solvent ratios, making flow cell LC/FT-IR spectrometry feasible. Regrettably, the chromatographic efficiency of this system is poor.

A few studies have involved reverse phase systems (21-23). These systems have fewer spectral windows than the normal phase systems and analysis is severely restricted. Even when deuterated mobile phases are used, the number of useful spectral windows is small. Although much has been accomplished with flow-through LC/FT-IR spectrometric systems, these designs are hardly applicable as a universal approach. Reverse phase systems are almost totally excluded from this technology, and normal phase HPLC systems operate under the severe handicaps of poor solvent transmission and very low eluite concentrations.

SOLVENT-ELIMINATION SYSTEMS

As stated above, the problem with flow-through systems is that the spectrum is always obscured by absorption bands of the mobile phase. To avoid this problem the mobile phase, or

solvent, must be removed to leave the eluite for spectrometric study. The first attempts at eliminating the solvent were applied to NP-HPLC systems and involved a two-step process (24,25). The first step was to concentrate the eluite by about a factor of ten by evaporating some of the solvent in a heated tube. The second step was to deposit the concentrated eluite onto a powdered potassium chloride (KCl) substrate where the remainder of the solvent was evaporated. Spectra were recorded by diffuse reflectance (DR) infrared spectrometry. DR spectrometry is well-suited to the measurement of small quantities of a sample; but this two-step process is time-consuming and necessitates long delays between elution and recording of the spectrum. This system has also been adapted to microbore columns (26).

One major disadvantage of the DR solvent elimination technique is that polar (reverse phase) solvents will dissolve the KCl DR substrate. A remedy for this shortcoming is to extract the eluite into a nonpolar solvent for deposition onto the KCl powder (27). This has been achieved in an extraction coil by mixing methylene chloride with reverse phase HPLC effluents, then physically separating the polar and nonpolar phases (aqueous and CH_2Cl_2) in a separation tee. The nonpolar phase is passed to a concentrator for deposition on a DR KCl substrate, as in the normal phase HPLC system. This has the disadvantage that an additional, low extraction efficiency, step is added to the process. An alternate method is to spray the HPLC effluent onto an insoluble substrate, such as industrial-grade diamond powder, using an ultrasonic nebulizer (28).

In the case of an aqueous mobile phase, the water can be removed by reaction with 2,2'-dimethoxypropane (DMP), that produces methanol and acetone when the reaction is acid catalyzed (29). The methanol, acetone, and excess DMP can be deposited on a DR substrate along with the eluite. All components, except the eluite, can then be evaporated readily. This is an elegant system, but it is restricted to simple mobile phases, such as H_2O:CH_3OH and H_2O:CH_3CN. If nonvolatile

ionic modifiers are added to the mobile phase, these modifiers can have concentrations exceeding that of the eluite, and hence dominate the spectra.

A different solvent elimination method is the buffer memory technique developed by Jinno (30-33). In this technique the effluent from a normal phase microbore HPLC column is deposited onto a slowly moving KBr plate. The solvent is removed by evaporation, and spectra of the eluites are recorded by transmission spectrometry. This technique, like the diffuse reflectance technique, is essentially an off-line method that cannot be used easily with polar mobile phases.

Other methods have been devised to remove the solvent from HPLC systems and deposit the solute for infrared spectral interrogation. Gagel and Biemann (34,35) have developed a continuous recording reflection-absorption interface. The interface involves taking the effluent stream from a chromatograph and mixing it with nitrogen gas. The nitrogen gas disperses the liquid effluent and sprays it onto a reflective surface. The nitrogen then evaporates the solvent and leaves the solute as a residue on the surface. The solutes are deposited on a spiral track on a reflective surface. Spectra of the solutes are obtained as the track is moved into an infrared beam and the spectra are obtained as reflection-absorption spectra. This system is capable of eliminating the mobile phase when it contains up to 55% water (with methanol), but in gradient elution systems the temperature of the nebulizing gas had to be computer controlled to evaporate the solvent as the mobile phase composition changed.

Griffiths has developed a similar interface, except that the spectra are collected as transmission spectra with an infrared microscope (36). The nebulizer for this apparatus is similar to the one reported by Gagel and Biemann, but the deposition is done onto an infrared transparent substrate, such as zinc selenide (ZnSe). The advantage to this system is that Griffiths realized that the ultimate detection limits will be achieved by concentrating the solute into a minimum cross-sectional area, then focussing the infrared beam onto that area. The general system has been

described (37,38), but these references reported only normal phase systems. Griffiths has shown one spectrum of methyl violet from 100% water using his HPLC nebulizer when the system is evacuated as opposed to the normal ambient pressure system (39).

All of the above solvent-elimination methods suffer from the need for complex steps to effect solvent removal or reverse phase systems cannot be accommodated on a routine basis. These solvent elimination steps are sometimes time-consuming and are not always very efficient. As with the flow-through systems, these solvent-elimination techniques work best with normal phase systems.

MAGIC-LC/FT-IR INTERFACE

The Monodisperse Aerosol Generation Interface for Combining (MAGIC) Liquid Chromatography (LC) with Fourier Transform Infrared (FT-IR) spectrometry provides an alternate interface that solves many of the problems exhibited by the above-mentioned interfaces. The MAGIC interface, in its generic form, is a transport based device that takes LC column effluent, removes the solvent with high efficiency, and passes the desolvated solute to a detector. As this device is a high efficiency desolvating interface, it has the property most desirable for an LC/FT-IR spectrometric interface.

MAGIC-LC has three primary components: (1) a monodisperse aerosol generator (MAG) (2) an atmospheric, ambient temperature, solvent evaporation chamber and (3) a momentum-based particle enrichment separator. A schematic of the MAGIC-LC/FT-IR spectrometric interface is shown in Figure 1. The MAGIC-LC device has already been described in some detail in the literature, in its application to mass spectrometry (40-42). Basically, the MAG is a device that converts the effluent stream into highly uniform droplets. This is accomplished by pumping the

effluent through a fine bore fused silica capillary tube, typically 25 μm in internal diameter. The jet formed at the end of the fused silica tube is unstable and forms an aerosol of uniform droplets, as originally modelled mathematically by Rayleigh (43). The droplets are dispersed by a gas sprayed perpendicular to the jet, to prevent the droplets colliding and forming a polydisperse aerosol. A detailed schematic of the MAG has been given elsewhere (40).

The dispersed droplets flow towards a nozzle at the opposite end of the desolvation chamber to the MAG. The pressure in the desolvation chamber is near atmospheric and the pressure is considerably reduced on the other side of the nozzle. The fact that the droplets are of uniform size, and that they are rather small (on the order of 50 μm in diameter), the rate of evaporation of the solvent is high. As the volume of the droplets decreases the relative surface area increases, and hence the evaporation of the droplet is rapid. The desolvation chamber serves the purpose of evaporating the solvent and passing the remaining solute, in droplet form, into the momentum-based separator. Both solute droplets and solvent vapor pass into the separator, but only the solute droplets have sufficient momentum to pass through the separator to a collection plate where the solute droplets are deposited. The momentum-based separator has been discussed in detail previously (42).

The collection plate is translated during deposition so that each eluite is deposited in a unique area on the plate. In this way each eluite is separated spatially for infrared analysis. Once the HPLC separation is complete, the deposition plate is removed and placed in an infrared spectrometer. Typically a beam condenser is used to focus the beam onto the eluite deposition. A spectrum is collected by transmission spectrometry as the collection plate is an infrared transparent window, such as KBr or KCl. An alternate approach is to use an infrared microscope instead of a beam condenser. An infrared microscope will focus a beam to a much smaller area than a beam condenser, and as long as an eluite deposition can be constrained to a small area, for example

100 μm in diameter, the microscope will give higher sensitivity than the beam condenser. The size of the deposition is dependent upon the quantity of component injected and the configuration of the MAGIC device. Depositions of approximately 100 μm have been achieved.

The MAGIC device as used for LC/FT-IR spectrometry differs somewhat from the device used for LC/MS. These differences are to accommodate changes in the aerosol to produce good depositions for FT-IR spectrometry, as opposed to producing an easily vaporized solute stream for mass spectrometry. The aerosol considerations for different spectrometric techniques are described in detail elsewhere (44).

Spectra have been collected successfully using the MAGIC-LC/FT-IR spectrometric device for a variety of solvent systems and at varying concentrations of analytes (45,46). Figure 2 illustrates a series of spectra of erythrosin B from different mobile phase compositions. Figure 2*a* is the erythrosin B from 100% methanol, in 2*b* the mobile phase is 80:20 methanol:water, 2*c* it is 60:40 methanol:water, and Figure 2*d* shows the spectrum when the mobile phase is 100% water. All four spectra are good representations of erythrosin B and match the reference spectrum closely. Figures 2*a-c* show some methanol trapped in the eluite depositions. This is residual methanol after the solvent elimination process. In the original solutions of erythrosin B the solute concentration was only a few parts per thousand, and after desolvation the solvent concentration is only a few percent of the solute concentration. Clearly the desolvation is not 100% efficient for some solvents, yet it is close to that efficiency. It is interesting to note that the spectra from 100% water mobile phase show no trapped solvent. The reasons why some solvents are trapped are currently being investigated in this laboratory, as well as methods to alleviate the problem. One immediate solution is to remove the spectrum of the trapped solvent by spectral subtraction.

MAGIC-LC/FT-IR spectrometry can also work well with pure normal phase separations. It can be argued that 100% methanol is not a normal phase solvent. Figure 3 shows the spectrum

of anthracene as deposited from 100% hexane. There is no hexane residue apparent in the spectrum. Figure 4 is a spectrum of caffeine from 100% water, a reverse phase solvent, and again there is no residual solvent apparent.

All the spectra shown thus far have been of rather large samples, on the order of a few tens of micrograms per injection. This is typically greater than standard injections for HPLC separations, and detection limits in the tens of nanograms or lower are desirable. The limiting factor for the detection of eluites by the MAGIC-LC/FT-IR spectrometric device is not in the solvent elimination step, but in the optics for the spectrometry. Figure 5 illustrates a spectrum of 100 ng of methyl red (injected) and analyzed using an infrared microscope. The spectrum is clearly identifiable, despite the interference of atmospheric water vapor. The baseline is skewed due to dispersion effects of the deposition; that is, the deposition is too thick. This spectrum was from an earlier version of the MAGIC-LC/FT-IR device that was rather inefficient. Only five to ten percent of the injected eluite was recovered at the deposition plate. Current models of the MAGIC-LC/FT-IR device appear to have efficiencies of 30%, and further improvements are anticipated. With microscopic optics instead of beam condensing optics, detection limits of less than one nanogram (injected) can be projected.

The interface functions well in the presence of buffered solvents (47). Even with buffer concentrations as high as 1F, spectra of the chromatographic eluites can be collected. Figure 6 shows the spectrum of caffeine deposited when the solvent contained 1F KHP buffer. Obviously the spectrum of the caffeine contains extra bands, and these are attributable to the buffer. As the buffer is involatile, it is deposited continuously. A spectrum of the buffer without the eluite is measured and subtracted from the spectrum of the mixture. In the upper half of Figure 7, a spectrum of the caffeine minus the KHP buffer is shown. A reference spectrum of caffeine is

shown in the lower half of the figure. The spectral differences are due to the protonation of the caffeine.

The only present shortcoming of the MAGIC-LC/FT-IR spectrometric device is that it is currently an "off-line" technique. Largely the mechanics of making it an "on-line" technique are only engineering changes, and systems previously devised for LC/FT-IR interfaces could be implemented (for example, those given in references 34-39). Clearly, MAGIC-LC/FT-IR spectrometry is a method that holds great promise for the interfacing of HPLC with FT-IR spectrometry. This is the first device that has been used successfully for both normal and reverse phase separations, and also the first to work with buffered reverse phase systems (47). Both KH_2PO_4 (potassium dihydrogen phosphate) and KHP (potassium hydrogen phthalate) buffers were used successfully. Effluent flow rates of up to 1 mL/m can be accommodated by the interface. One of the most beneficial aspects of the MAGIC-LC/FT-IR device is that the solvent elimination is done at ambient temperature; no heating of the effluent stream or of the desolvating gas is necessary. Not only can changes in the mobile phase composition be handled without changing the desolvation parameters, thermally labile components can be analyzed with no concern for thermal degradation.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

1. Schematic diagram of the MAGIC-LC/FT-IR spectrometric interface showing the three major components of the MAGIC device and the placement of the deposition plate for collection of the eluites from an HPLC separation.

2. MAGIC-LC/FT-IR spectra of 50 μg injections of erythrosin B using various different mobile phase compositions: (a) 100% methanol, (b) 80:20 methanol:water, (c) 60:40 methanol:water, and (d) 100% water. (Reproduced from Ref. (46).)

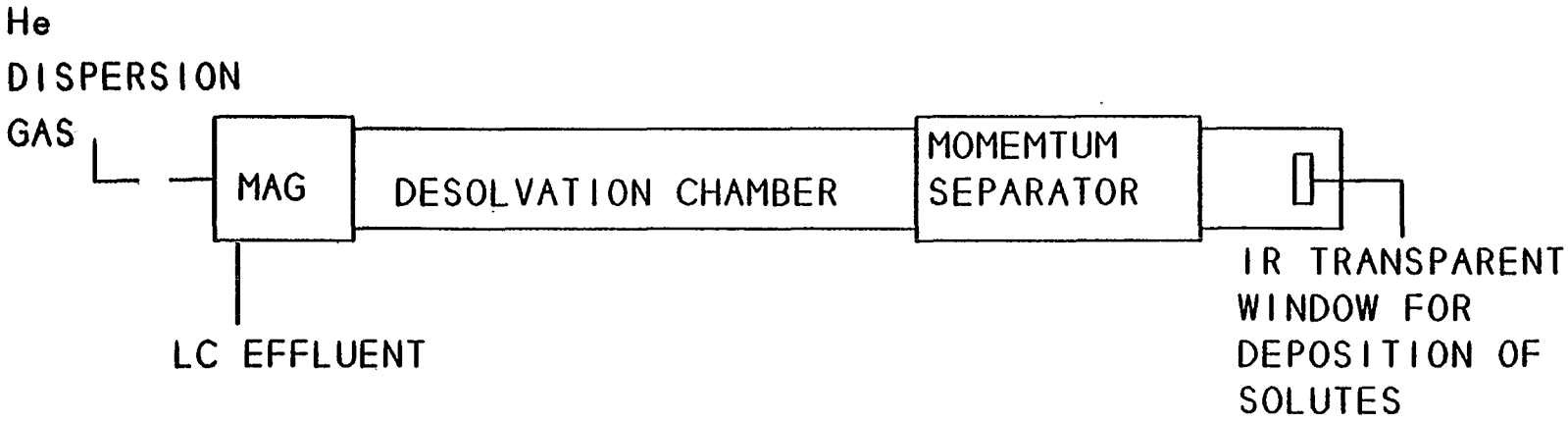
3. Spectrum of deposited anthracene using 100% hexane as the mobile phase.

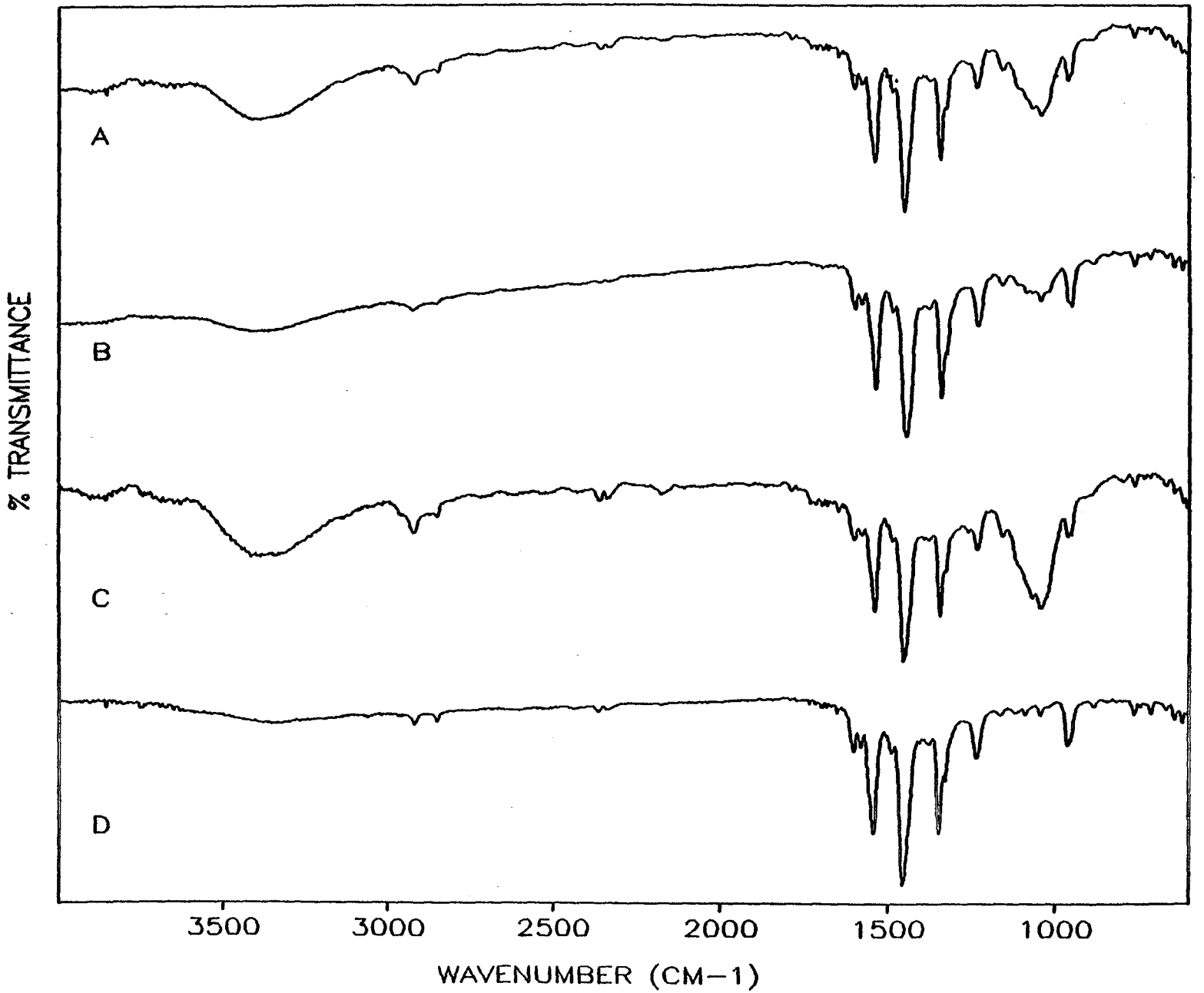
4. Caffeine as deposited from the MAGIC-LC/FT-IR device, when 100% water was used as the mobile phase.

5. Spectrum of 100 ng of methyl red (injected) from a 100% methanol mobile phase. (Reproduced from Ref. (45).)

6. Spectrum of caffeine and 1F KHP buffer. (Reproduced from Ref. (47).)

7. Spectrum of caffeine (upper) after spectral subtraction of the KHP buffer spectrum. A reference spectrum of caffeine is shown below. (Reproduced from Ref. (47).)


He
DISPERSION
GAS
MAG
DESOLVATION CHAMBER
MOMEMTUM
SEPARATOR
IR TRANSPARENT
WINDOW FOR
DEPOSITION OF
SOLUTES
LC EFFLUENT


% TRANSMITTANCE
A
B
C
D
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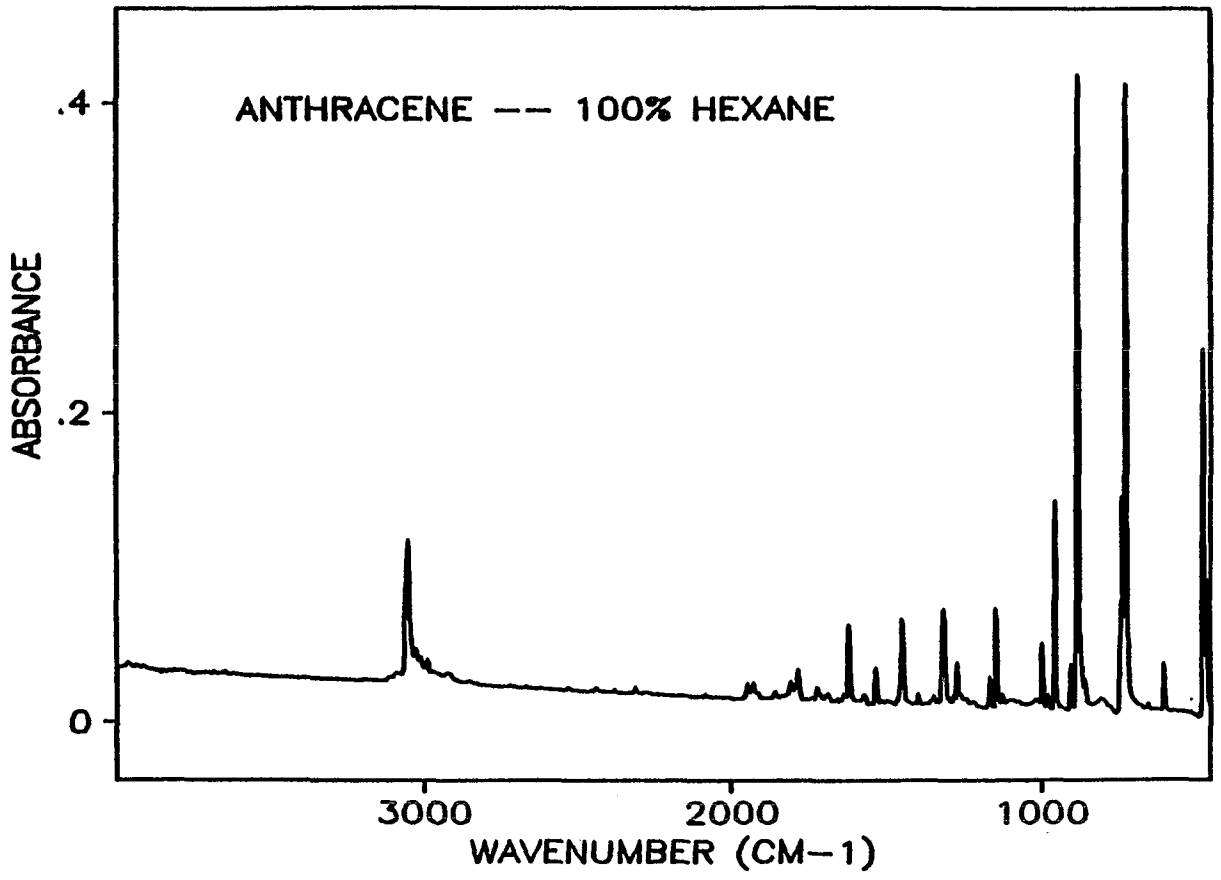
3000
2500
2000
1500
1000
WAVENUMBER (CM−1)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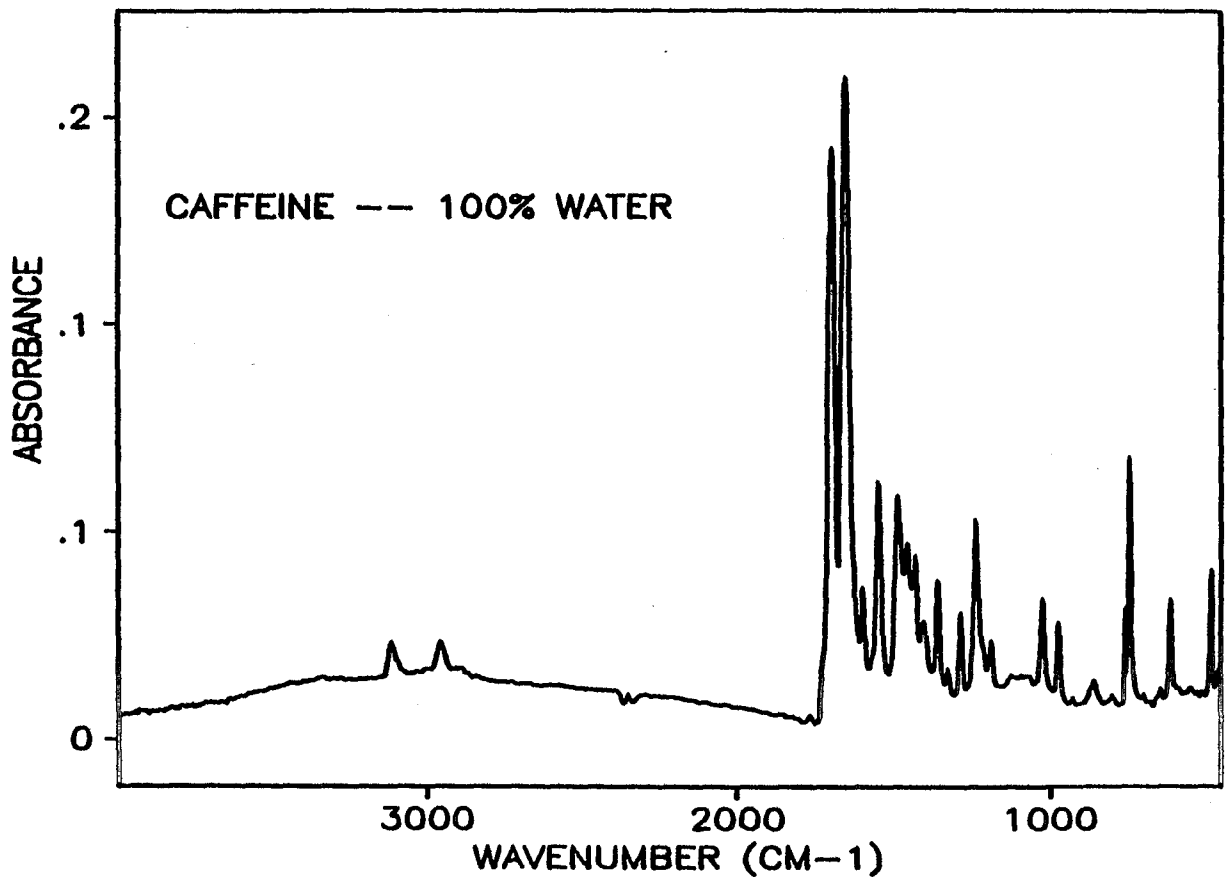
ABSORBANCE
.4
.2
0
3000
2000
1000
WAVENUMBER (CM-1)


CAFFEINE -- 100% WATER
ABSORBANCE
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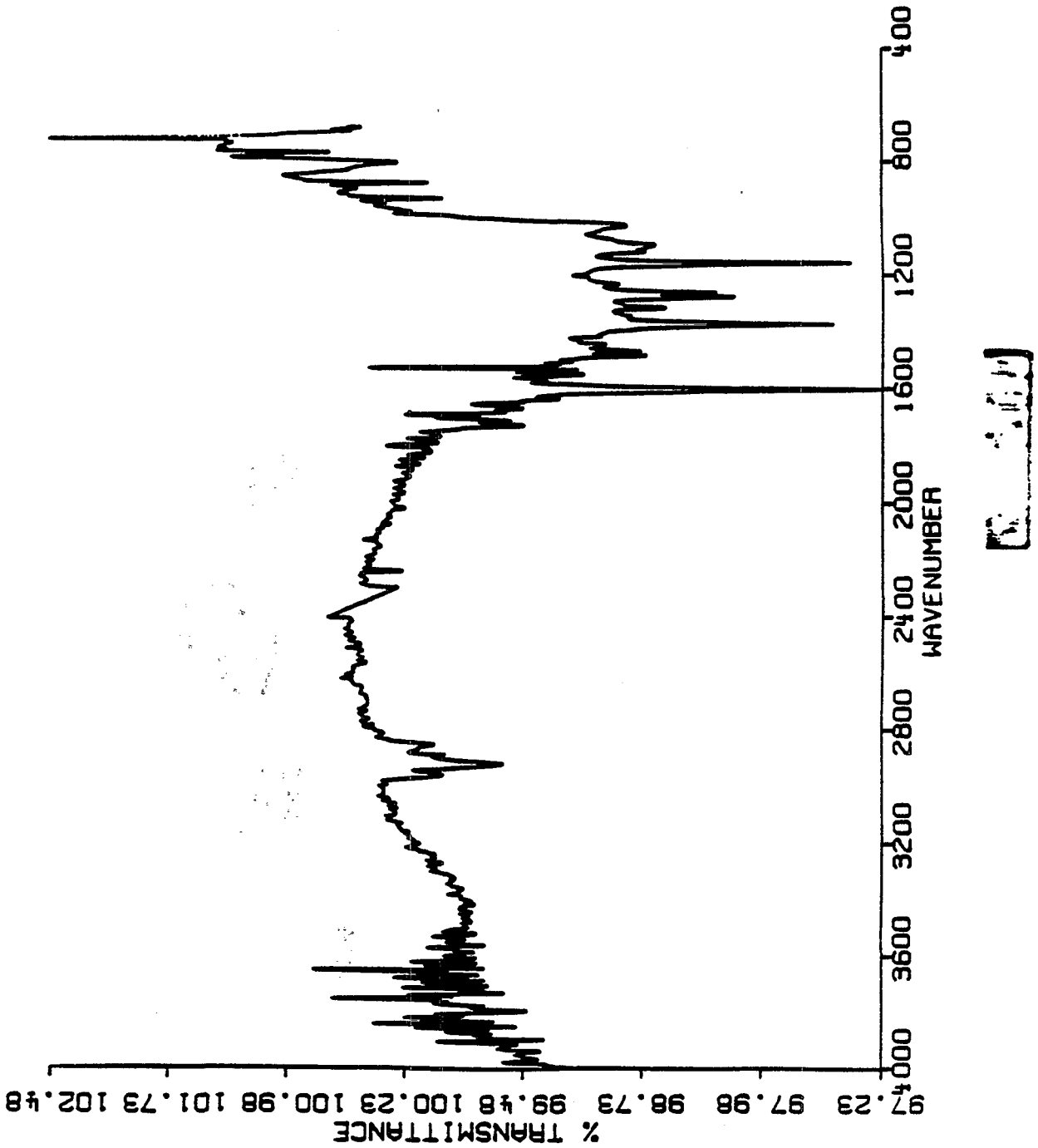
.1
.1
0
3000
2000
1000
WAVENUMBER (CM-1)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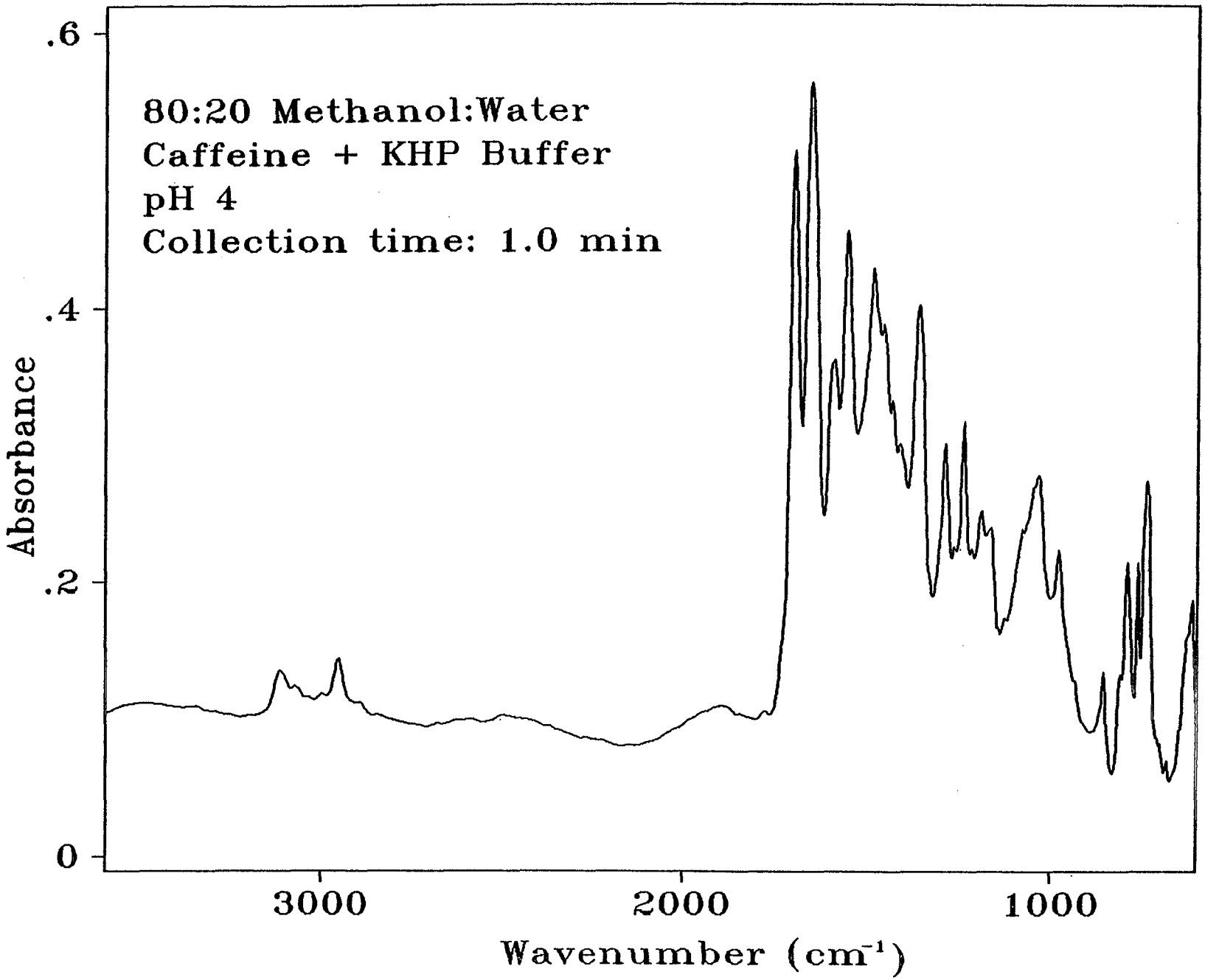
WAVENUMBER


80:20 Methanol:Water
Caffeine + KHP Buffer
pH 4
Collection time: 1.0 min
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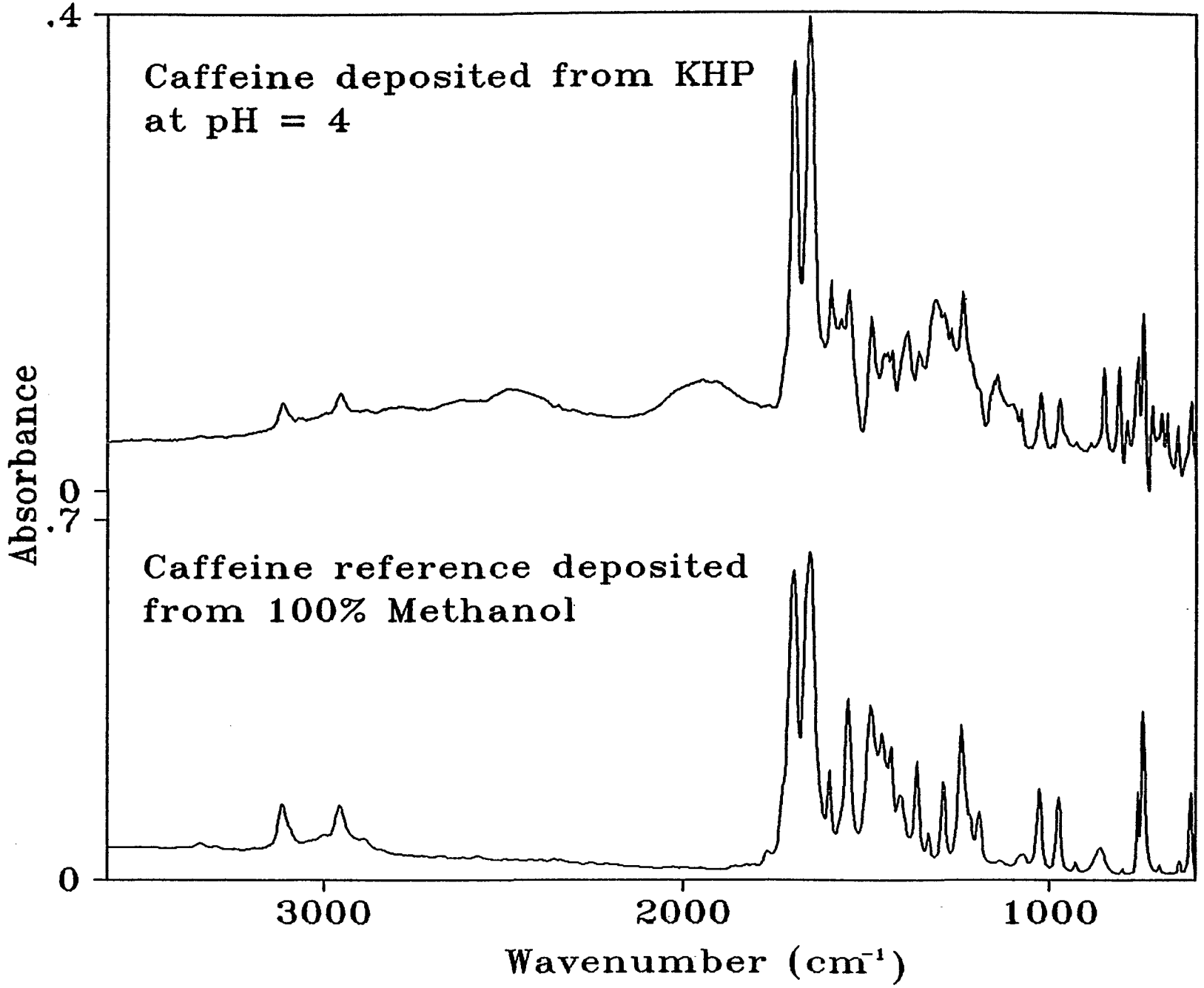
.4
.2
0
Absorbance
3000
2000
1000
Wavenumber (cm⁻¹)


.4
Caffeine deposited from KHP
at pH = 4
Absorbance
0
Caffeine reference deposited
from 100% Methanol
0
3000
2000
1000
Wavenumber (cm⁻¹)

Slide 2

LC/FT-IR Spectrometry

The mobile phase is the problem

In HPLC separations the compounds can have concentrations as low as 100 ppm

Slide 3

Dynamic Range

FT-IR spectrometer sensitivity is limited

by the dynamic range of the ADC

Slide 4

Two Basic FT-IR Approaches

1. Use flow-through cells
(keep the solvent)

2. Eliminate the solvent

Slide 5

Aerosol Beam Separator — Needed Properties —

- High Solute Transport Efficiency
- Effective Vapor Removal
- Minimal Peak Broadening
- No Memory Effects
- No Adjustments

Slide 10

MAGIC

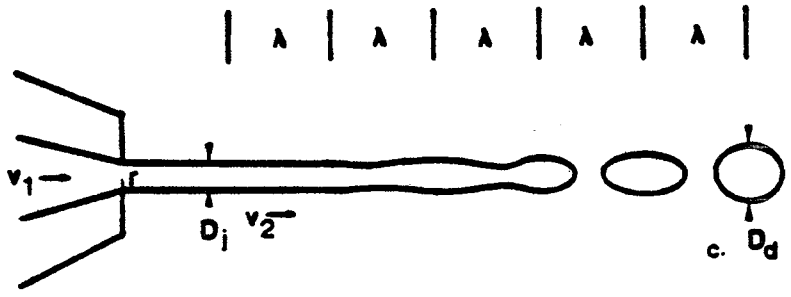
Monodisperse Aerosol Generation

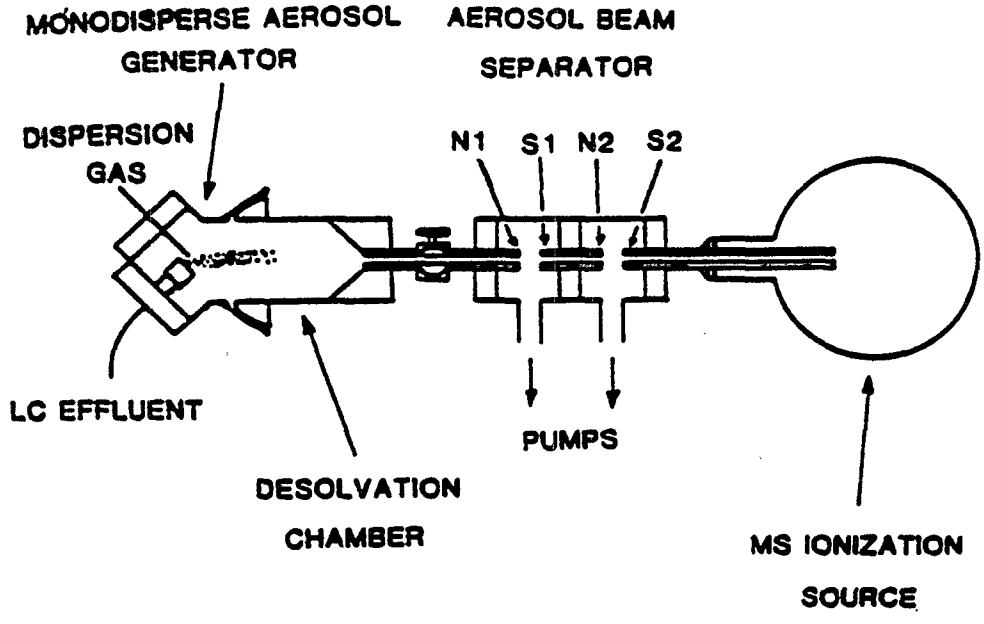
Interface Combining...

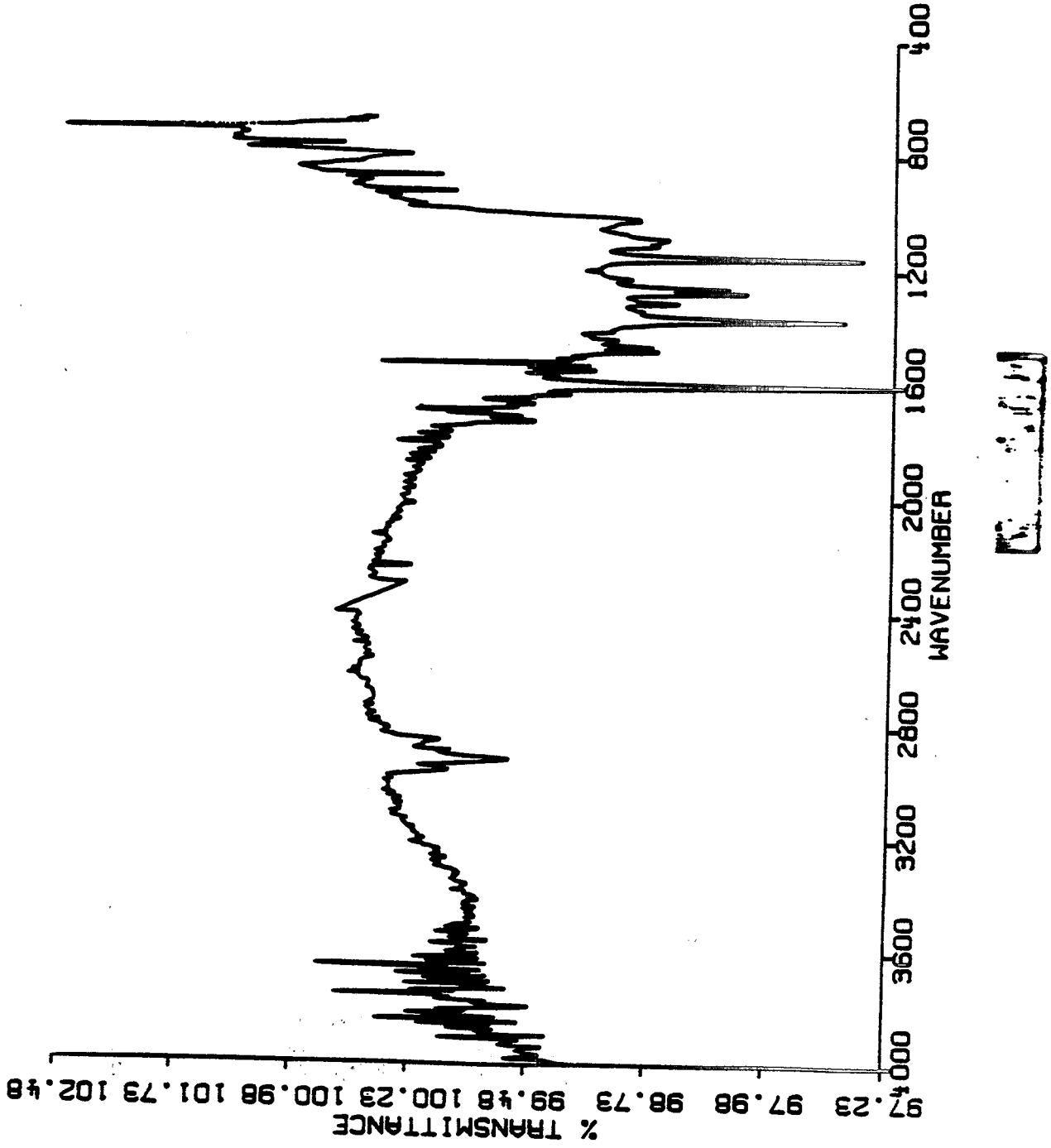
Slide 22

MAGIC-LC/FT-IR SPECTROMETRY CHARACTERISTICS

- Elimination of all the solvent
- Normal phase and reverse phase operation
- Mobile phase can be 100% aqueous
- LC flow rates to 1 mL/min
- No heating of the effluent


A
A
A
A
A
v_1
D_j
v_2
c.
D_d


MONODISPERSE AEROSOL GENERATOR
AEROSOL BEAM SEPARATOR
DISPERSION GAS
N1
S1
N2
S2
LC EFFLUENT
DESOLVATION CHAMBER
PUMPS
MS IONIZATION SOURCE


% TRANSMITTANCE
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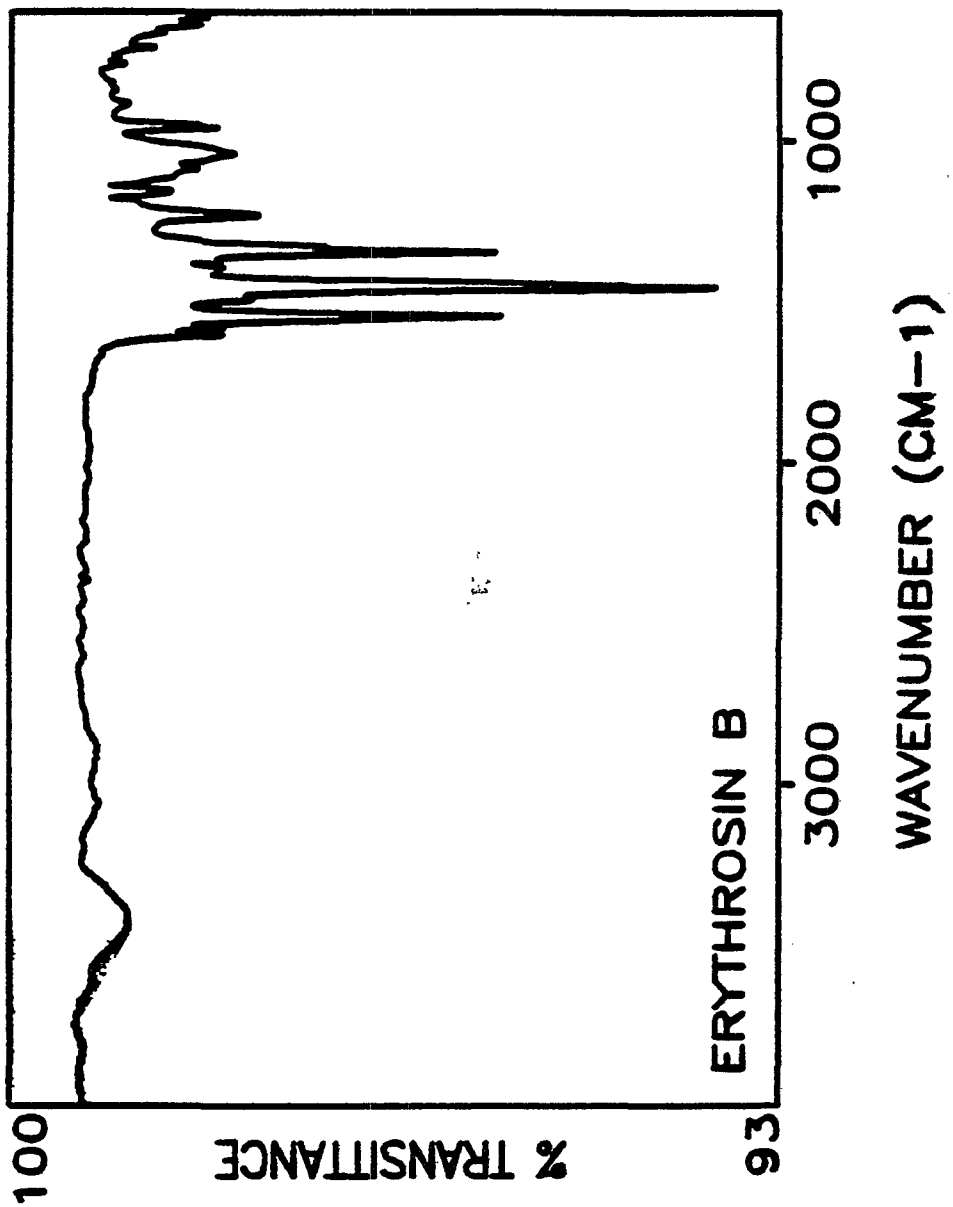
4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBER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% TRANSITTANCE
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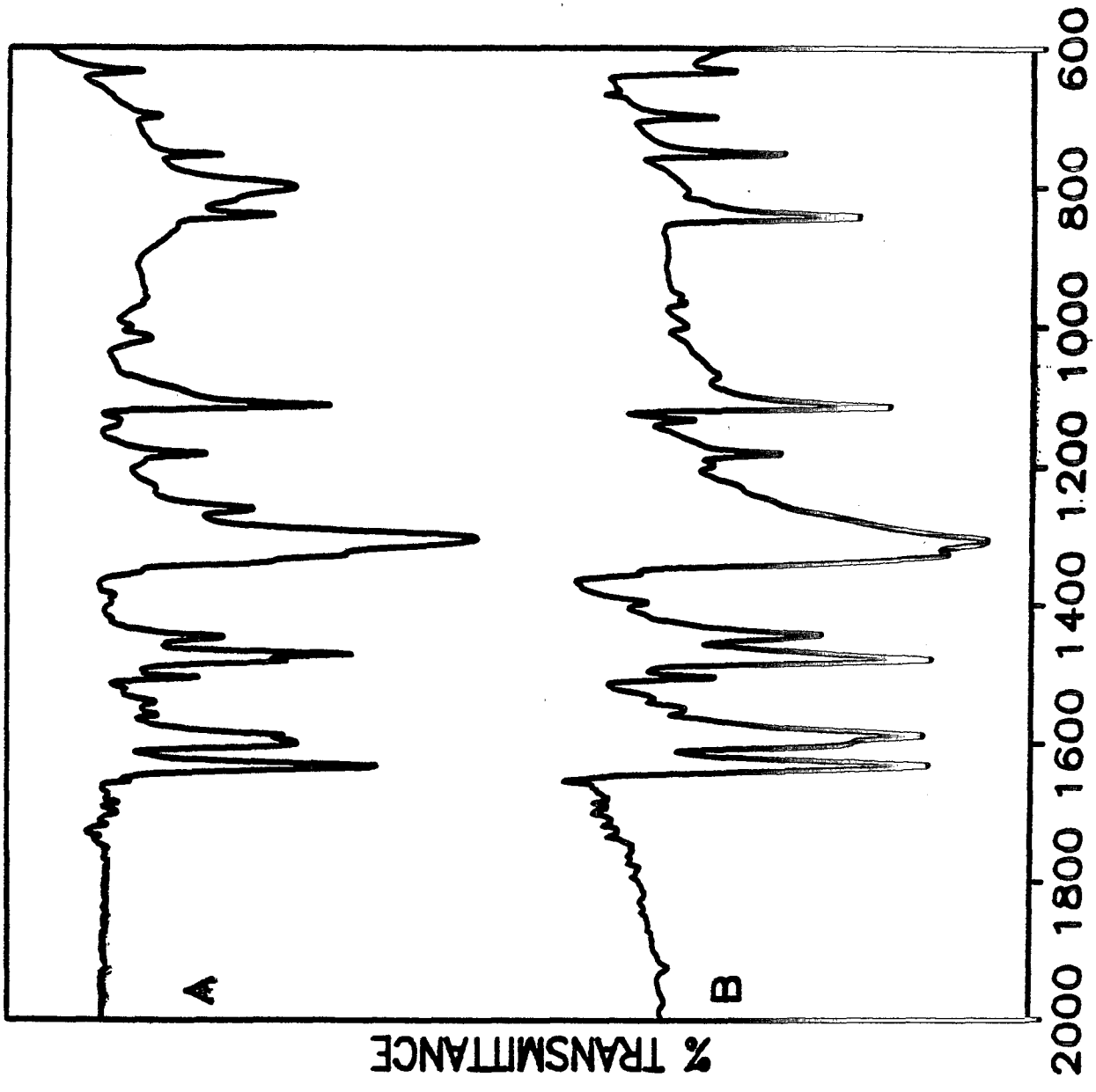
ERYTHROSIN B
3000
2000
1000
WAVENUMBER (CM-1)


% TRANSMITTANCE
A
B
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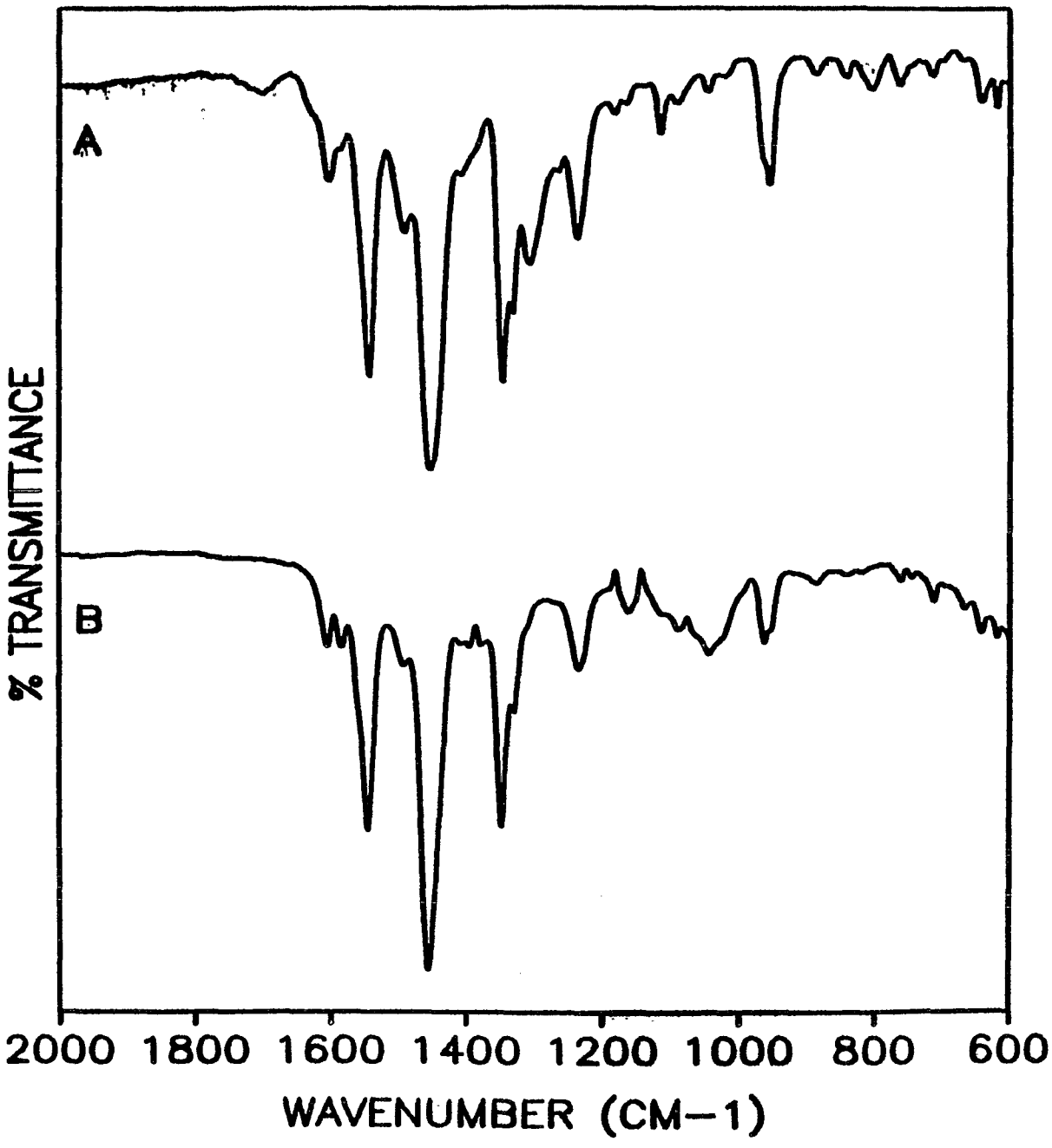
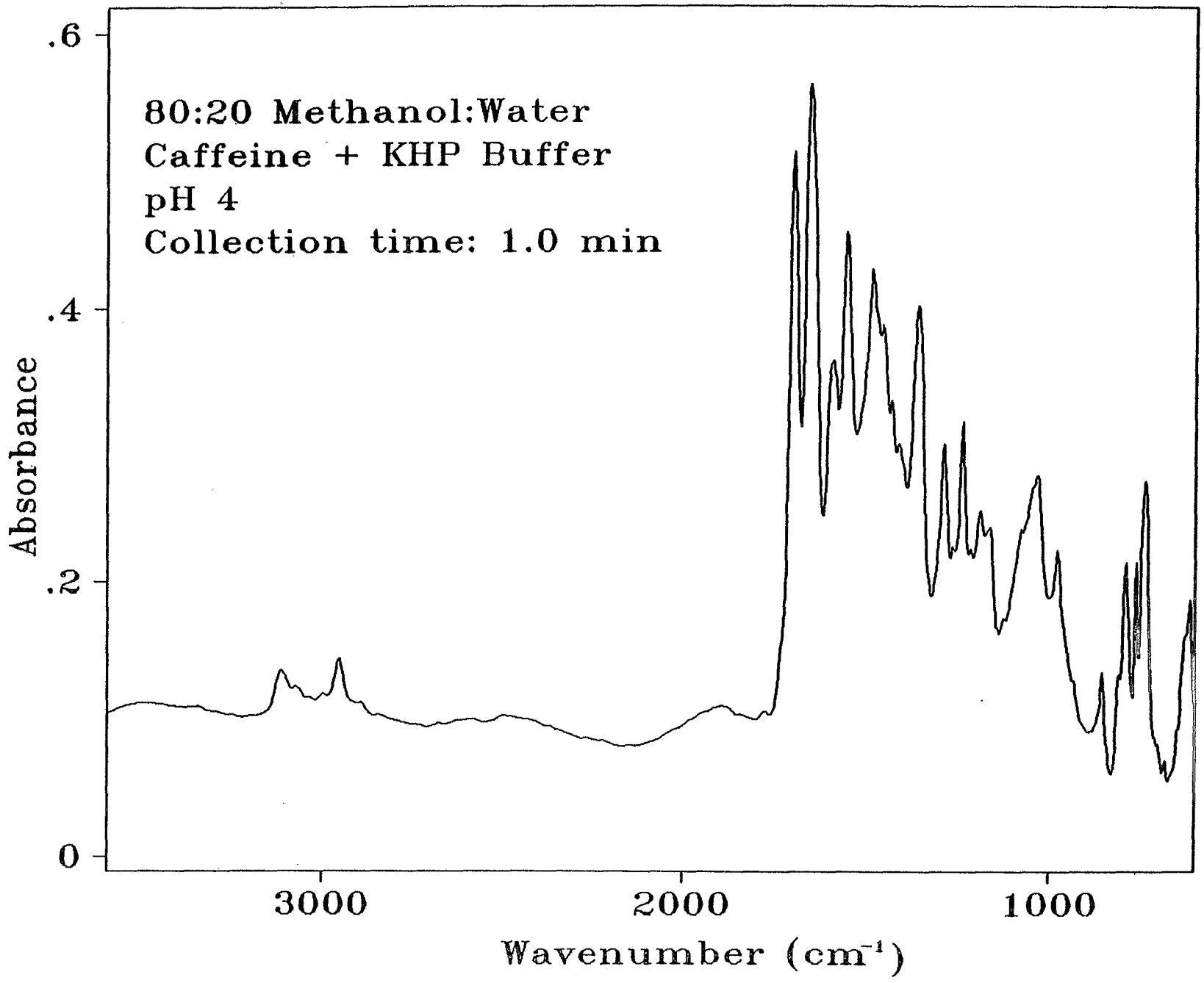
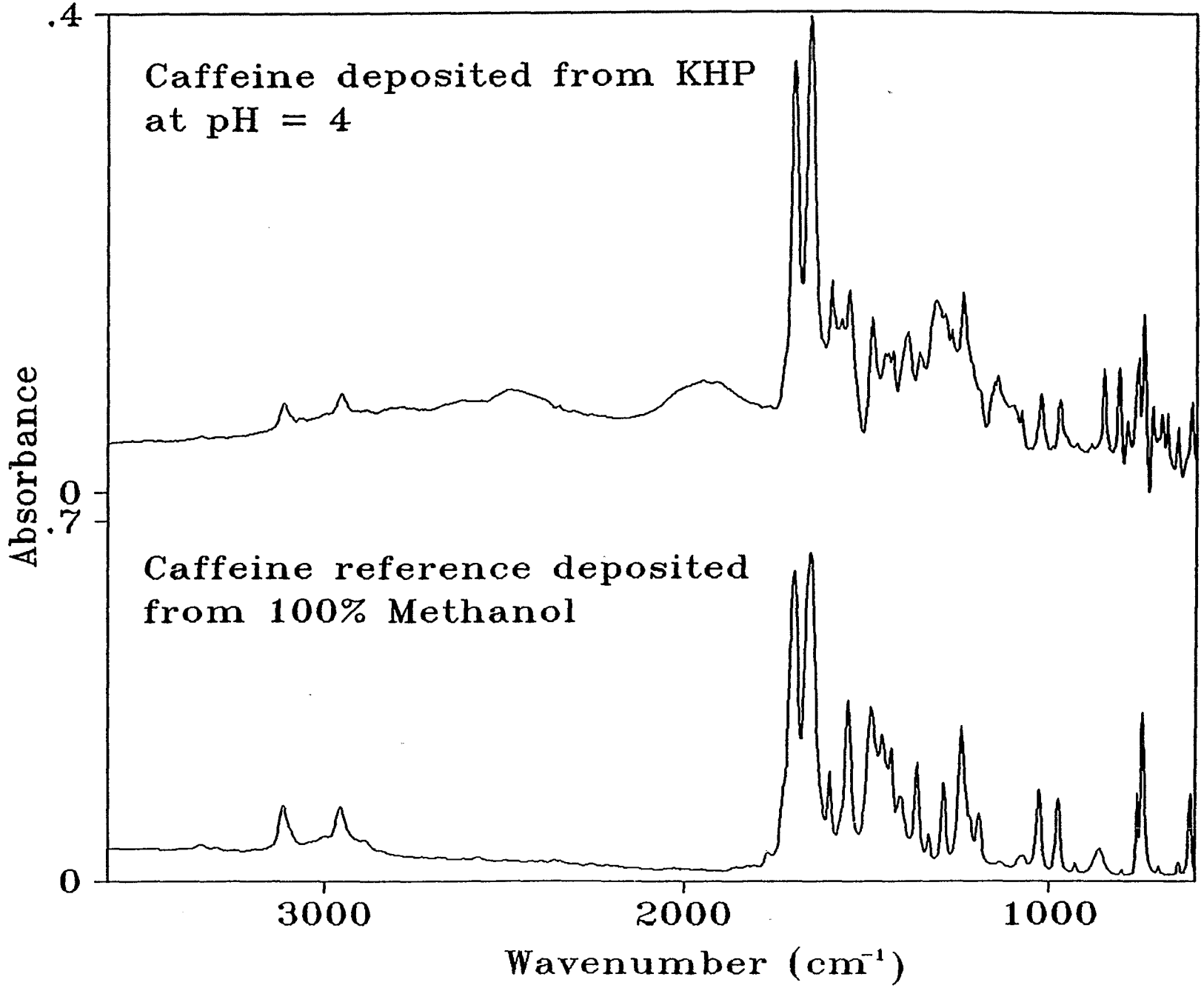
WAVENUMBER (CM-1)


A
B
% TRANSMITTANCE
2000 1800 1600 1400 1200 1000 800 600
WAVENUMBER (CM−1)


80:20 Methanol:Water
Caffeine + KHP Buffer
pH 4
Collection time: 1.0 min
Absorbance
.6
.4
.2
0
3000
2000
1000
Wavenumber (cm⁻¹)


.4
Caffeine deposited from KHP
at pH = 4
Absorbance
0
Caffeine reference deposited
from 100% Methanol
0
3000
2000
1000
Wavenumber (cm⁻¹)

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

DR. MSIMANGA: My name is Huggins Msimanga from Kennesaw State College in Marietta, Georgia.

It looks like to me you have to time...you have to specify the amount of time to allow for the deposition of the solute analyte. Supposing two components come off from the HPLC within a specified time of less than a minute, how do you take that into account? Suppose it is two different analytes on the window.

MR. DE HASETH: Well, the plate itself translates at a reasonable speed, the deposition plate. We can certainly separate two components one minute apart. That is a long time. We can complete for higher concentration components...by higher concentration, we are talking a few hundred picograms.

It has been demonstrated through direct deposition GC/FT-IR which is a parallel technique to this that you can get reasonable spectra a less than 200 picograms in 3 seconds of data collection time. So, all you need is about 3 seconds of analysis, not a minute.

The one I showed was through a beam condenser, and there, yes, we did need a minute, because that was a much

less efficient interface in terms of optics. With this new system, we can do the same analysis in a much shorter time.

The depositions are confined to a radius of about 100 to 150 micrometers. So, they are very small depositions. We can focus indirectly on that and collect our spectra.

MR. TELLIARD: Thank you very much, Jim.

MR. TELLIARD: Our next speaker is Tom Tiernan from Wright State University. Dr. Tom has been working on the joys of dioxin for the last few years and spent the last couple of years working on a new column which is going to save me a lot of money. Right?

DR. TIERNAN: Probably.

MR. TELLIARD: Okay. Tom is going to talk about the analysis of dioxins and furans.

DR. TIERNAN: You heard earlier this morning about chlorinated dibenzodioxins and chlorinated dibenzofurans from Les Lamparski.

Most of you who do environmental analyses . . . and I know that includes many of you . . . know that there are 75 polychlorinated dibenzodioxin (PCDD) isomers and 135 polychlorinated dibenzofurans (PCDF) isomers. No one, to my knowledge, is even contemplating doing a routine type of analysis for all 210 isomers of these, but in more recent years, there has been a focus on determining the 2,3,7,8-substituted isomers of the various chlorinated groups of PCDD and PCDF, particularly the tetra- through heptachlorinated congeners. The reason for this interest, of course, is that these are thought to be the more toxic of the PCDD/PCDF congeners. Clearly, the seventeen 2,3,7,8-substituted isomers are more readily analyzed than all of the 210 isomers.

Even though there are methods that purport to measure the 2,3,7,8-substituted PCDD and PCDF isomers, including some EPA methods, one of the problems with these methods is that, in order to achieve optimum reliability and specificity for the quantitation of the 2,3,7,8-substituted isomers the use of multiple GC columns is required. There is no single GC column that will resolve all of the 2,3,7,8-substituted dibenzodioxins and dibenzofurans in a single analysis.

We originally began the work which I will describe today with the objective of trying to come up with some better columns for resolving and quantitating the 2,3,7,8-substituted PCDD/PCDF isomers. At the outset, we focused primarily on just the tetrachlorinated isomers, because we were involved with the U.S. EPA and the paper industry (NCASI) in a program in which the primary objective was to measure uniquely and specifically, only 2,3,7,8-TCDD and 2,3,7,8-TCDF in sludges, effluents, pulp and other paper and pulp mill wastes and products.

The requirement in the latter case, of course, is somewhat simpler than to separate all of the 2,3,7,8-isomers, but, still, separating even those two tetrachlorinated isomers absolutely uniquely is something of a challenge. At the time when we began this work, there was no single GC column that would separate both 2,3,7,8-TCDD and 2,3,7,8-TCDF uniquely in a single analysis.

Of course, 2,3,7,8-TCDD had been routinely analyzed on a number of different GC columns, specifically and uniquely, including the DB-5, SP-2330 and other columns. Also, there was purported to be a unique separation of 2,3,7,8-TCDF from all other TCDFs on the DB-225 GC column. Thus, determining both 2,3,7,8-TCDD and 2,3,7,8-TCDF in a given sample using these columns required two separate GC-MS analyses.

Much of the early work which we did with the U.S. EPA and the paper industry (NCASI) in connection with developing a new

column for determining both 2,3,7,8-TCDD and 2,3,7,8-TCDF focused on the concept of using serially connected capillary GC columns. By that, I mean using two different portions of two different columns which are simply connected together. Typically, one does this using a dead volume fitting.

There is, in fact, in the literature a good bit of information about modeling the performance of these kinds of capillary columns, as well as columns which are coated with mixtures of different stationary phases. There has been little or no modeling, however, which would permit one to predict theoretically the composition of a single stationary phase or GC column coating containing multiple functional groups which would achieve the kinds of separations of interest here.

So, effectively, the initial goal of our work was to come up with a modeling procedure that would permit us to predict a stationary phase or coating for a capillary GC column which would contain multiple functional groups, and which would achieve the unique separations of these two isomers (2,3,7,8-TCDD and 2,3,7,8-TCDF). The next phase of this work was conducted largely by our partner in these studies, J & W Scientific, and involved synthesis of a specific polymer coating containing the desired functional groups in the predicted amounts (as indicated by the modeling results) and preparation of a bonded capillary GC column coated with this new stationary phase. Finally, testing of this column to determine its effectiveness for separating 2,3,7,8-TCDD and 2,3,7,8-TCDF was accomplished at Wright State.

I am going to describe to you today the outcome of these studies.

One might well ask, what is wrong with coupled

GC columns if they achieve the desired separation? Indeed, we previously developed a coupled column that would, in fact, separate 2,3,7,8-TCDF uniquely. In addition, we eventually developed a three-section capillary GC column combination, that is, portions of three capillary columns coated with different stationery phases which were coupled in sequence, that would resolve both 2,3,7,8-TCDD and 2,3,7,8-TCDF uniquely in a single analysis.

However, it is difficult to convince analysts to prepare and use these kinds of columns, and even more difficult to get a manufacturer to make them. Such coupled columns tend to be somewhat fragile, and the connections are difficult to make and the junctions tend to leak. Chromatographers are therefore reluctant to make and use such columns for routine analyses.

These, then, were some of the reasons for attempting to develop a single-phase coated column, using a specially tailored phase, which could be manufactured and supplied by a recognized gas chromatography specialty firm.

As we will see, what was required initially in terms of developing a model such as that mentioned was to measure GC retention times, capacity factors, and temperature dependences for the gas chromatographic separations of the tetrachlorinated dibenzodioxin isomers and the tetrachlorinated dibenzofuran isomers using several different capillary columns.

Among the columns that were evaluated here were DB-WAX, SP-2250, DB-17, DB-5, SP-2200 and DB-1. The data derived from isothermal measurements of the parameters cited were then incorporated into a multidimensional computer model, which I

am going to describe in rather general terms, to ultimately predict optimum combinations of the various functional groups which would be required as components of the specially synthesized phase in order to obtain the desired resolution.

J & W Scientific used the modeling predictions to synthesize the new polymer or stationary phase, and prepared a bonded capillary GC column coated with that phase.

Ideally, the first new column prepared would have yielded the desired separations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. In reality, of course, scientific methods are rarely that good, and some iteration of the modeling/synthesis procedure proved to be necessary.

One of the reasons that the model for predicting GC column performance did not work quite as well as expected initially is that, even when one synthesizes accurately the polymer or stationary phase containing the predicted functional groups in the predicted amounts, there are likely to be interactions between the functional groups on the polymer that vary the activity and the separation capability of the column coated with this polymer. We are unable to accurately predict these interactions.

What we do, therefore, is take the retention time and related data derived from the initially prepared column, feed these data back into the model, obtain new solutions, and come up with a second prediction of the optimum stationary phase composition. If necessary, this procedure is repeated still again.

Now, just to give you an indication of how difficult and sensitive these kinds of isomer separations are, I wanted to just show you some retention time data for several closely-eluting TCDF isomers which was obtained on two capillary GC columns at two not very different temperatures (Slide 5). The columns here are the SP-2330 and DB-5

capillary columns. What you can see if you compare the retention times for the several isomers that are shown there is that as you go from 220 to 250 degrees with both of these columns, you get some inversion in the order of elution of the isomers.

Obviously, if you look at all 22 TCDDs and 38 TCDFs, this becomes even more severe. You have frequent mixing, jumping, and shifting of positions in terms of the order of elution.

So, it is no easy feat to reliably predict where these numerous isomers are going to elute.

The next slides (Slides 6, 7 and 8) show flow charts which give you an idea of the procedure used in applying the model which I have mentioned. I am going to discuss in greater detail, a little later, what are the specific critical parameters here.

The first thing we have to do, of course, is write the software and develop the model, and this was accomplished for use with a PC type computer. The model was actually written in Turbo Pascal for an IBM-compatible 386 PC with a 387 co-processor. The model will generate about 1000 to 2000 solutions, in terms of

predicted retention times, in a minute, and in an hour or so, we typically get the bulk of the predictions we are after.

In applying the model, we first enter the relevant experimental parameters which include the column length, radius, film thickness, inlet and outlet pressures, and the dead times at a minimum of two temperatures. These are entered into an equation or formula from which we ultimately calculate capacity factors. Initially, we determine two experimental parameters or constants which are called K1 and K2. Of course, to get the K1 and K2 constants, we have to measure isothermal retention times for the group of isomers in which we are interested at different temperatures. Data obtained at a minimum of two different temperatures are required for each of the columns evaluated.

We then insert the retention time data obtained for a given column at two different isothermal temperatures into a set of simultaneous linear equations and solve them to determine the constants, K1 and K2 (Slide 9).

Finally, we utilize these constants in the third phase of the model which gives us the capability

to predict the effect on retention times of each functional group that we wish to incorporate into the polymer backbone that becomes the ultimate coating or stationary phase for the column. Finally, of course, we synthesize the phase, coat the column with this phase and test the column.

So here then, is the capacity factor relationship (Slide 9), and you can see from equation number 3 at the

bottom, which you eventually work down to . . . the input data, of course, is again retention time, dead time, isothermal temperature . . . one can see that by measuring the retention time parameters for a given column at two different T's, one can insert these data into equation (3) and solve the two resulting simultaneous equations, and come up with the K1 and K2 factors, which are the empirical factors which we must obtain initially.

Now, these constants are then used in the retention time relationship shown in Slide 10 (Equation 4A) to come up with retention time predictions at different temperatures, in other words, to predict the times at which isomers are going to elute on a given column as a function of temperature.

Once we have that data, we then go to the last stage. We put these retention times into equation 5 shown on Slide 11 and, again, by doing this at multiple temperatures and solving simultaneously, we come up with the K-prime factors which are characteristic of the actual functional groups, that is, the pure functional groups, methyl, phenyl, or whatever groups we want to incorporate into the polymer.

On Slide 11, for example, are shown the applicable equations for two different columns that we have tested in this study. Column 1, of course, is actually the DB-5 column, which incorporates 95 percent methyl and 5 percent phenyl components, and Column 2 is the DB-17 column which incorporates about 50/50 methyl/phenyl components.

After we have obtained the K prime factors, that is, the functional group factors, we get to the very end of the procedure. We put these back into the retention time relationship (Slide 12), and we determine, for any given combination of these several substituent groups in a polymer, what the predicted retention times for the various isomers to be separated are going to be.

So, in other words, we can now predict what a totally new column containing entirely different combinations of functional groups would yield in terms of retention times for the PCDD/PCDF isomers.

Of course, the experimental verification of the results requires actual measurements using a GC or GC-MS (Slide 13). In this case, we are using a low to medium resolution sector mass spectrometer, a Kratos MS-25. It is operated in the selected ion monitoring mode, of course, for monitoring TCDD and TCDF. Here, you see the sets of ions that are typically monitored as indicators of both native TCDF and the isotopically labeled TCDF and the same for TCDD.

The chromatograph used here is a Carlo-Erba, and in the development phase of this work, we used hydrogen as the carrier gas. Subsequently, we have demonstrated that the predictions are also applicable and the same column performance can be achieved when we use helium as the carrier gas.

Throughout this study, retention times were measured on the various columns for at least three different temperatures, typically 220, 235 and 250 degrees C.

Well, let's look now at some data obtained in the initial stages of this work where we attempted to predict the combinations of functional groups in a single stationary

phase column coating which would give us an adequate separation of both 2,3,7,8-TCDD and 2,3,7,8-TCDF from all other PCDD/PCDF isomers.

Clearly, you must have a separation of at least one peak width of the 2,3,7,8 isomer from the nearest eluting TCDD or TCDF congener which is adjacent to it. So, here you see (Slide 14) some of the predicted separations which resulted from the modeling calculations. It appears that the very first combination of functional groups shown on Slide 14 does, in fact, yield the optimum separation in terms of peak width separation for 2,3,7,8-TCDD from the other TCDD isomers, and this combination also results in a quite good separation of 2,3,7,8-TCDF.

So, initially, we indicated to J & W that they should synthesize a polymer that would contain the

40:25:25:10 proportions of the methyl:phenyl:cyano:WAX functional groups. WAX simply denotes a PEG (polyethylene glycol) functional group.

J & W Scientific synthesized a polymer substrate containing these functional groups in what they believed to be the proportions specified by us, and prepared a bonded column coated with this polymer. When we tested this column for its ability to separate 2,3,7,8-TCDD and TCDF, the observed column performance was different than that expected. When the experimentally observed retention times were compared with the predictions of the model, it could be seen that the column was acting as if the composition were that shown on the second line (Result 1st synthesis) of Slide 15. The first line on the slide shows the column composition predicted by the initial calculation, which J &

W attempted to obtain. The difference in the theoretically expected and experimentally observed behavior of the column was undoubtedly due to the fact that there were unpredictable functional group interactions in the newly synthesized stationary phase coating.

We next inserted the experimentally observed retention time data for the initial column back into the model and calculated a new solution, that is, an iterative prediction of the stationary phase composition.

Before looking at the new solution, let's just look at what the initial column did in terms of separating the isomers (Slide 16). Here you can see that the 2,3,7,8-TCDD is not at all well separated from adjacent TCDD isomers, and exhibits a strong overlap with 1,2,3,8- and 1,4,6,9-TCDD.

The separation of 2,3,7,8-TCDF is considerably better (Slide 17), but, there is a considerable valley between 2,3,7,8- and 2,3,4,6-TCDF and the other co-eluting isomers.

Well, the results of the second modeling prediction obtained by reiterating the model calculations, as described above, are shown in Slide 18 on the third and fourth lines. The second prediction of the optimum functional group composition of the column stationary phase which we selected was the 43:26:22:9 combination, and when a polymer with this expected composition was synthesized and a bonded capillary GC column was coated with this polymer, the performance of this column in terms of retention times of the separated isomers, corresponded closely to the composition which was originally predicted. The last column on Slide 18 (horizontal) shows the calculatedcomposition to which the experimental behavior corresponded.

This is, in fact, the composition of the capillary GC column that has now become known as DB-DIOXIN and is currently being marketed by J & W Scientific under that name.

The separation which this column achieves for 2,3,7,8-TCDD is illustrated in Slide 19, and as can be seen, this separation is quite good. Slide 20 shows the separation achieved with the DB-DIOXIN column for 2,3,7,8-TCDF, again, well within desirable bounds.

You can see from the comparison shown in Slide 21 that the retention time predictions derived from the model are quite close to the experimentally observed retention times. The second vertical column here shows the expected or calculated retention times for this set of isomers, while the third column shows the actual experimental retention times that were observed. You can see that, in most cases, these are extremely close to the predictions.

The sensitivity of the DB-DIOXIN column is excellent. The mass chromatograms shown in Slide 22, for example, which were obtained for a 2.5 pg injection of 2,3,7,8-TCDF, exhibit about a 25:1 signal to noise ratio for the responses at the ion masses which are indicators of both native TCDF and the isotopically-labeled TCDFs that would be monitored in a normal analysis run. The DB-DIOXIN column exhibits similar sensitivity for 2,3,7,8-TCDD, as shown on Slide 23.

We have now used the DB-DIOXIN column very extensively for analysis of extracts obtained from a large variety of sample matrices. Slide 24 shows some of the types of samples that have been analyzed with this column during the past year or so, during which time a total of about 500 samples have been characterized for 2,3,7,8-TCDD and TCDF. In fact, the very same DB-DIOXIN column was used for all of these analyses.

You can see that the samples analyzed with this column range from relatively clean biologicals and human tissues to very dirty chemical wastes. It turns out that pulp and paper samples and wastes pose a particular challenge here, partly because of the kinds and types of interferences.

The DB-DIOXIN column also exhibits good, long-term stability. You can see from the mass chromatogram shown in Slide 25 that even after some 600 analyses with the column, the resolution is essentially unchanged for the 2,3,7,8-TCDD. The same long-term performance of this column is observed for 2,3,7,8-TCDF, as seen from the results shown in Slide 26.

The conclusions from this study are summarized on Slides 27 and 28. The main conclusion is that the DB-DIOXIN column is quite effective for the analyses of both 2,3,7,8-TCDD and 2,3,7,8-TCDF in a single GC-MS run. Moreover, the theoretical model developed in this study appears to be capable of reliably predicting the combinations of functional groups in a polymeric stationary phase coating which will yield a capillary GC column capable of achieving the desired separation of virtually any closely eluting compounds.

Of course, we are not only interested in the separation of tetrachlorinated dioxins and dibenzofurans, but are also interested in developing capillary GC columns that will be useful for separating the entire chlorinated range of these compounds, and in particular, in uniquely separating all of the other 2,3,7,8-substituted congeners. We have done some preliminary work toward this end already.

Obviously, the first step in achieving this objective is to see what isomers the DB-DIOXIN column which we already have in hand is capable of resolving. We have already determined that this column will, in fact, separate all of the 2,3,7,8-substituted congeners of all the chlorinated groups from each other. However, we do not yet know that this column will separate all of the other isomers of each chlorinated group from the 2,3,7,8-substituted isomers.

Some overlap of the chlorinated group retention time windows occurs with the DB-DIOXIN column. For example, some of the TCDFs coelute with some of the PeCDFs, as indicated by Slide 29. So the DB-DIOXIN column is somewhat different than the DB-5 column, on which the respective chlorinated congener groups are quite well separated from each other, at least under the conditions that are usually applied, and the DB-5 column is therefore more useful for the total chlorinated congener group type of analysis. Nevertheless, at this point, it appears that the DB-DIOXIN column shows considerable promise for analyses of just the 2,3,7,8-substituted isomers.

We are in the process of evaluating the separation capability of the DB-DIOXIN column for the entire 210 isomer PCDD/PCDF set.

The last slide (Slide 30) shows you the separations that are achieved with this column for some of the 2,3,7,8-penta CDDs and CDFs.

In conclusion, let me just say that the DB-DIOXIN column is currently available from J & W Scientific, and, in their most recent catalog, which has just been issued, some very nice mass chromatograms are shown which exhibit the separations obtained for all of the TCDF and TCDD isomers, using both helium and hydrogen carrier gases.

So, here for the first time, we have developed a working, stable, commercially-available capillary GC column that will permit one to determine at least 2,3,7,8-TCDD and 2,3,7,8-TCDF in a single analysis and will, as Bill said, possibly save the agency a little money.

MR. TELLIARD: A lot of money, Thank you, Tom.

DR. TIERNAN: Thank you.

QUESTION AND ANSWER SESSION

DR. TELLIARD: Are there any questions?

MR. LEWIS: Michael Lewis of TC Analytics.

What was the optimum column dimensions that you are using for your . . .

DR. TIERNAN: Sorry, what was the question?

MR. LEWIS: What was the optimum column dimensions that you were using for your development work? And conditions. Were they standard?

DR. TIERNAN: Oh, yes. You mean like temperature programs and what not?

MR. LEWIS: A 30 meter or a . . .

DR. TIERNAN: Oh, well, the original coupled column we put together was about 40 meters in length. But the present DB-DIOXIN column can be anywhere from 30 to 60 meters. It just depends on what you want to achieve here. But these are standard length columns as compared to current technology, and the temperature programs one would use here are very standard, too.

I didn't mention it, but, typically, you would be programming the column from about 180 to 220 degrees at about 10 degrees C per minute and then holding at the higher temperature. We know, however, that this column will go as high as 250 to 270 degrees C with no degradation.

MR. LEWIS; Were you using attempt to look at more the megabore standard dimensions right now?

DR. TIERNAN: No, this is not a megabore column, and we probably are not going to do that at this point. No, this is a standard 0.25 micron dimension column.

MR. TELLIARD: Anyone else?

Tom, what is the run time when you use the hydrogen carrier roughly?

DR. TIERNAN: Actually, you can adjust the head pressure of helium or hydrogen to achieve the same effective separation with either carrier gas, and the run time is on the order of about 30 minutes for analyses of both 2,3,7,8-TCDD and 2,3,7,8-TCDF in the same run.

MR. TELLIARD: That is good.

DR. TIERNAN: Yes.

MR. TELLIARD: Thank you very much.

DR. TIERNAN: Thank you.

NEW CAPILLARY COLUMN FOR THE DETERMINATION OF PCDD's AND PCDF's

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Department of Chemistry
and Toxic Contaminant Reseach Program
Wright State University
Dayton, Ohio

and

R.M.A. Lautamo and R.R. Freeman
J & W Scientific
Folsom, California

BACKGROUND

1. Separation of the 2378- substituted isomers of the DibenzoDioxins and DibenzoFurans provides a difficult challenge for capillary GC columns.
2. Tetrachlorinated Isomers
   - Dioxins (TCDD)-22
   - Furans (TCDF)-38
3. Requirements:
   - Separate 2,3,7,8-TCDD from all other TCDDs
   - Separate 2,3,7,8-TCDF from all other TCDFs
4. While separation of 2,3,7,8-TCDD from all other TCDDs is routinely accomplished on several capillary GC columns (DB-5, SP-2330, SP-2340), no single liquid-phase coated column has been reported which separates 2,3,7,8-TCDF from all other TCDFs and 2,3,7,8-TCDD from all other TCDDs in a single GC-MS analysis.

BACKGROUND

5. Initial studies in our laboratory using retention time data obtained on seven columns (DB-5, DB-225, DB-1701, DB-WAX, SP-2250, SP2340, and SP2401) led to the development of two different columns consisting of coupled serially-connected sections of single-phase columns. A combination of two different phases (DB-5 and DB-225) successfully resolved 2,3,7,8-TCDF from all other TCDFs. A combination of three phases (DB-WAX, DB-225, and SP-2550) simultaneously resolved 2,3,7,8-TCDD from all other TCDDs and 2,3,7,8-TCDF from all other TCDFs.

6. Coupled columns, while capable of the required isomer resolution, are somewhat difficult to handle and reproduce.

OBJECTIVES OF PRESENT STUDY

1. Measure GC retention times, capacity factors and temperature dependences of separations for all TCDD and TCDF isomers using a variety of capillary GC columns.

2. Utilize data obtained empirically in a multidimensional computer model to predict optimum combinations of various functional group phases which will yield complete resolution of both 2,3,7,8-TCDD and 2,3,7,8-TCDF.

3. Synthesize a single liquid phase polymer coating incorporating the functional groups selected in the relative proportions predicted by the model and construct a capillary column coated with this phase.

OBJECTIVES OF PRESENT STUDY

4. Test the efficacy of the column for achieving resolution of 2,3,7,8,-TCDD and 2,3,7,8-TCDF in a single run.

5. Use data derived from initial column to obtain an iterative solution using the model, as necessary.

6. Synthesize new polymer coating based on revised model predictions, and construct new column.

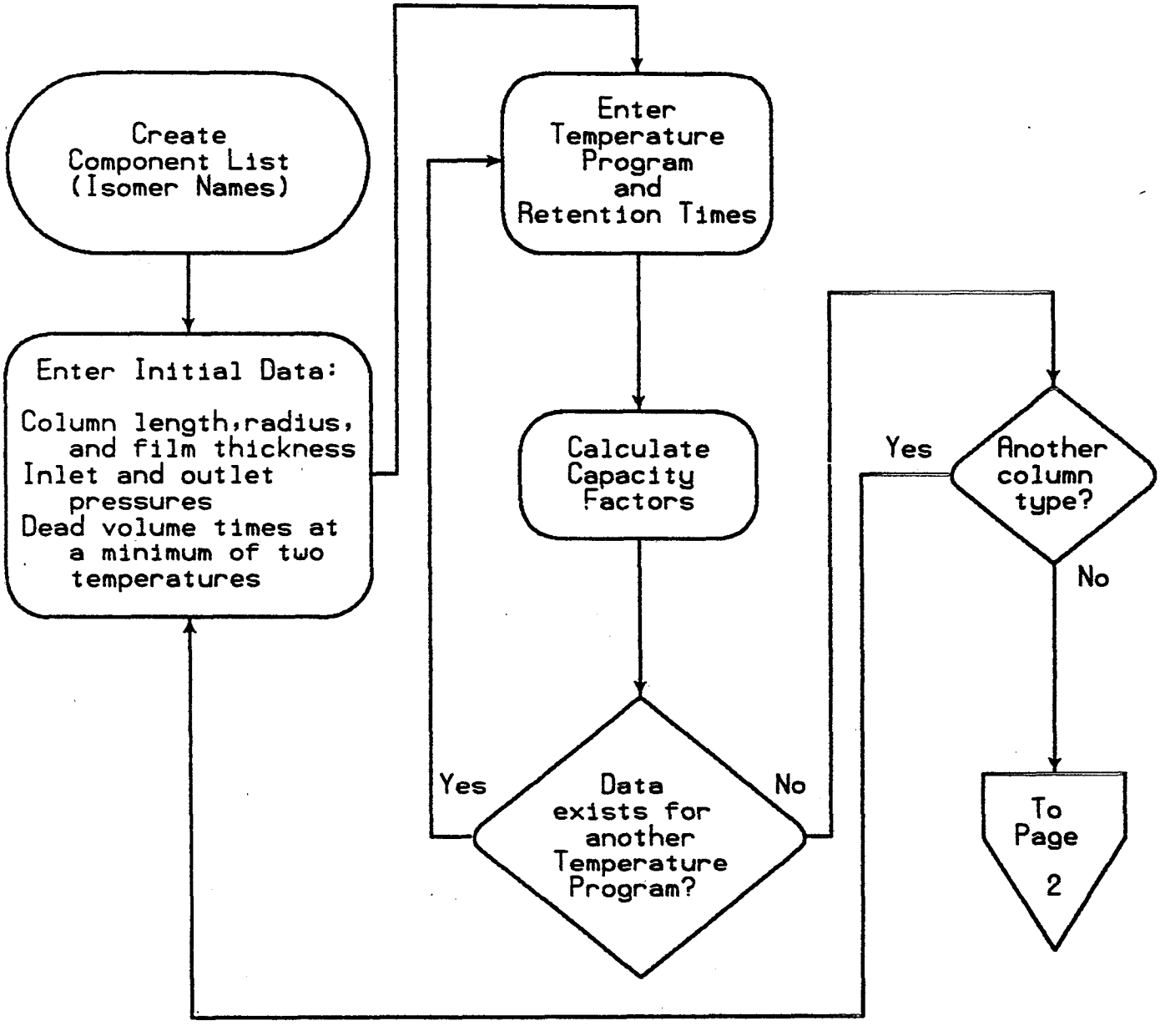
7. Demonstrate complete resolution of 2,3,7,8-TCDD and 2,3,7,8-TCDF using finally developed column.

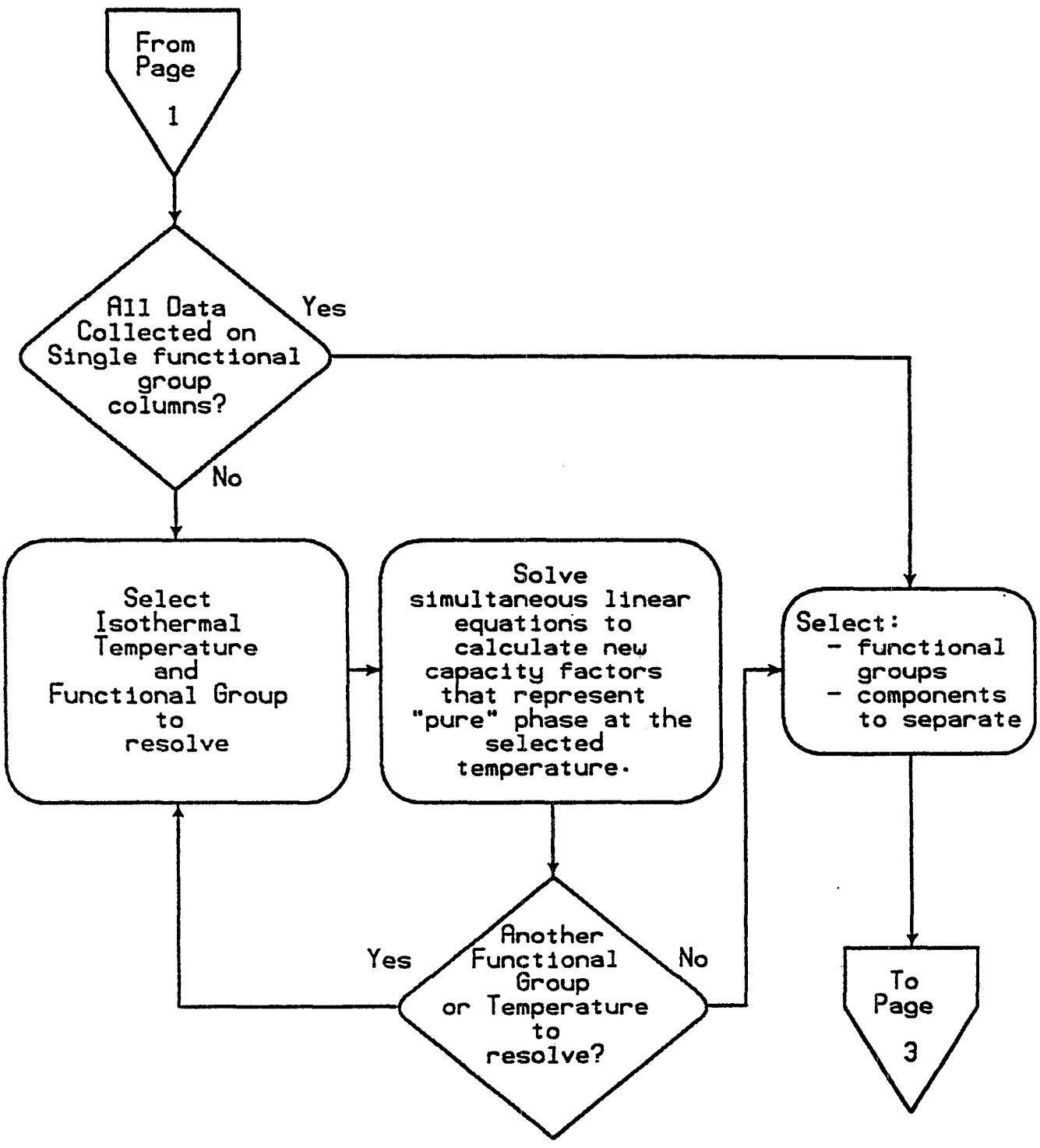
EFFECT OF TEMPERATURE ON TCDF ISOMER LOCATIONS

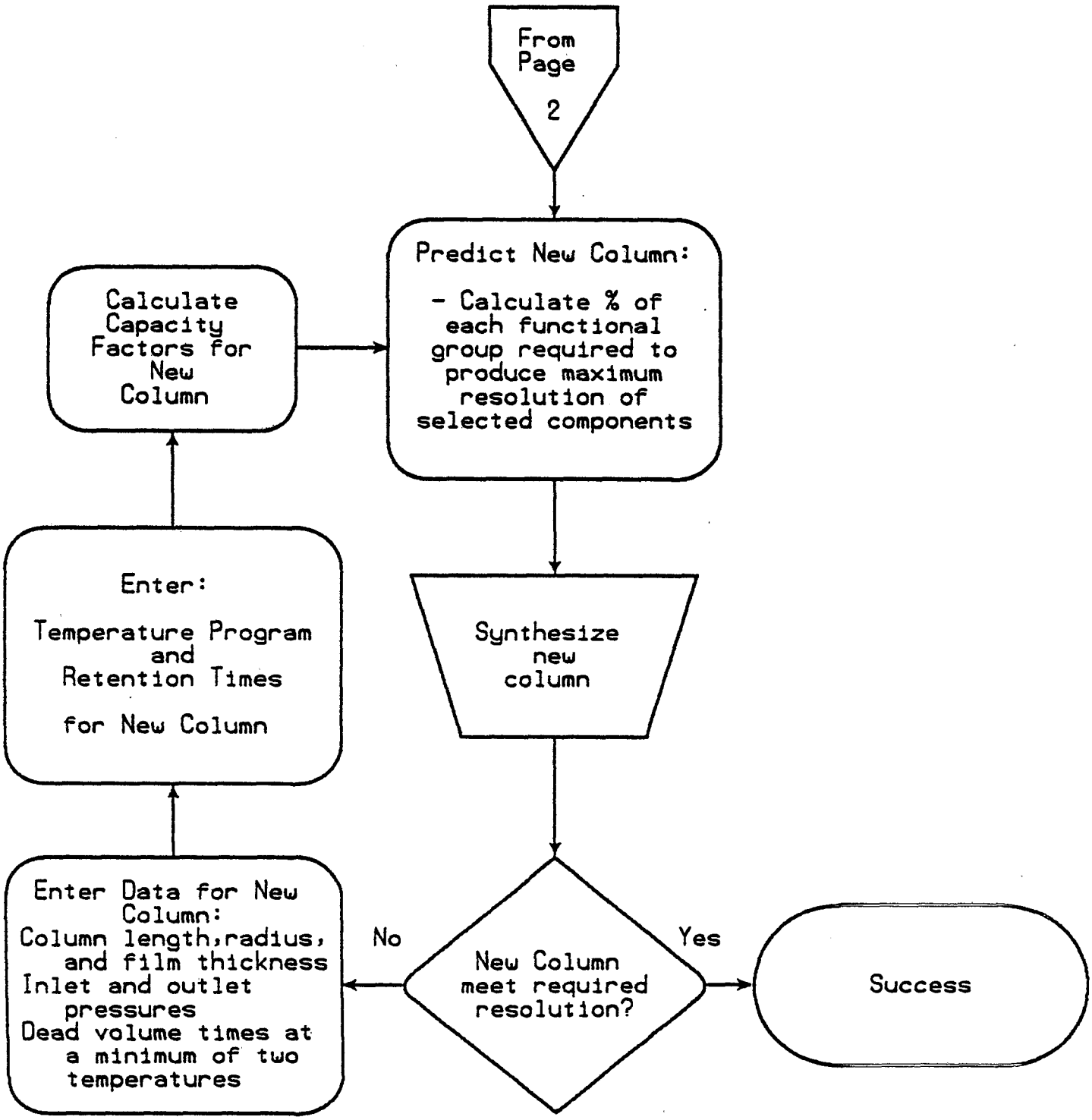
ISOMER	*SP2330 (220 C)*	*SP2330 (250 C)*
1,2,3,9	0.938	0.965
2,3,4,7	0.950	0.963
1,2,6,9	0.984	0.996
2,3,7,8	1.000	1.000
2,3,4,8	1.012	1.009

ISOMER	*DB-5 (220 C)*	*DB-5 (250 C)*
2,3,7,8	1.000	1.000
1,2,7,9	1.001	1.005
2,3,4,8	1.004	1.001
1,2,6,9	1.064	1.046
2,3,6,7	1.080	1.030
1,2,3,9	1.081	1.063

Retention times relative to 2,3,7,8


Create Component List (Isomer Names)
Enter Initial Data:
Column length, radius, and film thickness
Inlet and outlet pressures
Dead volume times at a minimum of two temperatures
Enter Temperature Program and Retention Times
Calculate Capacity Factors
Data exists for another Temperature Program?
Yes
No
Another column type?
Yes
No
To Page 2


From Page 1
All Data Collected on Single functional group columns?
Yes
No
Select Isothermal Temperature and Functional Group to resolve
Solve simultaneous linear equations to calculate new capacity factors that represent "pure" phase at the selected temperature.
Another Functional Group or Temperature to resolve?
Yes
No
Select:
- functional groups
- components to separate
To Page 3


From Page 2
Predict New Column:
- Calculate % of each functional group required to produce maximum resolution of selected components
Calculate Capacity Factors for New Column
Synthesize new column
Enter:
Temperature Program and Retention Times
for New Column
New Column meet required resolution?
No
Yes
Success
Enter Data for New Column:
Column length, radius, and film thickness
Inlet and outlet pressures
Dead volume times at a minimum of two temperatures

EXPERIMENTAL CONDITIONS
(FOR DEVELOPMENT)

Kratos MS-25 mass spectrometer

DS-90 Version 5.00 software

Selected-Ion monitoring mode

Ions monitored:

TCDF m/z 304, 306, 312, 316, 318

TCDD m/z 320, 322, 328, 332, 334

Carlo-Erba Mega 5300 series Gas Chromatograph

Splitless Injection

Hydrogen carrier gas 1.20 kg/square cm and 2.40 kg/square cm

Inlet and exit carrier gas pressures measured to
+/- 0.07 kg/square cm

Retention times measured at 220 C, 235 C, 250 C

Capacity Factor Calculations

Tr - Retention Time
Td - Dead Volume
T - Temperature
k' - Capacity factor at a given Temperature
k1 & k2 - Experimentally derived constants

$$Tr = Td (1 + k') \quad (1)$$

$$Ln (k') = Ln (k1) + k2 / T \quad (2)\ a.$$

Substituting Equation 1 into Equation 2 yields:

$$Ln ((Tr / Td) - 1) = Ln (k1) + k2 / T \quad (3)$$

Under experimental conditions Equation 3 contains two unknowns (k1 and k2). Values for k1 and k2 can be calculated by solving simultaneous equations for data collected at two or more isothermal temperatures.

a. Akporhoor,Vent,and Taylor, J. Chrom.,405 (1987)

New Retention Time Calculations

Tr - Retention Time
Td - Dead Volume
T - Temperature
k' - Capacity factor at a given Temperature
k1 & k2 - Experimentally derived constants

$$Ln (k') = Ln (k1) + k2 / T \qquad (2)\ a.$$

Equation 2 can be written as

$$Tr = Td [1 + k1 \exp (k2 / T)] \qquad (4)\ a.$$

Since k1 and k2 were determined during the capacity factor calculation, Equation 4 permits calculation of predicted retention times.

a. Akporhoor,Vent,and Taylor, J. Chrom.,405 (1987)

Calculation of Functional Group Capacity Factors

Existing column phases:

Column_1 : 95% Methyl, 5% Phenyl
Column_2 : 50% Methyl, 50% Phenyl

Column_1:

$$Tr = Td\,(\,1 + 0.95 * k'\_Methyl + 0.05 * k'\_Phenyl\,) \quad (5)$$

Column_2:

$$Tr = Td\,(\,1 + 0.50 * k'\_Methyl + 0.50 * k'\_Phenyl\,) \quad (6)$$

- Equations 5 and 6 each contain two unknowns (k'_ Methyl and k'_Phenyl). Effective capacity factors for each functional group can be calculated by simultaneously solving the above equations for data collected under the same experimental conditions.

PREDICTING A NEW COLUMN

Equation for retention time prediction for new combinations of "n" functional groups:

$$Tr = Td\,[\,1 + (\%\_Group\_1 * k'\_Group\_1) + (\%\_Group\_2 * k'\_Group\_2) + \ldots \text{additional groups} \ldots + (\%\_Group\_n * k'\_Group\_n)\,]$$

where $\%\_Group\_1 + \%\_Group\_2 + \ldots + \%\_Group\_n = 1$

After calculating the expected retention times, (Tr), for each component in a specific combination of functional groups, the isomer least resolved from the 2,3,7,8 isomer is used for the resolution value for that phase combination.

The best solution must be selected from those combinations giving a minimum resolution of one peak width.

