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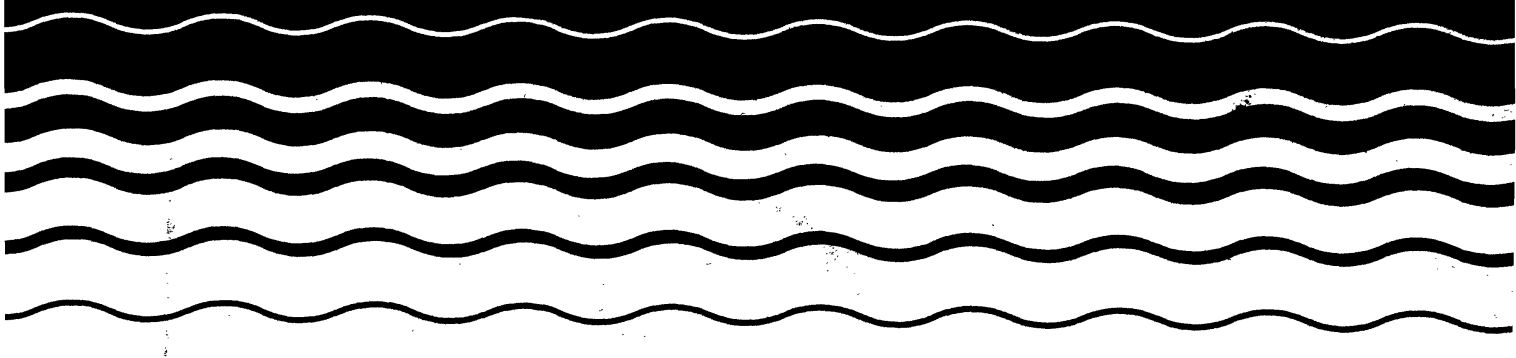

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF WATER
OFFICE OF SCIENCE AND TECHNOLOGY
ENGINEERING AND ANALYSIS DIVISION

FOURTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

MAY 8 & 9, 1991

FOREWORD

The Fourteenth Annual EPA Conference on Analysis of Pollutants in the Environment was a resounding success. The Conference was attended by over 300 scientists from industry, environmental laboratories, and state, local, and federal government agencies. The Conference provided the attendees with the opportunity to discuss the latest developments in analytical methodologies for the determination of pollutants in the environment.

These proceedings document 24 technical and policy presentations on subjects ranging from advanced sample preparation and data reduction techniques for GC/MS analysis to EPA's efforts towards analytical methods integration and the implementation of good automated laboratory practices.

We would like to thank Jan Sears of ERCE for coordinating the conference, Harry McCarty of Viar for his assistance in arranging the technical program and all the others who helped make the Fourteenth Annual Conference a success. We are looking forward to your attendance at the Fifteenth Annual EPA Conference in May of 1992.

W. A. Telliard

FOURTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

Office of Water
Office of Science and Technology
Engineering and Analysis Division

May 8-9, 1991
Norfolk, Virginia

TABLE OF CONTENTS - 1

FOURTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

TABLE OF CONTENTS - 2

FOURTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

TABLE OF CONTENTS - 3

FOURTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

TABLE OF CONTENTS - 4

PROCEEDINGS

MR. TELLIARD: Good morning. Welcome to the 14th Annual Norfolk Analytical Meeting. I'd like to welcome you. My name is Bill Telliard. I am with EPA and I am here to help you.

For those people who are new to the meeting, there are some rules that we abide by. There is no physical abuse to your neighbor; oral is always acceptable. In so doing, we'd like to have you during the proceedings, if you have questions of the speakers, come to the microphones that are around the room and state your name and your organization and ask your question. If for some reason you don't do that, these two women over here will physically abuse you.

The agenda is kind of a full one and we're going to try to stay on time for a change, which means that at the breaks when you go out and get your strawberry and coffee, if you would kindly get your tushes back in here so that we can keep the papers moving...

I'll have some more announcements later on, but I'd like to get the show on the road.

Our first speaker this morning is Tudor Davies.

Dr. Davies has been with the agency for about 20 years, unable to find gainful employment. Tudor has, in another life, been in charge of the Marine and Oceans Program prior to coming over the Office of Water just about a month ago or three weeks. So, he is going to give you an insight into some of the things that the Office of Water is going to be looking at and talk a little bit about the reorganization that has just occurred in the Office of Water.

DR. DAVIES: You're a large audience, and you sort of disappear off into the distance, so I'm a little bit intimidated--by the size of the audience as well as by looking at the program, which I saw last night....

Bill is a little irreverent in most things that he does, so I was bracing myself for his introduction--which turned out to not be too bad.

I was thinking last night about what I was going to say today....Yesterday I came from a meeting with sewage authorities, with a different sort of orientation--but at least I knew what they wanted me to talk about. Last night, I was wondering about Bill Telliard's motives for asking me to come here, and I thought about the worst things first: having looked at the program and knowing my analytical chemistry is 20 years behind me or more, I started to think perhaps Bill was out to intimidate me by the science here, to show me how much I didn't know. But then after awhile I ascribed a better motive to him, because he knows that in the Office of Science and Technology, which is where we both reside now, we do a lot of regulatory decision-making. He understands some of the leaps of faith we have to make, safety factors that we impose, and I began to think that what he was trying to show me was that--at least in the analytical chemistry area--the words, precision, improved quality, etc., all of these have meaning...and that we are at least moving progressively to improve the science, in order to reduce the minimum detection levels and even to automate the analytical methods and make them cheaper. I think Bill's motive today was to tell me that, at least in this area, we have good science and very capable people. I *hope* that was the message that he's giving me today.

I've been on the job in the Office of Science and Technology for a couple of weeks, and I'm going through a whole series of briefings on what goes on. And so I think the most appropriate thing to talk about today is to tell you a little bit about what we do--about why we reorganized and what we reorganized in the Office of Water at EPA. That's the thing that's on my mind

at the moment and I can be a little coherent about that.

What I'd also like to do is perhaps to tell you some of the things that we're doing in the Office of Science and Technology that are relevant to you and discuss some of those issues that might be of interest to you.

EPA has an administrator who's been on board two years, and he is looking for a change of agenda within the Agency. He sees that we've had success--particularly in the Office of Water over the last 20 years--in applying a technology-based approach to water-pollution control, and we've done this very much through command-and-control type operations. And what he's looking for--and I have some sympathy with this--is that we should be moving *beyond* command-and-control and dealing with issues such as cross-media pollution. Realizing that many programs have now been delegated from EPA to the states, many programs have been delegated from the states to the cities, and most pre-treatment and toxic reduction programs are done by the cities managing industrial input, we are looking at pollution prevention as much as control, and we should be taking advantage of any innovation that's out there. So we should be looking at some degree of flexibility in our systems.

Further, the administrator talks about taking advantage of the best science that we have in decision-making. In trying to move beyond command-and-control, trying to think ecologically as much as in the past we've focussed on human health, we have to start talking about geographic targeting, about focussing on specific environmental areas that are susceptible to management and control, and perhaps move beyond the basic command-and-control programs and do some new and innovative things. In that light, we reorganized the Office of Water.

[First slide. The Office of Water used to be seven offices. We've now focussed into four areas. (1) We have an Office of Waste Water Enforcement and Compliance that takes the old Enforcement, Permitting, and Municipal Control Office and "gloms" them all together so that the result is a spectrum that they like

to say "runs from white hat to black hat." (The old office director of that area said that perhaps the motto for that office should be, "I want to go out and crush someone.") (2) Then we have the Office of Science and Technology, which we'll talk about in a couple of minutes. (3) We put together some of the programs developed over that last couple of years on wetlands, the coastal area, storm water management, and things of that sort into the Office of Wetlands, Oceans, and Watersheds. That office will have a watershed function in the future. (4) Finally, we've put the drinking water program together with the ground water program.

We have three major statutes that we work with in the Office of Water. (1) We have the Clean Water Act, a major statute which is currently being reviewed for reauthorization on the Hill, and there's a great deal of activity within the Agency working with the Hill on the reauthorization. (2) We have the Safe Drinking Water Act. You probably saw that we were in the press yesterday on the lead rule and lead activities in the Agency, particularly for drinking water. (3) And then, finally, we have the "ocean dumping act," the Marine Protection, Research, and Sanctuaries Act, which has been very much narrowed over the last couple of years as we've gone away from permitting the dumping of industrial waste and sewage sludge into the ocean, so that now the only thing that we permit to be disposed of into the ocean is dredged material. We'll talk about sediments and some other issues in a moment.

[Second slide.] Again, the Office of Science and Technology...we've divided into three major groups. The first of those groups is the one that you are probably most familiar with, having had to suffer through with Telliard for the last 14 years: the Engineering and Analysis Division, which largely carries the responsibility for the Effluent Guidelines Program. This is the program that develops technology-based guidelines for specific categories of industry and is very much involved with your analytical program in terms of defining effluent, looking at the technologies available for managing effluent, and particularly, looking at the economics of that management and the significance of

regulating those industries.

EAD has perhaps more statutory and judicial deadlines than I like to think about. In fact, I think the whole office has about one judicial deadline per person to go around, which means that sets your agenda pretty closely.

One of the things I'd like to reflect on as we talk about the Effluent Guidelines Program is that what Bill Reilly has talked about is perhaps a "kinder and gentler" EPA--and that we're going to start moving away from command-and-control somewhat. In talking to EMSL yesterday, I kept on emphasizing that we were looking to flexibility and change...and the guy behind me on the program stood up and started to talk about all the things that we had done in enforcement, how we had fined this city $3 million and hit this industry for something else...and someone in the audience stood up and said, "You know, you have a very mixed message that you're giving here. On the one hand, you're talking about flexibility, and on the other hand, the Agency still has this command-and-control mentality."

I think we have a real problem with communicating in the Agency, and there's a little story I want to tell you, because I think we *all* have problems with communicating. I think you have a problem in dealing with biologists and regulators in terms of conveying chemistry to them and the depth and understanding of your techniques.

We often talk and hear very different things. I'd like to tell you a story that emphasizes that. It's a little bit off the point, but it adds a little light relief to the proceedings, and there is *no* religious connotation to this story at all. In fact, it was told by my minister about three or four weeks ago, and I thought it was very appropriate to the subject of communication.

In the Middle Ages, there was a Pope in Rome who was very, very flexible in terms of his beliefs, and the rest of the clergy in Rome was very, very conservative and wanted to get the Jews out of Rome. And the clergy pushed on this Pope, and they said, "You know, you've got to get them out."

And the Pope said, "Well, let's do it this way. We'll have a single combat between the Jews and the Catholics here to decide who will leave, and I will be part of the single combat, I will be the Catholic's champion, and they can choose their champion. To make the contest difficult, it will be a debate--and because I have such an enormous reputation as a debater, we'll do it in mime."

The Jewish community was very upset about this, but of course this was their chance to stay in Rome. And so they asked the most distinguished Rabbis if they would debate the Pope, and the Rabbis didn't want to do it. It eventually came down to a guy low in the structure who was a bit of the clown. He had to take on the Pope.

On the day of the debate, the Pope showed up in all of his finery with the clergy. And the little Jewish guy showed up, and he wasn't very well dressed, he looked sort of out of place among these people.

The Pope began in mime...I hope you can see me. He sort of took his arm...and just made a broad stroke, like this...and that was the opening shot of the debate.

His opponent looked at him for a while and did *that*...put his finger out and sort of shoved it down toward the ground, like that.

The Pope thought for a while and he made the next step...he moved three fingers toward his opponent, like that.

And his opponent stopped and thought about it and he just showed him one finger back, like that.

And then the Pope thought for a little while longer and then turned aside and pulled out the bread and the wine and showed it to his opponent. And his opponent looked at him for a while and took an apple out of his pocket and bit into the apple.

And the Pope said, "Oh, that's fantastic!" He said, "You have won, you can stay in Rome."

And so everybody left and all of the Cardinals, etc., said to the Pope, "Well, what happened? Interpret the debate for

us."

So the Pope said, "Well, I started off by saying, 'God made the heaven and the earth.' He came back and he did *that*, which meant to me that He also made man on the earth. And then I said, 'The Trinity,' and he again came back to me and said, 'He made man in his image.' And then I took out the sacrament and showed it to him, and he turned back to me and showed me the apple and he said, 'Man is human. He was tempted.' You know, that was wonderful. He had countered everything I said, so the Jews can stay."

So there was enormous celebration in the Jewish community, as you'd expect, and finally they got their champion aside and said, "Well, what happened?"

So he said, "Well, this is the way the debate went. He did *this,* which meant to me, 'All of you get out of town by nightfall.' And I said back to him, 'Not one of us is leaving.' Then he countered again and he said, 'You have three hours to get out of town.' And again I said, 'Not one of us is leaving.' So he said I had convinced him at that point. And so what we did then was he took out his lunch and I took out my lunch and we sat down and had lunch."

Think about how many conversations you've had that sort of worked like that.

Anyway, let me tell you a little bit about the rest of the office and the great difficulty we have in communicating some of the decisions that we make on regulatory matters.

We decided, when we put this office together, that we would try to pull some of the scientific people out of some of the other offices within Water, to try to consolidate and get a critical mass of scientific issues and people that we were dealing with. We thought that we would do that by having a risk assessment group outside of the Effluent Guidelines Program, the risk assessment group that you see in the middle there, and a risk management group.

The risk assessment group is charged with developing

health criteria for both drinking water and surface water regulation. If you'll look at that group, you'll see that we first analyze surface water (which we do very well) and then worry about the effect of the contaminants we find in the surface water on human health and the environment. Most of the work that we do in that area is based on translation from animal studies and aquatic toxicity studies that we do--so our ability to precisely measure chemicals in water and other media is really not matched by the science we have in looking at human and ecological risk assessment. We impose many safety factors, and we're often translating information from things like rat studies, trying to understand the impact of toxicity and perhaps cancer on human beings. So think about that as you consider the human health criteria that we've developed.

Often, one of the things that we're concerned about when we're setting drinking water standards is the reproducibility of the analysis method for water--and you're very helpful to us there. But again, there are those uncertainties in the risk assessment part of the program.

When we come to the ecologic criteria, we're interested in water quality. And we have a set of toxicity measurements and bio-concentration measurements that we make, particularly on a various file of animals, to come up with risk levels that are then incorporated into standards to protect the safety of surface water.

One of the areas that we're getting into is sediment criteria. When we look around the country, we see many, many areas in which the historical discharges, and perhaps the current discharges, are contaminating surface sediments. And that contamination doesn't stay in one place but recycles into the water column. There is exchange between the sediment medium and the biota so that we have a great deal of concern, particularly for those persistent toxic chemicals which bio-accumulate in humans. I'll talk in a moment about the Great Lakes, which is the site perhaps the furthest along in determining where those areas of sediment contamination are and in trying to deal with strategies to

remediate the problem.

The other part of the risk assessment area is the sewage sludge program. We have proposed a multi-media regulation for sewage sludge. It deals with placement of the material in certain environments, incineration of sludge, land filling, land spreading, etc. I think we've broken some new ground there in risk assessment. I know that Bill was very involved with the sewage sludge studies in terms of characterizing the toxicants in sewage sludge around the country...and we've had to work with many, many people across the Agency and deal with multiple statutes, as well as the Clean Water Act, in developing this regulation for sewage sludge, which will be proposed (we hope) next year. It will have multiple monitoring and assessment requirements what I'm sure some of you will be involved with. So we're dealing with human health in considering water, drinking water, and sewage sludge, on the assessment side.

On the risk management side, we're dealing with setting standards, particularly for surface water. We have a proposal that will be coming out shortly that will require all states to have standards for the materials that we've developed criteria for, and we see a further proposal coming out of the Great Lakes area, a proposal which is supported by all of the Great Lakes states, to set further, more specific water quality standards to protect the Great Lakes environment. The Great Lakes states are perhaps at the cutting edge in developing new techniques in that area. Those of you that are interested in development and implementation of water quality standards should watch the Great Lakes program to see what they are doing.

We are trying to develop standards for surface water, we're trying to develop standards for ecosystems, and we're developing standards for things like wetlands and sediments.

It's particularly interesting, I think, that we're developing standards and criteria for sediments, an area where we have a difficult medium to deal with and a whole series of different purposes at work.

We're looking, one, at preventing the toxic material from getting out into the environment in a concentration that can cause sediment contamination, and so we need criteria for our control programs for sources, particularly point sources. We have so much contamination out in the environment in Superfund sites and in contaminated sediments that we need criteria that will allow us to define the clean-up level. That's another purpose.

Then we have the problem of dealing with material that we want to move for navigation, material that is in the navigation channels and is contaminated: the dredge material program. In this program, we're trying to deal with sediments as a total medium. We're trying to deal with the whole toxicity, the whole potential bio-accumulation of toxics from those sediments, so we have a series of methods. And there is some controversy within the Agency about the methods that we use.

For non-polar organic chemicals, we're coming out with a predictive method for sediment criteria that's dependent upon partition coefficients and upon the organic carbon content of the sediment. We would look at these parameters and then determine concentrations for the particular chemicals. We're also looking at developing sediment criteria using a calculation based upon acid volatile sulfides within the sediment.

There's another group that says that what we should be doing is biological effects testing on those sediments, to see whether there is in fact a direct effect on benthic animals and, further, whether there is the possibility of any bio-concentration into the environment from those sediments...and they say *that* should be the regulatory framework.

Then there are a whole range of intermediate positions. We are concerned about whether this medium is binding chemicals, so that the direct chemical analysis doesn't reflect the biological availability of the chemicals.

This is an interesting debate, and we're having a great deal of interaction with the scientific community on this subject. It will be an interesting regulatory issue to follow, and I'm sure

that you will be called upon to develop very specific methods in this area.

Associated with the sediment issue is an issue related to fish advisories. Most of the contaminated sediments contain these bio-cumulative persistent chemicals. The thing that we're particularly concerned about is that these chemicals bio-accumulate and get into the fish and shellfish, and then we're called upon to issue fish advisories to the states to protect human health. There isn't a good procedure out there at the moment. There are FDA measures for interstate transfer of shellfish that are not very good, and there are methods that EPA has used that are again not very good.

We've recently had a symposium where the American Fisheries Society and the federal agencies got together with the states. Now we have a strategy that's working to develop better risk assessment and to look at fish consumption rates, and that's a critical component of any risk assessment. There is debate over whether subsistence fishermen eat a great deal more fish than people who are just recreational fishermen and what the normal population eats. Finally, we have to decide what level of protection to establish in setting a fish advisory.

We do not have a consistent methodology for looking at fish. Some people look at whole fish and some look at the edible portion, and the risk assessment varies accordingly. We also need a good standardized QA/QC program for sampling and analyzing fish tissue. We need to have a clearing house, so that all the states are dealing with these risk issues in a compatible way.

And then we come back to communication....We need a good risk communication strategy so that we don't frighten people, but we protect public health.

One of the final things that we're doing in this new office is trying to develop better load allocation methodologies. We can measure it. We can perhaps understand the environmental effects and the human health effects of chemicals in the environment. But what we have to do is develop a regulatory scheme

that allocates loads to specific sources, which in the future may include non-point as well as point sources. However, in most of the country, we are still doing dilution calculations, which is a pretty unsophisticated way to deal with controlling the release of contaminants into the environment. So that's an area that I think our office will focus upon.

I think that at this point I'll draw your attention finally to the Great Lakes, where we'll be dealing with these issues in a much more pro-active way. The Great Lakes community, along with Canada, is very concerned about the quality of the environment. We've had much success in dealing with nutrient issues. Bob Booth and I were talking over coffee this morning about activities that we'd had going on the Great Lakes 20 years ago during the International Field Year, and now we're back again to a very high focus on the Great Lakes. The eutrophication problems are largely solved, but the toxics problems in the environment are certainly not. We have significant inputs from the atmosphere. We have contamination in sediments and we have the normal land-based sources.

We have to develop a better standard methodology. We have to build sediment remediation methods that are economically acceptable, and those remediation methods are very slow in coming. But focus on the Great Lakes--I think that's where we'll be making a lot of new progress. And *that*, I think, is consistent with Reilly's intention of trying to work with local communities, work with the states, trying to develop political will for environmental control, and focusing on a geographic area that people can associate with. It's sort of difficult for the public to talk about technology-based standards for industry and for municipalities. I think people are more interested in *their* water body and protecting *that* in any way they can.

So we're going to think multi-media. Hopefully, we're going to use better science. I hope we can count on you to help with that, and I think we're going to try to be a kinder, gentler EPA, if that's possible. Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Are there any questions for Tudor? Silence.

In the back of the room during the break you'll find an organization chart for the Office of Water and a phone listing so you can call your favorite Office of Water person.

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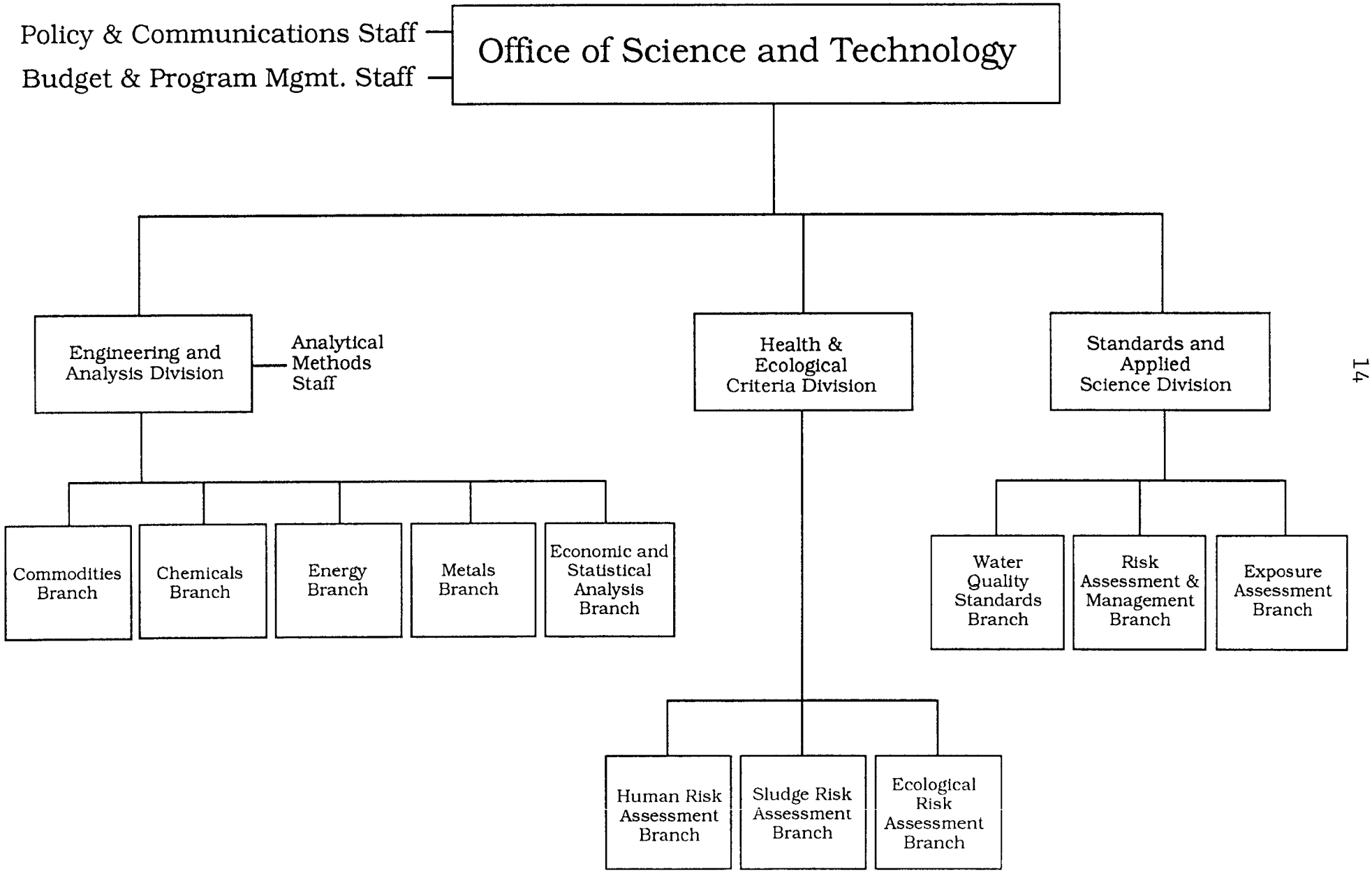
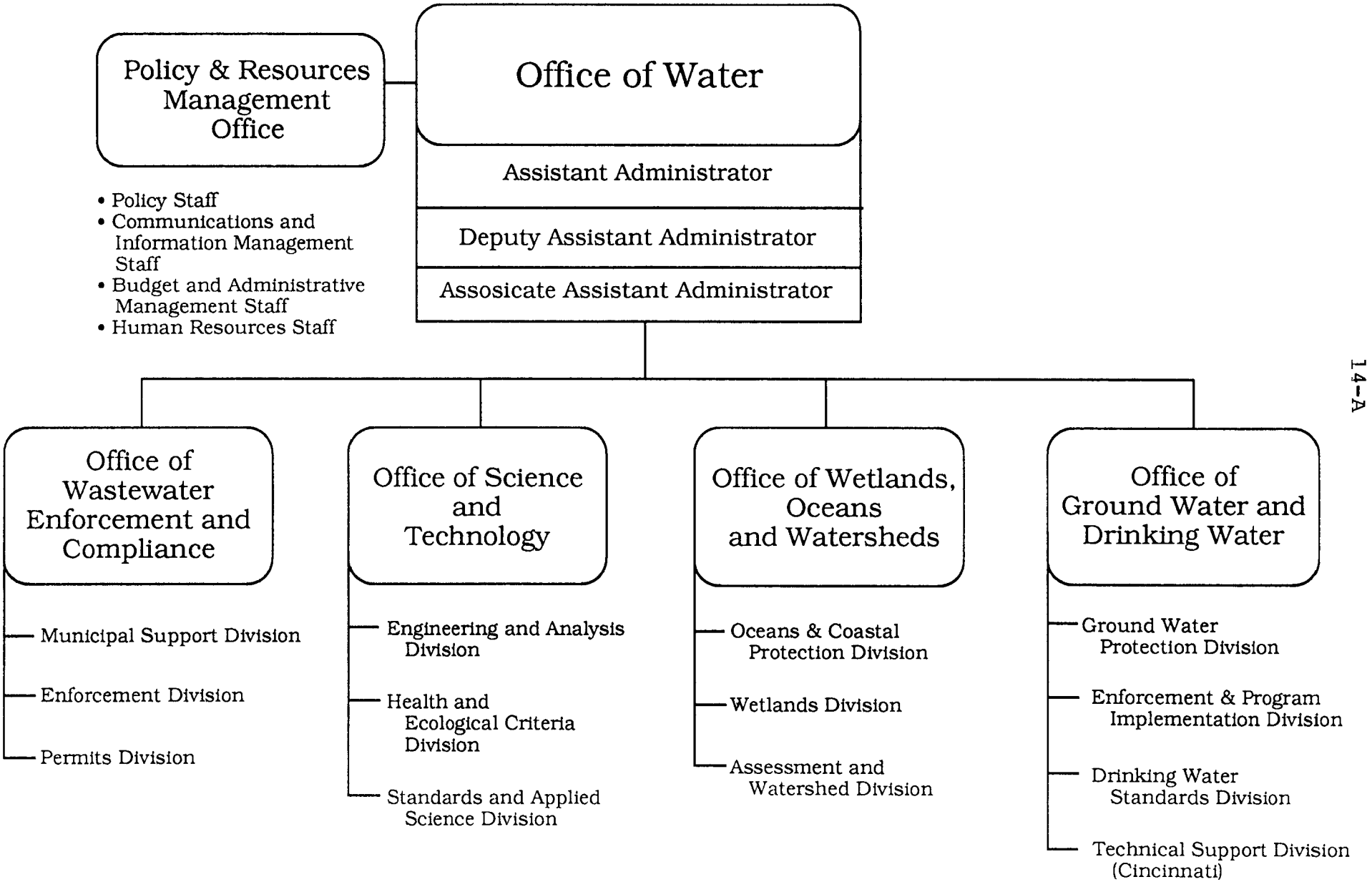


OFFICE OF WATER REORGANIZATION



MR. TELLIARD: Our next session is going to deal with hydrocarbon analysis and our first speaker is from Shell.

Ileana Rhodes and I met two children ago, she said, I had nothing to do with that. At that time we were looking into trying to measure some brines out of oil wells for laughs and she in her other job was to keep George Stanko in line. She's been fairly successful in that.

Ileana, do you want to come up?

DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS BY CAPILLARY GAS CHROMATOGRAPHY

Gasoline to Diesel Range Total Petroleum Hydrocarbons (TPH) and Approximate Boiling Point Distribution

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ABSTRACT

Assessment and remediation of soil contamination by petroleum products requires the identification of the type and extent of contamination. There are several analytical procedures that are used to obtain this kind of information. The term "total petroleum hydrocarbons" (TPH) is used to describe extent of contamination but the actual value determined is method dependent and, thus, must be defined by the method used. All procedures have limitations and care must be exercised in interpretation of data. None of the methods available provide information on boiling point distribution of the contaminants and limited information on product type.

A procedure was developed for the determination of product type, gasoline to diesel range TPH, and its boiling point distribution in soil. This procedure involves extraction of the soil followed by analysis of the extract using gas chromatography with flame ionization detection.

DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS BY CAPILLARY GAS CHROMATOGRAPHY

Gasoline to Diesel Range Total Petroleum Hydrocarbons (TPH) and Approximate Boiling Point Distribution

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INTRODUCTION

Assessment and remediation of soil contamination by petroleum products requires the identification of the type and the extent of contamination. There are several analytical procedures that are used to obtain this kind of information. The term "total petroleum hydrocarbons" (TPH) is used to describe the extent of contamination but the actual value determined is method dependent and thus must be defined by the method used. One of the most commonly used procedures is modified EPA Method 418.1 which is an indicator method that provides information on Freon extractable petroleum hydrocarbons measured using infrared spectrophotometry[1]. Other methods are based on extraction of the soil followed by gas chromatographic analysis of the soil extract using direct injection, headspace or purge and trap analyses with determination of selected components or sums of components[2-5]. All of these procedures have different advantages and limitations,thus care must be exercised in interpretation of data.

Most of the chromatographic procedures require two types of analysis. Volatiles (ie. gasoline range) are determined by extraction of the samples followed by analysis of the extract using purge and trap techniques. Semivolatiles (heavier than gasoline range) are determined using a different extraction procedure followed by concentration of the extract and then analysis of the concentrate using a direct injection approach. These methods are necessary for determination of low levels of TPH contamination (<100 ppm). However, it is often not necessary to determine TPH concentrations below 100 ppm. Cleanup standards in about half the states are at 100 ppm TPH and above[6]. Results from several analyses must be combined to obtain limited information on product type. The concentration steps are time consuming and are often not necessary since the concentrate may need to be diluted for analysis.

The method described in this paper was developed to meet the following requirements: 1) identify the type of contamination (gasoline range, diesel range, mixtures, crudes, etc.), 2) quantitate TPH from gasoline to

diesel range, 3) quantitate selected target analytes, and 4) determine approximate boiling point distribution of the material present in the soil to assist in selection of appropriate remediation technology. It was also desirable to develop a method with minimal sample handling and simple calibration/instrumentation techniques.

None of the methods currently available can provide information that satisfies all of the stated goals. EPA Method 418.1 cannot provide information on the type of hydrocarbon contamination, light boiling point components are easily lost during sample handling and calibration is only accurate if samples contains about 30% aromatics[1]. Headspace procedures are very sensitive but are biased towards the light ends. To fulfill the stated requirements, a method was developed using methylene chloride or methanol for extraction of the soil followed by analysis of the extracts using gas chromatography with flame ionization detection (GC/FID). These solvents were chosen because they are relatively low boiling, and are commonly used in EPA methods and other proposed methods[5].

The extracts are analyzed using capillary gas chromatography. Separation is done using a high resolution fused silica capillary column with bonded methyl silicone phase. This is a non-polar stationary phase in which separation essentially takes place by differences in boiling points of the components in a mixture. The areas under all peaks that elute after the extraction solvent are summed for both samples and calibration standards. Calibration solutions can be prepared of either gasoline or diesel range TPH in the same solvent as the extraction solvent. Alternatively, calibration can be done with a mixture of selected gasoline and/or diesel components. Individual target analytes such as benzene, toluene, and xylenes (BTX) can be identified and quantitated if desired.

This method takes advantage of the fact that the flame ionization detector response is essentially the same for all hydrocarbons as indicated in Table 1 where the response factors of an abbreviated list of hydrocarbons present in all commercial gasolines are tabulated and normalized with respect to n-heptane. Only methyl-t-butyl ether (MTBE) is significantly different. For heavier material, similar data is available in the literature (C14-C32 alkanes and C10-C22 polycyclic aromatic hydrocarbons)[7].

Approximate boiling point distribution is obtained by normalization of the cumulative areas of peaks between retention times of elution of compounds of known boiling points. The normal hydrocarbon of a homologous series has the highest boiling point for its carbon number and thus elutes last. The approximate boiling point distribution plots provide information on weathering of the material.

The method described in this paper has been applied for gasoline to diesel range (gasoline range only, diesel range only as well as mixtures) TPH concentrations from 50 to 10,000 ppm. Soil moisture (<10%) does not appear to have a significant effect on extraction efficiency. For samples with relatively high moisture, it is recommended that the sample be mixed with sodium sulfate prior to extraction if methylene chloride is used for extraction. Drilling muds fall in this category.

EXPERIMENTAL PROCEDURE

Sample preparation

The method involves weighing 10-20 g of sample in a vial with a Teflon lined cap. Sodium sulfate may be added for samples with moisture levels above 10%. The extraction solvent, 10-20 mL of methylene chloride or methanol, is added to the vial. Solvent purity is essential (99+% purity). A series of extraction steps involve mixing for 1 minute using a vortex mixer and shaking with a horizontal shaker or a wrist action shaker for at least 1-4 hours. The samples can be centrifuged if necessary. The extracts can then be directly transferred to autosampler vials and analyzed by gas chromatography using the parameters listed in Table 2. Typical chromatograms are shown in Figures 1-4. Figure 5 shows the chromatogram of a synthetic standard of selected gasoline to diesel range components.

Preparation of Standards

Calibration standards - Standards are prepared using gasoline and/or diesel of any grade or source or a blend of selected hydrocarbons in the concentration range expected in the sample. These standards are prepared by weighing the required amount of gasoline and/or diesel or of selected hydrocarbons and diluting by volume with the extraction solvent. Typical concentration ranges are 50 to 10,000 µg/mL. Calibration curves or average response factors can be used. It is desirable to have standards in a similar concentration range as the samples. Typical calibration plots using a regular gasoline, diesel, 1:1 gasoline/diesel and a synthetic standard of selected gasoline/diesel range components are shown in Figure 6-9.

Boiling point distribution reference standard - A solution containing approximately 200 ppm each of n-hexane through eicosane and pentacosane is used for determination of the retention times corresponding to the different boiling point fractions. Table 3 lists the boiling points of each of these n-alkanes and the retention times observed when the instrumental parameters specified in Table 2 are used. The boiling point distribution can be used to assess whether or not a site is amenable to soil venting. For that reason, detailed boiling point distribution is usually done only for the gasoline range (up to C12) and only a few markers are used for heavier materials. The heavy materials are usually described by the carbon number range rather than by boiling point range.

Instrumental procedure

The instrumental parameters used for the analysis of the soil extracts and standards are listed in Table 2. Any data system capable of grouping and summing selected peak areas can be used. A VG Multichrom data system was used throughout this study for collection of data and computation of results.

The method, as described in Table 2, is limited to determination of hydrocarbons up to ~C25. This cutoff was chosen for several practical reasons. Column phase bleed at oven temperatures above 280°C results in a rise in baseline. This rise in baseline makes integration of unresolved peaks (such as in diesel range material) quite difficult and blank baseline subtraction is often necessary. This added computation is not always appropriate primarily due to changes in the electronic zero at the beginning of each run. A final temperature of 280°C minimizes baseline rise while still allowing elution of components up to and over C25. Another reason for selecting a cutoff of C25 is that alkanes above C25 are not sufficiently soluble in methylene chloride or methanol and thus would not be effectively extracted from the soil. Carbon disulfide can be used to extract heavier hydrocarbons.

Determination of TPH

The areas of all peaks detected that elute after the extraction solvent peak and up to the retention time where pentacosane elutes are summed. The report includes both total area sums of all peaks detected up to and including pentacosane and area sums of peaks eluting between the n-alkane markers for both standards and samples. The total area sums are used for determination of the gasoline to diesel range TPH in samples. The information on area sums between selected markers is used to generate an approximate boiling point distribution plot for a normalized sample.

Calibration can be done using gasoline and/or diesel or synthetic mixtures of selected gasoline to diesel components. The total area sum for samples to be quantitated must be within the calibration range.

It is often desirable to determine what portion of the TPH present in samples is due to gasoline range and what portion is due to a heavier product such as diesel range material. Both of these products overlap to some extent. A recommended cutoff is C10. Generally, gasoline is 5-15% above C10 and diesel can be ~20% below C10. This is obviously a compromise.

Calculation of Approximate Boiling Point Distribution

The approximate boiling point distribution is calculated by normalization of sums of peak areas of portions of the chromatograms eluting between preselected retention times as indicated in Table 3. These retention times correspond to known boiling points selected as references. The chromatographic column used in this method is essentially a boiling point non-polar column and compound separation is achieved by boiling point differences. A homologous series of n-alkanes is used as approximate boiling point references. The cumulative boiling point distribution is graphically displayed by plotting the cumulative area percents versus boiling points of the n-alkanes. The plots are similar to those obtained from simulated distillation or true boiling point gas chromatographic analyses. Figure 10 includes several approximate boiling point distribution plots.

RESULTS AND DISCUSSION

A single analysis can be used to determine product type, TPH, target analytes and approximate boiling point distribution.

Product Type Identification

Product type can simply be determined by visual inspection of the chromatograms. The "fingerprints" of gasoline, diesel and mixtures of these two petroleum hydrocarbons ranges are shown in Figures 1-4. The chromatogram can get more complicated if crude oil, jet range material or other refined products are also present. Nevertheless, it may still be possible to determine that the contamination is due to some sort of fuel oil. Industrial solvents can interfere in the analysis, however, the chromatographic fingerprints would be noticeably different.

Determination of TPH

Preliminary experiments indicated that methanol is somewhat less efficient in extraction of diesel range material than methylene chloride. Thus all subsequent spiking experiments were done using methylene chloride as extraction solvent.

The method was tested by spiking known amounts of regular gasoline, diesel oil and mixtures of gasoline and diesel oil in soil. Typical chromatograms are shown in Figures 1-3. As previously stated and shown in Table 1, the method takes advantage of the fact that the response of flame ionization detector is essentially the same for all hydocarbons (on a weight basis) and based primarily on effective carbon number. It is therefore not essential that calibration be performed using material similar to the material in the samples. For example, any gasoline, diesel, synthetic mixture or single hydrocarbon can be used for calibration and calculation of TPH in samples with any type of petroleum hydrocarbon contamination. This is essentially true. However, because products such as gasoline or diesel are composed of more than 300 individual components, at low concentration of total product, many of the individual components are simply too small to be detected and cannot contribute to the total signal detected and thus linearity falls off. Conversely, when synthetic standards are used, typically no more than 10-20 components are used and thus the TPH is distributed among a few peaks which can be all detected for all concentrations of the standards above the stated practical quantitation limits. The use of synthetic standards always results in underestimation of the TPH present in the samples.

In addition, by using extraction solvents that are in the gasoline range (<C6) a portion of gasoline range material cannot be measured, thus adding an additional bias to the method. This bias can be somewhat corrected by using gasoline standards for calibration of samples containing gasoline range materials.

Figures 6-9 show the calibration plots using different types of materials. These calibrations were used to quantitate results tabulated in in Table 4 which summarizes the results obtained for the soil spiking studies. Soils were spiked with gasoline, gasoline plus diesel mixtures and diesel range materials. Quantitation was done using calibration standards of gasoline range only, gasoline plus diesel range only, diesel range only and synthetic standards. The extracts were analyzed each using two different instruments. Evaluation of the results compiled in Table 4 indicates that it is acceptable to use any type of standard. The overall accuracy average is ~90% and the overall accuracy average percent limits are 70 - 110%. As expected, the least accurate results for the lower concentrations were obtained when synthetic mixtures were used for calibration where the slope is the highest.

Determination of Selected Target Analytes

Selected components are indicated in Figures 1-4 and can be measured individually if desired. The most practical approach is to simply use the same calibration as that used for total TPH using the area of the target analyte in a given sample. In this study, target analytes were not determined since spiked samples were used.

Approximate Boiling Point Distribution

Approximate boiling point distribution similar to those obtained from simulated distillation or true boiling point types of analysis can be obtained using this procedure which uses the retention times of n-alkanes as markers for determination of boiling point distribution of the contamination. Figure 10 shows the cumulative boiling point distribution of super and regular grades fresh gasolines. The approximate boiling point distributions of regular gasoline, diesel and a mixture of gasoline and diesel spiked onto soils are also included. This type of information can be used to determine not only product type(s) but also to characterize the state of the material, such as severity of weathering and relative concentrations of mixed range materials. A soil sample from a service station was analyzed using this method and the boiling point distribution of the contamination is also included in Figure 10. It is evident that the source of contamination in this soil is gasoline range material but it is extremely weathered since there are essentially no components that boil below 125°C.

Typically, a detailed boiling point distribution is needed only for the gasoline range so as to obtain information in assisting selection of suitable remediation technology (for example, soil venting). The driving force for development of this method was the generation of boiling point distribution information to assist in determination of what service stations with soil contaminations can be remediated effectively using soil venting. Beyond the gasoline range (above C12), it is not as important to detail the boiling range of the material but it is more practical to simply define the carbon number range to categorize the type of material (for example, jet, diesel, motor oil, etc.)

The method described in this paper only allows the characterization of material beyond C6 since any material lighter that C6 is obscured by the extraction solvent (methylene chloride or methanol). As much as 25% of a fresh gasoline can be below C6. When a sample is known to contain only gasoline range material, an alternate method is recommended to properly characterize the approximate boiling point distribution of gasoline range contamination. This alternate method involves extraction of the soil with tetradecane (elutes beyond the gasoline range) which allows the estimation of boiling point distribution from C1 to C12[8].

METHOD LIMITATIONS

As with any gas chromatographic procedure using non-selective flame ionization detection, interferences are possible from coelution of gasoline components with other soil contaminants of other sources. Potentially, any compound with similar boiling point and polarity as the hydrocarbons of gasoline to diesel range may have retention times within the range of interest and may result in overestimation of the TPH concentration. For example, volatile industrial solvents, cleaners, and naturally occurring compounds not of petroleum origin may interfere with this analysis. It is often possible to assess the presence of solvents and cleaners since the characteristic fingerprint of gasoline, kerosene, diesel and heavier materials is altered.

Decisions must be made by the analyst in determination of cutoff points for quantitation of different product ranges when contamination is caused by a combination of sources. For example, if soils are contaminated with gasoline range and diesel range materials, there is an area of overlap where certain components are common to both types of petroleum fractions. A compromise cutoff for mixtures of gasoline with diesel fuel range material is C10. There is no appropriate cutoff for a mixture of jet fuel or kerosene and diesel fuel since there is a great deal of overlap. Crude oil contamination also contains a wide range of materials. In cases where mixed products are present, it is perhaps best not to quantitate how much is due to what type of product but to simply quantitate TPH.

In order to minimize quantitation problems due to column bleed, the method is best suited for analysis of materials up to diesel range. Heavier materials can be detected but not quantitated effectively.

SUMMARY AND RECOMMENDATIONS

A high resolution gas chromatographic method was developed for the determination of gasoline to diesel range total petroleum hydrocarbons which involves extraction of the soil with methylene chloride or methanol. The method can be used for obtaining information on the boiling point distribution of the contamination and, if so required, on individual components of interest. The method has been applied to the analyses of spiked soil samples, soils from service stations and marketing distribution terminals, and drilling muds.

A limitation of the method is that the practical quantitation limit is 50-100 ppm. However, these levels are compatible with cleanup standards for many states[6]. A practical approach to the determination of TPH and characterization of the material present is to follow the procedure described in this paper and outlined in Figure 11 where a flow chart is outlined and the decisions are based on data quality objectives. The approach proposed involves extraction and analysis of soil samples for characterization of TPH as described here. If TPH is above 50-100 ppm (ie. if peaks are detected with appropriate fingerprints), then information on product type, TPH, selected target analytes and approximate boiling point distribution can be obtained from a single simple extraction and analysis. If no peaks are detected, and if information is needed below 50-100 ppm TPH, then the samples can be analyzed using other more sensitive methods.

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QUESTION AND ANSWER SESSION

MR. CALLAMORE: My name is Martin Callamore, City of Tacoma. We have done some extraction work doing TPHs in sewage sludge and what we found is that the FID has a big humpogram that makes quantification very difficult. We'll get the classic distribution of your diesel, but it's riding on top of a very large hump that will vary. Apparently, the extraction is taking out some things other than TPH also.

Doing the silica gel cleanup to remove the carboxylic acids hasn't really helped.

MS. RHODES: I can't hear you very well...sorry.

MR. TELLIARD: That's better.

MR. CALLAMORE: Okay, sewage sludge TPHs...cleaning up with silica gel to remove the carboxylic acids doesn't seem to remove all the biogenic material so we have a real severe problem with interference in the chromatogram trying to determine TPH. The traditional, normal hydrocarbon distribution rides on top of a very large hump which makes quantification very difficult. I was wondering if you had ever run into that sort of thing before.

MS. RHODES: I couldn't hear your whole question. I don't know if this is working or not.

I couldn't hear your whole question, but essentially what you've got is you've got all of that biological material to deal with as well and, I don't know, you might try some GPC-type techniques to try to clean it up a little bit better. We usually don't deal with that kind of material, but I know what you're doing because we have experienced that in some other cases...not for TPH measurements. You have to go through a whole lot of cleaning to get rid of the bio mass. Sorry.

MR. PRONGER: Greg Pronger, National Environmental Testing. Have you experimented with any solvents that would move your solvent front out in front of the pattern of gasolines such as maybe carbon disulfide or any of those?

MS. RHODES: I tried carbon disulfide. I work with carbon disulfide quite a bit and carbon disulfide gives you a peak right on the same spot where methylene chloride does. Carbon disulfide, however, is a better solvent for heavier hydrocarbons. For example, one of the other reasons why I stopped at C25 is because you can't dissolve C30 in methylene chloride. CS_2 will work just as well, but it also would interfere in the front end of the chromatogram.

MR. PRONGER: Are you saying it's got an interferent? Is it the grade of carbon disulfide or it...

MS. RHODES: No, it gives you response right on the spot. The FID will respond to CS_2 when it's in a solvent amount right on the same spot with methylene chloride within a few...like a half a minute or so. It will come out on the same spot. But it's a good solvent as well; it can be used. It just stinks so much.

MR. PRONGER: There are some disadvantages of the solvent.

MR. TELLIARD: Thank you.

TABLE 1: RELATIVE RESPONSE FACTORS OF SELECTED GASOLINE RANGE COMPONENTS USING GC-FID. (NORMALIZED WITH RESPECT TO n-HEPTANE)

Methyl-t-butyl ether	0.70
n-Butane	1.00
i-Pentane	1.00
2-Methylbutene-1	0.96
n-Pentane	1.00
Cyclopentane	0.96
2-Methylpentane	1.00
n-Hexane	1.00
Methylcyclopentane	0.97
2,4-Dimethylpentane	1.00
Benzene	0.92
Cyclohexane	0.99
Cyclohexene	0.98
2-Methylhexane	1.00
3-Methylhexane	1.00
t-1,3-Dimethylcyclopentane	1.00
t-1,2-Dimethylcyclopentane	1.00
3-Ethylpentane	1.00
2,2,4-Trimethylpentane	1.00
n-Heptane	1.00
Methylcyclohexane	0.98
Ethylcyclopentane	0.98
2,4-Dimethylhexane	1.00
2,3,4-Trimethylpentane	1.00
Toluene	0.93
2-Methylheptane	1.00
3-Methylheptane	1.00
t-1,3- & c-1,4-Dimethylcyclohexane	0.99
n-Octane	1.00
n-Propylcyclopentane	0.99
Ethylbenzene	0.96
m-Xylene	0.96
p-Xylene	0.96
o-Xylene + 3-Methyloctane	0.98
n-Nonane	1.00
i-Propylbenzene	0.98
2,6-Dimethyloctane + n-Propylbenzene	0.98
1-Methyl-4-ethylbenzene	0.98
1,3,5-Trimethylbenzene	0.98
1-Methyl-2-ethylbenzene	0.98
4-Methylnonane	1.00
t-Butylbenzene + 1,2,4-Trimethylben.	0.99
n-Decane + 1,2,3-Trimethylbenzene	0.98
Indan	1.00
1,2,3,5-Trimethylbenzene	0.99
Naphthalene	0.96
n-Dodecane	1.00
AVERAGE RESPONSE FACTOR	0.98

TABLE 2: INSTRUMENTAL PARAMETERS

Gas Chromatograph:	Hewlett-Packard 5880 or 5890
Column:	Quadrex MS-007, fused silica capillary column 25 m X 0.25 mm ID, 1.0 µm film thickness methyl silicon
Carrier gas:	Helium, 15 Psig.
Make-up gas:	Nitrogen, 30 ml/min.
Split Ratio:	30:1 (minimum)
Sample size:	1-5 µL
Injector:	325°C
Detector:	Flame ionization, 350°C
Column program:	40°C hold for 4 min, program at 10°C/min to 280°C. Hold for 15 min at 280°C.
Data System:	VG Multichrom

TABLE 3:

RETENTION TIMES AND BOILING POINTS OF n-ALKANES FOR DETERMINATION OF BOILING POINT DISTRIBUTION OF GASOLINE TO DIESEL RANGE TPH IN SOIL USING DESIGNATED INSTRUMENTAL PARAMETERS

	BP °C	Retention Time (min)	Alkane Marker
GASOLINE RANGE	36	2.15	n-C5
	69	4.09	n-C6
	98	6.85	n-C7
	126	9.55	n-C8
	151	11.93	n-C9
	174	14.03	n-C10
	196	15.92	n-C11
	216	17.65	n-C12
	236	19.26	n-C13
	253	20.76	n-C14
	270	22.18	n-C15
	287	23.51	n-C16
	302	24.77	n-C17
	316	25.98	n-C18
	329	27.11	n-C19
	343	28.20	n-C20
	402	35.99	n-C25

TABLE 4: SUMMARY OF TPH RESULTS FOR SPIKED SOILS

RESULTS CALCULATED WITH RESPECT TO GASOLINE STANDARDS, GASOLINE AND DIESEL STANDARDS, DIESEL STANDARDS AND SYNTHETIC MIXTURE STANDARDS AS INDICATED.

PRODUCT TYPE	TARGET VALUE PPM	GAS STD PPM	G+D STD PPM	DIES STD PPM	SYN STD PPM	AVE PPM	ACC AVG %
GASOLINE	57	43	55	77	43	55	96
		46	61	62	23	48	84
GASOLINE	113	85	110	125	77	99	88
		96	110	120	60	97	85
GASOLINE	2300	1980	2530	2210	1670	2098	91
		2000	2040	2400	1470	1978	86
GASOLINE	4770	4580	5500	4750	3740	4643	97
		4600	4680	5400	3800	4620	97
GAS+DIES	58	38	48	71	44	50	87
		67	51	69	24	53	91
GAS+DIES	117	91	120	130	83	106	91
		85	78	102	44	77	66
GAS+DIES	2230	1680	2150	1900	1410	1785	80
		2250	2180	2630	1620	2170	97
GAS+DIES	4140	3300	4120	3580	2760	3440	83
		4110	4010	4730	2990	3960	96
DIESEL	52	40	50	73	39	51	97
		46	62	62	20	48	91
DIESEL	104	74	95	110	68	87	83
		62	86	94	35	69	67
DIESEL	2770	2140	2730	2390	1800	2265	82
		2400	2450	3000	1770	2405	87
DIESEL	6660	5310	6440	5540	4420	5428	81
		6100	6240	7000	4560	5975	90

ACCURACY AVERAGE % (PER CONCENTRATION LEVEL): 87
RELATIVE STANDARD DEVIATION ("): 8

OVERALL ACCURACY AVERAGE PERCENT LIMITS:

GASOLINE:	92 ± 20
GASOLINE+DIESEL:	86 ± 21
DIESEL:	85 ± 22

EXTRACTS ANALYZED USING 2 DIFFERENT GAS CHROMATOGRAPHS

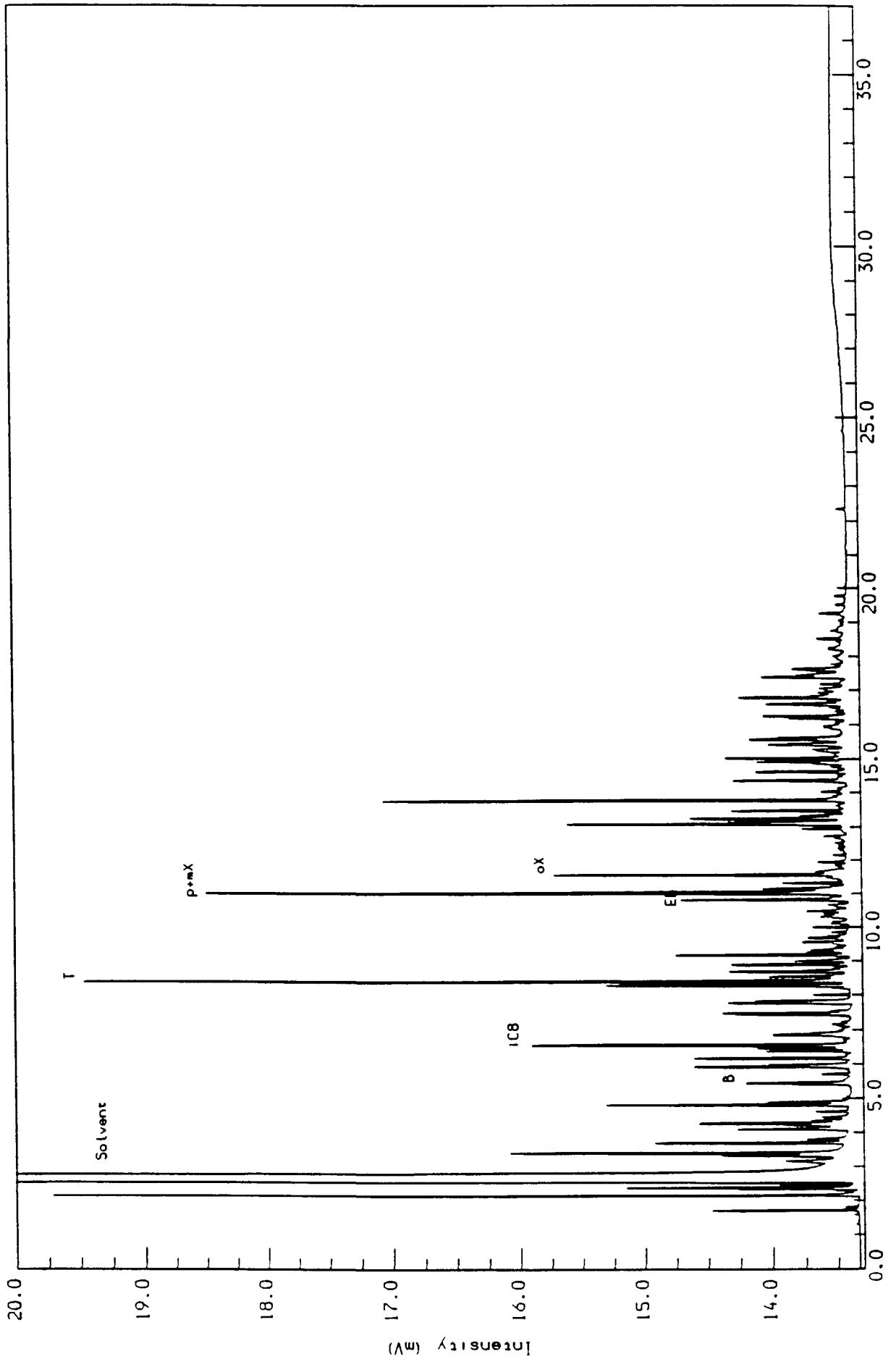


FIGURE 1: CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2300 PPM GASOLINE IN SOIL.

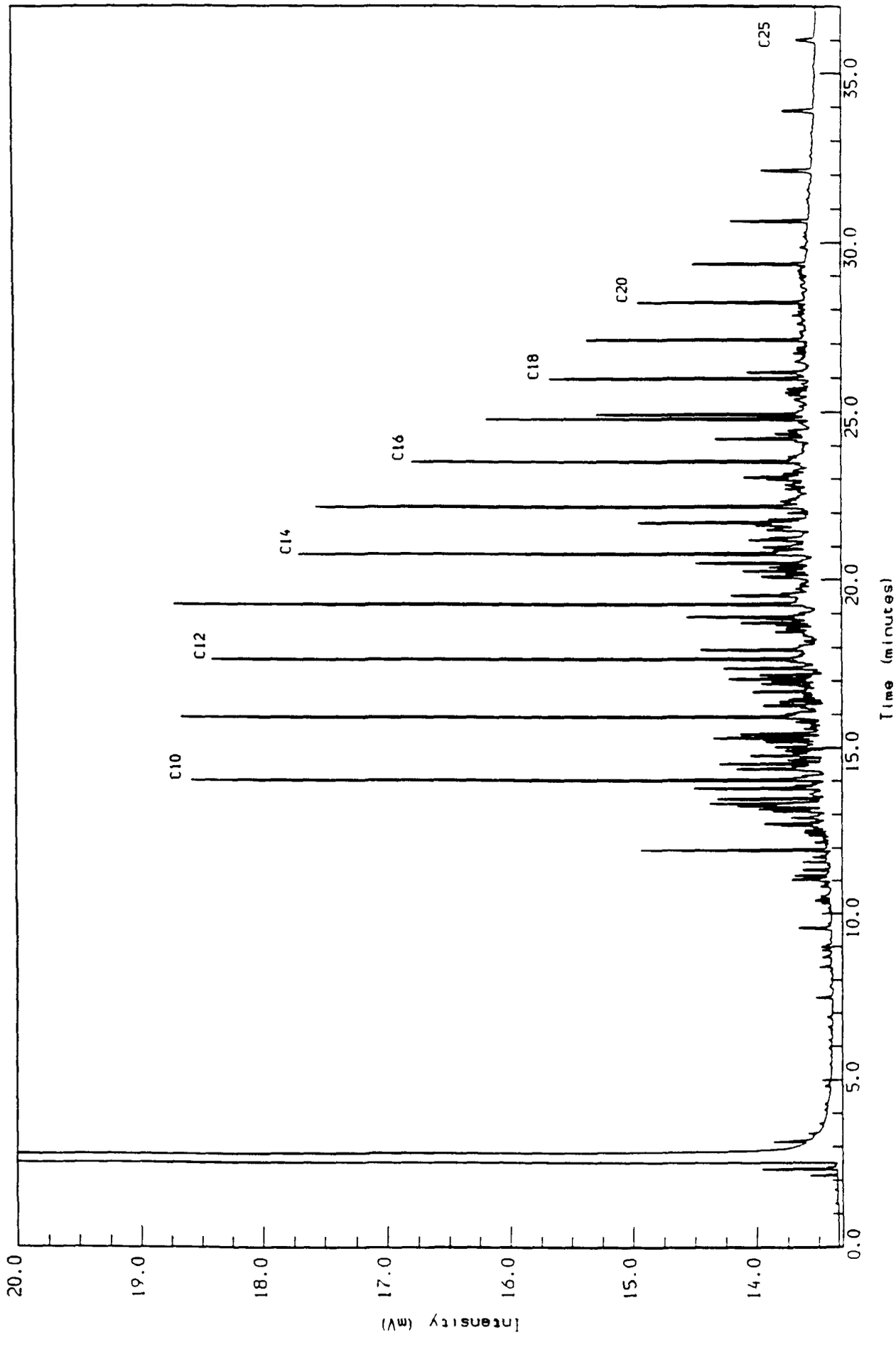


FIGURE 2: CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL.
2700 PPM DIESEL IN SOIL.

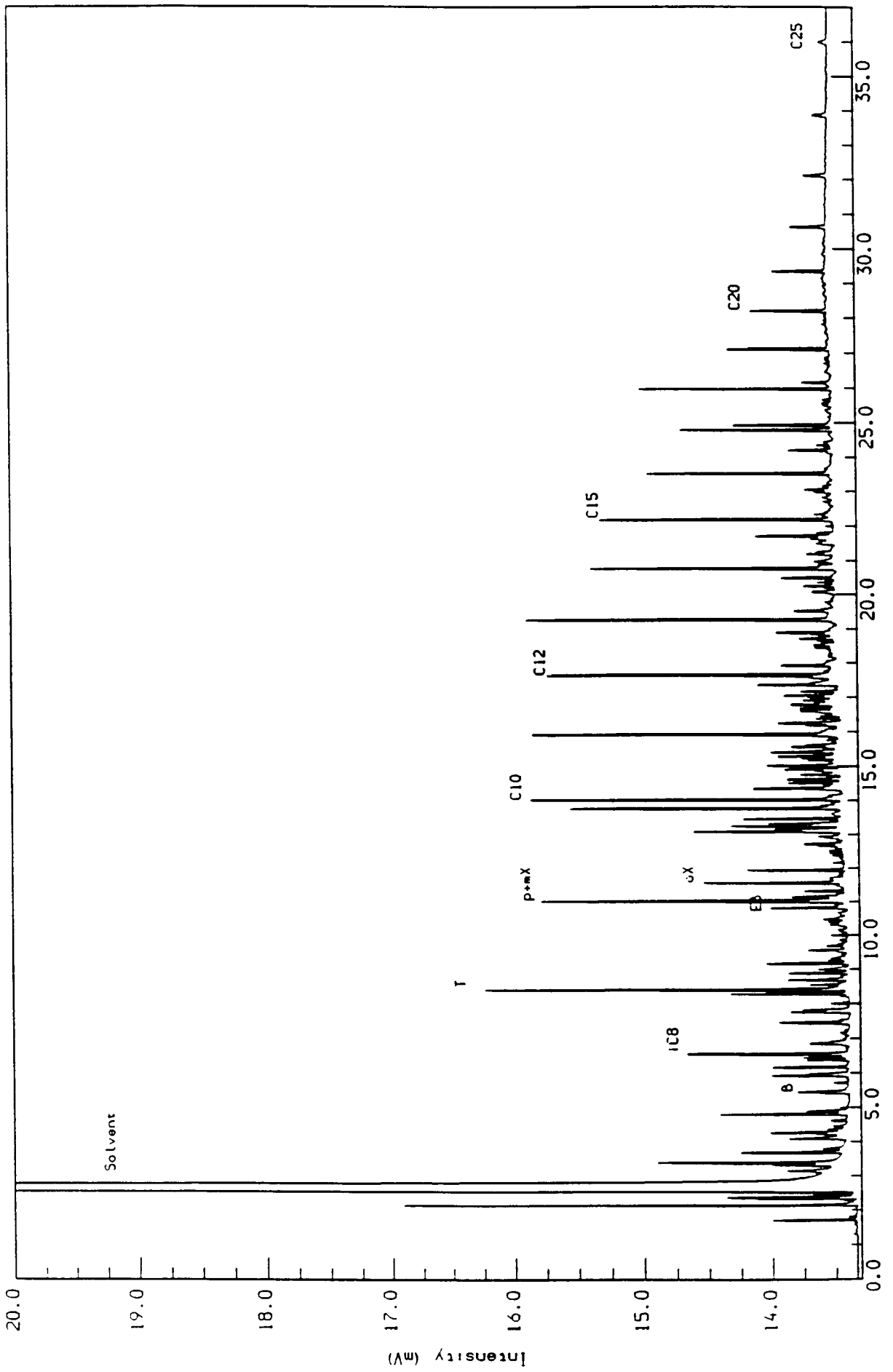


FIGURE 3: CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2200 PPM GASOLINE PLUS DIESEL (~1:1)

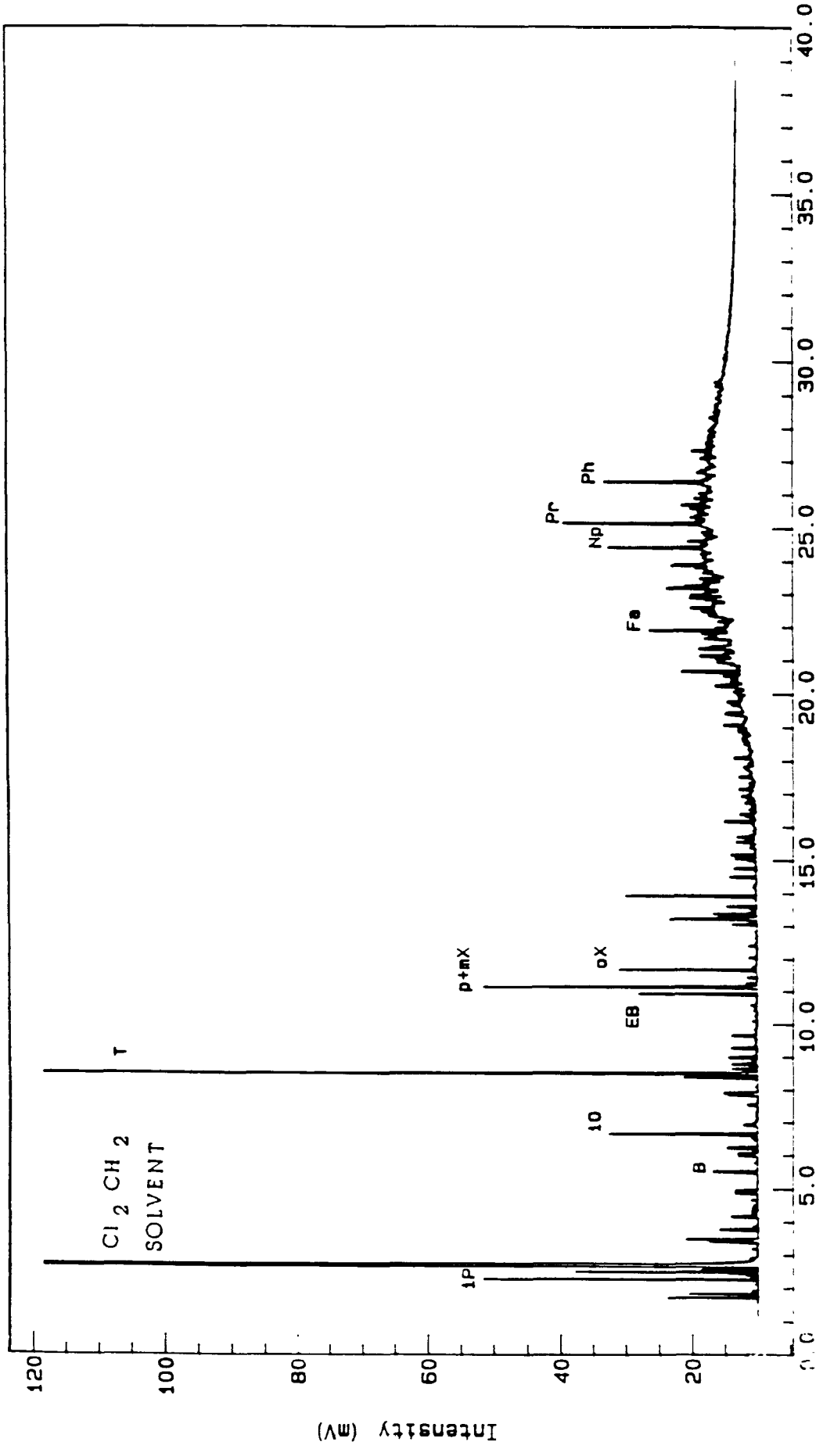


FIGURE 4: CHROMATOGRAM OF EXTRACT FROM A SOIL SAMPLE CONTAINING GASOLINE AND EXTREMELY WEATHERED DIESEL RANGE MATERIAL

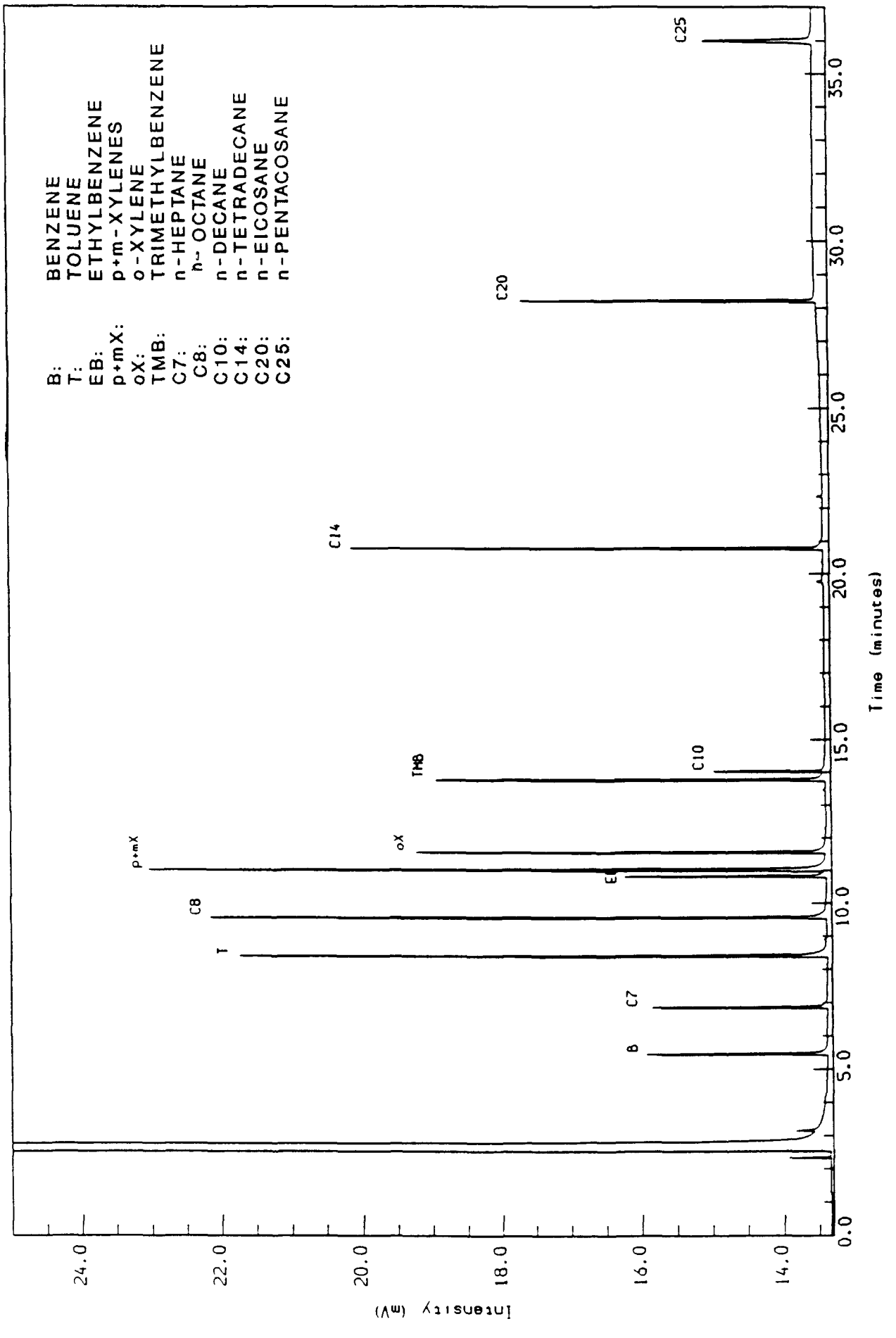
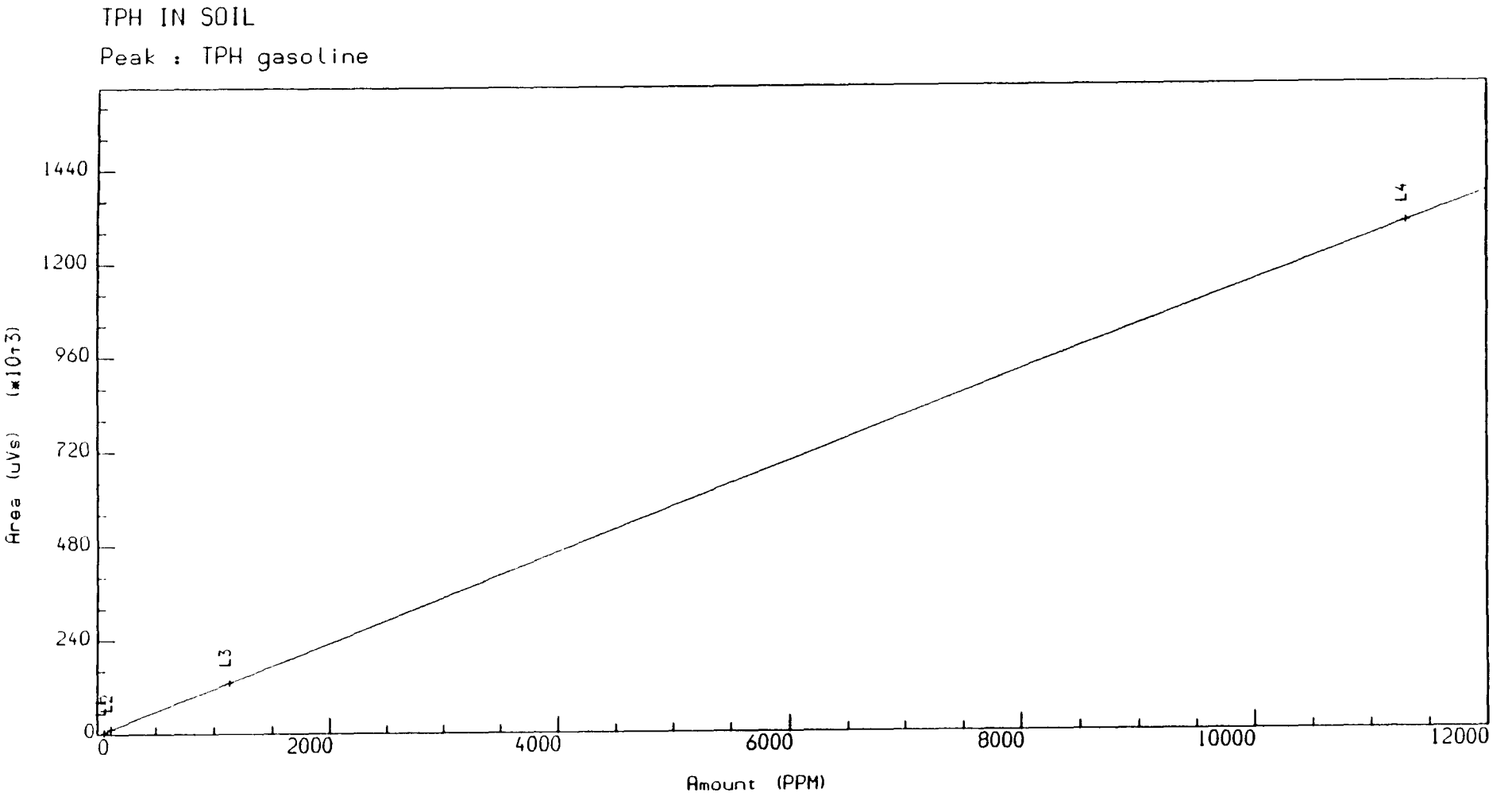


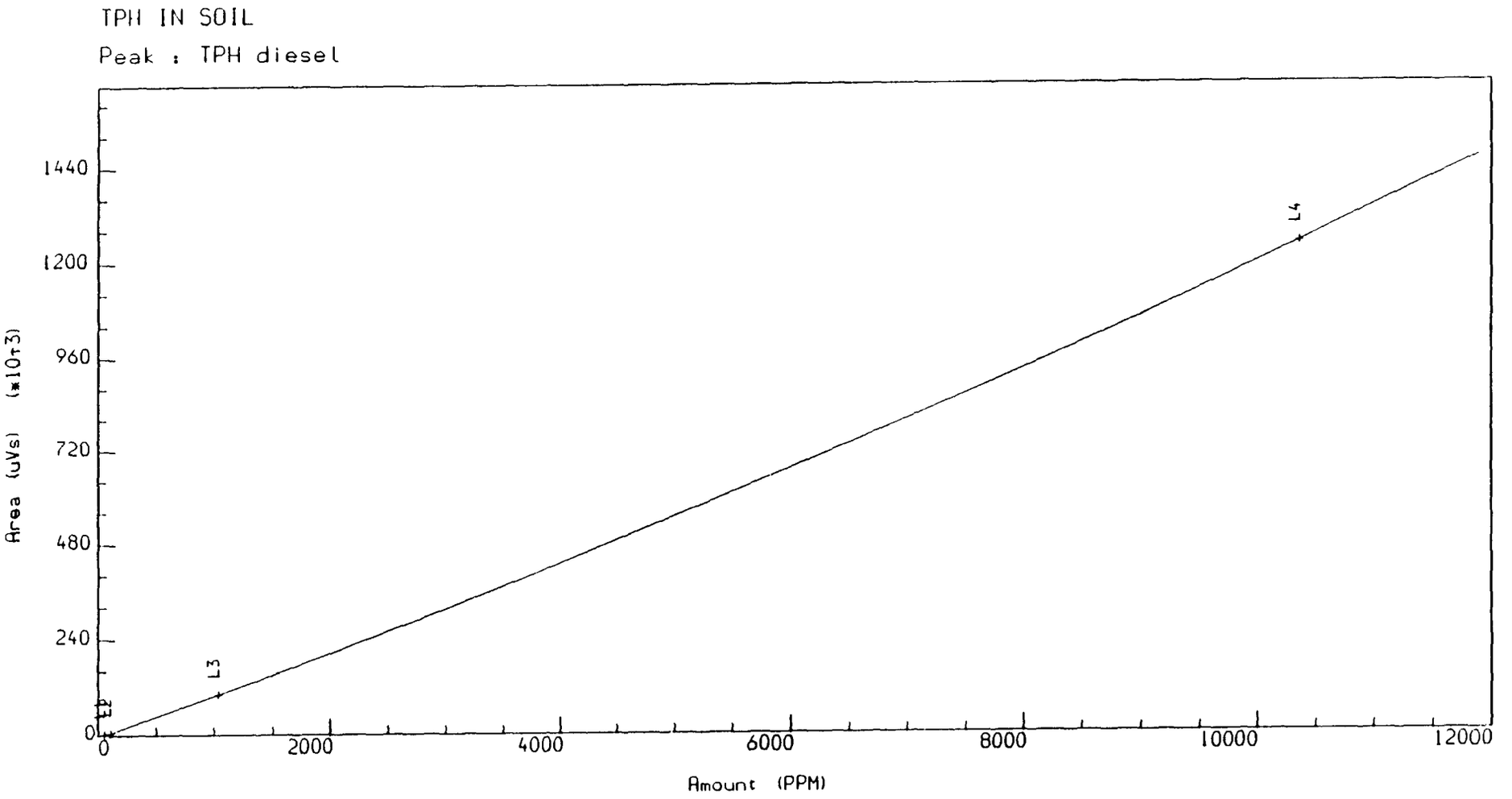
FIGURE 5: CHROMATOGRAM OF 1000 PPM SYNTHETIC MIX STANDARD



Constant : -1.266704E+3
1st degree : 1.16399E+2
2nd degree : -0.00015

Curve fit : Quadratic
Coeff of determination : 1.00000
Standard error : 1.23180E+3

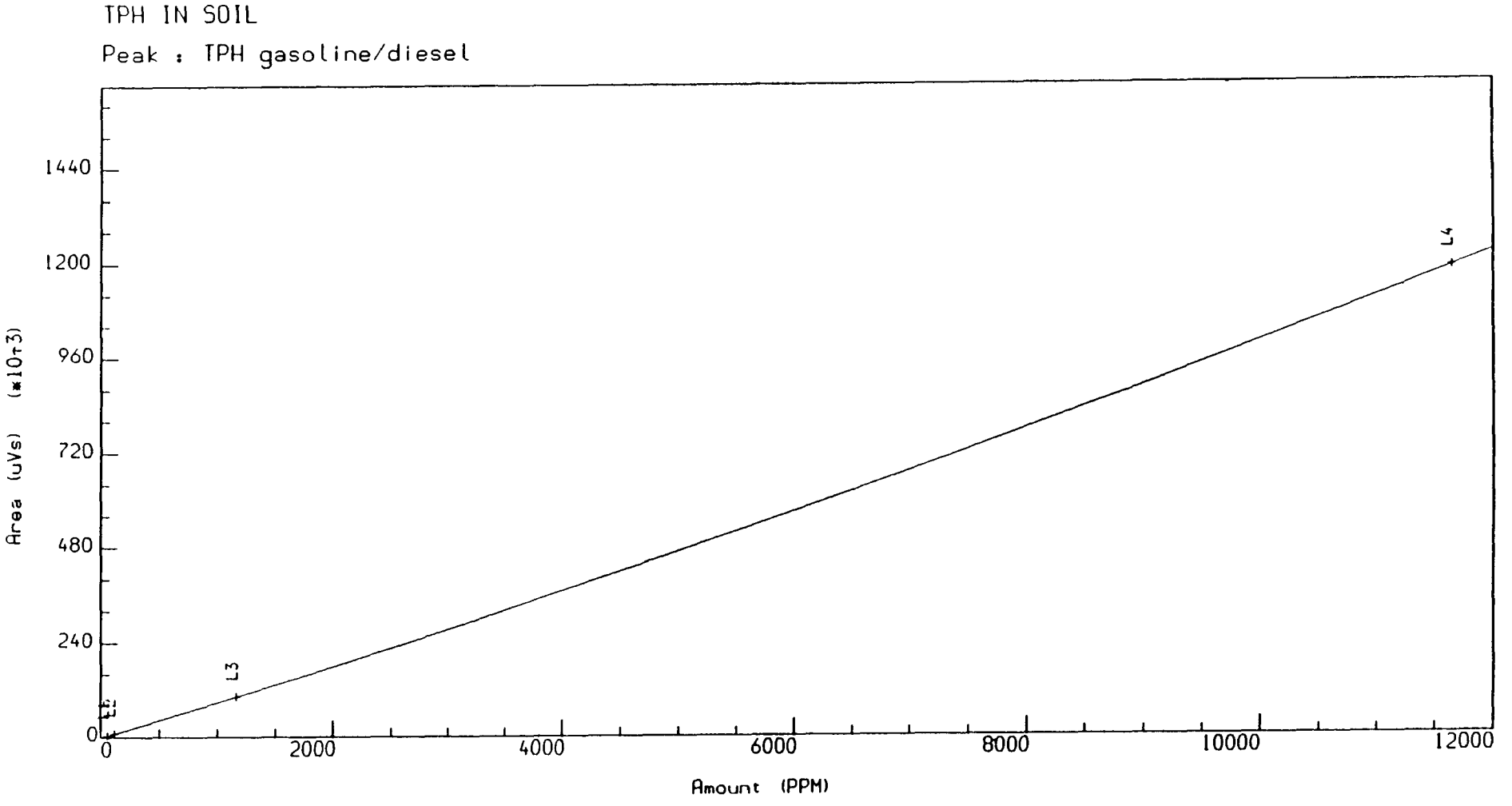
FIGURE 6: CALIBRATION PLOT USING GASOLINE STANDARDS. 50-10,000 PPM.



Constant : -4.030669E+3
1st degree : 1.00654E+2
2nd degree : 0.00193

Curve fit : Quadratic
Coeff of determination : 1.00000
Standard error : 1.34628E+3

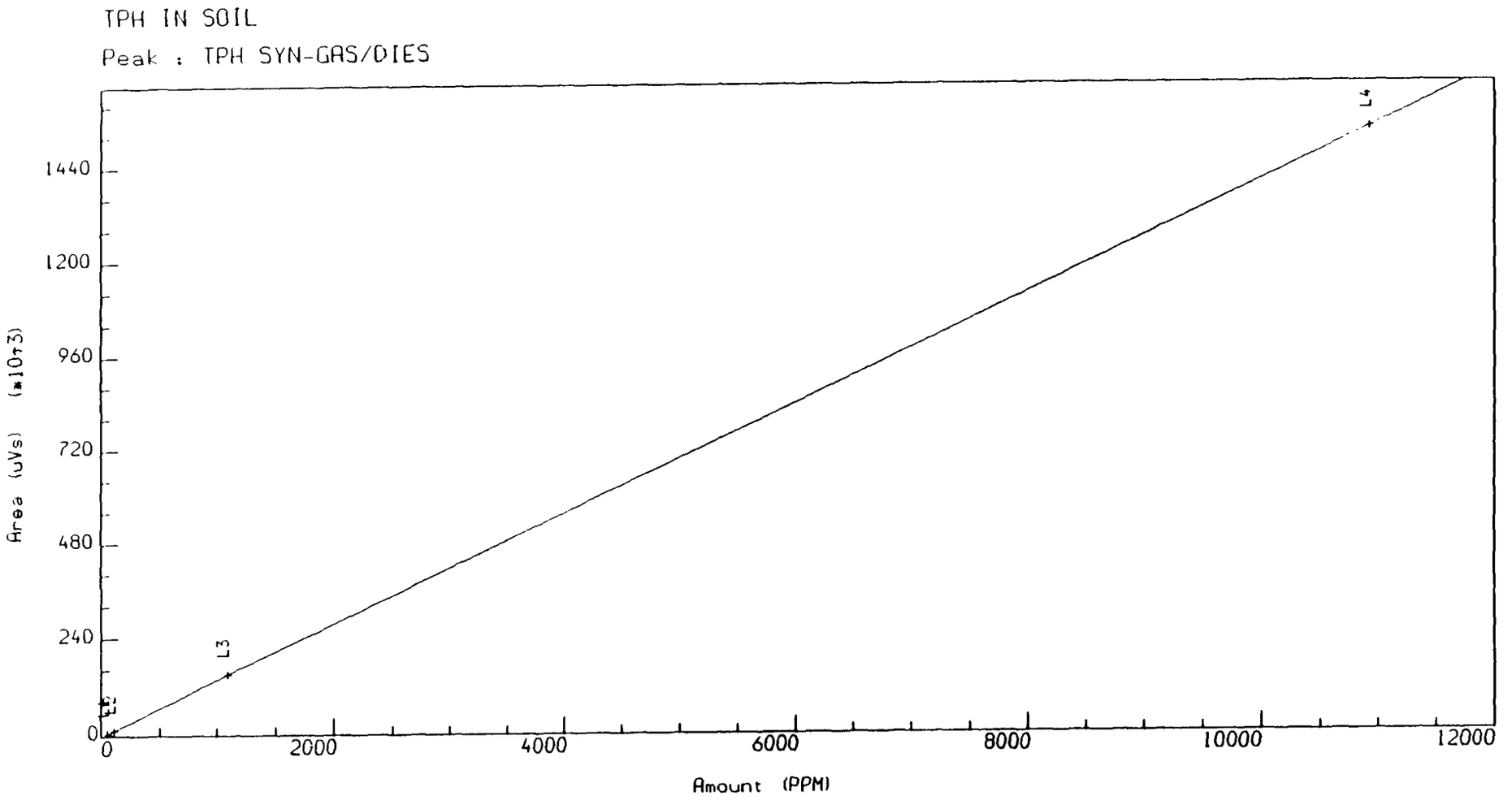
FIGURE 7: CALIBRATION PLOT USING DIESEL STANDARDS. 50-10,000 PPM.



Constant : -1.063288E+3
1st degree : 8.77609E+1
2nd degree : 0.00118

Curve fit : Quadratic
Coeff of determination : 1.00000
Standard error : 6.08165E+2

FIGURE 8: CALIBRATION PLOT USING 1:1 GASOLINE DIESEL MIX STANDARD. 50-10,000 PPM.



Constant : -2.085850E+3
1st degree : 1.38073E+2
2nd degree : 0.00022

Curve fit : Quadratic
Coeff of determination : 1.00000
Standard error : 6.86466E+2

FIGURE 9: CALIBRATION PLOT USING A SYNTHETIC MIX STANDARD. 50-10,000 PPM.

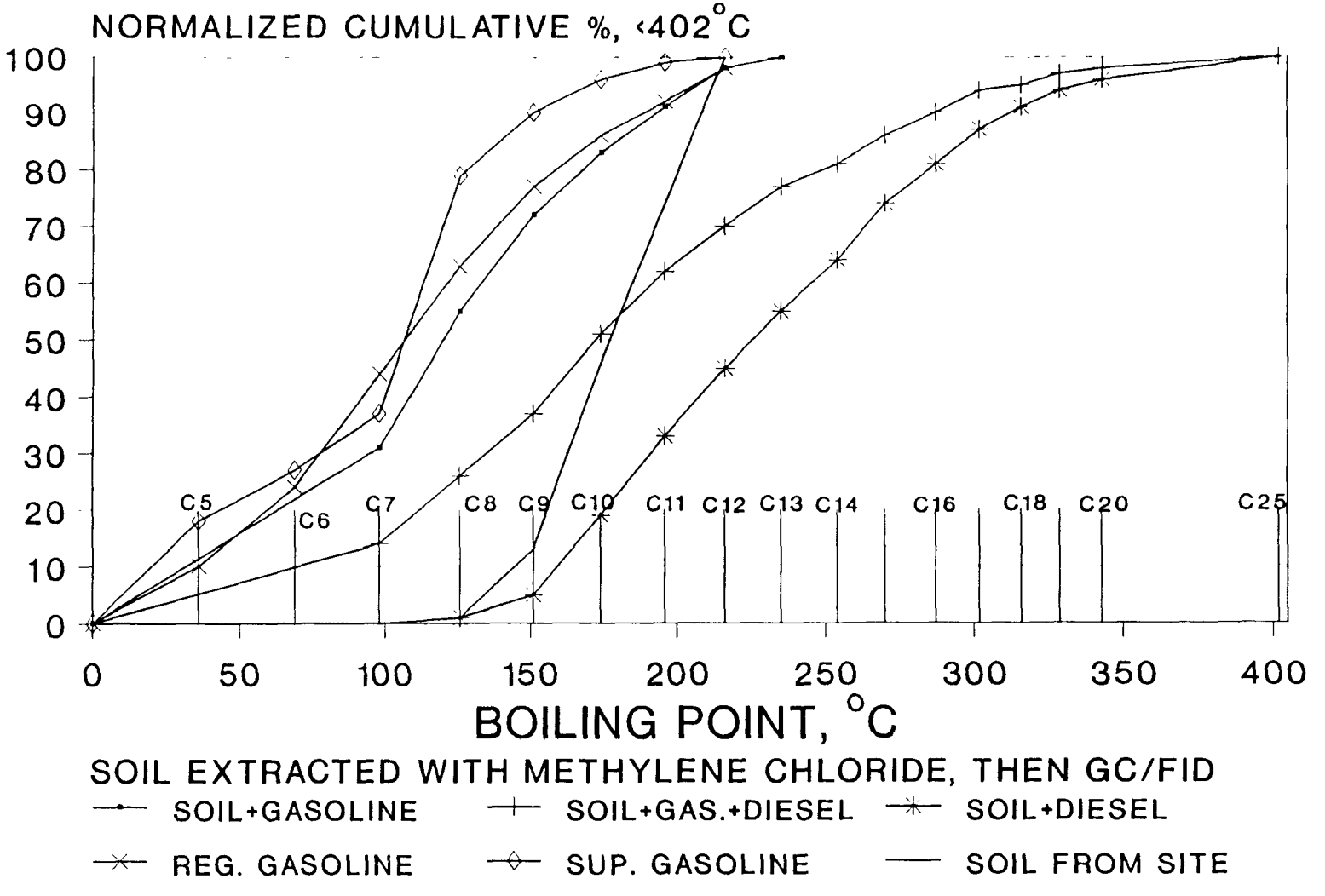


FIGURE 10: APPROXIMATE BOILING POINT DISTRIBUTION PLOTS.

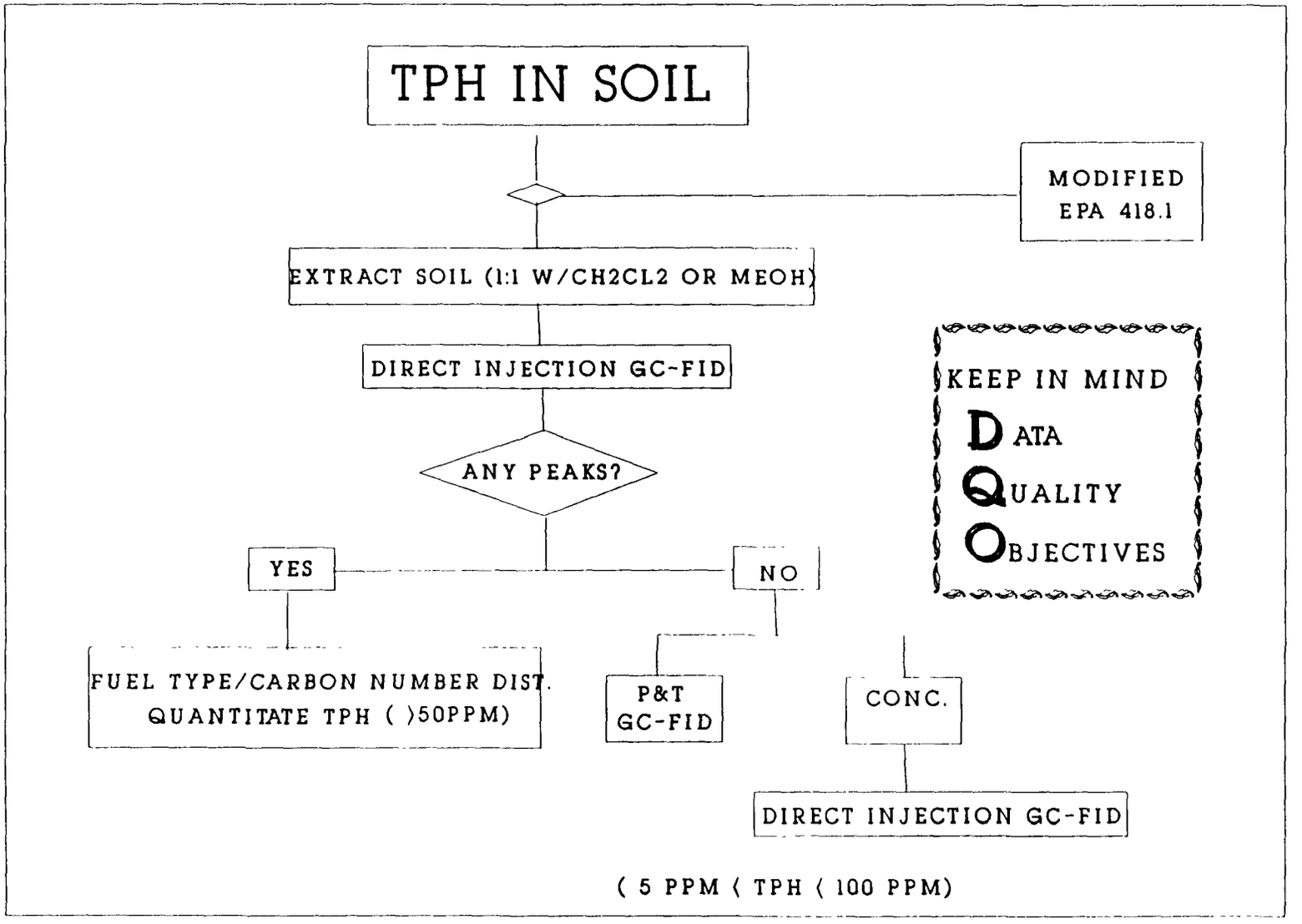


FIGURE 11: RECOMMENDED APPROACH TO DETERMINATION OF TPH IN SOILS.

DETERMINATION OF GASOLINE TO DIESEL RANGE TOTAL PETROLEUM HYDROCARBONS IN SOIL USING GAS CHROMATOGRAPHY

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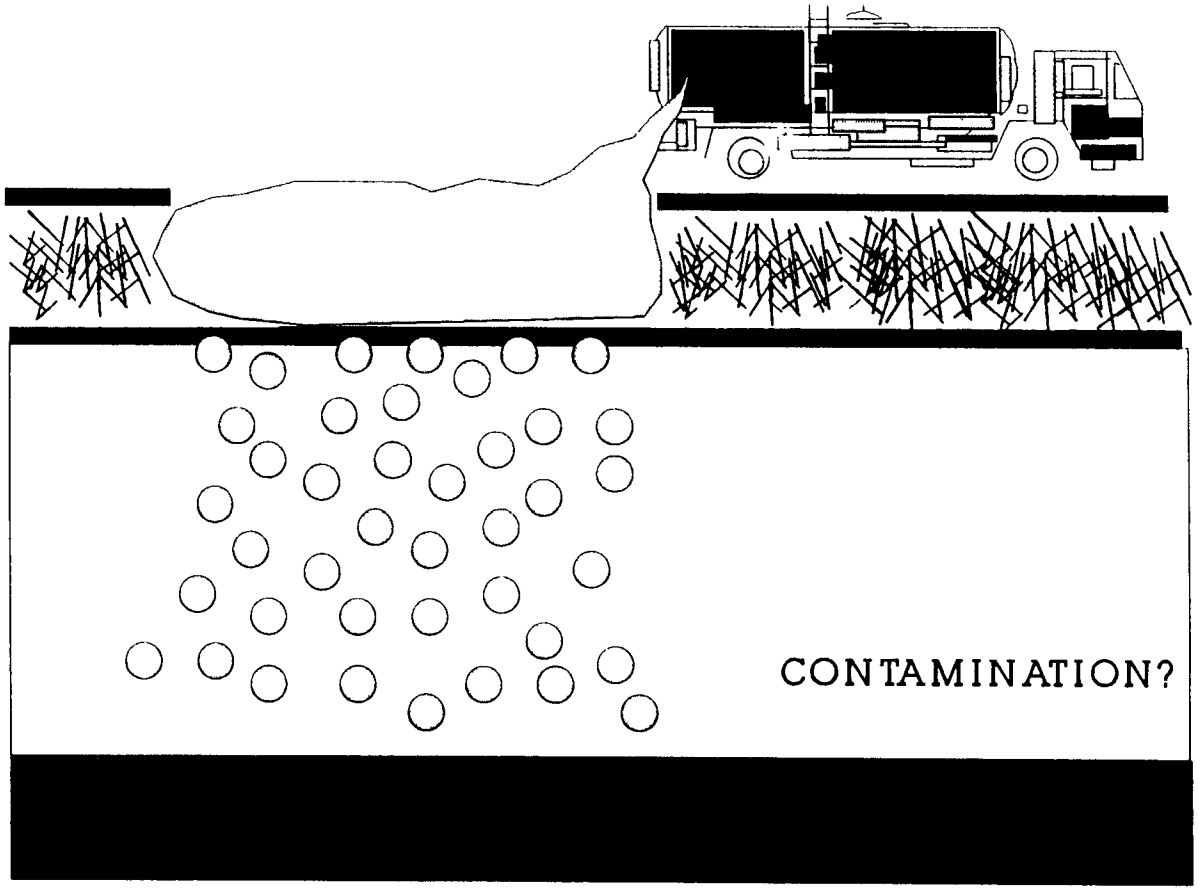
J. A. LEON
E. M. HINOJOSA



WHAT IS "TPH"?

THE TERM "TOTAL PETROLEUM HYDROCARBONS" IS USED TO DESCRIBE THE EXTENT OF CONTAMINATION IN WATER, SOIL AND WASTE. HOWEVER, THE ACTUAL VALUE DETERMINED IS METHOD DEPENDENT AND THUS IT MUST BE DEFINED BY THE METHOD USED

WHAT ELSE CAN BE MEASURED AS "TPH"?

ANY OTHER ORGANIC COMPOUND (CLEANING FLUIDS, SOLVENTS, POLAR COMPOUNDS, ETC)

WHAT IS NOT "TPH"?