Other factors that must be considered:
- number of functional groups contained in the prediction
- stability of the solution (width of solution window)

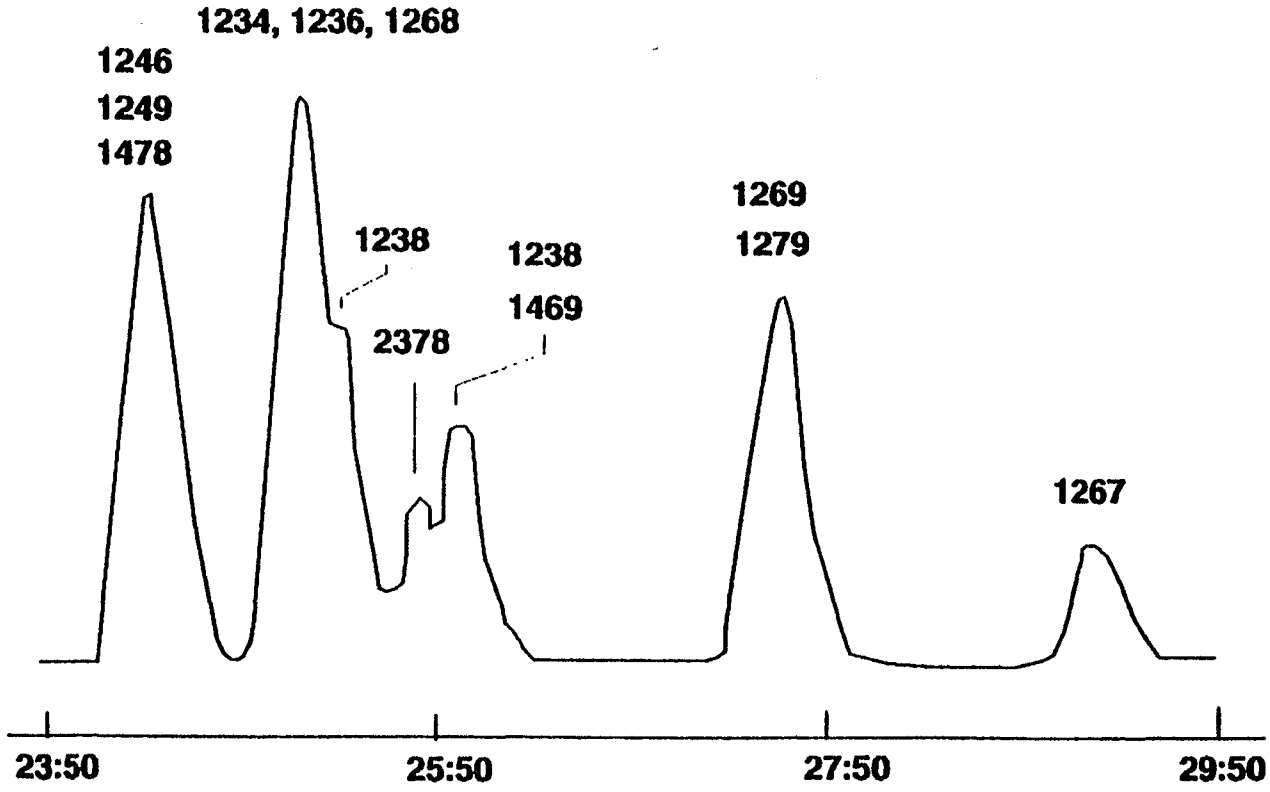
FORWARD PREDICTION FOR DB-DIOXIN

% Functional Group				Separation (Peak Width)	
Methyl	*Phenyl*	*Cyano*	*Wax*	*TCDD*	*TCDF*
40	25	25	10	1.19	1.59
40	25	30	5	1.15	1.78
40	25	20	15	1.09	1.42
45	25	15	15	1.05	1.34
40	30	20	10	1.03	1.32
40	25	25	10	0.99	1.53
45	20	5	10	0.95	1.11
45	30	5	15	0.89	1.16
45	25	10	15	0.83	1.32
45	35	5	10	0.75	1.10

PREDICTIONS FOR DB-DIOXIN COLUMN

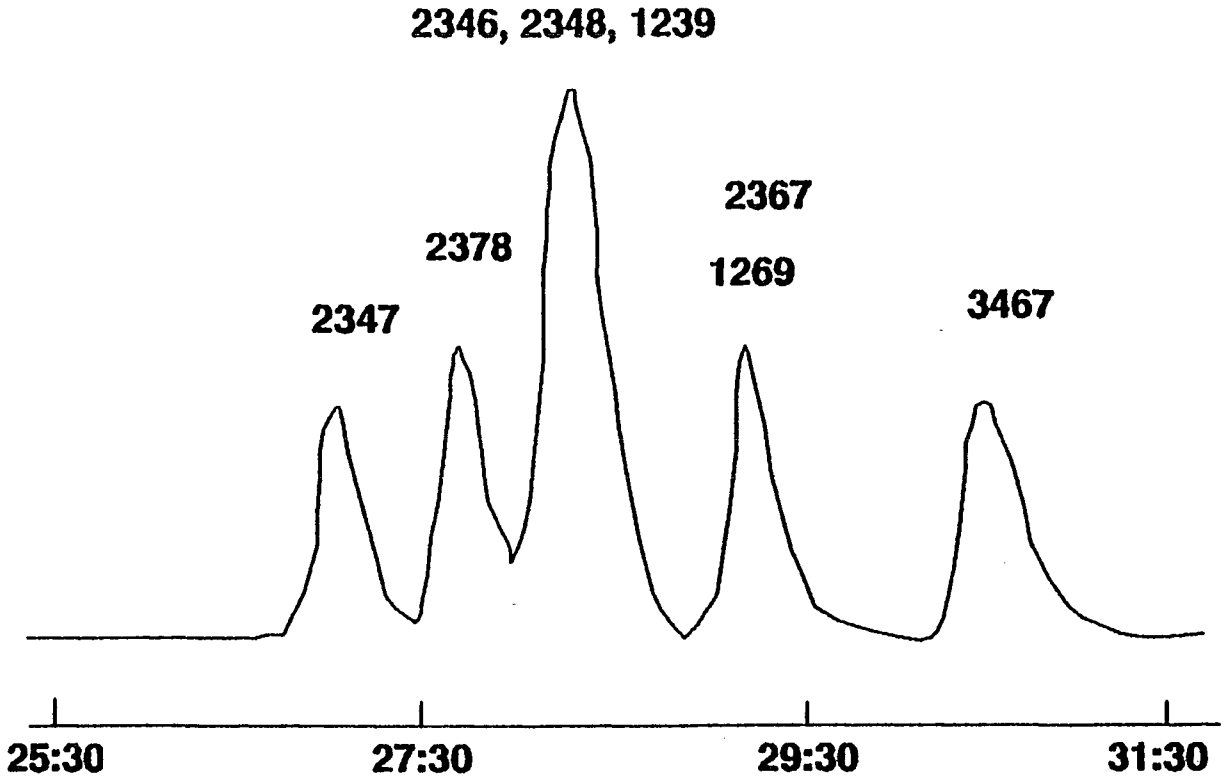
	% Functional Group			
	Methyl	*Phenyl*	*Cyano*	*Wax*
First Prediction	40	25	25	10
Result 1st Synthesis	45	32	13	10

RESOLUTION OF TCDD ISOMERS - FIRST COLUMN



Wright State University and J & W Scientific

RESOLUTION OF TCDF ISOMERS - FIRST COLUMN



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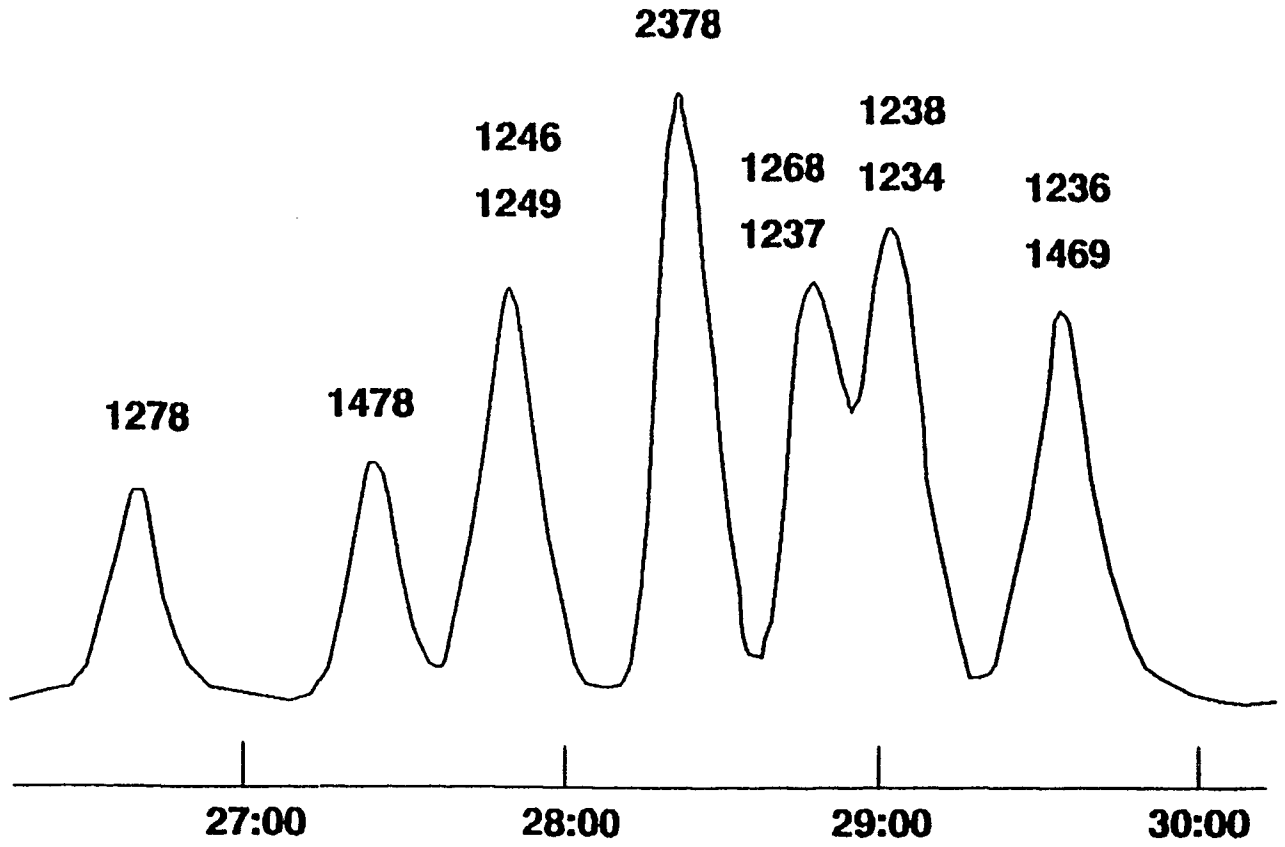
PREDICTIONS FOR NEW DIOXIN/FURAN COLUMN

DB-DIOXIN

	% Functional Group			
	Methyl	*Phenyl*	*Cyano*	*Wax*
First Prediction	40	25	25	10
Result 1st Synthesis	45	32	13	10
Second Prediction	43	26	22	9
Final Synthesis	44	28	20	8

RESOLUTION OF TCDD ISOMERS ON DB-DIOXIN COLUMN



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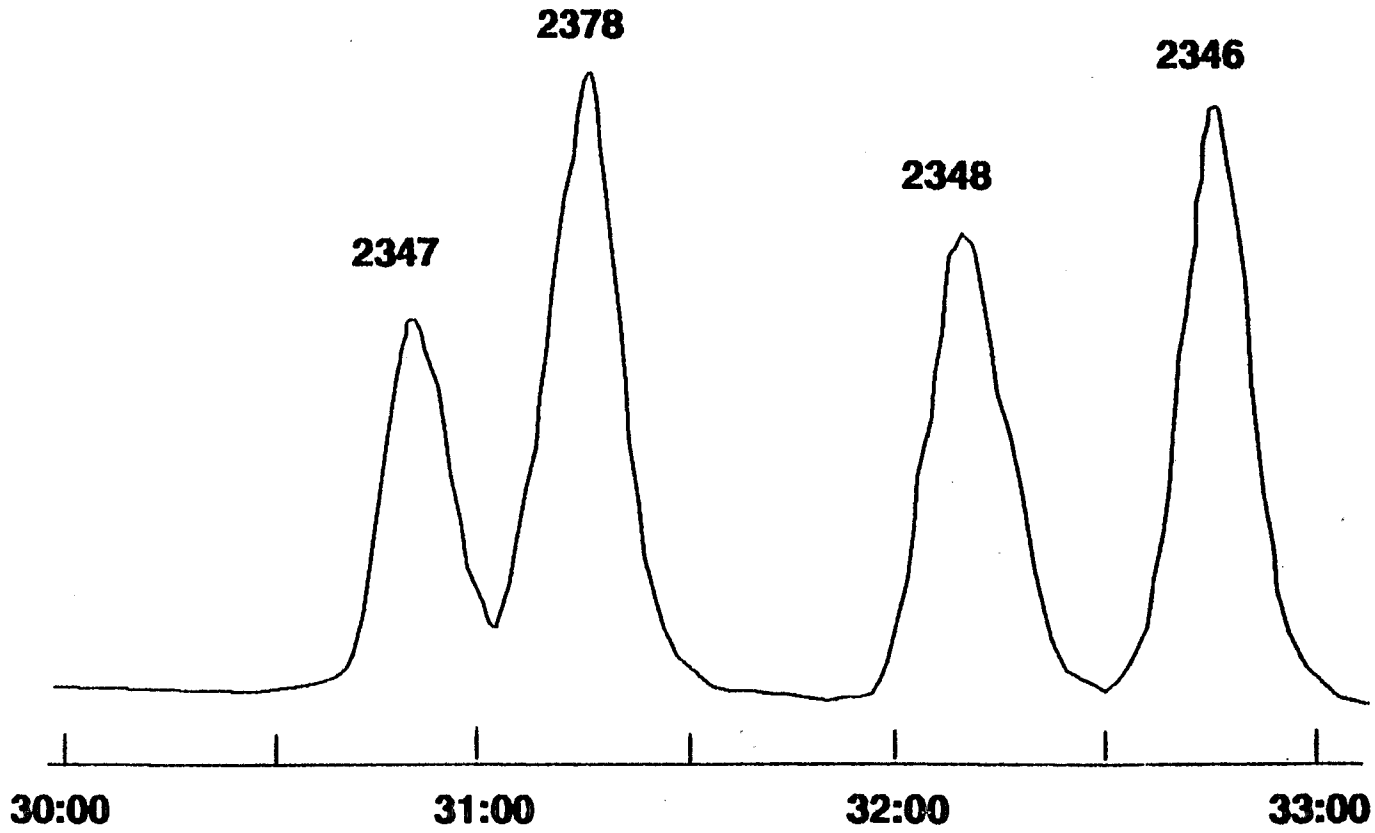
RESOLUTION OF TCDF ISOMERS ON DB-DIOXIN COLUMN



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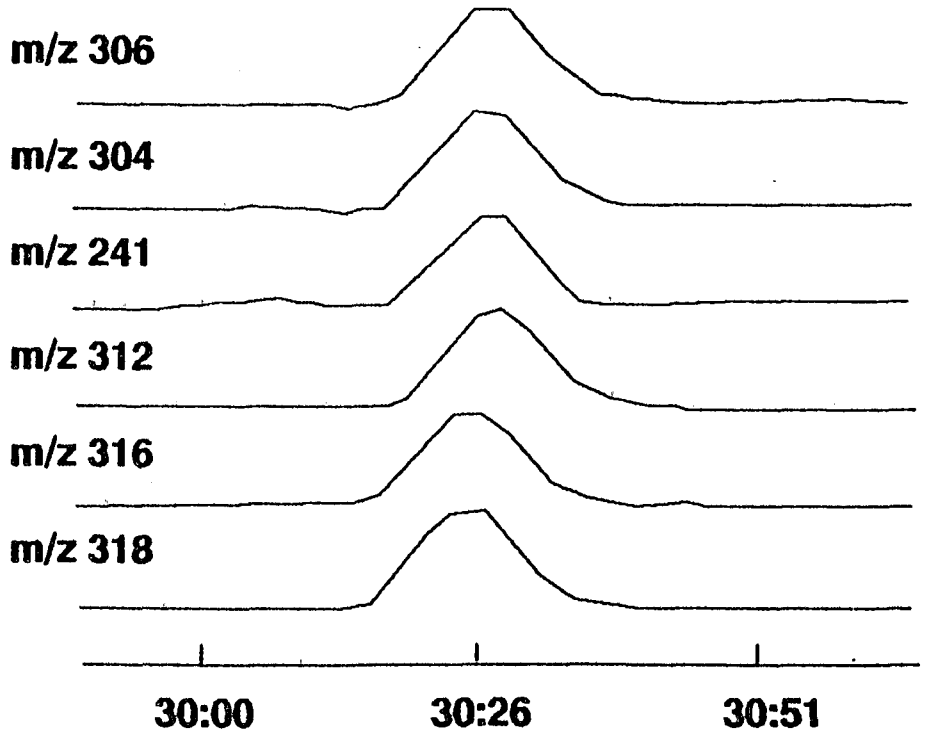
EXPECTED vs ACTUAL RT's FOR DB-DIOXIN

(TCDD REGION)

Isomer	*Expected Rt*	*Actual Rt*
1478	24:40	24:40
1249	24:44	24:38
1246	24:46	24:40
1268	25:00	25:22
1234	25:32	25:25
1236	25:28	25:26
2378	26:02	26:06
1469	26:14	26:14

2.5 PG OF 2378 TCDF ON DB-DIOXIN



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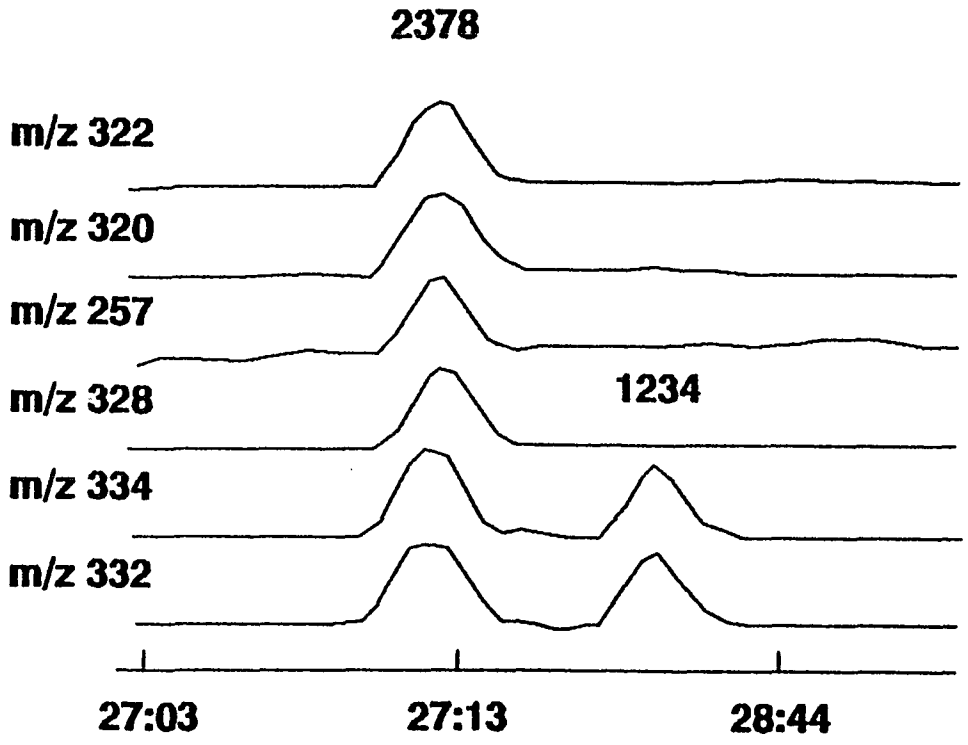
2.5 PG OF 2378 TCDD ON DB-DIOXIN



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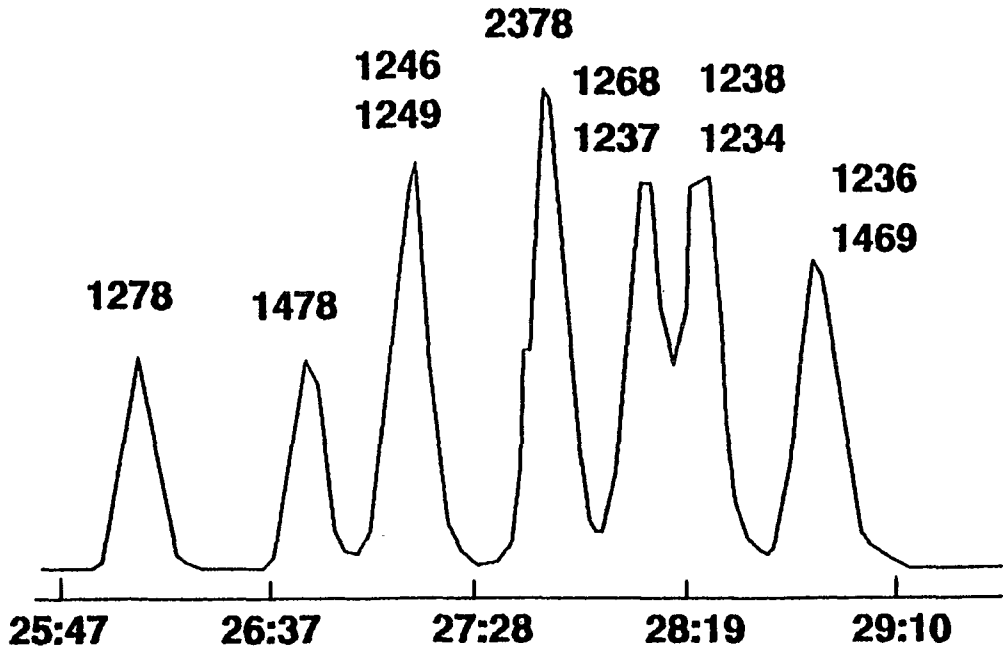
MATRICES ANALYZED ON DB-DIOXIN

- **Biologicals:**
  Beaver, fish, frogs, and mice
- **Human Tissues:**
  Blood and fat
- **Air Samples:**
  High volume ambient air and fly ash
- **Other Environmental Samples:**
  Soils, sludges, and waters
- **Chemical Wastes**
- **Paper/Pulp Products and Wastes**

500 Samples of Above Types Were Analyzed
Over a 12 Month Period Using This Column

RESOLUTION OF 2,3,7,8-TCDD ON DB-DIOXIN AFTER 250 STANDARDS AND 350 SAMPLE ANALYSES



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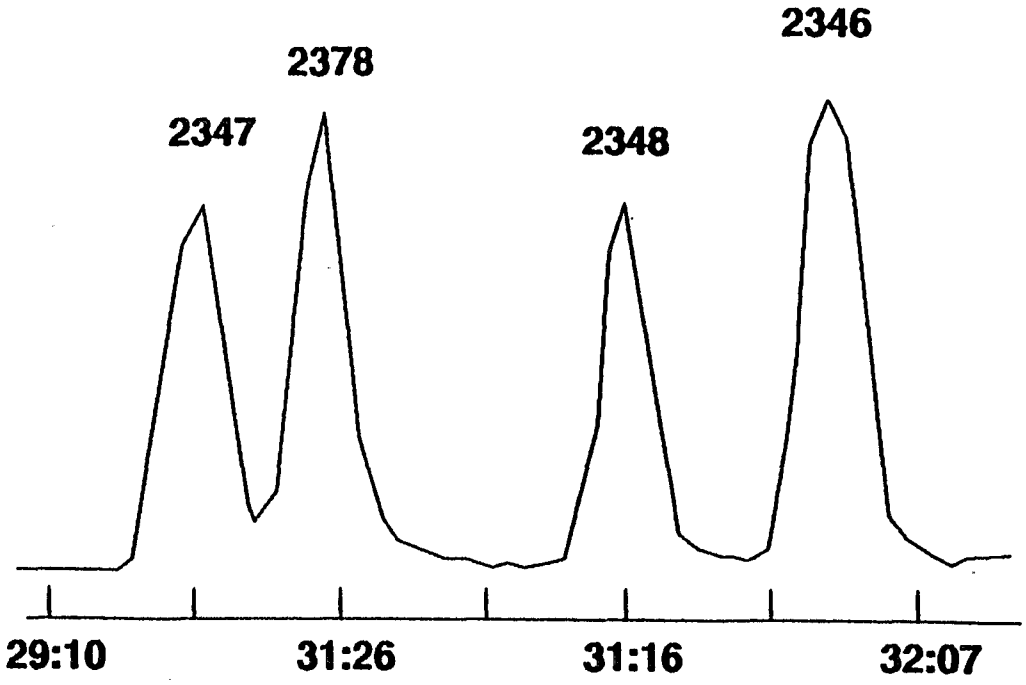
RESOLUTION OF 2,3,7,8-TCDF ON DB-DIOXIN AFTER 250 STANDARDS AND 350 SAMPLE ANALYSES



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CONCLUSIONS

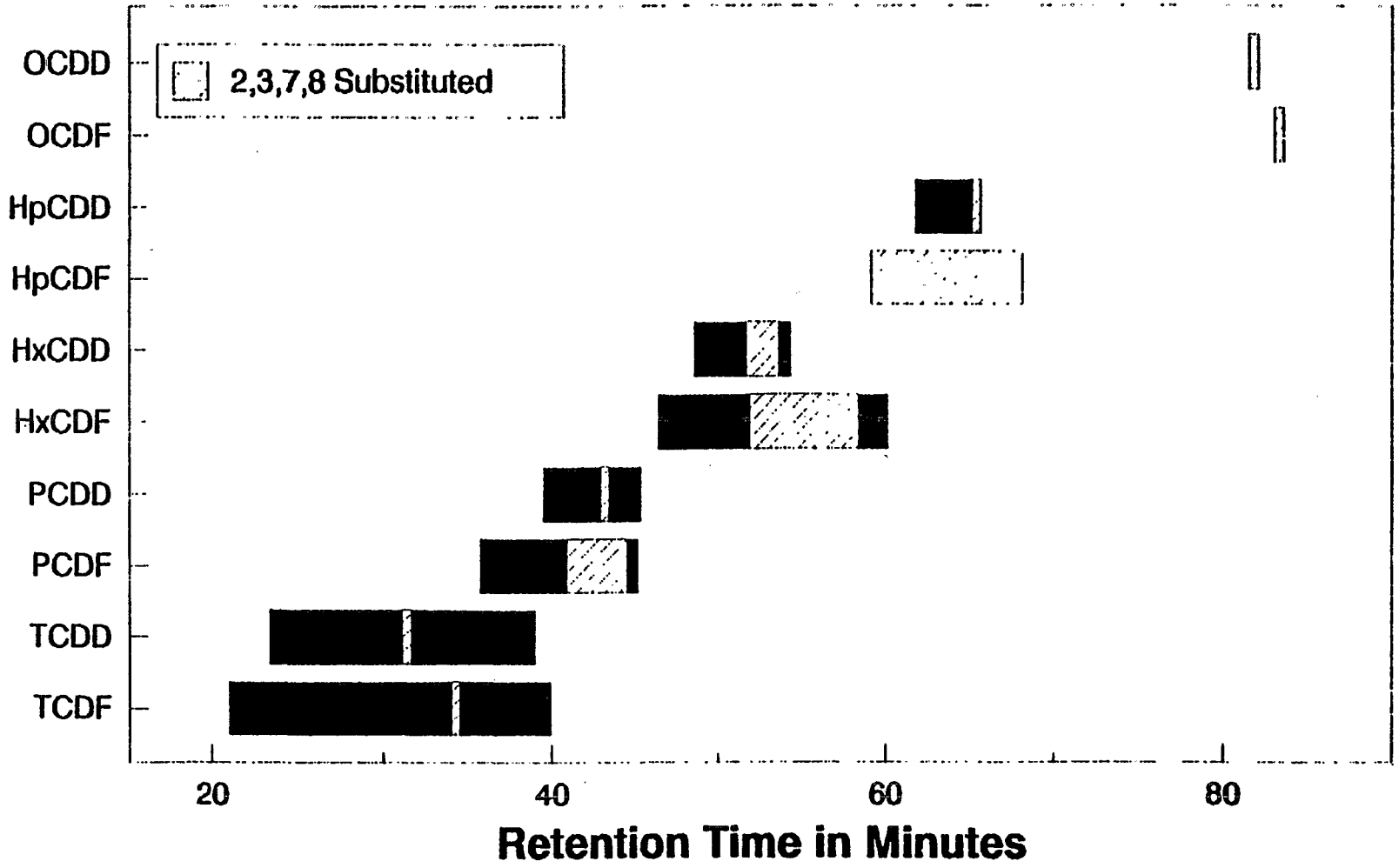
- An analytical approach has been developed to solve difficult separations of compounds. This approach has been successfully utilized to produce a capillary GC column capable of separating both 2,3,7,8-TCDD and 2,3,7,8-TCDF from all other TCDD and TCDF isomers in a single GC-MS analysis.

CONCLUSIONS

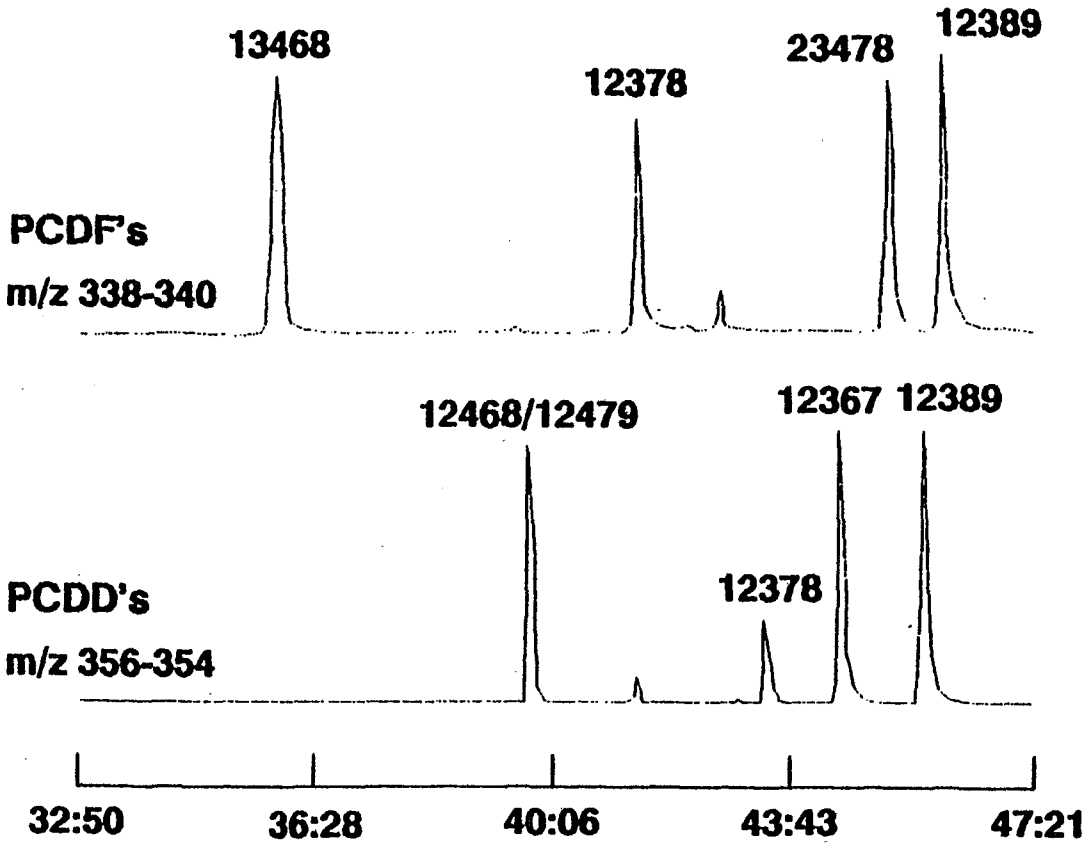
- The approach developed takes into account variances in:
  - -temperature programming
  - -head pressure
  - -column length
  - -film thickness
  - -functional group interactions

- The synthesis of a tailored bonded-phase column coating was essential in order to obtain a column of sufficient durability and reproducibility which would achieve the required separations.

RETENTION TIME WINDOWS FOR CONGENER GROUPS USING HELIUM CARRIER GAS



SEPARATION OF SOME PCDD & PCDF ISOMERS ON DB-DIOXIN



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AFTERNOON SESSION

MR. TELLIARD: Our next speaker is going to be Tom Fielding.

MR. FIELDING: Thank you.

Bill asked me to speak for 15 minutes this morning, and then he told me I was going to moderate the afternoon session, and I figured that was my 15 minutes right there. So, without further ado, let's start with our afternoon session.

Our first speaker is Mr. Ted Martin of the Chemistry Research Division, USEPA-EMSL who will talk about single laboratory evaluation of EPA Method 200.8.

Ted?

SINGLE LABORATORY EVALUATION OF METHOD 200.8, DETERMINATION OF TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

T.D. MARTIN, USEPA, EMSL-CINCINNATI AND
S.E. LONG, TECHNOLOGY APPLICATIONS, INC.

Inductively coupled plasma-mass spectrometry (ICP-MS) is currently receiving attention as the newest spectrochemical technique for trace element analyses of environmental samples. It is a multielement technique that provides extremely low limits of detection and freedom from the potentially complex interelement spectral interferences of atomic emission spectrometry. It is not without limitations, but when properly recognized and its strengths utilized, it is an extremely powerful tool for environmental analyses.

In this presentation certain procedural features of Method 200.8 and specific requirements for its use will be discussed. Also, presented will be detection limit data, single laboratory data compared with inductively coupled plasma-atomic emission spectrometry for the analysis of aqueous and solid matrices and the status of a joint EPA/AOAC multi-laboratory study currently being conducted.

SINGLE LABORATORY EVALUATION OF METHOD 200.8 DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY ICP MASS SPECTROMETRY

Theodore D. Martin
Environmental Monitoring and Systems Laboratory

and

Stephen E. Long
Technology Applications Inc.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

SINGLE LABORATORY EVALUATION OF METHOD 200.8 DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY ICP-MASS SPECTROMETRY

T.D. MARTIN, USEPA-EMSL AND S.E.LONG, TAI

The information that will be presented in today's talk can be divided into three topical or subject areas. The first portion will be a brief functional description of ICP-MS, the second part will be a discussion of certain procedural requirements of Method 200.8 followed by comparative data to inductively coupled plasma-atomic emission spectrometry (ICP-AES) and the final portion will be a status report of the joint EPA/AOAC multi-laboratory study currently being conducted.

ICP-MS offers some unique and distinct advantages to environmental analyses. Some of these are listed on the next slide (#2). The first item of particular importance is a linear range of 5 orders of magnitude, and up to 8, if the instrument is equipped with some type of extended range capability. This wide dynamic range is very useful for analysis of dilute solutions especially when viewed along with the low, PPT, detection limits. ICP-MS is considered to be a simultaneous analysis technique. This is achieved by repeated, rapid, sequential scanning of the ionized sample over the mass range 5-250 amu. This process provides multielement determinations of the entire periodic table with the few noteworthy exceptions (C, N, O, F, Si, P and S). By the very nature of the technique, isotope ratio information is available with each analysis. This feature gives the analyst the capability of doing very accurate determinations by isotope dilution. This same isotope information supplies recognizable patterns, like fingerprints, which can facilitate qualitative analyses. Sample throughput is rapid (5 min. per sample) while generally providing for some analytes detection limits that are equal or lower than graphite furnace atomic absorption spectrometry (GFAA).

The next slide (#3) is a functional schematic of the VG PlasmaQuad spectrometer. This is the instrument used in the single laboratory validation study to be discussed later. The slide is self-explanatory. However, it may be helpful to trace the analyte route through the system.

The sample solution is pumped to the nebulizer where the resulting aerosol droplets of the analyte traverse the spray chamber and enter the plasma through the injector tube of the torch assembly. The energy of the plasma desolvates, dissociates and ionizes the analyte. A portion of these ions enter the expansion chamber through a small hole in the sample cone interface. The ions are then drawn into the spectrometer through even a smaller hole in the skimmer cone and are focused by the lens supply past the photon stop into the quadrupole. By virtue of their mass-to-charge ratios, the ions sequentially pass through the charged rod assembly onto the detector. The resulting signals from the detector are processed by the multichannel analyzer and the data transferred to a dedicated computer.

It is important to note the most critical area of the instrument is the expansion chamber or cone assembly. It is in this area where the oxides and

polyatomic molecular ions are primarily formed and where analyte deposition can occur at the cone orifice causing instrument drift and memory effects.

The following slide (#4) shows the actual instrument. The stand alone unit on the right is the RF generator for plasma. The torch box assembly and spectrometer interface are enclosed behind the dark door in the center of the instrument. On the right are the gas controls for the plasma and on the left are the controls for quadrupole, vacuum pumps and readout systems. The rotary vacuum pumps and required cooling system are behind the instrument and cannot be seen on this slide.

The next slide (#5) shows the torch lighted and with the torch box assembly in the advanced or working position in front of the spectrometer sample cone interface.

The following slide (#6) shows the appearance of the sample cone interface of the spectrometer after a period of operation. The cone is made of nickel and when new is very shiny. The heat of plasma is the main cause for change of appearance. Two hours of operation can account for such a change.

A new sample cone is shown in the next slide (#7). Although shielded by the sample cone during operation, the heat also affects the skimmer cone shown at the right.

With all the advantages offered by ICP-MS there are still some limiting factors. On the next slide (#8) are listed the most common interferences that affect the technique.

Although the inorganic mass spectrum is far simpler and less complex than atomic emission, it is not free of spectral interferences. Spectral interference occurs as an isobaric interference from either an isotope of another element, that form singly or doubly charged ions of the same nominal mass-to-charge ratio, or from polyatomic ions commonly formed in the plasma or interface system from support gases and sample components. The mass range from 12 to 75 amu is the region most affected by polyatomic interferences. The analytes of this region include the first series transition metals - scandium through zinc. Fortunately, the elemental and most of the common polyatomic interferences have been identified.

In Method 200.8 only two of the recommended analytical isotopes experience isobaric elemental interferences. Ruthenium interferes on Mo-98 and krypton on Se-82. However, eight of the analytes can experience a polyatomic interference. These analytes are As, Cd, Cr, Cu, Mn, V and Zn with a remote, but possible interference on Ag. Again, the majority of these analytes are first series transition metals and the polyatomic interferences are well documented and noted in the method. The third spectral interference, abundance sensitivity, is a problem of resolution where the wing of a large ion peak contributes to a small ion peak. These occurrences can be minimized by selecting the proper instrument operating conditions.

The listed physical interferences also are best controlled by operational measures such as: (1) using a peristaltic pump to control and provide a steady rate of sample introduction to the nebulizer, (2) the use of a mass flow

controller to provide accurate gas flow and uniform aerosol transport to the plasma, (3) limiting dissolved solids to 0.2 % (w/v) to reduce the potential clogging of the orifice of the interface cone assembly (4) the use of a water cooled spray chamber to lower the water vapor content of the aerosol to reduce oxide formation and (5) the use of internal standards to correct for matrix suppression. Method 200.8 requires the use of all these procedural measures except the water cooled spray chamber which is listed as a recommendation.

Memory interference results when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sample and skimmer cones and from buildup of the analytes in the spray chamber and sample uptake system. Adequate flushing of the system with a rinse blank reduces the effect. Method 200.8 requires as a minimum, the use of a one minute rinse time. Also, the presence of a memory effect may be assessed during analysis by noting a consecutive drop in replicate integrations.

On the next slide (#9) is a summary of Method 200.8 features. The method is applicable to both aqueous and solid matrices for the analysis of 20 analytes. It should be noted that elements Ca, K, Mg, Na and Fe have not been included in the method because they are normally present at relatively high concentrations in environmental samples and can be determined accurately and more effectively by other techniques. However, the elements thorium and uranium are included because of the increasing interest of these elements in groundwater and because of the relatively good sensitivity of these elements by ICP-MS.

The method provides similar acid digestion procedures for aqueous and solid matrices. This occurs when the remaining particulate material in an evaporated aqueous sample is acid refluxed in the same manner as a solid sample. A combination of HNO_3 and HCl acids is used in both procedures. The resulting analyses are considered to be "total recoverable" determinations.

Prior to ICP-MS analysis, internal standards are added to an aliquot of the digestate. Method 200.8 requires the use of at least 3 internal standards; however, the use of the 5 listed on the slide is recommended and was used in the single laboratory validation study.

Outlined on the next two slides (#10 and #11) are the "total recoverable" sample preparation procedures for aqueous and solid samples, respectively. Specifics included in the outlines are the size sample used, the acid addition, the reflux time and dilution volumes. Note that prior to ICP-MS analysis an aliquot of the digestate is diluted further to limit the dissolved solids to 0.2% (w/v) and to control the chloride concentration to a level of 0.4% (v/v). In each case, the analytical determinations are multiplied by a dilution factor to obtain the sample analyte concentrations.

A combination acid "total recoverable" procedure was selected for sample preparation because it requires less time, is less labor intensive, and past studies have shown it to be equal or superior to the "hard digestion" (HNO_3 + H_2O_2) for solubilizing toxic and priority pollutant metals. With the "total recoverable" procedure insoluble oxides are less likely to occur while the HCl has been shown to stabilize Ag in solution and improves the solubilization of oxides and certain analytes such as Sb and Cr.

As a side note, it may be important to know, that in order to provide uniform sample preparation for the various spectroscopy techniques these same digestion procedures have been incorporated into the recently revised ICP-AES Method 200.7 and the new stabilized temperature graphite furnace atomic absorption methodology, Method 200.9.

On the next slide (#12) are shown the requirements of instrument calibration. After a 30 min warm-up period, a tuning solution containing 5 elements (Be, Co, In, Mg and Pb) is used to check instrument resolution and adjust mass calibration. The Mg isotopes 24, 25, 26 are used to check resolution for the low mass range while the Pb isotopes 206, 207, 208 are used for the high mass range. Mass calibration is adjusted if it has shifted by more than 0.1 amu from unit mass. This solution is also used to check the stability of the instrument.

After tuning is complete, the instrument is calibrated using a calibration blank and two composite standard solutions. Before beginning sample analysis, the calibration is initially verified for all analytes by analyzing a QC sample obtained from an outside source. The analytical result must not exceed ± 10% of the established values of the QC sample. The calibration is then verified on a continuing basis by analyzing a standard solution as surrogate sample at frequency of 10% with the determined value being within the QC window of ± 10% of the true concentration.

As mentioned before, at least three internal standards must be used and their response monitored. If their response falls outside the QC window of +25% to -40% of the original response, the situation must be corrected. This may require only sample dilution or may entail termination of the analysis to clean the sampling cone and/or retune the instrument.

On the next slide (#13) are given the quality control requirements of Method 200.8. For initial demonstration of performance, method detection limits or MDLs and the linear calibration range must be determined. Procedures for these two determinations are described in the method. These two determinations must be completed every six months or whenever there is a significant change in background or instrument response (e.g. changing the detector).

For assessing laboratory performance, a reagent blank and a laboratory fortified blank are analyzed with each batch of samples. If an analyte in the reagent blank determination exceeds its MDL, laboratory or reagent contamination should be suspected. Recovery of the analytes in the fortified blank should be within the established control limits or 85 to 115%, if control limits have not been developed. If recovery is outside the limits, the analysis is out of control. The analysis should be terminated and the problem identified and corrected before continuing the analyses.

To assess analyte recovery from the matrix, 10% of samples are fortified with the same analyte concentration as that used in the fortified blank. If recovery from the sample matrix falls outside the designated range of the fortified blank, a matrix affect should be suspected.

The method detection limits for Method 200.8 are given on the next slide (#14). The aqueous method detection limits are all 1 μg/L or less with the

exception of As, Se, V and Zn. Method detection limits for solids are 1 mg/kg or less with the exception of Se. These, along with instrument detection limits, are included as data tables in Method 200.8.

The next slide (#15) shows the analytical scheme used in the single laboratory validation study. A matrix set of five waters and three solids were used in the study. The five waters consisted of drinking water, well water, pond water, a sewage treatment primary effluent and an industrial effluent. The three solid samples were NITS sediment #1645, EPA electroplating sludge #286, and EPA hazardous waste soil #884. For each matrix, a total of five replicate sub-samples were analyzed in order to make an estimate of precision. Two further sets of duplicate sub-samples were fortified with a multielement analyte mixture, one set a low concentration (10 μg/L to 50 μg/L for aqueous and 20 mg/kg for solids), the other at high concentrations (100 μg/L to 200 μg/L for aqueous and 100 mg/kg for solids) in order to assess element recoveries in a given matrix. A total of nine samples were therefore analyzed for each matrix with the total number of samples 72. The digestate or aliquots of the digestate were analyzed by both ICP-AES and ICP-MS.

On the next slide (#16) are given the instrument operating conditions used in the single laboratory validation study. These are the same operating conditions that appear in Method 200.8 and Method 200.7, respectively. There is an error in the ICP-AES listed conditions. The time used for data acquisition was a 16 sec integration period not 20 sec as shown. Also, of the ICP-MS operating conditions given, only the minimum of 3 replicate integrations is required by Method 200.8.

During the course of the single laboratory validation study, spectral interferences were experienced by both technniques in the analysis of certain samples. Those which were most significant are listed on the next slide (#17). The analysis of all samples by ICP-MS required correction of the interference on As, V and Cr from the polyatomic ions of argon-chloride and chlorine-oxide. These corrections were anticipated and necessary because of the sample preparation procedure used and the inherent concentration of chloride in environmental samples. Cu-65 was use for copper analysis of the industrial effluent sample because the high sodium concentration caused a $NaAr^+$ interference on Cu-63. Also, correction of MoO on Cd-111 was necessary because the industrial effluent contained approximately 1 mg/L Mo.

The largest ICP-AES spectral interferences occurred in the analysis of the sediment and sludge samples. The interference was of an interelement direct spectral overlap nature from high concentrations of Cr (#1645-28,000 mg/kg and #286-7500 mg/kg) and Fe (#1645-89,000 mg/kg). The interferences effects in these two samples were so severe that it prevented the analysis of Th and Se in the sediment sample and caused the reporting of inaccurate data for Sb in both the sediment and electroplating sludge samples.

In the next slide (#18) are recovery data from the fortified primary sewage treatment effluent. Except for Ba and Th the recoveries are between 85-115%. The low Ba recovery is attributed to the presence of sulfate. However, the low Th recovery cannot be explained. In the other four aqueous

samples, Th recoveries were acceptable. The formation of insoluble phosphates during sample processing has been suggested, but not confirmed.

The next 5 slides (#19-23) are figures that contain ICP-MS/ICP-AES comparison plots for the elements Cu, Mn, Ni, Ag, and V. In each case the center bar represented the mean concentrations of the five replicates and the vertical bars represents two standard deviations of the replicates each side of the mean. The concentration of the analyte is noted on the y-axis, and the sample matrix along the x-axis. The ICP-MS data are noted by the wider bars. These five elements were selected for presentation because of the available data. We will step through these slides for your observation without additional discussion.

These five figures will not appear in the proceedings of this meeting because they are being published elsewhere. However, these figures, along with others, and a complete dicussion of the single laboratory validation study has been prepared as a draft report by Dr. Stephen Long of Technology Applications, Inc. For those interested in obtaining a copy of the report see me following this session or during the course of the conference.

Given in this slide (#24) is a brief summary of the single-laboratory validation study. Approximately 3000 analytical determinations were completed. The matrix analyte background data were used to compare the two spectroscopic techniques using a paired t test. A null hypothesis approach was used with the analyte means of the two techniques being compared at the 5% level of significance. For an analyte to be included in this comparison, a requirement was set that data must be available for at least two of the matrices. For aqueous matrices, 11 analytes qualified; for the solid matrices, 17 analytes qualified. Only Se, Tl and U did not meet the requirements. These comparisons represented 860 determinations. A significant difference between the two techniques exists if calculated p value is < the level of significance set at 0.05. The lowest p value calculated was 0.08 for Zn in water. Therefore, it would appear that the two techniques provide data that are equivalent in quality for the range of concentrations applicable to both techniques.

The summation of the precision determined in the study was the following. Intra-sample precision of the two techniques was similar being 1 to 2% RSD. Although the overall precision appears to be sample limited, for the matrices tested, the mean RSD was < 10% except for the hazardous waste soil. Higher RSDs for this sample were attributed to the inhomogenity of the sample material. Of the 298 spike duplicate determinations, only 8% had a relative percent difference (RPD) that exceeded 10%. If the hazardous waste soil duplicates were not included in the calculation, the number would drop from 8% to < 6%.

Recovery of the fortified analytes was very good. For the fortified blank, recovery ranged from 94% to 107%. For the fortified matrices < 10% of the recoveries were outside the 85% to 115% limits. As for specific analytes, Sb gave good recovery in the aqueous matrices but low recoveries (55.4% - 81.2%) in the solid matrices. Poor recoveries obtained for Ba in the sewage effluent, hazardous waste soil and electroplating sludge have been attributed to precipitation as the sulfate. Low recoveries of Th in the sewage effluent and hazardous waste soil cannot be explained at this time. However, all low

recoveries appear to be matrix related and with the exception of these three elements, recovery data indicates adequate method performance for the range of elements and matrices study.

On the last slide (#25) is a summary description of the joint USEPA/AOAC multilaboratory ICP-MS study currently being conducted. This project was started in early December, 1989 after concurrence by AOAC that a joint effort multilab study of Method 200.8 would be of benefit to the analytical community doing environmental analyses. The study design that you see here was completed and agreed upon by both parties in early January, 1990. Samples and ampul concentrates were shipped to the 18 participating laboratories on March 22, 1990, and as of May 3, seven of the participants had already forwarded data packages.

In addition to determining sample background concentrations, sample aliquots are to be fortified as Youden pairs with analyte concentrations necessary to collect the data required. For determinations in reagent, tap and ground water this is to be done at three levels of concentration. The participants will use their own reagent water and a local drinking water for sources of these two types of water. For the ground water determinations each laboratory has received for analysis one of the waters collected from five different sources. Besides the reagent, tap and ground water determinations, eight of the laboratories will receive for analysis a wastewater digestate and also will analyze a wastewater of their choice.

The data from this study will be compiled by EPA and presented to the AOAC Executive Board for approval along with a copy of the method in the AOAC format. The project and final report are scheduled to be completed by October 1990. The results of the study are to be presented as a poster paper on September 12 at the annual AOAC meeting in New Orleans, LA.

For more detailed information concerning this study, please contact James Longbottom of the Quality Assurance Division of EMSL-Cincinnati.

This concludes my presentation.

SINGLE LABORATORY EVALUATION OF METHOD 200.8 DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY ICP MASS SPECTROMETRY

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Environmental Monitoring and Systems Laboratory

and

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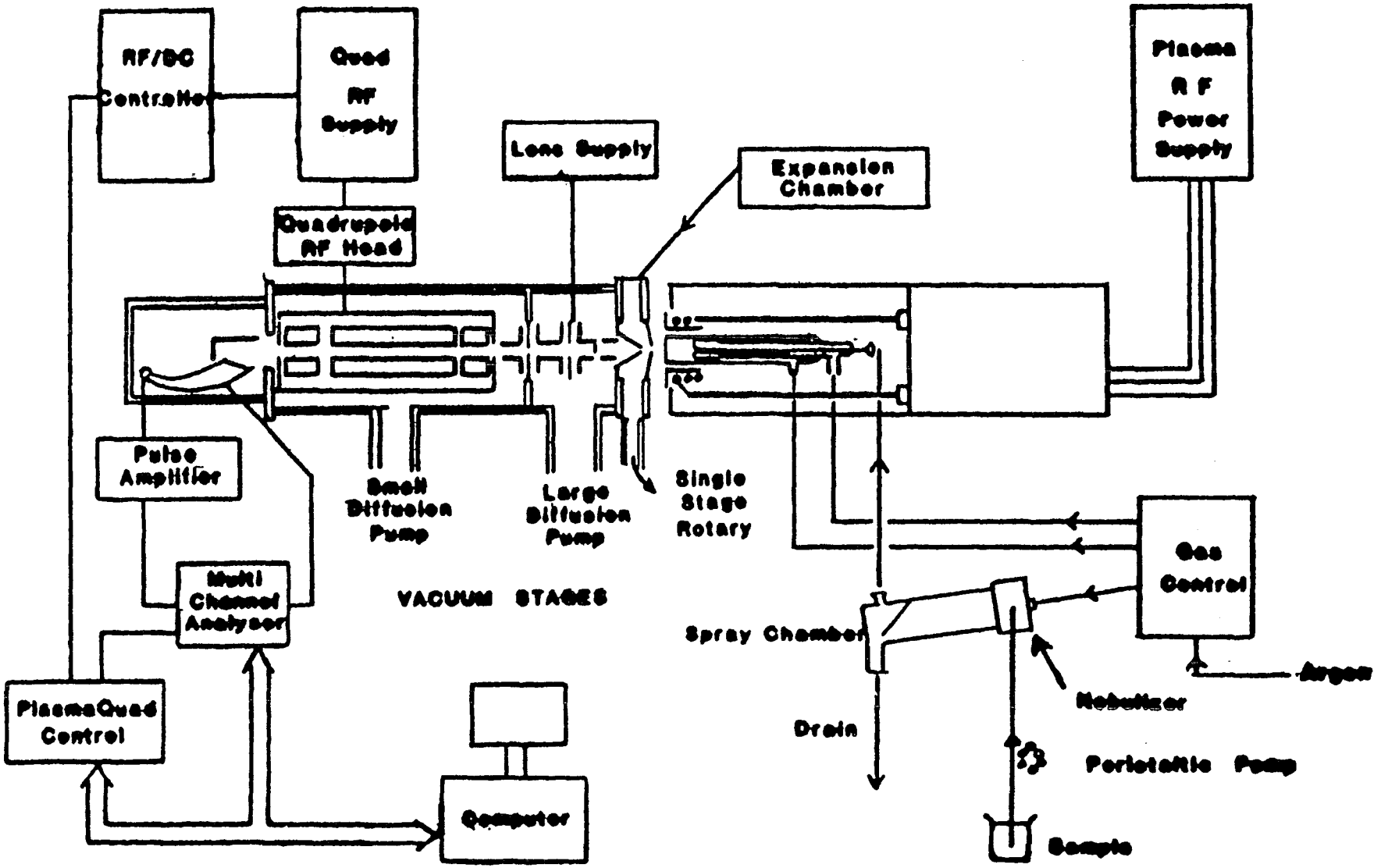
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

ADVANTAGES

1. LINEAR RANGE 5 - (8) ORDERS
2. PPT DETECTION LIMITS
3. "SIMULTANEOUS" DETERMINATION OF PERIODIC TABLE
4. ISOTOPE RATIO INFORMATION
   ISOTOPE DILUTION CAPABILITY
5. FACILITY FOR QUALITATIVE ANALYSIS
6. RAPID SAMPLE THROUGHPUT

PlasmaQuad Schematic



ICP-MS INTERFERENCES

SPECTRAL
1. ISOBARIC ELEMENTAL - Mo, Se
2. POLYATOMIC IONS - 8 analytes
3. ABUNDANCE SENSITIVITY - Resolution

PHYSICAL
1. VISCOSITY - Peristaltic pump
2. AEROSOL TRANSPORT - Mass flow control
3. DISSOLVED SOLIDS - Limit 0.2% (w/v)
4. OXIDE FORMATION - Cooled spray chamber
5. SUPPRESSION - Internal standards

MEMORY - ANALYTE BUILDUP
1. SAMPLE UPTAKE SYSTEM
2. CONE DEPOSITS
3. DROP IN REPLICATE INTEGRATIONS

METHOD 200.8 : SUMMARY FEATURES

SCOPE & APPLICATION : Ground, Surface and Drinking Waters
Wastewater, Sludge and Solid Waste

ELEMENT COVERAGE : Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb
Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn

SAMPLE DIGESTION : Nitric, Hydrochloric acid

DISSOLVED SOLIDS : 0.2% Limit

INTERNAL STANDARDS : Sc, Y, In, Tb, Bi

SAMPLE PREPARATION - TOTAL RECOVERABLE

1. AQUEOUS

100ml sample + 1ml conc. nitric
0.5ml conc. HCl

Heat to reduce volume to 15ml. Reflux for 30min. Cool and dilute to 50ml.

Dilute 20ml ⟶ 50ml and analyze.

0.4% HCl, 0.8% nitric. Dilution factor 1.25.

SAMPLE PREPARATION - TOTAL RECOVERABLE

2. SOLIDS

1g sample + 4ml (1+1) nitric
10ml (1+4) HCl

Reflux for 30min. Cool and dilute to 100ml.
Centrifuge or allow to stand overnight.

Dilute 10ml ⟶ 50ml and analyze.

0.4% HCl, 0.4% nitric. Dilution factor 0.5

METHOD 200.8 : CALIBRATION

DEMONSTRATION OF INITIAL CALIBRATION

- Tuning Solution (mass calibration)
- Quality Control Sample QCS

CALIBRATION VERIFICATION

- Standard run as surrogate sample at 10% frequency
  QC Window ± 10% of true value

INTERNAL STANDARDIZATION

- Minimum of Three Internal Standards
  QC Window + 25% of Original Response
  - 40%

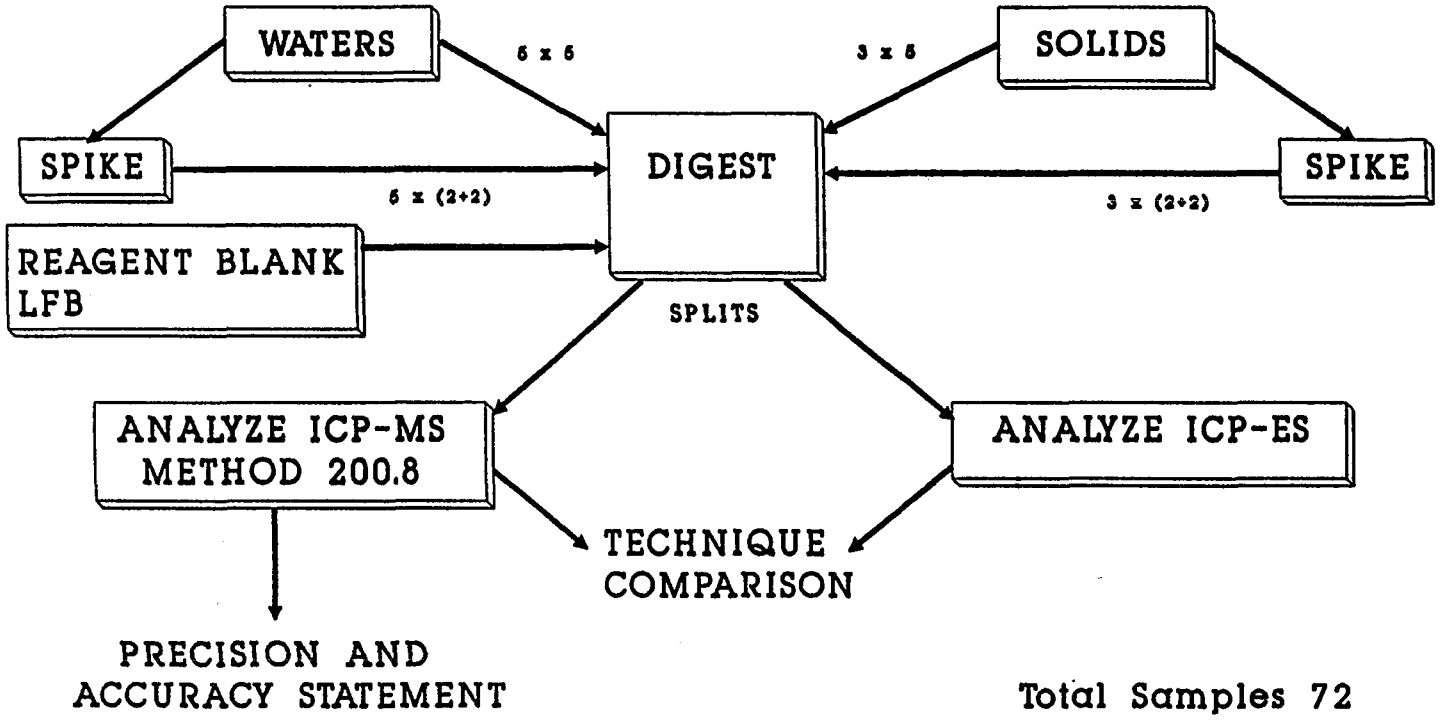
METHOD 200.8 : QUALITY CONTROL

1. INITIAL DEMONSTRATION OF PERFORMANCE
   - MDL, Linear Calibration Range
2. ASSESSING LABORATORY PERFORMANCE
   - Reagent Blank (LRB) - 1 per batch
   - Laboratory Fortified Blank (LFB) - 1 per batch
3. ASSESSING ANALYTE RECOVERY
   - Laboratory Fortified Sample Matrix - 10% of samples

TOTAL RECOVERABLE METHOD DETECTION LIMITS

ELEMENT	MASS	AQUEOUS (ug/l)	SOLIDS (mg/kg)
Al	27	1.0	0.4
Sb	121	0.4	0.2
As	75	1.4	0.6
Ba	137	0.8	0.4
Be	9	0.3	0.1
Cd	111	0.5	0.2
Cr	52	0.9	0.4
Co	59	0.09	0.04
Cu	63	0.5	0.2
Pb	208	0.6	0.3
Mn	55	0.1	0.05
Mo	98	0.3	0.1
Ni	60	0.5	0.2
Se	82	7.9	3.2
Ag	107	0.1	0.05
Tl	205	0.3	0.1
Th	232	0.1	0.05
U	238	0.1	0.05
V	51	2.5	1.0
Zn	66	1.8	0.7

ICP-MS METHOD 200.8 SINGLE LAB VALIDATION



Total Samples 72

METHOD 200.8 VALIDATION
INSTRUMENT OPERATING CONDITIONS

	ICP-MS	ICP-ES
Instrument	VG PlasmaQuad Type I	Jarrell-Ash AC 1160
Forward power	1.35 kW	1.1 kW
Coolant flow rate	13.5 l/min.	19 l/min.
Auxiliary flow rate	0.6 l/min.	0.3 l/min.
Nebulizer flow rate	0.78 l/min.	0.63 l/min.
Solution Uptake	0.6 ml/min.	1.2 ml/min.
Repl. Integrations	3	4
Data acquisition	320 us dwell 2048 channels 85 sweeps	1620s integration 48 channels

SPECTRAL INTERFERENCES 200.8 ELEMENT SUITE

- ICP-MS

    1. Chloride on As-75, V-51, Cr-52
    2. Na(Ar) on Cu-63 (effluent)
    3. Mo(O) on Cd-111 (effluent)

- ICP-ES

    1. Cr on Sb 206.8 nm (NIST 1645)
    2. Cr on Sb 206.8 nm (EPA 286)
    3. Cr on Th 283.7 nm (NIST 1645)
    4. Fe on Se 196.0 nm (NIST 1645)

SPIKE RECOVERIES - PRIMARY EFFLUENT

ELEMENT	BKGRD CONC. (ppb)	SPIKE (ppb)	RECOVERY (%)
Sb	1.5	10	95.7
As	<1.4	50	104.2
Ba	202	50	79.2
Be	<0.3	10	110.5
Cd	9.2	10	101.2
Co	13.4	10	95.1
Pb	17.8	10	95.7
Ni	84.0	10	88.4
Se	<7.9	50	112.0
Ag	10.9	50	97.1
Tl	<0.3	10	97.5
Th	0.11	10	15.4
U	0.71	10	109.4
V	<2.5	50	90.9
Zn	163	50	85.8

VALIDATION STUDY SUMMARY

- ANALYTICAL DETERMINATIONS - 3000
- MATRIX COMPARISON ICP-MS / ICP-AES
    1. Paired t test, $p = 0.05$ for $n > 2$
    2. Aqueous (11) - Solids (17) 860 determinations
    3. Aqueous Zn, $p = 0.08$
- PRECISION
    1. Intra-sample RSD 1-2%
    2. Matrices, mean RSD <10%
    3. 8% RPD >10% - 298 determinations
- RECOVERY
    1. Fortified blanks 94-107%
    2. <10% Fortified matrices >85-115%
    3. Sb, Ba and Th

JOINT USEPA/AOAC MULTILABORATORY STUDY

- STUDY PERIOD, DEC 1989 TO OCT 1990

STUDY DESIGN

WATER SOURCES	YOUDEN PAIRS	
REAGENT	3	
TAP	3	BACKGROUND
GROUND (5)	3	+ DATA
WASTE (Digestate)*	2	
WASTE (of choice)*	1	

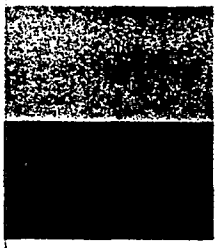
- PARTICIPATING LABORATORIES 18 - (8)*

MR. FIELDING: Our next speaker is Jim Rice who will talk about ICP performance for the measurement of 14 trace metals in power plant waste streams.

Jim?

EPRI

13th Annual EPA Conference on
Analysis of Pollutants in the Environment
Norfolk, Virginia
May 9-10, 1990



ICP PERFORMANCE FOR THE MEASUREMENT OF FOURTEEN TRACE METALS IN POWER PLANT WASTE STREAMS

By

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Redondo Beach, California

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Consulting Engineer
Olney, Maryland

and

Winston Chow, PE
Electric Power Research Institute
Palo Alto, California

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ABSTRACT

A 26 laboratory study by the Electric Power Research Institute determined the performance of an Inductively Coupled Plasma Atomic Emission Spectroscopic (ICP) method for measuring 14 elements (Al, Ba, Be, B, Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn) in typical power plant waste streams. The resulting single operator and overall precision were used to compute limits of detection and quantitation for each of the elements in each matrix. These limits of detection are compared to published EPA detection limits. In addition, an algorithmic approach was used to compare ICP precision and recovery results from the utility sample matrices to those obtained in reagent grade water samples. From this analysis the presence or absence of chemical matrix effects were investigated.

BACKGROUND AND OBJECTIVES OF THE ANALYTICAL METHODS QUALIFICATION PROJECT

The utility power industry is required under the Federal Water Pollution Control act to monitor their discharges for a number of parameters. As a result of the 1976 Consent Decree (National Resources Defense Council versus Train), the EPA was required to establish effluent limitation guidelines, pre-treatment standards, and also new source performance standards for 65 pollutant classes (129 specific priority pollutants). In anticipation of a requirement that utility discharges be monitored for some or all of the priority pollutants, EPRI Project RP 1851-1 was initiated both to collect concentration and frequency data about utility aqueous discharges and to assemble a set of sampling and analysis guidelines for the species of interest in those discharges. Utility chemists would then have a firm basis to select methods to monitor the species of interest in those discharges.

The data bases produced in Phase I of EPRI Project RP 1851-1, Sampling and Analysis of Utility Pollutants (SAUP), contain both the average steam electric power plant discharge concentrations for all conventional, nonconventional, and priority pollutants (1) as well as a comprehensive compilation of precision and bias data on the methods used to monitor the pollutants (2). In developing this latter data base, it was found that the validation data were often obtained for matrices and concentrations not representative of the steam electric industry. The lack of an independent data base derived from utility laboratory performance in typical discharge matrices placed individual utilities at a disadvantage during siting and permit negotiations. At the same time, there was a trend toward setting effluent discharge limits at the end of pipe or edge of the mixing zone at the water quality criteria concentration. Many of these water quality criteria are at or below the detection limit of current analysis methods. In order to determine whether current monitoring methodology is capable of detecting pollutants at the EPA detection limit or the water quality criteria concentration, EPRI instituted a project under RP 1851-1 entitled Utility Aqueous Discharge Monitoring - Analytical Methods Qualification (AMQ).

The primary objective of the AMQ Project is to collect precision and bias data for methods used to determine selected parameters and elements in utility discharge streams. The required analytical data are collected through collaborative testing using representative utility laboratories. The limits of detection and quantitation derived from this project thus provide a realistic estimate of the capabilities of EPA-approved methods in the compliance monitoring situation under utility process stream and laboratory operating conditions.

The specific AMQ project goals are to:

- Establish both the single operator and overall precision that can be expected from utility laboratories utilizing the selected compliance methods.
- Establish whether any statistically significant bias exists in a given matrix for the methods validated.

- Determine the expected limits of detection and quantitation of compliance methods when used by a utility analyst for utility matrices.

Table I provides an overview of the entire AMQ project. It is divided into four parts in order to minimize the impact on the participating industry laboratories and to permit modification of the test design to reflect changing environmental issues or regulatory requirements. The elements and parameters in each part were selected on the basis of their importance to the utility industry, regulatory interest, and a comparison of discharge and intake concentrations. Under the AMQ-III validation program, the subject of this paper, Inductively Coupled Plasma (ICP) was validated for 14 metals in 6 different utility matrices.

AMQ-III TEST METHODOLOGY

The AMQ project is based on the premise that a method qualification project should use matrices representative of those encountered by the analyst in routine work. Furthermore, since the shipment and storage of samples is part of the normal analysis procedure at most laboratories and comparison of the results from different laboratories on split samples is often encountered in compliance monitoring, the test program should include spiking the matrices and sending aliquots to each participant. A detailed review of the AMQ test and analysis protocols can be found in references (3,4). A summary of the test program protocols is provided in the following paragraphs.

Laboratory Selection

The participation of utility laboratories was solicited through the offices of EPRI and the Utility Water Act Group (UWAG). Twenty laboratories were eventually enlisted to validate the AMQ-III elements.

Laboratories were contacted before the test to determine which labs had the experience or interest in determining the elements in the seawater samples. These laboratories participated in a pre-test study to assist in selecting test concentrations, assessing sample stability, and providing the operators with some experience with those difficult matrices. The QA/QC vial was used as an absolute, independent measure of the bias associated with an individual laboratory.

Matrices Tested

A key component of this validation effort was the use of typical utility matrices. To that end, sufficient quantities of river water, ash pond overflow, seawater intake, seawater discharge (seawater with a proportional amount of fireside wash added to simulate routine plant discharges), and treated chemical metal cleaning wastes (TCMCW) were obtained from utility sources. Following the overall objective of simulating typical NPDES monitoring, the test matrices were homogenized, spiked and then split. In addition to these samples, spiked reagent grade water and a QA/QC vial supplied by the ERA (Environmental Research Associates) were also sent to

participating laboratories. All laboratories were required to analyze the reagent grade water and QA/QC vial while the analysis of the TCMCW sample was optional.

Test Concentration Selection

Depending on the background concentration, every effort was made to have the lower test concentrations near the expected detection limit of the method. This requirement was difficult to meet in some of the matrices, due to the high background. The remaining test concentrations were selected to stay within the published (5) estimate of the optimum analytical range, if possible. A total of 4 test concentrations (neat and three spiked) were prepared for each matrix and element.

Sample Preparation

Samples were prepared (3,4) by filling a polyethylene 120 L churn (Figure 1) splitter with the acid (HNO_3) stabilized test matrix. The volumes were determined by weight and density measurements and were accurate to ±100 mL based on the calibrated accuracy of the scale. After the volume was determined, weighed amounts of single element 1000 ug/L certified AAS standards were added to the churn splitter using Teflon beakers. After the addition of a spike, the churn was operated for 5 minutes before samples were removed from a spigot at the bottom of the churn. Each sample consisted of a 500 mL aliquot in a precleaned (HCl, HNO_3, high purity water) polyethylene bottle.

QA/QC Activities

A comprehensive QA/QC program was part of the sample preparation and dispersement effort. Internally, the sample spiking and disbursement activities were guided by a test plan whose adherence was audited by personnel not associated with the test program. In addition, test samples from each matrix were selected at random and analyzed prior to shipment to ensure their proper preparation. Samples were also analyzed by GFAAS to determine the stability with time. Based on the seawater pre-test, it was found that barium could not be stabilized in the seawater and TCMCW matrices at the test concentrations. Consequently, barium data from those matrices are not included in the results.

Test Procedures and Reporting Requirements

Each participating laboratory was sent a detailed test protocol describing the sample digestion and analytical procedures. The test protocol contained a copy of EPA Method 200.7 and detailed instructions on the reporting requirements. Each sample was analyzed in duplicate and the results reported to the TRW test coordinator on standardized reporting forms or on a hard-copy computer output from the ICP. A QA/QC survey, covering equipment used, background/experience of the operator, and laboratory practices, was included in this package.

Statistical Analyses

The design of the validation program was based on ASTM D2777-85 using replicate analyses. The data from the test program was reduced using a PC-based statistical program, which implemented the data analysis and outlier test protocols in ASTM D2777-85. All data received from the participants was initially screened for values greater than 5x and less than 1/5 of the expected true values. Laboratories exceeding those limits were asked to check their calculations and reports, but were not asked or permitted to re-analyze their samples. On this error-free data set, the statistical program performed the lab ranking and individual outlier testing to screen the data. The program then computed the single operator and overall precision and recovery at each test concentration along with its linear and curvilinear regression equation for precision and recovery. Figure 2 is an example of overall precision versus true value.

The true concentration was computed by taking the mean of the reported results for the lowest test level and then adding the known amounts of each element added during the sample preparation effort. In most cases for a given element, the lowest test level was the as-received matrix. For selected elements and matrices, small quantities of the element were added to the background concentration to raise their lowest test concentration near the expected ICP detection limit. This approach was taken based on previous test experience to avoid data drop-out due to concentrations below an element's detection limit.

CALCULATION OF THE LIMITS OF DETECTION AND QUANTITATION

Background

An important consideration in selecting an analytical method is its limit of detection (LOD). Over the years, several definitions for limit of detection and its companion concept, limit of quantitation (LOQ), have evolved (Table 2). Under Phase I of RP1851-1, a methodology for computing an LOD was developed utilizing open literature precision data. That approach will be discussed and its problems noted. An alternate approach utilizing the greater amount of data that was derived from the AMQ validation studies will be presented.

Definition of Limit of Detection

In reviewing the sources of LOD definitions (Table 2) several areas of agreement are apparent:

1. The consensus is that the LOD can be defined as some factor times the standard deviation of the blank.

2. The factor chosen depends on the risk level of making false positive identification of zero values and false negative identification of nonzero detectable values.

3. The blank should be well characterized (>10 replicates).

4. The blank sample must be processed exactly as the actual sample.

The key questions remain: What is the value for the factor and what type of standard deviation (single operator, S_0, or overall, S_T) should be used? Based on the definitions in Table 2, the consensus value for the factor appears to be at or near 3. The interpretation of this value in terms of a confidence level depended on the point of view of the reader. If one is only concerned about false positive identifications of zero values, then the 3 sigma limit provides <1% risk of making a false positive identifica- tion. The actual risk involved depends on the number of replicates used to calculate it. Should one also be concerned with the error of not identifying detectable levels of a species, then the 3 sigma LOD represents a 7% chance for both false positive and false negative responses. The 7% risk is for a large number of blank replicates, and the risk increases with a decrease in the number of replicates. It should be noted that most regulatory limits consider only the chance for false positive errors. In those cases, 3 sigma represents a risk level of <1% of falsely identifying a species as present when it is not.

The Environmental Monitoring and Support Laboratory (EMSL) has published an approach to LOD calculation stressing the complete analytical procedure, which includes specifying a matrix, an analytical procedure (calibration through the evaluation of results), and a particular instrument. EMSL proposes the concept of method detection limit (MDL) to describe processing a sample through all the steps comprising an established analytical procedure. The MDL is defined as "minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero" (10). The MDL is determined from replicate analyses of a sample in a given matrix containing the analyte at concentrations 1 to 5 times the estimated MDL. Two approaches are given (8); one employs seven replicate measurements and is expressed as:

$$MDL = t_{(N-1,\ 1-\alpha)} \times S_c \qquad (1)$$

where $N = 7$, $\alpha = 0.01$ and S_c is the standard deviation of the seven replicates. Substituting the appropriate one tail "t" value, equation 1 becomes:

$$MDL = 3.143\ (S_c) \qquad (2)$$

An alternative approach tests the reasonableness of the MDL estimate by using an iterative process (2 sets of seven replicates). The MDL is then defined as:

$$MDL = 2.8681 \times S_{pool} \qquad (3)$$

where S_{pool} is the pooled S_c for the two sets of seven replicates and 2.681 is the value for a single tail $t_{(12,\ 0.01)}$. The MDL approach has been incorporated in promulgated (49 FR 43430, Friday, October 26, 1984) regulations.

Implicit in the LOD discussions by all the quoted authors except Rice was the assumption that single operator precision data are used to calculate the LOD. The reasoning, as expressed by the ACS (9), is that the analyst needs to report his/her detection limit. From a regulatory standpoint, interlaboratory (overall) precision data may be more applicable, since split samples are involved. In our earlier studies (2), LODs were calculated using both single operator, S_0, and overall, S_T, data.

An estimate of the S_0 and S_T values at zero concentration can be obtained from the y-intercept of the precision versus mean test concentration linear regression equations. The drawback of this approach was twofold. First, precision is not a linear function of concentration all the way to zero (Figure 3). In practice, the precision tends to flatten to a value that could be equated to the instrument noise and effects due to a given matrix. A linear regression of precision data, especially with data points far from zero, can underestimate the precision at zero and produce negative intercepts. Negative intercepts were often obtained in earlier studies (2,3,4) and rendered the computation of an LOD impossible.

Recognizing this problem, the statistical program used in the AMQ-I and -II validation efforts was modified to compute curvilinear regression equations in the form:

$$S = ab^T \tag{4}$$

where T is the estimated true value at each test level. These curvilinear equations were found to fit the data from the test program much better than the linear regression equations.

Calculation of the Limit of Detection

The first step in calculating the LOD is to use the precision versus true value and recovery regression equations; they are used to compute a precision versus mean concentration equation. The resulting equations are used to compute the limit of detection in the following manner.

Starting with the EPA definition of an MDL (10, 13), the regression equation for precision based on the mean concentration will be substituted:

$$MDL = t*S \tag{5}$$

$$S = m\bar{x} + b \tag{6}$$

where t is the students t, S the standard deviation, and $\bar{x}$ is the mean concentration. Therefore:

$$MDL = t(m\bar{x} + b) \tag{7}$$

In order to satisfy the EPA requirement that the precision be obtained at a concentration 1 to 5 times an estimated MDL, x will be set equal to the MDL

$$MDL = t(m*MDL + b) \quad (8)$$

or

$$LOD = tb/(1-tm) \quad (9)$$

where t is the "t" value for the degrees of freedom of the precision versus mean concentration regression (related to the number of labs for single operator precision or the total number of data points for overall precision). Equation 6 can be solved directly to obtain an LOD. Using the same substitution approach, the curvilinear equation is:

$$(LOD)/(b^{LOD}) = ta \quad (10)$$

Equation 10 cannot be solved directly; but, using an iterative approach found in a commercial software package (TKSolver Plus), a root can be obtained.

Definition of Limit of Quantitation

In our review (2) of the literature definitions for limit of quantitation, several areas of agreement were noted:

1. The LOQ is equal to a factor times the standard deviation of the blank.

2. The factor is related to the expected/required precision at the LOQ.

As with the LOD calculation, establishing the factor and choosing the type of standard deviation are the key issues.

Compared to the LOD, the LOQ is established in a less rigorous manner. Currie (6) and the ACS (9) define the factor as inversely proportional to the relative standard deviation (RSD) at the LOQ. The ACS (9) has chosen ±10% RSD as the precision expected/required at the LOQ. The choice of ±10% is arbitrary and does not accurately reflect the day-to-day precision that an analyst finds at ppb levels. In TRW's review of the literature validation data (2), RSDs were calculated at the primary drinking water standard and at the average power plant discharge concentration using the overall precision linear regression equations for Flame AAS and GFAAS. The average of all the RSDs computed was 23.5%. This value represents the best generally attainable precision at levels which are encountered in real world analyses. Based on those data, expecting an RSD of ±20% at trace levels seems reasonable and defensible and will be used in the evaluation of the AMQ data.

Rice (12) has suggested that the LOQ be defined as "the lowest true concentration for which the relative overall precision is 20%." This definition parallels the EPA's Practical Detection Limit.

One approach to fulfill that definition is to use the computed linear regression equations for the precision versus mean. The regression equations are in the form of a linear equation:

$$S = m\bar{x} + b \tag{11}$$

Converting the S to relative standard deviation by dividing through by $\bar{x}$:

$$S/x = m + b/\bar{x} \tag{12}$$

Setting the $S/x = 0.2$ and solving for $\bar{x}$:

$$\bar{x} = b/(0.2-m) \tag{13}$$

or

$$LOQ = b/(0.2-m) \tag{14}$$

Using the curvilinear precision equation, the resulting equation would be:

$$b^x/x = 0.2/a$$

or

$$(b^{LOQ})/(LOQ) = 0.2/a \tag{15}$$

TKSolver Plus was also used to solve equation 15.

By taking this approach, the actual concentration which produces an RSD of 20% can be found. For comparison, both single operator and overall precision regression equations were used to produce a value for the LOQ. Negative LOQs are computed from the linear regression data when either the slope exceeds 0.2 or when the intercept is negative and the slope is less than 0.2. In the former case, a slope of >0.2 indicates that an RSD of ±20% was never obtained over the test range.

RESULTS

The linear and curvilinear precision (single operator and overall) versus mean concentration equations were computed using the respective precision versus true value and the recovery regression equations. Using the methodology described, the linear and curvilinear LODs and LOQs by precision type and matrix were computed. Those preliminary results can be found in Table 3 together with the EPA detection limit and the WQC.

Table 3 shows the problems associated with using a linear regression equation to estimate LODs. Most of the time the linear regression precision equations produced negative LODs, probably as the result of the test range being too far away from the detection limit. Even though every attempt was made to have the lower test concentrations near the detection limit, the background concentration of some elements in some matrices did not permit a test range as low as we would have liked. The curvilinear precision regression equations were less sensitive to this problem and, in most cases, were able to produce a positive LOD. Another problem with using the linear regression precision equations was negative slopes. In this case, the data is probably poorly correlated, since is would be quite unlikely that the precision (standard deviation of mean) would increase with decreasing concentration. Consequently, no LODs were computed from linear regression precision equations having a negative slope.

Similar problems with the calculation of an LOQ from the linear regression precision equations were also seen. If the slope was >0.2 (indicating that an RSD of 20% was not obtained over the test concentrations) or the intercept was negative, LOQs could not be computed from the linear regression equations. Once again, the curvilinear regression equations seemed to produce results much more reliably than the linear equations (Table 3).

As part of the final review effort, the LODs in Table 3 will be reviewed to determine whether they will meet EPA guidelines (13) for computing an MDL. As such, the results in Table 3 should be considered preliminary pending the formal review of the RP 1851-1 Project Advisory Committee.

Comparison of EPRI AMQ-III LOD and LOQ to the EPA Detection Limit

The preliminary single operator and overall precision based EPRI LODs and LOQs from the curvilinear regression equations were ratioed to the EPA detection limit in Table 3. To further highlight this comparison, the ratios were collated by matrix and plotted as a bar chart. Where there was no data from the curvilinear regression equation, the linear regression result was used. The overall precision based LODs and LOQs are presented here since they represent the situation (comparison of multiple laboratory data from split samples) found in most NPDES monitoring audits. In all cases, a ratio less than one indicates that the EPRI LOD or LOQ was lower than the EPA detection limit. A ratio greater than one indicates that the EPRI LOD or LOQ was greater than the EPA detection limit. For plotting and interpretation convenience, the y-axis (ratio) is a log scale.

Reagent Grade Water. Reagent grade water should be the closest to the EPA detection limits since the EPA ICP detection limits (5) are the concentrations which produced a net analytical signal three times the standard deviation of the background beneath the spectral line. In application of this definition, the resulting detection limits were based on single operator reagent grade water data. However, except for cadmium, all the EPRI computed LODs are above EPA detection limit (Figure 4). Most of the EPRI LODs are greater than a factor of 3 higher and, for beryllium, iron, and zinc, the LODs were greater than 10 times higher than the EPAs. The EPRI LOQs followed the same pattern; but, since they were usually 2 to 4 times higher than the LODs, most of them were 7 times higher than the EPA detection limit.

River Water. Based on the chemical characterization studies done on each matrix during the test program, river water could be considered the next most complex matrix. In this case (Figure 5), all of the EPRI LODs are greater than 3 times the EPAs and five elements (boron, beryllium, manganese, nickel, and zinc) are 10 times larger than the EPA detection limit. In most cases, the EPRI LOQs were 7 times higher than the EPA detection limit.

Ash Pond Water. The ash pond water sample was taken at the same plant as the river water and consists of the overflow from ash pond. It had a higher TDS and sulfate content then the river water. Both cadmium and chromium were below the EPA detection limit (Figure 6). The remaining elements were 2 times higher than the EPA detection limit. A substantial number of those elements (barium, beryllium, boron, iron, manganese, nickel, and vanadium) were 10 times greater than the EPA detection limit. All the EPRI LOQs were greater than the EPA detection limit and most (except cadmium) were 8 or more times higher than the EPA detection limit.

Seawater Intake and Discharge. Both seawater matrices, as expected, produced similar results (Figures 7 and 8). All EPRI LODs (except for copper in the seawater intake) were 10 times higher than the EPA detection limit. Most of the element's LODs were 20 times greater than the EPA detection limit. Boron and cadmium exhibited LODs 100 times higher than the EPA detection limit in one or both of the matrices. Comparison of the EPRI LOQ to the EPA detection shows an even worse situation as boron, beryllium, iron, nickel, and zinc LOQs were 100 times higher than the EPA detection limit.

Treated Chemical Metal Cleaning Wastes (TCMCW). The TCMCW sample was similar in composition (high sulfate and chloride) to the seawater samples, but with the added organic flocculating agents to remove iron and copper. The LODs computed from the precision data taken from this matrix are not as bad as the seawater samples, but show only 3 elements (cadmium, copper, and vanadium) having an LOD less than 10 times the EPA detection limit (Figure 9). All elements having data were 4 times higher than the EPA detection limit. Only the LOQ for aluminum was less than 10 times the EPA detection limit.

Summary of EPRI LOD Results. Figure 10 shows the percentage of reporting elements having an LOD between 0.1 to 1, 1 to 10, 10 to 100, and 100 times greater than the EPA detection limit. First, this three-dimensional bar chart shows that, though different, the results from the reagent grade water (RGW), river water (RW), and ash pond overflow (APO) are comparable. On the other hand, the seawater intake and discharge (SW-I and SW-D) and the TCMCW have similar results. Secondly, the performance, based on increasing LOD, is much worse in the complex matrices. Thirdly, even though the LODs in the RGW matrix were the lowest of the matrices studied, almost 70% of them were between 2 to 9 times higher than the EPA's and a significant (23%) were 10 times higher than the EPA's.

At the minimum, these results show that detection limits will vary by matrix, and that fact should be considered when a discharge or performance limit is set.

Comparison of EPRI AMQ-III LODs to EPA Water Quality Criteria

Water Quality Criteria (WQC) represent another benchmark that utility laboratories are being required to meet. A similar comparison of EPRI LODs for those elements having a proposed or approved WQC published in the Federal Register was performed. The results of those comparisons by matrix are found in Figures 11 through 16. The WQC limits are generally higher than the EPA detection limits and, for most of the elements having WQCs, the EPRI overall LOD was within a factor of 1 to 10 of the WQC. However, the EPRI LOD for lead is consistently a factor of 10 or 100 greater than the WQCs in all matrices. In the APO, SW-I/D, and TCMCW matrices, the EPRI LOD is 10 to 100 times the EPA WQC. The EPRI LOD for aluminum in the SW-D/I and TCMCW matrices was consistently a factor of 10 or more than the WQC limit. Finally, only one element, zinc, consistently had an EPRI overall LOD lower than the EPA WQC in all the matrices.

These data indicate that most laboratories would have a difficult time determining an element at its WQC.

Matrix Effects

As part of the data analysis effort, the slopes of the precision and recovery linear regression equations for each discharge stream were compared to the slopes for reagent grade water. Standard statistical tests were employed to determine whether the differences seen were significant. Table 4 summarizes the results of the analysis. No significant trends were seen based on significant differences between the slopes of the single operator and overall precision, and recovery equations. In fact, one would have expected more elements to have had significant slope differences for matrices such as the two seawater. This prediction did not turn out to be true. Part of the problem with this sort of statistical comparison is that the error bands associated with the slopes are relatively large and get worse with matrices such as seawater. As a result, differences tend to be obscured in the same matrices where one might predict there to be a matrix effect. Additional development effort is required to devise a statistical test to determine the presence of a matrix effect.

SUMMARY

The EPRI RP 1851-1 AMQ validation programs have developed a comprehensive data base of precision and bias data using utility laboratories analyzing typical utility discharge streams. These data have shown that EPA detection limits based on single operator tests in reagent grade water do not produce similar detection limits. In fact, detection limits 10 to 100 times the EPA detection limits have been seen. In light of these differences, consideration should be given to setting detection limits that are more representative of the real world performance of NPDES monitoring methods.

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Table 1

UTILITY AQUEOUS DISCHARGE MONITORING-
ANALYTICAL METHODS QUALIFICATION (AMQ)
OVERALL PROJECT PLAN

Project Title	Part	Round	Test Program Scope	
			Parameters	Method
Sampling and Analysis of Utility Pollutants	*		--	--
Analytical Methods Qualification	I	1	As, Se	GFAAS**
		2	Ni, Pb, Cr, Cu	GFAAS
Analytical Methods Qualification	II	1	Cd	GFAAS
			Hg	CVAAS
			Fe, Zn	Flame AAS
Analytical Methods Qualification	III	1	Al, B, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn	ICP

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* Initial effort under EPRI Project RP 1851-1 which involved collection and analysis of data on discharge rates and data on the analytical precision and bias for utility discharge species.

** Approximately 6 seawater laboratories determined As and Se by GHAAS.

GFAAS = Graphite Furnace Atomic Absorption Spectrometry

GHAAS = Gaseous Hydride AAS

CVAAS = Cold Vapor AAS

ICP = Inductively Coupled Argon Plasma Optical Emission Spectroscopy

Table 2

LOD DEFINITION FROM VARIOUS SOURCES

Author	Title	Definition	Mathematical Interpretation	Degrees of Freedom
Currie (6)	Decision Limit	$L_C = 1.645\sigma_B$	5% chance of reporting zero value as detected.	Infinite
	Detection Limit	$L_D = 3.290\sigma_B$	5% chance of reporting zero value as detected or not reporting a real value as >0.	Infinite
Kaiser (7,8)	Limit of Detection	$LOD = 3\sigma_B$	Approximately a 5% risk of reporting zero values as detected for normal distributions and as high as 11% risk of reporting zero values as detected for asymmetric or broad distributions.	Infinite
ACS (9)	Limit of Detection	$LOD = 3\sigma_B$	7% chance of reporting zero value as detected or not reporting a real value as >0.	Infinite
EPA/EMSL (10)	Method Detection Limit	$MDL = 3.143\sigma_B$	1% chance of reporting zero value as detected.	6
Rice (11)	Critical Level	$LC = 2.576\sigma_B$	0.5% risk of reporting zero value as detected or not reporting a real value as >0.	Infinite
	Limit of Detection	$LOD = 4.652\sigma_B$	1.0% risk of reporting zero value as detected or not reporting a real value as >0.	Infinite

* Rice also suggests using overall precision data from interlaboratory studies on real, spiked samples.

Table 3

Summary of AMQ-III ICP LOD and LOQ Data

			TOTAL	ESTIMATED TEST			LINEAR		CURVILINEAR		DETECTION	QUALITY								
			NUMBER OF	CONCENTRATION (ug/L)		MATRIX	COMPUTED	COMPUTED	COMPUTED	COMPUTED	LIMIT	CRITERIA	LINEAR		CURVILINEAR		LINEAR		CURVILINEAR	
ELEMENT	MATRIX	PRECISION	DATA PTS.	LOW	HIGH	EFFECT?	LOD (ug/L)	LOQ (ug/L)	LOD (ug/L)	LOQ (ug/L)	(ug/L)*	(ug/L)**	LOD/EPA	LOQ/EPA	LOD/EPA	LOQ/EPA	LOD/WQC	LOQ/WQC	LOD/WQC	LOQ/WQC
Al	RV	Single	142	180	443	Y/N/N	Neg. slope	Neg. slope	21.1	39.0	45	87.0			0.5	0.9			0.2	0.4
		Overall	142				78.9	189.4	182.0	399.0	45	87.0	1.7	4.2	4.0	6.6	0.9	2.2	2.1	3.4
	APO	Single	142	405	894	N/N/N	Neg. LOD	Neg. LOQ	80.1	160.0	45	87.0			1.8	3.6			0.9	1.8
		Overall	143				Neg. LOD	Neg. LOQ	106.0	240.0	45	87.0			2.4	5.3			1.2	2.8
	SW-I	Single	64	1510	6030	N/N/N	Neg. slope	Neg. slope	1059.0	1789.0	45	87.0			23.5	39.8			12.2	20.6
		Overall	64				549.0	1195.1	1224.0	2579.0	45	87.0	12.6	26.6	27.2	57.3	6.9	13.7	14.1	29.6
	SW-D	Single	72	1980	7490	N/N/N	Neg. LOD	Neg. LOQ	83.8	165.0	45	87.0			1.9	3.7			1.0	1.9
		Overall	72				Neg. LOD	Neg. LOQ	1817.0	NC	45	87.0			40.4				20.9	
	RGW	Single	144	193	809		Neg. LOD	Neg. LOQ	59.4	118.0	45	87.0			1.3	2.6			0.7	1.3
		Overall	144				Neg. LOD	Neg. LOQ	117.0	279.0	45	87.0			2.6	6.2			1.4	3.2
	TCNCW	Single	120	1390	2200	N/N/Y	Neg. slope	Neg. slope	208.0	371.0	45	87.0			4.6	8.7			2.4	4.5
		Overall	120				1597.0	843.2	1479.0	NC	45	87.0	1.3	3.4	32.9		0.7	2.8	17.0	
B	RV	Single	138	40	104	N/N/N	Neg. slope	Neg. slope			5									
		Overall	140				Neg. slope	Neg. slope	136.0	190.0	5				27.2	38.0				
	APO	Single	136	350	794	N/N/N	71.3	194.2	39.1	84.9	5		14.3	38.8	7.8	17.0				
		Overall	139				153.5	1373.9	176.0		5		30.7	274.8	35.2					
	SW-I	Single	64	4590	8810	N/N/N	Neg. slope	Neg. slope	1466.0	2288.0	5				293.2	457.6				
		Overall	64				Neg. LOD	Neg. LOQ	1139.0	2345.0	5				227.8	469.0				
	SW-D	Single	68	4590	9430	N/N/N	Neg. LOD	Neg. LOQ	369.6	729.0	5				73.8	145.8				
		Overall	69				Neg. LOD	Neg. LOQ	1004.0	2225.0	5				200.8	445.0				
	RGW	Single	136	25.2	97.2		Neg. LOD	Neg. LOQ			5									
		Overall	138				Neg. LOD	Neg. LOQ			5									
	TCNCW	Single	120	620	1020	N/N/N	Neg. LOD	Neg. LOQ	213.0	439.0	5				42.6	87.8				
		Overall	120				4994.5	861.9		NC	5		998.9	172.4						
Ba	RV	Single	136	15	143	N/N/N	3.4	6.5			2			3.3						
		Overall	140				Neg. slope	Neg. slope			2									
	APO	Single	144	190	447	N/N/N	Neg. LOD	Neg. LOQ	8.4	17.1	2				3.2	6.4				
		Overall	139				Neg. LOD	Neg. LOQ	21.8	44.3	2				10.9	23.2				
	SW-I	Single	64	N/A	N/A						2									
		Overall	64								2									
	SW-D	Single	68	N/A	N/A						2									
		Overall	70								2									
	RGW	Single	140	9.9	86.6		Neg. slope	Neg. slope	5.9	11.8	2				3.0	5.5				
		Overall	141				6.2	14.6	8.4	17.3	2		3.4	7.3	4.2	8.7				
	TCNCW	Single	128	N/A	N/A						2									
		Overall	128								2									

Table 3

Summary of AMQ-III ICP LOD and LOQ Data (continued)

			TOTAL	ESTIMATED TEST			LINEAR		CURVILINEAR		DETECTION	QUALITY								
			NUMBER OF	CONCENTRATION (ug/L)		MATRIX	COMPUTED	COMPUTED	COMPUTED	COMPUTED	LIMIT	CRITERIA	LINEAR		CURVILINEAR		LINEAR		CURVILINEAR	
ELEMENT	MATRIX	PRECISION	DATA PTS.	LOW	HIGH	EFFECT?	LOD (ug/L)	LOQ (ug/L)	LOD (ug/L)	LOQ (ug/L)	(ug/L)*	(ug/L)**	LOD/EPA	LOQ/EPA	LOD/EPA	LOQ/EPA	LOD/WQC	LOQ/WQC	LOD/WQC	LOQ/WQC
Be	RW	Single	132	2	27	N/N/N					0.3	5.3								
		Overall	134				5.5	9.6			0.3	5.3	11.5	31.5			0.7	1.8		
	APO	Single	134	7	45	N/N/Y	0.3	0.7			0.3	5.3	1.0	2.3			0.1	0.1		
		Overall	134				5.7	14.9			0.3	5.3	19.1	49.6			1.1	2.8		
	SW-I	Single	80	27	140	N/N/N	Neg. slope	Neg. slope	14.0	25.0	0.3	5.3			44.7	86.0			2.6	4.9
		Overall	79				3.4	8.4			0.3	5.3	11.2	28.0			0.6	1.6		
	SW-D	Single	78	39.8	179	N/N/N	Neg. LOD	Neg. LOQ	6.8	792.0	0.3	5.3			22.0	2640.0			1.2	149.4
		Overall	79				5.6	7.7	20.0	43.9	0.3	5.3	10.8	25.5	66.7	146.3	0.6	1.4	3.8	8.3
	RSW	Single	132	2.9	25.4		1.1	3.5			0.3	5.3	3.7	7.7			0.2	0.4		
		Overall	132				4.6	9.0			0.3	5.3	13.3	30.1			0.8	1.7		
	TCMCV	Single	104	25.2	90.1	N/N/N	Neg. LOD	Neg. LOQ			0.3	5.3								
		Overall	105				Neg. LOD	Neg. LOQ			0.3	5.3								
Cd	RW	Single	142	14.3	65.9	Y/N/N	Neg. slope	Neg. slope	14.8	83.3	4	1.1			3.4	5.8			12.4	21.2
		Overall	142				13.7	29.4	16.3	94.6	4	1.1	3.4	7.4	4.1	8.7	12.5	26.8	14.8	31.5
	APO	Single	138	22.6	86.6	N/N/Y	8.6	10.9			4	1.1	1.1	2.6			3.8	9.3		
		Overall	141				1.5	6.6			4	1.1	0.5	1.5			1.7	5.5		
	SW-I	Single	70	163	246	N/N/N	Neg. slope	Neg. slope	118.0	151.0	4	1.1			29.5	37.8			107.3	137.3
		Overall	71				Neg. slope	Neg. slope	152.0	295.0	4	1.1			38.0	73.8			138.2	268.2
	SW-D	Single	72	166	275	N/N/N	228.7	172.9			4	1.1	57.2	43.2			207.9	157.2		
		Overall	72				449.6	221.6			4	1.1	112.4	55.4			408.9	201.4		
	RSW	Single	144	17.1	99.3						4	1.1								
		Overall	149				8.6	11.5			4	1.1	0.1	0.3			0.3	1.2		
	TCMCV	Single	116	152	332	N/N/N	Neg. slope	Neg. slope	74.8	131.0	4	1.1			18.7	32.8			67.8	119.1
		Overall	117				Neg. LOD	334.8	37.3	NC	4	1.1		83.7	9.3			304.4	33.9	
Cr	RW	Single	138	31	67.9	N/N/N	4.8	9.6	11.8	870.0	7	11.0		1.3	1.6	126.3	0.4	0.9	1.8	79.1
		Overall	141				Neg. slope	Neg. slope	21.8	89.0	7	11.0			3.1	5.6			2.8	3.5
	APO	Single	136	31.6	80.3	N/N/N	Neg. slope	Neg. slope	18.9	20.3	7	11.0			1.6	2.9			1.8	1.8
		Overall	139				Neg. slope	Neg. slope	3.3	41.1	7	11.0			0.5	5.9			0.3	3.7
	SW-I	Single	70	276	447	N/N/N	Neg. LOD	Neg. LOQ	98.8	299.0	7	11.0			13.8	42.7			8.8	27.2
		Overall	71				Neg. slope	Neg. slope	254.0	345.0	7	11.0			36.4	52.1			23.3	33.2
	SW-D	Single	72	288	592	N/N/N	Neg. LOD	Neg. LOQ	5.7	158.0	7	11.0			0.8	22.6			0.5	14.4
		Overall	72				36.5	259.5	205.0	NC	7	11.0	5.2	37.1	29.3		3.3	25.6	18.6	
	RSW	Single	134	26.2	121		Neg. slope	Neg. slope	19.2	35.5	7	11.0			2.7	5.1			1.7	3.2
		Overall	138				10.1	44.6	22.4	35.7	7	11.0	2.6	6.3	3.2	7.7	1.6	4.0	2.0	4.9
	TCMCV	Single	114	240	780	N/N/N	Neg. LOD	Neg. LOQ	68.5	139.0	7	11.0			9.8	19.9			6.2	12.6
		Overall	115				Neg. LOD	Neg. LOQ	86.0	203.0	7	11.0			12.3	29.0			7.8	18.5

Table 3

Summary of AMQ-III ICP LOD and LOQ Data (continued)

			TOTAL	ESTIMATED TEST			LINEAR		CURVILINEAR		DETECTION	QUALITY	LINEAR		CURVILINEAR		LINEAR		CURVILINEAR	
			NUMBER OF	CONCENTRATION (ug/L)		MATRIX	COMPUTED	COMPUTED	COMPUTED	COMPUTED	LIMIT	CRITERIA								
ELEMENT	MATRIX	PRECISION	DATA PTS.	LOW	HIGH	EFFECT?	LOD (ug/L)	LOQ (ug/L)	LOD (ug/L)	LOQ (ug/L)	(ug/L)*	(ug/L)**	LOD/EPA	LOQ/EPA	LOD/EPA	LOQ/EPA	LOD/MDC	LOQ/MDC	LOD/MDC	LOQ/MDC
Cu	RV	Single	138	25.6	61.1	N/N/N	Neg. slope	Neg. slope	21.4	35.1	6	12.0			3.6	5.9			1.8	2.9
		Overall	139				Neg. slope	Neg. slope	25.6	43.3	6	12.0			3.9	7.2			2.0	3.6
	APD	Single	138	31.8	69.9	N/N/N	Neg. slope	Neg. slope	16.6	29.2	6	12.0			2.8	4.9			1.4	2.4
		Overall	141				11.1	24.6	20.2	44.3	6	12.0	1.9	4.0	3.4	7.4	0.9	2.0	1.7	3.7
	SV-1	Single	70	173	336	N/N/N	Neg. LOD	Neg. LOQ	18.6	39.8	6	12.0			3.1	6.6			1.6	3.3
		Overall	71				Neg. LOD	1943.5	32.3	86.3	6	12.0		257.2	5.4	14.4		128.6	2.7	7.2
	SV-D	Single	64	265	502	N/N/N	Neg. LOD	Neg. LOQ	21.9	41.9	6	12.0			3.6	7.0			1.8	3.5
		Overall	68				Neg. slope	Neg. slope	180.0	38.1	6	12.0			30.0	3.7			10.0	1.8
	RGV	Single	144	29	115		1.9	3.7	9.8	1774.0	6	12.0	0.3	0.6	1.6	295.7	0.2	0.3	0.8	147.8
		Overall	144				25.0	46.0	31.3	62.6	6	12.0	3.8	7.7	5.2	10.4	1.9	3.8	2.6	5.2
	TCMCV	Single	120	1490	1790	N/N/N	Neg. LOD	Neg. LOQ	49.7	97.6	6	12.0			8.3	16.2			4.1	8.1
		Overall	120				Neg. LOD	Neg. LOQ	34.5	69.2	6	12.0			5.7	11.5			2.9	5.8
Fe	RV	Single	142	300	549	N/N/N	Neg. LOD	Neg. LOQ	24.9	53.8	7				3.6	7.7				
		Overall	142				Neg. LOD	652.4	25.8	58.1	7			93.2	3.6	8.3				
	APD	Single	140	325	642	N/N/N	Neg. slope	Neg. slope	154.0	252.0	7				22.0	36.0				
		Overall	142				Neg. slope	Neg. slope	160.0	296.0	7				22.9	42.3				
	SV-1	Single	70	320	625	N/N/Y	Neg. slope	Neg. slope	216.0	331.0	7				31.1	47.3				
		Overall	70				Neg. LOD	Neg. LOQ	309.0	673.0	7				44.1	96.1				
	SV-D	Single	72	320	655	N/N/N	Neg. LOD	Neg. LOQ	84.2	168.0	7				12.0	24.0				
		Overall	72				Neg. LOD	Neg. LOQ	246.0	NC	7				35.1					
	RGV	Single	140	29.5	142		33.3	68.2	41	83.9	7		4.8	9.7	5.9	12.0				
		Overall	141				62.4	149.5	70.7	170.0	7		8.9	21.4	10.1	24.3				
	TCMCV	Single	112	244	1050	N/N/N	Neg. slope	Neg. slope	156.0	285.0	7				22.3	40.7				
		Overall	113				67.0	133.5	182.0	375.0	7		9.6	19.0	26.0	53.6				
													######							
Pb	RV	Single	134	153	342	N/N/N	Neg. LOD	Neg. LOQ	41.2	94.4	42	3.2			1.0	2.2			12.9	29.5
		Overall	135				Neg. slope	Neg. slope	130.0	247.0	42	3.2			3.1	5.9			40.6	77.2
	APD	Single	132	200	504	N/N/N	Neg. slope	Neg. slope	87.9	159.0	42	3.2			2.1	3.8			27.5	49.7
		Overall	134				Neg. slope	Neg. slope	137.0	247.0	42	3.2			3.3	5.9			42.8	77.2
	SV-1	Single	68	1190	1990	N/N/N	Neg. slope	Neg. slope	711.0	902.0	42	3.2			16.9	21.5			222.2	281.9
		Overall	69				Neg. LOD	Neg. LOQ	477.0	1476.0	42	3.2			11.4	35.1			149.1	461.3
	SV-D	Single	68	1570	2780	N/N/N	Neg. slope	Neg. slope	541.0	904.0	42	3.2			12.9	23.4			169.1	307.5
		Overall	70				Neg. LOD	Neg. LOQ	557.0	1504.0	42	3.2			13.3	35.8			174.1	470.0
	RGV	Single	128	196	470		Neg. slope	Neg. slope	86.9	165.0	42	3.2			2.1	3.9			27.8	51.6
		Overall	131				Neg. slope	Neg. slope	134.0	240.0	42	3.2			3.2	5.7			41.9	75.0
	TCMCV	Single	106	1190	1800	N/N/Y	Neg. LOD	Neg. LOQ	173.0	336.0	42	3.2			4.1	8.0			54.1	105.0
		Overall	109				Neg. LOD	Neg. LOQ	499.0	1197.0	42	3.2			11.8	28.5			154.7	374.1

Table 3

Summary of AMQ-III ICP LOD and LOQ Data (continued)

			TOTAL	ESTIMATED TEST			LINEAR		CURVILINEAR		DETECTION	QUALITY	LINEAR		CURVILINEAR		LINEAR		CURVILINEAR	
			NUMBER OF	CONCENTRATION (ug/L)		MATRIX	COMPUTED	COMPUTED	COMPUTED	COMPUTED	LIMIT	CRITERIA								
ELEMENT	MATRIX	PRECISION	DATA PTS.	LOW	HIGH	EFFECT?	LOD (ug/L)	LOQ (ug/L)	LOD (ug/L)	LOQ (ug/L)	(ug/L)*	(ug/L)**	LOD/EPA	LOQ/EPA	LOD/EPA	LOQ/EPA	LOD/LOQC	LOQ/LOQC	LOD/LOQC	LOQ/LOQC
Mn	RV	Single	140	77	242	N/N/N	20.5	38.7	18.4	33.8	2			19.3	6.3	12.2				
		Overall	141				45.1	91.8	39.1	179.0	2		22.5	45.9	19.8	39.7				
	APO	Single	140	220	348	N/N/N	Neg. LOD	Neg. LOQ	3.2	11.0	2				807.3	5.7				
		Overall	142				92.9	190.1	90.3	185.0	2		46.5	95.2	45.2	92.5				
	SW-I	Single	72	80.5	499	N/N/N	Neg. LOD	Neg. LOQ	17.1	31.8	2				8.6	16.8				
		Overall	72				Neg. LOD	43.2	74.6	NC	2			81.6	37.0					
	SW-B	Single	72	94.2	686	N/N/N	Neg. LOD	Neg. LOQ	13.1	30.4	2				6.7	13.2				
		Overall	72				Neg. LOD	83.9	90.5	NC	2			42.0	49.3					
	RGW	Single	136	10	31.7		Neg. LOD	110.4			2			59.3						
		Overall	136				7.5	30.7			2		3.7	15.4						
	TCHCW	Single	114	78.7	304	N/N/N	0.5	1.8	19.0	37.1	2		0.3	0.9	9.5	18.6				
		Overall	117				Neg. slope	Neg. slope	116.8	187.0	2				59.5	93.5				
Mo	RV	Single	126	33	191	N/N/N	21.8	35.0	14.9	44.0	8			6.9	1.9	45.5				
		Overall	123				64.5	150.0	58.4	150.0	8		8.5	18.9	7.3	16.3				
	APO	Single	120	44	202	N/N/Y	16.2	51.8	15.1	50.2	8		2.1	4.2	1.9	3.8				
		Overall	121				24.6	63.4	23.2	53.0	8		3.1	7.9	2.9	6.6				
	SW-I	Single	64	283	591	N/N/N	105.5	198.9	145.0	278.0	8		13.2	24.9	18.1	34.8				
		Overall	64				155.2	319.5	206.0	429.0	8		19.4	39.9	25.8	53.6				
	SW-B	Single	64	381	795	N/N/N	Neg. slope	Neg. slope	209.0	378.0	8				26.1	47.3				
		Overall	64				159.6	317.6	253.0	503.0	8		20.0	39.7	31.6	62.9				
	RGW	Single	122	39	127		7.6	18.1	18.4	41.8	8		1.0	2.3	2.3	5.1				
		Overall	123				19.9	79.9	32.0	NC	8		2.5	9.5	4.0					
	TCHCW	Single	102	295	792	N/N/N	Neg. LOD	Neg. LOQ	47.6	118.8	8				8.5	14.8				
		Overall	103				Neg. LOD	Neg. LOQ	143.8	298.0	8				17.9	37.3				
Ni	RV	Single	144	62.2	125	N/N/Y	Neg. slope	Neg. slope	31.4	88.5	15	160.0			3.4	5.9			0.3	0.6
		Overall	144				180.8	760.5	172.8	NC	15	160.0	12.6	50.7	11.5		1.2	4.8	1.1	
	APO	Single	138	71.6	149	N/N/N	Neg. LOD	Neg. LOQ	19.2	59.6	15	160.0			1.3	2.6			0.1	0.2
		Overall	138				127.8	258.9	159.8	496.0	15	160.0	8.5	16.7	10.6	33.1	0.8	1.6	1.0	3.1
	SW-I	Single	72	538	869	N/Y/N	Neg. LOD	Neg. LOQ	93.5	192.8	15	160.0			6.2	12.8			0.6	1.2
		Overall	72				Neg. LOD	254.3	187.8	NC	15	160.0		157.6	12.5			14.8	1.2	
	SW-B	Single	72	622	948	N/N/N	Neg. LOD	Neg. LOQ	98.5	192.8	15	160.0			6.6	12.8			0.6	1.2
		Overall	72				153.8	299.8	278.8	750.0	15	160.0	10.1	20.9	18.5	48.7	1.0	1.9	1.7	4.6
	RGW	Single	136	62.9	253		13.8	27.7	55.9	54.3	15	160.0	0.8	1.8	1.8	3.8	0.1	0.2	0.2	0.4
		Overall	136				24.8	69.8	41.5	102.8	15	160.0	1.6	4.7	2.8	6.8	0.2	0.4	0.3	0.6
	TCHCW	Single	122	598	1510	N/N/N	Neg. LOD	Neg. LOQ	79.5	156.8	15	160.0			5.3	10.4			0.5	1.0
		Overall	124				Neg. LOD	Neg. LOQ	191.8	520.8	15	160.0			12.7	34.7			1.2	3.3

Table 3

Summary of AMQ-III ICP LOD and LOQ Data (continued)

			TOTAL	ESTIMATED TEST			LINEAR		CURVILINEAR		DETECTION	QUALITY	LINEAR		CURVILINEAR		LINEAR		CURVILINEAR	
			NUMBER OF	CONCENTRATION (ug/L)		MATRIX	COMPUTED	COMPUTED	COMPUTED	COMPUTED	LIMIT	CRITERIA								
ELEMENT	MATRIX	PRECISION	DATA PTS.	LOW	HIGH	EFFECT?	LOD (ug/L)	LOQ (ug/L)	LOD (ug/L)	LOQ (ug/L)	(ug/L)*	(ug/L)**	LOD/EPA	LOQ/EPA	LOD/EPA	LOQ/EPA	LOD/WQC	LOQ/WQC	LOD/WQC	LOQ/
V	RW	Single	122	32.9	72.9	N/N/N	Neg. slope	Neg. slope	14.3	25.0	8				1.8	3.1				
		Overall	125				11.3	23.9	25.9	55.1	8		1.4	3.0	3.2	6.9				
	APD	Single	128	40.3	93.6	N/N/N	9.5	18.3	19.2	37.5	8		1.2	2.3	2.4	4.7				
		Overall	128				28.7	55.9	534.0	643.0	8		3.6	7.0	66.8	80.4				
	SW-1	Single	56	293	643	N/N/N	Neg. slope	Neg. slope	127.0	208.0	8				15.9	26.0				
		Overall	56				194.7	Neg. LOQ	267.0	NC	8		24.6		33.4					
	SW-D	Single	56	341	690	N/N/N	Neg. slope	Neg. slope	39.5	77.5	8				4.9	9.7				
		Overall	56				321.5	Neg. LOQ	396.0	NC	8		48.2		49.5					
	RGW	Single	126	56	111		0.3	0.6	7.8	15.7	8		0.0	0.1	1.0	2.0				
		Overall	127				24.5	54.8	31.9	69.5	8		3.1	6.8	4.0	8.7				
	TCMCW	Single	100	313	643	N/N/N	Neg. LOQ	Neg. LOQ	59.7	96.8	8				5.7	7.3				
		Overall	102				Neg. LOQ	Neg. LOQ	61.6	126.0	8				7.7	16.0				
Zn	RW	Single	140	7.8	69.2	N/N/N	29.5	57.4	26.5	53.7	2	110.0		26.7	13.3	31.4	6.2	0.5	0.2	
		Overall	142				48.6	144.9	50.8	NC	2	110.0	24.3	72.4	25.4		0.4	1.3	0.5	
	APD	Single	142	16	82.1	N/N/N	10.1	20.2	10.1	33.1	2	110.0	5.0	10.4	8.1	16.8	0.1	0.2	0.1	
		Overall	143				19.9	400.8	21.1	NC	2	110.0	9.9	200.0			0.2	3.6		
	SW-1	Single	88	77.1	636	N/N/N	Neg. LOQ	Neg. LOQ	49.7	94.1	2	110.0			14.9	29.1			0.3	
		Overall	88				Neg. LOQ	80.6	91.5	NC	2	110.0		40.3	45.8			0.7	0.8	
	SW-D	Single	88	108	682	N/N/N	Neg. LOQ	Neg. LOQ	18.2	34.8	2	110.0			9.1	18.4			0.2	
		Overall	88				Neg. LOQ	Neg. LOQ	97.2	323.6	2	110.0			48.6	161.5			0.9	
	RGW	Single	138	10.7	61.7		Neg. slope	Neg. slope	23.7	41.5	2	110.0			11.9	20.7			0.2	
		Overall	141				34.8	75.5	40.2	91.1	2	110.0	17.0	37.8	20.1	45.6	0.3	0.7	0.4	
	TCMCW	Single	114	78.2	196	N/N/N	Neg. LOQ	Neg. LOQ			2	110.0								
		Overall	116				Neg. LOQ	Neg. LOQ	27.8	74.6	2	110.0			13.9	37.3			0.3	

* EPA Methods for Chemical Analysis of Water and Wastes (EPA 600/4-79-020, Revised March 1983)

** Water Quality Criteria for freshwater aquatic, 100 mg/L hardness where applicable

Matrix effects: based on comparison of slope of single operator and overall precision, and recovery regression equations for each matrix compared to reagent grade water.

NC: No value was computed and implies that an RSD of 20% was not reached over the test range.

Table 4

ELEMENTS HAVING A MATRIX EFFECT BASED ON
REGRESSION EQUATION SLOPE DIFFERENCES

	Single Operator	Overall	Recovery
River Water	Al, Cd		Ni
Ash Pond Overflow			Be, Cd, Mo
Seawater-Intake		Ni	Fe
Treated Chemical Metal Cleaning Wastes			Al, Pb

Figure 1. Photograph of Churn Splitter Used During the AMQ-III Effort.

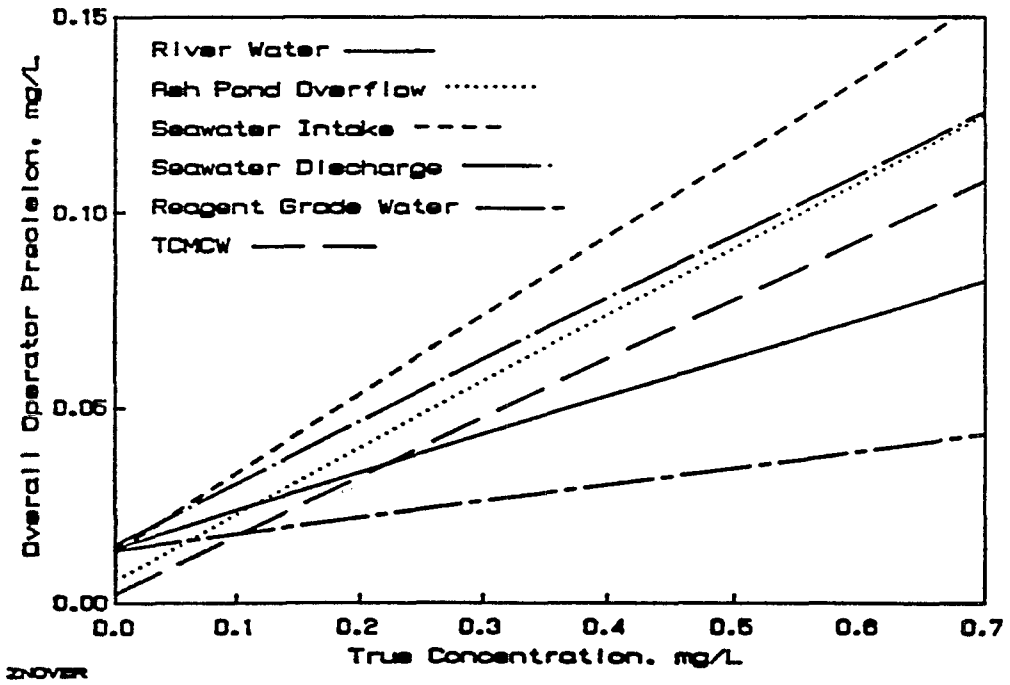


Figure 2. Zn by ICP
Overall Operator Precision vs True Concentration

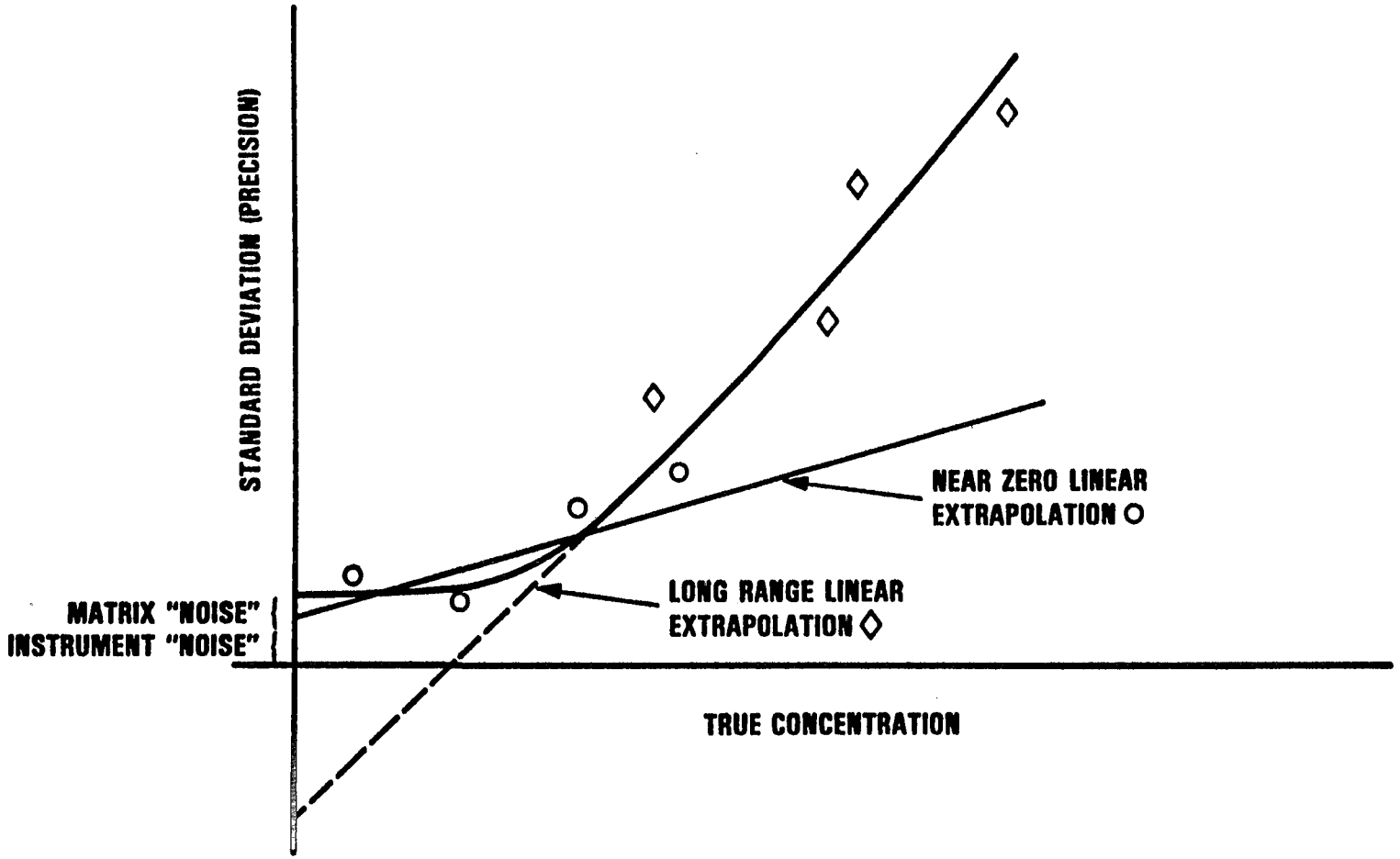
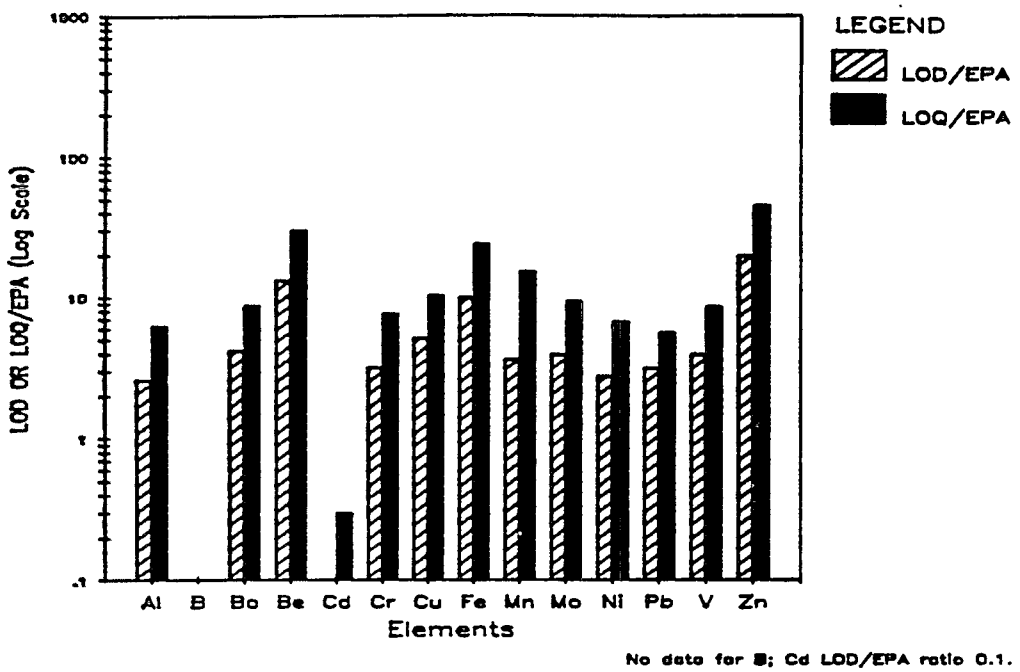
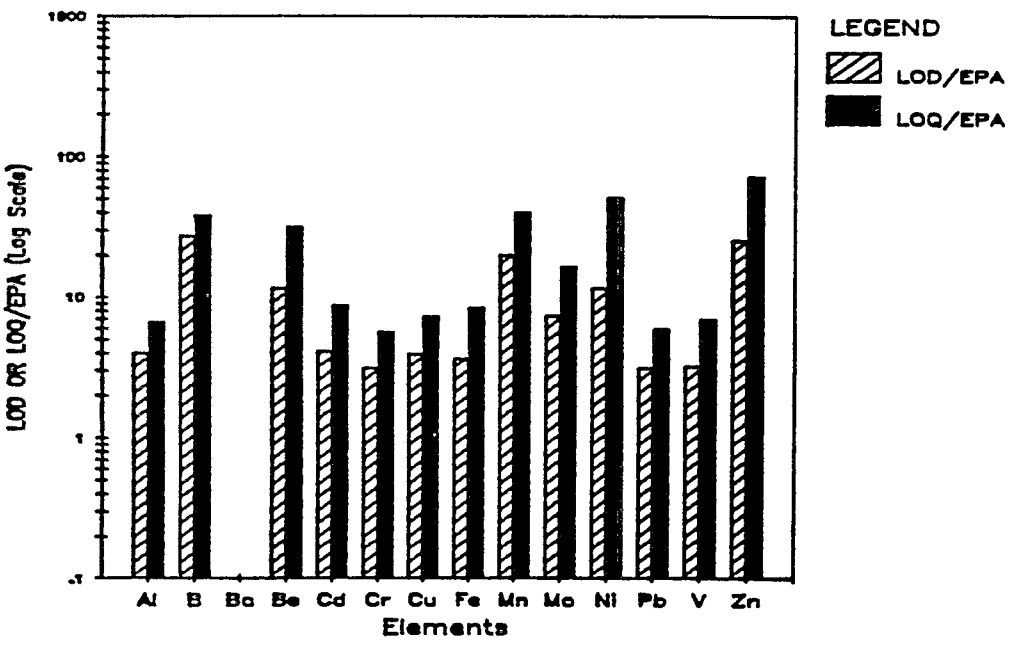


Figure 3. Effect of Test Concentration on the Calculation of LODs.



No data for B; Cd LOD/EPA ratio 0.1.

Figure 4. Ratio of EPRI LOD and LOQ to EPA ICP Detection Limit for Reagent Grade Water



No data for Be.

Figure 5. Ratio of EPRI LOD and LOQ to EPA ICP Detection Limit for River Water

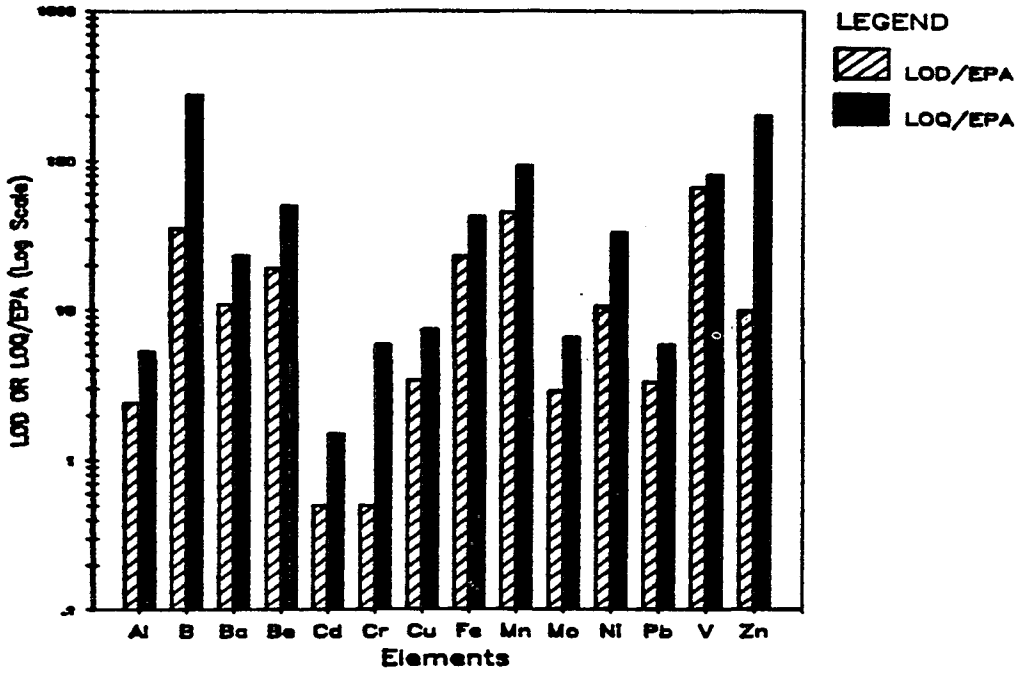
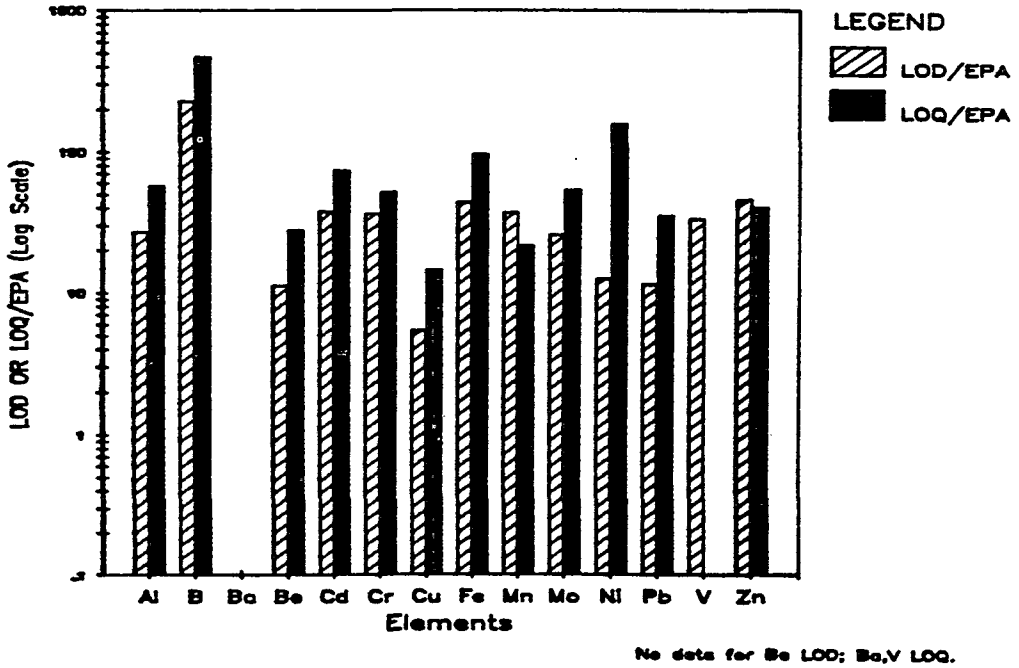


Figure 6. Ratio of EPRI LOD and LOQ to EPA ICP Detection Limit for Ash Pond Overflow



No data for Be LOD; Ba,V LOQ.

Figure 7. Ratio of EPRI LOD and LOQ to EPA ICP Detection Limit for Seawater Intake

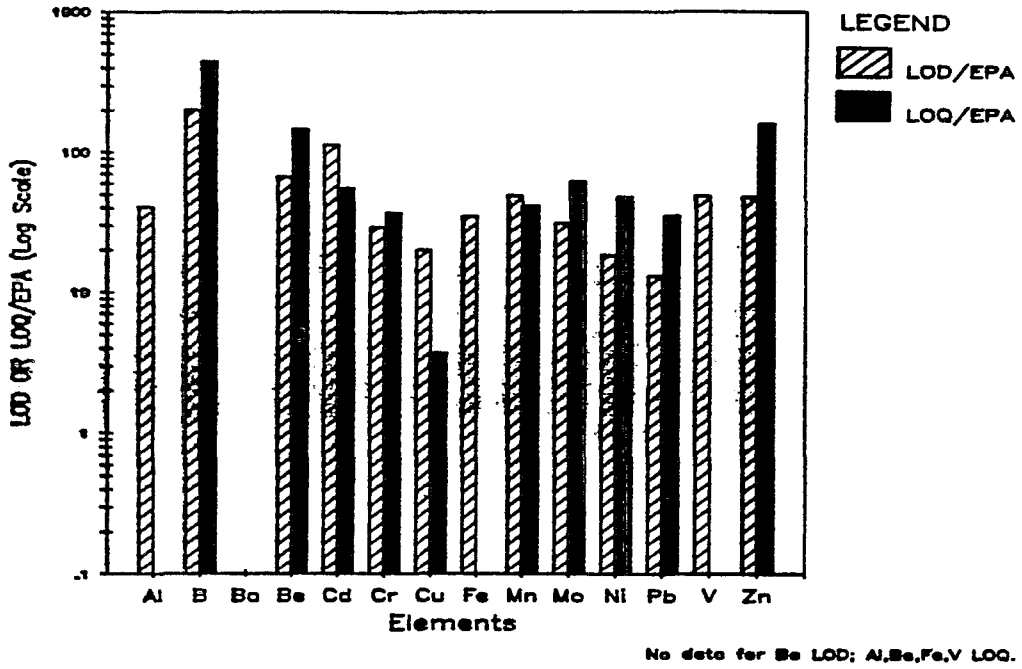


Figure 8. Ratio of EPRI LOD and LOQ to EPA ICP Detection Limit for Seawater Discharge

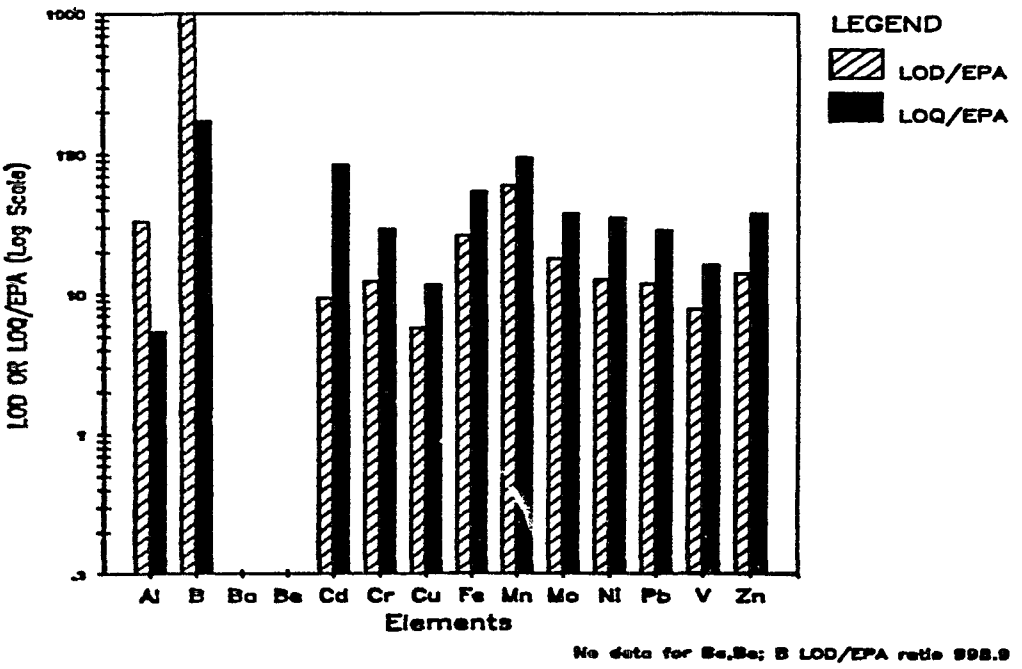


Figure 9. Ratio of EPRI LOD and LOQ to EPA ICP Detection Limit for Treated Chemical Metal Cleaning Waste

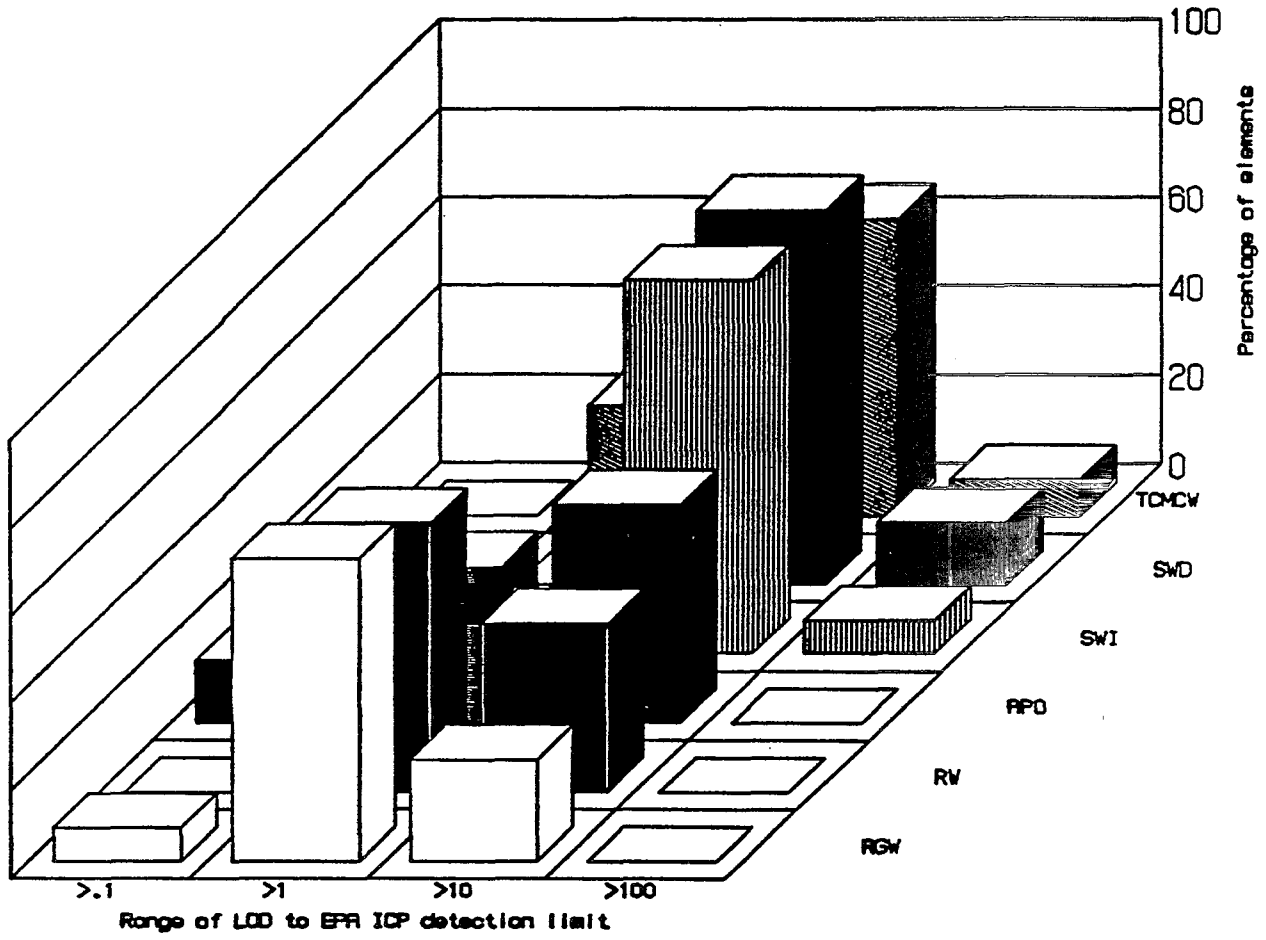


Figure 10. Percentage of Reporting Elements Having a Given Ratio

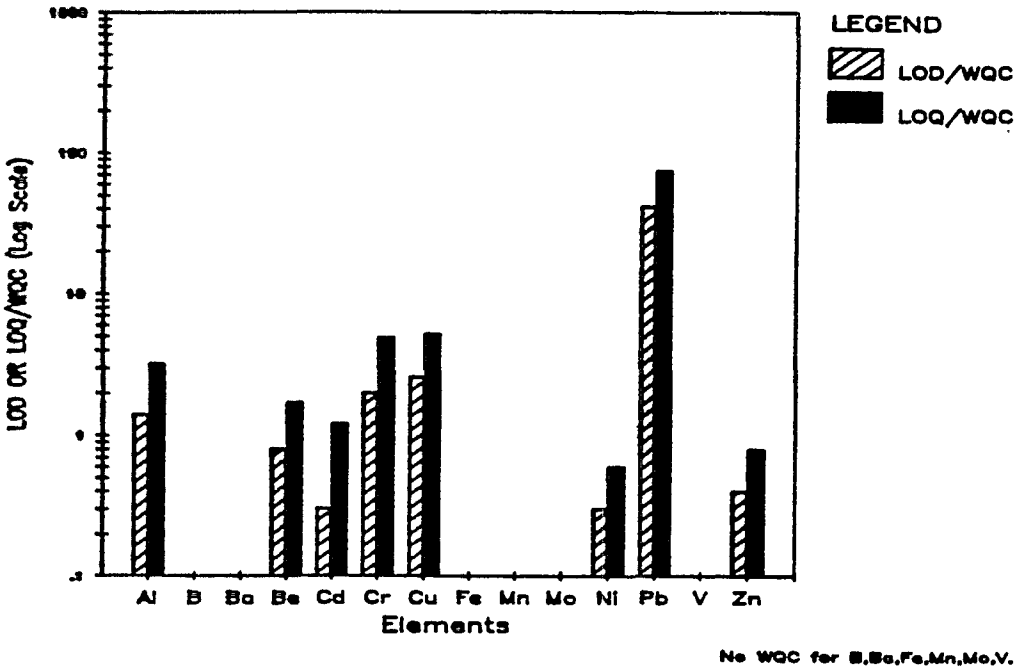


Figure 11. Ratio of EPRI LOD and LOQ to Water Quality Criteria for Reagent Grade Water

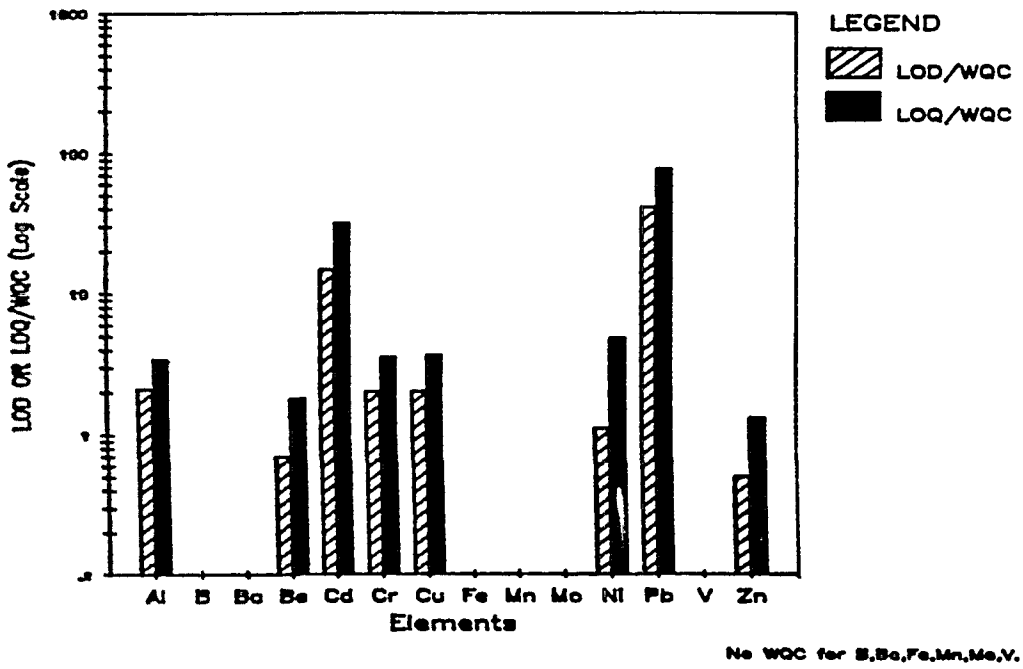


Figure 12. Ratio of EPRI LOD and LOQ to Water Quality Criteria for River Water

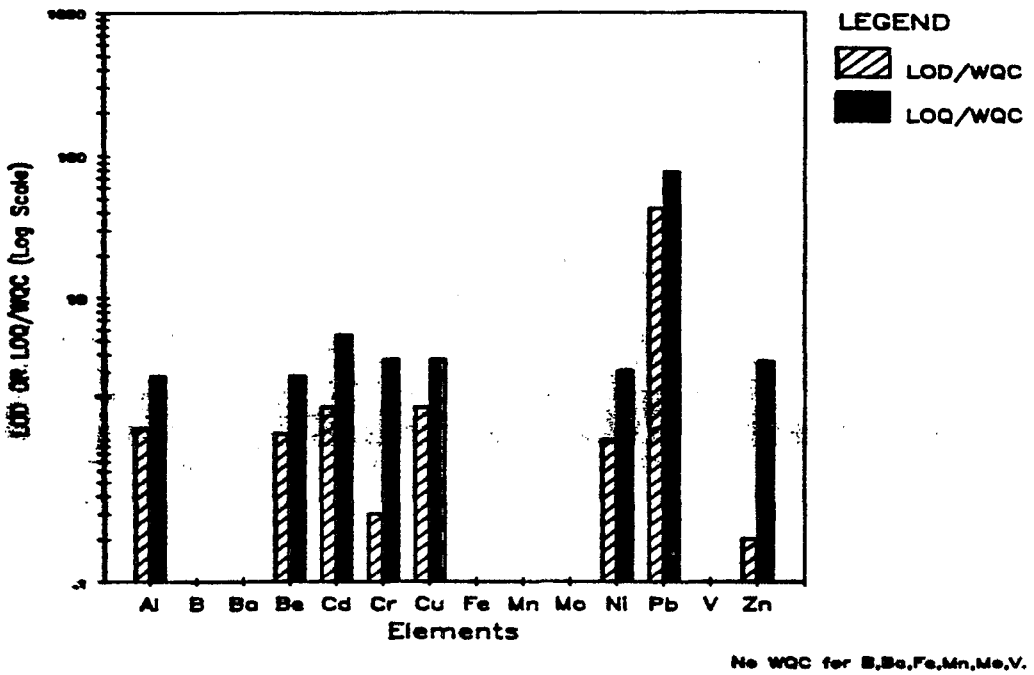


Figure I3. Ratio of EPRI LOD and LOQ to Water Quality Criteria for Ash Pond Overflow

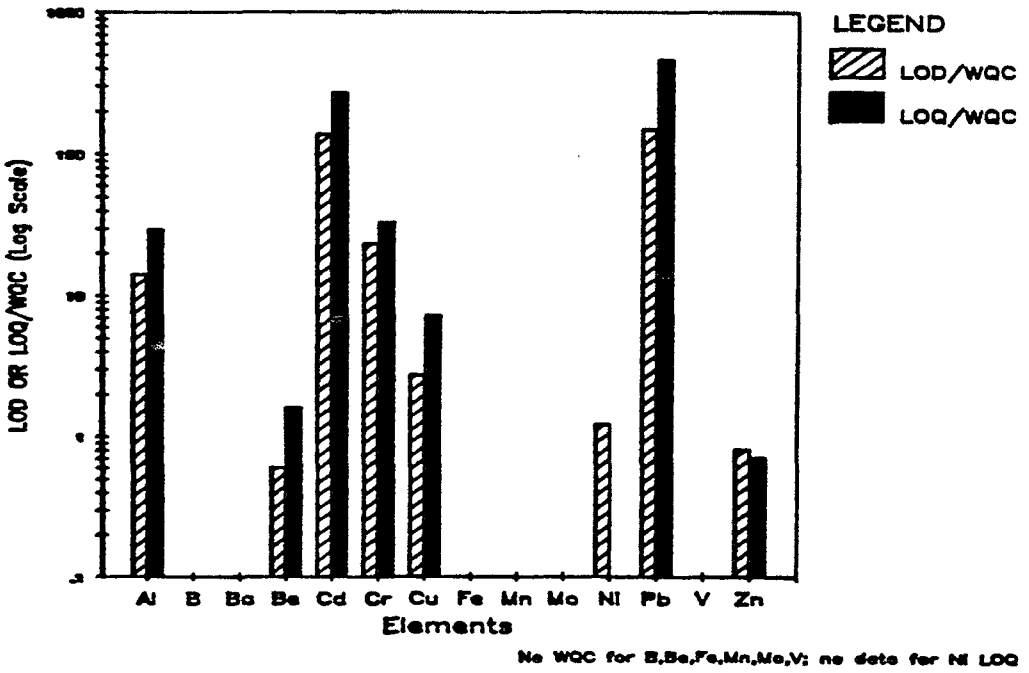


Figure I4. Ratio of EPRI LOD and LOQ to Water Quality Criteria for Seawater Intake

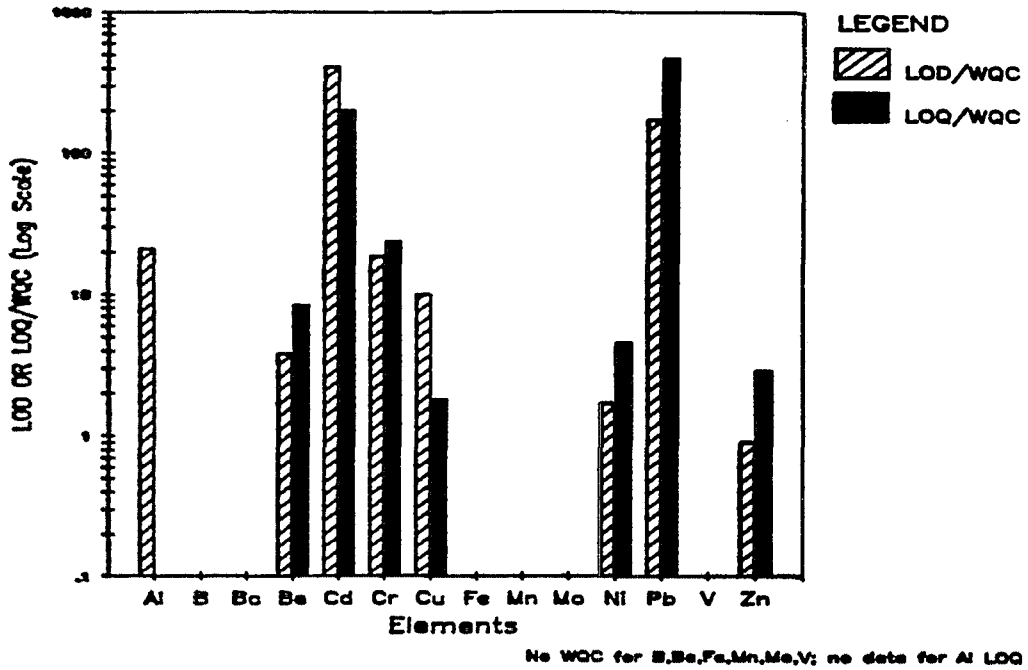


Figure 15. Ratio of EPRI LOD and LOQ to Water Quality Criteria for Seawater Discharge

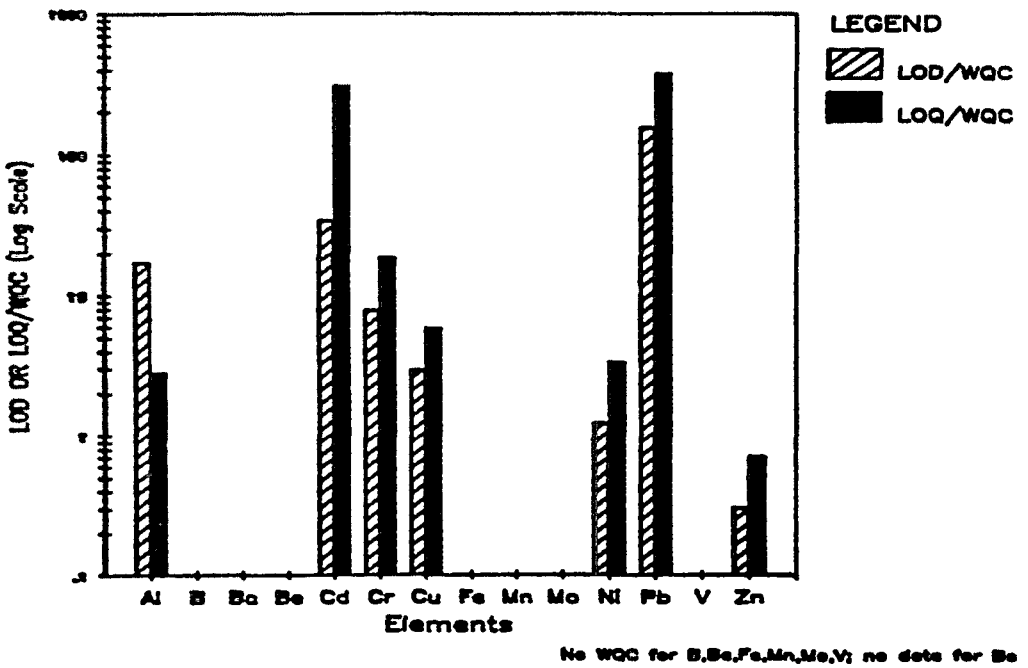


Figure 16. Ratio of EPRI LOD and LOQ to Water Quality Criteria for Treated Chemical Metal Cleaning Waste

QUESTION AND ANSWER SESSION

MR. HACHIGIAN: Lee Hachigian of General Motors.

I assume the intent was to use this data to work with your regulatory agency in establishing limitations on effluents from the utility industry. Do you foresee that during these negotiations, if you can call it that, you would be required to do site-specific...the same type of report site specific for each of the operations or you could use this data that you have already determined?

MR. RICE: That is a very good question. Obviously, the collection of the data was directly related to the entire compliance monitoring and permit negotiation effort.

Both things have happened. In some cases, the published information has been able to be used by a member utility in its negotiations of a permit limit.

In other instances, it has at least secured for the utility the opportunity to run a site-specific MDL or to obtain information on their recovery and reproducibility by a round-robin with a number of corresponding labs. We have used the latter situation in connection with and MDL when that was in question (no detectible discharge for a limit) to get two or three additional qualified laboratories

together with the utility laboratory in an approved round robin simply on MDL.

MR. HACHIGIAN: As a followup question, has it been effective?

MR. RICE: Pardon me?

MR. HACHIGIAN: Have your efforts been effective?

MR. RICE: Yes, very much so.

The entire method validation program has cost the Electric Power Research Institute close to $1.5 million to date including furnace AA and ICU on a range of metals and matrices. EPAL is now continuing with additional elements that were not run earlier but are now requested by members since they in turn are being requested by regulatory agencies to monitor or to control parameters not previously to subject of interest.

MR. HACHIGIAN: Thank you.

MR. FIELDING: Any other questions?

(No response.)

MR. FIELDING: Thank you.

MR. FIELDING: Our next speaker is Mr. Bill Krochta. He will be speaking about the quantitation detection limits in analysis of environmental samples.

QUANTITATION/DETECTION LIMITS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

W. G. Krochta, PPG Industries; L. I. Bone, The Dow Chemical Company; B. A. Cuccherini, CMA; T. L. Dawson, Union Carbide Chemical & Plastics Company, Inc; K. J. G. Hillig, BASF Corporation; R. A. Javick, FMC Corporation; N. E. Prange, B. M. Hughes, Monsanto Company; F. I. Saksa, CIBA-GEIGY Corporation; G. H. Stanko, Shell Development Company

QUANTITATION/DETECTION LIMITS
FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

I. INTRODUCTION

Analytical technology continues its unrelenting pace to develop methodology to lower the concentration limits at which the analytes can be measured. Picogram (10^{-12} grams) quantities are commonly reported as new detector systems for gas and liquid chromatography are developed. Advances in mass spectrometry are leading to lower levels of quantitation. For example, ion trap mass spectrometers and inductively coupled plasma-mass spectrometry (ICP-MS) are some highly sensitive techniques, which are becoming more commonly used for organic and elemental determinations respectively and capable of detecting subnanogram ($<10^{-9}$ gram) quantities. The statement following depicts the situation that we are encountering:

> "... the number of compounds detected in a sample of water is related to the detection level. As the detection level decreases an order of magnitude, the number of compounds detected increased an order of magnitude. Based on the number of compounds detected by current methods, one would expect to find every known compound at a concentration of 10^{-12} g/L or higher." - Dr. William T. Donaldson (EPA Athens Laboratory)

As the regulated community is required to perform within the level of increasingly restrictive compliance limits, the analytical chemist must emphasize to the public that all measurement data have an associated uncertainty interval(1). This information becomes critical as measurements are made approaching the lowest analytical capability of a given procedure.

II. ANALYTICAL LIMITS OF MEASUREMENT - DEFINITIONS

In their regulatory programs, the USEPA uses a variety of procedures to establish limits of measurement. In the following slide definitions are given to present an approach to define analytical capability.

LIMIT OF DETECTION (LOD) - Lowest concentration level that can be determined to be statistically different from a blank(7).

METHOD DETECTION LIMIT (MDL) - Minimum concentration of analyte that can be determined with 99% confidence that the true value is greater than zero(2,3,13).

INSTRUMENT DETECTION LIMIT (IDL) - Smallest signal above background noise that an instrument can detect reliably(7).

LIMIT OF QUANTITATION (LOQ) - Concentration above which quantitative results may be obtained with a specified degree of confidence(7).

PRACTICAL QUANTITATION LIMIT (PQL) - Lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions(5).

III. APPLICATION OF METHOD DETECTION LIMITS (MDL) SUBJECT TO MATRIX EFFECTS

The MDL is similar to the LOD except that the LOD is defined with a sample blank whereas the MDL is defined with either a blank or in each matrix being analyzed(2,3). In most cases, however, laboratories report MDLs determined at one point in time and routinely based on reagent water. They do not normally perform the MDL evaluation on the different matrices analyzed for regulations development, compliance monitoring, or tested to determine permit requirements.

In their proposal to set enforceable maximum contaminant levels (MCLs) for volatile synthetic organic chemicals in drinking water(5), EPA explains that the MDL could not be used as the basis for quantitative maximum contaminant levels: "The specification of such a concentration is limited by the fact that MDLs are variables affected by the performance of a given measurement system. MDLs are not necessarily reproducible over time in a given laboratory, even when the same analytical procedures, instrumentation, and sample matrix are used."

IV. PRACTICAL QUANTITATION LIMITS (PQL) AS A MEANS OF IDENTIFYING MEASUREABLE CONCENTRATIONS

Many observations for organic toxic pollutants are below the MDLs, thus creating difficulties in developing effluent limitations guidelines and permit limits. In such instances where analytical and effluent variability cannot be determined, only those concentrations above quantifiable levels (17) should be considered. It should also be recognized that there is a fundamental difference between detection and quantitation limits. Unfortunately these terms are too often misused as being synonymous. EPA has developed a method for establishing such quantifiable numerical limits for its proposed drinking water standards (50 FR 46902) and for its proposed organic toxicity characteristic (51 FR 21652), designated as the practical quantitation limit (PQL). EPA has developed this concept of a PQL for specific analytical methods and lists of chemicals.

A. RECOMMENDED PRACTICAL QUANTITATION LIMITS COMPARED TO METHOD DETECTION LIMITS

The EPA used PQLs which are recommended as 10 times the MDL for selected volatile organic chemicals when it proposed MCLs for drinking water. The Agency states that: "setting the PQLs in a range between 5 and 10 times the MDL achieved by the best laboratories is a fair expectation for most state and commercial laboratories" (50 FR 46907). At the PQLs chosen by EPA for this rulemaking, its performance evaluation studies indicate that 80% of the EPA and State laboratories in its water program evaluation studies could measure within ±40% of the true concentration. This was the basis for setting the PQL at 10 times the MDL. This is not a very high standard of performance as admitted by the Agency in the preamble to this proposed regulation. **Thus, even at the PQLs, over 20% of the "good" laboratories would not be expected to obtain results within ±40% of the concentration of a specific component.** At concentration levels below PQL, performance of even the best of "good" laboratories deterioriates rapidly.

B. PRACTICAL QUANTITATION LIMITS IN REAL MATRIX SAMPLES REFLECT EFFECT OF MATRIX INTERFERENCE

A recent presentation(12) described a study evaluating Method 8020, which is a gas/liquid chromatography procedure in SW-846 "Test Methods for Evaluating Solid Wastes, Physical Chemical Methods" for the determination of low concentrations of toluene, benzene, and xylenes in real matrix groundwater samples. The round robin study involved 20 commercial laboratories. Method 8020 lists the practical quantification limits for all three compounds as 2.0 μg/L. The PQLs derived from results achieved by the laboratories in this study are much higher. The PQLs at which 80% of the laboratories could achieve a recovery within ±40% of a true value from this study are 7.5 μg/L for benzene, >20 μg/L for toluene, and 18.5 μg/L for total xylenes. It is clear that the Method 8020 published PQLs are seriously underestimated when applied to this groundwater matrix and for these 20 laboratories.

The inability of these laboratories to perform within the method PQL criteria should not be surprising even to EPA. In the preamble to the final rule on the federal primary drinking water standards for eight volatile organic compounds (VOCs), EPA states that:

"PQLs for the VOCs were based on the MDL and surrogate test data ... The PQLs based on these laboratory data are considered a two step removed surrogate for actual laboratory performance, first because they are estimated from another measurement (the MDL) and second, because they are derived from laboratory performance under ideal circumstances. Therefore, they do not actually represent the results of normal laboratory procedures, but are a model of what normal procedures might achieve. Specifically:

(1) Laboratories receive performance evaluation samples in which a limited number of concentrations are analyzed and the samples do not have matrix interferences as might actual samples;

(2) PQLs are based on EPA and State laboratory data which are considered to be representative of the best laboratories, but not all laboratories; and

(3) Samples are analyzed under controlled ideal testing conditions which may not be representative of routine practices.

For these reasons, the PQL represents a relative stringent target for routine performance." (52 Federal Register 25699).

More specific to groundwater samples, EPA discussed the significance and reliability of the PQLs that are included in Appendix IX of the rule: "The PQLs listed were EPAs best estimate of the practical sensitivity of the applicable method for RCRA groundwater monitoring purposes. However, some of the PQLs may be unattainable because they are based on general estimates for the specific substance. Furthermore, due to site-specific factors, these limits may not be reached." 53 Federal Register 39721.

For solid wastes the matrix problem has also been demonstrated to be very significant(21). Member companies of the Hazardous Waste Treatment Council obtained initial information that showed 33 out of the 91 Best Demonstrated Available Technology (BDAT) standards promulgated for the First and Second Third Land Disposal Restrictions were set at levels below the PQLs. As a follow-up, a formalized interlaboratory study using incinerator ash samples was performed. In this matrix a range finder study was conducted by six member companies to determine appropriate spiking levels to determine MDLs for each of the constituents. As part of this study a matrix spike was prepared at the BDAT level and determined. The results of the study showed that 65 percent of the volatile constituents, 73 percent of the acid extractable constituents, and 23 percent of the base neutral extractable constituents were not detected at the spike performed at the treatment standard limit.

The PQLs and also MDLs published by EPA for its analytical methods are based on reagent water spiked with the compounds of interest, so they do not represent limits achievable where matrix interferences exist, as with actual samples. EPA does identify in Method 8020 that the PQLs are highly matrix-dependent and that they are listed only to provide guidance and may not always be achievable. **Unfortunately, these caveats or warnings are likely to be ignored, particularly by some regulatory agencies, when permit limits or other regulatory levels are set.**

V. PROPER TREATMENT OF THE DATA CAN AVOID MISREPRESENTATION OF THE FACTS

A. RULES FOR THE USE OF SIGNIFICANT NUMBERS

Despite the wide attention given to numbers for quantitative and qualitative limits the improper use of rules for use of significant numbers goes virtually unnoticed. As measurements are required more and more frequently to be made at decreasing concentrations, the relative analytical variability and uncertainty can increase substantially and the need to understand and recognize significant data is essential. Horwitz et al (22) reviewed data from over 50 independent Association of Official Analytical Chemists (AOAC) interlaboratory collaborative programs covering numerous AOAC drug and pesticide studies. The analytical methods covered were chromatography, atomic absorption spectrometry, absorption spectrometry, polarography, and biossay. In Figure 1 the % variation is expressed as powers of 2 with the mean concentration expressed as powers of 10. A convenient reference point is that at 1 ppm the variation is 16%. The % variation was found to double for each decrease of concentration by 2 orders of magnitude. It is important to note that this curve is independent of the analyte or analytical technique that was used to make the measurements. These relationships should also apply to environmental levels of measurement as well.

Analytical chemists must always emphasize to the users of the data that the single most important characteristic of any result obtained from one or more analytical measurements is an adequate statement of its uncertainty interval. Often in legal judgments there is an attempt to dispense with uncertainty and try to obtain unequivocal statements; therefore, an uncertainty interval must be clearly defined in cases involving litigation and/or enforcement proceedings. Otherwise, a value of 1.001 without a specified uncertainty, for example, may be viewed as legally exceeding a permissible level of 1(7).

The analytical inclusion of only significant numbers is vital to the accurate interpretation of data. Scientific personnel are not exempted from the tendency to retain all values, no matter how divergent or suspect they may be. One of the principles of handling the data of physical and chemical measurements is that a numerical result by itself should give an approximate idea of the precision of the value as indicated by the number of significant figures used in expressing the value. An inaccurate representation of significant figures may give one an impression nearly as erroneous as from an inaccurate value. Misuse of significant figures can cause reporting violations when indeed the measured value does not exceed the limit. Adherence to proper expression of significant numbers is especially important when permit limits are near the limit of quantitation for the procedure and its relative uncertainties are large.

The number of significant figures reported as a result of a scientific measurement depends on establishing previously the relative precision with which the measurement can be made as shown in Table II(11). In considering the proper use of significant figures for regulatory reporting, it is imperative that significant figures start at the laboratory bench and be adhered to by anyone who further treats or handles the data. Otherwise, false conclusions and misunderstanding will develop and possibly lead to serious consequences.

B. GUIDELINES FOR REPORTING DATA

EPA has recognized that data measured at or near the detection limit have considerably more uncertainty associated with them than when significant amounts are present(6). In this discussion EPA acknowledges the recommendations by the American Chemical Society Report(7). A graphical illustration of the relationship of LOD and LOQ is shown in Figure 2(7). The base scale is in units of standard deviation, which is assumed to be the same for all the measurements involved.

Confidence in the apparent analyte concentration increases as the analyte signal increases above the LOD. The value for LOQ = 10σ is recommended, where σ is the standard deviation of the measurements. Assuming a large number of samples, the LOQ then corresponds to an uncertainty of ±30% in the measured value (10σ $\pm 3\sigma$) at the 99% confidence level. The LOQ is most useful for defining the lower limit of the useful range of measurement methodology.

From these guidelines in Table III, if the measured value is less than the limit of detection, one should report "not detected" together with the value for the LOD. When the measured value is larger than the LOD but smaller than the limit of quantification (LOQ), report "detected but not quantifiable" together with the value for the LOQ. If the measured value is greater than the LOQ, report the value and its uncertainty.

VI. IMPACTING THE REGULATORY PROCESS

Data measured at or near the limit of detection may cause serious difficulty for the user in developing valid conclusions from any study. Not only can the amount of uncertainty approach and even equal the reported value, but also confirmation of the species reported is virtually impossible as the identification must depend solely on the selectivity of the methodology and knowledge of the absence of possible interferents. As the concentrations increase to measurable amounts these problems diminish. As stated previously, quantitative interpretation, decision-making, and regulatory actions should be limited to data at or above the limit of quantitation(7). The following discussion graphically illustrates how analytical variability can impact the regulatory process.

A. GRAPHICAL ILLUSTRATIONS OF THE IMPACT OF ANALYTICAL VARIABILITY ON COMPLIANCE LIMITS

Figures 3 through 7 were developed in order to visualize the impact of variability upon laboratory measurements of concentrations in plant effluents. Figure 3 shows the general probability distribution function for random error when the measured concentration is expressed in σ units. This curve can be thought of as a frequency distribution when a large number of effluent samples of the same concentration are analyzed repetitively. The x-axis is the concentration that a laboratory may measure; the y-axis is proportional to the frequency the laboratory measures a given concentration and is expressed in probability units. The y-axis data have been normalized so that the total area under the curve gives a value of 1.000. This curve applies to all analyses in which only random error occurs.

Several observations can be made regarding the probability distribution shown in Figure 3.

Observation #1: Only a small percentage of the total analyses may give the best estimate of the true value.

Observation #2: One-half the measurements are above the mean and one-half of the measurements are below the mean. Therefore, if the mean is some effluent trigger concentration above which a plant would be violating its permit, the plant would be failing one-half the time, if these data were treated as having no uncertainty.

Observation #3: The measured concentrations shown in Figure 3, 99.7% of the reported values would fall between plus or minus 3σ of the mean concentration; therefore, it can be seen that the σ of a determination is a very fundamental property of a distribution which must be used in evaluating data which contains uncertainty.

B. THE APPLICATION TO REGULATORY LIMITS

In order to translate this general probability distribution to real-world examples, Figures 4 through 7 were generated assuming different analytical uncertainty in the random errors. All figures were generated for the measurement of an effluent sample containing 100 μg/L of the target analyte. Figure 4 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 1μg/L for σ; Figure 5 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 10 μg/L for σ: Figure 6 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 30 μg/L for σ; and Figure 7 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 100 μg/L for σ. The probability distribution for the last case has been truncated at 0 μg/L since negative values of concentration are meaningless.

These four cases show clearly the impact of determinations which are carried out with different amounts of analytical uncertainty. Unfortunately, regulations are written as if data were being obtained with an uncertainty less than that shown in Figure 4. Permits which give a specific limit for a certain compound, fall into this category. However, the analytical data which are being obtained by a typical environmental laboratory for the analysis of reagent water are most likely analytical data obtained with the uncertainty shown in Figures 6 or 7. Figure 6 describes most analytical data obtained using EPA Methods 624 and 625 when the measured concentration is ten times higher than the method detection limit determined in reagent water. Figure 7 describes most analytical data obtained using EPA Methods 624 and 625 when the measured concentration is equal to the method detection limit which can be the case if the sample or sample extract must be diluted due to interfering substances. **The concern is that the probability distribution summarized in Figure 6 is used by the Environmental Protection Agency to characterize data obtained by analytical laboratories for effluent analyses. However, these data represent a best case, since method detection limits for Methods 624 and 625 are derived from the analysis of reagent water. Reagent water data should not necessarily be used to determine the random error associated with all plant effluents which may contain relatively high levels of inorganic salts, and unregulated organic compounds which may interfere with these methods.**

An additional important conclusion from this set of figures is that these case studies must be applied not only to analytical data obtained using the classical EPA Methods 624 and 625, but it also applies to BOD, COD, toxicity, opacity, etc. **Any time any measurement is being made which includes random error, this measurement contains the same types of uncertainty as described above which is certainly accentuated as the required concentration limits are decreased.** Therefore, regulations should not be written with wording that implies that Figure 4 uncertainties exist when in fact Figures 6 and 7 uncertainties are typical representations of analytical uncertainties associated with permit violation data.

Evaluation of permit violations cannot be properly made without first knowing the analytical uncertainty of the determination in the vicinity of the permit trigger concentrations and for the exact matrix under study. This means that σ data which are published with EPA Methods for the analysis in spiked reagent water should only be used as a guide. For application, however, this information should be developed for each compound/parameter in each laboratory performing these analyses.

C. THE APPLICATION TO BACKGROUND CONTAMINATION

As regulated limits go lower and lower, background contamination becomes an ever increasing problem. However, this topic can be treated in much the same way as were regulatory limits discussed above. The same analytical uncertainty must also be applied to the analysis of method blanks. In this case, method blanks are not defined as replicate injections of a sample extract, but are replicate extraction and extract analyses when representative glassware, solvents, instrumentation, etc. are used in the analyses. Using this same reasoning, an analysis of the mean concentration of the background contamination and the σ for that determination gives one the information needed to determine whether a measured quantity in a plant effluent sample is actually different from the quantity present in the method blank.

For commonly occurring background contaminants such as methylene chloride, acetone, toluene, 2-butanone, and common phthalates no positive sample results should be considered real which are within 10σ of the mean background concentration. All measured concentrations in all samples and method blanks should be reported, with qualifiers such as BBL (below background level) being used for those concentrations which are within 10σ of the blank concentration.

VII. RECOMMENDATIONS

There is a LOD or MDL which can be determined for every analyte in every matrix below which it is not possible to reliably ascertain that an analyte is present or absent. There is also a concentration range above the LOD or MDL where it is possible to qualitatively establish the presence of an analyte, but the concentration cannot be accurately and reliably quantified. It is also not practical to determine precisely the LOD or MDL for all analytes, in every matrix, and at all laboratories. All regulatory programs must recognize these facts. As a practical solution to this problem, every method should have published practical quantification limits (PQLs) which are at least media (water/soil) specific. Many of these PQLs have been published by media, and for most analytes these PQLs are representative of levels that can be achieved at most commercial laboratories. However, there should also be procedures for determining matrix specific detection and quantitation limits. Unfortunately it is not possible to analyze a large enough universe of matrices to establish generalized quantitation limits for comparison with regulatory levels. An approach must be established which will preserve the utility of published PQLs as guidance, while recognizing the significant number of compliance limits which are below their respective PQLs and thus require a variance procedure.

If a laboratory determines that it can not meet published detection and quantitation limits in their sample matrix, they should be allowed to measure these levels using established procedures which include mandated QA/QC requirements. These levels would then be used as reporting limits. If the quantitation limit, so established, is above the regulatory level, the compound would be considered to be in compliance until such a time that a level above the quantitation limit is measured. This assumption of compliance would apply whether or not the quantitation limit were a published PQL or a measured quantitation limit. EPA would also determine the frequency that these published PQLs would be re-evaluated pending method and equipment improvement. In some cases the Agency has suggested that a facility may petition for such a variance (24).

We also recommend that the EPA establish uniformity among the various regulatory programs for the determination of the method detection limit. Although the definition is essentially the same, the number of replicates and blanks may be different, therefore, the calculation is effected. This can further compound the current state of confusion in understanding and applying quantitation and detection limits. The corresponding quantitation limit should be established at five to ten times the MDL or substantially higher as the matrix would dictate (19). The use of such factors, however, must be used with extreme care as the method variability may well be underestimated by most laboratories (17). EPA recognized this need for consistency in its Report to Congress in CWA Section 518. It was reported that analytical methods are sometimes unnecessarily different for similar sample matrices, target analytes and data quality objectives. The Agency should move to greater method uniformity and more consistency in the use of quantitation and detection limits and use these concepts in regulatory compliance situations.

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DR. WILLIAM T. DONALDSON
(EPA ATHENS LABORATORY)

"... THE NUMBER OF COMPOUNDS DETECTED IN A SAMPLE OF WATER IS RELATED TO THE DETECTION LEVEL. AS THE DETECTION LEVEL DECREASES AN ORDER OF MAGNITUDE, THE NUMBER OF COMPOUNDS DETECTED INCREASED AN ORDER OF MAGNITUDE. BASED ON THE NUMBER OF COMPOUNDS DETECTED BY CURRENT METHODS, ONE WOULD EXPECT TO FIND EVERY KNOWN COMPOUND AT A CONCENTRATION OF 10^{-12} G/L OR HIGHER."

DEFINITION OF ANALYTICAL CAPABILITY

- LIMIT OF DETECTION (LOD) - Lowest concentration level that can be determined to be statistically different from a blank.

- METHOD DETECTION LIMIT (MDL) - Minimum concentration of analyte that can be determined with 99% confidence that the true value is greater than zero.

- INSTRUMENT DETECTION LIMIT (IDL) - Smallest signal above background noise that an instrument can detect reliably.

- LIMIT OF QUANTITATION (LOQ) - Concentration above which quantitative results may be obtained with a specified degree of confidence.

- PRACTICAL QUANTITATION LIMIT (PQL) - Lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions.

Comparison of Reportable Significant Figures as a Function of Relative Precision

Precision (%)	Significant Figures	Example	
		Calculated	Reported
±0.001 to ±0.01	5	54.8149	54.815
±0.01 to ±0.1	4	54.8149	54.81
±0.1 to ±1	3	54.8149	54.8
± 1 to ±10	2	54.8149	55
± 10 to ±30	1	54.8149	5×10^1

ACS GUIDELINES FOR REPORTING DATA

Analyte Concentration in Units of σ ($S_t - S_b$)	Region of Reliability
<3	Region of questionable detection (and therefore unacceptable)
3	Limit of detection (LOD)
3 to 10	Region of less-certain quantitation
10	Limit of quantitation (LOQ)
>10	Region of quantitation

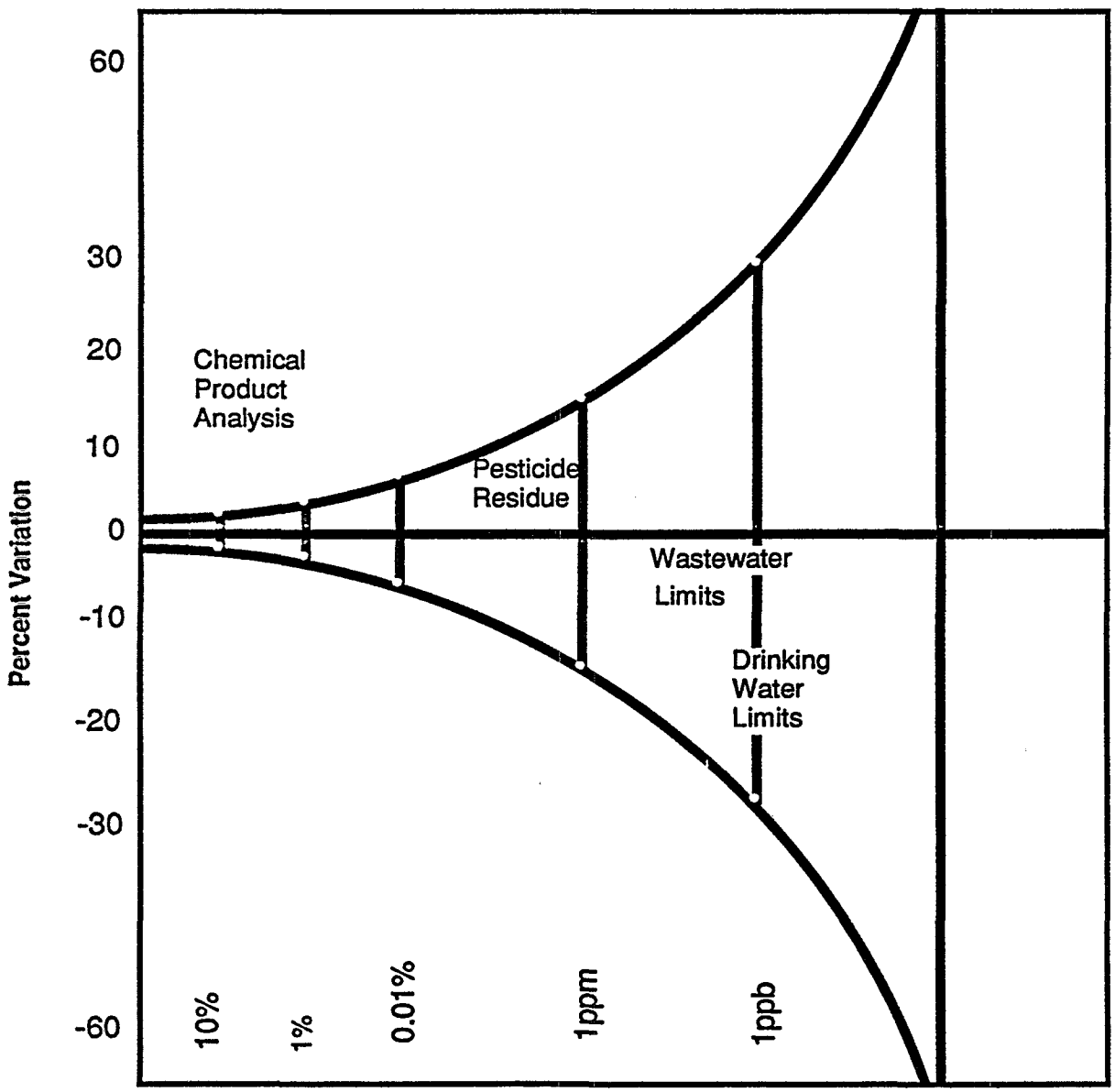

FIGURE 1. CURVE RELATING VARIABILITY BETWEEN LABORATORIES AND CONCENTRATION.

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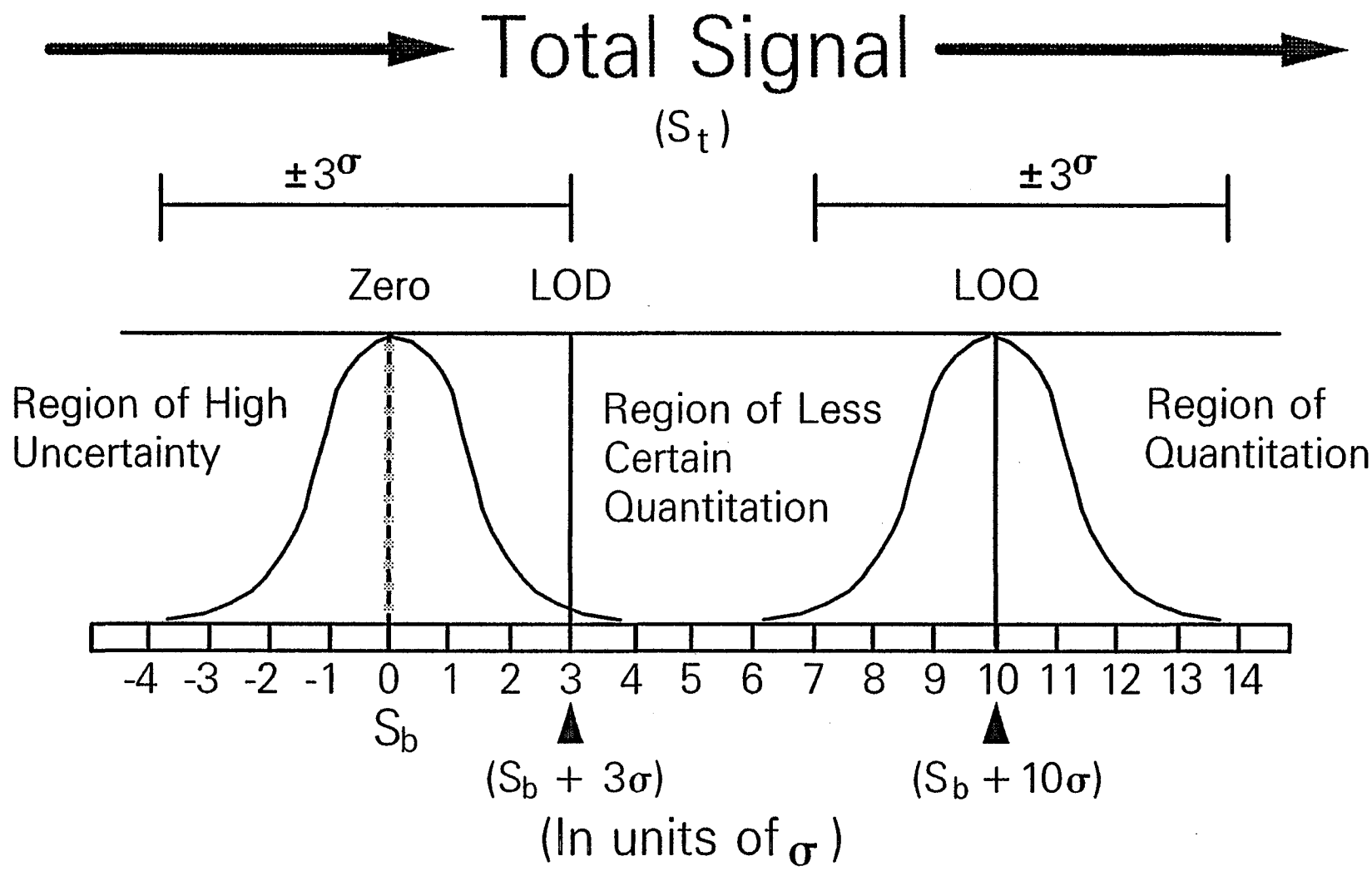

FIGURE 2, RELATIONSHIP OF LOD AND LOQ TO SIGNAL STRENGTH

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Figure 3. Normal Curve of Random Error (x in sigma-units from mean)

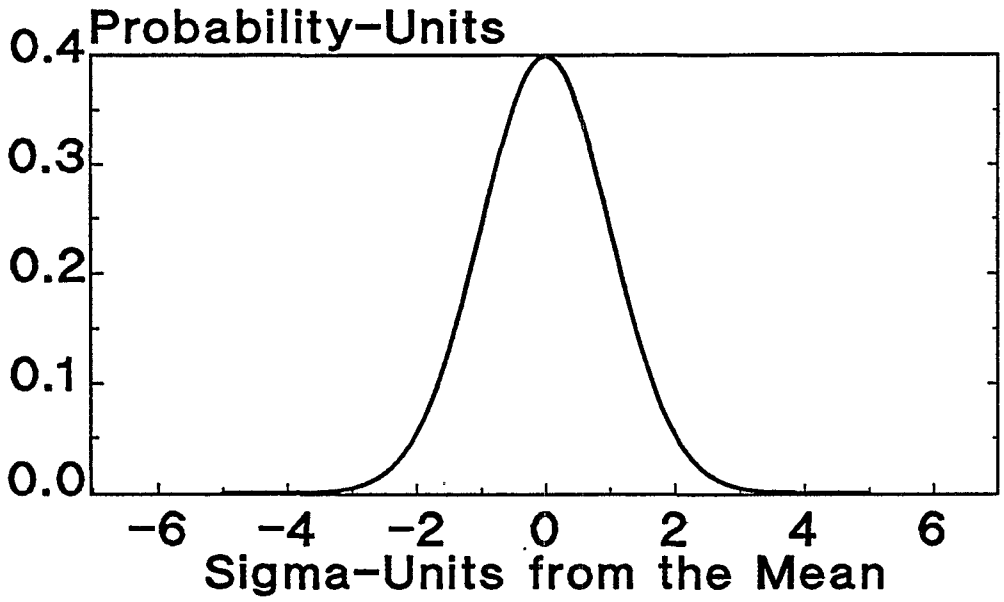


Figure 4. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 1 ug/L

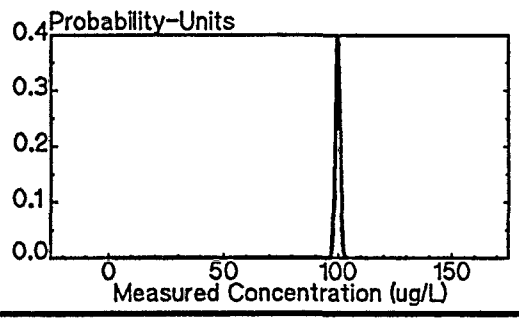


Figure 5. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 10 ug/L

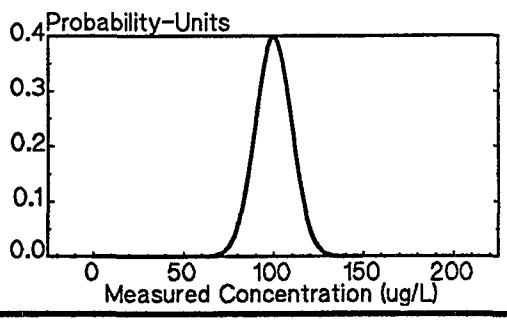


Figure 6. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 30 ug/L

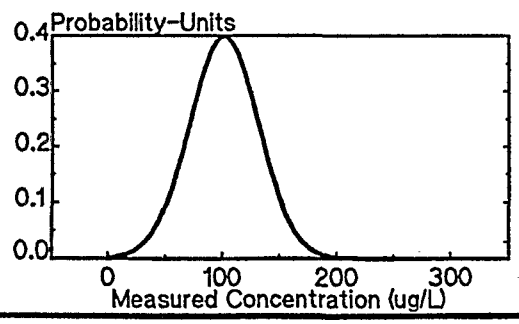


Figure 7. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 100 ug/L

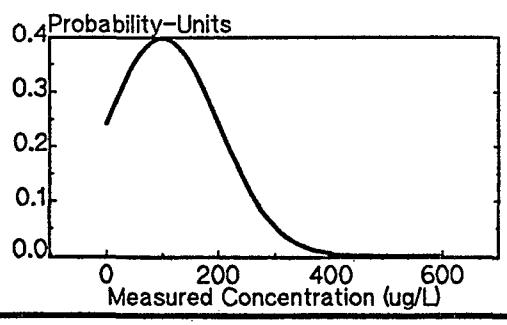


Figure 3. Normal Curve of Random Error
(x in sigma-units from mean)

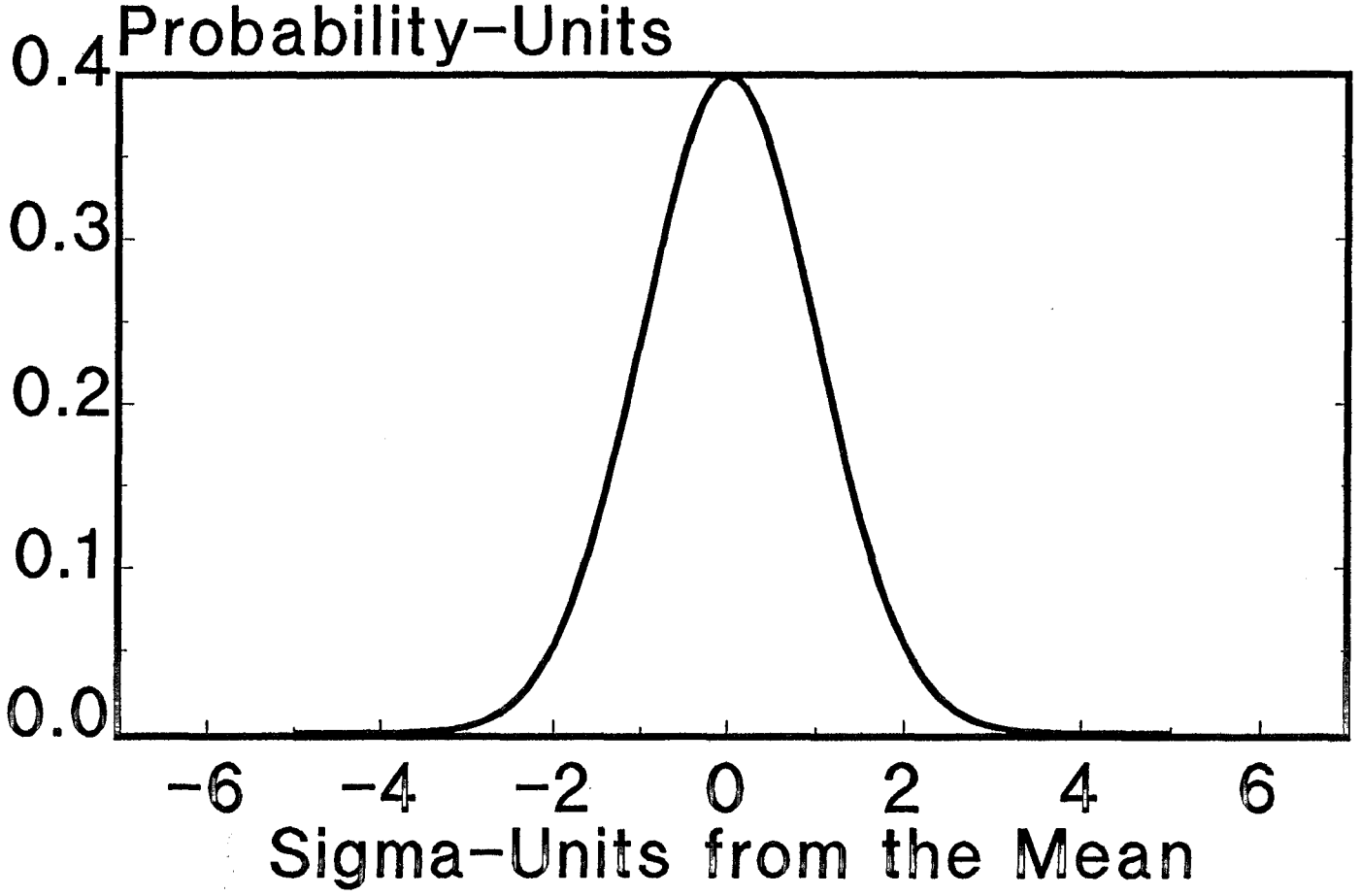


Figure 4. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 1 ug/L

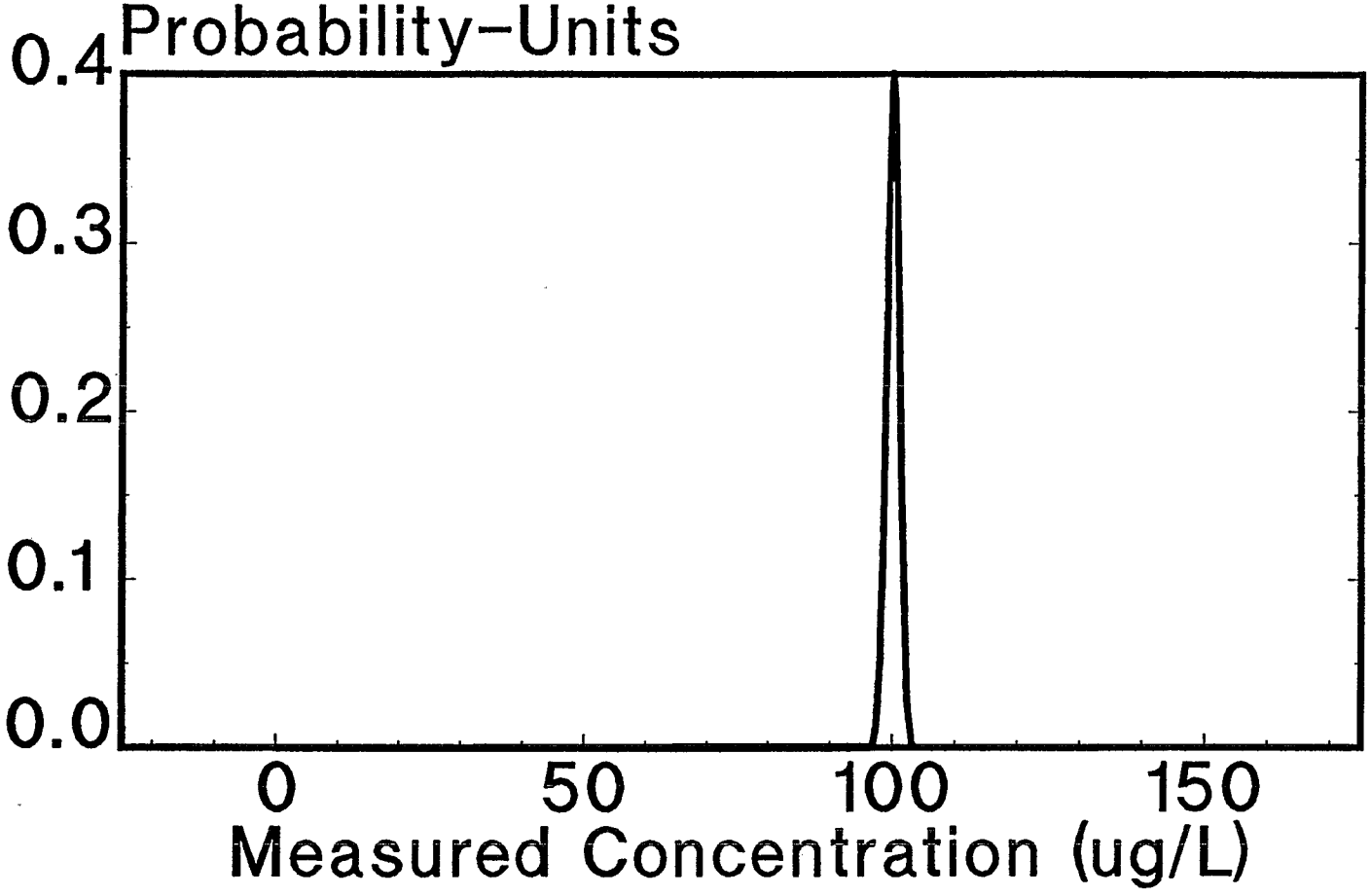


Figure 6. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 30 ug/L

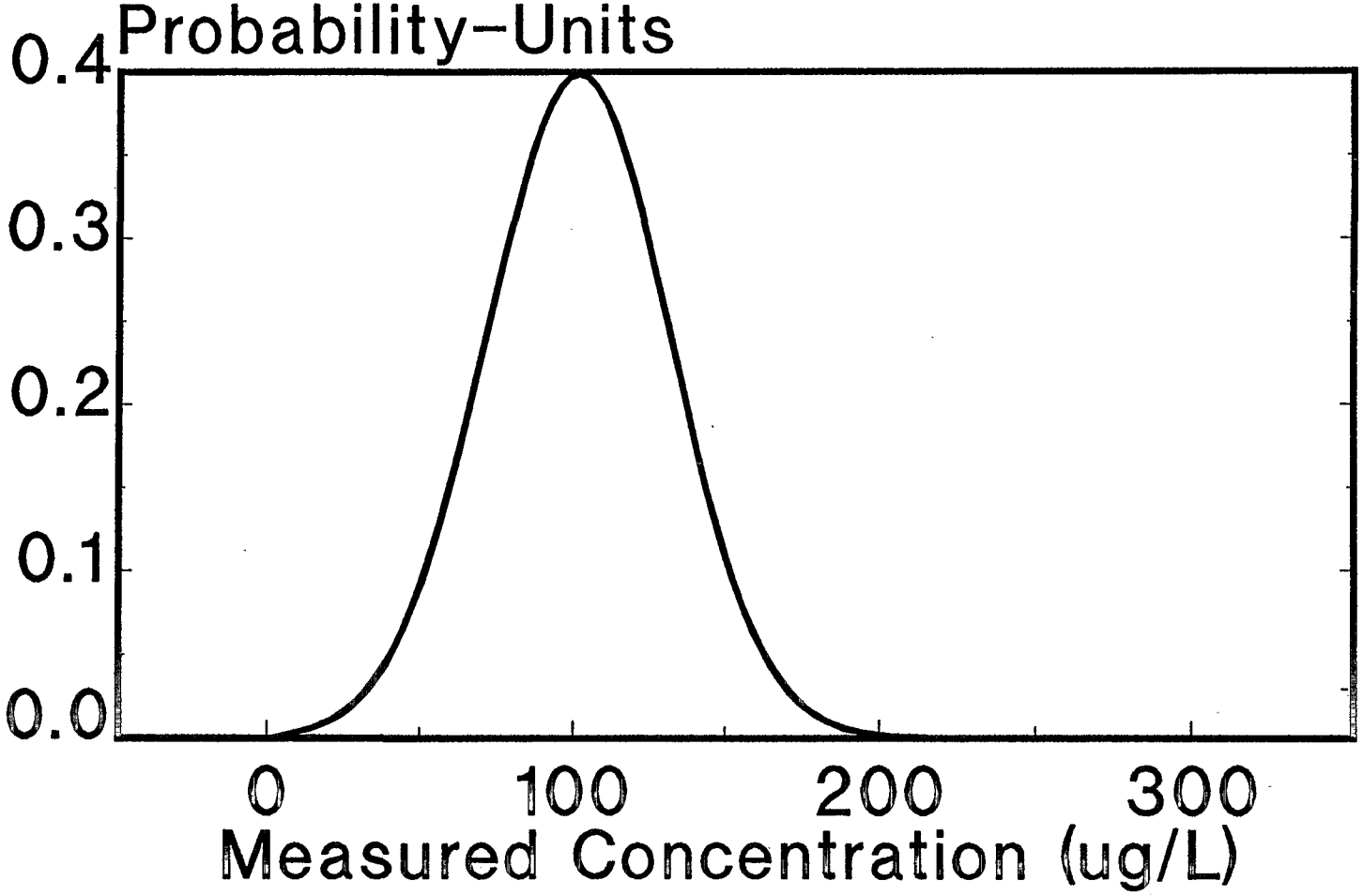


Figure 5. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 10 ug/L

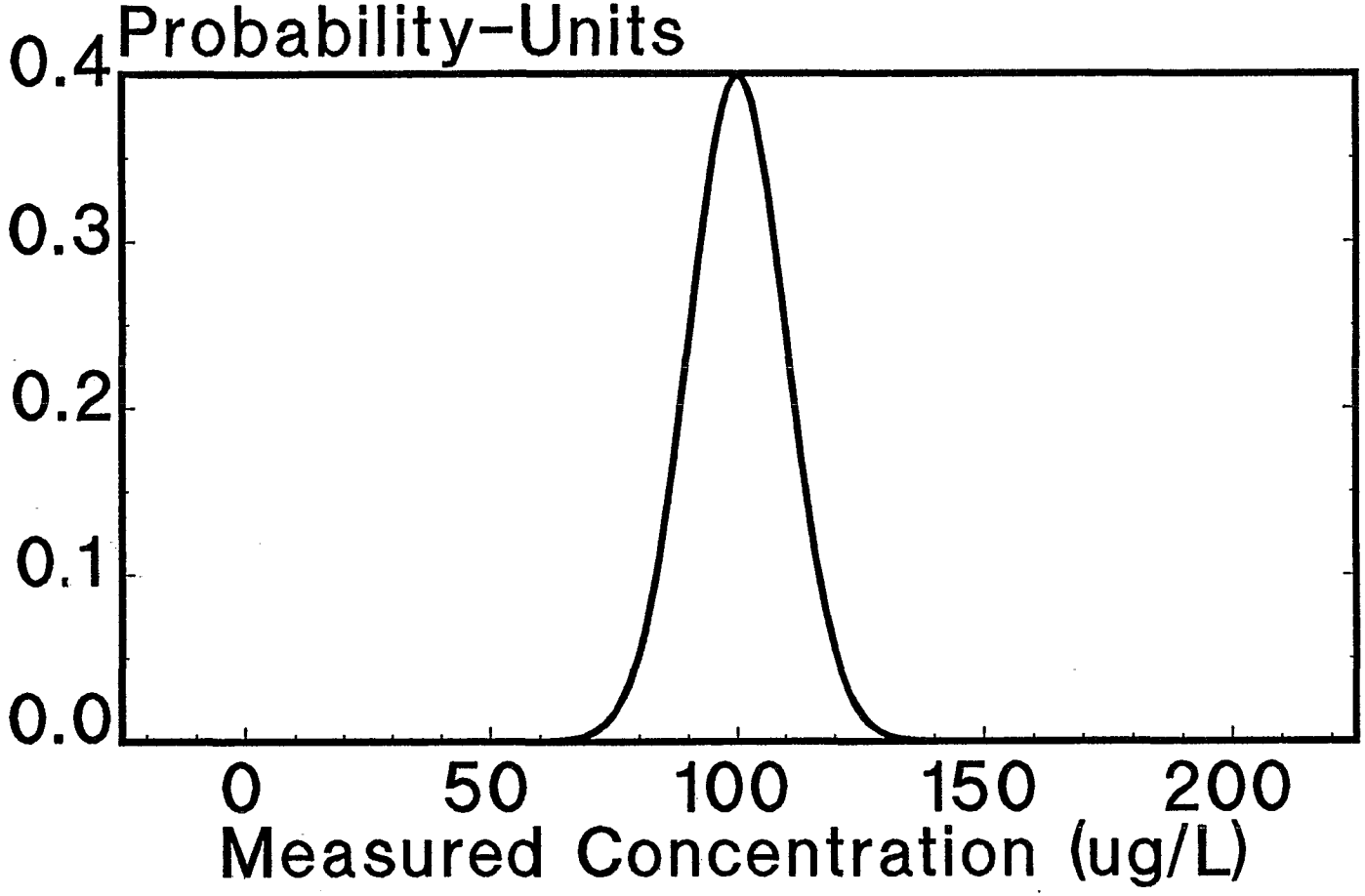
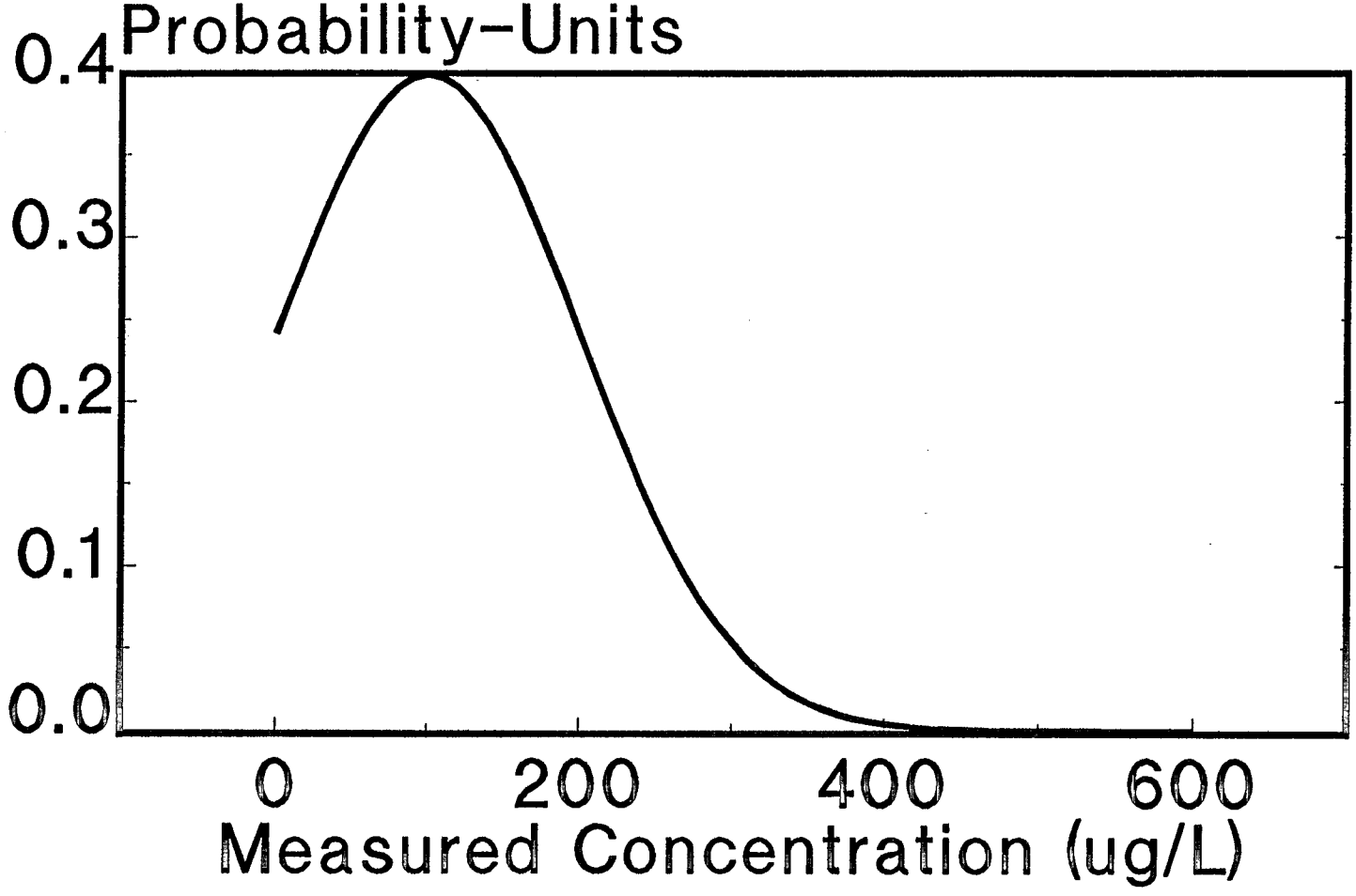


Figure 7. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 100 ug/L



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(2) PQLs are based on EPA and State laboratory data which are considered to be representative of the best laboratories, but not all laboratories; and

(3) Samples are analyzed under controlled ideal testing conditions which may not be representative of routine practices.

For these reasons, the PQL represents a relative stringent target for routine performance. (52 Federal Register 25699).

QUESTION AND ANSWER SESSION

MR. ENWEZE: I am Tony Enweze from EBASCO.

My question is, having looked at all these different values of method of detection limits, don't you think that one of the primary reasons EPA is using what they have now is something related to the risk level that has been documented that particular contaminants could cause certain kinds of diseases as certain concentration levels? You see, in order for them to maintain that every laboratory report a value within a certain range, they have established a value such that it will be compatible with that risk level for that particular compound.

Do you see that as a possible reason why they have these random values for detection limits?

MR. KROCHTA: I am not sure if I understand that question.

MR. ENWEZE: What I am trying to focus on here is that detection limits sometimes as established by EPA often are related to the risk level of a particular contaminant or any compound in the environment. It isn't necessarily that it might be coming from a practical approach, in other words, how this can be analyzed or how this can be found, but EPA values have been

established to give the limit above which the toxicity effect of a particular compound may impact a person who comes into contact with it.

So, do you think that those kinds of reasons is a major impact on why EPA has established their limits to be such in a random fashion?

MR. KROCHTA: Well, I am not sure if I understand the complete question. I may be the reasons, but our primary concern is that EPA will need to establish for these compounds PQLs that we should use as only guidance, because published PQLs are set primarily in specific matrices that are not necessarily site specific. We should only use them as a guidance as they may not be achievable even if for risk assessment purposes or routine practical applications.

As I mentioned earlier, work was done evaluating solid matrix effects, when they did a study on incinerator ash. It was found that about 33 percent of the EPA designated limits were actually below what could be measured in that particular matrix, in that site matrix.

Now, EPA has agreed that they do have a problem, and they are making an effort to establish more realistic method detection limits, but we have to recognize that they are only to be used as a guidance. Unfortunately, they are too often used, when they are setting regulations, as a level

that can be achieved, and that is not the case. They cannot be achieved.

One more comment, in our own opeation, we had a regulation limit set which was about 100 times below what we could actually measure in that particular matrix.

MR. ENWEZE: This is exactly what I am trying to get to. Don't you then think that for EPA to try to make it sort of arbitrary that wouldn't that put the environment...the people at some kind of risk to exposure to contaminants? If the detection limits...the results that are reported by labs often are reported than less than the detection limit which is considered from a risk point of view as not relevant, how would you then control that factor of the fact that...

Let me give you an example. Use the method detection limit of 5 ppb. It is clearly established that at 5 ppb, a particular contaminant can cause cancer to anybody who inhales it at this certain dose. So, how can you then control the public or the industries from polluting above those limits that could cause the risk that we are all worried about?

That is where my concern comes in, that what you are saying, leaving the public to decide where the method detection limit will be based on the analytical approach

might be risky to the public as a whole because of that factor of risk that is associated with each compound.

MR. KROCHTA: I can see your point. It is a problem. However, if they are going to establish a regulation, it should be at a level that can actually be measured. To be controlled, you have to be able to measure it.

You want to have a regulation that can actually protect the public, but if you can't measure it, it is very difficult to operate under it.

MR. ENWEZE: So, do you think then that the risk level that is established in risk assessment books are probably not valid or those values are reported with a method that was not capable of detecting that level?

MR. KROCHTA: I am not sure. I don't think we can answer that question right here.

MR. ENWEZE: Well, okay. I think I made my point that the values that we are talking about in detection limits, it is a little bit hard to leave the public exposed because the industry would like to see EPA compromise at a certain level that they consider practicable when in that quality it has been documented through research that below that level that can be detected

there is a high risk of possible diseases that could be inflicted on the public.

So, I find it difficult to let the system go to a higher detection limit when considering the risk level that might be encountered.

Thank you.

MR. FIELDING: Any other questions?

(No response.)

MR. FIELDING: All right. Let's take about a 15-minute break and be back about 3:15 or 3:20.

(WHEREUPON, a brief recess was taken.)

MR. TELLIARD: Over the last eon, the Office of Water Regulations and Standards has been working on a regulation for the offshore oil and gas industry. We feel that this regulation will outlast all of us. It is the longest known regulation in history. It has taken so long to write, most of the panel members have died. (Laughter.)

MR. TELLIARD: The youngest kid on the committee is 63, and he started out fresh out of school.

In this continuing story today, we have two presenters, both of them from the man who wears the star at Texaco, and we are going to talk about some applications and concerns about analysis of drilling fluids and drilling muds and cuttings.

Warren who is our first one up, followed by Mike Stephenson, are both involved in this program which we are trying to implement in relation to both offshore oil and gas and also, in the next year or 2 or 500, onshore oil and gas regulations.

So, Warren, would you like to lead off?

MR. HALTMAR: Thank you.

Good afternoon. Today, I will be talking about a method for determining diesel oil in drilling fluids Method 1651, Revision A. This is a proposed method for determining the total oil and identifying and determining diesel oil in drilling fluids which include muds and cuttings.

Proposed methods, I always believe, are not actual facts but are expected to undergo modifications.