- IT IS NOT TOTAL SINCE HEAVY HYDROCARBONS ARE NOT ALWAYS EXTRACTED, VOLATILES CAN BE LOST
- SOME METHODS NEGLECT AROMATICS
- SUMS OF ONLY SELECTED COMPONENTS IN SOME CASES

PROBLEM

WIDE ARRAY OF METHODS THAT PROVIDE DATA OF VARYING AND QUESTIONABLE UTILITY

WHAT ARE THE METHODS AVAILABLE FOR TPH DETERMINATION

1-MOST METHODS INVOLVE SOME SORT OF EXTRACTION PROCEDURE FOLLOWED BY ANALYSIS USING:

- GRAVIMETRY
- INFRARED SPECTROPHOTOMETRY
- GAS CHROMATOGRAPHY MEASURING

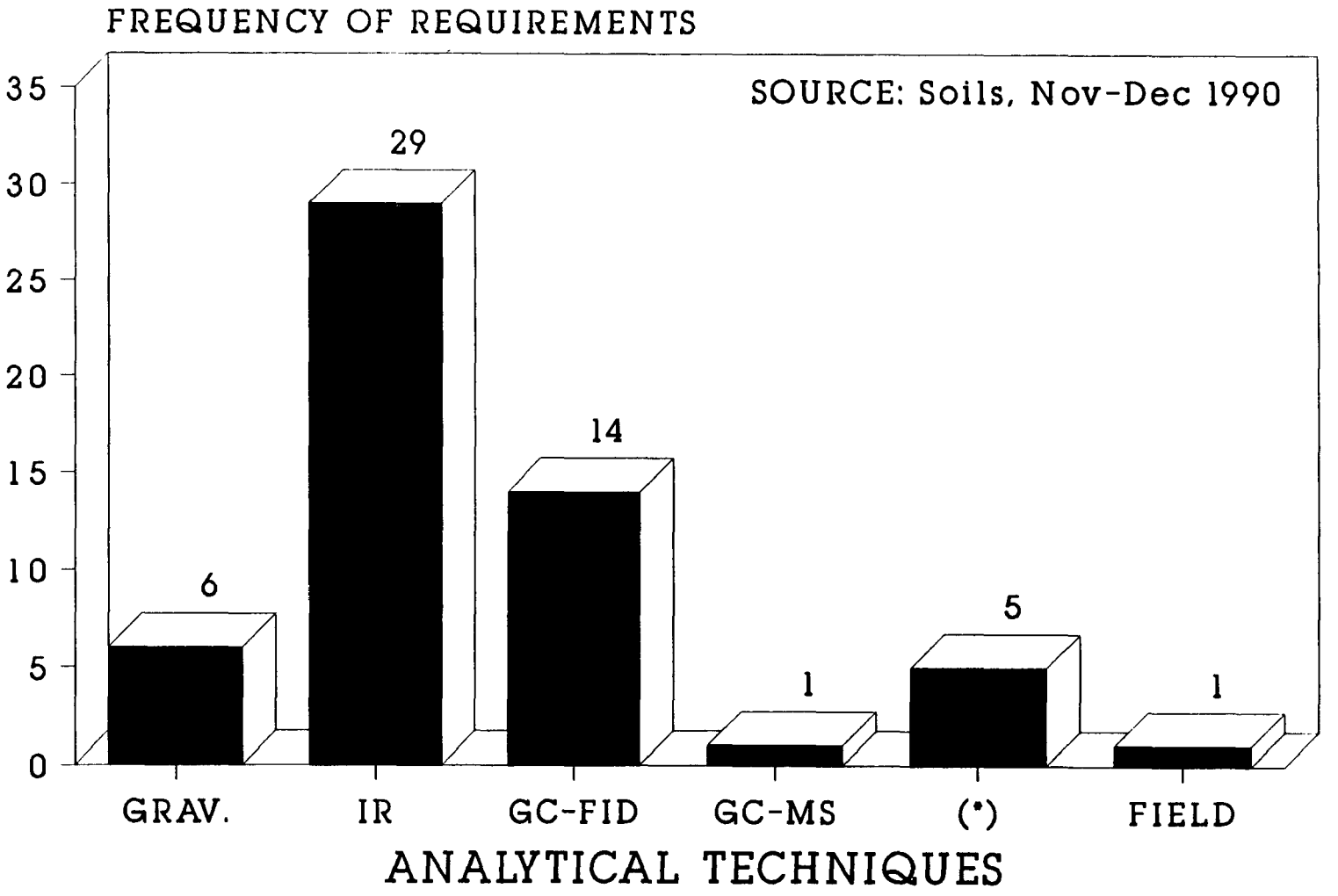
  -SELECTED COMPONENTS DETERMINATION

  OR

  -SUMS OF ALL COMPONENTS IN A GIVEN RANGE

2-HEADSPACE ANALYSIS USING GAS CHROMATOGRAPHY (WITH AND WITHOUT EXTRACTION OF THE SAMPLE)

WHAT METHODS ARE REQUESTED BY STATES?
"TPH" METHODS



(*) ANY APPROPRIATE SW846 METHOD (None without modification)

TOTAL PETROLEUM HYDROCARBONS (TPH)
SOLVENT EXTRACTION/GAS CHROMATOGRAPHIC METHODS

- SAMPLE IS EXTRACTED WITH A SOLVENT
- EXTRACT IS INTRODUCED INTO A GAS CHROMATOGRAPH EITHER BY DIRECT INJECTION OR BY PURGE AND TRAP TECHNIQUES (THE LATTER IS ONLY APPLICABLE FOR GASOLINE RANGE ORGANICS)
- THE CHROMATOGRAPHIC COLUMN SEPARATES COMPONENTS IN THE SAMPLE
- THE COMPONENTS ARE DETECTED PRIMARILY BY A FLAME IONIZATION DETECTOR WHICH RESPONDS TO ALL CARBON-HYDROGEN CONTAINING COMPOUNDS (THERE ARE OTHER DETECTORS THAT CAN BE USED, SUCH AS PHOTOIONIZATION DETECTORS AND MASS SPECTROMETERS, HOWEVER INCOMPLETE INFORMATION IS USUALLY PROVIDED)
- TOTAL AREA OF CHROMATOGRAM IS INTEGRATED AND QUANTIFIED BY COMPARISON WITH STANDARDS

TPH USING GAS CHROMATOGRAPHY

GAS CHROMATOGRAPHIC METHODS CURRENTLY USED INVOLVE:

- DETERMINATION OF GASOLINE RANGE MATERIAL
  - -Extraction
  - -Purge and Trap or Headspace Analysis
- DETERMINATION OF HEAVIER THAN GASOLINE RANGE MATERIAL
  - -Extraction
  - -Concentration
  - -Analysis of concentrated extract

ADVANTAGES

- DETECTION LIMITS IN THE LOW PPMs
- SIMILAR TO EPA METHODS / BASED ON EPA METHODS

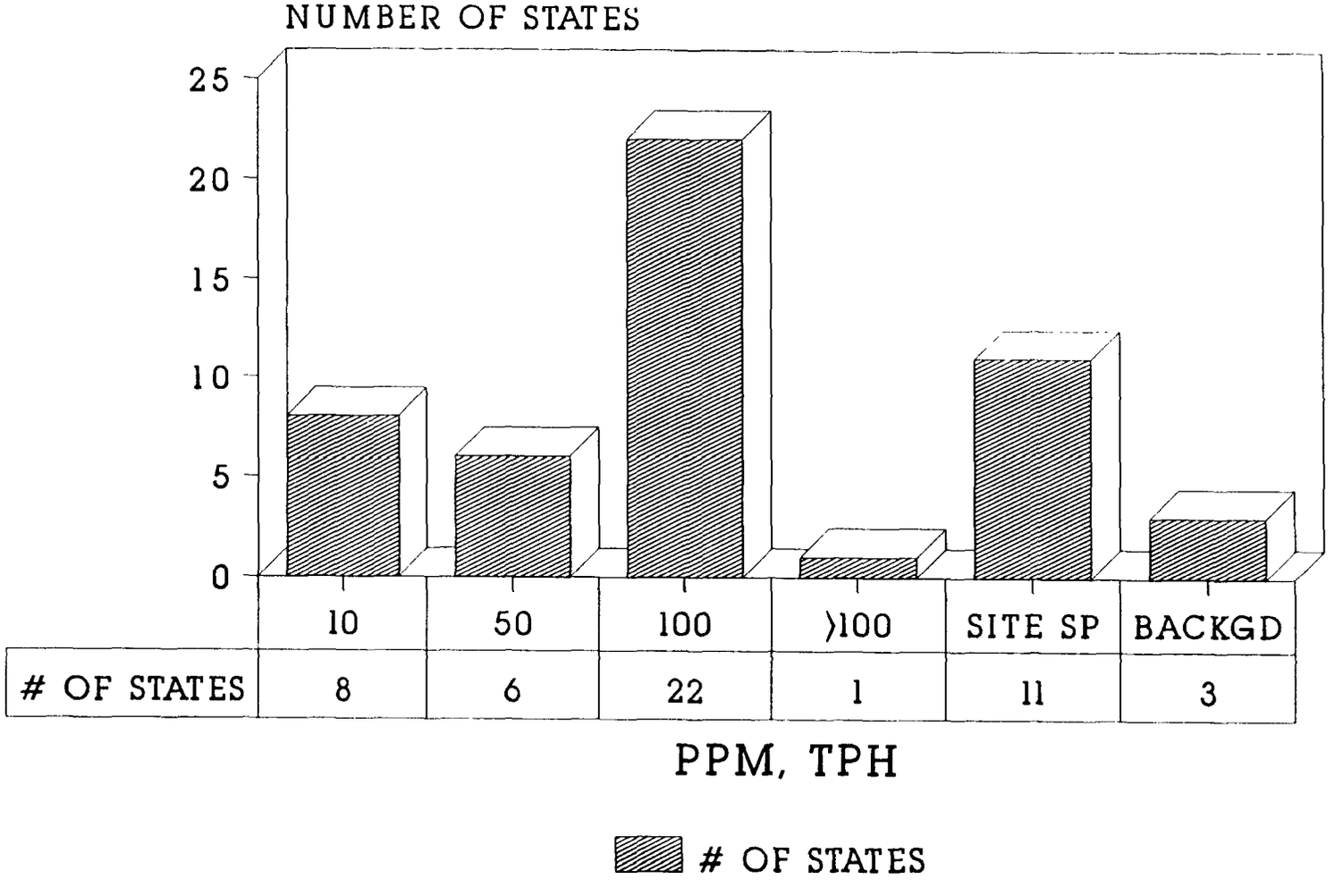
DISADVANTAGES

- TWO METHODS ARE REQUIRED
- INTENSIVE SAMPLE PREPARATION
- SCREENING NECESSARY
- LIMITED/SEGMENTED INFORMATION ON PRODUCT TYPE

WHAT ARE SIGNIFICANT TPH CONCENTRATIONS???

STATE BY STATE SUMMARY OF CLEANUP STDS

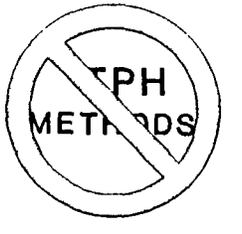
SOURCE: SOILS, NOV-DEC 1990



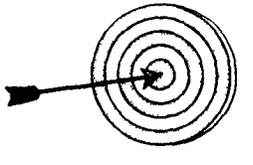
ANALYTICAL METHOD DEVELOPMENT FOR R&D SUPPORT

- REQUIREMENTS
  - Determine type of contamination range (gasoline, jet, diesel, crude, etc.)
  - Determination of TPH in soils at contaminated sites
  - Determination of selected target analytes (BTEX, etc.)
  - Boiling point distribution to aid in selection of appropriate remediation technology

- PROBLEM
  - There are no TPH methods that can satisfy requirements



- SOLUTION
  - Development of a soil extraction procedure followed by GC/FID analysis that provides information on
    - PRODUCT TYPE [redacted] TO DIESEL fingerprint
    - Gasoline range TPH
    - BTEX, etc.
    - Boiling point distribution

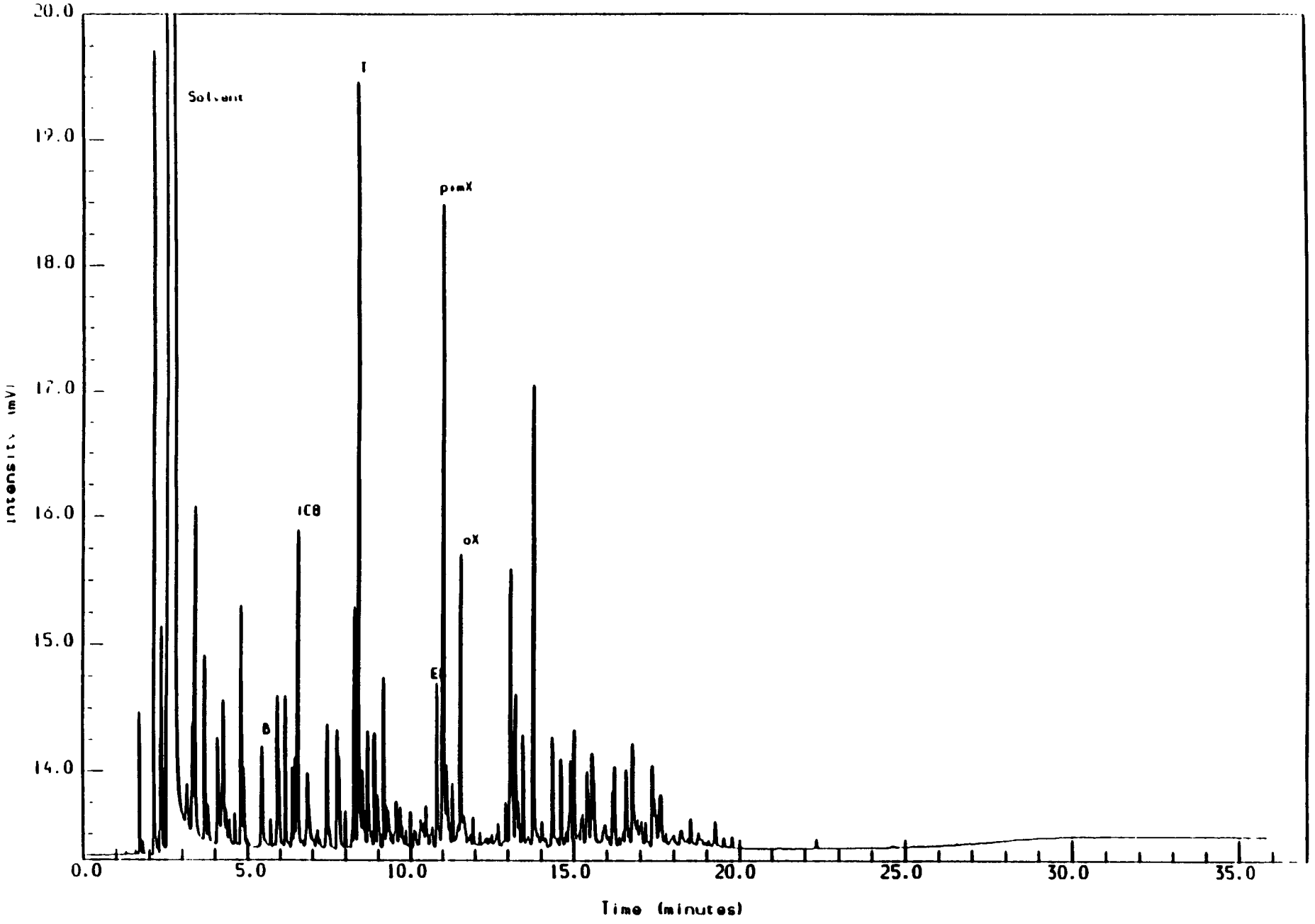


SOIL EXTRACTION AND ANALYSIS PROCEDURE

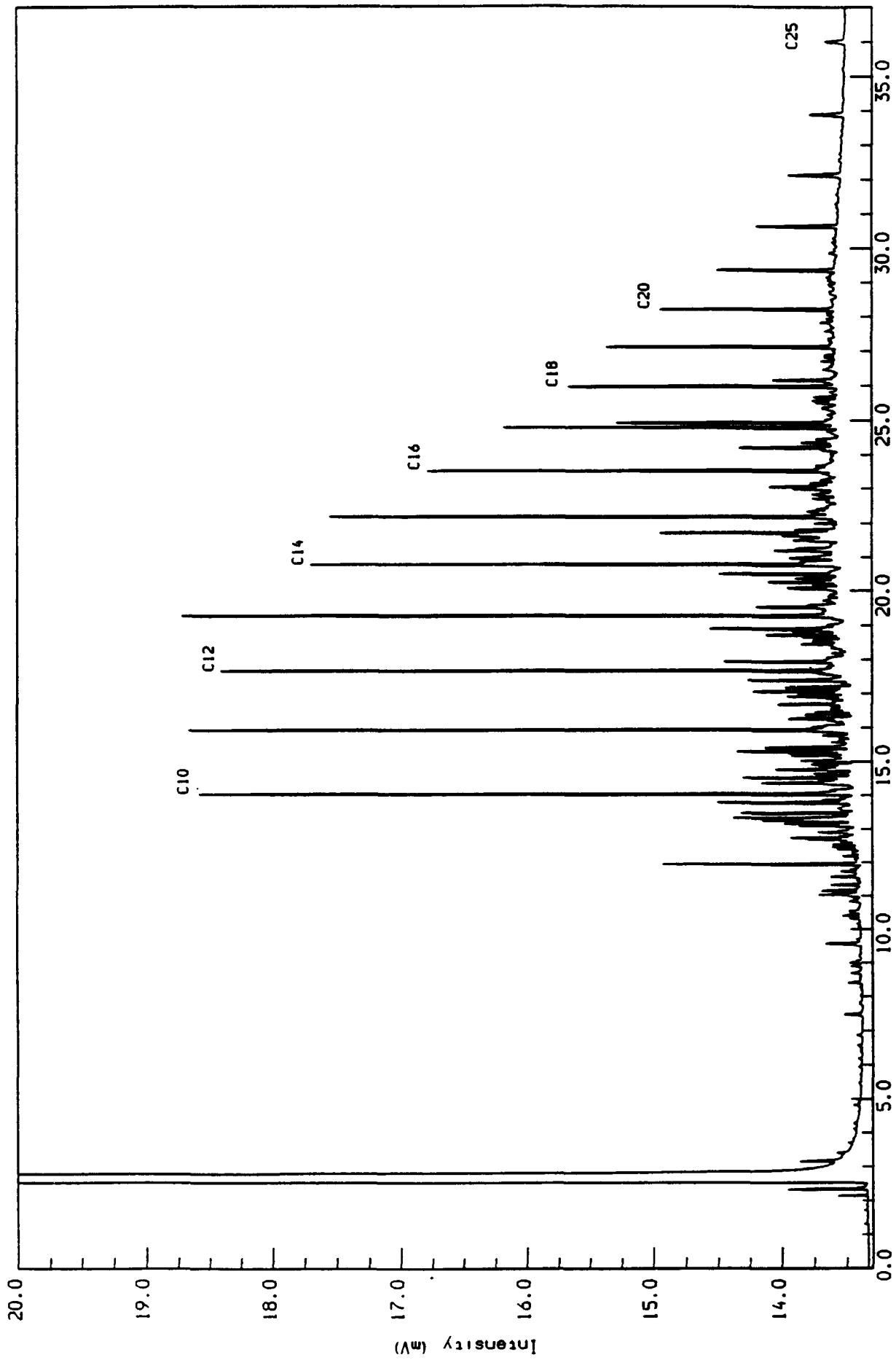
- Weigh a portion of the soil sample. Typically, 10-20 g are weighed directly in a vial. May add sodium sulfate
- Add 10-20 mL of methylene chloride or methanol and cap the vial. Purity of extraction solvents is essential
- Vortex for 1 minute
- Shake with a mechanical shaker for at least 1 hour
- Place vials in sonicator bath and sonicate for at least 1/2 hour
- Centrifuge if necessary
- Transfer portion of extract to autosampler vial
- Analyze extracts by GC/FID using designated instrumental parameters
- Calculate TPH in sample by comparison with standards either using response factor(s) or calibration curves. Use of calibration curves is recommended

INSTRUMENTAL PARAMETERS

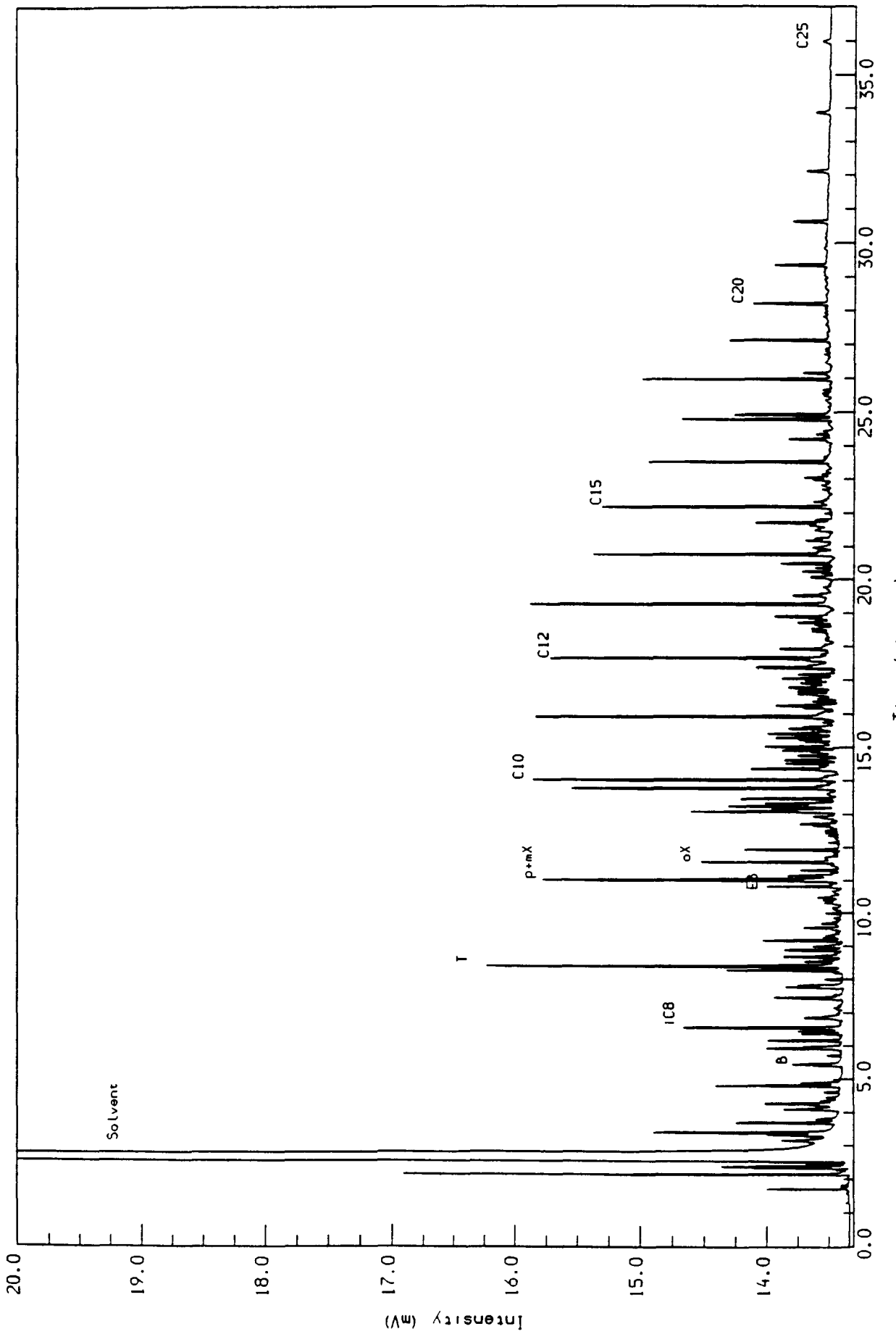
Gas Chromatograph:	Hewlett-Packard 5880 or 5890
Column:	Quadrex MS-007, fused silica capillary column 25 m X 0.25 mm ID, 1.0 µm film thickness methyl silicon
Carrier gas:	Helium, 15 Psig.
Make-up gas:	Nitrogen, 30 ml/min.
Split Ratio:	30:1 (minimum)
Sample size:	1-5 µL
Injector:	325°C
Detector:	Flame ionization, 350°C
Column program:	40°C hold for 4 min, program at 10°C/min to 280°C. Hold for 15 min at 280°C.
Data System:	VG Multichrom



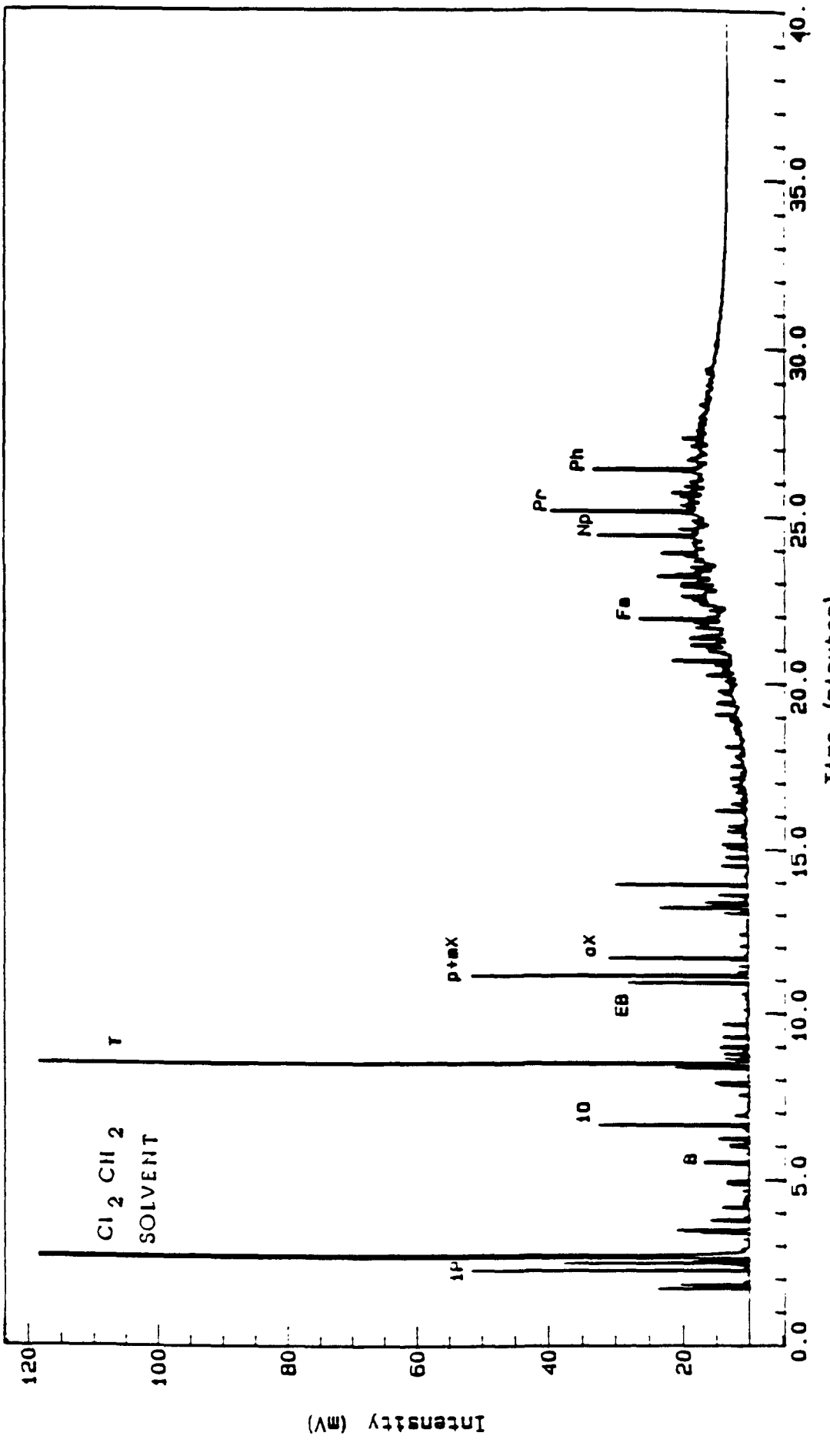
CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2300 PPM GASOLINE IN SOIL.



CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2700 PPM DIESEL IN SOIL.



CHROMATOGRAM OF EXTRACT FROM SPIKED SOIL. 2200 PPM GASOLINE PLUS DIESEL (~1:1)



CHROMATOGRAM OF EXTRACT FROM A SOIL SAMPLE CONTAINING GASOLINE AND EXTREMELY WEATHERED DIESEL RANGE MATERIAL

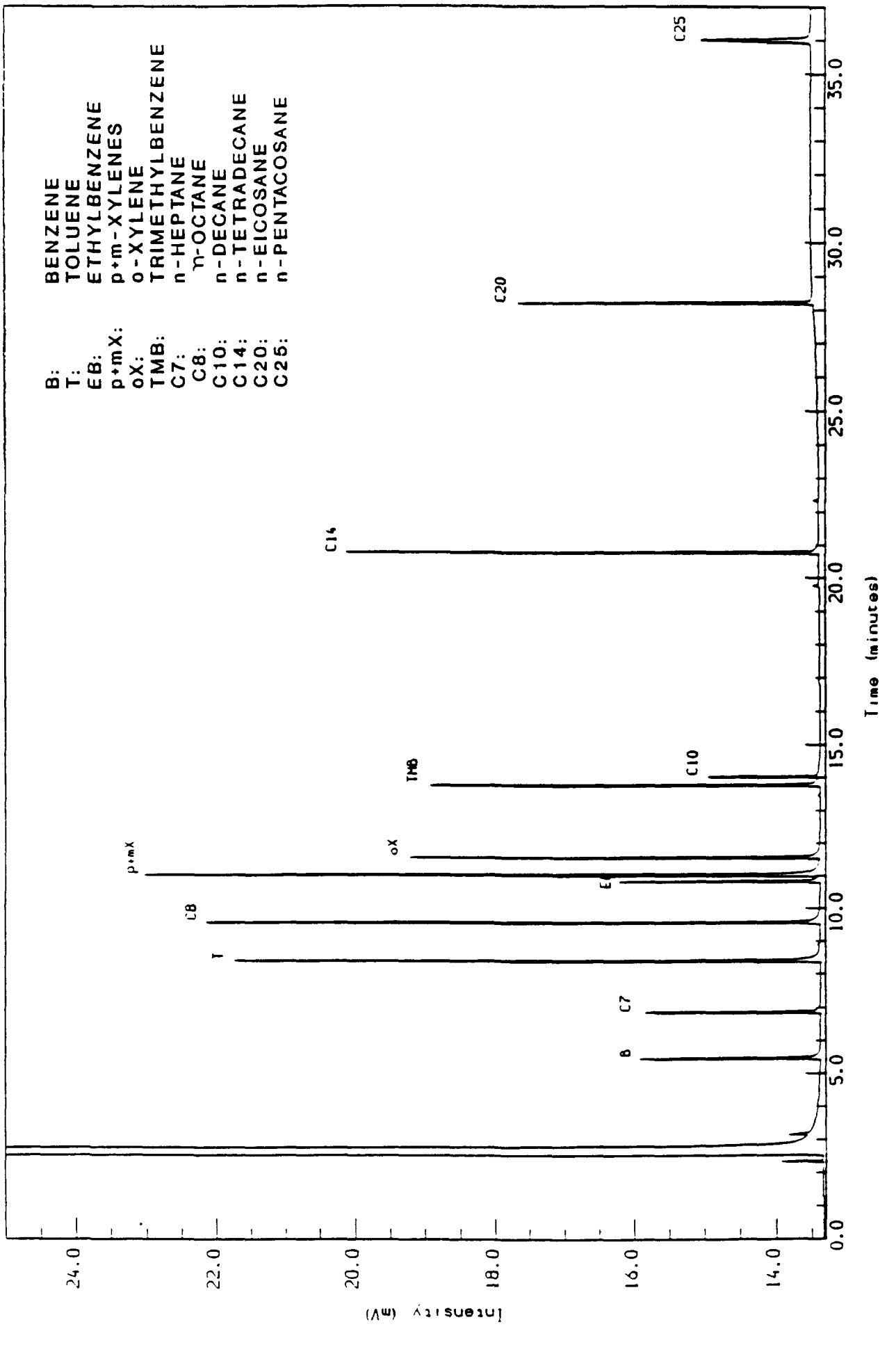
CALIBRATION STANDARDS

- TPH DETERMINATION

  - Can prepare standards using any grade or source of gasoline, diesel, mixtures of gasoline and diesel or selected target components. Prepare a 1% stock solution in the extraction solvent. Dilute from stock as needed to generate a calibration range that encompasses the range of concentrations in the samples under study

- BOILING POINT DISTRIBUTION DETERMINATION

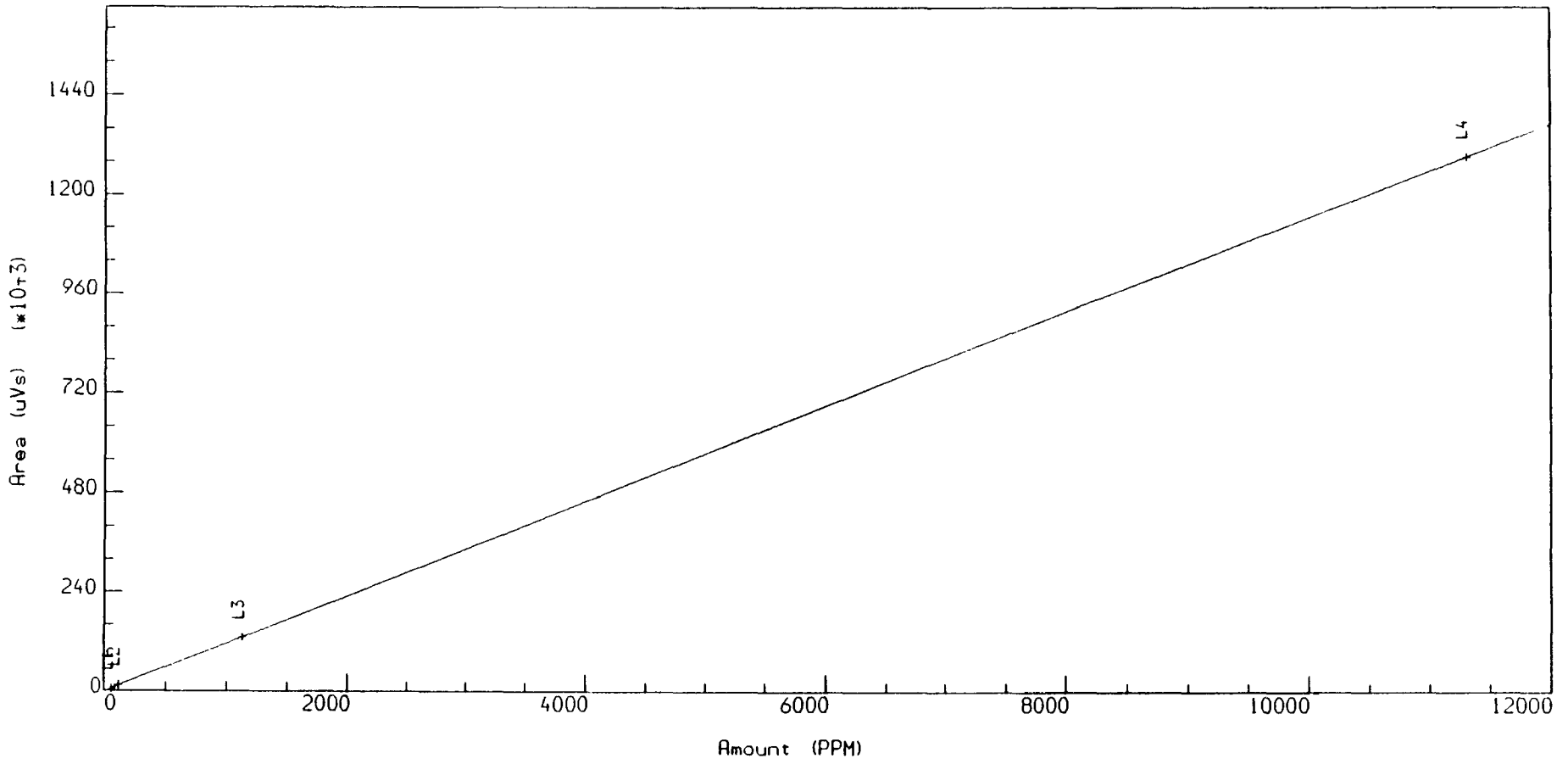
  - Prepare a standard containing n-C6 to n-C25 in methylene chloride or methanol at 100-1000 ppm total. Analyze a sample of this standard solution to detemine the retention times of these compounds and use the information to select cutoff points and boiling point distribution



CHROMATOGRAM OF 1000 PPM SYNTHETIC MIX STANDARD

TPH IN SOIL

Peak : TPH gasoline



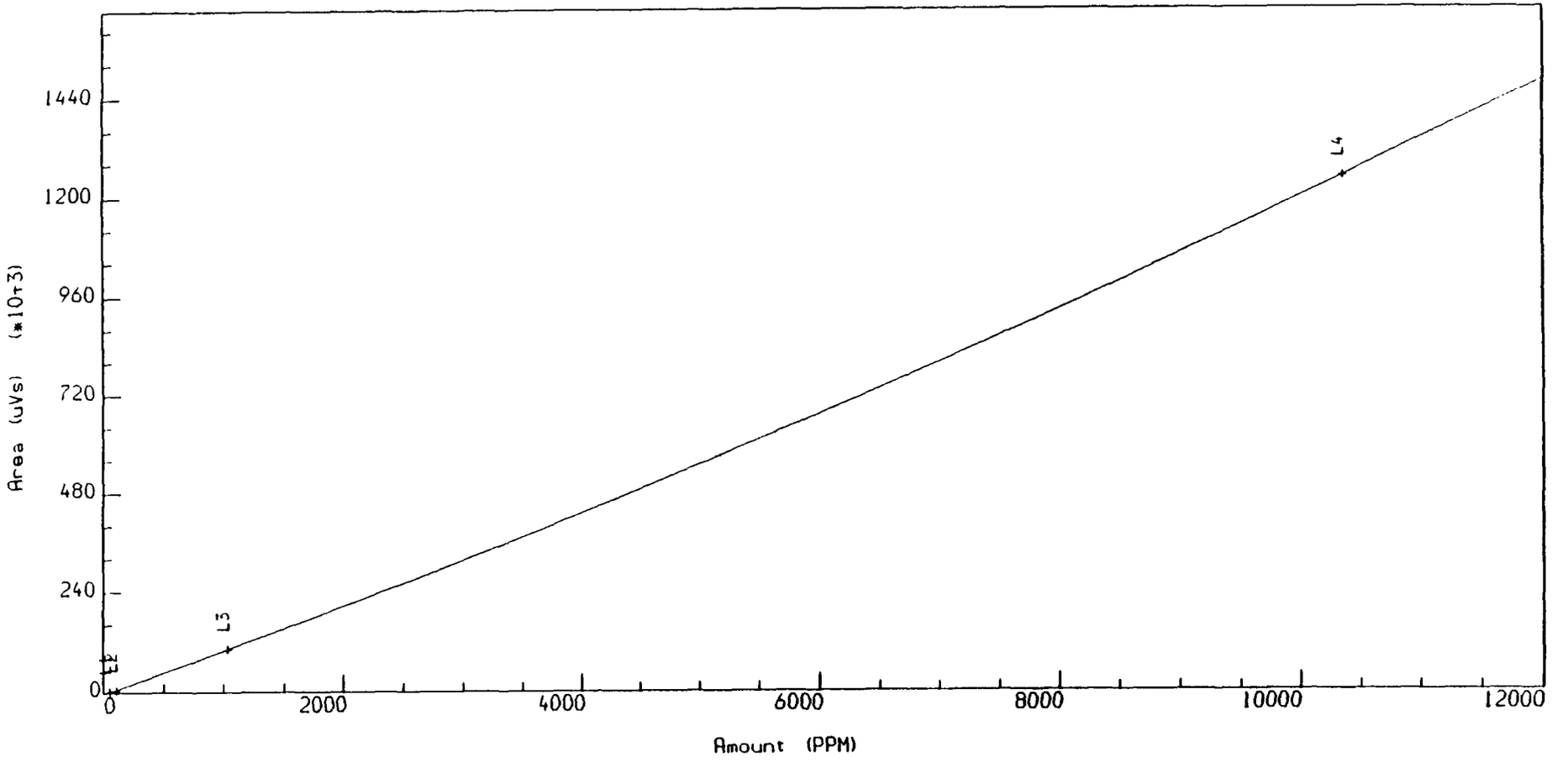
Constant	: -1.266704E+3	Curve fit	: Quadratic
1st degree	: 1.16399E+2	Coeff of determination	: 1.00000
2nd degree	: -0.00015	Standard error	: 1.23180E+3

CALIBRATION PLOT USING GASOLINE STANDARDS.

50-10,000 PPM.

TPH IN SOIL

Peak : TPH diesel

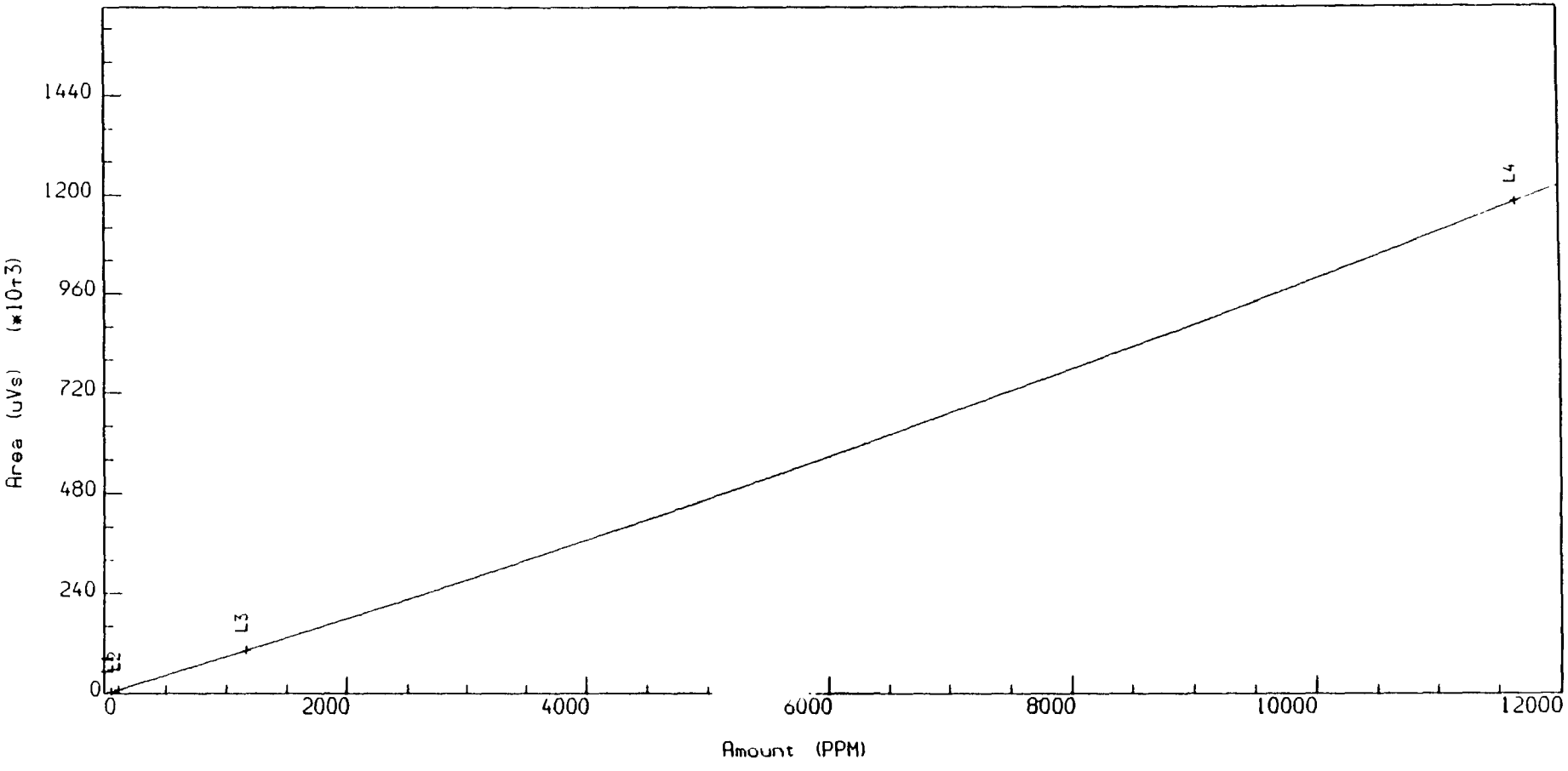


Constant	: -4.030669E+3	Curve fit	: Quadratic
1st degree	: 1.00654E+2	Coeff of determination	: 1.00000
2nd degree	: 0.00193	Standard error	: 1.34628E+3

CALIBRATION PLOT USING DIESEL STANDARDS. 50-10,000 PPM.

TPH IN SOIL

Peak : TPH gasoline/diesel



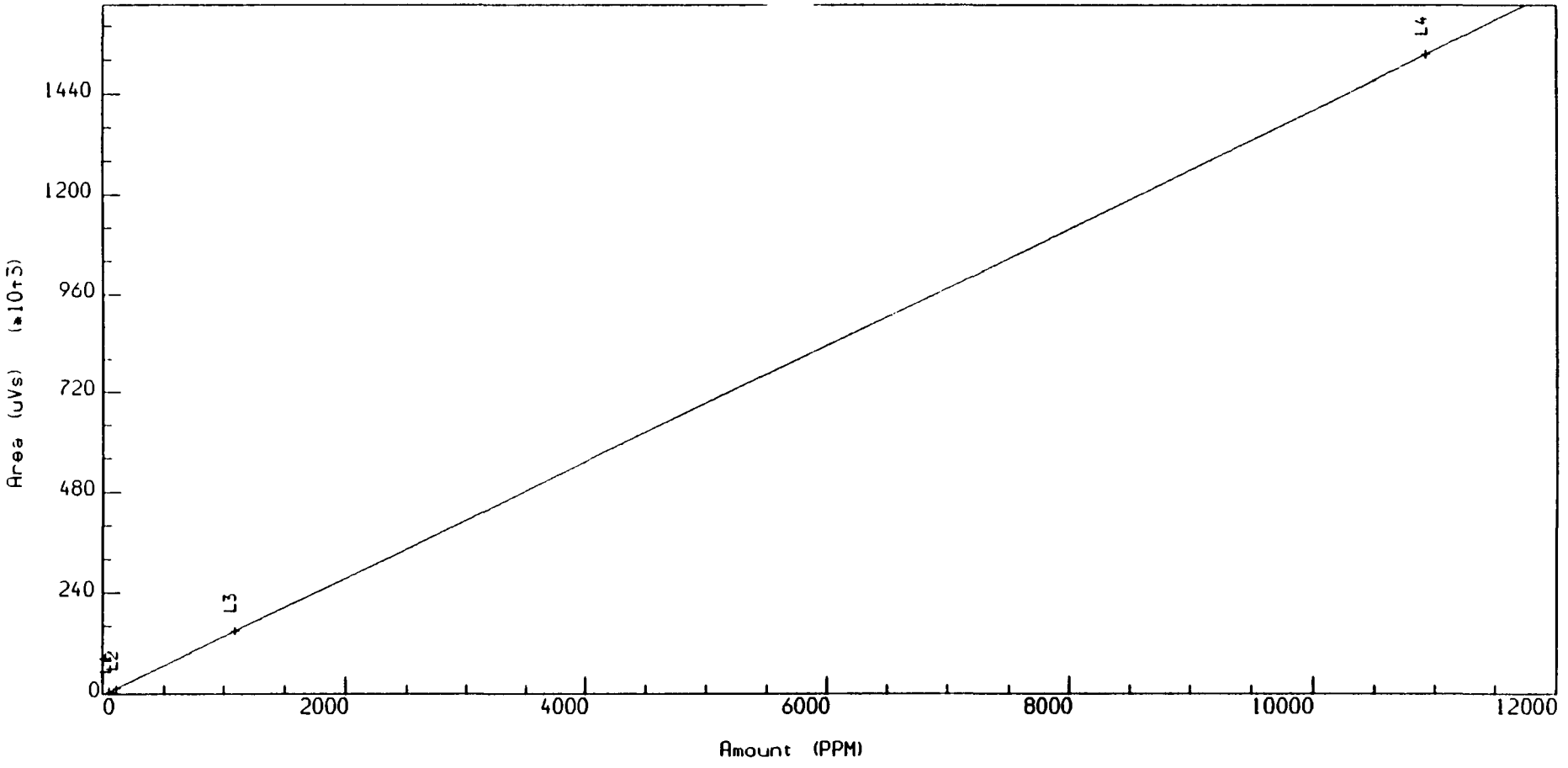
Constant	: -1.063288E+3	Curve fit	: Quadratic
1st degree	: 8.77609E+1	Coeff of determination	: 1.00000
2nd degree	: 0.00118	Standard error	: 6.08165E+2

CALIBRATION PLOT USING 1:1 GASOLINE DIESEL MIX STANDARD.

50-10,000 PPM.

TPH IN SOIL

Peak : TPH SYN-GAS/DIES



Constant	: -2.085850E+3	Curve fit	: Quadratic
1st degree	: 1.38073E+2	Coeff of determination	: 1.00000
2nd degree	: 0.00022	Standard error	: 6.86466E+2

CALIBRATION PLOT USING A SYNTHETIC MIX STANDARD.

50-10,000 PPM.

SUMMARY OF TPH RESULTS
SPIKED SOILS, PPM

PRODUCT TYPE	TARGET VALUE PPM	GAS STD PPM	G+D STD PPM	DIES STD PPM	SYN STD PPM	AVE PPM	ACC AVG %
GASOLINE	57	43	55	77	43	55	96
		46	61	62	23	48	84
GASOLINE	113	85	110	125	77	99	88
		96	110	120	60	97	85
GASOLINE	2300	1980	2530	2210	1670	2098	91
		2000	2040	2400	1470	1978	86
GASOLINE	4770	4580	5500	4750	3740	4643	97
		4600	4680	5400	3800	4620	97
GAS+DIES	58	38	48	71	44	50	87
		67	51	69	24	53	91
GAS+DIES	117	91	120	130	83	106	91
		85	78	102	44	77	66
GAS+DIES	2230	1680	2150	1900	1410	1785	80
		2250	2180	2630	1620	2170	97
GAS+DIES	4140	3300	4120	3580	2760	3440	83
		4110	4010	4730	2990	3960	96
DIESEL	52	40	50	73	39	51	97
		46	62	62	20	48	91
DIESEL	104	74	95	110	68	87	83
		62	86	94	35	69	67
DIESEL	2770	2140	2730	2390	1800	2265	82
		2400	2450	3000	1770	2405	87
DIESEL	6660	5310	6440	5540	4420	5428	81
		6100	6240	7000	4560	5975	90

ACCURACY AVERAGE % (PER CONCENTRATION LEVEL): 87
RELATIVE STANDARD DEVIATION ("): 8

OVERALL ACCURACY AVERAGE PERCENT LIMITS:

GASOLINE:	92±20
GASOLINE+DIESEL:	86±21
DIESEL:	85±22

EXTRACTS ANALYZED USING 2 DIFFERENT GAS CHROMATOGRAPHS

APPROXIMATE BOILING POINT DISTRIBUTION

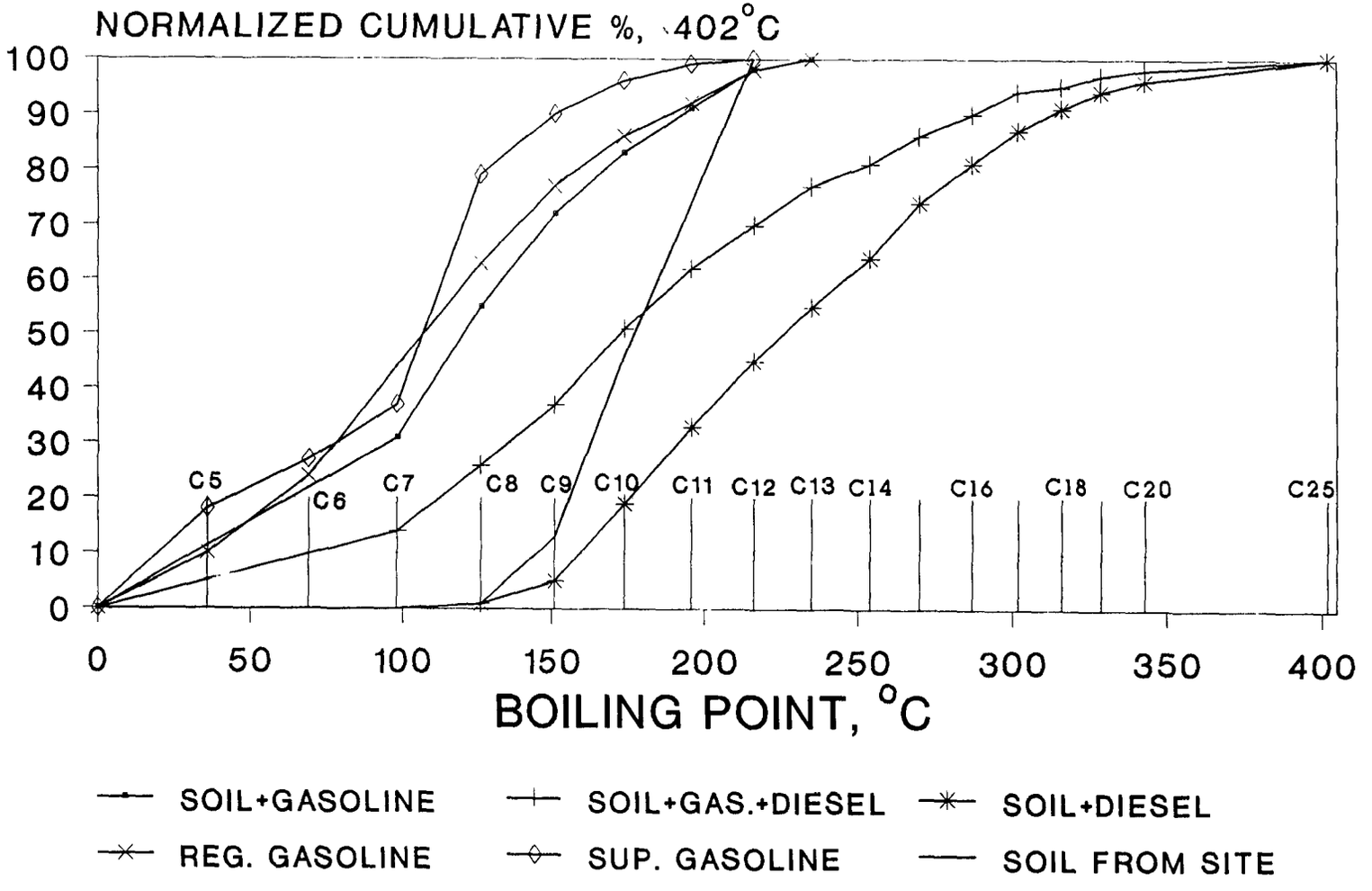
- The stationary phase in the chromatographic column used in this method is non-polar. Separation of compounds in a mixture is achieved essentially by differences in their boiling point. In this method, n-alkanes are used as references to determine the correlation of retention time with the known boiling points of the n-alkanes (C6-C25).

- Approximate boiling point distribution is calculated by normalization of sums of peak areas of portions of the chromatograms eluting between boiling points of interest.

RETENTION TIMES AND BOILING POINTS OF n-ALKANES FOR DETERMINATION OF BOILING POINT DISTRIBUTION OF GASOLINE TO DIESEL RANGE TPH IN SOIL USING DESIGNATED INSTRUMENTAL PARAMETERS

	BP °C	Retention Time (min)	Alkane Marker
GASOLINE RANGE	36	2.15	n-C5
	69	4.09	n-C6
	98	6.85	n-C7
	126	9.55	n-C8
	151	11.93	n-C9
	174	14.03	n-C10
	196	15.92	n-C11
	216	17.65	n-C12
	236	19.26	n-C13
	253	20.76	n-C14
	270	22.18	n-C15
	287	23.51	n-C16
	302	24.77	n-C17
	316	25.98	n-C18
	329	27.11	n-C19
	343	28.20	n-C20
	402	35.99	n-C25

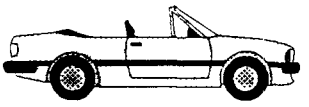
APPROXIMATE BOILING POINT DISTIBUTION
GASOLINE TO DIESEL RANGE



SOIL EXTRACTED WITH METHYLENE CHLORIDE, THEN GC/FID

ALTERNATE GASOLINE RANGE METHOD

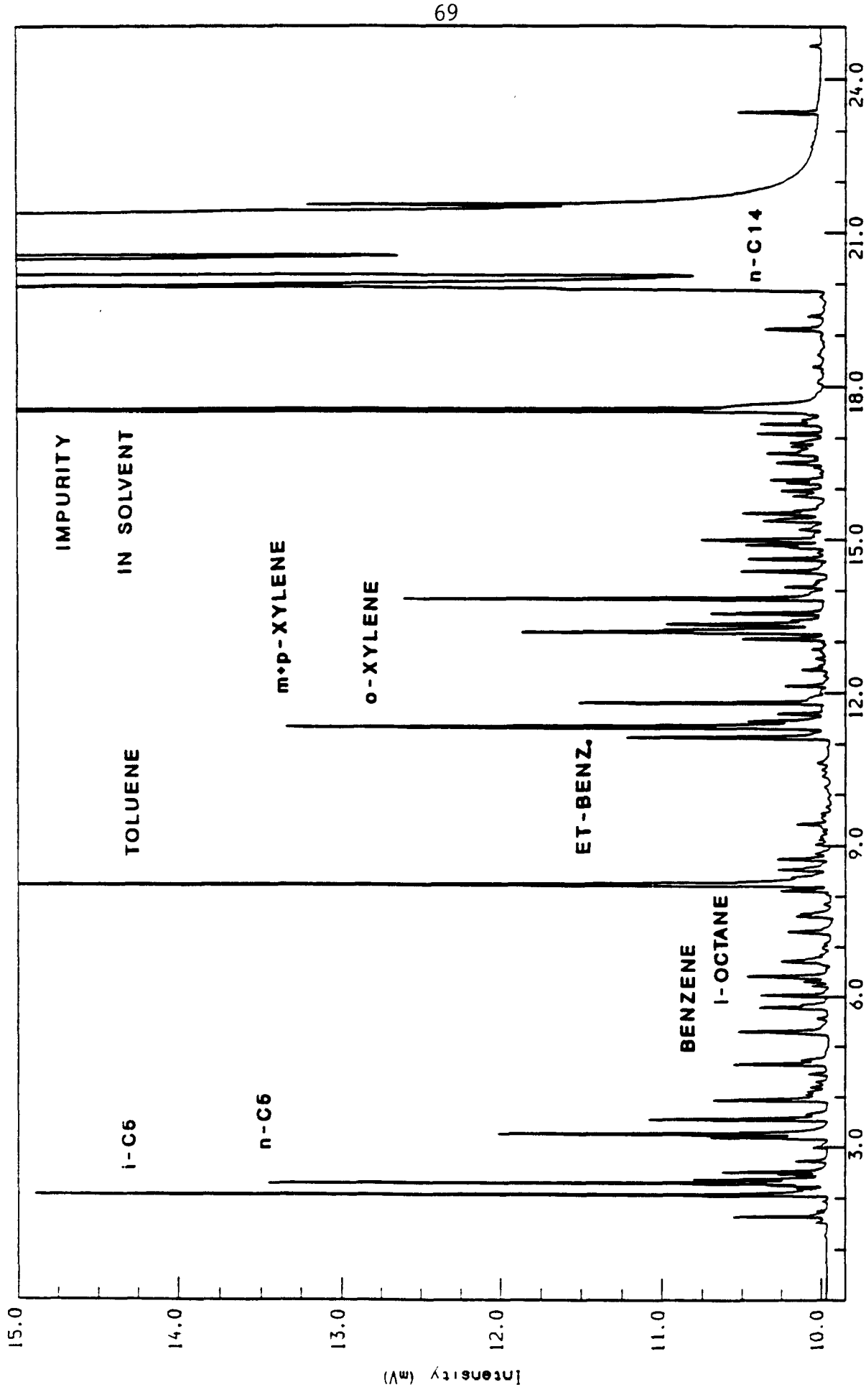
GASOLINE RANGE TPH



- Extraction of soil samples with methylene chloride or methanol results in inability to determine most gasoline components below C6. As much as 25% of gasoline is in this range.

- To assess properly gasoline range TPH as well as to estimate boiling point distribution of contaminants in soil, an alternate method was developed.

THE METHOD USES n-TETRADECANE (BEYOND GASOLINE RANGE) FOR EXTRACTION FOLLOWED BY ANALYSIS OF EXTRACT USING GC-FID



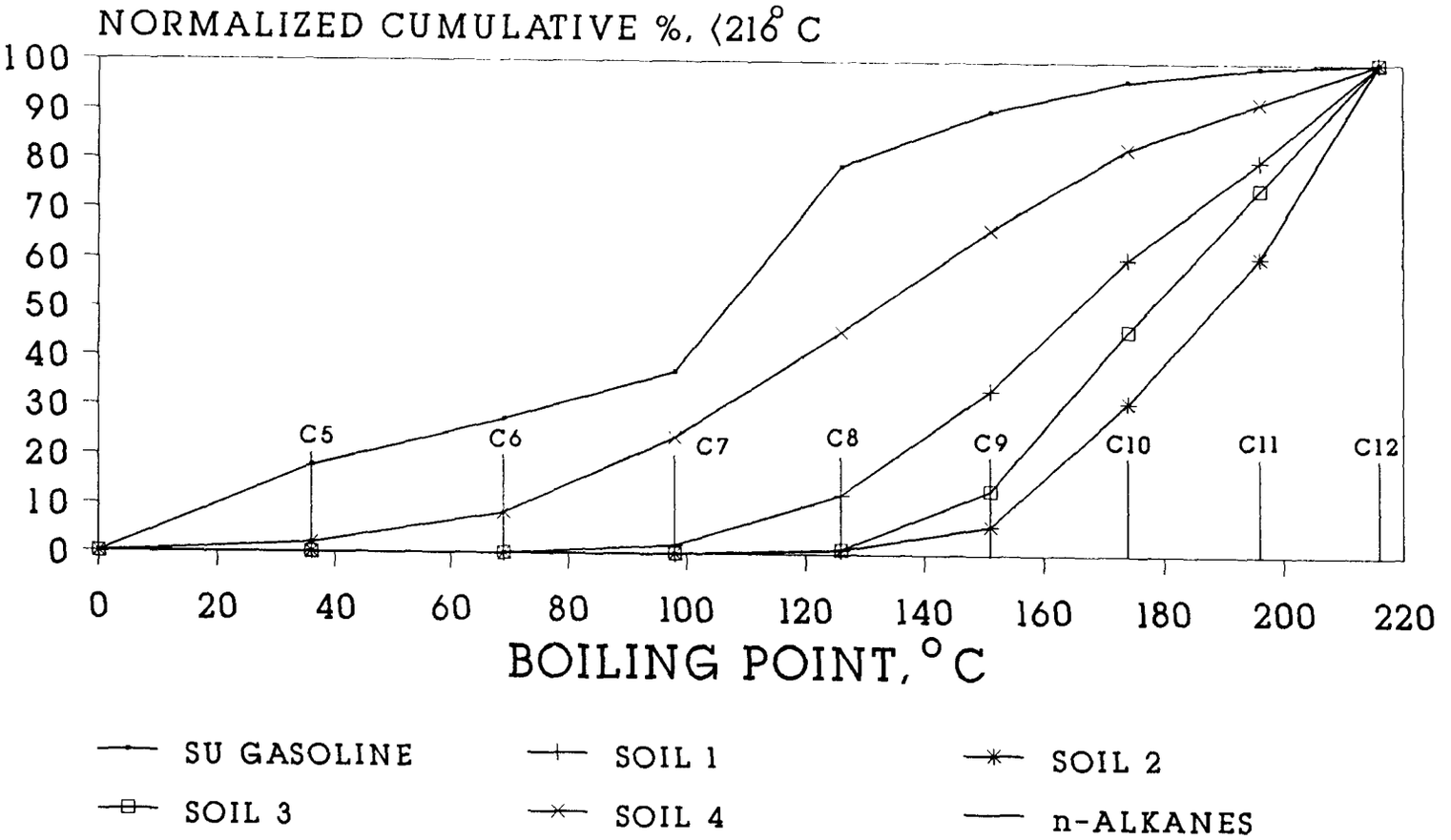
CHROMATOGRAM OF TETRADECANE EXTRACT OF SOIL SPIKED WITH GASOLINE (1500 PPM).

TETRADECANE EXTRACTION METHOD RECOVERY STUDIES. SAND AND SANDY LOAM (*) SPIKED WITH GASOLINE

SPIKED TPH ug/g	ADDED WATER %	FOUND TPH ug/g	TPH RECOVERY %
50	0	51	102
50	0	48	96
50	10	52	103
50	10	51	102
100	0	101	101
100	0	98	98
100	10	95	95
100	10	92	92
500	0	470	94
500	0	460	92
500	10	370	74
500	10	340	68
1000	0	880	88
1000	0	880	88
1000	10	950	95
1000	10	950	95
1020	0	1000	98
1020	10	990	97
*1000	0	940	94
*1000	0	950	95
*1000	10	900	90
*1000	10	870	87
12000	0	11600	97
12000	10	10500	95

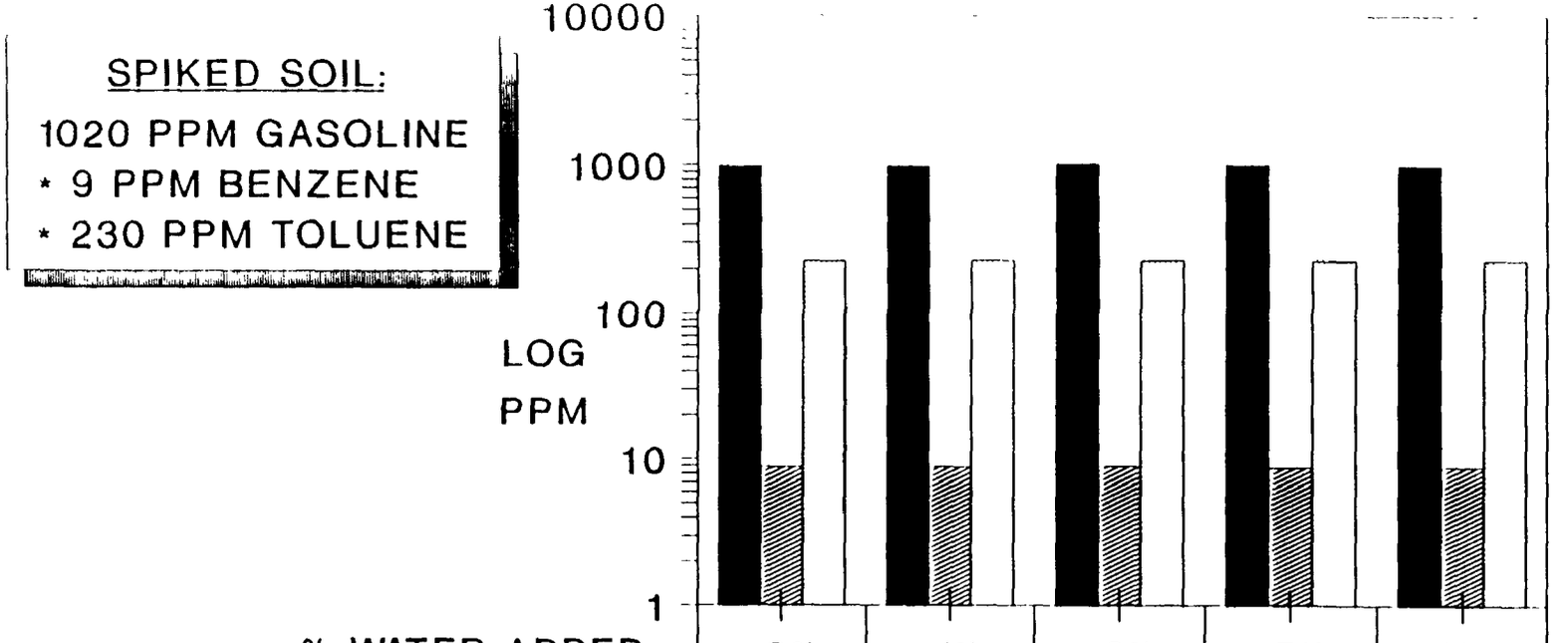
AVERAGE RECOVERY: 93±8%

APPROXIMATE BOILING POINT DISTRIBUTION GASOLINE RANGE TPH IN CONTAMINATED SOILS FROM GASOLINE STATION



SOIL EXTRACTED WITH n-C14, THEN GC/FID

EFFECT OF MOISTURE CONTENT OF SOIL ON EXTRACTION EFFICIENCY. 0 TO 10% WATER ADDED



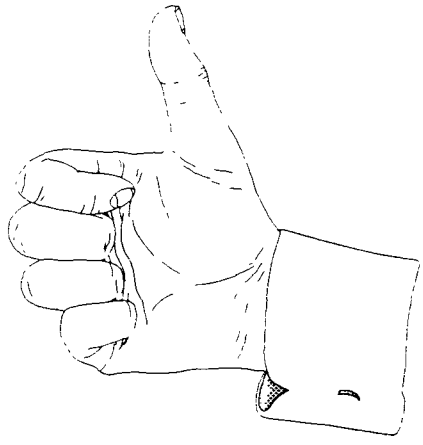
% WATER ADDED	+0%	+1%	+2%	+5%	+10%
MEASURED TPH	980	985	1020	1000	990
MEASURED BENZENE	8.8	8.8	8.9	8.7	8.8
MEASURED TOLUENE	228	230	230	227	229
% RECOVERY, TPH	96	97	100	98	97
% RECOVERY, BENZENE	98	98	99	97	99
% RECOVERY, TOLUENE	99	100	100	99	100

SUMMARY

- DEVELOPED SOIL EXTRACTION PROCEDURES FOLLOW BY GC-FID ANALYSIS THAT PROVIDES INFORMATION ON

  - PRODUCT TYPE FINGERPRINT
  - INDIVIDUAL TARGET COMPONENTS
  - GASOLINE TO DIESEL RANGE TPH
  - APPROXIMATE BOILING POINT DISTRIBUTION

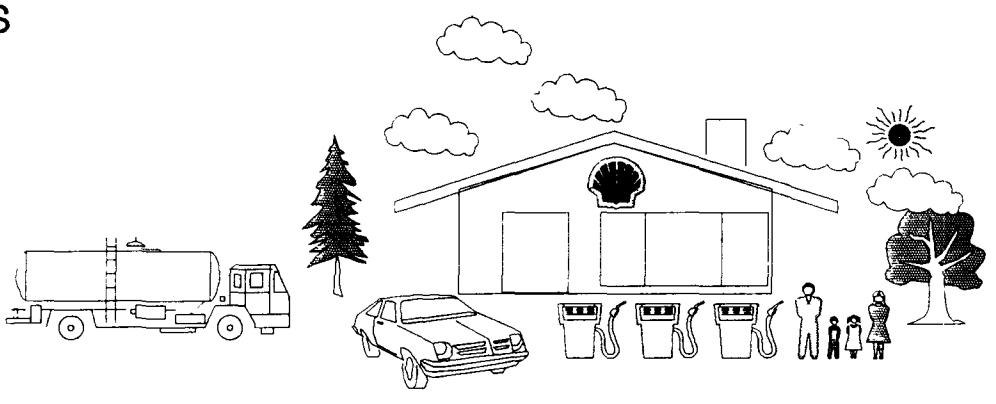
- THE TPH RANGE TESTED WAS 50 TO 10,000 PPM IN SOIL



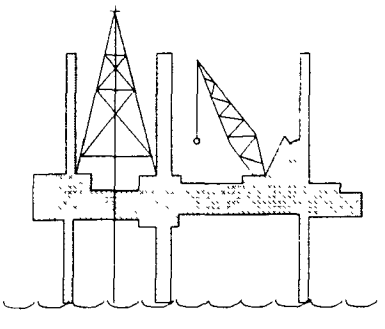
APPLICATIONS TO DATE
GASOLINE TO DIESEL RANGE TPH

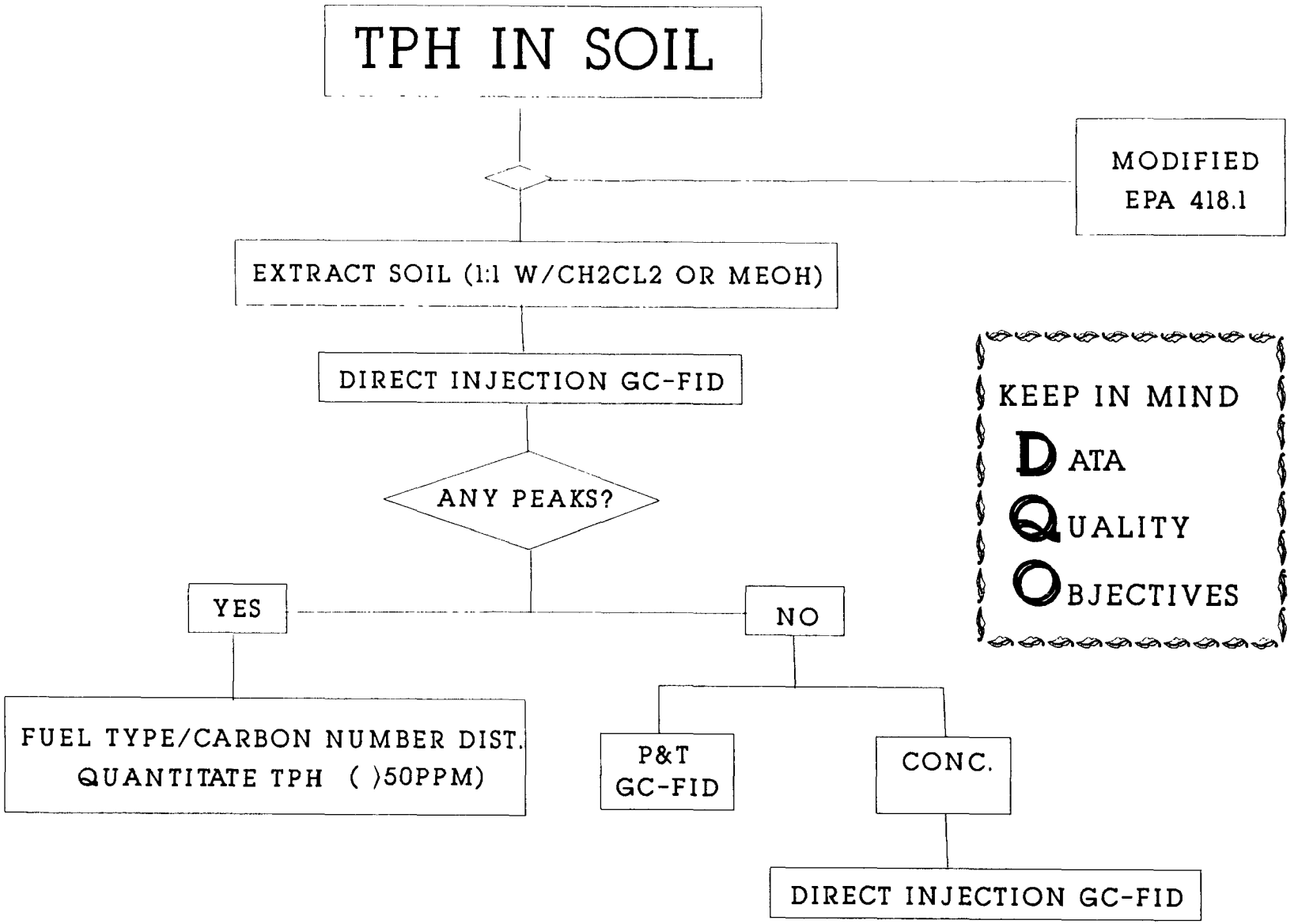
- SPIKED SOIL SAMPLES

- SOILS FROM SERVICE STATIONS AND DISTRIBUTION TERMINALS



- DRILLING MUDS




TPH IN SOIL
MODIFIED EPA 418.1
EXTRACT SOIL (1:1 W/CH2CL2 OR MEOH)
DIRECT INJECTION GC-FID
ANY PEAKS?
YES
NO
FUEL TYPE/CARBON NUMBER DIST.
QUANTITATE TPH ( )50PPM)
P&T GC-FID
CONC.
DIRECT INJECTION GC-FID
KEEP IN MIND
DATA
QUALITY
OBJECTIVES
5 PPM ⟨ TPH ⟨ 100 PPM)

MR. TELLIARD: I would like to read an announcement that I received from our laboratory in Cincinnati, EMSL. They're looking for a few good volunteers. They're looking for some labs to participate in three round robin studies, one on Method 8315A for the determination of carboxyl compounds by HPLC and that's going to be during June of '91, a method for marina nitrates for the determination of nitrate, nitrites in estuarine and coastal waters by automated color metric analysis and that's for June, '91, and method 524.2, determination of purge-able organic compounds in water by capillary column GC/MS and that's for October/November of '91.

If any of your folks from any of the labs are interested in participating, there's a sign-up sheet with a little more information on the back table in the corner for those of you who would like to.

Our next speaker is Rick Beach. Rick is the Director of Research and Development for Hydrosystems in Sterling, Virginia, and he's going to talk to us on a screening method for total polynuclear aromatics.

Do you want to use the walk-around microphone or do you want to use the podium microphone?

MR. BEACH: Good morning. Can I have the first slide?

My talk today will focus on a screening method for total polynuclear aromatics (TPNAs) that I developed at Hydrosystems. Actually the method goes a little farther in that it can resolve groups of polynuclear aromatics, the specifics of which I will discuss a little later in my talk.

I'd like to thank a number of people in my laboratory who contributed to this work: Kelly West, Lyle Silka, Mike Albertson and Arkady Gilchenok.

The technique I will be discussing today was developed for use in evaluating creosote residues at the L.A. Clarke Superfund site in Fredericksburg, Virginia.

The method works well for almost any PNA contamination, whether from creosote, petroleum hydrocarbons, or from coal tar. In addition, we're investigating some other applications right now.

This is a picture of actual operations at L.A. Clarke in, I believe, the 1970's. This photo illustrates the creosote wood treating operations used here during that time. Railroad ties, contained on railroad cars, were treated in large autoclaves filled with creosote and exposed to elevated pressures and temperatures. Under these conditions, the creosote permeates the wood. After treatment, the creosote was drained off, the autoclave opened, and the railroad car containing the treated ties was removed to what is called "drip tracks". At this point creosote was allowed to "drip" onto the ground below the drip tracks, resulting in substantial soil contamination. In the newer plants operating today, the drip process occurs in a concrete liner or some other type of liner, to prevent soil contamination.

Screening techniques are highly effective in evaluating large contamination sites such as the L.A. Clarke site. During on-going operations, it's very easy to tell where the contamination is; it sticks to the bottom of your shoes.

However, a couple of years later when the drip tracks are ripped up, the soil is moved around, and you have a little bit of surface biodegradation, you can't easily tell, other than by historical photos, where the main problem area was located. Furthermore, you can't always determine from drainage ditches and other spill activities where the highest concentrations of the contaminants may be on the site. Therefore, a screening technique is a highly efficient and cost effective tool for use in evaluating contamination of large sites.

For the work at L.A. Clarke, Hydrosystems inherited a screening method as part of a consent order between the Responsible Party and the EPA prior to our taking over the Superfund work. The initial RIFS work on the first operable unit was done by R.F. Weston. They developed a technique in 1985 or '86 that was based on a fluorescent scanning technique of acetonitrile extracts of soils. The technique was set up to quantitate two different groups of PNAs by evaluating 2 & 3 ringed compounds and the second group was to evaluate 3 to 6 ringed compounds.

R.F. Weston had used this method to report areas of major contamination at the L.A. Clarke site. We had planned on using their method in our subsequent investigations there. In fact, part of the clean-up standards for this site are based on the Weston screening technique.

However, before tackling the L.A. Clarke site, we decided to use the Weston screening method for a separate investigation of oil and fuel contamination at a railroad switching yard. We surveyed approximately 50 acres of the 500 acre site. This slide is a photo of a portion of the whole switching yard. Pictured here is an area containing a braking system and an automatic lubricator, as well as the beginning of the distribution yard. There is extensive contamination in these areas resulting from general railroad activity, as well as from accidental spills, leaks from cars, etcetera.

Unfortunately, the Weston method did not work well

here. We found that we could not get consistent matrix spike recoveries or sample precision on the analyses. We are really disturbed about this because we had just obligated to doing several hundreds of thousands of dollars worth of work on the L.A. Clarke Superfund site with a technique that had significant problems. So we went back to the data that Weston had generated from the RIFS for this site to hopefully resolve the discrepancies with the method.

The first thing we noticed when we went through the data was that no data for matrix spike recoveries or sample duplicates existed in the RIFS report. I asked some of the people that were involved in the work about the ommision and they explained that they had not performed such QC measures. They considered their method to be a very gross screening technique and therefore felt that the matrix spikes and duplicates weren't warranted.

Their raw data did contain a range of dilution results from a number of individual samples. We used this data to estimate whether or not they actually encountered the same matrix effects that we did. To make this estimate, I looked at the ratio of the diluted concentration of a given sample corrected for its dilution factor to the non-diluted concentration. In the absence of matrix interferences or non-linearity of response, this value should equal 100 percent. I did this for all of the samples within a factor of two of the calibration limits. For the two groups of PNSs identified by the Weston method, their analyses resulted in values of over 200 percent. In my view, a two and a half fold increase in response is stretching it a little bit too far for only being at most a factor of two out of the linear working range.

To constrain these results further, we narrowed down the samples to just those in the linear working range. These are samples in which the original analyses and the diluted analyses are both in the linear range. Unfortunately, only nine samples from group 1 and none from group 2 fit this criteria. In fact,

in this case, the ratio got even higher than the previous group, suggesting that there may be a strong negative interference - the greater the dilution, the greater the deviation above 100 percent. This result was very disconcerting, and overwhelmed any attempt to use matrix spike recoveries in conjunction with the Weston method.

We were therefore forced to scrap the Weston method and develop a new screening method that could use matrix spike recoveries and sample replicates to evaluate accuracy and precision. The results of these QC measures could then be used to insure that the project data quality objectives are met.

Weston used their method to map large areas of the site and to identify certain problems, but we were at a disadvantage. We took over the method with the job and had to incorporate data quality objectives into our quality assurance plan prior to our discovering the inherent problems with the technique. I had made up what I thought were a fairly wide range of data quality objectives but found that with the Weston technique, we would not be able to achieve the goals. So we tried using the same acetonitrile extraction that Weston used, but substituted an HPLC setup with a low resolution, reverse phase column to give us more group information than what the Weston method had provided. We calibrated on equal concentrations of the 16 priority pollutant PNAs. It's also a very easy standard to come by commercially.

This slide illustrates what you get on your chromatogram with the setup that we utilized. The first thing you may notice is there are four groups identified and the first group is titled, one to three rings. Well, if you have one ring, it's not really a PNA. But what we found out is that it was going to be too much work to try to resolve the difference between the earliest eluting PNA, which is naphthalene with two rings, and some natural or non-natural fluorescing one-ringed compounds that are co-eluting. So what we did is to lump them all together in this case. Therefore the title is somewhat misleading. However, we are doing more studies to try to narrow

this group down without making the method too unwieldy.

For soils, however, we found that there wasn't very much in the way of early eluting compounds that would need to be separated from naphthalene. The signal was very small in this case, so we just let it ride.

The other groups are four ring compounds, five and six ring compounds, and what I have indicated with a question mark is greater than six ring compounds. Primarily, they're substituted six ring compounds. Later, I'll explain why we wanted these last two groups resolved this way.

Let me back up for a second.

The distribution of the priority pollutant PNAs is this: there are six priority pollutant compounds in the one to three ring group, four compounds in the four ring group, and six compounds in the five to six ring group. So there's a nice distribution of the compounds across the majority of the groups that we can resolve.

The calibration curve takes a little interpretation if you're not used to group concentrations. The x-axis on this slide is the concentration of each of the PNA compounds in the 16 compound standard mixture. The y-axis represents the cumulative area for each of the groups of PNA compounds.

To establish calibration factors, you first multiply the compound concentration by the number of compounds in each group to determine the group concentration. The group calibration factor is the group concentration divided by the cumulative area of the compounds within that group.

The curve shown is one of our first calibration curves from last summer. Since then we've extended the linear range to 10 parts per million liquid concentration. The soil concentration gives a range fairly nice dynamic range from approximately 0.5 parts per million of each TPNA group to between 400 and 500 parts per million of total PNA. This is a very nice, large range for doing screening analyses.

This slide is courtesy of Hewlett-Packard. Our

analyses were conducted on a Hewlett-Packard 1050 quaternary HPLC system. We're using a binary format right now with a program going from 40 percent acetonitrile to 100 percent acetonitrile at eight minutes with water as the balance of the solvent. The fluorescence detector we're using is the model 1046, set up with excitation at 235 nanometers, emission at 420 nanometers, and a cutoff filter at 380 nanometers.

The sample preparation involves extracting two grams of non-dried soil or sediment with 10 mLs of acetonitrile in a simple vortexer, allowing it to settle, and filtering the suspension with a 0.2 micron a crodisc. It's a very simple procedure with the matrix spike incorporated prior to the extraction.

The data that you see in this slide is actual QC data from the project. This is not a traditional method of validation where you take one fairly unitern soil type, homogenize it completely, spike it, run duplicates and create nice statistics. These project statistics were generated from actual field samples.

For this project our matrix spike data quality objective was 40 to 160 percent recovery. The recovery we got for the three groups that we have standard compounds for ranged between 126 and 142 percent recovery. This includes all rejected data. By rejected data, we mean data from soil samples with other evidence of being heterogeneic. If you excluded the rejected data, the average percent recovery would drop approximately 20 percentage points here. So the data for the actual project on the average worked out very well. The actual number of samples that we used to calculate statistics was 300 screening analyses. We ran matrix spikes and duplicates on one out of every 10 samples. We also ran GC/MS confirmations on the basis of one in 10 samples, which you'll see the results of a little bit later.

This slide shows the sample duplicate results. We evaluated the precision as the relative percent difference

between the soil duplicates. The data quality objective was set at less than 67 percent. This DQO is easy to evaluate,if the duplicate values are within a factor of two of each other, the data quality objective of less than 67 percent is attained. The average relative percent difference ranged between 42 and 45 percent. Again, the data would be better if we had excluded the rejected data, but we did not. These are real sample points.

The number of samples evaluated as part of the statistics varied depending on whether the matrix spikes were diluted out or below detection. The same criteria applies for the sample duplicates.

This work was performed over a one and a half month period back last summer. All analyses were done under one initial calibration. The initial calibration agreed with check standards performed daily on every 10 to 20 samples for the entire period. My acceptable criteria was a relative standard deviation of not more than 25 percent. In actuality, trend analyses showed that the relative standard deviation increased with time. So if I had put a smaller RSD on my check standards, I would have perofrmed a new intital calibration and gotten a better set of data for the overall project. But again, it wasn't needed for these project goals, which was to evaluate large areas of the site. The idea was to come up with a very economical screening technique that fit within reasonable data quality objectives, which is what the new method did.

This slide demonstrates the increased accuracy that we got out of our approach. The ROD for the site specified cleanup standards based on the Weston screening technique and its' correlation to the standardized EPA methods. We were confused as to what to apply as cleanup standards if we weren't using the same exact screening techniques. Therefore one of the things we had to do was to come up with a new correlation between the GC/MS data and the new screening technique.

What we have plotted on this slide with a log-log scale is a sum of all the PNAs that we reported from the GC/MS

confirmation analyses. The GC/MS data included three groups of PNA compounds. The first group was called carcinogenic PNAs (CPNAs). This group of compounds is the result of a lot of risk assessment work and has created particular problems for the analytical methods. The CPNAs consist of 24 compounds, seven of which are priority pollutants, 17 are not. Of those 17 that are not priority pollutant compounds, you can only get commercial standards for seven of the PNAs. That left 10 PNAs without standards. You have to estimate concentrations for these compounds using relative response factors of the closest eluting standard.

Therefore the first group of GC/MS data was carcinogenic PNAs. The second group was the remainder of the priority pollutant PNAs, which consisted of nine other compounds, and the third group which was the tentatively identified compounds based on library searches and estimated concentrations.

After you lump GC/MS data from all 3 groups together, you get a number which we included as the TPNAs for the GC/MS. We plotted those values versus the TPNAs of all the four groups that we had from the TPNA screening technique and we got this great correlation of 0.942. For a screening analysis, this was totally amazing and I was really surprised by this result. I confess that I did throw out one data point out stat 25 values. The data point was located two orders of magnitude off the line. When I first saw it plotted on the graph, I went back and searched for the archived sample, planning to re-analyze the soil. Unfortunately I couldn't find the sample. I went through the calculations and chromatogram for the sample and found some inconsistencies in the TPNA groups. Therefore given this uncertainty in the result, I felt somewhat justified in excluding that one sample point. I can undoubtedly justify the exclusion statistically if I use a Q test on it.The other nicety of the correlation information was that the slope came out close to one. This was really surprising, considering the fact that I had all of these non-compound specific calibrations. But the slope of

0.885 resulted in an easy comparison of GC/MS to screening data for project personnel. The same correlation coefficient, to three decimal places, was calculated from the correlation of CPNAs to the two comparable groups of the TPNA screening technique, the five to six ring and the substituted six ring group. It came out quite well. The same correlation coefficient, but, the slope, 0.787, fell off a little bit. But we can still use this comparison to plot a limited sub-set of the data that's very useful in terms of evaluating remedial alternatives for the CPNAs.

We've used this information to the data in terms of CLP equivalents because that's the procedures upon which we're basing our standardized analyses. This approach also makes the results more palatable to project people looking at the data. They can get confused when interpretting results of screening analyses. Therefore we put the values in familiar terms and units, even though in this case there wasn't very much of a change in the actual numbers. The screening results discussed here are from the analyses of soils and sediments from a floodplain area of the site. The extensive data set allowed us to develop isopleths over the whole flood plain area with very good delineation of areas of contamination. It was a particularly troublesome area to investigate. The area was 1,700 feet long and 700 feet wide. The floodplain is on an old stream bed which gets flooded several times a year. Over the years, all the streams' paths have meandered and resulted in changes in the depositioned areas. During creosoting operations over the last 50 years, some of the drainage ditches from the site emptied to the floodplain and you may hav had pure creosote contaminating the area. But due to the changes in the stream paths you can't just go to the stream beds where they exist now to locate contamination. Unfortunately, I can't present that data right now, but we found contamination in areas you wouldn't have located if you had to use a more limited number of samples.

The final flood plain survey consisted of 360 screening

analyses and 36 GC/MS analyses on soils from 180 stations (two depths). Given the approximate 10:1 cost ratio between the two types of analyses, the costs for each type of analyses were the same. The total analytical cost for this investigation turned out to be approximately $36,000.00. If you had used the budget only for GC/MS analyses, it would have only given you 72 analyses on soils from 36 stations. When you begin evaluating data from a very complicated site, with the potential of isolated soil source areas, you really need that fivefold increase in site information. The increased information is particularly useful if you can evaluate contamination within a factor of two and be assured of quality control measures that you can use to verify that the system is under control. This approach is advantageous if the TPNA group results are adequate for your specific data usage.

Our current work in progress using the TPNA method involves analysis of soil types other than flood plain soils and sediments. We're analyzing different types of geologic matrices, including clays, loams, and rocks. We're also analyzing TPNAs in surface and groundwaters. There are some problems that we're working on for water samples, primarily the lack of resolution between the one and two ringed compounds. The resolution of the early fluorescence peaks becomes very critical in the water samples. This problem is aggravated in water samples due to the high percentage of one and two ringed compounds relative to that found in soils. There's very little in the way of the higher ringed compounds in the water samples since these compounds are very insoluble and are so "particle active."

We've also used the TPNA screening method for monitoring bioremedial activities on the L. A. Clarke site. We're currently using batch reactors, thin film reactors, and artificial wetlands. We plan on using it for monitoring activities associated with land farming and soil flushing. We have a fairly wide latitude from EPA in terms of evaluating bioremedial techniques and we're at the pilot scale on a number

of the different remedial studies for this particular site.

We're also using the TPNA method to create an internal database to further expand the application of the method. Any sample that comes into our laboratory as part of a UST investigation, which could include contamination from gasoline, lubricating oils, and motor oils, is also analyzed for TPNAs. We don't normally report the results. We add the results to the internal database that we can correlate with other petroleum hydrocarbon techniques, primarily the TPH technique by IR which is the most commonly requested method in our area.

In summary, we've come up with a screening technique that's applicable to PNA contamination from a variety of sources and believe that the method is a very economical technique which can utilize QC measures to confirm the validity of the results and provide valuable site information. It's reliable and rock-solid in terms of the analytical technique and may have a lot of different types of applications.

Are there any questions?

QUESTION AND ANSWER SESSION

MR. BEACH: Any questions? Are you letting me off easy?

Thank you.

MR. TELLIARD: Thank you, Rick.

A SCREENING METHOD FOR TOTAL POLYNUCLEAR AROMATICS

Richard B. Beach, Kelly M. West, Lyle Silka,
Michael D. Albertson, Arkady Gilchenok

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SLIDE OF CREOSOTE WOODTREATING SITE

SLIDE OF RAILROAD SWITCHING YARD SITE

EVALUATION OF WESTON TPNA RESULTS AT L.A. CLARKE WITH DILUTED AND NON-DILUTED VALUES

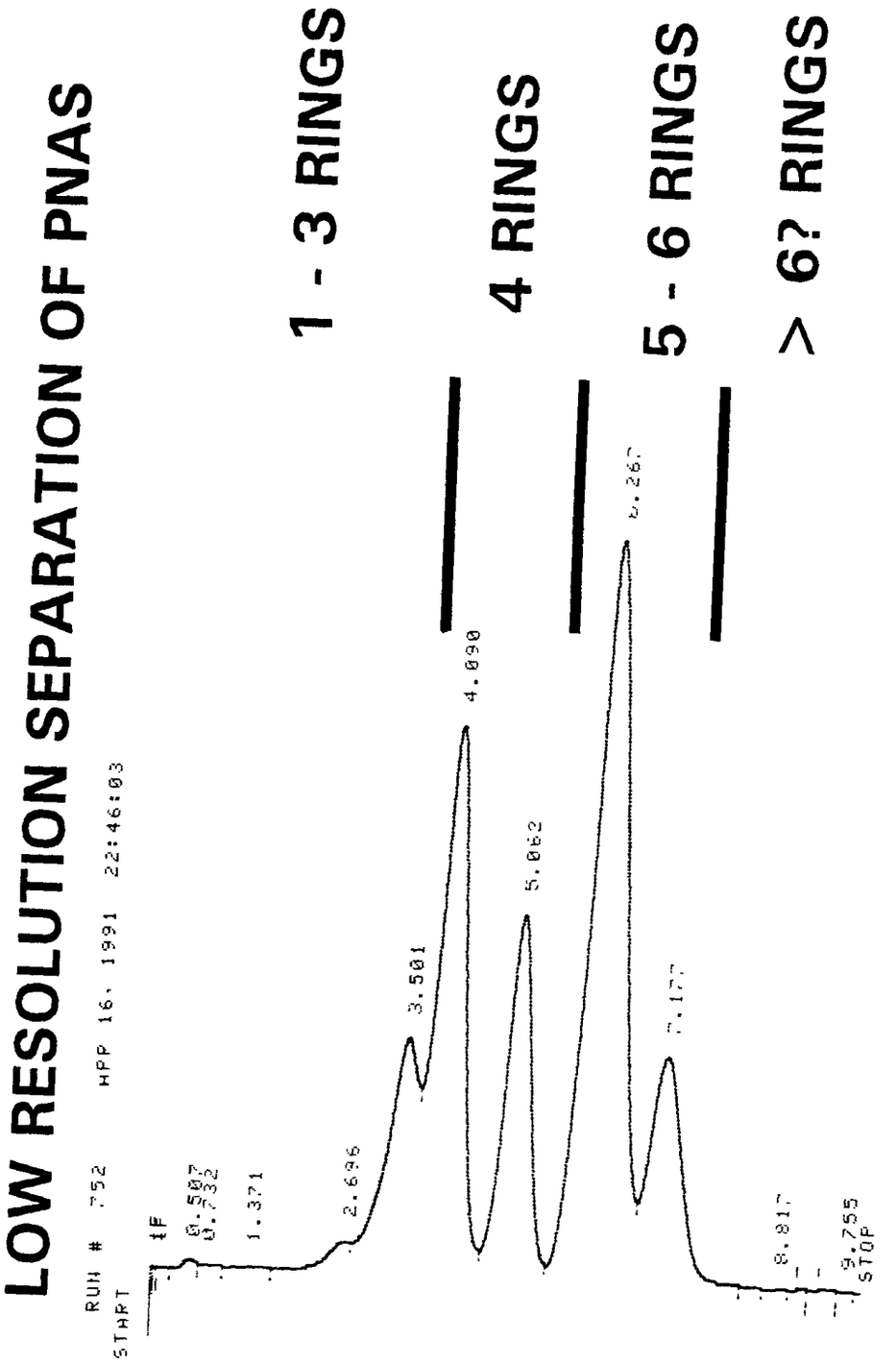
% DILUTED/NON-DIL. VALUE

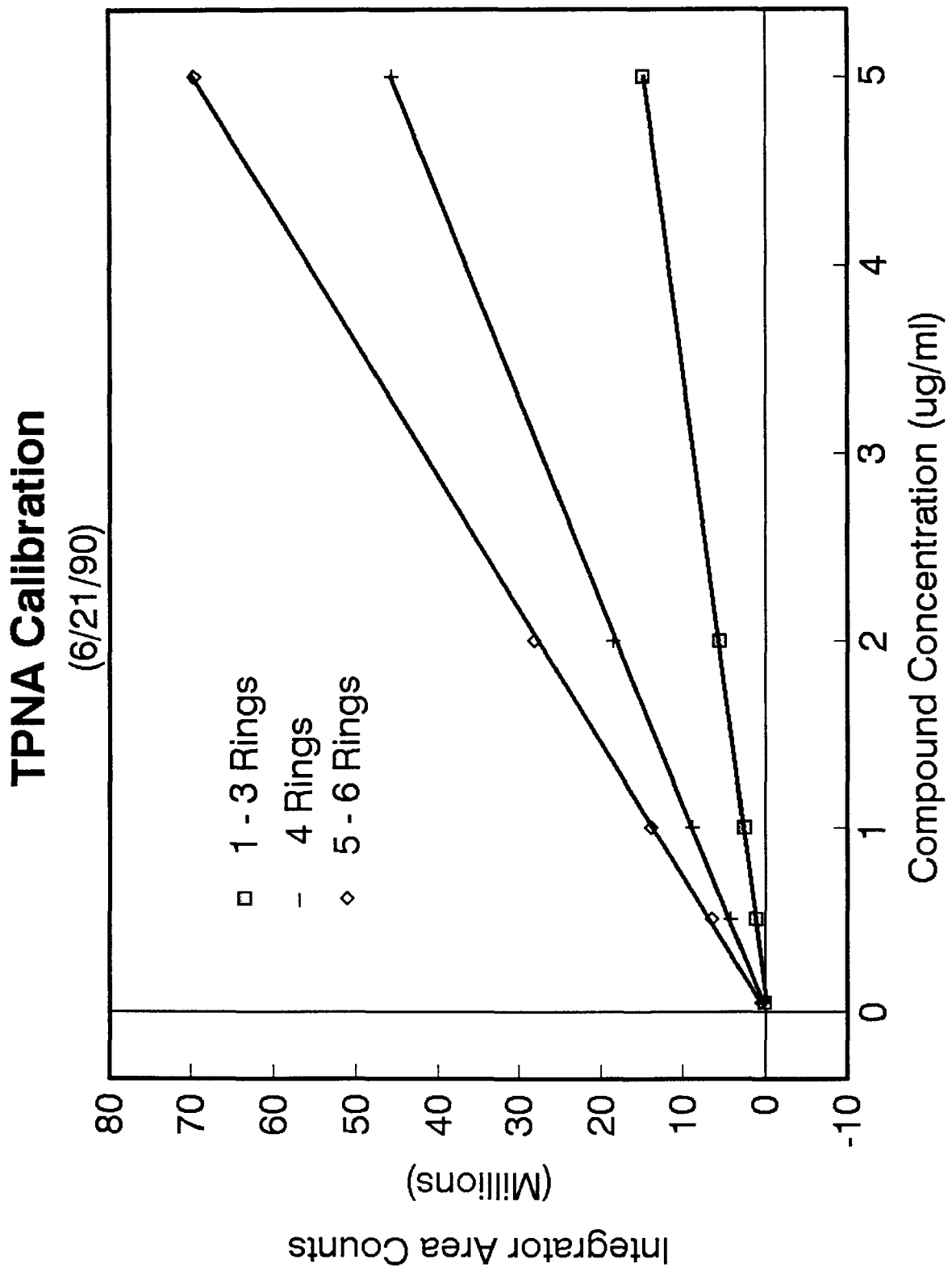
DATA DESCRIPTION	GRP I	GRP II
OVERALL AVERAGE	258 n = 16	204 n = 16
AVG. WITHIN CALIB. RANGE	273 n = 9	NA

NA - Not applicable, no data within calib. range

NEW TOTAL PNA (TPNA) METHOD

- ACETONITRILE EXTRACTION OF SOILS
- HPLC - LOW RESOL. C-18 RP
- FLUORESCENCE DETECTION
- CALIB. ON GROUPS OF THE 16 PP PNAS


LOW RESOLUTION SEPARATION OF PNAS
RUN # 752 HPP 16, 1991 22:46:03
START
tF
0.507
0.732
1.371
2.696
3.501
4.090
5.062
6.267
7.177
8.817
9.755
STOP
1 - 3 RINGS
4 RINGS
5 - 6 RINGS
> 6? RINGS


TPNA Calibration
(6/21/90)
1 - 3 Rings
4 Rings
5 - 6 Rings
Integrator Area Counts
(Millions)
80
70
60
50
40
30
20
10
0
-10
0
1
2
3
4
5
Compound Concentration (ug/ml)

SLIDE OF HEWLETT PACKARD 1050 HPLC SYSTEM

SAMPLE PREPARATION FOR SOILS

- 2.0 G. NON-DRIED SOIL/SEDIMENT
- IF MS, ADD 10 UG OF STD. MIX
- 2.0 G. ANHYD. SODIUM SULFATE
- 10.0 ML ACETONITRILE
- VORTEX 1 MINUTE
- SETTLE AND FILTER WITH 0.2 U ACRODISC

TPNA ACCURACY - % RECOVERY OF SOIL MATRIX SPIKES
(DQO = 40 - 160%)

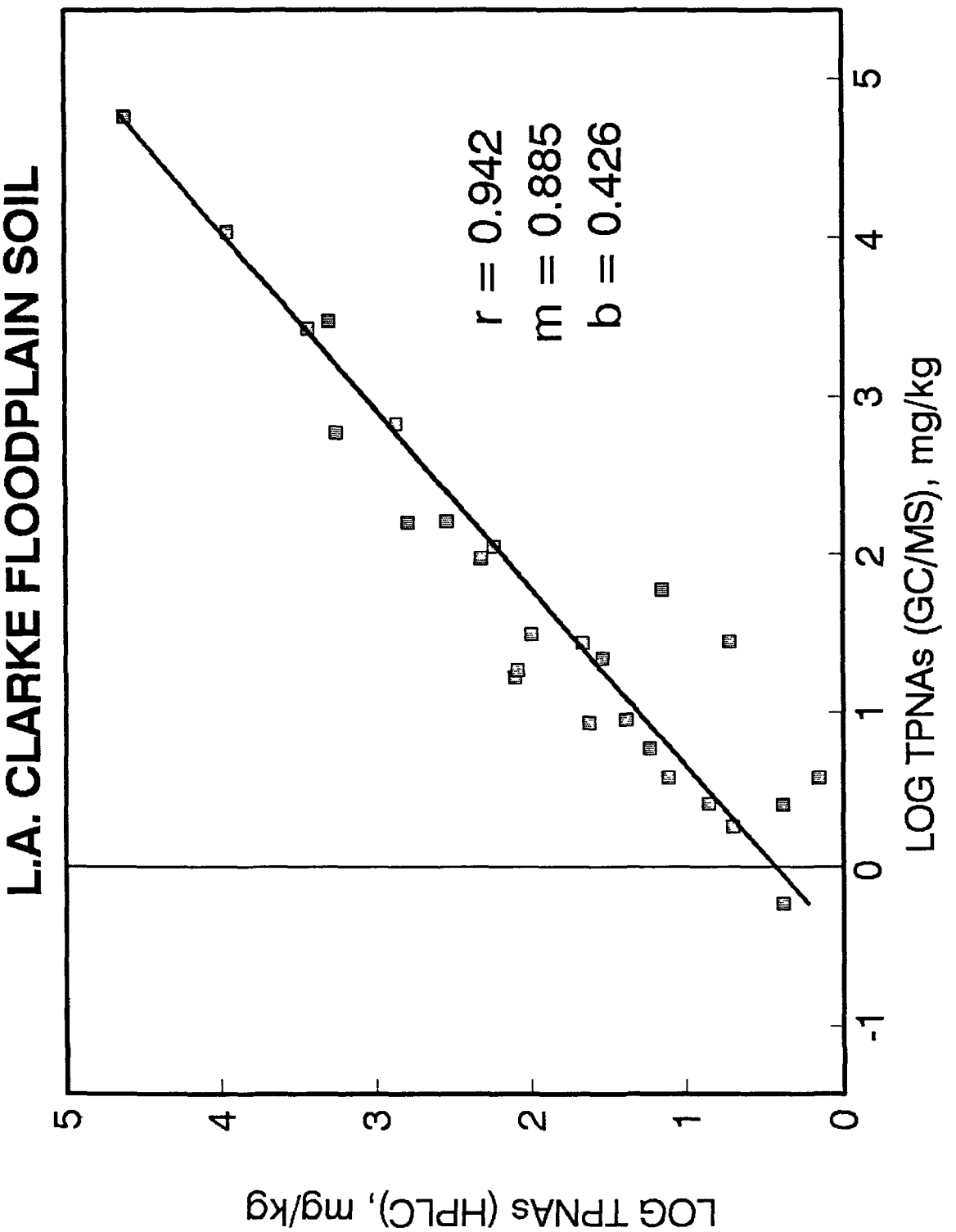
	1-3 RINGS	4 RINGS	5-6 RINGS
AVG. RECOVERY	126	142	130
1 STD. DEV.	43	75	37
N	25	24	24

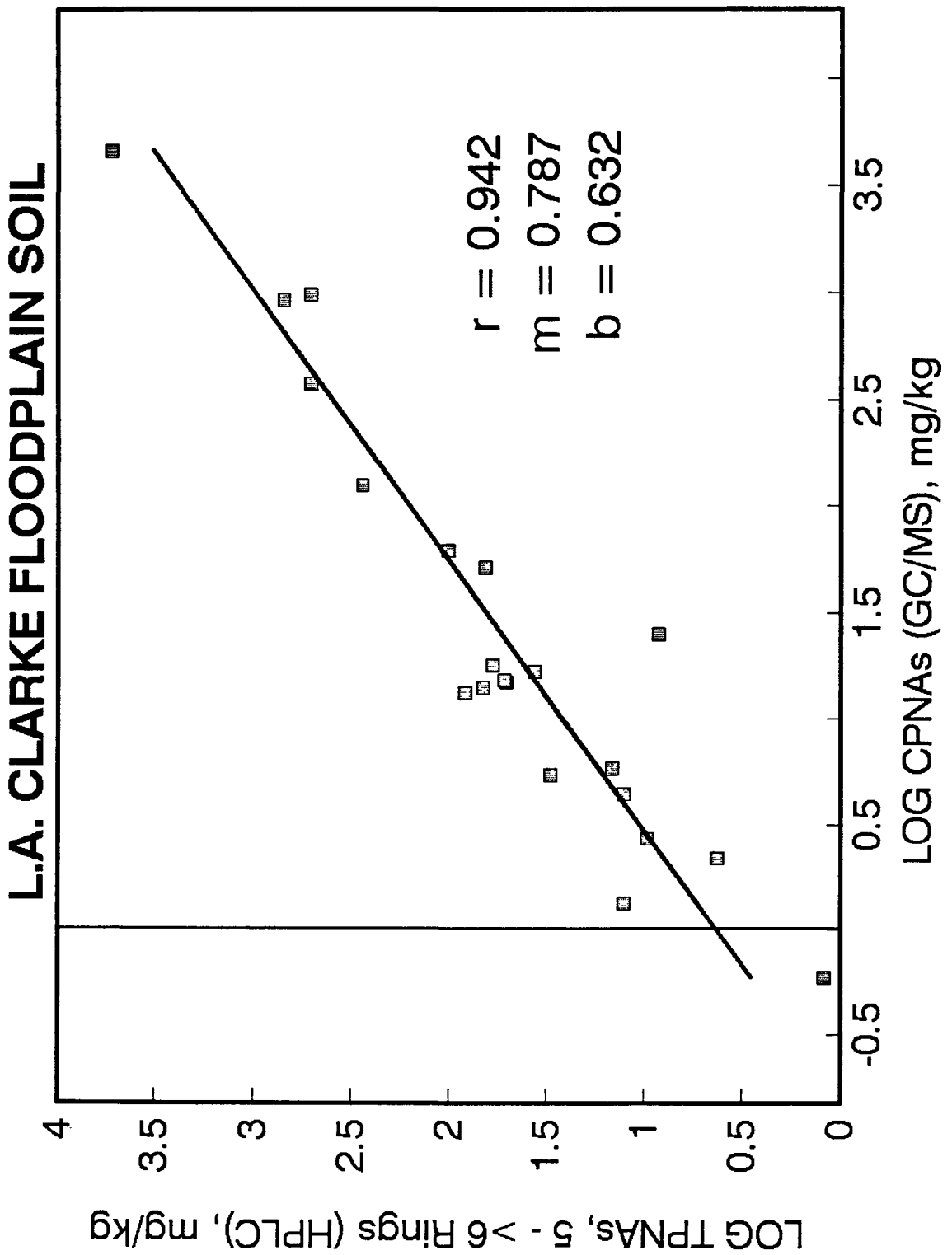
QC PERFORMED 6/22/90 - 8/06/90

TPNA PRECISION - RPD OF SOIL DUPLICATES
(DQO = <67%)

	1-3 RINGS	4 RINGS	5-6 RINGS
AVG. RPD	42	45	44
1 STD. DEV.	43	39	38
N	23	19	16

QC PERFORMED 6/22/90 - 8/06/90


L.A. CLARKE FLOODPLAIN SOIL
r = 0.942
m = 0.885
b = 0.426
LOG TPNAs (GC/MS), mg/kg
LOG TPNAs (HPLC), mg/kg
-1
0
1
2
3
4
5
0
1
2
3
4
5


L.A. CLARKE FLOODPLAIN SOIL
r = 0.942
m = 0.787
b = 0.632
LOG TPNAs, 5 - >6 Rings (HPLC), mg/kg
LOG CPNAs (GC/MS), mg/kg
0
0.5
1
1.5
2
2.5
3
3.5
4
-0.5
0.5
1.5
2.5
3.5

INFORMATION/ECONOMY RATIO OF THE TPNA METHOD FOR SITE INVESTIGATIONS

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360 TPNA @ $ 50 = $18,000
36 GC/MS @ $500 = $18,000
$36,000

$36,000 YIELDS 72 GC/MS ANALYSES ALONE

360 TPNA/72 GC/MS = 5 TIMES THE SITE INFORMATION

IF THE TPNA RESULTS ARE ADEQUATE FOR SPECIFIC DATA USAGE

TPNA WORK IN PROGRESS

- DIFFERENT SOILS
- SURFACE AND GROUNDWATERS
- MONITORING BIOREMEDIAL ACTIVITIES
- PETROLEUM RESIDUES FROM USTs

MR. TELLIARD: Continuing on with the petroleum part of the program, our next speaker is Greg Douglas. Greg is presently Senior Research Scientist with Battelle Ocean Sciences in Duxbury, Massachusetts, and his work is again talking about fingerprinting petroleum hydrocarbons in water.

MR. DOUGLAS: The currently approved analytical protocols that are traditionally recommended for oil-spill response and remediation programs are often without the necessary sensitivity or selectivity to address program objectives and regulatory limits. As a result, we've developed our own techniques for the quantitation and identification of hydrocarbons in marine and terrestrial systems to better understand the fate and transport of these materials in the environment.

These methods either are in the marine chemistry literature or are modifications of standard Environmental Protection Agency (EPA) methods. In many cases, we are able to enhance the quality, improve the sensitivity by almost three orders of magnitude for many of the analytes, and provide detailed information to help us to understand the fate and transport of petroleum products in the environment.

The methods have been developed to support natural resource damage assessment programs, so they have a very high level of quality assurance and quality control.

The analytical objectives after an oil and gasoline spill are to provide chemical information to evaluate the presence or absence of the petroleum in the sample. We would like the analysis to yield a reasonably quantitative measure of total petroleum hydrocarbons, assist in product identification, and provide the analytical information to evaluate the degree of weathering. Such information helps us to understand the potential toxicity and transport of the spilled product in the environment.

The method that one selects may vary according to the requirements and the particular situation. How quantitative does it have to be? Can one rely on a semiquantitative procedure? What kind of sensitivity is necessary? What matrix will one be working with? Does one need to know the identity of the product, or is that not important in this particular situation? Are there any special-interest compounds that one wishes to track? Does

one require any relative weathering information? Cost is always a factor when considering methodologies, and so the required turnaround time. The more sophisticated the analytical procedures, the longer the time needed for completion. Also, is the work to be used in litigation? That consideration could affect the methods used and the type of deliverables that one must produce.

A few of the petroleum hydrocarbon methods currently in use include Method 418.1, modified for soils and for waters; ultraviolet fluorescence analysis in marine systems and ground waters; EPA Method 8270, a gas chromatography with mass spectrometry (GC/MS) analysis used for a variety of compounds, including the polynuclear aromatic hydrocarbons; a modified EPA GC/MS methodology that we use in our own program; and a gas chromatography with flame ionization detection (GC/FID) analysis, which is a modification of EPA Method 8100.

I shall begin by discussing the applications and limitations of one of the most common methods in use today: EPA Method 418.1. The sensitivity of this method in water is approximately 1 mg/L (1 ppm). In soils one can achieve a detection limit of 1 to 10 mg/kg dry weight. The sensitivity of this method is rather limited because the solubility of many of the compounds in petroleum is significantly less than 1 ppm. The procedure is not very quantitative. At best, it's semiquantitative, and should be viewed as a screening tool. EPA Method 418.1 doesn't really provide product identification unless one modifies the method and uses a full-scan Infrared (IR) Spectrometer and reviews the data. This method does offer a rapid turnaround time, and it should be used primarily when data are needed to make rapid field decisions. Method 418.1 involves a freon extraction of the water or sediment and analysis on an IR system at a very specific wavenumber, 2930 cm-1. The calibration standard is composed of an n-hexadecane, chlorobenzene, iso-octane mixture to replicate the molar absorptivity of a standard petroleum product (fuel oil). Figure

1 shows that the 2930-cm-1 wavenumber region encompasses chiefly the CH_2 stretch.

Unfortunately, this method is not very quantitative when comparing different hydrocarbon products. For example, we find that the analysis of a gasoline standard, yields only 49% recovery because of the dominance of the CH_2. Some of the wide-band IR systems provide a little better quantitation in that respect inasmuch as they overlap both wavelengths in many cases.

For fuel oil #6, there is a relative dominance of the CH_2 stretch that results in about 115% recovery. For the creosote oil, which is composed primarily of aromatic components whose peaks are seen in Figure 1, there is a shift away from the CH_2 to the aromatic C-H stretch; only 16% is recovered in a creosote standard.

The problem is that the molar absorptivity of the defined calibration standard differs from that of many petroleum products in the environment. This results in a wide variation in response, depending on the product type.

The apparent percent recovery using IR, for a variety of products is charted in Figure 2. The results range from 145% to about 16% recovery, depending on the product.

In addition to these calibration problems, products undergo physical and chemical weathering, which also changes the relative amount of CH_2 stretch. Figure 3 shows a GC/FID chromatogram of a groundwater sample containing fuel oil #2. We see the unresolved complex mixture and the resolved aliphatic components. We also have the isoprenoids pristane and phytane, which often are used as weathering indicators. When this material is released into the soil, the more soluble aromatic components of petroleum will be washed out and dissolve into percolating rainfall. The peaks in the lower chromatogram of Figure 4 are mostly aromatic compounds. As a result of the different solubilities of the individual components of diesel, a groundwater sample may be contaminated primarily with aromatic

hydrocarbons, including naphthalenes and fluorenes and a variety of other soluble aromatic components. If one were to analyze water samples of the water-soluble fraction of petroleum, using the IR method, one may get not-detected (ND) responses because the method is insensitive to those aromatic components. We have seen situations where one could smell the contamination, but the IR method yielded only an ND. There is a slight absorbance of aromatics because of the alkyl side chain associated with those compounds, but the relative absorbance is low when compared to the total mass.

Biodegradation and weathering of products create further difficulties with the interpretation of results when using Method 418.1. Figure 5 shows chromatograms of a crude oil and of a sample of the same oil after degradation. A series of aliphatic hydrocarbons is evident on the upper chromatogram of the crude oil. They comprise a much higher percentage of the sample than they do in the lower chromatogram of the environmental sample. If one were to compare the results by IR for the same mass of material, there would be much less mass detected for the lower sample because the specific IR absorbing species had been degraded to a large degree.

In addition, natural hydrocarbon interferences will not be removed by the silica cleanup step because plants produce $n\text{-}C_{25}$, $n\text{-}C_{27}$, $n\text{-}C_{29}$, and $n\text{-}C_{31}$ plant waxes. There have been many situations near peat bog areas, swamps, and sewage systems where one obtains high numbers for IR measurements because of background interferences.

In summary, there are a number of problems associated with quantifying petroleum hydrobarbons with the EPA Method 418.1. Analytical results obtained by using it should be interpreted with an understanding of the applications and the limitations of the technique.

Figure 6 illustrates a protocol that we follow. Most of the methods either are modifications of EPA protocols to

improve selectivity and sensitivity or they are reported in the marine environmental literature.

In this example, we have a sediment sample (but it could be extracted water, as well, following the EPA Method 3510). The sample is spiked with appropriate surrogate compounds (Table 1) and extracted following EPA protocols for sediments (and for waters, using a separatory funnel, liquid-liquid extraction). We then filter the extract, and concentrate it using Kuderna-Danish (KD) apparatus or rotary evaporation techniques. An aliquot of the extract is then weighed to obtain a total extractable weight, prior to column cleanup. We then process the extract through an alumina column cleanup, slightly modifying standard EPA Method 3610 by combining the F1 saturated hydrocarbon and F2 aromatic hydrocarbon fractions to obtain a total recoverable hydrocarbon fraction. Next, we again concentrate the extract to a small volume. We then weigh an aliquot of the extract to get pre- and post-column total oil values. We calculate the percent polars, {(precolumn oil-postcolumn oil)/precolumn oil}, which can be very useful in evaluating the degree of biodegradation. Then, we add our internal standards and analyze the sample extract by GC/FID (modified EPA Method 8100). The method is calibrated very specifically, using a suite of n-C_8 to n-C_{36} alkanes with alkane response factors relative to the internal standard androstane.

Total recoverable petroleum hydrocarbon is calculated from the total GC/FID baseline corrected area and the average response factor (RF) of the n-C_8 to n-C_{36}. With care, one can obtain RFs across that whole range that vary by no more than 10%, even at the heavy end (i.e., greater than about n-C_{27}), where one can run into some mass discrimination problems. All in all, the detector responses are uniform, and one can, in fact, quantify the GC/FID-detectable components with reasonable accuracy.

If the sample was extremely weathered, we then examine the aromatic compounds by using GC/MS. We also look at another

class of compounds that many may not be aware of: the triterpanes, steranes, and diterpanes. These compounds are very specific to various sources of petroleum. They are resistant to degradation, and they have specific fingerprints. As we examine the more weathered oils, those fingerprints can help us to identify the kinds of products that are present. Because steranes, triterpanes, and diterpanes are resistant to degradation, one can use them as internal normalizers to calculate the amount of oil lost after a spill.

The analytes determined via GC/FID and GC/MS analyses are shown in Table 1. For analyzing petroleum products, this list is more selective than is Method 8270. Rather than just look at, for example, the 16 priority pollutant PAHs, of which only a few are present in petroleum, we have expanded the analyte list for PAHs to include the alkylated PAHs and dibenzothiophenes because the ratios of the sulphur compounds to the nonsulphur aromatics are also characteristic of specific sources. We still analyze for priority pollutant PAHs, including the pyrogenic PAHs, benzapyrene, fluoranthene, and pyrene. These PAHs help to separate pyrogenic sources from petroleum sources of PAHs. In marine systems, we often find evidence of a number of pyrogenic sources, including atmospheric deposition of combustion products into the bays and harbors.

We also study the full suite of alkanes from n-C_7 up to n-C_{36}. We also examine the isoprenoid hydrocarbons, pristane and phytane. The ratio of n-C_{17} to pristane or n-C_{18} to phytane may be used as an indicator of weathering because the organisms in marine systems soils and ground waters tend to preferentially degrade the straight-chained alkanes relative to the isoprenoids.

The detection limits for total petroleum hydrocarbons insediment is around 1 to 10 mg/kg (parts per million). Alkane detection limits are typically 0.1 mg/kg, and the PAH detection limits are 1 to 10 mg/kg.

In water samples, we can detect PAHs down to about 1 to

10 parts per trillion. Such low detection limits are useful for plume tracking because one obtains much information in advance of the arrival of the heavily contaminated portion of a plume. Also, one gets data on a lot more analytes, which allows one to start fingerprinting more effectively by having a full suite of compounds.

In addition to these components, we use the triterpanes and the steranes as conservative oil indicators, mainly in the heavier oils, fuel #4, fuel #6, lubricating oils, and crude oils. There is also a suite of diterpanes in diesel fuels. I'm also looking into jet fuels to see if we can find those components there as well. Again, these are components that originally were biologically derived, are very resistant to degradation, and have very specific fingerprints.

Table 2 lists products that we have analyzed and included in our computer library. We have analyzed the products by using, GC/FID or GC/MS and measured their biomarker components. We are using principal-component analysis and ratio analysis to try to cluster various classes of components so that even under weathered conditions we can still identify the product.

Figure 7 shows two GC/FID chromatograms of gasoline and its water-soluble fraction. Again, the quantification is based on the total area response relative to an internal standard. We also quantify each individual alkane.

Figures 8 and 9 also show chromatograms of products and their water-soluble fractions. Our standards include not only the pure products but also degraded products and water-soluble fractions, especially for groundwater studies. To get good correlation between sample results and possible contamination sources, one looks at the components in the water-soluble fraction of the potential sources.

We take the data that we generate and enter them into an electronic spreadsheet and plot the distributions of the individual n-alkanes, pristane, and phytanes. Figures 10 through

15 illustrate the results obtained for selected petroleum products.

One problem to be aware of when working with GC/FID analysis of petroleum hydrocarbons is one of mass discrimination. One can actually lose a large fraction of the heavier components of a sample if the capillary column is not appropriately positioned and the injection liner is not of the proper diameter. Mass discrimination should be monitored routinely.

Figure 16 shows two superimposed chromatograms of the same oil run twice: one where there is a problem with mass discrimination and one where there isn't. As much as 50% of the product could be lost in some cases of mass discrimination. To monitor mass discrimination, we examine the n-C_{36} response factor relative to the n-C_{21} response factor. They should be within a few percent of each other. In many cases, we have seen the ratio of n-C_{36} to n-C_{20} response factors near 0.1 or 0.2, indicating that there is a severe problem that could result in false negatives.

Figure 17 depicts an example of an alkane standard that we run. It shows the response of each individual alkane standard of the same concentration from n-C_8 to n-C_{36}. The two largest peaks in the chromatogram are quantitation internal standards (QIS) and surrogate internal standard (SIS) compounds. The response should be linear across the full alkane range as it is here. The peaks should not drop off after n-C_{25}, which unfortunately is common in much of the GC/FID work that we have reviewed.

One would use this procedure to look at an actual sample. One would examine the distribution of the unresolved complex mixture, where it begins and where it ends. And one also would examine the distribution of these resolved compounds because pristane and phytane (Figure 3) are still there even after fairly significant degradation.

As shown in the lower chromatogram of Figure 5, the straight-chained alkanes have been almost completely degraded in

this sample.

Comparing the lower chromatogram to the upper one is not fruitful because of the extent of degradation that has taken place. As weathering proceeds, the qualitative accuracy of the measurement decreases. In this case, one would go to the next level, using aromatic distributions and biomarkers.

The kind of problems that can occur when using the standard EPA protocols are illustrated in Figure 18, which shows the GC/FID output for diesel and JP5 and their water-soluble fractions. Assume, for example, that there has been an oil spill, and that one is interested in the potential toxicity of the contaminated water to marine life. You would collect the water sample, send it to the analytical laboratory and request a Method 8270 analysis. What you might get back is depicted in Figure 19. You might get a plot of the PAHs to include in some cases, the naphthalene, perhaps C_1 naphthalene and perhaps phenanthrene. The detection limit for this method is about 10 parts per billion, and does not measure the alkylated PAHs. If one uses the modified GC/MS approach for the same sample (Figure 20), one obtains a full distribution of parent and alkylated PAHs that can be used to interpret the data and determine the source of the oil spill and the transport, fate, and potential effects of it.

Using the modified GC/MS procedure (Figure 6), one can analyze a whole spectrum of products (Figures 21 through 26), including creosote, which has a very distinct distribution where the major peaks are the parent PAHs. The PAH concentration within a homologous series in creosote decreases rapidly as alkylation increases.

The used of petroleum-specific GC/FID and GC/MS methods can improve our understanding of the proceses that influence oil degradation in the environment. Biodegradation rates of hydrocarbons are dependent on the type of bacteria, presence of limiting nutrients, temperature, and types of hydrocarbons.

Bacteria generally degrade hydrocarbons according to the following sequence: n-alkanes>branched alkanes>aromatic hydrocarbons>cyclic alkanes. If a conservative compound in the spilled oil can be identified, then, as degradation of the oil proceeds, the concentration of that compound will increase. This increase can be compared to the source oil and the percent depletion of the oil can be estimated according to the following equation: % Total Oil Depletion = $(1-C_0/C_1)x100$, where C_1 is the conservative compound concentration in the degraded oil and C_0 is the conservative compound concentration in the source oil.

Individual analyte depletion can be estimated by the equation: % Analyte Depletion = $\{1 - (A_1/A_0) \times (C_0/C_1)\} \times 100$, where A_1 is the analyte concentration in the degraded oil and A_0 is the analyte concentration in the source oil.

If the source oil cannot be identified at the site, C_0 can be substituted with the conservative compound concentration in the oil prior to application of the remediation agents (water, bacteria, nutrients, oxygen).

There are technical advantages to using the above approach rather than traditional methods to estimate site remediation. Because of spatial variability, the traditional attempts to evaluate the effectiveness of oil spill remediation often require large numbers of samples to determine the mass loss with reasonable precision. The use of an internal chemical indicator reduces spatial variability, thereby reducing the number of samples required to monitor effectiveness of the remediation option. By adjusting the operational remediation parameters, it may be possible to tune the selected remediation approach to maximize the degradation of the more toxic components.

Butler et al. (1991) presented a paper at the In Situ and on-site Bioreclamation symposium in San Diego using the above relationship. In their paper, they assumed 17(H),21B(H)-C_{30}Hopane(hopane) was the most conservative analyte measured in

their degraded crude oil samples. Figure 27 from Butler et al. (1991) shows the GC/FID chromatograms from that study of oiled beach sediment exhibiting increasing degrees of degradation. Butler et al. (1991) then examined traditional measures of degradation for four weathered samples (Figure 28a). Their results demonstrated that, in the four degraded samples, the traditional weathering indicators were not very useful. They then examined the percent total oil depletion, n-C_{18}, and phytane depletion relative to hopane. The results presented in Figure 28 indicate that as weathering proceeded percent total oil depletion increased to 45%-50% relative to the 30% depleted NSC reference oil. The n-C_{18} and phytane demonstrated substantial percent depletion as the oil degradation increased. These data suggest that the use of the n-C_{18}/phytane ratio ceases to be a good weathering indicator in moderately to heavily degraded oil samples.

In conclusion, the GC/FID and GC/MS methods presented today provide the analyte selectivity and sensitivity required to evaluate the fate and transport of spilled petroleum products in environmental samples. The results from these analyses can be compared to other large environmental databases such as from NOAA Mussel Watch program or to established and proposed sediment and water quality criteria to evaluate potential environmental effects and relative levels of contamination. Finally, the use of conservative chemical indicators, such as hopane to estimate oil degradation may improve our ability to evaluate the effectiveness of remediation options after an oil spill.

I would like to thank Dr. Rojer Prince of Exxon Research and Engineering (Clinton, NJ) for his review of this work. This work was supported by the Battelle Research and Development Program.

QUESTION AND ANSWER SESSION

MR. CASTLE: Do you utilize the pristane/phytane ratios, and, if you do, have you found that, as the weathering increases, the pristane/phytane ratios remain stable or do they alter?

MR. DOUGLAS:They alter somewhat in heavily degraded samples. I can't say that they degrade at equal rates, but they do vary enough where it's hard to use them after they degrade beyond Sample D (in Figure 30), say, which would be difficult to use.

MR. CASTLE: That's what we found also. Thank you.

In your simultaneous ion monitoring work, typically how many ions would you follow?

MR. DOUGLAS:We're looking at between 6 and 15 ions.

MR. WESTON: Would you attempt to optimize your SIMS sensitivity, for example, by lowering the mass spectral resolution? Would you attempt to optimize sensitivity specific to the SIMS method?

MR. DOUGLAS: We tried to reduce the number of ions that we had to look at, which would improve sensitivity. We calibrated it in favor of, say, the midrange ions. Our sensitivity was good enough to detect about 100 ng of analyte per milliliter of extract.

MR. WESTON: Right. Thank you.

MR. STANKO: In one of your slides, you showed that your detection limit with the modified Method 8270 was somewhere in the range of 1 to 10 parts per trillion.

MR. DOUGLAS:Right.

MR. STANKO: I'd like to ask you, what did you do to Method 8270, which is essentially a part per billion, at best, to get it down to the parts per trillion level?

MR. DOUGLAS: Basically, we were able to increase sensitivity by using single ion monitoring

(SIM), concentrating the final extract to 250 ml and increasing sample size to 2 L.

MR. STANKO: Thank you.

MR. TELLIARD: Thanks a lot, Greg.

I'd like to thank this morning's speakers for their efforts.

It's break time. Please get your goodies and get back in here in about 15 minutes. Thank you for your attention.

TABLE 1. PETROLEUM FINGERPRINTING ANALYTE LIST

Polycyclic Aromatic Hydrocarbons	Aliphatic Hydrocarbons Normal Alkanes	TARGET REPORTING LIMITS Waters	Sediments
naphthalene	n-C_7	Total PHC = 50.0 µg/L	Total PHC=10 mg/kg
C1-naphthalenes	n-C_8	Alkanes = 0.2 µg/L	Alkanes= 0.1 mg/kg
C2-naphthalenes	n-C_9	PAHs = 0.01 µg/L	PAH's= 0.0005 mg/kg
C3-naphthalenes	n-C_{10}		
C4-naphthalenes	n-C_{11}	Oils	
acenaphthylene	n-C_{12}		
acenaphthene	n-C_{13}	PHC=80,000 mg/kg	
fluorene	n-C_{14}	Alkanes=320 mg/kg	
C1-fluorenes	n-C_{15}	PAHs=16 mg/kg	
C2-fluorenes	n-C_{16}		
C3-fluorenes	n-C_{17}		
phenanthrene	n-C_{18}		
anthracene	n-C_{19}		
C1-phenanthrenes	n-C_{20}		
/anthracene	n-C_{21}	Surrogate Compounds	
C2-phenanthrenes	n-C_{22}		
/anthracenes	n-C_{23}	PHC = Ortho terphenyl	
C3-phenanthrenes	n-C_{24}	PAH = d_8 naphthalene	
/anthracenes	n-C_{25}	d_{10} fluorene	
C4-phenanthrenes	n-C_{26}	d_{12} chrysene	
/anthracenes	n-C_{27}		
dibenzothiophene	n-C_{28}		
C1-dibenzothiophenes	n-C_{29}		
C2-dibenzothiophenes	n-C_{30}	Internal Standard Compounds	
C3-dibenzothiophenes	n-C_{31}		
fluoranthene	n-C_{32}	PHC = 5α Androstane	
pyrene	n-C_{33}	PAH = d_{10} acenaphthene	
C1-fluoranthenes	n-C_{34}	d_{10} phenanthrene	
/pyrenes	n-C_{35}	d_{12} benzo[*a*]pyrene	
benzo[*a*]anthracene	n-C_{36}		
chrysene			
C1-chrysene			
C2-chrysene			
C3-chrysene			
C4-chrysene			
benzo[*b*]fluoranthene	Isoprenoid Hydrocarbons		
benzo[*k*]fluoranthene			
benzo[*a*]pyrene	1380 pristane		
dibenzo[*a,h*]anthracene	1470 phytane		
benzo[*g,h,i*]perylene	1650		
indeno[1,2,3-*cd*]pyrene			

The highlighted PAH compounds represent the 16 priority pollutants list.

TABLE 2. PETROLEUM FINGERPRINT PRODUCT LIST

#	PRODUCT
1.	Gasoline
2.	White Gasoline
3.	Paint Thinner
4.	Turpentine
5.	Jet A
6.	JP4
7.	Kerosene
8.	Diesel #1
9.	Diesel #2
10.	Fuel Oil #2
11.	Fuel Oil #4
12.	Fuel Oil #6
13.	Lubricating Oils
14.	Syltherm
15.	Transformer Oils
16.	Creosote Oil
17.	Coal Tar
18.	Prudhoe Bay Crude Oil
19.	NBS 1580 Shale Oil
20.	NBS 1582 Crude Oil
21.	EPA Bunker Oil
22.	Gunk Super Oil
23.	NBS Coal
24.	NBS Fly Ash
25.	Combustion Soot
26.	Aviation Gasoline
27.	Mineral Oil
28.	NBS Residual Fuel Oil

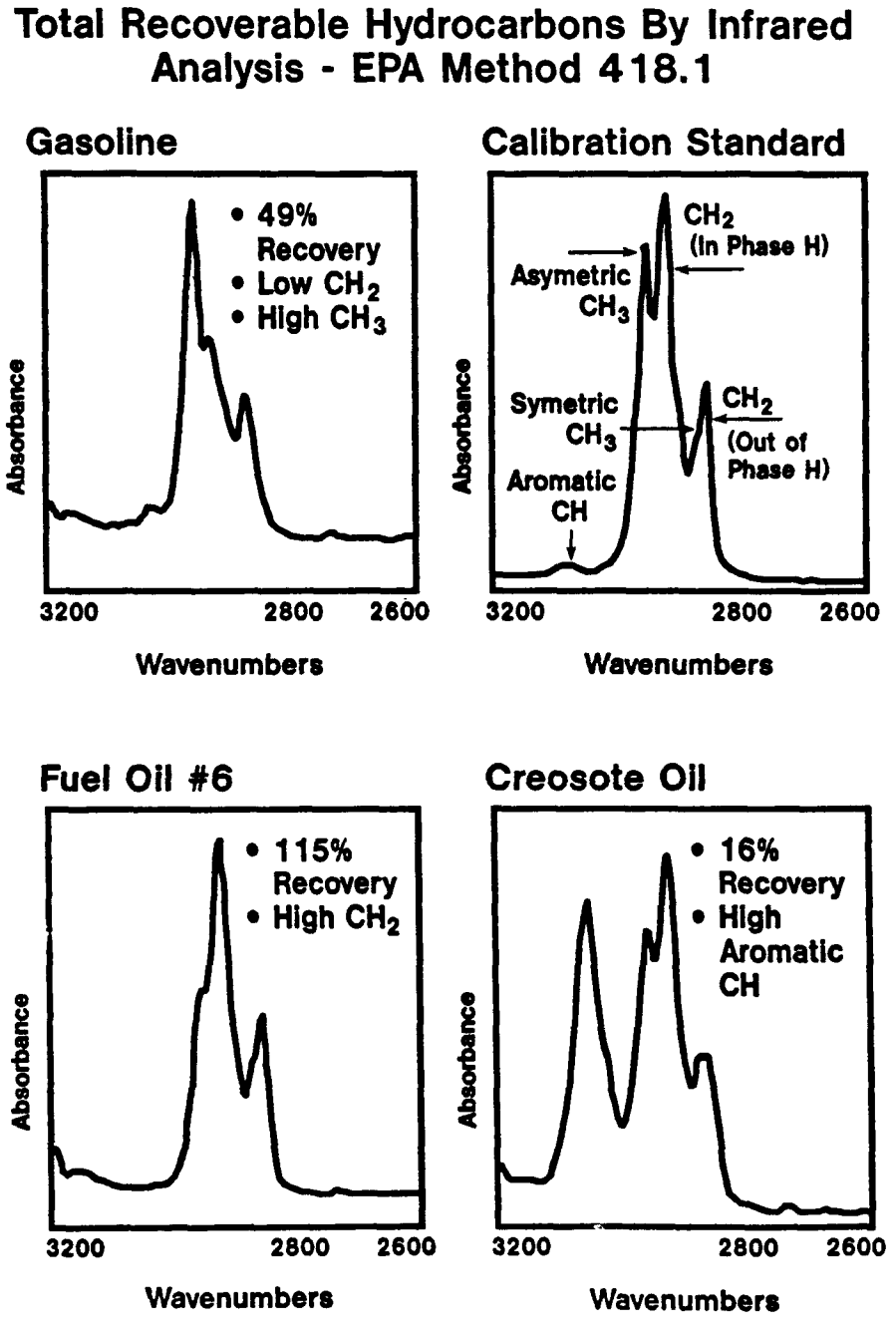


Figure 1. Infrared absorbance patterns of a calibration oil, gasoline, fuel oil #6, and creosote vs wavenumber (2600 to 3200 cm^{-1}). These samples were prepared in freon and analyzed according to EPA Method 418.1 by using a quantification absorbance of 2930 cm^{-1}.

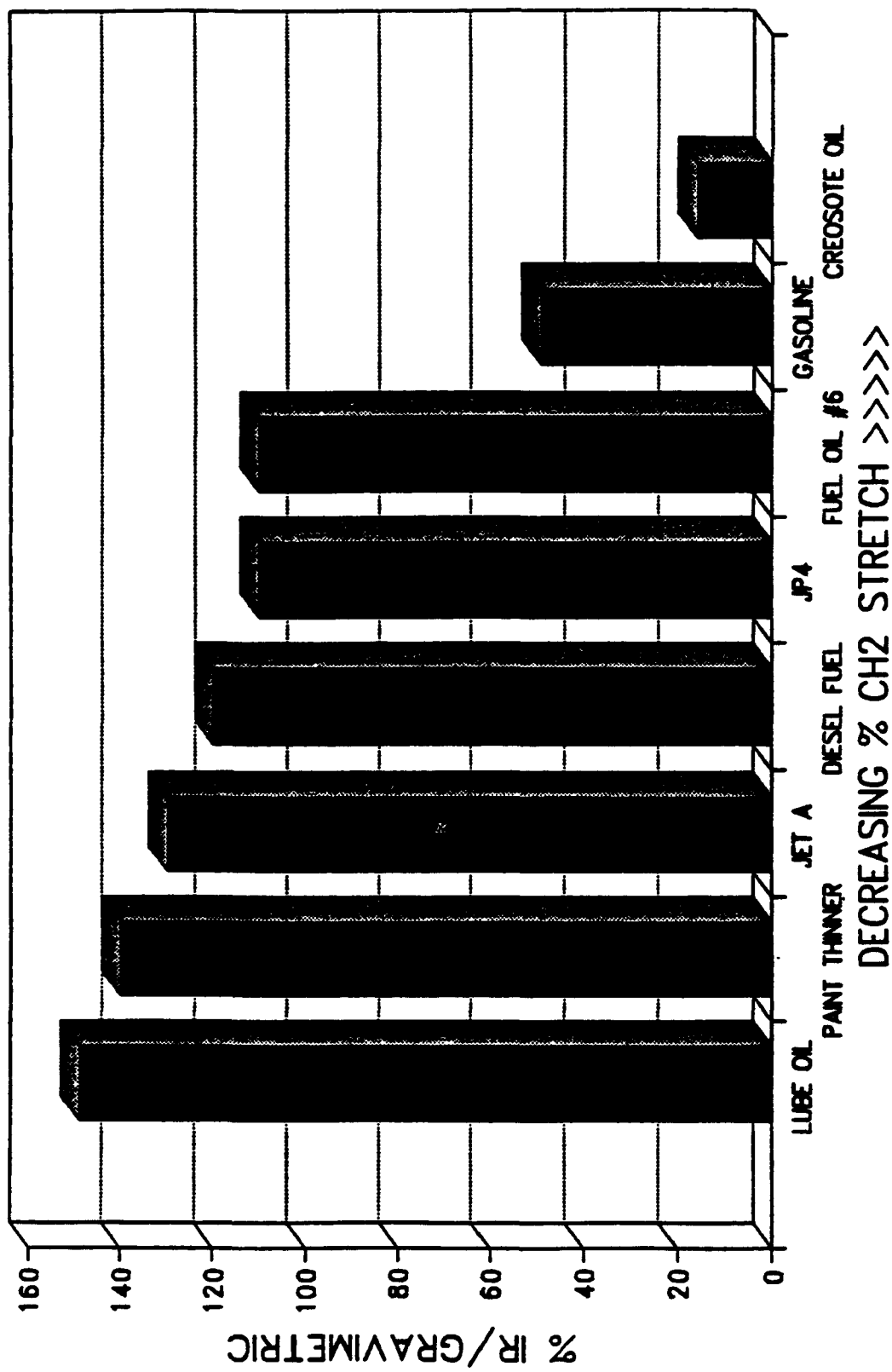


Figure 2. Comparison of the percent recovery of eight hydrocarbon products analyzed according to EPA Method 418.1. A positive bias (>100% recovery) is observed in products that contain a higher percentage of saturated compounds than are present in the calibration oil. The negative bias (<100% recovery) is observed in products containing a higher percentage of aromatic hydrocarbons than are present in the calibration oil.

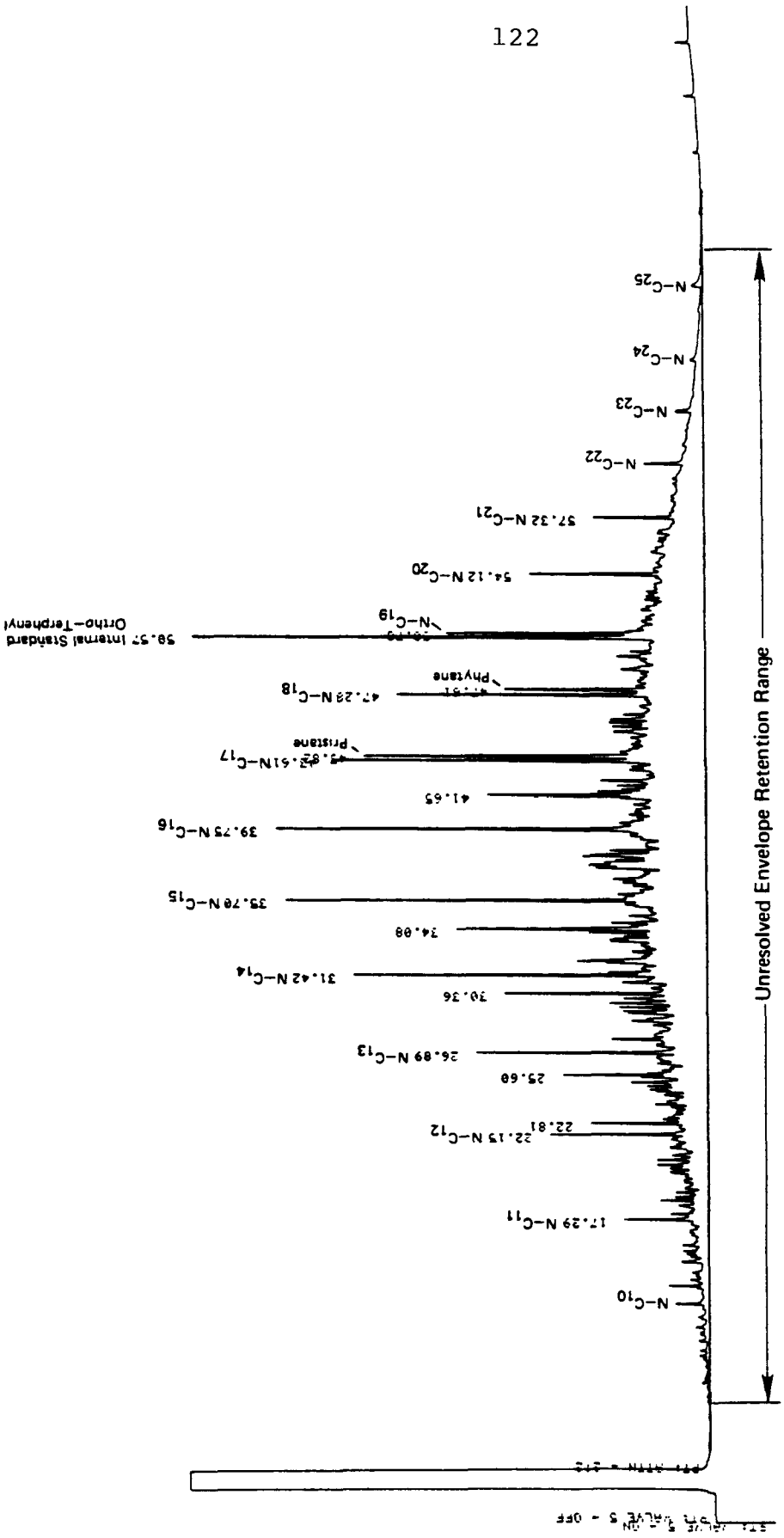


Figure 3. GC/FID chromatogram of a groundwater sample contaminated with fuel oil #2.

Gas Chromatographic Analysis of JP5 and Diesel Oil, Water Soluble Components

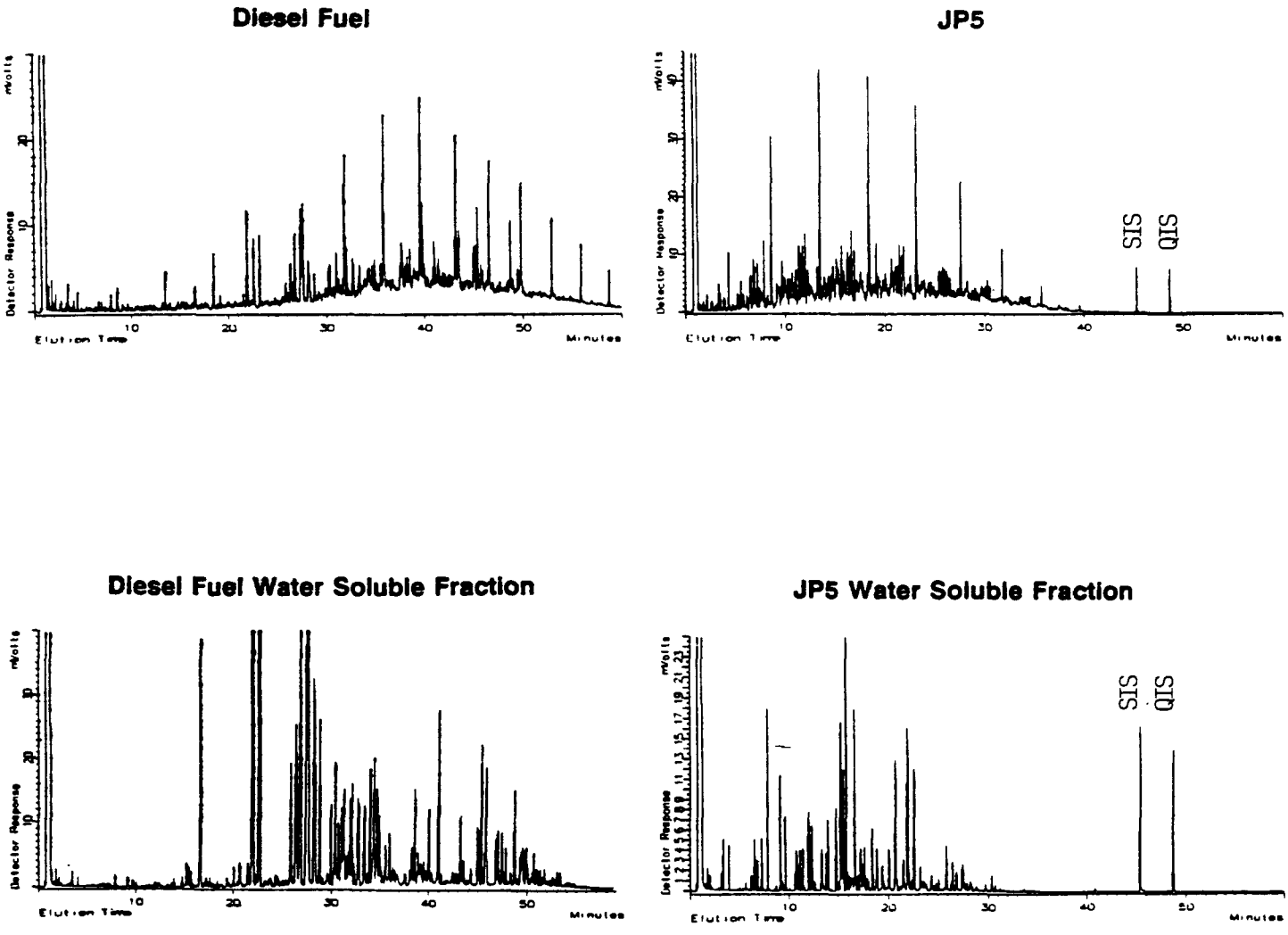


Figure 4. GC/FID chromatograms of diesel and JP5 fuel oils and their respective water-soluble fractions. The water-soluble fractions were prepared by floating the products on 1 L of distilled water in a separatory funnel for 5 days, after which time the water-soluble fraction (WSF) was drained from the bottom. This WSF is composed primarily of 2- to 3-ring aromatic hydrocarbons. Using WSF standards for fingerprinting improves water sample product-identification accuracy.

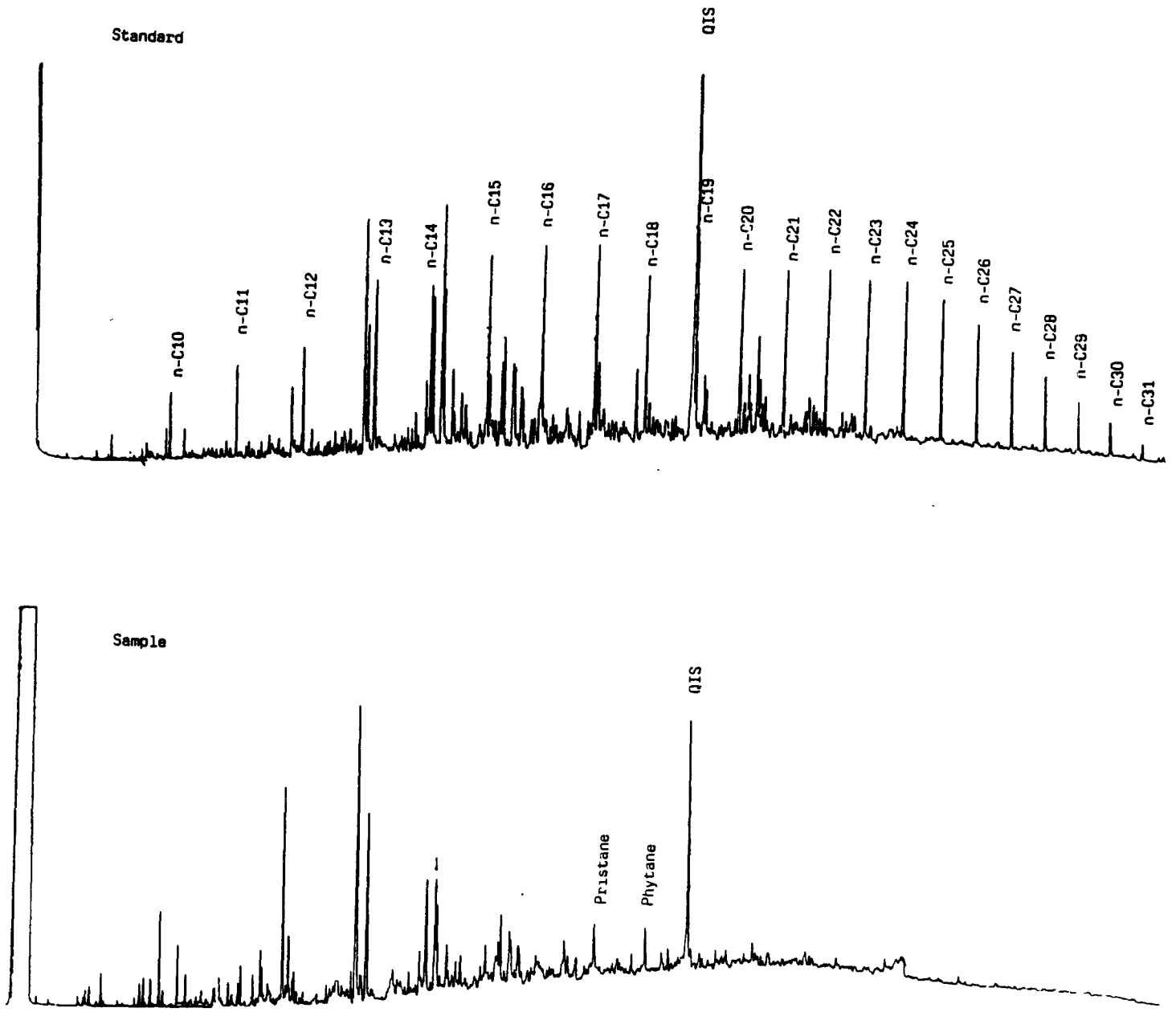


Figure 5. **GC/FID chromatograms of fresh and degraded crude oil. The quantitation internal standard (QIS) is ortho-terphenyl.**

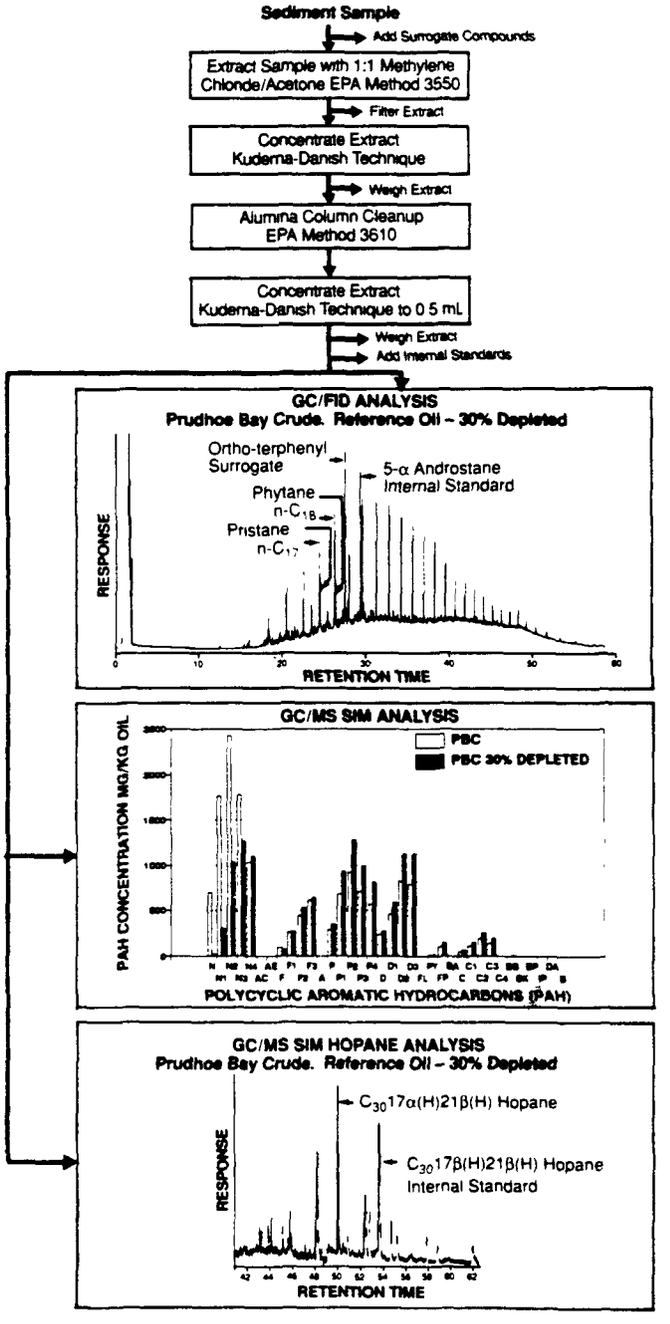


Figure 6. Battelle Fingerprinting Program method summary. For water-sample analysis, EPA Method 3510 would be used to extract the samples.

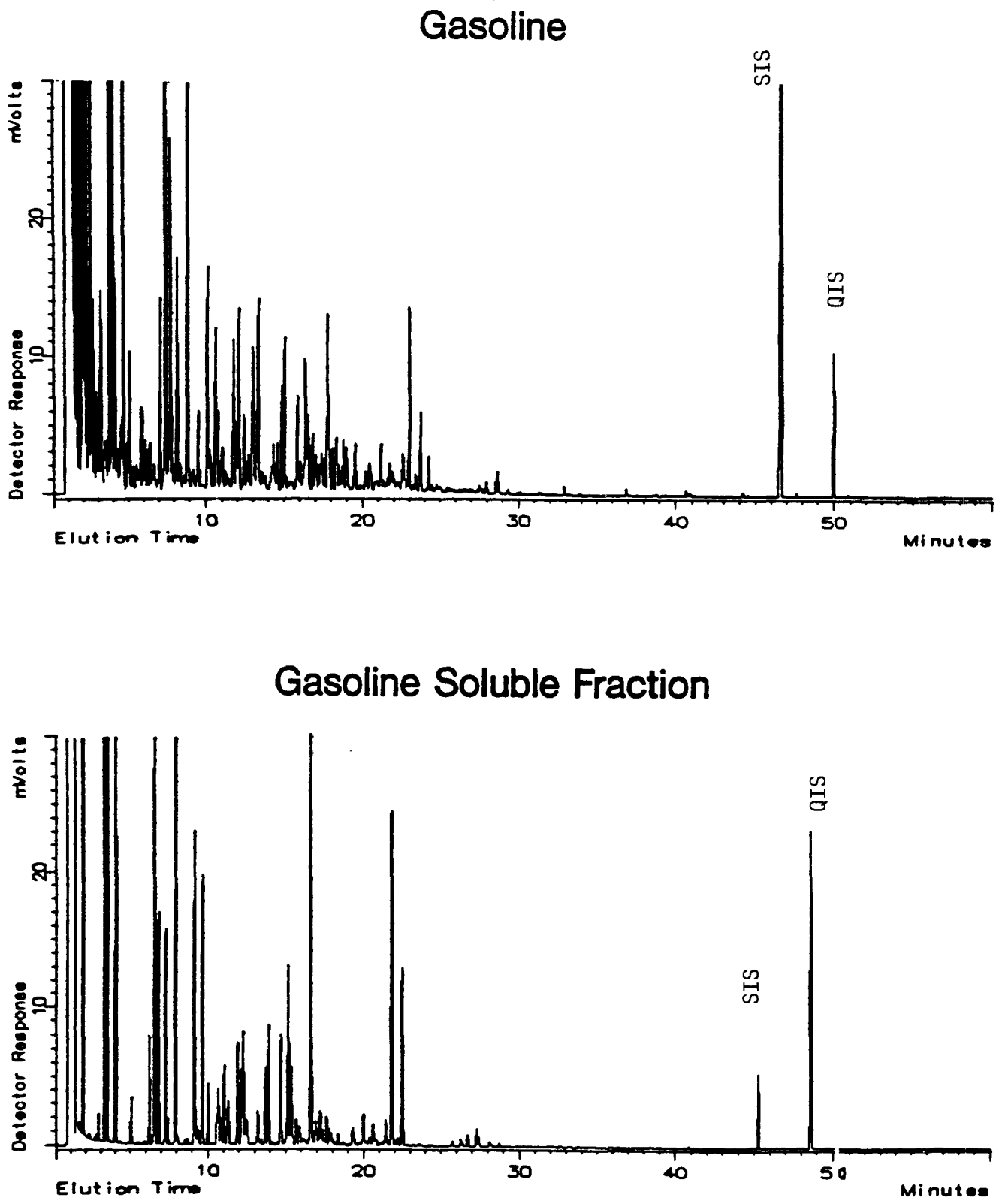


Figure 7. GC/FID chromatograms of gasoline and its water-soluble fraction. The surrogate internal standard (SIS) is ortho-terphenyl and the quantitation internal standard (QIS) is 5-α androstane.

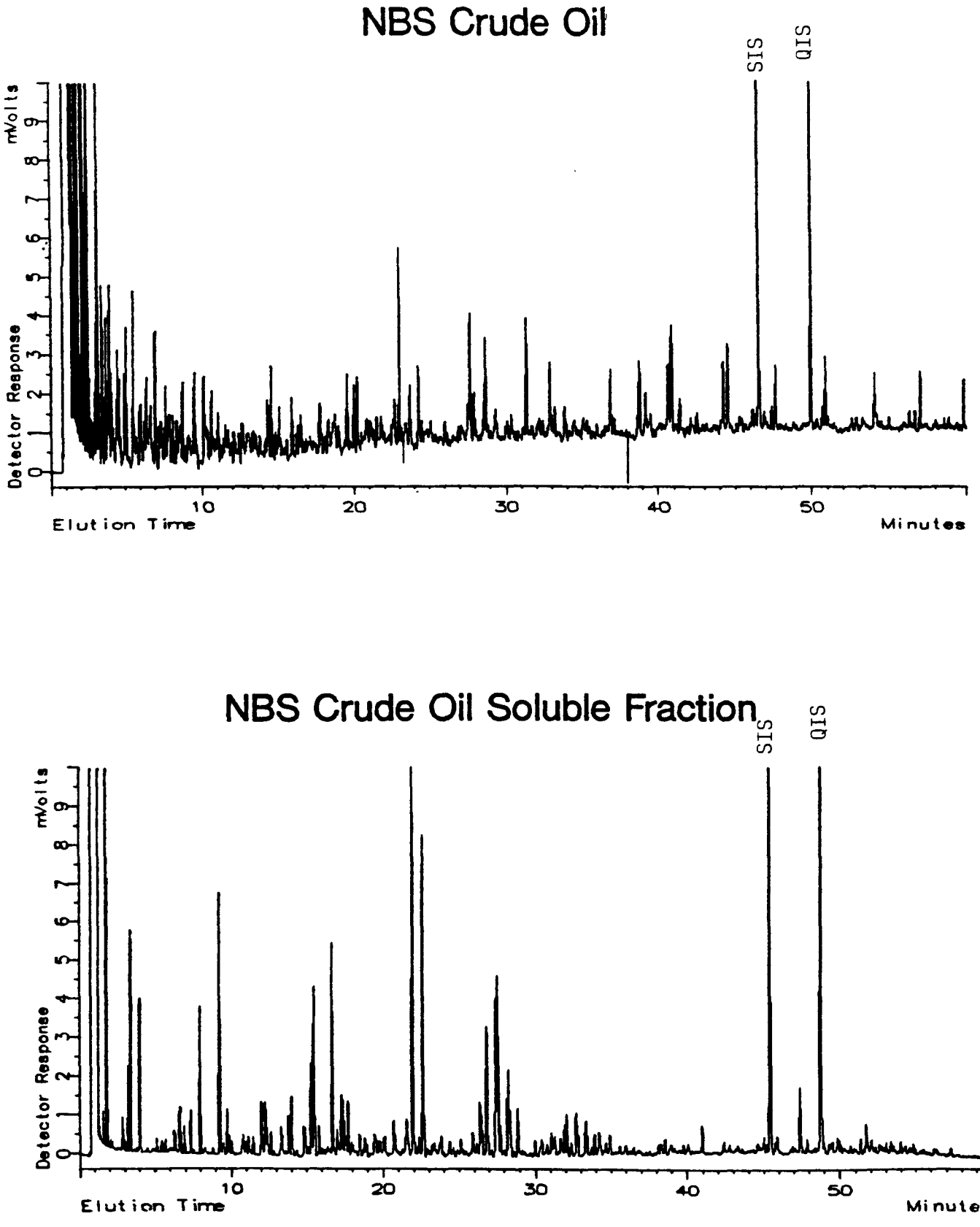


Figure 8. GC/FID chromatograms of National Bureau of Standards (NBS) crude oil standard and its water-soluble fraction.

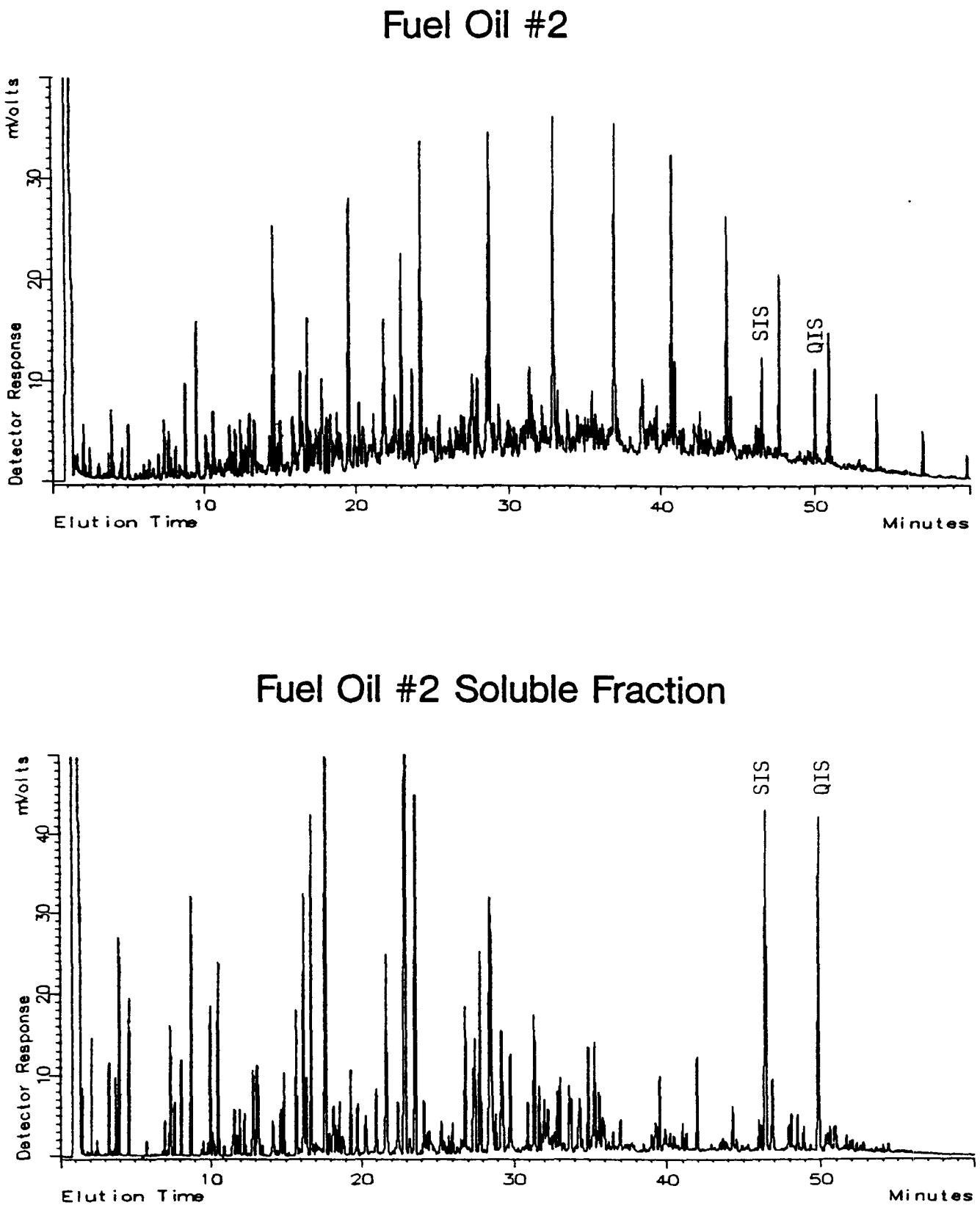


Figure 9. GC/FID chromatograms of fuel oil #2 and its water-soluble fraction.

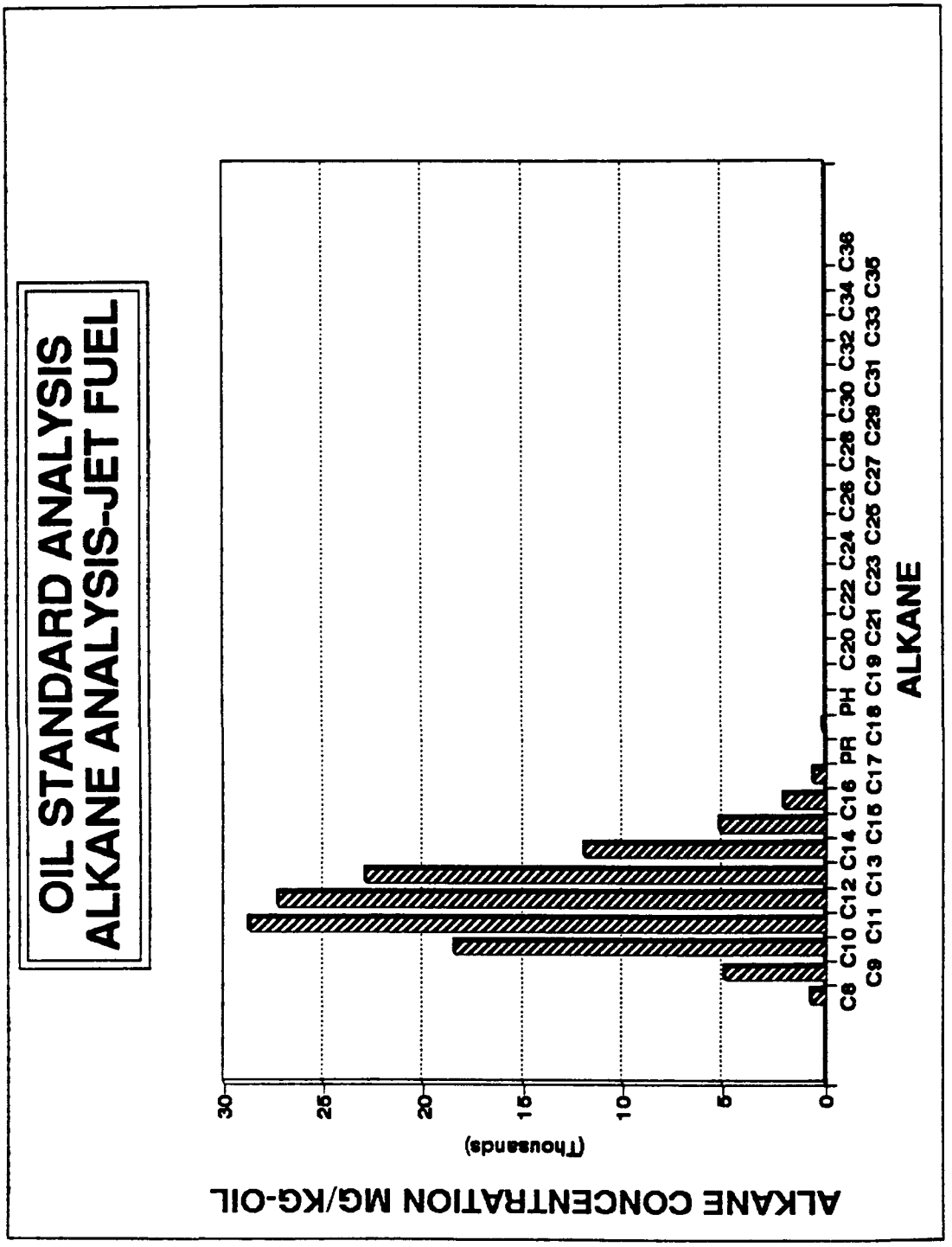


Figure 10. Concentration and distribution of saturated hydrocarbons in jet fuel.

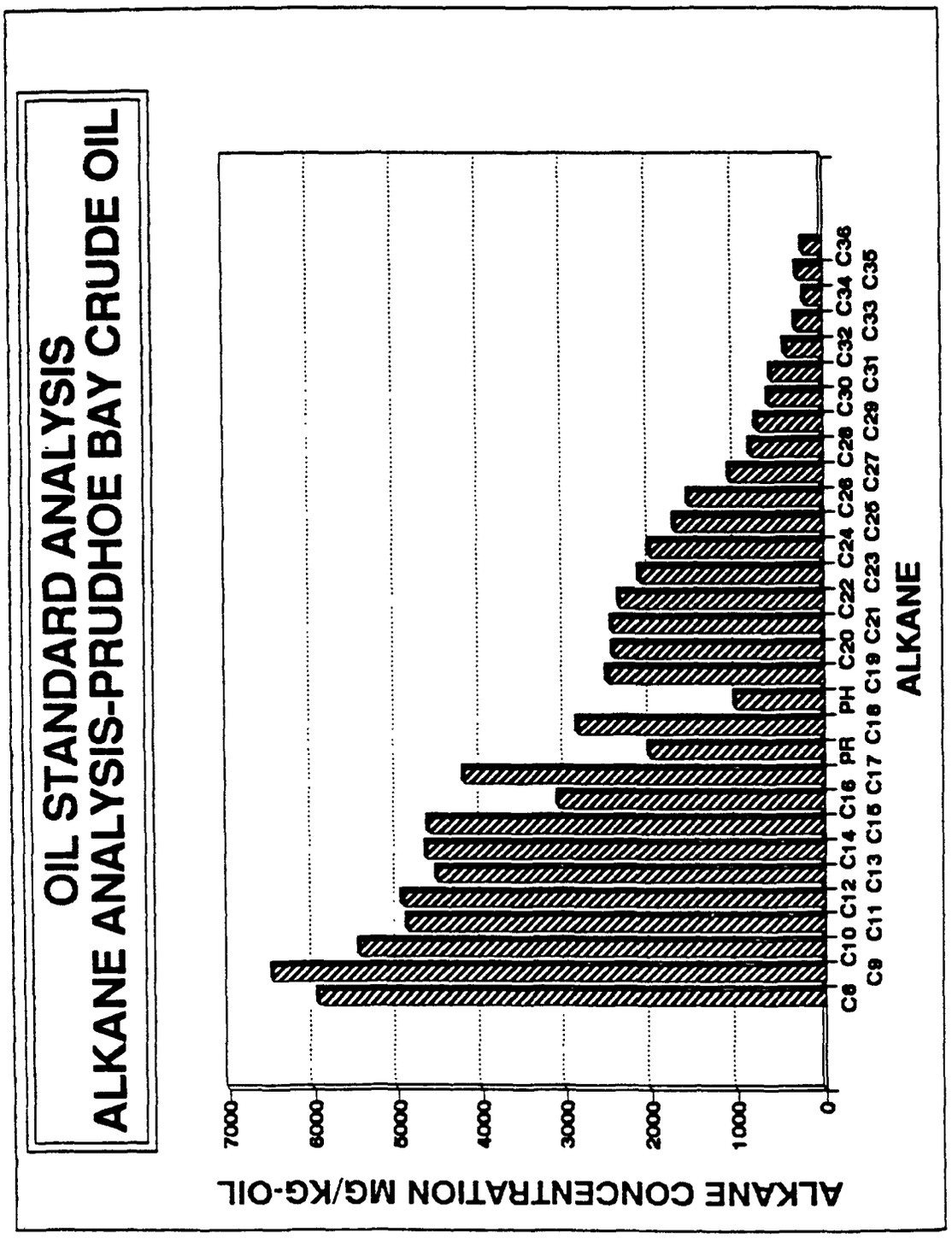


Figure 11. *Concentration and distribution of saturated hydrocarbons in Prudhoe Bay crude oil.*

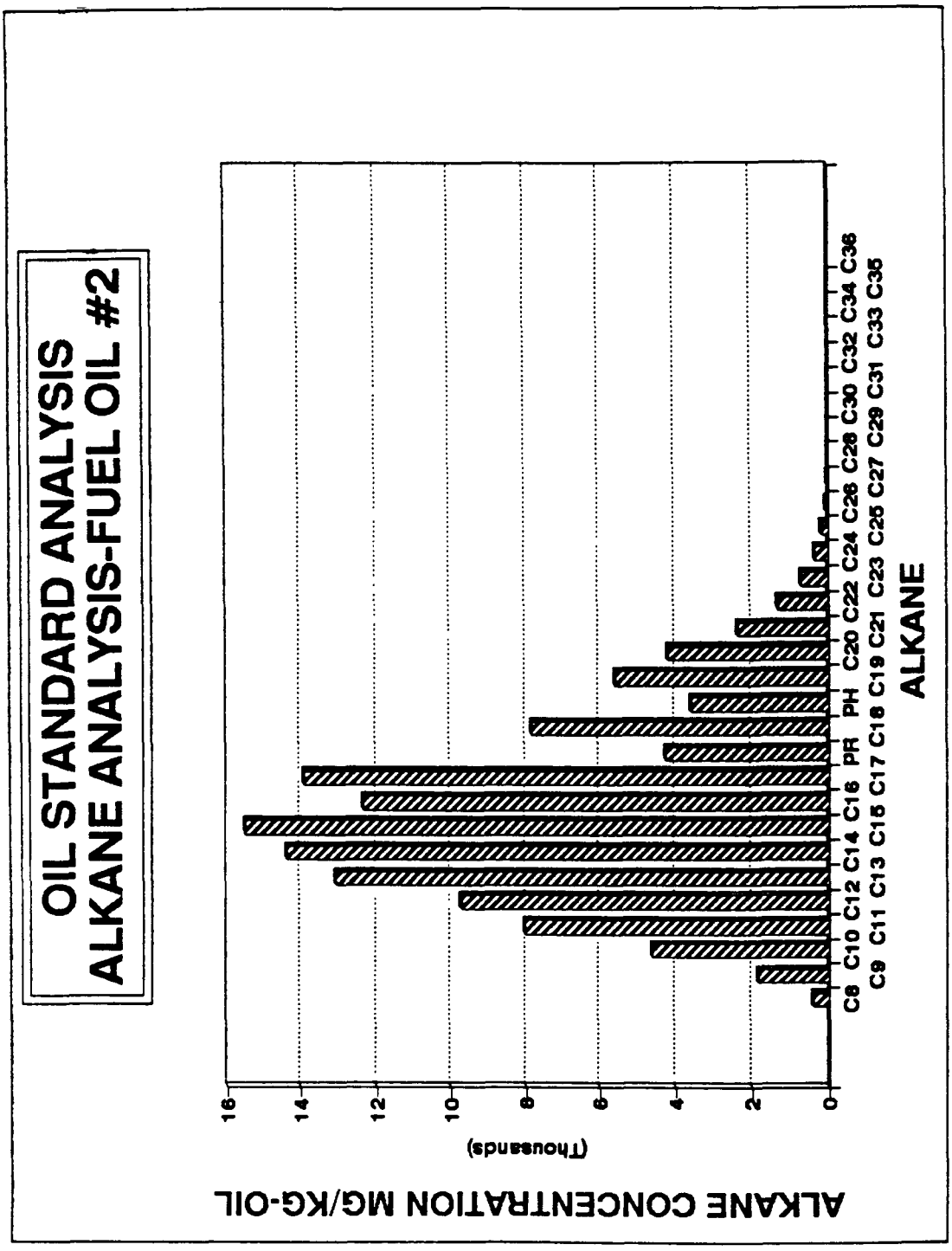


Figure 12. Concentration and distribution of saturated hydrocarbons in fuel oil #2.

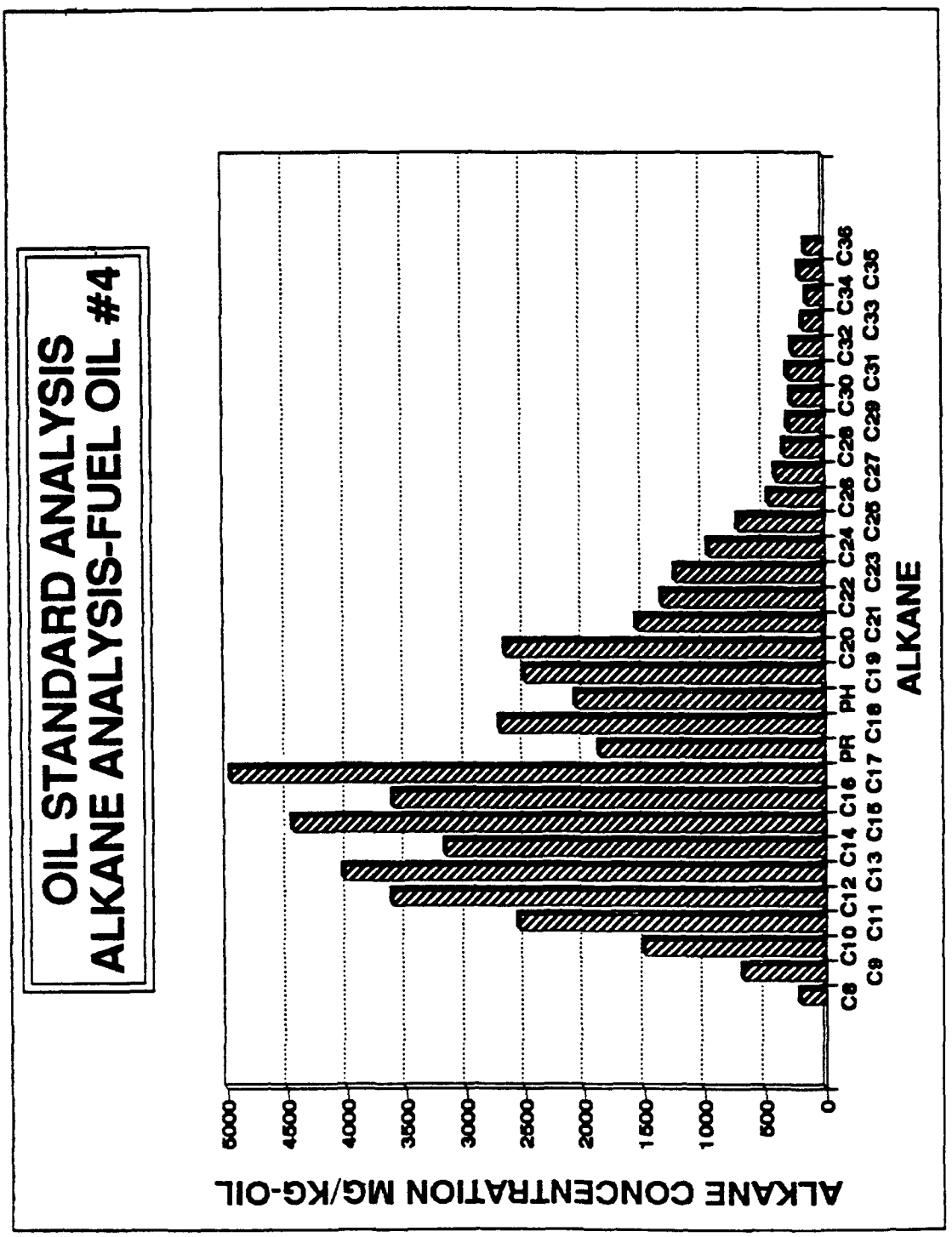


Figure 13. Concentration and distribution of saturated hydrocarbons in fuel oil #4.

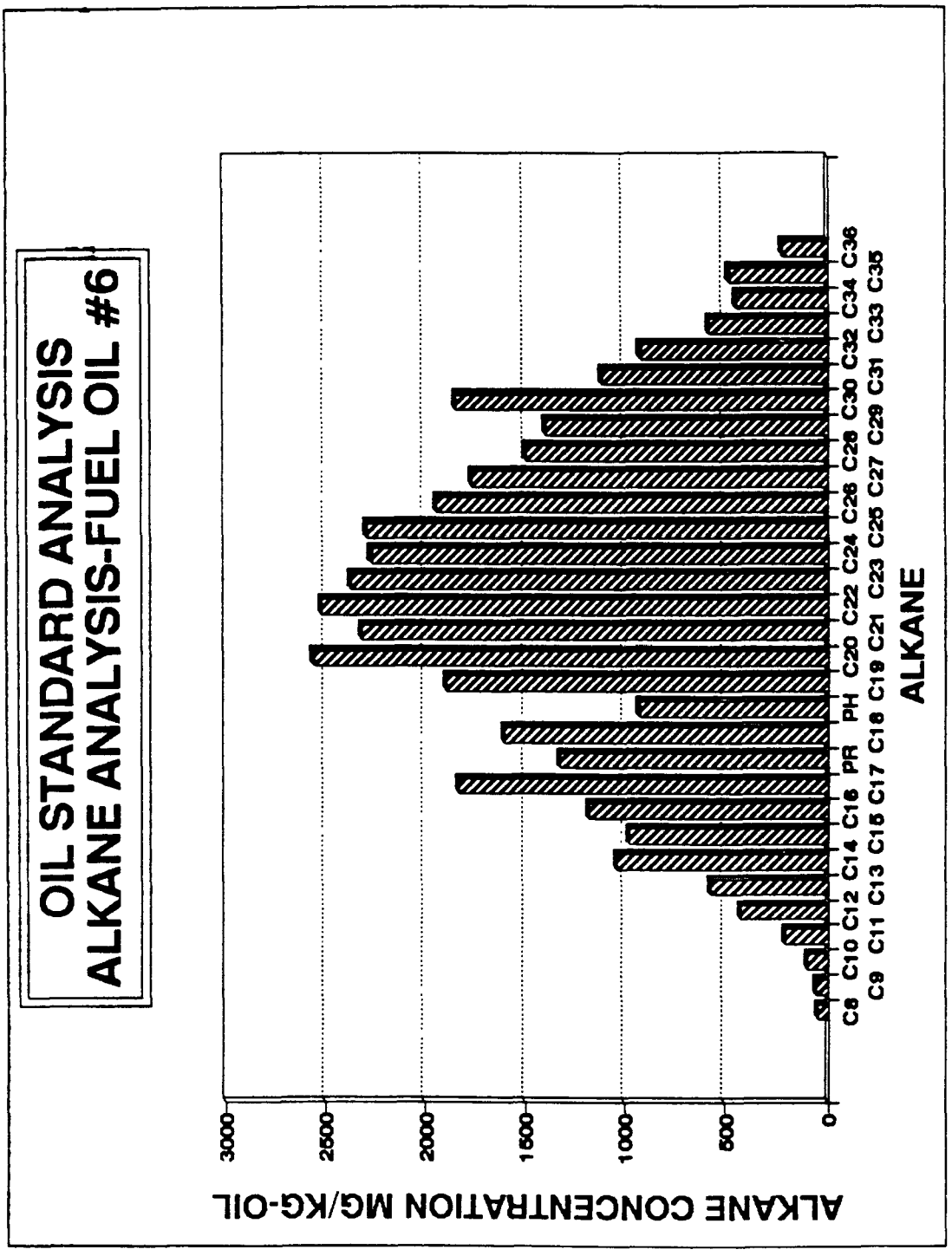


Figure 14. Concentration and distribution of saturated hydrocarbons in fuel oil #6.

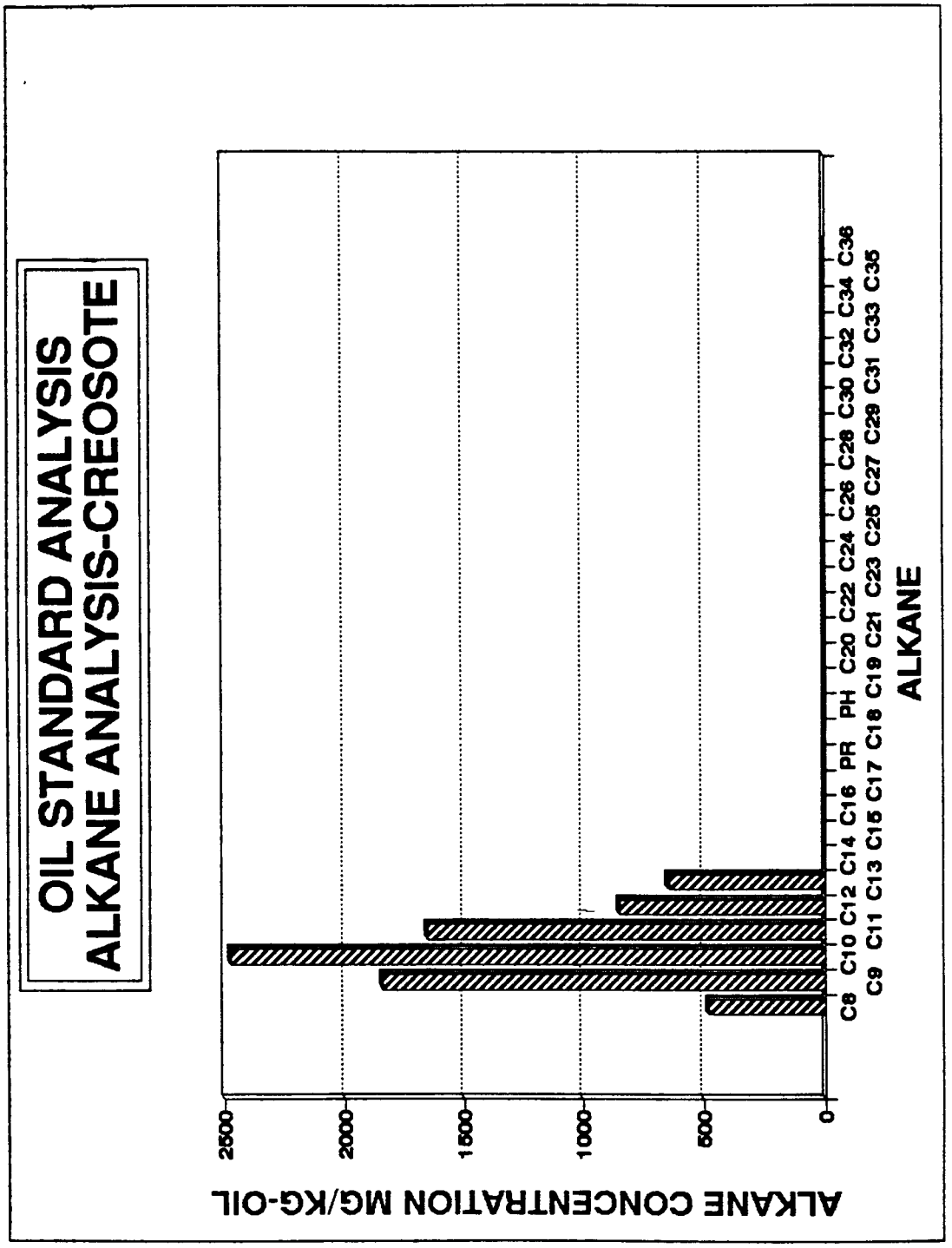


Figure 15. Concentration and distribution of saturated hydrocarbons in creosote.

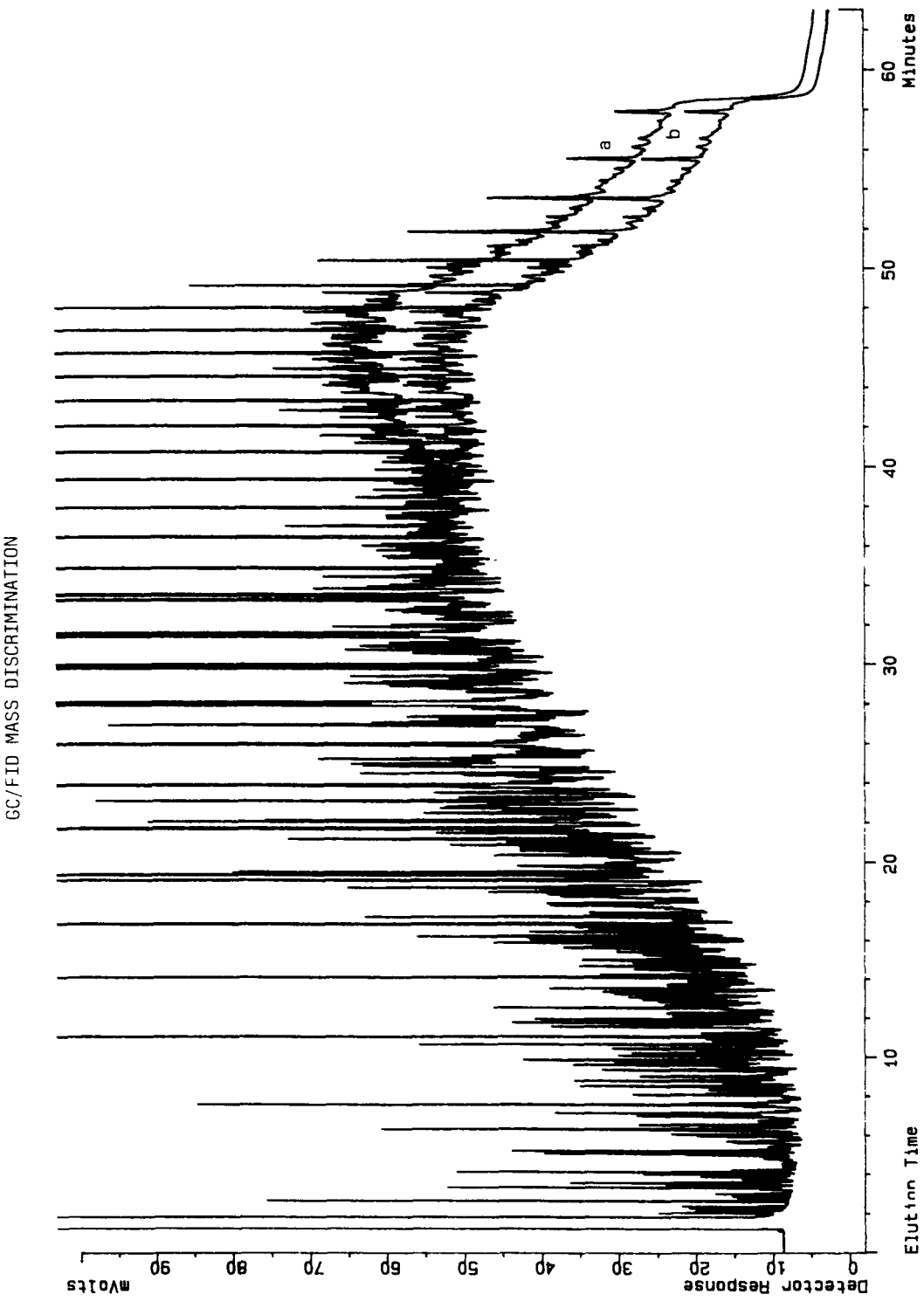


Figure 16. GD/FID chromatograms of a crude oil sample analyzed with (a) acceptable mass discrimination and (b) unacceptable mass discrimination.

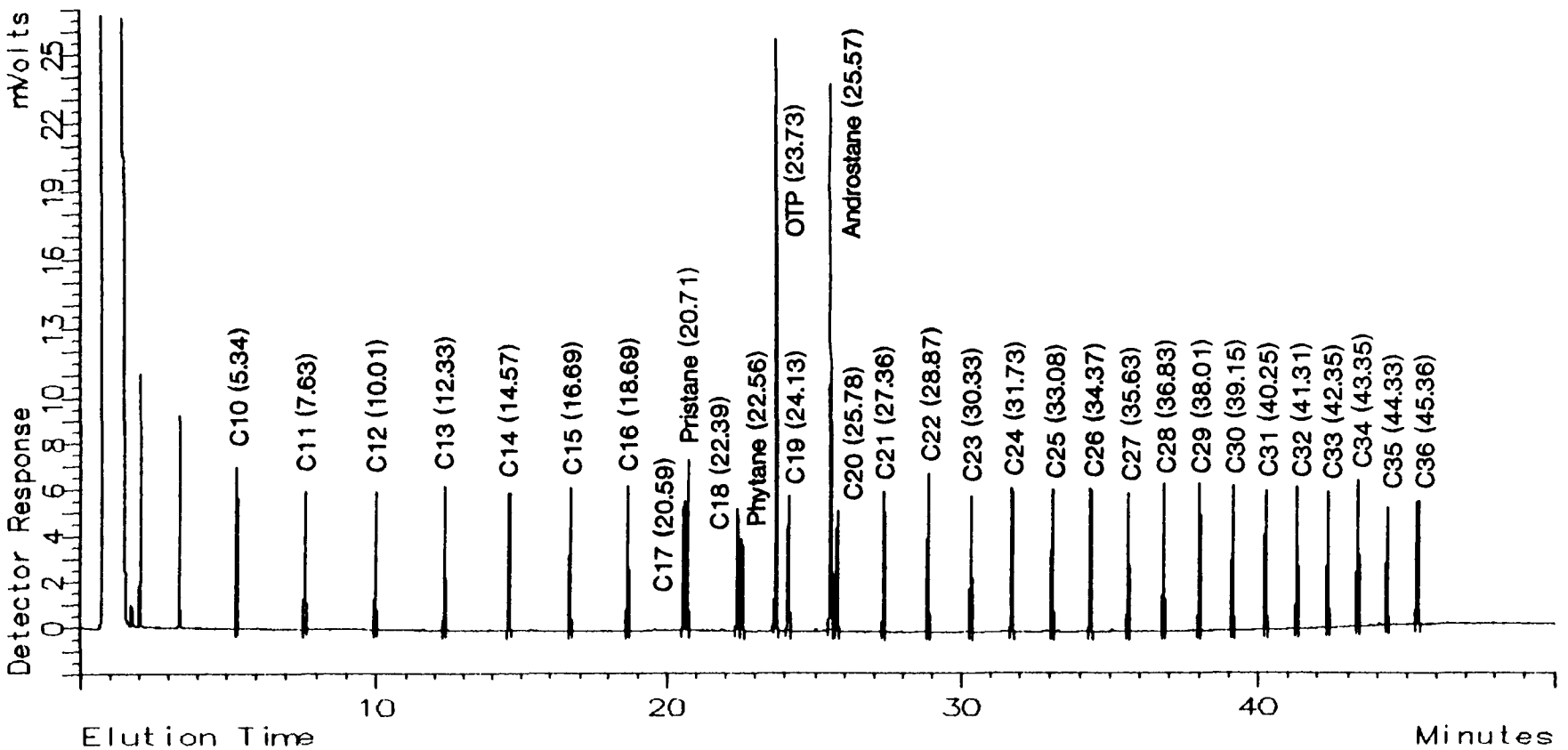


Figure 17. GC/FID chromatogram of a 5-ng/μL alkane standard. This chromatogram demonstrates the acceptable level of resolution (separation of n-C_{18} and phytane) and mass discrimination as indicated by the response of n-C_{34}/n-C_{21} (>0.8).