The detection limits for this method are 200 mg of total oil and 100 mg of diesel oil in our samples. This amounts to, if are taking a 20 gram sample, 2 mg of diesel oil.

Again, this is a proposed method. I got involved in this last year in validating the GC portion of this method. This year, I became a participant in a round-robin study to determine how effective this method is.

Today, I will talk about only the high points of the method, retorting or distillation of the sample, the gravimetric determination for total oil, and then the capillary gas chromatography method for determining diesel oil.

Then I am going to talk about possibly a few modifications to this method. Some of them are drastic modifications. I really originally thought they might be a

pie in the sky type thing, but maybe they are more down to earth than I originally thought.

Finally, I am going to bring you my conclusions about the method.

For those of you who are not familiar with drilling fluids, the definition of a drilling fluid is it encompasses all of the compositions used to aid the production and removal of cuttings from a borehole.

For our case, we are looking at a water-based mud, and this is made up of three major components: water, clays, and additives. The additives can be weight enhancers, viscosity enhancers, viscosity reducers, fluid loss agents and lubricating agents. Diesel oil is not supposed to be added to these drilling fluids.

Occasionally, a driller will add it because he has problems. The problem is he is getting a drill bit stuck in a hole, he left his lubricating agents back on shore, he is off shore, he only has a finite time to do something. So, he sees diesel oil is handy, and he mixes it in the drilling fluid.

This first step of the procedure is to retort the sample. Retorting is a simple distillation procedure, which is semi-quantitative at best. The device has been around the oil industry for a long time and consist of a metal sample cylinder, an aluminum condenser and a graduated

cylinder to correct the distillate. The drilling fluid sample is retorted until liquid stops coming from the sample.

Once we have our distillate. Total oil is determined gravimetrically. We extract the distillate with methylene chloride. The methylene chloride removes the hydrocarbon material, which includes total oil and diesel oil from the distillate.

The methylene chloride is removed using a Kuderna-Danish concentrator to give a gravimetric determination of total oil. I was unsuccessful in removing all of the methylene chloride from the sample using this device. The Kuderna-Danish Apparatus is a concentrator not a device to bring to dryness.

What I finally did with this apparatus is I took the receiver off the bottom after I had removed as much methylene chloride as I could. I put it in a sand bath, warmed it gently, and blew dry hydrogen on it. I knew when I did that I was probably going to lose some of the light ends of the diesel oil, and, indeed, we did.

One of the interesting things that I did with the Kuderna-Danish is that once I removed all the methylene chloride, I still had methylene chloride in my sample. I took a sample of that, injected it into my GC, and I got a chromatogram very similar to what I was expecting from my

diesel oil. So, it really didn't look like the retort was having no adverse effect on the diesel oil.

For the gas chromatography, section of the procedure, we redissolve the sample in methylene chloride and added an internal standard, 1,2,5-trichlorobenzene. We inject this into our GC. We essentially fingerprint the sample, to identify the diesel oil by looking at the alkanes. We are looking at ten alkanes eluting after the internal standard.

Gas chromatography conditions, we are using a DB-1 column or equivalent, 30 meters long, 0.25 mm inside diameter with a film thickness of 1.0 micron.

The method calls for a split ratio is 0 to 120. When I did the verification on the calibration method, I found out when we use the high split ratios, we came up with the old bugaboo of discriminating distillation. If we reduced the split ratio down to 40:1 or less, then eliminated the discriminating distillation.

Our detector and injector temperature is 275. Our oven temperatures are programmed from 90 to 250 degrees C at 5 degrees per minute. This can change. There is a criterion in the procedure that calls for relative retention times to elute at a particular time. The internal standard must elute at 8 minutes.

I had some difficulties making my G.C. meet the retention time requirements of the method. Because of the

many variables associated with G.C. retention times, many manufacturers test mixes would be a better check for G.C. and column operating efficiency. This is especially true when analyzing complex samples.

Finally, a data system is needed that can store and process data from the G.C.

A typical chromatogram of #2 diesel is this right here. We have our internal standard. We are looking at these 10 alkane peaks. We start with C_{12}. The method does allow that if we run into some interferences with these alkanes, say, from a crude oil, that we can use some of the lesser peaks, possibly some of the aromatics here. The aromatics are really the compounds that could be harmful to our environment.

The data we obtained on our calibration samples is shown here. The first three standard samples have relative retention times and response factors in agreement with the procedure. The last sample is our lowest standard and failed to meet the requirements for response factors.

There is a caution here that I think everybody needs to be when aware of using data systems. Data systems can have problems picking the correct baseline for samples ranging over a wide range of concentrations. The expanded chromatograms show an alkane region in and out of the

calibration range. Large differences do exist because of baseline differences.

Taking a look at the data generated from the method, it was found that the light ends of the diesel oil were lost. This occurs when the methylene chloride is evaporated to dryness. This data was obtained by spiking mud samples with known amounts of diesel. As can be seen, 40 to 50 percent of the diesel oil is lost during the gravimetric analysis.

Earlier, I stated that the retort device is a semiquantitative device. We ran a blank down here of just water, and lo and behold, we find out that there are 61 mg of diesel oil in that water blank.

To see what effect this loss has on our chromatogram, we took two samples, spiked with known weights of diesel oil. One of them was dissolved in methylene chloride; one of them we carried through our retort procedure. What we want to see is differences in the chromatograms of the two samples.

Here we have our internal standard, and you can see this chromatogram is very, very similar to what I showed you earlier.

Now, if we carry diesel through the retort, the extraction, and the concentration, this is our diesel. We have lost all the light ends. This is our internal standard. Before, on the other chromatogram, the maximum

alkane was peaking about 17 minutes retention time. Here, we have pushed our maximum alkanes out to 20 to 24 minutes. So, we have drastically altered the diesel oil.

If we look at the aromatic fraction in here and compare the two different samples, we see that we have also lost part of our aromatics.

Some of the modifications that could improve the method. We need larger samples. Two mg of diesel is a rather small sample to work with. The retort evidently is retaining some of the diesel oil. So, possibly, a glass distillation device would be better.

The split injection mode of the gas chromatograph reduces sensitivity. Performance and sensitivity could be improved by reducing the split ratio or by splitless or on-column injection. If additional sensitivity is needed then widebore or megabore columns could be used.

The problems were encountered with one internal standard, but in complex matrices it is advisable to use multi-internal standards.

Working through this method, it became apparent that the internal standard should be added to the drilling fluid. This would allow tracking the sample all the way through the procedure, not just the G.C. portion.

The method uses only an FID detector. Because the aromatics are the compounds of concern, it is suggested that a PID detector be used along with the FID detector.

One of the major modifications would be to use FT-IR. FT-IR's with the latest in software techniques, like partial-least-squares could be used to determine solvent (methylene chloride), crude oil and diesel oil. This procedure would still need a suitable extraction technique.

Another possible method would be fluroescence. This would monitor only fluroescening compounds (aromatics) a non-fluroescening solvent would be needed for the extraction.

Finally, a method that I am not too familiar with is SFE/SFC. This method appears to be ideal for this type of analysis. The method could be one continuous procedure using on-line extraction. The chromatography could give chromatograms similar to the G.C. or it could give only total saturates and total aromatic.

In conclusion, I was unable to determine how effective the retort separated the hydrocarbons from the drilling fluids (gravimetric analysis). Chromatograms of diesel oil versus retorted diesel oil were similar.

Methylene chloride is a problem with the gravimetric analysis. A little bit of error can cause a large error in total oil and diesel oil.

The gas chromatography proved satisfactory with one internal standard with low split ratios.

If you all have any questions now, I will be glad to entertain them. Thank you.

MR. TELLIARD: Thank you, Warren. Thank you very much.

LABORATORY DETERMINATION OF DIESEL OIL IN DRILLING FLUIDS

BY: WARREN C. HALTMAR

ABSTRACT

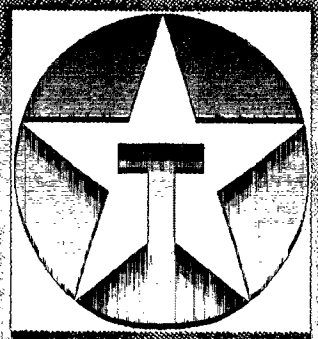
Drilling muds and/or drill cuttings occasionally become contaminated with diesel oil, which contains toxic compounds and could be harmful to the environment if discharged in an improper manner. The Environmental Protection Agency (EPA) has proposed a method (Method 1651) for determining total oil and diesel oil in drilling fluids (cuttings and muds). This method involves the retorting, gravimetric determination of total oil, and the capillary gas chromatography determination of diesel oil.

Detection limits are estimated to be 200 mg/kg for total oil and 100 mg/kg of diesel oil in the drilling fluids. This translates to 2 mg of total oil or 1 mg of diesel oil per 10 gram sample. After retorting the distillate (water and oil) is extracted with methylene chloride to separate oil from the water coming from the drilling fluid. The methylene chloride is evaporated to give a gravimetric determination of total oil, which includes diesel oil. The dried extract (oil) is dissolved into methylene chloride with an internal standard and analyzed by split injection capillary G.C..

This is a proposed method and is expected to experience modifications before final acceptance. The merits and possible modifications of this method will be discussed.

LABORATORY DETERMINATION OF DIESEL OIL IN DRILLING FLUIDS

• by: Warren C. Haltmar



METHOD 1651 REVISION A

- The method is used to determine total oil content and identify and determine diesel oil concentrations in drilling fluids (muds and cuttings).

- The detection limits of METHOD 1651 is 200mg/kg total oil and 100 mg/kg diesel oil.

- Retort or Distillation
- Gravimetric for Total Oil
- Capillary Gas Chromatography for Diesel Oil
- Modifications
- Conclusion

DEFINITION

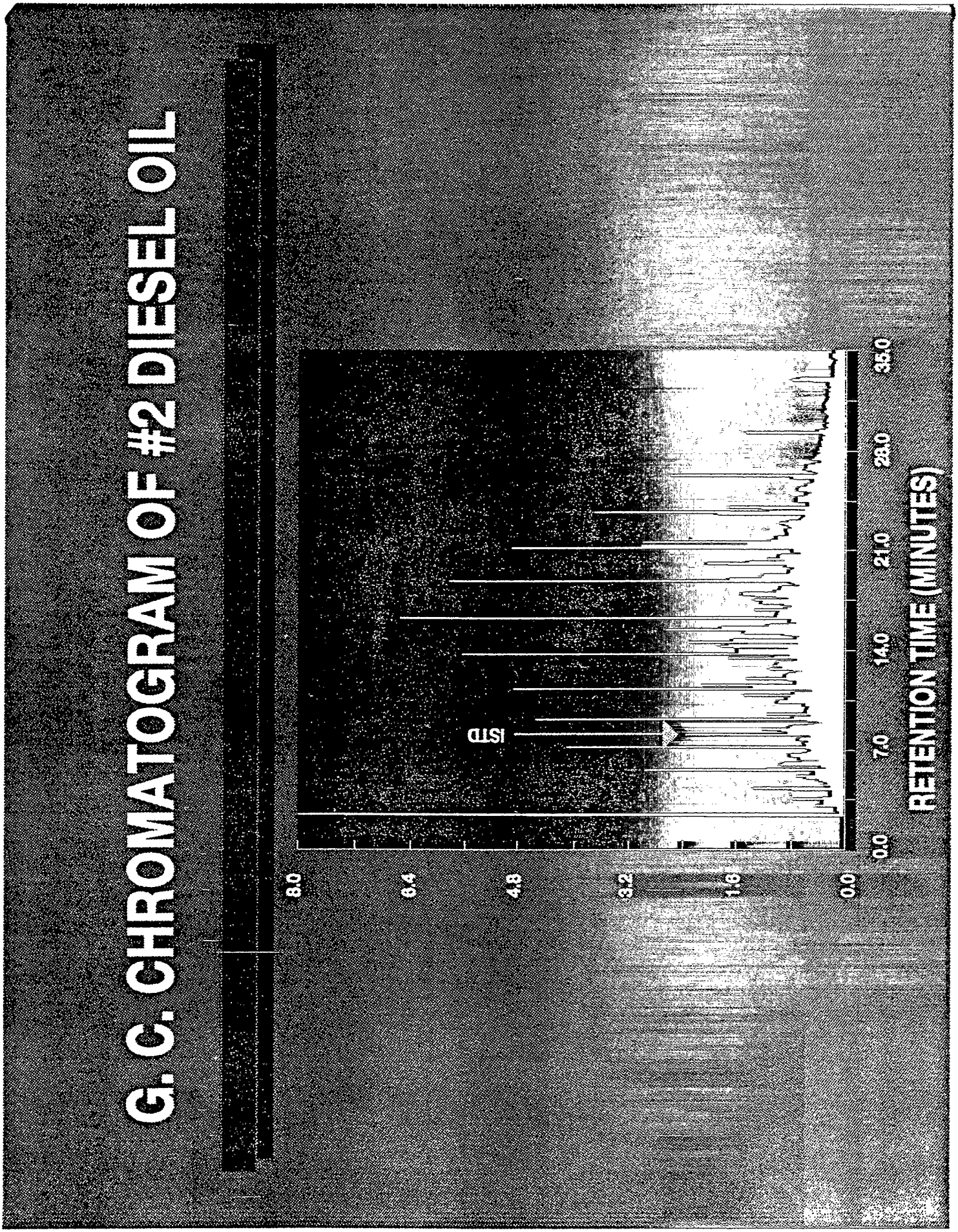
- Drilling Fluids — Encompasses all of the compositions used to aid the production and removal of cuttings form a borehole in the earth.

- Retorting — Involves placement of a precise amount of mud in a steel container, and heating it in the retort until no more distillate collects in a graduated cylinder.

- Gravimetric for Total Oil
  - Extraction— Methylene Chloride
  - Concentration — Kuderna — Danish Apparatus
- Gas Chromatography — Calibration
  - Internal - Standard — 1, 2, 5, — Trichlorobenzene
  - Fingerprinting — Alkanes

GAS CHROMATOGRAPHY — CONDITIONS

- Column — DB-1, 30M X 0.25mm 1.0, 1.0µm Film Thickness
- Spilt Ratio — 0 - 120:1
- Detector and Injector Temperature — 275°C
- Oven Temperature (Programmed) — 90-250°C @ 5°C/min
- Data System with Storage


G. C. CHROMATOGRAM OF #2 DIESEL OIL
8.0
6.4
4.8
3.2
1.6
0.0
ISTD
0.0
7.0
14.0
21.0
28.0
35.0
RETENTION TIME (MINUTES)

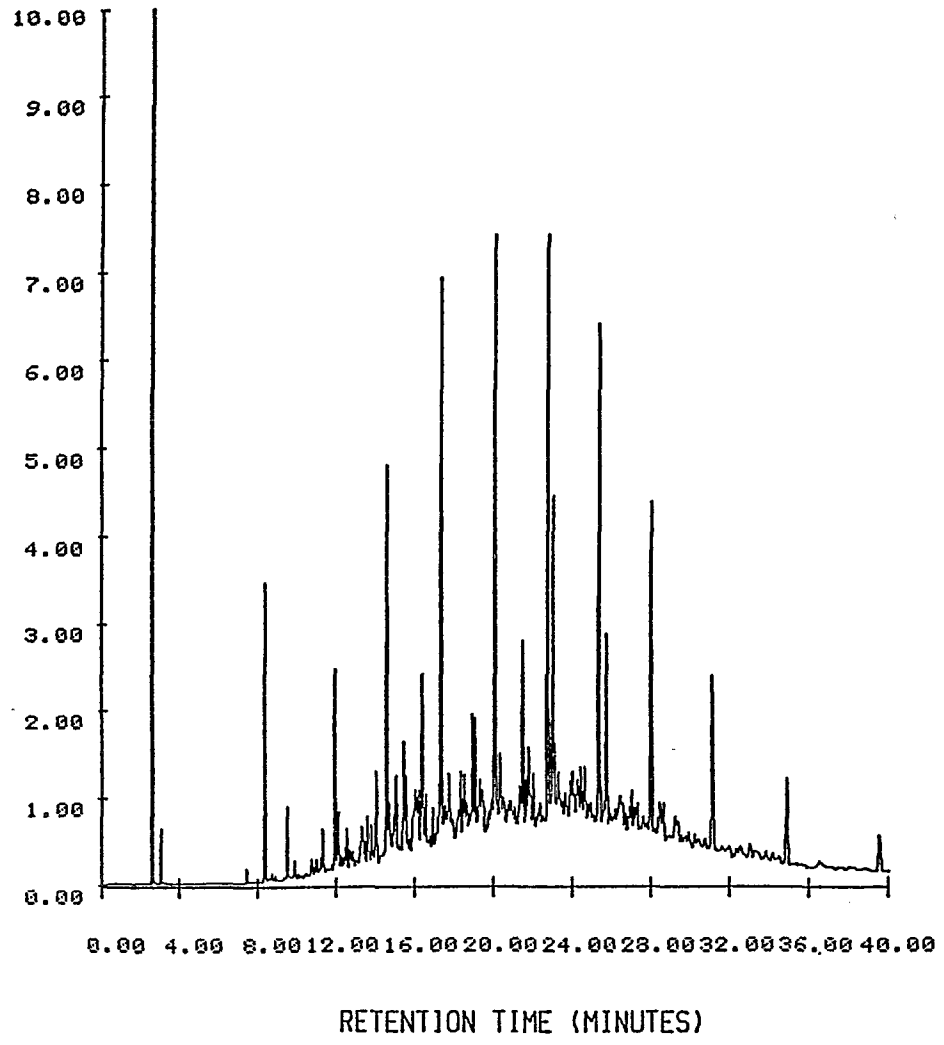
G. C. CALIBRATION DATA FOR #2 DIESEL OIL

	760 STD		300 STD		150 STD		60 STD	
PEAK	REL RET	RF	REL RET	RF	REL RET	RF	REL RT	RF
ISTD	1		1		1		1	
1	2.64	0.013	2.62	0.016	2.62	0.019	2.79	0.370
2	4.99	0.013	4.97	0.016	4.96	0.019	5.13	0.393
3	7.48	0.024	7.45	0.030	7.43	0.033	7.60	0.253
4	9.98	0.018	9.94	0.021	9.92	0.023	10.09	0.407
5	12.41	0.018	12.36	0.020	12.35	0.023	12.53	0.458
6	14.98	0.018	14.73	0.014	14.71	0.023	14.88	0.512
7	17.01	0.012	16.97	0.009	16.96	0.016	17.13	0.792
8	19.15	0.009	19.12	0.009	19.11	0.012	19.26	0.988
9	21.2	0.005	21.18	0.005	21.18	0.009	21.36	1.467
10	23.16	0.003	23.15	0.002	23.15	0.004	23.34	2.768

GRAVIMETRIC RESULTS FOR DIESEL OIL IN DRILLING FLUIDS

SAMPLE	mg DIESEL OIL ADDED	mg DIESEL OIL RECOVERED	% RECOVERY
1	408.7	205.4	50.2
2	384.3	230.7	60.0
3	403.0	228.8	56.8
4	404.0	262.6	65.0
	0	61.2	

SAMPLE D-1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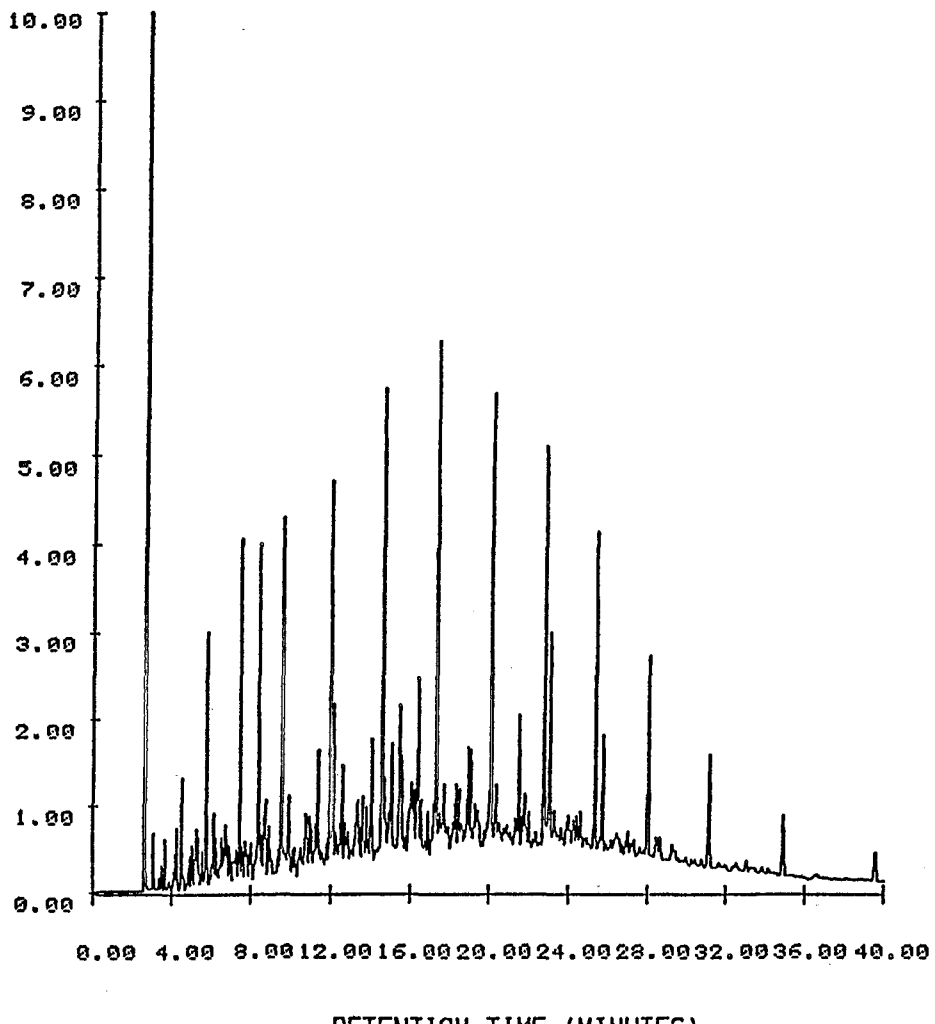
RETENTION TIME (MINUTES)

SAMPLE D STD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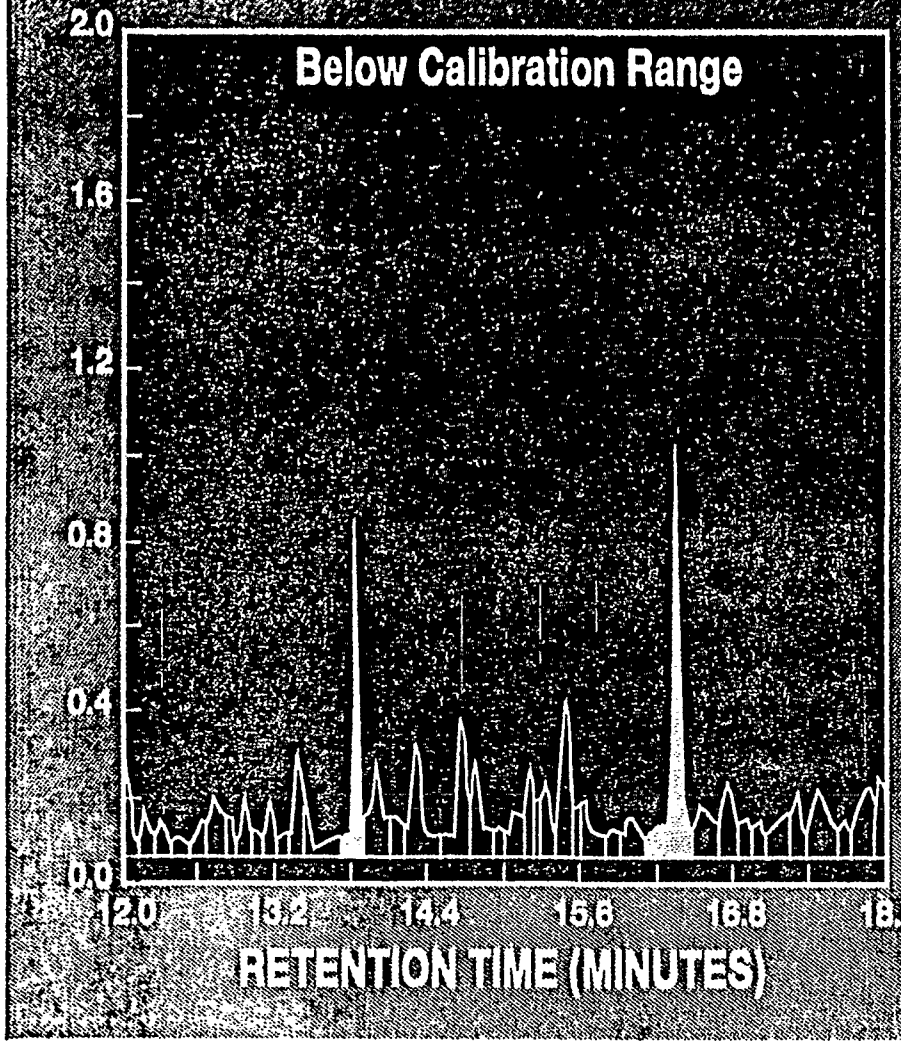
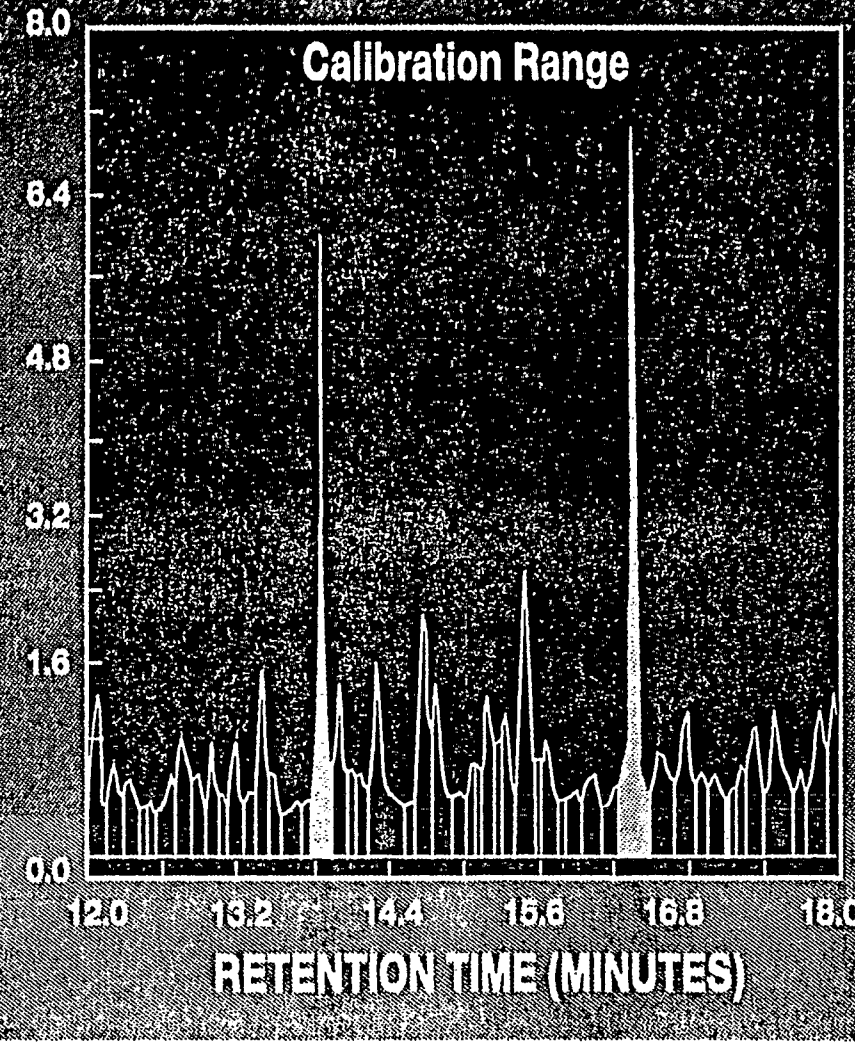
RETENTION TIME (MINUTES)

G. C. CHROMATOGRAM OF C14 – C15 HYDROCARBONS IN #2 DIESEL OIL





MODIFICATIONS

- Retort — Larger Samples
- Gas Chromatography
  - Injection Mode
  - Mega-Bore Columns
  - Internal Standards
  - FID/PID Detectors
- Spectroscopic Method — Total Oil
- Diesel Oil — Fluorescence
- SFE/SFC

CONCLUSIONS

- RETORT — Unable to determine effectiveness on low concentrations of diesel oil. Retorting does not appeal to effect fingerprinting of diesel oil by GC.

- GRAVIMETRIC ANALYSIS — Concentration step presents problems in removing Methylene Chloride.

- GAS CHROMATOGRAPHY — Reproducible results are attainable with one internal standard. Diesel oil concentrations must be in appropriate range.

MR. TELLIARD: In the same drilling mode, Mike Stephenson is going to come up and explain how nice the method is and how he really likes it.

MR. STEPHENSON: Warren got up and told you something about the nuts and bolts of this Method 1651. What I want to talk about is the validation of the method.

In order to get to where we can talk about the validation study that we are undergoing, I want to go through a little bit of history that is involved with this elusive Method 1651.

The purpose of the method is to identify the presence of diesel oil in drilling fluid and to quantify the amount of diesel oil present. Diesel oil is a highly aromatic fuel, and aromatic compounds are known to be bad for the environment. One of the most famous ones is benzene. Naphthalene is a known poison. They use it in moth balls.

So, we don't want to put these in the ocean. The agency saw the wisdom of doing that, and banned the discharge of drilling muds that contain diesel in them. Very logical.

The next thing we had to do was say, how do we know whether there is no diesel in it? That means you have to have a way of analyzing for it.

So, back in...I think the first official proposal of this method was in August of 1985. It was unofficially proposed some time before that, and we have been sort of at

cross purposes with Bill on it since the first day he mentioned it.

One of the things that brought us to cross purposes was the method that we were talking about using. We were analyzing a highly aromatic fuel by using aliphatic compounds as the labels. The agency's recommended substitute for using diesel fuel was to use mineral oil which has very low to no aromatic content. Since it doesn't have any aromatics, it has as lot of aliphatics which makes it look almost the same as diesel.

In fact, one of the studies that we conducted as an industry showed that from the chromatograms, you couldn't tell the difference between diesel and mineral oil in some cases.

MR. TELLIARD: If you were blind, you couldn't. That is true.

(Laughter.)

MR. TELLIARD: There was an incident.

MR. STEPHENSON: Okay, there were two.

After the method was originally proposed, one of the things that we as an industry tried to convince Bill and the rest of the agency, was that we needed to be able to use diesel for periodic operational requirements.

It costs a lot of money to move these drilling rigs around out there, so we like to park in one place and drill two or three holes from one location. In order to do that, you do a lot of bending of your pipe and drilling off at angles. You can imagine, if you will, a bent shaft with something that is inside it turning, that it ends up binding periodically.

In order to reduce that binding, historically, one of the best lubricating agents that we knew as an industry was diesel oil. It would unstick our pipe, and we could get on with drilling pretty effectively.

If we put a slug of diesel in the mud to unstick our stuck drilling pipe, then if we recovered all of that diesel, we should end up with no diesel left in the mud. And it turned out that we ended up having to recover a large slug of mud.

At any rate, I am not here to talk about the diesel pill monitoring program. That was a long winded program that did a lot of analyses, and it is the source of a lot of the operational history with Method 1651.

That method came out and was published. As an industry, we had a few problems with it. There were typographical errors in a couple of the formulas and...

MR. TELLIARD: Conclusions.

MR. STEPHENSON: Yes, conclusions.

Also, one of the things that it didn't do was address, from our viewpoint, the possibility of interferences. If we were using a recommended substitute such as a mineral oil in our drilling fluid and we happened to get lucky and drill through an oil bearing zone, then we ended up with a little bit of oil in the drilling fluid.

How can you tell that what you measure isn't diesel? Or, how can you tell if there is any diesel there or how much is there? You end up with an interference problem from the formation oil.

If you drill a dry hole and don't find oil, it becomes a pretty simple system, but if you find oil or you put a little diesel oil and a little mineral oil in the mud, it becomes very complicated. And that issue is not resolved yet.

At any rate, we made our comments on the first publication , and they came out with Revision A. When they came out with in October of 1988, we had 14 rigs that were out in the Gulf of Mexico drilling; drilling not using diesel and not using oil based muds.

So, we went out and took some samples. We took a sample before they hit an oil bearing formation, a sample after they hit an oil bearing formation, and a sample at the

end of the well. We were going to analyze all those samples using Method 1651 to see how much total oil was in the mud and if there was any problem with interferences with diesel. We were trying to convince Bill that we needed to do something else.

When we started out, and we had difficulty with the method. Our contract laboratory spent about $30,000 just trying to do the calibration according to the method. At that point, we decided he could stop trying to calibrate.

We had an emergency meeting with Bill and Dale Rushneck and the contractor that was doing the work. We got a little advice from Dale on how to get on the right track, and our contractor went back and tried some more. We finally decided to stop.

At that point, I said, okay, we have a problem. I knew I had a good analytical chemist. So, I called Warren, and I gave him the method. I asked him to go down to the local Texaco station, get some diesel, and do the calibration. However, he couldn't calibrate following the letter of the method, either.

So, I said okay, that is wonderful. Then I asked him to go back and see what had to be done to make the method calibrate. So, he did.

Then we had another meeting. We are good at meetings. We meet all the time. We had another meeting, and we made

some modifications to the method. At that point we decided that with those modifications, we needed to do a study by several laboratories of this whole method. The purpose was to determine just exactly how good the method was and what it was going to accomplish, and we weren't even going to talk about such things as interferences at this time. We were just going to see if we could do straight analyses.

So, what I am talking about in this validation study is the purpose of the study, the laboratory samples, the control of the study, and what results we intend to get.

As you see, we had a joint study, industry and government. You can see Bill is the guy over there in the blue coat and the white beard.

The purpose of the study was to determine the difficulty of the method. One of my colleagues, Dan Caudle, and I have maintained for a long time that this was a very difficult method. So, one of the things we wanted to find out because Bill wanted to show that it really wasn't all that difficult, was just what the degree of difficulty of it was.

We also wanted to find out what the reproducibility of the method was.

And finally, we wanted to get some rough idea of the detection limits, because we weren't comfortable with the limits that were set forth in the proposed method.

And Bill said, okay, I will let you do that. I will even donate one laboratory to do that. Very magnanimous of me.

MR. TELLIARD: Nice guy, nice guy.

MR. STEPHENSON: Yes, nice guy. He is here to help us.

The laboratories that we are using for the study include, of course, Warren Haltman of Texaco as one of the laboratories. Conoco Research Center up in Oklahoma is another one of the laboratories. Since we already have laboratories that have good analytical capability, and since we are not going to be reported on these results, and we are just doing some research, we figured that we might as well use them to do this little study.

We did use an independent laboratory, CORE Laboratories in Lafayette which used to be known as Weintritt Testing Labs. That was the laboratory that did the bulk of the testing in the diesel pill monitoring program, and that was the laboratory that was trying to do the calibration in the 14 rig study.

Then, of course, we have Bill's laboratory, Dave Thompkins at ETS Analytical Services.

And then as a matter of interest, there is a new technology that has arisen at Ruska Instruments. They call it thermal chromatography, but it is controlled distillation

through a detector. It is an interesting device, and he has some data that shows good results. In fact, it is so good, Bill to uses it for another method.

Since Dan Caudle from Conoco and I had been arguing with Bill about this for several years, we decided that we were a little prejudiced in what was going on; and since Texaco and Conoco had provided two of the laboratories to do the testing, we ought not be involved as being the control officers. That would mean we would know what the unknown samples were, and we might prejudice our own people.

So, we asked Joe Raia from Shell Development Company act as the industry control officer. Our good friend here acts as the other one.

The next topic is the results that we intend to achieve. Each of the laboratories, when they turn in their analysis package, are supposed to turn in the chromatogram of each run, the oil content from each retort, the diesel content as a result of doing the GC runs and doing the calculations as set forth in the method, and the QA and QC requirements of the method. That was the way we set up the program with triplicates and so forth, to make sure we got sufficient data. This program provides 23 retorts and 23 G.C. runs.

At $250 a run, it costs the industry about $5750 for CORE Laboratories. I would hate to see what Warren has spent on the testing.

What about the data received to date? Well, one laboratory, CORE Labs, has turned in its data. The others are still working on it. I saw Dave Thompkins the other day, and ETS is still working on it. Texaco still has not finished all of their analyses. Conoco hasn't finished theirs. We have heard from Ruska and they are still working on it.

It is taking a little longer to do this than we first envisioned. But, when we get all the data in to Bill and Joe, we are going to get back together again, probably at Texaco, to discuss all of this data and what it means. Hopefully, we will come to some way of either modifying the method to make it suitable to all of us and something we can live with or inventing some new method. Who knows?

At any rate, I want to thank Bill for inviting me to come speak and for being our control officer. I want to thank Dan Caudle who dragged me, kicking and screaming, into this debate; Joe Raia from Shell who worked with Warren a great deal on some of our comments and on the recommended revisions to this method; Warren who has done a lot of work and consultation with me; the API for paying for Weintritt Laboratories; and, of course, the EPA for paying for ETS.

That is basically all I wanted to say, except I wanted to know if you had any questions, because we have a bunch.

QUESTION AND ANSWER SESSION

MR. HOPPE: My name is Eric Hoppe. I am with Battelle.

I am kind of wondering if I am missing a point here. I am not sure I understand what the difficulty of the method is. I think there are a lot of commercial laboratories that have done this for years and years, although I don't think there has been any check as far as their recovery limits or anything.

MR. TELLIARD: We have not met before the meeting, right?

MR. HOPPE: No, we have not.

(Laughter.)

MR. TELLIARD: And before you went to Battelle, you worked in which part of the EPA? Just kidding.

MR. STEPHENSON: Actually, the basis of one of our sets of comments describing the difficulty of this method was a Battelle report, just to keep things in perspective.

It turns out that we end up doing things like evaporating to dryness in a Kuderna-Danish. A Kuderna-Danish, you know, is not a dryness device. It is not designed for that. It doesn't do that well. Hence, it

doesn't do it. And that is one of the problems we have with the method.

Another problem is the fact that the retort is not a fully quantitative distillation procedure. The recoveries that we get here, the recoveries that Weintritt got in their work were low.

So, you know, there are some problems with it.

One of the reasons we went to doing the retort...maybe this will help clarify it and why it becomes such a problem to us...we started out initially...and Bill had this idea for doing this...and we wanted to have a method that we could do out on this platform bobbing up and down on the ocean.

MR. TELLIARD: You didn't like my first idea. I recommended we wouldn't have this difficulty if they just used GC/MS. They didn't think it was a good idea to put a mass spectrometer on an oil rig. I thought they had a very narrow window to look through. You had room for a Coke machine, but you didn't have room for a mass spectrometer.

(Laughter.)

MR. STEPHENSON: What can I say? It is a matter of priorities. We didn't want to do this in the first place.

And we may end up going back to GC/MS. I can see it coming.

MR. TELLIARD: Five years.

Go ahead. It is your show. I shouldn't be heckling you from the side.

MR. STEPHENSON: That is all right. I heckle you.

So, we chose what would be a method we could do out on this rig that is bobbing up and down out there in the ocean. One of the things that the companies that sell us our drilling muds and all the components have is this retort. It was designed as a means of measuring the amount of solids that were in the mud. All they did was put a weighed mud sample in this device, and they heated it up, and drove off all the liquids. Hence, they could weigh what was left, because it was a tared flask in the beginning, and knew what their solids content was.

We decided we would pervert this method and use it as a method of collecting the oil and water. The water we didn't care about, but the oil was important. So, we tried to use that as our distillation, our oil recovery method from the mud, and it has its problems.

The other thing is we wanted a simple GC method. GC is a pretty simple thing. Graduate students use them; undergraduate students use them. I know of a trucking

company that that is how they monitor what comes in on the 18-wheelers off the road. They have some guy who didn't finish high school yet who takes a sample off of this truck and goes and runs it in a GC, and he interprets the data, and they spend thousands of dollars based on his interpretation.

So, we figured a GC method was a good idea. Howsomever, by the time we got through with all the QA, QC, and everything else that we cranked into it to make it a good, reliable EPA method, it was no longer a field method. The calibration restrictions are also extremely tight.

So, we are shifting the samples back to shore to be analyzed anyway. I think Bill is going to win.

Did I cover it? I still haven't answered it?

MR. HOPPE: I still don't know what the problem is.

(Laughter.)

MR. TELLIARD: You can't make up for the weaker players is the problem.

MR. STEPHENSON: We have been trying to compensate for Bill, but...

Maybe at the break, you can talk to Warren. He has been doing this, and he can maybe discuss some of the details. As I say, he is the nuts and bolts man. I am the guy who has to go meet with Bill.

Do I have any other questions?

(No response.)

MR. TELLIARD: Thank you, Mike. Thanks a lot.

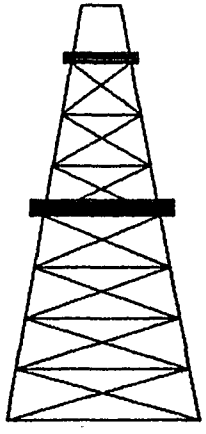
VALIDATION OF A METHOD FOR THE DETERMINATION OF DIESEL OIL IN DRILLING FLUIDS

M. T. STEPHENSON
TEXACO INC.

CHAIRMAN
TECHNOLOGY WORK GROUP
API OFFSHORE GUIDELINES STEERING COMMITTEE

PURPOSE OF METHOD

- IDENTIFY THE PRESENCE OF DIESEL OIL IN DRILLING FLUIDS
- QUANTIFY THE DIESEL OIL PRESENT



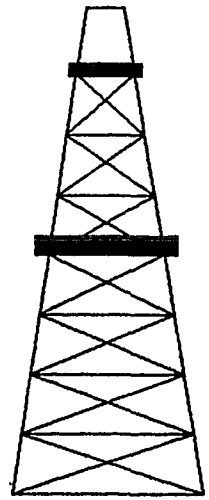
TEXACO INC.

HISTORY OF THE METHOD

- ORIGINAL PROPOSAL - AUG 26, 1985
- DIESEL PILL MONITORING PROGRAM
- API COMMENTS
- REVISION A
- 14 RIG STUDY
- TEXACO RESEARCH

VALIDATION STUDY

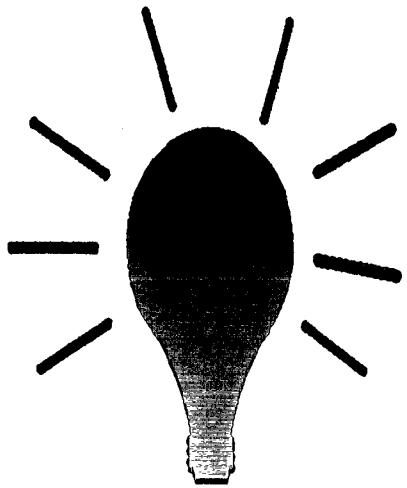
- PURPOSE
- LABORATORIES
- SAMPLES
- CONTROL
- RESULTS



TEXACO INC.

PURPOSE OF STUDY

- DETERMINE DIFFICULTY OF METHOD
- DETERMINE REPRODUCIBILITY OF METHOD
- DETERMINE "ROUGH" DETECTION LIMITS

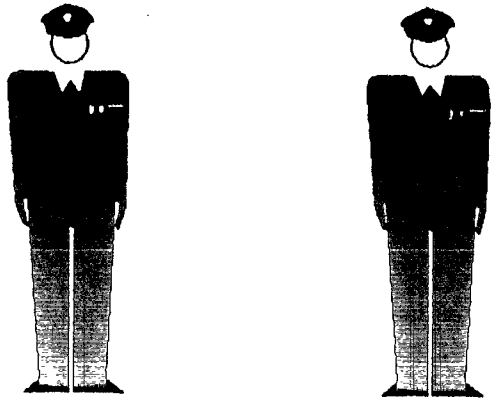


PARTICIPATING LABORATORIES

- TEXACO E&P TECHNOLOGY DIVISION
- CONOCO RESEARCH CENTER
- CORE LABORATORIES - LAFAYETTE, LA.
- ETS ANALYTICAL SERVICES
- RUSKA INSTRUMENTS

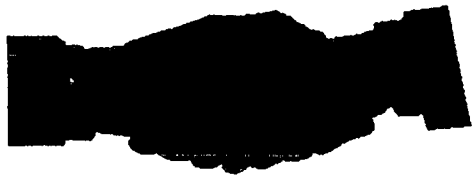
STUDY CONTROL

- INDUSTRY CONTROL OFFICER:
  J. C. RAIA
- AGENCY CONTROL OFFICER:
  W. A. TELLIARD



STUDY RESULTS

- CHROMATOGRAMS OF EACH GC RUN
- OIL CONTENT ANALYSES
- DIESEL CONTENT ANALYSES
- QA/QC
- DATA RECEIVED TO DATE?



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- W. C. HALTMAR, TEXACO INC.
- AMERICAN PETROLEUM INSTITUTE
- ENVIRONMENTAL PROTECTION AGENCY

QUESTIONS?

MR. TELLIARD: Our next speaker is from EPA and our lab at RTP, Larry Johnson who has spoken with us before. It has been a while since he has been back. Larry is going to talk to us on some air source methods they have been working on at RTP.

MR. JOHNSON: As Bill mentioned, we are the air methods people. Of course, we don't really talk all that much with the water people except when we get water in our air and they get air toxics coming out of the water.

Some of the push for looking at air samples comes from a couple of different directions. There is lot of interest now because of the new Clean Air Act that is coming through, air emissions from Superfund sites, air emissions from lagoons. The sewage sludge incineration regs are well into coming out, and we have been looking at the emissions from incinerators.

What I am going to try to do today is just a quick look at some of the kinds of samples that you might see coming into your laboratories related to air.

Just like with water samples, air samples have three major phases that have to be dealt with. The sampling part of the operation is greatly different, of course, than taking samples out of water or sludge.

The preparation steps, you will find as we get into them, are going to look fairly familiar to you with just a few differences. You will be getting new kinds of samples, but you are going to use old familiar techniques, although on different matrices.

After the sample is extracted, the analysis methods are really quite similar except in fairly rare cases.

I am going to go through some of the sampling methods just briefly to show you what kind of equipment these samples are taken with and, therefore, where some of these samples are coming from. I am skewing this discussion quite a bit towards stack emissions mostly because that is our specialty.

In the interest of time, I am going to talk mostly about organics, and only the more frequently used sampling trains. There are a lot of other trains available, especially if you start trying to look for a wide variety of compounds.

So, I am not going to make any pretense that this is complete. We are just going to hit the high spots, basically.

Most of the work has been done on stack emissions from combustion sources. We started out working on power plants. We worked on a whole variety of combustion sources, and a lot of our funding and, therefore, our focus in the last few years has been hazardous waste incineration related.

The new Clean Air Act is going to focus attention combustion stacks, but also vents and similar sources.

Where are these methods provided? In fact, somebody asked me a very good question out in the hall before the

talk. Is there a compendium somewhere of all of the air methods? The answer is not quite. A list of the better references will help.

Most of the Federal Register methods that are used in relation to the air part of our program are in 40 C.F.R 60 and 61. There are air and stack methods in SW-846, and we have a number of them in various stages of review and clearance for inclusion in SW-846. There are also other sources. We have a number of guidance documents and other references. In the hard copy of the paper, I will list a few of those.

Also, there is an operation called EMTIC, Emission Measurements Technical Information Center, that has been set up at RTP, and its function is primarily to supply methods information to the States and to the regions. The number is (919) 541-1059.

One of the methods I am going to talk about is Method 0010, and that is an SW-846 method.

We are also going to talk about 0030. A lot of stack samples and some ambient samples are taken in Tedlar bags. Metal cylinders are very popular, and sometimes they are great and sometimes they are terrible. Usually, for stacks, they are terrible, but we will talk a little bit about their use for ambient sampling, too. Likewise, sorbent tubes are used for source and for ambient sampling.

A lot of the time we will spend on 0010. This is a very flexible method, so a lot of the samples will come in from this hardware. It is also one of the more complicated methods, so you will get more subsamples to deal with.

It is the same thing as Modified Method 5. The term Modified Method 5 became so ambiguous that we had to quit calling it that.

It is also the same train as the so-called Semi-VOST which is less ambiguous but a poor name also.

This method is used for compounds with boiling points greater than 100 degrees C. So, we are talking about what I call the semi-volatiles and the non-volatiles. It doesn't necessarily correspond exactly to what you would call those things, based on water analysis terminology.

This is a diagram of the Modified Method 5 train. If you haven't seen one of these stack sampling train before, it looks like a glass blower's nightmare, but, believe me, you need all of these pieces there to get the samples.

From your standpoint, the important thing is what samples will be generated from this device probe rinse sample comes from this part of the train, a sorbent or a filter sample is also generated there. The sorbent is usually XAD-2. A condensate sample is also produced.

We will talk a little about how each of those sample types is handled in the laboratory.

Solvent extraction is used to recover organic compounds from the samples. Usually, it is methylene chloride, almost a universal solvent, which, sometimes, we do have to follow up with another solvent. In the vast majority of cases, methylene chloride is the solvent of choice for all the usual reasons.

The probe rinse has two sub-samples to it, in effect. The particulate material, and the solvent that the probe was rinsed with. The rinse is filtered and the two sub-samples dealt with separately. Usually, they are combined in with some of the other subsamples. The solvent is combined with an extract, and the particulate is combined with the filter. Depending on the information needed the combination might be different.

The sorbent and the filter are where most of the sample is collected in this train. If you have any luck at all, it will be distributed between those two, and you should never try to figure out what this means in terms of what was in the vapor state and what wasn't in the vapor state in the stack. It is totally meaningless if you do try that, and unfortunately, a lot of people do.

Again, the samples are Soxhlet extracted. We went out of our way to misspell Soxhlet here. I think about four of senior scientist types looked these things over and didn't see the mistake until I started packing the slides. The

sorbent which is usually XAD-2 is well-behaved compared some solids like soils and sludges. XAD-2, assuming it has been cleaned and treated properly, is consistent from batch to batch, and you know what to expect from it.

The particulate is another matter. It is a little bit like a soil sample in that respect. It may be very docile for months and months and then turn around and bite you by not giving back some of the material that you are interested in recovering.

Very much like your water sample, once you have extracted the sample, you have to concentrate the extract, and then you have to do an analysis. We almost always go with GC/MS or GC, and when we can't, we go with HPLC. It is very much like water or sludge analysis in that respect.

The condensate has passed through the filter, and has been through XAD-2, so most of the organics are stripped out. It is relatively clean. It is not something you want to drink, but compared to a dirty water sample with a lot of organics in it, it is relatively clean, and you analyze this material just to prove that nothing broke through. It is almost a QC sample.

In some cases, if you have enough history, you can quit running this sample. Unfortunately, a lot of people have quit when they shouldn't, and we are tightening up requirements on running it.

A separatory funnel extraction is required very much like a water sample, and like with a water sample, sometimes another extraction with a second solvent may be required. Once the extract is obtained, it is concentrated in a K-D and analyzed with one of the unusual analytical methods.

Method 0030 is the VOST or VOST, depending. The pronunciation is like tomatoes or tomatoes. It is designed for compounds that boil between 30 and 100 degrees C. We have found that most of the compounds that boil between 100 C and 132 C will also work, but we don't allow the train to be used above 132 C, because things up in that range can be involved with the particulate, and the particulate is discarded in this method.

Here is the location of the particulate filter. You throw it away. The sample stream passes through a cooler, then into a tenax cartridge. There will be condensate, which is usually minimal. This is a low volume train which is why it will catch the volatiles. There is a back-up tenax tube and charcoal which we included in sheer desperation. Most of us have wished we hadn't put it in there for years now. We are going to replace it one of these days.

Most of the sample typically collects on the front tenax tube, but you have to analyze the condensate to prove

it contains no compound of interest, and you always analyze the second tenax tube, because it is not unusual for it contains some of the compound of interest.

You only have two subsamples here, two sets of sorbent tubes. In fact, a sampling run usually consists of approximately six sorbent tubes.

The condensate must be dealt with, even though some people discard it when it should be analyzed. Again, it is more of a QC sample just to prove that nothing got through the rest of the train. It protects against breakthrough, channeling, things like that.

This is what the tenax tubes look like. We actually adopted the biggest ambient air sampling tubes that we could find. There is about 2 grams of tenax in the one, and the other has about a gram of tenax and a gram of charcoal in it.

Method 5040 which, again, is a SW-846 method is used to analyze these tubes. It is just a heat desorption method with a twist. You heat desorb into a purge and trap chamber, because these tubes are going to have maybe a milliliter of water on them sometimes. You get rid of the water by running it into water.

We have tried a lot of more elegant techniques, and so far, none of them have worked very well for us. That is not

to say they wouldn't if we spent enough money to really make them work.

We have a draft Method 5041. 5040 is in the book, and it is a packed column. In fact, it is the old 624 method. We didn't want to develop an analytical method. We were busy with the sampling method, so we just adopted the analytical method.

5041 is a megabore version of 5040, and it will give you a lot better resolution. It is under review, and a year or less it will be in SW-846.

The condensate is analyzed by purge and trap whenever possible. If you have something like acetonitrile that doesn't purge and trap well, you may have to use direct injection which I know all of you love.

Tedlar bags is a viable way to sample, but one problem with these bags is that they are deceptively simple, and there is a multitude of ways to use them wrong. You use them only for low boilers because you don't want things condensing out in the bag. It is necessary to run through a water trap if there is any moisture in the stack. You usually do the analysis by GC/MS, and if there is any condensate in the trap, you have to analyze that however you can, usually purge and trap.

Some of the sampling trains that are available for bags right now don't have the condenser, but most of the time,

you need that if there is any moisture in the stack. Moisture can't be allowed in the bag, because if any condensation occurs in the bag, the sample is invalid. Metal cylinders are very popular. The Summa polished cylinders are used a lot for ambient air. Method TO-14 uses these devices. The summa polishing is just a pacification technique that is applied to the cylinder. Cryo-focused GC/MS is usually used to do the analysis, sometimes just GC.

Method 25 is an attempt to obtain a total organics concentration. A metal cylinder is used, and then an FID analysis is performed after running the sample through some treatment to convert it into methane.

All of these metal cylinder techniques only really work when you don't have high levels of acid gases like HCl and SO_2 and other corrosive agents. High moisture levels interfere with the cryo-focusing analysis. Most of the time canisters don't work well for stack sampling.

Sorbent tubes, you can use those same tenax tubes to do ambient air samples from around dumpsites and off of lagoons. The technique is a very similar to Method 0030. You heat desorb, but don't usually run through the purge and trap procedure, because the water isn't present..

The QA/QC is very important for all of these methods, and we are just realizing how truly important it is. We are

being forced to tighten up on the sampling QC and on the laboratory workups.

Because we had clean sample matrices in a lot of cases, we would typically demonstrate that the technique worked and then only have minimal safeguards against analysts performing poorly in the laboratory. We have found that that is not enough. Poor performance has occurred all too often.

We have recent guidance on QA, especially related to hazardous waste incineration. I will put the references to that in the written version of the paper. We are going to tighten many of the QC requirements and use more labeled spikes. There is going to be less combining of subsamples allowed, and I think where we can, we are going to have to utilize isotope dilution.

Isotope dilution procedures are not yet developed for stack samples, but if funding allows, we would like to work on them. We have typically fewer things to look for in a given sample, so it is not quite as big a cost burden as if you are looking for 200 or 300 things at once.

Audit samples are available for a lot of these methods. VOST audit samples are available at RTP. They have to be requested by an EPA person. So, if you want to be audited asks an EPA person to call RTP and request the audit samples.

There are audit sample development and validation work going on right now on the TO-14 canister method for use around Superfund sites. There are two different groups in a real laboratory that are doing that work. So, there will be audit samples available.

Are there any questions?

MR. TELLIARD: If there are no questions, thanks a lot, Larry. We appreciate it.

PREPARATION AND ANALYSIS

OF

AIR EMISSION SAMPLES

SAMPLING

PREPARATION

ANALYSIS

SAMPLING METHODS

STACK EMISSIONS

ORGANIC

MOST FREQUENT

COMBUSTION CONNECTION

WHERE?

40 CFR, PARTS 60 & 61

SW-846

OTHER SOURCES

METHOD 0010

METHOD 0030

TEDLAR BAGS

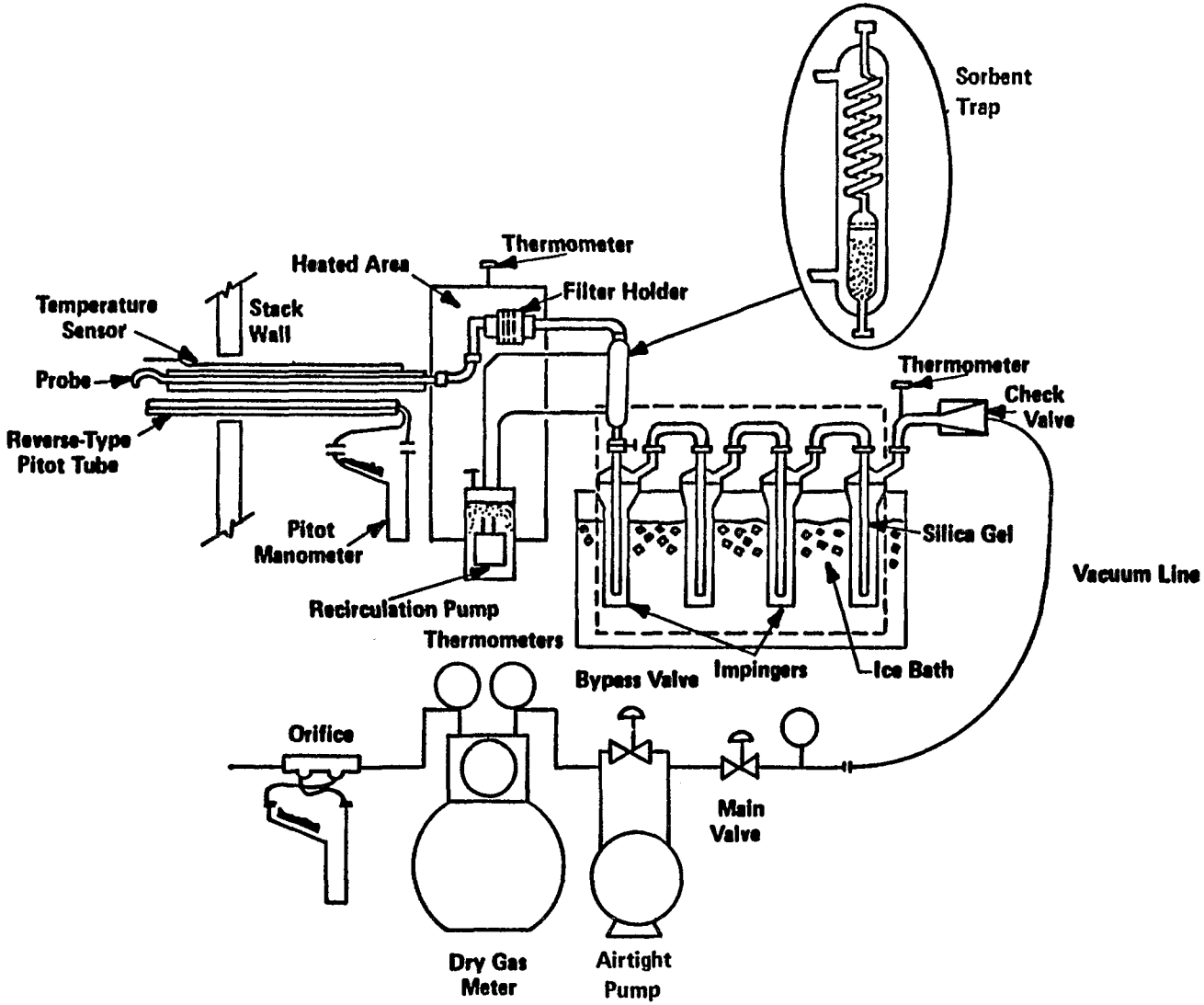
METAL CYLINDERS

SORBENT TUBES

METHOD 0010

MODIFIED METHOD 5

B.P. GREATER THAN 100 °C



Modified Method 5 train.

PROBE RINSE

FILTER

SORBENT

CONDENSATE

SOLVENT EXTRACTION

PROBE RINSE

PARTICULATE/SOLVENT

SORBENT

FILTER

SOHXLET EXTRACTION

SORBENT CONSISTENT MATRIX

PARTICULATE MAY BE INCONSISTENT

EXTRACT CONCENTRATION

ANALYSIS

CONDENSATE

CLEAN, PREDICTABLE

SEP. FUNNEL EXTRACTION

SECOND SOLVENT

EXTRACT CONCENTRATION

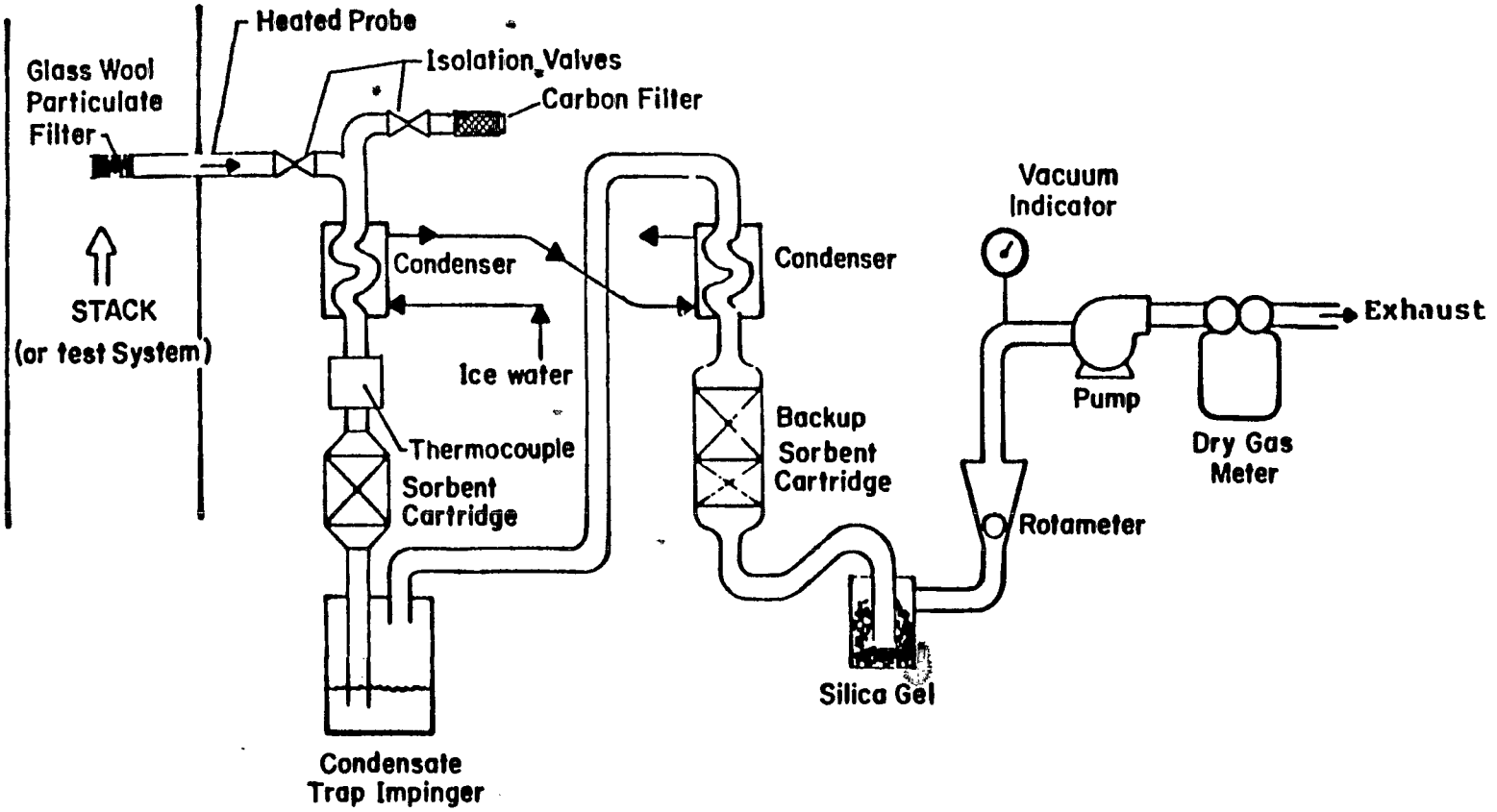
ANALYSIS

METHOD 0030

VOST

B.P. 30 °C TO 100 °C

RANGE EXTENDED TO 132 °C



Volatile organic sampling train (VOST).

SORBENT TUBES

CONDENSATE

SORBENT TUBES

ANALYZE BY METHOD 5040

DRAFT METHOD 5041

CONDENSATE

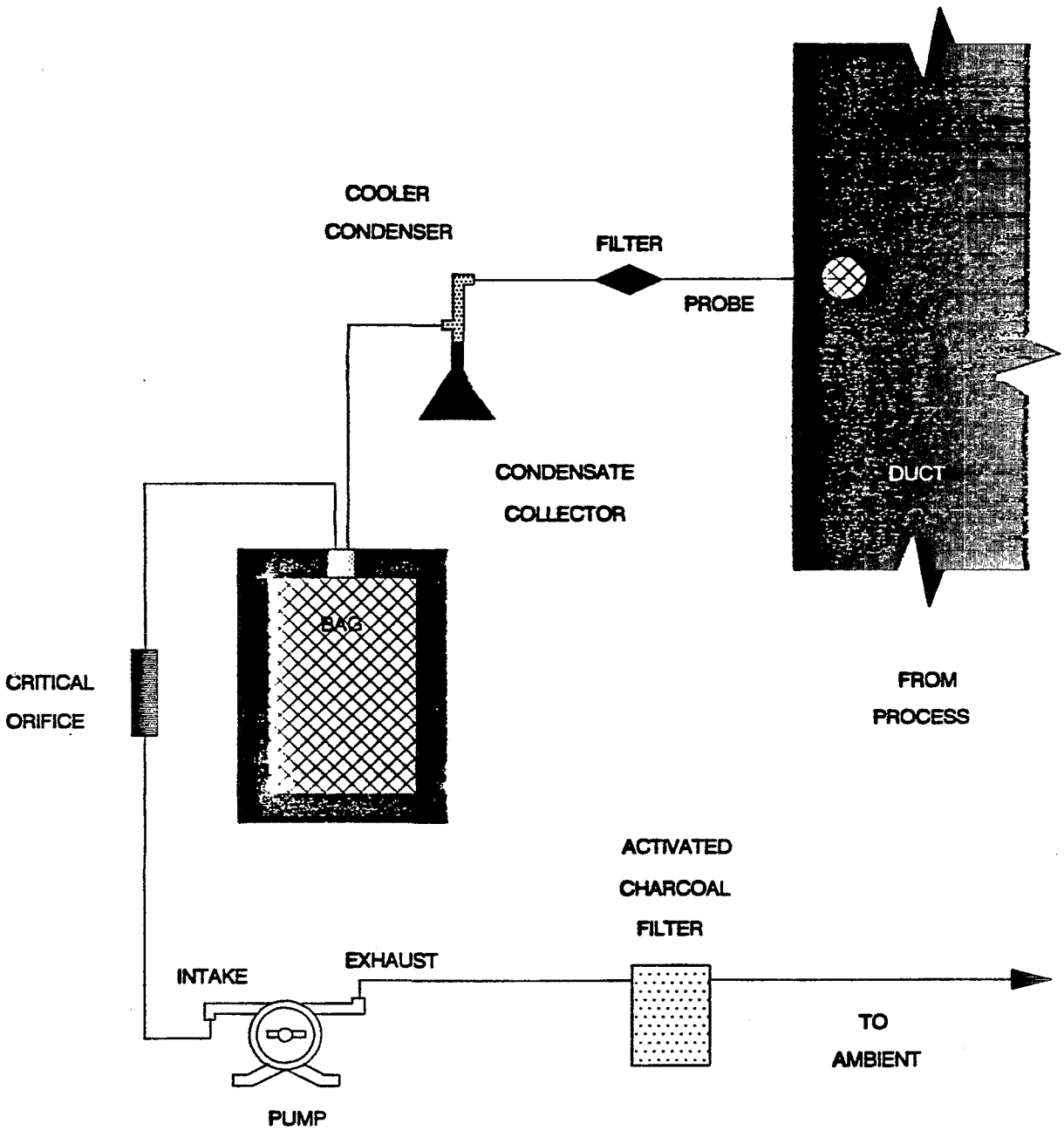
PURGE AND TRAP

TEDLAR BAGS

LOW BOILERS

ANALYSIS BY GC/MS

ANALYZE CONDENSATE



BAG SAMPLE COLLECTION APPARATUS

METAL CYLINDERS

METHOD 25

FID ANALYSIS

METHOD TO14

CRYOFOCUS GC/MS

SORBENT TUBES

SIMILAR TO METHOD 0030

HEAT DESORB

QA/QC

VALIDATION LIMITED

RECENT GUIDANCE

MORE LABELED SPIKES

ISOTOPE DILUTION?

AUDIT SAMPLES

QUESTIONS?

MR. TELLIARD: Our last speaker today...which means this will also be on the final...is going to talk about the Chesapeake Bay and the joys thereof. Tina Fletcher from Region III and the Bay Office is going to talk about the nutrient measurements that the folks have been spending a great deal of time on in the last couple of years.

The Chesapeake Bay Program: Experience with Nutrient Analytical Methods in the Estuarine Environment

Five years into the mainstem monitoring program for nutrient, demand and physical parameters the program is involved in a re-evaluation of the project design and implementation. This test of our assumptions has involved an analysis of the data available for the detection of trends in nutrient levels which have a direct bearing on the availability of oxygen and thus the survival of our living resources in the Chesapeake Bay waters. Concurrent with this trend estimation is a power analysis to determine the theoretical sensitivity of the current database with respect to its temporal and spatial coverage and the detection limits available from the existing field processing and analytical methodologies. Were the initial assumptions which set us out on this first five years of perhaps a twenty year journey correct? But I am getting ahead of my story.

Here in Norfolk, we are close to the mouth of this the largest and most productive estuary in the continental U.S. The Bay as we presumptuously call her stretches 195 miles along a mainstem with 7,000 miles of shoreline 18 trillion gallons of water and an average depth of less than 30 feet. Formed 10,000 years ago as melting glaciers flooded the Susquehanna River Valley she is home to 200 species of fish along with 2,700 other plant and animal species, 12 million people and their hundreds of thousands of pleasure boats. The resource is too valuable to let go and we at

the Chesapeake Bay Program, a consensus organization of representatives from federal, state and local governments along with citizen groups, and universities from Maryland, Virginia, Pennsylvania and the District of Columbia take that responsibility very seriously.

The drainage basin for the Chesapeake spans 4,500 square miles from the states of Maryland, Virginia, Pennsylvania, Delaware, West Virginia, New York and New Jersey. Data are received from environmental organizations in each of these regions. The quality of these data must be understood so that they may be effectively used in the management decisions.

From before 1950 through the 1970s many state and university groups conducted research oriented studies some of which operated over a protracted period but most of which were both spatially and temporally very limited. Between 1978 and 1983 the Chesapeake Bay Program as coordinated by the Environmental Protection Agency was in its research phase where it sought to characterize the Bay's water quality, sediment quality and resources.

This period was devoted to determining what data were available from historical sources and to identifying the issues at hand for the Chesapeake. The infamous "Appendix F- A Monitoring and Research Strategy to Meet Management Objectives", defined the Chesapeake Bay Water Quality Monitoring Program Objectives as:

* Characterizing existing water quality Baywide
* Determining trends in water quality that might develop in response to management actions or additional sources of pollution
* Integrating the analyses of various monitoring components with a view toward achieving a more comprehensive understanding of processes affecting water quality and the linkage with living resources

In 1984 the Chesapeake Bay Program entered the Implementation Phase in which the designs of the Research Phase took form. Within the committee structure of the Chesapeake Bay Program, the Monitoring Subcommittee attempted to translate the research questions into an EPA funded mainstem monitoring program for physical, nutrient, demand and biological parameters. The Mainstem Monitoring Program was based upon the segmentation scheme developed by researchers to encapsulate the variable portions of the Chesapeake's central trunk and near tributaries. The MMP was designed as a 50 station network which would be sampled 20 times per year. As with any monitoring effort, the scope of the program was heavily linked to the budgetary constraints. The extent to which existing laboratory capabilities and configurations could be utilized would be pivotal in moderating the costs of the program. Data from the tributaries would be taken from the monitoring programs within each of the states vastly increasing the reach and complexity of the database.

The MMP measures more than 25 forms of nutrient, demand, physical and biological parameters. The Mainstem Monitoring Program is not a regulatory program and as such there is no EPA mandated set of methods. The EPA water chemistry manual, "Methods for Chemical Analysis of Water and Wastes" describes most of its methods as suitable for the analysis of saline waters. However, the degree to which this has been evaluated should not be overestimated. There were no Agency guidelines for the selection of analytical methods. The Chesapeake Bay Program was on its own to identify its needs and to determine the analytical methods which would satisfy those requirements.

With strong input from EPA and those organizations which would be implementing the analytical work, it was decided by the Monitoring Subcommittee that EPA water methods and procedures would be adopted for this program. There was a sense that this would provide a continuity with the historical database and would provide a linkage with the tributary data which was generated by the principal state laboratories which were driven by these same EPA methods required under the National Pollution Discharge Elimination System., the workhorse of those labs at that time.

While the Chesapeake Bay Program is a consensus organization, this consensus is not instantly achieved. A series of laboratory and field consensus workshops were held to thrash out the program design beyond the work done in the Monitoring Subcommittee. A

strong objection to the analysis of these estuarine waters with TKN as the measure of total nitrogen was made by Chris D'Elia and the University of Maryland representing a strong linkage with standard oceanographic methods. Intense challenge was brought to the analysis of the crucial particulate phase of nutrients by difference between the total and dissolved determinations. Detection limits were said to be unacceptably high. However, the analytical program was in place and it was determined that "comparability" would have to be demonstrated before a change would be made.

Change, the enemy of trend analysis. Nonetheless, change is inevitable in any monitoring program. A learning curve is present initially and then with each new analyst, each new piece of equipment and so forth. Trend analysts may argue that consistency is more important than "truth". However, new instrumentation is inevitable and should be embraced. Improvement in system efficiencies which lead to lower detection limits are always desirable as long as the cost equation is not shifted. It is the role of the formal comprehensive quality assurance program to provide the documentation and management of that change so that the needs of the data users can still be met.

In 1986, two years into the monitoring program, special studies outside the normal monitoring program were initiated to accommodate the recommendations for change while maintaining a linkage to the on-going monitoring program. These special studies addressed recommendations that freezing be allowed as a method of preservation and that .45 micron membrane filters be replaced by .8 micron effective pore size glass fiber filters.

Further, special studies were initiated to evaluate the comparability between the EPA methods and those coming from the oceanographic protocols. It was determined that the recommended changes would benefit the goals of the Mainstem Monitoring Program for a variety of reasons from improved detection limits, greater analytical throughput, improved recoveries and even the lessening of hazardous waste materials. Field analytical procedures did not change, however, many changes were adopted in the laboratory analytical methods.

As a reflection of the Appendix F concerns and with the strong realization that there was no natural barrier at the tributaries, a Baywide Quality Assurance Program was initiated in 1986. Work was begun to bring the tributary monitoring programs in line with changes underway in the Mainstem Monitoring Program. As a beginning a Coordinated Split Sampling Program was designed to identify the variability associated with the processes used to collect, process, analyze and report the data which are stored in the Chesapeake Bay Program database.

The Coordinated Split Sampling Program utilizes four organizational components to collect and distribute split samples to a varied group of federal, state and university laboratories who routinely produce data from the mainstem and tributaries. The attempt is to establish the comparability between organizations so that the data will be of known quality and apparent differences can be evaluated for possible organizational artifacts. Triplicate samples, spiking, duplicate samples and standard reference materials all facilitate the evaluation of sources of variability. An established statistical protocol is used to evaluate the data produced in this split sample program and rapidly turn it back to the organizations for evaluation and implementation of changes as indicated.

Some of the data which have come out of the Coordinated Split Sampling Program clearly indicate the need for change. In the case of Total Dissolved Phosphorus, it was quite apparent that the university laboratories who are responsible for the analysis of the Mainstem Monitoring Program were reporting data which were nearly an order of magnitude lower than the principal state laboratory. This is not surprising considering the bulk of the sample load for that laboratory is from point source and hazardous waste sampling locations. State management used the data from the Coordinated Split Sampling Program to leverage changes in laboratory arrangements which would allow the production of data which were not a function of the analyzing laboratory.

Conversely, it has been heartening to see how tightly bunched the data are for field and lab precision for TDP overall. Silica split sample results are hard to separate lab to lab. Each of the other parameters has its own characteristics and trends point to a tightening of limits. Organizations are using these data to track and implement changes in their field and laboratory operations.

Split sample data provide a measure of the comparability between the different sampling and analytical organizations which have been crucial in the evaluations of the trend. The role of the Coordinated Split Sampling Program and the Baywide Quality Assurance Programs can only be expected to expand as the CBP attempts to utilize more effectively the data from myriads of historical and on-going monitoring programs throughout the basin as identified in the Chesapeake Bay Basin Monitoring Program Atlas. The Living Resources Monitoring Plan seeks to forge a link between habitat requirements of the biota and water quality. The quality of data throughout all of these programs must be known to permit their use in the decision making process.

The Chesapeake Bay Monitoring Program represents an evolving data collection network and a process of providing information necessary for management of the Chesapeake Bay's Resources. If the support of management decisions is the reason for data collection, then a database is only as good as its match with the needs of those decision makers. Five years into the monitoring program an

intense process of re-evaluation is in process to be certain that the data produced to date are of known quality. To determine if the monitoring program is able to detect a trend if one develops is the task at hand. Will the existing monitoring program be able to track the 40 % reduction in nutrients by the year 2000 as stipulated by the Governors in the Chesapeake Bay Agreement? The users of this database need to be identified and their concerns prioritized. Then, they must stipulate explicitly the quality of data they require to meet the needs of the sophisticated computer models or to satisfy the monitoring of the Living Resources Habitat Criteria.

The configuration which is represented by the Mainstem Monitoring Program in the future will be a combination of the original perspectives of the Research Phase with clear direction from the users of this evolving database. Analytical systems will be honed to produce data of the quality required by the program, not just by the goal of "how low can you go?"

What have we learned? In the area of monitoring, consensus may be an impossible form of management but it is essential to the success of the multi-jurisdictional nature of estuarine monitoring. The success of a monitoring program is directly related to the clarity of the needs of the decision makers who will use these data. Program objectives and the specific questions must be understood and translated into a network design. Trends resultant from management actions will rarely be seen in two to five years.

Natural variability in rainfall and other cycles has a much longer period. Monitoring of this type is there for the long haul and must have a long term stable source of funding to provide consistent implementation of a program of the quality required.

A comprehensive quality assurance program is crucial for the success of any monitoring program. A coordinated split sampling program is necessary to establish the comparability between multiple organizations involved in the monitoring effort. Data must be statistically evaluated and returned to the participants for action. The technical consensus of experts must be utilized in the design and implementation of the monitoring program.

Data management cannot be ignored. A well designed, thoroughly documented and consistently implemented data management system must be in place to facilitate the accurate and efficient acquisition of data and to effectively make the data available to the user communities. Close attention must be paid to the handling of historical data sets where the quality is often unknown.

Data analysis must not be an afterthought. Rather, it should be leading the process. Data which sit on the shelf often are of inappropriate quality since they have not had the benefit of feedback from the data analyst. The strongest organizations are clearly correlated with those operations who routinely utilize the data generated by the Mainstem Monitoring Program for their own purposes.

The Chesapeake Bay Program experience with nutrient analytical methods has been or is being repeated in some form in each of more than a dozen estuarine programs nationwide. The isolation of the technical communities of the Agency's estuarine programs is clear. Regions II and III have been involved in a year long effort to identify the analytical needs of the estuarine and marine communities. Last week we held with support from the Office of Marine and Estuarine Protection the first annual Estuarine and Marine Analytical Methods Workshop in an attempt to establish a network of technical experts in the estuarine and marine matrices. The Estuarine and Marine Analytical Methods Committee was formed.

Analytical needs were coordinated under four workgroups who are charged with the compilation of candidate methods, as well as the evaluation of existing methods and SRMs. Round-robins which can be organized within the community will be encouraged and the interest and support on the part of the Office of Research and Development is clear. It is an idea whose time has come as we seek to promote each estuarine program with through the experience of the other in this most challenging matrix.

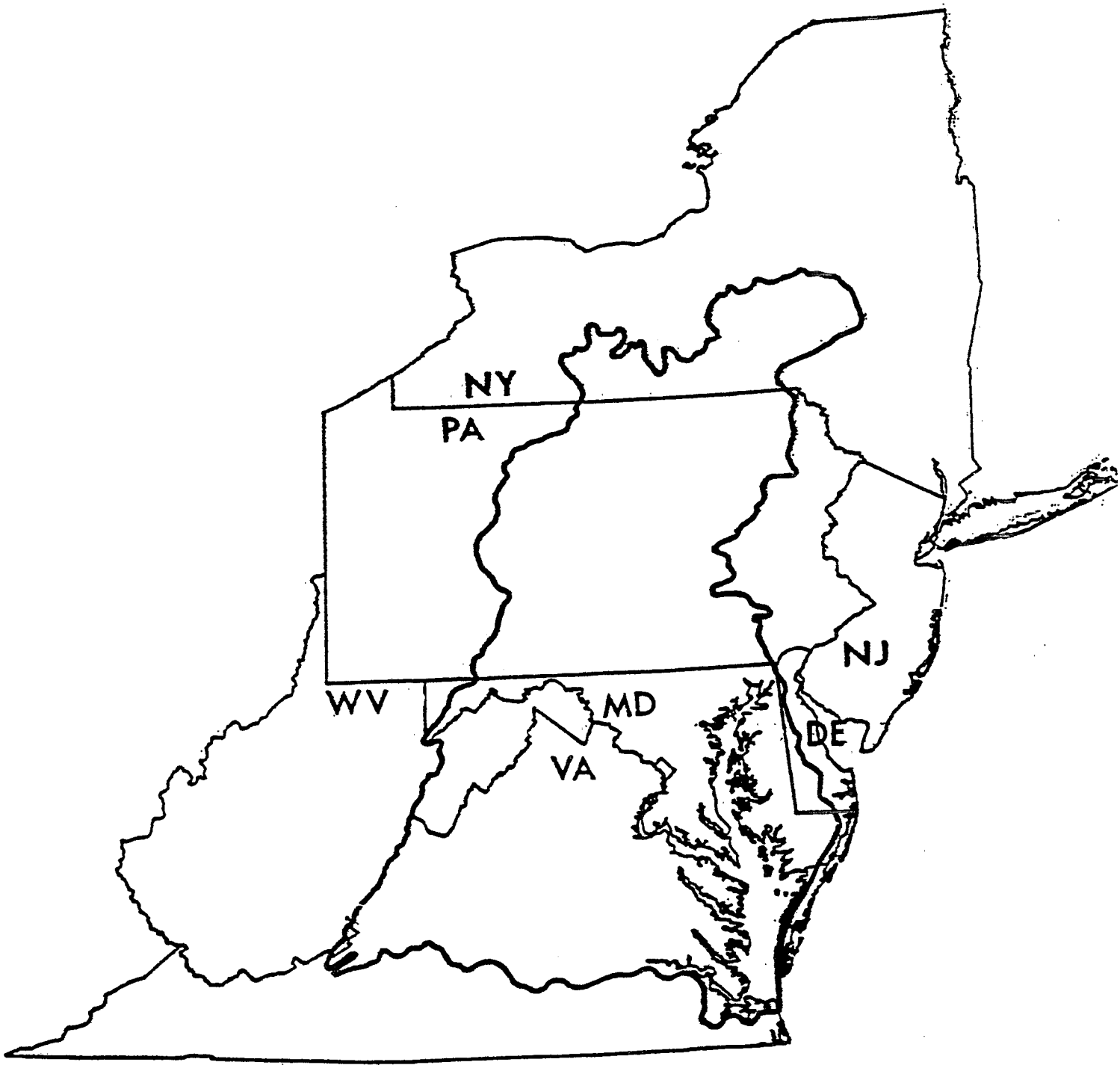
I would like to offer special thanks to Peter Bergstrom and Rodney Buckingham of CSC and Rich Batiuk of the Chesapeake Bay Liaison Office for their assistance in the preparation of these materials.

OVERHEAD

THE CHESAPEAKE BAY PROGRAM

Experience with Nutrient Analytical Methods in the Estuarine Environment

CHESAPEAKE BAY BASIN



CHRONOLOGY OF THE CHESAPEAKE BAY MONITORING PROGRAM

1950s–1970s Independent data collection efforts, often more research oriented and short-term in nature

1978–1983 Chesapeake Bay Program Research Phase

- Characterization of the Bay's water quality, sediment quality and resources
- Compilation of historical water quality data
- Chesapeake Bay Synoptic Survey
- Chesapeake Bay Segmentation Scheme
- "Appendix F – A Monitoring and Research Strategy to Meet Management Objectives"

CHRONOLOGY OF THE CHESAPEAKE BAY MONITORING PROGRAM (cont'd)

1984 – Present	Chesapeake Bay Program Implementation Phase
1984	Monitoring Subcommittee established
	Chesapeake Bay Water Quality /Biological Resource Monitoring Program implemented in July 1984
	Technical Monitoring Program Consensus Workshops
1985	Expansion of definition of the Chesapeake Bay Monitoring Program to include non-tidal data collection programs
	First Biennial State of the Chesapeake Bay Report published
	Increased emphasis on coordinated data management

CHESAPEAKE BAY PROGRAM BASIN SEGMENTS

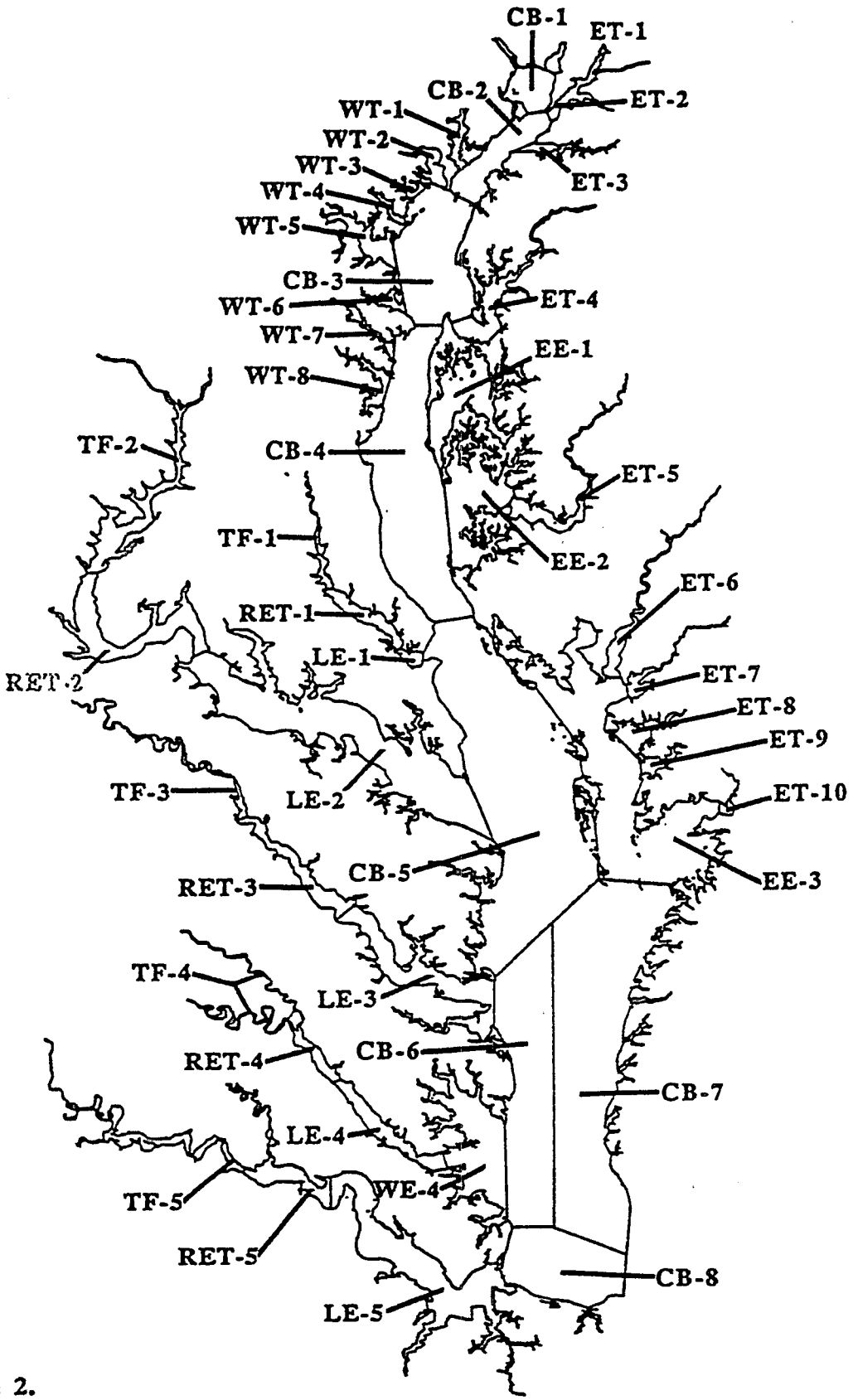
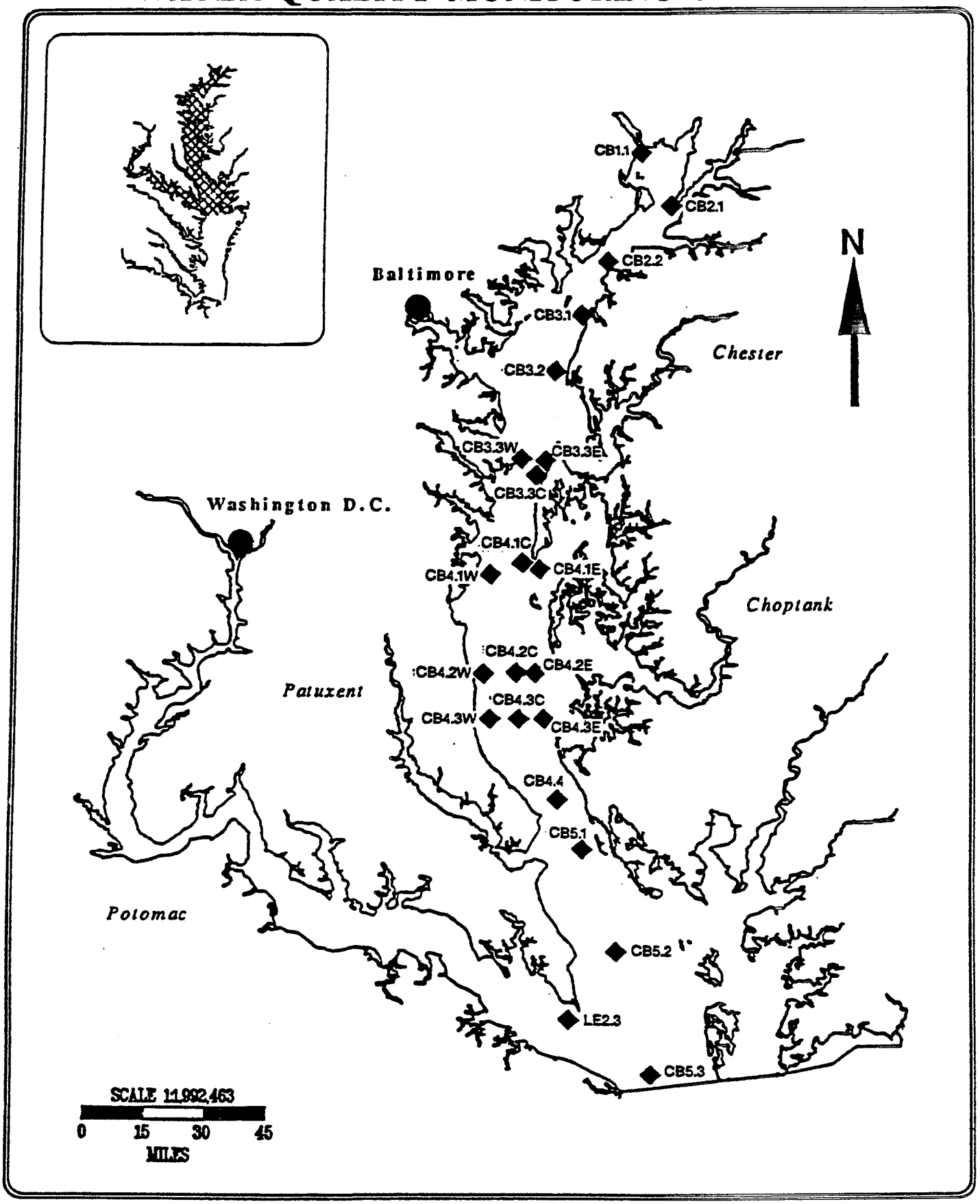
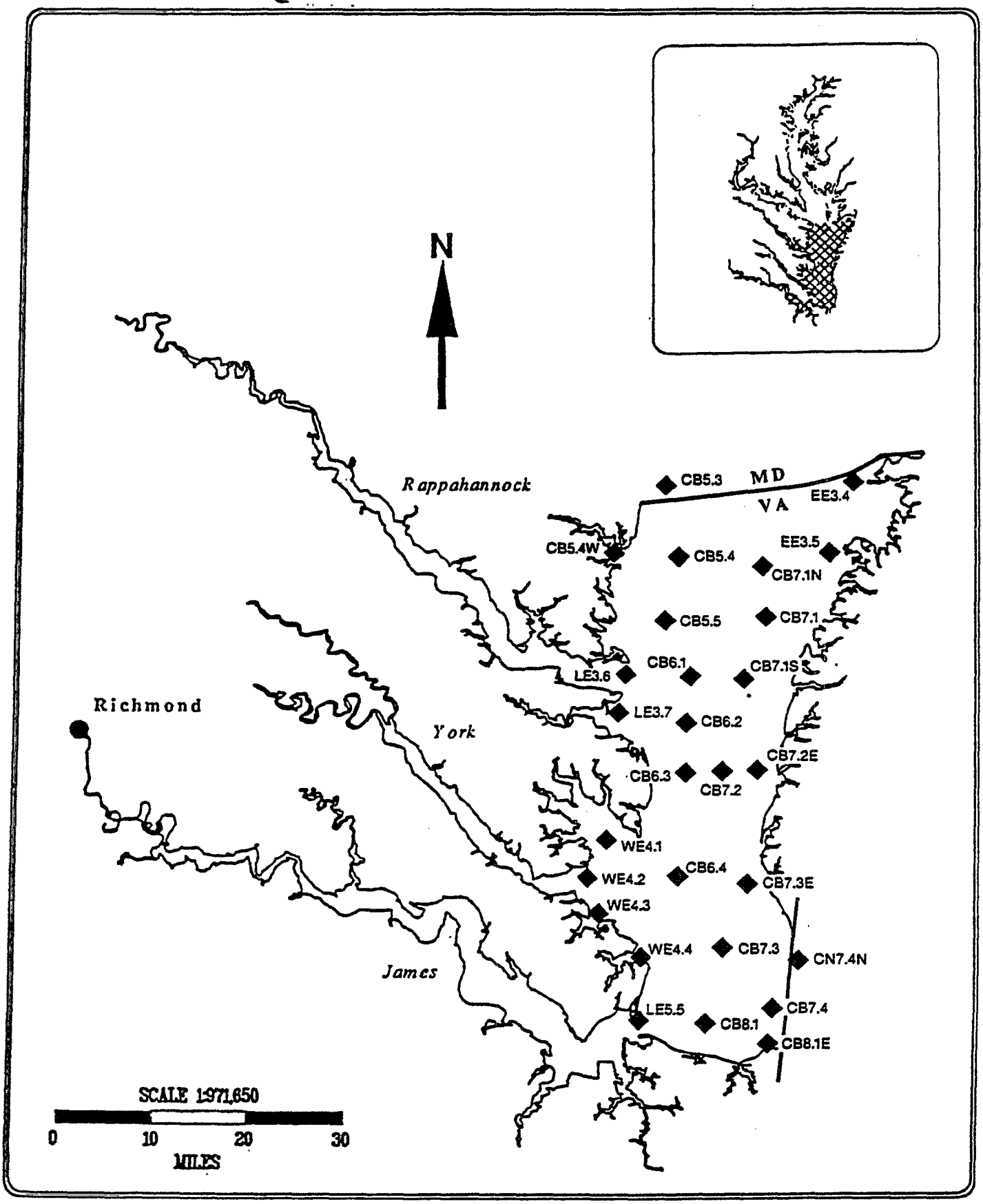


Figure 2.

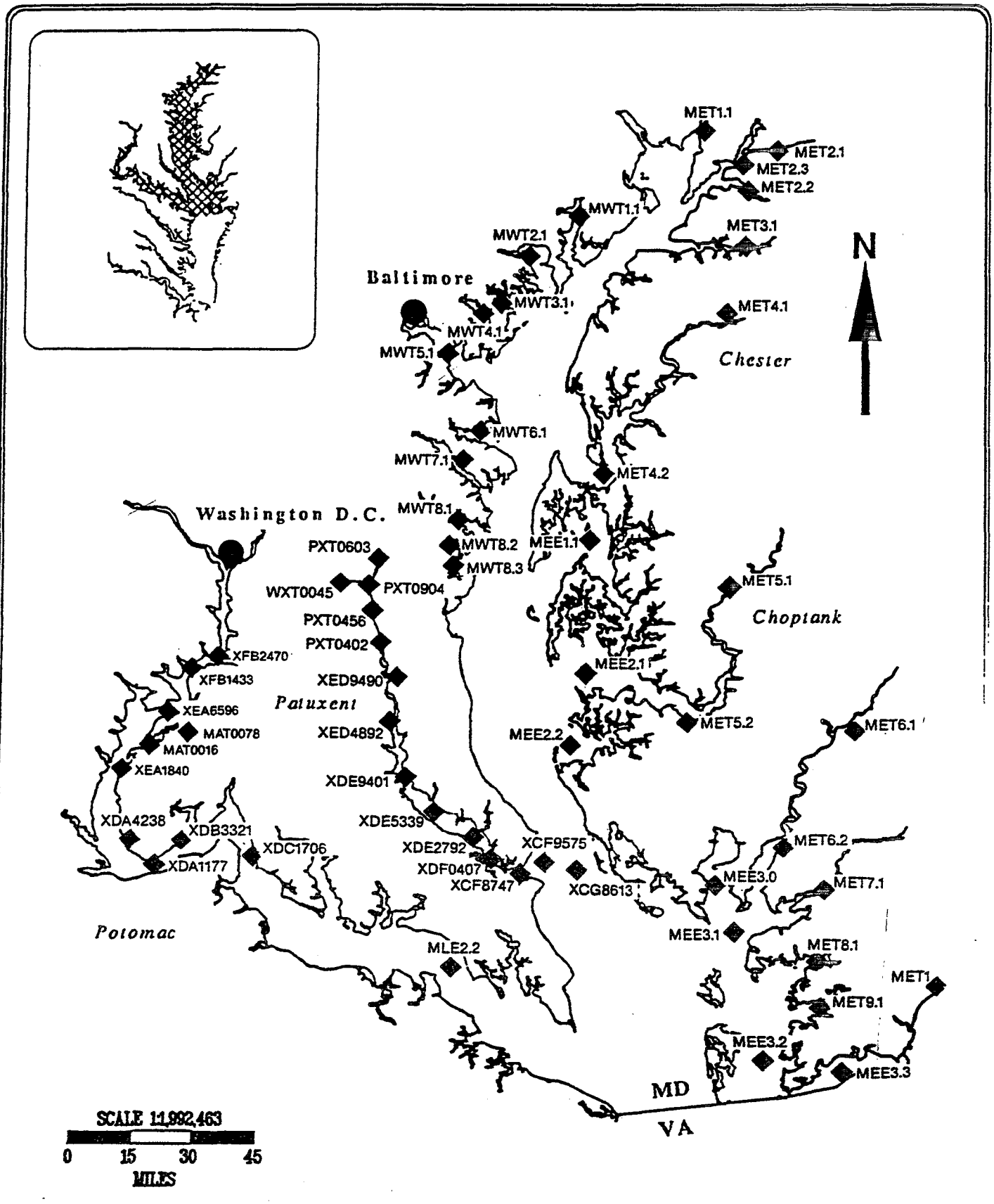
MARYLAND CHESAPEAKE BAY MAINSTEM WATER QUALITY MONITORING STATIONS



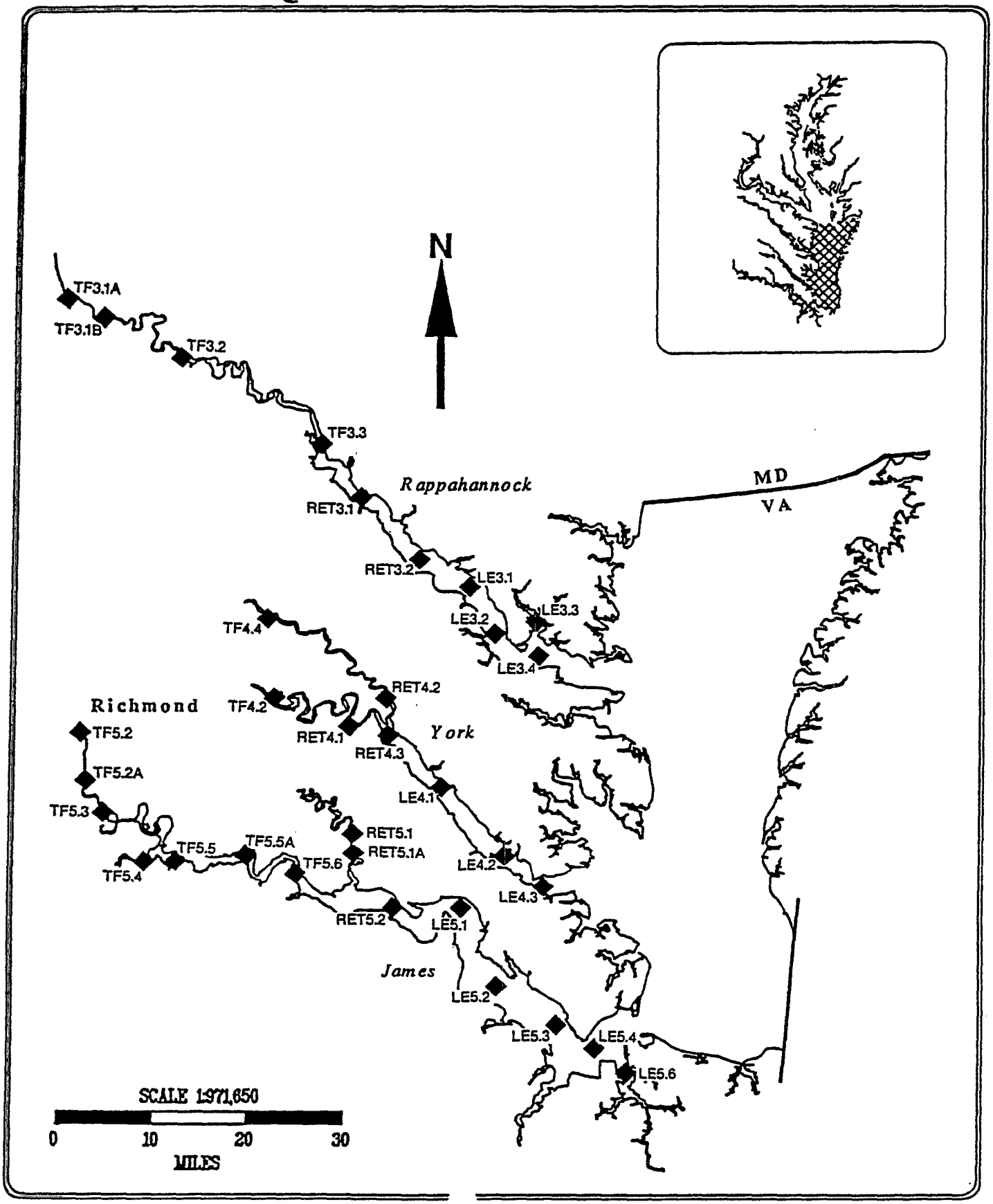
VIRGINIA CHESAPEAKE BAY MAINSTEM WATER QUALITY MONITORING STATIONS



MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM: TRIBUTARY CHEMICAL /PHYSICAL STATIONS



VIRGINIA CHESAPEAKE BAY TIDAL TRIBUTARY WATER QUALITY MONITORING STATIONS



WATER QUALITY PARAMETERS MEASURED IN TIDAL MONITORING PROGRAMS

Temperature
Dissolved Oxygen
Specific Conductivity
Salinity
pH
Secci Depth
Total Phosphorus
Total Dissolved Phosphorus
Particulate Phosphorus
Dissolved Inorganic Phosphorus
Dissolved Organic Phosphorus
Total Nitrogen
Total Dissolved Nitrogen
Particulate Organic Nitrogen
Dissolved Inorganic Nitrogen
Dissolved Organic Nitrogen
Nitrate
Nitrite
Ammonia
Total Organic Carbon
Dissolved Organic Carbon
Particulate Organic Carbon
Dissolved Silica
Total Suspended Solids
Chlorophyll *a*
Phaeophytin

CHRONOLOGY OF THE CHESAPEAKE BAY MONITORING PROGRAM (cont'd)

1986	Comprehensive nutrient analysis and sample storage comparison studies funded by the Monitoring Subcommittee
	Baywide Quality Assurance Program initiated
1987	Second Biennial State of the Chesapeake Bay Report Published
	Expansion of program coordination to include fisheries/shellfish resource monitoring
	1987 Chesapeake Bay Agreement signed by the states and the EPA
1988	Sediment processes monitoring expanded to support Time Variable Chesapeake Bay Water Quality Model development
	Baywide Coordinated Split Sample Program implemented

LABORATORY ANALYTICAL METHODS

VARIABLE	EPA METHOD	CBP METHOD
Silica, dissolved	EPA 370.1 (AA)	EPA 370.1 (AA)
TOC	EPA 415.1 (Infrared)	PC + DOC
DOC	EPA 415.1 (Infrared)	EPA 415.1 (Infrared)
Particulate Carbon	TOC - DOC = PC	High Temp Oxidat. Combustion
TSS	Standard Methods (Gravimetric)	Standard Methods (Gravimetric)
TKN	EPA 351.2	Not Analyzed
TDN	TKN(f) + NO3 + NO2	Alk. Pers. Dig. EPA 353.2
PN	TKN (W) - TKN (F)	High Temp Oxidat. Combustion

LABORATORY ANALYTICAL METHODS

VARIABLE	EPA METHOD	CBP METHOD
Ammonia	EPA 350.1 (AA) Automated Phenate	EPA 350.1 (AA) Automated Phenate
NO2 + NO3	EPA 353.2 (AA) Cad. Red, Diaz.	EPA 353.2 (AA) Cad. Red, Diaz.
NO2	EPA 353.2 (AA)	EPA 353.2 (AA)
TP	EPA 365.1	TDP + PP
TDP	TP (w) - TP (f)	Alk. Pers. Dig. EPA 365.4 (AA)
OrthoP	EPA 365.1 (AA)	EPA 365.1 (AA)
PP	TP (w) - TP (f)	High Temp Oxid. Dig., EPA 160.2-1
Chlorophyll "a"	Spectrophot.	Spectrophot.
Phaeophytin "a"	Spectrophot.	Spectrophot.