Gas Chromatographic Analysis of JP5 and Diesel Oil, Water Soluble Components

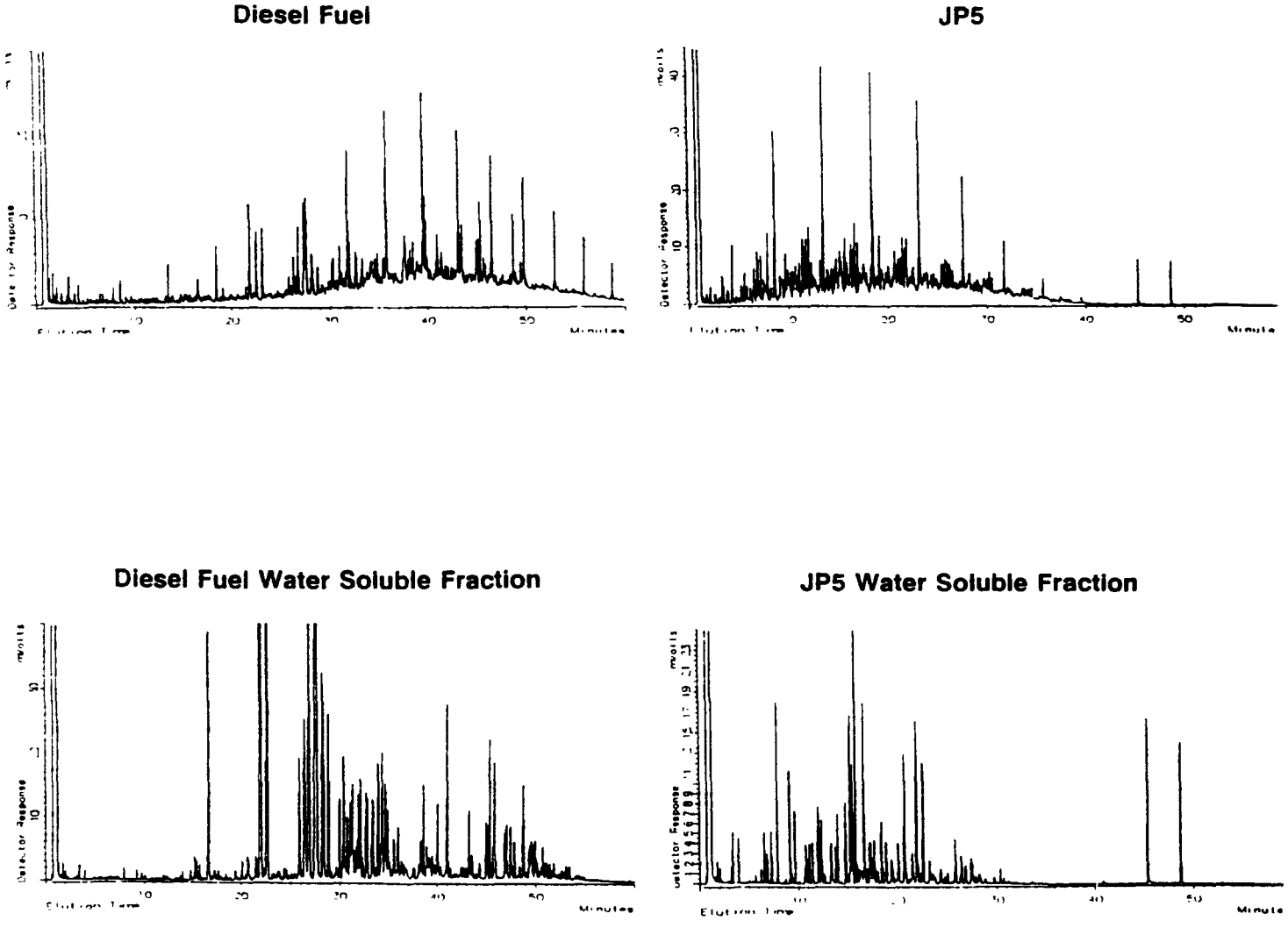


Figure 18. GC/FID chromatograms of diesel and JP5 fuel oils and their respective water-soluble fractions. The water-soluble fractions were prepared by floating the products on 1 L of distilled water in a separatory funnel for 5 days, after which time the water-soluble fraction (WSF) was drained from the bottom. This WSF is composed primarily of 2- to 3-ring aromatic hydrocarbons. The use of WSF standards for fingerprinting improves water sample product-identification accuracy.

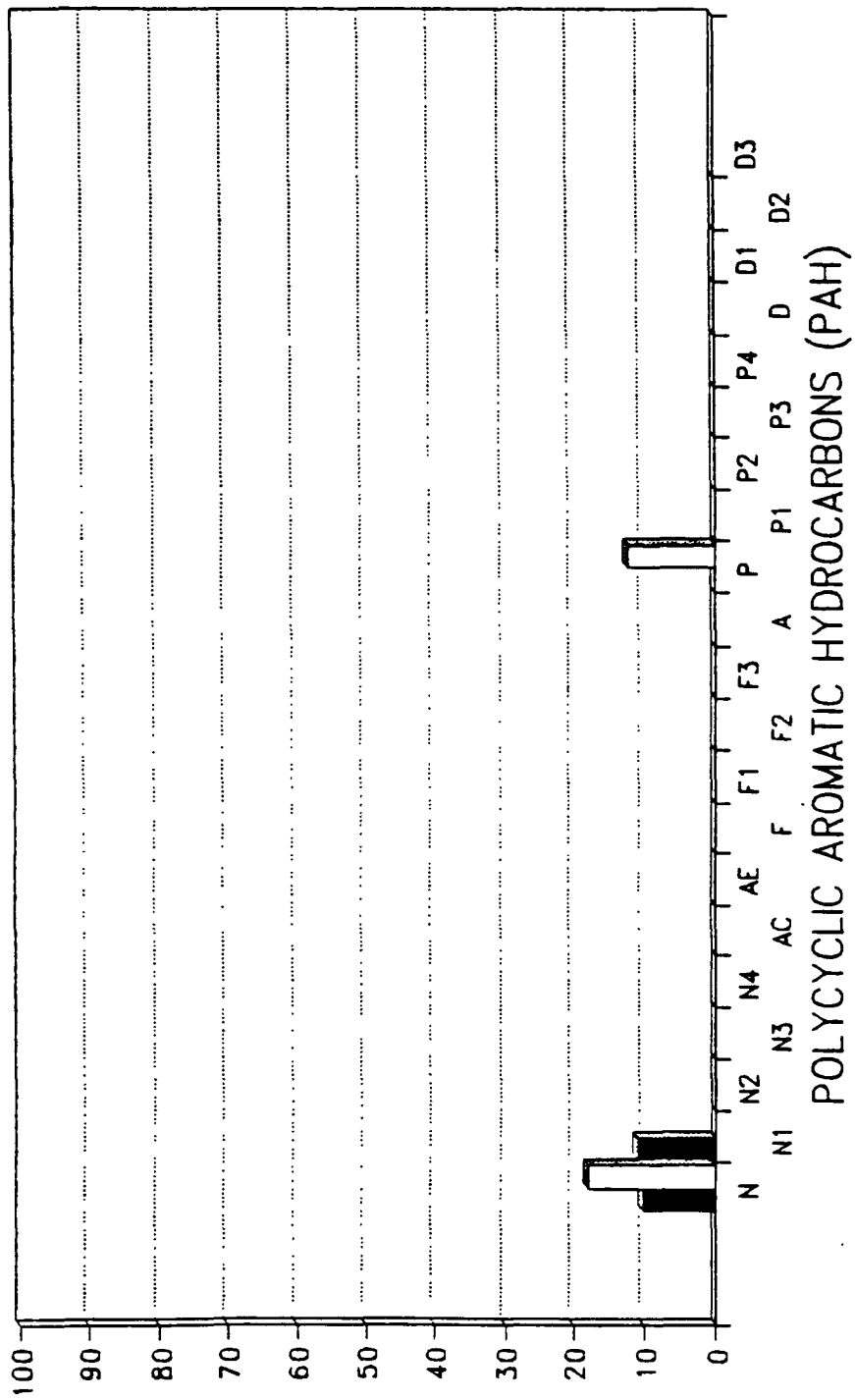


Figure 19. PAH distribution of the water-soluble fractions of JP5 and diesel fuel as measured by EPA Method 8270 for the analytes listed in Table 1. This method has limited utility for oil-spill assessment owing to the relatively high reporting limits and lack of petroleum-specific alkylated PAH homologs.

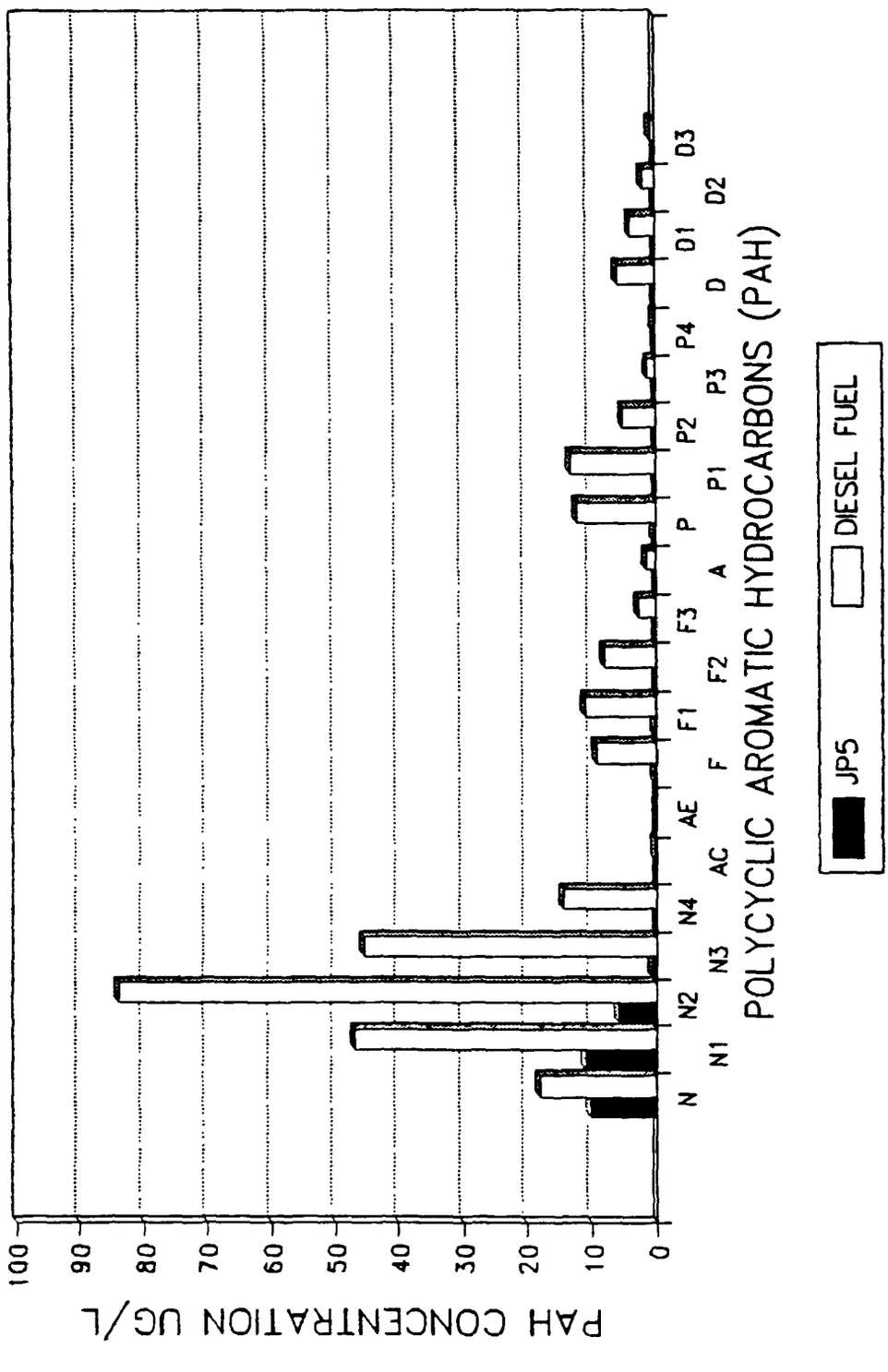


Figure 20. PAH distribution of the water-soluble fractions of JP5 and diesel fuel as measured by the GC/MS method described in this presentation. The additional chemical data gained by this analysis is critical for evaluation of the transport and fate of these materials in environmental samples.

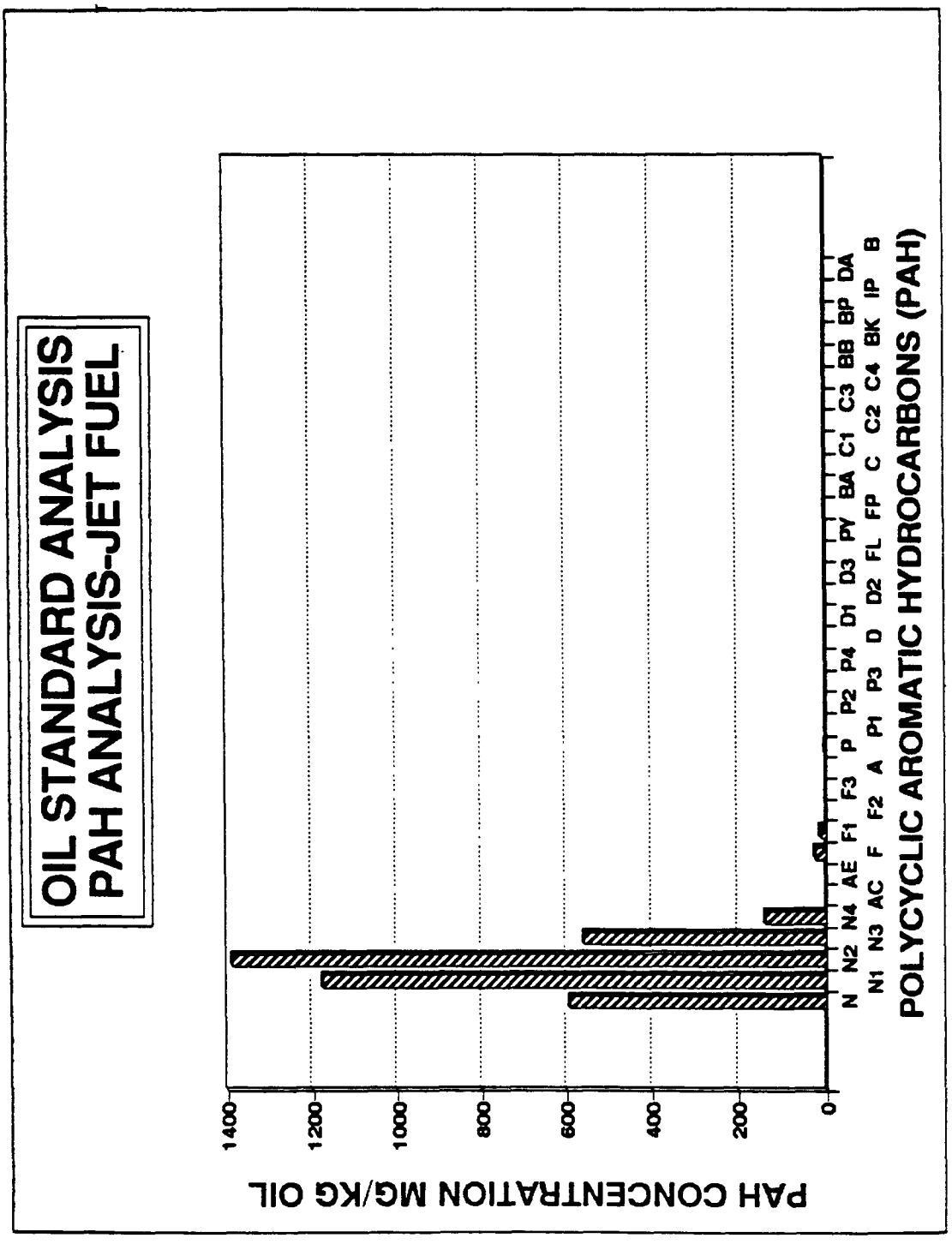


Figure 21. Distribution and concentration of PAHs in jet fuel.

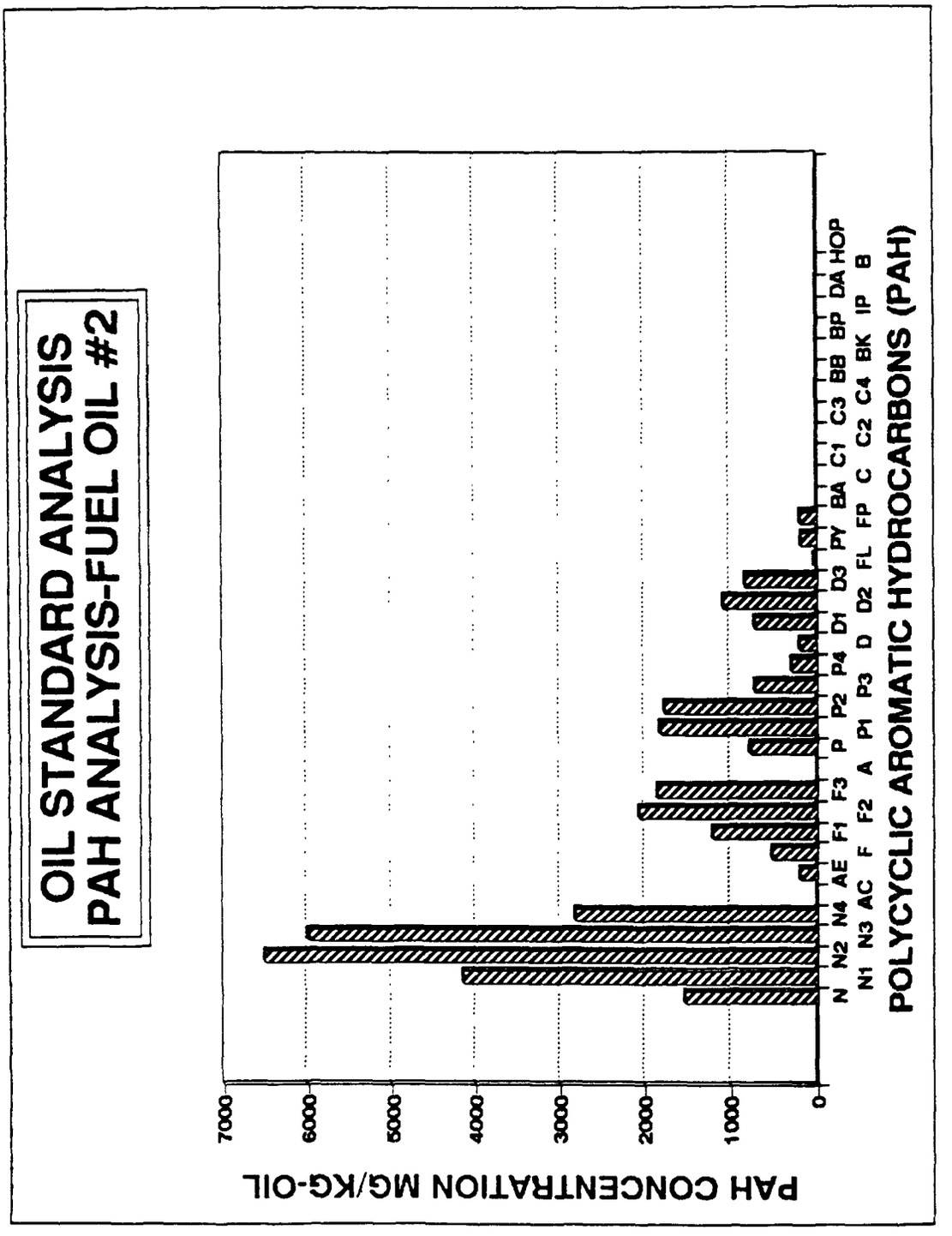


Figure 22. Distribution and concentration of PAHs in fuel oil #2.

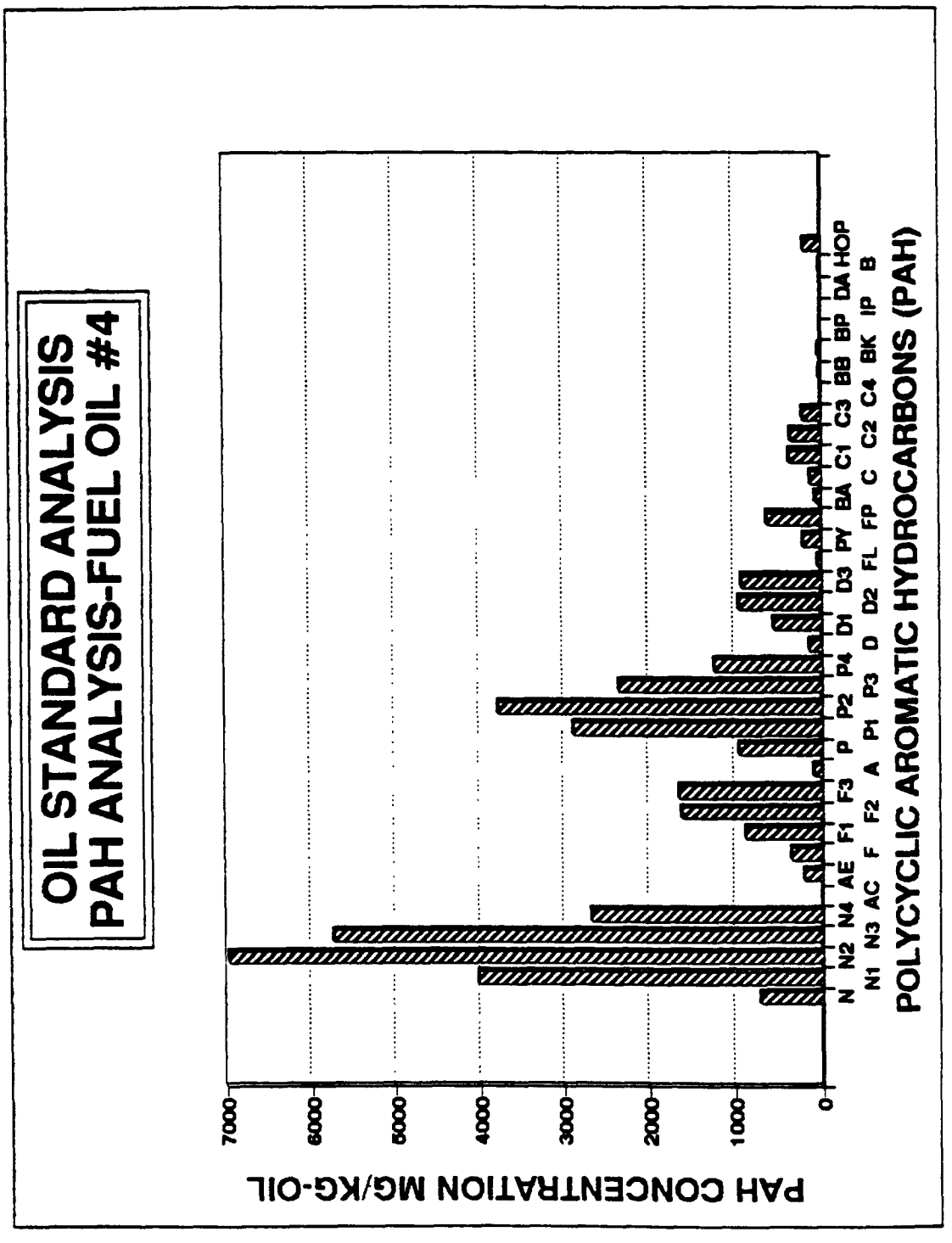


Figure 23. Distribution and concentration of PAHs in fuel oil #4.

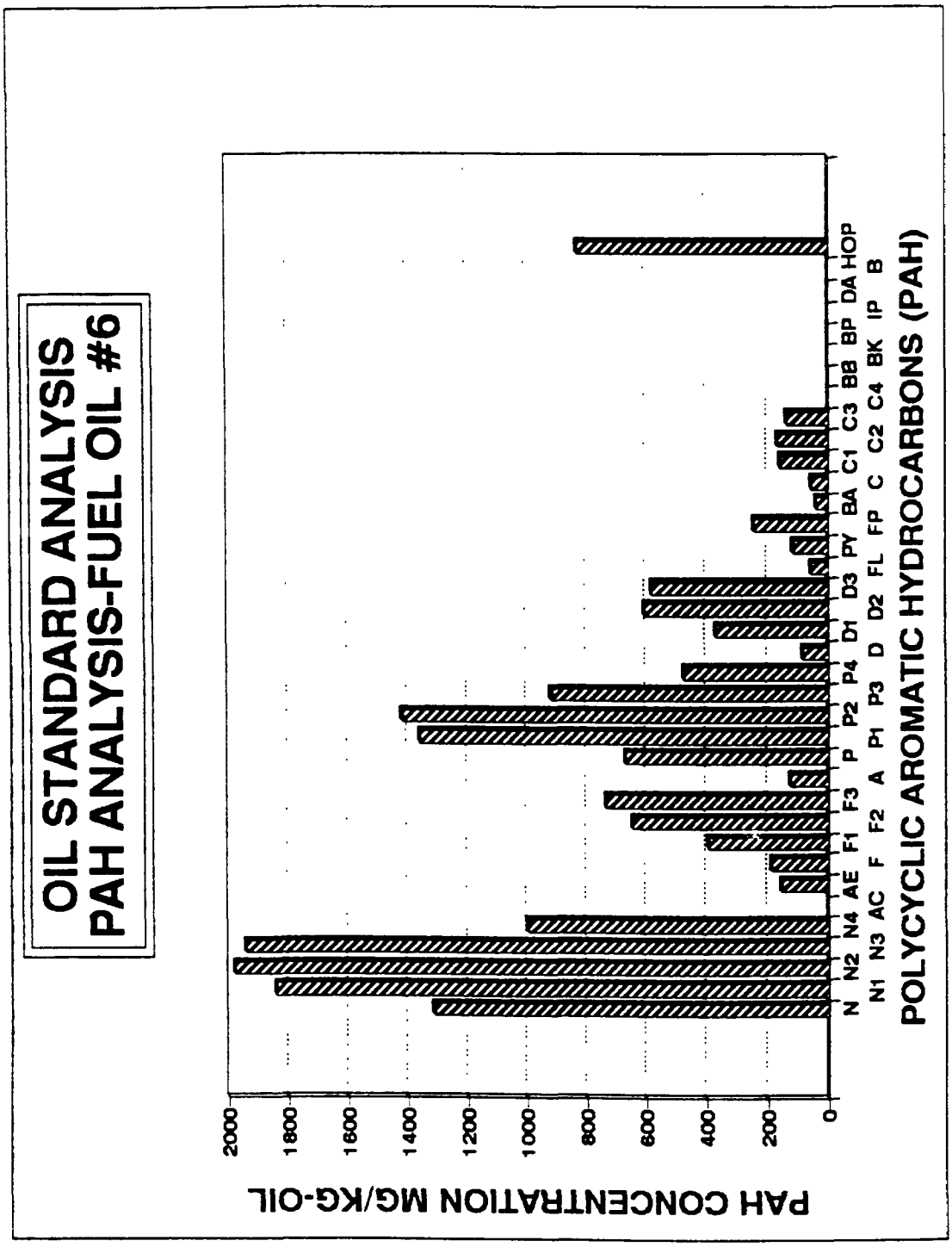


Figure 24. Distribution and concentration of PAHs in fuel oil #6.

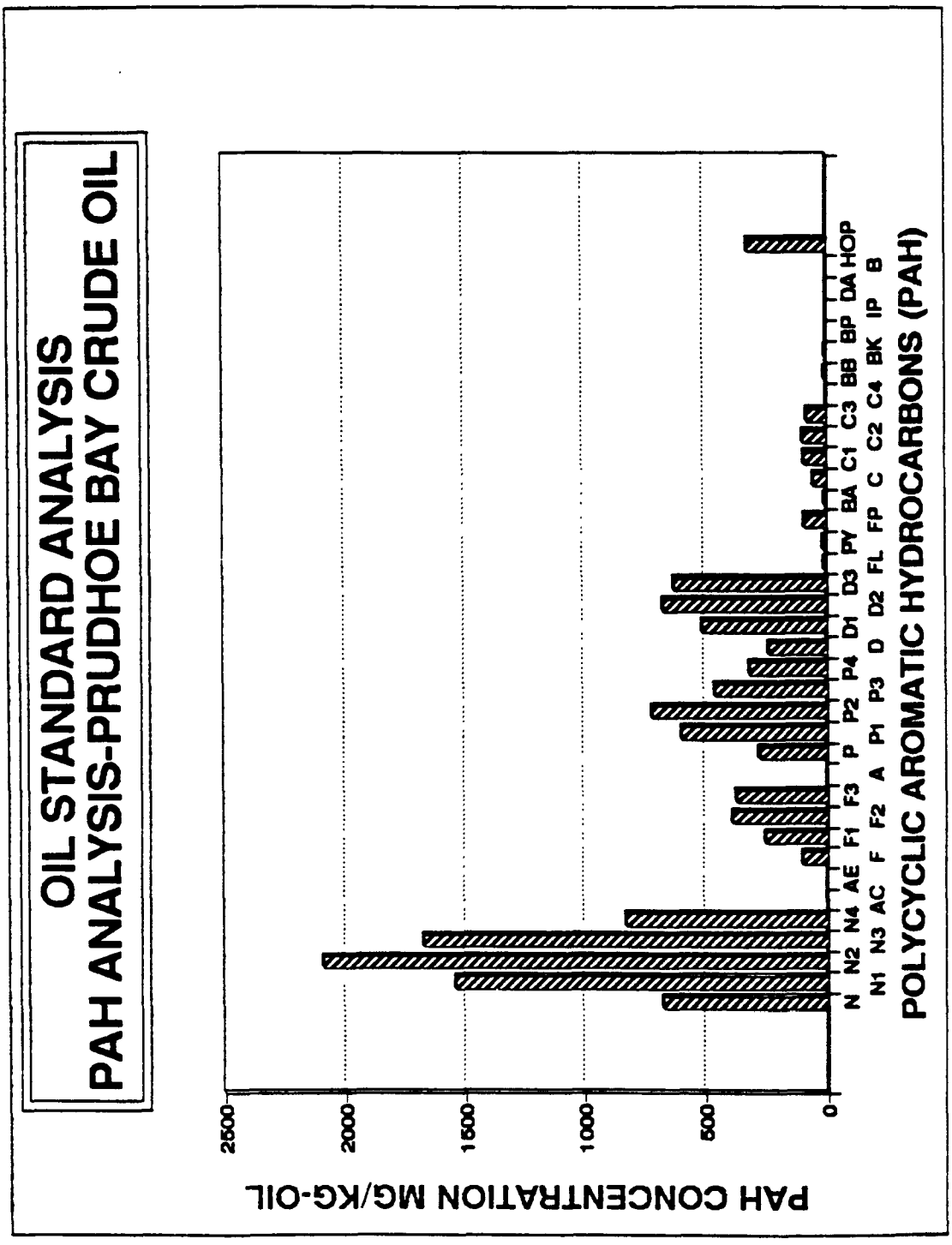


Figure 25. Distribution and concentration of PAHs in Prudhoe Bay crude oil.

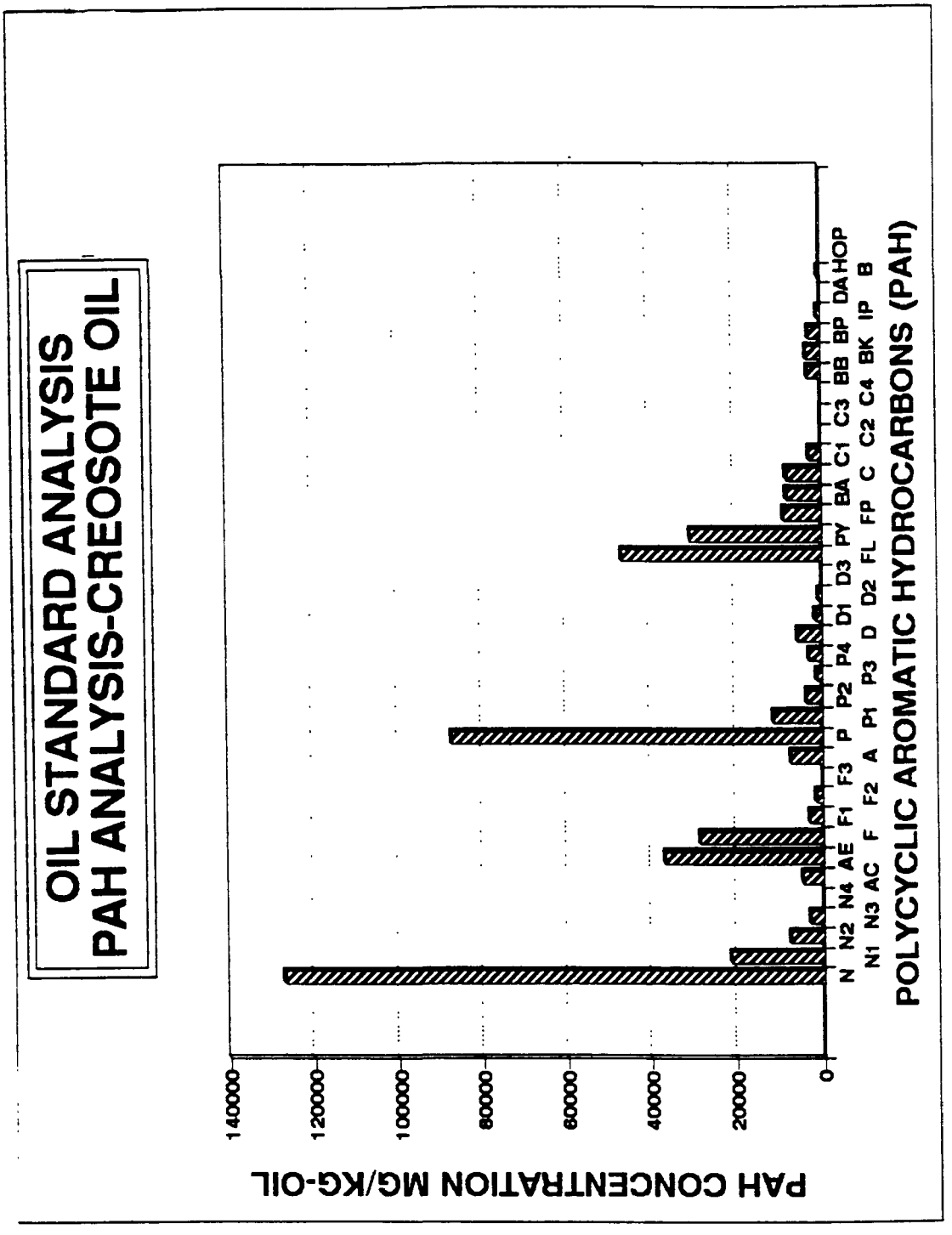
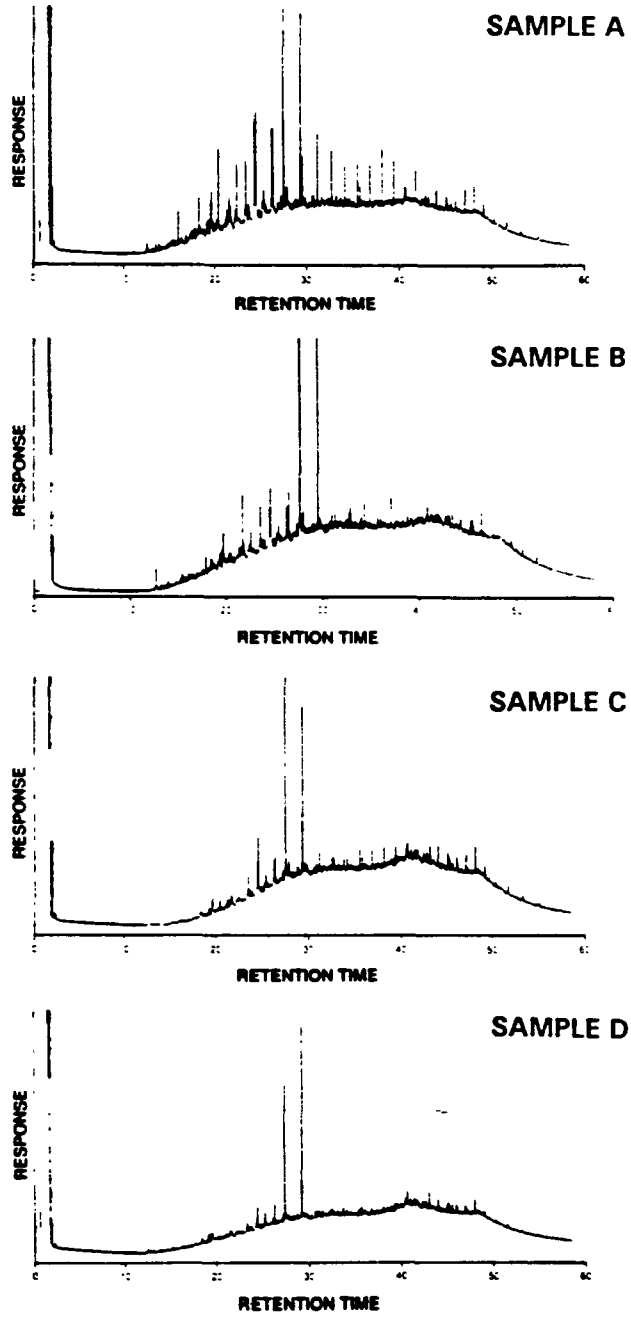
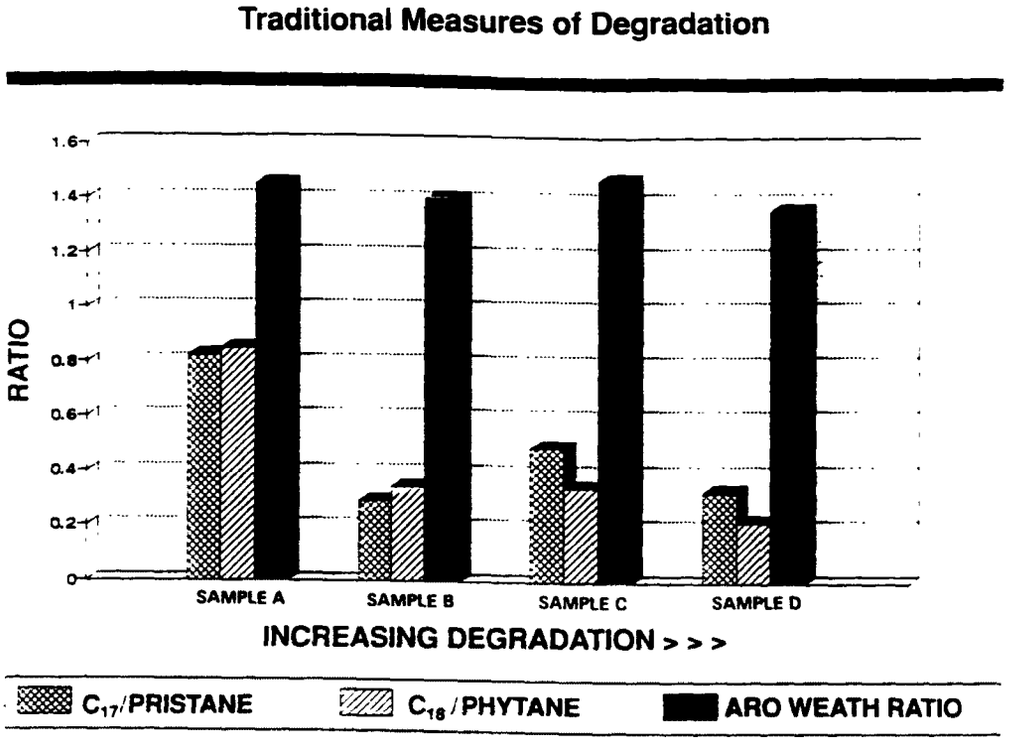


Figure 26. Distribution and concentration of PAHs in creosote oil.



GC/FID Chromatograms from Selected Sediment Samples.

Figure 27. GC/FID chromatograms of a crude oil samples that exhibit increasing amounts of oil degradation.



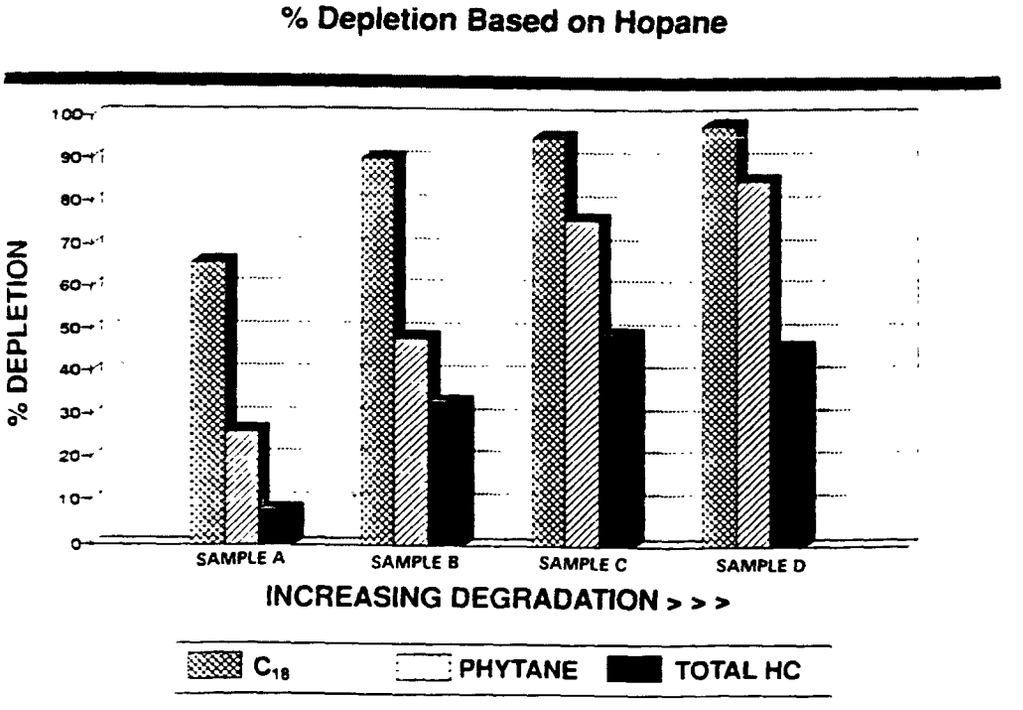


Figure 28. (a) Traditional measures of degradation vs increased oil degradation.
(b) Percent depletion of n-C_{18}, phytane, and total hydrocarbons (HC) relative to 17α(H),21β(H)-C_{30} Hopane.

MR. TELLIARD: Can we get the folks in from the outside with their coffee and their toast or whatever they're bringing?

It kind of reminds me of the story about the Aggie that was on the boat and this guy from the University of Texas and another fellow from the University of Houston and the ship ran aground and sank and the three men were left in a lifeboat for months on end. Finally, a small bottle appeared in the water and they opened it and a genie came forth and granted them for freeing him one wish each. So the fellow from the University of Texas said, I can't wait. You just send me right back there to Austin in them hills and I'm going to be happy. And (snap) he's gone.

The other fellow said, I'd like to go back to Houston and have a little crab and sit around and eat some. (Snap) He's gone.

And there sat the Aggie, bobbing in the lifeboat all by himself, looking around. And the genie said, what would you wish?

He said, well, actually, I'd like to have my friends back.

Our first speaker in the pesticide section is Cary Jackson. Cary is presently associated with Colorado State University in a company called Support Systems.

Cary is going to talk about a novel approach to extraction and analysis of chlorophenoxy-acid herbicides. I think novel is kind of neat. I've never heard of a novel approach.

ANALYSIS OF CHLOROPHENOXY-ACID HERBICIDES IN SOIL AND WATER

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ABSTRACT

Due to the chemical nature and behavior of chlorophenoxy-acid herbicides in soil and water, and the traditional use of non-specific or semi-specific detection systems, currently practiced analytical methods often fail to provide accurate and precise measurements for making environmental and toxicological assessments. As a result of the phenoxy-acid group $-OC_nH_{n+2}COOH$, phenoxy-acid herbicides of 4 C or less are easily subjected to alkaline and acid hydrolysis. In order to partition the free acid form of the herbicides from soil and water to organic solvent, the entire soil matrix is required to be at a pH of less than 2. This often becomes difficult to achieve, especially in calcareous soils where $CaCO_3$ buffers the addition of acid. Once the herbicides have been favorably partitioned to organic solvent, difficulty in detection and identification may arise from non-analyte interferences that are electrophilic and respond to electron capture detectors. Often, hydrolysis cleanup procedures are required to remove or minimize interferences. However, these cleanup procedures have been shown to have an unfavorable effect on the accuracy and precision of the target-analyte measurement.

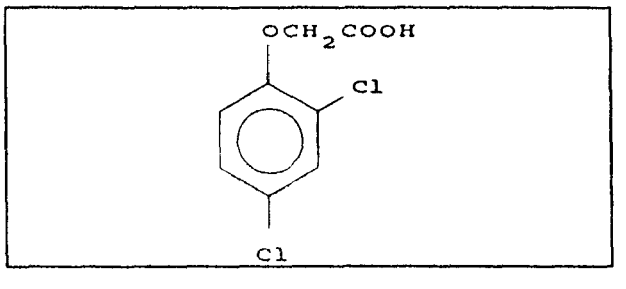
The objective of this study was to develop a new extraction and analysis procedure for chlorophenoxy-acid herbicides in soil that eliminates acidifying the soil, minimizes hydrolysis cleanup steps, eliminates the use of ethyl ether as an extraction solvent

in exchange for a less water soluble, non-flammable solvent, maximizes the accuracy and precision of the measurement, and uses a specific detector that does not respond to traditional electron capture detector interferences.

In order to meet the above objective, chlorophenoxy-acid herbicides spiked in soil were subjected to alkaline hydrolysis and partitioned to the aqueous phase of a soil suspension. Upon flocculation of the soil suspension, an aliquot of the supernate was acidified and extracted with dichloromethane. The extracted herbicides were methylated with diazomethane and analyzed by gas chromatography using a halide-specific electrolytic conductivity detector. Reported accuracy and precision results are equal or superior to those reported in U.S. EPA analytical methods.

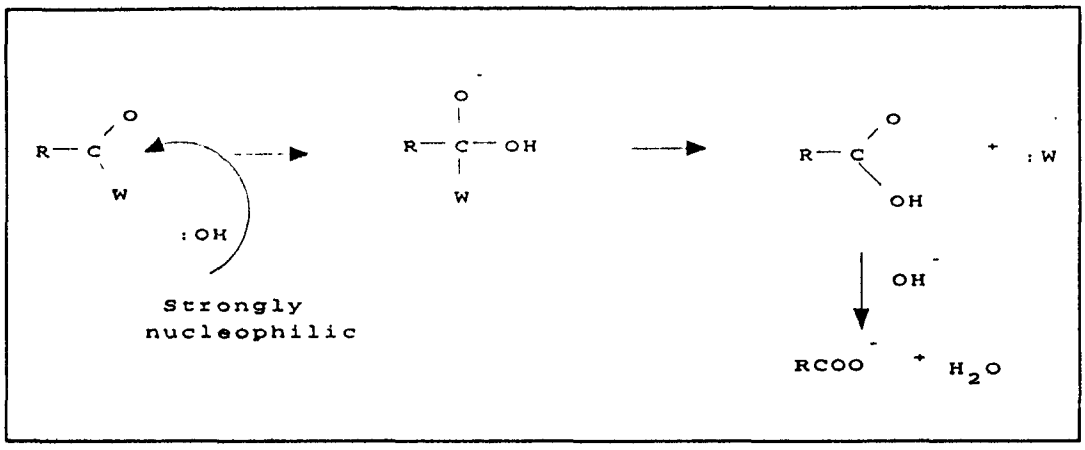
INTRODUCTION

Due to the chemical nature and behavior of chlorophenoxy-acid herbicides in soil and water, and the use of non-specific or semi-specific detection systems, currently practiced analytical methods (1,2,3,4,5) often fail to provide accurate and precise results for making environmental and toxicological assessments. First, chlorophenoxy-acid herbicides fall under the general structure of $ROC_nH_{n+2}COOH$, where R represents a chlorinated benzene ring. For example, 2,4-D has the following structure:

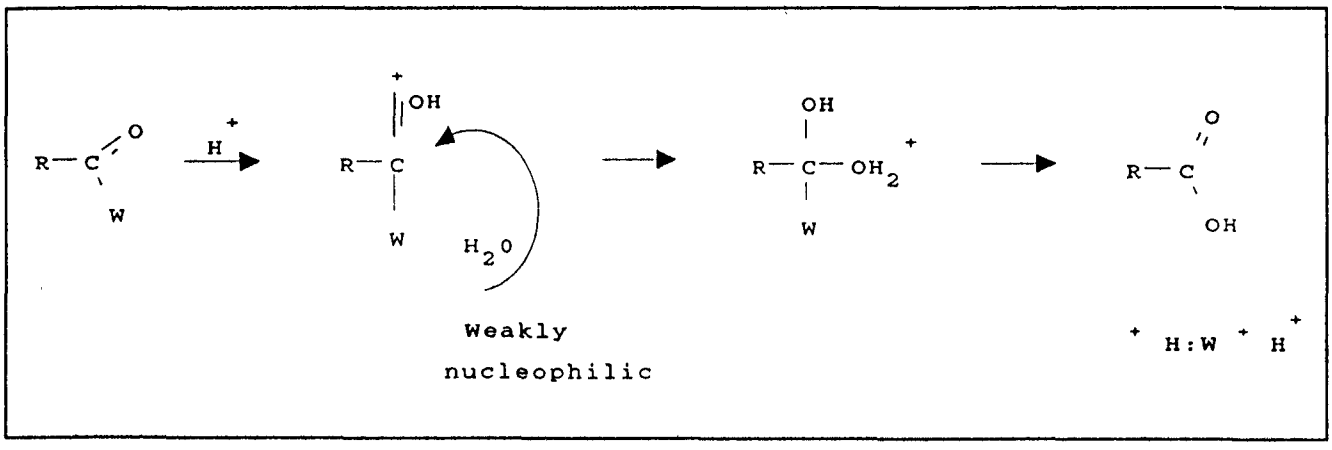


As a result of the phenoxy-acid group $-OC_nH_{n+2}COOH$, phenoxy-acid herbicide compounds are easily subjected to alkaline and acid hydrolysis.

Alkaline hydrolysis

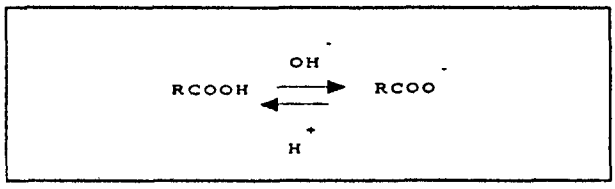


Acidic hydrolysis



In alkaline hydrolysis, the hydroxide ion acts as a strong nucleophilic reagent and replaces the leaving group,-W (-OH, -Cl, -OOCR, $-NH_2$, -OR'. Whereas in acid hydrolysis, the hydrogen ion attaches itself to carbonyl oxygen and renders itself vulnerable to attack by the weak nucleophilic reagent, water. As expected, salts formed during alkaline hydrolysis are soluble in water but insoluble in non-polar solvents. The free acids of four C or less, formed

during acid hydrolysis, are both soluble in water and in organic solvent. However, only with very polar solvents or when the pH is less than 2, will the free acid herbicides favor the organic solvent.



Because chlorophenoxy-acid herbicides act as strong organic acids, standard methods for the extraction of herbicides in soils are often inadequate, tedious, and time-consuming. For example, EPA Method SW-846; 8150, requires sufficient HCL be added to 50 g of soil to obtain a pH of less than 2. Continuous monitoring of the pH for 15 min is required to insure the pH remains below 2. Achieving a pH of less than 2 is often difficult, especially in calcareous soils where $CaCO_3$ can play a significant role in buffering the addition of HCL. After the pH is stabilized, three 20-min sequential extractions with acetone and diethyl ether, respectively, are required. The solvent extracts are combined with a fourth extraction using only diethyl ether. The solvent extract is then subjected to alkaline hydrolysis by the addition of reagent water and KOH. Evaporation of the diethyl ether on a water bath is required for 90 min. The alkaline solution then undergoes further diethyl ether extraction to remove non-ionic neutral and basic organic substrates.

At this point in the extraction process, the herbicides have undergone acid hydrolysis, solvent extraction, and alkaline hydrolysis. The next step is to convert the salts of the acids to the free-acid form, partition the herbicides into diethyl ether, and remove any residual water with the addition of acidified anhydrous

Na_2SO_4. The solvent extract is then concentrated and esterified with diazomethane (6,7). Finally, after removal of residual diazomethane, the extract is ready for GC analysis employing an electron capture detector (ECD).

The use of an ECD in the analysis of chlorophenoxy-acid herbicides may also lead to mis-identification and/or poor integration of the chromatographic peaks. Because the ECD responds to molecules that are deficient of electrons in their outer most energy shell, a wide variety of compounds can be detected. For example, compounds that contain atoms of Cl, Br, I, F, N, S, P, and O respond to the ECD. Compounds that contain pi bonds such as aromatic rings, also respond to the ECD. The most common interferences in the analysis of herbicides are organic acids that include chlorinated phenols and phthalate acid esters. However, with highly contaminated waste soils, many different interferences can be encountered. Additionally, ECDs are sensitive to GC oven temperature programming; Thus, causing chromatographic base-line rise that could interfere with peak integration.

The purpose of this study was to develop a new extraction and analysis method for chlorophenoxy-acid herbicides in soils and water that would meet the following criteria: 1) simple to use in that the method minimizes hydrolysis and clean-up steps; 2) replaces diethyl ether in favor of a less water-soluble, non-flammable, and non-explosive solvent; 3) maximizes the accuracy and precision of the analysis; 4) uses a specific detector that minimizes or eliminates interference from non-target substrates and avoids chromatographic base-line rise due to oven temperature programming.

MATERIALS AND METHODS

Extraction

Soil from 0- to 10-cm depth of a Larimer County Paoli (8) sandy clay loam was air-dried and reduced to a particle size of less than 2.0 mm. The soil had 24 g kg^{-1} organic matter, a pH of 7.7 (1:1 soil/water), an EC of 28 ds m^{-1}, and a CEC of 17.4 cmole kg^{-1}. An herbicide spiking solution was prepared in methanol and contained 25 μg mL^{-1} of Silvex (2,4,5-trichloropropionic acid), 2,4-D (2,4-dichlorophenoxy-acetic acid), Dalapon (2,2-dichloro-propanoic acid), 2,4-DB (4-(2,4-dichlorophenoxy)butyric acid), Dicamba (3,6-dichloro-2-methoxy-benzoic acid), Dichlorprop (2-(2,4-dichlorophenoxy)-propanoic acid), 2,4,5-T (2,4,5-trichlorophenoxy-acetic acid), MCPA (4-chloro-2-methylphenoxy-acetic acid), MCPP (2-(4-chloro-2-methylphenoxy)-propanoic acid isooctyl ester), and a surrogate, (2,4-dichlorophenyl-acetic acid).

A 0.5 mL aliquot of the herbicide solution was added to 100 g of soil and mechanically tumbled for 0.5 h at 32 rpm. The soil was then saturated with 1500 mL of reagent-grade water, pH adjusted to 12 with 6M NaOH, and mechanically tumbled for 0.5 h as previously described. The study was run in quadruplicate at an herbicide concentration of 125 μg kg^{-1}. Assuming a 100% partitioning of the herbicides from soil to water, the water concentration would be 8.3 μg L^{-1}. The soil extract was then treated with 18 μmol of $CaCl_2$ and allowed to stand for 10 min. A 500 mL aliquot of the soil extract was brought to 1000 mL with reagent water, adjusted to a pH of less than 2 with concentrated sulfuric acid, and extracted with dichloromethane in a continuous liquid extractor for 18 h. The solvent extract was then passed through acidified Na_2SO_4 and concentrated to less than 2 mL

using a Kuderna-Danish concentrator. Immediately prior to analysis, the extract was esterified with diazomethane and exchanged to hexane. The final extract volume was adjusted to 1.0 mL under a stream of purified nitrogen.

Analysis

All analytical standards and sample extracts were analyzed using an HP-5890 GC coupled with an OI-4420 electrolytic conductivity detector. The detector was set up in the halogen mode using a reactor temperature of 950° C. The reactant gas, H_2, was set at a flow rate of 100 mL min^{-1}. Chromatographic separations were performed using either a 30 M J&W DB-608 or DB-1701 fused silica megabore capillary column. The liquid phase film thickness used was 0.83 μm and 1.0 μm respectively. The carrier gas, He, was set at a flow rate of 8 mL min^{-1} and the makeup gas at 30 mL min^{-1}. The GC oven conditions were 65° C, for 4 min; 25° C min^{-1} to 150° C for 0.5min; 3° C min^{-1} to 225° C; 20° C min^{-1} to 270° C. Standard and sample extract injection volumes were 3 μL. Finally, chromatographic peaks were collected and integrated using a Maxima 820 data system developed by Dynamic Solutions.

RESULTS AND DISCUSSION

A summary of the chlorophenoxy-acid herbicides from soil and water is shown in Table 1. Accuracy used here, is defined as the mean percent recovery and error associated within a particular determination, and is calculated as:

$$\text{Mean Percent Recovery} = 100\ \frac{(\Sigma\ \text{Replicate Values}/\ \text{No. Values})}{\text{True Value}} \qquad (1)$$

and

$$\text{Mean Percent Error} = 100\ \frac{(\text{Measured Value} - \text{True Value})}{\text{True Value}} \qquad (2)$$

Precision, defined as the variability amongst the replicate values and measured as the percent relative standard deviation (RSD) or coefficient of variation is calculated as:

$$\text{Percent Relative Standard Deviation} = 100 \frac{\text{Standard Deviation of Measured Values}}{\text{Mean of Measured Values}} \quad (3)$$

Relatively high recovery and low RSD (coefficient of variation) was achieved as illustrated in Table 1. Only dicamba failed to be recovered above the 90% level and showed a mean percent error above 10%. However, the reported mean recovery and RSD for dicamba is consistent with results reported in other EPA analytical methods.

Figures 1 and 2 are chromatograms of the herbicide standards and a single soil extract analysis. It has been Our experience with the ELCD is that instrument detection limits are approximately 50 times lower than the standard concentration of 8.3 mg L^{-1} represented in Figure 1.

The ability to achieve such accuracy and precision is believed to be directly related to the following: 1) partitioning the salts of the herbicides directly from soil to water; 2) minimizing adsorption of herbicides to colloidal surfaces by flocculating the soil suspension with the addition of $CaCl_2$; 3) minimizing or eliminating further hydrolysis procedures for matrix clean-up purposes; 4) the use of a non-or low water-soluble extraction solvent such as dichloromethane; and, 5) using an electrolytic conductivity detector that is selective only for halogenated species and is unaffected from temperature programming of the GC oven as shown in Figure 2.

CONCLUSIONS

By performing a simple soil-water extraction under basic conditions and reducing the zeta potential of the soil suspension with

$CaCl_2$ to encourage flocculation, significant partitioning of chlorophenoxy-acid herbicides from soil to water is achieved. Further extraction of the flocculated soil suspension with dichloromethane, derivitization with diazomethane before solvent exchange, and analysis of the solvent extract using an electrolytic conductivity detector, yields accuracy and precision results that are equal or superior to those reported in EPA analytical methods.

ACKNOWLEDGMENTS

We are grateful to Bob Jump of ATI for performing the GC/ELCD analyses. We also would like to thank Drs. Ken Barbarick and John Tessari and Ms. Kristy Lynch for their review of this manuscript.

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(3) U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wasterwater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.

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(5) U.S. EPA, "Method 515.1. Determination of Chlorinated Acids in Water by Gas Chromatography With An Electron Capture Detector," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, 1990.

(6) Aldrich, Technical Information Bulletin No. AL-180.

(7) Black, T.H., The Preparation and Reactions of Diazomethane, *Aldrichim. Acta,* 1983, 16 (1), 3.

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Table 1

Single Operator Accuracy, and Precision

Herbicide	Spiked Soil Conc ($\mu g\ kg^{-1}$)	Detected Conc ($\mu g\ kg^{-1}$) Rep# 1	Rep# 2	Rep# 3	Rep# 4	Mean Percent Recovery	Mean Percent Error	Percent RSD
Surrogate	125	129	116	130	131	101	0.4	5.5
MCPP	125	123	106	125	122	96	4.8	7.7
DICAMBA	125	111	100	115	116	88	11.6	6.6
MCPA	125	113	106	121	119	92	8.2	5.9
DICHLORPROP	125	128	116	128	130	100	0.4	5.1
2,4-D	125	122	120	135	134	102	2.2	6.1
SILVEX	125	122	113	122	123	96	4.0	3.9
2,4,5-T	125	131	122	137	134	105	4.8	4.9
2,4-DB	125	135	127	136	136	107	6.8	3.3

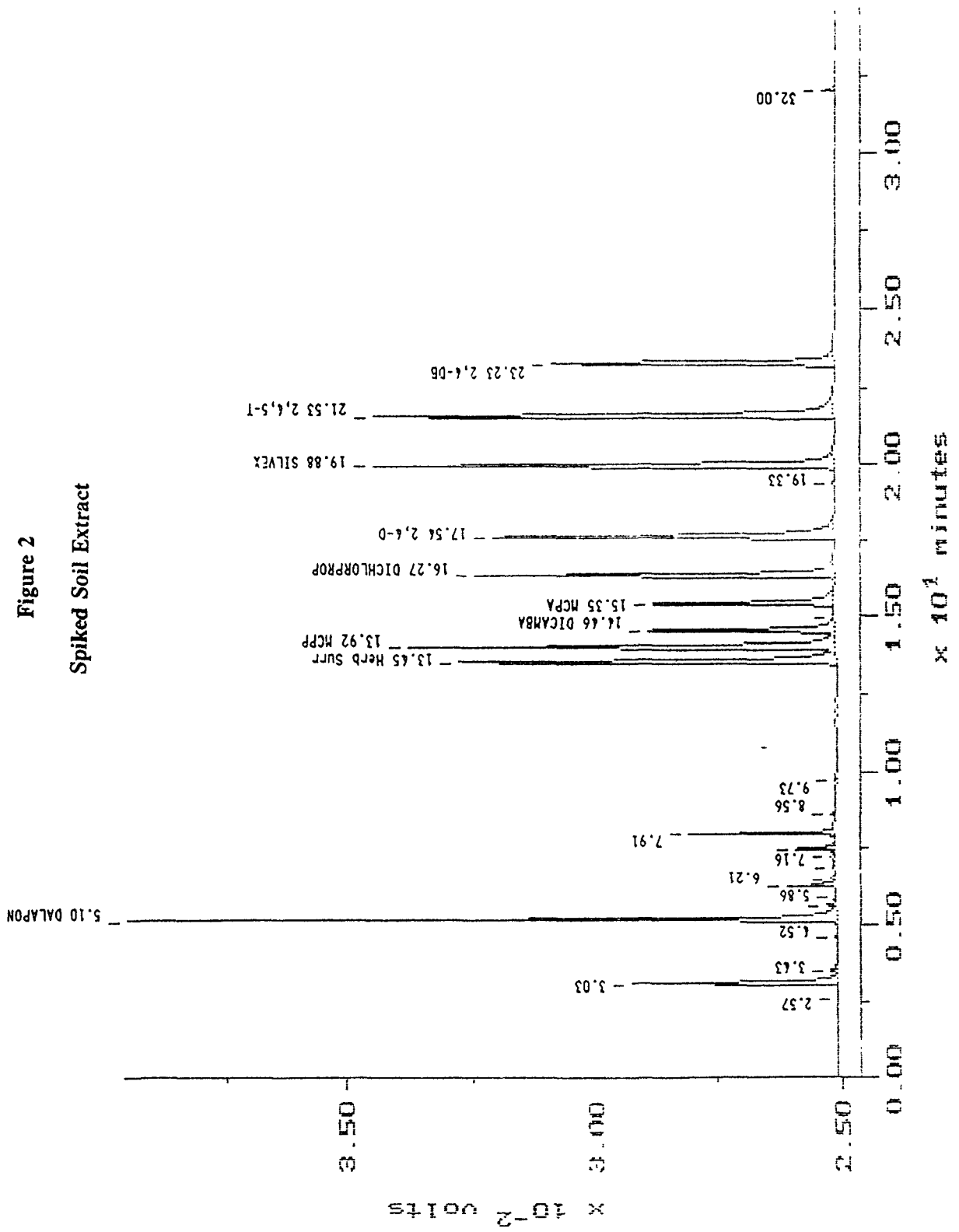

Figure 2

Spiked Soil Extract

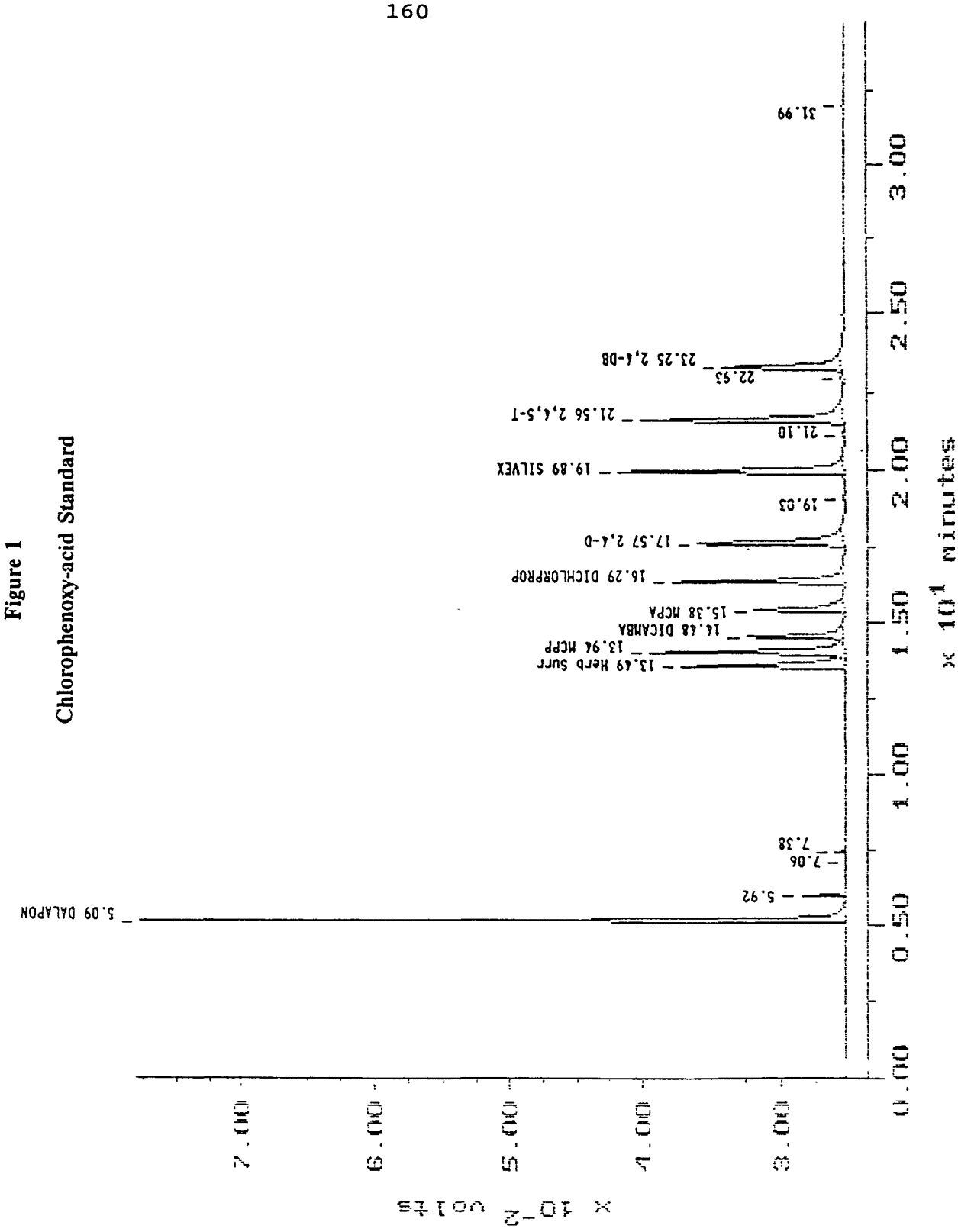

Figure 1

Chlorophenoxy-acid Standard

QUESTION AND ANSWER SESSION

MR. YOUNG: Yes, my name is Michael Young from NET, Atlantic.

I have a question regarding the hydrolysis step on your method. As I understand it, the hydrolysis step of Method 8150 is to convert naturally esterified forms, that is, the phenoxy acids that are not in the free acid state that are esterified either to natural alcohols or phenolic groups present in, say, humic matrix or something of that sort in the soil.

Are you sure from your analysis method that a half an hour shake at room temperature at pH2 will accomplish this hydrolysis and have you considered doing a method recovery study using esterified forms of your phenoxy acids in order to accomplish this?

MR. JACKSON: I haven't gone into any rigorous tests. Basically, what I've done is taken the free acids in a methanolic solution and spiked them into soil. The soil was calcareous so they readily formed a salt and then added the water and partitioned them. So, I don't really have any data to look at that.

MR. VANOPAL: My name is Howard Vanopal and I work at the Army Environmental Hygiene Agency at Aberdeen.

I've been doing some extensive work with this type of these herbicides like you have for the last couple of years and I've discovered a couple of things. In reference to the gentleman's other question, I also have grave doubts that this method will hydrolyze, for example, some of the long chain herbicide esters and these are the type that are used in agriculture. You have some of these esters that are quite long like isopropyl esters, propylene glycol, butyl ether esters. These require a fairly rugged hydrolysis with heat in order to completely work.

In reference to the dicamba, I think the problem with low recoverage is due to its volatility. It is far more volatile

than any of those others and you must take care when you do solvent transfers and things like this. Otherwise, you can get good recovery of it. But overall, your approach is somewhat similar to what we are working on.

MR. JACKSON: This method was basically tested only on the 8150 compounds and from the chemistry, it works very well on four carbon phenoxy acids and less. The higher carbons do have a problem. Since these were not the targeted compounds, they were not addressed and this method may not be applicable at all to those other ones that are being used.

MR. ELLEMAN: Dave Elleman of Columbia Analytical Services.

Have you actually done this in a real world sample, a side-by-side comparison between the two methods?

MR. JACKSON: In the laboratory, 8150 was practiced...before it was practiced commercially, the four replicate precision and accuracy test was done and the results were acceptable as to the method. That was done approximately two years ago and then this method here was developed, oh, about six to seven months ago and we took these results and compared them and these were equal or superior. So, we did do a side-by-side, but not at the same time.

MR. ELLEMAN: What I really was comparing is on a real world matrix, when you're actually taking a soil sample and you've done one soil sample by one method and the same soil sample by the other. We did some supercritical fluid extractions on hydrocarbons and it worked great in sand, but it didn't work a hoot on a real clay kind of sample. I wondered if that might play a role also in this tumbling kind of episode...get into the matrix with a water by comparison to using a real solvent to get into it.

MR. JACKSON: Well, the half hour tumbling time was arbitrary. We had to start somewhere and I was looking to reduce method time. So I started at a half hour and

when I got the results back for that typical soil, and that's a sandy clay loam that has morilanite type clays in it. It also has some very simple minerals, kaolanites and then gypsite and things like that. So there's lots of active sites on that soil that you can get hydrogen bonding or you can get bridging. You get absorption and the half hour seemed to work real well. I haven't found a soil yet that the surrogate recovery, and that's all basically that we can monitor in real samples...that the surrogate recovery was low. We've been getting very good surrogate recoveries.

MR. ELLEMAN: But there's a difference between a spike and a surrogate. It's already dissolved in some methanol by comparison to the soil itself because everything is already contaminated inside of it for a side-by-side comparison.

MR. JACKSON: Yes, I don't really have any exact side-by-side comparisons. Based on the results here, what I tried to do was show that this method was equivalent or better to the regulatory method.

MR. TELLIARD: Thank you, Cary.

MR. TELLIARD: Our next speaker is Dr. Hodgeson. He's from our laboratory in Cincinnati, EMSL, Environmental Monitoring Methods Systems...

MR. HODGESON: Laboratory.

MR. TELLIARD: Laboratory. I always forget the systems. He's going to talk to us on the measurement of acid herbicides and disinfection products in aqueous media. Jimmy?

ADVANCED TECHNIQUES FOR THE MEASUREMENT OF ACIDIC HERBICIDES AND DISINFECTION BYPRODUCTS IN AQUEOUS SAMPLES

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ABSTRACT

Acidic herbicides and haloacetic acids are two important classes of organic acids, which may occur in aqueous matrices and are subject to current and pending regulations, respectively. The haloacetic acids are formed along with the trihalomethanes as ubiquitous components of chlorinated drinking water supplies. The techniques currently used for monitoring both classes of compounds are complex liquid-liquid extraction procedures, which employ large volumes of organic solvents. The hydrophilic nature of many of these analytes places a significant limit on method performance. Another problem with current gas chromatographic methods is the use of diazomethane as the methylation reagent. Many laboratories are reluctant to use this reagent, even when applied in a relatively safe manner.

This presentation will discuss our recent work on liquid-solid extraction as a promising means for both simplifying the methodology and improving method performance. The acidic herbicides may be extracted from aqueous samples by either reverse phase or ion exchange media. The hydrophilic haloacetic acids are efficiently recovered by ion exchange. Recovery data will be presented for packed columns as well as commercially available filter disks. Data will also be presented on the use of acidic methanol as an alternative reagent to diazomethane. This reagent provides recoveries comparable to diazomethane for phenoxyacid herbicides and haloacetic acids.

INTRODUCTION

Among the most complicated of EPA drinking water methods is 515.1 for acid herbicides. This paper will discuss a much simplified approach for this class of analytes, as well as an improved means for the measurement of haloacetic acids in drinking water. The latter are ubiquitous components of chlorinated supplies and are subject to regulation under EPA disinfection byproduct rules in the 1994-1995 timeframe. Several of the acid herbicides are currently regulated and more are subject to future drinking water regulations.

A brief summary will be given of the current methodology for acid herbicides (EPA 515.1) and haloacetic acids (EPA 552). These methods are published in EPA drinking water manuals available from the National Technical Information Service. Two major means for the simplification and improvement of these methods will be discussed. These are the use of liquid-solid extraction (LSE) for sample pre-concentration and the use of acidic methanol for methylation as an alternative to diazomethane. Many laboratories in this country have been reluctant to use diazomethane, even when provided with the quite safe micromolar procedure of Method 515.1. As a point of emphasis, the two techniques discussed here are still in the developmental stage. When completed, these procedures will be published in the open literature and will be available to the public as EPA Methods 515.2 and 552.1 for the acid herbicides and haloacetic acids respectively.

DISCUSSION

ACID HERBICIDES: The analytes of 515.1 are listed in the slide presentation. These include the commonly employed phenoxyacid herbicides, some phenolic compounds and benzoic acid derivatives, bentazon and dalapon (2,2-dichloropropanoic acid). Several of these compounds were not determined quantitatively by this method during the National Pesticide Survey because of poor precision, namely acifluorfen (blazer), chloramben, dalapon and 4-nitrophenol. The latter compound does not methylate and does not belong in the analyte list of 515.1 or the new 515.2 discussed below. Dalapon is a hydrophilic analyte, which does not partition favorably by liquid-liquid extraction or by the reverse phase LSE procedure of 515.2. It is efficiently extracted from water by anion exchange LSE and has logically been included in the analyte list for the new LSE procedure for the haloacetic acids (552.1). Both acifluorfen and chloramben are efficiently recovered and quantitatively determined by the reverse phase LSE method outlined below.

Method 515.1 begins with an aqueous phase hydrolysis step at pH 12 to convert commercial ester forms of the herbicides to the free acids. At the basic pH the acids are present as anions and

the aqueous sample is washed with methylene chloride to remove potentially interfering neutral and basic organics. After acidification, the 1 liter sample is serially extracted with ethyl ether. Drying of the ether extract with sodium sulfate is a tedious step with the potential for analyte losses. The ether volume is reduced to 1-2 mL by Kuderna-Danish evaporation with a solvent exchange to methyl-tert-butyl ether (MTBE). A florisil clean-up of the extract is included to remove potential interferences from, e.g., high humectant ground water. The acids are methylated by a safe procedure employing micromolar amounts of diazomethane. The analytes are determined quantitatively by gas chromatography with an electron capture detector (GC-ECD). Overall, this is a tedious, time-consuming method requiring a high level of operator skill. Even a skilled operator is limited to approximately six samples a day for the sample preparation step alone.

Two mechanistic options are available for the extraction of acid herbicides from water, anion exchange and reverse phase extraction on a hydrophobic substrate. We have done sufficient work on anion exchange to demonstrate feasibility. However, reverse phase extraction is a simpler approach. Of the reverse phase options, extraction by 3M Empore 47mm disks is faster and more efficient than by extraction cartridges. We have successfully employed both C-18 and the newer resin disks. The resin disks provide somewhat better efficiency and certainly faster extraction times than C-18.

An outline of the procedure is given in the slide tables. Anhydrous sodium sulfate (20% w/w) is added to a 100 mL sample and the sample pH is adjusted to 1.0 with reagent grade HCl. The disks are conditioned by sequentially passing through the disk 20 mL 10% methanol in MTBE, 5 minutes air (under vacuum), 20 mL methanol and 20 mL reagent water. The sample is then extracted without allowing the disk to dry and under a vacuum of 5 inches Hg. The disk is air dried under vacuum for 20 minutes and eluted with two 2 mL aliquots of 10% methanol in MTBE. Approximately 8 mL of MTBE is used to rinse the sample bottle, frit and funnel. The combined MTBE extract is dried through a wide bore Pasteur pipet packed with anhydrous sodium sulfate (described in Method 552). The sample volume is reduced to approximately 4 mL under a nitrogen purge and the sample methylated by the diazomethane technique of Method 515.1 or 552.

All of the data in the slide tables was obtained with a sample volume of 100 mL and a concentration factor of 20. Larger sample volumes and concentration factors are feasible. However, a significant drop in recovery was observed for some of the analytes at a sample volume of 1 liter. The determination of optimum sample volume and concentration factor for overall method performance are parameters yet to be determined.

Representative recovery data are presented in three slide tables. These tables compare C-18 versus resin for unsalted

reagent water, C-18 versus C-18 salted, and the effect of washing the sample bottle for a salted high humectant ground water. Several conclusions can be drawn from these data. Salting the water sample is necessary for optimum recovery and this salting largely washes out the significant differences between C-18 and resin recoveries for unsalted reagent water. The recovery data on fortified ground water show that high humectant levels do not adversely affect recovery. These data also indicate that the florisil clean-up procedure of Method 515.1 will not be required. The disk appears to effect sample clean-up in that a substantial portion of the humics appear to pass through without retention. Any humics retained are apparently not eluted with MTBE. This same table illustrates the importance of rinsing the sample bottle. The reagent water data on 5-hydroxy-dicamba is suspect, possibly because of a problem with the fortification standard used. We believe this analyte is recovered greater than 60% and the ground water data is supportive.

The data indicate that all of the analytes may be recovered sufficiently, with the exception of Dalapon. Method 515.2 will be written to require the extraction of aqueous standards to correct for extraction efficiencies. Dalapon is too hydrophilic to be collected by reverse phase and it is thus included in the anion exchange procedure for haloacetic acids discussed below.

HALOACETIC ACIDS AND DALAPON: While not as complicated as Method 515.1, Method 552 also requires serial extraction with MTBE and evaporation of the considerable excess solvent. The latter must be accomplished by a gentle nitrogen purge because of the volatility of the monohaloacetic acids. The acids are methylated by the same diazomethane procedure used in Method 515.1 and analyzed by GC-ECD. A skilled analyst is still limited to 6-8 samples per day.

The anion exchange extraction procedure was developed with a number of objectives in mind - method simplification and pollution prevention (i.e., eliminate evaporation of large volumes of solvent), development of a much needed method for the regulated analyte, Dalapon, and inclusion of a simple alternative methylation procedure to diazomethane. While method development has not been completed at this time, accomplishment of these objectives appear imminent. Accomplishment of the latter is particularly satisfying in that methylation is efficiently accomplished directly in the elution solvent, acidic methanol.

A brief summary of the method is given. The anion exchanger is analytical grade AG 1-X8 resin, 100-200 mesh, from Bio-Rad. The commercial resin is washed liberally with deionized water and stored under deionized water. One mL solid phase extraction tubes (Supelco) are loaded with the resin dropwise as a slurry until a height of 10 mL wet resin is attained. The resin is maintained under water until used. The column is conditioned by sequential addition under vacuum of 10 mL aliquots of methanol, reagent water, 1 M HCl in methanol, reagent water, 1 M NaOH and

reagent water, without allowing the bed to dry. A 100 mL sample is extracted immediately after addition of the last reagent water aliquot. The analytes are eluted with a small aliquot (2-4 mL) of H2SO4/methanol and quantitatively converted to their methyl esters by simply heating this aliquot with a small aliquot of MTBE added as cosolvent for 30 minutes at 50°C. For a 4 mL aliquot of 10% H2SO4/methanol (the probable final eluant of choice), the methyl esters are partitioned into the organic phase by the addition of 10 mL of 10% by weight of sodium sulfate in reagent water. The organic phase is removed and the aqueous phase is washed with several more small aliquots of MTBE to a total volume of 8-10 mL. The small excess of solvent is removed by nitrogen purge to a final volume of 5 mL for a concentration factor of 20. The analytes are analyzed by GC-ECD.

The bar graphs shown in the slide tables show the recoveries obtained for all the analytes with 4 successive 2 mL aliquots of 25% H2SO4/methanol. The recovery is essentially maximized after the first two aliquots and the final method version will probably call for a single 4 mL aliquot of H2SO4/methanol. The next slide table shows some preliminary haloacetic acid and Dalapon recoveries in reagent water and simulated high ionic strength water. The presence of high concentrations of competitive anions is expected to present the greatest challenge to the method. These data in fact show reduced recovery for the monohaloacetic acids. We have since shown that the anion responsible for the displacement is sulfate. One solution for high sulfate waters is sample dilution, but this would raise MDL's. Another possibility is sulfate clean-up with cation exchange resins in the BaII form, but this approach has not been tested.

ESTERIFICATION EFFICIENCIES: The remaining slide tables provide esterification efficiencies using both diazomethane and the H2SO4/methanol technique. Absolute esterification efficiencies have been determined for those analytes, for which methyl esters are available. Esterification is quantitative for all the haloacetic acids, Dalapon, all the phenoxyacids and a few others. A critical factor for the acidic methanol procedure is the addition of an organic cosolvent. This serves to shift the equilibrium esterification reaction to the right.

Toluene was added as a cosolvent for the esterification data shown for the acid herbicides. Only the true, relatively strong acids are methylated by this procedure. No yield is obtained for phenolic compounds. In our current procedure for Dalapon and the haloacetic acids, the elution solvent is 4 mL of 10% by volume of H2SO4 in methanol and 2.5 mL MTBE is added prior to heating for 30 min. at 50°C. Under these conditions, the esterification is quantitative for all of the analytes, contrary to the data shown in the final data table.

QUESTION AND ANSWER SESSION

MR. McCARTY: To remind questioners, please come to the microphone and identify yourself and your affiliation.

MR. VANOPAL: Yes, I've got one question on this. Is this designed to do just acid forms of herbicides or can you do all forms that would be commonly found in the environment?

MR. HODGESON: The techniques that I've been talking about, this liquid-solid, you first would have to do the same thing on the front end of the method. You'd have to hydrolyze. You know, I didn't address that, but you'd still have to hydrolyze these acids. By the reverse phase, you could collect these compounds, but then you're going to have to still do something before you do your final analysis in terms of a hydrolysis step probably.

MR. VANOPAL: Okay.

MR. HODGESON: The halo acids, of course, are not a problem. They're present only as a free acid.

ADVANCED TECHNIQUES FOR THE ANALYSIS OF ACIDIC HERBICIDES AND DISINFECTION BYPRODUCTS IN AQUEOUS SAMPLES

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CONTENTS

Organic Acids by GC

- CURRENT DRINKING WATER METHODS
  - Method 515.1 - Herbicides
  - Method 552 - Haloacetic Acids
- LIQUID SOLID EXTRACTION
  - Herbicides - Ion Exchange
    - Reverse Phase
  - Haloacetic Acids - Ion Exchange
- ALTERNATIVE ESTERIFICATION REAGENTS
  - Acidic Methanol
  - Performance Relative To Diazomethane

METHOD 515.1(CURRENTLY)

1 Liter sample pH 12 with NaOH
Shake 1 hour to hydrolyze derivatives

Solvent wash with CH2 Cl2

Adjust pH 2 with H2SO4 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

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 552 DESCRIPTION
Haloacetic Acids

- SAMPLE COLLECTION AND PRESERVATION
  - 100 mL Sample Dechlorinated with NH4CL
- SAMPLE CLEANUP
  - Alkalination and Organic Wash
- LIQUID-LIQUID EXTRACTION
  - Acidification
  - Extract with Methyl-t-butyl-ether(MTBE)
- EXTRACT CONCENTRATION
- ESTERIFICATION WITH DIAZOMETHANE
  - Micromolar Procedure
- CAPILLARY GC-ECD ANALYSIS

HALOACETIC ACIDS

Analyte List

ANALYTE	FINISHED(1)	RAW(1)
Monochloroacetic Acid	0.82	NA
Monobromoacetic Acid	NA	NA
Dichloroacetic Acid	7.3	42
Trichloroacetic Acid	4.5	98
Bromochloroacetic Acid	3.8	3.2
Dibromoacetic Acid	0.7	1.4
2,4-Dichlorophenol	NA	NA
2,4,6-Trichlorophenol	NA	NA

1)Concentration in chlorinated sample, uG/L

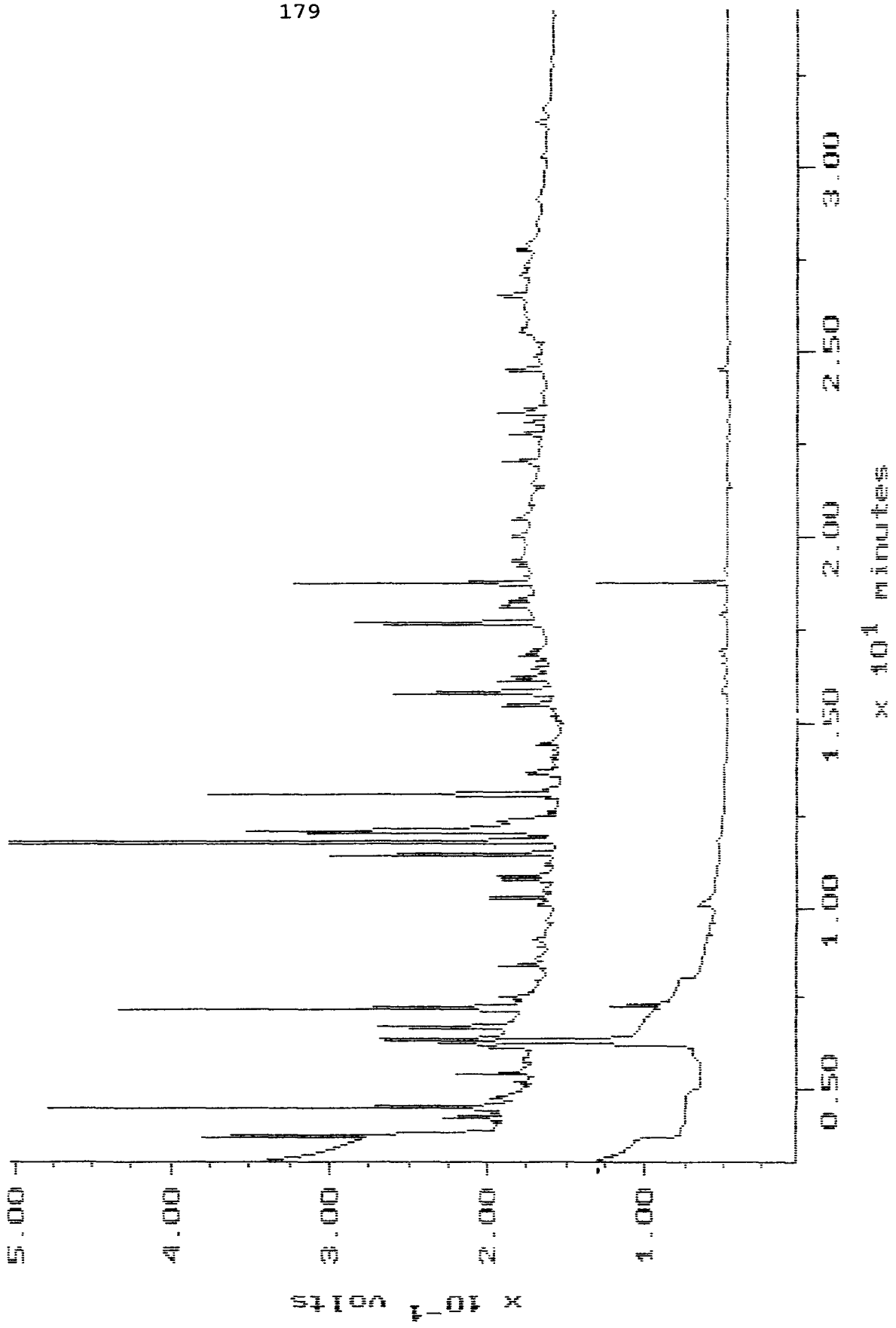
LIQUID-SOLID EXTRACTION OPTIONS
Organic Acids/Phenols

- Anion Exchange versus Reverse Phase
- Extraction Columns versus Teflon-based Disks
- MATRIX : Silica versus Styrene/Divinylbenzene Copolymer(PS-DVB)
- ANION EXCHANGE : Strong Sites(Quartenary Ammonium) verus Medium(Tertiary Ammonium)
- REVERSE PHASE : C-8 And C-18(silica based), Pure PS-DVB Resin Particles

ORGANIC ACIDS

Anion Exchange Procedure

- Condition Anion Exchanger - Disk or Cartridge
- Extract 100 mL Water Sample, pH > 7
- Elute with Acidic Methanol(ca. 4 mL)
- In situ Methylation, 15-60 min. at 50-90 C
- Phase Separation, Reagent Water + Solvent
- Analysis by Capillary Column GC-ECD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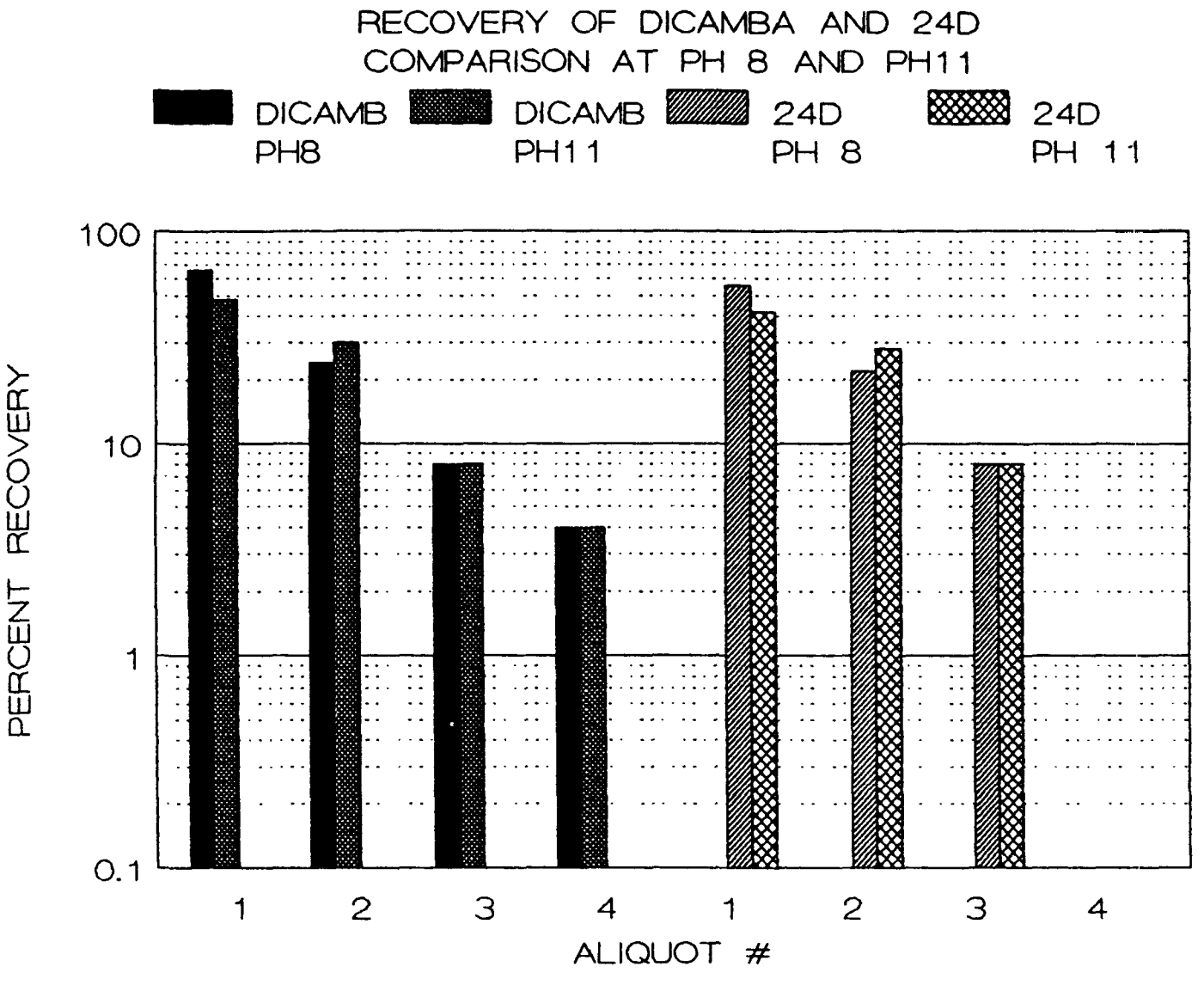
4.00
3.00
2.00
1.00
x 10^-1 volts
0.50
1.00
1.50
2.00
2.50
3.00
x 10^1 minutes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COMPARISON AT PH 8 AND PH11
DICAMB PH8
DICAMB PH11
24D PH 8
24D PH 11
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10
1
0.1
PERCENT RECOVERY
1
2
3
4
1
2
3
4
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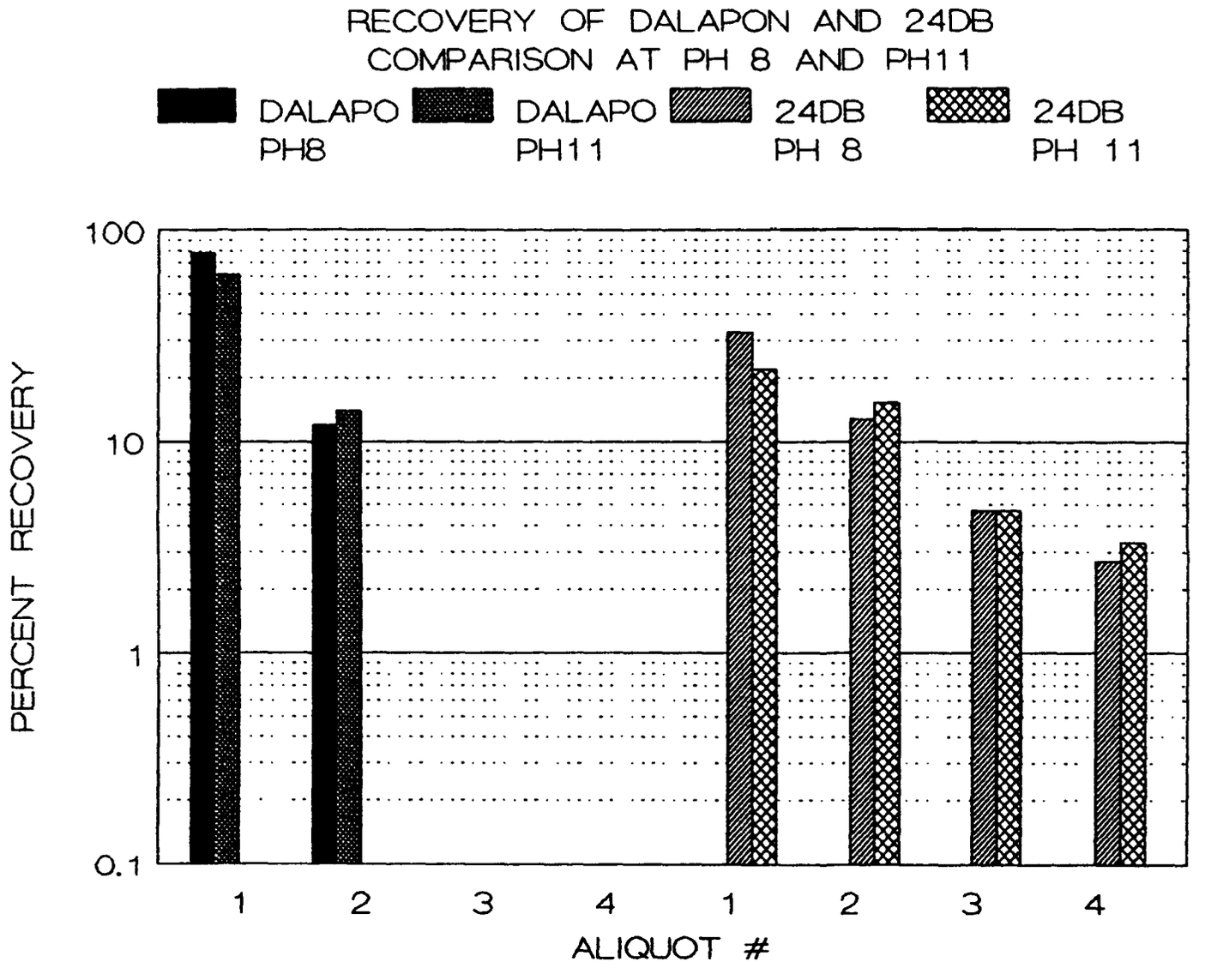
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COMPARISON AT PH 8 AND PH11
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DALAPO PH11
24DB PH 8
24DB PH 11
100
10
1
0.1
PERCENT RECOVERY
1
2
3
4
1
2
3
4
ALIQUOT #

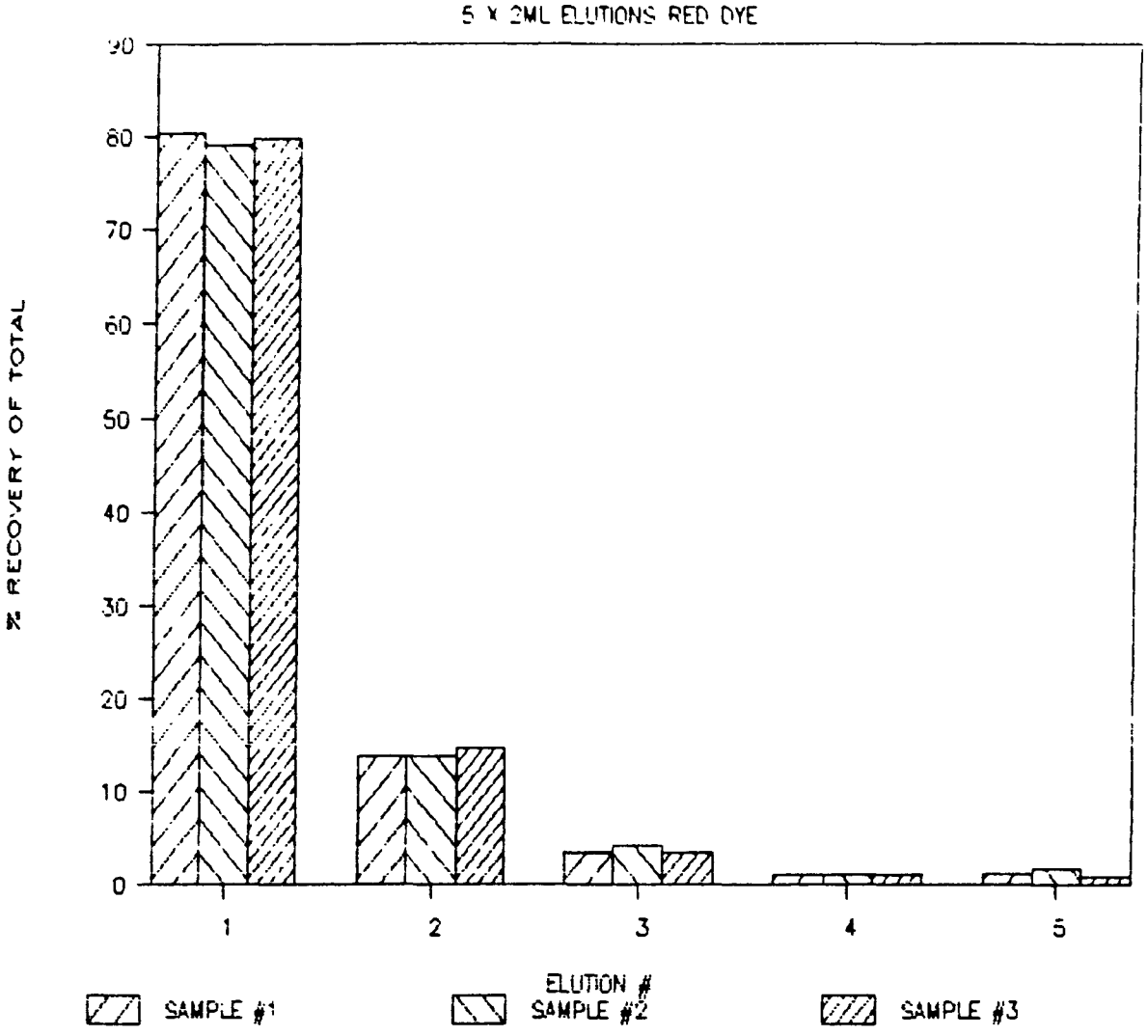
ORGANIC ACIDS

Reverse Phase Extraction(1)

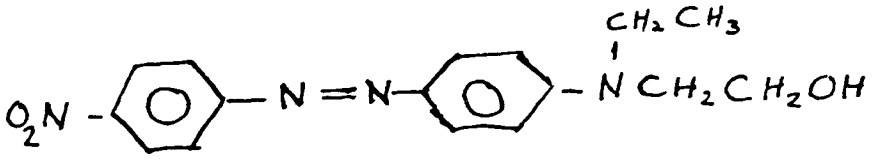
- Condition Disks
- Extract 100 mL Sample at pH < 2
- Elute with 2-4 mL of Polar Solvent(e.g. MTBE)
- Esterify Extract with Diazomethane or H_2SO_4/Methanol
- Analysis by Capillary Column GC-ECD

1) EMPORE C-8 or C-18 Extraction Disks

C8 EXTRACTION DISK ELUTION TEST



RED DISPERSE 1 OPTICAL PROBE



λ_{max} = 480 nm

HERBICIDES REVERSE PHASE EXTRACTION - DISKS
Reagent Water Recoveries ± Rel. Std. Dev.