FIELD VARIABLES AND ANALYTICAL METHODS

Variable	Analytical Method
Temperature	CTD
Depth	CTD
Dissolved Oxygen	DO Sensor w/ Winkler Cal.
Conductivity	CTD
pH	pH Probe
Secchi Depth	20 cm disk after Welch
Salinity	Calculated from Conductivity

Figure 6. Chesapeake Bay Coordinated Split Sample Program

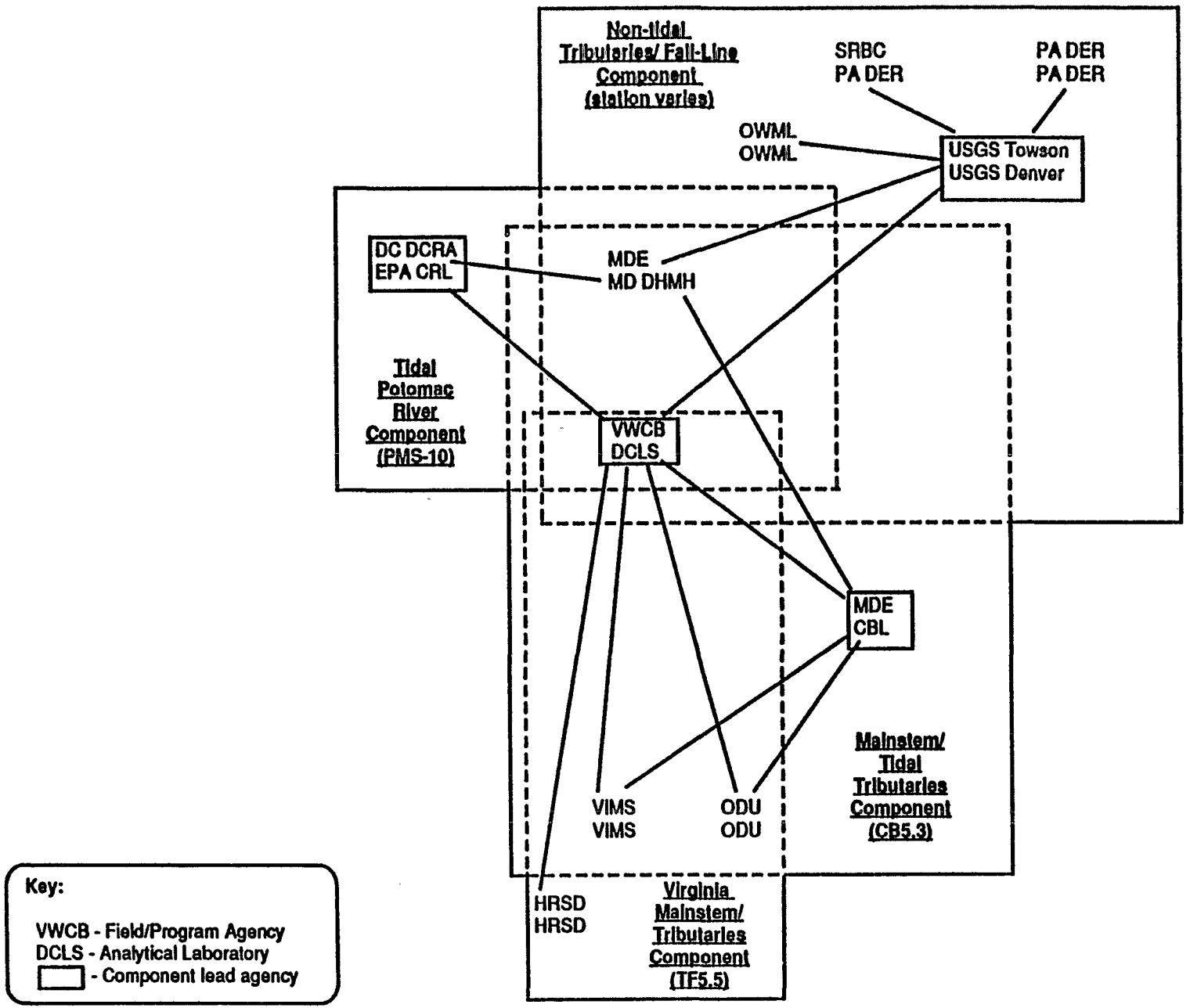
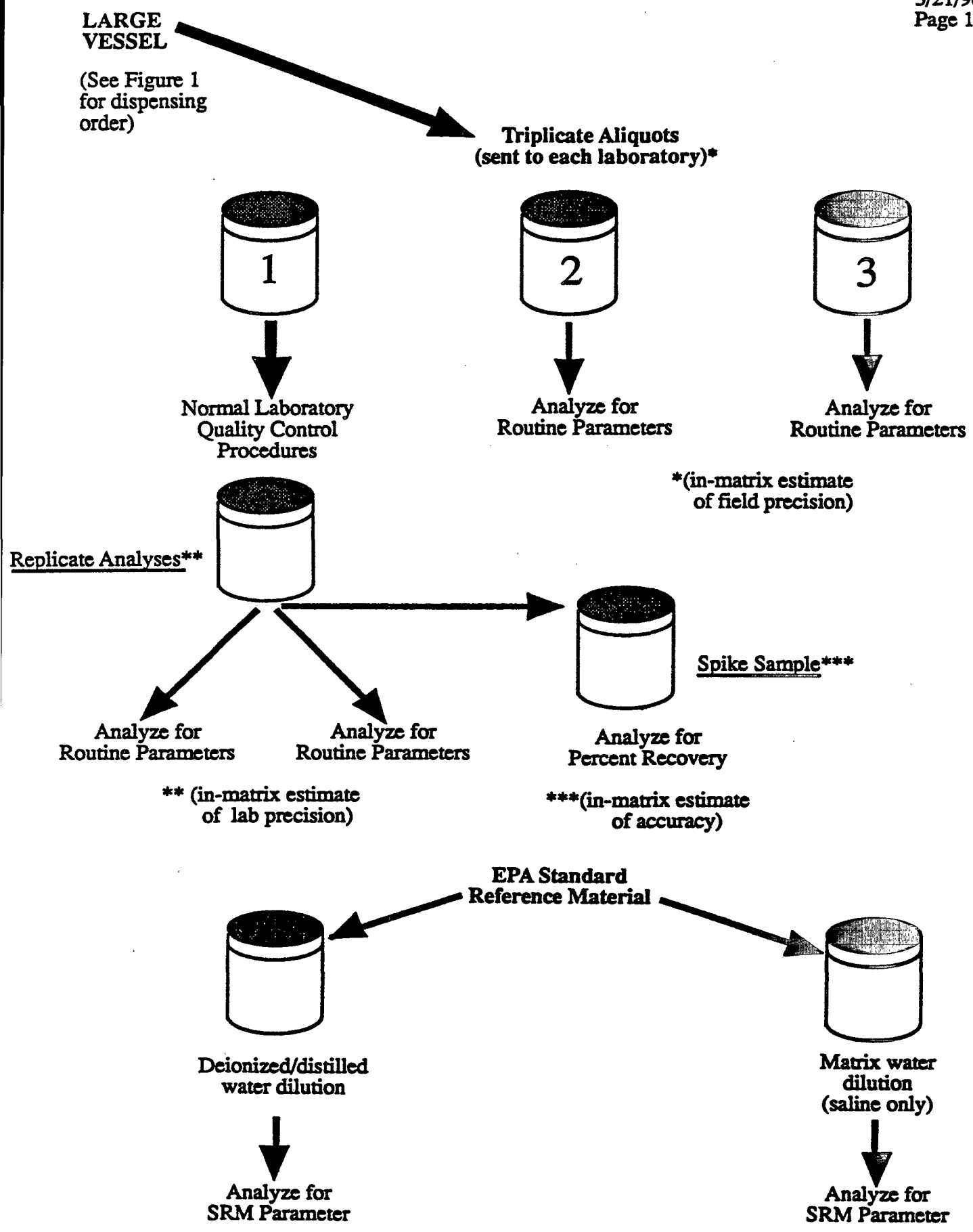
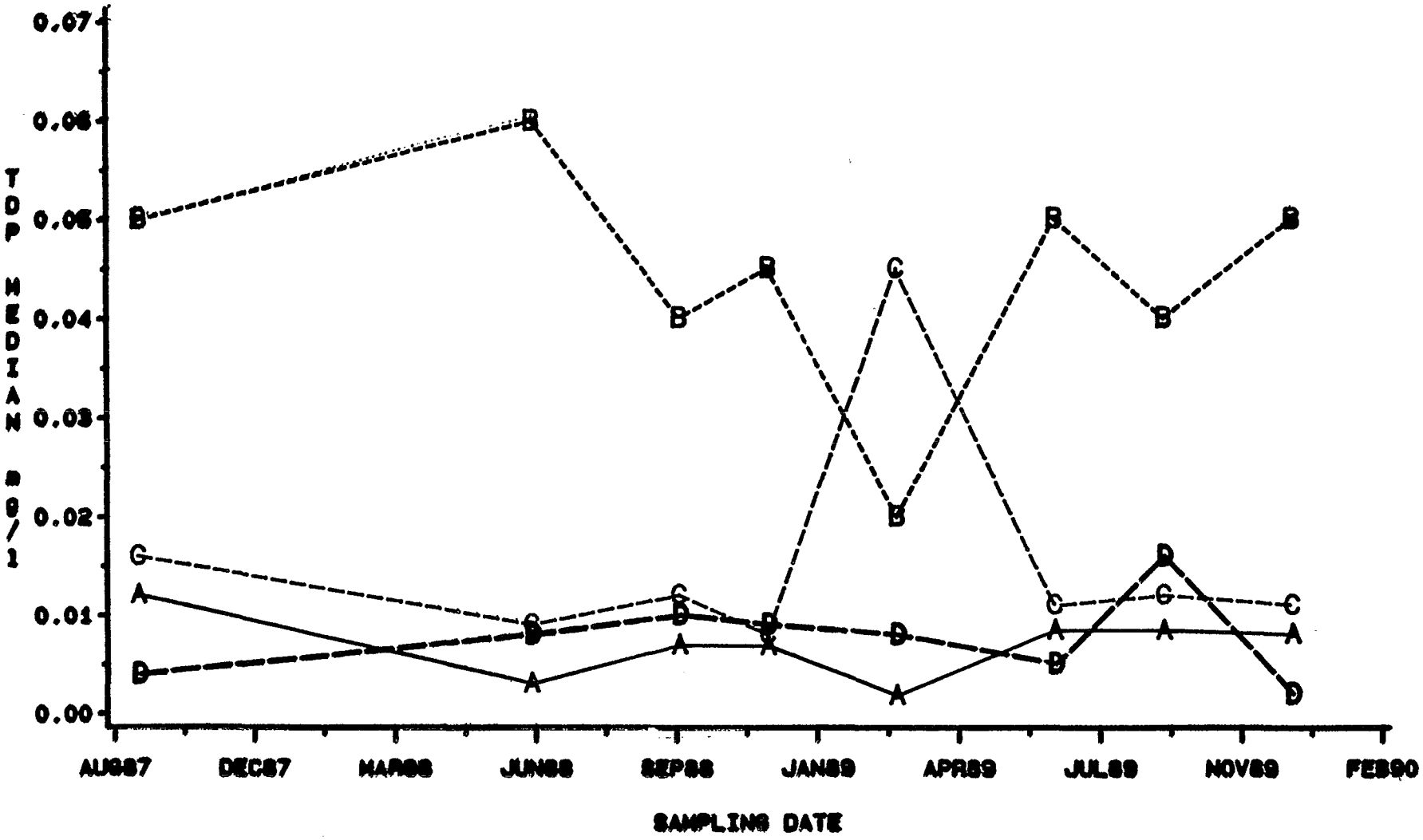


Figure 4. Schematic of the Operational Flow of Analyses, Coordinated Split Sample Program



Split sample results at four labs, TDP

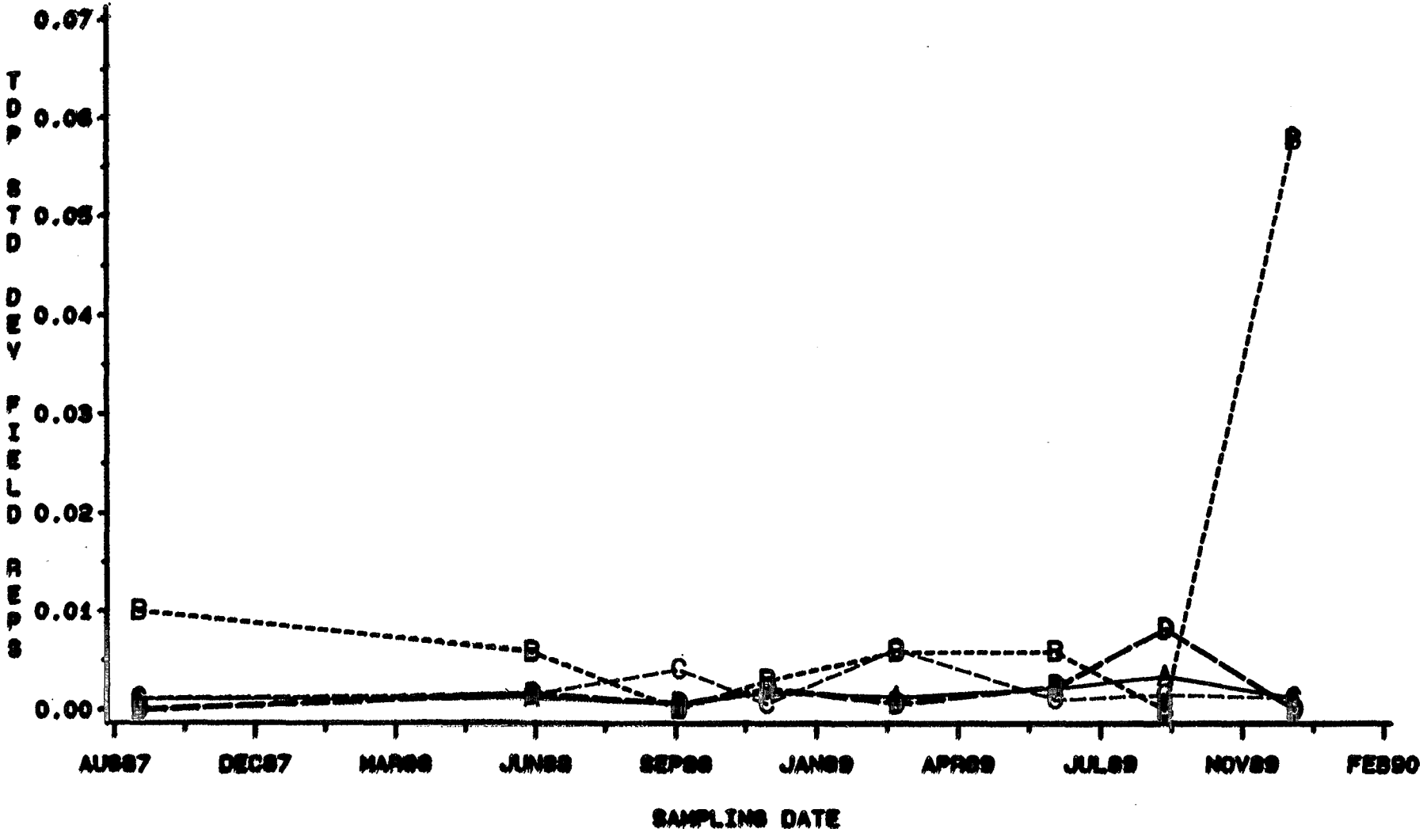
Medians of three aliquots for Total Dissolved Phosphorus, mg/l
Data from four-way split samples done quarterly at Station 085:3



Letters show analysis laboratory (A, B, C, D)

Field Precision at four labs, TDP

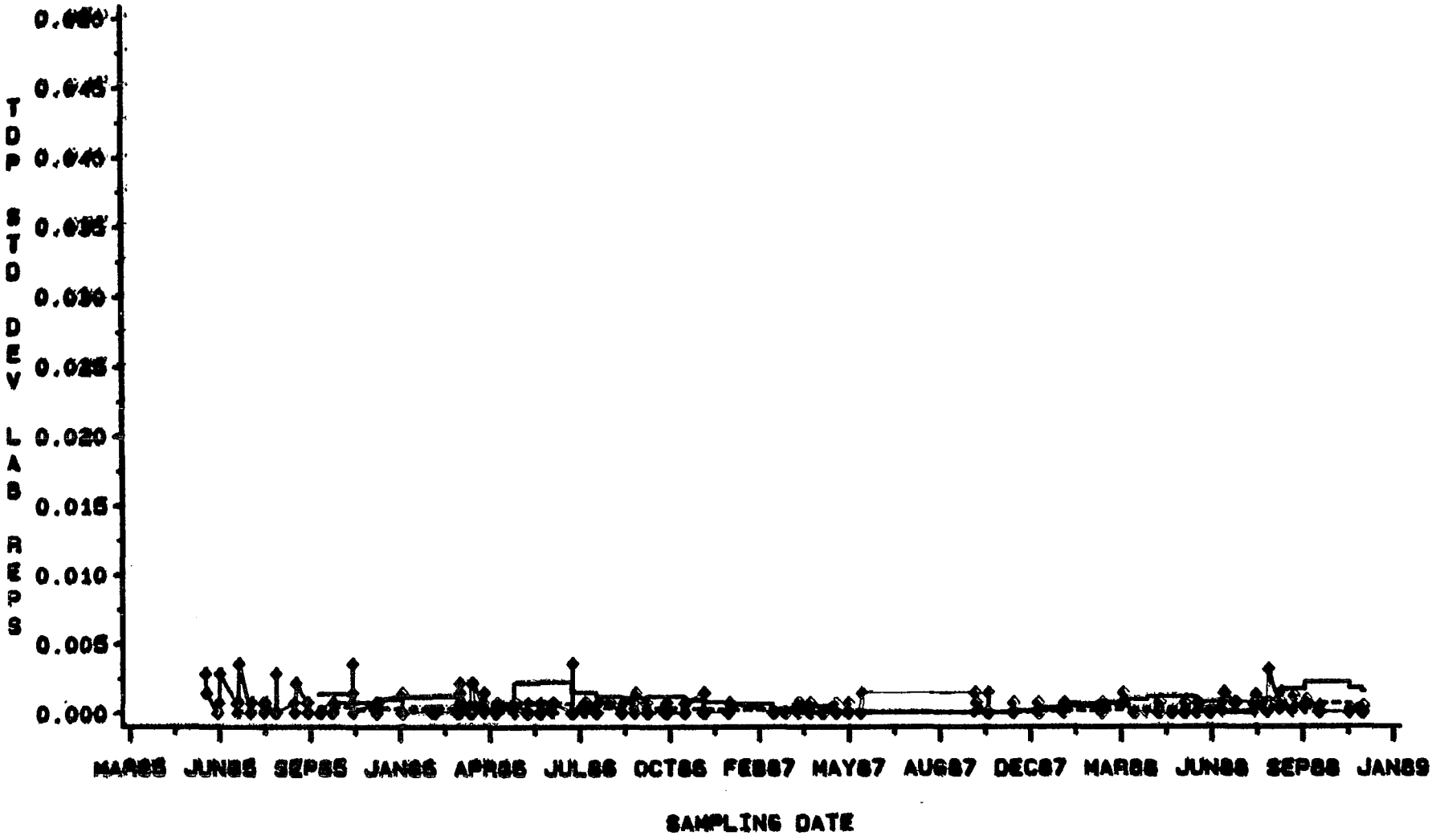
Standard deviations of three aliquots for Total Dissolved Phosphorus
Data from Four-way split samples done quarterly at Station 055.3



Letters show analysis laboratory (A, B, C, D)

Laboratory Precision at Lab A, TDP

Standard deviations of Total Dissolved Phosphorus lab duplicates
Monthly Control Limits from Rolling 25 mean



Blue=raw data, solid red=monthly UCL, dashed red=monthly mean

COMPONENTS OF THE CHESAPEAKE BAY MONITORING PROGRAM

- Mainstem Chesapeake Bay Water Quality Monitoring Program
- Maryland, Virginia and District of Columbia Tributary Water Quality Monitoring Programs
- Citizen Monitoring Program
- Fall Line (River Input) Monitoring Programs
- Baywide Phytoplankton and Zooplankton Monitoring Programs
- Baywide Benthic Monitoring Programs
- Fisheries Independent Shellfish Monitoring Programs
- Fisheries Independent Beach Seine and Trawl Survey Programs

COMPONENTS OF THE CHESAPEAKE BAY MONITORING PROGRAM (cont'd)

- Submerged Aquatic Vegetation Aerial and Ground Survey Program
- Sediment Toxicant Monitoring Programs
- Finfish and Shellfish Tissue Monitoring Programs
- Baywide Waterfowl Survey Programs
- Sediment Processes Monitoring Programs

OTHER CHESAPEAKE BAY BASIN MONITORING PROGRAMS

- State Ambient Water Quality Monitoring Networks
- State Shellfish Bacteriological Monitoring Programs
- Utilities Monitoring Programs
- USGS NASQUAN Program
- USGS Streamflow Gauging Network
- State Groundwater Observation Network
- Nonpoint Source Watershed Monitoring Programs

OTHER CHESAPEAKE BAY BASIN MONITORING PROGRAMS (cont'd)

- Point Source Compliance Monitoring
- Radiological Monitoring Programs
- NOAA NWS Meteorological Data Networks
- State Air Quality Monitoring Networks
- State Acid Depostion Networks
- NOAA Tidal Height Network

CHESAPEAKE BAY LIVING RESOURCE MONITORING PROGRAM OBJECTIVES

- Document the current status of living resources and their habitats in Chesapeake Bay

- Track the abundance and distribution of living resources and the quality of their habitats over time

- Examine correlations and relationships between water quality, habitat quality and the abundance, distribution and integrity of living resource populations

THE CHESAPEAKE BAY MONITORING PROGRAM

An Evolving Data Collection Network
and Process Providing Information
Necessary for Management of the
Chesapeake Bay's Resources

MONITORING PROGRAM DESIGN AND IMPLEMENTATION

Chesapeake Bay Monitoring Program Experience:

- Institutionalized the program through an effective committee/technical workgroup structure
- Planned adequately for water quality network design but not for living resource components; monitoring of toxics still not fully addressed

Recommendations:

- Establish a multi-jurisdictional monitoring committee
- Clearly state the program objectives using them in developing Data Quality Objectives and the network design
- Continually seek long-term, stable funding sources
- Integrate existing monitoring programs into the design of a coordinated monitoring program
- Consider future modeling needs during network design

DATA MANAGEMENT

Chesapeake Bay Monitoring Program Experience:

- Did not adequately plan up front for data management needs
- Centralized computer data base networked with other data bases
- Working with numerous data submitting organizations demanded specific data submission formats and data management requirements

Recommendations:

- Plan adequate resources for data management prior to monitoring program implementation
- Seek consensus on and require adherence to specific data submission requirements
- Clearly state objectives for data base development up front and adhere to them when structuring the data base
- Target acquisition of key historical data sets early on
- Establish procedures for quality assurance of all data entered onto a common data base

QUALITY ASSURANCE

Chesapeake Bay Monitoring Program Experience:

- More than 15 laboratories analyzing water quality samples alone eventually contributing to the centralized computer data base
- Significant effort required to ensure use of comparable sample collection and analysis methods across component programs
- Routine analysis and interpretation of QA data critical to future quality of data

Recommendations:

- Establish quality assurance as an integral part of all monitoring program components (QAOs, audits, QA plans)
- Set up a coordinated split sample program between analytical laboratories
- Seek technical consensus on sample collection and analysis procedures in view of program objectives and implementation of resultant consensus

DATA ANALYSIS AND INTERPRETATION

Chesapeake Bay Monitoring Program Experience:

- Insufficient resources were devoted to data analysis
- Direct connections between information resulting from the program and management decisions were limited until adoption of the Baywide Nutrient Reduction Strategy and setting of Baywide restoration goals
- Establishment of consensus on data analysis priorities up front and sharing of data management and data analysis resources between agencies was necessary

Recommendations:

- Dedicate resources for analysis and interpretation of monitoring data
- Establish a tiered reprting system to force routine analysis and synthesis of data targeted toward various levels of agency managers and the public
- Create a dependence on using results from the monitoring program for management decision-making

ANALYTICAL METHODOLOGY

Chesapeake Bay Program Monitoring Experience:

* Adopted EPA Water and Wastewater Analytical Methods
* Hostage to continuity with the "historical database"
* CBP special studies to establish comparability
* Some data usability compromised

Recommendations:

* Develop performance data for estuarine and marine analytical methods through round robin and validation studies
* Evaluate and develop SRMs
* Develop a network among technical estuarine/marine professionals

ESTUARINE

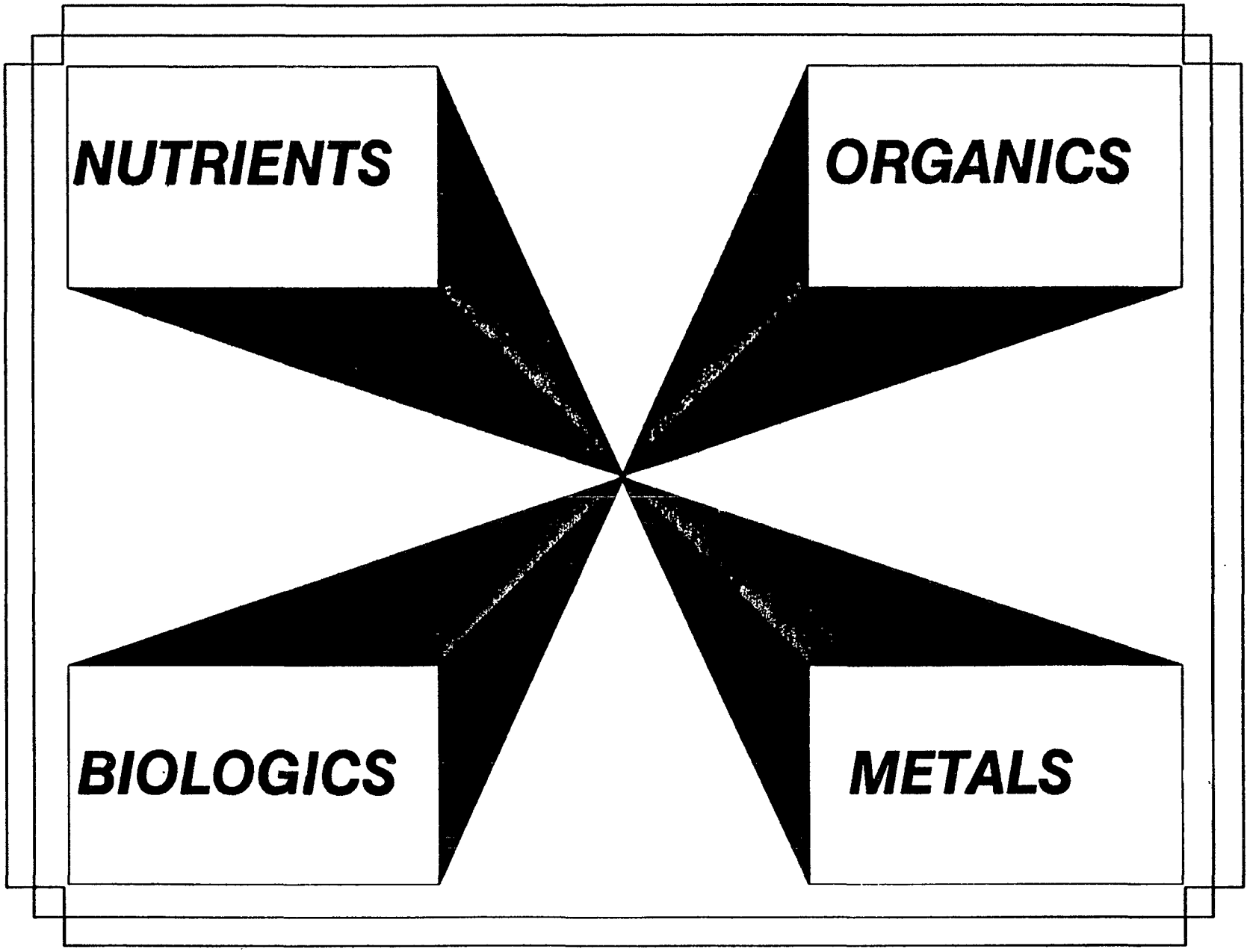
AND

MARINE

ANALYTICAL METHODS

COMMITTEE

WORKGROUPS


NUTRIENTS
ORGANICS
BIOLOGICS
METALS

MR. FIELDING: Good morning.

I have one announcement to make. EMSL-Cincinnati is soliciting labs for two interlaboratory method validation studies. The first is a joint EPA/AOAC effort to validate NPS Method 6 for ethylene thiourea in water by GC/NPD. The second is a joint ASTM/EPA study announced in the Federal Register for Cr_6 ion chromatography.

If anyone is interested in participating in either of these two method studies, information will be provided at the table in the rear of the hall.

I hoped everybody survived last evening's excursion on the HMS Sinkfast. If you didn't, let us know.

We have several interesting papers today. We would like to start off with a paper by Yves Tondeur of Triangle Laboratories who will discuss the determination of semi-volatile organic compounds in river water at the ppq level by high resolution GC and high res mass spec.

Yves?

MR. TONDEUR: Good morning.

Sometime last fall, the Canadian Government, which is engaged in a study of pollutants in the Niagara River, established a list of some 23 organic chemicals for which methodologies capable of achieving parts per quadrillion detection limits were necessary, and the U.S. Environmental Protection Agency, in the spirit Of international cooperation, has offered to help and subcontracted the work to our lab.

The objectives (Fig. 1) of the study were to develop an analytical procedure that would be able to detect and quantify 21 target compounds in river water sample extracts at the parts per quadrillion level. Originally, the list was for 23 compounds, and we had to reduce it to 21, primarily because one of the compounds, the trichlorotoluene could not be obtained as a standard at the time of the study, and the other one was a series of chemicals called toxaphene for which we didn't think we could develop a procedure at the parts per quadrillion level within the required 21-day turnaround.

So, during that short period of time, we were involved in the evaluation of short and long-term reproducibilities of the response factors for the various analytes relative to internal standards and also somehow evaluate the procedure

on simulated matrix spike or laboratory control spike extracts.

The method itself calls for isotope dilution mass spectrometry during which a group of 16, labeled standards, mostly deuterium labeled, were used. The mass spectrometer uses a detector which is operating in the selected ion monitoring mode and with a resolving power of 10,000 for selectivity.

The samples are introduced inside the system through a capillary GC column. The samples were supposed to be obtained from the extraction of a 40-liter sample size and analyzed following a concentration step down to 25 microliters. In other words, a million-fold concentration, and that was the requirement set for us.

The target analytes (Fig. 2) represent a broad range of compounds ranging from compounds such as acenaphtene, benzidines, a group of halogenated aliphatics and aromatics such as chloroethylether or bromophenylphenylether and also chlorinated benzene and brominated benzene. We have also a series of nitrosamines (n-nitrosodimethyl, dipropyl, and diphenylamines), DEHP and di-n-octylphthalate, along with some phenolic compounds such as tetrachlorophenol and dinitrophenol.

So, the very first thing we did was to prepare a set of calibration solutions whose composition is summarized on

Figure 3. Two types of compounds: 1) A series of 21 unlabeled analytes representing the target compounds, and 2) A group of 16 labeled internal standards.

The analyte concentrations along these five calibration solutions vary from 25 picograms per microliter in concentration all the way to 300 picograms per microliter, while the concentrations of the internal standards remain constant at either 100 picograms per microliter or 200 picograms per microliters, depending on the compound.

Now, if we consider a sample size of 40 liters and a final extract volume (if achievable) of 25 microliters, then the concentration domain represented by this set of calibration solutions covers approximately the 15 ppq level up to about 200 ppq level, which was part of the requirement of the study.

Since I am going to be showing quite a few tables this morning, I will just show a few selected current ion profiles obtained on as little as 5 picograms of selected compounds such as the chloroethylether for which a 5-picogram injection gives you a very reasonable and respectable signal-to-noise ratio (Fig. 4). The same can be said for the chlorinated and brominated benzene (5-picograms of material injected) (Fig. 5).

Acenaphthene and its internal standard, D_10-acenaphthene (Fig. 4). eluting slightly before or the

chlorophenylphenylether with the M and M+2 responses, the M+2 becoming kind of a noisy thing at the 5 picogram level.

Another final example is the one obtained on tetrabromobenzene. Figure 6 represents 5-picograms of material injected on the GC column for which a noisy signal is obtained.

I am not saying here that all the target compounds could be analyzed at the 5 picogram injection level. These examples are the only ones for which a reasonable signal could be obtained. They reveal that the methodology itself could very well exceed the required detection limits requested by the Canadians.

So, an aliquot from each of these calibration solutions were then injected once and the response factors of the various analytes calculated for each of the calibration points. The means of those five points were calculated along with the relative standard deviations of the means. (Fig. 7).

As you can see from this summary table, with the exception of acenaphthene, the standard deviation remained below the 20 percent mark, and most of the time, it is even less than 10 percent, which is quite remarkable considering t the levels at which we are working. The results are in agreement with expectations from the use of isotope dilution techniques.

There are a few analytes for which we were not able to measure a response factor. Benzidine and dinitrophenol: Those two compounds were never seen at those levels in the chromatogram. We suspect that the benzidine, being a basic compound, and nitrophenol, an acidic compound, reacted together and, therefore, make their detection very difficult.

We also believe that at those very low concentrations, picogram per microliter range, that the reaction is much more noticeable. We are able to see benzidine and nitrophenol simultaneously in the solution when their concentration in the solution exceeded the nanogram per microliter level.

Other compounds such as the DEHP for which we were not able to generate a response factor because of a problem with the mass spec operator who did not cover the right retention time window. This was, in fact, corrected afterwards during the matrix spike studies.

Nitrosodiphenylamine constituting another exception. Since we use a splitless injection technique, we observed almost quantitative conversion of nitrosodiphenylamine into diphenylamine.

As far as the relative retention time for these analytes, the mean relative retention times are summarized in Figure 8. They were determined using the internal

standards that were used during the computation of the response factors.

As you can see, over the 5-point calibration curve, these standard deviations are extremely small which makes it evident that isotope dilution will provide pretty reliable results as far as qualitative characterization of the analytes in the samples.

We then looked into the continuing calibration (con-cal), that is, after a 48-hour and 4-day periods following the initial calibration. Figure 9 contains the summary results obtained after 48 hours.

The middle point of the calibration curve was used to determine the relative response factors for each of the analytes, we then compared those response factors to the mean that were obtained during the initial calibration (I-cal), and then calculated the percent difference between the con-cal and the I-cal response factors.

As you can see, for most of the analytes for which we could measure a response factor, the percent difference remained within 20 percent of the I-cal, which is quite remarkable.

Then we also looked at the response factors obtained for these various analytes four days following the initial calibration (Fig. 9). Four days may not be a lot, but when

you have a 21-day period to develop and evaluate a method, 4 days is a significant amount of time.

So, again, the daily response factors calculated here from the middle point of the calibration curve were compared to the I-cal response factors and then the deviation from the I-cal summarized in the last column. And with the exception of acenaphthene, dichlorobenzidine and diphenylamine, the deviation remained within 20 percent of the I-cal.

Even though some of these analytes exceeded 30 percent deviation, we believe that the initial calibration can be used for routine analysis at least after 4 days after establishment.

We then evaluated the overall procedure of high-resolution GC and high resolution mass spectrometry on what we called matrix spike analysis (a laboratory control spike). The sample is supposed to be obtained from the extraction of 40 liters of water, then concentrated down to 1 ml methylene chloride and sent out to the lab in vials of 1 ml. The lab is then required to add the internal standards to that 1 ml solution before blowing it down to 25 microliters.

So, what we have done since we were not able to obtain actual river samples, we simulated a matrix spike by taking 1 ml of dichloromethane and spiking known quantities of the

unlabeled compounds shown here along with the internal standards. The spike level is expressed here in parts per quadrillion and varies from some 30 ppq to 63 ppq, and for a couple of analytes, the concentration of the spike is 125 ppq (Fig. 11).

The second column shows the result obtained from the triplicate set of matrix spike studies. These are the mean and the relative standard deviation of the mean.

The last column, which is called here percent accuracy, is in fact is the recovery (amount found in the sample relative to the amount spiked in the sample), and offers an idea on how accurate the procedure is.

There are a few compounds, acenaphtene and the phthalates along with tetrabromobenzene, tribromobenzene and diphenylamine for which these percent accuracies were very high, exceeding what we would call an acceptable limit of 150 percent. For the remaining compounds, the percent accuracies were close to the 100 range.

With the exception of the phylates for which an obvious explanation can be offered simply because of background contamination, we cannot come with any reasonable explanation for the acenaphthene observation. For the others, one can always assume that tetrabromobenzene and tribromobenzene, are not actually measured using isotope

dilution, need their measurement are more susceptible to instabilities during the GC/MS run.

In conclusion, the procedure developed here of high-resolution GC and high-resolution mass spectrometry could definitely offer parts per quadrillion detection limits on most of the target compounds, that is, provided that 40 liters of extract can be blown down to 25 microliters without any form of a cleanup.

Some of the limitations we encountered were primarily associated with chemical reactivity between some of the components but also background contamination.

As far as the precision and accuracy of the method (as measured on matrix spike studies for 18 analytes), the precision, was in the neighborhood of 15 percent (mean), ranging from 3.5 to 50 percent, which is kind of remarkable considering the low levels at which we were working.

Finally, the accuracy gained here from matrix spike studies gave us a mean of 157 percent, ranging from 86 to 374. Of course, that mean is biased high because of a couple of extremely high data points originating from tetrabromobenzene and the phlalates.

Finally, we recommend strongly that: 1) Separate analyses be done for the acidic compounds. It is not a very good idea to mix the acid and the base neutral fractions of the extraction; 2). The actual testing of river water

sample be evaluated directly so that one can really determine the applicability of the method at the parts per quadrillion level; and, 3) finally, as we go to lower and lower levels, special precautions will have to be taken to minimize or control the contribution from background such as phlalates. Otherwise, the method will not be applicable to analytes for which we have some background contribution.

As far as the determination of nitrosodiphenylamine and diphenylamine goes, they will have to be analyzed separately at this time perhaps by using other GC conditions (we found that nitrosodiphenylamine was degrading into diphenylamine using cold on-column injection.

Thank you for your attention, and if you have any questions, I would be glad to answer them.

QUESTION AND ANSWER SESSION

MR. FIELDING: Are there any questions?

MR. STANKO: George Stanko, Shell Development Company.

I would like to point out that one of the definitions of practical quantitation limit is that 80 percent of the labs can get within plus or minus 40 percent of the true value. I don't think you got there.

Thank you.

MR. FIELDING: Any other questions?

(No response.)

MR. FIELDING: Thank you, Yves.

DETERMINATION OF SEMI-VOLATILE ORGANIC COMPOUNDS IN RIVER WATER AT THE PART-PER-QUADRILLION (PPQ) LEVEL BY HIGH-RESOLUTION GAS CHROMATOGRAPHY / HIGH-RESOLUTION MASS SPECTROMETRY

Yves Tondeur, Mick Chu & Don Harvan

TRIANGLE LABS

OBJECTIVES

1. Develop Methodology (21 target compounds, river water sample extract, ppq level)
2. Demonstrate an I-Cal with Reproducible Response Factors
3. Demonstrate Con-Cal with Reproducible Response Factors
4. Demonstrate Matrix Spike Recoveries after Spiking and Concentration Steps

TRIANGLE LABS

METHOD

Isotope - Dilution Mass Spectrometry

Fifteen Deuterated or Carbon-13 Labeled

Selected Ion Monitoring M S

Electron Ionization

Positive Ion Mode

Resolving Power of 10,000 for Selectivity

Capillary GC Column (60-m DB-5) to Insure Adequate GC Resolution

Extraction to be from 40-L River Water

Concentration of the Final Extract to 25 uL

Greater than a Million-Fold Concentration

TRIANGLE LABS

ANALYTES of INTEREST

Acenaphthene

Benzidine

Bis(2-chloroethyl)ether

Bis(2-ethylhexyl)phthalate

4-Bromophenylphenylether

4-Chlorophenylphenylether

3,3'-Dichlorobenzidine

Di-n-Octylphthalate

N-Nitrosodimethylamine

N-Nitrosodipropylamine

N-Nitrosodiphenylamine

Diphenylamine

1,2-Diphenylhydrazine (or decomposition product azobenzene)

1,2,3,4-Tetrachlorobenzene

1,2,3,5-Tetrachlorobenzene

1,2,4,5-Tetrachlorobenzene

2,4,5-Trichlorotoluene

2,3,4,5-Tetrachlorophenol

2,4-Dinitrophenol

1,3-Dibromobenzene

1,3,5-Tribromobenzene

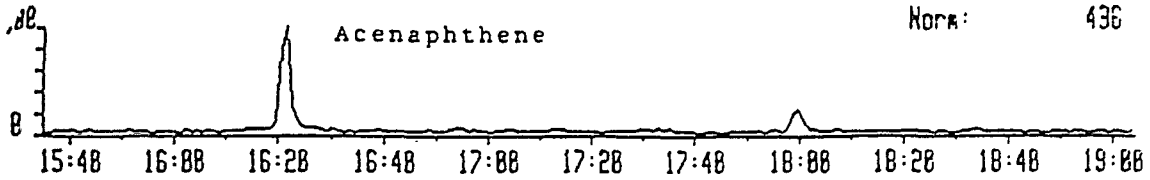
1,2,4,5-Tetrabromobenzene

INITIAL CALIBRATION SOLUTIONS

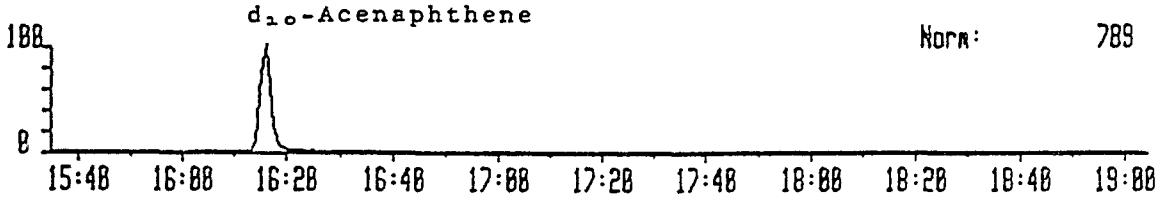
Compound / Solution Number	Concentration (pg/uL)[a] 1	2	3	4	5
Unlabeled Analytes					
Acenaphthene	25	50	100	200	300
Benzidine	25	50	100	200	300
Bis(2-chloroethyl)ether	25	50	100	200	300
Bis(2-ethylhexyl)phthalate	25	50	100	200	300
4-Bromophenylphenylether	25	50	100	200	300
4-Chlorophenylphenylether	25	50	100	200	300
3,3'-Dichlorobenzidine	25	50	100	200	300
Di-n-Octylphthalate	25	50	100	200	300
N-Nitrosodimethylamine	25	50	100	200	300
N-Nitrosodipropylamine	25	50	100	200	300
N-Nitrosodiphenylamine	25	50	100	200	300
Diphenylamine	25	50	100	200	300
1,2-Diphenylhydrazine	25	50	100	200	300
1,2,3,4-Tetrachlorobenzene	25	50	100	200	300
1,2,3,5-Tetrachlorobenzene	25	50	100	200	300
1,2,4,5-Tetrachlorobenzene	25	50	100	200	300
2,4,5-Trichlorotoluene	25	50	100	200	300
2,3,4,5-Tetrachlorophenol	25	50	100	200	300
2,4-Dinitrophenol	25	50	100	200	300
1,3-Dibromobenzene	25	50	100	200	300
1,3,5-Tribromobenzene	25	50	100	200	300
1,2,4,5-Tetrabromobenzene	25	50	100	200	300
Internal Standards					
d_{10}-Acenaphthene	100	100	100	100	100
d_8-Benzidine	200	200	200	200	200
d_8-Bis(2-chloroethyl)ether	100	100	100	100	100
d_4-Bis(2-ethylhexyl)phthalate	100	100	100	100	100
d_5-4-Bromophenylphenylether	100	100	100	100	100
d_5-4-Chlorophenylphenylether	100	100	100	100	100
d_6-3,3'-Dichlorobenzidine	200	200	200	200	200
d_4-Di-n-Octylphthalate	100	100	100	100	100
d_6-N-Nitrosodimethylamine	100	100	100	100	100
d_{14}-N-Nitrosodipropylamine	200	200	200	200	200
d_6-N-Nitrosodiphenylamine	100	100	100	100	100
d_{10}-Diphenylamine	100	100	100	100	100
d_{10}-1,2-Diphenylhydrazine	100	100	100	100	100
$^{13}C_6$-1,2,4,5-Tetrachlorobenzene	100	100	100	100	100
d_3-2,4-Dinitrophenol	200	200	200	200	200
$^{13}C_6$-1,4-Dibromobenzene	100	100	100	100	100

(a) Based on a 40-L sample size, 25 uL final extract volume, 25 pg/ul represents 15.6 ppq. (Calibration Range: 15.6 ppq to 187.5 ppq.)

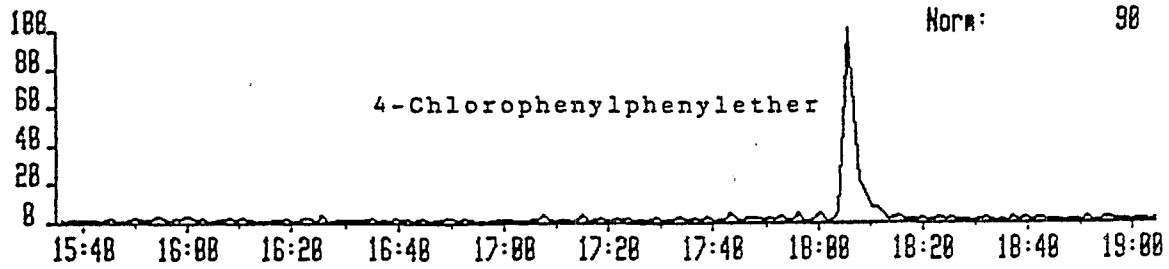
18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
ple 1 Injection 1 Group 5 Mass 154.0783



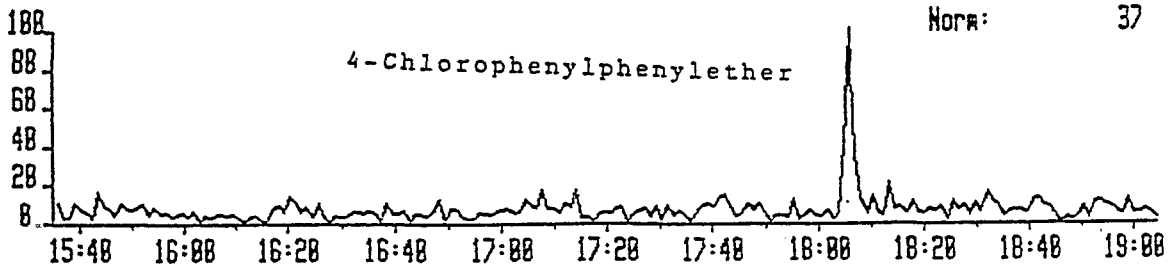
TL16 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 5 Mass 164.1441
Text:

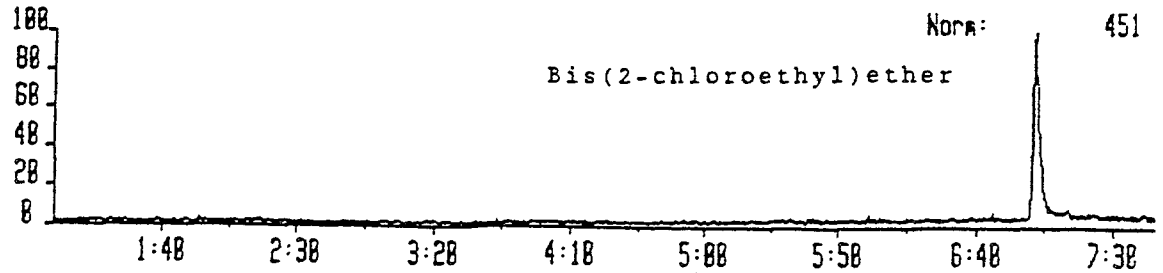


TL16 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 5 Mass 204.0341
Text:

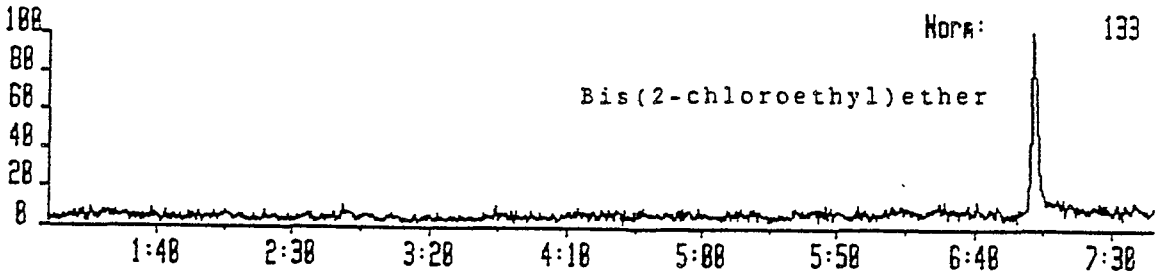


TL16 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 5 Mass 206.0312
Text:

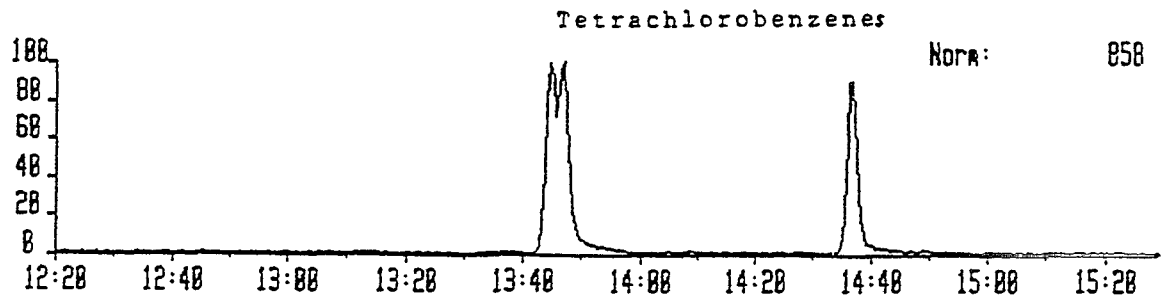




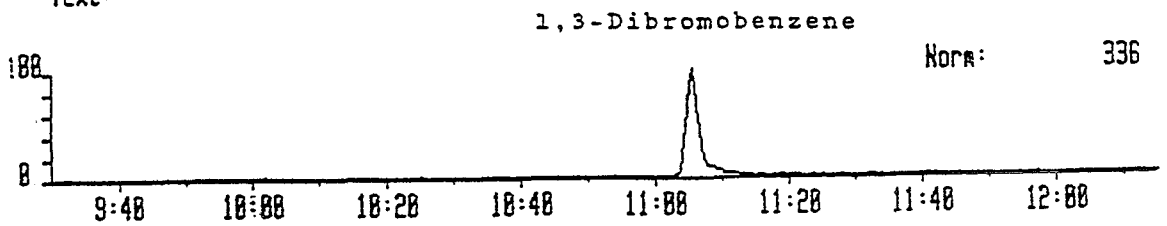
TLI6 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 1 Mass 95.0070
Text:



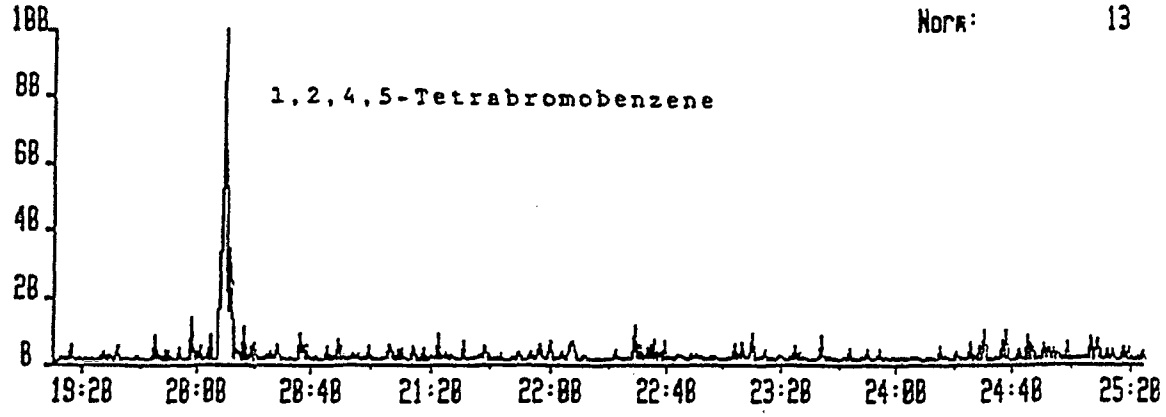
TLI6 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 4 Mass 215.8883
Text:



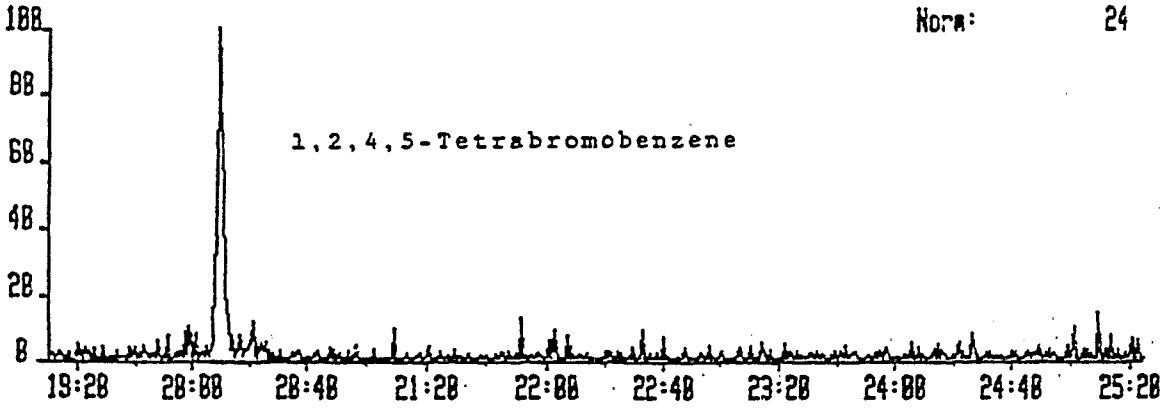
TLI6 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 3 Mass 235.8659
Text:



TLI6 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 6 Mass 391.6869
Text:



TLI6 18-SEP-89 Sir:Voltage 70-250SEQ Sys: TLI
Sample 1 Injection 1 Group 6 Mass 393.6849
Text:



INITIAL CALIBRATION RESULTS

Analyte	Mean RRF	RRF % RSD
Acenaphthene [e]	1.69	25
Benzidine	rj[a]	--
Bis(2-chloroethyl)ether	0.84	4
Bis(2-ethylhexyl) phthalate	[b]	
4-Bromophenylphenylether	0.70	8
4-Chlorophenylphenylether [e]	1.31	6
3,3'-Dichlorobenzidine	1.44	12
Di-n-Octylphthalate [e]	0.89	5
N-Nitrosodimethylamine	0.79	4
N-Nitrosodipropylamine	0.85	6
N-Nitrosodiphenylamine	[c]	
Diphenylamine [de]	1.04	12
1,2-Diphenylhydrazine [e]	1.28	18
1,2,3,4-Tetrachlorobenzene	1.04	5
1,2,3,5-Tetrachlorobenzene	0.91	5
1,2,4,5-Tetrachlorobenzene	1.15	6
2,3,4,5-Tetrachlorophenol	0.04	1
2,4-Dinitrophenol	rj[a]	--
1,3-Dibromobenzene	0.36	2
1,3,5-Tribromobenzene	0.11	0.3
1,2,4,5-Tetrabromobenzene	0.10	0.8

(a) rj = rejected data point (fails to meet acceptable initial calibration criteria).

(b) The signal corresponding to DEHP was not detected due to improper selection of retention time window.

(c) N-Nitrosodiphenylamine is quantitatively converted into diphenylamine inside the GC injector and on the GC column.

(d) Contains a contribution from N-Nitrosodiphenylamine.

(e) Corrected for isotope impurities using equations 6-9.

INITIAL CALIBRATION RESULTS

Analyte	Mean RRT	RRT % RSD
Acenaphthene	1.005	0.00
Benzidine	--	--
Bis(2-chloroethyl)ether	1.013	0.09
Bis(2-ethylhexyl) phthalate	--	--
4-Bromophenylphenylether	1.002	0.03
4-Chlorophenylphenylether	1.002	0.00
3,3'-Dichlorobenzidine	1.001	0.04
Di-n-Octylphthalate	1.001	0.00
N-Nitrosodimethylamine	1.012	0.55
N-Nitrosodipropylamine	1.015	0.11
N-Nitrosodiphenylamine	--	--
Diphenylamine	1.002	0.00
1,2-Diphenylhydrazine	1.003	0.00
1,2,3,4-Tetrachlorobenzene	1.054	0.00
1,2,3,5-Tetrachlorobenzene	0.998	0.00
1,2,4,5-Tetrachlorobenzene	1.001	0.00
2,3,4,5-Tetrachlorophenol	1.228	0.07
2,4-Dinitrophenol	--	--
1,3-Dibromobenzene	0.832	0.01
1,3,5-Tribromobenzene	1.101	0.05
1,2,4,5-Tetrabromobenzene	1.034	0.01

CONTINUING CALIBRATION RESULTS

(48 hours following the initial calibration)

Analyte	RRF i-cal	RRF con-cal	Percent Difference
Acenaphthene [f]	1.69	1.15	-21.4
Benzidine		[a]	
Bis(2-chloroethyl)ether	0.84	0.87	3.5
Bis(2-ethylhexyl)phthalate	[b]	5.08	--
4-Bromophenylphenylether	0.70	0.73	4.6
4-Chlorophenylphenylether [f]	1.31	1.49	14.3
3,3'-Dichlorobenzidine	1.43	1.60	11.5
Di-n-Octylphthalate [f]	0.89	0.77	-13.5
N-Nitrosodimethylamine	0.79	0.83	4.4
N-Nitrosodipropylamine	0.85	0.77	-9.6
N-Nitrosodiphenylamine		[c]	
Diphenylamine [df]	1.04	1.12	7.1
1,2-Diphenylhydrazine [f]	1.28	1.43	11.7
1,2,3,4-Tetrachlorobz	1.04	1.04	0.1
1,2,3,5-Tetrachlorobz	0.91	1.02	11.5
1,2,4,5-Tetrachlorobz	1.15	0.99	-14.3
2,3,4,5-Tetrachlorophenol	0.04	0.05	20.4
2,4-Dinitrophenol		[a]	
1,3-Dibromobenzene	0.36	0.43	20.9
1,3,5-Tribromobenzene	0.11	0.12	3.7
1,2,4,5-Tetrabromobenzene	0.10[e]	0.11	6.2

(a) Benzidine and 2,4-dinitrophenol are not detected at low levels.

(b) No response factor is available for DEHP in the initial calibration.

(c) Thermal decomposition.

(d) Contribution from the decomposition of N-nitrosodiphenylamine.

(e) Ion-abundance ratio was outside the expected QC limit.

(f) Corrected for isotope impurities using equations 6-9.

CONTINUING CALIBRATION RESULTS

(4 days following the initial calibration)

Analyte	RRF i-cal	RRF con-cal	Percent Difference
Acenaphthene [f]	1.69	0.93	-35.9
Benzidine		[a]	
Bis(2-chloroethyl)ether	0.84	0.92	9.0
Bis(2-ethylhexyl)phthalate	[b]	4.60	--
4-Bromophenylphenylether	0.70	0.77	10.6
4-Chlorophenylphenylether [f]	1.31	1.49	14.2
3,3'-Dichlorobenzidine	1.43	1.90	32.7
Di-n-Octylphthalate [f]	0.89	0.94	-4.8
N-Nitrosodimethylamine	0.79	0.76	-4.2
N-Nitrosodipropylamine	0.85	0.79	-6.5
N-Nitrosodiphenylamine		[c]	
Diphenylamine [df]	1.04	1.40	33.9
1,2-Diphenylhydrazine [f]	1.28	1.11	-13.0
1,2,3,4-Tetrachlorobz	1.04	1.04	-0.4
1,2,3,5-Tetrachlorobz	0.91	1.03	12.4
1,2,4,5-Tetrachlorobz	1.15	1.12	-2.9
2,3,4,5-Tetrachlorophenol	0.04	0.05	20.7
2,4-Dinitrophenol		[a]	
1,3-Dibromobenzene	0.36	0.35	-2.1
1,3,5-Tribromobenzene	0.11	0.11	0.0
1,2,4,5-Tetrabromobenzene	0.10[e]	0.09	-6.2

(a) Benzidine and 2,4-dinitrophenol are not detected at low levels.

(b) No response factor is available for DEHP in the initial calibration.

(c) Thermal decomposition.

(d) Contribution from the decomposition of N-nitrosodiphenylamine.

(e) Ion-abundance ratio was outside the expected QC limit.

(f) Corrected for isotope impurities using equations 6-9.

MATRIX SPIKE ANALYSES

Analyte	Spike Level (ppq)	Found Conc. (ppq)	RSD %	Accuracy %
Acenaphthene	31.3	63.4	23.1	203
Benzidine	-	-	-	-
Bis(2-chloroethyl)ether	31.3	31.4	3.4	100
Bis(2-ethylhexyl)phthalate	31.3	113.7	-	364
4-Bromophenylphenylether	62.5	81.8	13.8	131
4-Chlorophenylphenylether	31.3	80.2	13.4	257
3,3'-Dichlorobenzidine	125	108	7.8	86.2
Di-n-Octylphthalate	31.3	67.1	17.2	215
N-Nitrosodimethylamine	62.5	66.9	16.2	107
N-Nitrosodipropylamine	62.5	58.9	10.1	94.3
N-Nitrosodiphenylamine	-	-	-	-
Diphenylamine	62.5	352	40.8	563
1,2-Diphenylhydrazine	31.3	29.0	9.9	92.7
1,2,3,4-Tetrachlorobenzene	31.3	40.2	7.6	129
1,2,3,5-Tetrachlorobenzene	31.3	36.5	3.9	117
1,2,4,5-Tetrachlorobenzene	31.3	34.9	4.8	112
2,3,4,5-Tetrachlorophenol	125	293	14.1	235
2,4-Dinitrophenol	-	-	-	-
1,3-Dibromobenzene	31.3	31.0	7.5	99.3
1,3,5-Tribromobenzene	31.3	53.0	3.6	169
1,2,4,5-Tetrabromobenzene	31.3	117	51.1	374

CONCLUSIONS

1. PPQ Detection Limits Achievable for Most of the Target Analytes

2. Chemical Reactivity Limitations

3. Background Contamination

4. Precision :

   18 Analytes (MS Studies)

   Mean: 14.3%

   Range: 3.4% to 51.1%

5. Accuracy :

   16 Analytes

   Mean: 157%

   Range: 86.2% to 374%

RECOMMENDATIONS

1. Separate Analysis for Acidic Substances
2. Testing on Actual River Water Samples
3. Special Precautions to Control Background Contamination
4. Different Approach Necessary for Reporting Separately

N-Nitrosodiphenylamine

&

Diphenylamine

MR. FIELDING: There is a substitution next. Gordon Wallace from MIT was unable to get here, so we are substituting a very nice paper by Larry Keith of Radian Corporation who will talk about his sampling and analysis methods data base.

MR. KEITH: Thanks, Tom.

Good morning. The sample and analysis methods data base I am going to talk about a little bit this morning originated in Cincinnati at EPA. The overall objective is very similar to Jim King (Viar) and Bill Telliard's (EPA) List of Lists. In some places, the data are similar and in other places it is different.

Jim King and I have talked about these programs and our conclusion is that, basically, these are complimentary programs. They use different searching techniques, and there are some significant differences between them. Why are we interested in databases of methods and analytes? The answer is because the world has become a jungle of analytes and methods, and it is growing all the time. I can remember back not too long ago when life was a lot simpler, and there were relatively few pollutants that people looked for. In the 1970s there were some lists of pesticides, and we didn't have very many methods. We had GC with electron capture detectors, but we didn't have mass spectrometry back in the late 1960s and early 1970s.

However, since that time, people have become interested in more and more different kinds of organic compounds, and, with that interest, we environmental analytical chemists have become craftier and smarter and developed many more techniques.

The result is a proliferation of methods that we have today.

A compounding factor is that many analytes have multiple methods that can be used for their analysis. So, the question is, what method should be used?

There are some obvious things, of course, that method selection well depends upon (Figure 1). First of all, one must consider the available instrumentation. If the method of choice uses a GC/MS method and your lab doesn't have a GC/MS, you can't use that method. The same analogy may be made using an I-cap method for elemental analysis. If you only have atomic absorption spectrometers available, then you cannot use I-cap methods.

Another important factor to consider is the environmental matrix. A third factor to consider is whether or not there are interferences present. Different methods and techniques may introduce or be prone to different interferences. So, sometimes you may need to select the best technique for your purposes by considering what the interferences may be in the samples.

A fourth factor to consider is that various methods have different detection levels. When the need for the greatest sensitivity is paramount, this may be the deciding factor in selecting a method.

Not very often, but sometimes, you may also run into the problem of maximum holding time. Some of the methods have different holding times and in these cases this may influence method selection.

Some examples will illustrate the influences that the above factors can have. Take, for example, 1,2-dichlorobenzene. If you want to do the analysis by GC with a packed column and a photoionization detector, there are at least three different methods that use that particular technique (Figure 2).

However, if you wish to use an electroconductivity detector, then there are at least three other GC methods that use packed columns with that detector.

On the other hand, if you wish to use a capillary column instead of a packed column with an electroconductivity detector, then you may use Method 502.2. But, if you wish to use an electron capture detector with a capillary column, then Method 8120 is applicable.

Finally, if you wish to use a mass spectrometer for a detector then there are at least six other methods with packed or capillary columns.

Consider the same example influenced by its environmental matrix (Fig. 3). If you want to analyze for 1,2-dichlorobenzene in drinking water, EPA's 500 series of methods will apply. If you want to analyze for 1,2-

dichlorobenzene in wastewater, then EPA's 600 series of methods will apply. If you want to analyze for 1,2-dichlorobenzene in sludges, soils, groundwater, and various other matrices, then EPA's 8000 series of methods will apply.

Each of these methods differ in required instrumentation, sample preparation, detection levels, etc.

Next consider the problem of interferences with method selection. If a non-selective detector (e.g. an electron capture detector) is used then phthalate esters may interfere with the analysis. Or taking elemental analyses using I-cap as another example, some elements will cause interferences with that technique that would not exist if atomic absorption methods were used and vice versa.

Thus, knowledge of potential interferences can also be very important in making method selections.

Next, consider the influence of detection levels on method selection (Fig. 5). Using I-cap to analyze for total chromium, one can select EPA Methods 200.7 and 6010 which are essentially identical; they both have a method detection level of 7 ug/L.

I-cap instrumentation is expensive and not all laboratories have such instruments. However, most laboratories do have atomic absorption (AA) instruments. Direct aspiration AA methods have a detection level of 50

ug/L. On the other hand, if you use a graphite furnace technique (EPA Method 7191), then the detection level for total chromium is 1 ug/L. In this example graphite furnace AA provides the most sensitive detection and also a less expensive instrumentation than the I-cap.

The above example is just one of hundreds of variations where method detection levels may influence method selection.

Thus, the overall problem becomes how do you find and select the most appropriate method for sampling and analysis without having to be an expert on all of these or without reading through mountains of EPA reports, the Federal Register and the literature?

Although environmental chemists may be familiar with this detailed information, the people who have to work with environmental chemists (i.e. engineers, regulators, etc.) do not often have the knowledge to make the best decisions involving sampling and analytical methods. How can we help them?

One solution is to provide method summaries from a sampling and analysis database that can be searched by the criteria of interest in order to find applicable method summaries (Fig. 6). This is essentially what we have done. In 1987 and 1988, Bill Mueller and David Smith started compiling a sampling and analysis database at EPA 's Risk

Reduction Engineering Lab in Cincinnati, Ohio. (Fig. 7). They began compiling this database primarily for engineers and contractors who worked with EPA so that the best methods for sampling and analysis of a large variety of pollutants in many matrices could be selected.

The records were compiled using d-Base III and, as the database got larger and larger, the searches got slower and slower.

At the ACS meeting in Los Angeles in September of 1988, and suggested that we use a software program written in C language that we had developed at Radian. It is a " free-text" searching program that may be used to search ASCII text files.

In October of 1988, I received an ASCII dump of the d-Base files. In December, 1988, we did some trials with the free-text searching program and made minor changes.

Then in March of 1989, I sent final copies of the program to EPA and, during the next nine months, we essentially doubled the size of the database and used a revised format. Finally, in March of 1990, the program was sent to Lewis Publishers for publication in the summer of 1990.

A private publishing firm was used so that the publication would get wide distribution and be made easily accessible to everybody.

This publication is the first-of-its-kind, electronic reference book (a book on diskettes) with environmental sampling and analysis methods (Fig. 9).

Each method and analyte summary is self-standing and it is about one page long. What I mean by self-standing is that all of the information is there to allow you to make a selection for a method and an analyte combination without having to go to any other reference.

There are 150 methods, and 660 Method-analyte summaries. The EPA List of Lists program has about 1700 method-analyte summaries.

One of the main differences between EPA's Sampling and Analysis Methods Database and EPA's List of Lists is that, the former has fewer analytes, but contains more information and in a different format List of Lists program. The Sampling and Analysis Methods Database is completely menu driven, so it is very easy to run.

The program performs and/or searches.

It has a hypertext "feel" to its use. It is not a hypertext program, but it has a hypertext "feel" to it. The menu has a highlight bar, which is moved to the analyte-method summary of interest. When the "Enter" key is pressed, the selected summary is instantly displayed.

Once the files have been searched and the appropriate summaries have been found any of them may be displayed easily and very rapidly in any order desired.

Once a summary is displayed, you can page up and down and browse through it. The length of each summary is about two or three computer screens.

Any or all of the summaries may be printed either to a disk file or to your printer.

Within the text on the screen, the key words that were used for searching are reversed video, so they are highlighted. This immediately locates in the text the key words that were of interest. The highlighted keywords do not appear any differently from the other text when printed. Key word highlighting is only used with video screen presentations.

The publication comes complete with an illustrated tutorial. In addition, it has a printed manual.

The publication is provided in three volumes (Fig. 9). Volume I covers industrial chemicals. It has three diskettes of data, plus Systems Diskette. Within Volume I, there are files on chlorinated aliphatic volatile organics; all the other halogenated volatile organics (e.g., aromatics, bromo, chloro and fluoro compounds); non-halogenated volatile organics; and selected semi-volatile compounds.

The second volume is on one diskette. It contains method-analyte summaries of pesticides, herbicides, PCBs, and polychlorinated dioxins and furans.

The third volume also is on one single diskette. It contains one file with elemental methods and another file with water quality parameters (e.g. BOD, suspended solids, pH, etc.).

The information was grouped into three volumes because some people may only be interested in selected groups of analytes and, therefore, no want or need all of the data.

Figure 10 shows the menu for the searching program. It is very simple. When you select "Search" the program searches the active file.

"File" is an option that allows you to move from one file to another without going back through the menu. When you select the option "menu", you are returned to the main menu.

When you select the "Print" option, you may print either to diskette files or to paper.

The "criteria" option is used to enter key words that are to be used to search the files selectively. Five lines of search criteria may be entered. (Fig. 11). If criteria are placed on each line, they are additive during a search. Thus, if "sludge" is on line 1 and "water" is placed on line 2, the program will only find methods that

have both sludge and water as key words somewhere in the summary. In this example, both sludge and water would have to be present for a method summary to be selected.

As a second example, if you want to do "or" searches, where one or another key word is in a summary (for example, aromatic or aliphatic), then the piping character is used to separate those key words on the same line. Thus, if "aromatic:aliphatic" was placed on line 1, "water" on line 2 and "sludge" on line 3, then the searching program would only find those method summaries that had the words "aromatic" or "aliphatic" and "water" and "sludge" in their text.

Each summary contains the primary name of a chemical, its CAS number and the applicable EPA method number (Fig. 12). It also contains a brief description of the EPA method; a short one-paragraph description of the method. In addition, each summary contains the applicable matrices that the method may be used to analyze. A very important section of each summary includes common interferences and solutions for removing those interferences if they are known.

Another part of each summary lists the instrumentation required -- not just the major instrumentation required but, very importantly with respect to the organics, the gas chromatographic columns that are needed.

The sections involving quality control include the published concentration range and the published method detection level (MDL) for the method analyte combination. In addition, practical quantitation limit factors are listed when those are available for the RCRA methods.

The method-analyte precision and accuracy data includes another part of the QC information summarizes sampling and preservation instructions, including the maximum holding time (M.H.T.). Quality control requirements for performing the method are also summarized in this section. The final information presented lists the EPA reference source.

An example of the data is illustrated with Aroclor 1242 using Method 8080. This is shown in Figures 13-15.

There are also some limitations with this publication (Fig. 16). First, not all of EPA's method-analyte summaries are included yet -- specialized analytes, (e.g. organophosphorous pesticides, and many of the semi-volatile compounds with GC/MS methods) are not yet summarized.

These may be added later if there is sufficient interest in this publication format.

Second, the publication is not available in the Macintosh format. However, people with no computers or who have Macintosh computers will be able to get a printed version by the end of 1990.. Of course, that can't be searched.

Lastly, you can't perform the analyses using only the summaries. There is not sufficient detailed information included in the summaries to perform the analyses, but that is not the purpose of this publication. Its purpose is to enable one to make an informed decision as to which EPA method to select for any given situation.

QUESTION AND ANSWER SESSION

MR. FIELDING: Does anybody have any questions?

MR. PRONGER: Greg Pronger from National Environmental Testing.

I was wondering if this program or the List of Lists programs allows the user to append compounds or methods to it.

DR. KEITH: I will have to let Jim King from Viar Corporation answer with respect to the List of Lists. Jim, will you answer that?

MR. KING: The List of Lists in the form that we use actually allows us to enter the information. A number of EPA program offices also can enter information if they have programming capabilities with System J language. However, the average person could not add information to this program.

DR. KEITH: With EPA's Sampling and Analysis Methods Database, you would be able to add compounds or methods to it because, essentially, it is in two pieces. The searching program is a run-time program that can't be changed, but that searching program goes out and loads an ASCII file into the computer's memory. One can easily append information to the ASCII files so, yes, it would be possible.

MR. PRONGER: Thank you.

DR. KEITH: Any other questions? Yes?

MR. LEWIS: Mike Lewis.

How much is the software?

DR. KEITH: Well, I hate to get into costs in a technical meeting. Let me just say that it is...

MR. LEWIS: Free?

DR. KEITH: No, it is not free, of course, because it is produced by a commercial publisher, so they hope to make a profit on it. One never knows whether they will or not. Volume 1, the industrial chemicals, will be in the same range of cost as the List of Lists will be. It will be under $100. The other volumes will be even cheaper than that.

I brought some information sheets, and for those of you who may be interested further in this publication, I will put the information sheets back on the back table. If you are interested, you can pick them up, and they will give you more details.

Any other questions? Yes?

MR. GILLENWATERS: Bill Gillenwaters, Newport News Shipbuilding.

Any thought about including the spectra to be tagged in with it when you call the compound?

DR. KEITH: No, there is so much trouble to do it with words, that spectra would just be beyond the intended scope. I will never put spectra in it. It is just too damn much trouble and not worth it.

MR. NEIN: John Nein from the Naval Supply Center.

Have you considered correlating any non-EPA methods such as ASTM, USGS standard methods or AOAC into this database, or do you feel that would just add to the confusion?

DR. KEITH: Yes. Actually, I have thought about doing that, and, again, it depends on how much interest there is in this type of thing. Of course, this data base only has EPA methods in it, because it was compiled by EPA chemists in Cincinnati. So, that is what their interest was.

But there are many other methods, the ASTM methods and Standard Methods, etc., all of which could be quite readily, with a slight massive amount of work, be added to this database.

So, I have thought about it. Really, this publication is an experiment. The List of Lists is also an experiment,

and the key is how helpful these databases will be to the technical community. Are people really going to find these databases to be useful? If so, then we are on the right track, and, of course, we can add other data to them. If people don't need these types of database summaries, then there is no point in adding to them in the future.

Looking at it from my own point of view, since I don't know the details of all these methods, I find it to be pretty useful. In fact, let me digress and tell you the first time I ever used EPA's Sampling and Analysis Methods Database.

A lady called me to inquire about inorganic methods. I am an organic chemist; therefore, I don't know the details of the many inorganic methods. She told me that she had a laboratory...and it wasn't Radian Corporation...perform some analyses for chromium, and the results were inconsistent.

So, I had my computer on, and I quickly accessed the EPA inorganic method summaries. I searched all the chromium methods while I was talking to her. Of course, she didn't know that I had this information available at my fingertips. I asked what method the lab used and she told me. I quickly displayed the summary of that method and I observed it was a method for direct aspiration atomic absorption for chromium. However, when I asked about the type of matrix, the samples were in, she told me that they were solid samples.

The interferences section of the summary warns that high solids content can cause significant interferences. So, I told her that the lab used the wrong method.

When I searched for chromium and for solids, the computer program found a different method that used graphite furnace atomic absorption. Thus, the lab did use atomic absorption spectroscopy, but it didn't use a graphite furnace. It used the direct aspiration technique and suffered from interferences.

The client was appreciative of this information and said they were going to resample and, this time, send them to Radian. So I said okay, that sounds good. (Laughter.)

So, the client thought that I knew whereof I was speaking about elemental analyses, and, as I have told you, being an organic chemist, I didn't know anything about it. But that was the first time that I personally used EPA's Sampling and Analysis Methods Database to try to help someone find correct methodology.

Yes?

MR. RICE: Jim Rice.

I have a question. I noticed that you stated that all of the methods contained in the database were EPA methods since that was the original objective.

DR. KEITH: Yes.

MR. RICE: My questions involves information that you show for method detection limit and for precision and accuracy and performance, in effect, of the methods in various matrices. Have you limited yourself to just using the information furnished by EPA, or have you gone further than that to other major study results?

DR. KEITH: No, the data has been limited to just the information that was published in the EPA methods.

MR. PRONGER: If a user would buy one of the early versions, is there going to be some way for him to get an update if there would be further updates without having to rebuy the entire package?

DR. KEITH: I really don't know, but let me philosophize. The publisher publishes books, and their concept is, instead of treating this publication like a software program and selling it for know, a lot of money, to instead treat it like a book and make it cheap so that everybody will buy it.

Therefore, I suspect that like when a new edition of a book comes out, you rebuy the book, right? And I suspect that that is probably what they will have to do because the price is so low. That is what they will probably have to do to recover their advertising and production costs.

So, my guess is that if there are updates, they will probably be not at the full price but not free either -- probably at some reduced price in between. But that is just a guess. That would be the logical way to do it if I were the publisher.

Okay, thank you very much.

MR. FIELDING: Thank you, Larry.

SUGGESTED READING

1. Johnson, L.D., "Detecting Waste Combustion Emissions," Environmental Science and Technology, 20, 223 (1986).

2. Johnson, L.D., James, R.H., "Sampling and Analysis of Hazardous Wastes" in Standard Handbook for Hazardous Waste Treatment and Disposal, H.M. Freeman, Editor, McGraw Hill, New York, New York, 1988.

3. Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods. SW-846 Manual, 3rd ed. Document No. 955-001-0000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.

4. J.H. Margeson, J.E. Knoll, M.R. Midgett, D.E. Wagoner, J. Rice and J.B. Homolya, An evaluation of the semi-VOST method for determining emissions from hazardous waste incinerators, J. Air Pollut. Control Assoc., 37(9) (1987)1067.

5. R.G Fuerst, T.J. Logan, M.R. Midgett and J. Prohaska, Validation studies of the protocol for the volatile organic sampling train, J. Air Pollut. Control Assoc., 37 (4)(1987) 388.

6. Johnson, L.D., "Trial Burns: Methods Perspective," Journal of Hazardous Materials, 22, 143, (1989).

7. "Handbook, Hazardous Waste Incineration Measurements Guidance Manual", EPA-625 / 16-891021, June 1989.

8. "Handbook, Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration, EPA-625/6-89023, January 1990.

Selection of best method depends on:

- Analytical instrumentation;
- Environmental matrix;
- Interferences present;
- Detection levels; and
- Maximum holding time.

Analytical Instrumentation

Example: 1,2-dichlorobenzene

- GC, packed column, PID
  - Methods 503.1, 602, 8020
- GC, packed column, HECD
  - Methods 502.1 601, 8010
- GC, capillary column, HECD
  - Method 502.2
- GC, packed column, ECD
  - Method 8120
- GC/MS, packed and capillary columns
  - Methods 524.1, 524.2, 624, 625, 1624, 1625

Environmental Matrix

Example: 1,2-dichlorobenzene

- Drinking water
  - Methods 502.1, 502.2, 503.1, 524.1, 524.2
- Wastewaters
  - Methods 601, 602, 624, 1624, 625, 1625
- Soils, sludges, groundwater, wastes
  - Methods 8010, 8020, 8120

Methods differ in sample preparation, instrumentation, detection limits, holding times, etc.

Interferences Present

Example: PCBs, pesticides, chlorinated organics

- Methods using nonspecific detectors have problems when phthalate esters, other oxygen- and sulfur-containing compounds are present.
  - Method 8120, GC with ECD

Detection Levels

Example: total chromium

- ICP
  - Methods 200.7 and 6010 : MDL = 7 ug/L
- AA direct aspiration
  - Method 7190 : MDL = 50 ug/L
- AA graphite furnace
  - Method 7191 : MDL = 1 ug/L

Problem: How to find and select most appropriate method for sampling and analysis without being an expert or reading massive volumes of information scattered throughout **Federal Register**, EPA reports, and the literature.

Solution: A Sampling and Analysis Database in a convenient **widely accessible** format.

Background

1987-1988: William Mueller and David Smith (EPA-CI RREL) compile S & A Base.
Oct. 1988: Larry Keith obtains ASCII dump.
Nov. 1988: Revise presentation format.
Dec. 1989: Trial with "free text" searching
Mar. 1989: Provide EPA with copies
Dec. 1989: Double size of database in new format
Mar. 1990: New version sent to Lewis Publishers

Jul. 1990: **Sampling and Analysis Methods Database** published

Features

- First of its kind electronic reference book on sampling and analysis methods;
- Each method/analyte summary "self standing";
- 150 methods;
- 650 method/analyte summaries;
- Menu-driven program;
- Performs "and/or" searches of multiple key words;
- Hypertext "feel" to program use;
- Page up/down browsing of each summary;
- Print any or all summaries to file or paper;
- Highlights the searched text in each summary;
- Tutorial with illustrations on disk; and
- Printed manual.

Volume I - Industrial Chemicals (3 diskettes)

- Chlorinated Aliphatic Volatile Organics
- Other Halogenated Volatile Organics
- Nonhalogenated Volatile Organics
- Semivolatile Organics

Volume II - Pesticides, Herbicides, PCBs, Dioxins and Furans (1 diskette)

Volume III - Elements and Water Quality Parameters (1 diskette)

Menu Selections

Search Criteria File Print Menu

You can search for five different criteria by entering in the 5 lines below.

The criteria placed on each line are additive - sludge on line 1 and water on line 2 will only find entries that have BOTH sludge AND water in them.

To search for two or more criteria separate them on a line by PIPING (|). Thus, aromatic|aliphatic on a line will find EITHER aromatic OR aliphatic.

Partial words may be searched: vol will find volatile, volume, volt, etc.

Press Function Key F10 when finished; then select SEARCH from the main menu.

1.
2.
3.
4.
5.

Each one page summary contains:

- Primary name and CAS number
- EPA Method No. and its description
- Applicable matrices
- Interferences and solutions (if known)
- Instrumentation required
- Concentration range and MDL
- Practical quantitation limit factors
- Precision and accuracy
- Sampling and preservation instructions
- Maximum holding time
- Quality control requirements
- EPA reference source

PRIMARY NAME: Aroclor 1242 (PCB-1242) Method 8080

TITLE: Organochlorine Pesticides & PCBs

MATRIX: Groundwater, soils, sludges water miscible liquid wastes, and non-water miscible wastes

CAS #: 53469-21-9

APPLICATION: This method is used for the analysis of 19 pesticides and 7 Aroclor (PCB) mixtures. Samples are extracted, concentrated and analyzed using direct injection of both neat and diluted organic liquid into a gas chromatograph (GC).

INTERFERENCES: Solvents, reagents and glassware may introduce artifacts. Other interferences may come from coextracted compounds from samples. Phthalate esters are common interferences when using an electron capture detector (ECD) so all plastics must be strictly avoided. Exhaustive cleanup of reagents and glassware may be required to eliminate phthalate contamination. Use of a halogen specific microcoulometric or electrolytic conductivity detector will eliminate phthalate interference.

INSTRUMENTATION: GC capable of on-column injections and an ECD or a halogen specific detector (HSD). Column 1: 1.8 meter by 4 mm with 1.5% SP-2250 / 1.95% SP-2401 on Supelcoport. Column 2: 1.8 meter by 4 mm with 3% OV-1 on Supelcoport.

RANGE: 8.5 to 400 ug/L MDL: 0.065 ug/L (in reagent water)

PRACTICAL QUANTITATION LIMIT FACTORS FOR MULTIPLYING TIMES FID MDL VALUE:

Matrix	Multiplication Factor
Groundwater	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludge by sonication	10,000
Non-water miscible waste	100,000

PRECISION: 0.21X + 1.52 ug/L (overall precision)

ACCURACY: 0.93C + 0.70 ug/L (as recovery)

SAMPLING METHOD: Use 8 oz. widemouth glass bottles with Teflon lined caps for concentrated waste samples, soils, sediments and sludges. Use 1 or 2 1/2 gallon amber glass bottles with Teflon lined caps for liquid (water) samples.

STABILITY: Cool soil, sediment, sludge and liquid samples to 4 deg. C. If residual chlorine is present in liquid samples add 3 mL of 10% sodium thiosulfate per gallon of sample and cool to 4 deg. C. M.H.T. = 14 days for concentrated waste, soil, sediment or sludge. M.H.T. = 7 days for liquid samples. All extracts must be analyzed within 40 days.

QUALITY CONTROL: A quality control check sample concentrate containing each analyte of interest is required. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. Use appropriate trip, matrix, control site, method, reagent and solvent blanks. Internal, surrogate and five concentration level calibration standards are used. The quality control check sample concentrate should contain Aroclor 1242 at 50 ug/mL in acetone.

REFERENCE: Method 8080, SW-846, 3rd ed., Nov 1986.

Limitations:

- "Specialized" analytes and many semivolatiles using GC/MS methods are not included yet. May be added if user interest is sufficient.
- Not available with Macintosh formats. Printed version, **Compendium of EPA's Sampling and Analysis Methods** will help people with no computers or only Macintosh computers, but it can't be searched.
- Can't perform analyses from summary information - only select the best method.

MR. FIELDING: Let's take about 15 minutes for some coffee. Can we get back at about 10:20?

(WHEREUPON, a brief recess was taken.)

MR. FIELDING: Before we start, I would like to remind people if they have a question, give your name and the company name so the young ladies on the side there can get it correctly. "Voice from the audience" doesn't look quite as good as it might, and you don't get credit for your comments.

Our next speaker is Bruce Colby of Pacific Analytical who will talk about microextraction isotope dilution GC/MS determination of volatile organic compounds.

Bruce?

MR. COLBY: Good morning.

Since we are running about half an hour behind schedule, I am going to stretch my talk out so that we can catch up. I knew that would excite you all.

I am going to talk this morning about a technique that has been around for a long, long time. It was used, at least, I recall people using it probably about 10 years ago when the organic chemicals industry was being screened by the Effluent Guidelines Division at the time. It is called microextraction, and we, I guess, kind of resurrected it recently to help solve a problem that we encountered where no other solution seemed viable.

The problem we encountered was a series of samples that contained relatively high levels of some ketones, relatively high being in the 1 percent or just under 1 percent type level, and we were looking for the volatile organic species in the samples. If we tried purge and trap on these, the ketones would absolutely wipe out any chance of making a reasonable determination of the other targets.

The options we felt we had with respect to dealing with this problem were to approach the situation by two possible routes. One was direct injection of the aqueous sample, and the other was to resurrect this microextraction technology.

Well, we decided before we were to strike off on things that we should establish a few goals for ourselves. They

are pretty standard sorts of goals for what, in effect, would be a method development effort, not a big one, just a little one.

We have to determine these volatile organics in the presence of what I call semi-purgable organics, fairly polar but nevertheless volatile species. The ketones fall in that category. Phenol, we know, falls in that category. If you have a sample with a tremendous amount of phenol in it, it will get in the purge and trap device and cause trouble for days to come.

And we wanted to have a system that was sufficiently precise, accurate, and with enough sensitivity that it would be close to the purge and trap technology.

Direct injection, we pretty much decided, wouldn't provide us with enough sensitivity. Purge and trap allows one to put the equivalent of a 4 or a 5 ml water sample in the instrument. The water does not go in but all of the volatile organics in the water presumably do.

Clearly, you can't inject 5 ml. A few microliters is more like it. So, this is roughly a factor of 1000 in loss of sensitivity with direct injection.

Microextraction falls somewhere in between, and it provides a couple of interesting things. One is that it provides a mechanism to generate a little bit of additional chemical selectivity. By properly selecting the solvents,

we can discriminate against things that are more polar and keep them out of our extracting solvent and leave them in the water. That was the big key for what we were up to.

The other thing is it is relatively simple, but when you are trying to solve a problem that is tough, even if you have to go at it a tough way, that seems okay.

The problem with microextraction historically has been that it is not really as sensitive as purge and trap and it doesn't really have the accuracy and precision that you expect to get with purge and trap or direct injection, for that matter.

The sensitivity problem we thought we had a decent shot at by using one of the newer GC/MS instruments that is on the market. They seem to have gotten much more sensitive in the last year or so. We used a VG Trio 1 on this job. I suspect that there are several other instruments out there that could do the job just as well.

Our older equipment, we know, cannot do the job. So, it really is confined to the newer GC/MS instruments.

We thought we could beat the old problems of the accuracy and precision that are associated with microextraction by going to isotope dilution. The problems with accuracy and precision, incidentally, are associated with the fact that there can be some pretty significant matrix effects. We heard something about matrix effects

yesterday, and isotope dilution does help us get around these to a reasonable extent.

The method I have outlined in my first slide. We take 35 ml of the water sample, add the labeled compounds to it. We are using a 40 ml VOA vial, we call them.

We then add 1 ml of hexadecane, cap the vial, shake it up, let the layers separate, pull off 1 ul of the hexadecane, shoot it onto a 30 m DB-624 megabore column that is directly coupled to the GC/MS ion source through a restrictor, use a reasonable sort of temperature program, acquire full scan mass spec data.

Hexadecane elutes after all of the target analytes. So, at that point, we shut down the filament and let the solvent through, getting the targets out before the solvent rather than after it which is the more conventional way.

The target analytes are identified and quantified, basically, according to the methodology described in 1624.

Well, a blank looks something like this which I guess, might look a little bit horrifying, but these peaks are actually very, very small, as you will see in the next slide or two.

We see the air come through. Principally, it seems to be argon, the CO_2 staying behind. This blank is a water sample that we know to be clean extracted with the hexadecane and just shot.

We see some silicon compounds. The silicon compounds are not reproducible. We suspect they probably are associated with the analyst not properly cleaning or handling the teflon caps on the vials. We don't know that for a fact, but that is what we suspect, and we haven't been back to verify it. They don't cause a problem in the actual analytical work, so we haven't made a big issue of it.

There appears to be a little bit of hexane in the hexadecane as well.

A chromatogram for a standard. This is the high point on the calibration curve, 10 ng/ul injection. It gives us some pretty nice looking peaks. I cut the chromatogram off just about at the point where we shut the instrument down and the hexadecane starts to come out.

Low concentration standard. Now you can just start to see the silicon compounds in there. So, you can see that even though they looked really huge in the previous one, when we get down to injecting 100 picogram per analyte, that is still a pretty small quantity of that silicon compound.

Looking for targets in the sample, we use a software that comes with the instrument. This is looking at a 1 ng spike into a water sample. Here you are looking at 1,2-dichloropropane. Just picked one at random.

The top trace is the total ion chromatogram. You see a little bit of a blip in that. Again, it is only 1 ng, so quite a small quantity.

Quantitation mass area is shown in the center drawing. The bottom one I won't bother with.

So, the targeting that we used was all automatic. We didn't go back and edit any of the data. We did take a look at it, but whatever was there we accepted, because we just didn't have enough time to fool around with it, basically.

Spectra, again, looking at that dichloropropane that we had before. It is an unbackground subtracted spectrum or raw data spectrum on top. You have a lot of peaks from background within the equipment.

If you do a background subtraction, you get the center kind of a spectrum. It certainly has all the major peaks. It even picks up the minor isotope peaks. There is a set at 97 and one at 112. There are a few other peaks that show up as well.

The bottom spectrum is a spectrum from the NBS library.

So, there seems to be plenty of sensitivity for what we are up to.

What we do now is calibrate the instrument at a very low level compared with conventional GC/MS technologies. We are starting at a high level of 10 ng/ul and going down to 100 picograms per microliter using a 5 point calibration.

That is roughly equivalent to the Method 525 sort of calibration system. I think we are going to get a little bit more information on that from another speaker later on.

Basically, it is a drinking water method. Here, we are using the kind of instrument sensitivity you would use for that drinking water method, but we are applying it to volatile analytes in a wastewater, but the key is the sensitivity.

The calibration compounds are spiked into a water sample. They are prepared in methanol, then extracted from the water sample with the hexadecane, and we do our calibration of the target analytes, again, by isotope dilution, and the labeled compounds we do by a mean response factor calculation.

Target analyte calibration curves were generally very good. What I have plotted here for about...I think it is 23 compounds...is the correlation coefficient that we get for that 5-point calibration curve.

The two on the far right actually were correlation coefficients of 1.0000. I don't know what the fifth decimal place would have with it, but that was pretty impressive.

We have a couple that don't look quite as good on the far left. Those turn out to be tetrachloromethane and toluene. I went back and checked those, and it turns out that each of those had a bad measurement, and we just left

it in the data because we were taking the philosophy we would do it all automated.

So, we have a couple of calibration curves that are a little bit suspect. They, nevertheless, are pretty good calibration curves.

We wanted to look at calibration a little bit more carefully, because we are pushing down into a very low concentration regime with this method. So, we also look at the data with respect to higher order regression fits to the line. This is an allowable part of the Method 525 technology.

In order to compare the quality of calibration curves in these higher order fits, we can't really use correlation coefficient. We have to go to some other statistic to evaluate the quality of the curve.

What we use is a statistic called the mean residual. Basically, what we do is take the calibration data and generate a regression line of some type through the calibration data, in this case, a linear fit to the data. We then plug those calibration data back into that regression line and calculate concentrations.

Now, we know the concentrations, because they are our standards. We made them up, and we are now plugging the data back into the calibration curve, and we get some

concentrations that are slightly different than the true values.

It is the difference between the true value and the determined value as having plugged it back into the curve that is the residual, and what I have plotted here is that correlation coefficient from the previous slide on top versus the mean residual.

The mean residual also has the advantage that it can be expressed in terms of a measurable quantity, in this case, ng/ul.

For the isotope dilution measured compounds, we have a mean residual of approximately 1.28 ng/ul. So, our low end of the calibration curve, on the average, is probably going to be roughly plus or minus 100 percent. So, we are pushing it kind of hard down there.

Now, that average includes those two bad actors up there, and if we take those two out, then the mean residual is quite a bit nicer.

Well, we looked at a second order calibration curve in addition to the linear one, and we got what I would call a pretty substantial improvement in the statistic known as the mean residual. You can see that on here. Essentially, all of the second order fit residuals were lower than the linear regression residuals.

It is tempting, in that sense, to want to use a second order calibration curve, but we will look at some implications of that later on that may change your minds.

It turns out that we had a couple of compounds in there that we calibrated by internal standard because we didn't have the labeled analogs for them. I just throw them up here because we did make the measurements on them, and we do have some information on them. The mean residual on the internal standard compounds is really fairly similar to that of the linear regression isotope dilution values with the exception that they literally had to be done by a second order fit, and I suspect that has something to do with matrix effects associated with spiking of methanol into the samples and the quantities of solvents used.

We also had to quantitate the labeled analogs in order to get some kind of an evaluation of recovery. So, I have again plotted the mean residual for the labeled analog measurements here. Again, these were done by mean response factor, and the mean residual on this is on the order of about 0.13 ng/ul.

In a quick summary on the calibration, isotope dilution looked pretty good by linear regression. Internal standard data looks like it is going to have to be done by secord regression, second order fit. And labeled analogs, as they are in there at a constant amount and we only want...our

interest in them was fairly basic and single point calibration. Our mean response factor was all we were after there.

The next thing after the instrument is calibrated is to back off and say okay...I almost hate to bring up the term...what are the method detection limits? In this calculation, we used the equation that is in the Federal Register, basically, the student's t value times the standard deviation. So, it is roughly three times the standard deviation of...I guess we used eight replicate measurements, and these were prepared and measured separately.

When we look at these, now we can see the difference between linear regression and second order calibrations. It is pretty clear that there is not much difference between the two, and if you try to sort out where the lines go on the screen, it is just about next to impossible, but you can only see what, in effect, is one set of data.

So, even though the calibration curve looked better with the second order fit, when we start applying it to actual measurements of spiked samples, we don't see that improvement. I don't think that we are at a stage where we can definitely say that a second order fit isn't needed, but the implication is at this point that a linear fit will probably be okay.

The few compounds we did by internal standard. The mean detection limits there were about roughly a ballpark factor of 2 to 3 higher than they were by isotope dilution.

And we could calculate a detection limit for the labeled analogs. I don't know quite what it means, but at least it gives you some sense for the reproducibility of the data at the level at which they were spiked. Again, they are roughly the same as the internal standard measured numbers.

The method detection limits I broke out in a summary slide here with the gases and the non-gases separately. It turns out that the compounds that are generally considered gases, chloromethane, vinylchloride, and so forth, they were on the method detection limit slides, those were the compounds on the left. They are harder to handle. They are less reproducible, and using this method detection limit calculation, they then have a higher detection limit.

It appears that the method detection limit for most of the volatile compounds, i.e., the non-gas compounds, is about 6.4 ug/l according to the calculation. The gases are substantially worse. I think we probably could improve that some by fine-tuning our sample handling a little bit and spiking. For what we were involved in, they were not terribly relevant, however.

The internal standard and labeled analog values, again, are very similar to one another.

I put the standard deviation up there so you could see how much variation there was involved in the mean method detection limits that I put up there. The isotope dilution values are reasonably tightly packed around that 6.4 value. So, most of them were behaving quite well.

We also looked at the recoveries of the spiked compounds. Keep in mind now that isotope dilution has an inherent recovery correction associated with it. We did the isotope dilution measured compounds using both linear and second order polynomial fits on the calibration curve. As we saw with the detection limit numbers, the way we calibrate for isotope dilution doesn't appear to be very significant when it comes to measuring values in the samples.

The percent recoveries we would expect to average out around 100 percent for the non-gases. They were about 109 percent using a linear fit and about 108 percent using a second order fit. So, there is effectively no real difference.

For the gases, they weren't quite as good. There appeared to be a positive bias that may have been associated with the order in which the compounds were spiked into the sample. I am not sure.

Internal standard values, again, as we are spiking our standards into a water and extracting them out, there is an inherent recovery correction going on here, and, again, we would expect to see the recoveries showing up at around 100 percent. There appear to be some biases in this, three compounds being quite high and three quite low, but I don't really personally believe there is enough data there to say much. Certainly, there is a lot more spread in these recoveries than there was in the isotope dilution values.

The labeled analogs, like the internal standard measured compounds, had recoveries over a fairly wide range from roughly 50 to 250, but what we are interested in the labeled analogs is can we get a decent signal from it, and if we can, we are generally quite happy. If we can't detect the labeled analog, then we are pretty darn sure we can't detect the naturally abundant compound and we know we have a problem with the analysis.

So, we are basically at this point interested in seeing the labeled analog, not so much concerned about whether we got 47 or 82 percent recovery.

Percent recoveries, in summary, we are looking at isotope dilution non-gases again, about 109 percent, pretty tightly grouped. Standard deviation of 7 percent.

Isotope dilution, gases, again, there appears to be some positive bias, but there is quite a bit of variation in that, a 16 percent standard deviation.

Internal standards, even more variation. Interestingly, quite similar to the labeled analogs and some bias with the labeled analogs, again, possibly having to do with the order in which things are spiked in.

In summary, we have a method that for most of the volatile organic compounds that are not highly polar, we have pretty decent detection limits with this technology using the new GC/MS instrumentation that is available to us. For the gaseous compounds, not quite as good. We know they are tougher to handle.

Recoveries are in the vicinity of 100 percent. So, it starts to look like a fairly viable technique for dealing with some kinds of samples. We believe the technology could be pushed into applications where other kinds of complex or interference situations are an issue, and we expect to be trying a little bit with the base neutral and acid fractions in the future.

I might add that the base neutral and acid fractions may have an additional benefit, and that is that by working with relatively small samples and, in particular, smaller quantities of solvents, we are involved a pollution reduction problem which is, for some of us in the analytical

community, becoming more and more of an issue, the chlorinated solvents. We know where they go, and the regulators are figuring it out, and I think EPA is probably coming under a little pressure on all this, too.

That takes me to the end of the data that I had. I think I am doing a little bit in helping catch up, but I would be more than happy to try to answer a few questions.

QUESTION AND ANSWER SESSION

MR. FIELDING: Does anybody have any questions?

MR. MCCARTY: Harry McCarty, Viar and Company.

Bruce, presumably, your calibration data, since you are spiking your standards into the reagent water, you are spiking varying volumes to get the different concentrations, did you look at making up an equivalent volume of methanol so that all of them end up with the same amount of methanol? Because that may explain some of the problems.

We have done a couple of studies, and it seems to help some of the calibration data. I would assume with isotope dilution, it would just make it even better.

MR. COLBY: I don't think it would affect the isotope dilution data at all. I believe it would probably have some effect on the internal standard compounds, but they were not of real interest to us in this. They were in there just because they happened to be there, and we looked at them as a consequence, but yes, I am quite sure you are right. That would be an improvement.

MR. MCCARTY: It is a relatively simple thing, you know, when people are doing it in practice, and it may make a significant difference there.

MR. COLBY: Quite true.

Anybody else awake?

(No response.)

MR. COLBY: If not, okay, thank you.

MR. FIELDING: Thank you, Bruce.

MICROEXTRACTION ISOTOPE DILUTION GC/MS DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

by

Dante J. Bencivengo and Bruce N. Colby

PacificAnalytical

and

James S. Smith

Trillium, Inc.

EXPERIMENTAL GOALS

- Determine volatile organics in the presence of large quantities of semi-purgable organics.
- Provide detection limits equivalent to purge & trap GC/MS.
- Provide accuracy and precision equivalent to purge & trap GC/MS.

MICROEXTRACTION

Advantages:

- Chemical selectivity
- Simplicity

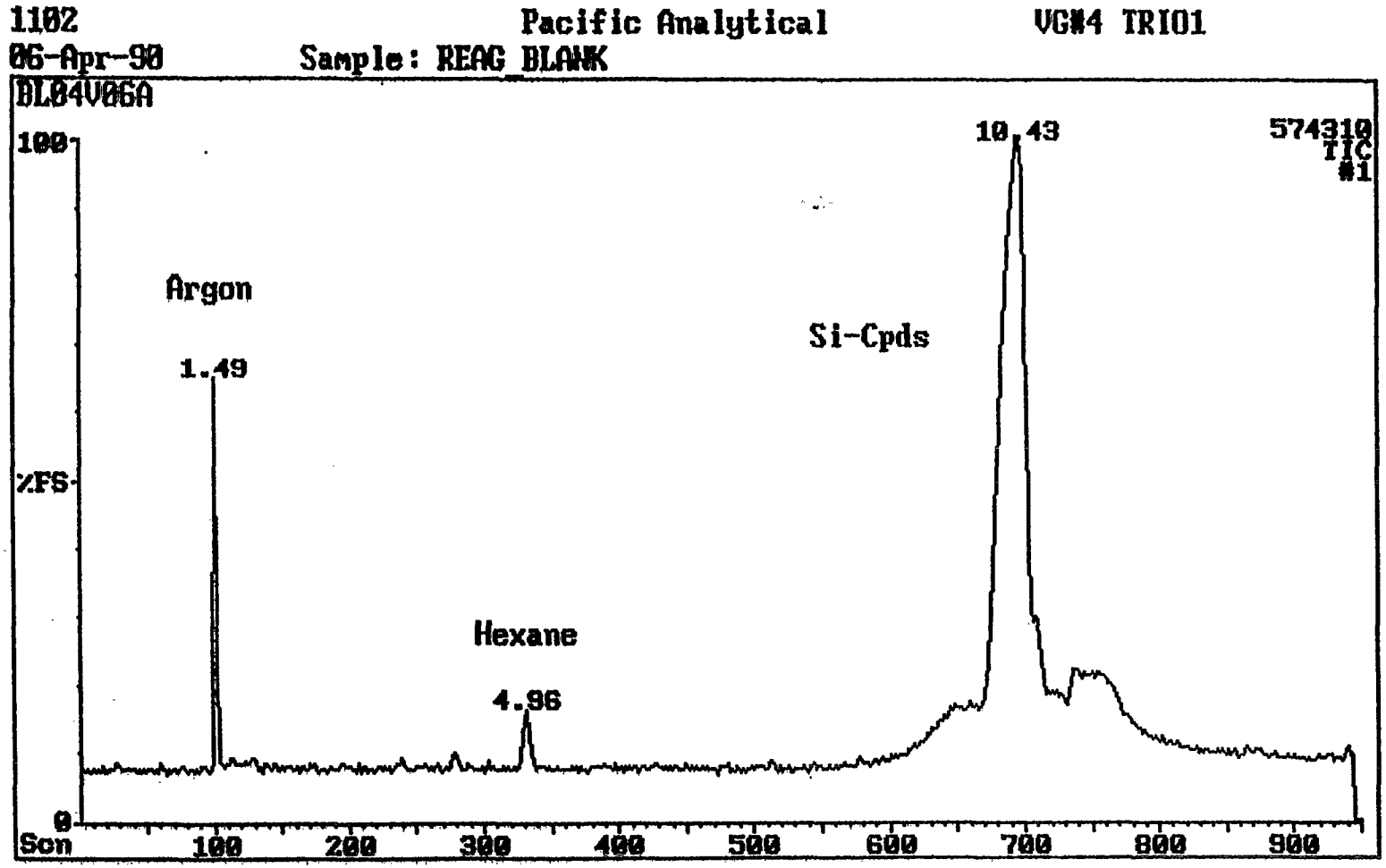
Disadvantages:

- Sensitivity
- Accuracy
- Reproducibility

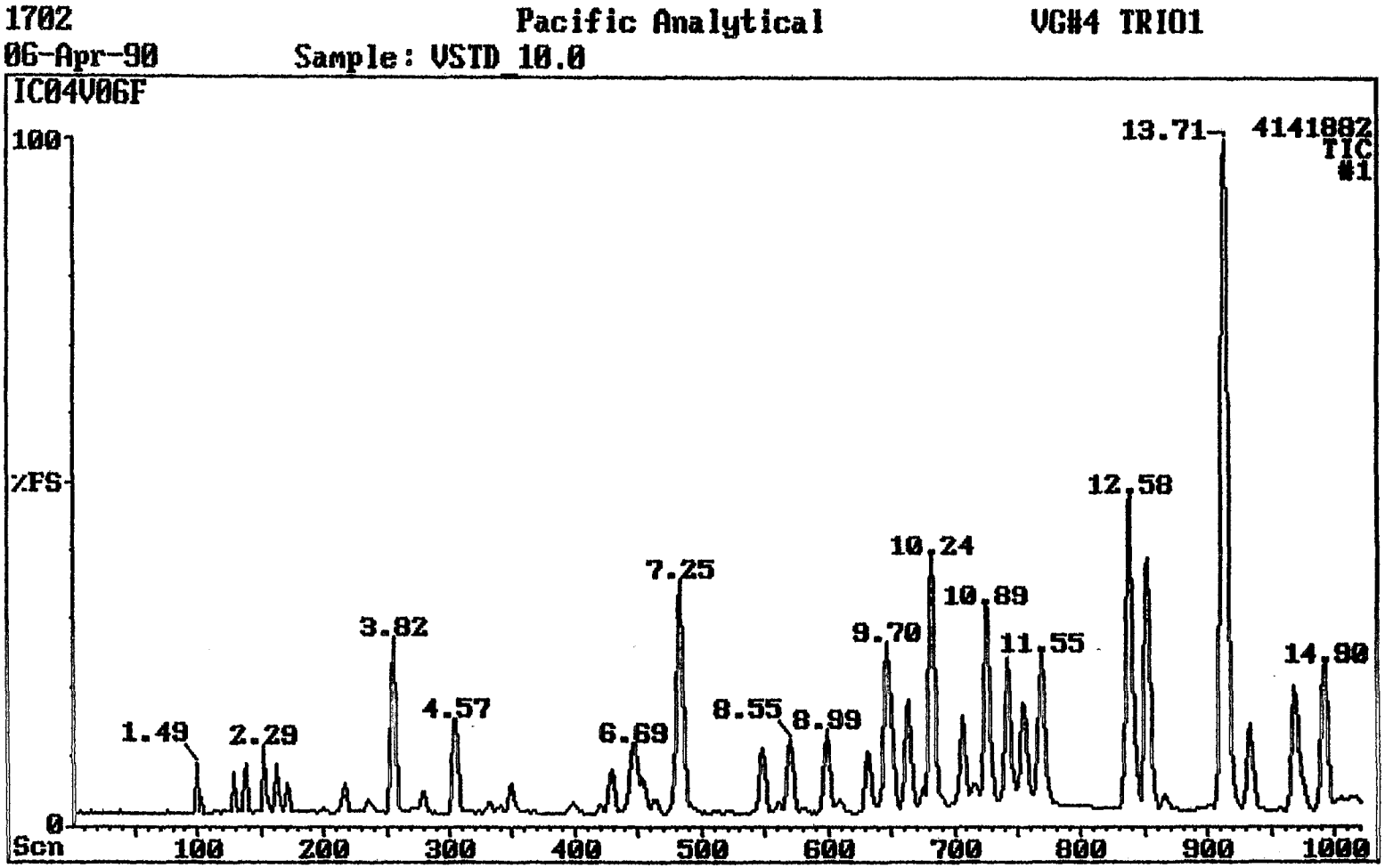
METHOD SUMMARY

- Spike 35 mL sample with Method 1624 labeled compounds and internal standards.
- Add 1 mL hexadecane, shake and wait for layers to separate.
- Inject 1 uL onto a 30 m DB-624 Mega-bore column directly coupled to the GC/MS ion source through a 1 m 0.25 mm restrictor.
- Program from 40 to 180 ^{o}C at 8 ^{o}C/min with initial and final holds of 3 and 20 min respectively.
- Acquire full scan data until just before hexadecane is eluted (filament turned off while solvent is eluted).
- Identify targets and quantitate via isotope dilution.

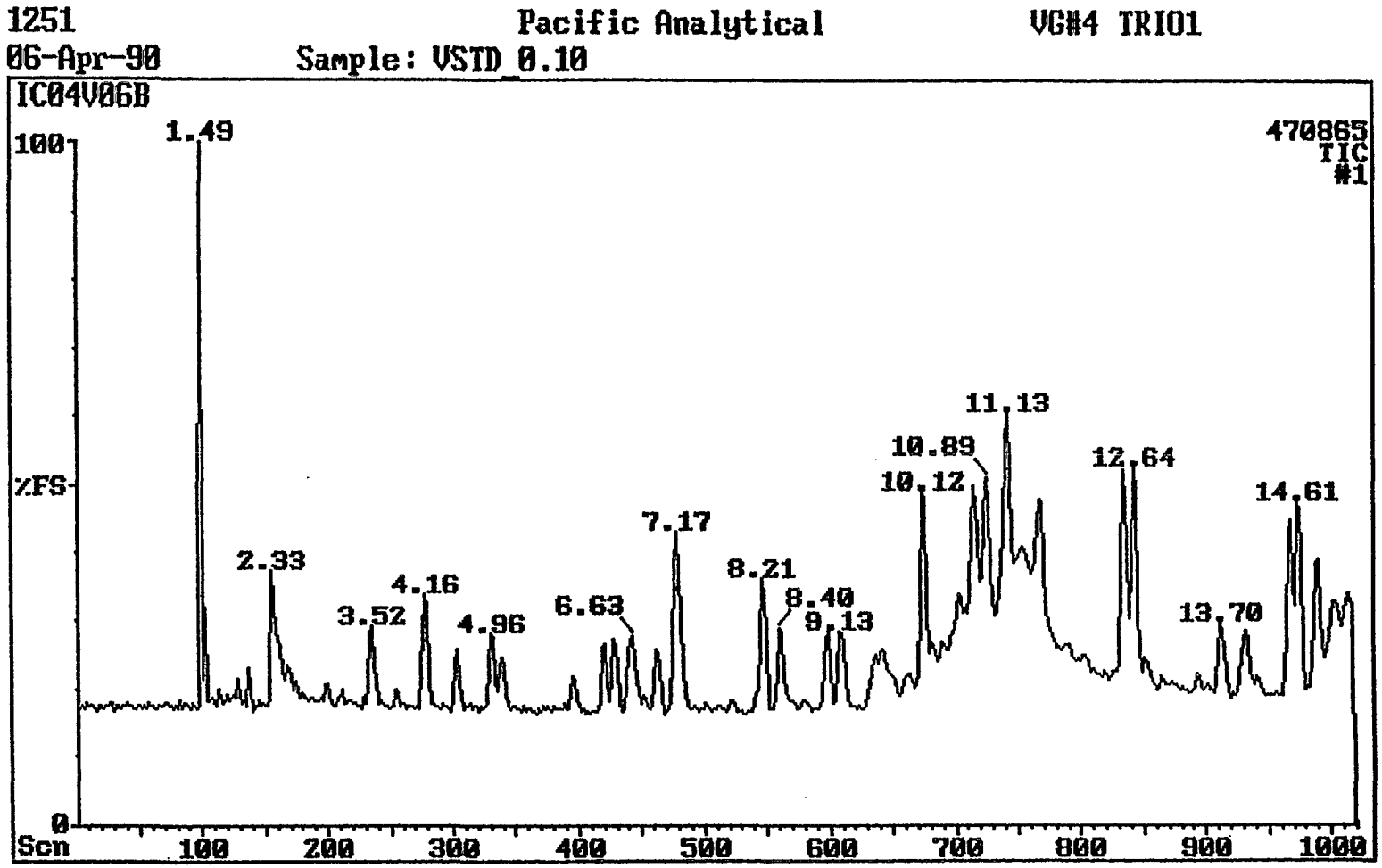
BLANK SAMPLE CHROMATOGRAM



STANDARD CHROMATOGRAM (10 ng/uL)

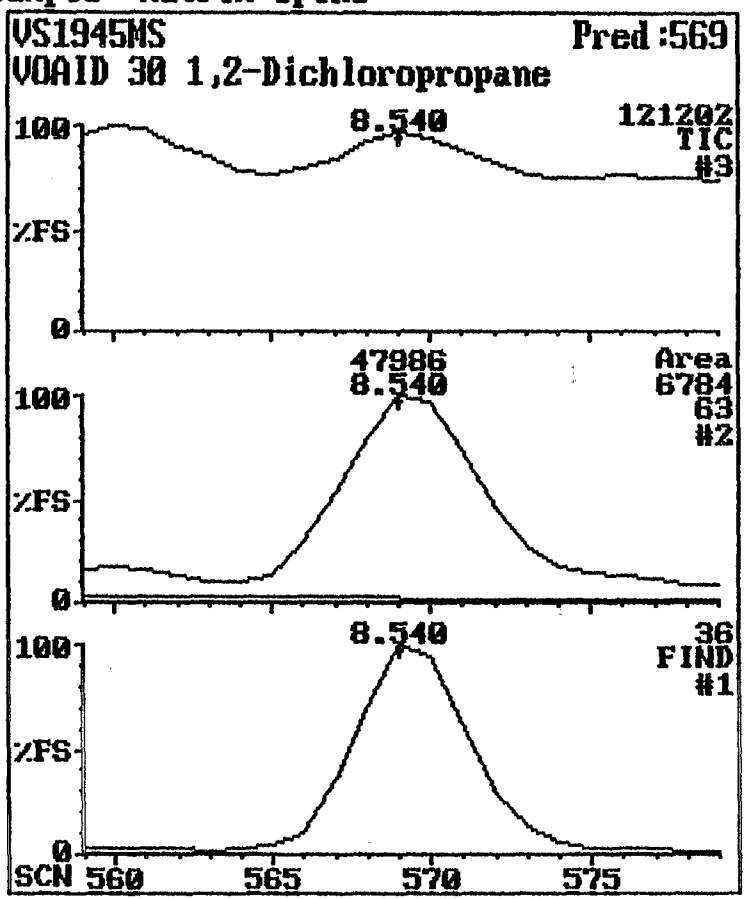


STANDARD CHROMATOGRAM (0.1 ng/uL)

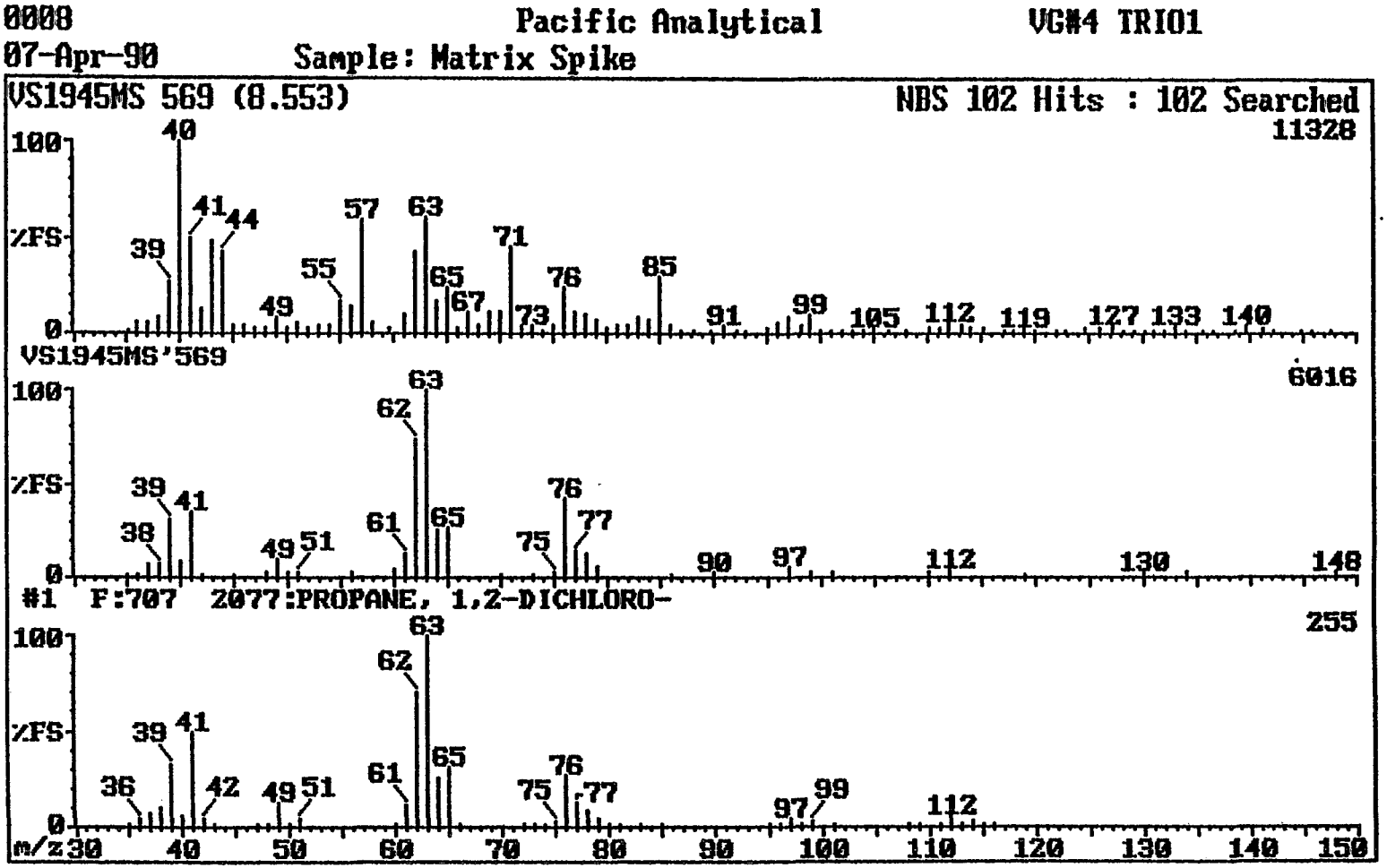


TYPICAL TARGETING (1ng/uL)

0008 Pacific Analytical VG#4 TRIO1
07-Apr-90 Sample: Matrix Spike



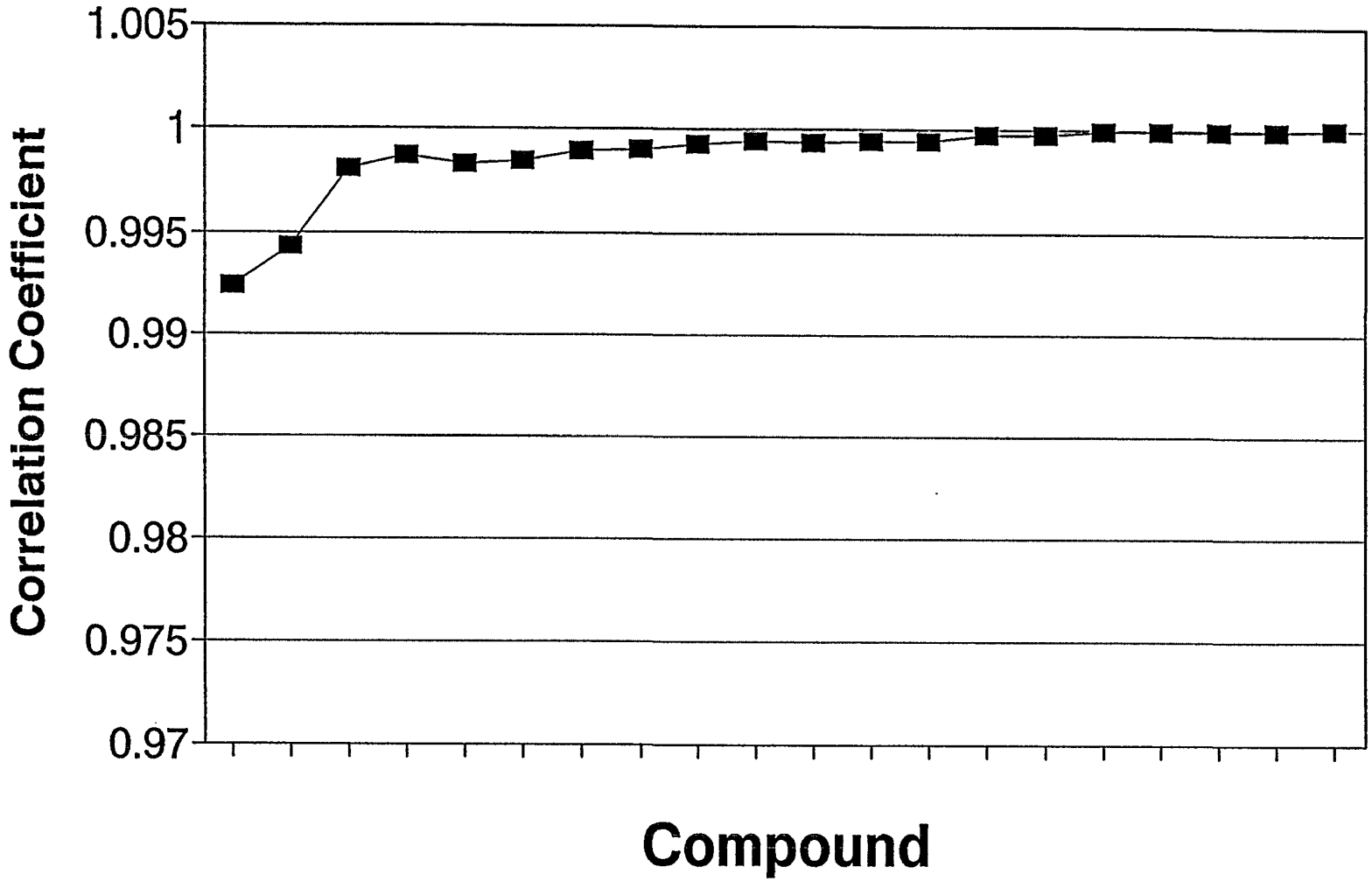
TYPICAL MASS SPECTRUM AND LIB SEARCH



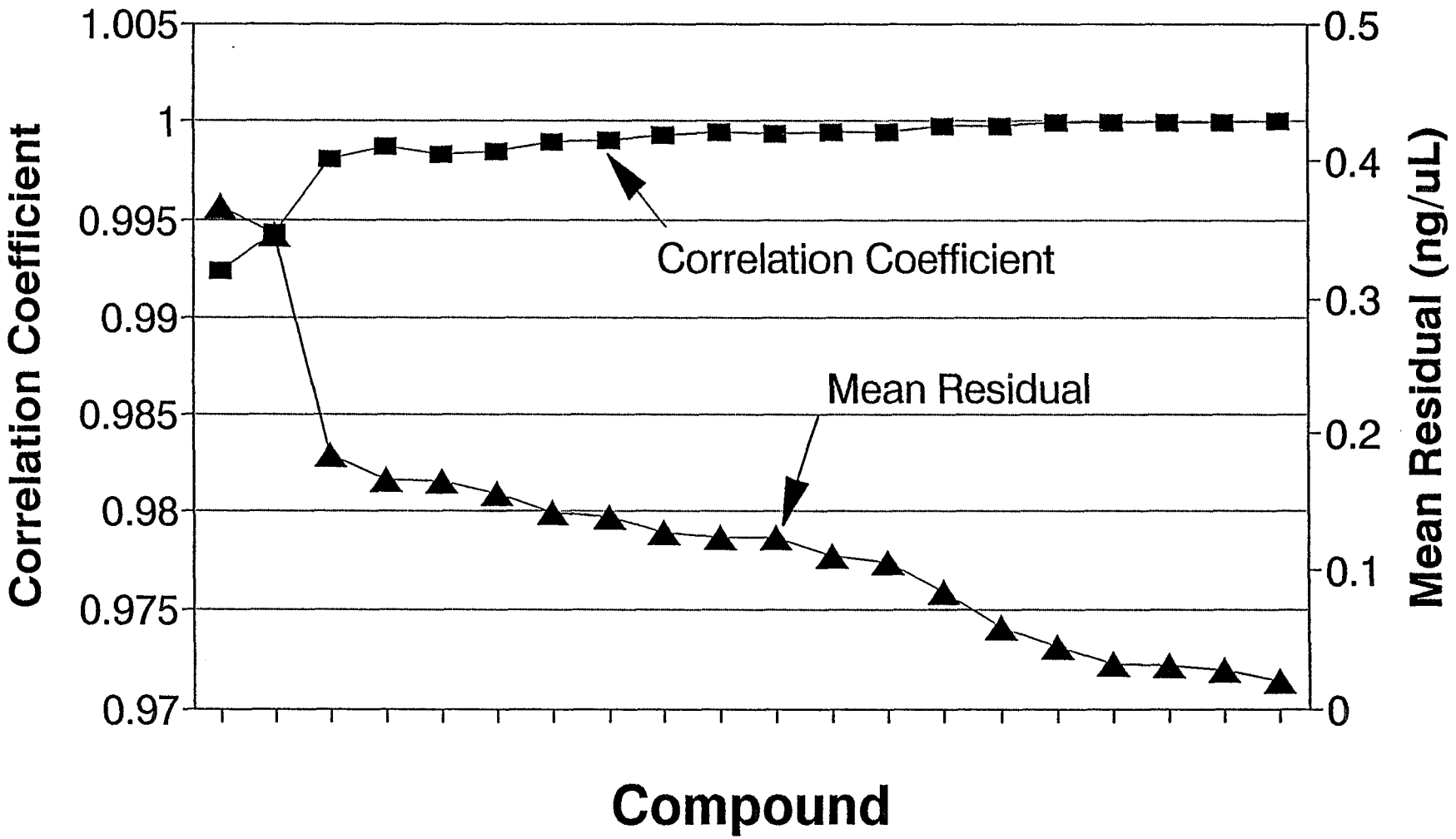
INSTRUMENT CALIBRATION

- Calibrate at 0.1, 0.5, 1, 5 and 10 ng/uL.
- Prepare working standards in methanol.
- Spike into water and extract into hexadecane.
- Calibrate Labeled Analogs using mean response factors.
- Calibrate Target Analytes by isotope dilution.

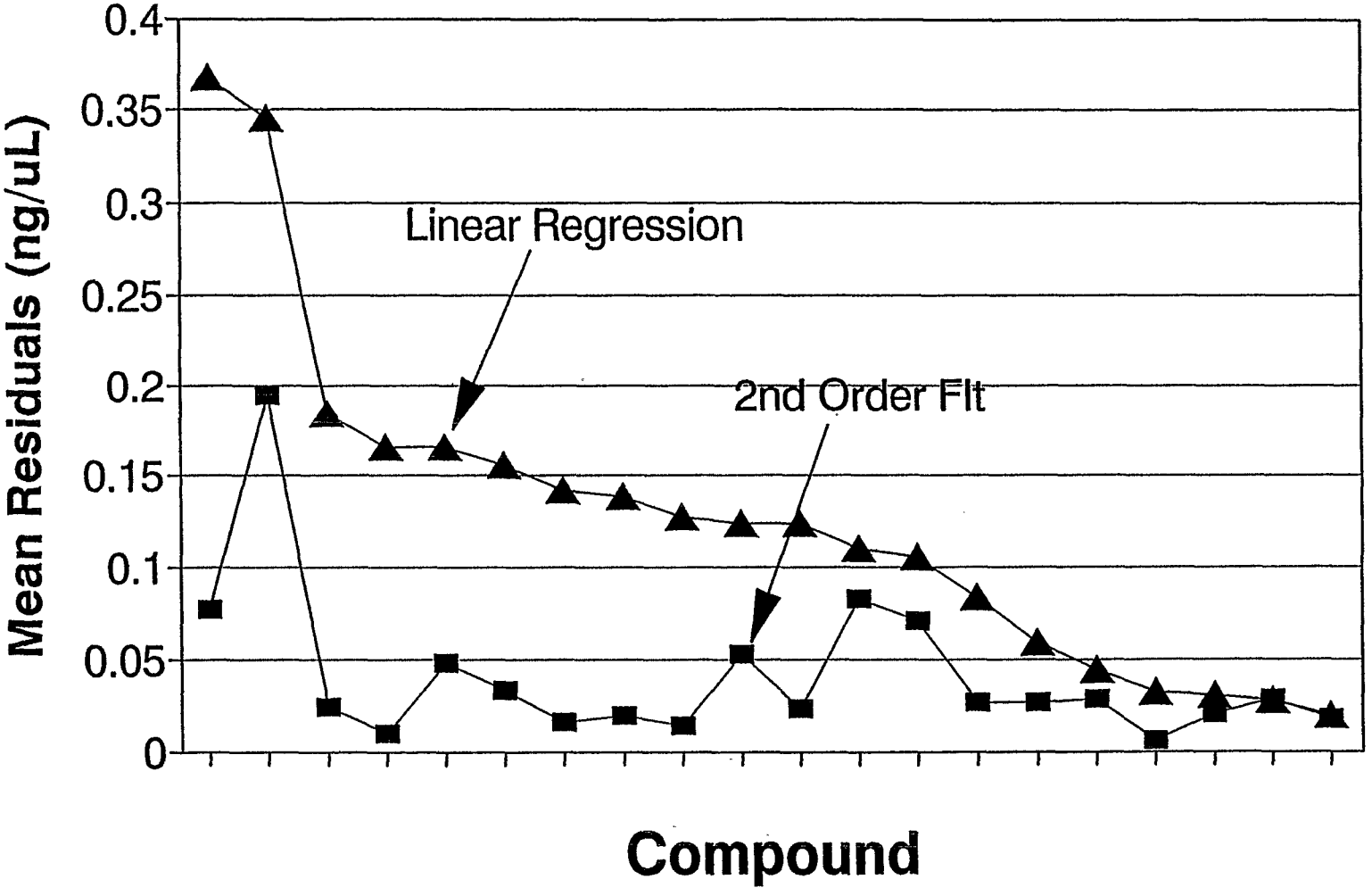
ISOTOPE DILUTION CALIBRATION



ISOTOPE DILUTION CALIBRATION

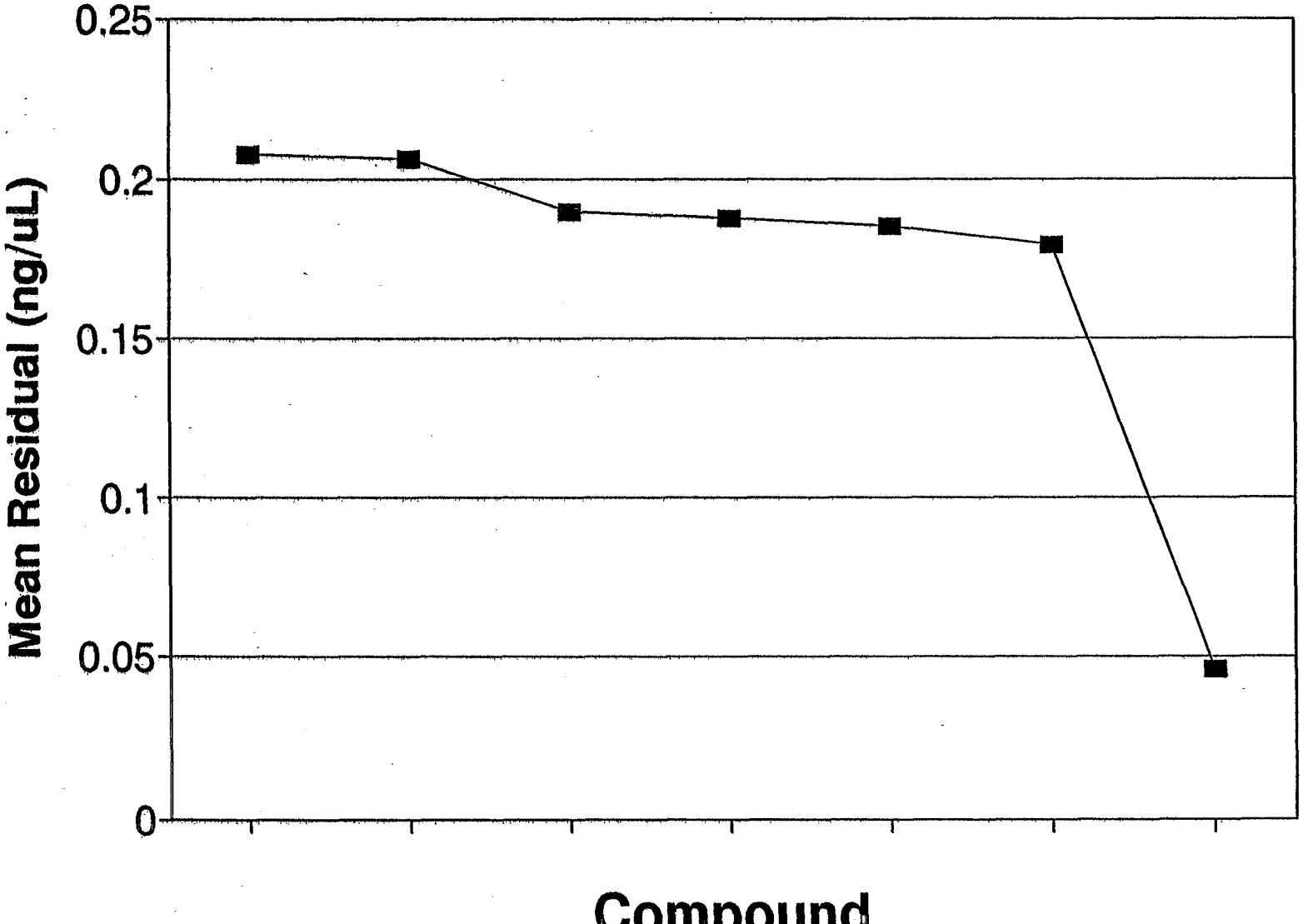


ISOTOPE DILUTION CALIBRATION

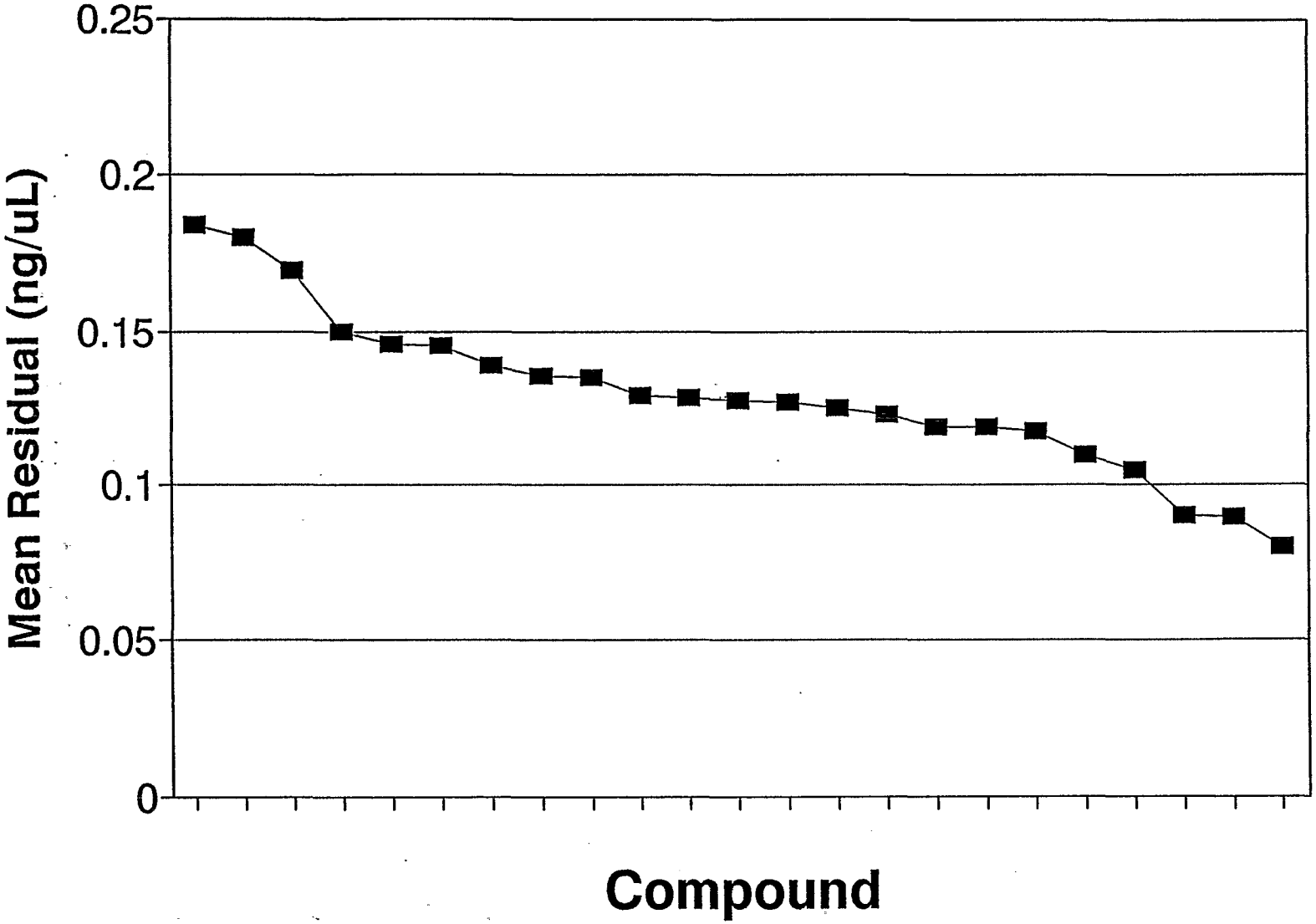


INTERNAL STANDARD CALIBRATION

(2nd Order Fit)



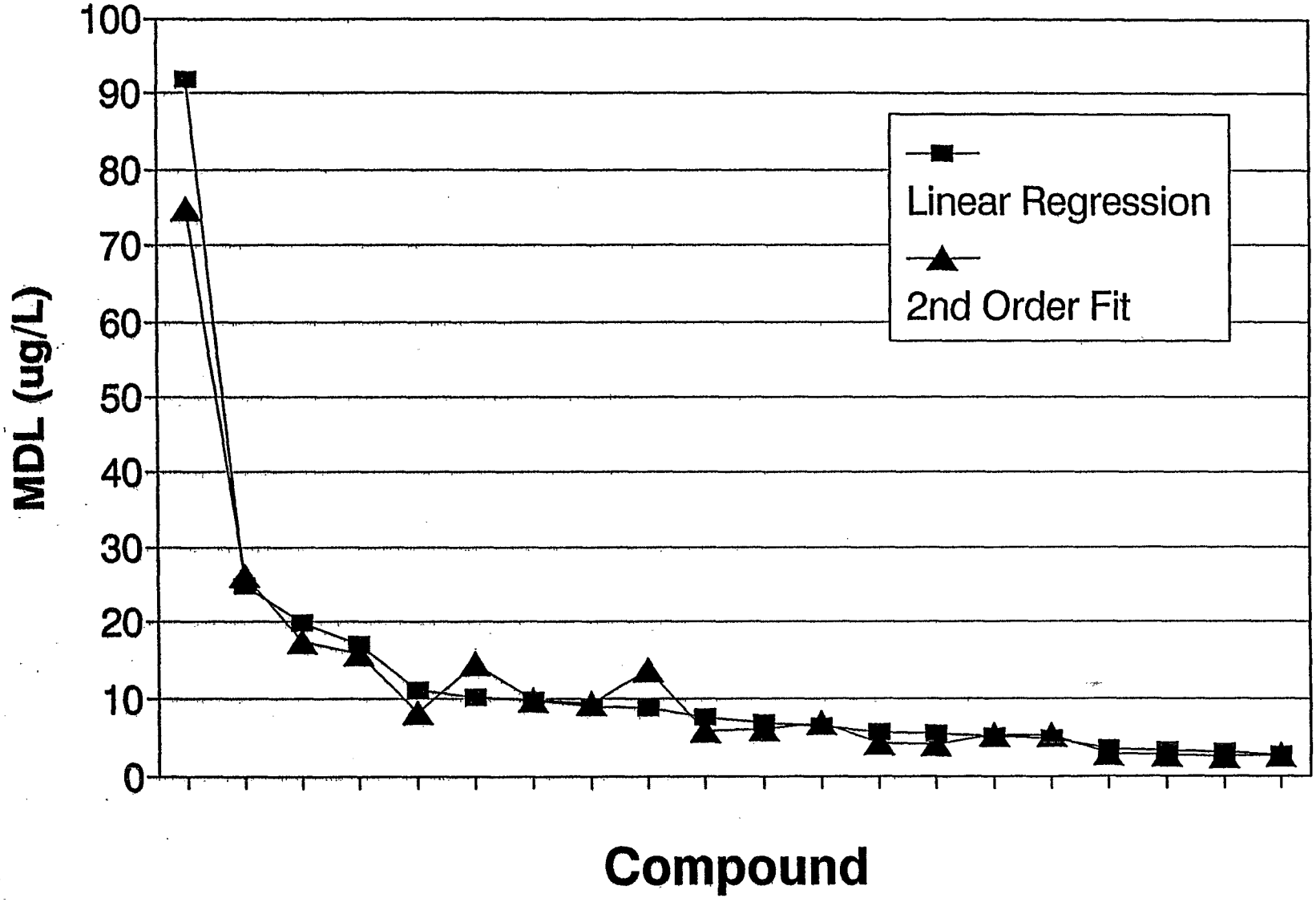
LABELED ANALOG CALIBRATION



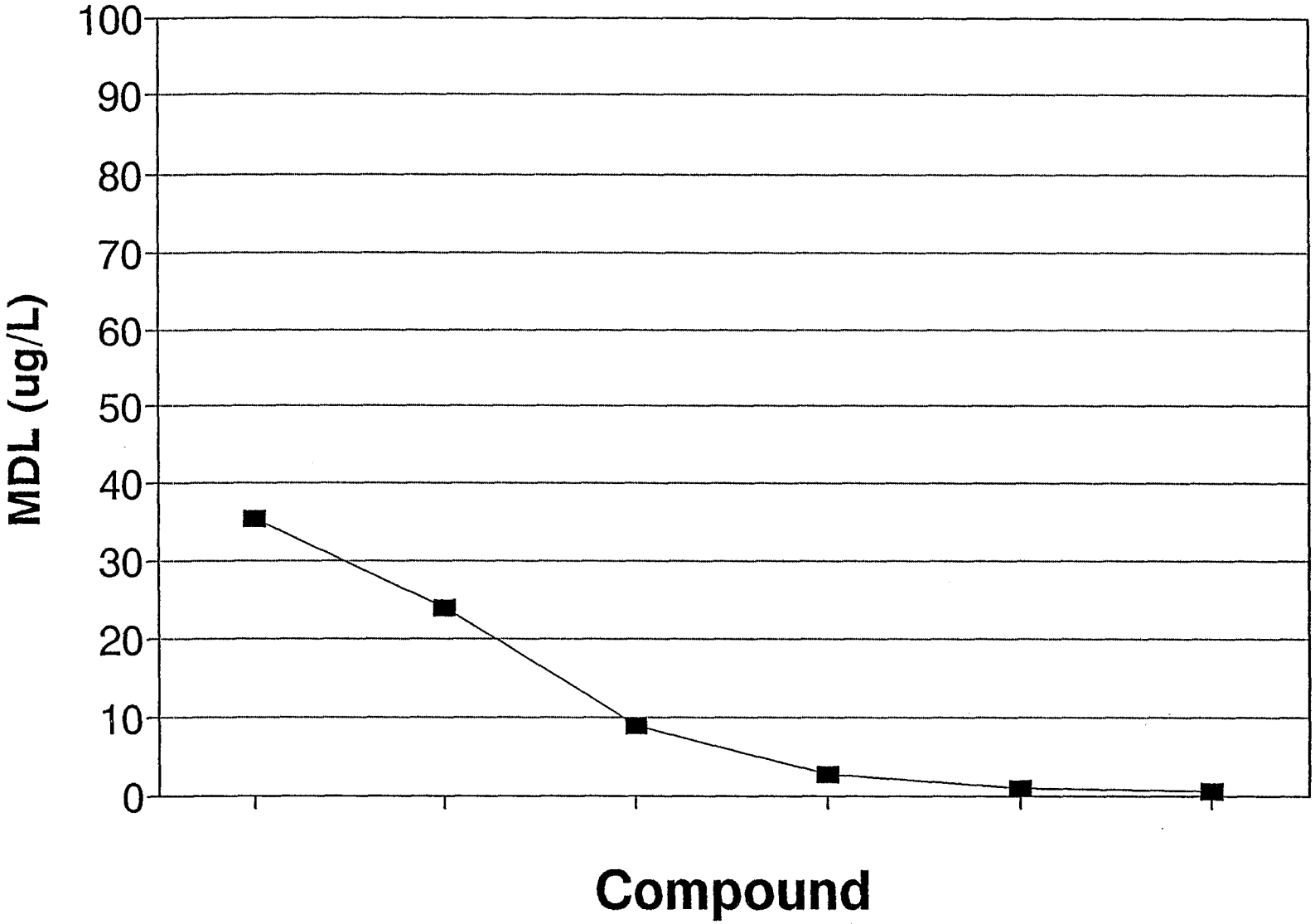
CALIBRATION SUMMARY

Category	Calibration	Mean Residual
Isotope Dilution	Linear Regression	0.128 ng/uL
Internal Standard	Second Order Regression	0.172 ng/uL
Labeled Analogs	Mean Response Factor	0.129 ng/uL

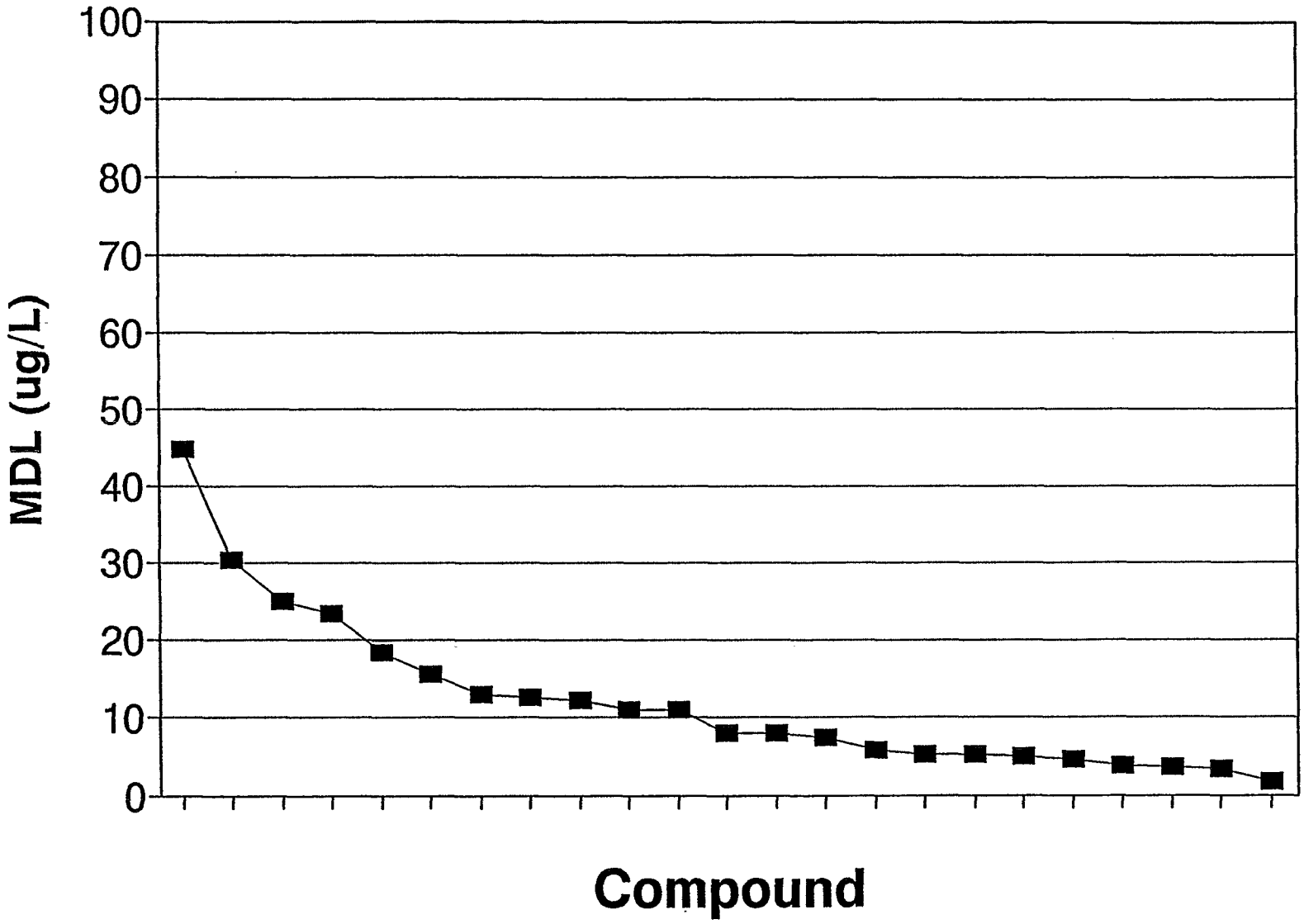
ISOTOPE DILUTION DETECTION LIMITS



INTERNAL STANDARD DETECTION LIMITS



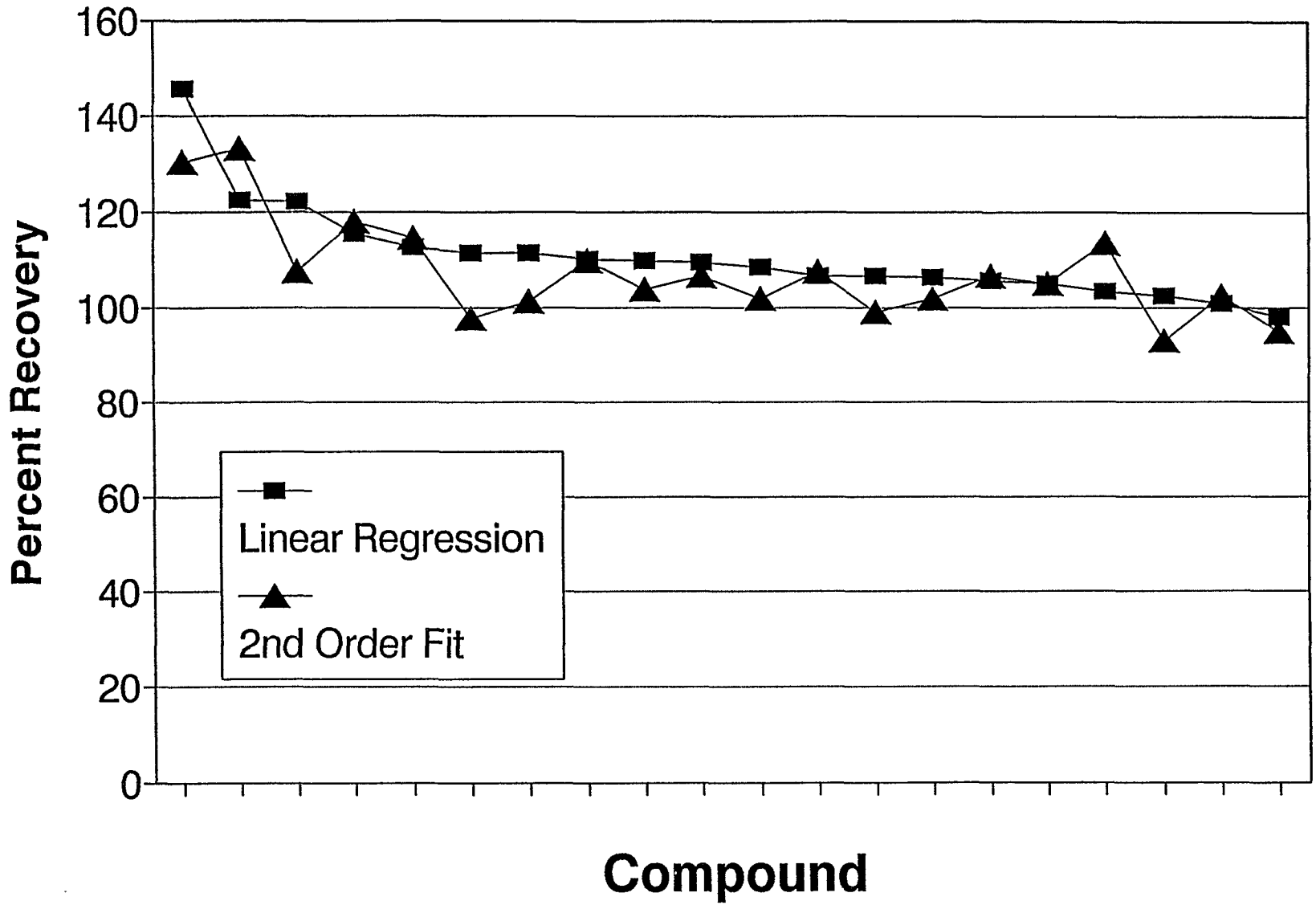
LABELED ANALOG DETECTION LIMITS



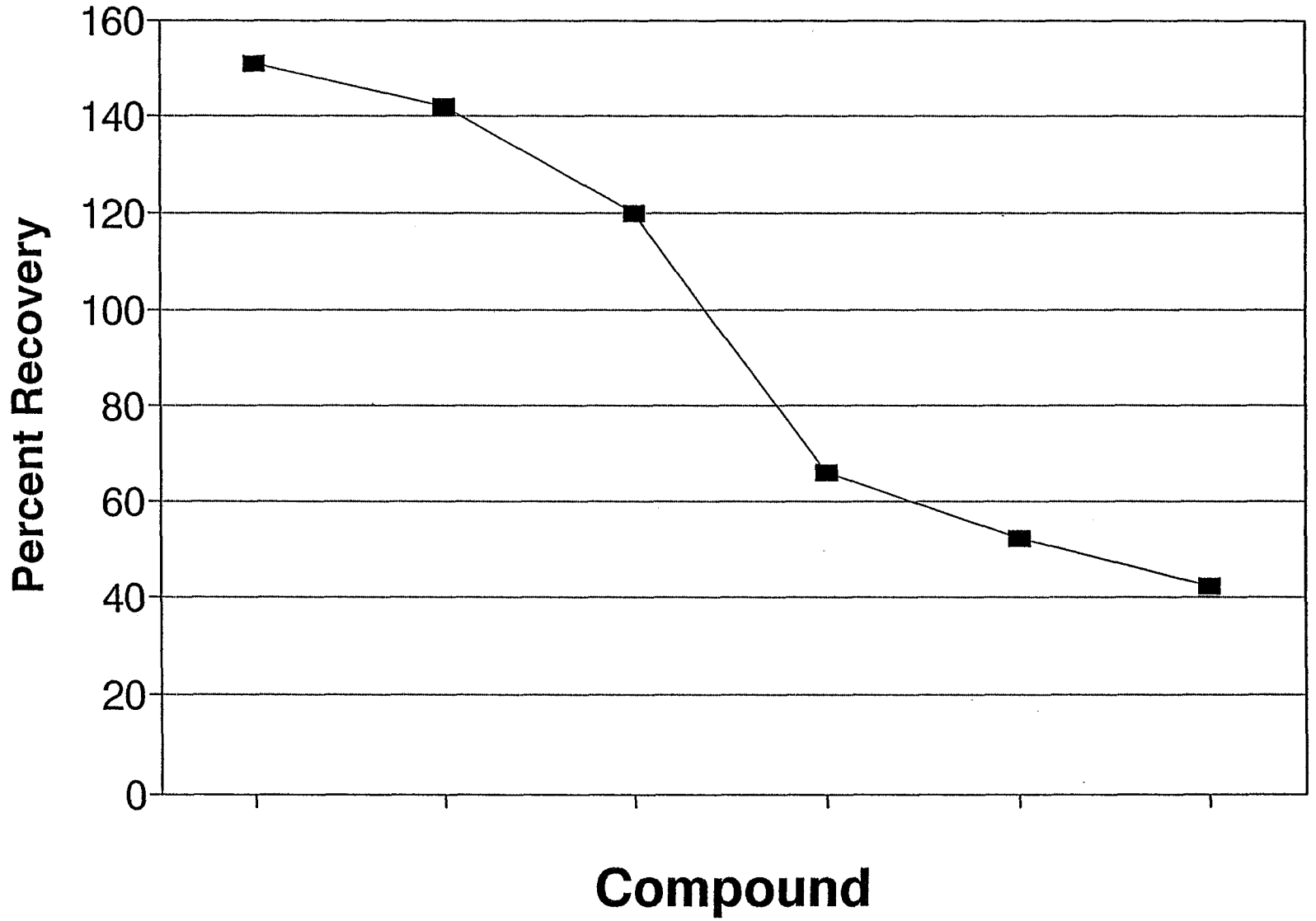
METHOD DETECTION LIMITS SUMMARY

Category	MDL (ug/L)	SD
Isotope Dulution, non-gases	6.4	2.7
Isotope dilution, gases	38.4	30.9
Internal Standard	12.1	13.2
Labeled Analogs	12.0	10.2

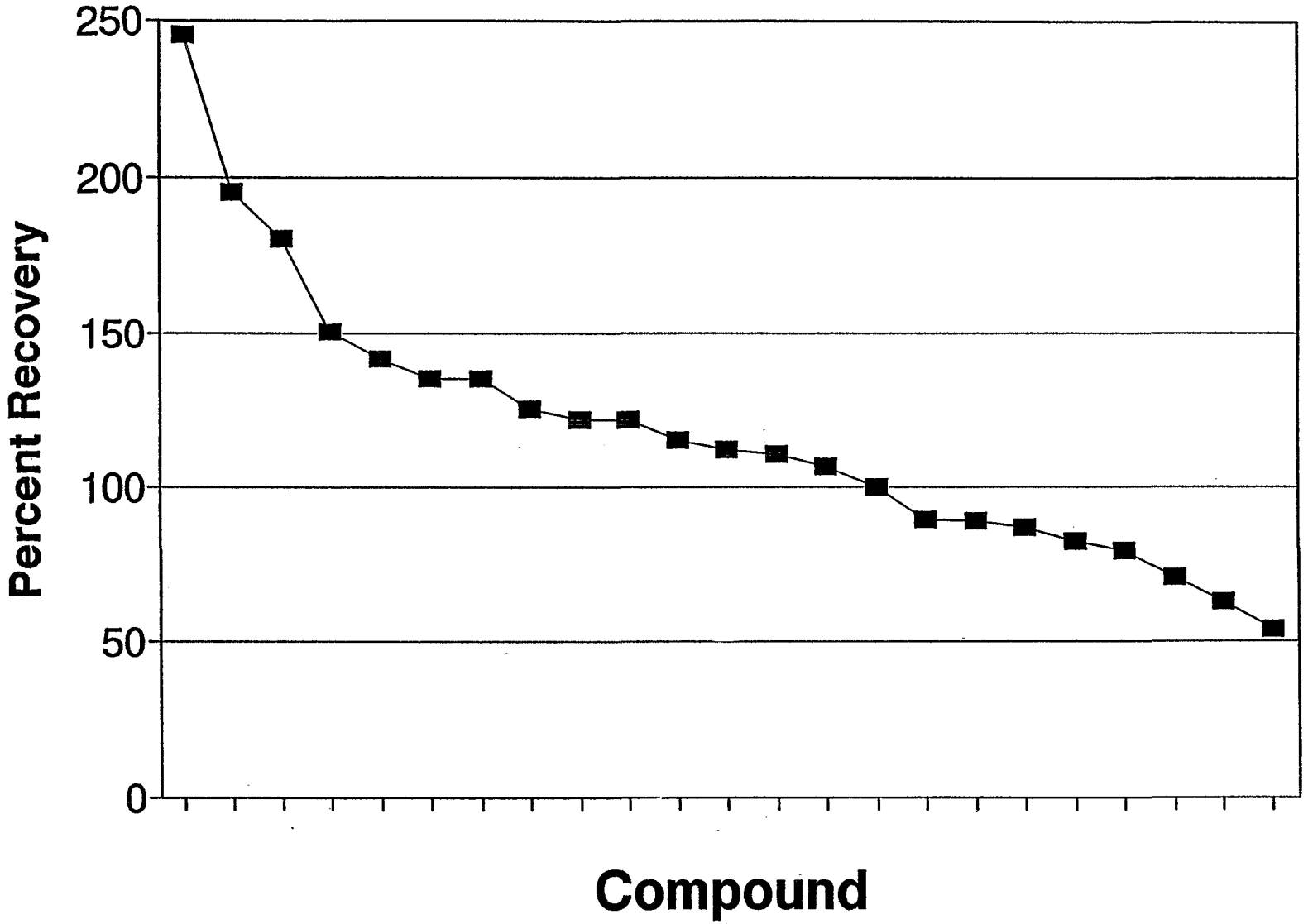
ISOTOPE DILUTION RECOVERIES



INTERNAL STANDARD RECOVERIES



LABELED ANALOG RECOVERIES



PERCENT RECOVERY SUMMARY

Category	% R	SD
Isotope Dulution, non-gases	109	7
Isotope dilution, gases	119	16
Internal Standard	96	44
Labeled Analogs	118	44

METHOD SUMMARY

Category	MDL (ug/L)	% R
Isotope Dulution, non-gases	6.4	109
Isotope dilution, gases	38.4	119
Internal Standard	12.1	96
Labeled Analogs	12.0	118

MR. FIELDING: Our next speaking will be Mr. Jim Eichelberger of EMSL-Cincinnati who will discuss the liquid-solid extraction for determination of acid herbicides in drinking water.

MR. EICHELBERGER: Good morning.

Actually, what I am going to try to do today is give you a status report of two projects we have going on in the laboratory in Cincinnati, and one of them is the subject on the agenda. The second is a project we have going on to develop a cleanup procedure for sludge extracts.

The reason they are status reports is because neither one of them is completed yet, and we hope to have them completed later this year.

The first project I would like to talk about a is drinking water project that is an attempt to use disk technology, solid phase disk technology, for the extraction of the chlorinated acids, the herbicides, from groundwater and finished drinking water. This project is being conducted by Jimmie Hodgeson in our laboratory in EMSL-Cincinnati, and he couldn't be here.

For those of you who would like some more details on this work, you might want to take down his phone number. I know he will be happy to talk to you.

Actually, what we are trying to do is develop a procedure that is better than what we have on the books right now for doing chlorinated herbicides. That procedure is Method 515.1 which is currently in the drinking water methods manual that was published in December of 1988.

A summary of that method is the following: it uses a 1 liter sample in which the analyst adjusts the pH to 12 with sodium hydroxide and shakes it for an hour to hydrolyze the derivatives. Then he does a methylene chloride extraction, which is a solvent wash, to remove all possible interferences, then readjusts the pH to 2 with sulfuric acid. He then does the conventional three serial extractions with ethyl ether, concentrates that extract, and does a solvent exchange to methyl tertiary butylether in methanol. Methylation is achieved with diazomethane, and the separation and determination are done by capillary column GC with an electron capture detector.

Folks in the lab tell me that this procedure for a set of five to seven samples takes approximately eight to ten hours.

So, what we have is a fairly cumbersome method that uses a liquid-liquid extraction with an undesirable solvent, and is time consuming. So, we are trying to eliminate some of the undesirable features of Method 515.1.

This is the set of analytes for 515.1, and we are using that same set in our study to come up with a better method. You have your garden variety phenoxyacetic acids, some phenols, and some other types of compounds, all being herbicides.

Next, the disk technology. The disks are manufactured by the 3-M Corporation. Currently, there are only two types of disks available commercially, and they contain the C_8 and the C_{18} adsorbents.

This is one of the sets of equipment that you can use to employ this technology. I don't think it is a good idea to grab the disk with your fingers, but you could put it on with a tweezers and seal the funnel to keep the apparatus from leaking, and the entire thing sits on a suction flask to which you apply a certain amount of vacuum. and put your samples through the disk. It's a fairly simple, straightforward technology.

I showed this slide last year, but for those of you who weren't here, this is a picture of one of those disks. The is a C_{18} disk, if I am not mistaken shown from the side. You are looking at the thickness of it.

What you see are the silica particles coated with the C_{18} and interspersed in a teflon matrix. I don't know what the degree of magnification is, but it is a whopper. I like to show this slide.

This is another picture of a disk from the side showing the adsorptive capacity. We used Disperse Dye #1 as a surrogate. It demonstrates the disk technology and how compounds are going to behave. The red layer there is adsorbed right at the very top of the disk. So, you can see

the concentration right there on the top. It doesn't penetrate down into the disk far at all.

So, after some experimentation...and bear in mind that this isn't final yet, this is where we were about three weeks ago...we have decided to use a 100 ml sample. We tried liter samples, but we saw some breakthrough. So, the ideal, and probably the volume that we will decide on, is between a liter and 100 ml. I think it is going to be around 0.5 liter.

You adjust the pH of the sample to 2, but before you put the sample onto the disk, you have to pretreat the disk. This is standard operating procedure for solid phase extractions.

First, you elute the disk with 20 ml methyl tertiary butylether. That is going to be the final eluting solvent. So, the attempt here is to remove any interferences that possibly could end up in the final elution.

Then you pull a little air through it for a few minutes and put some methanol through which is supposed to activate the disk, and then introduce some reagent water before putting the sample through.

Right now, they are using a throughput time of 5 minutes for 100 ml. The 3-M guys tell us that they routinely put 100 ml a minute through the disk and find no detrimental effects using that quick throughput.

Then you air dry the disk after the sample has passed through. That really doesn't remove all the residual water, but it removes a great portion of it. Then you elute with the eluting solvent which is 10 percent methanol in methyl tertiary butylether.

You dry that over a little sodium sulfate just to remove the residual water, and methylate with gaseous diazomethane. The separation is done on a GC capillary column, and the determination with an electron capture detector.

Now, the sample prep time here...by the way, that line is supposed to be at the bottom of the slide, but my Harvard Graphics expertise isn't good.

The sample prep time for the same size set of samples is now cut to two hours. So, we think we have a fairly simple, straightforward procedure with little concentration and no solvent exchange. You methylate in the eluting solvent, and it looks as though we have a simple, straightforward procedure.

This is a little graph I put together on some results testing the C_8 and the C_{18} disks. The third bar on the right of each group will be discussed in a second or two. You can see the C_{18}, in general, seems to be a better matrix for the adsorption. The C_8 gave a little bit lower recoveries for the compounds on the x-axis than the C_{18} did.

We noticed when we were doing the initial work that when we used metal funnels, the old millipore type systems that we had around the lab for a long time, and some of the metal had peeled off, we would get reduced recoveries, and we would find a little green precipitate in the bottom of the eluate.

It must be that the low pH is reacting with those metal funnels. So, in our final report, we are going to recommend that glass funnels and glass filter holders be used, and not the metal which will eliminate that problem.

Again, we tried the old salting out trick. We used a 15 percent ammonium sulfate added to each 100 ml, and we studied the compounds on the x-axis at 5 ug/l. That is not very focused, but the lighter bars on the left of each group are the salted results, and the grey or striped or whatever they are on the right of each group are the unsalted.

You will notice, except for one compound, dichlorprop, that the unsalted results are always higher. In solid phase extraction work, that is common, and the only thing I can think of is the compounds are salted out of the water before they get to the disk. They are plated out on the glassware and whatever else they come in contact with. So, salting out in solid phase technology just doesn't work.

This is a list of some comparisons of recoveries and relative standard deviations of some of the compounds that

are analytes in Method 515.1. The column on the left of the recovery section is from the disks, and on the right is from liquid-liquid extraction.

You can see there are still a few problems. Bentazon still is lower on the disk. Jimmie assures me that these aren't insurmountable problems and we will overcome all this.

In some cases, we are better off with the disk than we are with liquid-liquid extraction. For the DCPA, we have come quite a ways, and dalapon is another problem with the disk. So, we are working on those problems right now, and we should have them resolved when the final report is published.

In the relative standard deviation portion of that slide, the disks look much, much better than the liquid-liquid extraction. So, it looks like the disks will work for these compounds. The jury is still out on a few of them, but I think we can resolve the problems.

I know there are some of you out there interested in looking at alternate forms of methylation. We have been looking for the last year or two, at some of the different methods, and they are listed here.

I have data today on the one that looked most successful out of those four. The borontrifluoride-methanol

is just not an efficient methylating agent for the number of compounds that we have in the method.

Sulfuric acid-methanol looked promising, and I will show you some results of that in a minute.

The bottom two we tried, and the results were pretty miserable. So, we really haven't come up with anything great in those three areas.

Now, the sulfuric acid...and, by the way, this was done by taking a small amount of methanol to which a 5 percent by volume sulfuric acid solution had been added, spiking in these compounds, and heating the solution to 70 degrees C for two hours. Then the solution was diluted with reagent water a microextraction was done with methyl tertiary butylether.

For these compounds, this the good news. Everything worked really well here. The phenoxy acids seemed to esterify real well with this form of methylation, sometimes better than the diazomethane. This is the bad news. The phenols are terrible, and some of the other compounds just don't methylate under those conditions.

So, we still haven't found a suitable replacement for diazomethane for all the compounds on the list.

This project should be completed sometime this summer. Jimmie is going to write up the results. We will publish it in one of the journals, and we will put a method together

that should be available to the Office of Drinking Water maybe in the fall.

The second topic I wanted to talk about a little bit is a cleanup procedure that we have been working on for sludge extracts. Back in September of last year, we delivered a method to the Office of Water for extracting priority pollutants from municipal sludges, mostly digested sludges and filter cakes.

The method uses 200 ml of sample. We were trying to come up with an extraction procedure that would allow us to handle highly contaminated sludge samples so we didn't have to dilute them, and end up with method detection limits in the parts per million range.

So, our method consisted of taking 200 ml of sample or a 10 g equivalent of dry solids, centrifuging that sample, separating the liquid from the solids, and doing a continuous liquid-liquid extraction on the liquid and a sonication sample preparation on the solids.

The sonication consisted of three steps, first using methanol followed by 1:1 methanol:methylene chloride, and the third was the methylene chloride step.

Then the methanol was separated from the solution. All the analytes were contained in the methylene chloride, and we tried to concentrate that down to 10 ml.

Well, what we did was create a bit of a monster. We created a procedure that extracted the analytes more efficiently, but it also extracted all the unwanted gunk that is found in a sludge sample just as efficiently. So, we immediately realized that we had a problem and that we needed an efficient cleanup procedure if this extraction procedure were ever going to work. So, we did some work with silica gel adsorption, gel permeation chromatography (GPC), and solid phase cartridges.

The two that showed the most promise were the silica gel and the GPC. Since those techniques were already being used in analytical laboratories that were doing sludge samples, we pursued those two approaches.

We tried to determine if varying the deactivation state of the silica gel could improve the efficiency of cleanup of sludge extracts. We varied the deactivation state up to 30 percent water, and found that 10 percent deactivation was about the optimum condition for silica gel cleanup of sludge extracts.

This slide just demonstrates on three different sludges the amount of cleanup we can get with silica gel. The three sludges were collected in Cincinnati on three different days to show you the variability in the sludges from one source. The second column shows the mg/ml of residue that contained in the sludges. After the silica gel cleanup, which

consisted of 65 g of 10 percent deactivated silica gel we eluted with 425 ml of methylene chloride, you can see the percent cleanup in the column on the far right.

The percent cleanup is the difference between column 3 and column 2 divided by column 2. So, in the case of sludge A, it was almost not worth the effort. In sludge C, it did a fairly decent cleanup job.

So, we figured that, at this point, we had a technique that could possibly, when used with another technique, give us a decent cleanup.

We tried coupling this with gel permeation chromatography. We studied it with the silica gel process prior to the GPC, and the GPC prior to the silica gel. Results showed no difference. It makes no difference which one you do first. You end up with the same amount of total cleanup, about 30 percent, which wasn't enough to give us the ability to concentrate the sludge extract to get decent method detection limits.

Then we studied a number of different bio-beads. We had done all the original work with SX-3. We thought maybe SX-2 or SX-4 would be more efficient in the GPC process. It turns out that no matter how we studied it, silica gel first or second, the bio-beads gave us no improvement in overall recovery.

By the way, the GPC that we had been using up to now was done with all methylene chloride as the mobile phase.

Due to the nonpolar nature of the types of materials that we wanted to remove from the sludge extract, we thought that it might be advantageous to add a less polar solvent.

So, we experimented with different amounts of normal hexane in the mobile phase in the methylene chloride, and this slide shows you what we found. The bar to the left of each group is the gel permeation chromatography alone, and the shaded bar is the silica gel plus the GPC result.

As we increased the hexane in the methylene chloride, our cleanup was increasing dramatically. If we added 90 percent hexane to methylene chloride, we were getting almost 100 percent removal of all the gunk in the sludge extract. However, that presented problems.

In the GPC, when you add that much hexane, you have memories in the column, and you have to rinse the column before putting the next sample on, and this is too time consuming. So, we had to back off, and the work that we are doing right now is with hexane in methylene chloride at about 65 to 75 percent.

We put a standard set of analytes together, and evaluated the method...which is typical in a method development...backwards. We looked at the analytical determinative step first, GC/mass spec. Then we looked at

how efficiently we were K-D'ing all the samples, the GPC recoveries, and the silica gel/GPC recoveries. Then we did the entire procedure with a fortified sludge extract.

That extract, before we cleaned it up, contained almost 78 mg/ml of residue. After the silica gel and the GPC, it was down to 22.9 mg which is a 71 percent cleanup.

This enabled us to concentrate our extracts down to 1 ml with no trouble. The silica gel step that we used here was 60 g of 10 percent deactivated silica gel, and we eluted with 425 ml of methylene chloride. The GPC was done with the SX-3 bio-beads, and eluted with 75 percent hexane:25 percent methylene chloride.

These are some of the results we got for what we felt would be a representative batch of analytes. We were pleasantly surprised with the amount of recovery that we got for most compounds.

There is a problem with isophorone and another with benzyl alcohol. It turns out the problem is coming from the silica gel step. We think we can solve that problem. So, presently we are evaluating this procedure on a large number of analytes and with a number of different types of sludges. We hope to have this method completed by late summer, and available for anybody who would like to try it.

There is one question which might come to mind. What happens to the GPC calibration when you add this much

hexane? Well, this picture here is a typical UV trace of what happens when you have pure methylene chloride as the mobile phase.

The analytical envelope starts right before dioctylphthalate and ends right before sulfur. When you put 40 percent hexane in the methylene chloride, it doesn't change at all. It stays exactly the same. The sulfur is still a useful peak.

But when you increase the amount of hexane to 60 percent hexane and 40 percent methylene chloride, the analytic envelope spreads out, and the sulfur is incorporated into the extract. We haven't found any problems with this so far. The sludges that we have been looking at haven't had much of a sulfur background. However, it could be a problem, and we are working on that.

So, both of those products should be done by fall, optimistically, late summer and will be available in publications and methods.

I would be glad to answer any questions anybody may have.

QUESTION AND ANSWER SESSION

DR. WILLIAMS: Dan Williams, Kennesaw State College.

Have you looked at alternate techniques such as something like silation as opposed to methylation, something like hexamethyldisilizane or whatever?

MR. EICHELBERGER: I think Jimmie has been doing some work on that, but we don't have any results yet. Yes, that is a good point.

MR. LEWIS: Do you see any changes in your recovery between the difference in your detection source when you GPC versus RI or fluorescence detection, or did you limit it to UV?

MR. EICHELBERGER: I think all they used was UV. I never was really involved in either one of these projects, but I think they used UV solely.

MR. FALLICK: I am Gary Fallick from Waters.

A question for you on the first procedure. Have you also looked at conventional SPE cartridges as an alternative to the disks?

MR. EICHELBERGER: We haven't yet, but it is a good point. We are going to do that.

DR. ARMSTRONG: I am David Armstrong from Southern Research Institute.

Have you looked at any other solvents but hexane? Let me give you a little more information.

When I was at S-CUBED, we did a study on hazardous wastes using butylchloride. Are you familiar with that? I don't know if you remember any of that work. It turned out we were using about...I think it was 50 percent butylchloride, and we were getting much better recoveries in GPC of the analytes out of hazardous wastes. So, that is an option you might consider.

MR. EICHELBERGER: How about your ability to remove the extraneous interfering materials?

DR. ARMSTRONG: It worked pretty well. Again, this isn't exactly the matrix you are looking at, but it seemed to work pretty well.

MR. EICHELBERGER: That is a good point, too. This procedure might just work for sludges. Hopefully, it will work for all sludges, but at this point, we don't know. It is tough to try out all sludges.

MR. YOCKLOVICH: I am Steve Yocklovich from Burlington Research.

Concerning 515, there was a noticeable salt effect, and I imagine there is a big effect when there is a large amount

of some of the analytes. Will that be clearly stated in the interferences section of the method?

The reason I ask that is regulators in our State are starting to use waste water methods for groundwaters and everything.

MR. EICHELBERGER: I never thought about that. When you are in the methods production mode, you just can't do everything that everybody expects, but, yes, we could put that in there. I mean, we could recommend no salting out, because it is detrimental to our recoveries.

MR. YOCKLOVICH: Well, salting out and also, you know, just a clear statement in the interferences that the people that are writing regulations can see that it is inappropriate in certain situations.

MR. EICHELBERGER: Well, you see, at this point, this technology has not been proven for anything but waters with no particulate matter in them. And if somebody wants to try to use this technology for samples other than drinking water, they might run into big problems. So, I don't think States are going to be able to do that. They are not going to be able to make you use a method that won't work.

Of course, I don't know. States make you do a lot of things.

(Laughter.)

MR. FIELDING: Are there any other questions?

(No response.)

MR. FIELDING: Thank you, Jim.

EXTRACTION OF CHLORINATED ACIDS FROM GROUND WATER AND FINISHED DRINKING WATER USING DISK TECHNOLOGY

Researcher: Dr. Jimmie Hodgeson
Environmental Monitoring Systems Laboratory
Cincinnati

(513) 569-7311

LIST OF ANALYTES

Acifluorfen
Bentazon
Chloramben
2,4-D
2,4-DB
Dalapon
Dicamba
3,5-Dichlorobenzoic acid
Dichlorprop
DCPA-AM
Dinoseb
5-Hydroxydicamba
4-Nitrophenol
Pentachlorophenol
Picloram
2,4,5-T
Silvex

METHOD 515.1(CURRENTLY)

1 Liter sample pH 12 with NaOH
Shake 1 hour to hydrolyze derivatives

Solvent wash with CH_2Cl_2

Adjust pH 2 with H_2SO_4 and
3 serial extractions with ethyl ether

KD add MTBE + MeOH

Methylate with diazomethane

Determine with capillary column GC-EC

Sample prep time: 5-7 samples in 8-10 hours

METHOD 515.1 USING DISK LIQUID-SOLID EXTRACTION

100 mL sample pH < 2

Pretreat disk-20 mL MTBE
-air dry 5 min.
-20 mL methanol
20 mL reagent water

Sample throughput time = 4 min.
at 5 in. Hg vacuum

Air dry 10 min.

Elute with two 2.5 mL 10% MeOH in MTBE

Dry over anhydrous Na_2SO_4
Sample prep time: 5-7 samples in 2 hours
Methylate with gaseous diazomethane

Determine with cap column GC/ECD

DISK LSE PRECISION AND ACCURACY
100 ML 5 UG/L C-18 DISK

ANALYTE	% RECOVERY		%RSD	
	Disk	LLE	Disk	LLE
Acifluoufen	96	90	7	4
Bentazon	56	90	8	22
Chloramben	65	55	1	4
2,4-D	89	94	9	13
2,4-DB	115	87	8	15
Dalapon	21	100	9	20
Dicamba	75	79	8	4
3,5-DiClbenzoic acid	114	88	9	6
2,4,5-T	85	73	7	4
Dichlorprop	66	90	8	12
DCPA-AM	79	23	8	74
Dinoseb	35	74	8	10
Silvex	88	77	1	6

ALTERNATIVE METHODS OF METHYLATION

- BF_3 - METHANOL
- SULFURIC ACID - METHANOL
- AMBERLITE RESINS - METHANOL
- IN SITU ALKYLATION ON SOLID SORBENT WITH NUCLEOPHILE - EXAMPLE
  $CH_3I + RCOOH(ADSORBED) = ROCH_3 + HI$

SULFURIC ACID METHYLATION

Analyte	% Recovery
Dalapon	117.4
35DCBA	114.0
Dichlorprop	110.8
2,4-D	86.2
Chloramben	84.2
Silvex	97.2
2,4,5-T	87.0
2,4-DB	97.4

100 mL Fortified Reagent Water - 5ug/L

SULFURIC ACID-METHANOL METHYLATION

Analyte	% Recovery
Dicamba	2.0
Acifluorofen	37.0
Pentachlorophenol	0.0
DCPA - AM	0.0
Dinoseb	0.0
Bentazon	0.0

100 mL Fortified Reagent Water - 5ug/L
AG1-X8 Resin Bed, 0.11 mL Volume

Analyte	% Recovery	%RSD
Acifluorfen	80	7
Bentazon	70	4
Chloramben	53	16
2,4-D	90	13
2,4-DB	98	5
Dalapon	68	13
Dicamba	75	6
3,5-DCBA	81	19
Dichlorprop	72	28
Dinoseb	18	19
4-Nitrophenol	51	1
Pentachlorophenol	83	12
Picloram	66	11
Silvex	78	3
2,4,5-T	77	2

A METHOD FOR THE DETERMINATION OF ORGANICS IN MUNICIPAL SLUDGES

200 mL sample(10 g eq. dry solids)
Centrifuge
Liquid-CLLE
Solids-sonication-MeOH
- 1:1 MeOH:CH_2Cl_2
-CH_2Cl_2
Concentrate extract to 10 mL ???

Attempted cleanup
Silica gel
GPC
Solid phase cartridges

DEACTIVATED(10%) SILICA GEL CLEANUP OF CRUDE SLUDGE EXTRACTS

Sample	Crude Ext. mg/mL	Clean Ext. mg/mL	% Cleanup
A	64.4	59.9	7
		62.2	4
		61.9	4
		60.8	6
B	82.4	71.6	13
		66.7	19
		70.0	15
		66.8	19
C	59.0	47.0	20
		47.6	21
		42.0	29
		44.9	24
		47.5	19

65 g SG 425 mL MeCl- 10mL

Comparison of DSGF/GPC and GPC/DSGF with a Single Sludge C Crude Extract - 59 mg/mL

DSG/GPC		GPC/DSG	
	mg/mL res		mg/mL res
	DSG		GPC
1	47.0	1	42.7
2	46.7	2	42.0
3	42.0	3	42.0
	GPC		DSG
1	39.7	1	38.0
2	41.0	2	37.6
3	35.8	3	38.3
Total	Cleanup	Total	Cleanup
1	33	1	36
2	31	2	36
3	39	3	35

Final Extracts Concentrated to 1 mL by KD

Cleanup of Sludge Extracts Using Silica Gel and Different Bio-Beads

Silica gel - SX-3	SX-3 - Silica gel
Silica gel - SX-2	SX-2 - Silica gel
Silica gel - SX-4	SX-4 - Silica gel

No improvement in GPC or overall cleanup was observed by either of the alternate stationary phases, SX-2 or SX-4

Methylene chloride used as the mobile phase

Average Recovery and RSD From Fortified Sludge Extract - 100ug/mL - 5 Reps

Analyte	%rec	RSD
2-Cl phenol	75.2	9.6
2-Nitrophenol	74.6	7.2
Aniline	23.6	25.0
Naphthalene	73.8	8.4
Isophorone	4.9	36.7
2-Flourobiphenyl	93.2	1.6
Acenaphthylene	83.2	3.6
Diethyl phthalate	60.6	5.6
N-Nitroso DPA	92.6	8.9
Benzyl alcohol	5.6	32.1
Dieldrin	88.5	14.0
4,4'-DDT	70.2	9.1
Benzo(a)pyrene	89.0	6.9
Benzo(b)fluoranthene	87.8	1.8
2,6-Dinitrotoluene	80.6	18.3
Hexachlorobenzene	78.5	5.3

GPC: 60g SX3 75% Hex 25% MeCl

SAMPLE AND ANALYTICAL CONDITIONS

Each analytical step individually evaluated
GC/MS KD GPC DSGF/GPC FORTIFIED EXTRACT

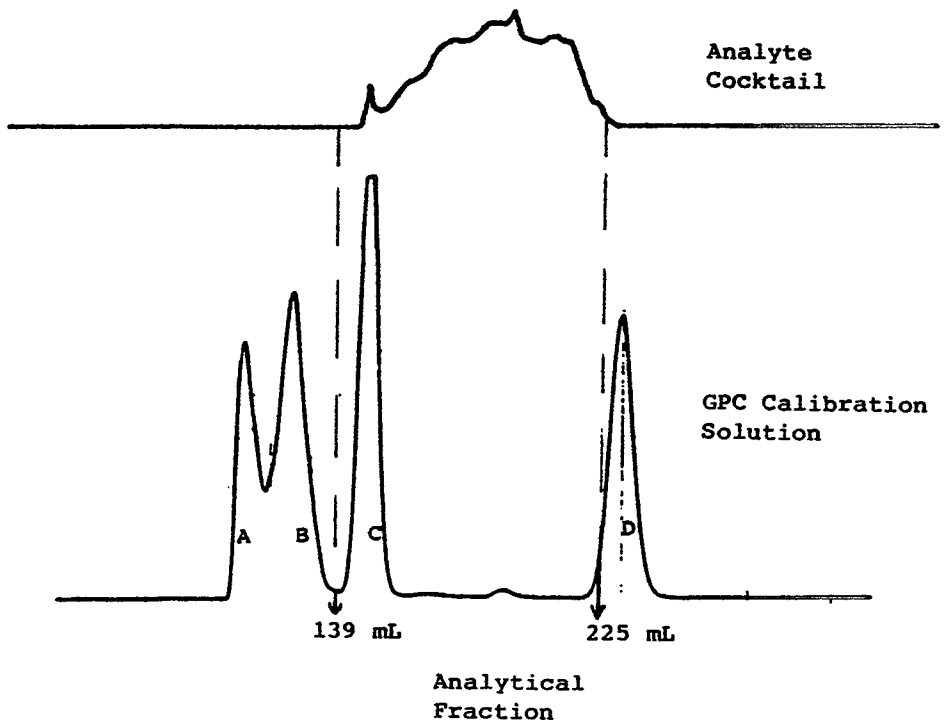
Residue before cleanup 77.9 mg/mL
Residue after GPC cleanup 23.6 mg/mL (66%)
Residue after DSGF/GPC cleanup 22.9 mg/mL (71%)
All extracts KDed to 1 mL before analysis

DSGF: 60g 10% deactivated silica gel
425 mL MeCl elution solvent

GPC: SX-3 bio beads
75% hexane 25% MeCl mobile phase

GPC CHROMATOGRAMS (UV)

Mobile Phase - $MeCl_2$
Stationary Phase - SX-3



MW = 280,000

A. Polystyrene
B. Corn Oil
C. Dioctylphthalate
D. Sulfur

SLUDGE CLEANUP BY GPC

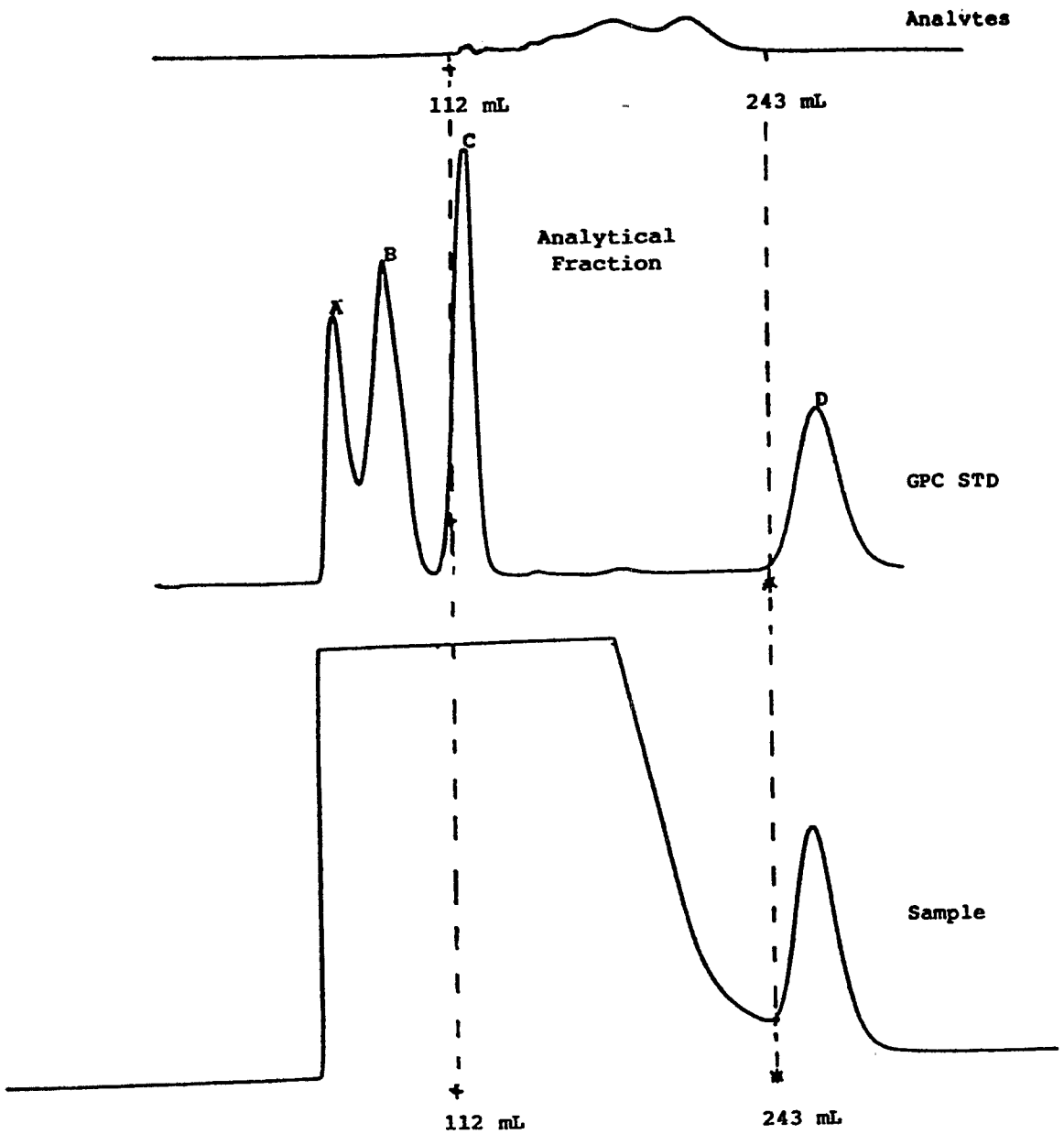


Figure . GPC Chromatograms of Analytes, GPC Standard and Sample

Stationary Phase = SX3
Mobile Phase = 40% Hexane and 60% Methylene Chloride V/V
+ = Start of Collection
* = Stop of Collection
A = Polystyrene
B = Corn Oil
C = Dioctylphthalate
D = Sulfur

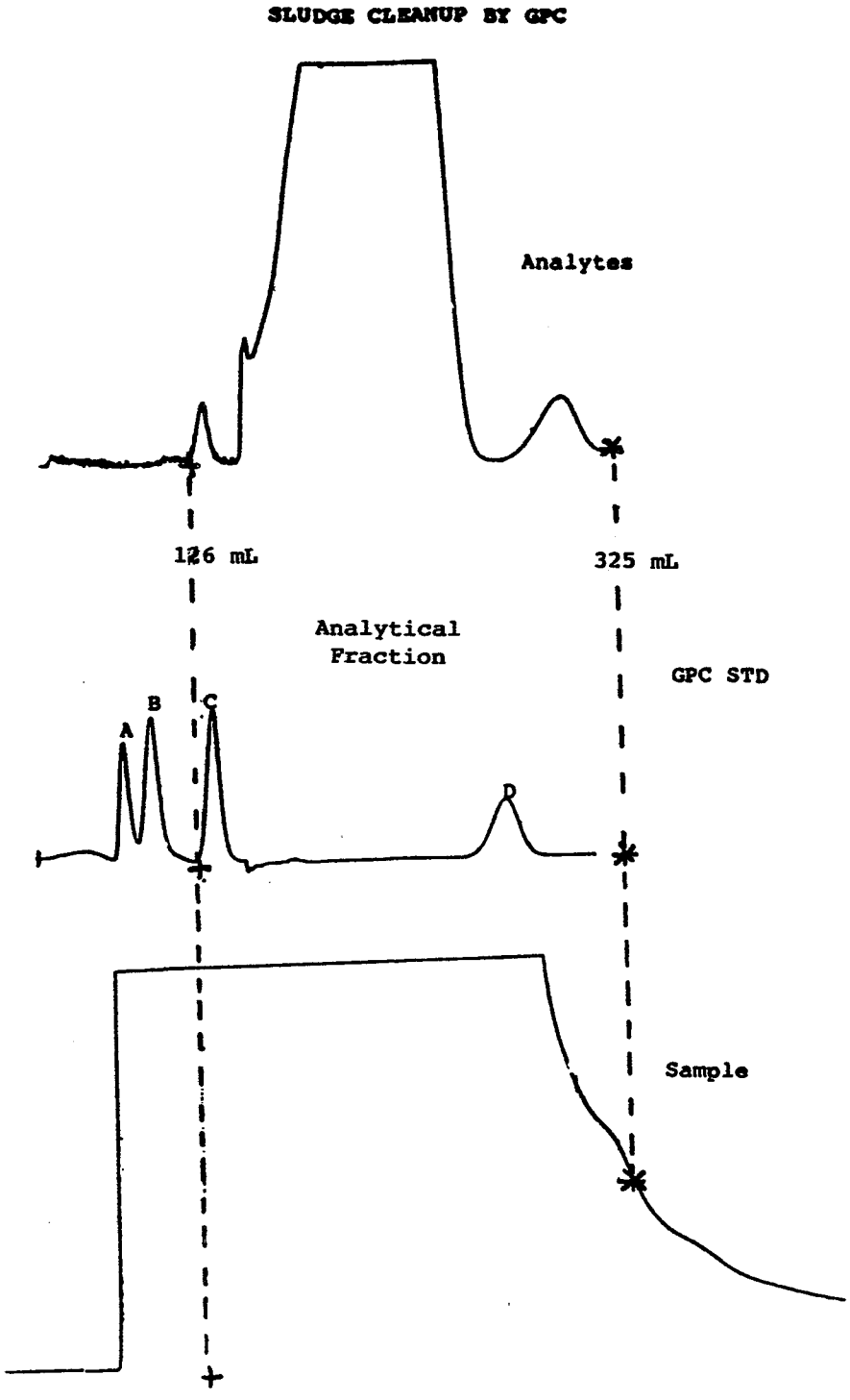
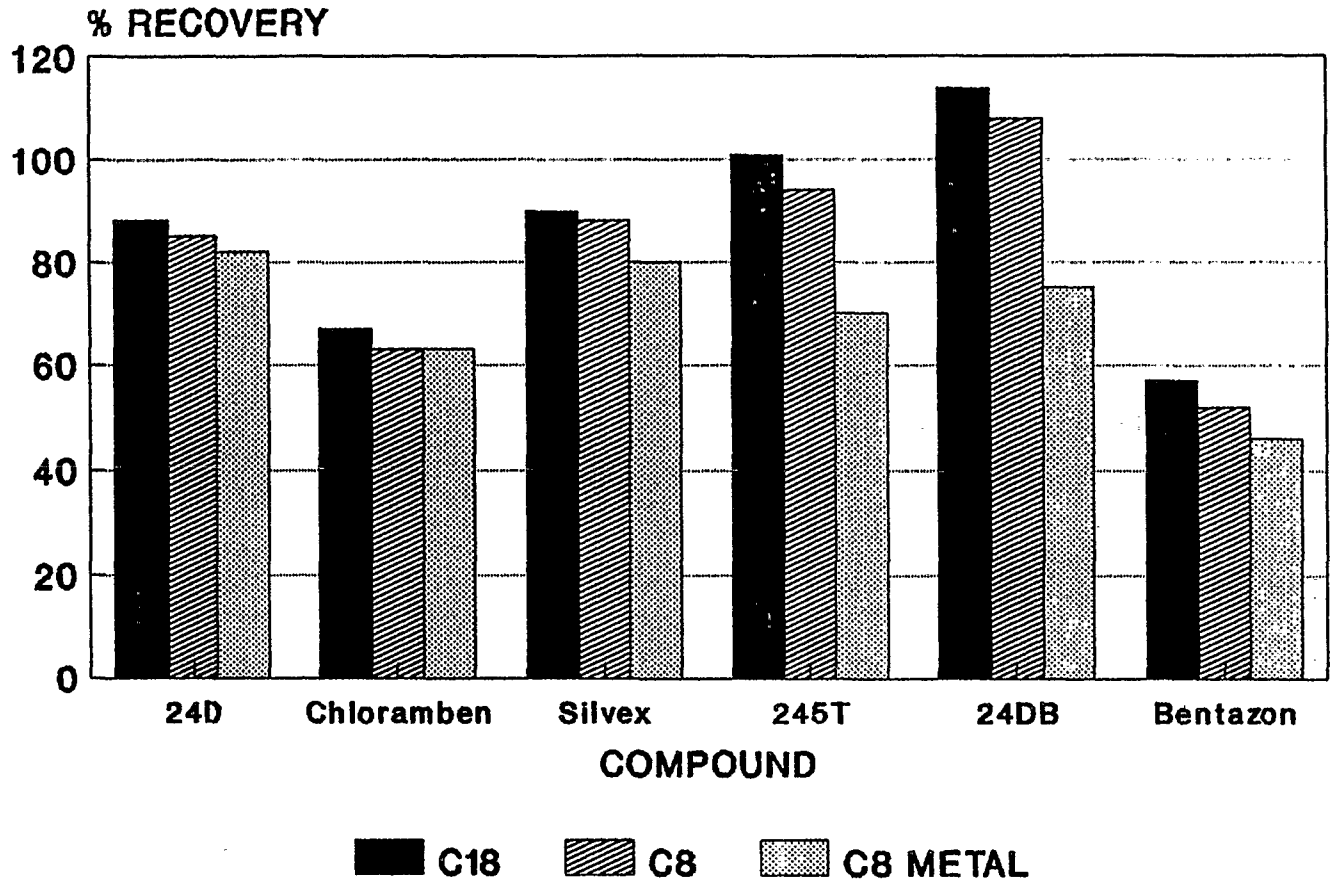


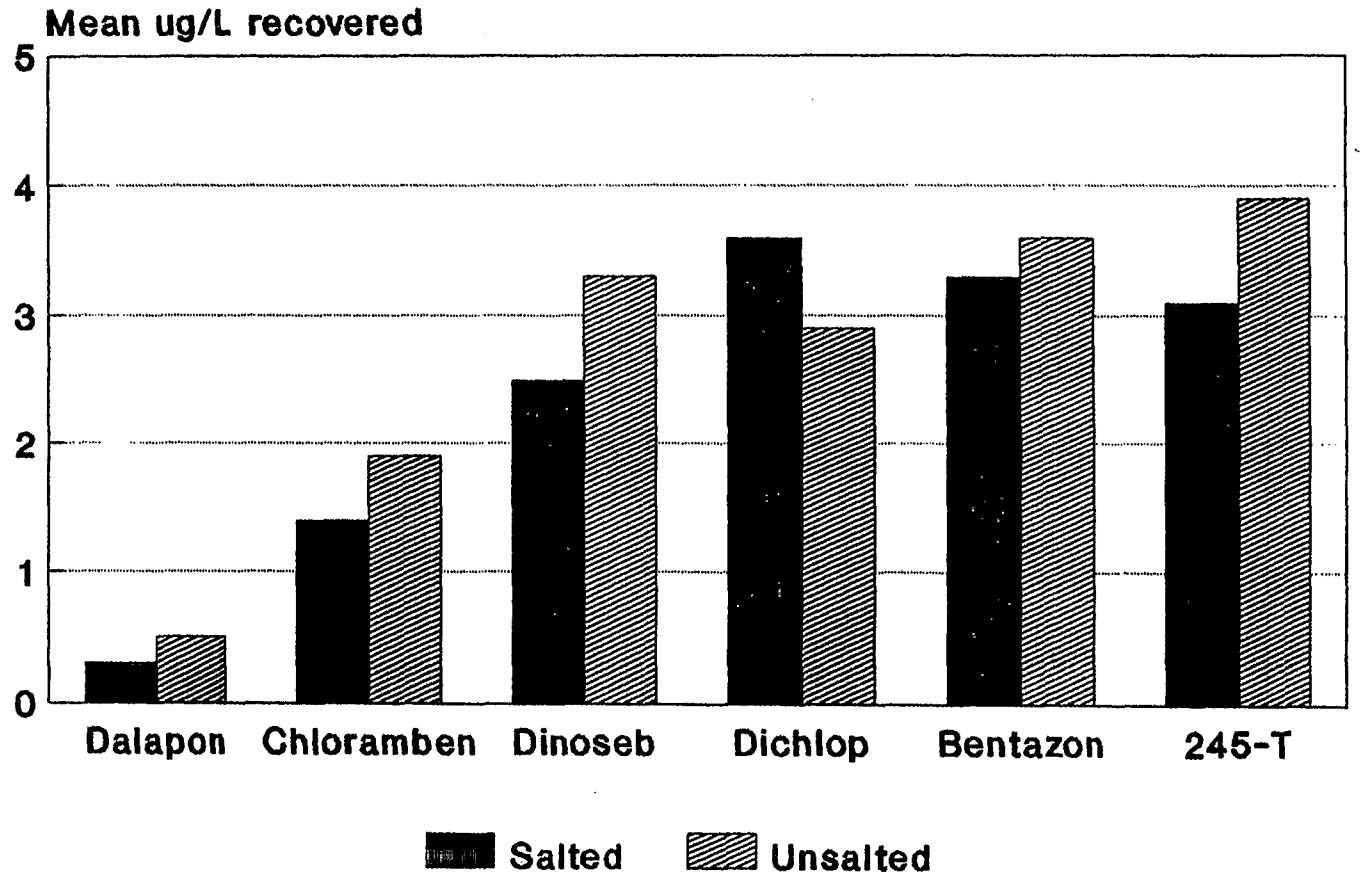
Figure GPC Chromatograms of Analytes, GPC Standard and Sample

Stationary Phase = SX3
Mobile Phase = 60% Hexane and 40% Methylene Chloride V/V
+ = Start of Collection
* = Stop of Collection
A = Polystyrene
B = Corn Oil
C = Dioctylphthalate
D = Sulfur

COMPOUND EXTRACTION FROM REAGENT WATER USING DISKS



Salted vs. Unsalted 15% (NH4)2SO4
Reagent Water C18 Disks 5ug/L



100 mL sample

MR. FIELDING: Our next speaker is Susan Richardson of Environmental Research Laboratory, USEPA at Athens, who will talk about application of multispectral techniques to the identification of aldehydes in a combined sewer overflow.

MS. RICHARDSON: My talk today will cover the application of multispectral techniques which are a combination of mass spectral and infrared techniques for the identification of organic compounds in environmental samples. Specifically, I will focus on the identification of straight-chain aldehydes in a combined sewer overflow sample.

This work has recently appeared in an EPA report, and I have listed the report number here for anyone who is interested in reading more about this work. I also have some flyers on a back table with more information about how to obtain this report.

The use of multispectral techniques for identifying organic compounds in environmental samples has been a major part of what I have been involved with at EPA's Environmental Research Laboratory in Athens, Georgia.

The multispectral techniques that were used for this specific study, the identification of the aldehydes, are shown in the red blocks. Each technique incorporated the use of gas chromatography with it.

The techniques that we used for this study were, first of all, low resolution electron-impact mass spectrometry, EI-MS; high resolution EI-MS; low resolution chemical ionization mass spectrometry, CI-MS; high resolution CI-MS; and Fourier transform infrared spectroscopy.

The techniques shown below that you can probably barely see in the green block are fast atom bombardment mass spectrometry and thermospray LC/mass spectrometry. These techniques are currently available on our instrumentation, but they weren't used for the study that I will talk about today.

The techniques shown at the very bottom are currently being developed, and we would like to incorporate those techniques into our multispectral techniques analysis program as they are developed. Those are supercritical fluid chromatography coupled with nuclear magnetic resonance spectroscopy and supercritical fluid chromatography coupled with infrared spectroscopy.

The instrument that was used for the mass spectral work is shown on this slide, and it was a VG 70SEQ High Resolution Hybrid mass spectrometer. It has a double focusing sector composed of electrostatic analyzer plates and an electromagnet. This double focusing sector allows us to do the high resolution work that I will talk about later. It also has, in tandem, a quadrupole analyzer which allows us to do MS/MS work as well.

I want to mention that I was primarily involved with the mass spectral work, as was John McGuire and Al Thruston who are also listed on your program. Tim Collette was

responsible for the infrared work that I will talk about later.

The purpose of this slide is to emphasize just how few compounds are typically targeted by common analysis methods. I have shown here specifically EPA Method 1625, which I am sure most of you are familiar with. It uses low resolution electron impact mass spectrometry to target less than 200 analytes.

Just this year, Chemical Abstract Services has gone over the 10 million mark for the total number of chemicals it has given a registry number to. So, it is clear that we are typically only targeting a very small percentage of the total amount of compounds that could be found in environmental samples.

Part of my laboratory's mission since the Consent Decree of 1976 has been to analyze environmental samples for compounds other than those targeted by current EPA methods.

There are three main obstacles to obtaining identifications of organic compounds in environmental samples using common analysis methods that generally involve an extraction of the sample into organic solvent followed by low resolution GC/MS using EI conditions and, finally, library data base matching.

First of all, since the sample is generally extracted into an organic solvent such as methylene chloride, there

will be compounds that will not be extracted and will be missed at this stage in the identification process. Compounds that are highly water soluble would fall into this category.

Of those compounds that are extracted, there will be those for which GC/MS is not applicable. High molecular weight compounds or thermally labile compounds would fall into this category.

Of the compounds which are GC/MS applicable, there will be those that won't have spectra in the library data base, inhibiting a structural assignment by library data base matching.

Part of my work is involved in using multispectral techniques to, first of all, identify those compounds which do not show spectra in the library data bases and then enter that spectrum into a library data base to make the next identification a little easier. We also use multispectral techniques to add confidence in the structural assignment for compounds which may have an entry in a library data base.

Many times, particular compounds will show similar library fits from library data base matchings. I am sure all of you are aware of that, and there is not always a clear choice available. So, using these multispectral techniques which complement each other, we are able to

obtain very precise identifications on compounds which would not have been possible just using low resolution electron-impact mass spectrometry and library data base matching.

As I mentioned earlier, this sample was taken from a combined sewer overflow, and it was extracted into methylene chloride. Bill Telliard of ITD was responsible for the program which provided this sample for us, and Jim King of the Sample Control Center was responsible for storing the sample for us.

This slide shows the GC/MS chromatogram obtained under low resolution EI conditions. Among the many compounds that we identified in this sample, the peaks labeled 1 through 8 represent the eight straight-chain aldehydes that we identified in the sample.

There were four saturated aldehydes: n-hexanal, n-heptanal, n-nonanal, and n-octanal; and four unsaturated aldehydes: 2-heptenal, 2-octenal, 2-decenal, and 2-undecenal. The low resolution EI data led us to believe that we could possibly have these assignments that I have shown you. However, in this case, there were many similar library fits, and there was no clear choice available from library data base matching.

So, at this point in the identification process, these assignments were only tentative.

Also, for those four unsaturated aldehydes, there were typically only two possible isomer choices in the library. For instance, for the compound 2-heptenal, 2-heptenal was in the library and 4-heptenal was in the library, but other possible isomer choices such as 3-heptenal, 5-heptenal, and 6-heptenal were not.

So, we could not be sure of a correct structural assignment from library data base matching.

Part of the reason that the low resolution EI data was so inconclusive was that there was very little molecular weight information present in the EI spectra. I have listed here the relative abundances of the molecular ions obtained under EI conditions for the aldehydes listed at the left. You can see that most of these aldehydes show extremely small molecular ions.

Shown here are n-hexanal at 0.1 relative abundance; for n-heptanal, 0.2; n-octanal, 0.1; for 2-octenal, 0.3. The one exception was 2-heptenal which did show a molecular ion at a reasonable relative abundance. The three aldehydes listed at the bottom, n-nonanal, 2-decenal, and 2-undecenal, did not show a molecular ion at all.