ANALYTE	C-18	PS-DVB Resin
Dalapon	0	42 ± 25
Pentachlorophenol	69 ± 4	70 ± 2
Chloramben	8 ± 11	3 ± 15
5-Hydroxydicamba	0	0
Picloram	49 ± 19	74 ± 7
Dinoseb	72 ± 16	75 ± 5
Blazer	77 ± 20	82 ± 5
Dicamba	73 ± 13	71 ± 14
2,4-D	86 ± 12	83 ± 6
Silvex	73 ± 14	74 ± 15
2,4,5-T	76 ± 11	75 ± 14
2,4-DB	81 ± 13	80 ± 14
Dachthal	53 ± 17	99 ± 8
Bentazon	0	9

Triplicate Analyses at 5 µg/L

HERBICIDES REVERSE PHASE EXTRACTION - DISKS
Reagent Water Recoveries ± Rel. Std. Dev.

ANALYTE	C-18	C-18, Salted
Dalapon	0	28 ± 2
Pentachlorophenol	69 ± 4	75 ± 8
Chloramben	8 ± 11	68 ± 12
5-Hydroxydicamba	0	9 ± 6
Picloram	49 ± 19	77 ± 14
Dinoseb	72 ± 16	76 ± 13
Blazer	77 ± 20	85 ± 8
Dicamba	73 ± 13	95 ± 8
2,4-D	86 ± 12	77 ± 4
Silvex	73 ± 14	77 ± 7
2,4,5-T	76 ± 11	91 ± 11
2,4-DB	81 ± 13	128 ± 10
Dachthal	53 ± 17	74 ± 8
Bentazon	0	86 ± 8

Triplicate Analyses at 5 µg/L

HERBICIDES REVERSE PHASE EXTRACTION - DISKS
Selected Analyte RW Recoveries ± RSD

ANALYTE	C-18, Salted	Resin, Salted
Dalapon	28 ± 2	31 ± 30
Chloramben	68 ± 12	77 ± 7
5-Hydroxydicamba	9 ± 6	8 ± 40
Picloram	77 ± 14	99 ± 21
Dachthal	74 ± 8	97 ± 5
Bentazon	86 ± 8	71 ± 5

Triplicate Analyses at 5 µg/L

HERBICIDES REVERSE PHASE EXTRACTION - DISKS
Ground Water Recoveries ± Rel. Std. Dev.

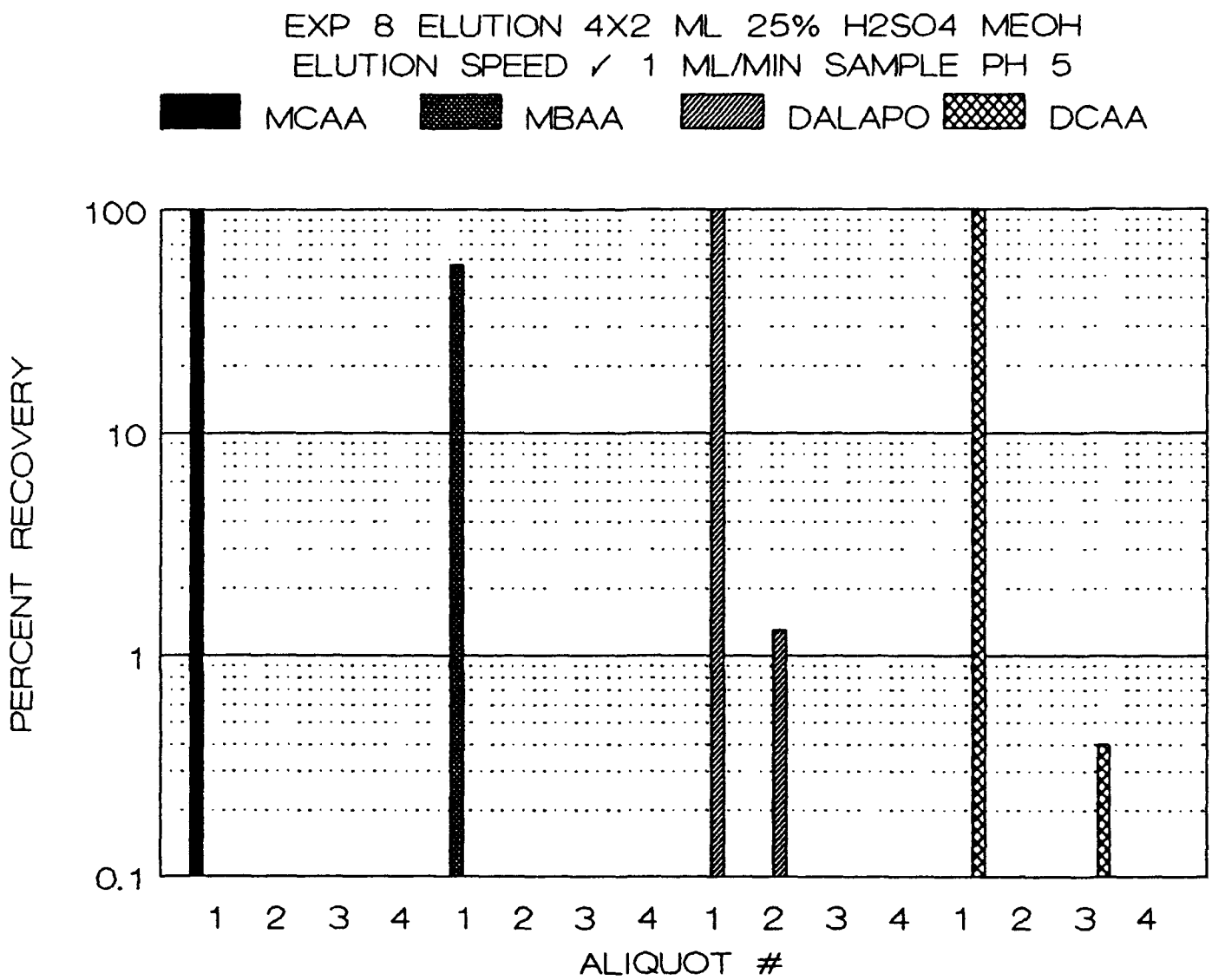
ANALYTE	C-18, S	C-18, S,+Wash
Dalapon	10 ± 69	34 ± 31
Pentachlorophenol	72 ± 4	81 ± 8
Chloramben	64 ± 11	73 ± 6
5-Hydroxydicamba	64 ± 8	71 ± 20
Picloram	102 ± 9	122 ± 10
Dinoseb	90 ± 18	89 ± 7
Blazer	116 ± 8	130 ± 12
Dicamba	88 ± 12	90 ± 9
2,4-D	98 ± 11	100 ± 7
Silvex	81 ± 16	87 ± 9
2,4,5-T	96 ± 13	100 ± 9
2,4-DB	108 ± 13	121 ± 8
Dachthal	63 ± 13	84 ± 10
Bentazon	88 ± 11	93 ± 8

Triplicate Analyses at 5 µg/L, High Humectant Fla. GW

ORGANIC ACIDS

DOWEX STRONG ANION EXCHANGE RESIN PROCEDURE

- 100 mL WATER SAMPLE, pH = 7
- AG1-X8 RESIN COLLECTION, HYDROXIDE FORM, 0.2 mL VOLUME
- ELUTION WITH 2 mL 10% HCL/METHANOL
- SOLVENT EXCHANGE TO MTBE
- ESTERIFICATION
- CAPILLARY COLUMN GC-ECD


EXP 8 ELUTION 4X2 ML 25% H2SO4 MEOH
ELUTION SPEED ✓ 1 ML/MIN SAMPLE PH 5
MCAA
MBAA
DALAPO
DCAA
100
10
1
0.1
PERCENT RECOVERY
1 2 3 4 1 2 3 4 1 2 3 4 1 2 3 4
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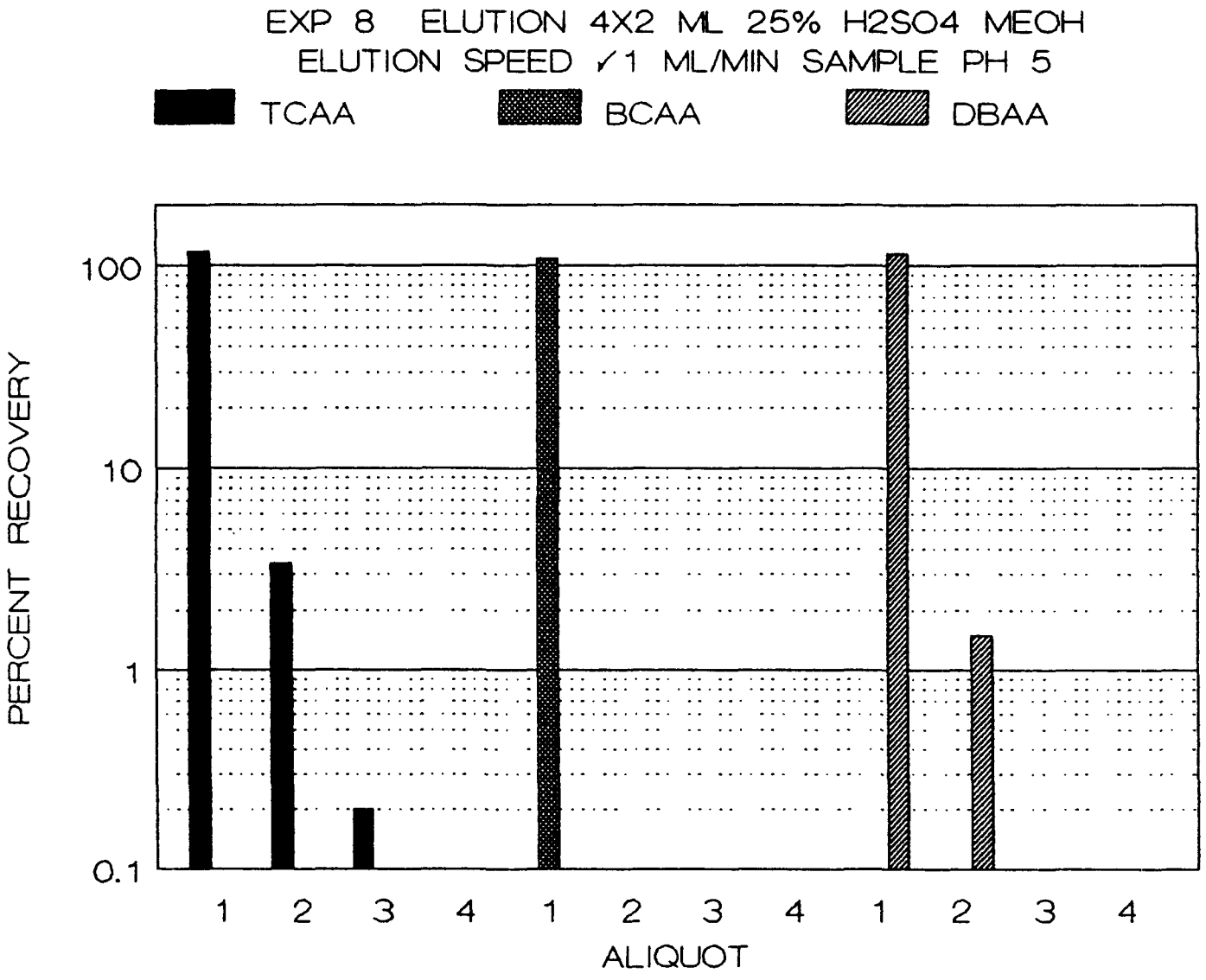

EXP 8 ELUTION 4X2 ML 25% H2SO4 MEOH
ELUTION SPEED ✓1 ML/MIN SAMPLE PH 5
TCAA
BCAA
DBAA
PERCENT RECOVERY
100
10
1
0.1
1 2 3 4 1 2 3 4 1 2 3 4
ALIQUOT

ABSOLUTE ESTERIFICATION EFFICIENCIES
Diazomethane Methylation

Method 515.1 Analytes	Recovery, %(1)
Chloramben*	107
Dalapon	95
Dicamba	99
Dinoseb*	118
2,4-D	107
2,4-DB	106
2,4,5-T	100
5-Hydroxydicamba	25
Pentachlorophenol*	96
Picloram	89
Silvex	106

1) Based on Methyl Ester Standards

SULFURIC ACID/METHANOL PROCEDURE

- RCO2H + CH3OH(ACID) = RCO2CH3 + H2O
- Reduce Extract Volume to 1-2 mL(MTBE,Toluene)
- Add 1 mL 35% H2SO4/Methanol
- React 15-60 min. at 50-90 C
- Add 5 mL Reagent Water(salted)
- Extract to 2-5 mL Organic Phase

ESTERIFIICATION EFFICIENCIES
Acidic Methanol(1)

Method 515.1 Analyte	Recovery, %
Dalapon	95
3,5-Dichlorobenzoic Acid	111
MCPA	111
Dichloroprop	98
Pentachlorophenol	0
Chloramben	0
5-Hydroxydicamba	<5
Picloram	78
Dinoseb	0
Acifluorfen	67
Dicamba	21
2,4-D	89
Silvex	97
2,4,5-T	89
2,4-DB	87
Dachthal	0
Bentazon	0

1) 35% H2SO4/Methanol, 1 hr, 90 C, Toluene Extract

FEDERAL REGISTER CITATIONS

Acidic Methanol Methylation

Analyte Cited	Type of Regulation	Methylates?
2,4-D	Regulated	Yes
Silvex	"	Yes
Pentachlorophenol	"	No
Dalapon	Unreg., Monitoring	Yes
Dicamba	"	Marginal
Dinoseb	"	No
Picloram	"	Yes
Bentazon	1991 Priority List	No
Dacthal	"	No
Dicamba	"	Marginal
Acifluorfen	"	Marginal
2,4,5-T	"	Yes
Haloacids	"	Yes

1) Yes:>80% ; Marginal:20-80% ; No:<20%

MR. McCARTY: Our next speaker this afternoon is going to be Bob Beimer from S-Cubed Laboratories. For those of you who have been here before, Bob is a fixture at Norfolk. As a matter of fact, we're not sure he ever actually goes home. That's where the tan comes from, I think.

He's going to be speaking today on temperature-programmable on-column injector for GC/MS work. He got off easy because Telliard would have raked him over the coals.

MR. BEIMER: I have long been convinced that the EPA believes all detectors are linear and a corollary to that premise is that detector response curves, all pass through the origin.

It's a frustrating fact that virtually all of the methods EPA publishes require response linearity of the detectors. I'm associated mainly with mass spectrometers and I guess I've been doing GC/MS now for about twenty years, as a result of this, I've determined that mass spectrometers response is not linear.

In a continuing effort to improve detector response, we have recently focused our attention on at the front end of the system to try to determine if the injector on the gas chromatograph has an influence on linearity.

I have pleaded with various instrument manufacturers and think maybe they're starting to listen and will at least look at linearity of response as an important aspect of selling hardware. Reliability, dependability, precision, accuracy, resolution, sensitivity, all of this is important, but nobody's really bothered with response linearity.

As a part of this effort, we embarked on a program in association with Hewlett-Packard to evaluate a cool on-column injection system. The main focus of this effort was response linearity.

We have compared the traditional splitless injection system to the new on-column system by using a single instrument. The instrument was a Hewlett-Packard 5970 MSD, equipped with a splitless injector on one side and an on-column injector on the other. We literally set the instrument up in the splitless mode, ran a calibration curve and then turned around and took the same column and hooked it into the cool on-column injector and ran another curve to compare the two.

I'm going to give you just a brief tutorial on what a splitless injector looks like compared to an on-column injector. Slide 1 shows a Hewlett-Packard splitless injector. In the

splitless injector, you shoot your sample onto a liner, which is located inside the injection area here, which is typically heated to 300 degrees centigrade. A small flow of gas goes down through here and onto the column. When the purge is off, the gas is diverted out in this direction and you don't have a purge gas blowing through the injector. As a result a slight flow of one milliliter a minute or so pushes the sample onto the column and then after some pre-determined period of time, a couple of minutes, usually this valve opens and allows the purge gas to flow through the injector. At this point anything that's left in the injector is blown out through this second line. The technique results in some discrimination, both thermal discrimination because of the volatility of your compounds, but also if you don't get all of your sample out of that injector while the purge valves are closed, it's going to be blown away. Some of the data that I'll show you later will illustrate this graphically.

Slide 2 is a schematic of an on-column injector. It's a very low mass injector so that it can be rapidly heated or cooled. In use, it is cooled to the same temperature as the starting point of the column program. It's then temperature programmed with the column so that it heats as the column heats and is cycled back for the next injection.

There are a lot of guides in here. This area right in here serves as a needle guide. There's another needle guide located about here so that the needle from the syringe actually gets onto the column. You're dealing with some fairly fine needles and they tend to be a bit prone to bending, so guiding them is extremely important.

At this point down here, the needle deposits the sample directly onto the column. About two meters of 0.5 mm ID uncoated fused silica column is butt connected to a traditional .2 millimeter ID DB5 GC column for determination of semi-volatile analytes.

As a result all of the sample is placed on the column

directly as a liquid. It disburses over this two meter uncoated column and then as the temperature is programmed, it's accumulated at the front of the analytical column and chromatographed.

The cool on-column injector has some fundamental advantages and I'll just touch on a couple of these.First of all, if your analyzing thermally-labile materials, the low temperature minimizes degradtion. The injector is never any hotter than the GC column and you're not having to vaporize the sample in the injection port.

The amount of sample that can be injected using cool-on column is not as high as that which you can get for the splitless injector, but when doing trace analysis, it's certainly adequate.

Slide 3 is a chromatogram of a series of base neutral compounds, the typical CLP/BNA standard, run using splitless injection. Please note the relative intensities of the later eluting compounds. These two right here are higher molecular weight polynuclear aromatics eluting late from the column.

Slide 4 is the same sample using cool on-column injection you can see the relative height of these peaks is significantly greater. In fact, there's a general trend to higher transmission of material as the retention time increases. More data will point this out graphically. It should be noted that this is not a distortion in the cool-on column; it's because the splitless injector discriminates against higher boiling materials. That is they are not getting onto the GC column during the injection process and they're being blown away when the split valves open.

Now, to get back to my favorite topic, linearity. Slide 5 is the response of phenol as a function of concentration. This axis is the area generated for the quantitation mass for phenol, versus the concentration at five points...20, 50, 80, 120 and 160. The sad part about this curve is, as I was hoping that I would be showing this type of curve for the splitless injector, and a straight line going through the origin

for the on-column injector. But, as you can see, they both have the same shape. I started this study with a wonderful plan about how this was going to solve the world's problems. But the fact is, the non-linearity in this case is not associated with the injector.

The RSDs that you see printed on the curves are the traditional EPA calculation for response. The percent RSD of 18 for the on-column injector and 4 for the splitless injector is a measure of the linearity of the lines. I should point out here is that phenol is a fairly polar compound. It elutes early in the chromatographic program and the splitless injector and the on-column injector yield primarily the same results.

A little later in the chromatogram, fluoranthene exibits much the same behavior. RSDs are a little different, but, not significantly. One is five and one is eight. They certainly meet all EPA criteria.

But if you notice the absolute intensity of the peaks for the on-column injector, they are almost twice that of the splitless injector. What that's saying is that even for a compound like fluoranthene, the splitless injector is discriminating by about a factor of two.

It should be pointed out that these runs were set up so that all voidables were controlled as closely as possible. We literally took the column off of one injector and put it onto the other. We changed no mass spectrometer conditions, used the same auto sampler for the two runs and ran them essentially back-to-back.

I should also point out that the splitless injector has a pressure programming feature and as a part of that pressure programming feature, we were pressure bursting the front end of the chromatographic run so that we would help drive as much of the material out of the injector and onto the column as possible. We were able to put this pressure ramp in the front end of the chromatogram to help transfer as much of the material onto the column as possible. The standard injector on the HP-5890 does

not have this feature and therefor the factor of two is probably closer to eight or ten in terms of the transmission efficiencies, especially for the later eluting compounds.

Pentachlorophenol behaves similarily to fluorthane.

Finally, I thought I'd look at a base. This is 4-nitroanaline and the results again are about the same. You see this difference of about a factor of two. If I were to show the late eluting polynuclear aromatics, such as the benzo/pyrenes and perylene, there would be about a factor of three, using the pressure burst injection and without it, a factor of eight to ten.

Not everything is rosy, however. This is total ion trace for three of the analytes at three different concentrations. This is 20 nanograms, 60 stet nanograms and 160 nanograms. The three analytes in this trace are benzyl alcohol, 2-methylphenol. Between the 20 and the 80 peak broadening. At 160 there's radical peak broadening occurring. We puzzled over this and puzzled over this for sometime, played with the length of the pre-column and finally when all else failed consulted the literature. Sure enough, this was expected. It is suggested that if you use a thicker film column and this problem will go away. Sure enough, we put in a thicker film column and the problem went away.

This is basically column overload because of the injection efficiency of the on-column. We were using thin film columns initially and had to change to thick film.

This slide shows the same set of data with splitless injection some peak broadening is observed as you go to higher concentrations but the peak broadening is much less than with the on-column.

As a result of what we have seen, we are limiting on column to low concentration work, drinking water type analyses as opposed to hazardous waste and higher concentration materials.

The title of this talk mentioned on-column injection and the HP 5971 GC/MS. When I put the title together, I really

thought we were putting the on-column system on a 5971. It turns out we put it on a 5970 and used the 5971 for looking at low concentration, high sensitivity analyses such as Method 525.

I've got four slides here I'll just run through quickly to show that the 5971 works quite well for this application.

I'm not sure the 5971 is the answer for Method 525 since the detection limits are challenging.

This is a linear regression response curve for phenanthrene. This axis is the amount ratio that represents the amount of material injected, divided by the amount of the internal standard. The internal standard concentration is five and the concentrations injected were from .1 up to 10 or two orders of magnitude of concentration range.

This axis is the area ratio on the area of the analyte, divided by the area of the internal standard. This results in some normalization correcting for injection vandelites.

Method 525 allows for a little flexibility in terms of response since you can use linear regression or even a polynomial without having to force the origin. As a result it is probably one of the more progressive EPA methods. Phenanthrene is an easy material; it chromatographs very well and has a very strong molecular ion.

This is a spectrum of the low concentration point of the curve, 100 picograms of the phenanthrene. Note the molecular ion is clearly visible.

Hexachlorobenzene, a little tougher compound to deal with. It's got a lot of chlorine on it and doesn't like to form positive ions. Again, the response is reasonably linear. Again, it fit with the linear regression.

Finally, the spectrum. A lot more grass on the baseline. You've really got the gain cranked up on the instrument in order to achieve these detection limits.

We've been pleased with the system. It's worked out very well and I think there are some real applications for it.

QUESTION AND ANSWER SESSION

MR. PRONGER: Greg Pronger, National Environmental Testing.

Have you tried HP's nanoliter adapter in the injector?

MR. BEIMER: I don't even know what it is.

MR. PRONGER: One of our laboratories has been playing with the same technique for the standard 8270 type of analysis and what they've found is they get almost scary straight lines when they go down to a .2 microliter injection, taking advantage of the better transfer of analyte into the column. They're making .2 microliter to .5 microliter injections. Some of the problems with the percent RSDs just completely went away. They saw no increase in loss of the more sensitive analytes like 4-nitrophenol, 4-nitroanaline, penta-chlorophenol. They remained with very strong response at the low end standards and very good results that way. It might be something worth looking at in that aspect.

MR. BEIMER: We'll try.

MR. BEACH: Richard Beach from Hydro-Systems.

On your cool on-column work, you're showing the difference in the response curves there. Was that with the pressure programming or without? Did you try just cool on-column without the pressure?

MR. BEIMER: The cool on-column was without pressure programming. MR. BEACH:That's what you were showing there?

MR. BEIMER: Yes.

MR. BEACH: And so if you used pressure...

MR. BEIMER: The only pressure programming that was used was on the splitless injector. We did not use any of the other pressure programming features.

MR. BEACH: So you didn't use the

pressure programming on the on-column work either?

MR. BEIMER: Right.

MR. BEACH: Thank you.

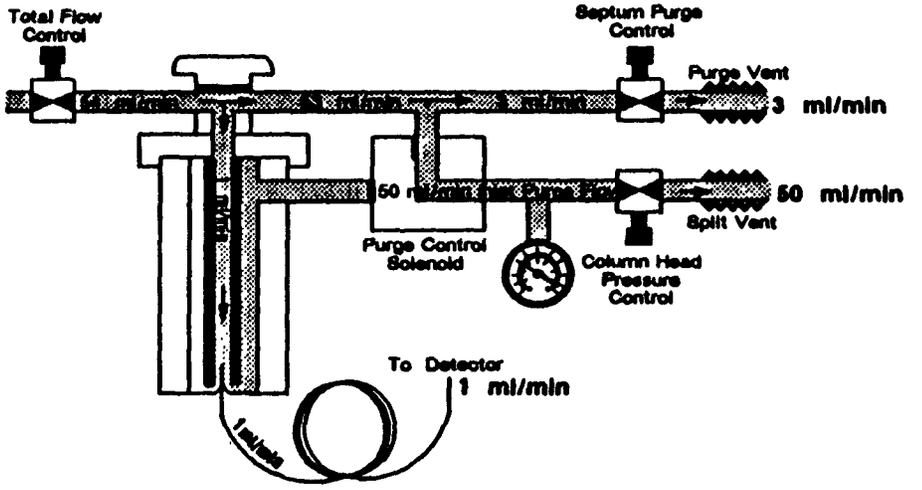
EVALUATION OF THE HP5971-A GC/MS EQUIPPED WITH A TEMPERATURE-PROGRAMMABLE ON-COLUMN INJECTOR

Robert Beimer
Mark Hatcher
Turner Smith

S-CUBED, SAN DIEGO, CALIFORNIA

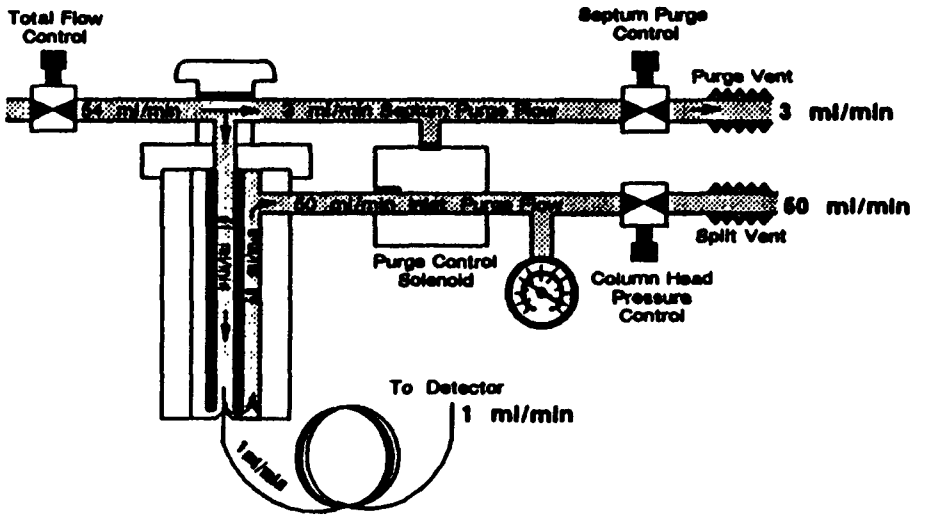
MAXWELL
S-CUBED Division

Splitless Inlet
Purge OFF



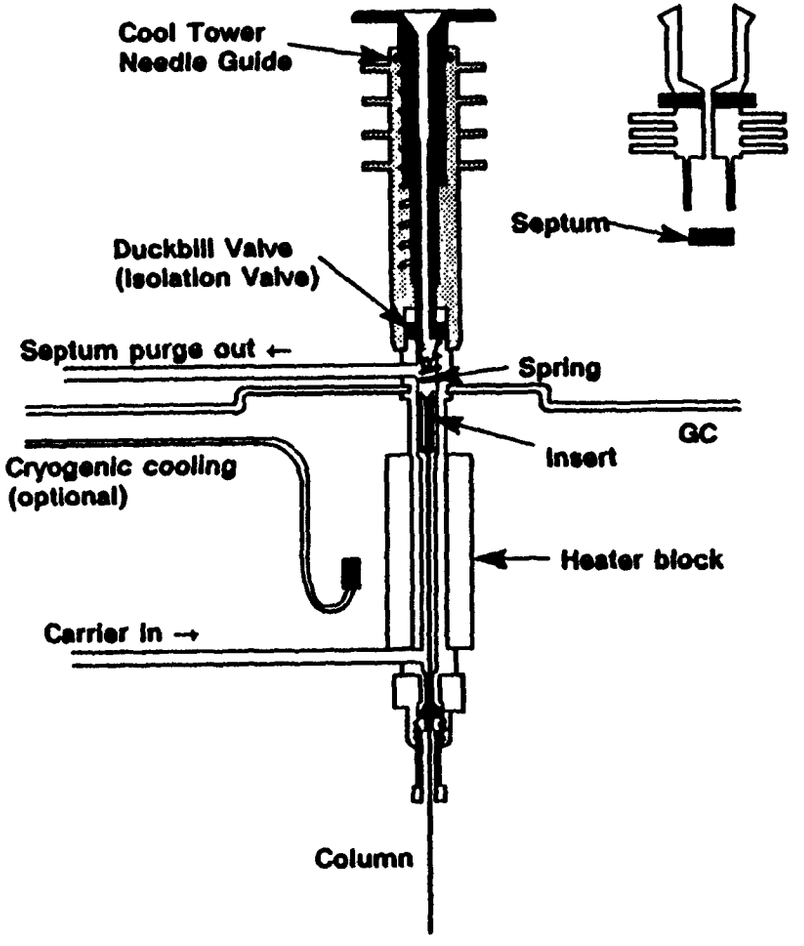
HEWLETT PACKARD

Splitless Inlet
Purge ON



HEWLETT PACKARD

Cool On-Column Inlet



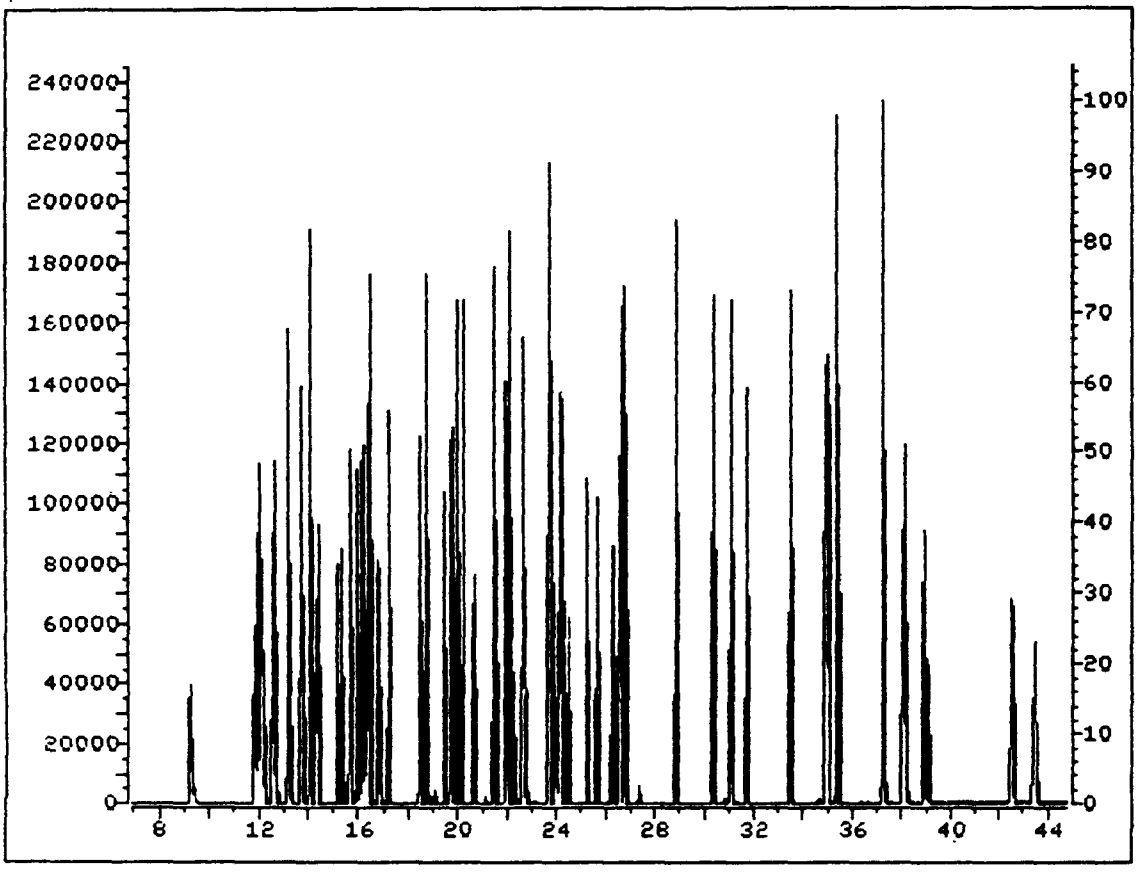
HEWLETT PACKARD

GC Capillary Inlet Comparison

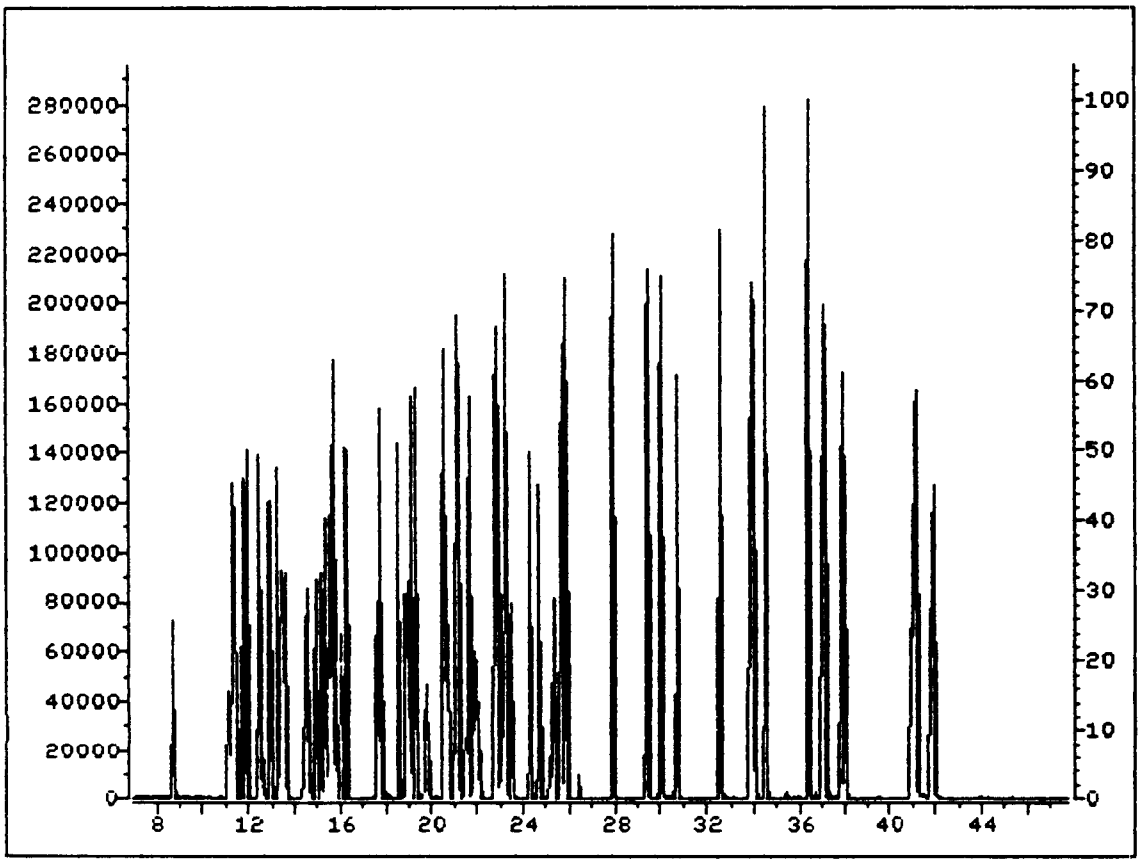
		Split	Splitless	Cool On-Column
Sample Attributes	Concentration	High	Low	Medium-Low
	Minimun Thermal Stability Required	Medium	Medium-High	Low
	BP Range	Medium	Low-Medium[2]	Wide
	Typical Injection Volume	Large	Small-Medium	Small-Medium
Inlet Features	Vaporizing	Yes	Yes	No
	Discrimination Possibility	High[1]	Medium	Low
	Sensitivity to Sample Cleanliness	Low	Medium	High
	Usefulness for Trace Analysis	Good	Better	Best
	Reproducibility with Manual Injection[1]	Good	Good	Best
Other	Ease of Use	Easy	Moderate	Moderate[1]
	Minimum Column id (mm)	0.1	0.2	0.2

1. Can be improved with automatic injection.
2. The "splitless" effect only occurs for solutes with BPs slightly higher than that of the solvent.

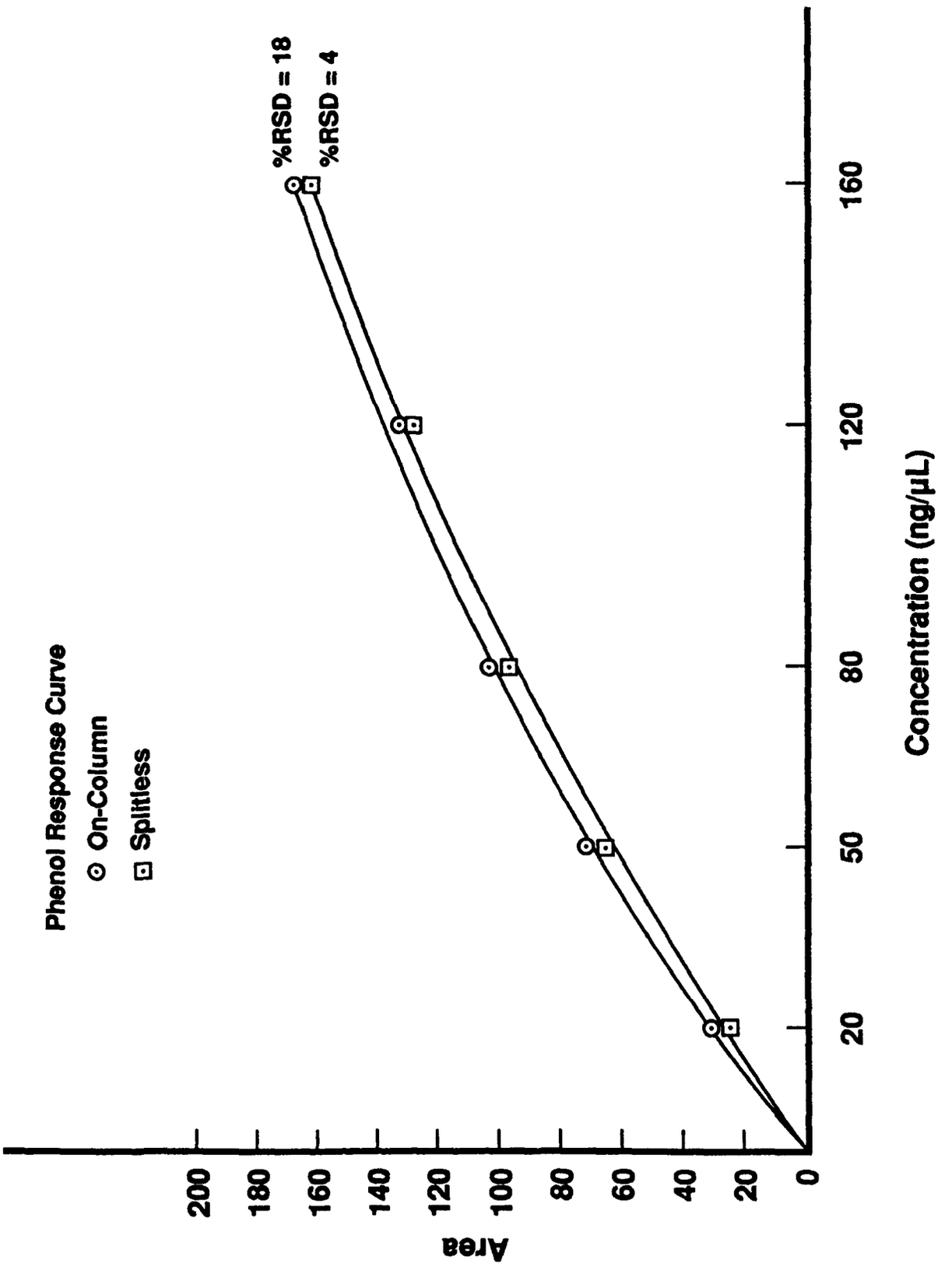
HEWLETT PACKARD

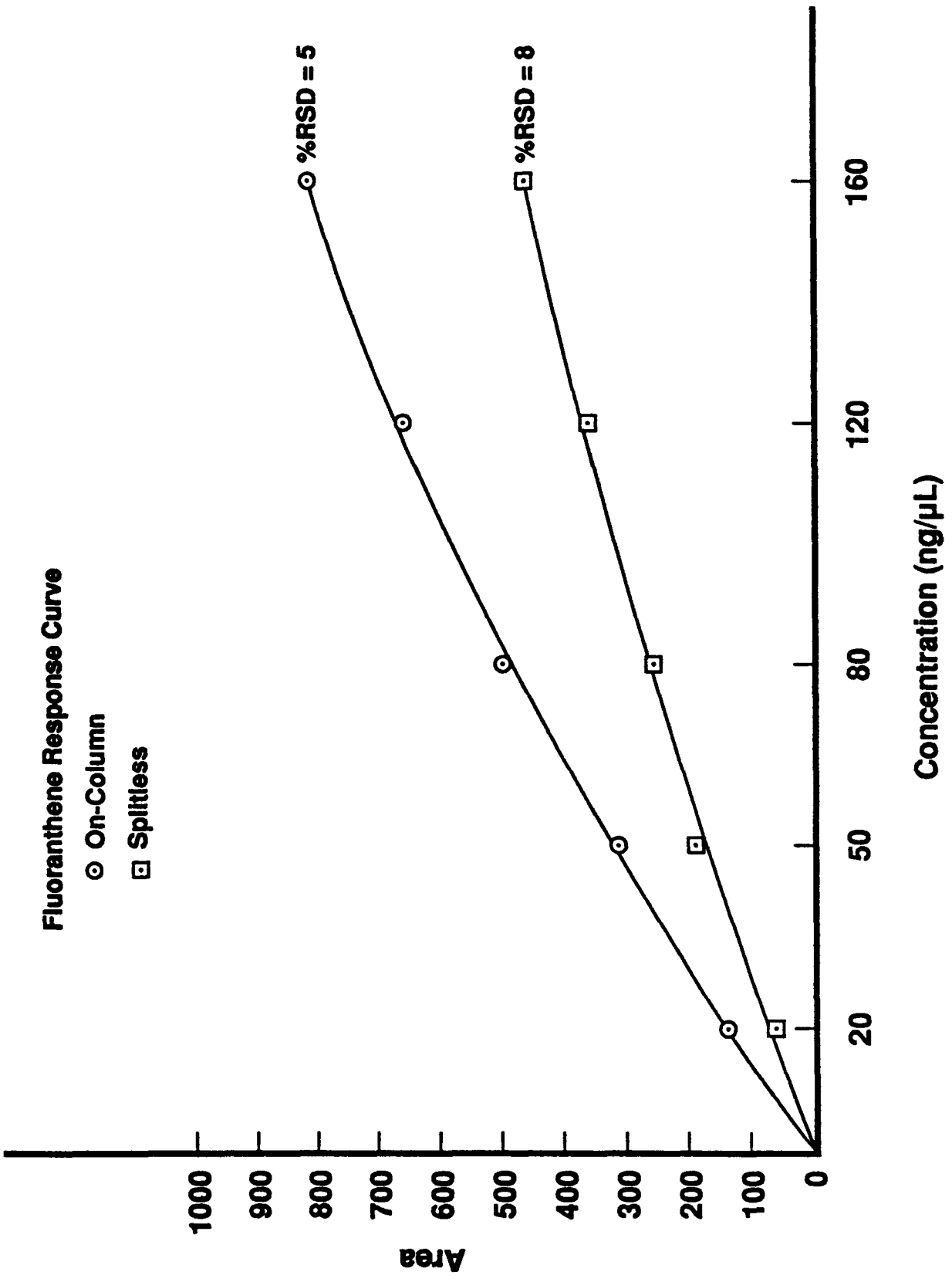


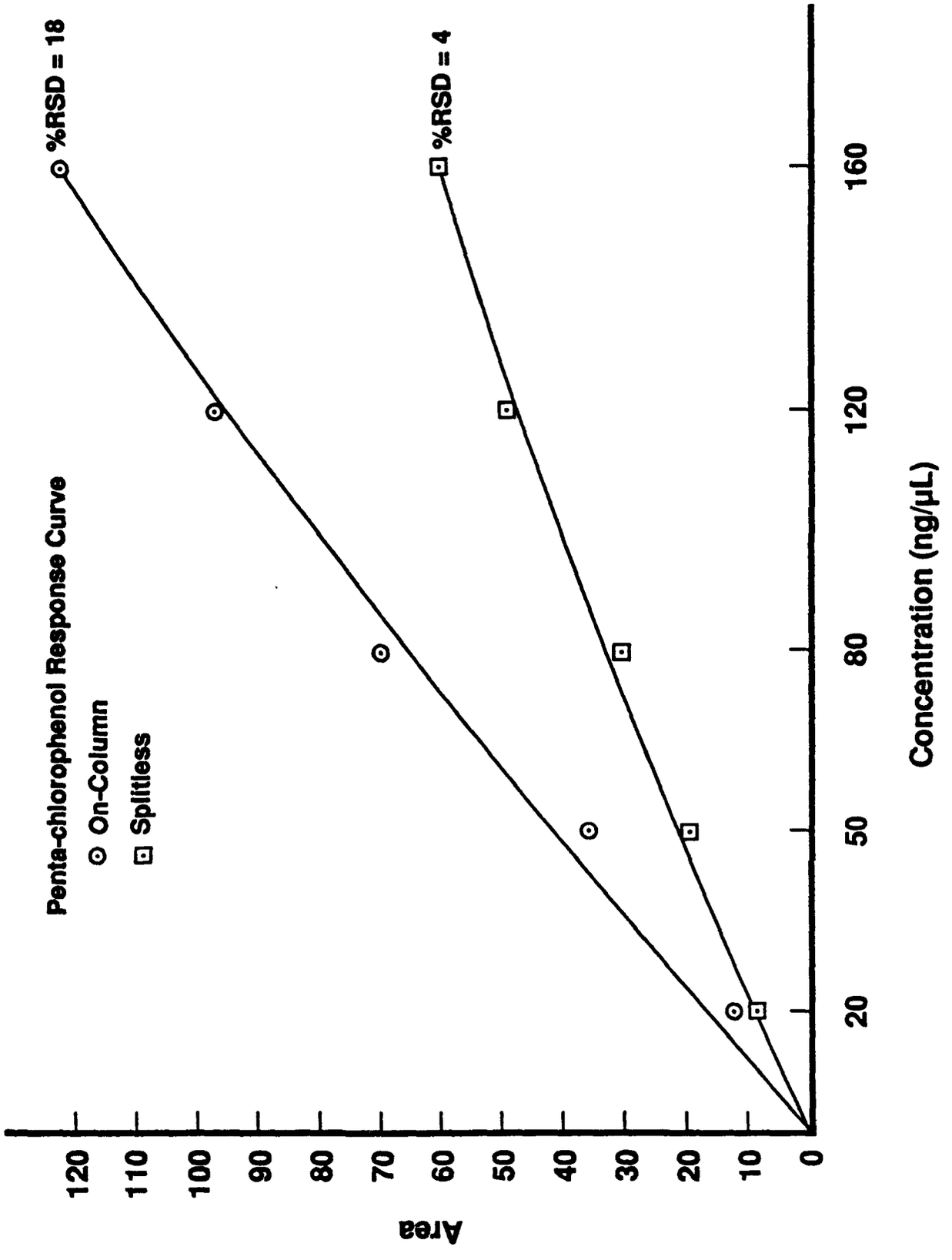
SPLITLESS CHROMATOGRAM (80 ng)

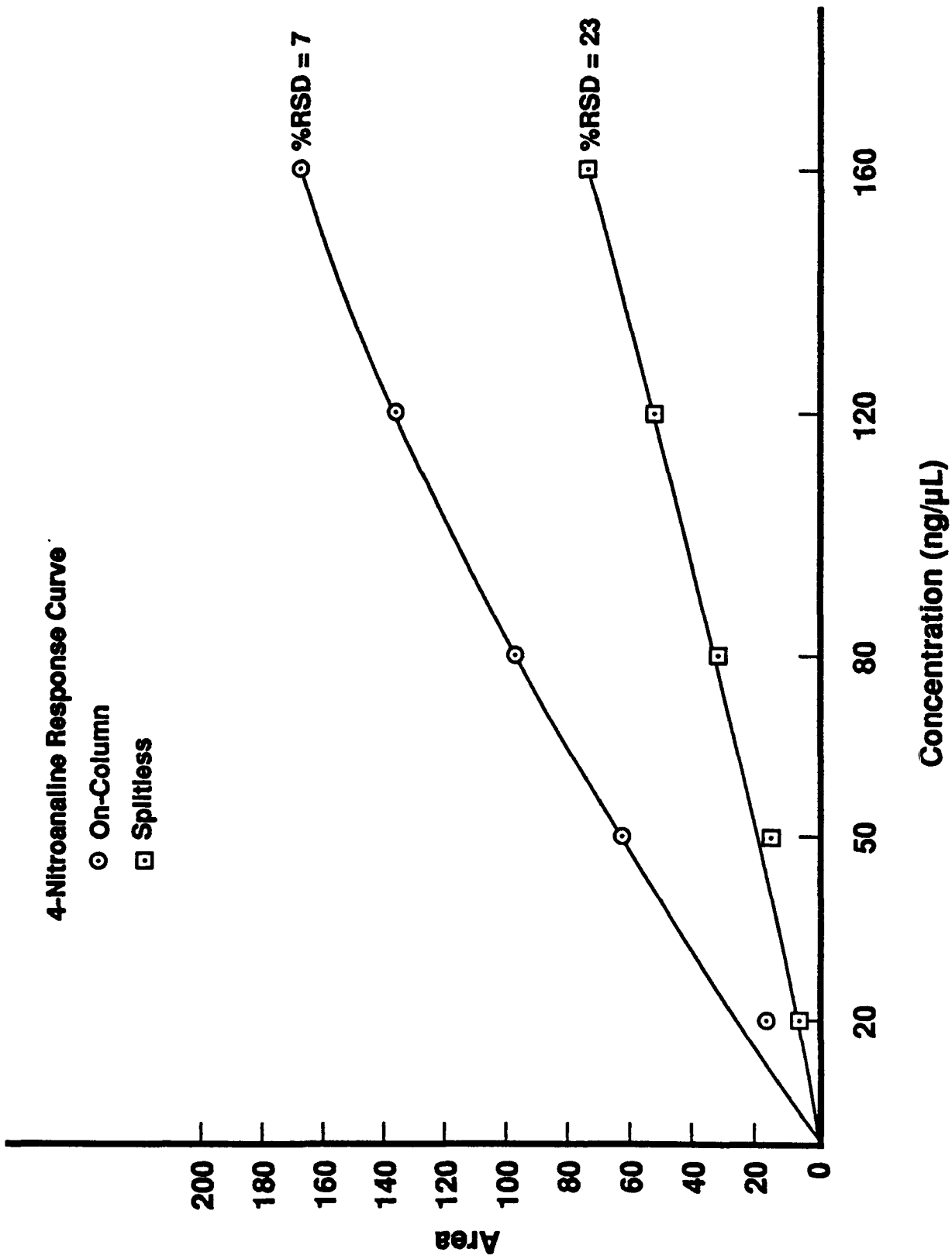


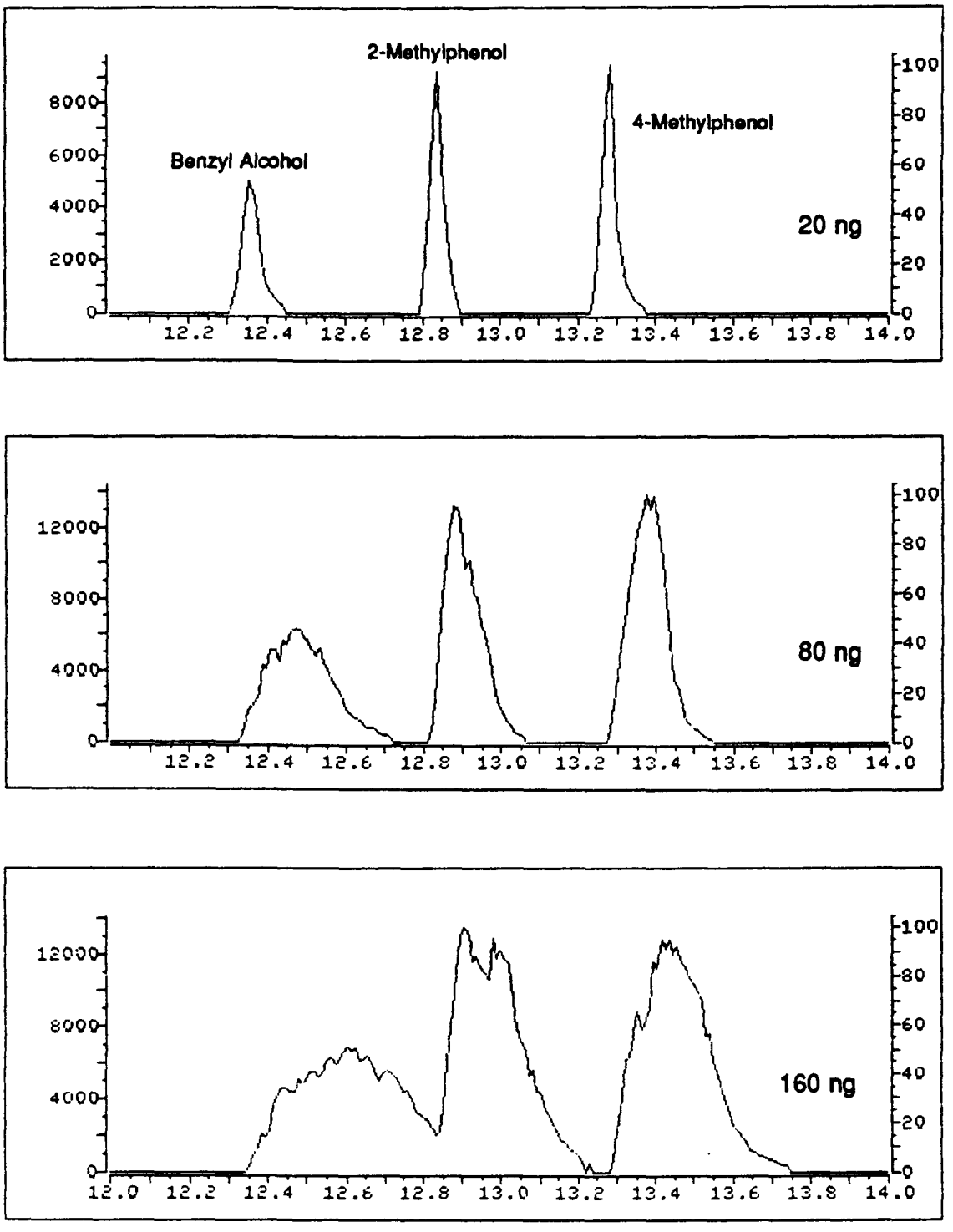
ON - COLUMN CHROMATOGRAM (80 ng)


Phenol Response Curve
On-Column
Splitless
%RSD = 18
%RSD = 4
Area
0
20
40
60
80
100
120
140
160
180
200
20
50
80
120
160
Concentration (ng/µL)

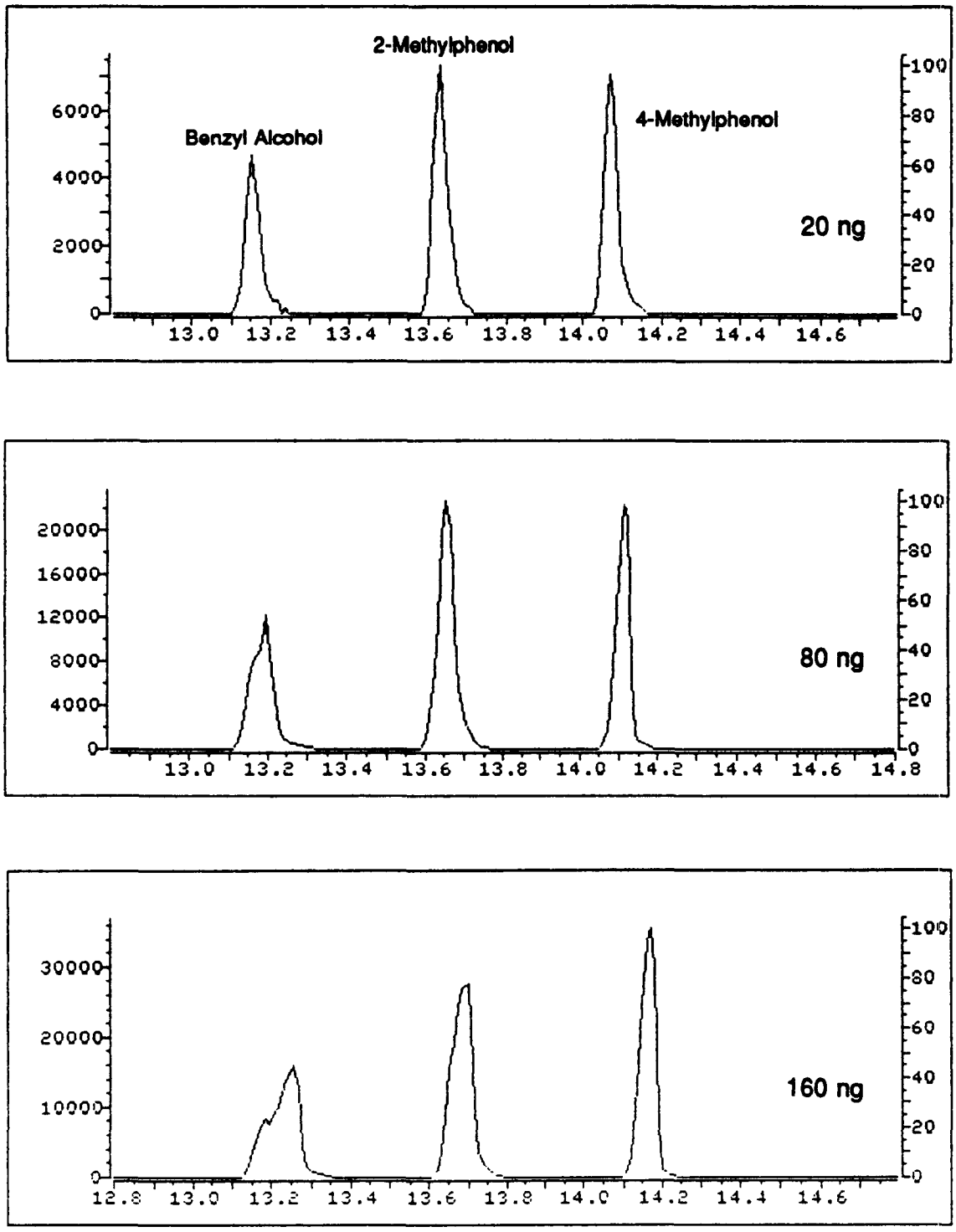

Fluoranthene Response Curve
On-Column
Splitless
%RSD = 5
%RSD = 8
Area
1000
900
800
700
600
500
400
300
200
100
0
20
50
80
120
160
Concentration (ng/µL)


Penta-chlorophenol Response Curve
On-Column
Splitless
%RSD = 18
%RSD = 4
Area
Concentration (ng/µL)
0
10
20
30
40
50
60
70
80
90
100
110
120
20
50
80
120
160

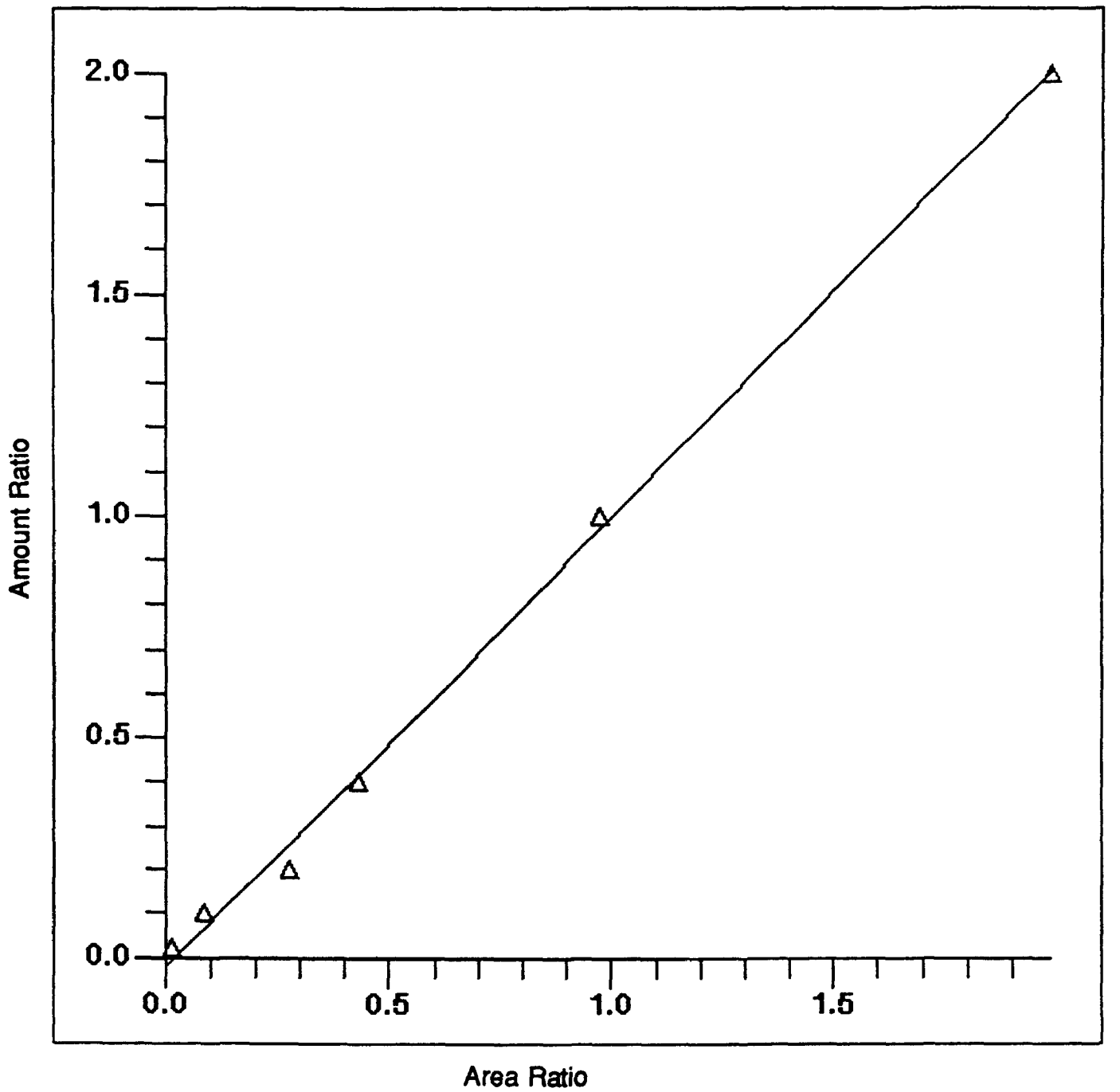

4-Nitroanaline Response Curve
On-Column
Splitless
%RSD = 7
%RSD = 23
Area
Concentration (ng/µL)
0
20
40
60
80
100
120
140
160
180
200
20
50
80
120
160



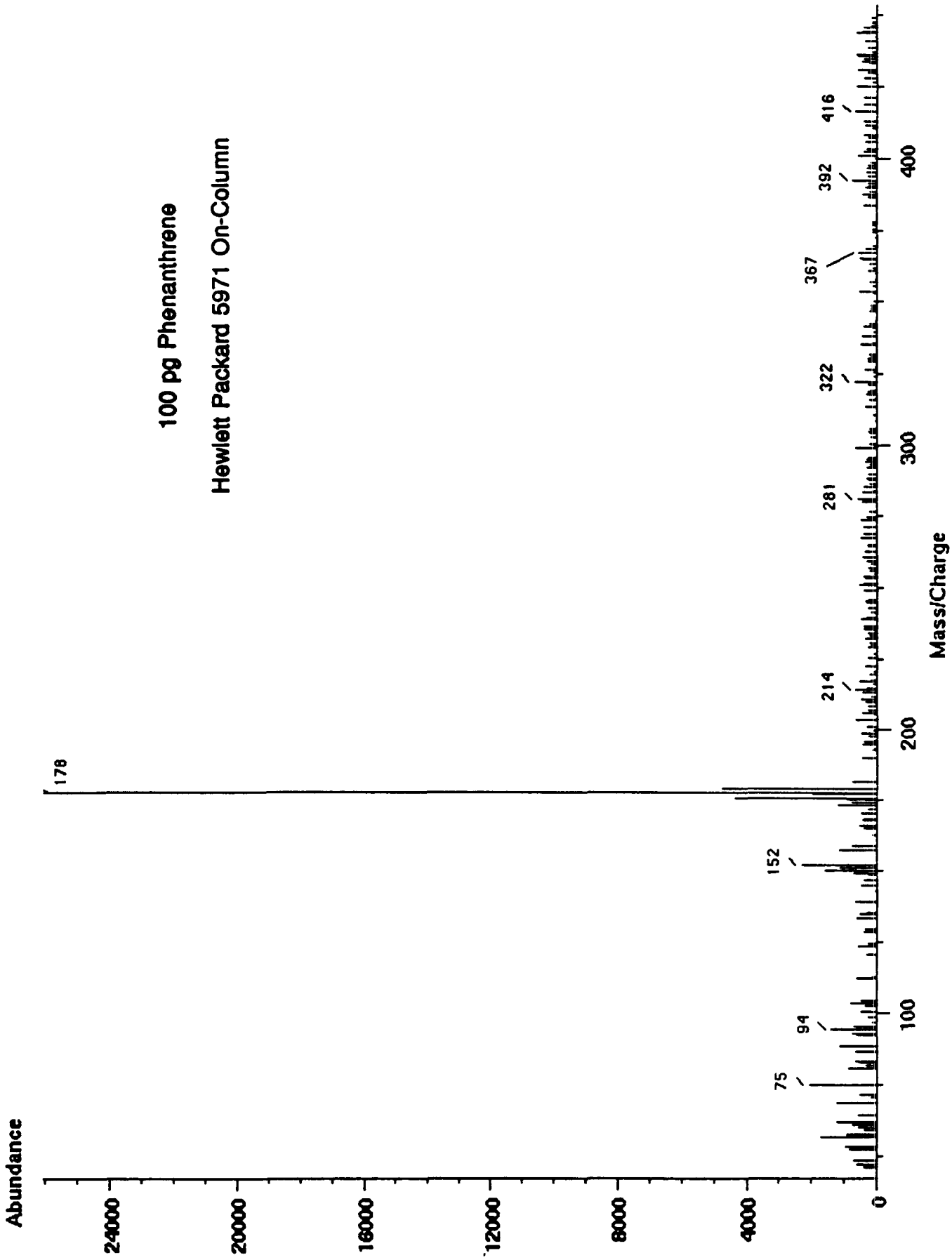
ON - COLUMN RESOLUTION WITH INCREASING AMOUNT INJECTED

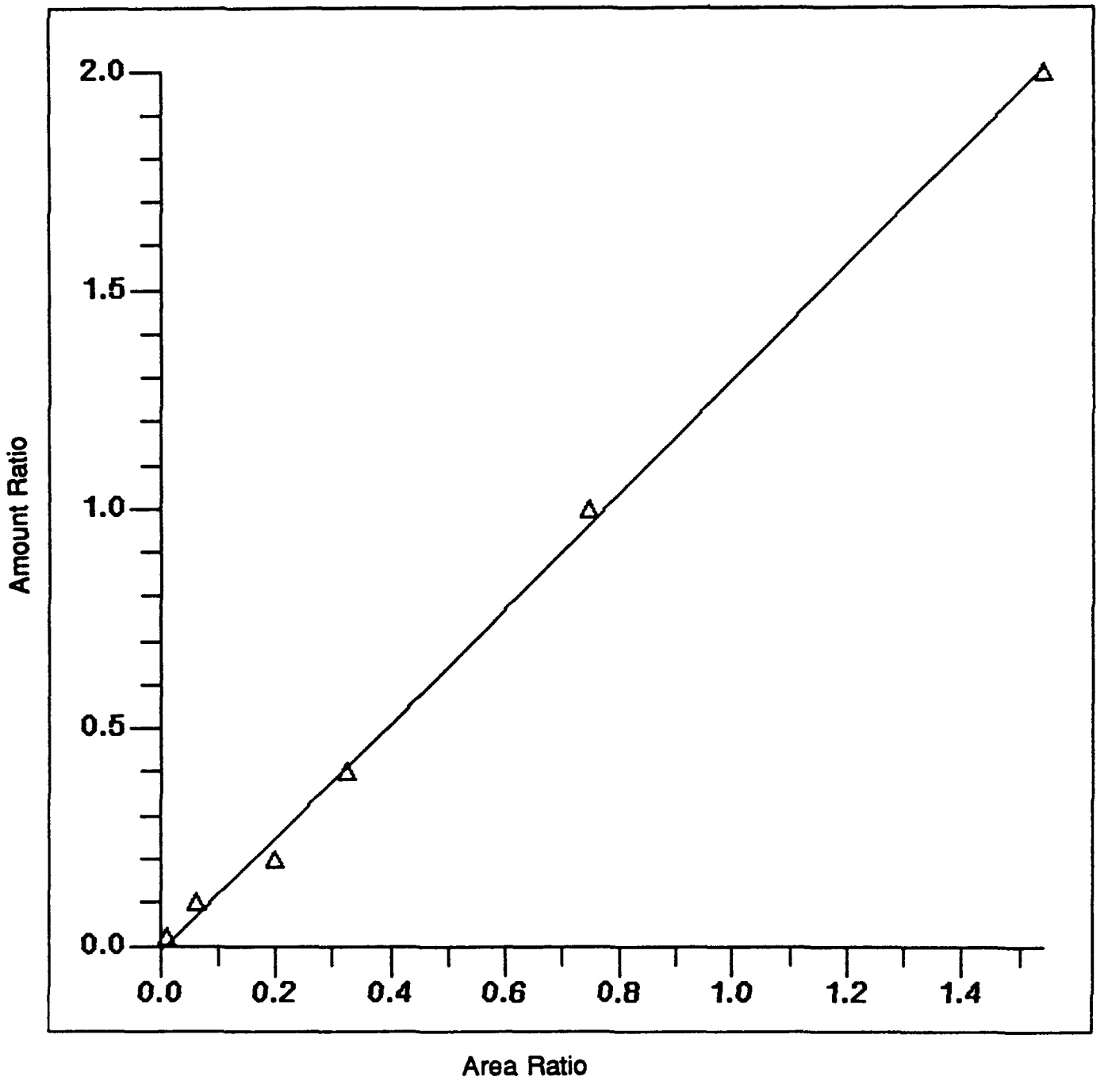


SPLITLESS RESOLUTION WITH INCREASING AMOUNT INJECTED

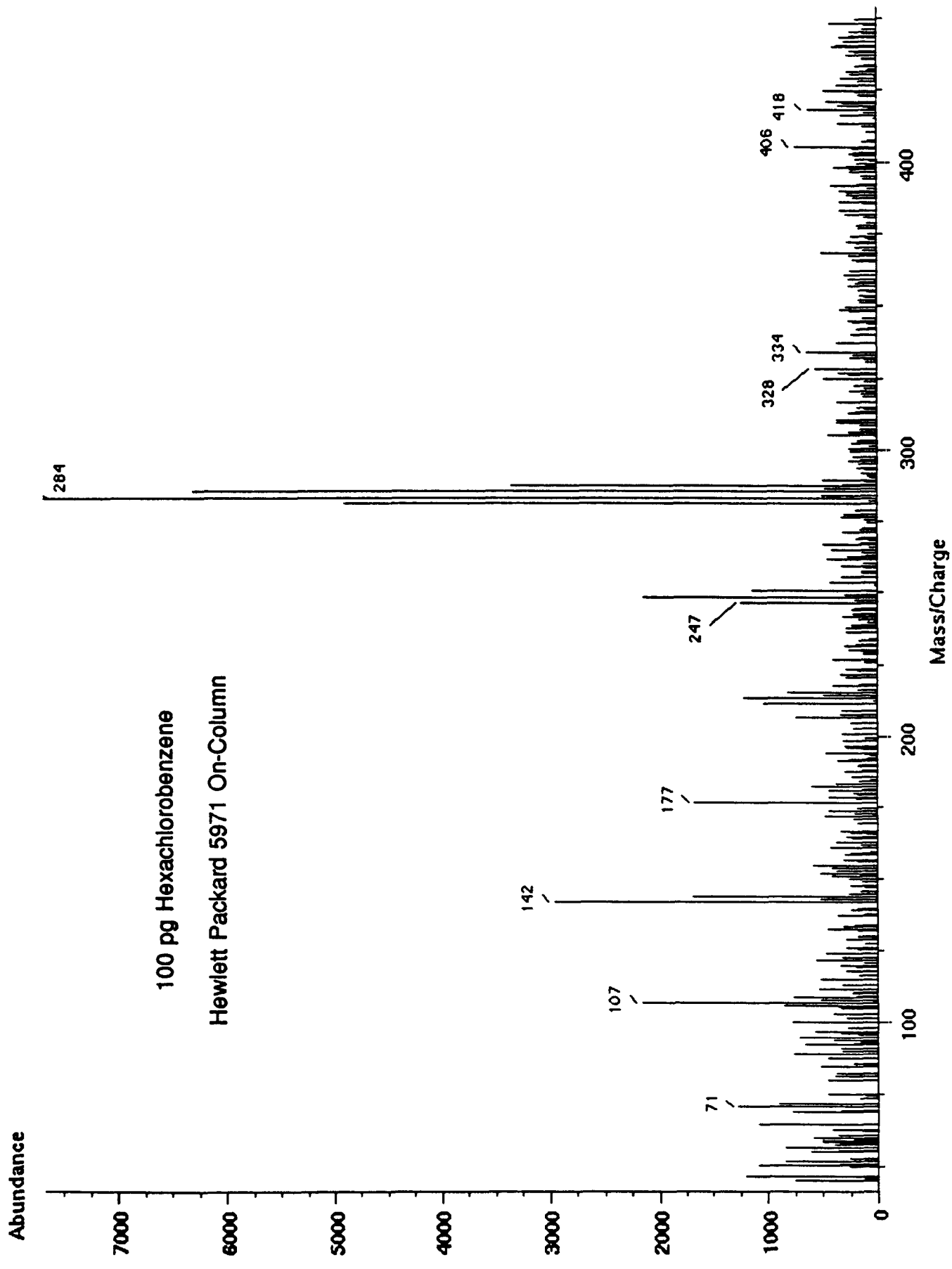


PHENANTHRENE RESPONSE CURVE (METHOD 525)


100 pg Phenanthrene
Hewlett Packard 5971 On-Column
Abundance
24000
20000
16000
12000
8000
4000
0
100
200
300
400
Mass/Charge
178
152
75
94
214
281
322
367
392
416



HEXACHLOROBENZENE RESPONSE CURVE (METHOD 525)


100 pg Hexachlorobenzene
Hewlett Packard 5971 On-Column
Abundance
Mass/Charge
0
1000
2000
3000
4000
5000
6000
7000
100
200
300
400
71
107
142
177
247
284
328
334
406
418

MR. McCARTY: Our next speaker this afternoon is Margaret St. Germain from Midwest Research Institute. Margie has been doing a lot of work with Bill Telliard's program, certainly with isotope pollution methods over the years. But she's taken a really unique approach. She's actually looked at historical data. When you go back and look at the data, you've got to answer all sorts of questions about what happened, and I think Margie's going to tell us, maybe, things we don't want to hear. But she's going to compare some historical data for complex samples in which the isotope dilution methods did not work very well, I think, and look at the criteria that are specified in the latest revisions, Method 1624 and 1625C.

Margie gave me a little bit of a background for an introduction and one of the things that I find very interesting is that when she got out of college, she had one job interview and was immediately hired at MRI and has stayed there ever since. That kind of longevity, I think, is also a reason she can look at historical data, because she's got some. If you bounce around, you can always blame it on..."well, that was the old lab and they didn't know how to do it". So, hopefully, Margie will be able to tell us something about what's wrong with the criteria, as well as what's right.

THIS IS AN UNEDITED VERSION OF THE PRESENTATION BY THE SPEAKER

MS. ST. GERMAIN: Good afternoon. I thought I'd start out by telling you that I'm a quarter Polish and I thought there was a rash of Polish jokes awhile back and I thought that had died until I got to the conference and I heard a whole bunch more. So, just to let you know that during that last rash of Polish jokes I heard about a gentleman who decided that with all of that publicity, he thought that he'd become Polish because he thought there had to be something good about Polish people. And so he looked around and he finally went to a surgeon and said, well, I really want to become Polish. Is it possible and what does that entail?

So, the surgeon said, well, you know, it's an awfully serious operation. I have to remove half of your brain.

And the doctor said, I'm not going to let you make that decision. You go home and think about it.

And the guy thought, well, it's possible. And he got real excited and said, I definitely want to become Polish.

So he went back to the surgeon and said, let's do it.

And so they scheduled the surgery and got through the surgery. Everything went smoothly. The guy was recovering from the surgery and was starting to wake up and the surgeon came in and said, we made a very small mistake.

The guy just kind of looked at him and the surgeon said, instead of removing half of your brain, we removed 95 percent of your brain.

And the poor old guy just looked at him and said, mama mia.

So, this was the wake-up call. So, I'd like to get onto some of this data. When I got into it, I thought that sure enough I've got this database to look at all of this historical data. It should go real smoothly, very fast. Needless to say, it's taken me three months to get through about 18 compounds...just trying to get all of the data loaded, organized,

go back and check for all the problems. So what I'm going to do is try to give you an overview of some of the things that I did find and also remind you as it compares to two other specific types of methods.

The other thing I should let you know is I have been doing isotope dilution for two and a half years. In that time, I've analyzed over 550 samples from six different matrices, including pesticide industries, pulp and paper, creosote paper plant, municipal sludges, Superfund sites, and oil and gas. In trying to collate this volume of data, I ended up focusing on the OPR criteria to start with because I knew that if that did not meet the method, then we should look back at the method. My next step would be then to go back to these different matrices and see what kinds of recoveries I got on my surrogates for each matrix. And so I was concerned to see how close to the method I really was and what can happen over that two and a half year period.

Just to give you an overview, what I've done is set up in the next few slides references to two other methods...two other series of methods, the solid waste methods, including 8240 and 8270 for volatiles and semi-volatiles, respectively, and those are for solid waste and for the water samples, the 624, 625 samples and then, of course, 1624 and 1625 for complex samples.

Now, as you notice in this slide, the comparison of this data, what I focused in is what the QA requirements or criteria were. So on this slide we've indicated what the internal standards are, how many there are, how many surrogates, how many target analytes and this is specific for the analytes that must pass criteria, additional compounds and tentatively identified compounds.

If we go through the volatile method, there are three internal standards for each of the methods, although for 8240 they are different internal standards. The surrogates will range from three for 8240 up to eight for 624, although they do recommend a minimum of three surrogates. Up to 31 for the isotope dilution method. So, already we're generating a lot of

volume of data just for volatiles.

The target analytes, on the 8240 there are 10 analytes that I've listed and these are what they call the SPCCs and the CCCs for the system performance check compounds and the calibration check compounds. All of the other compounds listed in that method are recommended to meet the criteria. They are not required. And so that's why I've listed them as I have there.

Okay, the isotope dilution methods, the 1624, 1625, also list criteria for how to identify additional GC peaks, which is not found in the other methods. The same kind of information is available for the semi-volatile method, as listed on the table.

Going on, let's look at the internal standards for volatile methods just to point out that the first two methods have the same internal standards. 8240 maintains the bromochloromethane...

Hmmm? No. Uh-oh. Okay. There's one slide out of line, so please try to remember that one. I'll discuss that later. Okay.

Bromochloromethane is the only common internal standard to all three methods.

Going onto the next slide is the internal standards for the semi-volatile methods. And you'll notice that two of the methods only require one internal standard. 8270 requires six of them.

The other thing we want to look at are the surrogates for the volatiles methods and you'll notice that 8240 has three surrogates, 624 has up to eight, although not all eight are necessarily used. But keep in mind that isotope dilution, which you can't read, has 31 of them and this just starts giving you an indication of what kind of QA is actually built into the method.

Okay, if we go on and do the same thing for semi-volatiles, we have a similar situation with six surrogates for 8270, up to 17 for 625 and 81, which takes up two slides to even

half-way read the slide, with about 81 surrogates.

Okay, that one slide that was out of line, that had to do with developing valid data and you have to have several pieces of information about QA. What I'm going to focus on is instrumental QA and method QA. So, the next couple of slides will focus in on that.

The instrumental QA basically has to do with the calibration of the instrumentation and monitoring of that calibration via an internal standard. And so, all the methods require some kind of mass spectrometer calibration, including the mass assignment and the mass ratio or mass intensity. The internal standards, they monitor area and retention times for two of those methods, although one of them does not specify any criteria.

The gas chromatographic criteria has to do with resolution more than anything else and the 8240 does apply some of that by using CCC compounds. The isotope dilution does have that same kind of criteria for all of its surrogates and also includes a resolution criteria of D8 toluene-toluene. However, that criteria right now is impossible on a packed column.

We've come up with a recommendation for a different resolution that truly indicates degradation of the packed column. We can go and look at the same kinds of information for the semi-volatile methods and an additional item, if you go through it and look at it. The additional item for the semi-volatiles is that they've thrown in penta-chlorophenol to monitor tailing and that is what monitors the degradation of the capillary column. Isotope dilution has also taken that same standard, added DDD and is looking for degradation of the standard, as well as the column chromatography. When DDD degrades, it goes to DDT and so they're looking for additional degradation of the standard and degradation of the column within one's standard mix.

Okay, that was the instrumental QA. Now we're going to the method QA and as we can see, the isotope dilution methods...what I call isotope dilution methods or the 1600 series

methods...have much stricter...have a lot more criteria, although they are not quite as strict and I'll be able to show you how that can be done. So, we're looking at initial calibration which all the methods require, and a continuing calibration. Again, most of the methods have very specific criteria that are written into the methods. A lot of additional criteria are added because of the statements within the methods that you must maintain a QA program and as part of that program, some of the additional QA that are in other methods are being incorporated into running 624.

Okay, along with that method QA you also have to monitor that QA for samples and some of the things that they monitor are the internal standard areas, the internal standard retention times, surrogate recoveries, and target identification by retention time and by spectra verification.

All the methods do require some kind of matrix spiked samples...at least recommend, if not require, and duplicate samples. And that's just to observe some of the statistics involved with each matrix.

Okay, we can look at the same kind of thing for the semi-volatile methods, including initial calibration with the curves, IPRs, number of samples, continuing calibration. What I found interesting is that two of these three methods did specify a maximum shift length where at the end of that shift you must perform more QA in order to continue past that number of hours.

Going on, we can look at some of the sample criteria and, like I said, this is just a quick review to give you an idea on the perspective of what we're trying to do here.

As far as that information, what we do is we receive the sample, extract it, analyze it, transfer the quantitation data to a PC that has a database and that's how we can monitor our ongoing precision and recovery and check to see if we're within specs or not. And so, what we've done is we've taken the information from the quan reports...I'm ready to strangle this thing...and for each compound in the quan reports for the isotope

dilution methods, we have 10 items that are collated into that database for each compound and they include the sample file name, the EGD number, the compound name, retention time in seconds and scans, relative retention time, area, the amount calculated by the isotope dilution method, relative response factor, and the average response factor from the current curve for that data.

In compiling the data that I did just for the ongoing precision and recovery standards, I had 231 volatile files for 92 compounds. Of those, only 67 of them I have enough data to even look at. The other 29 are additional compounds that do not have necessarily very strict criteria.

For semi-volatiles, I had 171 files for 257 compounds, of which 157 of them I really do have lots of data. So if you look at that, I've got on the order of 641,000 pieces of information in the database and it's taking up about 35 meg of space in my 40 meg hard drive, so I'm running on a very tight system right now.

Okay. Some of the key features of the data that you're going to see is that this data was acquired over a two year period. We generated several calibration curves based on failing curve or daily responses. We used several columns and on occasion, we have been able to pass previous curves because we've been real careful about the capillary columns we've purchased. We've also been careful about trying to reproducibly pack our own packed columns. We've even collated the data from several instruments for the same compounds and for each OPR summary that you will see, there are over 150 points.

When looking at all that data, it was obvious when there is truly a problem and when it was a statistical outlier. In the data that you will see, the X axis will always be the file number, the Y axis will change and I'll try to discuss that as we go through some of the data.

We're going to look at the internal standards for retention times in areas and three compounds from volatiles and semi-volatiles. I purposely picked one CCC and one SPCC so you

can see what some of the relationships are between the other methods.

Okay, so this next slide is the retention times of the three internal standards and the method specifies very specific ranges for retention times for those internal standards. The Y axis in this case is the scan number which converts to...each scan is three seconds. And so, the bromochloromethane, the lower line of dots, has a requirement of 653 seconds to 782 and for the most part, we did meet the criteria. There is one outlier that I'll discuss in a second. The same is true for the bromochloropropane and then, finally, for the dichlorobutane. They all have method criteria, specific retention time windows.

The one outlier...I went back and looked at the file and the notebook read, started the run...computer didn't start...started the computer acquisition 30 seconds late. Therefore, we have 30 seconds to add onto that to make it more of a real time and it does fall in at that point.

And I thought, well, you know, this is nice. It shows straight lines. But what does that tell me about my internal standards? So, I decided to look at the areas and they're really spread out. And I started looking at some of the data and came up with an additional criteria that my lab is starting to recommend and that's for bromochloromethane that the area counts be between 10,000 and 30,000. Below 10,000 we notice that we start having detection limit problems. Above 30,000 we notice that we have saturation problems for the high level standards. And so if we can maintain that internal standard within a tighter internal standard area, then we should be able to have a lot more reproducible data.

I looked at the same kind of thing for 2-bromo 1-chloropropane and, again, they're spread all over the place and came up with new limits for that also and they end up focusing on similar ranges, although the absolute intensity is much higher for this compound.

And then we looked at 1,4 dichlorobutane. The first 60

files or so are significantly different from the scatter that you saw previously and we are currently trying to identify what the possible difference is for that.

Okay, so let's go on and look at an SPCC for volatiles, tetrachloroethane. This is real data with nothing thrown out. The center solid point that's way above that you can see... The hollow points you may not be able to see. That point...we went back and it's a labeled compound. We discovered that it was calibrated incorrectly. When we recalculated it on the correct peak with the correct areas, then it fell in line. There are two additional hollow points and they were standards that were run at the end of the day after high level samples, so it's obvious that there was carry-over. But in looking at the data, the next morning, the point fell in and so therefore the system cleaned up overnight and we were ready to continue on.

That's a lot of points to look at, so what I've done is focused in on two areas. One is from file 130 to 160 and the first point that's low was again an end of the day standard where we had some very dirty samples. You can see the very next day the point is back up again. You also notice two more points later on that were low and we discovered that our column was degrading. We packed a new column and we were again to pass the same curve in this case and we were back up to where we were once we had packed a new column.

Tetrachloroethane is one of those compounds that we analyzed on two separate instruments during the month of February, 1990, and, as you can see, all the solid points are scattered generally over a range. The hollow points are the same and the hollow points are all the natives on two different instruments and the acceptable criteria range for tetrachloroethane in the method is from 7 to 34 micrograms, which we definitely passed in this case.

Going on to a CCC, again we have wide scatter. We do have a couple of points that are outside of the criteria. Acceptable ranges for the labeled compound...the method says,

detected up to 65. After the method was written, then they changed the labeled compound concentration to 100 micrograms and, of course, then you fail the criteria. So, by multiplying that range by a factor of five, which is how they raise the standard, then you have detected to 325 to monitor as a criteria base that your labeled standard should be, right around 100.

What we've done is looked at files 130 to 160 again. The hollow points are staying fairly consistent, right at 20 micrograms, where they ought to be since our native is at 20 micrograms and you can notice that there's a general downward trend of the labeled compound at the conclusion of that particular run and then we made up a new solution and started over and we are back up at 100 micrograms again. So, we've been using that as a criteria for how far it degrades and then change over rather than just go until it goes to not detected.

Okay, we've got similar data on two instruments. And again, you can see that the general scatter is within an acceptable range for the two instruments.

Going on to chloroform, this was one of the few compounds that I did not have any outliers and I was, frankly, surprised. The acceptable range was eight to 30 micrograms and concerning how tight those spots are or those data points, it looks real good to me, concerning some of the other plots that you've just seen. However, I do have about eight outliers within that two year period that need to be addressed that I haven't gone through yet to identify the problems.

Let's focus in on a couple of areas. From file 130 to 160 again and within that criteria, within that set data, we did meet the criteria all the time very easily. And I got to thinking, say, well, how does this compare to the 624 Method and the 8240? So, what I did was I took chloroform. I have shown the response factor for chloroform, calculated by the isotope dilution method. The response factor should be right around one and has been. I do have one outlier in that respect.

Taking that same data and recalculating the areas,

based on an internal standard method using bromochloromethane, we can see we've got quite a few more outliers. Most of them are right around a general response factor of one. But towards the end, we start seeing a lot of scatter. So in that case, it's not working as well as the isotope dilution method.

Okay, going into the semi-volatiles, we'll go through the same kind of data and I'll probably go through this fairly quickly.

We have the retention times for the internal standard, 1,4-difluorobiphenyl and as you can see, we did meet the criteria of 1,078 seconds to 1,248 seconds. Again, I looked at the areas and decided that any areas above 600,000 counts, which we've got about four points on that graph, I start having difficulties with saturation of the mass spectrometer for higher levels.

Okay, I'm going to look at phenanthrene, which is a good reactor. And as you can see, the criteria for the method on the semi-volatiles the labeled compounds have a wider range. The native compounds are much tighter. And so, the labeled compounds for phenanthrene have an acceptance window of 34 to 168 micrograms, based on a 100 microgram standard, and this is micrograms per liter. The natives, however, are from 87 to 126, so we're looking generally at a plus or minus 20 percent for the natives.

Going on and looking at a selected window from files 40 to 60, we can see that was real easy to meet. Things were fairly consistent, although I do have a section where things didn't work so well and I do have two outliers. The first one at this point I cannot explain. The second one was at the end of a day of a dirty sample and so we were seeing some things...but the very next day we were back in spec. So, we're seeing that something does happen if you run shifts back to back...that there are some difficulties.

The next thing I tried was 4-nitrophenol...first off, a bad reactor and also a SPCC. And I do have quite a few points that are above the majority of the points, the solid points being

the labeled compounds and the hollow points being the native compounds. And again, for the labeled compound on this 4-nitrophenol, the method says there's no specification for what kinds of numbers you get. What's important is that your native compounds must meet a 51 to 178 microgram per liter criteria.

Looking at that, we obviously had a small problem towards the end of that section from about file 135 to 150. In looking at that data, all the acids failed. At that point, I refused to run acid extracts. However, all of my base neutrals passed. So at that point, I ran only base neutral fractions in order to try to meet holding times and at the same time meet specific criteria.

Another compound that I looked at was hexachlorobutadiene. The criteria for the labeled compound was not specified on the low end. It went up to 413 micrograms on the high end. The native, however, was from 43 to 287 micrograms and, as you can see, for over 150 files, I did meet that criteria.

I decided to do the same kind of thing to compare this to the other two methods by response factor information since that's the one thing I could manipulate. And so, here we had the response factor for hexachlorobutadiene using the isotope dilution calculation and we do have a spread, but generally most of the points are between 1 and 2.5. Calculating against D,10-phenanthrene, we have a range from 0 up to .6 with most of the points being around .3. Okay, when you run into response factors this low, you start running into difficulties in quantitation and reproducibility. I went and looked at that against D,8-naphthalene which would be the 8270 Method and saw a similar situation, although in this case, I did find a lot more scatter.

So, in conclusion, I was surprised at the number of points that did meet criteria and the ones that I could identify what the problem was either related to previous sample analyses or a bad column situation. I was able to identify additional internal standard area criteria that should help me monitor

what's going on in real time a lot sooner than the day or two later and have to rerun a set of samples. With the database that I've developed, I can compare this data to other methods since most of the surrogates and internal standards are already in the isotope dilution mixes. So we have the potential of re-evaluating OPRs based on other methods, other surrogates and also looking at different matrices and surrogate recoveries.

So I'd like to conclude with expressing my thanks to Bill Telliard for sending me all of those scuzzy samples to deal with and to Jim King and his group for sending us all the samples and doing all the footwork for the organization and especially to the MRI staff who performed the analysis. Without them, we could not have gotten through that number of samples.

I'll take any questions now.

(No response.)

MR. McCARTY: Thanks, Margie.

NO SLIDES AVAILABLE
FOR THIS PRESENTATION

MR. McCARTY: Our next speaker is going to be Lance Steere, who is also from S-Cubed Laboratories. Lance tells me he's a member of an endangered species; he's a native San Diegan. Apparently, the reintroduced species out there are getting pretty bad. The water shortage seems to drive the native species away for some reason.

He's going to be talking today about heated purge and trap GC/MS analysis as a way of dealing with the water soluble compounds and alcohols that are often attempted by Method 1624C.

MR. STEERE: Good afternoon. I'm here to talk about heated purge and trap and isotope dilution. What originally got me into this area was back during the National Sewage Sludge Survey in the summer of '88 through the winter of '89, S-Cubed analyzed over 200 sewage sludge samples and I personally had the opportunity to run, about 150 of these analyses myself on the volatiles which, of course, means smelling them and dealing with them very up-front and personal. What I came across in about 25 percent of these samples was the simultaneous QC failures of the so-called water soluble compounds. These are acetone, acrylonitrile, diethyl ether, methylethylketone, acrolein and p-dioxane and it was interesting to see QC failures among this same special group of compounds. I sort of picked up the pattern after a couple of months of doing sewage sludge samples and, gee, these same ones keep failing in some samples and I wondered why. This really was of concern because among the corrective actions for when you have QC failures in isotope dilution methods, the first corrective action is to rerun the sample at a 1:10 dilution. Of course, this is not always necessary as far as analyzing the targets to bring them in the calibration range. It's just a matter of seeing whether the method is working on that particular sample matrix. So this problem generated a lot of reruns, a lot of extra work.

Another thing you have to do for corrective action is check your daily calibration, your ongoing precision and recovery, or OPR as they call them in the isotope dilution biz. Our system always seemed to check out, so it really did seem to indicate a problem with the samples themselves and not with our system. And, of course, if your dilution also fails, then you're supposed to calculate the target amounts based on internal standard quantitation, which is equivalent to tossing out the isotope dilution method in favor of the old internal standard method and the issue arose as to whether which set of data would be more reliable, isotope dilution quantitated values or internal standard quantitated values?

Actually, the two sets of data weren't all that dissimilar. They varied by about a factor of two, depending on the magnitude of the XS recovery that the labeled standards were showing.

Well, originally when I was running these samples, I was pretty much convinced that there was some non-purged compound in there that was somehow modifying the solvent and creating this phenomenon of enhanced purgability. So, like Bob, I went ahead and wrote up an abstract real quick saying that this was going to be the topic of my discussion here today. Which was OK until I went to do the actual experiment and nothing that I seemed to add to the aqueous media I was testing seemed to give this same enhanced purgability effect.

The only other plausible explanation that occurred to me was the mild heating that we routinely gave these solid samples. The method recommends that you run high solid samples around 40 degrees, as opposed to room temperature and it helps get all of the nasties off the solid matrix that you're running. So, I ran a standard at 40 degrees and I observed excess recoveries of these water soluble compounds very similar in magnitude to what I observed with the sewage sludges. So, my idea was to test the isotope dilution method under hot purge and trap conditions.