So, in general, the low resolution EI data was void of molecular weight information.

This slide shows an example of one of the EI spectra obtained, in this case, for nonanal which has a molecular

weight of 142. You can see that there are no ions in this molecular weight region.

Generally, the highest mass ion present for most of these aldehydes in the EI spectra was due to the loss of water from the parent compound, shown here at m/z 124 for nonanal.

In order to determine the molecular ion for these aldehydes, first of all, low resolution chemical ionzation mass spectrometry was used. The reason low resolution was used before high resolution was to prevent the interference of a calibration compound such as pfk that would have been necessary for the high resolution experiment.

So, we first of all determined to a nominal mass what the molecular ion was for each of these compounds using low resolution CI, and then we used high resolution CI to determine the accurate mass.

I have listed here the observed masses obtained experimentally for the (M+H) ions under high resolution CI conditions. You can see that these observed masses do compare very favorably with the calculated masses based on the assignments given at the left.

So, this high resolution CI data did support our structural assignments. However, we haven't yet shown clearly where the location of the carbon-carbon double bond

is for the unsaturated aldehydes, 2-heptenal, 2-octenal, 2-decenal, and 2-undecenal.

In order to determine the location of that carbon-carbon double bond, we used high resolution electron impact mass spectrometry. I am choosing to use an example here, in this case, 2-octenal, to show you how we used high resolution EI mass spectrometry to determine the location of the double bond, but we used the same procedure for each of the other three unsaturated aldehydes as well.

The premise that we used was this: carbon-carbon double bonds will rarely fragment across the carbon-carbon double bond under EI conditions. So, if we could show we had a fragment ion owing to cleavage at each of these other carbon-carbon bonds along the hydrocarbon chain and if we see an absence of an ion owing to cleavage at this particular location, then we could determine that this must be the location of the carbon-carbon double bond.

The reason that high resolution was necessary for this work over the corresponding low resolution experiment was that under low resolution EI conditions, many of the fragment ions obtained could be represented by more than one possible empirical formula and, thus, by more than one particular site of cleavage. So, in order to determine that site of cleavage accurately, we did need high resolution EI mass spectrometry.

This slide shows an example of that. Using low resolution EI mass spectrometry conditions, we obtained an ion at m/z 83 for the compound that I showed you on the previous slide, 2-octenal. This ion at 83 could be represented either by C_6H_{11} which corresponds to a particular site of cleavage along the hydrocarbon chain and also a possible location for the carbon-carbon double bond, or that ion at 83 could be represented by C_5H_7O corresponding to yet another particular site of cleavage along the hydrocarbon chain and another possible location for the carbon-carbon double bond.

High resolution electron impact mass spectrometry provided us with the accurate mass that determined that the C_5H_7O assignment was the correct assignment for the ion at 83. Thus, we can assign that specific site of cleavage at the location shown here.

We used the same methodology for each of the other fragment ions obtained under high resolution EI conditions, and we showed that we did have cleavage of each of these carbon-carbon bonds along the hydrocarbon chain, but we did see an absence of an ion owing to cleavage at this location. So, we concluded that the double bond must be located at this particular position, which is at the carbon-2 position.

Incidentally, this particular location for the carbon-carbon double bond allows it to be in conjugation with the

aldehyde carbonyl group, making it a more thermodynamically stable compound, something you might expect for a compound found in the environment.

Keep in mind that this double bond is in conjugation with that aldehyde carbonyl group. That will become important in the next slide.

This slide shows the infrared spectrum of 2-octenal. Again, I am choosing to use 2-octenal to show you how we used infrared spectroscopy to identify all of these aldehydes. I use this as one particular example.

Infrared spectroscopy was a nice complement to mass spectrometry, because it, first of all, confirmed some structural assignments that we had made using mass spectrometry, and it also provided new information that mass spectrometry was not able to provide.

First of all, the peaks shown here which are due to the stretching fundamental of the hydrogen atom attached to the carbonyl carbon and also due to a corresponding overtone peak, those peaks, along with the peak due to the stretching of the carbonyl shown here at 1715 cm^{-1} are clear evidence for an aldehyde group

So, first of all, IR spectroscopy confirmed the existence of the aldehyde group for all eight straight-chain aldehydes we identified. Secondly, infrared spectroscopy

confirmed the existence of the carbon-carbon double bond for the four unsaturated aldehydes.

The peaks shown here at 1634 cm^{-1} is clear evidence of a carbon-carbon double bond.

The third piece of information that infrared spectroscopy provided was the location of that carbon-carbon double bond along the hydrocarbon chain for those unsaturated aldehydes. If this carbon-carbon double bond had not been in conjugation with that carbonyl group, this particular frequency shown here at 1634 cm^{-1} would have been shifted to a much higher frequency, to about 1650 cm^{-1}. Also, the carbonyl frequency would have been shifted to about 1742 cm^{-1}.

So, because these frequencies are located where they are at 1634 and 1715 cm^{-1}, that is clear evidence for conjugation of that carbon-carbon double bond with the aldehyde carbonyl group, thus confirming that the double bond is located at carbon-2, as high resolution electron-impact mass spectrometry had suggested.

Finally, infrared spectroscopy allowed an exact isomeric determination for the four unsaturated aldehydes, that is, whether we had a cis or a trans double bond. This was something that mass spectrometry was not able to provide.

The peak shown here at 976 cm^{-1} is clear evidence for a trans double bond. So, we did determine that we had a trans double bond for each of those four unsaturated aldehydes.

To summarize, using the multispectral techniques, which were low and high resolution electron-impact mass spectrometry, low and high resolution chemical ionization mass spectrometry, and Fourier transform infrared spectroscopy, we were able to precisely identify these compounds that would not have been able to be identified this way using the common analysis methods of low resolution electron-impact mass spectrometry and library data base matching.

First of all, low resolution chemical ionization mass spectrometry allowed us to accurately determine the molecular ion since it was either very small or wasn't present at all in the EI spectra for most of these aldehydes.

Secondly, high resolution CI-MS provided us the accurate mass which allowed us to determine the exact empirical formula of the molecular ion.

Thirdly, infrared spectroscopy confirmed the existence of the aldehyde group for all eight aldehydes.

Fourthly, both high resolution EI mass spectrometry and infrared spectroscopy together determined the position of the carbon-carbon double bond for the unsaturated aldehydes.

Finally, infrared spectroscopy allowed an exact isomeric determination, that is, whether we had a cis or a trans double bond. We did determine that we had a trans double bond, and this, again, was something that mass spectrometry was not able to provide.

You can see how nicely these techniques complemented each other and how they worked very well together to allow us to make these precise identifications.

I would like to conclude by saying that the observation of these straight-chain aldehydes in a combined sewer overflow sample was very unexpected. What we have typically found in those types of samples are primarily fatty acids and fatty acid methyl esters. So, the observation of these aldehydes in that particular type of sample was unusual from that standpoint.

It was also unusual from the standpoint that there are very few reports of similar straight-chain aldehydes in the literature where they were found in the environment at all. So, we did feel that this finding was significant.

There are many other types of aldehydes that are commonly observed such as benzaldehyde, acetaldehyde, and formaldehyde, but, evidently, straight-chain aldehydes are not that common.

I do want to mention, however, that I have been recently told that there have been some tentative

identifications of some similar straight-chain aldehydes in Superfund samples, but these identifications are only tentative at this point.

I would like to thank you for your attention. If there are any questions, I would be happy to try to answer them.

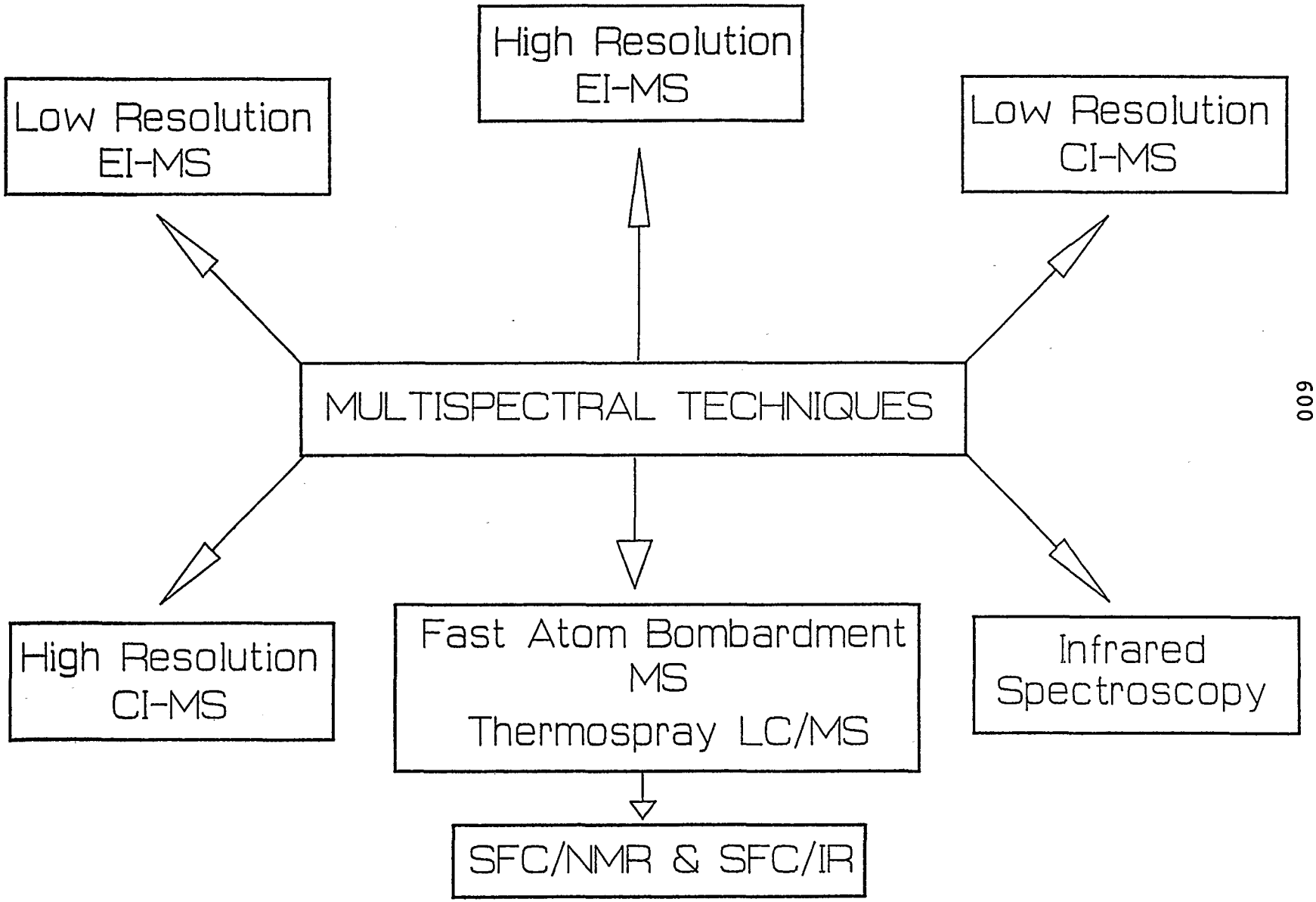
MR. FIELDING: Does anybody have any questions?

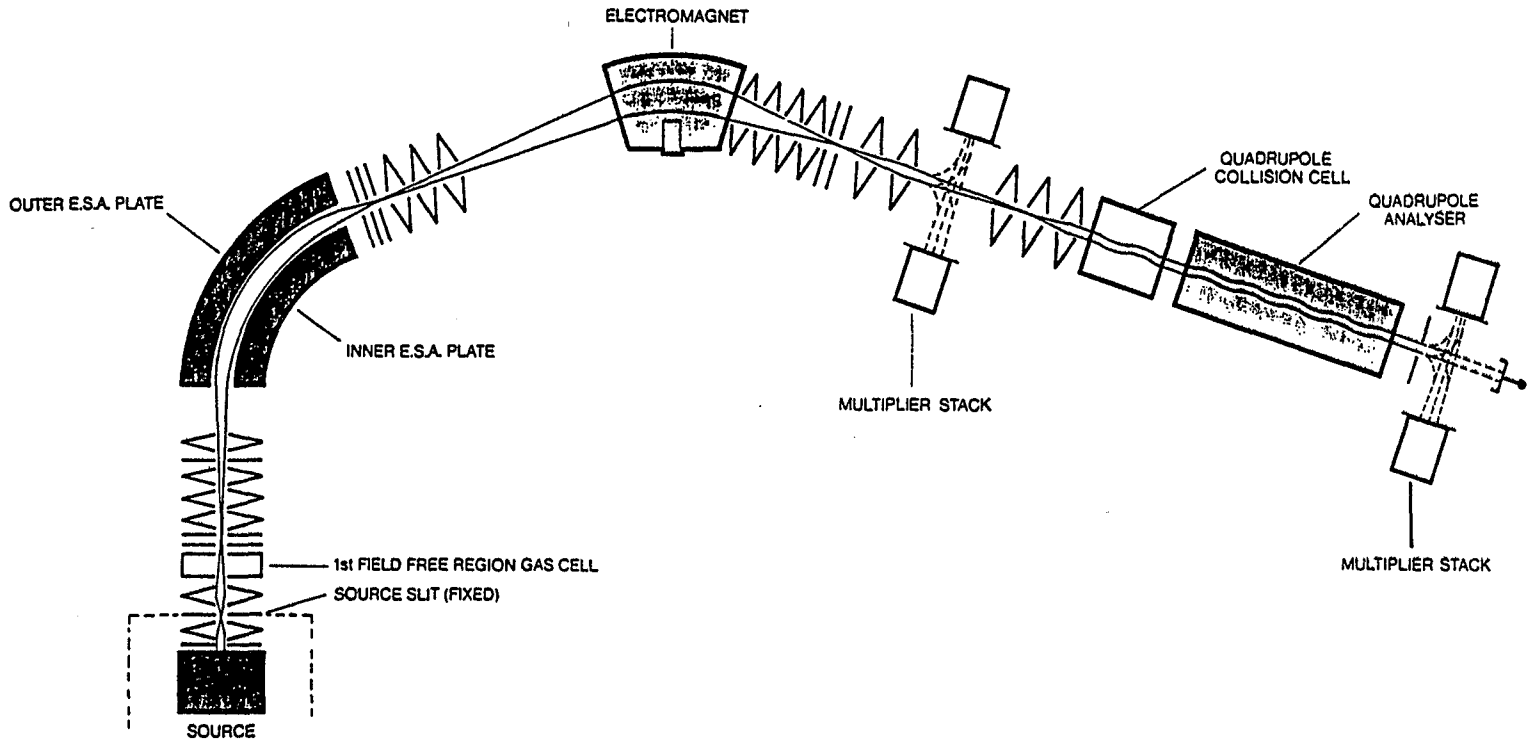
(No response.)

MR. FIELDING: If not, we thank you very much, Susan.

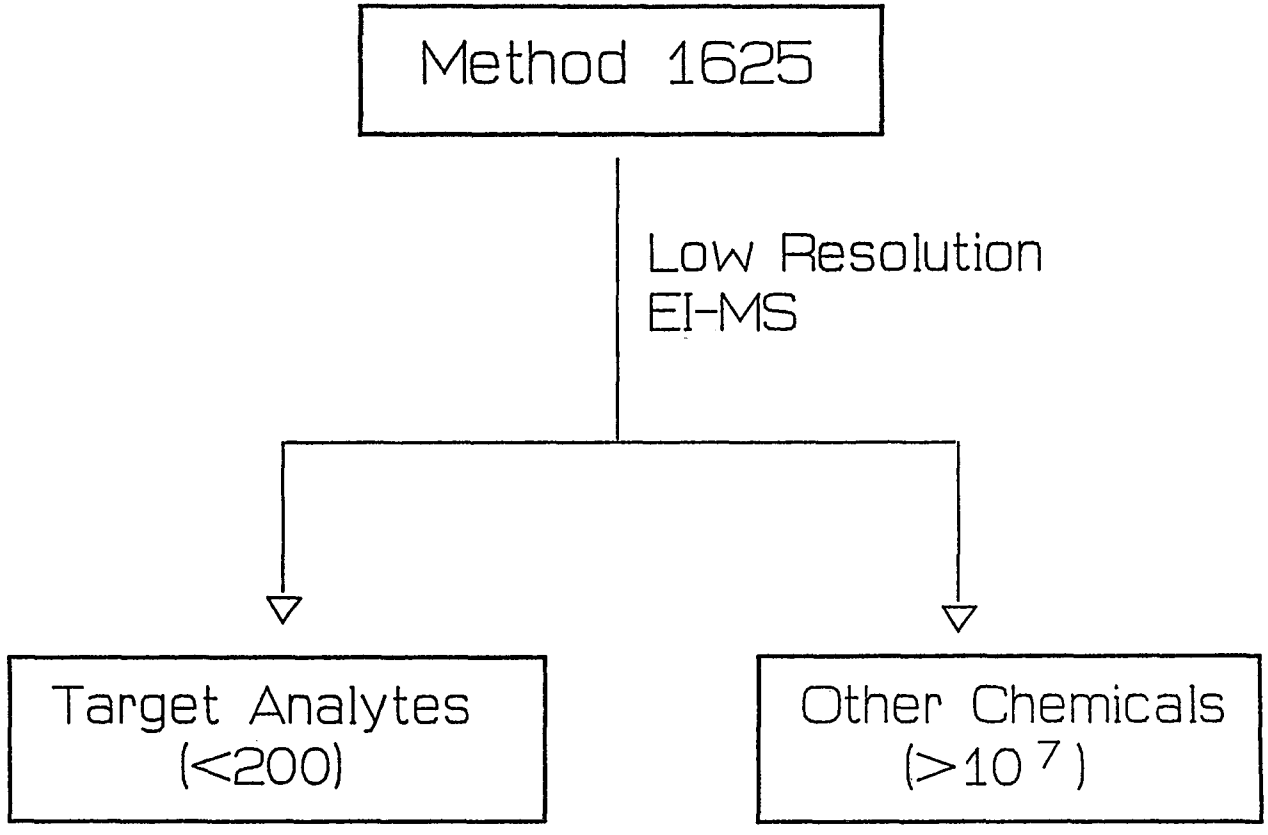
Application of Multispectral Techniques To the Identification of Aldehydes In a Combined Sewer Overflow

EPA/600/4-90/002
NTIS No. PB 90 160 995/AS


High Resolution
EI-MS
Low Resolution
EI-MS
Low Resolution
CI-MS
MULTISPECTRAL TECHNIQUES
High Resolution
CI-MS
Fast Atom Bombardment
MS
Thermospray LC/MS
Infrared
Spectroscopy
SFC/NMR & SFC/IR



GC inlet
Solid probe inlet
FAB/FD inlet
Thermospray LC/MS inlet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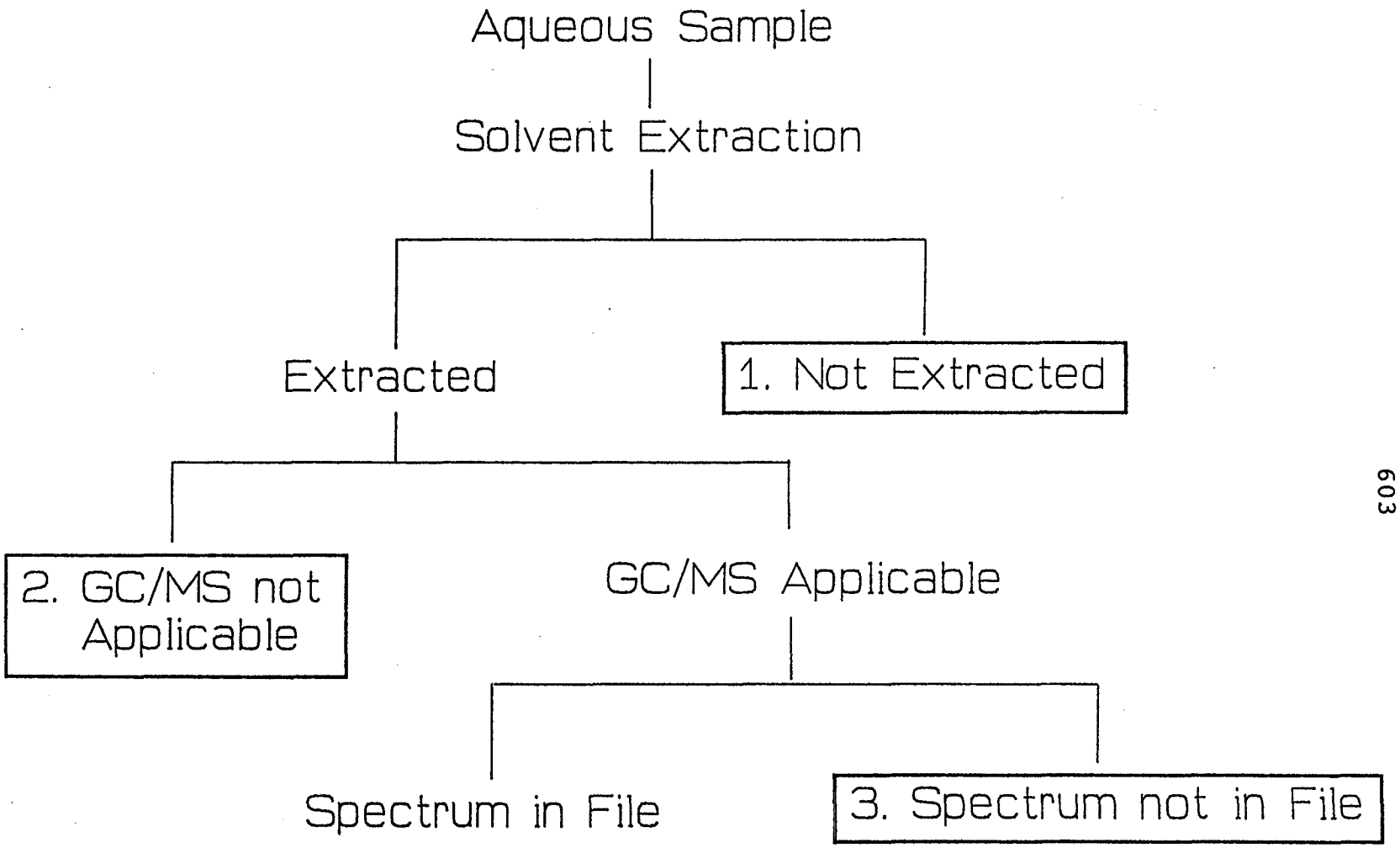
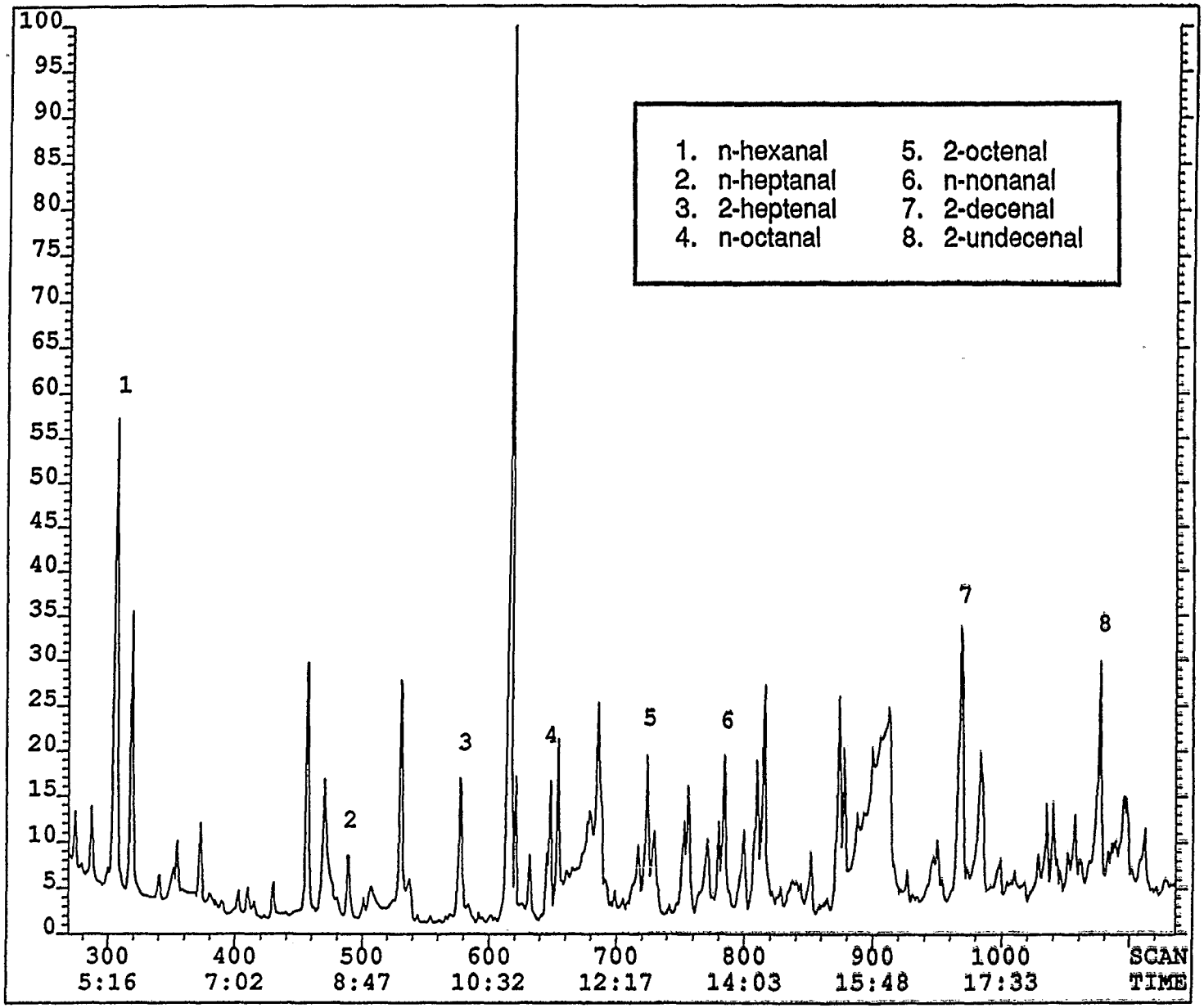
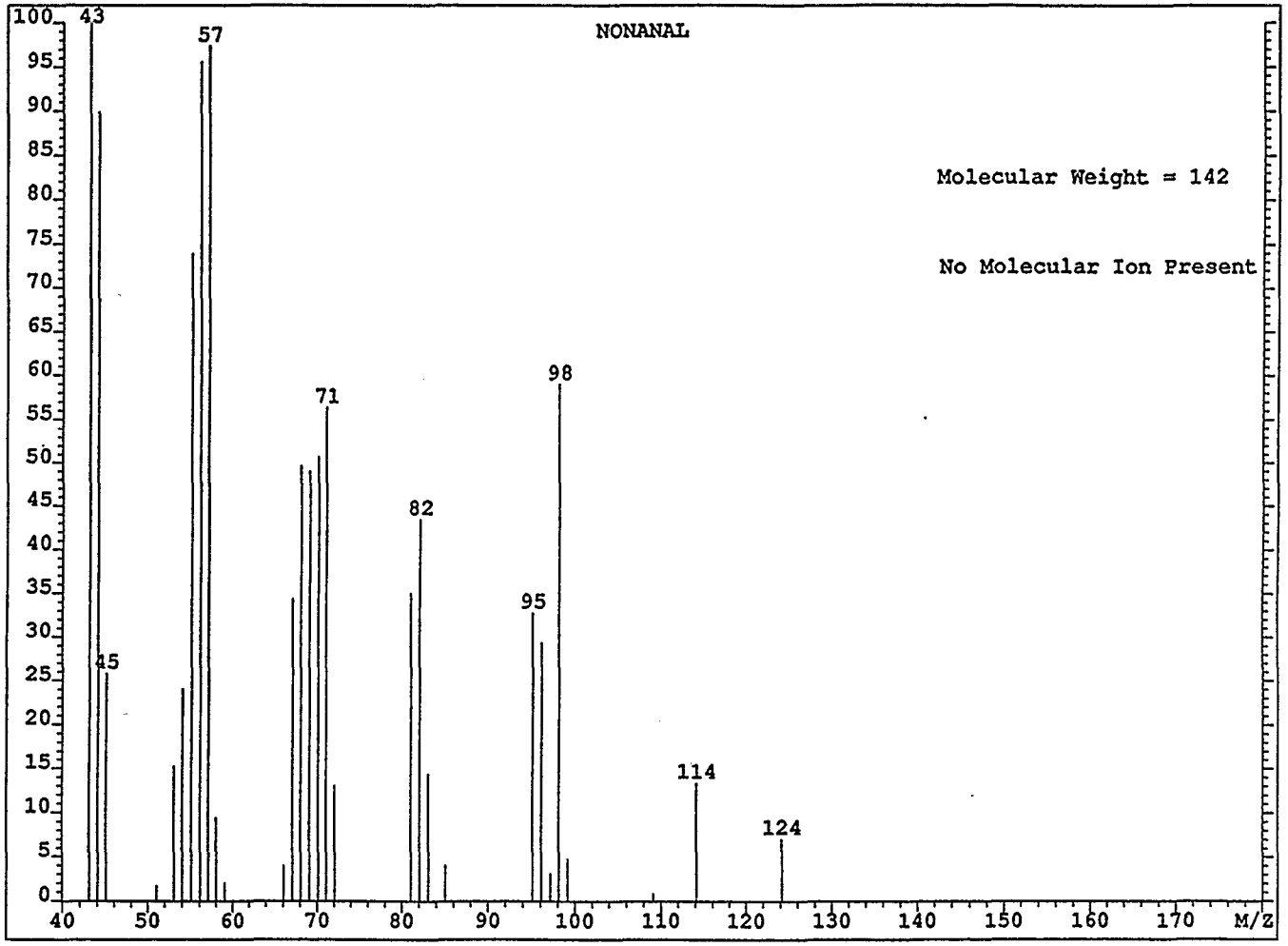
Low Resolution
EI-MS
Target Analytes
(<200)
Other Chemicals
(>10 7)


Aqueous Sample
Solvent Extraction
Extracted
1. Not Extracted
2. GC/MS not Applicable
GC/MS Applicable
Spectrum in File
3. Spectrum not in File


1. n-hexanal
2. n-heptanal
3. 2-heptenal
4. n-octanal
5. 2-octenal
6. n-nonanal
7. 2-decenal
8. 2-undecenal
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
300
5:16
400
7:02
500
8:47
600
10:32
700
12:17
800
14:03
900
15:48
1000
17:33
SCAN
TIME

Electron Impact Relative Abundance
Of Molecular Ions

Compound	Relative Abundance
n-hexanal	0.1
n-heptanal	0.2
2-heptenal	10
n-octanal	0.1
2-octenal	0.3
n-nonanal	---
2-decenal	---
2-undecenal	---

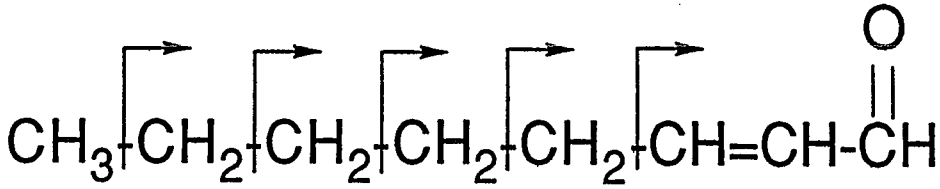

NONANAL
Molecular Weight = 142
No Molecular Ion Present
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
43
57
71
82
95
98
114
124
45
40
50
60
70
80
90
100
110
120
130
140
150
160
170
M/Z

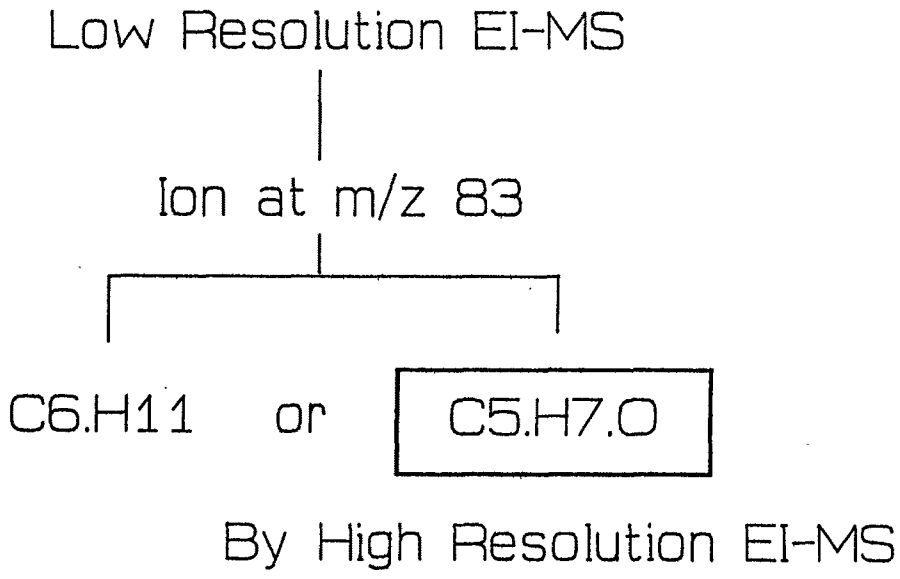
High Resolution CI Accurate Masses

$[M+H]^+$

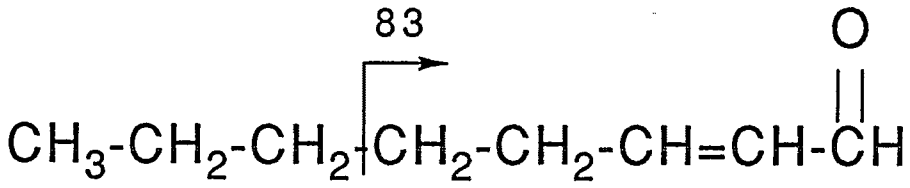
Compound	Empirical Formula	Observed Mass	Calculated Mass
n-hexanal	C6.H13.O	101.096	101.097
n-heptanal	C7.H15.O	115.111	115.112
2-heptenal	C7.H13.O	113.097	113.097
n-octanal	C8.H17.O	129.130	129.128
2-octenal	C8.H15.O	127.113	127.112
n-nonanal	C9.H19.O	143.143	143.144
2-decenal	C10.H19.O	155.144	155.144
2-undecenal	C11.H21.O	169.158	169.159

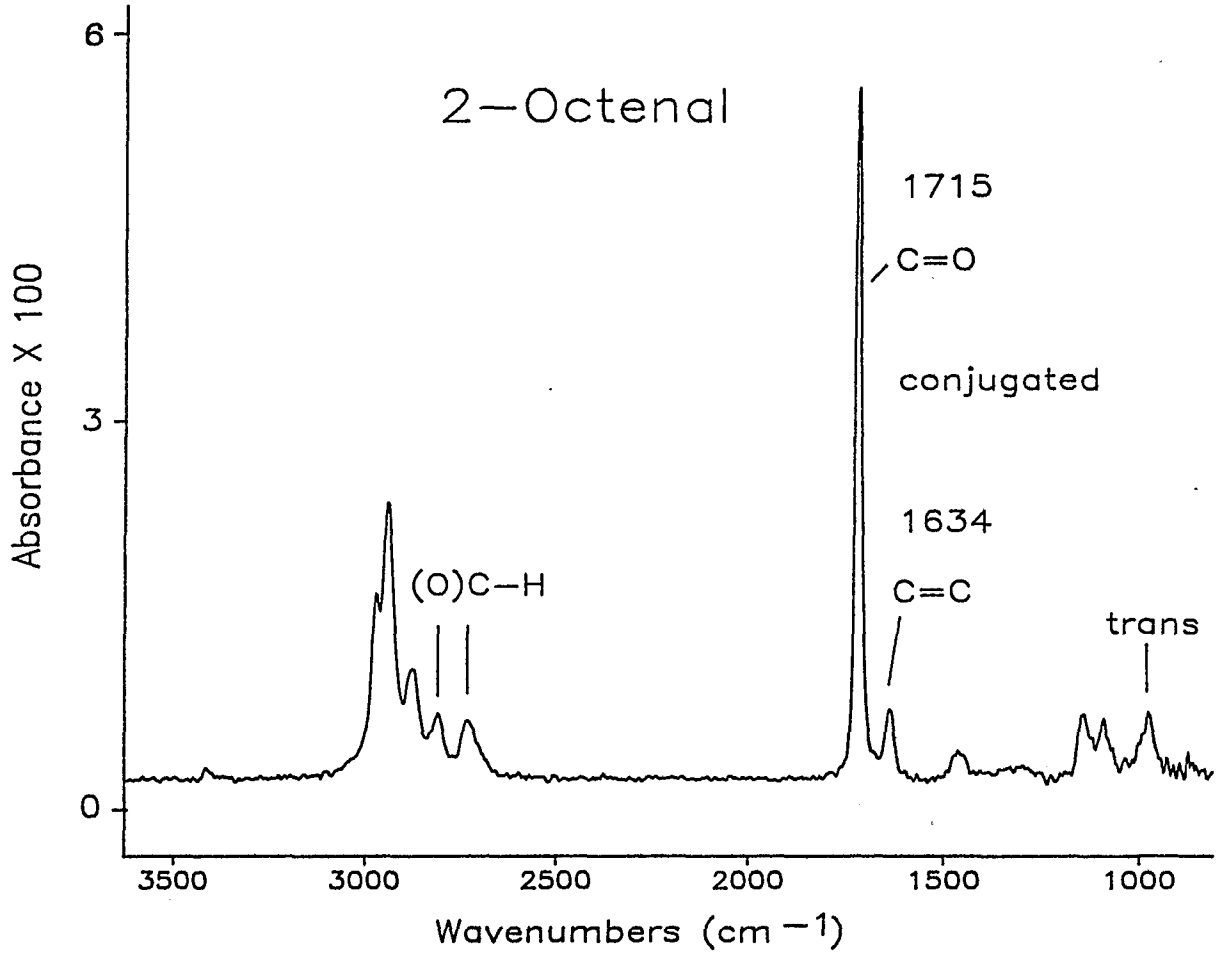
2-Octenal




Low Resolution EI-MS
Ion at m/z 83
C6.H11
or
C5.H7.O
By High Resolution EI-MS

2-Octenal




2—Octenal
1715
C=O
conjugated
1634
C=C
trans
(O)C—H
Absorbance X 100
6
3
0
3500
3000
2500
2000
1500
1000
Wavenumbers (cm⁻¹)

Summary

- Accurate Determination Of Molecular Ion → Low Resolution CI-MS
- Exact Empirical Formula Of Molecular Ion → High Resolution CI-MS
- Confirmation of Aldehyde Group → Infrared Spectroscopy
- Position of Carbon-Carbon Double Bond → High Resolution EI-MS Infrared Spectroscopy
- Exact Isomeric Determination (Cis or Trans Double Bond) → Infrared Spectroscopy

MR. FIELDING: It is time for lunch. Can we try to get back about 1:00 o'clock? We have a full afternoon, and I know some people have to leave on early flights. We will see you at 1:00 o'clock.

AFTERNOON SESSION

MR. TELLIARD: We would like to get going for this afternoon's session, please.

One small announcement. We routinely take the proceedings down and put it out in a book called "Proceedings." As I alluded to before, last year's proceedings are sitting waiting to be printed. I called my management, I called Washington, and they said yes, it is sitting here. The word is that we won't be able to print it until September when we get new money. So, when it is available, I will mail it to you, he said.

That also means that these proceedings that we are taking down now will hopefully be out in September when we get the new budget. New money comes in in a big truck and they dump it in the office. We roll around in it for a day or two and then spend it.

So, I am sorry about this. It is kind of embarrassing, but the Office of Water took about a $1 million intramural cut this year. Apparently, we made somebody unhappy up on the Hill, and now they have made us unhappy. It works.

So, because of that intramural cut, we have not been able to print almost anything. So, on those cards you filled out, on some of those documents, you will get a little notice that says "in printing" which means there is

no money right now, and we will get those in September. Those that are available we will mail out to you.

So, our first speaker this afternoon is Joe Raia. Joe is going to speak about one of his favorite persons, a robot, and the joys of doing suspended solids using a robotic method.

MR. RAIA: Good afternoon.

At Shell Development Company at the Westhollow Research Center, I have the Environmental Wastewater Analysis group, and in this laboratory we process a large number of samples for the environmental research at this facility. One of the goals and focuses of our group is to try to automate methods where it makes sense to do so in order to perform these analyses as cost effectively as possible.

The total suspended solids method was one of these methods that we thought was a real good candidate for automation. It was highly repetitive, we did relatively large numbers per year, on the order of about 2000, and it really wasn't that much fun to do.

We got together with our systems development group...and the co-author up there on the slide, Al Telfer...and began thinking about how we could automate this procedure. The result of that effort is what I will be talking about this afternoon.

Automation in the laboratory is really nothing new. It has been around for a number of years. We have had laboratory information management systems for identifying the sample when it comes into the laboratory and to do sample tracking.

We can skip over the sample preparation part shown here on the slide for a minute, and looking at the analysis side,

there are all sorts of automated instrumentation with autosamplers, continuous flow type systems,and instrumentation which are run by microprocessors. Then, in the results and reports section of the analysis, we know computerized data reduction has been around for years.

One important step in this whole process has been sample preparation. About, I guess, 1982 or so, a company out of Hopkinton, Massachusetts, the Zymark Corporation, took a look at that and decided that it was a spot where we really needed to do some work in terms of automation and time savings efforts. So, they have come up with their Zymate system for primarily the sample preparation part of the analysis procedure.

The TSS analysis robotic system that I am talking about here in this presentation is one that measures total suspended solids in water. We developed the method to follow the standard EPA protocol, Method 160.2, which essentially is a filtration of the sample through a 1 micron filter and then followed up by a gravimetric finish after removal of the water at 105 degrees in an oven.

The procedure will also allow us to measure the volatile residue according to EPA Method 160.4 with what we call a minimum of operator intervention. As I go through and describe the lab robot...and many of you here have already seen them around for quite a few years, you will see

that the hands of the robot would not be able to stick the sample into a 550 degree furnace that is used for the volatile residue part of the test. So, we intervene at that point and place the samples in a rack and manually insert them into that type of a furnace.

Now, in the beginning of our story here, this is a photograph of the way we used to do suspended solids in the lab. We typically had our setup to do eight samples at a time, batchwise. At that time, we tried to automate at least the end part of the procedure by linking the balance to a computer so that you could start the analysis, get your tare weight, store that weight in the data system, then perform the filtration, the drying, the weighing, reweighing, and then from the data system memory of the initial and final weight, the computer would calculate the suspended solids that were captured on the filter.

This slide shows the system that we developed to perform that analysis. This is the Zymark Zymate system that we purchased from Zymark Corporation, and this is their controller to automatically operate the instrumentation.

It is not shown here, but we have linked this system to an IBM PC for report generation. I have another schematic that I will put up here in a second to show you the layout of the system.

This whole apparatus is on about a 7 foot by 4 foot table top, and the electronics for performing part of the analysis are housed below here.

The sample starts out in this sample rack. Typically, we use 100 ml of sample. This is the oven for drying at 105 degrees C, a dessicator for conditioning before weighing in the balance, and these items here are the stands to hold the Gooch crucible for the filtration.

To simulate our original earlier days with this method, we stayed with a batch of 8 sample at a time, although we can actually do 16 in two batches of 8.

This next slide shows schematically what the photograph is trying to show there.

The feedback sensor is an item that I want to point out. This turned out to be the real challenge in terms of trying to automate this procedure; the reason being, " how to determine when the filtration had finished". In order to do that, we ended up using a capacitance type sensing device which allowed you to essentially tell the liquid level in the Gooch crucible.

The oven and dessicator were built in our shops at Shell in Westhollow, and they are pneumatically operated. The balance is a Mettler balance with a pneumatic door, and I have already mentioned the data system.

This next slide shows the step by step operation that the robot does to perform the test. I am going to read through here as we go. The sequence is as follows:

The robot gets the Gooch crucible with filter from the dessicator and moves it to the balance where the tare weight is obtained. Next, the robot takes them to the rinse station where a small volume of water is placed on the filter. This helps seal the filter to the Gooch crucible.

The robot then places them in the filter station and backs away. The vacuum is turned on to that filter station, and the capacitance electronics system takes a reading of the base capacitance. That is the base point that will be compared to determine when the sample is finished filtering.

This is accomplished using the switched outputs available to the power and event controllers as well as the A/D input. The output of the capacitance electronics is a 4 to 20 milliampere signal. This is converted to a volatage at the PEC switches using a 50 ohm resistor. This voltage reading is stored in the robot controller's memory for further use.

The robot then gets the proper sample flask from the storage rack and inverts the flask into the crucible. The robot leaves the flask in a holder on top of the filter station with the neck of the flask below the top of the crucible.

This allows us to filter up to 100 ml of sample into a 40 ml Gooch crucible. You can kind of think of this as a chicken feeder principle where the Gooch will not overflow because of the hydrostatic pressure that won't allow the rest of the 100 ml volume to fill until some of it filters through.

The robot backs away, and a second capacitance measurement is made. Now, if the filtration is complete, this second reading will approach the base reading and the vacuum will automatically be shut off for that filter station. If not, the robot proceeds with loading the next sample and rechecks all loaded stations for capacitance until filtration is complete.

The rest of the procedure operates in exactly the same way, and we rinse three times according to the protocol.

The sample can sit for some time without affecting performance as long as the vacuum is off. We found that if the filter gets too dry, some samples seem to get a waterproof like coating that may hinder a rinse procedure that follows. Conversely, the filter must not be too wet, particularly when the crucible is placed in the oven.

For this reason, the program pauses after the final rinse and before the crucible is loaded into the oven while vacuum is applied to all occupied filter stations.

After drying at 105 degrees, the crucible is moved to the dessicator to condition and then weigh. Constant weight is verified by redrying the crucible for a half an hour and then reweighing.

If the volatiles are measured, the crucible and dry solids are moved by the analyst to a 550 degree furnace, and after 45 minutes, the crucibles are allowed to cool to ambient conditions and then placed in a dessicator before being weighed as before.

What I have here is a series of photographs to show some of the steps that the robot is taking to carry out the procedure that I have just described. This one shows getting the crucible out of the dessicator at the beginning of the analysis before placing it in the balance.

The door of the balance is activated and pneumatically opened, and the crucible is placed on the pan. The arm moves back, and the door is closed, and a weighing is made. The average of 10 weighings is done.

The arm goes back to get the crucible and moves it to the filtration station. The arm then goes to get the sample of water that is in a 100 ml volumetric flask and moves it to pour the sample into the Gooch crucible.

Programming that step was a little tricky to make sure that no water was dripping during the pouring process so that we didn't have any loss of sample. You can see how the

filtration stations were designed to hold the flask in place inverted as the water passed from the flask into the Gooch crucible, and this is the place where the 100 ml of sample is poured into a 40 ml volumetric Gooch crucible without overflowing.

The neck of the flask is just below the top part of the Gooch crucible. The filter has already certainly been put in place early on in the procedure.

Then the arm goes to get the flask and moves it over to a rinse station where the rest of the sample is quantitatively transferred back onto the filter.

This shot was taken with a pen light put on the robotic arm and a time delay photograph to show all the different motions that are involved in carrying out this procedure by the robot to do eight samples.

This next slide shows the linearity with sample volume. It turns out that you have to select samples that are real high in solids. You use a reduced volume of sample for those type samples, and we wanted to see what sort of linearity we were getting down in the lower sample volume range and felt comfortable that it was linear down in that range.

This slide shows comparison data using the robotic and manual methods for a couple of samples that were generated in our research in the Environmental Science Department, in

benchscale biotreaters, at two different TSS levels. The mean standard deviation and coefficient of variation at these two levels were essentially about the same.

We feel that we don't see any bias in the robotic versus the manual method. At the 100 mg/l level, there seemed to be a lower robotic recovery for this particular set of data than for the manual, but that did not turn out to be the case in later results comparison work.

This data here shows percent recovery using samples provided to us by the Analytical Products Group out of Belpre, Ohio. This vendor will supply proficiency testing type samples to various laboratories who participate.

So, we had a comparison here of about 40 different labs around the country who were also getting the TSS proficiency sample, and we were able to compare it by the robotic procedure and the manual method performed in our laboratory, and compare it to the manual procedure in these other laboratories... and we felt satisfied with this recovery comparison.

The benefits of lab automation, as I conclude here, are first the obvious one of unattended operation. The sample can be run at night or on weekends.

Reduced time for analysis. We have been operating this system for about three years in our laboratory and have been able to demonstrate a cost savings over that period of time.

Typically, you can get improved precision. With the TSS system however, I think the nature of the sampling itself is such that we really don't see any benefit of improved precision over the manual method if the manual method is done real carefully.

Finally, there is what we call gained "new" time for R&D that we end up with for doing more interesting and challenging tasks in the environmental area. A lot of work needs to be done.

I believe that is it. I will take any questions, if you have any.

QUESTION AND ANSWER SESSION

MR. TELLIARD: I have a question.

When you take the sample and you have a lot of solids, do you shake it and then take 100 ml of that, or do you just get it from...when you get to your 100 ml volume? What do you start with, 2 liters or a liter that comes out of a sampler or something like that?

MR. RAIA: That is right. So, you take that sample, and you shake it initially to get that aliquot.

MR. TELLIARD: And then you put that in the volumetric and transfer it to the system?

MR. RAIA: Right.

MR. TELLIARD: Any problems with solids like sticking to the walls?

MR. RAIA: We haven't seen any, but that is something to be concerned about.

MR. TELLIARD: Any other questions as I am up here hogging the microphone?

MR. COLLAMORE: Martin Collamore, City of Tacoma.

How do you handle larger sample sizes than 100 ml?

MR. RAIA: We don't. We don't run a sample size larger than 100 ml.

MR. COLLAMORE: But you can handle lower samples? You can handle smaller samples?

MR. RAIA: Yes, we can handle smaller samples. We do handle samples more concentrated by diluting down if we need to, but in terms of total volume, we have only used up to 100 ml. You are limited to some extend there by the weight of that flask with the water. We really have not gone to larger sample sizes, and I don't know what maximum volume we could end up with, but this particular setup has been able to handle the type of samples that we typically deal with.

Some of our manufacturing locations also have a similar type of robotic system for doing TSS, and they are using a 100 ml sample volume also.

MR. TELLIARD: Thank you very much, Joe.

A LABORATORY ROBOTIC METHOD FOR THE AUTOMATED DETERMINATION OF TOTAL SUSPENDED SOLIDS IN ENVIRONMENTAL WATER SAMPLES

by

Joe C. Raia and Al Telfer
Shell Development Company
Houston, Texas

For Presentation at the

The Annual U.S. EPA Conference
on
Analysis of Pollutants in the Environment
Norfolk, Virginia
May 9-10, 1990

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ABSTRACT

This paper presents a new laboratory robotic procedure which automates the standard method for the determination of Total Suspended Solids (TSS) in environmental water and wastewater samples. The method also determines Volatile Total Suspended Solids (VTSS) with a minimum of operator intervention. The automated equipment, robotic procedure, and results are presented. The benefits of automation in the environmental analysis laboratory are discussed.

ACKNOWLEDGEMENT

The authors wish to acknowledge P. J. Drymala and R. A. Balderas of Shell Development Company for their assistance in this project.

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INTRODUCTION

Automation has been used in the analytical chemistry laboratory for many years. This has primarily included microprocessor controlled analytical instrumentation with dedicated autosamplers, continuous flow systems, and computerized data collection, calculation, and report generation. In recent years, laboratory automation has been extended by the use of robotics, combined with programmable computers, to new tasks which include sample preparation and even entire analytical determinations.

This article presents a laboratory robotic system for the determination of total suspended solids (TSS) in environmental water samples. The method adheres to the standard protocol that is specified for the manual procedure (US EPA Method 160.2) (1). It also performs Volatile Total Suspended Solids (VTSS) with a minimum of operator intervention. The robotic TSS procedure required the development of new robot-friendly modules and sensors not yet commercially available. These components and the automated analysis method are described. Results are presented which compare the robotic and manual procedures. The method has been validated and is currently in routine operation in our environmental analysis laboratories.

a) A portion of this paper is to be published in American Environmental Laboratory

THE TSS ANALYSIS LABORATORY ROBOTIC SYSTEM

The TSS analysis laboratory robotic system and associated equipment are shown in Figures 1 and 2. The system consists of the following major components:

1. A laboratory robot and controller (Zymark Corporation, Zymate I upgraded to a Zymate II system)
2. Three Zymate Power and Event Controllers (PEC)
3. A printer for the Zymate controller
4. A computer (IBM-XT) and printer with programms for communication with the Zymate, data calculation and report generation
5. A balance (Mettler AE163) with electronic interface and a remote pneumatic controlled door
6. An Oven, thermocouple controlled with pneumatic controlled door
7. A Desiccator with a remote pneumatic controlled door
8. Eight filtration stations
9. Capacitance sensing devices for eight positions
10. A pump and reservoir system to supply rinse water
11. A rinse dispenser station with pneumatic valve
12. A storage rack to hold 16 polypropylene, volumetric flasks (100ml) used for the samples
13. A custom built table top support frame with castors and leveling jacks to hold the robot table and hardware
14. Various actuators, sensors, and controls required by the system

One of the challenges encountered with the design of the robot system was the problem of how to sense that filtration had been completed. This problem also exists for sensing rinse completion. These problems were solved by detecting the amount of water in the Gooch crucible using a commercially available capacitance electronic package usually used for level sensing in tanks and vessels. The holder for the Gooch crucible in the filter station is made of two stainless steel parts. They are electrically separated by a rubber gasket, and form two plates of a capacitance measurment system. If a small amount of water is present within the Gooch crucible, a significant change in the capacitance output signal occurs.

In operation, the sequence of events is as follows: The robot gets the Gooch crucible with filter from the desiccator and moves it to the balance where the tare weight is obtained. Next, the robot takes them to the rinse station, where a small (2-3 ml) quantity of water is placed on the filter. This helps seal the filter to the crucible. The robot then places them into the filter station, and backs away. The vacuum is turned on to that filter station, and the capacitance electronics system takes a reading of the base capacitance. This is accomplished using the switched outputs available at the Power and event controllers, as well as the A/D input. The output of the capacitance electronics system is a 4-20 milliampere signal. This is converted to a voltage at the PEC switches using a 50 ohm resistor. This voltage reading is stored in the robot controllers memory for further use. The robot then gets the proper sample flask from the storage rack and inverts the flask into the crucible. The robot leaves the flask in a holder on top of the filter station, with the neck of the flask below the top of the rucible. This allows up to 100 ml of sample to be filtered using a crucible of about 40 ml capacity. It will not overflow since the neck of the flask is sealed below the liquid surface. The robot backs away and a second capacitance measurment is made. If the filtration is complete, this second reading will approach the base reading, and the vacuum will be shut off for that filter station. If not, the robot proceeds with loading the next sample and rechecks all loaded stations until filtration is complete. The rinse procedure operates in exactly the same way. The samples can sit for some time without affecting performance as long as the vacuum is off. If the filter gets too dry, some samples seem to get a water-proof like coating that may hinder rinse procedure. Conversely, the filter must not be too wet, particularly when the crucible is placed in the oven. For this reason the program pauses after the final rinse and before the crucible is loaded into the oven, while vacuum is applied to all occupied filter stations. After drying at 105 C, the crucible is moved to the desiccator to condition and then weighed. Constant weight is verified by redrying the crucible for a half hour and reweighing. If volatile suspended solids are measured, the crucibles and dried solids are moved by the analyst to a 550 C furnace. After 45 minutes, the crucibles are allowed to cool ambiently, and then placed in the desiccator before being weighed as before.

The Zymate II system is interfaced with an IBM-XT-PC to perform the data calculation and report generation of the TSS and VTSS results.

RESULTS

The robotic procedure has been validated for unattended operation, and for precision and accuracy. Comparison data of the robotic and manual procedures are shown in Tables 1 and 2. Results in Table 1 show that the precision of both methods is good and the values are comparable for the biotreater aeration basin samples tested. Any precision gains offered by robotics are likely obscured by variability in the sampling of these wastewaters. The robotic procedure resulted in a 7% lower mean TSS value than did the manual method for the aeration basin samples tested. No consistent bias in the data, however, has been found for either procedure. Results in Table 2 compare the recovery of the robotic and manual procedures for TSS in standard samples prepared at various concentration levels for round-robin testing. Data for an in-house control are also given. The robotic and manual procedures both showed comparably good recovery for these round-robin samples. The robotic method values were in the 94% - 107% range, and the manual method values were in the 83% - 97% range. The mean recovery of the fifty labs which participated in this APG sample set were in the 91% - 95% range. Linearity of TSS with volume of sample filtered is shown in Figure 3 for the robot and manual methods. Typically, the volume of sample taken for analysis is such that it can be filtered in a reasonable time period and yet be enough to yield sufficient solids for accurate weighing.

Analyst time required for the robotic procedure is less than one-third that for the manual procedure. The capital investment required for the robotic TSS method has been recovered in about the first 200 days of operation with the current sample throughput demand. The analyst has welcomed the automated robotic TSS procedure. The responsibility for operating the robotic instrumentation is viewed as a more interesting task than the manual procedure, and gained "new" time can now be focused on more creative method development and special problem solving challenges in the environmental analysis area.

REFERENCES

1) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

TABLE 1. COMPARISON OF TSS RESULTS BY ROBOTIC AND MANUAL METHODS

SAMPLE:	BENCH SCALE BIOTREATOR		AERATION BASIN	
METHOD:	ROBOTIC TSS MG/L	MANUAL TSS MG/L	ROBOTIC TSS MG/L	MANUAL TSS MG/L
	10670.	9670.	122.4	139.2
	10130.	10590.	115.2	152.0
	11631.	10250.	125.6	127.6
	11219.	11130.	123.2	130.0
	10820.	10540.	118.4	128.8
	9981.	10320.	122.8	128.4
	10761.	11530.	116.8	126.4
	10200.	10640.	141.2	124.8
MEAN	10676.	10584.	123.2	132.2
S.D.	566.	562.	8.1	9.1
C.V.(%)	5.3	5.3	6.6	6.9

TABLE 2. RECOVERY RESULTS FOR TSS BY ROBOTIC AND MANUAL METHODS

SAMPLE	TRUE TSS MG/L	ROBOTIC % RECOVERY	MANUAL % RECOVERY	MANUAL APG*** MEAN % REC.
APG # 1*	36.5	107.	83.0	92.5
APG # 2*	52.7	94.9	96.8	90.7
APG # 3*	77.0	93.5	92.2	90.7
APG # 4*	287.0	107.	94.8	94.2
APG # 5*	316.8	98.7	97.2	94.6
APG # 6*	498.6	94.9	96.3	94.2
KAOLIN CONTROL**	100.	104.	95.6	

* Proficiency Environmental Testing Program Samples: prepared and provided by Analytical Products Group(APG), Inc., Belpre, Ohio

** In-house control sample

*** Mean Recovery of 50 labs participating in the APG Program

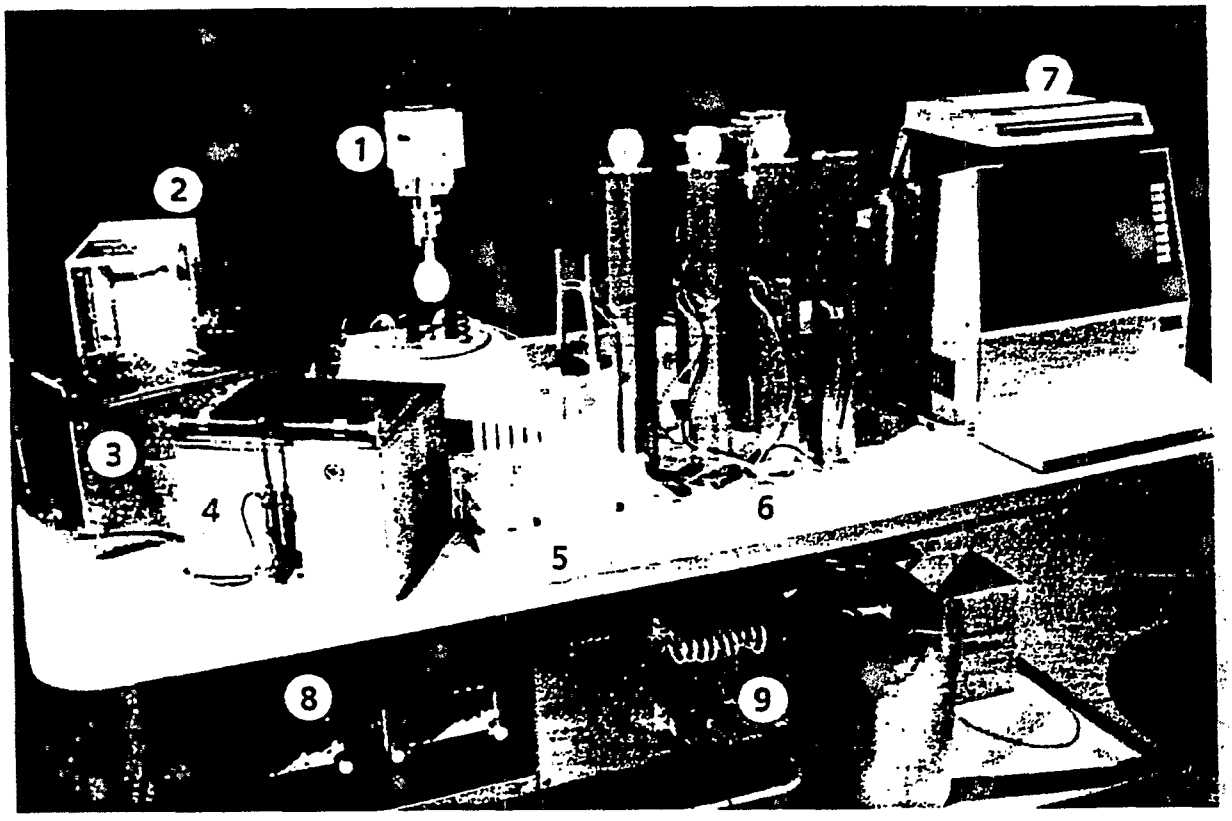

Figure 1. Robotic TSS Equipment

1. Zymark Robotic Arm
2. Balance
3. Desiccator
4. Oven
5. Flask Rack
6. Filtration Stations with Capacitance Sensors
7. Zymate Controller
8. Capacitance Sensors Electronics
9. Pneumatic Valves for Vacuum and Pressure

09941

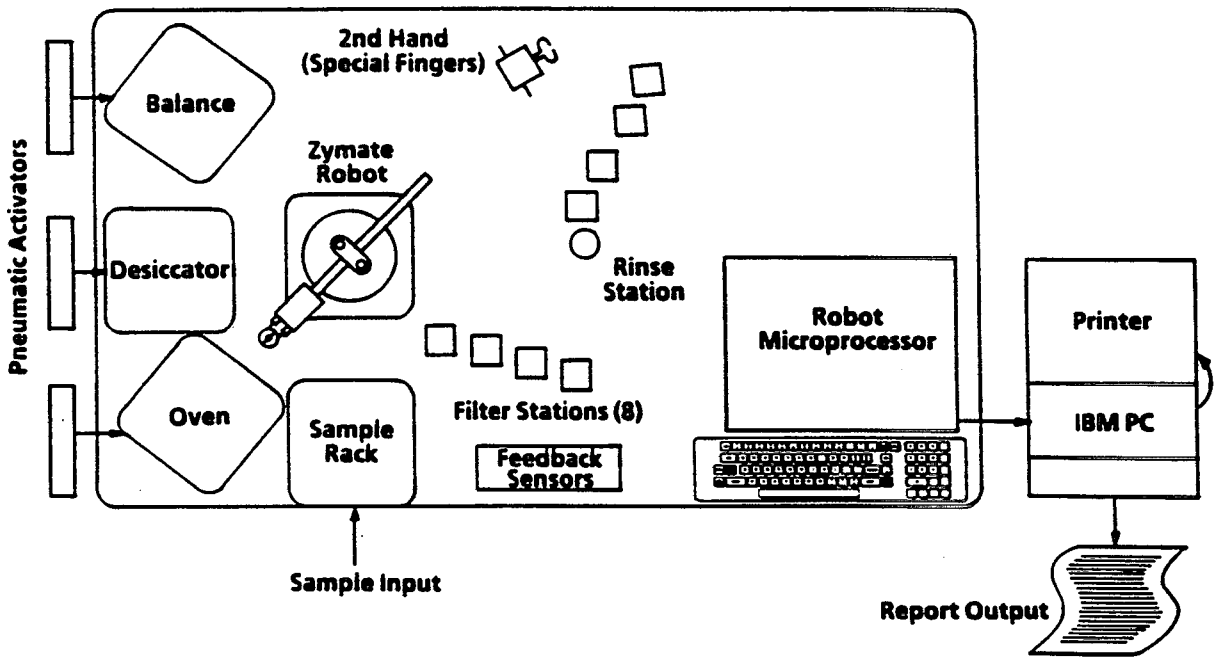

Figure 2. TSS Robot

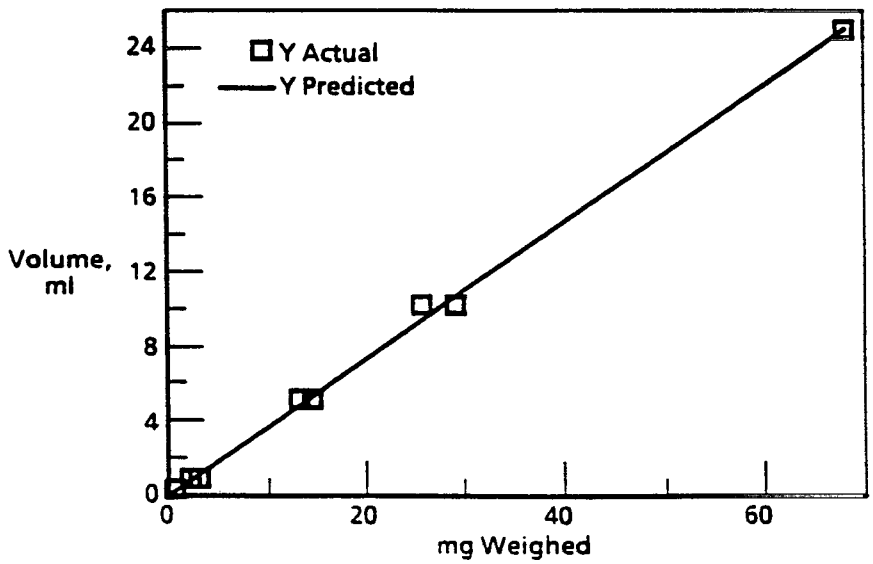

Figure 3. TSS Linearity with Sample Volume
mg Weighed vs. Volume, Manual and Robot

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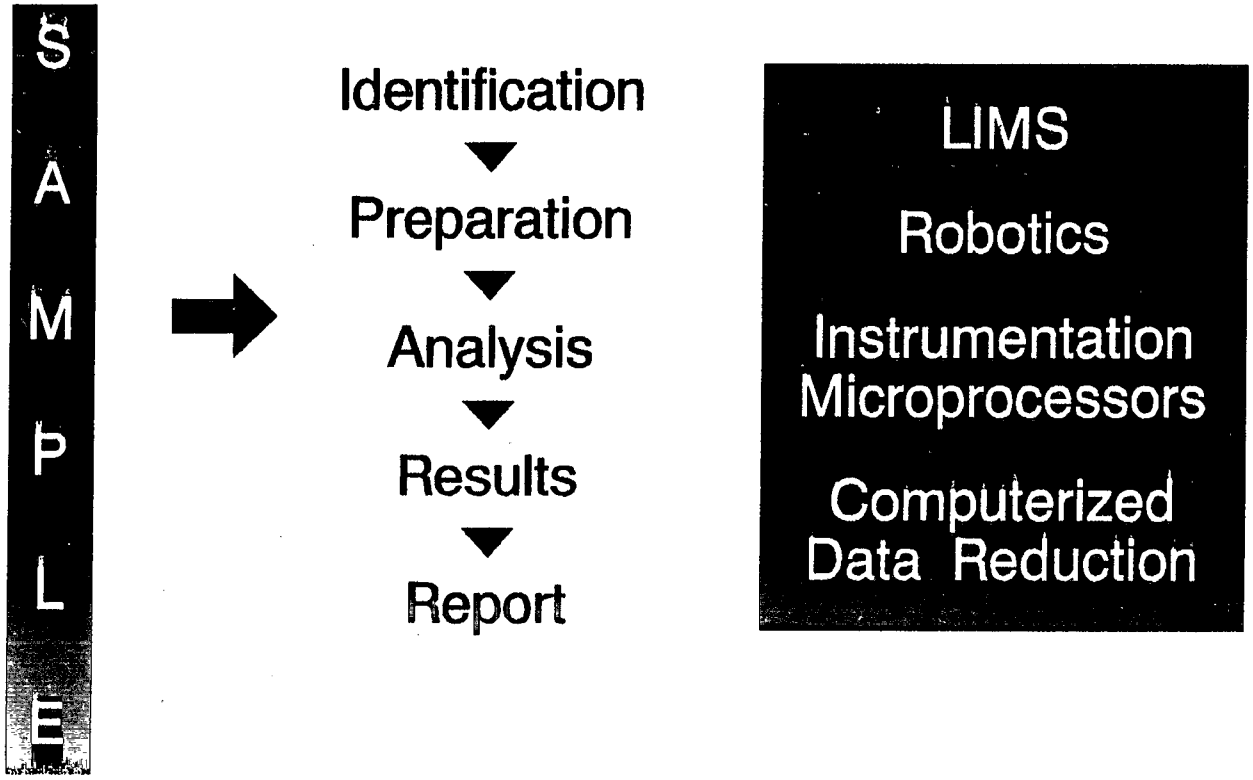
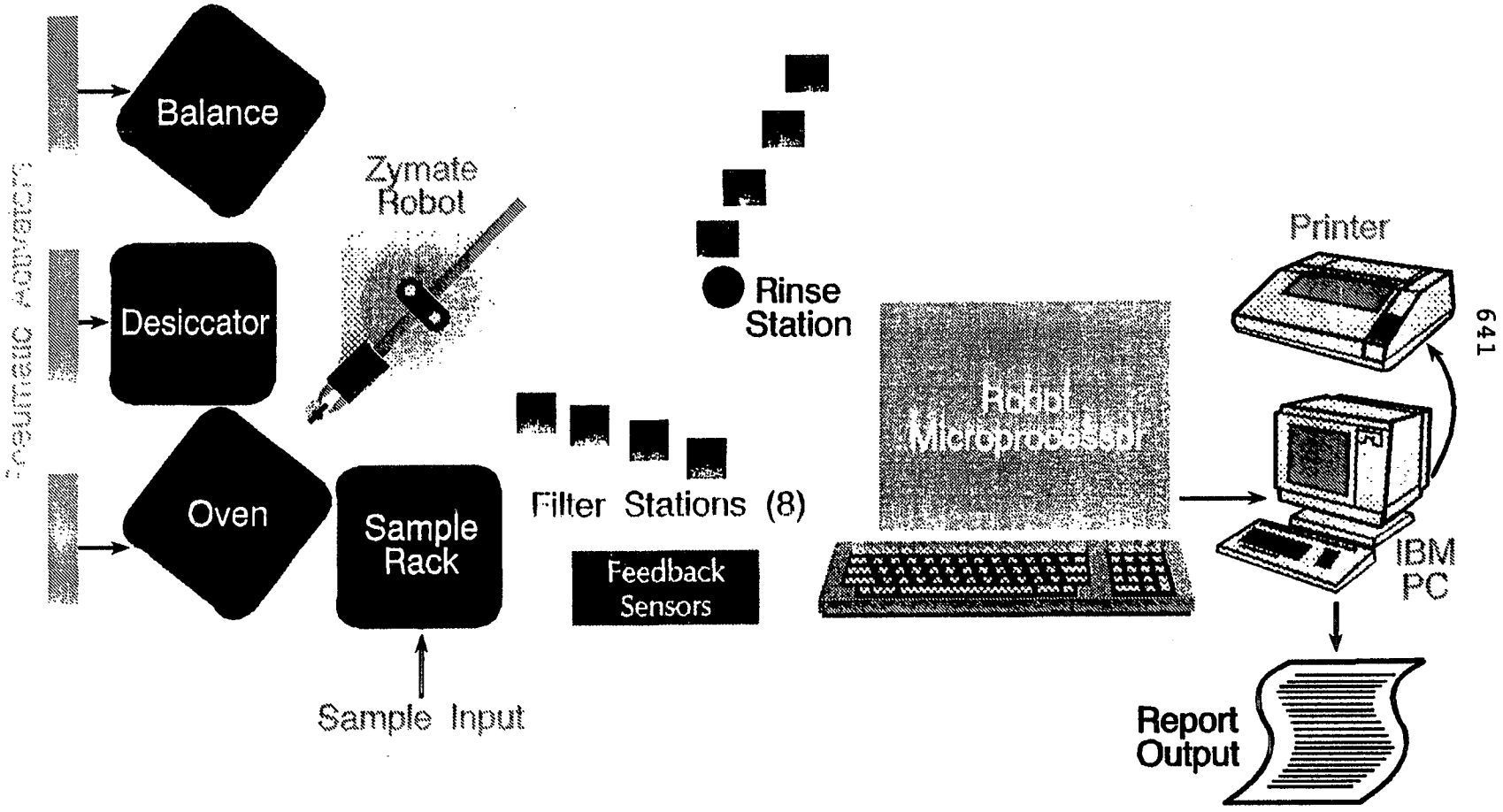
Automation in the Analytical Chemistry Laboratory



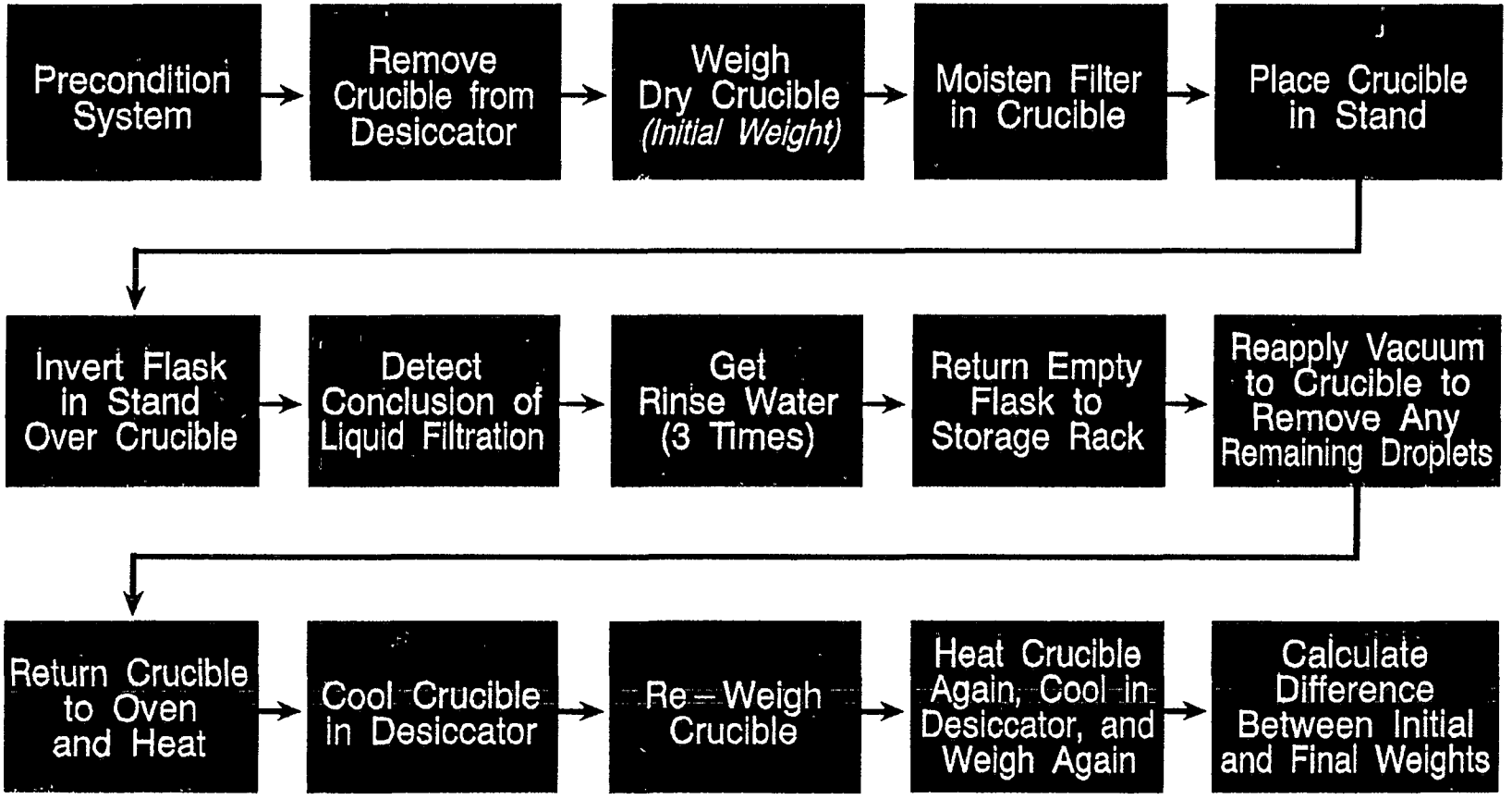
The TSS Analysis Laboratory Robotic System

- Measures Total Suspended Solids in Water
- Follows the Standard Procedure (EPA Method 160.2)
- Measures Volatile Residue (EPA Method 160.4)

TSS Robot


Balance
Desiccator
Oven
Zymate Robot
Sample Rack
Sample Input
Rinse Station
Filter Stations (8)
Feedback Sensors
Printer
IBM PC
Report Output

Robotic TSS Procedure



Comparison of TSS Results by Robotic and Manual Methods

	Bench Scale Biotreater Aerator 61786		*Aerator Basin*	
	Robotic TSS, mg/l	*Manual TSS, mg/l*	*Robotic TSS, mg/l*	*Manual TSS, mg/l*
Method	10670	9670	122.4	139.2
	10130	10590	115.2	152.0
	11631	10250	125.6	127.6
	11219	11130	123.2	130.0
	10820	10540	118.4	128.8
	9981	10320	122.8	128.4
	10761	11530	116.8	126.4
	10200	10640	141.2	124.8
Mean	10676	10584	123.2	132.2
S.D.	566	562	8.1	9.1
C.V.(%)	5.3	5.3	6.6	6.9

Recovery Results for TSS by Robotic and Manual Methods

	True TSS, mg/l	*Robotic WRC % Recovery*	*Manual WRC % Recovery*	*Manual APG Mean % Rec* [c]
APG #1[a]	36.5	107.0	83.0	92.5
APG #2[a]	52.7	94.9	96.8	90.7
APG #3[a]	77.0	93.5	92.2	90.7
APG #4[a]	287.0	107.0	94.8	94.2
APG #5[a]	316.8	98.7	97.2	94.6
APG #6[a]	498.6	94.9	96.3	94.2
Kaolin Control[b]	100.0	104.0	95.6	

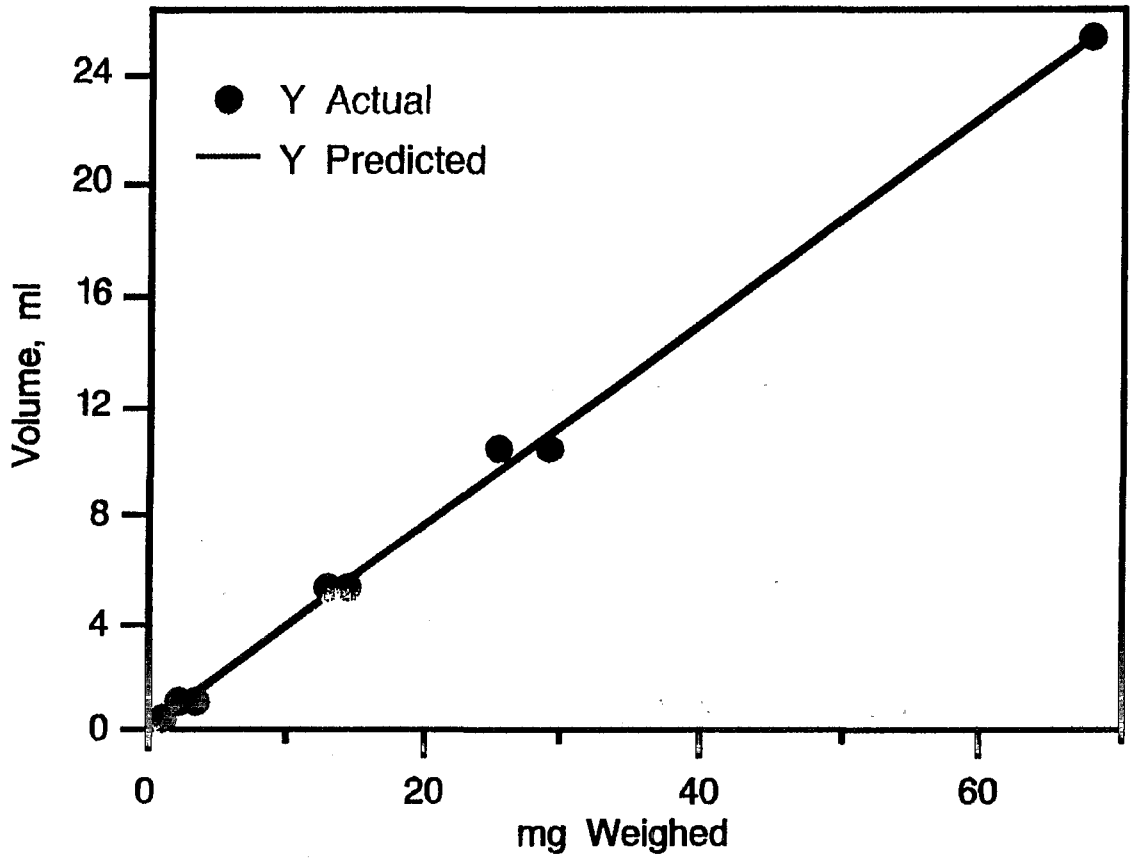
a) Proficiency Environmental Testing Program Samples: prepared and provided by Analytical Products Group (APG), Inc., Belpre, Ohio.

b) In-house control sample.

c) Mean recovery of 50 labs participating in the APG Program.

TSS Linearity with Sample Volume

mg Weighed vs. Volume, Manual and Robot



Benefits of Lab Automation

- Unattended Operation
- Reduced Time/Analysis
- Improved Precision
- Gained "New" Time for R&D

MR. TELLIARD: Our next speaker was supposed to be Cary Jackson, but I found out they had some real technical work to do at the lab, so instead of him, they sent Dale. Dale is going to talk about some pesticide analysis using the Dean Stark extractor and isotope dilution GC/MS.

Determination of Semivolatile Pollutants in Sewage Sludge by Soxhlet/Dean-Stark Extraction, High Performance Liquid Chromatography Cleanup, and Isotope Dilution Gas Chromatography/ Mass Spectrometry

Cary B. Jackson and D.R. Rushneck, Analytical Technologies, Inc., 225 Commerce Drive, Fort Collins CO 80524, and John Tessari, Colorado Epidemiological Pesticide Study Center, Colorado State University, Fort Collins CO 80523.

ABSTRACT

This paper gives the results of the determination of semi-volatile pollutants in sewage sludge using Soxhlet/ Dean-Stark (SDS) extraction, preparative scale high performance liquid chromatography (HPLC) cleanup, and isotope dilution gas chromatography/mass spectrometry (GCMS).

Large scale (70 gram) sludge samples were extracted by SDS, continuous liquid/liquid, soxhlet, and ultrasonic extraction techniques. All of these techniques resulted in large amounts of interferences being co-extracted with the compounds of interest.

Results showed that SDS extraction is more efficient at extracting the compounds of interest than the other techniques, but it is also more efficient at extracting interfering compounds.

HPLC improves cleanup slightly, but not sufficiently to make this technique desirable as a standard cleanup procedure.

The conclusion from these tests is that large-scale sewage sludge samples will require further, alternative cleanup techniques before reliable measurements of the semi-volatile pollutants at the part-per-billion level in the solid phase of the sludge can be made.

BACKGROUND

EPA has been attempting to measure the semi-volatile and pesticide pollutants in sewage sludge at the part-per-billion (ppb) and sub-ppb level since the early 1970's. Those familiar with the determination of these analytes in sewage sludge will expound at length on how difficult these determinations are, mainly because of the large concentrations and large number of interfering substances in the sludge. A variety of different approaches have been tried in attempts to improve the precision and accuracy of measurements, and to lower the detection limit for the pollutants of interest.

The use of isotope dilution gas chromatography/mass spectrometry (GCMS) and gel permeation chromatography (GPC) have been helpful in improving the measurement of pollutants in sludge. Further improvements in cleanup are limited by the desire to measure analytes with a wide variety of chemical species. Thus, the normal cleanup techniques that may be effective for a small group of similar compounds (e.g., sulfuric acid cleanup of sludge extracts for determination of polychlorinated biphenyls) cannot be used for cleanup of normal and polynuclear aromatic hydrocarbons, amines, phenols, ethers, and other species because of the destruction or removal of many of these species by the cleanup

technique.

Against this background, this study attempted to employ Soxhlet/Dean-Stark (SDS) extraction and preparative scale high performance liquid chromatography in addition to GPC and isotope dilution GCMS as techniques for selective extraction and for large scale cleanup of sludge extracts. The study objectives are shown in Figure 1.

SLUDGE

The sewage sludge used for all measurements was filter cake obtained from a nearby publicly owned treatment works (POTW). The characteristics of this sludge are shown in Figure 2.

The sludge contained 14 percent solids. EPA Method 1625, the isotope dilution method for determination of semi-volatile pollutants, employs either continuous liquid/liquid extraction (CLLE) or ultrasonic (sonic) extraction, depending on the solids content of the sample. If the percent solids is less than one, the sample is extracted directly. If the percent solids is in the range of 10 - 30, the sample is diluted with reagent water to one percent solids (10 grams in one liter) and extracted using CLLE. If the percent solids is 30 percent or greater, the sample is extracted using the sonic technique.

In order to test SDS and other extraction techniques, a mass of 10 grams of solids was chosen. At 14 percent solids, the weight of sludge sample was therefore 70 grams. The 10 gram mass of solids is at the break point between the use of CLLE and sonic extractions; i.e., this mass would be required if the sludge contained 30 percent solids.

Method 1625 requires the use of a "dilute aliquot" when interferences are know or suspected. For the dilute aliquot, the sample is diluted by a factor of 10 and this diluted sample is then analyzed. The dilute aliquot was not employed in this study because it is well known that one gram of sludge solids can be successfully analyzed by Method 1625 as written.

OVERVIEW OF EXTRACTION/CLEANUP

In order to determine the effectiveness of SDS extraction, the SDS technique was compared to several other techniques, as shown in Figure 1. The solvent systems used are given in the figure.

An overview of the extraction and cleanup processes are shown in Figure 3. For each extraction technique, an aliquot of sludge was extracted after spiking with the stable isotopically labeled compounds, a second aliquot was extracted after spiking with the labeled compounds and pollutants, and a third aliquot was extracted unspiked. The spiking level was 100 ng for each component.

Extracts were concentrated to 10 mL final volume and processed through the GPC. In this process, 50 percent of the extract is recovered. Each 5 mL GPC eluate was concentrated to 0.5 mL (to compensate the 50 percent loss). The 0.5 mL concentrated eluate was split in two. One of these splits was spiked with internal standard and a one microliter aliquot was injected into the GCMS. This aliquot permitted comparison of the extraction techniques.

The remaining halves of the concentrated GPC eluates from the SDS extraction technique were subjected to HPLC cleanup. The

concentrated GPC eluate from the unspiked sludge was spiked with the pollutants and labeled compounds so that losses associated with the sludge matrix during HPLC cleanup could be quantified. In addition, a standard containing the pollutants and labeled compounds was processed through the HPLC to measure losses in the absence of the sludge matrix.

After HPLC cleanup, the HPLC eluates were re-concentrated to 250 uL, the internal standard was added, and one microliter aliquots were injected into the GCMS.

SOXHLET/DEAN-STARK EXTRACTION

SDS extraction employs a moisture trap in combination with a Soxhlet extractor, as shown in Figure 4. The successful application of this technique to determination of chlorinated dioxins and furans has been reported (reference 1), and the technique is part of EPA Method 1613 for dioxin/furan measurements.

The apparatus uses a lighter than water solvent that forms an azeotrope with water for the extraction. Most commonly, the solvents employed have been benzene and toluene. The azeotrope is condensed and falls into the moisture trap where the water settles to the bottom of the trap. The water can be drained and measured either gravimetrically or volumetrically. The percent moisture in the sample can then be calculated based on the sample weight.

In applying the SDS extraction technique, we believed that the use of a slightly polar solvent (benzene) would reduce the quantity of interferences co-extracted from the sludge, yet would permit extraction of the components of interest.

HPLC CLEANUP

This cleanup employed a preparative scale column with the characteristics shown in Figure 5. The column was operated isocratically with acetonitrile as the eluting solvent in a Waters HPLC system with an ultra-violet (UV) detector operated at 254 nm.

RESULTS

Chromatograms

Figures 6 - 10 show reconstructed ion current (RIC) chromatograms comparing the various extraction techniques. These chromatograms are scaled to the largest peak. The fine structure in these chromatograms give an indication of how much material is being extracted and how readily the components of interest can be measured.

The small, well defined peaks at the beginning of these chromatograms are the labeled compounds and can be used to compare the total amounts of material extracted, and to indicate the degree of difficulty in locating the labeled and native compounds in the sample matrix.

Chromatograms of the base/neutral and acid extracts are analyzed separately in Method 1625. As shown in Figures 6 and 7, keeping these extracts separate provides an improvement over the bulk simultaneous extraction of the base/neutral and acid analytes, as evidenced by Figures 8 - 10.

The chromatogram in Figure 10 gives an indication that much more material is extracted using the SDS extractor than with the other extraction techniques. Nearly all of the analytes are

masked by the large amount of material extracted from the sample matrix. The two large peaks in this chromatogram, and at or near the same retention time in all of the chromatograms are hexadecanoic and octadecanoic acid.

Comparison of Extraction Methods

Figure 11 compares the concentrations of pollutants detected by the various extraction methods. In reducing the GCMS data, a formidable problem is presented in attempting to identify the pollutants. Spectra are heavily contaminated by interfering compounds, and the quantitation m/z is frequently inflated by a contribution from one or more of these compounds. It must be reiterated that the sample size used for these analyses is larger than normally attempted, so the lack of complete success in rigorously determining the concentration and identity of the pollutants of interest is attributable to this large sample size.

Further, the seeming lack of success of identifying pollutants from the SDS extraction can be attributed to the large amounts of interfering materials co-extracted from the matrix.

HPLC Cleanup

Figures 12 and 13 allow comparison of the HPLC chromatogram of the 100 ug/mL pollutant standard with that of the spiked SDS extract. The similarities in the chromatograms exist because the UV detector responds primarily to the polynuclear aromatic compounds in these solutions and a lack of naturally occurring polynuclear aromatics in the sludge. The detector is attenuated to bring the chromatograms on scale. Even so, saturation of the

detector occurs in the beginning of the HPLC run for the SDS extract.

Figure 14 compares the number of compounds detected before and after HPLC cleanup with that of a standard containing all 74 labeled and 82 native compounds. As can be seen, HPLC cleanup improves the number of compounds detected in the SDS extract, but HPLC cleanup also removes some of the analytes of interest. The analytes removed consist mainly of the normal hydrocarbons that elute on the tail of the chromatogram (see Figures 12 and 13).

CONCLUSIONS

From the test results presented in this report, it can be concluded that:

(1) Soxhlet/Dean-Stark extraction is more efficient at extracting substances from the sludge matrix. Unfortunately, the greater numbers and amounts of substances extracted mask the compounds of interest.

(2) HPLC provides a slight improvement in cleanup of sludge extracts. Unfortunately, some analytes of interest are lost in this cleanup.

(3) Large amounts of sludge (10 grams of solids) cannot be effectively extracted and cleaned up by the techniques tested in this work. Based on experience with other sludge samples, smaller amounts of sludge (1 - 3 grams of solids) can be effectively extracted and cleaned up using continuous liquid/liquid extraction and gel permeation chromatography.

REFERENCE

Lamparski, L.L., and Nestrick, T.J., "Novel Extraction Device for the Determination of Chlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Matrices Containing Water", Chemosphere, 19:27-31, 1989.