My goals for this were several. First was to establish that the hot purge and trap method would be useful in an actual analytical situation. I wanted to verify that the detection limits would be adequate. I expected that they would be better since the hot purge should get these compounds out of solution easier. I also wanted to verify that there would be a sufficiently wide calibration range. In case it was too sensitive, you too narrow a range and it's not really useful for running routine samples. Secondly, I wanted to establish that the method performance is satisfactory under the hot purge and trap conditions and towards this end, I decided I would run an initial precision and recovery analysis. And, lastly, I wanted

to see if the isotope dilution quantitation method would correct for temperature variances. I thought that it would, but I kind of wanted to push the system and see just how much temperature change could be tolerated. And then looking back at the National Sewage Sludge Survey problem, I wanted to see if this information might shed some light on what had been happening during the sewage sludge excess recoveries.

For my tests, I focused on the six water soluble compounds listed there and I also selected three alcohols. Ethanol and isopropanal are of special interest in the pharmaceuticals industry and I've been asked on a number of occasions to use hot purge conditions to analyse for these particular compounds. Also, I had to limit myself to compounds for which I already had labeled analogs available. After all, I was on overhead for this whole project and couldn't really justify to my boss buying a lot of expensive standards for this project.

So, after setting up my compound list, and narrowing it down to these compounds, I did the instrument detection limit studies with the results shown here. Most of the compounds are very well detectable around the 5-ppb range.

Acetone experienced somewhat of a problem due to the use of bulk solvents in the extraction labs upstairs at S-Cubed. There's always a background of acetone in the air and you have to go to sort of extreme conditions, such as pre-purging your water and using heat to get the acetone on out of it. The background level is around five to ten ppb, but if you took those extraordinary measures, you could actually detect fairly consistently in the one to five ppb range.

Ethanol and n-butanol both experienced some sort of interference that I never really did trace down. Even if you didn't purge anything on the system, you got peak areas that, at the base temperatures I established at 75 degrees, would correspond to ethanol at about 10 ppb and n-butanol at about five...even if you didn't purge anything. So, there was some

sort of interference going on there.

There's substantial improvement in sensitivity for these compounds using the hot purge and trap conditions of 75 degrees.

Here I show the hot purge and trap curve at 75 degrees that I ran three weeks ago with the average response factors listed there and the relative standard deviations in those response factors, as compared to a room temperature curve that I ran for the PE sample for the recent isotope dilution RFP a couple of months ago. Across the board, about an order of magnitude improvement.

Notice that acrolein and p-dioxane, two of the ones that show the lower sensitivities, show great improvement as far as relative standard deviation once you bump up the response factor to something that's a little more palatable to our system.

I went on and ran a calibration curve at that point. I chose the same calibration range that the six water soluble compounds get in the method, which is from 50 to 1,000 ppb. Because of their general lower sensitivity in aqueous media, they're given a calibration range that's actually five times higher than all of the other analytes, such as chloroform and tetracholoethylene and like that. Those are usually analyzed in the 10 to 200 ppb range. And I got these results. Actually, the sensitivity for four of the compounds, acrylonitrile, isoproponal, diethyl ether and MEK were so much better that I got a little bit of saturation on my system while running the 1,000 point. You can see some of the relative standard deviations for the targets. Here's MEK at about 19, diethyl ether around 21. Those are approaching what I consider to be the warning limit in the method. The method allows you to use average response factors, as long as your relative standard deviation in your curve is below 20 percent. Above that, you have to go to all of the trouble of deriving linear regression response factors or, even worse yet, graphical response factors. Generally, linear regression will work fine for these.

If I exclude the 1,000 point, the relative standard deviations drop by about a factor of two so some of the variance displayed by the target compounds here is due to the 1,000 point being biased somewhat low.

With a calibration curve in hand, I went on to an initial precision and recovery analysis, which is four replicates all spiked at the 100 ppb level. Ideally, you get a mean recovery in all cases right around 100 and you can see that these conform pretty well, except for acrolein which is really one of the bad boys. We've only learned to detect acrolein on our system just in time for the last PE sample. Historically, we've never been able to see that one.

One thing I noticed...you might have noticed on my very first slide, that when the labeled standards of the acetone, acrylonitrile and MEK were high in sewage sludge samples, I'd actually see the labeled acrolein. So I knew that it existed and knew that it might be able to be detected on my system, but I had to find the trick and eventually I did.

The relative standard deviations in the IPR's are all much more than adequate. Anything under 10 percent is just great. Up to 20 percent is good. Up to 30 percent is fair. Around 40 percent is, well, marginal and 50 percent okay. Actually, for the six compounds that are included in the method, there are established criteria for IPRs and all of these compounds pass. Even acrolein manages to slip under the wire here. So, standard deviation criteria under the IPRs are really rather liberal for these compounds, because historically they're of lower sensitivity. Which goes hand-in-hand with higher variability. But, under hot purge and trap conditions, you get better sensitivity, so correspondingly lower variability in the data.

Here's a really bad slide that I'm not going to bother showing you because they said you ought to graph this stuff so it's easier to see.

Here's the results I got, running different

temperatures...seeing the temperature variability effect.

Here's room temperature at 25 degrees and the "boiling" purge and trap at 90 degrees. The labeled alcohols...see, there's a lot of condensation you get in the system. You have to worry about water carrying over onto your trap and screwing up the next analysis. You see, the labeled alcohols shown here all show the type of response you'd expect to see.

Here's the reference temperature of 75 degrees where all the calibrations took place, so you'd expect them to cross the 100 line here at 75 and they do. At higher temperatures, you get improved purgability and at lower temperatures, you get miserable purgability. But the target compounds here all get corrected with the isotope dilution method to be around 100, which is the level where they were spiked.

Notice that ethanol and n-butanol really take off when you get really low recoveries of the labeled alcohols. They are biased very high. Ethanol is something like 240 ppb. This is due to the background interference levels that were seen on the system. If you have a small area that's there no matter what you purge on, then that's going to have such a tremendous effect. By the time you correct for less than 10 percent recovery of labeled alcohol, the values there go sky high. But isopropanol didn't have such a problem and so it's recovery is about 100 all throughout.

Acetone, MEK and acrylonitrile all were very well behaved compounds. They show the classic low recovery at low temperatures, higher recovery at higher temperatures and about 100 at 75 degrees and all of the target compounds are corrected adequately to show right around 100.

Here's diethyl ether and p-dioxane. P-Dioxane shows the classic behavior, temperature dependent low recovery, high recovery, the target compound biased somewhat low below 100, but pretty constant throughout the range. Diethyl ether, on the other hand, shows both the target and the labeled compounds are about 100 throughout the entire temperature range. That's

because the boiling point of ether is down around 34 degrees and this may have had some influence on its getting out of the water solution fairly easily. Maybe they should drop diethyl ether from this water soluble list. You don't tend to think of it as being water soluble, although it does have the capability of hydrogen bonding, which is probably why it's included here.

So, the implications for my problems back on the sludge survey... It appears that the high observed recoveries of those labeled compounds was due to the mild heating and my results in this study indicate that the target values reported using isotope quantitation were probably perfectly adequate and therefore we didn't have to go to any great extra effort to recalculate using internal standard areas and so forth and, of course, skip all of the reruns that weren't needed because of the target being outside of the CAL range.

So, in general, what I want you to go away with today after this talk is for you to know that the hot purge and trap method works just fine with isotope dilution. You get very good detection limits, very good calibration range, although perhaps you get too much sensitivity at the high end and you have to trim that a bit, the IPRs are as good as at room temperature, and it corrects for temperature variances just thumbs up...just great.

It's too bad I didn't have these results in at the time when I did the National Sewage Sludge Survey because I had this little voice in my head saying, trust your labeled compounds, Lance. Use the power of the method. But, unfortunately, I was a little bit more pragmatic in those days and went strictly by the book.

Are there any questions? I guess I should have seeded a few questions.

I thought of a question, why didn't I calibrate my system for the 40 degree...

MR. McCARTY: Do you want to identify yourself, please?

MR. STEERE: My name is Lance

Steere and I work at S-Cubed and I ran some of these myself and what I want to know, Lance, is why didn't you calibrate your system at 40 degrees in the first place?

Well, the answer to that, young lad, is that the Sewage Sludge Survey samples came in literally one or two a week for several weeks and we were running them along with a lot of aqueous samples. So, it was very convenient just to set it on up with your calibration curve already in place. We really only experienced troubles with a few compounds and a few samples, so it didn't really seem to be calibration curve related. As I got more and more into it, I finally began to see the pattern. But, I didn't have time at that point to think about running extra calibration curves for sewage sludge samples because we were then doing 20 of them a week and that was just about impossible. So, the problem kind of crept up on me and I didn't think of the solution until I had to come up with a topic for the talk today.

No questions? Thank you very much.

HEATED PURGE AND TRAP GC/MS ANALYSIS OF WATER SOLUBLE COMPOUNDS AND ALCOHOLS BY METHOD 1624

BY

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SIMULTANEOUS QC FAILURES FOR 'WATER SOLUBLE' COMPOUNDS IN ~25% OF SEWAGE SLUDGE SAMPLES

Labeled Compound	Acceptance Criteria (ppb)	Range of Values in High Recovery Samples (ppb)
d_6 Acetone	35-165	165-300
d_3 Acrylonitrile	NS-204	204-350
d_{10} Diethyl Ether	44-156	156-250
d_8 MEK	42-158	158-300
d_4 Acrolein	37-163	Observed*

*Usually not detected in any calibration or daily standard (OPR) analyses.

Instrument: Finnigan 4021 with Tekmar LSC-1 purge and trap

CORRECTIVE ACTIONS FOR LABELED RECOVERY OUTSIDE RECOVERY LIMITS ...

1 Rerun sample at 1:10 dilution.

2 Check system calibration by running another daily standard (OPR).

3 Calculate target amounts based on internal standard quantitation method.

WHY THE XS RECOVERY OF LABELED 'WATER SOLUBLE' COMPOUNDS?

- SOLVENT MODIFIER? - not supported by experiment
- MILD HEATING (~40°) - observed XS recoveries similar to sludges

Test the ability of Method 1624C to correct for purge temperature variability

GOALS FOR ISOTOPE DILUTION HOT PURGE AND TRAP DEMONSTRATION ...

1 HPT method is useful for analyses:

- Adequate detection limits.
- Sufficiently wide calibration range.

2 Method performance is satisfactory under HPT conditions.

- Initial precision and accuracy analysis.

3 Isotope quantitation can correct for temperature variances.

- How much change in temperature can be tolerated?
- What do results suggest for sewage sludge survey sample problems?

Method 1624C *Water Soluble Compounds*:

- Acetone
- Acrolein
- Acrylonitrile
- Diethyl Ether
- Methyl Ethyl Ketone
- 1,4-Dioxane

Selected alcohols:

- Ethanol
- Isopropanol
- n-Butanol

INSTRUMENT DETECTION LIMITS (IDL) UNDER
HPT CONDITIONS (75°C)

Compound	IDL (ppb)	
Acetone	1-5	Backround level 5-10
Acrolein	1-5	High variability, raises effective detection limit
Acrylonitrile	0.1-2	
Diethyl Ether	0.1-2	
MEK	1-5	
1,4-Dioxane	5-10	
Ethanol	10-15	Interference near 10-ppb level
Isopropanol	1-5	
n-Butanol	5-10	Interference near 5-ppb level

IMPROVEMENT IN SENSITIVITY FOR HPT CONDITIONS VERSUS ROOM TEMPERATURE PURGE

Labeled Compound*	HPT Curve at 75°C (04/15/91)		Room Temperature Curve at 25°C (01/21/91)	
	Average R_f	%RSD	Average R_f	%RSD
Acetone	.815	6.5	.101	12.8
Acrolein	.042	9.8	.0064	23.7
Acrylonitrile	2.50	5.7	.412	2.0
Diethyl Ether	1.66	2.1	.957	1.5
MEK	1.08	1.8	.082	3.7
p-Dioxane	.169	8.9	.011	26.3

*Labeled compounds are spiked at the 100-ppb level in all CAL runs.

HPT CALIBRATION RESULTS

Labeled Analog/ Compound	CAL Range 50-1000 ppb		%RSD (Excluding 1000 ppb CAL)
	Mean R_f	%RSD	
d_6 Ethanol	.103	9.7	
Ethanol	1.76	13.4	
d_6 Acetone	.815	6.5	
Acetone	1.36	15.0	
d_4 Acrolein	.042	9.8	
Acrolein	19.3	15.3	
d_3 Acrylonitrile	2.50	5.7	
Acrylonitrile	.982	11.6	6.6
d_8 Isopropanol	1.73	3.5	
Isopropanol	1.08	9.3	5.4
d_{10} Diethyl Ether	1.66	2.1	
Diethyl Ether	.859	20.8	11.6
d_8 MEK	1.08	1.8	
MEK	1.27	18.7	11.4
d_8 p-Dioxane	.169	8.9	
p-Dioxane	1.19	5.1	
d_7 n-Butanol	.177	3.6	
n-Butanol	1.28	14.3	

INITIAL PRECISION AND RECOVERY (IPR) RESULTS UNDER HPT CONDITIONS

IPR = 4 replicates spiked at the 100-ppb level.

Labeled Analog/ Compound	Range of Recovery	Mean Recovery	% RSD
d_6 Ethanol	87-117	102	13.6
Ethanol	92-102	96	4.8
d_6 Acetone	120-124	122	1.4
Acetone	86-95	91	4.0
d_4 Acrolein	145-169	154	7.1
Acrolein	60-74	69	8.5
d_3 Acrylonitrile	105-110	107	1.7
Acrylonitrile	99-104	101	2.2
d_8 Isopropanol	97-116	106	8.6
Isopropanol	94-94	95	2.4
d_{10} Diethyl Ether	100-105	102	2.0
Diethyl Ether	109-114	111	2.2
d_8 MEK	110-113	111	1.2
MEK	95-100	98	2.6
d_8 p-Dioxane	85-113	99	13.1
p-Dioxane	90-97	93	3.5
d_7 n-Butanol	99-118	109	7.9
n-Butanol	88-93	90	2.8

COMPARISON OF HPT IPR RESULTS WITH METHOD 1624C
IPR CRITERIA (SECTION 8.2; TABLE 6)

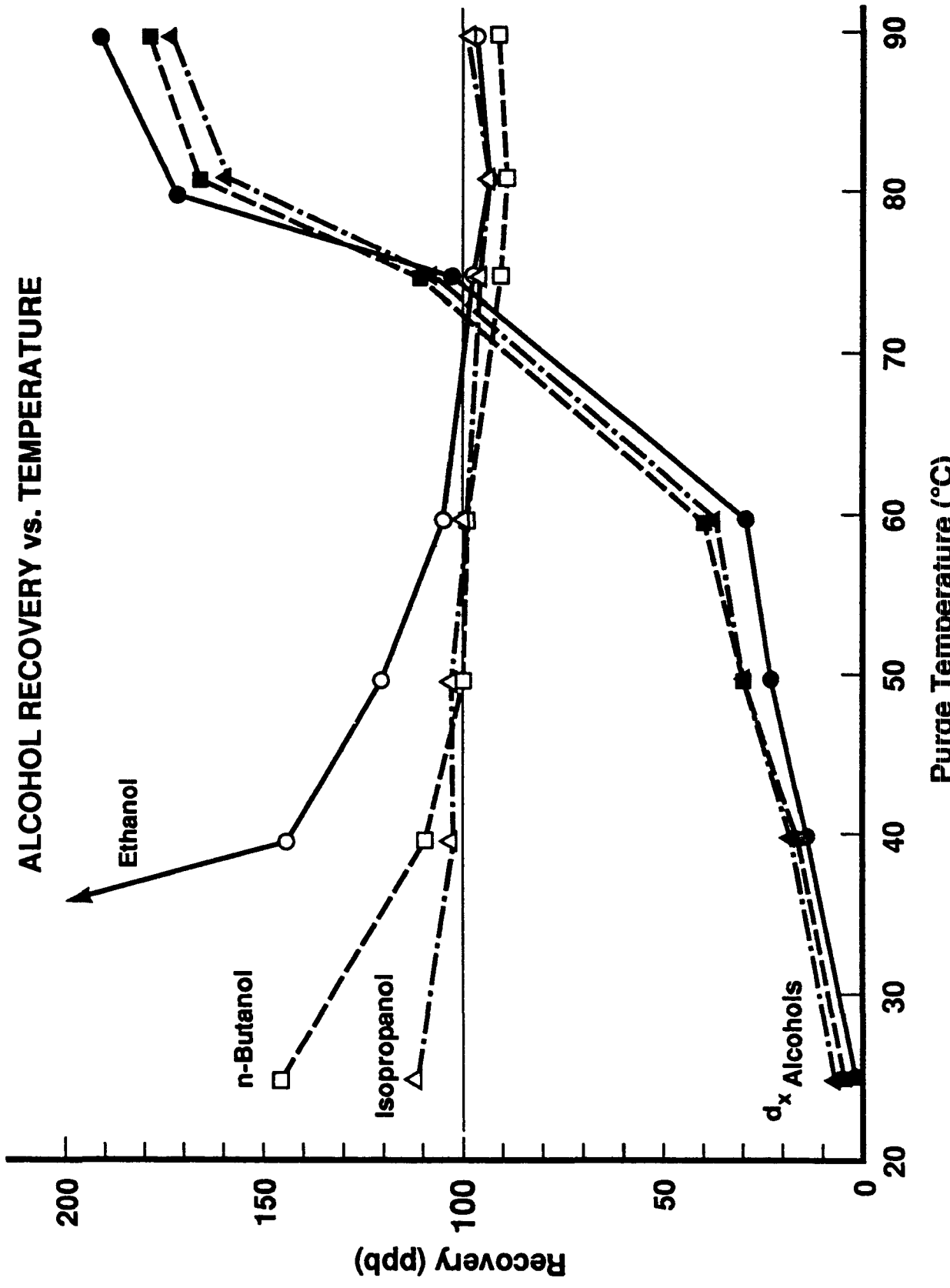
Analog/ Compounds	Acceptance Criteria Versus HPT Results			
	Mean	HPT	Standard Deviation	HPT
Acetone	77-153	122/91	51	4
Acrolein	32-168	154/69	72	8
Acrylonitrile	70-132	107/101	16	2
Diethyl Ether	75-146	102/111	44	2
MEK	66-159	111/98	57	3
p-Dioxane	65-135	99/93	36	4

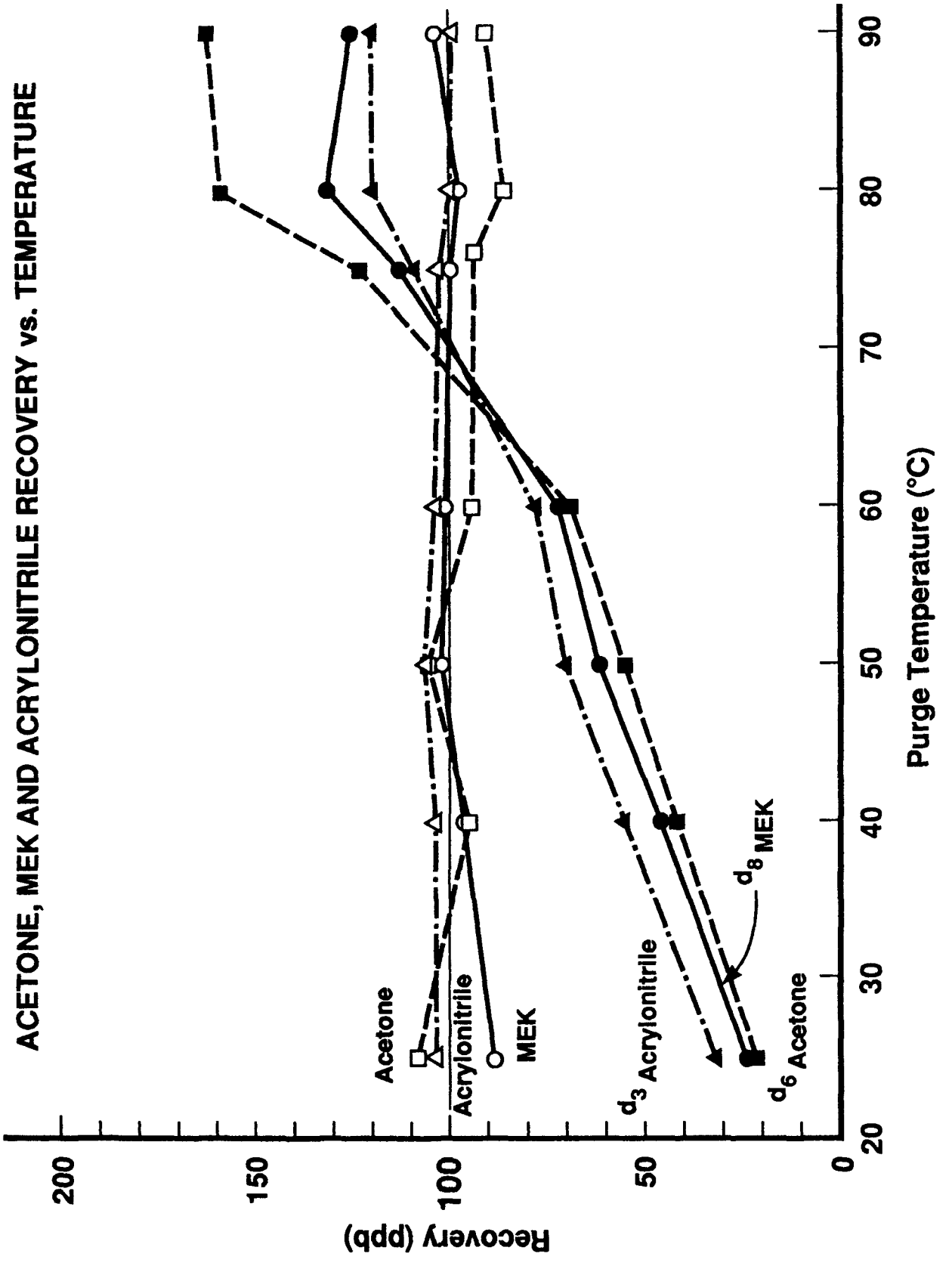
HPT RECOVERIES UNDER VARIABLE TEMPERATURE CONDITIONS

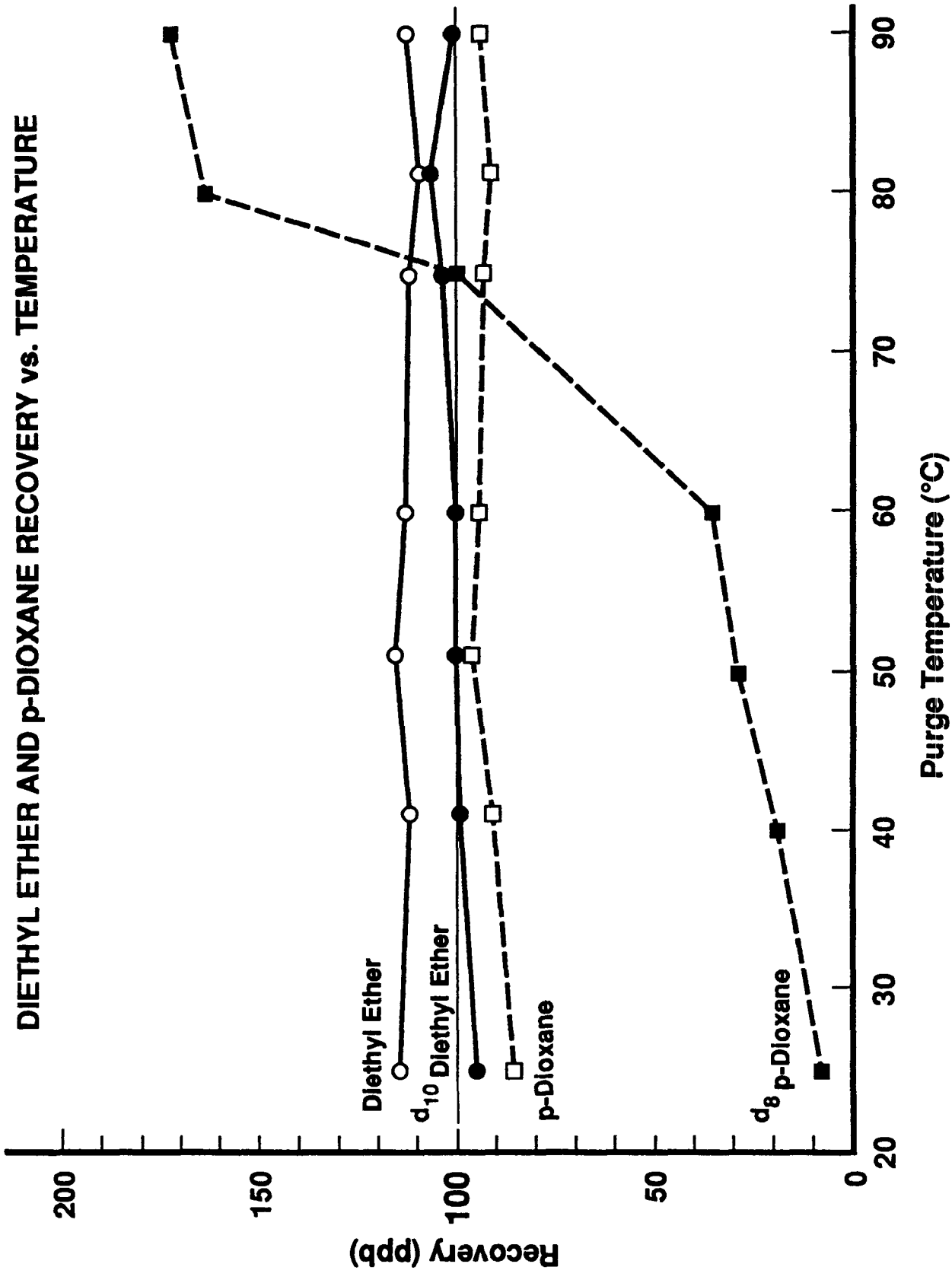
All compounds and analogs spiked at the 100-ppb level.

Analog/ Compound	Purge Temperature (°C)						
	90	80	75*	60	50	40	25
d_6 Ethanol	189	171	102	28	23	13	2
Ethanol	95	92	96	104	120	144	340
d_6 Acetone	160	157	122	67	54	41	21
Acetone	88	84	91	92	105	93	107
d_4 Acrolein	199	237	154	108	80	78	51
Acrolein	46	39	69	64	95	67	62
d_3 Acrylonitrile	119	119	107	76	69	54	31
Acrylonitrile	97	98	101	102	105	102	102
d_8 Isopropanol	172	159	106	36	29	17	6
Isopropanol	96	93	95	99	102	102	111
d_{10} Diethyl Ether	100	106	102	100	100	99	95
Diethyl Ether	111	108	111	112	115	111	114
d_8 MEK	123	130	111	70	60	44	21
MEK	101	95	98	100	101	94	87
d_8 p-Dioxane	171	163	99	36	30	20	8
p-Dioxane	94	91	93	94	96	91	86
d_7 n-Butanol	176	165	109	37	29	16	5
n-Butanol	90	88	90	99	100	109	145

*Average of 4 IPRs.


ALCOHOL RECOVERY vs. TEMPERATURE
Ethanol
n-Butanol
Isopropanol
d_x Alcohols
Recovery (ppb)
200
150
100
50
0
20
30
40
50
60
70
80
90
Purge Temperature (°C)


ACETONE, MEK AND ACRYLONITRILE RECOVERY vs. TEMPERATURE
Recovery (ppb)
200
150
100
50
0
20
30
40
50
60
70
80
90
Purge Temperature (°C)
Acetone
Acrylonitrile
MEK
d3 Acrylonitrile
d8 MEK
d6 Acetone


DIETHYL ETHER AND p-DIOXANE RECOVERY vs. TEMPERATURE
Recovery (ppb)
200
150
100
50
0
20
30
40
50
60
70
80
90
Purge Temperature (°C)
Diethyl Ether
d_{10} Diethyl Ether
p-Dioxane
d_8 p-Dioxane

IMPLICATIONS FOR NATIONAL SEWAGE SLUDGE SURVEY RESULTS ...

1 High observed recoveries of *water soluble* labeled compounds was caused by mild heating.

2 Target values reported using isotope quantitation are more reliable.

3 Recalculated values using IS method are not needed.

4 Reruns at dilution are not needed if original recovery is within CAL range.

GOALS FOR ISOTOPE DILUTION HOT PURGE AND TRAP DEMONSTRATION ...

1	*HPT method is useful for analyses:*	**You Bet!** 
	• Adequate detection limits.	**Order of magnitude better than RT!**
	• Sufficiently wide calibration range.	**May need to trim high end!**
2	*Method performance is satisfactory under HPT conditions.*	**Of Course!** 
	• Initial precision and accuracy analysis.	**As good as RT!**
3	*Isotope quantitation can correct for temperature variances.*	**Like a Champ!** 
	• How much change in temperature can be tolerated?	**± 15°C or more!**
	• What do results suggest for sewage sludge survey sample problems?	**"Trust your labeled compound quantitations; Use the power of the method!"**

MR. McCARTY: That's the problem when you throw up a lot of data. People have to assimilate it. Lunch is settling in at this point.

Our next speaker this afternoon is Bruce Colby from Pacific Analytical Laboratories.

I'm going to be real nice to Bruce. I'm not going to give him a hard time about the money he borrowed from me in Europe last September or the grappa we drank until all hours or anything like that.

Bruce has done a lot of work over the years on library search results. He's one of the few people I know who drives to work thinking about library search data, and goes to bed thinking about library search data, and wakes up at 4:00 in the morning and writes a paper, and actually submits the abstract before there's been a call for papers.

He's going to talk about some improvements in the TIC spectral assignments through a technique known as peak centroid analysis.

Bruce?

MR. COLBY: Thanks, Harry. I'm going to break this afternoon's tradition here in two ways. First of all, I'm going to talk about something I did before I wrote the abstract. I guess I just don't have enough imagination to do it any other way. Secondly, I'm going to talk about qualitative aspects of methodologies.

I don't really want a slide yet.

The qualitative aspects of any of these GC/MS methods have to be dealt with before you worry about the quantitative aspects. If you can't make a qualitative analysis correctly...in other words, identify the compound correctly...there's not much point in worrying about how well you can do your quantitation.

Well, the specific part of qualitative, spectral dealings I'm going to concern myself with is the TIC area. The technology I'm going to describe is actually applicable to identifying overlapped target components, as well. But I'm going to concentrate on the TICs because that's what I started out to deal with.

The reason I got involved in the TICs in my own mind recently was a consequence of watching people in a lab struggle with trying to identify non-target analytes in relatively messy samples, like isotope dilution samples or anything that our illustrious Mr. Telliard might send us.

The problem we run into is that the non-target analytes are often co-eluted or closely eluted with materials we've spiked in, labels compounds and base neutrals. Margie said we had about 80 of them; that sounds around right and in the volatiles, roughly half that many.

The problem we run into in terms of what happens when we look at data, what I've got here is a nice peak on the left hand side. It's nicely shaped, it's pointed, there's not much background. The reaction to that is, yes, that must be some kind of compound.

All of the examples I'm going to show, by the way, are actually for targets. But I'm going to treat them as if they

were not targets because going into it, I needed to know what the compounds were.

You can see on top the spectrum we get for a retention time of 14.03 minutes and the best library search is a spectrum below it. At first glance there is a lot of agreement there, but there are a few things that are a little bit off in left field. You'll see there are some peaks out in this area in the library that don't correspond with any in the sample. The same in here. Worse yet, when you get into this collection of peaks, there's a big 104 not there. There are differences.

The first reaction to it might be, yes, that must be it. It must be this benzene ethanamine beta methyl. The only problem is that we're looking at a purge and trap sample and there's no way that could have come out of a purge and trap device and made it through the column in that time frame. So what we have is a mystery compound.

The problem with the TICs in particular is a combination of things. There are, I believe, two issues in particular that we have to fight. One is the database that we search our unknown spectra against and come up with reference spectra; it is incomplete. It's only got a little more than 50,000 or so entries in it and there may be a few million possibilities. So there's not a very good coverage there. It also has a lot of things in it that won't find their way through a GC column and I thought some about trying to work on that, but decided that was too big of a problem for me to deal with, so I'd concentrate on another aspect of the problem and that is a lot of times the spectra that we feed into our library search program are the result of more than one component generating peaks in the mass spectrum. In case you're not already guessing it, there's probably more than one compound here and we'll look at that a little bit later.

Well, if we've got a situation with two components, either very closely eluted to each other or overlapping to some extent that makes it difficult to use normal data system

technology to extract clean spectra for each component, then there has to be some other way that we can go at it, unless we're just going to give up and say, that's an unknown. So, I thought, what is it that we have? What pieces of information do we have that we might be able to extract from the data file to give us this additional handle to work on the library search? In other words, how are we going to get a cleaner spectrum?

Basically, there are only two things we have. One is that we can have sort of a supposition that if we have two components next to each other, they have different mass spectra. If we say that, then we have something we might be able to work with.

The other thing that we can say fairly emphatically is that if we have two separate components here, each of those components will have its own retention time. Now, obviously if they have a different enough retention time, you'll see two peaks on the TIC. But I'm going to try to push that technology to separate things that give you peaks like that.

What I'm going to do basically is to attack my data file, in particular, a peak that I believe to be multi-component and extract for each mass that has a peak associated with this particular collection of masses, that spectrum up there...extract a mass chromatogram and calculate for that mass chromatogram a centroid corresponding to the retention time for the elution of the component that that mass belongs to. We'll then do that for each mass in the spectrum and see if I come up with more than one group of centroids.

Now, before we get that far, it would probably be best to try something very simple and clean. So, take our old friend, DFTPP, which we have many spectra of in the laboratory. This is an NBS library spectrum. It's a nice spectrum to work with because it's got lots of peaks across the mass range...down here at 51 all the way up to 442. It's got little peaks, 365 and what not. So, it's a nice kind of test compound.

I went to the lab, grabbed a floppy disk, hauled off a

couple of data files and tried the centroid calculation and what I've done here is plot that TIC trace for DFTPP and next to it I've plotted the time at which the centroids for all peaks greater than or equal to one percent of the base peak happen to come out at. In other words, how closely do we calculate a centroid for all of those roughly 65 peaks or whatever.

It turns out that the centroids for DFTPP masses were within... Well, the standard deviation was .04 seconds. We were scanning the instrument at one scan per second over sort of a traditional BNA mass range. So, if in fact there was another component in here, three standard deviations away, that would be about .15 seconds away, we should get two groups of centroids showing up there.

Now, if we know that mass X belongs to the first group, then we say, okay, that intensity belongs to this compound and then any mass that belongs to the second group of centroids belongs to another compound and then all of a sudden we're starting to separate these spectra, one from the other.

Just to show you what the spectra actually look like for the DFTPP, we've got the...these are the centroids that eluted within a plus or minus three standard deviation window of the center of the centroid and this is that NBS reference spectrum. Basically, they're indistinguishable from each other. So, certainly we're not hurting the data by messing around with these centroid things.

I thought, well, let me take something where I know there's probably going to be a little bit of an interference...something that will be eluted fairly closely. I took a peak and in this case for... This is the TIC trace here. It's a peak for D34-hexadecane. When I break that down into groups of centroids, I get one major centroid and one little bitty group right next to it at a slightly longer retention time. In fact, it's .48 seconds difference. And again, you can see that the peak up here, you know, would be pushing 10 seconds wide. Anyway, this first collection of centroids produces a

spectrum...a very nice spectrum for the D34-hexadecane.

The second group of centroids produces another nice spectrum. Masses are all offset by one in the lower mass direction, the less-deuterated compound having a longer retention time than the deuterated. Well, obviously that's the impurity in this deuterated hexadecane. There's a D33-hexadecane that was in there when it got spiked into this particular sample and we can see that we can actually separate those. They're less than a half second apart in retention time. So, I'm starting to get happy.

Let's take a look at that thing we had up there first, the spectrum for one sort of peak that gave us a crummy library. We run the centroid analysis and lo and behold, we get two groups. Now, those people in the audience who are highly familiar with volatiles analysis ought to already know what those are. For those of you who don't fall into that category, I'll show you the spectra...or try to.

Here is a spectrum of the first group of centroids. Any volatiles analyst will pick that one out very quickly. The second group of centroids, most of you should recognize that. Anyway, if you don't, we stick these into the library search. Here's the first component in our first group of centroids. Actually, it's orthoxylene, so it's a 1,2-dimethylbenzene, but in these spectra these are indistinguishable from each other. So, now we're getting somewhere. We've got a pretty good fit on that one.

The second group of centroids, the masses in there correspond to this spectrum and what we've got is styrene, another pretty good match.

Well, maybe that was too easy of an example, so let's move on here and try something a little bit more complicated. Here we've got a couple of components coming out here. I'm going to concentrate on the more intense of the two. If we take the data spectrum for the 19.61 retention time and library search it, we get something that is clearly useless. We can look at the

sample spectrum and we can say certainly there's chlorines in here and, yes, this library search produced chlorines. But also, there's no way that's the right compound. So, let's run out little centroid analysis thing on it and we get a nice single collection of centroids corresponding to this and here we have three groups of centroids. So, well, let's have a look and see what those are.

The first of this collection of three gives us this spectrum. The second gives us this spectrum and the third one gives us this spectrum.

Now, if we take those and submit that to library search, we get a very good match for dibromochloromethane, followed by a very good match for the 1,1,2-trichloroethane.

This, the middle one of the three, is a very match for 1,3-dichloro 1-propene. We know really what those particular components are because, again, they are targets in this particular sample and this particular sample is, in fact, a volatile standard I've run on a packed column. The previous data we worked with were volatiles run on a capillary column. This is run on an instrument...about a five or six year old instrument. The other one was a much newer instrument. It doesn't seem to make much difference what kind of data we attempt to deal with. Anyway, that was only three things. So, let's attack a situation where maybe it's even worse.

Here we've got a TIC trace. It's got a shoulder on there, so we know going in that we've got some kind of potential interference situation.

If we take the spectrum for the peak top, 18.81, we get a spectrum that has some peaks in it...all kinds of peaks in it. If we library search it, it says it's a hydrocarbon. That doesn't really look like a hydrocarbon. It looks like it may have some chlorines in it out here. It looks like it may have some aromatic character to it, based on those intense higher mass peaks. One thing we can do with this, going in and knowing that there's a shoulder on it, is we can run some spectral cleanup

software on it. This is a technology called or basically referred to as a Biller-Beaman cleanup. If we do that to the spectrum, now we've...this is like a single scan enhance in a Finnegan system. You can see that those chlorine clusters went away and we still have some hydrocarbon character and aromatic character; we still get a hydrocarbon answer that the spectrum comes up with for the best fit. Still not too impressive, so let's run this centroid business on it and see what happens.

Well, this one's even worse yet, isn't it? This time, we've got one, two, three, four, five, six different components showing up in this and since I don't have any good way to show six spectra all at once, I'll just pick these three here in the middle since they're the ones that are most closely eluted to each other. Now we have spectra for those three middle ones at the top. Here's a spectrum. It's about .9 seconds later. This is capillary column BNA one second scan stuff. About 1.3 seconds later, we get this spectrum with some chlorinated things in it. That's kind of encouraging. So, we send that off and do some library searching on it. The first component that we looked at, biphenyl. Well, that's dead easy, isn't it?

The second one...well, it's some kind of hydrocarbon. They all give these sort of similar spectra, so that's about what we do as we look at it and say, yes, it's a hydrocarbon.

And the last one, we get a very nice comparison with 2-chloronaphthalene.

So, what we've managed to do is come up with a way that allows us to take spectra for components that are eluted fairly close together and, in theory, based on the standard deviation for the centroids of the DFTPP spectrum, you would predict that you have about a 99 percent change of getting a good separation of spectra that are eluted as components...eluted as closely as about .15 seconds for a capillary column run. I haven't found an example that close. The closest we've managed to find one was that deuterated hexadecane. That was about .48 seconds. But

clearly, we're separating things that are coming very, very close together in retention time.

So, now we have a better show at sending a good spectrum off to library search and I think this has the potential of improving our ability to do reasonable TIC identifications.

Well, what's the down side? There's got to be one; it can't be all good. Two things...if two compounds have the same masses in their spectrum, the calculated centroid will come out between the two. So that's a little bit of an issue. The styrene and ortho-xylene that were in the first example, if you recall, weren't fully separated one from the other in the centroid groupings. That is a consequence of some common low mass ions.

If two compounds had exactly the same retention time, they'll have exactly the same centroids and we won't be able to tell those apart.

So, those are the two limiting factors on it that we're aware of at this point. We continuing to pursue some other variations of this and I expect you'll be seeing it in commercial data systems, I would say within the year. It's been quite fun working on it. If anyone has any kind of question to ask, I'd be more than happy to try to answer.

QUESTION AND ANSWER SESSION

MR. McCARTY: Bruce, one question I have is in terms of practicality, what would you estimate is the time increase this would put on TIC searches for, say, your 10 to 20 most intense TIC type of situation?

MR. COLBY:It appears that the centroid analysis time, processing that, well, certainly it's going to be system-dependent and data-dependent. It adds in the vicinity of about four or five seconds per collection of things. So, basically it will double the amount of time people spend on a TIC.

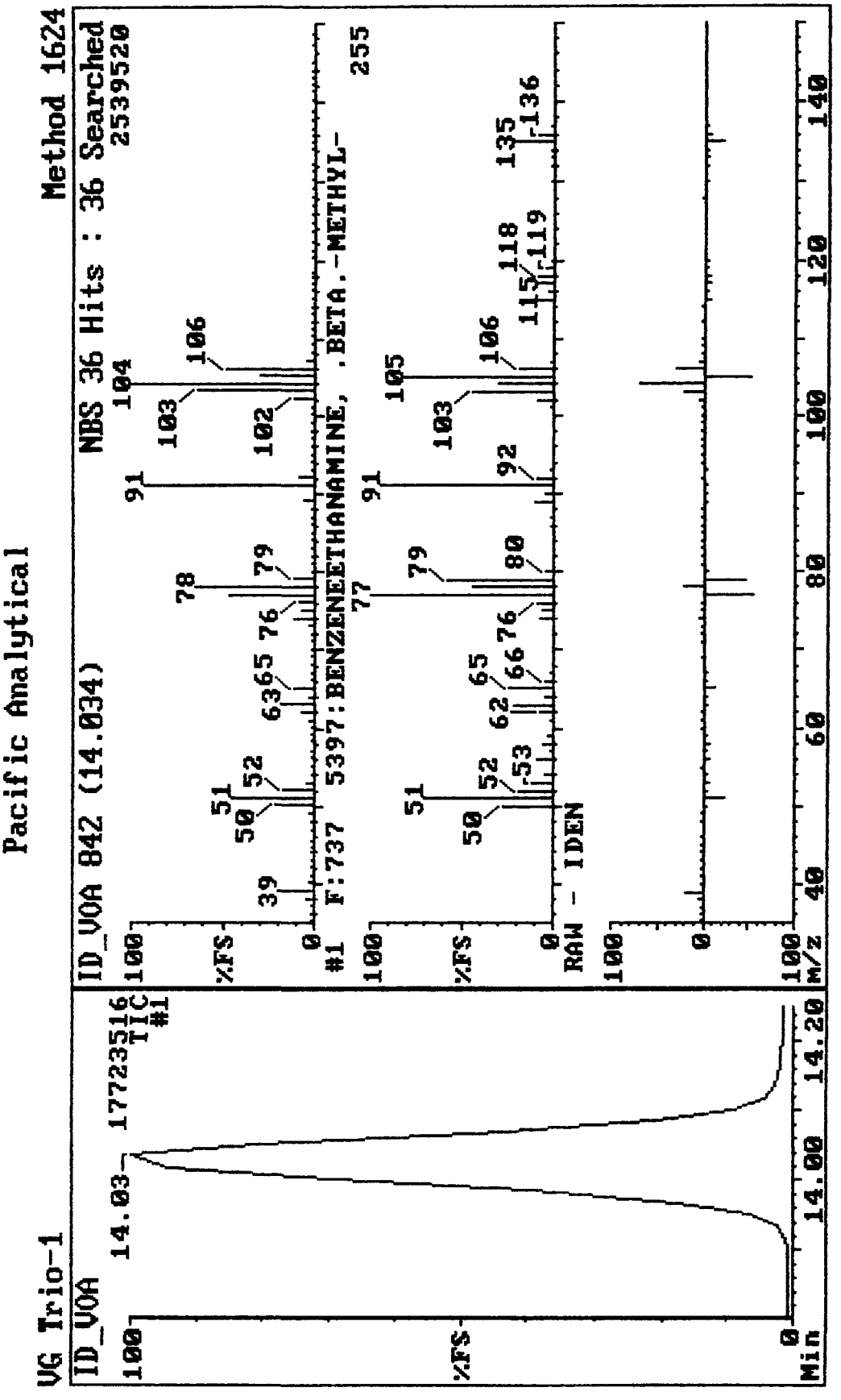
MR. McCARTY: From four seconds to eight seconds?

MR. COLBY: Four to eight.

MR. McCARTY: Any other questions?

MR. COLBY: Everybody knows how I did those calculations? I didn't think so.

MR. McCARTY: There will be a test later.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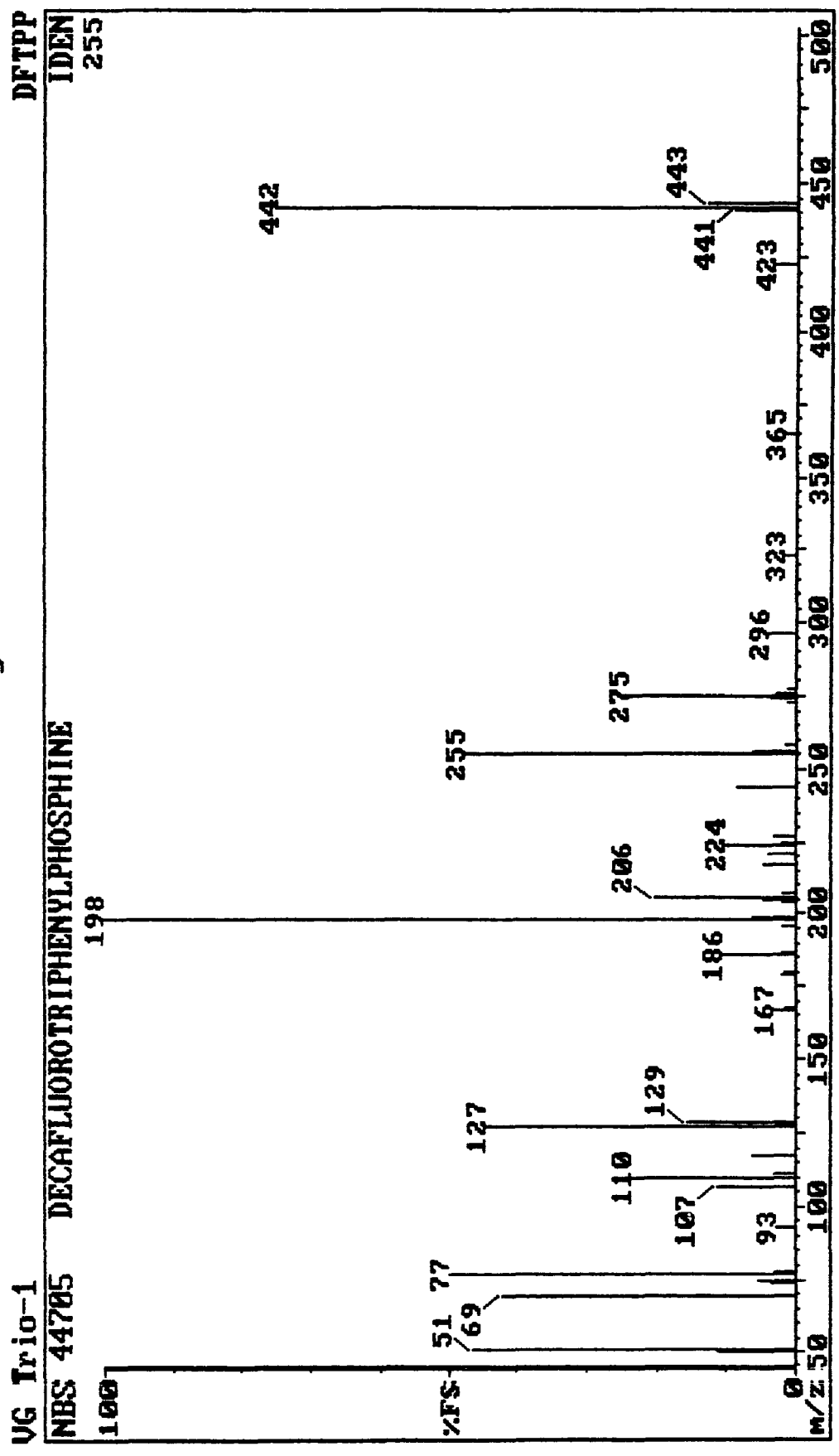
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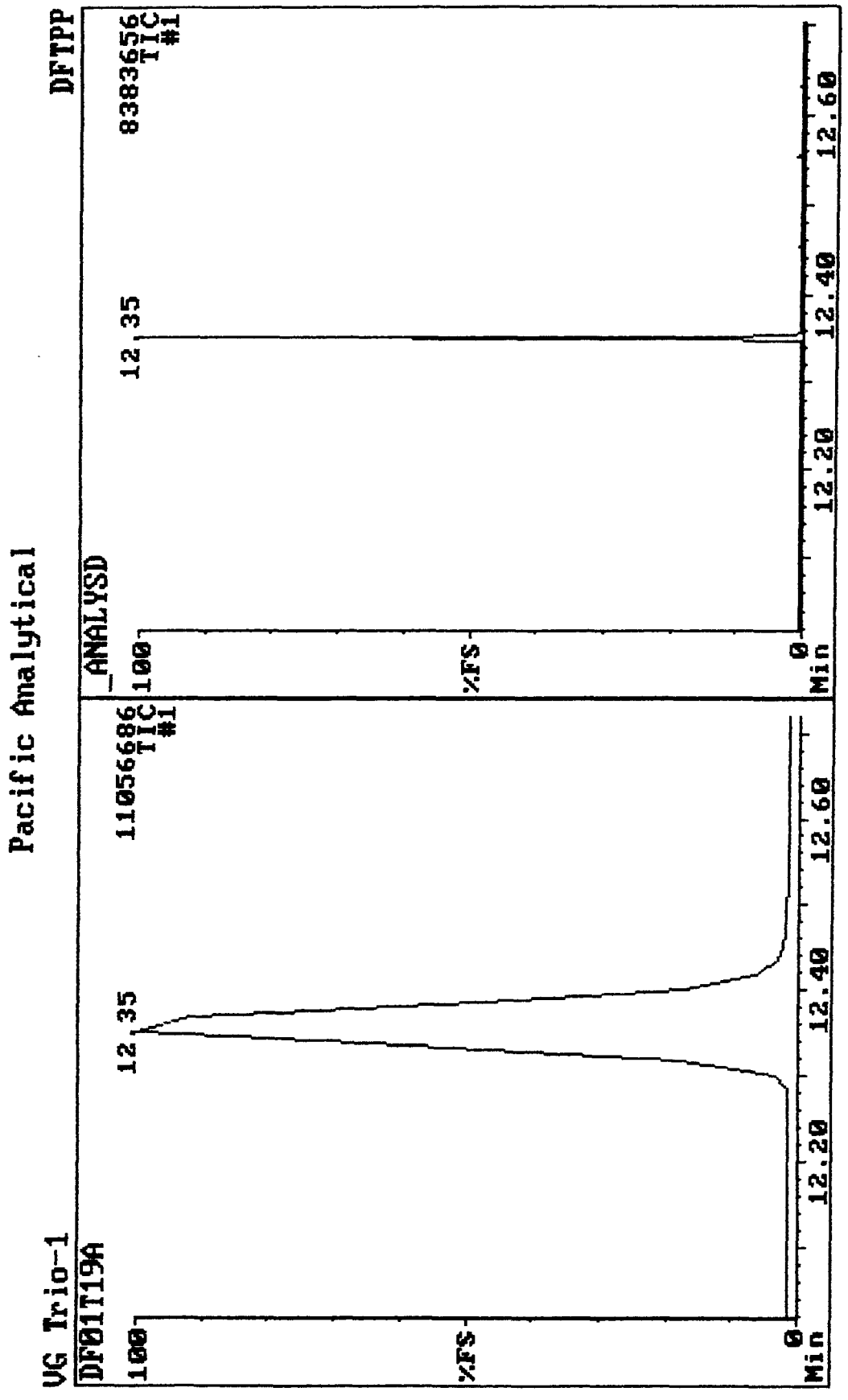
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Pacific Analytical

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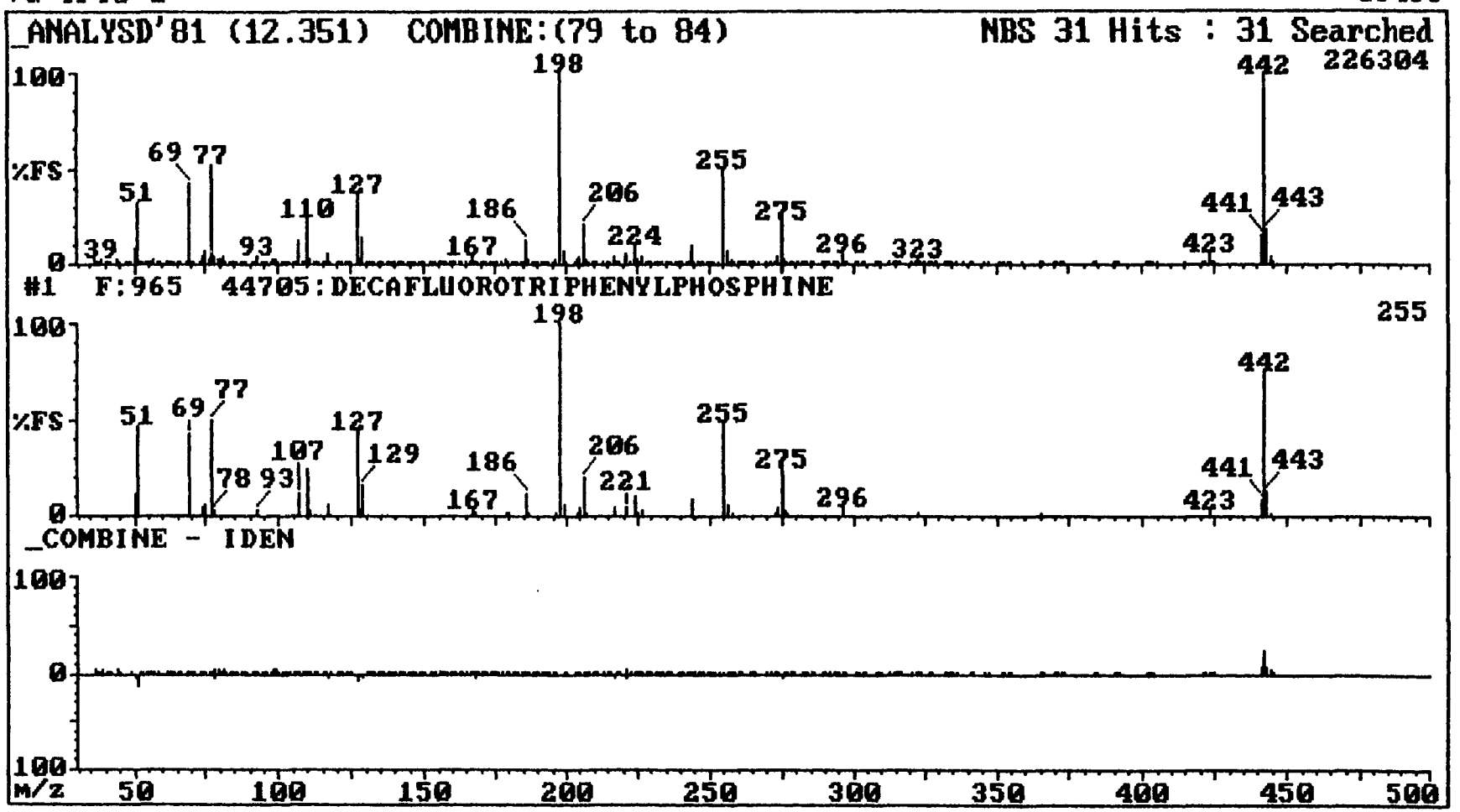

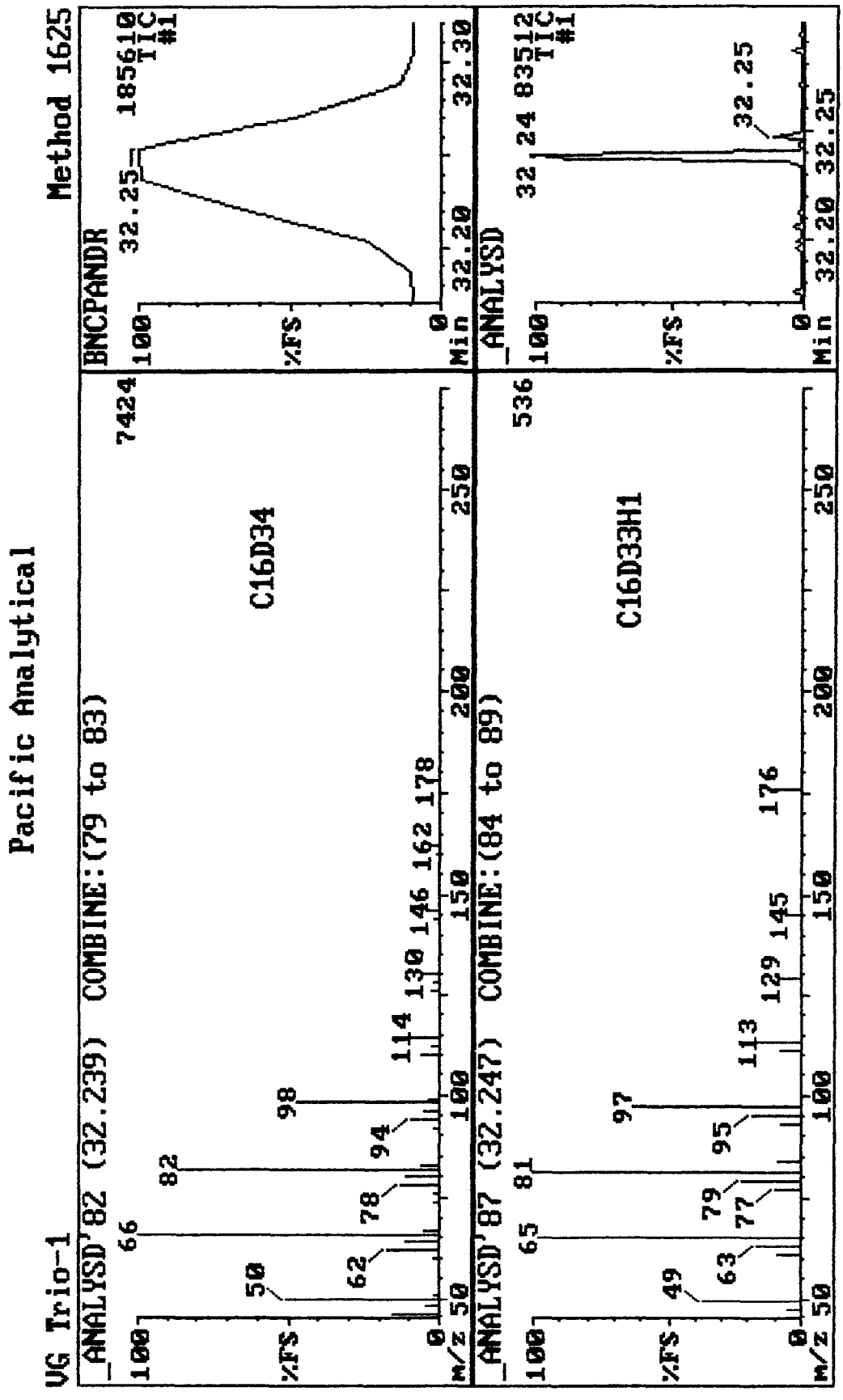
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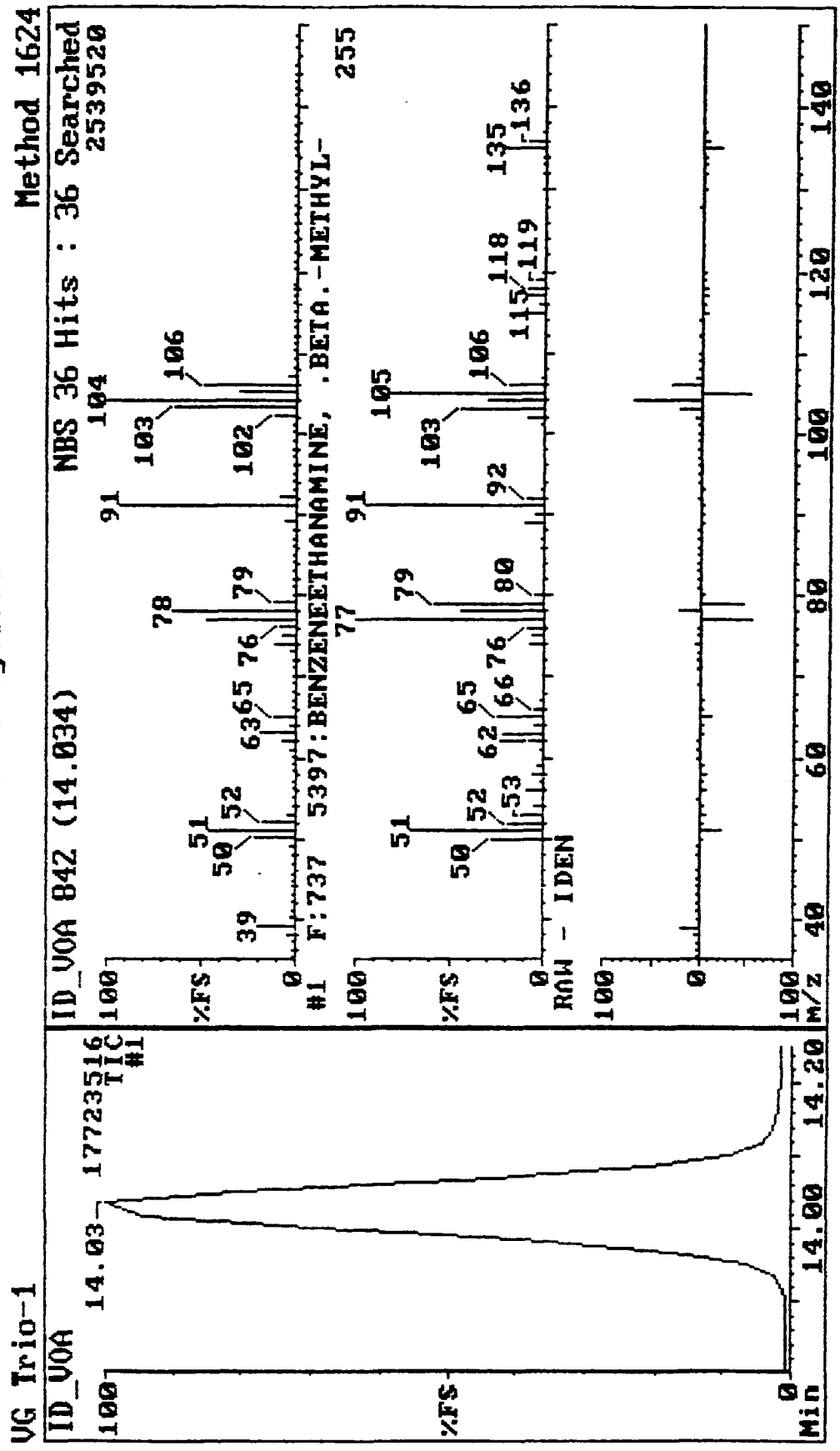
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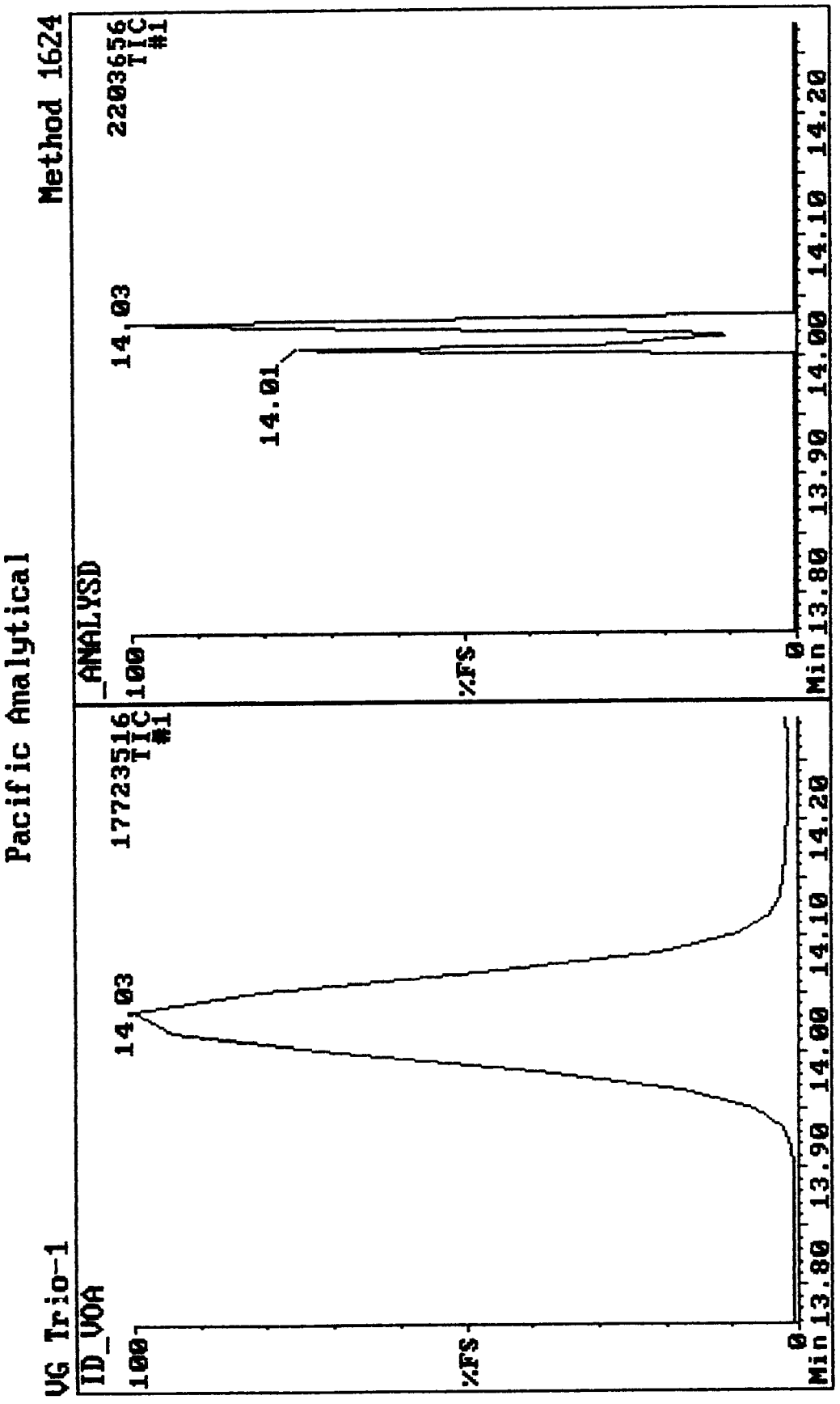
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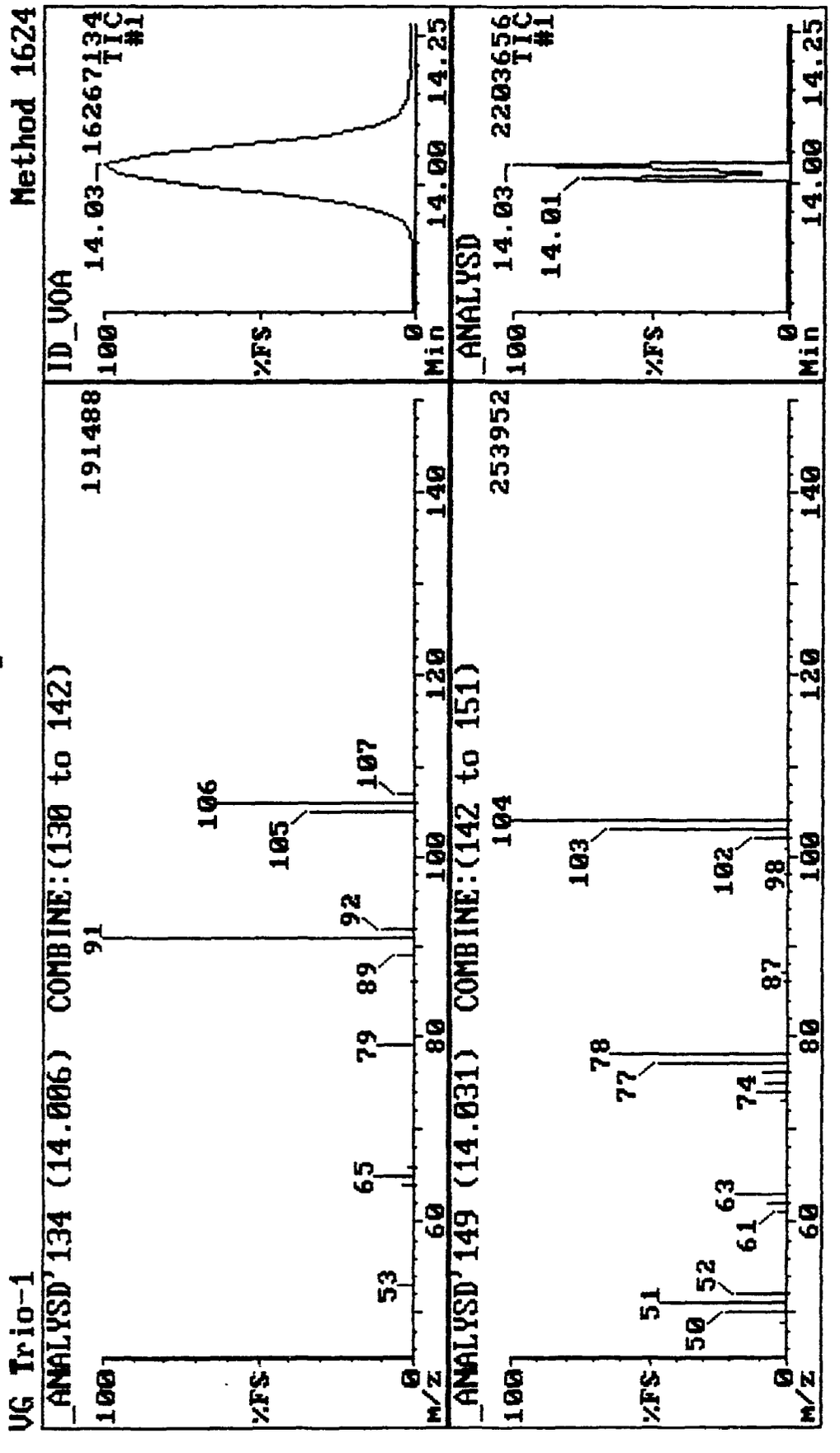
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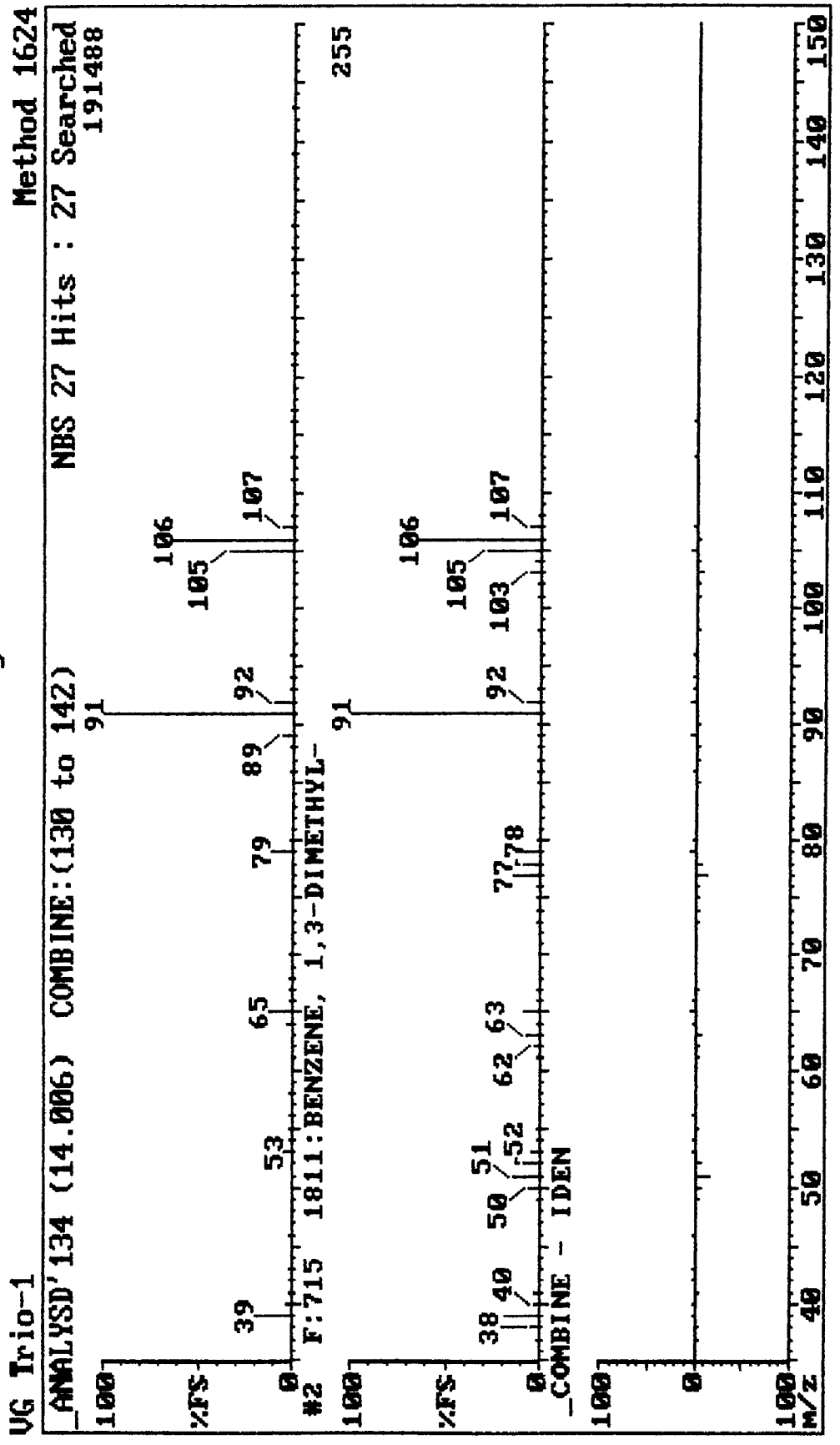
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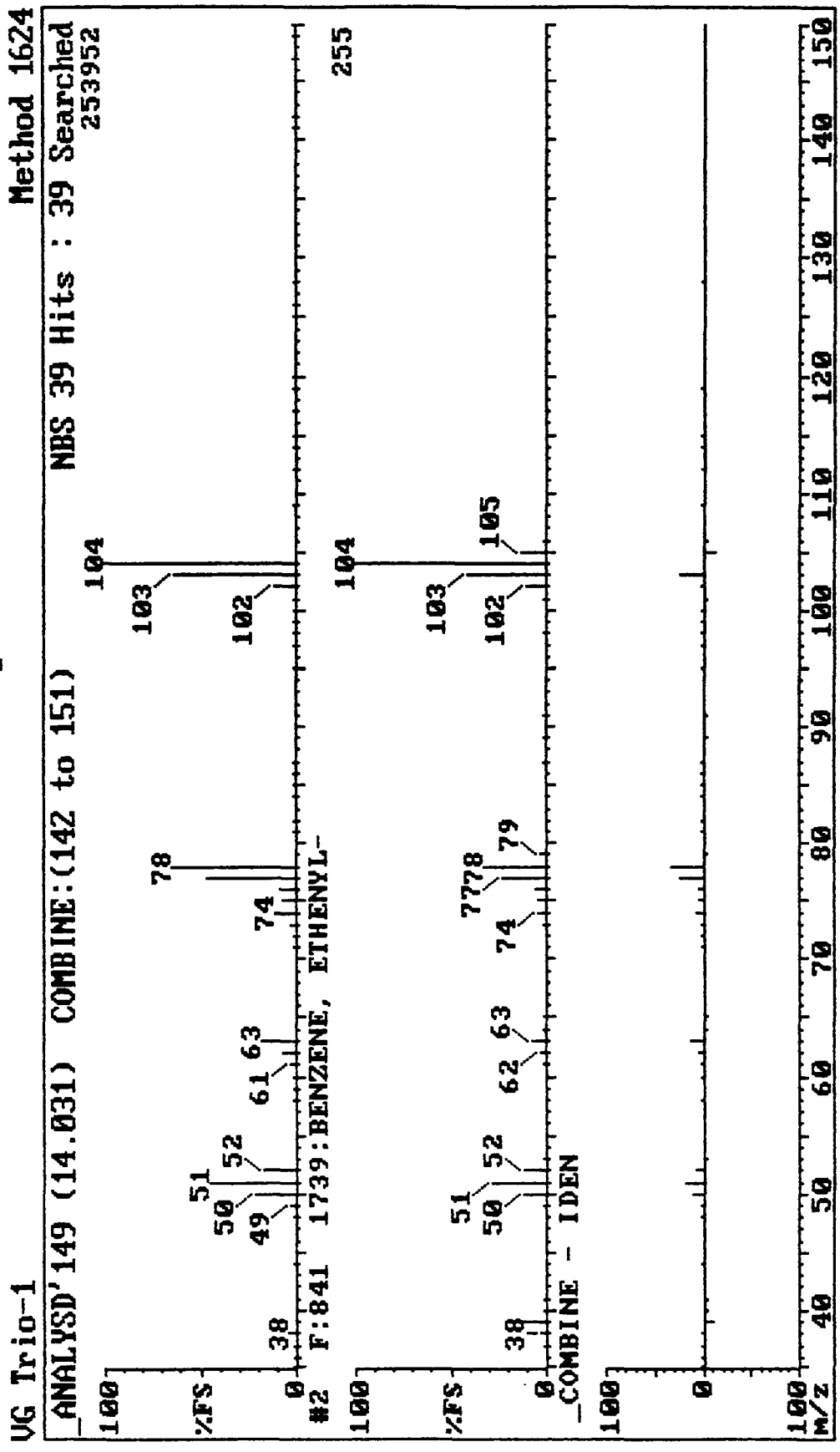
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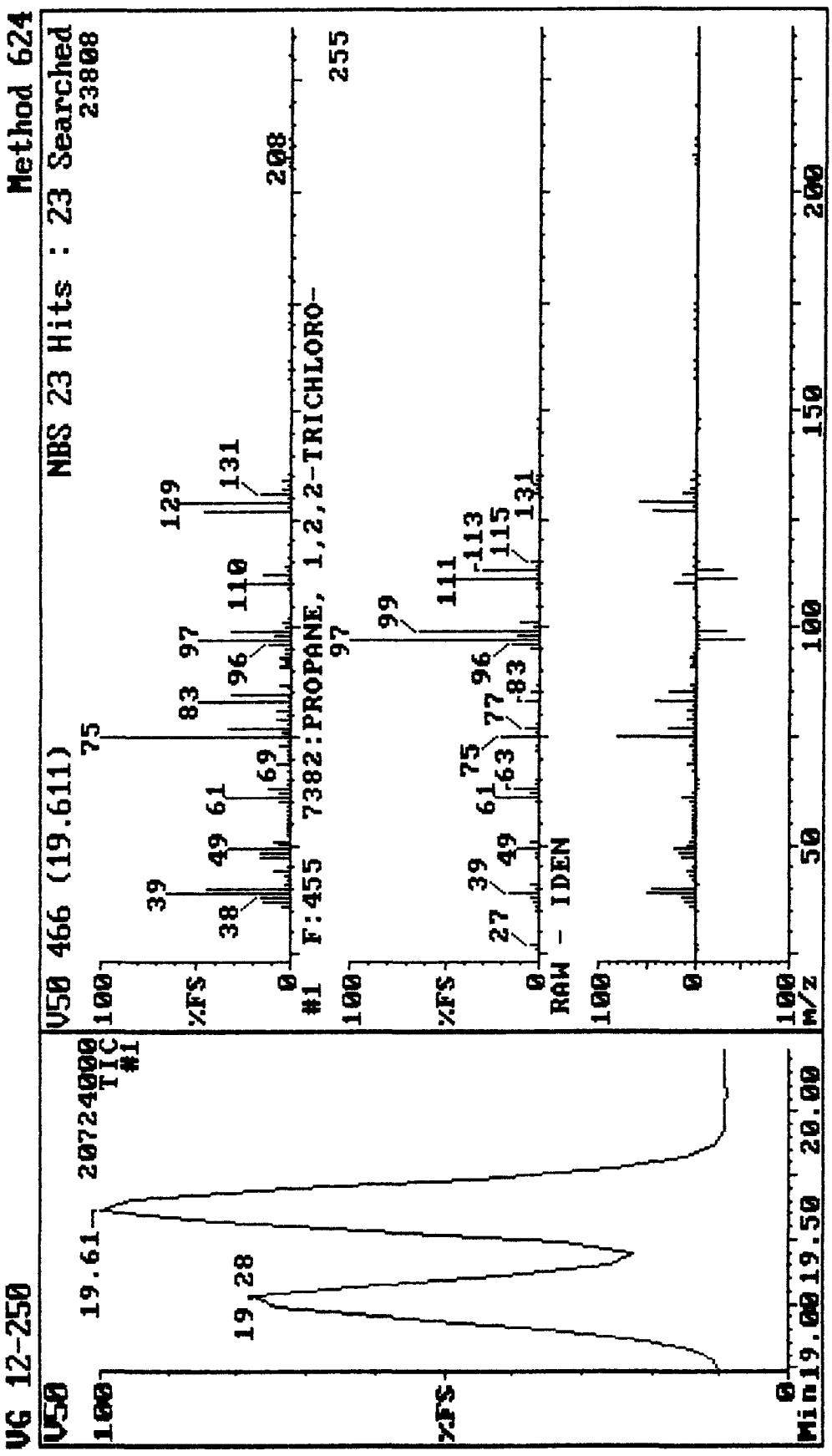
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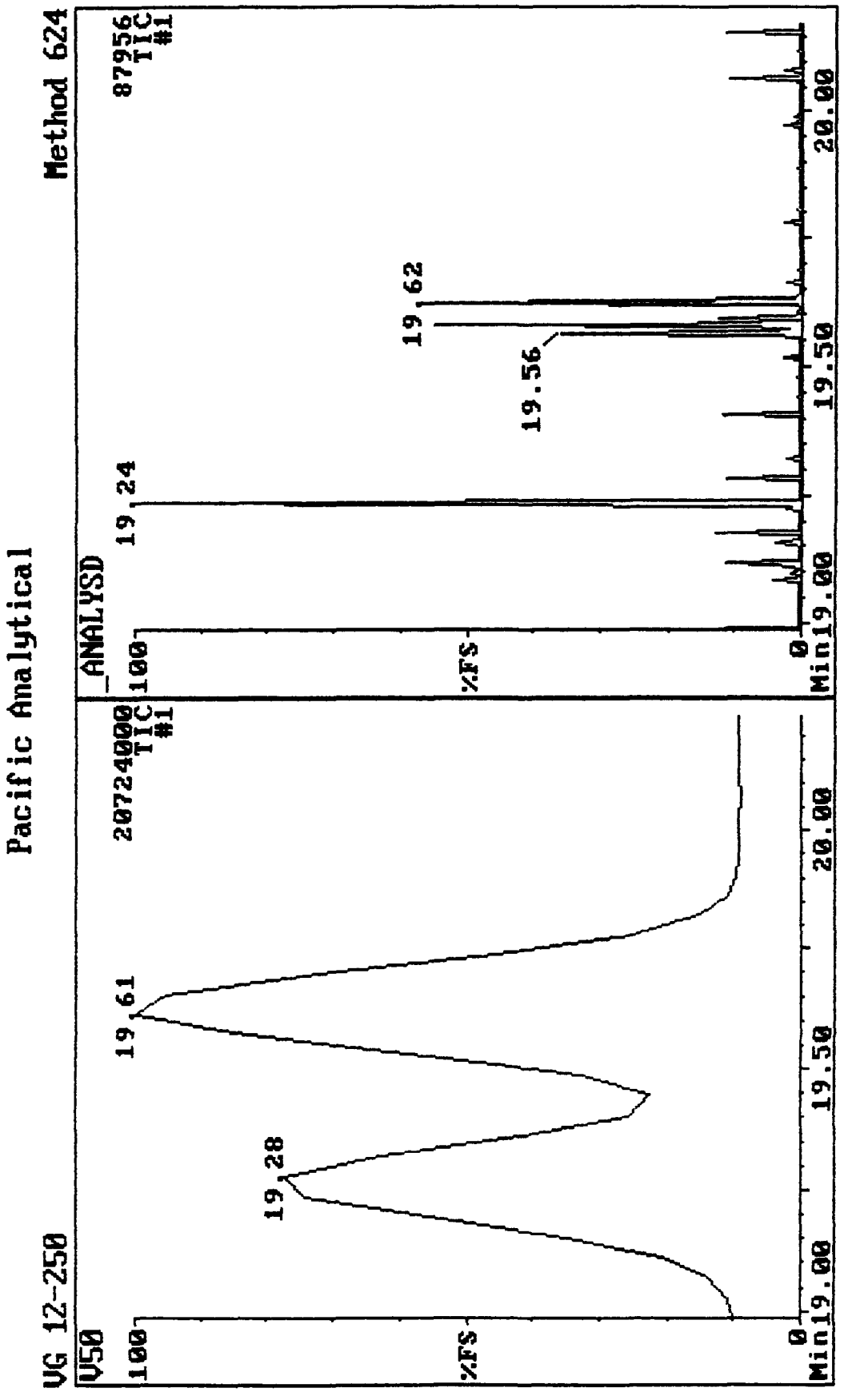
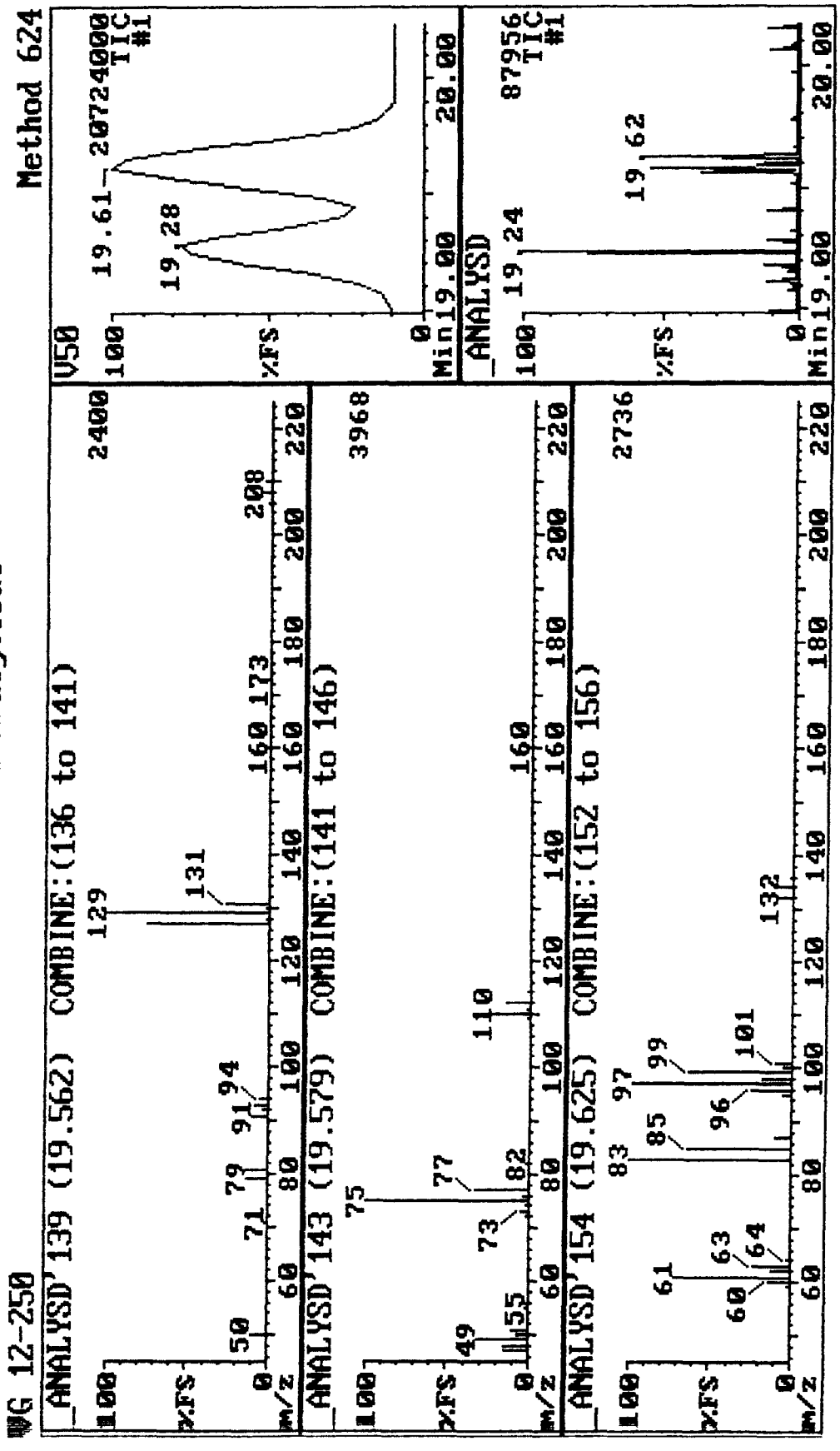
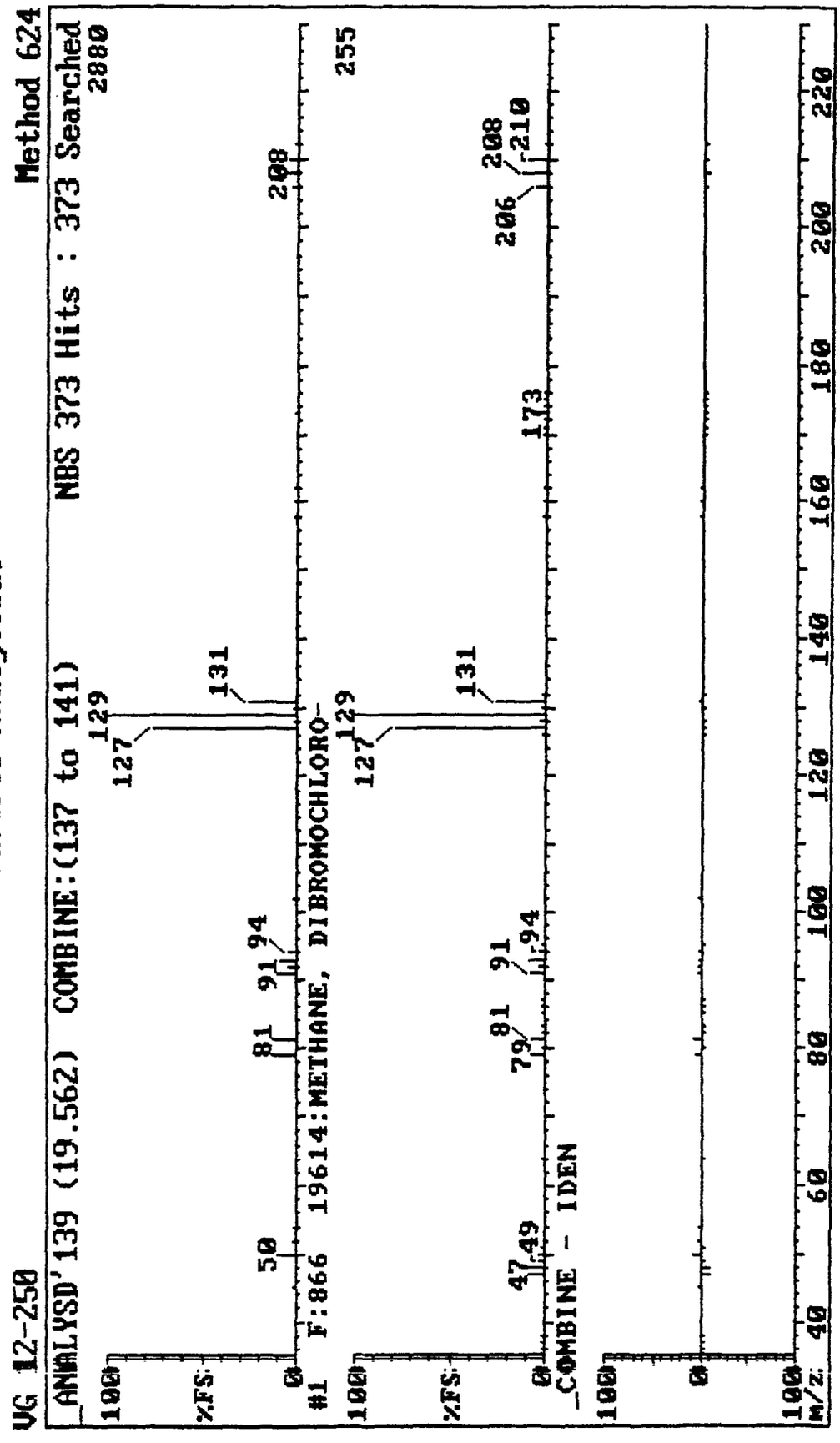
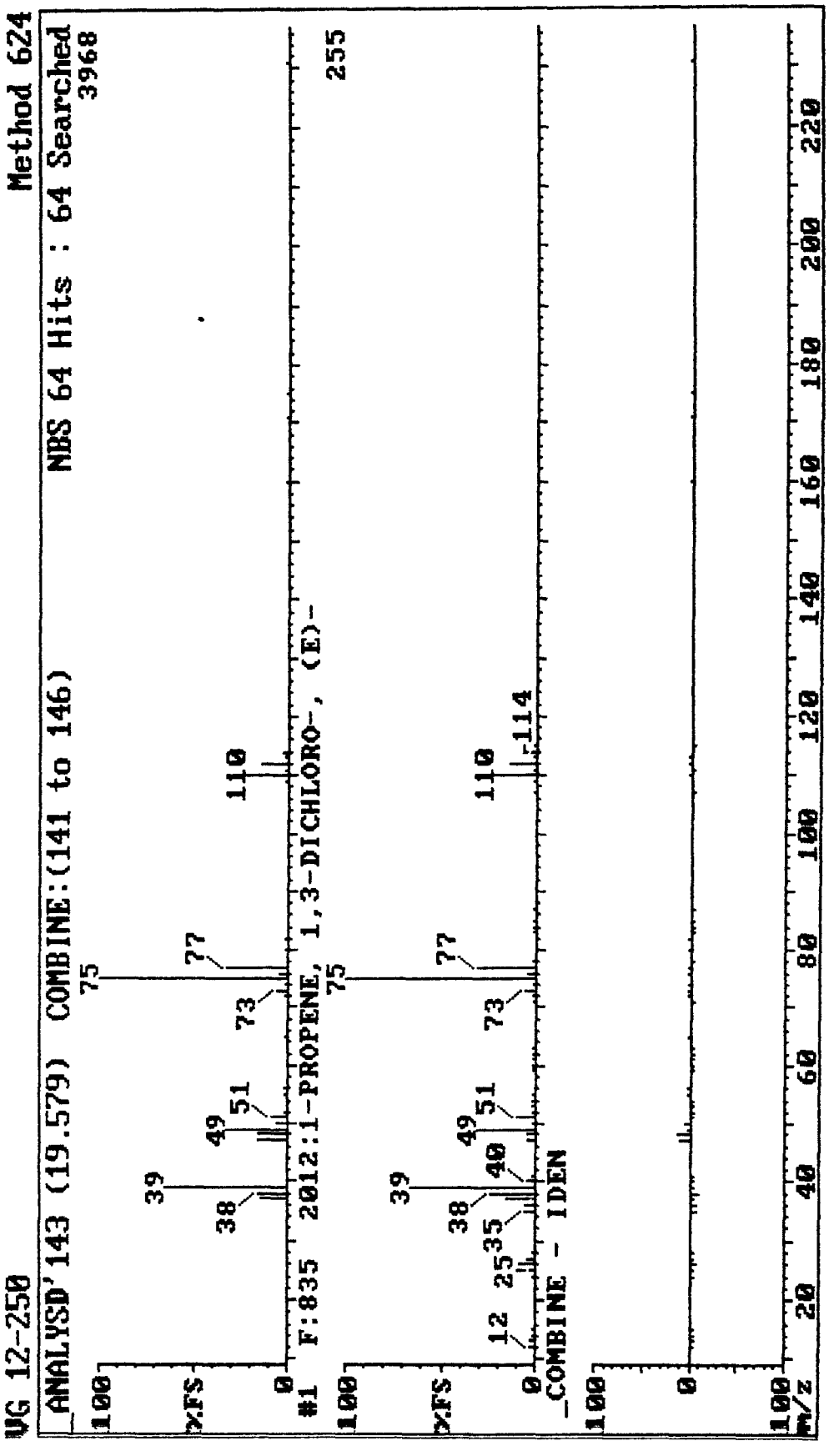
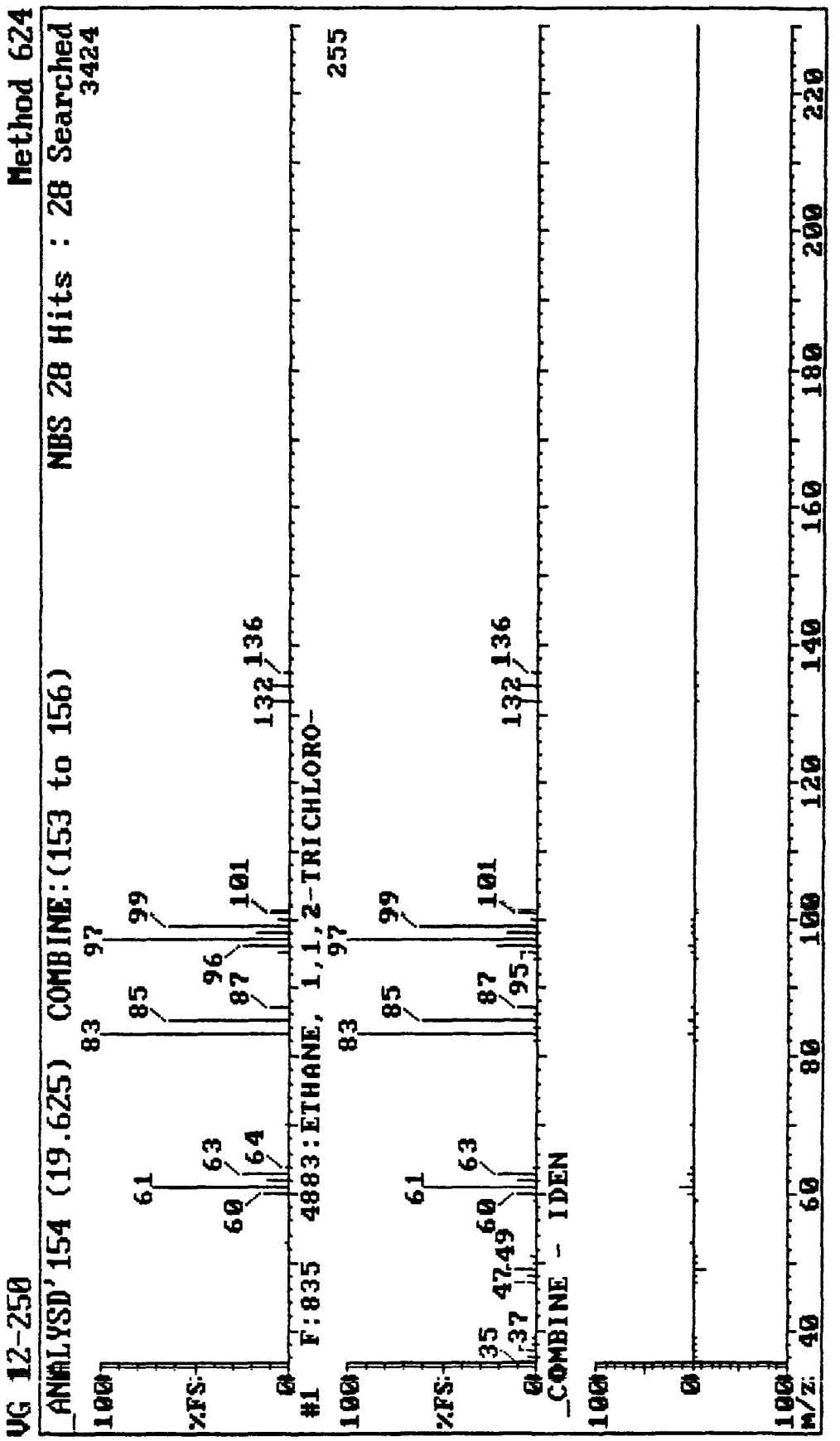
V50
TIC
#1
19.61
19.28
%FS
Min
19.00
19.50
20.00
V50 466 (19.611)
NBS 23 Hits : 23 Searched
#1 F:455 7382:PROPANE, 1,2,2-TRICHLORO-
RAW - IDEN
m/z

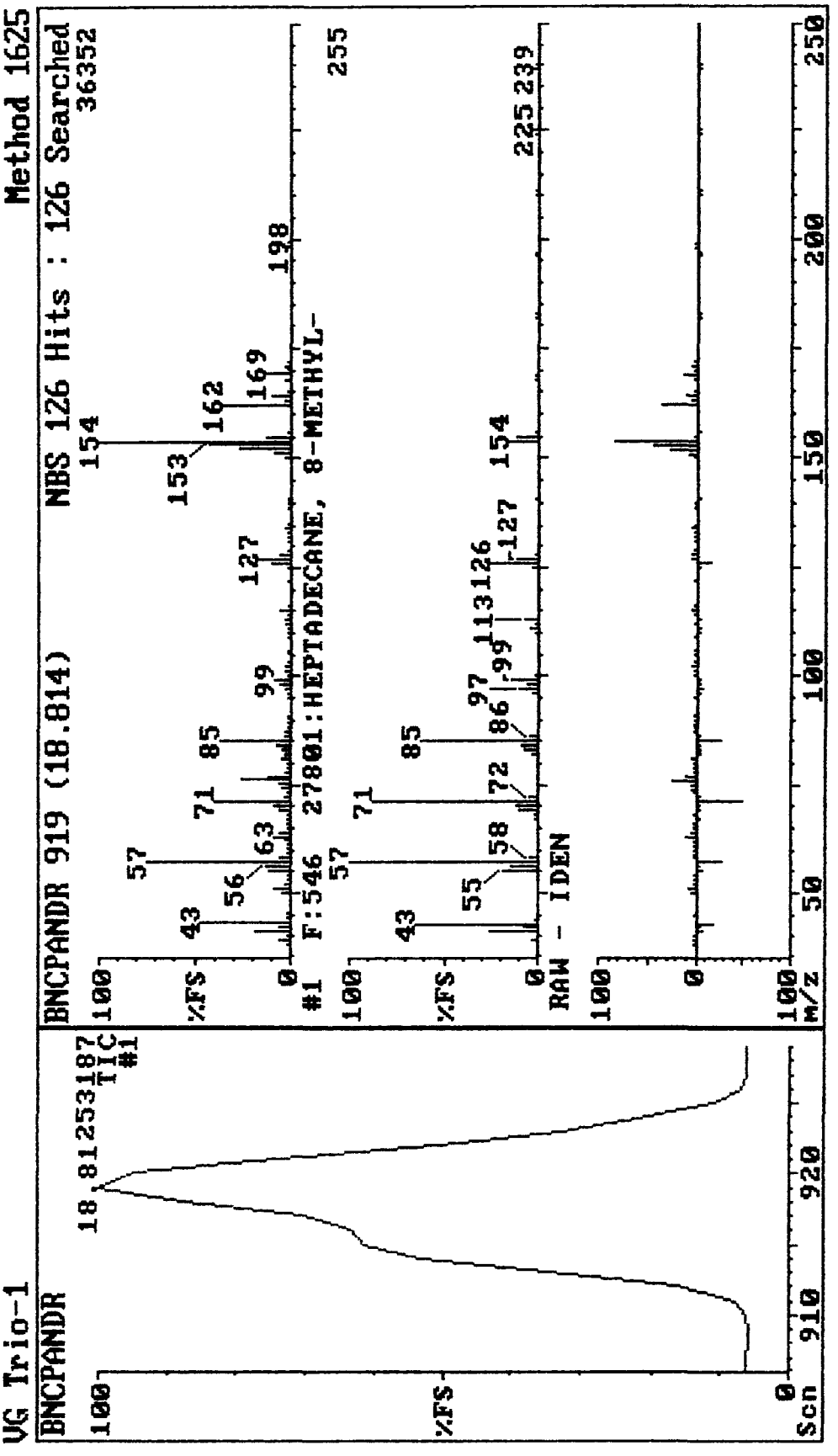

Pacific Analytical
Method 624
VG 12-250
V50
100
%FS
0
Min19.00
19.50
20.00
19.61
19.28
207240000
TIC
#1
_ANALYSD
19.24
19.62
19.56
87956
TIC
#1

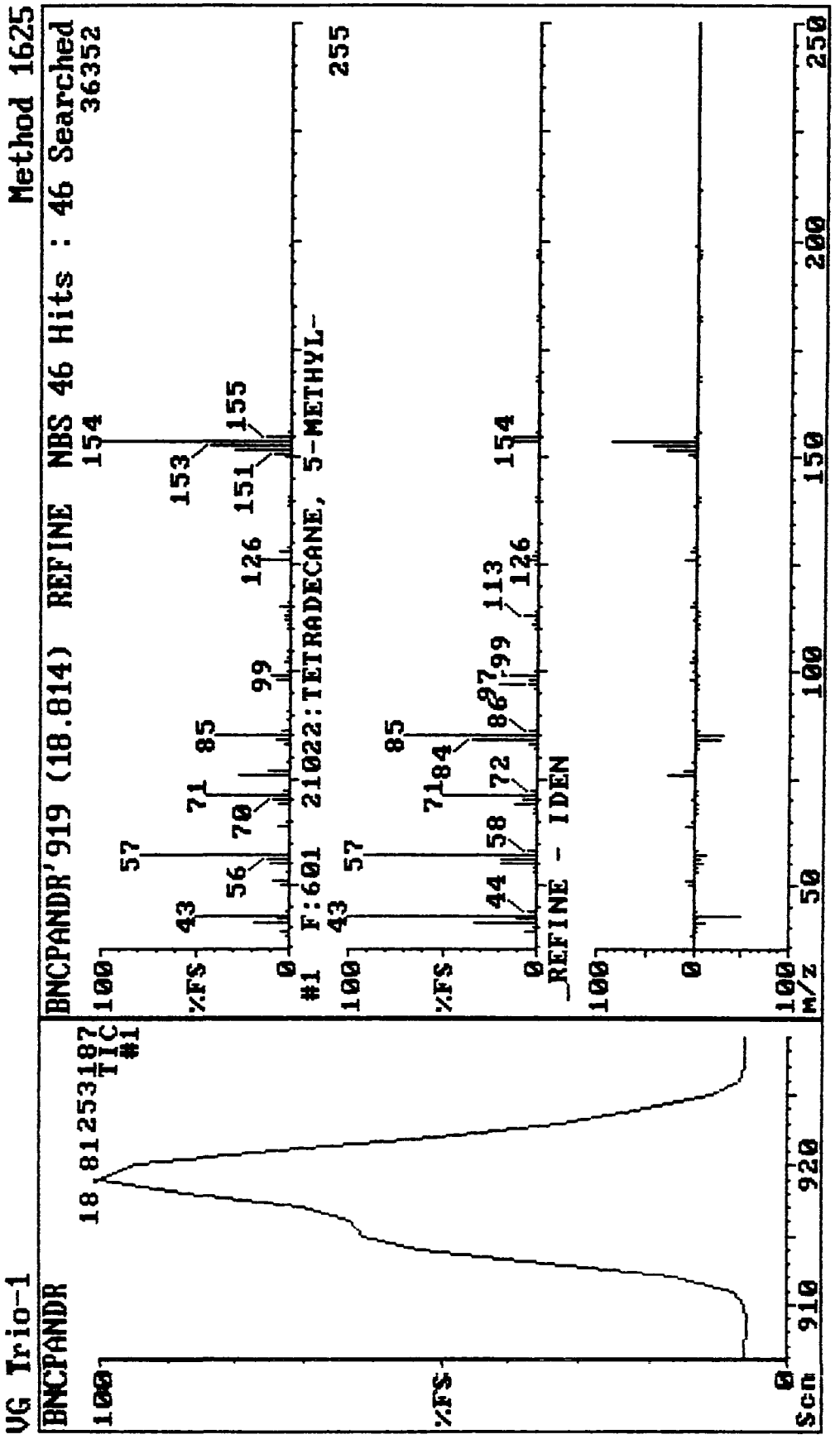

Pacific Analytical
Method 624
WG 12-250
_ANALYSD 139 (19.562) COMBINE:(136 to 141)
_ANALYSD 143 (19.579) COMBINE:(141 to 146)
_ANALYSD 154 (19.625) COMBINE:(152 to 156)
_ANALYSD
VSO
TIC #1
TIC #1
19.61
19.28
19.24
19.62
20724000
87956
2400
3968
2736
%FS
m/z
Min

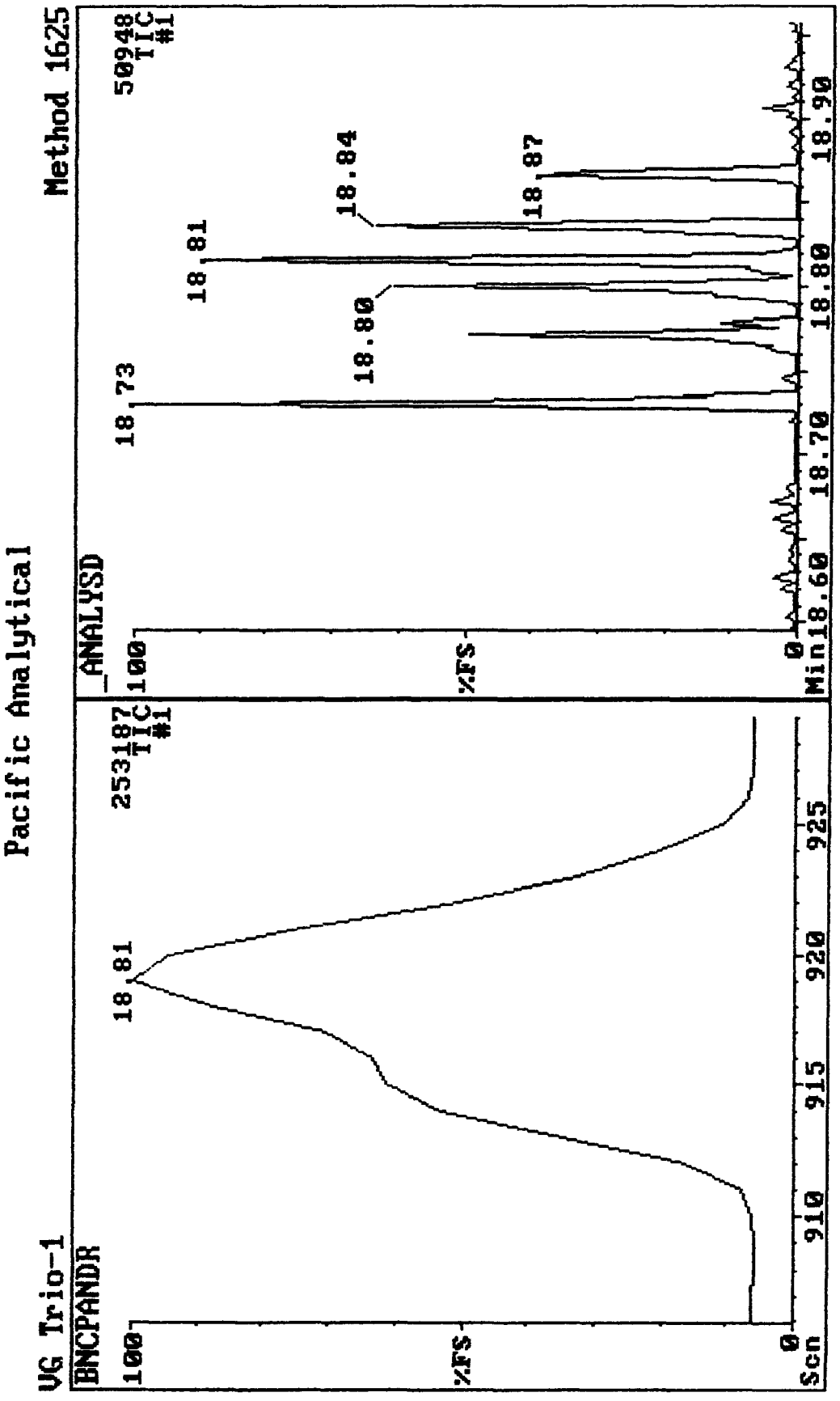

Pacific Analytical
Method 624
VG 12-250
_ANALYSD'139 (19.562) COMBINE:(137 to 141)
NBS 373 Hits : 373 Searched
2880
255
#1 F:866 19614:METHANE, DIBROMOCHLORO-
_COMBINE - IDEN
%FS:
M/z:
129
127
131
208
206
210
173
81
91
94
50
47
49
79
40
60
80
100
120
140
160
180
200
220

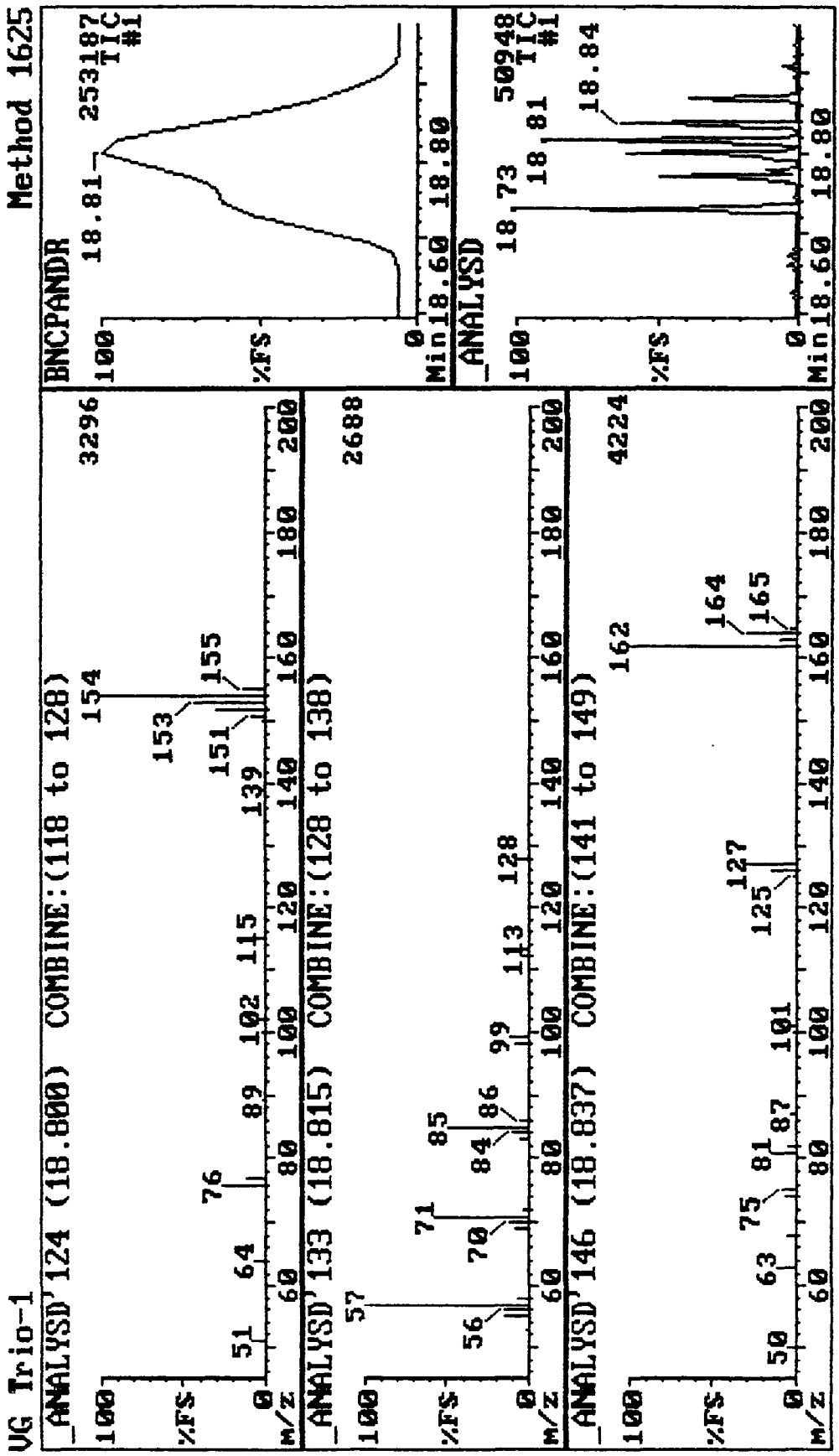

Pacific Analytical
Method 624
UG 12-250
_ANALYSD'143 (19.579) COMBINE:(141 to 146)
NBS 64 Hits : 64 Searched
3968
255
#1 F:835 2012:1-PROPENE, 1,3-DICHLORO-, (E)-
_COMBINE - IDEN
%FS
m/z
100
0
20
40
60
80
100
120
140
160
180
200
220
75
77
39
38
49
51
73
110
12
25
35
40
114

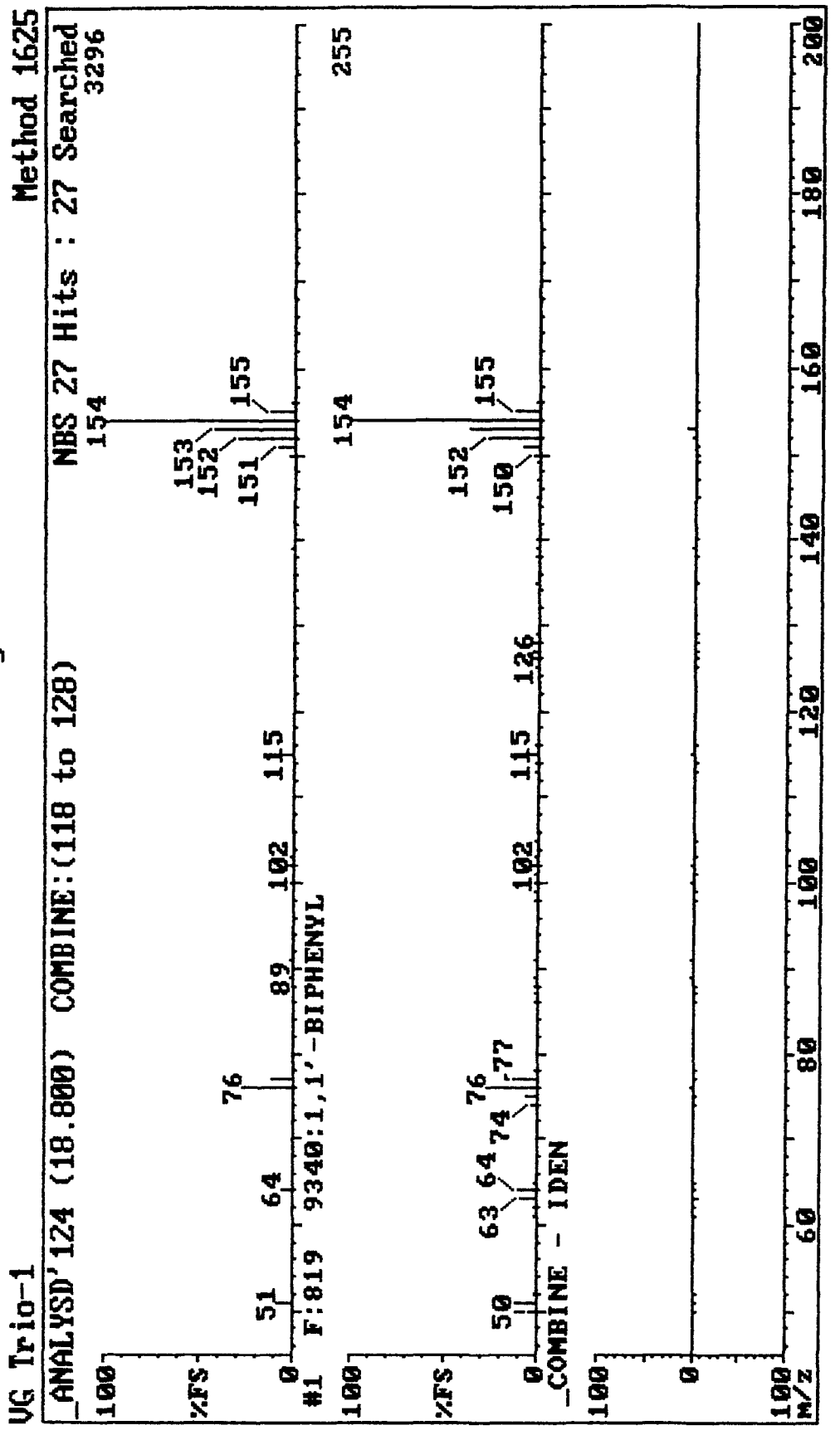

Pacific Analytical
VG 12-250
Method 624
ANALYSD'154 (19.625) COMBINE:(153 to 156)
NBS 28 Hits : 28 Searched
3424
#1 F:835 4883:ETHANE, 1,1,2-TRICHLORO-
255
_COMBINE - IDEN
%FS
m/z:

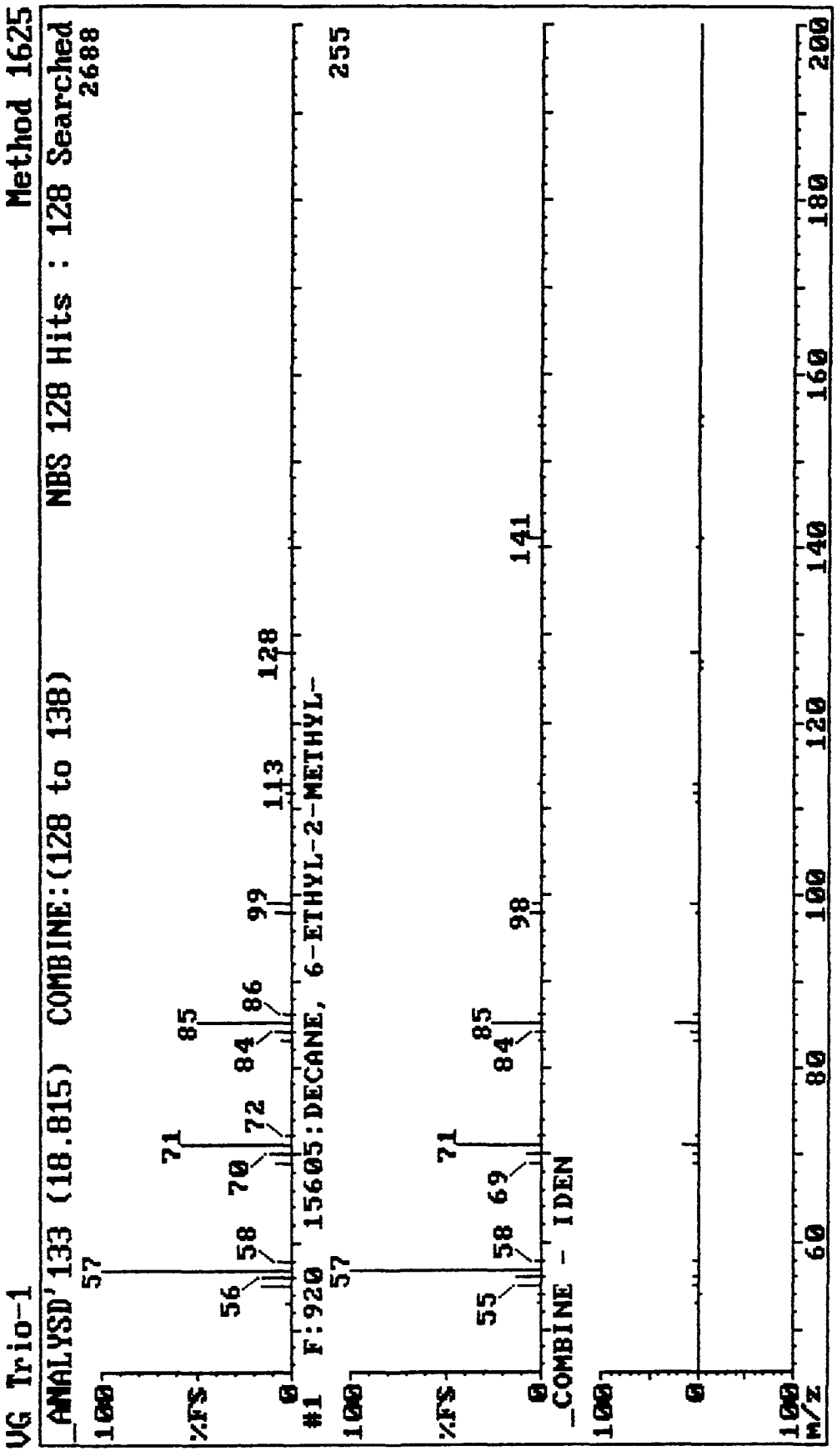

VG Trio-1
Pacific Analytical
Method 1625
BNCPANDR
TIC
#1
18.81
253
187
%FS
Scn
910
920
BNCPANDR 919 (18.814)
NBS 126 Hits : 126 Searched
36352
#1 F:546 27801:HEPTADECANE, 8-METHYL-
RAW - IDEN
m/z
50
100
150
200
250
255
225
239
154
153
162
169
198
127
126
113
99
97
86
85
72
71
58
57
56
55
43
63

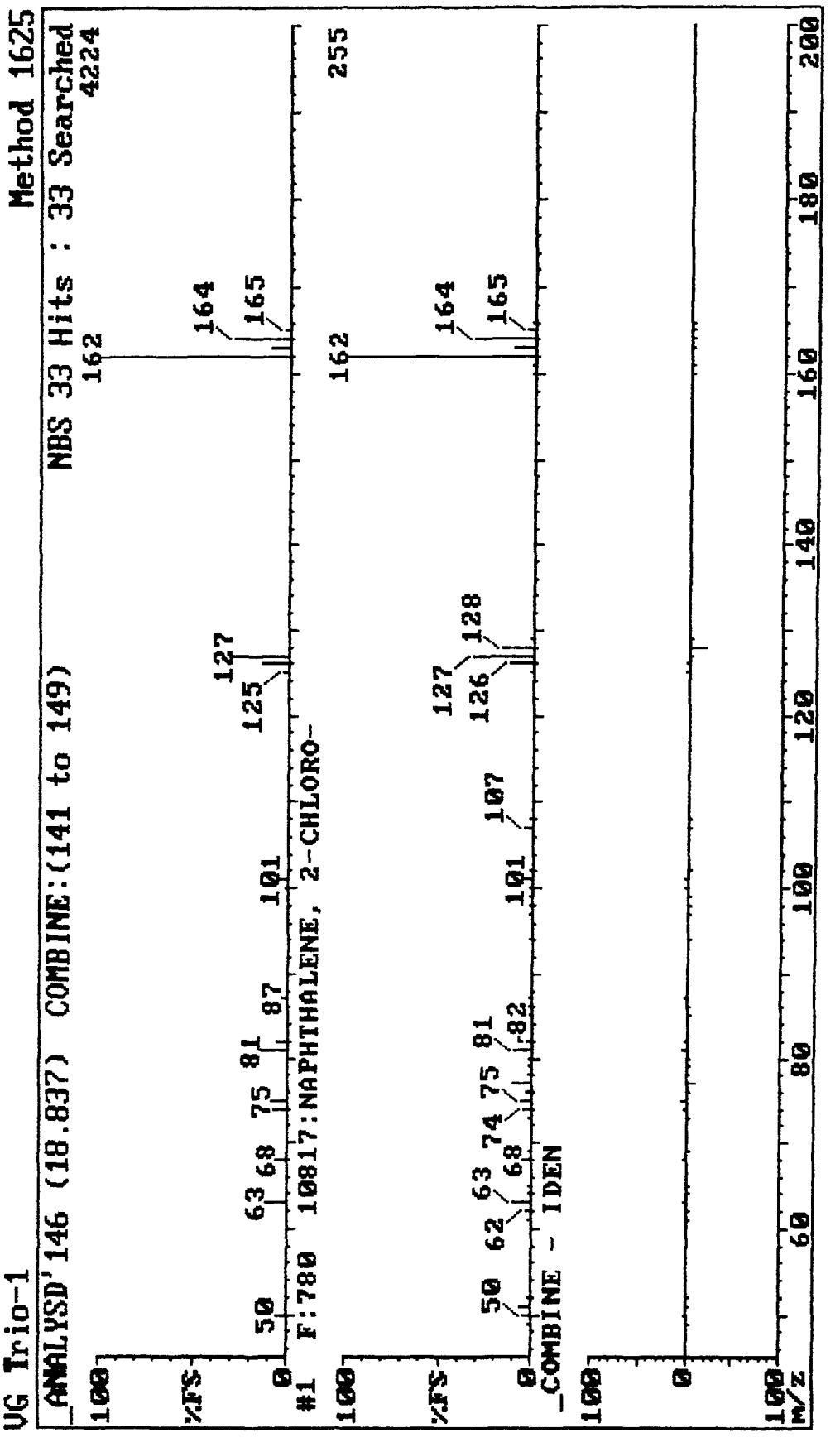

VG Trio-1
Pacific Analytical
Method 1625
BNCPANDR
%FS
Scn
TIC
#1
BNCPANDR'919 (18.814) REFINE NBS 46 Hits : 46 Searched
#1 F:601 21022:TETRADECANE, 5-METHYL-
REFINE - IDEN
m/z


VG Trio-1
Pacific Analytical
Method 1625
BNCPANDR
100
%FS
0
Scn
910
915
920
925
18.81
253187
TIC
#1
_ANALYSD
100
%FS
0
Min18.60
18.70
18.80
18.90
18.73
18.80
18.81
18.84
18.87
50948
TIC
#1


Pacific Analytical
Method 1625
VG Trio-1
BNCPANDR
18.81
253187
TIC
#1
Min 18.60 18.80
%FS
100
0
ANALYSD 124 (18.800) COMBINE:(118 to 128)
3296
154
153
155
151
139
76
89
102
115
64
51
ANALYSD 133 (18.815) COMBINE:(128 to 138)
2688
57
71
85
86
99
113
128
70
84
56
ANALYSD 146 (18.837) COMBINE:(141 to 149)
4224
162
164
165
127
125
101
87
81
75
63
50
m/z
60
80
100
120
140
160
180
200


Pacific Analytical
VG Trio-1
Method 1625
_ANALYSD'124 (18.800) COMBINE:(118 to 128)
NBS 27 Hits : 27 Searched
3296
#1 F:819 9340:1,1'-BIPHENYL
_COMBINE - IDEN
%FS
M/z


Pacific Analytical
Method 1625
VG Trio-1
_ANALYSD' 133 (18.815) COMBINE:(128 to 138)
NBS 128 Hits : 128 Searched
2688
255
#1 F:920 15605:DECANE, 6-ETHYL-2-METHYL-
_COMBINE - IDEN
%FS
m/z
57
56
58
71
70
72
85
84
86
99
113
128
141
98
55
69


Pacific Analytical
UG Trio-1
Method 1625
ANALYSD'146 (18.837) COMBINE:(141 to 149)
NBS 33 Hits : 33 Searched 4224
#1 F:780 10817:NAPHTHALENE, 2-CHLORO-
_COMBINE - IDEN
%FS
m/z

MR. McCARTY: Our last speaker in this session immediately before the break on GC/MS issues is William Eckel from Viar and Company. Bill has been with Viar for something on the order of 10 or 11 years. He started out as a member of the group that works on one of our projects for Superfund scheduling samples, and he has worked his way up to the point where he can now deal with exciting topics like reverse search compounds. Bill is also the two time apple bobbing champ at the Viar Company picnic. He works very hard at this. He spends a hell of a lot of time with his head in a bucket, sometimes under water.

Bill, if you still want to go on, it's up to you.

REVERSE SEARCH COMPOUND STUDY: METHODS 1624C AND 1625C

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Sample Control Center
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Alexandria, Virginia 22314

ABSTRACT

Four laboratories participated in an inter-laboratory study to establish Relative Response Factor (RRF) and Relative Retention Time (RRT) data for 118 Reverse Search (RS) compounds to be published in ITD methods 1624C and 1625C. The laboratories performed five-point calibrations using standards of the Reverse Search compounds supplied by one of the participating laboratories. The resulting data were reported to, and statistically analyzed by the Sample Control Center. The results of the statistical analysis indicate that the best qualitative and quantitative results for Reverse Search compounds would be achieved by requiring each laboratory which uses these methods to establish its own RRF and RRT data.

INTRODUCTION

A inter-laboratory study was conducted in the first half of 1990, under SCC episode 1878, to revise the RRF and RRT specifications for the Reverse Search (RS) compounds in methods 1624C and 1625C, which are presently based on one laboratory's data. One of the participating laboratories obtained standards for the 118 RS compounds, prepared combined standards for the two methods, and distributed the combined standards to the three other participating laboratories for analysis. The study results were reported to the Sample Control Center and were then subjected to statistical analysis to determine the suitability of the data for establishing new RRT and RRF specifications for the RS compounds in methods 1624C and 1625C.

METHODOLOGY

Laboratory Analysis

The participating laboratories performed five-point calibrations as specified in methods 1624C and 1625C, using the combined RS compound standards supplied to them. Data were reported in both computer-readable and hardcopy formats.

Statistical Analysis of Laboratory Data

1. Relative Retention Times (RRT)

The RRT data submitted by the four participating laboratories were analyzed by the same methods used for the inter-laboratory study which established the RRT windows for the Target compounds in method 1625 (SRI International, "Interlaboratory Validation of U.S. Environmental Protection Agency Method 1625A", Draft Final Report, June 1984). Briefly, the GC temperature programs used by each of the laboratories were reviewed for adherance to

those specified in the methods. Data from laboratories which did not use the temperature ramps specified in the methods were rejected. (This resulted in the rejection of one laboratory's data in both fractions). Data from the remaining laboratories was subjected to an outlier analysis, which rejected 2% of all the data points as outliers. Next, 95% Prediction Intervals (95% PI) were calculated from the remaining data to establish RRT windows. These windows were compared to the RRT specifications for RS compounds presently given in methods 1624C and 1625C to see whether or not the 'old' RRTs fell within the 'new' RRT windows.

2. Relative Response Factors

The RRF data were reviewed using Analysis of Variance (ANOVA), by calculating Percent Relative Standard Deviations (%RSDs) for the five-point calibrations, and by plotting RRF versus concentration for each compound and laboratory. The ANOVA was used to detect differences between laboratories, between laboratories and the method specifications, and between concentration levels within laboratories. The %RSD calculations were used to follow up the results of the ANOVA, and to evaluate calibration linearity and stability of Response Factors.

RESULTS AND DISCUSSION

1. Relative Retention Time data

The 'new' RRT windows for RS compounds calculated in this study are presented in Tables 1 (method 1624C) and 2 (1625C). Compounds whose 'old' method RRTs do not fall within these windows have an asterisk in the 'flag' column. The discrepancies between the 'old' RRTs and the 'new' RRT windows are detailed in Tables 3 (1624C) and 4 (1625C). In Tables 3 and 4, the column 'deltaRRT' shows how far outside the 'new' RRT window the 'old' RRT is. Figures 1 (method 1624C) and 2 (1625C) plot the midpoint of the RRT windows versus the widths of the windows.

Most of the RRT values currently in method 1625C fell within the RRT windows calculated by the above-mentioned methods; only 14 of 94 RS compounds' 'old' RRT values fall outside the new windows (see Table 4). For eight of these compounds, the difference between the 'old' RRT and the RRT windows from this study is marginal (0.014 RRT units or less). The other four compounds have more substantial differences.

For the volatiles, over half (14) of the 24 compounds studied have 'old' method RRT values outside the RRT windows from this study (see Table 3). Again, however, the differences are marginal (0.019 RRT units or less) for seven of the twelve. The two with the largest differences (the xylenes) are the last compounds to elute. This may be due to differences in the final isothermal period of the GC temperature program used (between this study and the one used to establish the original single RRT values). The last three compounds in Table 3 are all "hot purge" compounds and none of the three was detected at all five levels of the initial calibration by the three laboratories (this may be because the "hot" purge was not used).

Figures 1 and 2 demonstrate, as expected, that the width of the RRT windows becomes relatively larger as the RRT departs from 1.0. (Note the difference in the vertical scale in figures 1 and 2). This appears to serious for early-eluting compounds in method 1625C, for

some of which the width of the window is greater than the RRT. For example, the RRT window for 1,2:3,4-diepoxybutane is 0.143 to 0.459 ('old' RRT, 0.352). Such wide RRT windows would seem to be of little use in compound identification. Referencing compounds in this part of the chromatogram to an early-eluting internal standard (or labelled compound) would alleviate this problem. The obvious outlier in Figure 2 at an RRT just below 1.2, is 1,4-naphthoquinone. The calibrations for this compound were badly saturated, which may have had some effect on the RRT data.

In the course of the analysis, it was noted that there was no overlap in RRTs between some of the laboratories using different GC temperature programs. RRT data from two laboratories did not fall within a 95% Confidence Interval (which is narrower than the 95% Prediction Interval mentioned above) calculated from all four laboratories' data. This points out the necessity of matching the analysis conditions which a laboratory is using to those used in generating the reference RRT data, in order for the reference RRT data to be valid for compound identification under the conditions of use.

2. Relative Response Factor Data

Analysis of Variance (ANOVA) was performed on the RRF data to answer three questions:

1) Are there significant differences between RRFs at different calibration levels within laboratories?

2) Are there significant differences between mean RRFs between laboratories?

3) Are there significant differences between laboratories' mean RRFs and the present RRF specifications in the methods?

The ANOVA results allowed us to conclude that:

1) Except for three compounds, there were no significant differences (95% level) between RRFs at different calibration levels within laboratories. Percent Relative Standard Deviations (% RSDs) were, in general, acceptably low (less than 25%).

2) There were significant differences (95% level) between laboratory mean RRFs (for all compounds which all of the laboratories were able to detect). At most two of the four laboratories had mean RRFs that were not significantly different for a particular compound.

3) There were significant differences (95% level) between laboratory mean RRFs and the method-specified RRFs. All four labs had significant differences for 43 compounds, three labs had significant differences for 49 compounds, two labs for 19 compounds, and one or no labs for only six compounds. Clearly the majority of the results were different than the method-specified RRFs.

Because each laboratory's data appeared well-behaved, we concluded that the differences were due to normal inter-laboratory variability. However, because the differences are significant, no one set of RRF specifications can be recommended for inclusion in the methods that would give equally accurate results from the four study laboratories.

Figures 3 through 10 show plots of RRFs versus calibration levels for selected compounds. These plots illustrate the differences between laboratories, and between the laboratories and the method-specified RRF, which is shown as a horizontal line.

CONCLUSIONS AND RECOMMENDATIONS

We recommend that laboratories using methods 1624C and 1625C be required to make their own RRT and RRF measurements, on a less-frequent basis than is required for the Target compounds. This could be done at the same time that Relative Retention Time measurements are being made, as mentioned above in the RRT section. A reasonable schedule might be to require a five-point calibration for the Reverse Search compounds at the time of the Initial Precision and Recovery (IPR) study, and then to require a one-point calibration at a lesser frequency than is required for the Ongoing Precision and Recovery (OPR) analysis (say, once a week or once a month). An early-eluting internal standard for method 1625C would help to narrow the RRT windows for early-eluting Reverse Search compounds. Measurements of RRT and RRF data for 'hot purge' compounds should be made under both hot and room-temperature conditions by individual laboratories.

We believe that the development of laboratory-specific RRT and RRF data is the best method to ensure the reliable identification and quantitation of Reverse Search compounds. The problems encountered by the laboratories in this study illustrate the qualitative and quantitative errors which could potentially be made by using RRT and RRF data which do not apply to the specific analytical system being used.

If laboratories are not to be required to generate their own RRF and RRT data for the reverse search compounds, then we recommend that this study be repeated, with strict adherance to the analysis conditions in the methods, and with proper Quality Control guidance. The methods would then need to be modified to require strict adherance to the analysis conditions, to ensure that use of the reference RRT and RRF data would result in reliable identification and quantitation of reverse search compounds.

QUESTION AND ANSWER SESSION

MR. McCARTY: Nobody seems to wants to ask questions about search compounds.

MR. ECKEL: It's a messy, messy subject.

MR. McCARTY: Nobody wants to do them either!

Surprisingly, we've finished up a little bit early. What I would like to do, in order to give you people more time to relax before we go out for our evening cruise this evening, is to take our break now and come back earlier than 4:15, since I see our 4:15 speaking standing at the back of the room, chafing at the bit. What say we reconvene about 4:00 here? Go out and have a few refreshments outside, and then we'll get out about 5:00, hopefully.

TABLE 1

METHOD 1624C (VOA) : NEW RELATIVE RETENTION WINDOWS
FOR REVERSE SEARCH COMPOUNDS

EGD NUMBER	COMPOUND NAME	OLD METHOD RRT	95% LOWER LIMIT	95% UPPER LIMIT	FLAG
532	2-PROPEN-1-OL	0.960	1.026	1.042	*
533	CARBON DISULFIDE	0.860	0.778	0.861	
535	CHLOROACETONITRILE	1.210	1.282	1.387	*
536	3-CHLOROPROPENE	0.950	0.940	0.969	
537	CROTONALDEHYDE	0.840	0.806	0.863	
538	1,2-DIBROMOETHANE	0.980	0.980	0.984	
539	DIBROMOMETHANE	1.250	1.261	1.351	*
540	TRANS-1,4-DICHLORO-2-BUTENE	1.000	1.000	1.000	
541	1,3-DICHLOROPROPANE	0.920	0.918	0.928	
542	CIS-1,3-DICHLOROPROPENE	0.870	0.862	0.879	
543	ETHYL CYANIDE	0.920	0.898	0.946	
544	ETHYL METHACRYLATE	1.030	1.028	1.041	
545	2-HEXANONE	0.980	0.967	0.979	*
546	IODOMETHANE	0.680	0.555	0.661	*
547	ISOBUTYL ALCOHOL	1.320	1.380	1.475	*
548	2-PROPENENITRILE, 2-METHYL-	1.260	1.266	1.326	*
549	METHYL METHACRYLATE	1.060	1.044	1.059	*
550	4-METHYL-2-PENTANONE	0.920	0.901	0.915	*
551	1,1,1,2-TETRACHLOROETHANE	1.080	1.072	1.093	
552	TRICHLOROFLUOROMETHANE	0.910	0.852	0.903	*
553	1,2,3-TRICHLOROPROPANE	0.980	0.975	0.980	*
554	VINYL ACETATE	0.790	0.746	0.790	*
951	M-XYLENE	1.510	1.298	1.422	*
952	O+P XYLENE	1.570	1.326	1.480	*

TABLE 2

METHOD 1625C (SEMI) : NEW RELATIVE RETENTION WINDOWS
FOR REVERSE SERACH COMPOUNDS

EGD NUMBER	COMPOUND NAME	OLD METHOD RRT	95% LOWER LIMIT	95% UPPER LIMIT	FLAG
555	ACETOPHENONE	0.703	0.654	0.729	
556	4-AMINOBIPHENYL	1.334	1.320	1.363	
557	ANILINE	0.597	0.519	0.636	
558	O-ANISIDINE	0.827	0.802	0.835	
559	ARAMITE	1.635	1.591	1.708	
560	BENZANTHRONE	1.811	1.791	1.888	
561	RESORCINOL	0.936	0.901	0.960	
562	BENZENETHIOL	0.574	0.455	0.638	
563	2,3-BENZOFLUORENE	1.661	1.631	1.721	
564	BENZYL ALCOHOL	0.675	0.613	0.692	
565	1-BROMO-2-CHLOROBENZENE	0.757	0.674	0.820	
565	1-BROMO-2-CHLOROBENZENE	0.757	0.674	0.820	
566	1-BROMO-3-CHLOROBENZENE	0.734	0.736	0.739	*
567	4-CHLORO-2-NITROANILINE	1.222	1.211	1.235	
568	O-TOLUIDINE, 5-CHLORO-	0.947	0.938	0.955	
569	P-CHLOROANILINE	0.874	0.830	0.863	*
570	1-CHLORO-3-NITROBENZENE	0.875	0.858	0.892	
571	O-CRESOL	0.700	0.651	0.708	
572	CROTOXYPHOS	1.567	1.508	1.662	
573	2,6-DI-TERT-BUTYL-P-BENZOQUINONE	1.095	1.100	1.116	*
574	TOLUENE, 2,4-DIAMINO-	1.021	1.025	1.034	*
575	1,2-DIBROMO-3-CHLOROPROPANE	0.721	0.674	0.749	
576	2,6-DICHLORO-4-NITROANILINE	1.083	1.301	1.344	*
577	1,3-DICHLORO-2-PROPANOL	0.506	0.356	0.557	
578	2,3-DICHLOROANILINE	0.997	0.991	1.008	
579	2,3-DICHLORONITROBENZENE	1.044	1.041	1.054	
580	1,2:3,4-DIEPOXYBUTANE	0.352	0.143	0.459	
581	3,3'-DIMETHOXYBENZIDINE	1.797	1.753	1.883	
582	DIMETHYL SULFONE	0.558	0.415	0.572	
583	P-DIMETHYLAMINOAZOBENZENE	1.653	1.617	1.720	
584	7,12-DIMETHYLBENZ(A)ANTHRACENE	1.964	1.945	2.060	
585	N,N-DIMETHYLFORMAMIDE	0.350	0.131	0.439	
586	3,6-DIMETHYLPHENANTHRENE	1.516	1.499	1.562	
587	1,4-DINITROBENZENE	1.079	1.067	1.074	*
588	DIPHENYLDISULFIDE	1.396	1.380	1.429	
589	ETHYL METHANESULFONATE	0.548	0.450	0.583	
590	ETHYLENETHIOUREA	1.187	1.148	1.207	
591	MESTRANOL	1.899	1.856	1.992	
592	HEXACHLOROPROPENE	0.871	0.830	0.874	
593	2-ISOPROPYLNAPHTHALENE	1.078	1.092	1.107	*
594	ISOSAFROLE	0.986	0.957	1.036	
595	LONGIFOLENE	1.053	1.051	1.071	
596	MALACHITE GREEN	2.048	2.035	2.147	
597	METHAPYRILENE	1.531	1.491	1.574	
598	METHYL METHANESULFONATE	0.439	0.290	0.518	
599	2-METHYLBENZOTHIOAZOLE	0.945	0.932	0.959	
900	3-METHYLCHOLANTHRENE	2.097	2.063	2.219	
901	4,4'-METHYLENEBIS(2-CHLOROANILINE)	1.791	1.752	1.878	
902	4,5-METHYLENE PHENANTHRENE	1.453	1.446	1.496	
903	1-METHYLFLUORENE	1.302	1.295	1.327	
904	2-METHYLNAPHTHALENE	0.944	0.930	0.962	
905	1-METHYLPHENANTHRENE	1.459	1.450	1.502	

TABLE 2

METHOD 1625C (SEMI) : NEW RELATIVE RETENTION WINDOWS
FOR REVERSE SERACH COMPOUNDS

EGD NUMBER	COMPOUND NAME	OLD METHOD RRT	95% LOWER LIMIT	95% UPPER LIMIT	FLAG
906	2-(METHYLTHIO)BENZOTHIAZOLE	1.217	1.215	1.238	
907	1,5-NAPHTHALENEDIAMINE	1.441	1.427	1.474	
908	1,4-NAPHTHOQUINONE	1.052	0.775	1.591	
909	1-NAPHTHYLAMINE	1.168	1.161	1.175	
910	5-NITRO-O-TOLUIDINE	1.223	1.212	1.232	
911	2-NITROANILINE	1.047	1.048	1.055	*
912	3-NITROANILINE	1.115	1.115	1.125	*
913	P-NITROANILINE	1.230	1.214	1.239	
914	BIPHENYL, 4-NITRO	1.409	1.395	1.445	
915	N-NITROSODI-N-BUTYLAMINE	0.914	0.906	0.917	
916	N-NITROSODIETHYLAMINE	0.490	0.372	0.557	
917	N-NITROSOMETHYLETHYLAMINE	0.338	0.179	0.512	
918	N-NITROSOMETHYLPHENYLAMINE	0.865	0.855	0.986	
919	N-NITROSOMORPHOLINE	0.717	0.664	0.727	
920	N-NITROSOPIPERIDINE	0.770	0.709	0.772	
921	PENTACHLOROBENZENE	1.152	1.149	1.167	
922	ETHANE, PENTACHLORO-	0.585	0.506	0.641	
923	PENTAMETHYLBENZENE	0.931	0.920	0.941	
924	PERYLENE	2.020	2.013	2.137	
925	PHENACETIN	1.300	1.274	1.330	
926	PHENOTHIAZINE	1.554	1.529	1.592	
927	1-PHENYLNAPHTHALENE	1.493	1.399	1.451	*
928	2-PHENYLNAPHTHALENE	1.490	1.474	1.536	
929	PRONAMIDE	1.357	1.332	1.397	
930	PYRIDINE	0.325	0.090	0.384	
931	SAFROLE	0.937	0.932	0.944	
932	SQUALENE	1.753	1.897	2.119	*
933	1,2,4,5-TETRACHLOROBENZENE	0.981	0.969	0.993	
934	THIANAPHTHENE	0.835	0.812	0.865	
935	THIOACETAMIDE	0.660	0.550	0.798	
936	THIOXANTHE-9-ONE	1.579	1.557	1.621	
937	O-TOLUIDINE	0.714	0.664	0.734	
938	1,2,3-TRIMETHOXYBENZENE	0.970	0.948	0.967	*
939	ANILINE, 2,4,5-TRIMETHYL-	0.938	0.932	0.948	
940	TRIPHENYLENE	1.795	1.768	1.866	
941	TRIPROPYLENEGLYCOL METHYL ETHER	0.758	0.927	0.979	*
942	1,3,5-TRITHIANE	0.764	0.938	0.971	*
943	BENZOIC ACID	0.835	0.782	0.866	
944	P-CRESOL	0.717	0.677	0.730	
945	BENZONITRILE, 3,5-DIBROMO-4-HYDROXY-	1.273	1.271	1.299	
946	2,6-DICHLOROPHENOL	0.844	0.829	0.867	
947	HEXANOIC ACID	0.641	0.557	0.653	
948	2,3,4,6-TETRACHLOROPHENOL	1.179	1.177	1.192	

TABLE 3

METHOD 1624C (VOA) : COMPOUNDS WHOSE PRESENT RRT IS OUTSIDE
THE RRT WINDOW FROM REVERSE SEARCH COMPOUND STUDY

EGD NUMBER	COMPOUND NAME	OLD METHOD RRT	95% LOWER LIMIT	95% UPPER LIMIT	Δ RRT
952	O+P XYLENE	1.570	1.326	1.480	0.090
951	M-XYLENE	1.510	1.298	1.422	0.088
546	IODOMETHANE	0.680	0.555	0.661	0.019
552	TRICHLOROFLUOROMETHANE	0.910	0.852	0.903	0.007
550	4-METHYL-2-PENTANONE	0.920	0.901	0.915	0.005
549	METHYL METHACRYLATE	1.060	1.044	1.059	0.001
545	2-HEXANONE	0.980	0.967	0.979	0.001
554	VINYL ACETATE	0.790	0.746	0.790	0.000
553	1,2,3-TRICHLOROPROPANE	0.980	0.975	0.980	0.000
548	2-PROPENENITRILE, 2-METHYL-	1.260	1.266	1.326	-.006
539	DIBROMOMETHANE	1.250	1.261	1.351	-.011
547	ISOBUTYL ALCOHOL	1.320	1.380	1.475	-.060
532	2-PROPEN-1-OL	0.960	1.026	1.042	-.066
535	CHLOROACETONITRILE	1.210	1.282	1.387	-.072

TABLE 4

METHOD 1625C (SEMI): COMPOUNDS WHOSE PRESENT RRT IS OUTSIDE
THE RRT WINDOW FROM REVERSE SEARCH COMPOUND STUDY

EGD NUMBER	COMPOUND NAME	OLD METHOD RRT	95% LOWER LIMIT	95% UPPER LIMIT	Δ RRT
927	1-PHENYLNAPHTHALENE	1.493	1.399	1.451	0.042
569	P-CHLOROANILINE	0.874	0.830	0.863	0.011
587	1,4-DINITROBENZENE	1.079	1.067	1.074	0.005
938	1,2,3-TRIMETHOXYBENZENE	0.970	0.948	0.967	0.003
912	3-NITROANILINE	1.115	1.115	1.125	-.000
911	2-NITROANILINE	1.047	1.048	1.055	-.001
566	1-BROMO-3-CHLOROBENZENE	0.734	0.736	0.739	-.002
574	TOLUENE, 2,4-DIAMINO-	1.021	1.025	1.034	-.004
573	2,6-DI-TERT-BUTYL-P-BENZOQUINONE	1.095	1.100	1.116	-.005
593	2-ISOPROPYLNAPHTHALENE	1.078	1.092	1.107	-.014
932	SQUALENE	1.753	1.897	2.119	-.144
941	TRIPROPYLENEGLYCOL METHYL ETHER	0.758	0.927	0.979	-.169
942	1,3,5-TRITHIANE	0.764	0.938	0.971	-.174
576	2,6-DICHLORO-4-NITROANILINE	1.083	1.301	1.344	-.218

FIGURE 1

VOA RRT WINDOW WIDTH VS RRT (METHOD 1624 C)

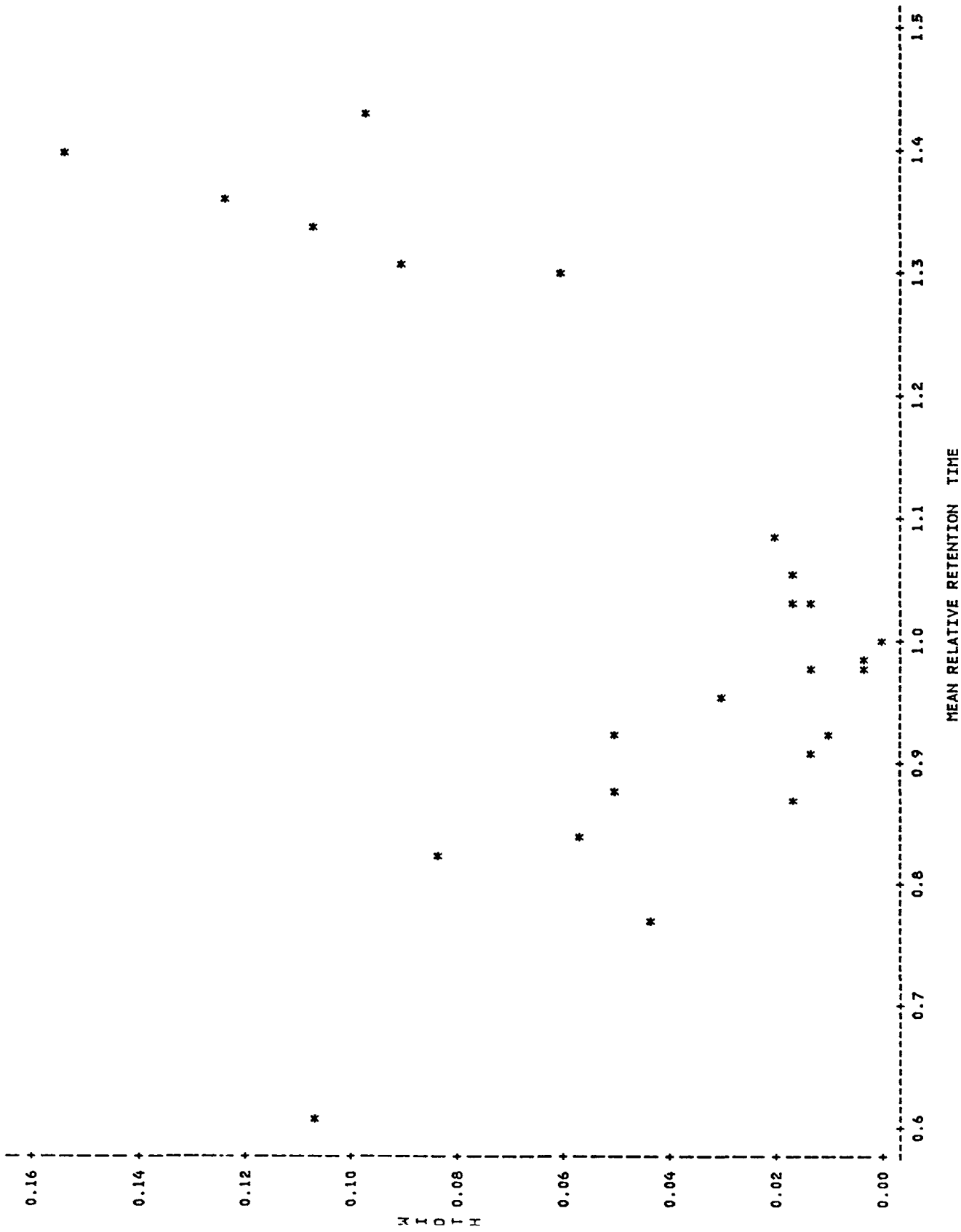
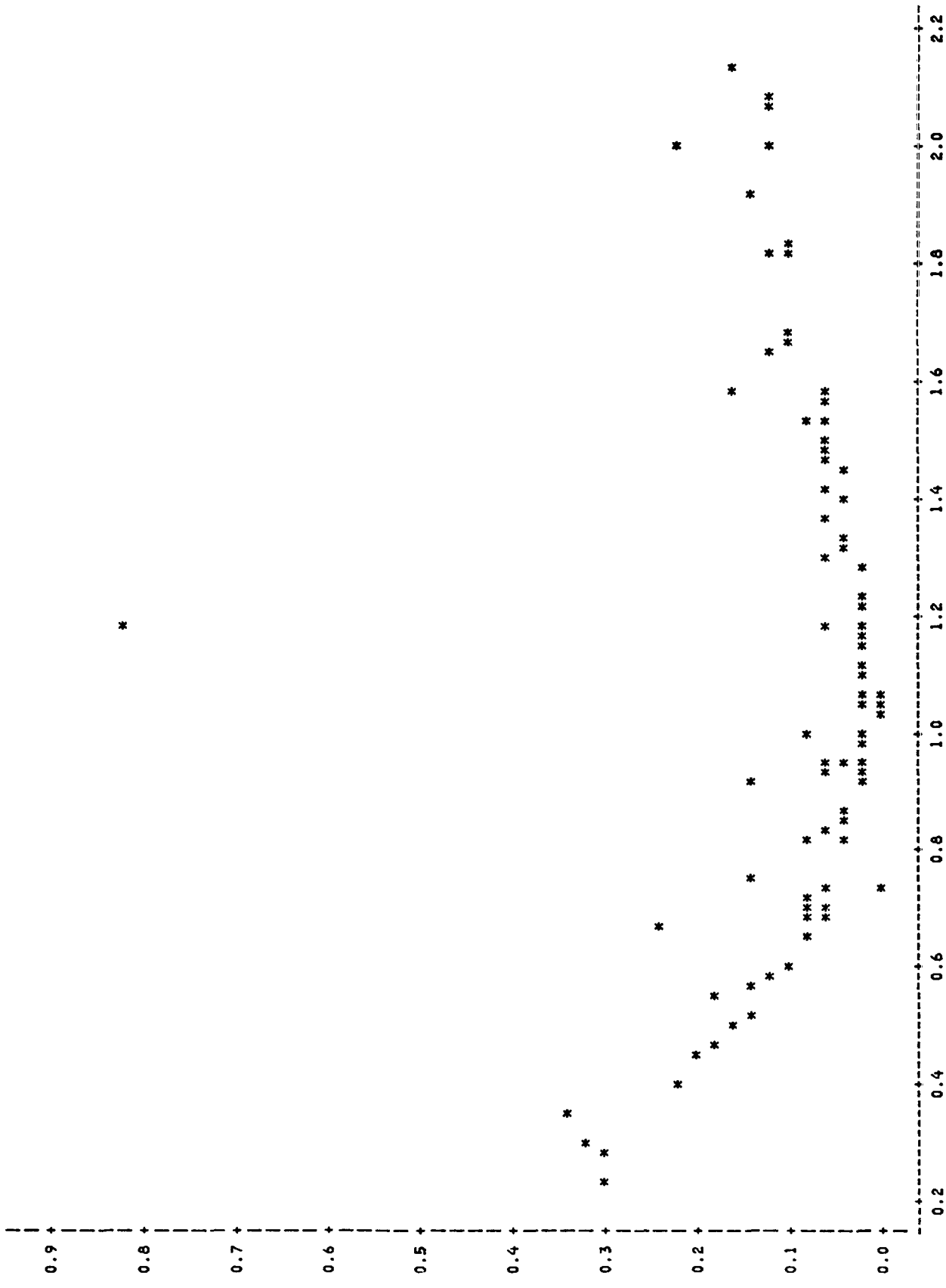


FIGURE 2

SEMI RRT WINDOW WIDTH VS RRT (METHOD 1625 C)



NOTE: 15 obs hidden.

FIGURE 3

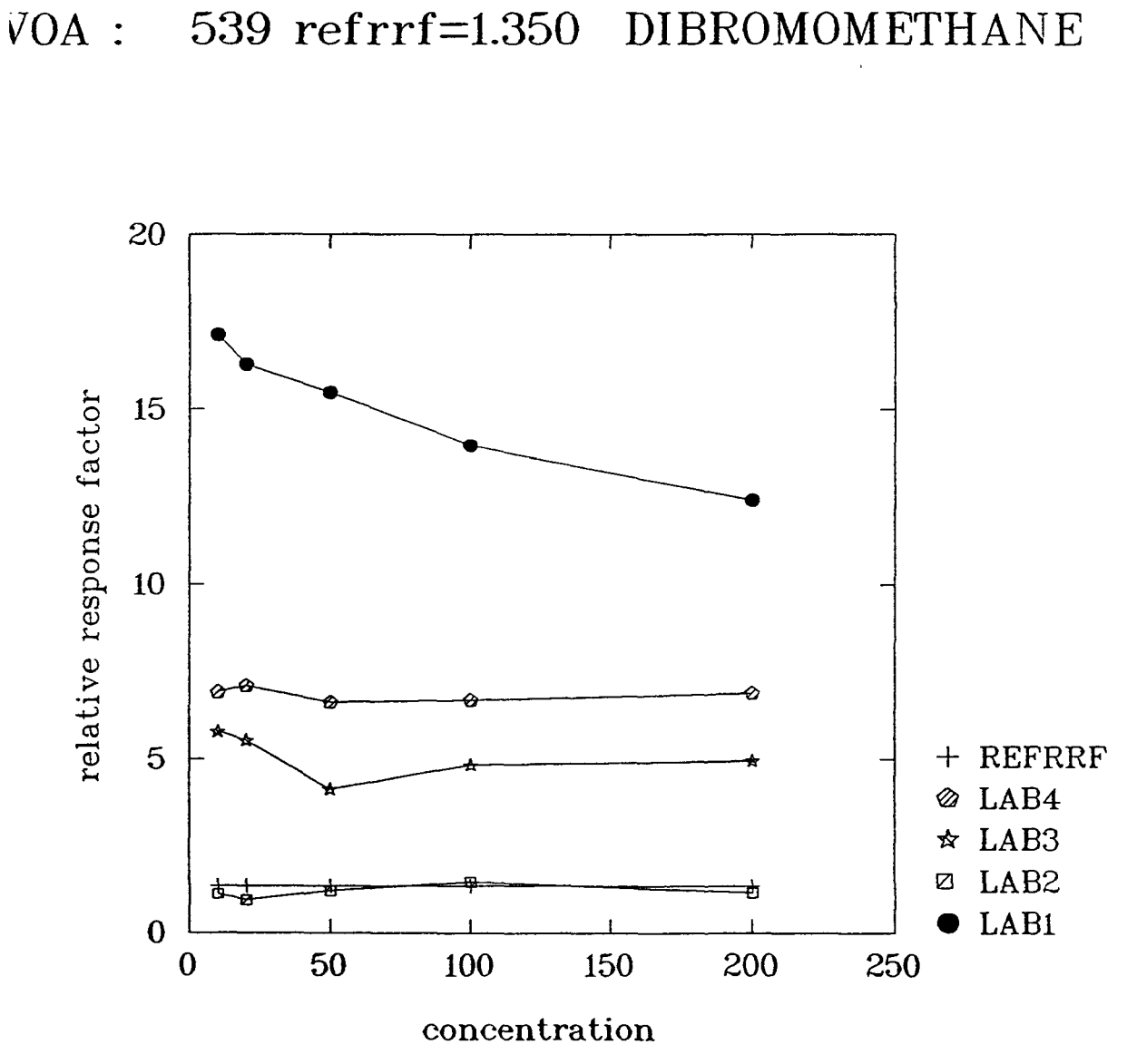

VOA : 539 refrrf=1.350 DIBROMOMETHANE
relative response factor
20
15
10
5
0
0
50
100
150
200
250
concentration
+ REFRRF
LAB4
LAB3
LAB2
LAB1

FIGURE 4

VOA : 550 refrrf=0.150 4-METHYL-2-PENTANONE

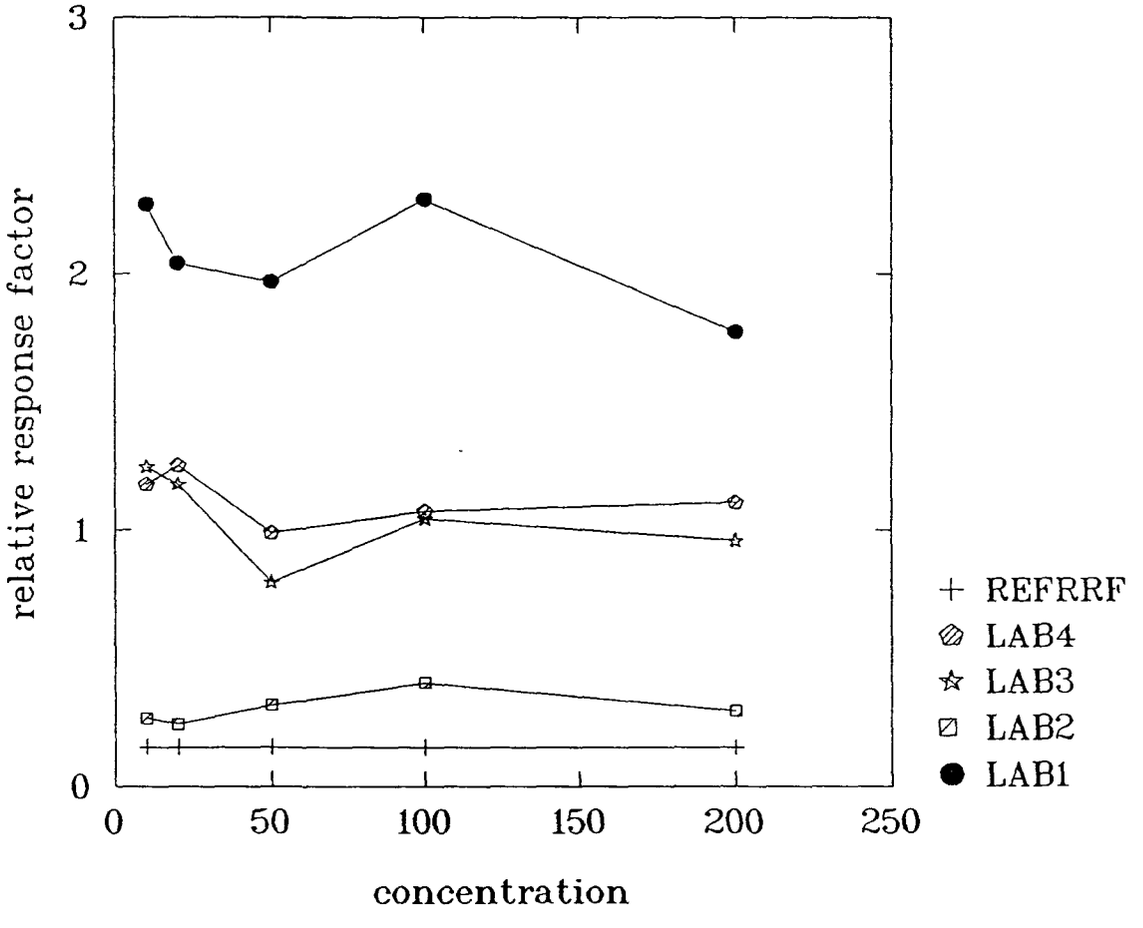


FIGURE 5

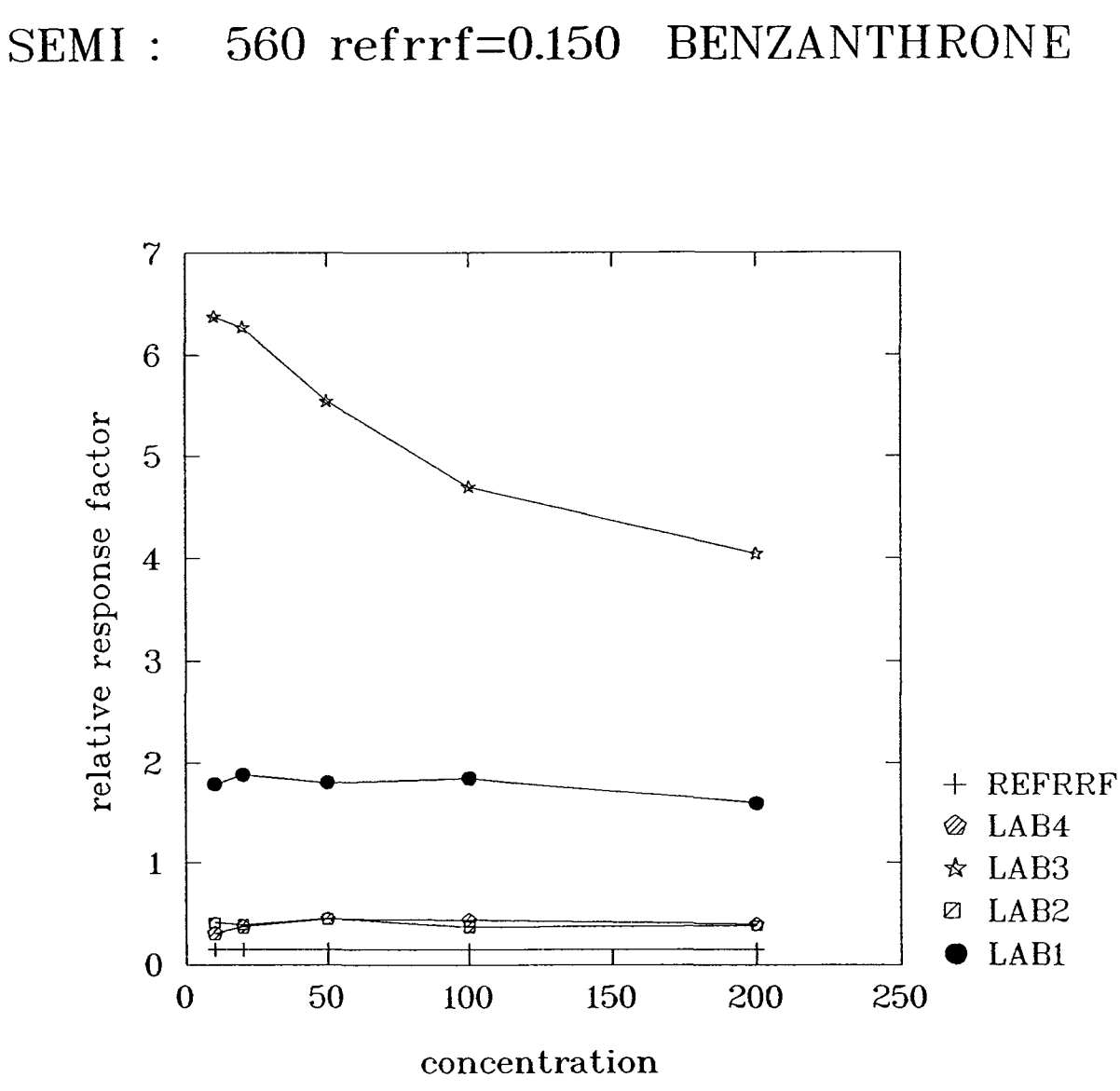

SEMI : 560 refrrf=0.150 BENZANTHRONE
relative response factor
concentration
0
1
2
3
4
5
6
7
0
50
100
150
200
250
REFRRF
LAB4
LAB3
LAB2
LAB1

FIGURE 6

SEMI : 579 refrrf=0.110 2,3-DICHLORONITROBENZENE

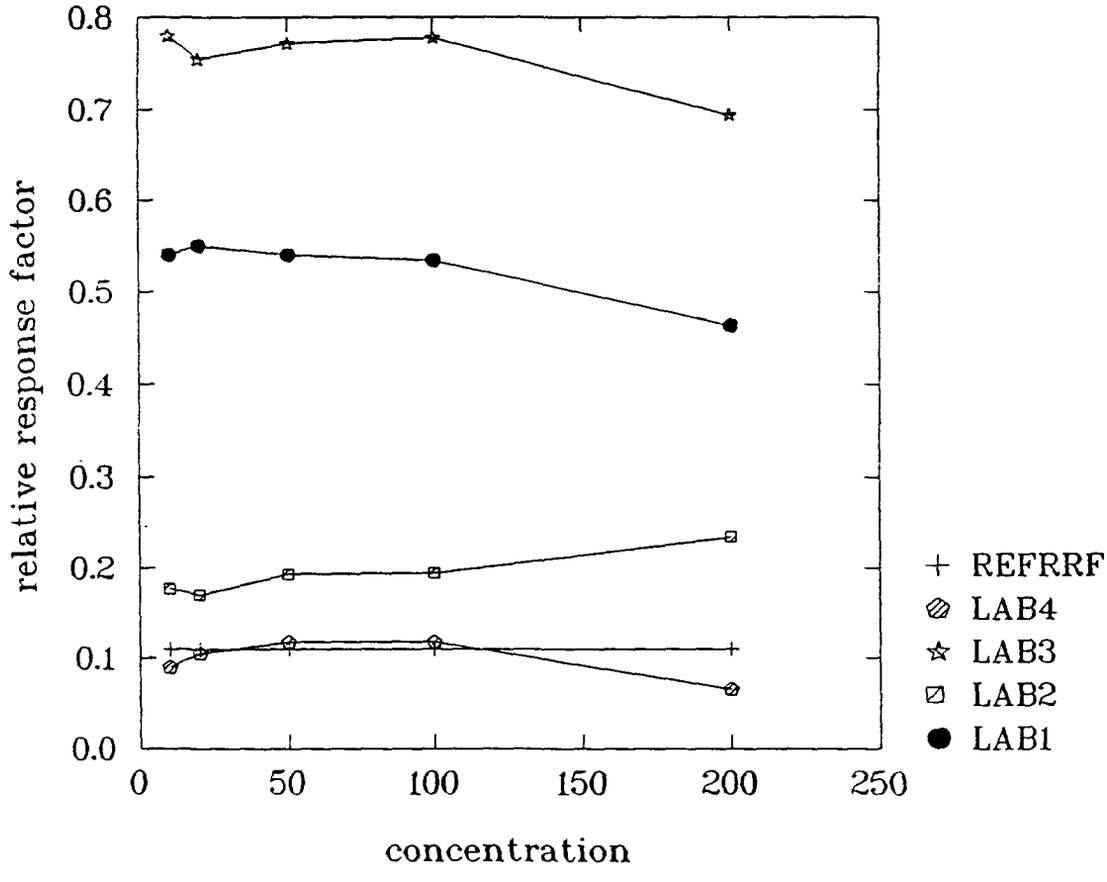


FIGURE 7

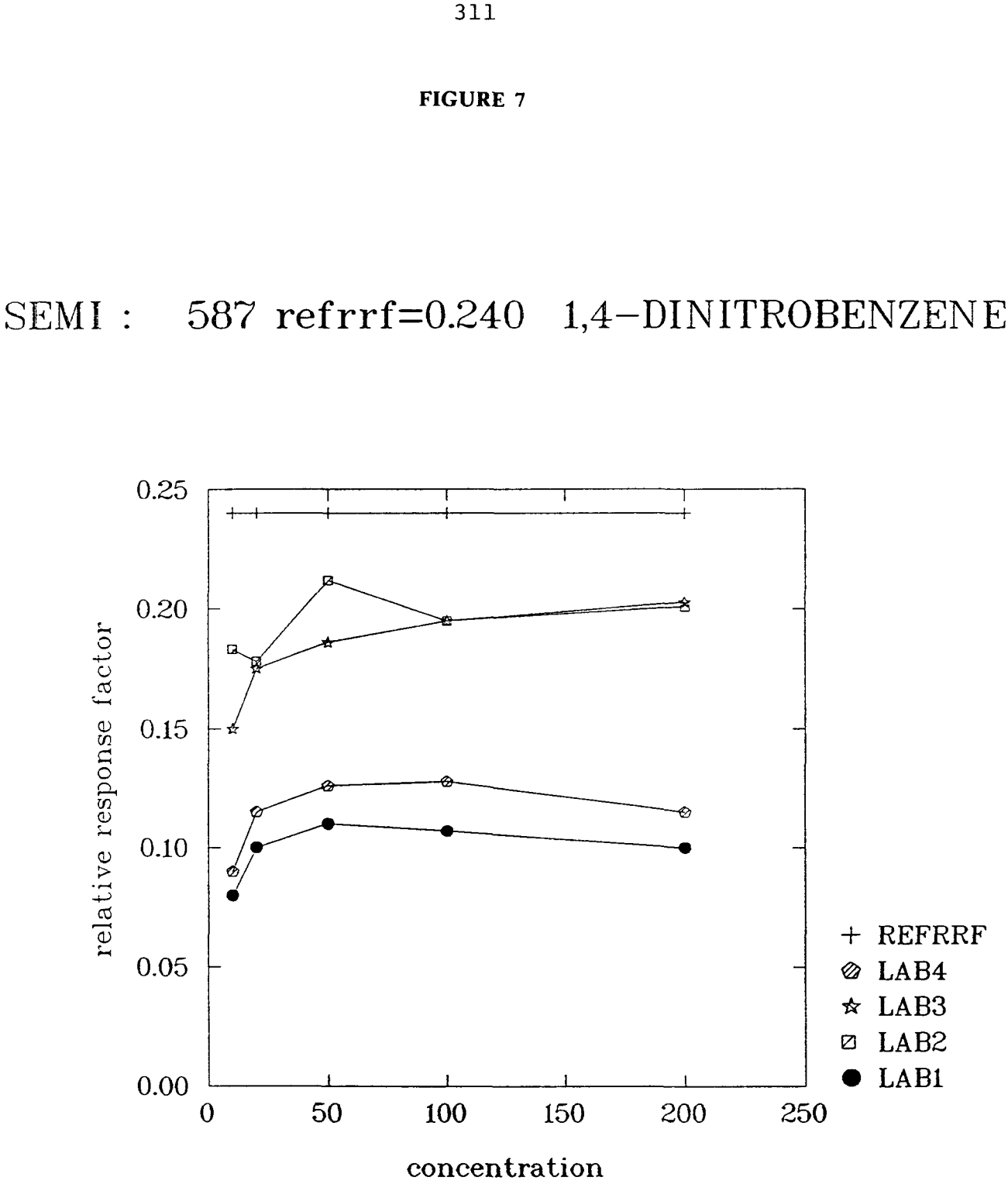

SEMI : 587 refrrf=0.240 1,4-DINITROBENZENE
0.25
0.20
0.15
0.10
0.05
0.00
relative response factor
0
50
100
150
200
250
concentration
REFRRF
LAB4
LAB3
LAB2
LAB1

FIGURE 8

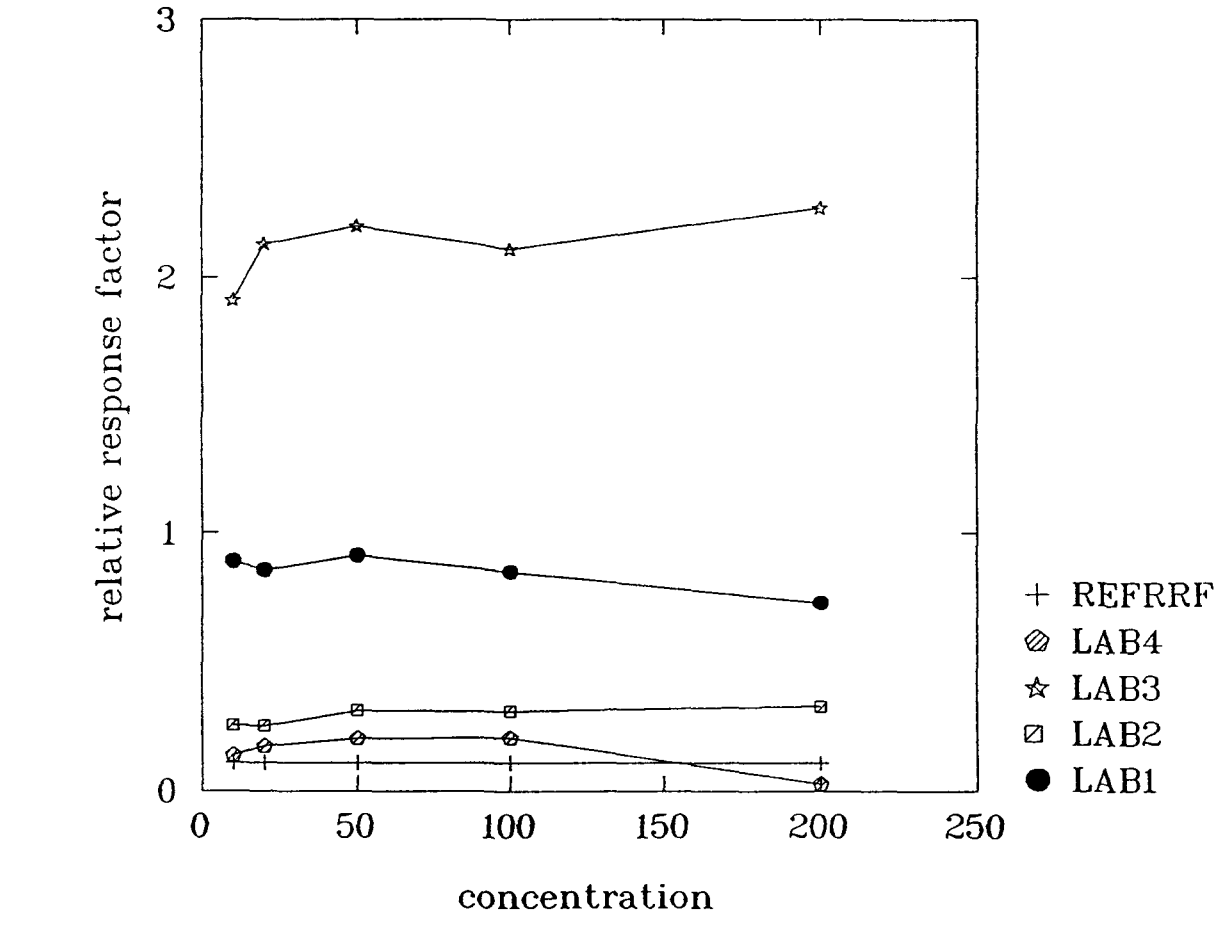

SEMI : 913 refrrf=0.110 P-NITROANILINE
relative response factor
concentration
0
1
2
3
0
50
100
150
200
250
REFRRF
LAB4
LAB3
LAB2
LAB1

FIGURE 9

SEMI : 915 refrrf=0.470 N-NITROSODI-N-BUTYLAMINE

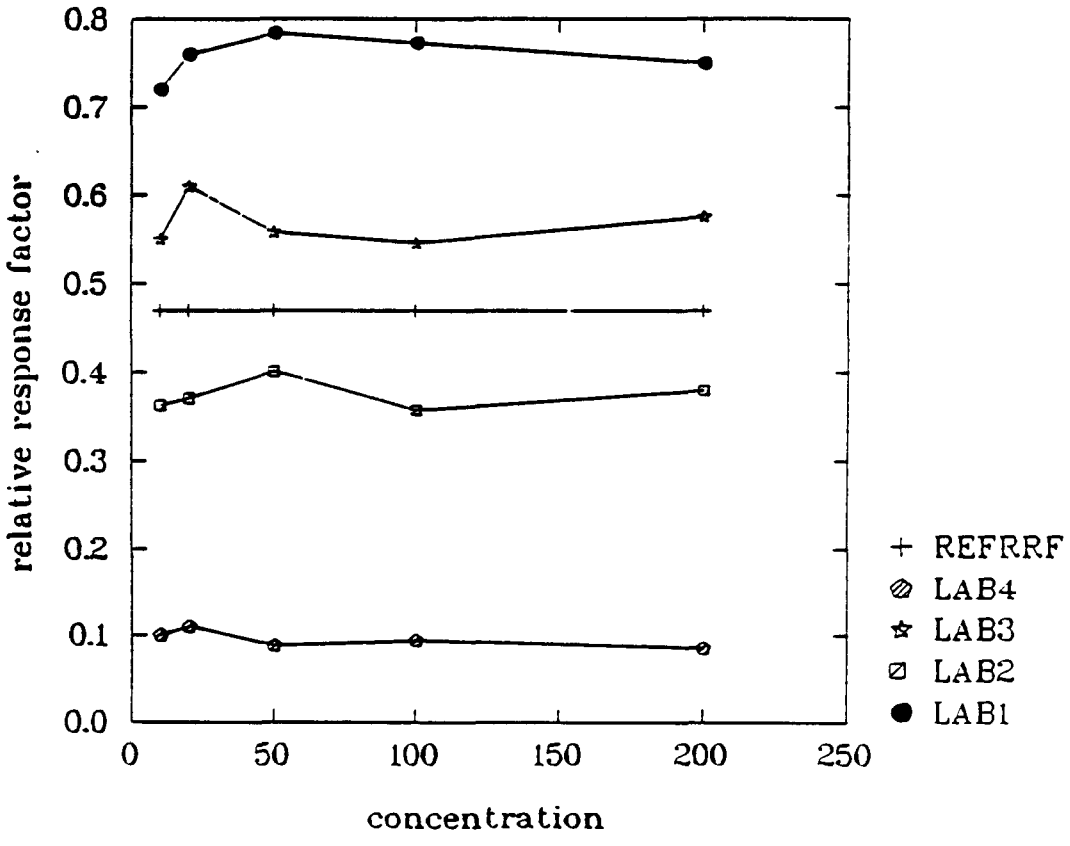
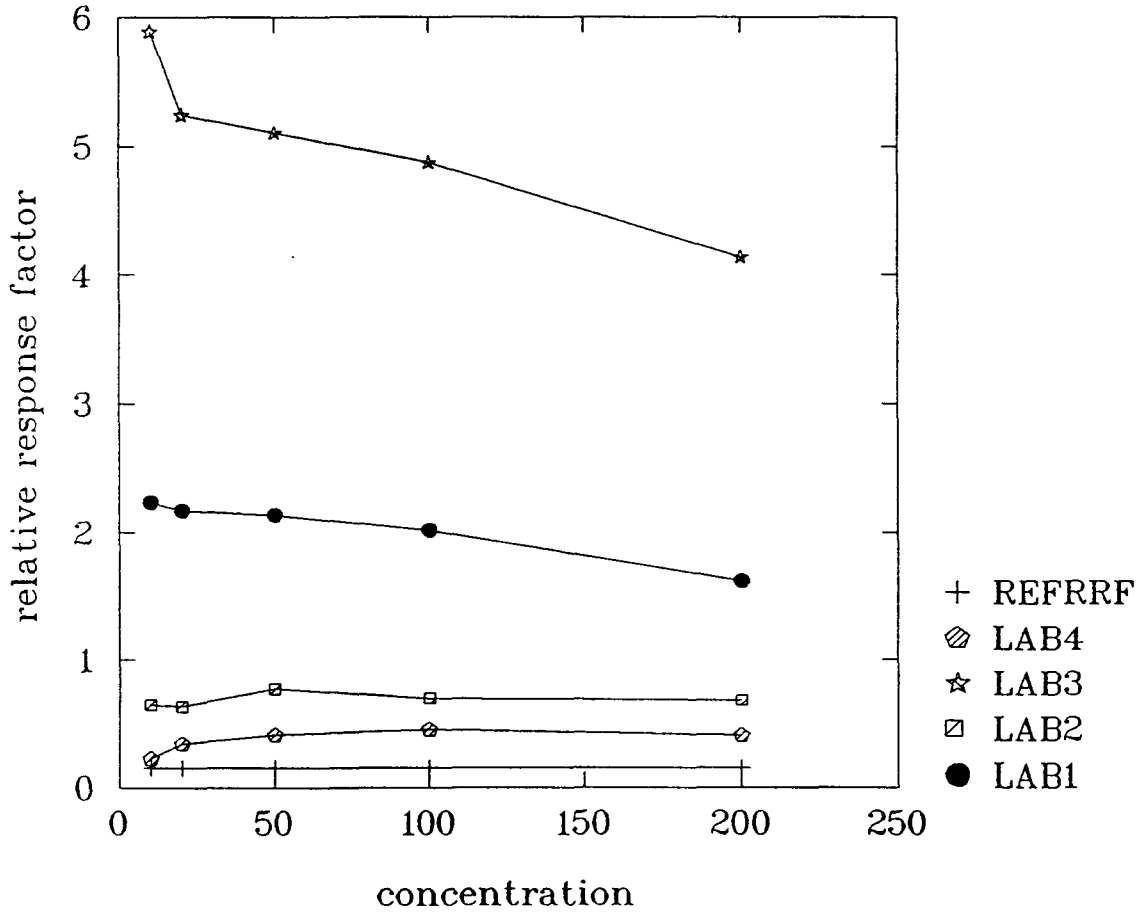


FIGURE 10

SEMI : 926 refrrf=0.150 PHENOTHIAZINE



MR. TELLIARD: Our last session today is going to deal with the joys and relationships with chlorinated phenolics, one of the more exciting things.

Two speakers are going to be addressing two programs that the agency has underway to help out the pulp and paper industry. As you know, a number of them have felt neglected so we haven't written any regulations for them and in an attempt to dispel that feeling of neglect, we're busily trying to get them more regs so they'll have something to talk about at their meetings. In lieu of that, our first speaker today is Larry LaFleur who is from the National Council of the Pulp and Paper Industry for Air and Stream Improvement. Over the last couple of years, Larry and I have been seeing each other in very strange places and talking about very strange things. Larry has taken on the dubious pleasure...honor...whatever...of being responsible for tying off many of the analytical issues that are facing both the agency and the industry and trying to measure some of these compounds in this rather complex effluent. So, he's going to speak a little bit today on chlorinated phenolics in the pulp and paper industry.

MR. LaFLEUR: Thanks, Bill.

Much of the pulp that's produced in the United States and throughout the world is bleached in order to improve the brightness, cleanliness, strength properties, color stability and absorptive properties of the final pulp. Current practices for bleaching utilize oxidation with chlorine and chlorine dioxide to break up the lignin molecule which is then subsequently dissolved in a strong caustic solution.

The reactions responsible for the de-lignification that occurs have been extensively studied and reported in the literature. A number of de-methylation reactions and de-alkylation reactions occur to break ether bonds, giving an increased phenolic content to the residual lignin and to begin to break up the lignin polymer backbone. There are a series of reactions on the ring, itself, some forming quinones and others leading to ring opening that increases the carboxyl content.

The next reaction that's important in the de-lignification process is electrophilic displacement of the three carbon side chain. All of those reactions lead to increased solubility of the residual lignin, breaking up of the lignin backbone and reducing the molecular weight, thereby, facilitating the subsequent extraction with sodium hydroxide.

Concurrent with those reactions are some reactions that do not improve the bleaching properties; specifically, these reactions include electrophilic substitution reactions on the aromatic ring and some substitutions on some definic groups that are on the propyl side chain.

Amongst the wide variety of chlorinated organics that are produced as a result of the bleaching process, is a whole series of chlorinated phenolic materials. The bleaching of softwood pulps, yields chlorinated phenols, chlorinated guaiacols, (ortho-methoxy phenols) chlorinated catechols (ortho dihydroxy bezene) and chlorinated vanillins which have the basic structure of the guaiacol with an aldehyde group para to the hydroxy group.

Due to the difference in the chemical makeup and structure of lignin that is in hardwood species, all of these types of materials are formed, along with chlorosyringols, (2.6 dimethoxy phenol) and syringaldehydes, (2.6 dimethoxy-4-formyl phenol).

A common misconception is that the bleaching process produces essentially all possible isomers of chlorinated phenolics. In actuality there is a number of very characteristic compounds that are formed.

This slide summarizes the most frequently detected materials organized by different process streams.

Generally, what is observed is a predominance of two to four chloro substitutions. The 4-chloro substituent occurs largely as a result of that de-alkylation reaction and breaks up the lignin molecule and subsequently releases the lower molecular weight chlorinated phenol.

Higher concentrations of chlorocatechols are observed in the C stage (first chlorination stage) than in some of the other stages because they are more stable under the high acid conditions. In the E stage because the purpose of that is to extract these materials as their phenolate salts. Thus, the E stage typically has the highest concentrations in the bleaching process.

The next table summarizes the least frequently detected compounds. The reactions that are responsible for the formation of these tend to be electrophilic aromatic substitution. The thermodynamics dictates ortho para substitution so what you see is anything that has substituents in the three and five position are virtually never found.

There are some other compounds, such as the catechols which are only occasionally detected in the E stage, but are frequently detected in the C stage.

You'll also note that the frequency of detection in the final treated effluent is significantly lower than any other process streams. That's in part due to the dilution of the

bleach plant waste waters with the pulping process waste waters. But it's also due to the removal of these compounds in the biological treatment system.

Chlorinated phenols came to the attention of the pulp and paper industry in the early 1970s when it was determined that they were significant contributors to fish toxicity in some untreated process waste waters. The next groups chloriodrenolics by chlorination level and plots them versus the toxicities to salmonids and/or fathead minnows. The toxicities range from the 300 to 500 ppb all the way up to several ppm. If you look within each chlorination level, you see quite a range of toxicities. But in general, if you look at the average for each chlorination level, there is a trend towards increasing toxicity with an increasing degree of chlorine substitution.

A number of studies have been undertaken to determine the environmental fate in the receiving environment of chlorinated phenolics, particularly of the guaiacols and catechols. What's begun to emerge is what is being described as the hypothetical guaiacol cycle. In biota, it has been shown that both the guaiacols and the catechols are readily conjugated, forming constituents like glucuronides. We've measured and determined that the uptake rates by the fish and the depuration rates are quite rapid. As a result, overall the bio-concentration potential, particularly for the lower chlorinated compounds, is quite low.

In the aqueous environment, which is essentially an aerobic environment, a number of studies have looked at the kinds of microbial transformations that occur. What seems to be the predominate metabolism is either demethylation of the guaiacol to form catechol structures which then can behave essentially as a catechol would normally behave or alternatively...methylation of the free phenol group to form a veratrole compound. Veratroles are fairly important when you consider that they may, in fact, be co-contaminants of the chlorinated phenolics and guaiacols in the receiving environment.

There's a number of other metabolic pathways that have been looked at, many of which lead to ortho-hydroxylation or para-hydroxylation, both with or without subsequent dehalogenation. Those products then ultimately undergo the same sort of demethylation and methylation chemistry mentioned before so the complexity of the compounds that one might encounter in the environment are substantially greater than what is observed in the bleach plant.

Materials that find their way into the sediments, have been shown to bind very quickly and very tightly with the solids. Generally, simple solvent extraction procedures are not very effective in recovering these materials and it required methanolic KOH to release what the authors of the work are terming bound materials. Sometimes the ratios of bound versus free are on the order of 100 to 1,000 times.

Some of the early analytical schemes that were used to monitor for chlorinated phenolics involved simple solvent extraction and then derivitization; often with diazomethane. These methods were found to be not very useful. A series of different substitution patterns become indistinguishable when methylated so that these different trichloroguaiacols are indistinguishable as the corresponding veratrole derivative.

Catechol recoveries in the solvent extraction systems were found to be very low and highly variable. The catechols that were extracted also methylated to produce an indistinguishable veratrole-type compound. Using this approach, you couldn't tell the difference between guaiacols, isomeric guaiacols, catechols and any veratroles that might have been present in the sample.

In early 1981, Ron Voss of the Pulp and Paper Research Institute in Canada reported the procedure shown here and it resolves many of those problems. In the procedure, a 50 mL sample...is neutralized, and 2,6-dibromophenol is added prior to derivatization as an internal standard. The sample is then buffered to a pH of 11.6, using potassium carbonate. Acetic

anhydride is added to the separatory funnel and mixed into the sample. A carbonate buffer forms phenolate salts of the phenols which then react with the acetic anhydride and directly form chlorophenol acetates in-situ, that is, right in the aqueous phase. Once that reaction has occurred, the resulting neutral chlorinated phenolics are much more amenable to extraction with a non-polar solvent like hexane. Following extraction, the analyses in the original method were performed on an electron capture detector with an unconcentrated sample.

One important aspect of this technique is that the analytical standards were prepared in an exactly identical manner. That is, for calibration purposes, you spike internal standards and un-derivatized target analytes into reagent water, buffer, acetylate, extract and analyze. Thus, the resulting response factors or calibration curve reflects not only the electron capture response, but the overall derivitization and extraction efficiency of the analytes.

The figure illustrates that the resulting acetates are, in fact, chemically distinguishable and the chlorophenol accetates can be separated and analyzed uniquely.

To summarize the advantages of the Voss procedure, the method overall was quite sensitive, using a 50 mL sample for compounds with two or more chlorines. One could obtain low part per billion detection limits which made the method ideally suited for the laboratory bleaching studies, for which it was originally developed. It had improved selectivity, both in terms of being able to differentiate the different isomers of chloroguaiacol that are formed and it could also differentiate guaiacols from catechols and guaiacols and catechols from veratroles.

The accuracy and precision I'll talk a little bit more about, but it was certainly better than anything we had seen to date using more traditional approaches.

Finally, the method was quite rapid and that really lent itself to the research environment where you're trying to generate a great deal of information.

In support of the current effluent guidelines program review that Bill Telliard just mentioned, EPA has been utilizing an adaptation of this in-situ acetylation procedure. The method was originally developed as a research tool with an idea of generating large databases for essentially comparative purposes. Considering it in the context of a regulatory compliance method, you need to go back and review the suitability of the method in the context of single analyses compliance/non-compliance determinations. Ideally, a method that's to be used for a regulatory purpose ought to have well-defined and known accuracy, precision, and ideally it should be reliable and rugged.

What I'd like to do is talk about how the in-situ acetylation procedure stacks up against these kinds of criteria.

Starting with accuracy, in the context of the in-situ acetylation, you're dealing with a balance between specificity and sensitivity. The in-situ acetylation procedure itself provides a means of cleaning up the sample. It optimizes the recovery of the target analytes and minimizes the recovery of undesirable co-contaminates. Obviously, detector selection is going to be important to both specificity and selectivity.