SDS EXTRACTION AND HPLC CLEANUP OF SEWAGE SLUDGE

OBJECTIVES

COMPARE SDS EXTRACTION WITH OTHER METHODS
ASSESS CLEANUP PROVIDED BY HPLC
ACHIEVE LOW DETECTION LIMITS IN SLUDGE

EXTRACTION METHODS COMPARED

METHOD	SOLVENT
SOXHLET/DEAN-STARK	BENZENE
SOXHLET	CH2CL2
CONTINUOUS	CH2CL2
SONICATION	CH2CL2/ACETONE

FIGURE 1
STUDY OBJECTIVES

SDS/HPLC

SLUDGE USED

TYPE: FILTER CAKE

PERCENT SOLIDS: 14

SAMPLE SIZE: 70 GRAMS
14 % SOLIDS x 70 g = 10 g SOLIDS
10 g SOLIDS IS CLLE/SONIC BREAKPOINT IN 1625

FIGURE 2
SLUDGE CHARACTERISTICS

OVERVIEW FLOW CHART

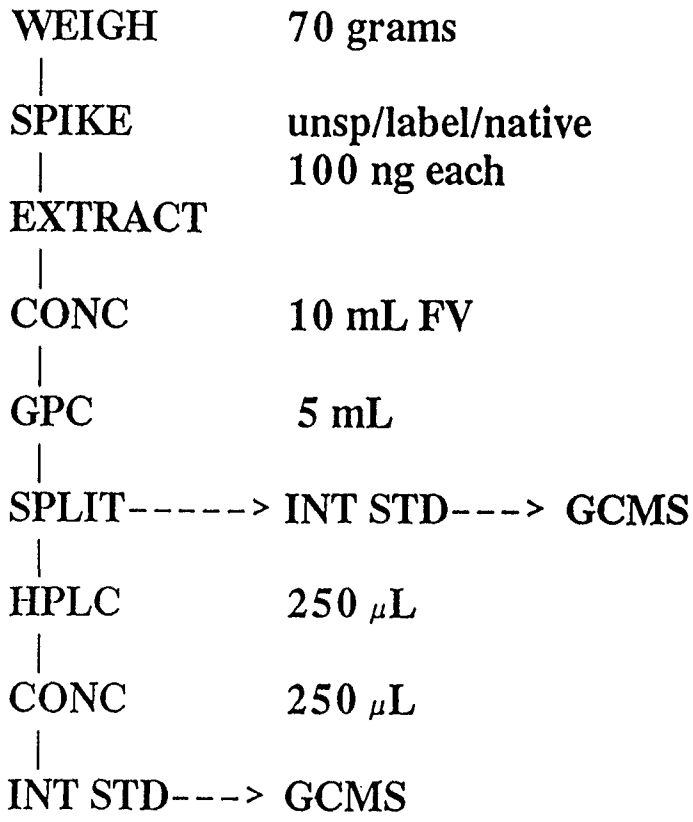


FIGURE 3
OVERVIEW OF EXTRACTION AND CLEANUP

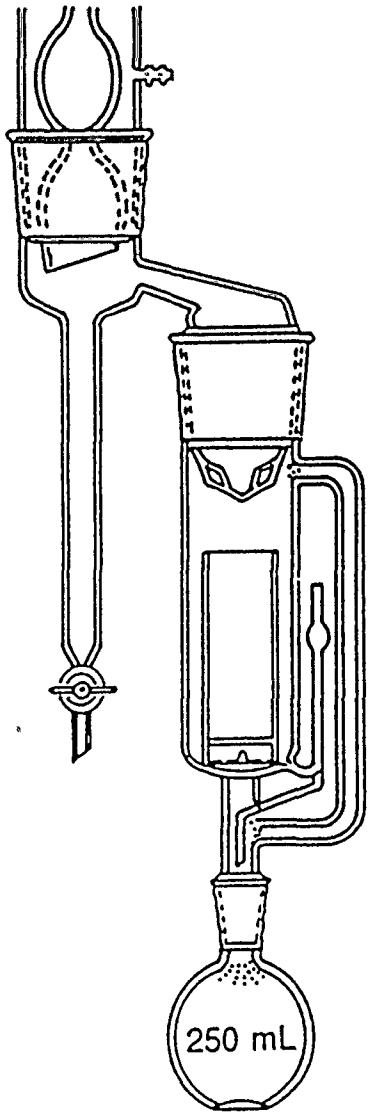


FIGURE 4
SOXHLET/DEAN-STARK EXTRACTOR

HPLC CLEANUP

COLUMN
TYPE: μBONDAPAK (WATERS)
DIMENSIONS: 2.5 X 10 CM
MATERIAL:
C18
125 Å; 10 μ
MOUNTING DEVICE: RADIAL MODULE

SOLVENT & FLOW RATE
ACETONITRILE
ISOCRATIC @ 5 ML/MIN

T99

FIGURE 5

CLLE ACID EXTRACT AFTER GPC

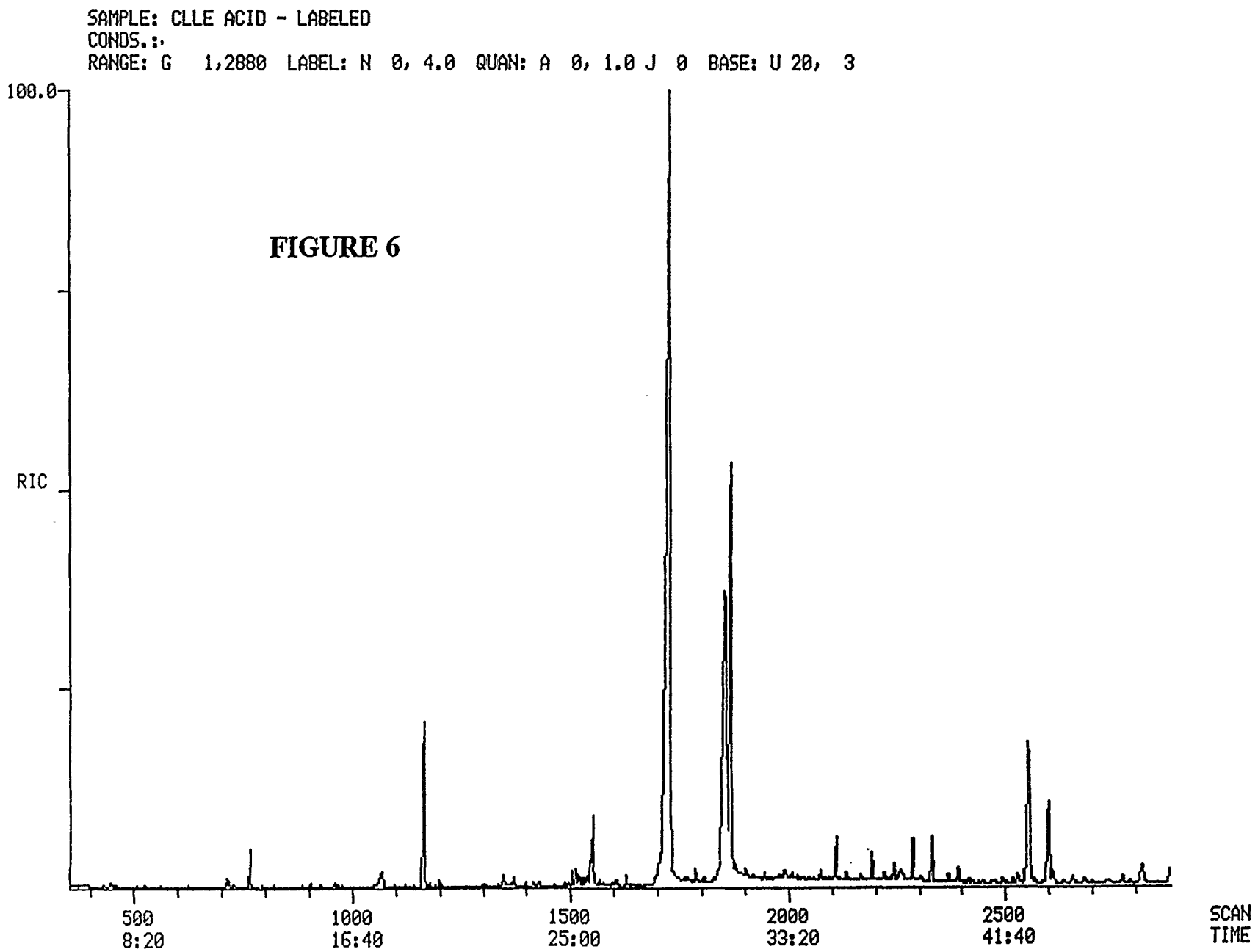


FIGURE 6

CLLE B/N EXTRACT AFTER GPC

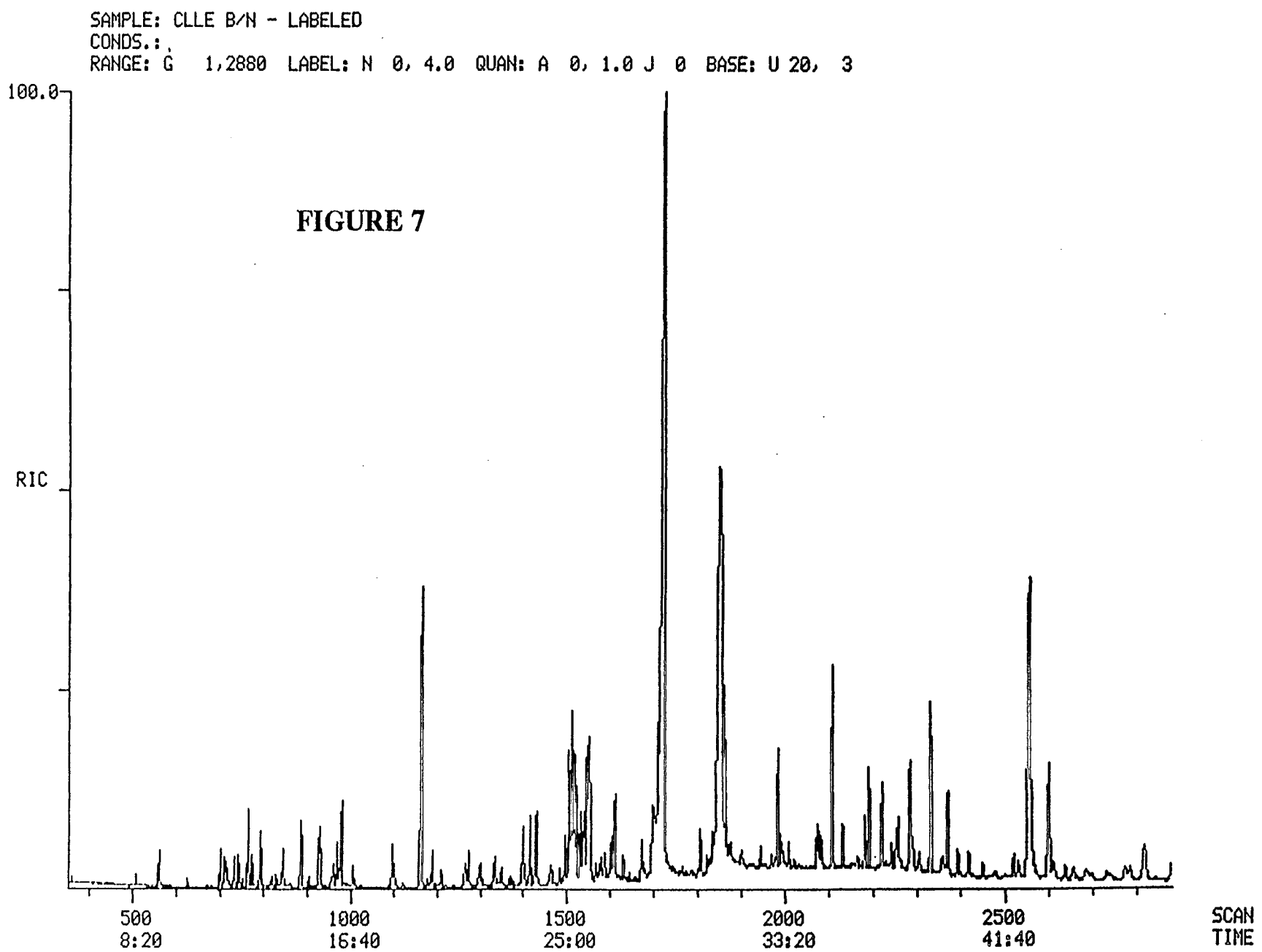


FIGURE 7

SOXHLET EXTRACT AFTER GPC

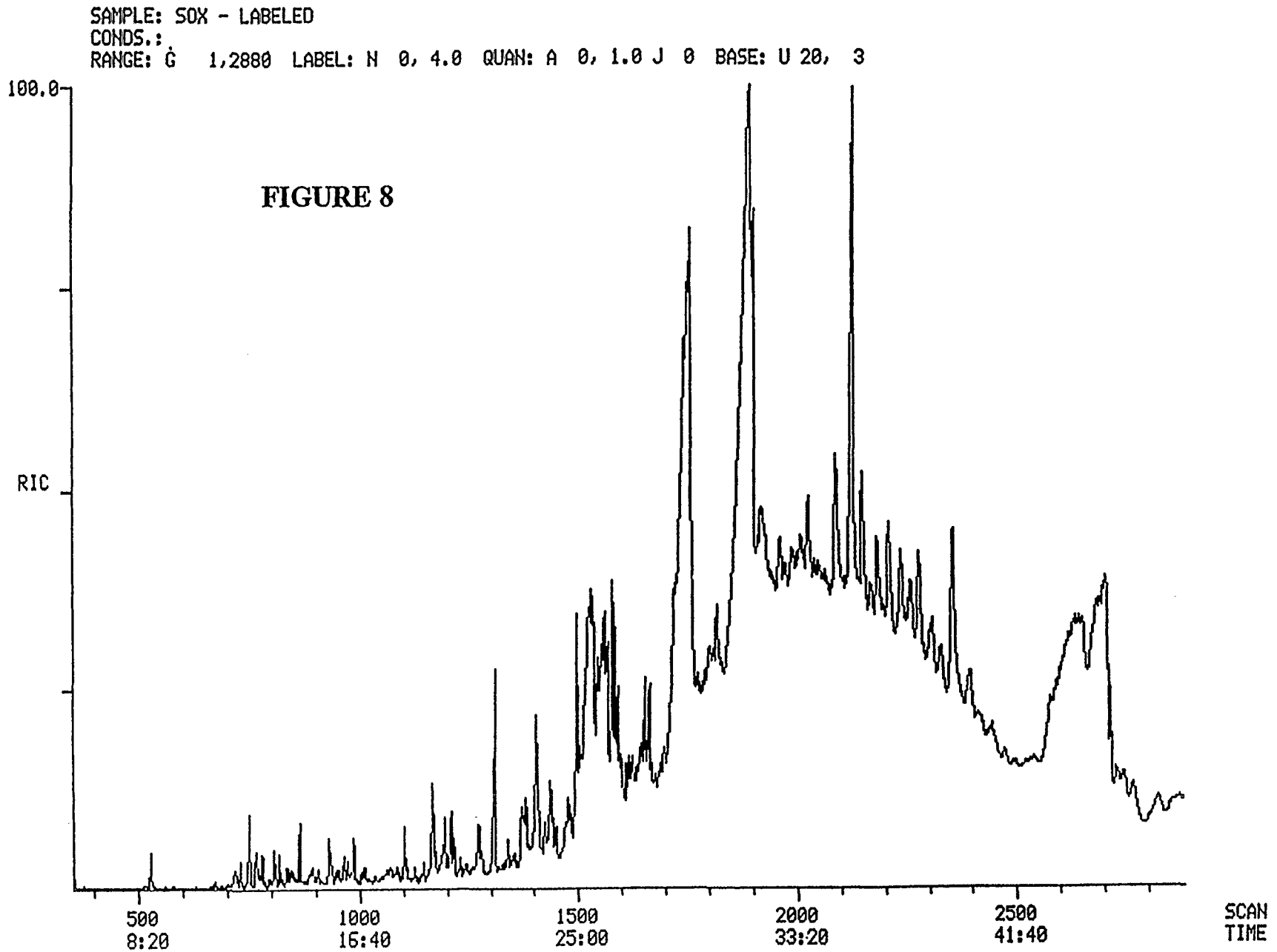


FIGURE 8

SONIC EXTRACT AFTER GPC

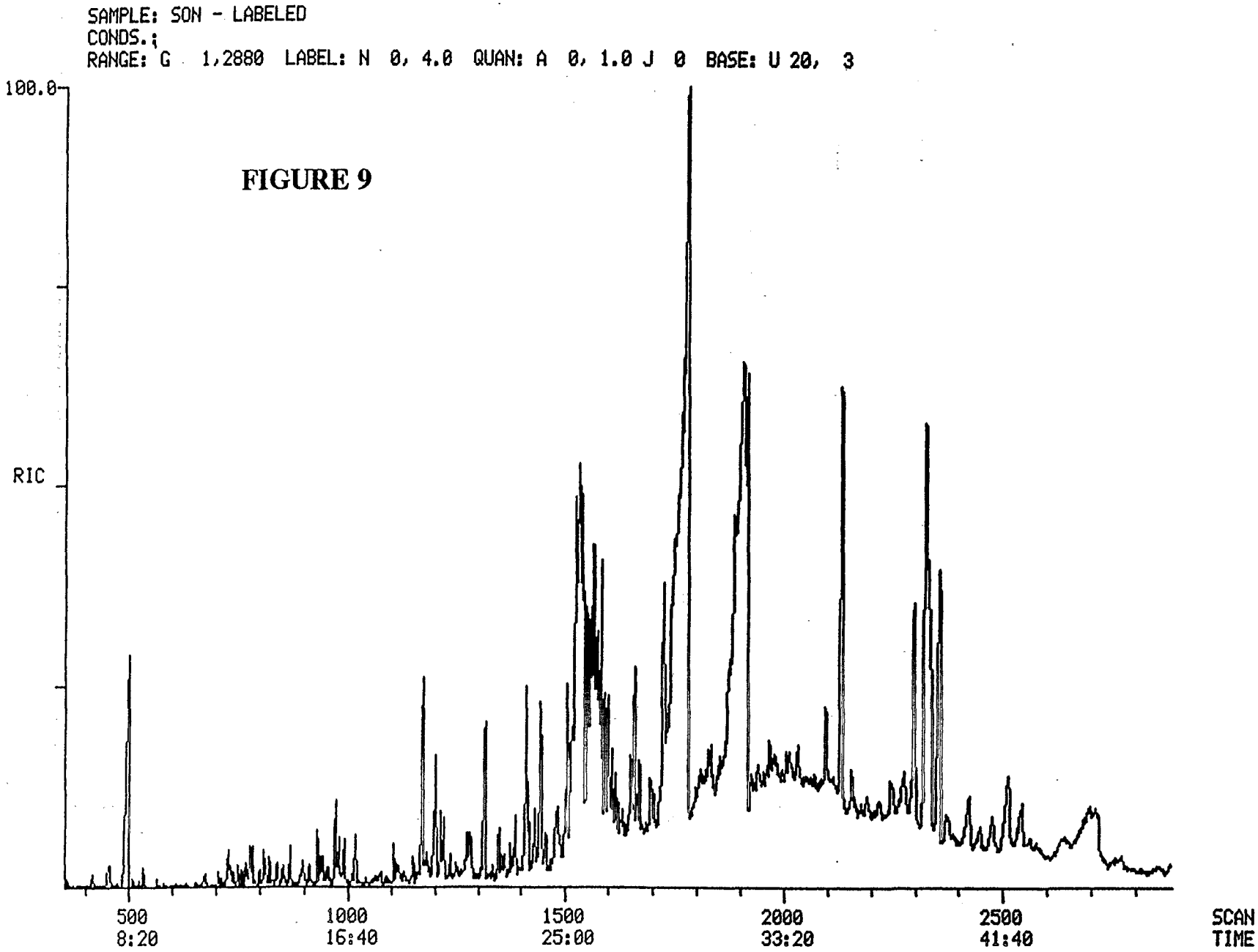


FIGURE 9

SDS EXTRACT AFTER GPC

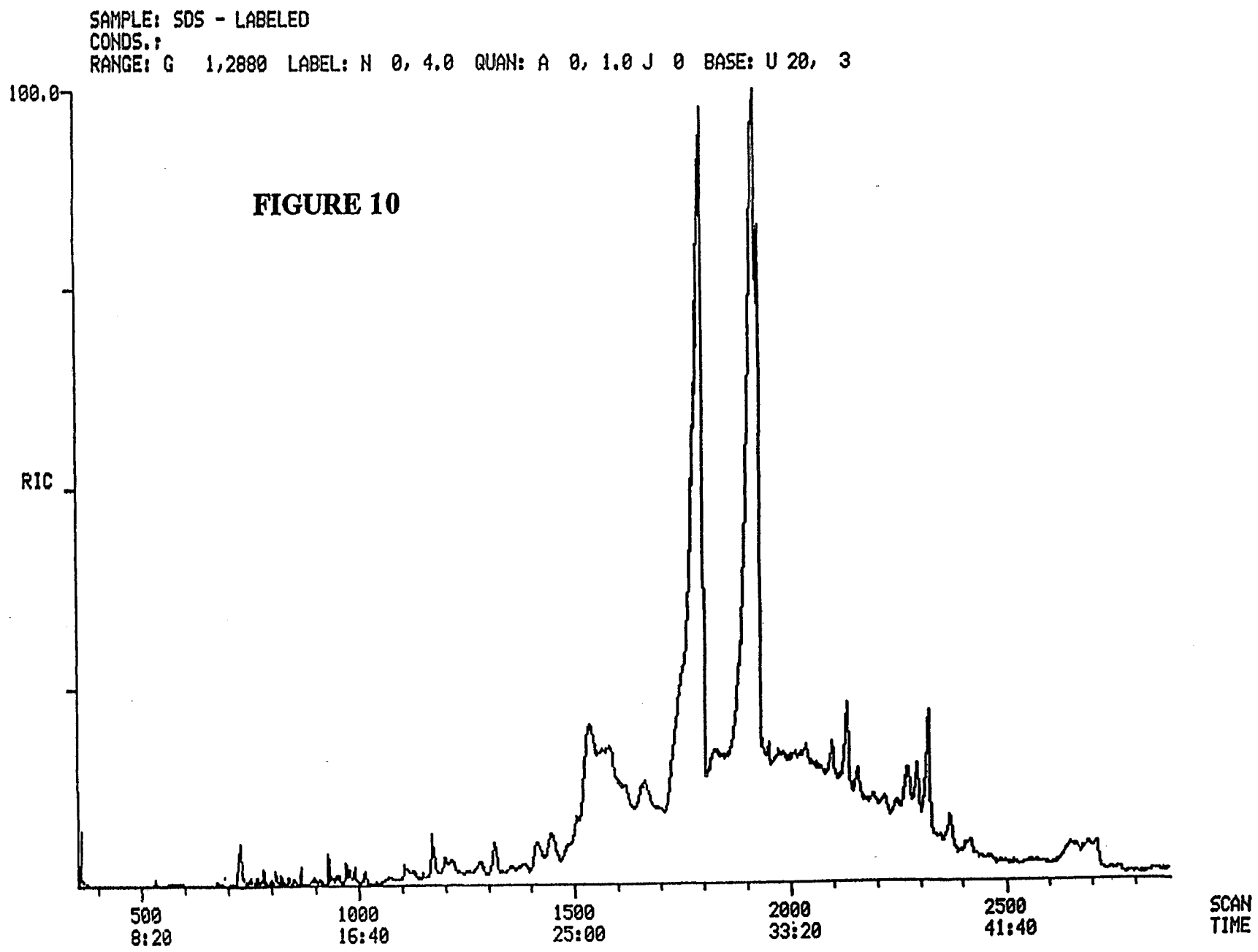


FIGURE 10

COMPOUNDS DETECTED

	CONC IN SOLIDS (mg/kg)					
	ACD	B/N	SOX	SDS	SON	SDS
PHENOL	1	-	7	-	-	-
n-C10	-	1	43	7	24	-
1,3-DICHLROBZ	-	1	4	1	1	-
p-CYMENE	-	3	24	8	6	-
NAPHTHALENE	-	1	2	2	1	2
n-C12	-	-	2	2	1	-
BIPHENYL	-	-	26	16	4	24
ACENAPHTHENE	-	-	1	0.1	1	-
n-C16	-	5	32	3	9	-
DIBUTYLPHTH	-	3	0.5	-	-	0.7
n-C20	-	1	57	14	0.5	9
BIS(2ETHEX)PH	140	12	150	-	1500	112
n-C30	31	3	8	-	-	-
PHENANTHRENE	-	-	-	-	-	2
DIOCTYLPHTH	-	-	-	-	-	3

FIGURE 11
RESULTS OF EXTRACTION METHODS

HPLC OF SDS EXTRACT (AFTER GPC)

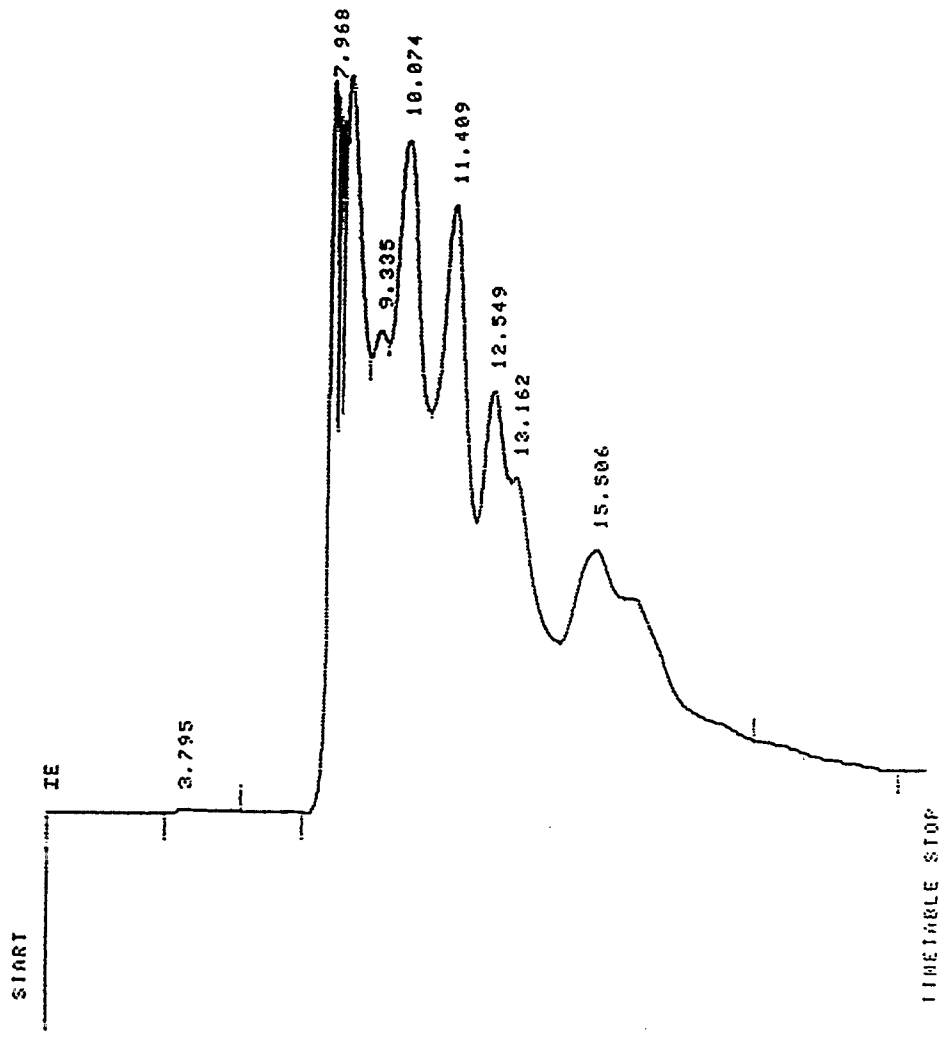


FIGURE 12

HPLC OF 100 μg/mL NATIVE STANDARD

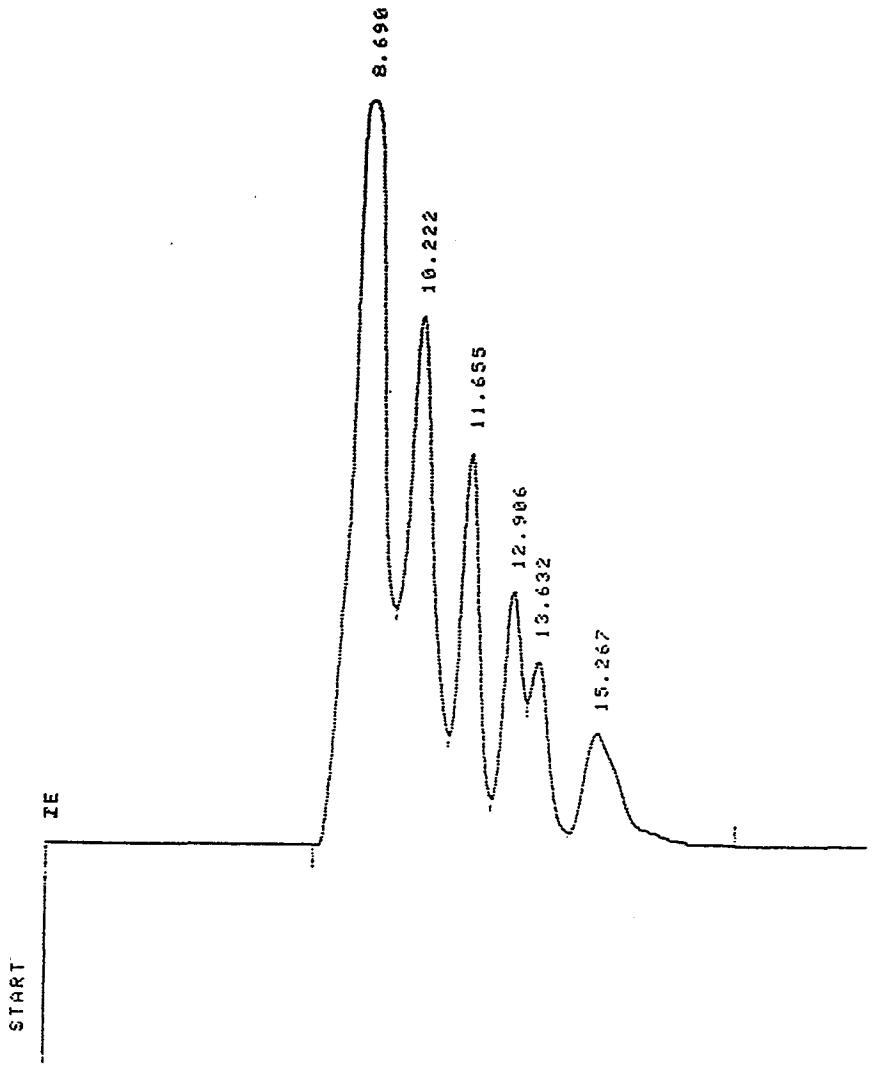


FIGURE 13

SDS + HPLC RESULTS

	SDS EXTRACTED EXTRACT		SDS EXTRACTED AFTER HPLC			
					SPIKED	
	LBL	NAT	LBL	NAT	LBL	NAT
NUMBER*	29	42	41	43	52	58
AVE % REC	13	103	31	97	81	106

*OF 74 LABELED & 82 NATIVE

FIGURE 14
EFFECT OF HPLC CLEANUP

MR. TELLIARD: Are there any questions?

(No response.)

MR. TELLIARD: No questions?

MR. RUSHNECK: No questions. Everyone can go home and do sludge now. Wonderful

MR. TELLIARD: Thank you, Dale. Thank you very much.

MR. TELLIARD: A couple of notes. The following speakers are going to be talking about one of our favoritest subjects, laboratory certification and reciprocity. We have beat this horse so many times it is wounded and dying, but we are going to do it again. We are going to do it until we get it right.

The agency has done something between our last discussion on the subject and today in that a committee was formed with is called the Methods Management Committee which is part of the agency that is looking at monitoring and methods across all media and in all program offices.

One of the ad hoc committees that has been formed under that is a committee to look at the issue of certification. Whether the agency is going to do it...as you know, part of our agency does do that, Drinking Water...but what the other program offices are going to do and what form it might look like and take. So, you will hear some of that kicked around today, I hope.

So, our next speaker will be Rhonda Whalen of the Department of Health and Human Services who will talk about the Federal Government perspective on the regulation of laboratories under CLIA of 1988. She will explain that.

MS. WHALEN: Good afternoon.

I am Rhonda Whalen. I am with the Health Care Financing Administration with the Health Standards and Quality Bureau, and we are charged with the responsibility of implementing the Clinical Laboratory Improvement Amendments of 1988.

Basically, the law that was enacted October 31, 1988 pertains to all entities that test human specimens. To set this in context, I am going to give you a little background information on what we currently do, what our current framework is, and then what it is we are going to be doing in the future.

At present, the Health Care Finance Administration regulates laboratories under two federal programs, the Medicare/Medicaid programs and the Clinical Laboratories Improvement Act of 1967. Medicare and Medicaid are reimbursement or payment programs, Medicare for beneficiaries over 65 and Medicaid for recipients through the State program. The Clinical Laboratories Improvement Act of 1967 regulates laboratories that test specimens that cross State lines.

At present, we have approximately 4900 Medicare-approved independent laboratories, and we have approximately 6600 Medicare-approved hospital laboratories. Of the 6600 Medicare-approved hospital laboratories, about 5200 are

accredited by either the Joint Commission on Accreditation of Health Care Organizations or the American Osteopathic Association.

What this means is that the Federal Government does not directly inspect these hospitals. Rather, we deem the accrediting organization's inspection programs, and the way we conduct inspections is that we have agreements with all 50 States, and the States do the direct inspections, and the Health Care Financing Administration has regional offices that oversee the State operations.

There are about 2900 laboratories subject to the Clinical Laboratories Improvement Act of 1967, that is, they test human specimens in interstate commerce.

So, the total universe of regulated laboratories by the Health Care Financing Administration is approximately 12,000. As I mentioned, for half of those, we deem the accreditation programs of JCAA or the American Osteopathic Association to inspect the hospital laboratories.

Beginning in 1987, a series of newspaper and magazine articles were published on the quality of laboratory testing, and, simultaneously, television programs were aired concerning the number of laboratories that were not subject to either Federal or State regulations.

Congress held hearings in 1988 and heard testimony from victims of faulty laboratory testing. Specific concerns

were raised about the validity of cholesterol screening and the accuracy of pap smear results.

Now, in that environment, we currently are responsible for regulating laboratories based on location. I mentioned independent laboratories, hospital laboratories. We also have laboratory services in nursing homes and dialysis facilities, et cetera.

In order to run the regulatory program for laboratories, we had interagency agreements with the Public Health Service. We have a memorandum of understanding with the Centers for Disease Control for provision of scientific and technical expertise on questions related to advances in instrumentation, new technology, proficiency testing, and cytology services. We also have a memorandum of understanding between the Health Care Financing Administration and the Food and Drug Administration for the provision of technical assistance concerning blood bank services.

So, at present, we work very closely with the Public Health Service and both CDC and FDA. This is based on long-standing arrangements, because prior to 1979, the Centers for Disease Control had responsibility for regulating the interstate laboratories. In 1979, the Health Care Financing Administration became responsible for licensing and

inspection of laboratories that test specimens in interstate commerce.

In 1980, the Health Care Financing Administration assumed responsibility for the inspection of approximately 4500 registered blood establishments that also participate in Medicare. These transfusion facilities that are primarily located in the private hospitals either collect or transfuse whole blood or packed cells or collect other blood components in emergency situations.

Both of these arrangements were generated on the premise that we were trying to reduce inspections. The Department of Health and Human Services had simultaneous programs and, per FDA, CDC, and the Health Care Financing Administration, was conducting inspections on an annual basis. So, what we were attempting to do was reduce the numbers of inspections.

Therefore, we proceeded in negotiations with agreements with both the Centers for Disease Control and FDA which took over the inspection responsibility, leaving the Centers for Disease Control and FDA with the responsibility for providing HCVA with the technical expertise necessary to run those two programs while we continued to carry on our primary responsibility which is to inspect facilities for approval for payment under Medicare and Medicaid.

Now, there is an historical basis which was occurring during this timeframe prior to the enactment of CLIA. One piece of legislation was the Omnibus Budget Reconciliation Act of 1987. This was Congress' first attempt to say that the laboratories located in physicians' offices that we currently reimburse for services provided to Medicare beneficiaries should be subject to regulations.

Essentially, what Congress said was that a physician's office laboratory that performs more than 5000 tests per year should be subject to regulation, and they charged the Department with regulating those laboratories.

In the meantime, this omnibus law that we are charged with implementing was enacted on October 31, 1988, and it is bigger than physician office laboratories. It says that all entities, certainly including physician office laboratories, that perform laboratory testing would be subject to federal regulations.

The main impact of the law is that it affects all testing entities, dramatically increasing the Health Care Financing Administration's role from regulating the current 12,000 laboratories to include an estimated 100,000 physician office labs and perhaps another 200,000 to 300,000 or 400,000 laboratories.

A unique aspect of the Clinical Laboratory Improvement Amendments of 1988 is that the law specifies the regulation

of laboratories according to testing performed. I mentioned a few minutes ago that we are responsible for regulating laboratories based on location. It is the current basis of our regulation.

This law says we should regulate based on the testing performed. It certainly is a reasonable basis for establishing regulation, but it is somewhat difficult because we have no data. We have no information on adverse impact of incorrect laboratory results, and we are being asked to establish regulations on the basis of the complexity of laboratory testing, meaning that the if the testing is more complex, we should have more strenuous regulations.

Therefore, if a particular test requires more interpretation, more objectivity, more judgment, then that type of regulation or that type of testing should be more heavily regulated, and we are without data to establish that type of regulatory program.

Now, one thing that Congress did in December of last year is it withdrew the OBRA '87 law which said we would regulate physician office labs that do over 5000 tests. This was extremely helpful to us, because, number one, it was this OBRA '87 was in conflict with CLIA '88. CLIA '88 says you regulate all entities. It doesn't specify physician office labs, and it doesn't talk about volumes of

tests performed in a laboratory. It talks about the kinds of tests performed.

So, we were faced with a problem that regulates by location, being asked to implement a law that designates physician office labs to be regulated and specifies volume simultaneously with a law that says no, you should regulate on the basis of testing. So, we were in somewhat of a dilemma.

Congress helped us out by withdrawing the Omnibus Budget Reconciliation Act of 1987 in December of 1989. Therefore, we have one omnibus law that we must implement.

The other thing that the Omnibus Budget Reconciliation Act of 1989 did is tie in Medicare payments with CLIA. What that means is that in order for a laboratory to be paid under Medicare, that laboratory will have to be certified under CLIA.

That has always been true for Medicare-approved independent labs or hospitals or nursing homes but has not been true for physician office labs. Presently, physician office labs are paid simply on the basis of the physician's name and receiving a billing number. The physician's lab does not have to meet any standards.

So, CLIA '88 changes that and says that, number one, those labs will be regulated, and then the Omnibus Budget Reconciliation Act of 1989 came along and said not only were

those labs to be regulate, but in order to be paid, those laboratories will have to have a certificate.

Now, as I mentioned, at present, we are regulating 12,000 labs under Medicare and have the potential of regulating over 300,000 labs under CLIA. Therefore, the CLIA program will be the largest program and Medicare will then be a smaller subset of the CLIA program.

During this time period in which Congress was hearing testimony on the faulty laboratory testing practices, the Health Care Financing Administration, in conjunction with the Centers for Disease Control and the Food and Drug Administration, was attempting to revise the current regulations that we have for laboratories. We had a Notice of Proposed Rulemaking which was published August 5, 1989, and we stated our proposed regulations to revise our current requirements for personnel, quality control, record keeping, proficiency testing, and we were attempting to establish new quality assurance requirements.

The closing date for the comments was November 3, 1988. CLIA was enacted October 31, 1988. So, we had somewhat of a dilemma, that dilemma being would we throw out our proposed rule and ignore the over 1600 comments we received and just start with the implementation of CLIA '88.

We determined that what we had proposed as a revision to our current requirements was in keeping with the

requirements that we would have to implement under CLIA '88. Therefore, we considered the 1600 comments, we analyzed them, and we responded to them in the preamble to the regulations that we published in final on March 14, 1990.

Those regulations will be effective September 10, 1990. They will affect those laboratories currently regulated under Medicare and those laboratories that test specimens in interstate commerce. What this rule does is it establishes the basis or the framework for the regulations that we will implement under CLIA '88.

This regulation published in final on March 14 establishes uniform proficiency testing requirements, a grading system, criteria for approving proficiency testing programs, the types of samples that should be sent by an approved proficiency testing program to participating laboratories, the kinds of challenges that should be included, and the frequency of the testing events.

We revised our quality control requirements to be current with new methodology and changes in technology. We established quality assurance requirements that would encompass the outcome measurements of laboratory quality, and the self-implementing provisions of CLIA '88, that is, the language in the statute that is so clear it doesn't require interpretation or rulemaking we put in this rule. We just lifted out the statutory language, and we put those

requirements into the March 14 rule so that we could go forward and implement those provisions of CLIA '88 that are self-implementing.

Now, we determined that the Clinical Improvement Amendments of 1988 are so far reaching and so extensive that we could not propose one rule to implement CLIA '88. Therefore, we have five rules all of which will require comment period and evaluation of the comments and then publication of a final rule.

The first rule is the most controversial rule, and I called this morning to see where we were. There is a strong possibility that that rule is going to be published the end of next week. We have just about achieved the Office of Management and Budget clearance needed for publication in the Federal Register.

This rule will establish standards based on the complexity of test performed. It will propose a list of tests for waiver or exemption from the requirements, that is, those tests that are so simple, accurate, and low risk and pose no reasonable risk of harm if performed incorrectly, then if laboratories do only those tests, the laboratory would be exempt from meeting Federal standards.

We are also going to propose personnel requirements based on complexity of testing. This is also quite controversial since heretofore we have not done that, and

anytime you specify personnel requirements, that always generates a lot of comments. That rule will have a 90-day comment period, and one of the most difficult things about this whole activity is that we don't know the number of labs we need to regulate, we don't know the testing performed in those laboratories, we do not know the types of personnel employed in those laboratories.

So, that brings me to the second rule that we are going to attempt to implement. Probably in June it will probably be published as a proposed rule and will have a 60-day comment period.

That rule is an interim procedure for provisional registration of laboratories. That is where we will sign laboratories up. They will pay a registration fee, and we will find out how many laboratories there are in the United States, what kinds of testing the laboratories conduct, and the types of individuals employed in these laboratories.

Also, this is a self-implementing law, that is, Congress is not appropriating any budget, any funds, to run this program. Therefore, we have to charge the laboratories a fee which we determined it would be most appropriate to charge each laboratory the portion of the amount necessary to determine compliance. That is, if the lab is smaller, less complex, fewer tests are performed, that laboratory would pay a smaller fee. Ultimately, what we are proposing

to do in this regulation is to set forth our fee schedule methodology.

That rule will have a 60-day comment period, and that is probably the rule that we will implement first. It is not quite as controversial and, obviously, we do need to get the laboratories registered, and we do need to start collecting money in order to maintain the program.

Now, the third rule that we need to publish as a proposed rule is the criteria for recognition of accreditation programs. The law specifies that we can recognize private non-profit organizations' accreditation programs and State programs with equivalent standards.

So, what we want to do is propose the criteria for recognition of those programs, the kinds of information we are going to request, the kinds of data that we are going to need on an ongoing basis, and then as soon as we establish our standards, then we can accept applications from interested accreditation programs and State programs. That rule is probably going to be published later on this summer.

The fourth rule is the proposed regulations that would implement the intermediate sanction and adverse action procedures, that is, the penalties that will accrue to a laboratory that does not meet the requirements. There are monetary sanctions and various penalties that laboratories

are subject to that do not meet the requirements. That rule will also be published later on in the summer.

The important thing about the hearings attached to CLIA are that in Medicare, if a laboratory does not meet the requirements, we terminate that laboratory's approval at that time. The laboratory then is allowed an opportunity for a hearing.

Under CLIA '88, since any adverse action against a laboratory, if it went to conclusion, would prohibit that laboratory from conducting testing in this country. If you lose your certificate, then you can't conduct testing in the United States. The laboratory is allowed an appeal process prior to any action on the certification.

So, we have to propose the hearing process, the types of evidence that will be allowed. It particular pertains to the judicial proceedings.

Along with that rule, there is a particular statutory provision that says that the department will make lists of these laboratories available to the public that are subject to intermediate sanctions, Medicare approval terminations, and loss of certification. So, that information is going to be available to the public.

The fifth and final rule will set forth the responsibilities and functions of the State survey agencies that we employ to do the direct surveys for us and also the

responsibilities of the Health Care Financing Administration in carrying out the activities of CLIA '88.

There continues to be a great deal of interest from individual laboratories, laboratorians, physicians, laboratory equipment manufacturers, and the media in the implementation of CLIA. For four nights in February, Channel 4 TV news in Washington, D.C. aired a program called "Deadly Mistakes: Promises Broken" which continued to focus on individuals who have died or were irrevocably harmed due to incorrect laboratory results. There is a continued emphasis by the media and a focus on the need for implementing these requirements. We have felt a good deal of pressure to get these regulations out, the comment period allowed, and then publish these rules in final to start regulating laboratories under CLIA.

Congress held hearings on March 7, and our administrator testified, and the thrust of the hearings, basically, from the Senate was, why don't you have these regulations published? Why aren't you regulating laboratories under CLIA? We enacted these laws because we wanted to protect the American public, and we don't see the Department responding.

So, essentially, we are about ready to at least be able to say that we are doing something, but while the media and Congress are concerned that we have not acted, the soon to

be regulated entity is very concerned that we are moving too fast.

There are five studies that are mandated under CLIA '88 all of which would be very useful in establishing regulations. Those studies were supposed to be out in May. They are not completed. That is the charge of the Public Health Service. In fact, they are in their very embryonic stage.

So, in the meantime, we are going to establish regulations in the absence of the information that would be gained from these studies.

Thank you.

MR. TELLIARD: Thank you.

MR. TELLIARD: Are there any questions?

MS. ORDONA: I have a question. My name is Alicia Ordona. I am from the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

My next question is, is the State laboratory going to be included in this regulation?

MS. WHALEN: Is the State laboratory what?

MS. ORDONA: Going to be included under this regulation.

MS. WHALEN: If the State laboratory does tests on human specimens, yes.

MS. ORDONA: Really?

MS. WHALEN: Yes, and all Federal laboratories.

MS. ORDONA: Thank you.

MR. RUSHNECK: Rhonda, Dale Rushneck of ATI.

I am curious about the fee schedule methodology. I know you don't have to have the rule out until late summer, but can you give us your thinking? Is it going to be based on size dollar volume of the laboratory, on the number of

tests performed, is it going to be split and a fee associated with each test? What is the current thinking?

MS. WHALEN: What we did, we really did look at what we currently...our current costs related to the inspection of laboratories and the determination of laboratory compliance. It is somewhat difficult right now, because we are budgeted an overall amount, and we negotiate with every State survey agency a different hourly rate, because the States are our contractors, so to speak.

The part that makes it complicated is that our data right now is somewhat limited because it is by State, not by laboratory, and it is also based on our current regulatory program which we are attempted to change and certainly strengthen the requirements and the amount of time that will be necessary to determine compliance.

So, with all of that, then I am going to tell you that we used our current information and attempted to establish fees. It is not a particular secret, but the fees will be biennial, every two years, because that is specified by law. If the laboratory is eligible for a certificate of waiver, it is a nominal fee, and the nominal fee that we came up with for the proposed rule is around $150.

The certificate fee, that is, the administrative cost for issuing the piece of paper, will be between $200 and

$300 for a certificate, a provisional certificate, or an accreditation certificate. Now, the fees that we are proposing for determining compliance...and remember again this is for every two-year period...runs from around $800 to...it seems like it is up around $2000.

Now, we have set what we believe to be our base costs. If it turns out that it costs us more to determine a laboratory's compliance, meaning that the laboratory was not ready for an inspection, had a lot of deficiencies, we had to go back, we had to conduct a follow-up inspection, the laboratory will get a second bill.

So, the first bill is going to be based on the extent of services and the volume of services, and that will set a base cost, and it is the minimum fee. If we incur additional costs, then the laboratory will get a second bill.

And as we gain more information on our costs relative to determining compliance under CLIA '88, we will upgrade our fees or downgrade if it turns out that we should be charging less, although I kind of doubt that, because CLIA '88 is going to require many more things. Therefore, I think that fees will go up, not down.

MR. TELLIARD: All right, thank you very much.

Baldev, did you have a question?

MR. BATHIJA: A quick question. Will you be allowed to keep that fee you collect, or does it revert back to the...

MS. WHALEN: Federal Treasury, and then we get budgeted out of that money, we hope.

MR. TELLIARD: I would like to have the panelists come up during the break that we are about to have so that you can go get your Coke and Pepsi and come back in, and if the panelists would come up and take a chair up here so that you are sitting target for the rest of the audience, if you would do that right after the break, I would appreciate it.

Thank you. Please get back in here in 15 minutes.

(WHEREUPON, a brief recess was taken.)

MR. TELLIARD: Our next speaker is Gerald Hoeltge who is going to carry on with the program of talking about program and laboratory certifications. He comes from our great town, Cleveland, and is connected with the Cleveland Clinic.

Gerald?

DR. HOELTGE: Thank you very much.

In the next few minutes, I want to present the College of American Pathologists' laboratory accreditation program as an example of what the private sector can accomplish in terms of laboratory certification.

This particular program began about 1965 quite informally when a group of pathologists got together and realized that there was no good mechanism for interlaboratory inspection directed towards improvement. They agreed to inspect each other's laboratories to offer constructive criticism and helpful suggestions. That activity has grown over the years to the point at which now it has a fairly substantial structure. We accredit now just under 4100 clinical laboratories.

I want to talk about some of the characteristics of the program, to give you an idea of the philosophy behind it so that the operational aspects, will be a little more understandable.

First of all, this is a voluntary program. Now, when I say voluntary, I am talking about the inspectors for the program. They are all practicing laboratorians. They are volunteering their time and expertise to the program. They are recompensed only for meals and mileage. It is also voluntary for the laboratory directors who choose to be

involved in this program. I say that with a little bit of caution because, in fact, many directors feel compelled to get their laboratories accredited. It comes from several different directions. Ms. Whalen talked about CLIA '67. Those laboratories which are in interstate commerce have to be licensed.

The inspection agency for such laboratories, of course, is the Centers for Disease Control or one of its contract organizations. However, a laboratory which is interstate licensed and accredited by the College can apply to the Health Care Financing Administration for a waiver from regular CDC inspections, and that means that the laboratory has one fewer inspection to suffer through on each cycle.

Also, the Joint Commission on Accreditation of Healthcare Organization recognizes CAP program for hospital laboratories. As Ms. Whalen pointed out, the Joint Commission is one of two private agencies that can qualify a provider for Medicare reimbursement. So, that means that if a hospital laboratory is certified by the College, that certification will be accepted by the Joint Commission. If the laboratory using that Joint Commission accreditation to qualify for Medicare reimbursement, then the CAP program is, qualifying the laboratory for Medicare reimbursement. Some laboratories find that to be a compelling reason.

Thirdly, we are seeing increasing numbers of private carriers who are offering provider contracts for competitive bidding, and they are including CAP laboratory accreditation among the bidding specifications. Points are given to those laboratories that have chosen to be measured by the accreditation criteria. That has brought a lot of commercial laboratories into the program who had never expressed an interest before.

So, those external characteristics aside, it is a voluntary program, and it certainly is voluntary on the part of the inspectors.

Secondly, it is a peer review program. The inspectors are all practicing laboratorians, and the management of the program, the commissioners for laboratory accreditation, are all practicing laboratorians. I run the blood bank and the transfusion service at the Cleveland Clinic Foundation. About an hour or two of my day, however, is devoted to CAP activities, and we manage the accreditation for about 450 laboratories in the Ohio, Indiana, Michigan, and Ontario area.

Thirdly, the inspection covers the entire laboratory. We will not accept an application from a facility that wants only part of the laboratory inspected. We are going to look at the entire facility, even those areas for which we have no technical expertise (such as in vitro fertilization or

environmental water quality). But we can look at any laboratory at least in terms of safety requirements.

Fourthly, it is based upon the Standards for Laboratory Accreditation. I will talk about that a little bit more in a moment.

Fifth, it combines on-site inspection with proficiency testing. Both of them go together. Neither one suffices for accreditation by itself.

Now, the Standards. This is a document that is the basis for our program. It has about a five-year review cycle. It is written generally to address the general case. It is the only part of the program that the Board of Governors of the College reviews very carefully. (All the operational aspects are managed by the Commissions on Laboratory Accreditation).

There are only five standards, each one of which is about a paragraph long, and then there is explanatory material that goes along with each. I will mention a few of the highlights.

The first is that it vests the responsibility for the management of the laboratory with the director. We have very specific personnel requirements for the director.

A director must be a physician or a doctoral level clinical scientists, an individual whose education and laboratory training is appropriate for the span of

disciplines that are represented in that particular laboratory.

And the director must discharge a whole series of responsibilities that you would find appropriate for any director to discharge: ensuring that there are sufficient numbers of people and the proper equipment and the quality control and the safety requirements and the educational aspects of laboratory medicine.

What we find is that in a number of commercial laboratories, for example, or in hospital laboratories where the medical director is not an employee of the laboratory but is a consultant, the director does not have sufficient authority to discharge those particular responsibilities. Those laboratories do not meet the Standards.

We also have personnel standards for employees other than the director. They are not as stringently defined. They are, in fact, performance standards.

Quality assurance is an important standard. We make a distinction between quality assurance and quality control. Quality control we define as those intralaboratory practices that contribute to the accuracy and timeliness of the clinical laboratory data. Quality assurance includes quality control, but it also includes the pre-analytic issues and the post-analytic issues all of which together

will impinge upon accuracy and timeliness in the healthcare system.

There is a standard that describes the need for adequate facilities and operational procedures. The laboratory must participate in the laboratory improvement programs of the College, that is to say, on-site inspection and proficiency testing.

That is a picture of the cover of the book in its current edition.

Now, our organization. At the top is the Board of Governors of the College, and there are four councils. The council to which the laboratory accreditation reports is the Council on Clinical Pathology. There are two commissions within that council. The Commission on Scientific Affairs includes 16 scientific resource committees each of which is devoted to a specific clinical laboratory discipline.

A second commission is the Commission on Laboratory Accreditation. The Commission includes 14 regional commissioners and 4 additional special commissioners. To support us are 61 State commissioners. Some States, such as New York, California, Ohio, and Pennsylvania, have more than one State commissioner, and the State commissioners have approximately 1,800 inspectors working for them.

Now, there are about 17,000 pathologists in the country. About 11,000 belong to the CAP. So, that means

that somewhere around 10 percent of all pathologists or about 15 percent of our membership serve as inspectors for the program.

Our inspection cycle is a two-year cycle. It begins with the date of the first successful inspection.

In alternate years, the laboratory will undergo an on-site inspection and a self-inspection. The self-inspection is a very serious inspection. The director uses exactly the same tools as an on-site inspector would use. The self-inspection is followed by the same post-inspection data entry routines to record the results of that inspection. The accuracy of the data is verified by the next year's on-site inspector. If the laboratory does complete the self-inspection with appropriate thoroughness, it is a very egregious deficiency indeed.

About 120 days before the lapse of accreditation, the laboratory director is sent a reapplication packet of materials. He or she has 30 days to fill that out and to return it to the program office in Northfield, Illinois. That gives us about 90 days, then, to find an inspector, for that inspector to get together an inspection team, and for the inspection to be scheduled and completed.

I can't emphasize enough how important it is for all deadlines to be met for this whole process to stay on schedule. Most of the problems that we have had running

this program have been due to delays, and we have had to adopt a "get tough" policy to stay on the inspection schedule.

The application packet that the director completes includes an extensive questionnaire. Specific information is requested. A list of all equipment, all of the tests that the laboratory is doing, and the volume of those tests have to be appended.

We ask the director to insert description of the quality control and the quality assurance programs that are operative in that laboratory.

We will get a floor plan of the facility, and we ask for a diagram table of organization that depicts the reporting relationships. The latter is particularly important in trying to identify sites in which there is a titular director only. The credentials of the key personnel. (the department heads, section heads, and the technical supervisors) are included.

To that information, the Central Office in Northfield adds the results from the last two inspections, (last year's self-inspection and the previous year's on-site inspection), all the computer commentary that was generated from those inspections, all relevant correspondence and, a statement of surveys participation.

By "surveys", we are talking about the proficiency testing program of the College. The laboratory must participate in this program. It is interesting to note that about 10 or 20 percent of all of the subscribers to our proficiency testing program, never send in their results for evaluation. So, it is important that the inspector know to which surveys the laboratory has enrolled in and does have data for even if that data was not submitted to the program office for evaluation.

The whole packet, is shipped to the inspector. We will try to choose an inspector who is a peer of the laboratory director. That means that we will try to identify an individual from a facility of a similar size who can relate to the kinds of problems and patient care issues that the laboratory director is facing, somebody whose scope of practice is comparable. We will not, for example, send a pathologist who limits his practice to cytopathology to a clinical laboratory that is involved only in toxicology and therapeutic drug monitoring.

One walks a fine line, however, because some of the peer review considerations make it difficult to preserve objectivity, especially when one must worry about competition. For example, to inspect a proprietary laboratory, peer review considerations would suggest that the most appropriate inspector would come from another

proprietary laboratory: but, to do so might require selecting an individual from a very long distance away so that competitive interests will no interfere with objectivity.

Once the director has applied for accreditation, all the materials have been received, and the inspector has been assigned. It is now up to the inspector to schedule an inspection. He or she will do so at a date that is mutually convenient with the director.

If it is a very large laboratory, the inspector will want to bring a team of individuals. A typical team is about 5 or 6 people. There may be a chemist, a microbiologist, a couple of pathologists, and perhaps a computer expert.

We have very specific rules for the qualifications of the inspector, but the selection of the inspection team members is entirely at the discretion of the inspector. This allows as much flexibility in the program as possible. The individuals who come are appropriate to the special needs of that particular laboratory. At a very big facility like Mayo Medical Laboratories or Metpath, we will have to take 12 or 15 people to do the laboratory well. Most of us who do inspections try to get the whole thing done in one day simply to minimize the amount of time that we take away

from our own practice. So, to do so often requires generally a fairly large team.

Then the inspector completes the checklists and returns them to the Centra Office. We have a checklist of questions that right now numbers around 2200 items, and they are enclosed in about 15 different booklets each of which focuses upon a different discipline within the laboratory.

The checklists are what give our inspection its structure. They standardize the program from region to region, from State to State, and from inspection to inspection.

Each of the questions have a value, and we talk about Phase I and Phase II items. A Phase I item is the less serious of the two. In some ways, you can think of it as a recommendation. A Phase II item is a requirement for accreditation. In fact, the laboratory must document correction of any Phase II deficiency before accreditation will be conferred.

We do sometimes deny accreditation on the basis of Phase I deficiencies if there is a very large number of them or if they have been recurrent and the director has shown no interest in correcting them.

Each item can be answered as "yes", as "no", or as "not applicable". It is the "no" items that drive the next part of the process: the generation of a checklist commentary.

Each question has a commentary. The commentary, which is generally quite a bit longer than the question, explains the meaning of the question. Appropriate journal references are included.

The specific set of checklist commentaries then is sent back to the director who must respond in writing to each deficiency, documenting correction of the Phase II deficiencies. The director has 30 days to prepare this reply. It is reviewed then by the regional commissioner who may decide that there is sufficient information there to render a decision or may ask for supplementary information. Once there is sufficient information, the recommendation can be to accredit the laboratory, or the recommendation may be to deny accreditation.

The Commission as a whole meets three times a year. Our first order of business is always to accredit all those laboratories for which accreditation has been recommended. Then we spend the rest of our time talking about the individual facilities for which denial has been recommended by the regional commissioner.

There is another document that is very important to the process. That is the inspector's supplemental report. This is a narrative, confidential document. The inspector can use this to amplify upon any items in the checklist. And if the inspector senses conflict between, let's say, the

director and the medical staff or between the laboratory and the hospital administrator, the issue should be described in the inspector's supplemental report.

The director will not see the information in this particular report, as a general rule. The regional commissioner may extract information from the report for inclusion into a personal letter that goes to the director. Especially when the commission is considering denial of accreditation, the feelings that are expressed in the supplemental report can be very important in shaping the course of the discussion.

Now, let us discuss proficiency testing. (We call that the "surveys program" or the CAP Interlaboratory Comparison Program). At the present time, there are over 90 different packages that are offered, including clinical chemistry, hematology, microbiology, toxicology therapeutic drug monitoring, histocompatibility testing, cytogenetics, and forensic pathology. New ones are being produced in molecular biology and in andrology.

Each one includes a set of analytic tests. There are more than 300 analytes available. An accredited laboratory must participate in the surveys program according to its repertory and complexity. A large laboratory will have to subscribe to many surveys, and a sophisticated laboratory

will have to choose the comprehensive versions of certain surveys.

We had mentioned the resource committees briefly before as being within the Commission on Scientific Affairs. You will remember that they are independent of the Commission on Laboratory Accreditation. The resource committees write the survey specifications, and they evaluate the results. Each reported result can be scored as acceptable or not acceptable.

The unfavorable results are printed in a report that goes to the regional commissioner once every three months, called the surveys results exception reports. In it we look for evidence of a possible systematic problem. All laboratories will have certain problems from time to time, but if it is a systematic problem, it will be recurrent.

We will often ask the laboratory director to check into a particular analytic test. In fact, I send out about 100 such letters every three months.

You can see how important it is that the laboratory participate appropriately, because, in fact, the commission is using the PT program as its mechanism for monitoring the performance of laboratories between on-site inspections.

Now, each of these resources committees is composed of nationally recognized experts. They are the scientific base for the College, and all sorts of scientific questions are

referred to them. For purposes of this discussion, they write the survey specifications and evaluate the results, and they also develop the technical portions of the checklists that we are using out there in the field, a very important contribution to the program.

We have an appeals process. The appeals process, as you might expect, will follow denial of accreditation. The director has 30 days to file the appeal. The appeal board, in fact, is the Commission on Laboratory Accreditation as a whole. The director is invited to come to the next meeting of the commission to plead his or her case.

If the commission affirms its original decision, then that particular appeal can be extended to the Board of Governors of the College, which is the final appeal board.

What are the qualifications for our inspectors? The inspector must be a Fellow of the College. Now, since fellowship in the College is limited to board-certified pathologists, that means that the inspector will be a board-certified pathologist.

It is also required that the inspector be affiliated with an accredited laboratory, and that he or she has undergone appropriate training.

Now, the training is, in most cases on-the-job. The experienced inspectors will take a prospective inspector along on two or three inspections to learn some of the

operational aspects, but we are really not depending upon the inspector for operational support. We are depending upon the inspector for expertise in evaluating a laboratory.

We also conduct new-inspector workshops where we train inspectors from scratch. I almost did not make this particular meeting, because I was originally scheduled to host one inspector's workshop in Cincinnati this evening. One of my fellow commissioners very graciously is covering for me at that particular event.

We also have update workshops that we hold periodically throughout the country to refresh and revitalize the inspectors who have been doing these inspections for many years.

Like any big program, it has a set of policies and procedures that codify all of the operational rules. Having such policies in writing, ensures fairness and uniformity.

Our policies and procedures are on a three-year review cycle.

Computer support is essential to the program. I cannot emphasize enough how important computers are to us in this. For example, we must hold to the inspection cycle. If I had to keep track of all of these laboratories in my own region, I would fall way behind. That would not serve the inspection process well at all. The computers keep the process moving.

The whole surveys program is run on computer. Most of the survey results are analyzed by computer. We talked about the survey results exception report by which the survey results are monitored by the commission. What I did not mention in that in that the report is not a simple listing of the unacceptable results. There is a fairly sophisticated algorithm that selects for us those laboratories that appear to have a higher probability of a systematic bias.

Of course, all of our inspector lists and other demographics are kept on computer. Each of the regional offices has a terminal to access the Chicago computer. The checklists and the commentaries are all on computer in a desktop publishing type of a format. This allows us to update these rules every 6 to 12 months to keep them current with technologic change. That can be a real challenge as new instrumentation and methodology comes onto the market.

Lastly, let me just make a couple of comments about finances. This is a self-supporting program. The revenue comes from the annual subscription fees that the laboratories pay. Now, the surveys program also generates revenue for the College, but we also incur significant expenses in the manufacture of the PT materials.

The expenses that are generated by these revenues primarily are for personnel support. We have about 75 full-

time employees in the program office in Chicago who are supporting the lab improvement programs of the College. There are also part-time staff, such as the secretaries in the regional office.

There are direct expenses that one incurs with each inspection (travel, lodging, meals, and such), and those are all charged to the program.

What is not charged to the program is the time of the individuals who are working on its behalf, and this is substantial. We have some solo practitioners, for example, who work as inspectors, and when they go out once a year or twice a year to do an inspection, they, must hire a locum tenens pathologist to come in and cover their practice for them. They pick up those costs themselves.

So, our inspectors and our team members are not paid, at least not by the College. They may very well, of course, be paid by the sponsoring organization that recognizes that these people bring back to their laboratories, more new information than they can confer onto the inspected laboratory. So, it is a two-way laboratory improvement program.

The voluntary contribution to the program really cannot be overestimated. It is immense when you include 1800 inspectors, 75 commissioners, approximately 200 scientists

that are on these resource committees, and then all the officers of the College. All are volunteers.

So, in those few words, I hope I have conveyed kind of an overview of the whole program. In the panel discussion, I will be happy to follow up on any items that you care to.

Thank you very much for your attention.

Laboratory Accreditation Program

College of American Pathologists

325 Waukegan Road Northfield, Illinois 60093-2750 708/446-8800

Characteristics

voluntary

peer-review

must cover entire laboratory

based on Standards of Laboratory Accreditation

combines inspection with proficiency testing

Standards for Laboratory Accreditation

- Vests the responsibility in the Director
- Personnel standards
- Quality assurance
- Adequacy of facilities and procedures
- Participation in CAP Laboratory Improvement Programs

Organization

- Council on Clinical Pathology
  - Commission on Scientific Affairs
    16 Resource Committees
  - Commission on Laboratory Accreditation
    - 13 Regional Commissioners
      - 60 State Commissioners
        - ~4,100 laboratories
        - ~1,800 inspectors

Inspection Cycle

- Begins with date of first successful inspection
- On-site and self-inspections in alternate years
- Reapplication begins 120 days before date of expiration
- *All deadlines must be met to stay on schedule!*

Application materials

- questionnaire
- list of all equipment and scope of analytic testing
- statement of quality control and quality assurance methods
- floor plan
- diagram of table of organization
- credentials of key personnel

Application packet also includes

- All results from the last two inspections
- Statement of Surveys enrollment
- Relevant interim correspondence

Choosing an inspector

- Peer-review considerations
  - facility of similar size
  - similar scope of practice
- Objectivity must be maintained
  - non-competitive practice

Process

- Director applies for accreditation
- Application materials are reviewed for completeness
- Inspector is assigned by state commissioner
- Application packet is sent to the Inspector
- Inspection is scheduled, arranged, and conducted by the Inspector and his/her team
- Inspection materials are returned to the Program Office

Process (cont'd)

- Checklist Commentary is printed and mailed to the Director
- Director responds to each deficiency in writing with appropriate documentation
- Reply is reviewed by Regional Commissioner
- Accreditation may be recommended or not recommended
- Commission votes on recommendation

Inspector's Supplemental Report

- confidential document
- may amplify individual checklist items
- appropriate location for sensitive information

Surveys Program (CAP Interlaboratory Comparison Program

> 90 proficiency testing surveys

> 200 analytes

Participation is required for laboratory accreditation.

Monitoring of Proficiency Testing

- Resource Committee evaluate results
- quarterly reports go to Regional Commissioners (Surveys Results Exceptions Reports)
- importance of appropriate participation

Resource Committees

- Each disciplinary committee is composed of nationally recognized experts.
- Write survey specifications
- Develop checklists

Inspector Training

- Required for all new inspectors
- Recommended periodically for all inspectors
- Conducted throughout country

Policies and Procedures

- codification of all operational rules
- special importance in a distributive program
- three-year review cycle

Appeals

- Follows denial of accreditation
- Director has 30 days to file
- Appeal heard by
  - entire Commission on Laboratory Accreditation
  - Board of Governors

Computer support

- inspection cycle
- Surveys monitoring
- inspector lists
- updating checklists and commentary

Financial

- self-supporting
- revenues come from
  - annual subscription
  - Surveys program
- expenses include
  - full-time staff in Program Office
  - part-time staff in regional offices

  direct expenses incurred in performing inspections
- Inspectors and team members are not paid.*The voluntary contribution to the Program is immense!*

MR. TELLIARD: What we would like to do now is there are five panelists. The sixth one is at National Airport in the fog.

Each of the panelists is going to make a brief presentation. Some of them you have heard before. Then when they are done with each presentation, we will open it up to the panel.

So, I guess Al is the first one.

DR. TIEDEMANN: I am Albert Tiedemann. I am the director of the Virginia Division of Consolidated Laboratory Services which is a central State laboratory system, providing most of the State Laboratory Services. Except for Highways and Transportation, none of the agencies have their own labs. We are their laboratories.

We feel we are in the middle where we can recognize both sides of problems in approving laboratories. We are subject to receiving approval from several Federal agencies. We are also responsible for some different types of programs for which we must give approval within the State, drinking water being the biggest. But these programs include venereal disease, driving under the influence of alcohol and drugs, and commercial blood banks. So, we feel we see both sides of the picture.

Since we are primarily in an environmental meeting here. I'm talking about the drinking water program.

States actually are EPA surrogates if they have primacy, that is, they conduct the laboratory approvals in the States for EPA. I am a little disappointed to look at the attendance list. There must be only about half a dozen people from the States here today, because, basically, as

acting for EPA, we are sort of under the gun. The laboratories in the States look to us for information as well as the piece of paper that says you are approved.

In Virginia, internal Virginia, we divide the laboratories into two classes. One is the government-owned laboratories, and most of these are water works. The large ones which produce more than 3 million gallons a day have to have at least an on-site approved microbiology lab. We do not charge fees for government laboratory approvals. That is funded by the general fund.

The others are the commercial profit-making laboratories for which we are not funded by taxpayers' money. Therefore, we do charge a fee. We break the fee into four categories: microbiology, inorganic chemistry, organic chemistry, and radiology. Depending on how many categories the lab wants to be approved for, the fees will range from $200 to $680 every three years. It is a three-year cycle.

In running the approval program, the basic requirement is we have to be at least as stringent as EPA. But within that overall guideline, we try to take an attitude or approach of being flexible, practical, and realistic. That is, we don't try to mandate a lot of very specifics. Do what you have to do with some flexibility in the way you do it. Keep good records, but we don't tell you how.

Our on-site visits analysts do not have to come back and find something in that visit that they can report as a deficiency. I am very pleased when I can sign a report that says no problems, no deficiencies, no recommendations, lab is doing excellent work.

You do find deficiencies, of course. We class them major and minor, and we base an approval for the lab overall on an evaluation of all of its pluses and minuses, its past performance, and the results it has obtained on proficiency evaluation samples. Basically, we want to know if we approve a lab that that lab has shown it can produce valid data. That is the bottom line.

Reciprocity. We do participate by giving reciprocity to out of State laboratories. We have three conditions. The first is they must show us that they have a need for certification because of the business they have in the State. We found that too many labs just wanted something on their letterhead, and it takes a lot of time to keep the records. So, they have to have business in Virginia.

Secondly, they have to provide us with the documentation of their approval by EPA or by another primacy State.

Third, because the number seems to keep increasing...several years ago, we had to hire some part-time clerical people to help with paperwork and had other

costs...they pay an annual fee of $100 per category, that is, the four categories I mentioned. I don't think there are probably many that pay more than $200 or, at the most, $300.

Because of the various time cycles in other states, we do require that reciprocal certification be renewed each year.

We have some problems with terminology. We talk about certifying labs, but we are not really certifying labs. If we do, we are in trouble, because if we take the word certification in its essence and say that lab is certified, that means we are guaranteeing that that lab's work is always accurate, we are assuring that it is absolutely correct.

So, what we are really doing is saying we approve the lab as being able to do good work or we are accrediting the lab. So, really, this term certification needs to be examined, because it could possibly, the way the lawyers get into things these days, come back to haunt the certifier.

Let me mention a few problems. I've noted that there are only a few state professionals here. I've gotten data from a number of states.

A key problem is information that EPA is considering discontinuing supplying Performance Evaluation (PE), quality control, and standard reference samples. I say

"considering: because program people in other states and others are concerned over the lack of positive, direct information from EPA Washington. We are receiving only rumors or bits and pieces of information from EMSL, the regions, and/or third-parties.

The term used is privatization. EPA has yet to define officially what they mean by privatization. We've received no plan, no details.

We hear that EPA will stop providing these samples. We hear laboratories will have to purchase the samples. Will we be able to buy the samples from any vendor? Who will certify the quality?

One rumor says that EPA will designate a sole source vendor. Many state procurement laws require competitive bidding.

One third-party source, which seems to be a valid source, stated that in addition to being a sole source vendor, that vendor would pay EPA a royalty on each sample. Therefore, EPA would reduce costs and also generate revenue.

What is the true story? We don't know. But someone in authority in EPA Washington needs to provide direct, factual information to the states. The states then need to transmit this information to the laboratories for which the states have approval responsibility.

A typical problem of failure to coordinate that exists today. If you are in the drinking water area, you are probably well aware by now that EPA several months ago approved the new COALERT procedure for microbiology testing for coliform. We can't approve anybody to use that procedure. We can't use it ourselves, because EPA says the method is approved. But EPA hasn't come out and said what are the laboratory criteria, what does your laboratory have to have in the way of everything from QA to detailed procedures before EPA will accept the data.

This is like the other things that pop up. There is a new requirement, a new parameter, something new to be regulated, but the analytical procedure doesn't exist, at least not in an approved form.

Last July the Journal of Environmental Laboratories published a series on laboratory certification. Bill says this Certification problem keeps coming up. It keeps coming up because the problems are still there. They are not really changing.

MR. CARTER: I am Mike Carter. I work for EPA in the Superfund program. More specifically, I am one of the managers of the contract lab program.

A lot of you know more about that program than you might want to. For those of you who are somewhat unfamiliar with it, we are the primary source of analytical data for the Superfund program. That means we are responsible for the analysis of 80,000 to 100,000 samples a year. Our budget is, in round numbers, $45 million per year for analytical services. That includes both quality assurance activities and the actual payment for the analyses.

We are frequently referred to as a de facto certification program, and I suppose that is an apt term. Before contracts are awarded to laboratories, there is an accreditation step. Normally, we do not award a contract to a laboratory without an on-site visit and a finding that they have adequate personnel, facilities, procedures, et cetera.

I said normally. The Small Business Administration can choose to issue a certificate of competency which we are obligated to accept. Our experience says that, in many cases, the laboratory was actually given a disservice when it got that certificate, because they do have lots of trouble performing.

During the course of the contract, we have a great deal of oversight. That includes, normally, four performance evaluation samples per year. They are intended to be double

blinds. Most people recognize them right away. So, at best, they are single blinds.

And we do have a certification activity. The former speaker's concern about nomenclature we happen to share. We accredit a laboratory, but then we exert fairly extensive and intensive efforts in product certification. By that I mean virtually ever data package is inspected at least once.

We a great deal of in-house activity. We have computer programs that are checking for compliance with our deliverable requirements. We utilize close to $3 million a year in computing services just maintaining data bases and cranking through these inspections.

We would like to see and hope to move toward more self-certification in which we do less and the laboratories do more so that we get out of kind of vicious circle where we get data, find some defects, notify the lab, give them a chance to rectify it. This is all taking time and effort. In the lab's case, efforts cost.

Another critical part of any credible accreditation program was mentioned earlier by Ms. Whalen, and that is for a program to be...and Dr. Hoeltge...for a program to be credible, there has to be some provision for a deaccreditation or a decertification. We have historically had administrative type actions that were, in essence, at least an interim deaccreditation. We would stop sending

samples to laboratories that were having certain problems, technical or through-put.

Some of those decertification efforts have recently become a whole lot more critical, sensitive, attention-getting. At the moment, we have three different audits underway by EPA's Office of Inspector General and somewhere in excess of ten investigations underway by the Inspector General's office.

There was an article in a journal that I had never before. Most of you have probably never heard of it before, either. It is called the Legal Times. The week of April 23rd of this year, it was on the front page. It wasn't at the top of the page, but it was on the front page. The headline said, "Superfund Effort Jeopardized by Suspect Data." It goes ahead to quote our Assistant Inspector General's investigation that says at least ten contractors are under investigation for potential fraud.

There have been three formal actions taken to date with only one of them being final. The final action was regarding Roy F. Weston Company. Basically, they signed a settlement agreement with the government in which they agreed to pay $750,000, and one of their labs was then voluntarily suspended for 4 to 12 months from doing any work for Superfund.

I must note here that the company has stated that they did not and do not admit any wrongdoing. It was strictly a settlement.

Subsequent to that, we had two laboratories, companies, that were suspended under suspension and debarment activities which are part of contract regulations. A suspension means that that entity is not allowed to compete from any Federal Government work from any Federal agency, and it probably extends to any cooperative agreement with a State in which Federal money has been passed on to a State.

An important little consideration here. Suspension is intended to be an interim action and may lead to debarment which is a longer-term, even more final type determination. The other important note is that the suspension does not in any way hold up the investigations that also precede it.

We now have inspectors general come to a lot of our program meetings just to make sure everybody knows the environment we are operating in. The fact of the matter is that if data are falsified or changed, there is the potential that three felonies have been committed. The falsified data that is submitted to the government is considered a false statement. To then send a bill to the government in which you are asking for payment for these falsified data is a false claim. And this one is a nice

catch: if you send in your invoice or you get your check back through the mail, that is mail fraud.

Each one of those felonies is punishable, as they tell us, by up to five years in federal prison and a $10,000 fine. So, falsify some data and, potentially, somebody is looking at 15 years in jail and $30,000.

The IG does tell us that indictments for felony charges are in the works and probably will be applied to both companies and individuals. So, we are in an entirely different world in terms of decertification. That is a fairly stringent decertification of a company or an individual.

So, we are still considered a de facto certification program, and I guess it would be fair to say that a lot of elements that are part of the certification program are active in our program. Certainly, it is a whole new world for us and for a lot of people that have been working for us.

MR. PERLER: I am Arthur Perler from the Environmental Protection Agency Office of Drinking Water. I suppose it is the folks that bring you laboratory certification for drinking water. I don't know if that is popular or not in this room. I have never spoken to this particular crowd before.

I just want to review briefly the authorities and the status of our program and some of the directions we are thinking about moving in I feel you all might be interested in.

Our basic program of laboratory certification derives from two elements of the Safe Drinking Water Act. The first one you see, we feel, gives us the basis for establishing analytical methods and all things related to doing the analyses concerning drinking water compliance, compliance under the Safe Drinking Water Act, and the key words there are, of course, are including quality control and testing procedures to ensure compliance.

Recently with the passage of the Lead Contamination Control Act, an additional kicker was added that we must, in a way, provide a program to ensure that the laboratories testing for lead are providing reasonably good results.

From that flows certain national primary drinking water regulations which apply to the public water supplies which have to provide the compliance analyses and provide those analyses either in their own labs or through commercial laboratories or State laboratories and certain requirements also on State offices for the approval of those laboratories.

EPA's lab certification program and requirements are basically, as most of you know, first of all, specified in

the laboratory certification manual the third edition of which is at the printers right now and would have been available at this meeting, but I think it is just maybe a week or two behind schedule. Some of you have advance copies of that.

This manual is used as the official policy of EPA within its own part of the decentralized program that we have for operating laboratory certification. That is that EMSL-Cincinnati, the EPA's headquarters laboratory program, certifies EPA regional laboratories. EPA regional laboratories then certify a principal State lab in each State, and then it is up to those State labs either to do all the analyses or to certify the commercial laboratories.

So, EPA is not in the business of certifying laboratories. For the business that we are in which is certifying regional labs and principal State labs, we use the lab certification manual as our official policy, and the States, we understand, for the most part pick up most elements of that manual as they certify commercial labs or the labs with which they do business or do business in the States.

State requirements then are pretty much again use of the lab cert manual, utilization of the EPA PE program, and then on-site evaluations either through State auditors or third party auditors.

Let me say just quickly in response to what Al said about PE samples, I will add to the rumor mill and tell you what I know about it. On the privatization or the program under which people may have to pay for a more limited number of PE samples, it is not expected to apply, I don't believe, to PE samples in its initial stages. What is under consideration now are basically the QC samples and the check samples that EPA provides, and I don't believe that PE samples in what is known as the water supply programs will be covered for quite a while. There is just too much backlash against that, and I believe that the program that we will be looking at won't be a sole source or a program that drives up the cost.

Let me point out also that there is nothing in the drinking water regulations that requires that PE samples be provided by EMSL, and there are a number of private entities and some States that have contracted with those private entities to provide samples except, let me say, for the trihalomethane regulations. The rest of the national primary drinking water regulations allow you to use a privately generated PE sample.

Our biggest problem and really what I wanted to focus on, although time is running fast, are the problems as we see them with laboratory certification. First of all, since it is a decentralized program, there are divergent State

requirements which we know now lead to a difference in acceptability and a difference in reliability in the results generated by laboratories in different States.

I don't want to call it a difference in quality, because I am sure everybody is out there trying to generate the highest quality data, but because we all in this room understand reliability in terms of, let's just say, precision and accuracy, there is a difference in that because of the different ways that States implement their programs.

These differences have led to limited reciprocity, differing fee structures, we believe higher costs, and limited availability of labs. That bothers us somewhat, especially since the number of drinking water regulations, the number of required analyses, and the number of drinking water systems required to perform them is going up and will be growing exponentially over the next 10 or 15 years.

The PE and audit requirement portions of the program provide us with a little heartburn also. Simply performing on a PE sample acceptably once a year is no measure of how a laboratory does on routine samples.

I point your attention to an article in the April-May, I guess it is, issue of Environmental Lab, the cover story by Stan Blacker, cover article, which represents a position which EPA and, I believe, the Office of Drinking Water may

be moving towards. In that article, he points out that laboratories that perform perfectly acceptably on PE samples and that even have reasonably good precision and bias still have relatively high probability of making a false positive or a false negative compliance determination because of the interval that precision implies and the statistics that are involved.

And the result of that is exactly what Blacker says. We believe that especially when environmental results are close to standards, there are probably an unacceptably high frequency of compliance determination errors, either false positives or false negatives being made.

Now, we were criticized also fairly severely for allowing a program to proceed which does have such limited reciprocity and without any ability for the private sector to prosecute the same kind of a program. So, we have had on the books a number of years, although it has been largely ignored by most States, policies which do encourage reciprocity and third party, and I am here to try to do that some more. I will take the opportunity to do that whenever I can.

The benefits of that, of course, are that there will be shared capacity, and many States have deficient numbers of laboratories. There will be increased competition. We think it will reduce costs, especially since we are getting

into regulating things which have quite expensive analytical methods associated with them.

And, also, according to the possibility of reciprocity and some other program changes which I don't want to address today, we feel that laboratories will be able to adopt new methodologies more quickly. Let me say that it is not that the laboratories will be able to adopt them; EPA will accept the adoption of laboratories of newer methodologies more quickly.

These are not meant to be alternatives. These are just various things that we are considering and some possibilities of changes in the program.

We would hope that any policy that we would put forward would allow more uniform State requirements...would end up in more uniform State requirements in order that we have more uniform reliability and probability of making correct compliance decisions in the drinking water program.

We would encourage those States that have...and I understand there are not many States here to listen...that many States that have changed their statutes and their regulations to provide programs which are less amenable to reciprocity to change those.

We are considering a complete overhaul of the system, as I said. We expect to come out with proposed regulations which would more likely provide evidence that laboratories

are performing within acceptable standards on a routine basis. Again, I would direct your attention to the general revisions that Stan Blacker discussed in that article, revisions that would attach to each piece of data the appropriate quality information, and those kinds of changes, by the way, could very well end up with environmental regulations, especially under the Safe Drinking Water Act, no longer even specifying the required analytical methodology, that kind of requirement being unnecessary within that type of program.

Now, that certainly is a program that only assesses quantitative analysis, and there are qualitative aspects of that program as well as on-site inspections and audits which I think we will maintain.

As Bill and others have talked about, the agency has gone into high gear on its EMMC which is an attempt to unify quality assurance and quality control in all of the programs and an attempt to unify, where possibly, analytical methodologies, and that is something that I hope you will all stay aware of, and as different solutions are proposed or put somehow into either the Register or put forward in meetings like this that you will comment on those.

Let me skip to the last bullet and say that all of these changes we are trying to move as quickly as possible on and we look for data and support from the laboratory

community, because I think that the last thing that we both want to happen, both within the Office of Drinking Water Programs and from, I think, the laboratories' side is some direct Congressional action which would alter the program, because, actually, we don't want to end up where we feel that we are being forced to make changes. The last changes that were forced on us that way resulted in drinking water regulations which we think probably went a little bit too far.

So, that is the end of what I have prepared, and I think we have questions at the end.

THE 13th ANNUAL EPA CONFERENCE
on
ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

Laboratory Certification & Reciprocity

Arthur H. Perler
Baldev L. Bathija
Office of Drinking Water

LABORATORY CERTIFICATION & RECIPROCITY

- DRINKING WATER LABORATORY CERTIFICATION
  - STATUTORY REQUIREMENTS
  - CURRENT SDWA REGULATIONS
- LABORATORY CERTIFICATION REQUIREMENTS
  - EPA
  - STATE
- ADVANTAGES OF INTERSTATE LAB CERTIFICATION
- DIFFICULTIES WITH RECIPROCITY
- POSSIBLE SOLUTIONS

NRFK-002

CURRENT STATUTORY REQUIREMENTS

SAFE DRINKING WATER ACT - Section 1401(1)(D)

" .... criteria and procedures to assure a supply of drinking water which dependably complies with maximum contaminant levels; including quality control and testing procedures to insure compliance with such levels ..."

LEAD CONTAMINATION CONTROL ACT - Section 4

"EPA shall assure that programs for certification of testing laboratories which test drinking water supplies for lead contamination certify only those laboratories which provide reliable accurate testing."

NRFK-003

CURRENT SDWA REGULATIONS

- Section 142.10(b)(4)

  "Assurance of the availability to the State of laboratory facilities certified by the Administrator and capable of performing analytical measurements of all contaminants specified by the State primary drinking water regulations."

- Section 141.28 - Approved Laboratories

  (a) "For the purpose of determining Compliance .... samples may be considered only if they have been analyzed by a laboratory approved by the State ...."

NRFK-004

CURRENT SDWA REGULATIONS - Cont.

- Section 142.10(b)(3)(i)

"The establishment and maintenance of a State program for the certification of laboratories conducting analytical measurements of drinking water contaminants ..."

"The requirements of this paragraph may be waived by the Administrator for any State where all analytical measurements .... are conducted at laboratories operated by the State and certified by the Agency."

NRFK-005

EPA LAB CERTIFICATION REQUIREMENTS

- Specified in Lab Cert Manual
  - Third Edition - Published - June 1990
- Manual is Official Policy for:
  - EMSL Certification of EPA Regional Labs
  - Regional Certification of Primary State Labs
- Manual is Guidance for:
  - State Certification of Local Labs

NRFK-006

STATE LAB CERTIFICATION REQUIREMENTS

- EPA Lab Cert Manual
- PE Samples
  - EPA, State, Commercial
- On-Site Evaluations
  - State Auditors
  - Third-Party Auditors

NRFK-007

INTERSTATE LABORATORY CERTIFICATION

- GAO Report Criticized Lack of Reciprocity Among States Resulting in High Costs of Multi-State Certification
- ODW Policy Encourages Reciprocity Among States
- ODW Policy Encourages Use of Third-Party Auditors
- Benefits of Inter-State Certification
  - Shared Capacity
  - Increased Competition
  - Reduced Costs
  - Faster Adaptation of Latest Methodologies

NRFK-008

INTERSTATE LABORATORY CERTIFICATION
(Perceived Hindrances)

- State's Rights - DW Primacy Regs
- Acceptable On-Site Evaluations
  - Qualifications of Other State Auditors
  - Qualifications of Third-Party Auditors
- Restraint of Trade
  - Selection of Third-Party Auditors
- Differing State Laws - Due Process

NRFK-009

RECIPROCITY AMONG STATES

(Limited Information Available)

- Reciprocity Possible

  AL, GA, IL, MI, MN, MO, MT, NC, ND,

  NV, NM, RI, SC, TN, TX, WA, WI, WV

- Reciprocity Not Permitted

  AR, CA, FL, LA, KS, KY, MA, ME,

  NH, NJ, OH, OK, OR, PA, UT

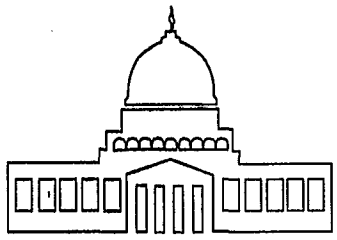
NRFK-010

POSSIBLE SOLUTIONS

- Uniform State Requirements - ODW Survey of States
- Third-Party On-Site Evaluations Sent to States - State Lab Cert Officer Decides if On-Site by State Team is Necessary
- Encourage States to Change Statutes
- National Federal Regulations
- Complete Overhaul of ODW System
    - New QAMS Approach to QA/QC
- EPA Environmental Monitoring Management Council (EMMC)
- Consortium of Quality Environmental Data (CQED)
- Congressional Action

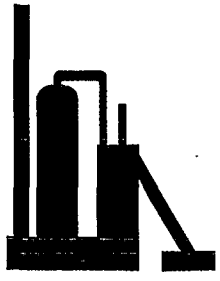
NRFK-011

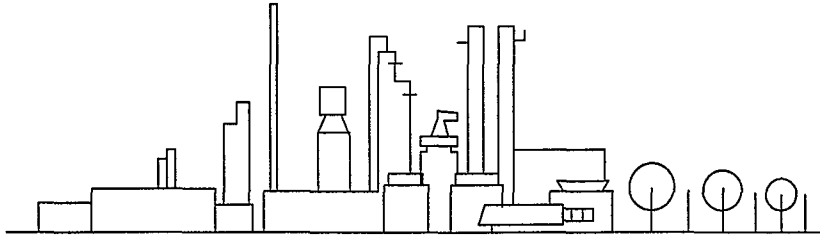
INDUSTRY PERSPECTIVE FOR A NATIONAL PLAN FOR LABORATORY ACCREDITATION

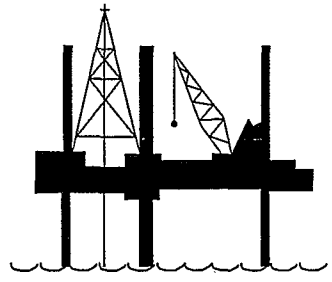


by

GEORGE STANKO







SHELL DEVELOPMENT CO.
HOUSTON, TEXAS

CONCERNS WITH CURRENT SYSTEM OF ACCREDITATION

NUMEROUS STATE ACCREDITATION PROGRAMS

A. COSTLY FOR LABORATORIES

B. CUSTOMER PAYS THE PRICE

C. REDUNDANCY BECAUSE OF NUMEROUS PROGRAMS

D. LABORATORIES SUBJECTED TO FAR TOO MANY AUDITS

E. IMPROVEMENTS IN DATA QUALITY ARE MARGINAL AT BEST

F. GENERAL LACK OF EFFECTIVE PERFORMANCE EVALUATION PROGRAMS

G. LABORATORY CUSTOMERS HAVE LITTLE UNDERSTANDING FOR CURRENT ACCREDITATION PROGRAMS

H. EXPERIENCES WITH SOME ACCREDITED LABORATORIES WAS DISAPPOINTING IN SPITE OF ACCREDITATION

CONCERNS WITH CURRENT SYSTEMS OF ACCREDITATION

INDUSTRY (CUSTOMERS) EXCLUDED FROM CURRENT ACCREDITATION PROGRAMS

A. ACCREDITATION PROGRAMS FUNDED BY INDUSTRY

B. NO CONTACT WITH INDUSTRY

1. PROBLEMS
2. HOW PROGRAMS COULD BE IMPROVED.
3. EFFECTIVENESS OF PROGRAMS.

WHO SUPPORTS NATIONAL ACCREDITATION OF ENVIRONMENTAL LABORATORIES?

1. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
2. AMERICAN COUNCIL OF INDEPENDENT LABORATORIES
3. MOST COMMERCIAL LABORATORIES
4. INDUSTRY:
   - A. CHEMICAL MANUFACTURERS ASSOCIATION
   - B. AMERICAN PETROLEUM INSTITUTE
   - C. OTHERS
5. STATES??????????????????????????

ELEMENTS OF STATE CERTIFICATION PROGRAMS

1. MANDATED BY STATE LEGISLATION
2. REQUEST FROM LABORATORIES FOR CERTIFICATION
3. CERTIFICATION REQUIRES FEES FROM LABORATORIES
4. ON-SITE INSPECTION BY STATE AUDITORS
5. DEMONSTRATION OF LABORATORY PERFORMANCE WITH EPA WP/WS PE SAMPLES
6. MUST MEET CRITERIA FOR PE SAMPLES
7. PERIODICALLY RECERTIFIED
8. SUBJECT TO STATE ENFORCEMENT ACTION
9. SOME PROVISIONS FOR RECIPROCITY BUT SELDOM PRACTICED

MAJOR ROADBLOCKS TO NATIONAL ACCREDITATION OF ENVIRONMENTAL LABORATORIES

1. STATES RIGHTS
   - A. CERTIFICATION AUTHORITY
   - B. ENFORCEMENT ACTION
   - C. STATE PROGRAMS (PEOPLE)

2. RECIPROCITY
   - A. ON-SITE VISIT/AUDITING
   - B. CERTIFICATION FEES
   - C. CERTIFICATION

SOLUTION TO CURRENT ROADBLOCK FOR NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION

1. FORGET ABOUT EC92 AS THE DRIVING FORCE.

2. CONSIDER ONLY ENVIRONMENTAL LABORATORY ACCREDITATION

3. IDENTIFY THOSE ELEMENTS OF CURRENT PROGRAMS THAT ARE ONEROUS

   A. CERTIFICATION FEES

   B. MULTIPLE ON-SITE VISITS/AUDITS

   C. INCONSISTENCIES BETWEEN STATE PROGRAMS

   D. GENERAL LACK OF RECIPROCITY

   E. OTHERS

SOLUTION TO CURRENT ROADBLOCK FOR NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION

4. FORM A NATIONAL COALITION FOR ENVIRONMENTAL LABORATORY ACCREDITATION

   A. REPRESENTATIVES FROM USEPA, STATE AGENCIES, ACIL, INDUSTRY

   B. PREPARE A LABORATORY ACCREDITATION GUIDANCE DOCUMENT BASED ON ASTM/ISO PRACTICES

      a. ASSESSOR CHECKLIST

      b. QUALIFICATIONS OF ASSESSORS

      c. PROTOCOL FOR ACCREDITATION RECOGNIZED AND ACCEPTED BY ALL

   C. LET STATES RETAIN THE RIGHTS FOR PROGRAMS

      a. COLLECT CERTIFICATION FEES

      b. RIGHT TO VERIFY ASSESSORS REPORTS AND ACCREDITATION

      c. RIGHT OF ENFORCEMENT ACTION

      d. RIGHT FOR ADDITIONAL PERFORMANCE EVALUATION

      e. MODIFY STATE LEGISLATION TO ALLOW FOR ALL THE ABOVE

OTHER CONSIDERATIONS

1. IF WE DON'T DEVELOP A WORKABLE PROGRAM, CONGRESS WILL BE FORCED INTO MANDATING ONE STATES WILL HAVE TO ACCEPT AND WE MAY NOT LIKE.

2. BEFORE NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION IS POSSIBLE THERE IS A NEED FOR STANDARDIZATION OF METHODOLOGY AND ANALYTICAL PRACTICES ACROSS ENVIRONMENTAL PROGRAMS.

MR. TAMPLIN: We have been asked to keep this short, so no slides, no overheads. We will try to keep you all bright-eyed and bushy-tailed.

I am Ben Tamplin from the State of California, Department of Health Services, Division of Laboratories. I am Chief of the Sanitation and Radiation Laboratory. We, also, are a centralized laboratory service, although there are a few laboratories in other agencies.

We have a long history of environmental laboratory accreditation going back to the late 1940s when the Porter-Cologne Water Quality Control Act was passed. In 1951, drinking water laboratories came under the purview of the Health Department, and this laboratory approval program grew at the request of Regional Water Quality Control Boards to include wastewater laboratories as well. Wastewater laboratories were dropped in 1981, because the State Water Resources Control Board could no longer afford to support their part of the program.

In 1985, Hazardous materials laboratories were required to become accredited in a separate program. A third program exists in California, but it is really a program of registration by the California Department of Food and Agriculture for laboratories doing pesticide analyses on raw produce.

California began consolidating these programs several years ago with the passage of two bills in our legislature, one which brought together drinking water laboratories, wastewater laboratories at the request of the State Water Resources Control Board, and hazardous materials laboratories. Just last year, a bill was passed that brought the Department of Food and Agriculture's registration program under our purview, but full regulation of these laboratories won't really occur until about 1992.

The old drinking water and the hazardous materials laboratories' regulations stay in effect in California until the Environmental Laboratory Accreditation Program regulations are in place. We expect this to occur by the end of the year, but recognize that it may require more time.

It should be no surprise that this combined program follows the systems that were used by the drinking water and hazardous materials programs, that is, that the certification was granted upon approval of an application, upon approval of a quality assurance plan, upon successful participation in a performance evaluation study, and following an uneventful site evaluation.

One other thing: there is the payment of a fee, and that check is the very first step in the accreditation

process. When one sends in an application, the check comes right off the top and in it goes to the cashier.

Currently, the basic fee in California is $913.28. For each field of testing a fee of $411.34 is added. These fees are adjusted on July 1 or shortly after July 1 of each year by the Department of Finance. It is, in a sense, a COLA.

Incidentally, we levy this fee every year.

The main problem before us right now is completion of our regulations package. We are getting help here...and we think we have done the right thing from an ad hoc committee that is made up of representatives of the American Council of Independent Laboratories, the Association of California Testing Laboratories, the California Association of Public Health Laboratory Directors, the California-Nevada Section of the American Water Works Association, and the California Water Pollution Control Association.

We are ready for public hearings now, and we expect these regulations will be in effect by January 1, 1991.

The lack of regulations has forced us to use existing regulations and has resulted in a very large backlog of inspections. We have to address this backlog in the next three months. We can give interim accreditation without a site evaluation so long as we get the money.

But we need to simplify our process and consolidate our fields of testing. We presently have 23 fields of testing.

That is absolutely ridiculous. We used to have the same 4 that Virginia has, but in the writing of our statute, people got carried away, and we now have, as an example, separate fields of testing for organics by GC/MS for drinking water, for wastewater, and for hazardous materials. Now, that is really ludicrous, because, as you know, once you get the lumps out of wastewater, the analysis is just as easy as that for drinking water.

We have to find a way to simplify accreditation,to get back to where we were. That may be difficult.

We also feel we have to have an effective system of reciprocity. The requirements for analyses in California are soon going to outstrip the State's laboratory resources. We need to accredit out of California laboratories, non-California laboratories.

We need to accredit them in order to provide a resource for some of the programs that are in the wings. We have an omnibus pesticide bill, a pesticides in food bill, which will add perhaps 40 people to our laboratory staff looking for pesticide residues in raw and processed foodstuffs. I don't know how many analyses this is going to take State-wide, but our share will be immense.

Also, we have something going in California now called the Big Green Initiative. It is the environmental plank of our Attorney General's candidacy for Governor. It is an

all-encompassing environmental protection act. It covers food safety and pesticides, agricultural worker safety, greenhouse gas reduction, ozone layer protection, commercial and residential tree planting, estuarine and ocean water protection, water quality protection, and marine resources and human health standards.

We don't have enough laboratories in California to do the monitoring that will be required under this initiative. We have an initiative system in California in which, if you don't like what the legislature is doing, you may go to the ballot box through the initiative process. This particular initiative came into the Secretary of State's office with two times the required number of signatures. It is estimated in the polls to be running 4 to 1 in favor. It is expected to pass and we will need laboratory resources, so we will have to go outside.

Also, some of our California laboratories are divisions of companies with laboratories in other States, and some of them have different capabilities. At the present time, there is no way they can trade samples back and forth to get the biggest bang for their buck. That is to say, both laboratories must be approved in California before the movement of samples back and forth can occur, and that is all wrong. We are not supposed to be restraining trade.

Many California laboratories are accredited in other States, some in 12 or more States, and I am certain there is a very high cost involved for them to comply with all the regulations. It is particularly costly in the area of proficiency testing. Here we really need an effective centralized system of performance evaluation.

Our current regulations allow us to recognize other programs, and we have told other laboratories if you are in the EPA program and you are analyzing Water Supply or Water Pollution Evaluation Samples or both, that is fine. We will accept those data. So far our legislature has gone along with this approach.

The reason we have recognized EPA PE Studies is that we really don't want to make our own PE samples. We don't want to create an empire. We think it is wasteful when a program like EPA's already exists, a program that really does work pretty well. We do criticize a lot, but we also recognize that this performance evaluation program is a good one, and it needs to stay in place.

We are ready in California to join other States and EPA in establishing some sort of nationwide centralized PE system. We have authority to charge laboratories for these samples, and even if we didn't, we could finance it ourselves out of the fees that we charge for accreditation.

We are happy that EPA has reversed at least part of its stand on the phase-out of some of its PE activities, and we call upon you at EPA to take a leadership role and help us establish a national program. If you want to come out to California to discuss it, we would be happy to have you. Just bring rain.

MS. PREVOST: I am Margaret Prevost from the New York State Health Department, the Environmental Laboratory Approval Program which is the program that certifies all environmental labs in New York State and out of the State.

I think you just heard the West Coast. You are going to hear the East Coast.

In our program, we certify labs in four categories, drinking water, wastewater, solid and hazardous waste, and air emissions. We have a little under 850 certified labs. Close to 300 of those are out of State labs.

We make our own proficiency samples. We have never used EPA's, probably for a lot of reasons. One of them is that our program really started, although it had a history...we certified drinking labs since the early 1950s...but the ELAP program to make it short, as it is called, became official in late 1985, and about at that time, there was already a little bit...I wasn't with the

program then, so excuse me if I am making a mistake...but there was concern about that perhaps EPA was going to cease making samples. So, we do make our own proficiency samples.

A laboratory in our program is inspected once a year and proficiency tested twice a year for what they are certified for.

I spent most of the day trying to get here. You had already started when I got here, so I don't know what the newest rumor is about the PT samples and maybe it has all been clarified now, but we received a number of calls from other States when the announcement first came that the wastewater samples were no longer going to be available. We are able to provide them to other States if that is necessary.

It sounds like now that isn't going to be necessary, but because we have the whole system in place and it has been in place for five years.

I think we could go toe to toe with California trying to explain our fee system. If there are any New York labs here, they would agree with me.

We had one fee system. It changed as of April 1, the beginning of our permit year. We now have a base fee of $500 plus an analyte fee for every analyte you are certified for plus a volume fee paid on the volume of your analysis of those analytes you are certified for on New York State

samples only. The legislature came up with this one; we didn't.

But none of our laboratories are in revolt yet, because the New York State budget has not passed. It is now 41 days overdue, and I can't send out any bills until they pass the budget.

I think one of our concerns...and we hear it from our laboratories. We have very active laboratory associations in New York. One of the things is we are very aware that a large lab that is certified in many States spends a great deal of time and a great deal of money. Actually, they were less concerned about our fees...they didn't like our fees, but they were less concerned about that than the idea of the time and money that is spent on doing proficiency testing, inspections, people come to inspect.

They would like that resolved. We understand that. In fact, the legislature just passed a bill saying that we are going to have an advisory board, a 7-member advisory board, and its mission, among other things, but its first mission is to discuss reciprocity and come up six months after it is formed with a report to the legislature.

One of the problems...and I think this is worthy of discussion...is the fact that as a northeastern State where we have a lot of pollution...and I think it is true that different regions have different problems...our legislature,

our Governor, and our Commissioner of Health have concerns. So, how it is done on a national certification program or the PT samples.

For instance, with EPA, it is 7 VOCs. In our State, a lab has to be certified for 52 VOCs.

So, I don't think it is that easy to put together something that would be universal, because then you would still have these subprograms, because you know how States are. You never go backwards. You only add. We don't have the Big Green coming down which sounds awful, but they never stop. I mean, you just keep testing for more and more.

It is the argument that we have to be this stringent and we go along with anything that is as stringent or more stringent. I am not quite aware of any other State...there probably is...that does annual inspections, but we do, and I don't think the Governor or the Commissioner of Health is going to back down on that.

So, there are a lot of issues, but we see the need for some type of reciprocity.

I think it is very important for your contiguous States especially, even if it is almost sort of a regional. So many labs are on borders; large labs go right over.

I don't know the answer. I do think that if one of the things is the proficiency test, if that can be addressed.

My concern is on having some sort of uniform proficiency test.

What do you do about the individual State requirements like ours where you have to do 52 VOCs? How is that going to be addressed? How will that prevent the labs from having just two levels, three levels, four levels? Other States probably have specific things they want tested. I don't know how that will be addressed.

Thank you.

MR. STANKO: I would like to present to you the industry perspective towards national laboratory certification. We will go through some of the concerns we in industry have.

I am not going to elaborate on any one of these specific things. The main thing is we have concerns with the numerous State accreditation programs. Other people also have concerns, and these are some of the items that lead to that concern: costly for laboratories; the customer pays the price.

We are still bottom line people. Essentially, all the certification fees that States are charging, the laboratory user has to pay it, and we are the laboratory user.

Another major concern that we have is that industry is left out of the entire system completely. We, industry, are

the customers of these contract labs more or less getting data for regulatory purposes, and nobody from the State agencies ever asked us, are there problems with the program, how could the program be improved, and are the programs effective? In other words, has it done anything for data quality?

The first question I am going to ask is who really supports national accreditation for environmental laboratories? I think the United States Environmental Protection Agency does and the American Council of Independent Laboratories does. I think most of the contract laboratories do and certainly industry does. The Chemical Manufacturers Association the American Petroleum Institute have gone on record as supporting national accreditation of laboratories, and there are others.

On item number 5, I needed 50 question marks, but they wouldn't quite fit. But in fairness to the States, I think you have to look at what are the elements of all the State programs, and this could be difficult to summarize. There is no way anyone can go through all 50 certification programs and do a good job of it.

What I have done is I have isolated some of the things that are common to all of them. Most of them are mandated by some sort of State legislation. They also require request from the laboratories for the certification. In

other words, the State requires that the laboratories ask for certification in that State so that certain requirements have to be met.

Number 3 you have heard a lot about. Certification requires fees from the laboratories. No new taxes, huh?

On-site inspection by State auditors, demonstration of laboratory performance with the EPA WP and WS samples, must meet criteria for PE samples, periodic recertification, as we have heard, and they are subject to State enforcement.

There are some provisions in all of these certification programs for the big R word, reciprocity, but it is seldom practiced. If it is practiced at all, most of the State programs rely on WP and WS samples, and that is about where the reciprocity is.

Now I would like to show you major roadblocks to national accreditation of laboratories. Number 1 is State rights. Once you give States the right to do something, you can never get it back. They have this certification authority. Someone has granted that authority, and now it is difficult to take it back.

A lot of States feel very strongly on enforcement action, and here I agree that the States should enforce this type of a program.

Number 3, the State programs. Most people think that if you have a national accreditation program, all the State

people involved in their own certification programs lose their jobs.

The big R word. On-site visiting and auditing. Every State feels that they have a need to send their auditors to that laboratory to inspect it. Some of the laboratories tell me that half of their staff is involved in nothing but working with auditors. The other half do the samples.

We have heard a little bit about certification fees to five significant figures at one point, and then who grants certification?

These are some of the major roadblocks, and now I am going to do something unusual. Instead of being critical and criticizing which Bill Telliard tells me I am good at, I am going to try to see if I can give some solutions to our current roadblocks.

Many of us thought that EC92 would be the driving force for a national accreditation of laboratories. Many of us thought that the environmental labs that we deal with could go in on the coattails of those product testing laboratories that are going to be affected or impacted by the EC92 regulations.

The first thing we have to do is forget EC92. Just as clinical laboratories are different from environmental laboratories, the product testing laboratories associated with EC92 are entirely different from the environmental

laboratories. That is one of the major flaws we have to address.

Consider only environmental laboratory accreditation. That goes along with divorcing ourselves from EC92. Groups like CQED and IAETL have tied themselves with EC92. I think they are going to have to step back and divorce themselves from EC92.

What can we do to identify those elements of the current program that are really onerous to us? We don't like certification fees, but just like I said, no new taxes. Have you ever seen anybody give anything back yet? I don't think we stand a chance on that.

Multiple site visits and audits. I think this is one area where if we have reciprocity we can really do away with some of this nonsense of having 50 States going to audit each single laboratory. I think this is one area where we can have reciprocity.

There are lots of inconsistencies in the State programs. Here again, I think we have to look to the national EPA to try to come up with some kind of a guidance so that we can have consistency between the State programs.

There is general lack of reciprocity. We have heard that R word enough times from a number of speakers. I don't have the solution to that.

I think we need to form a national coalition for environmental laboratory accreditation and environmental laboratory accreditation only. I think we need representatives from the USEPA, the State agencies, ACIL, and the industry as well.

I think we need to prepare a laboratory accreditation guidance document based on ASTM and ISO guidelines. They are out there. We don't have to make these up. They are available.

We need to come up with an assessor checklist that is uniform and acceptable to all State agencies as well as the Federal EPA. We need some sort of guidance and some sort of qualifications for the assessors so that no matter which assessor is used, all States and the Federal EPA and industry and the laboratories will recognize the assessor as being qualified and being able to conduct these audits.

I think we need a protocol for accreditation recognized by all and accepted, and this is where I think we look to the national EPA to look at the State programs and see what we have in common and come together with something that all the States can accept.

The politics involved says we are going to let the States retain the rights for some of these programs. The collection of certification fees, I don't see any answer to that. The right to verify assessor reports and

accreditation. Here, again, I think the States should have that right.

I think the States ought to maintain the right for enforcement action, and I think the States ought to have the right for additional performance evaluations if they are not willing to accept WP and WS or, like the last speaker said, they have their own program. Shell has its own program. I think the States have to be recognized and that they can do something additional or accept WP and WS.

The last thing, I think, is to modify the State legislation to allow for all of the above.

This slide has nothing to do with the actual accreditation. There are other considerations. If we don't develop a workable program, Congress will be forced into mandating one that the States will have to accept and we may not like at all. I also am giving a pitch for the EPA EMMC. We also need to address the 518 report issue. Before a national environmental laboratory accreditation program is possible, I think there is a need for standardization of methodology.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Thank you, George.

Now, for any of you who would like to ask questions or make comments, all of the panel is available at this time. Would anybody like to start?

MS. ORDONA: I am Alicia Ordona from Virginia, and I want to address this one to the California representative. What is your main objection to reciprocity? I mean, at least New York has said about VOCs, but what is the State of California's main objection to reciprocity in certification for drinking water?

MR. TAMPLIN: We have no objection.

MS. ORDONA: You don't?

MR. TAMPLIN: No. We have the authority in the statute. We don't have a mechanism in the regulations yet. That will probably be about the first of the year.

MS. ORDONA: In that case, I think I am going to recommend to my boss that we are not going to write reciprocal certification for laboratories from States that don't write reciprocal certifications from Virginia.

MR. LEVY: Nathan Levy with A&E Testing in Baton Rouge.

George, thank you. I wish that everybody in the agency and in the State governments had your feelings. I think most of us contract labs do have your feelings, and I guess my question becomes to anybody who wants to take it.

Why not? Why can't we do it? Why can't we take one person from every State and a few from the EPA and lock them in a room and tell them they can't come out until they have a program? Why not?

MR. FARRELL: Well, that gentleman just stole my thunder. I am Jack Farrell from Enseco.

George, I would also like to extend my thank you. I don't think it could have been said better.

I don't really have a question. I have a couple of comments I would like to make.

The first one is, very few of the programs that were talked about and very few of the programs that I know of, excluding the CLQ, deal with more than a capability discussion of what a laboratory can do. We need to add ongoing performance to whatever program or programs come up.

The second comment I would like to make is while we have half a dozen approval programs up there, there has to be at least 100 of them out there. There is also starting

to be a lot of different groups that are focusing on this accreditation issue, and I applaud that.

The request that I have is...and, Bill, maybe you can help or somebody can help...let's bring it all together so that it is one group that is addressing this issue and coming up with one consensus standard. If there is any way that IATA or CQED or anybody can help do that, that is what they are there for.

Fifty groups looking at fifty different certification programs is only going to cost us a lot more.

MR. TELLIARD: Anyone else?

MR. HOLT: I am Phil Holt from Occidental Chemical.

I would like to preface my remarks by saying I am in favor of lab accreditation. I think it has accomplished a lot, but as a matter of curiosity...and I will address this to New York since that is a program I am familiar with...I would like to know what we are accomplishing with the ongoing programs.

We started five years ago. What percentage of laboratories did we weed out as being not acceptable five years ago, and on an ongoing basis, are we continuing to weed out bad laboratories, or has it kind of leveled out now and only good laboratories are participating?

MS. PREVOST: Very honestly, only because I got a question a week ago from the New York Times or I wouldn't really be up on this, you are right. Everybody is suddenly getting interested in this. Just out of the blue, the New York Times wants to do a series on environmental laboratories. They haven't done it yet, and I wonder how they will manipulate what information I gave them. It is always a matter of concern.

Since the program won't be give years old, actually, until November of 1990, 342 labs have...records have not actually been kept of why 342 labs that were in the program are no longer in. I think I should preface this by saying before this, except for the drinking water labs which was a voluntary program...

By the way, New York State's laboratory ELAP program is a voluntary program in that wonderful way they like to define voluntary. The fact is that no laboratory can do work for the State of New York or any of its political subdivisions which means anything that is paid for by public monies must be done in a certified lab, but if you want to limit yourself to the private sector or just to drinking water in private homeowners' wells, you don't have to be certified. Obviously, most people are certified because the public sector money is very important.

Now, this was a group of laboratories that had never been regulated before, the environmental labs in New York State. Actually, the mission of the program at the time was to ensure there were competent labs for environmental analysis. It wasn't really to take labs in and throw them out.

The whole point of it was to sort of put on a layer of standards or regulations and then...and I do believe they have been made somewhat more stringent over the last four and a half years...the mission really is to try to bring laboratories in compliance. We don't really like to throw them out.

What they do do is many labs have withdrawn. We certify by specific analysis in New York what you want. If you fail your proficiency test enough times, you know, finally some laboratories actually shrink down to have so few analyses that they are certified for that they withdraw.

But the real mission of the program was not to throw a lot of labs out. It was to bring them up to a level of competency and, yes, it has leveled out. It has leveled out. There are still labs that become withdrawn, as we like to call it. We withdraw them from the program or they choose to be withdrawn, but certainly from the earlier, say, the first two years, it has leveled out.

Of course, you cannot say that every lab in our program is or very well...you do a proficiency sample. They are the best sample works that have been done. I mean, you know, you only have so much.

We do have unannounced inspections in New York, so nobody can kind of gear up for our inspections.

MR. CARTER: I would like to make kind of a response to what you said and pick up on something Jack Farrell said.

In our program, we do accreditation, and I guess the best way to say this is good labs have bad days. In some internal meetings that we have had to discuss some of these implications of accreditation, one thing I would say that most of us that have thought about it within EPA have a concern about is that the purchasing public, industry, or whomever really should understand that it is up to them to verify that this capable laboratory performed on their particular work.

Like I say, the best labs and the best people have bad days. So, being accredited or certified does not assure that the individual piece of data you got is exactly what you wanted.

MR. HOLT: I would like to ask one other piece of information of New York. Since things have sort of leveled out, is it time to start

thinking about maybe annual testing instead of biannual or if you are participating both in drinking water and wastewater quarterly testing?

MS. PREVOST: Did you say quarterly testing?

MR. HOLT: Yes. The drinking water and the wastewater were on opposite three-month cycles, so you were getting samples in every quarter.

MS. PREVOST: Oh, yes, right. No, there has been absolutely no move by the Commissioner to go to that type of...to reduce the number of proficiency tests.

Actually, if you will notice, we keep adding things that we proficiency test for. That seems to be, very honestly, the way the direction goes in New York. I am being honest.

MR. TELLIARD: Anybody else?

MR. PRONGER: I am Greg Pronger of National Environmental Testing.

The first thing I would like to say is that there seems to be an irony in the situation. For the first time, the USEPA has somebody coming up to them asking them to be regulated, basically, and the USEPA is having huge problems trying to figure out how to do this. It is probably the first time in history.

Normally, everybody is complaining about the EPA coming in and regulating them. Here is somebody looking to be regulated and having trouble doing that.

What seems to me one of the problems with getting anything implemented is the level of discussion going into it. If something would be promulgated just to get a program started, if the COP instead of...a problem that a lab has, if you perform on a COP sample but your bid isn't low enough, you technically aren't part of the program.

If there were a two-tier level where you could pass a performance sample, be a part of the program and not receive a sample, but if your bid is not high enough not become part of it and have to pay for that, the sites visits and such, that would at least be a step in the direction where it is a mechanism already established for going out checking on laboratories, taking care of that.

If you could then say you are a so-called COP lab and just not receiving samples, it would address some of the problems that the environmental labs are seeing, because the COP program kind of initiated the problem in that the laboratory was caught in the situation that you could pass every PE sample, keep bidding on them, getting PEs, and never become part of the program because your dollar bid is too high.

Then, if a client would call and say no, are you a COP lab, you would have to say no. Even though you could pass the samples forever, pass any type of inspection, you never get any place like that.

If something like that were started just to initiate that and then build from that on trying to get reciprocity from the States, trying to get some reciprocity between the different programs, it would be a building block, and I don't think anything will occur with this until there is just some type of initial action taken.

Thank you.

MR. CARTER: One of the problems with the de facto COP certification is that it is not just a PE and accreditation system. The fact that there is this ongoing, literally daily, inspection of deliverables means that we don't just do the quarterly PE samples. In essence, there is, like I say, almost a daily assessment of lab performance, and we make decisions on lab eligibility for samples under our program on a weekly basis.

So, performance on periodic PE samples is a relatively small part of the program.

We have problems right now with requests from media, various places, under Freedom of Information Act for PE sample results. What do you do about the lab that has passed the most recent one but they failed the last four?

Do we say yes, they passed the last one and they have done one right out of four? Is that really an accurate assessment of the laboratory?

The other problem is funding and authorization. We don't have any authority to sell our PE samples. We are prohibited by statute from giving away anything from Superfund.

So, as I say, there is a kind of an inherent problem in our passing on our de facto certification outside our program, and we find ourselves in a position where, due to the various scrutinies we are under, we can't really cut it back and accept other accreditations.

I guess the best thing I can say is we understand the problem.

Recently, the Office of Waste Programs Enforcement indicated they were considering making part of their consent agreements with responsible parties a requirement that they use COP laboratories. We assured them that was improper and at most what they could require is adherence to COP protocols and COP reporting requirements.

So, as far as I know, we have prevented them from further contributing to the problems inherent in a COP de facto certification.

MR. TELLIARD: I would like to thank the panel.

MR. TELLIARD: I want to thank you all for coming. I would like to thank Jan Sears in the blue dress in the back who makes all this happen every year. Jan, would you like to stand up?

I would like to thank the court reporters whose proceedings we can't print until September, but we will.

And I would like to thank you all for coming. I hope you have had a good meeting. I hope to see you back here next year, probably same time, same station. Anybody who has any ideas on subject panels or papers, please give me a call or drop me a line. We are always looking for new material.

Thank you so much for coming and thanks for your attention.

13th ANNUAL EPA CONFERENCE ON ANLYSIS OF POLLUTANTS IN THE ENVIRONMENT

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