Column selection is probably most important to specificity and certainly there's an obvious relationship between the sample size and the overall method sensitivity.

Looking first at the detectors, a number of detectors have been used in connection with this methodology. The original work done by Ron Voss used an electron capture detector. Shortly after Dr. Voss published his work, MCASI reviewed the method and published a GC/MS full scan version and recently in the Effluent Guidelines Program, EPA has been looking at the use of an electrolytic conductivity detector. If you compare those in the context of selectivity, we feel that the GC/MS offers, at least in full scan mode, clearly the best selectivity and we think there's reason to believe the electrolytic conductivity is more selective than the original electron capture. If you view those detectors from the point of view of sensitivity, the order is

essentially reversed. We're very interested in which of these detectors is going to provide the optimum compromise between selectivity and sensitivity. In order to do that, we went back to re-evaluate the original electron capture method. We looked at 23 different paired samples, covering the entire gamut of different matrices experienced in the pulp and paper industry collected from a variety of different pulp mills. We split the samples, analyzed them by both electron capture detection method and GC/MS. We used the GC/MS data as our reference point and only made comparisons where we had comparable detection limits. We flagged samples that had a positive by the electron capture detector, but showed non-detect by the GC/MS as a false positive and samples that showed a factor of two higher result in the electron capture detector, compared to the GC/MS as a positive bias.

For a wide number of different analytes that we were monitoring at this point, we flagged at least some percentage of the samples for false positives, some for a positive bias, some for both.

Overall, when we look at the full set of 23 paired samples, there were only actually three samples or 13 percent that had complete agreement between the GC/MS and the ECD data. Based upon this, it was determined that this is probably not a real good compliance monitoring tool.

EPA had adapted the Voss method to use a two column confirmation approach to enhance the selectivity of the Hall's detector that was used and thus complimenting its improved sensitivity over the full scan GC/MS. This sounded like a very good approach, so we set about evaluating it. The first step in that process, we thought, would be to do the best job we could of getting the best separations between all potential analytes and potential interferences.

We spent a couple of weeks working on different temperature programs and what you see here is the results of that effort. It's a pretty complicated program. We optimized the

separations on two columns. The original DB1 is the column that MCASI used since the beginning when Ron Voss originally published his work and the Rtx-35 column was the one that EPA was using as their confirmatory column.

Even after spending a couple of weeks trying every program we could think of, there were still a number of unresolved pairs. There's basically several sets of compounds that can't be resolved. On the Rtx-35 column, there was even a larger number of compounds that couldn't be resolved.

Improving resolution of any given pair of close elating compounds simply results in degrading the resolution in another area of the chromatogram. The temperature programs given in the figure offer the optimum compromise in terms of getting the maximum number of analytes separated. This is only with known standards or known constituents of pulp mill effluents and a few of the veratroles that might be co-contaminants in environmental samples.

Even if we could get all of the standards separated, that doesn't necessarily solve all potential problems. This is a chromatogram of 10 ppb standard on the Hall's detector, using a DB1 column and a typical C-stage filtrate, both run under identical instrumental conditions. The C stage filtrate chromatogram clearly illustrates that finding the target analyte in the presence of a myriad of potential co-eluting peaks is the challenge.

The next series of evaluations we performed involved six different typical pulp mill samples. These included some E-stage filtrates, C-stage filtrates from the process and some final treated effluents. We analyzed them both by the electrolytic conductivity detector and by the GC/MS. Since the GC/MS detection limits weren't as low, we enhanced the sensitivity by analyzing the samples first by a full scan procedure which we had been using for years and then repeat the analyses using a selected ion monitoring approach. Again, we used the GC/MS data as a reference point.

For the dual column data shown in the table we used the criteria that EPA had established for positive identifications. The analyte had to show up at the right retention time on both of the columns and the concentration had to agree within a factor of two. There are 40 different analytes in the six different samples giving a total of about 240 determinations.

Using the two column confirmation procedure, you see a fairly small number of false positives, but a fairly significant number of false negatives. One other thing we considered was the selectivity achieved using the Hall's detector without two column configeration. As you might expect, we about doubled the number of false positives, but we significantly reduced the number of false negatives. What's probably happening here is on one or the other columns we have a major chemical contaminant which is moving under the target analyte and then throwing the concentrations off.

The other point that I'd like to make is that this extends down into a concentration range below one part per billion. Some of the values were as low as half a part per billion. I'm sure that this whole treatment of the data would change significantly if a different lower detection threshold was used.

Based upon these preliminary evaluations, we feel that the electrolytic conductivity may offer some advantages over the electron capture detector, but it clearly has significant problems with process streams. We still feel that in terms of the optimum compromise between sensitivity and selectivity, the GC/MS procedure is the preferred method.

Due to the unique nature of the in-situ acetylation procedure, there's a number of factors that can contribute to the overall precision of the method. The first is the acetylation efficiency or yield and I'm going to talk more about that in a minute. The second factor is the extraction efficiency. We found that the extraction efficiency using the hexane is greater than 95 percent. We've done some studies looking at more polar

solvents to see if that might further improve that, but what we found was that you run into two problems: One, you start extracting some of the acetic acid, which was formed as a byproduct of acetic anhydride in water. This causes a lot of chromatographic problems. Secondly, you start to pull out more interferences. Given these two observations, hexane remains the optimum solvent.

The third factor affecting precision is concentration losses. Unless you boil the extract down to dryness, we haven't seen a real problem with concentration losses of these chlorophenol acetates. We think the method is fairly rugged with respect to concentration.

The last item here is the GC analysis. Clearly, that is a problem, particularly for the chlorinated catechols. We frequently have to replace the injection port liners and are often cutting off the front part of the columns. So, the method does require fairly careful chromatography.

In order to give you an idea of what the reproducibility of some of the spike recoveries are, I've tried to tabulate some of our older electron capture data. This represents approximately 100 determinations of matrix spikes made in various different pulp and paper industry waste waters and process streams. The recoveries are uniformly high with the one exception of the tetrachlorocatechol, which is in the 73% range. From this data, it is readily apparent that high recoveries can be routinely maintained.

The chlorinated phenols and guaiacols, the relative standard deviation of the recoveries are fairly consistently in the 16 to 23 percent range.

The vanillins recovery relative standard deviations are 30 to 38 percent. Thus, they are not as reproducible as the guaiacols and phenols.

The relative standard deviations for the chlorocatechols are 40 to 57 percent making them the least reproducible. It is very hard to maintain consistent higher

recoveries with the chlorocatechols.

Looking more specifically at method precision, we summarized some of our GC/MS data. These are seven replicate analyses of C-stage filtrate, an E-stage filtrate and a final treated effluent. A select group of analytes are included to illustrate the precision of the different analyte groups.

The overall precision of the chloroguaiacols and phenols is the best of all the analytes and the relative standard deviation is fairly low. The 4,5-dichloroguaiacol was at about a 2 ppb level so we probably are running into problems with concentration there. The vanillin relative standard deviations are fairly similar but slightly higher than the chloroguaiacols and phenols, the chlorocatechols consistently show poorer precision.

Clearly, the catechols are the weak point in the analytical methodology. If there is anything wrong with this method, it's the poor ruggedness or reliability of catechol data.

Looking into this a little more closely, I think a brief review of basic catechol chemistry begins to help illustrate some of the reasons why this might be the case. Catechols are known to undergo oxidation reduction reactions forming the corresponding orthobenzoquinone, particularly in alkaline solutions. This is an equilibrium-type reaction and the distribution of the products is very much dependent upon the presence of other oxidants in the sample, including oxygen.

A second reaction that may give rise to the degradation of the catechols is just simple base degradation. In fact, this reaction occurs very extensively in a caustic extraction stage. Compounds like tetrachlorocatechol are known to form chloranilic acid in the presence of the strong base and that's essentially why we see very little catechol in the E-stage filtrates.

These observations give us a little bit of an idea of how we might be able to go about solving the problem. The first thing that you can look at is the addition of a preservative, a reducing agent such as thiosulfate and bisulfite that are added

to quench residual chlorine and is generally practiced as a field preservation technique. Addition of thiosulfate has been pratical for years and the catechol problem still exists. Thus, that isn't the solution to the problem.

We have seen that the addition of ascorbic acid can, in fact, reduce the orthobenzoquinones back to the catechols and thus offers at least one approach to solving the problem.

Another consideration we might explore is to lowering the pH of the buffer. If these compounds are degraded in a strong base, use a weaker base. Along those same lines, we're looking at the possibility of shortening the exposure time to the high pH.

Of these three general approaches, clearly the most commonly practiced is the addition of ascorbic acid. What we wanted to do is evaluate just what that does to the results. Generally we can control our catechol recoveries fairly well. A series of paired analyses of samples with and without the addition of the ascorbic acid were performed. What was observed is that in the E-stage where most of these base labile compounds don't exist, there's no difference between the two analyses. Also, virtually no difference was observed in the treated effluents. The most significant differences were observed in the C-stage where there is a great deal of labile material and in one of the primary influents. The differences are fairly consistent with the one exception of the 3,4-dichlorocatechol where it's significantly greater. We think that these differences are directly attributable to the presence of chloroquinones.

We looked into this 3,4-dichlorocatechol a little more closely. Going back to the literature, back in the early '80s a compound 2,6-dichloroparaquinone was reported as a constituent in C-stage filtrates. This compound hadn't received a great deal of attention because nobody had good analytical methods for quinones. We've taken the compound and have shown that it is, in fact, reduced to the corresponding hydroquinone, (i.e. 2,6-dichloro-p-dihydroxy benzene) in the presence of ascorbic acid.

The diacetate that is formed upon acetylation has exactly the same retention time as 3,4-dichlorocatechol. By inspection of the spectra of the two compounds, it is readily apparent that, it would be hard to tell, if those two compounds were co-eluting, whether it was from a catechol or a paraquinone.

In general, we feel that although the ascorbic acid may offer some advantages in solving this catechol problem, it does so at the expense of the selectivity of the method. In particular, that means that we're no longer talking about catechols; we're talking about catechols plus quinones and, in fact, we may even be grouping in paraquinones with orthoquinones.

We are currently investigating solutions for solving this catechol problem which do not compromise the selectivity of the method. We went back and looked at the pH of the buffer. The figure summarizes a series of experiments performed investigating buffers from 8.2 up to pH 12. The original Voss procedure uses a buffer at 11.6, which is included in our study for reference. For a number of compounds, we actually saw a slight peak but otherwise, these are pretty flat curves. So first of all, there's very little sensitivity to pH. Secondly, if there is any sensitivity, it would actually indicate that on some of the compounds, we actually saw an increase at pH 9.9. There was very little difference between the original pH 11.6 buffer that we had originally used and buffers as low as pH 9.1. We concluded that we may have a handle on minimizing the catechol degradation and the data certainly suggests it's worth pursuing. What remains to be seen is whether or not the dropping the pH from 11.6 to 9.9, or even as far as 9.1, will be sufficient to adequately stabilize the catechols and at the same time we have to make sure that these buffers will work well on some of the samples. The experiment was just spiked reagent waters.

Another approach we're looking at involves reviewing the way we conduct the buffering in order to try and minimize the time it takes to get the sample acetylated after the pH adjustment. In order to look at that, we plotted here titrations

of several different samples against the carbonated buffer we use for the calibration standards.

The samples themselves have a native buffering capacity in the range of pH 8 to 10. In the early stages of our method, we actually found that when we added the buffer, we were only getting the pHs in the 11 range and we thought that was important at the time and so we added a step to increase the pH up to a target equal to that which we were using for calibration. All of that takes a lot of time. You've got to remove the pH electrode, rinse it off, take out the stir bar, and transfer the sample from the beaker to the separatory funnel, all of which extends the time that the catechols are sitting there degrading.

We are presently investigating a modification rather than making the initial pH adjustment to seven, the adjustment is made to pH 9 to 9.5. This takes the pH beyond the inherent buffering capacity of the sample. Then we go through all the business of taking the pH electrode out and transferring the sample to a separatory funnel. At that point, you are at a milder pH and the time may not be as critical. The carbonate is added and there is no check on the pH; the analyst immediately adds the anhydride. Hopefully, that will get us beyond any pH degradation. Preliminary experiments show that samples will not always hit pH 11.6, but from the data presented in the previous slide, we're convinced now that that's not anywhere near as important as we originally thought.

Both of these later modifications to the method are being considered specifically to enhance the ruggedness of the method, without compromising the accuracy or the precision.

I'd like to conclude that basically, we feel that the GC/MS provides the best selectivity, particularly in light of the complex nature of the effluents we were trying to analyze and we feel it has adequate sensitivity for most applications. The precision for all of the analytes is acceptable, with the exception of the chlorinated catechols. The reliability of the catechol analyses certainly needs improvement. Most people

struggle, trying to get 20 or 30 percent recoveries. Clearly, the method needs to be more rugged with respect to those analytes.

MR. TELLIARD: Thank you.

QUESTION AND ANSWER SESSION

MR.TELLIARD: Questions?

MR. CASTLE: Bill Castle, California Fish and Game Department.

I was wondering if you had tried what seems to be the obvious use assumed under GC/MS for quantitation of these compounds?

MR. LaFLEUR: The use of what now?

MR. CASTLE: Selected ions?

MR. LaFLEUR: Well, we've done it in the research context, but generally we didn't think that we needed detection limits much lower than we had for most of our research purposes. When you're working in the process streams, detection usually isn't a problem. You're not really worried about a sensitivity issue.

MR. CASTLE: Well, it just seemed in your two comparisons that you put it last under detection and you could have increased that by going to that...under your sensitivity that you listed on the one slide.

MR. LaFLEUR: Oh, okay, yes. If we were primarily after sensitivity, that would be one option to consider. The target analyte list we work with in our program typically is about 45 compounds and when you get that many compounds what you have to resort to, to use selected ion monitoring is only a couple of ions for each peak and at that point you have to really ask yourself, is that sufficient information to an unambiguously identify a contaminant.

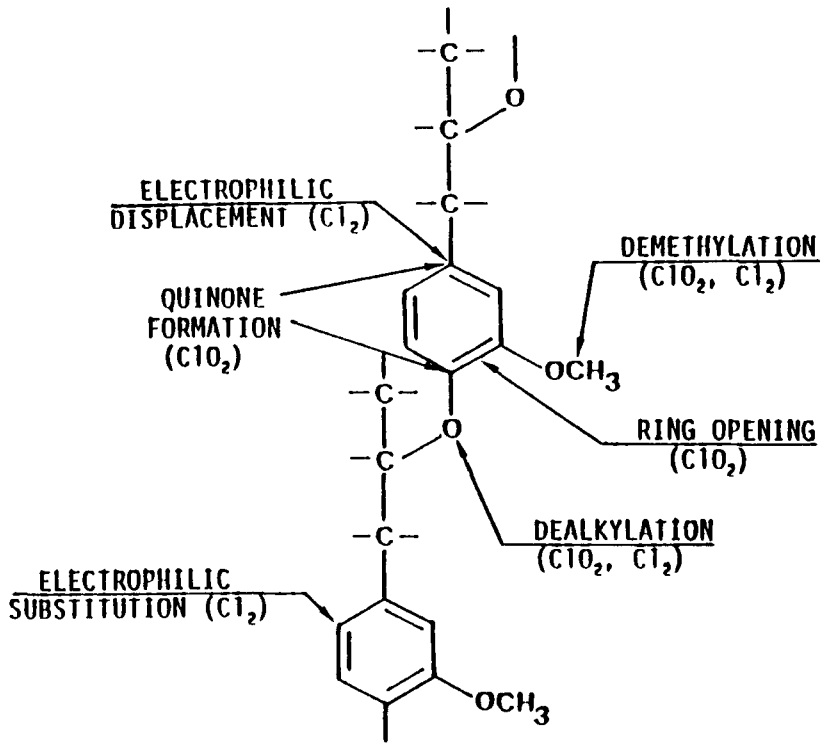
MR. TELLIARD: Thank you, Larry.

In-Situ Acetylation Analysis of Chlorinated Phenols in Pulp and Paper Industry Wastewaters: Further Investigations and Refinements

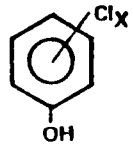
L. LaFleur, J. Louch, G. Wilson, and G. Dodo

National Council of the Paper Industry
For Air and Stream Improvement

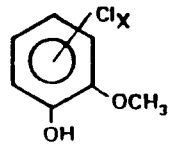
ncasi



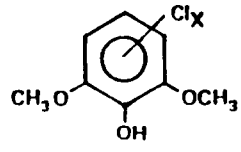
SOFTWOOD EFFLUENTS



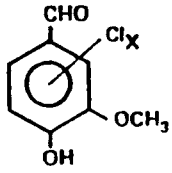
CHLOROPHENOLS



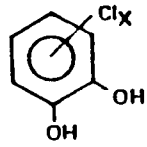
CHLOROGUAIACOLS



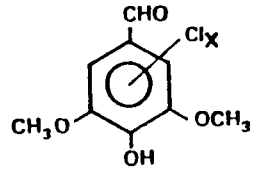
CHLOROSYRINGOLS



CHLOROVANILLINS



CHLOROCATECHOLS



CHLOROSYRINGEALDEHYDES

HARDWOOD EFFLUENTS

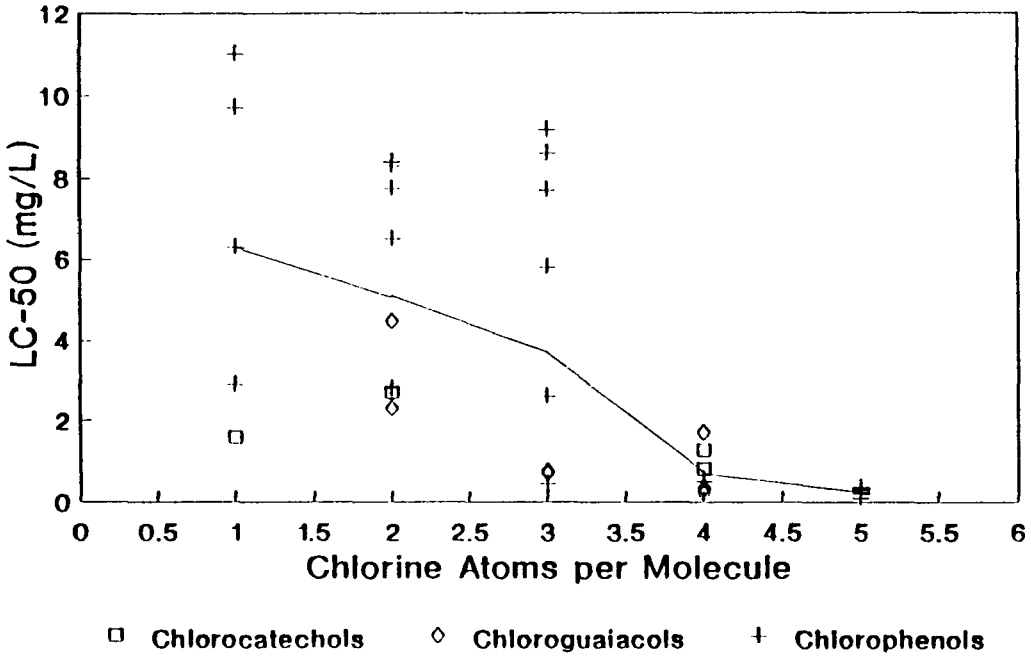
MOST FREQUENTLY DETECTED CHLORINATED PHENOLICS
FREQUENCY OF DETECTION

	C Stage Filtrate n = 23	E Stage Filtrate n = 23	Process Sewers n = 39	Treatment Effluent n = 30	Treated Effluent n = 63
2,4-Dichlorophenol	48%	78%	59%	77%	27%
2,4,6-Trichlorophenol	57%	100%	64%	80%	38%
4,5-Dichloroguaiacol	43%	87%	59%	90%	57%
3,4,5-Trichloroguaiacol	35%	74%	67%	83%	30%
4,5,6-Trichloroguaiacol	13%	96%	49%	60%	22%
3,4,5-Trichlorocatechol	100%	70%	85%	93%	75%
Tetrachlorocatechol	78%	13%	49%	63%	22%
6-Chlorovanillin	57%	83%	64%	83%	57%
5,6-Dichlorovanillin	13%	83%	56%	83%	56%

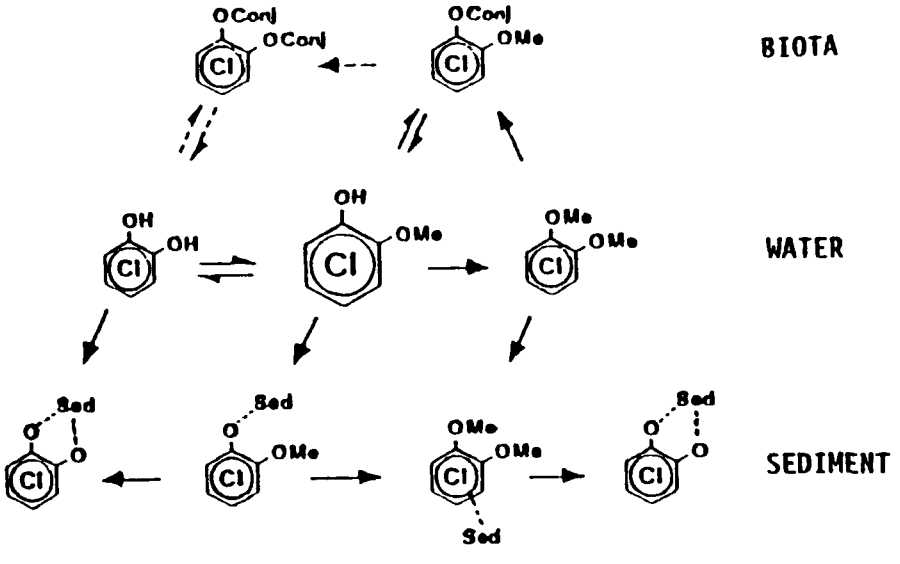
LEAST FREQUENTLY DETECTED CHLORINATED PHENOLICS
FREQUENCY OF DETECTION

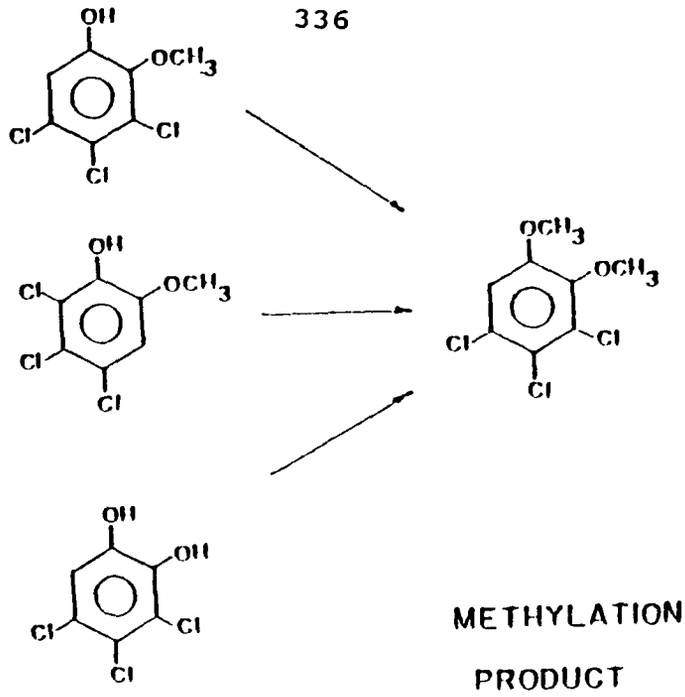
	C Stage Filtrate n = 23	E Stage Filtrate n = 23	Process Sewers n = 39	Treatment Influent n = 30	Treated Effluent n = 63
2-Chlorophenol	0%	9%	0%	3%	0%
4-Chlorophenol	43%	43%	49%	73%	5%
2,6-Dichlorophenol	0%	4%	0%	0%	0%
3,5-Dichlorophenol	0%	0%	0%	0%	0%
2,3-Dichlorophenol	0%	0%	0%	0%	0%
3,4-Dichlorophenol	0%	0%	0%	0%	0%
2,3,6-Trichlorophenol	0%	0%	0%	0%	0%
2,4,5-Trichlorophenol	0%	0%	0%	0%	0%
2346-Tetrachlorophenol	0%	9%	15%	0%	6%
Pentachlorophenol	0%	4%	10%	0%	3%
4-Chloroguaiacol	22%	35%	25%	63%	0%
4,6-Dichloroguaiacol	0%	35%	31%	60%	17%
Tetrachloroguaiacol	9%	65%	56%	20%	14%
4-Chlorocatechol	48%	4%	13%	43%	14%
3,4-Dichlorocatechol	65%	9%	54%	47%	5%
4,5-Dichlorocatechol	65%	4%	54%	83%	51%
346-Trichlorocatechol	70%	17%	69%	37%	8%
5-Chlorovanillin	4%	57%	33%	63%	24%
Chlorosyringaldehyde	13%	57%	15%	20%	3%
Trichlorosyringol	30%	87%	33%	30%	3%
3,5-Dichloro-4-hydroxy-benzaldehyde	0%	65%	38%	57%	3%

Chlorinated Phenolics Fish Toxicity

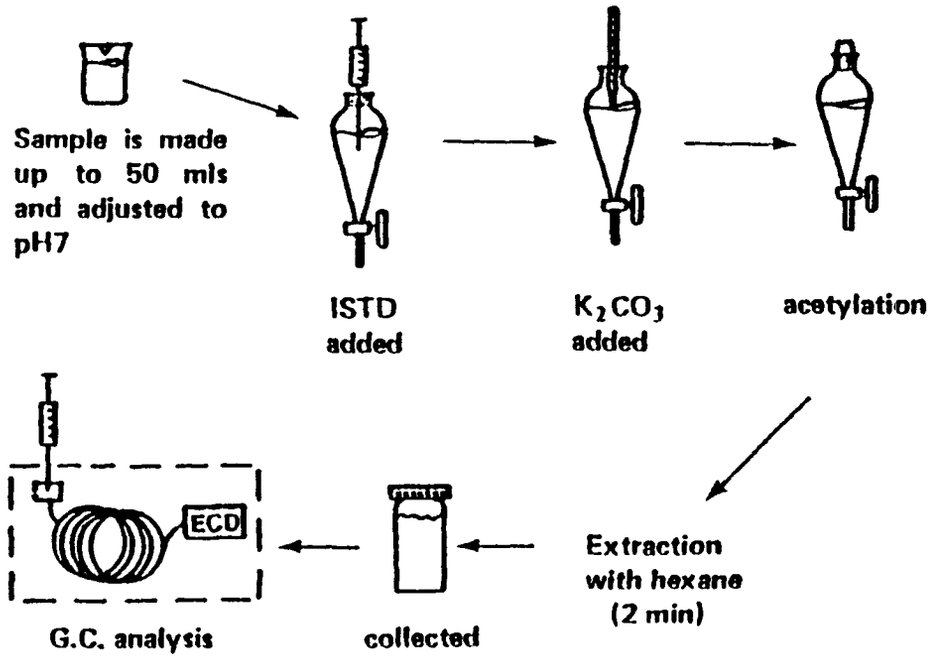


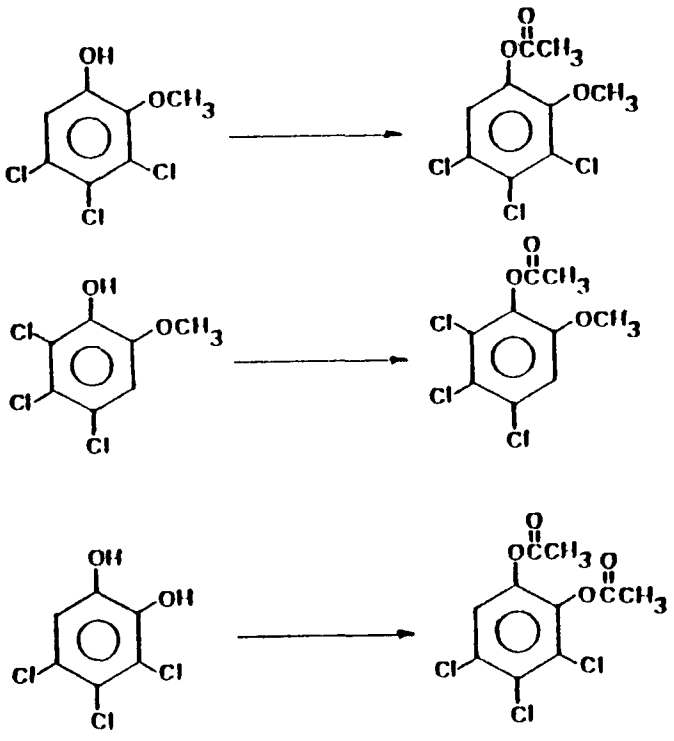
HYPOTHETICAL "GUAIACOL CYCLE"





EFFLUENT: IN SITU METHOD





ACETYLATION

PRODUCTS

Advantages of Voss In-Situ Acetylation Technique

- Sensitive

  Small sample size

- Improved Selectivity

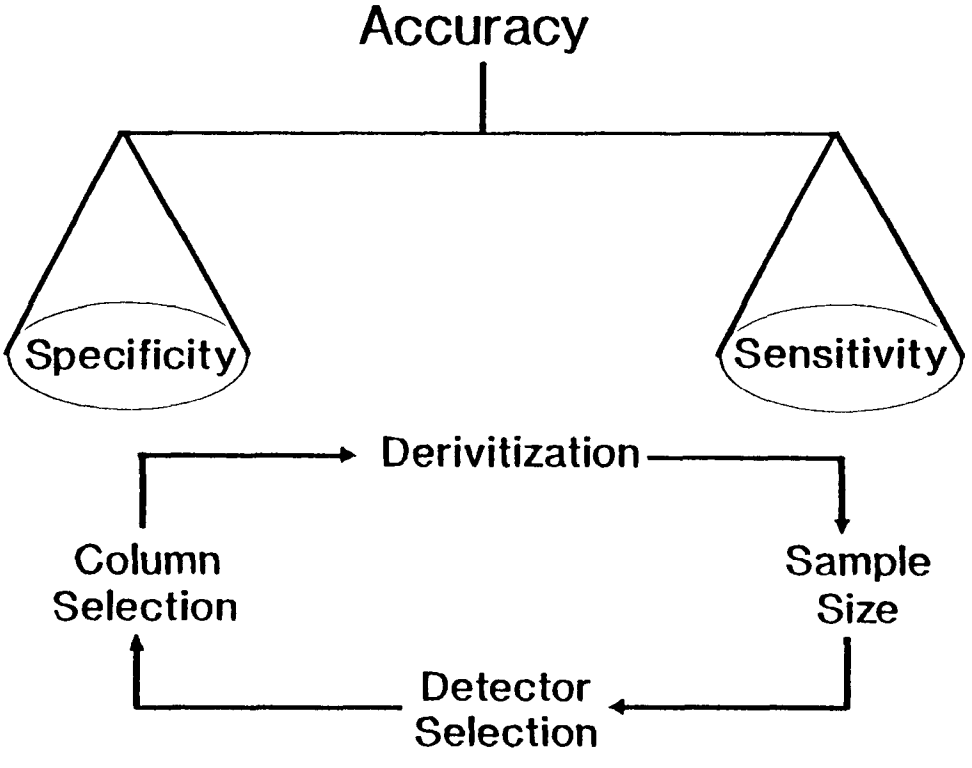
  Differentiates Isomeric Chloroguaiacols
  Differentiates Chloroguaiacols and Chlorocatechols

- Improved Accuracy and Precision

- Rapid

Requirements for Compliance Methods

- Accuracy
- Precision
- Reliability
  (Ruggedness)



Detector Comparison
Chlorophenol Acetates

- Selectivity

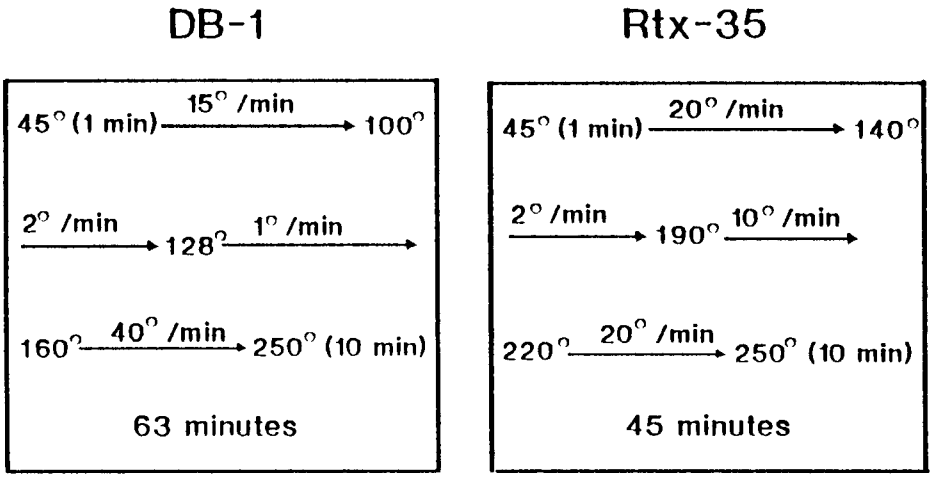
  GC/MS (full scan) › ELCD › ECD

- Sensitivity

  ECD › ELCD › GC/MS (full scan)

Comparibility of GC/ECD vs GC/MS Data

	False Positives	Positive Bias
2,6-Dichlorophenol	35%	
2,4-Dichlorophenol	17%	13%
3,5-Dichlorophenol	9%	
2,3-Dichlorophenol	17%	
3,4-Dichlorophenol	22%	
2,4,6-Trichlorophenol	9%	
2,3,6-Trichlorophenol		
2,4,5-Trichlorophenol	4%	
2,3,4,6-Tetrachlorophenol	17%	
Pentachlorophenol	13%	
4,6-Dichloroguaiacol	17%	4%
4,5-Dichloroguaiacol	22%	17%
3,4,5-Trichloroguaiacol	4%	
4,5,6-Trichloroguaiacol	4%	
Tetrachloroguaiacol	4%	4%
3,4-Dichlorocatechol	4%	
4,5-Dichlorocatechol		4%
3,4,6-Trichlorocatechol		
3,4,5-Trichlorocatechol	4%	
Tetrachlorocatechol	13%	
6-Chlorovanillin	4%	17%
5,6-Dichlorovanillin	4%	4%
Chlorosyringaldehyde	9%	9%
Trichlorosyringaldehyde	9%	



Compounds that Co-Elute

DB-1	Rtx-35
6-Chloroguaiacol	3,5-Dichlorophenol
3,4-Dichlorophenol	2,6-Dichlorophenol
	2,4-Dichlorophenol
2,4,5-Trichlorophenol	
4,5-Dichloroveratrole	4-Chloroguaiacol
	5-Chloroguaiacol
4,6-Dichloroguaiacol	
3,5-Dichloro-4-Hydroxybenzaldehyde	3-Chlorocatechol
	3,4,5-Trichlorophenol
5-Chlorovanillan	4-Chlorocatechol
3,5-Dichlorocatechol	
	4,5-Dichloroguaiacol
3,4,5-Trichloroguaiacol	Tetrachlorophenol
Tetrachloroveratrole	3-Chlorosyringol
	3,4-Dichlorocatechol
	4,5-Dichlorocatechol
	5-Chlorovanillin
	Tetrachloroveratrole

Comparibility of GC/ELCD vs GC/MS Data
All Matrices

	2 Column Confirmation	DB-1 Only
False Positives	4%	9%
Positive Bias	17%	24%
False Negatives	23%	2%
Negative Bias	3%	7%

Total Number of Samples = 6
Total Number of Analytes = 40

Percentage of Dual Column Confirmations in Replicate Analyses (>/= 5 ppb)

	Final Effluent n = 7	C Stage Filtrate n = 6	E Stage Filtrate n = 4
4-Chlorophenol		100%	100%
2,4-Dichlorophenol		100%	100%
2,4,6-Trichlorophenol		100%	100%
Tetrachlorophenol			100%
Pentachlorophenol			100%
6-Chloroguaiacol			50%
4-Chloroguaiacol		33%	
4,6-Dichloroguaiacol			100%
3,4-Dichloroguaiacol			100%
4,5-Dichloroguaiacol		17%	100%
3,4,6-Trichloroguaiacol			100%
3,4,5-Trichloroguaiacol	100%	33%	100%
4,5,6-Trichloroguaiacol	86%	67%	100%
3,6-Dichlorocatechol			25%
3,5-Dichlorocatechol		100%	75%
3,4-Dichlorocatechol			50%
4,5-Dichlorocatechol		100%	
3,4,6-Trichlorocatechol		100%	25%
3,4,5-Trichlorocatechol		33%	100%
5,6-Dichlorovanillin			100%

Percentage of Dual Column Confirmations in Replicate Analyses (</= 5 ppb)

	Final Effluent n = 7	C Stage Filtrate n = 6	E Stage Filtrate n = 4
4-Chlorophenol	14%		
2,4-Dichlorophenol	100%		
3,5-Dichlorophenol			50%
2,3-Dichlorophenol		83%	
2,4,6-Trichlorophenol	100%		
2,3,6-Trichlorophenol			25%
2,4,5-Trichlorophenol			25%
Tetrachlorophenol	29%		
Pentachlorophenol	71%		
5-Chloroguaiacol	29%		
4,6-Dichloroguaiacol	100%		
3,4-Dichloroguaiacol	100%		
4,5-Dichloroguaiacol	100%		
3,4,6-Trichloroguaiacol	100%		
Tetrachloroguaiacol	100%		
3,6-Dichlorocatechol		17%	25%
3,5-Dichlorocatechol	57%		
4,5-Dichlorocatechol			100%
3,4,5-Trichlorocatechol	29%		
6-Chlorovanillin	43%		
5,6-Dichlorovanillin	29%	17%	
Trichlorosyringol	43%		50%

In-Situ Acetylation Procedure

Factors Contributing to Precision

- Acetylation Yield / Efficiency
- Extraction Efficiency
- Concentration Losses
- GC Analysis

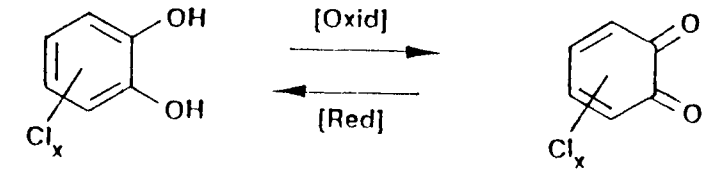
GC/ECD Matrix Spike Recovery Summary 3-84 to 1-86

	$\bar{X}$	Relative Standard Deviation
2,4-Dichlorophenol	110	23%
2,4,6-Trichlorophenol	102	16%
4,5-Dichloroguaiacol	103	19%
3,4,5-Trichloroguaiacol	99	19%
Tetrachloroguaiacol	93	18%
4,5-Dichlorocatechol	83	57%
3,4,5-Trichlorocatechol	94	58%
Tetrachlorocatechol	73	49%
6-Chlorovanillin	108	38%
5,6-Dichlorovanillin	83	32%

GC/MS PRECISION

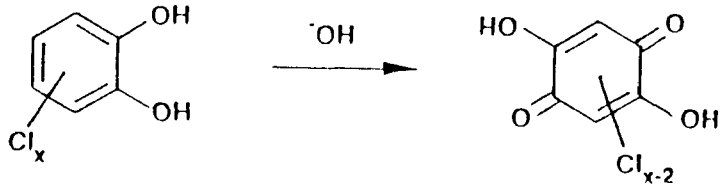
	Relative Standard Deviation		
	C Stage Filtrate n = 7	E Stage Filtrate n = 7	Treated Effluent n = 7
2,4-Dichlorophenol	7%	4%	2%
2,4,6-Trichlorophenol	8%	5%	4%
4,5-Dichloroguaiacol	4%	3%	11%
3,4,5-Trichloroguaiacol	6%	3%	1%
Tetrachloroguaiacol	4%	5%	2%
4,5-Dichlorocatechol	11%	16%	3%
3,4,5-Trichlorocatechol	5%	16%	4%
Tetrachlorocatechol	9%	17%	49%
6-Chlorovanillin	8%	5%	8%
5,6-Dichlorovanillin	13%	5%	5%

CHLOROCATECHOL pH STABILITY



CHLOROCATECHOL

CHLORO-O-BENZOQUINONE



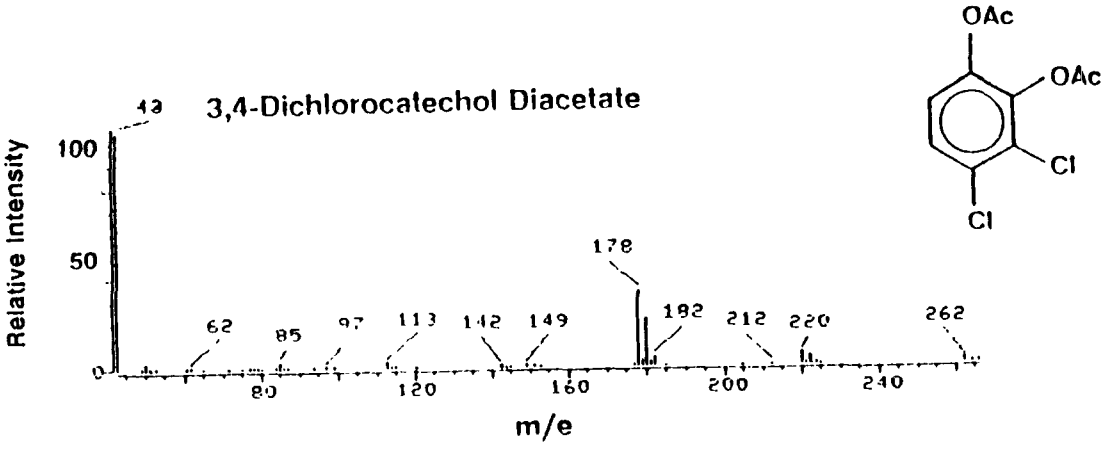
CHLORANILIC ACID

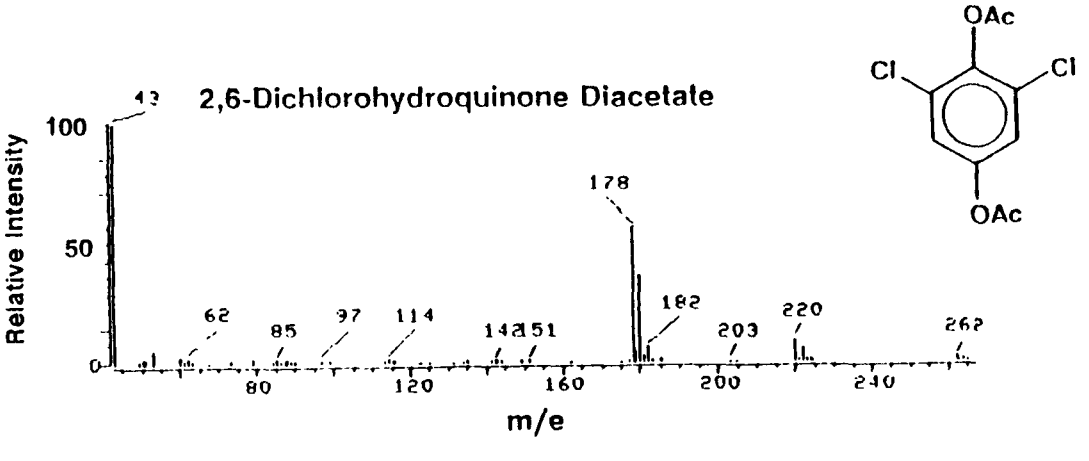
Possible Solution to Chlorocatechol Problem

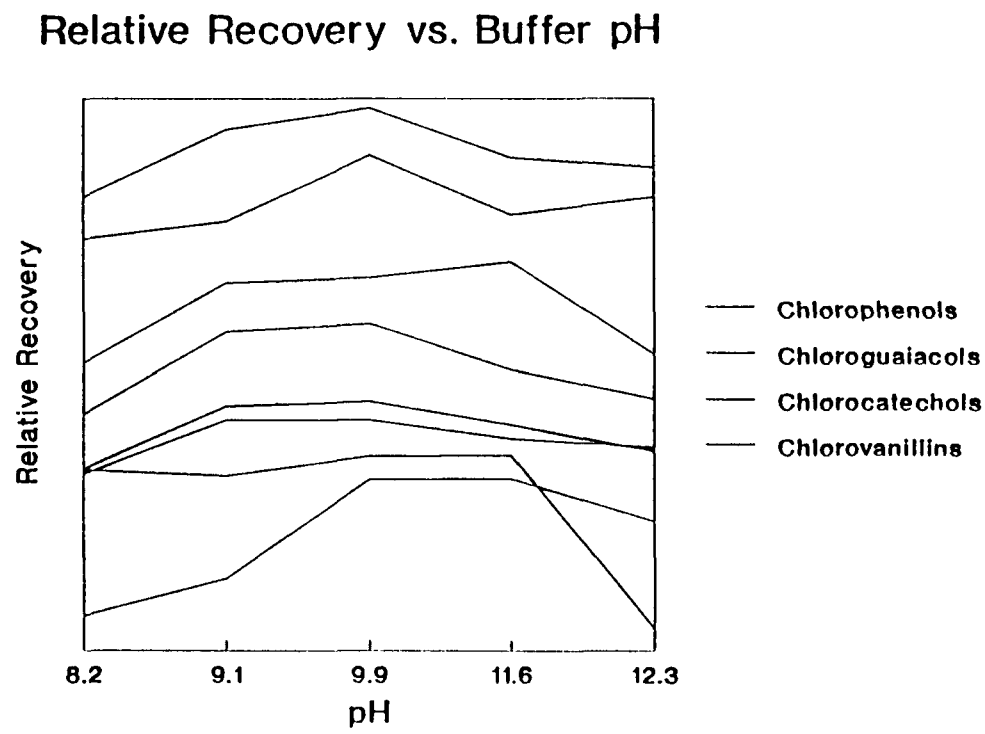
- Addition of Preservative
  Reducing agent - ascorbic acid
  thiosulfate
  bisulfite
- Lower pH Buffer
- Shorten Exposure Time

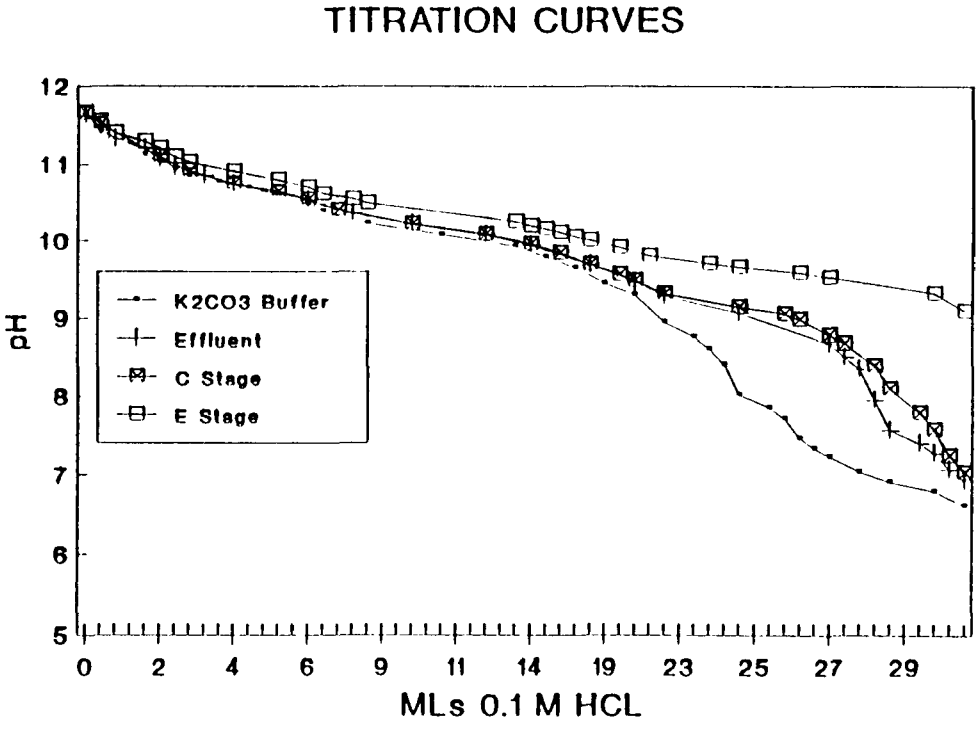
Percent Increase Due to Use of Ascorbic Acid

Analyte	C-Stage Filtrate n=3	E-Stage Filtrate n=1	Primary Influent n=2	Treated Effluent n=6
4-Chlorocatechol	0-11	0	0	0
3,4-Dichlorocatechol	0-311	0	0-137	0
4,5-Dichlorocatechol	0-73	0	0	0
3,4,6-Trichlorocatechol	0-56	0	0	0
3,4,5-Trichlorocatechol	0-42	0	0	0
Tetrachlorocatechol	0-38	0	0	0






Relative Recovery vs. Buffer pH
Relative Recovery
8.2
9.1
9.9
11.6
12.3
pH
Chlorophenols
Chloroguaiacols
Chlorocatechols
Chlorovanillins


TITRATION CURVES
pH
12
11
10
9
8
7
6
5
0
2
4
6
9
11
14
19
23
25
27
29
MLs 0.1 M HCL
K2CO3 Buffer
Effluent
C Stage
E Stage

Conclusions

- GC/MS Provides Best Selectivity with Acceptable Sensitivity
- Precision Acceptable for all Analytes Except Chlorocatechols
- Reliability for Chlorocatechol Analyses Needs Improvement

MR. TELLIARD: I saved the best until last. Our next speaker has presented here before. Peggy presented some work that she had done on isotope dilution when she was at Weyerhaeuser. Since then, she had a total conversion and now works for our Region X laboratory in Seattle and is going to continue the same thing, the in-situ acetylation and look at the method for chlorinated phenolics again in pulp and paper effluent.

MS. KNIGHT: I thought I'd give you a look at where I currently come from. This is the EPA Region X ESD Lab. It's located in Manchester, Washington, very close to Port Orchard, Washington, a little bit south of Bremerton. One of the advantages of the Manchester lab is it's not located in the exact place as the administrative offices - that can be quite an advantage. The administrative offices are located across the water. This is one of the views that we see from the laboratory, a ferry boat going across the Puget Sound. If you look in a slightly different direction, you would see Seattle.

This slide is included for Bill's benefit. I know that he likes ships and this is the Nimitz. We can frequently see the Nimitz coming into Bremerton. We get aircraft carriers...not battleships.

Larry has given you an outline of how the NCASF's method CP-86.01 works. I'll continue a discussion of that and how we at the Region X lab have been using the GC/MS portion of the method.

We've made a couple of changes that we think are appropriate for us. One of them is scaling up from combining three separate 100 milliliter extractions in a separatory funnel to extracting up to three liters by stir bar.

There isn't much you can really see with this slide except the vessels we do the stir bar extraction in. They are the sample containers that come into the laboratory. A stir bar is put into the bottom of the containers and a very strong vortex is formed.

Actually, I'm a little bit ahead of myself. I wanted to mention what the other changes were first. We have had trouble losing catechols, so we add a reducing agent, ascorbic acid. Another change we've made to the method is the incorporation of an injection internal standard or an instrument internal standard, whichever the current terminology is, something that's added before the analysis of the sample on the

GC/MS so that we can determine the recovery of the method internal standard, either 3,4,5-trichlorophenol or 2,6-dibromophenol, both of which have been used with success. We like to monitor the recovery of the method internal standard to find out how well we are doing. Along the same lines, we also add a series of surrogate compounds to monitor the method.

About the stir bar method. One of the characteristics of the in-situ derivitization procedure is that it proceeds very rapidly so mixing of the sample is exceptionally important. After the addition of acetic anhydride, the pH rapidly drops from 11.6, if you've reached that valve, down to about 7 within about 30 stet and the reaction is complete.

In order to make sure that everything is well mixed, we pull a very strong vortex as we're mixing the sample, adding the buffers, adjusting pH and adding the acetic anhydride is added. It seems to ensure good mixing during a very rapid reaction. Carbon dioxide is evolved rapidly during the reaction. The green vessel does not build up pressure as a separatory funnel would.

The same vessel is used for extraction with hexane of the reaction products. This is a picture of the apparatus that we use to extract the reaction products with hexane. We use a vacuum system. The parts that contact the sample are teflon or glass. The top hexane layer is pulled off into the sep funnel, then we use the sep funnel to separate aqueous phase from the hexane, the water is returned to the sample container for further extraction, and the hexane is saved as the extract.

You might think that the stir bar method would prevent emulsion formation. Pulp and paper mill effluents form terrific emulsions. However, the stir bar extraction method does help. We still have emulsions with these samples and usually use a centrifuge to break them.

As I mentioned before... Larry, could I have the first overhead. We've had a fairly substantial problem with catechol recovery even in our standards, so we now add ascorbic acid. The chlorinated catechols, as you can see from this slide, which is

derived from the same source as Larry's hypothetical guaiacol cycle, readily oxidize to orthobenzoquinones under alkaline conditions. In the presence of ascorbic acid, the benzoquinones are reduced to catechols which can then be derivatized and extracted. There is industry concern, especially in process streams that quinones and catechols will both be lumped together, but we need to find some way to at least have a look at the catechols.

Some Fathead Minnow larvae testing that we have done on tetracholo-orthobenzoquinone indicates that it is on the same order of magnitude toxicity as tetrachlorocatechol. We plan on testing other species, perhaps oyster larvae.

The injection internal standard that we use to monitor the recovery of our internal standard is 2,6-dibromophenol. NCASI in the past has used 3,4,5-trichlorophenol, which is not apparently found in pulp mill effluents. Both of these stet have problems. 3,4,5-Trichloroguaiacol is formed from tetrachlorophenol and also from pentachlorophenol under anaerobic conditions on some matrices. 2,6-Dibromophenol has been found to be produced naturally in infaunal worms and we've also found it in English sole. So, if one were to use this method, you'd have to be careful in internal standard selection to use it with marine tissue.

We selected a group of surrogates monitor how the method was proceeding and the ones that we selected were ones that are relatively easily available, D_5-phenol, 2-fluorophenol, 2-ethoxyphenol, which I was convinced was going to mimic guaiacol, 2,4,6-tribromophenol and D_6-resorcinol. After we had done about 20 matrix spikes, we looked at the correlation of every compound to every other compound to see what reflected what with SCOUT, a statistical package developed by Lockheed for EPA, turned out that the surrogates that we had selected were really only monitoring the recoveries of non-chlorinated and low chlorinated phenolics. We didn't really have appropiate

surrogates for any of the tri and tetrachloroguaiacols or catechols. So, what we'd really like is to have a ^{13}C labeled representative of each of those groups.

Well, how do the method mosifications on these work? We've got a couple of ways that we've tested this. This slide represents our method detection limit determination. It was done in blank water, so it represents the best case and detection limits. Of course, you could not expect this in real mill effluents and I'll show what happens with those in a minute.

There are a couple of things I should say about this slide. All of the detection limits that we determined were sub-parts per billion. The spiking level was 0.83 micrograms per liter and we extracted seven replicates of three liters of sample using the stir bar procedure. There are a couple of compounds, 4-propenylguaiacol and tetrachlorocatechol, which should be spiked at a higher level in order to more accurately determine the method detection limit. There are another four or five compounds that we should actually spike at a lower level in another set of seven replicates. I'm a little hesitant to try and spike less than .8 parts per billion.

Next slide.

This slide shows what the mass spectrum one of the trichloroguaiacols looks like at this level. There are enough masses there that I think we can identify the compound.

Next slide.

These are three masses present in this trichloroguaiacol and they maximize within plus or minus one scan.

Next slide.

Clean water is one thing and real samples are another. This is a set of 18 matrix spikes that were run on everything from in-process streams to pulp mills effluent samples. There were a couple of receiving water samples in here. The reason that they don't all have 18 valves is some had to be tossed

because the spiking level, which varied from 15 to about 50 parts per billion, sometimes was greatly exceeded by the natural amount in the sample so we couldn't include that data. There were also a couple of compounds that were added as we went along in this study.

These data were found using stir bar extraction and ascorbic acid. These data compare well with the NCASI precision and accuracy data, except for the catechols which are better, as you might expect from the addition of ascorbic acid.

Next slide, Larry.

This is representative of a real sample I thought you might like to see what it looks like. Somewhere around here is the region that we will be looking at a little later.

Next slide.

This is that same sample. The top trace represents a 25 microgram per liter spike of that sample. You can't really see many differences. Overall it's difficult to tell that the spiked sample is any different then the unspiked.

Okay, Larry.

The unspiked sample contained five parts per billion 3,4,5-trichloroguaiacol. This isn't a lot of area so 0.8 parts per billion for this sample would be very difficult. What you can detect mostly depends on what else is in the matrix.

Okay, Larry.

Again, this shows three masses and the addition of a fourth that is in this particular compound, but you wouldn't be able to see the maximum of that particular mass due to matrix effects.

Okay, Larry.

I just included this to show you what the spike would look like with 25 parts per billion added.

Okay.

This is a different sample, a treated effluent whereas the previous one was untreated.

Okay, Larry.

Although it looks messier, if you looked at the intensity on the right hand side, you would see that it's about 20 percent of the intensity of the untreated sample. This is actually quite a bit cleaner. We'll be again looking between 2,700 and 2,800 scans. Okay, Larry.

It is a lot easier to detect the compound in this sample at 2.5 parts per billion than in the untreated effluent.

These have been our experiences with the GC/MS method of in-situ acetylation on pulp and paper mill effluents. The detection limits are ultimately determined by what kind of sample you have, whether it's influent into a primary treatment or a secondary effluent. It also depends on the mill process. If we were to need lower levels, we'd probably need a cleanup technique, foe example silica gel or alumina.

If there are any questions, I'll entertain them.

QUESTION AND ANSWER SESSION

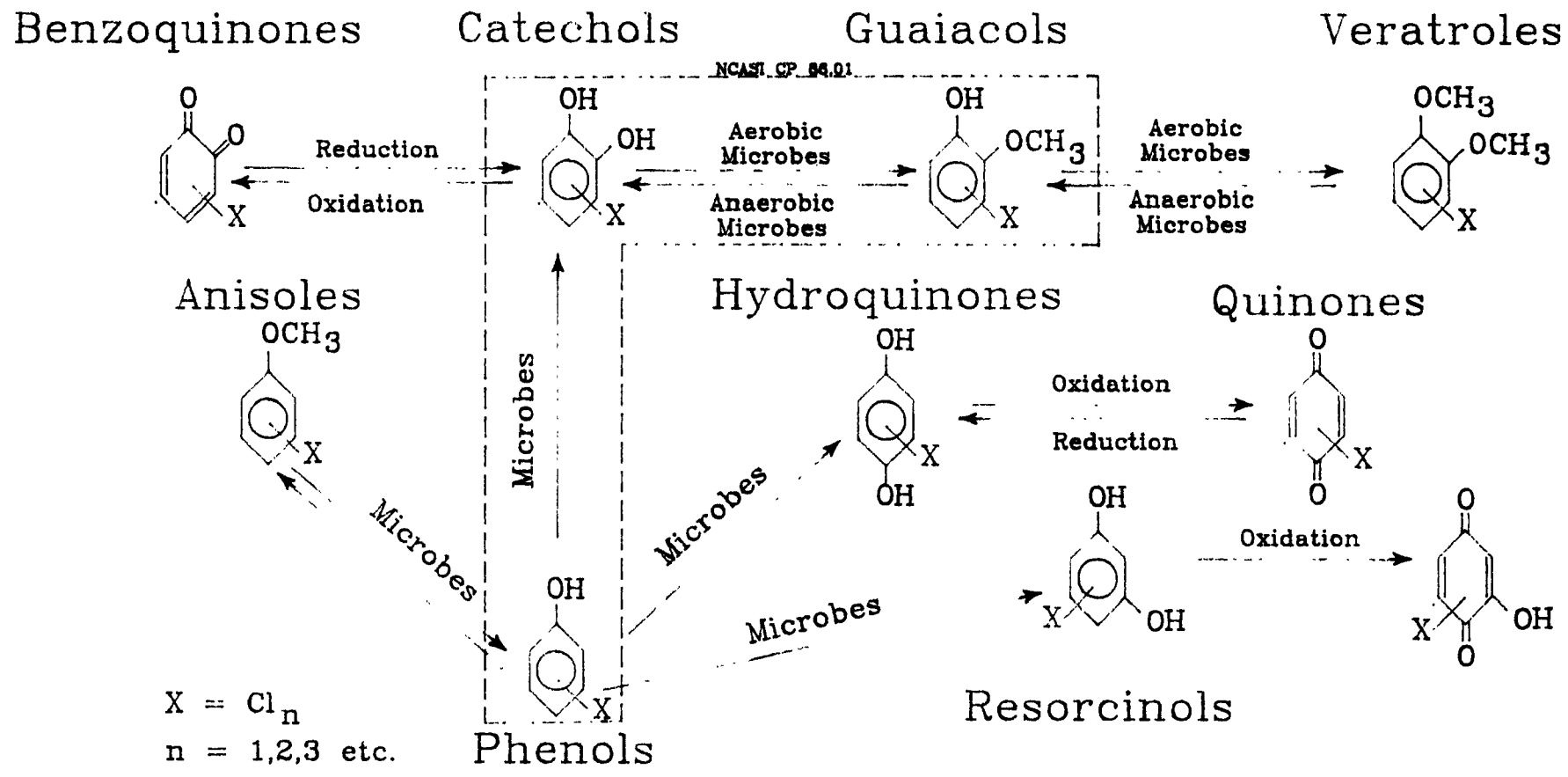
MR. TELLIARD: Any questions? Thank you, Peggy.

Thank you very much. I'd like to thank this afternoon's speakers.

Thank you for your attention. See you tomorrow morning and see the rest of you at the boat tonight.

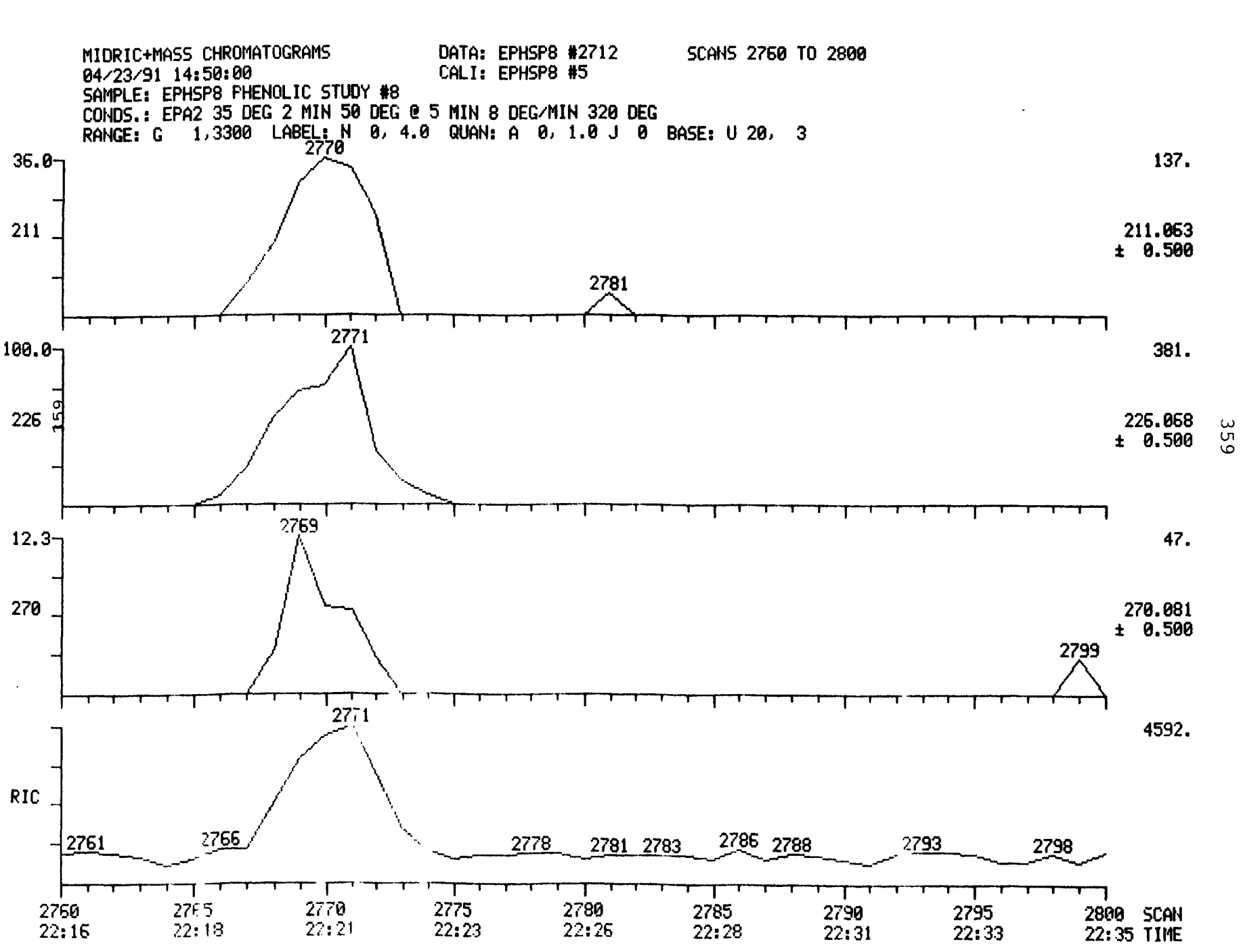
Thank you very much.

Fig 1. ENVIRONMENTAL CHEMISTRY OF SELECTED PULP PROCESS PRODUCTS



References: Environmental Chemistry of Penatchlorophenol, Pure and Applied Chemistry Vol. 53, pp 1051–1080, 1981.
Allard et al,"Environmental Fate of Chloroguaiacols and Chlorocatechols" Wat. Sci. Tech., Vol 20, No. 2, pp 131–141, 1988

	Average in ppb	STD in ppb	MDL in ppb	Recovery
Phenol	Ø.84	Ø.24	Ø.77	1Ø1
2-Methylphenol	Ø.84	Ø.11	Ø.35	1ØØ
4-Methylphenol	Ø.97	Ø.Ø8	Ø.24	117
2-Chlorophenol	Ø.78	Ø.Ø6	Ø.19	93
2,4-Dimethylphenol	1.Ø9	Ø.Ø8	Ø.26	131
4-Chloro-3-methylphenol	Ø.9Ø	Ø.Ø5	Ø.15	1Ø8
2,4-Dichlorophenol	Ø.81	Ø.Ø6	Ø.18	97
2,3,6-Trichlorophenol	Ø.78	Ø.Ø7	Ø.21	94
2,3,4-Trichlorophenol	Ø.82	Ø.Ø4	Ø.12	99
2,4,6-Trichlorophenol	Ø.76	Ø.Ø7	Ø.23	92
2,4,5-Trichlorophenol	Ø.85	Ø.Ø9	Ø.27	1Ø3
Pentachlorophenol	1.25	Ø.17	Ø.54	15Ø
Guaiacol	Ø.66	Ø.Ø9	Ø.27	79
4-Chloroguaiacol	Ø.78	Ø.Ø5	Ø.15	94
4-Allylguaiacol	1.77	Ø.19	Ø.6Ø	213
4,5-Dichloroguaiacol	Ø.83	Ø.Ø6	Ø.18	1ØØ
4-Propenylguaiacol	Ø.41	Ø.22	Ø.69	49
4,5,6-trichloroguaiacol	Ø.81	Ø.Ø4	Ø.14	98
3,4,5-trichloroguaiacol	Ø.86	Ø.Ø8	Ø.26	1Ø3
Tetrachloroguaiacol	1.ØØ	Ø.18	Ø.56	12Ø
4-Chlorocatechol	Ø.4Ø	Ø.Ø9	Ø.29	48
4,5-Dichlorocatechol	Ø.4Ø	Ø.Ø7	Ø.21	48
Tetrachlorocatechol	Ø.41	Ø.29	Ø.9Ø	49
alpha-Terpineol	Ø.73	Ø.12	Ø.38	88
6-Chlorovanillin	Ø.58	Ø.Ø6	Ø.2Ø	69
5,6-Dichlorovanillin	Ø.65	Ø.17	Ø.52	78
Trichlorosyringol	Ø.89	Ø.1Ø	Ø.3Ø	1Ø7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RANGE: G 1,3300 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
36.0
211
2770
2781
137.
211.063
± 0.500
100.0
226
159
2771
381.
226.068
± 0.500
12.3
270
2769
2799
47.
270.081
± 0.500
RIC
2771
4592.
2761
2766
2778
2781
2783
2786
2788
2793
2798
2760
22:16
2765
22:18
2770
22:21
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2795
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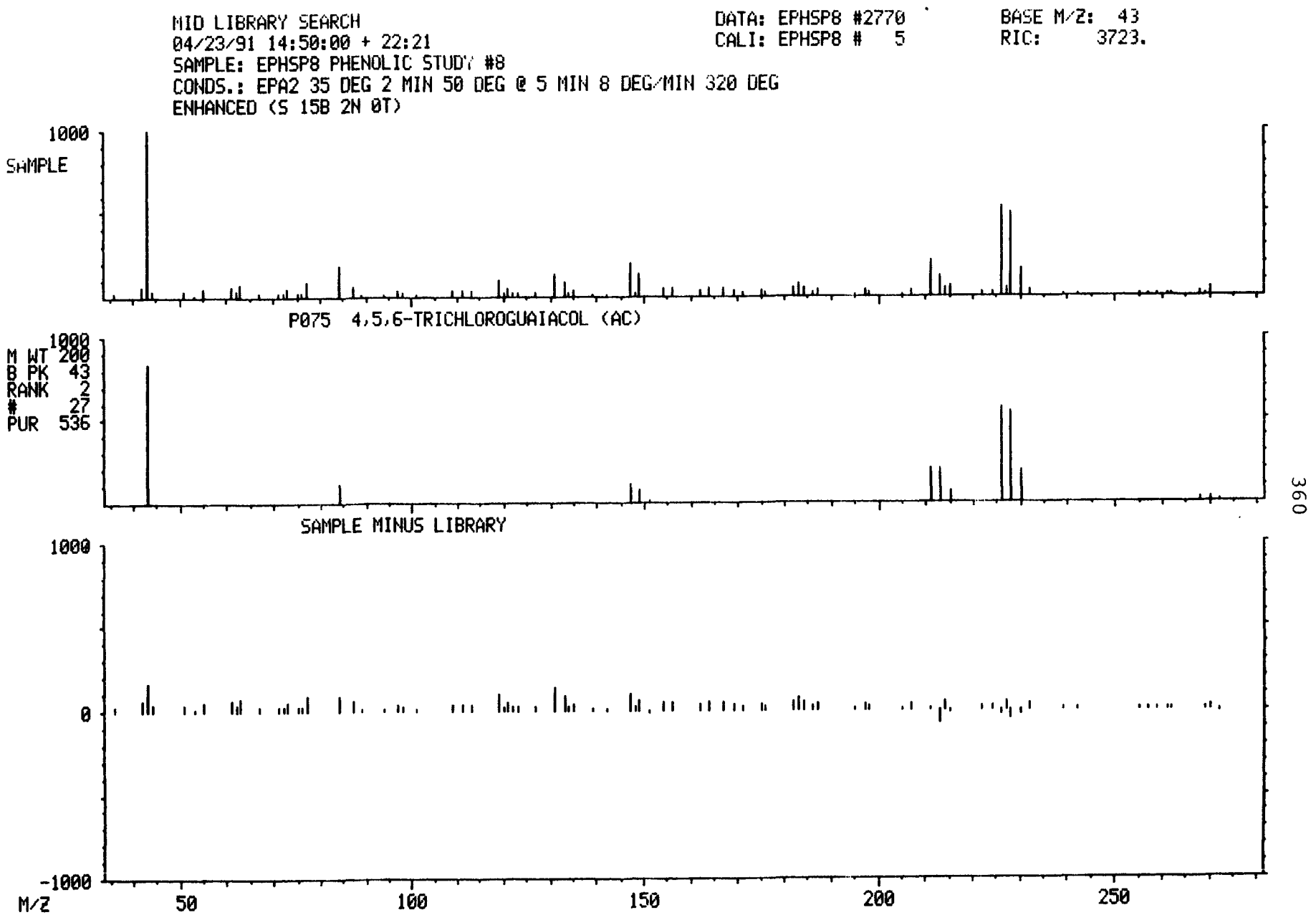
SCAN
TIME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ENHANCED (S 15B 2N 0T)
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BASE M/Z: 43
RIC: 3723.
1000
SAMPLE
P075 4,5,6-TRICHLOROGUAIACOL (AC)
1000
M WT 200
B PK 43
RANK 2
27
PUR 536
SAMPLE MINUS LIBRARY
1000
0
-1000
M/Z
50
100
150
200
250

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SAMPLE: E078133G [redacted] 100% 1ML/2UL
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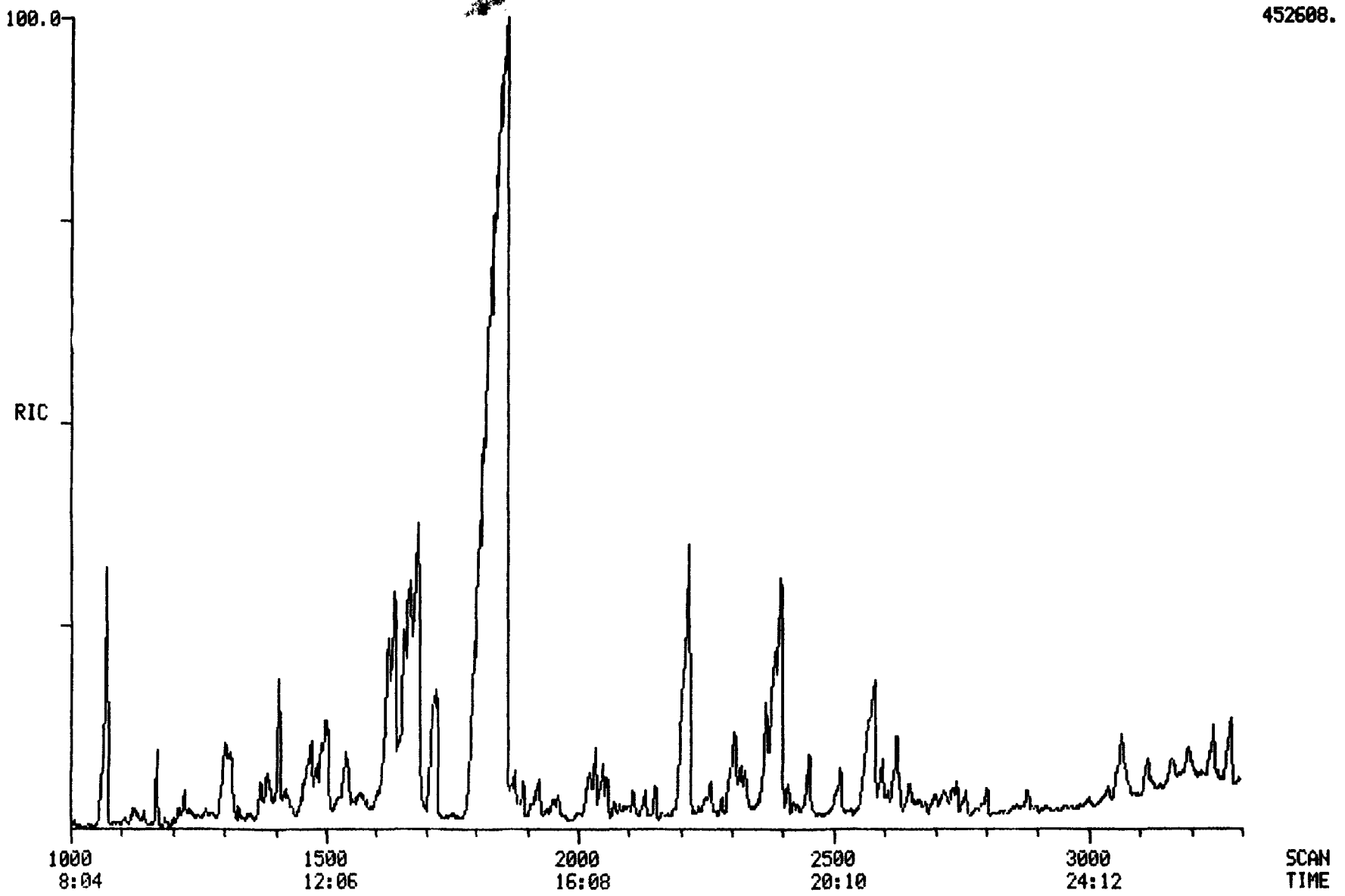

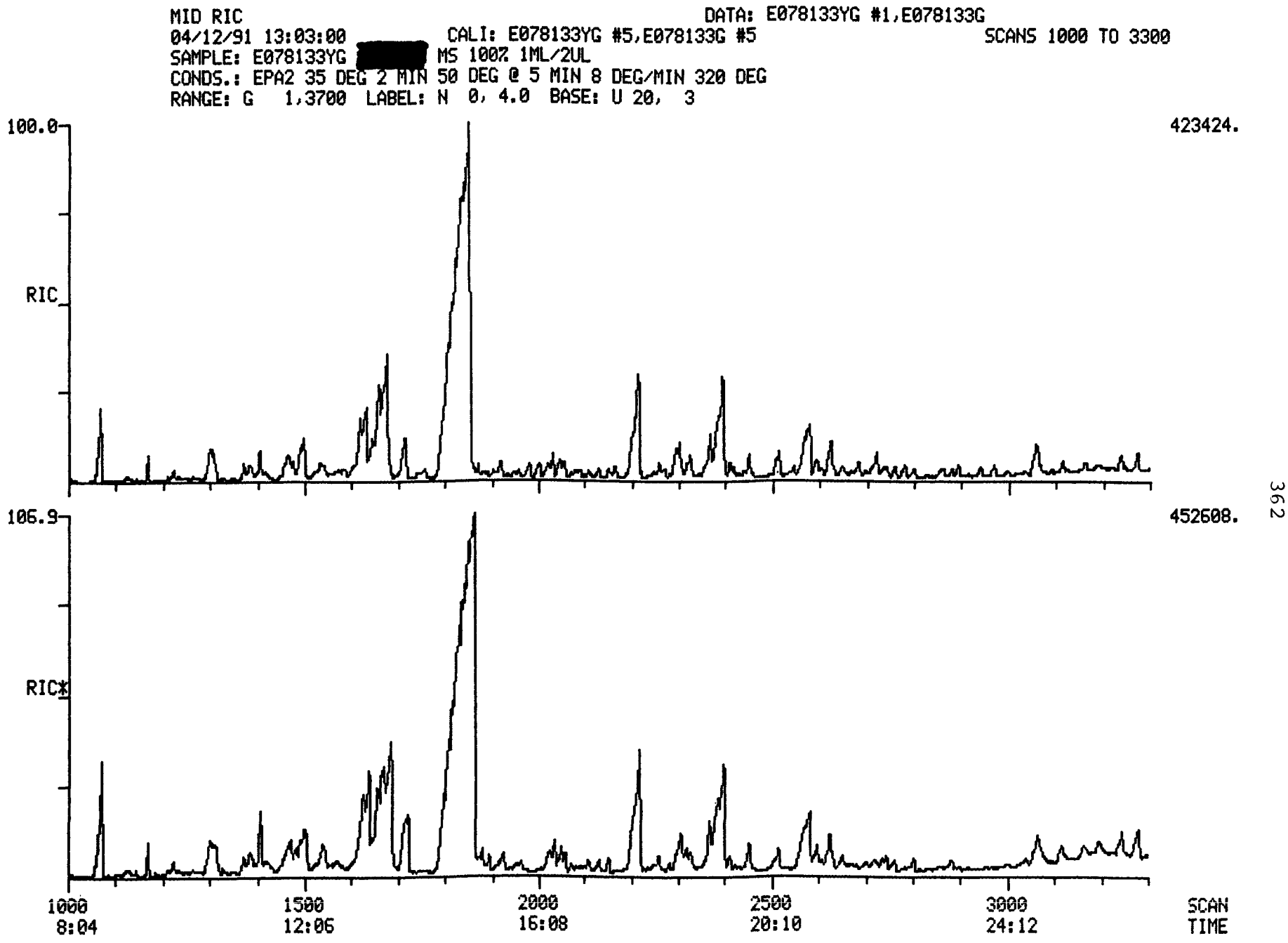
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RIC
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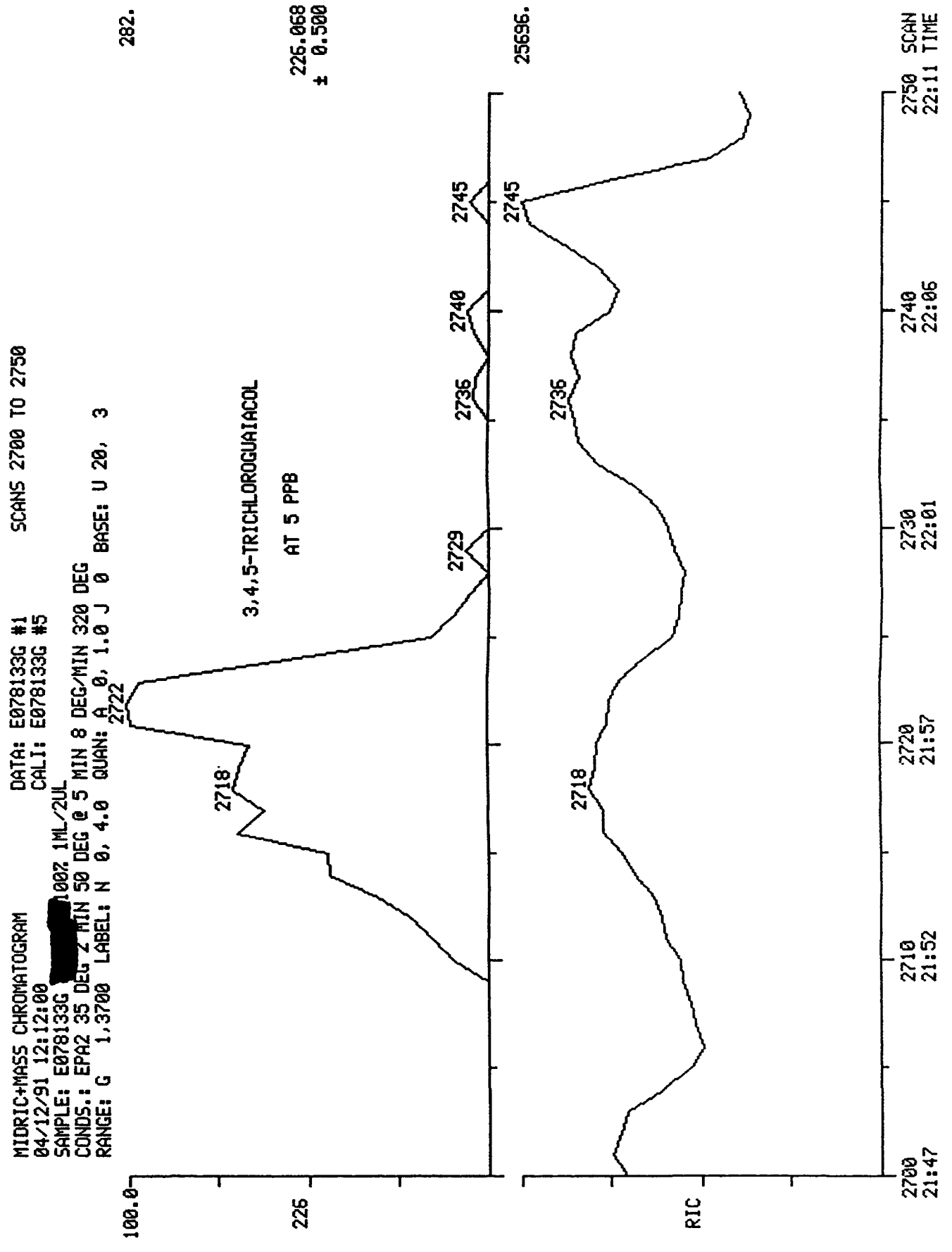
SCAN
TIME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SCANS 2700 TO 2750
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226.068
± 0.500
3,4,5-TRICHLOROGUAIACOL
AT 5 PPB
25696.
100.0
225
RIC
2700
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2710
21:52
2718
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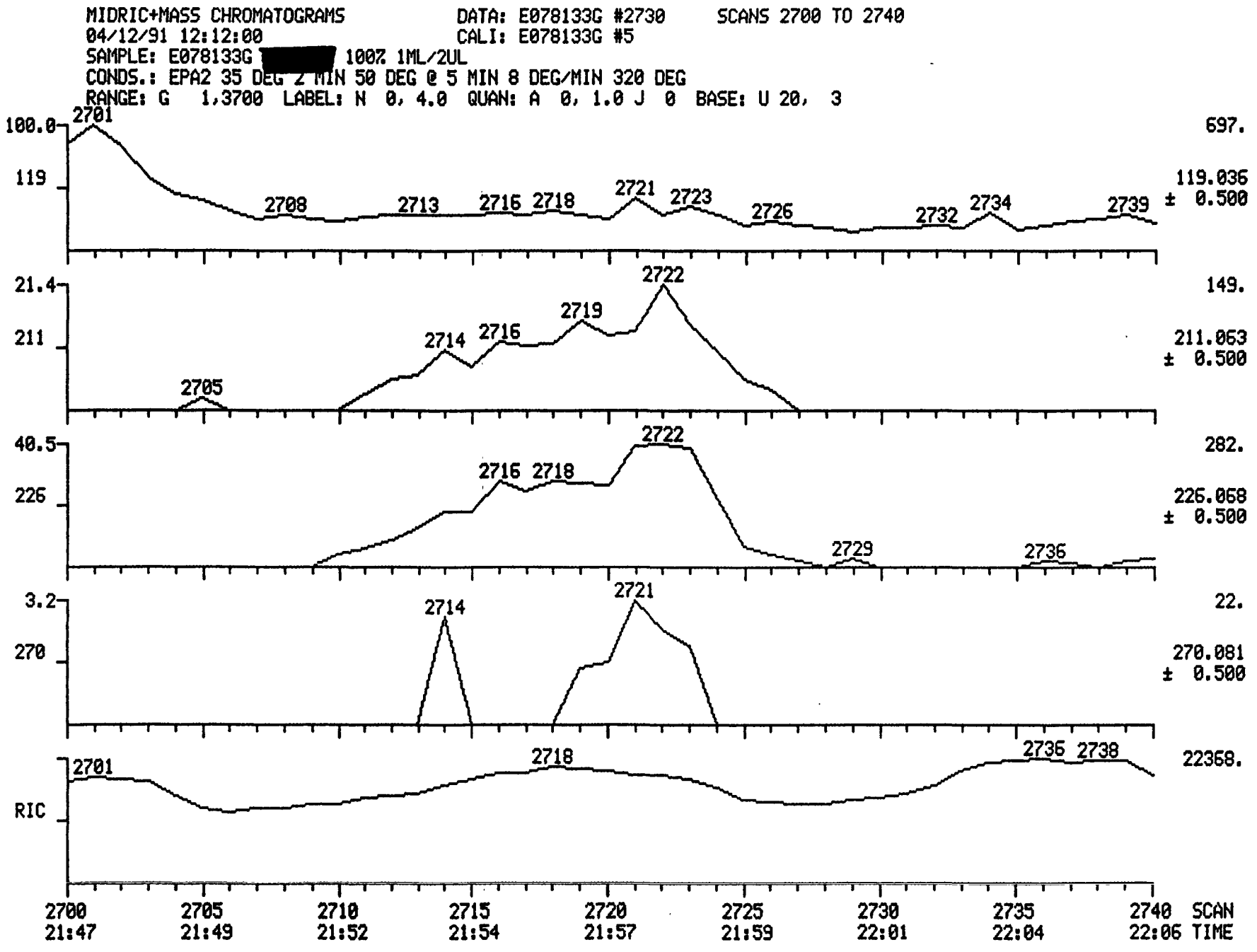
SCAN
TIME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RANGE: G 1,3700 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
100.0
119
2701
2708
2713
2716 2718
2721
2723
2726
2732
2734
2739
697.
119.036
± 0.500
21.4
211
2705
2714
2716
2719
2722
149.
211.063
± 0.500
40.5
226
2716 2718
2722
2729
2736
282.
226.068
± 0.500
3.2
270
2714
2721
22.
270.081
± 0.500
RIC
2701
2718
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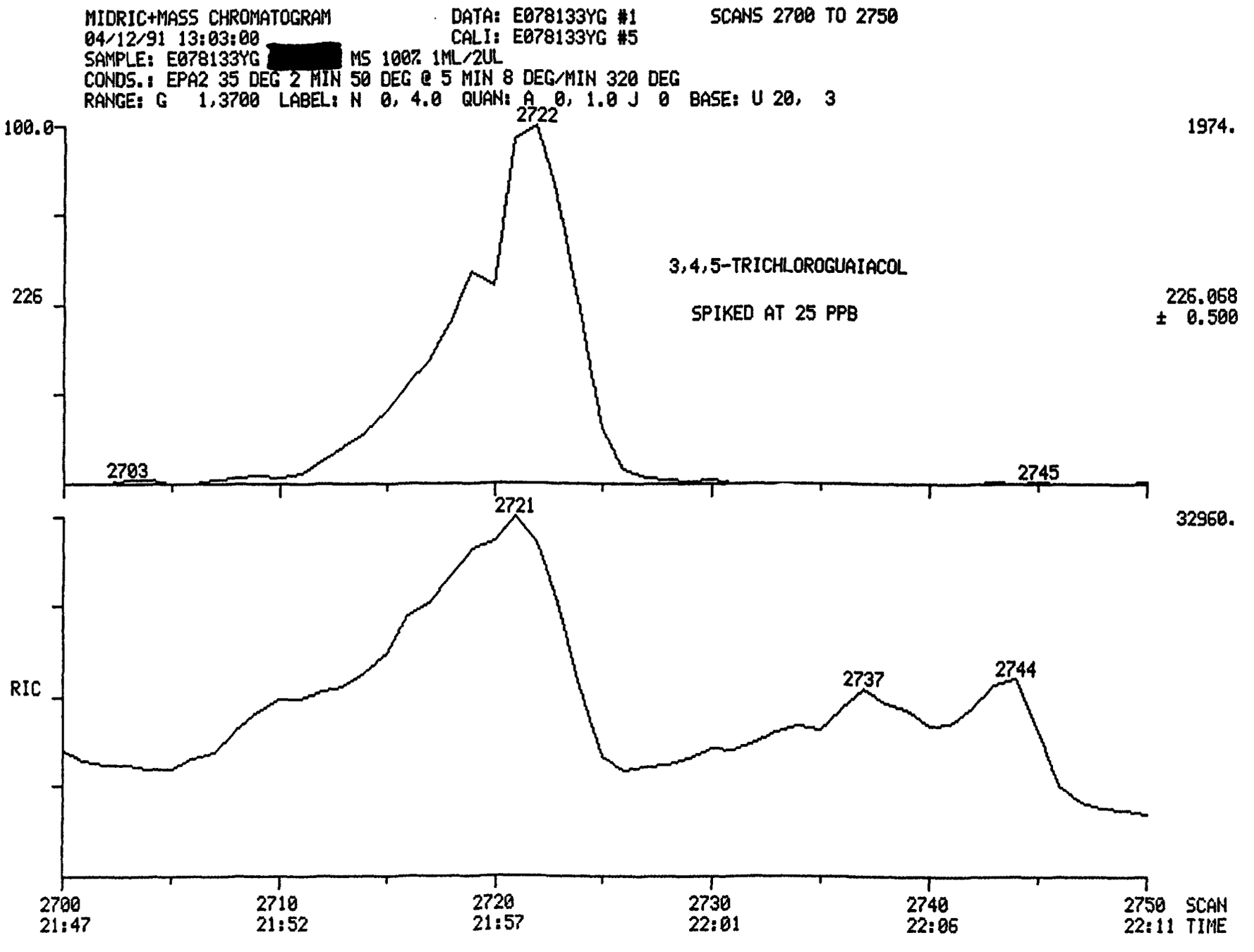
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2722
1974.
3,4,5-TRICHLOROGUAIACOL
SPIKED AT 25 PPB
226.068
± 0.500
2703
2745
2721
32960.
RIC
2737
2744
2700
21:47
2710
21:52
2720
21:57
2730
22:01
2740
22:06
2750
22:11
SCAN
TIME

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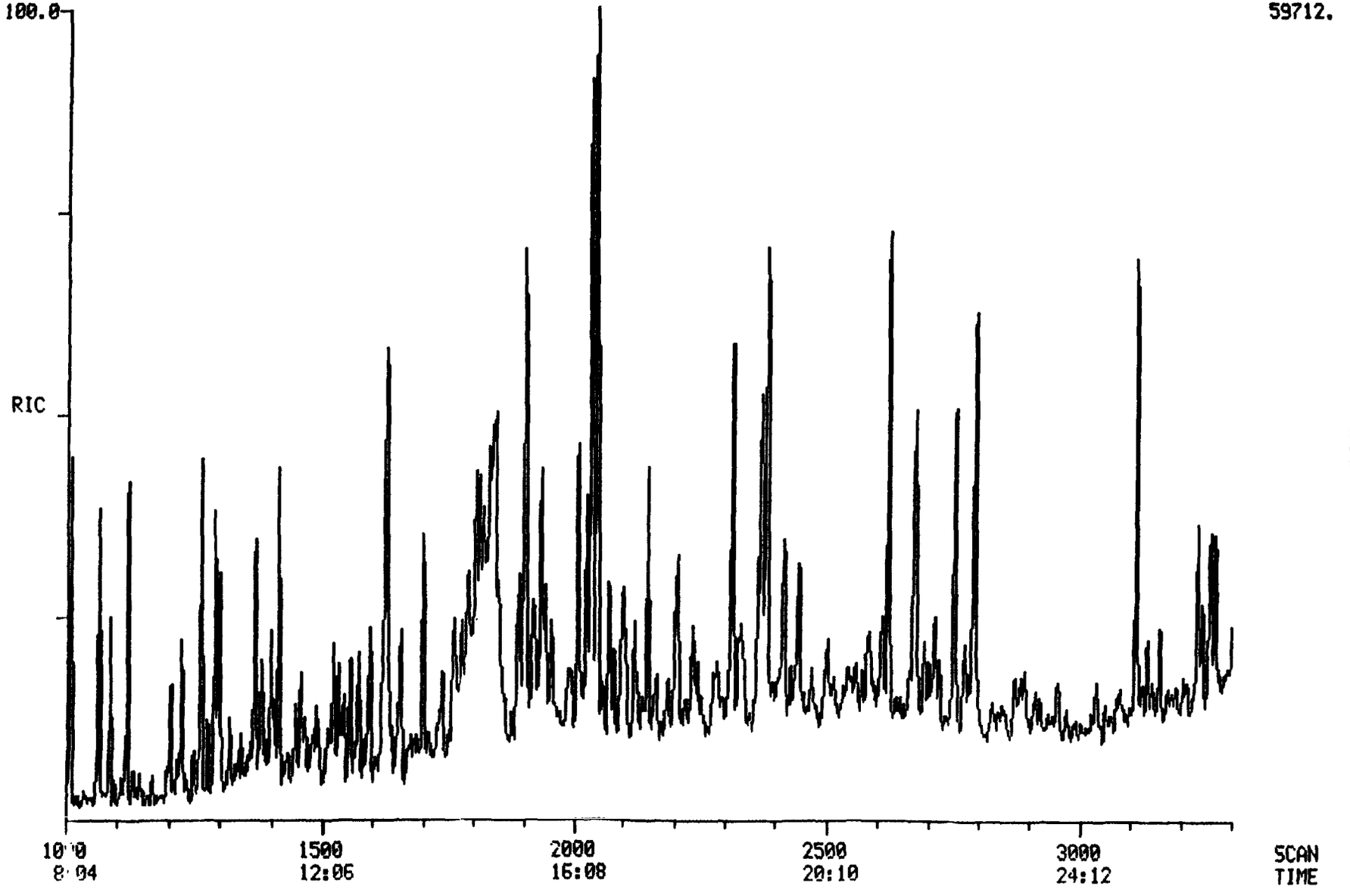

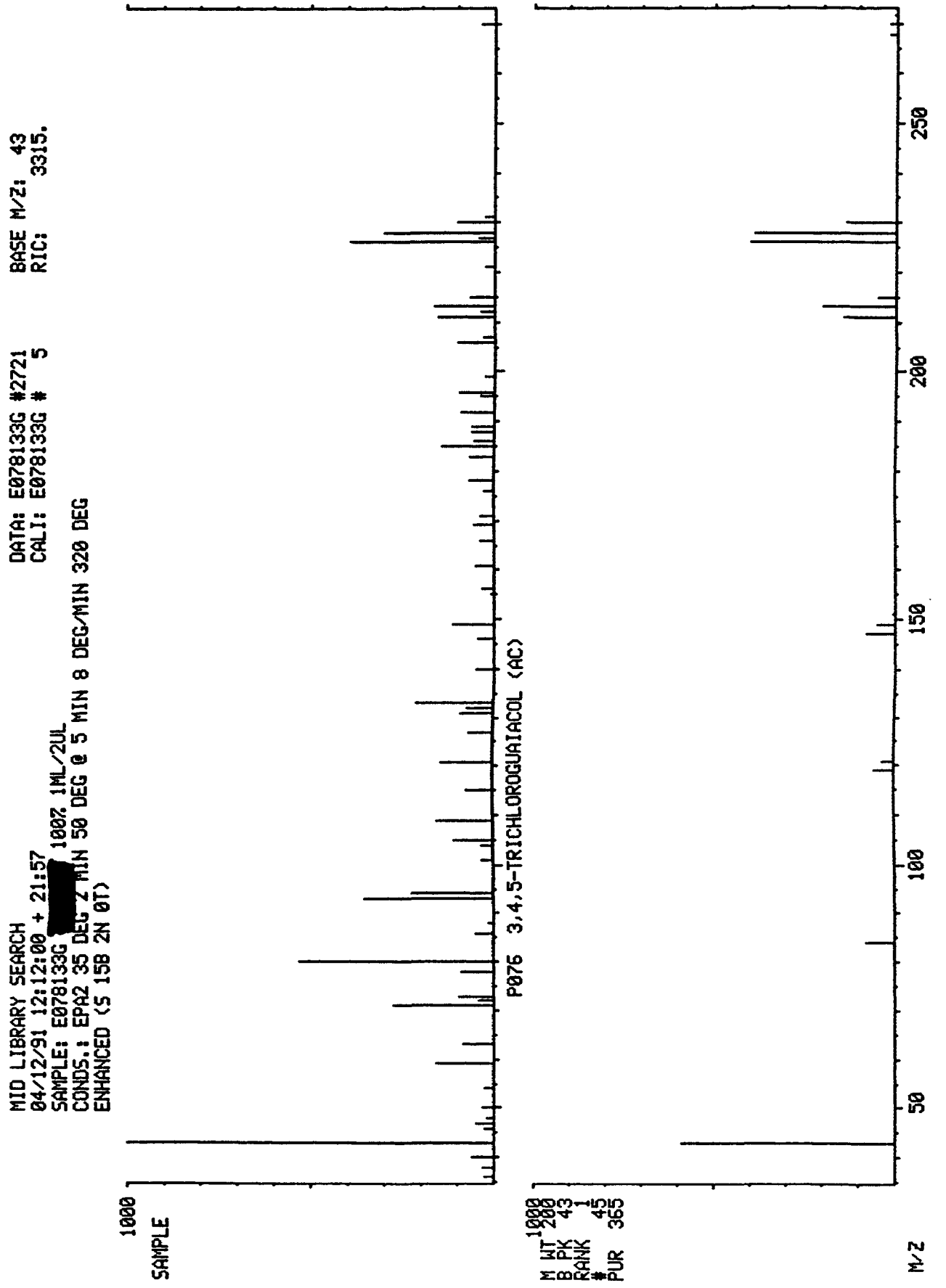
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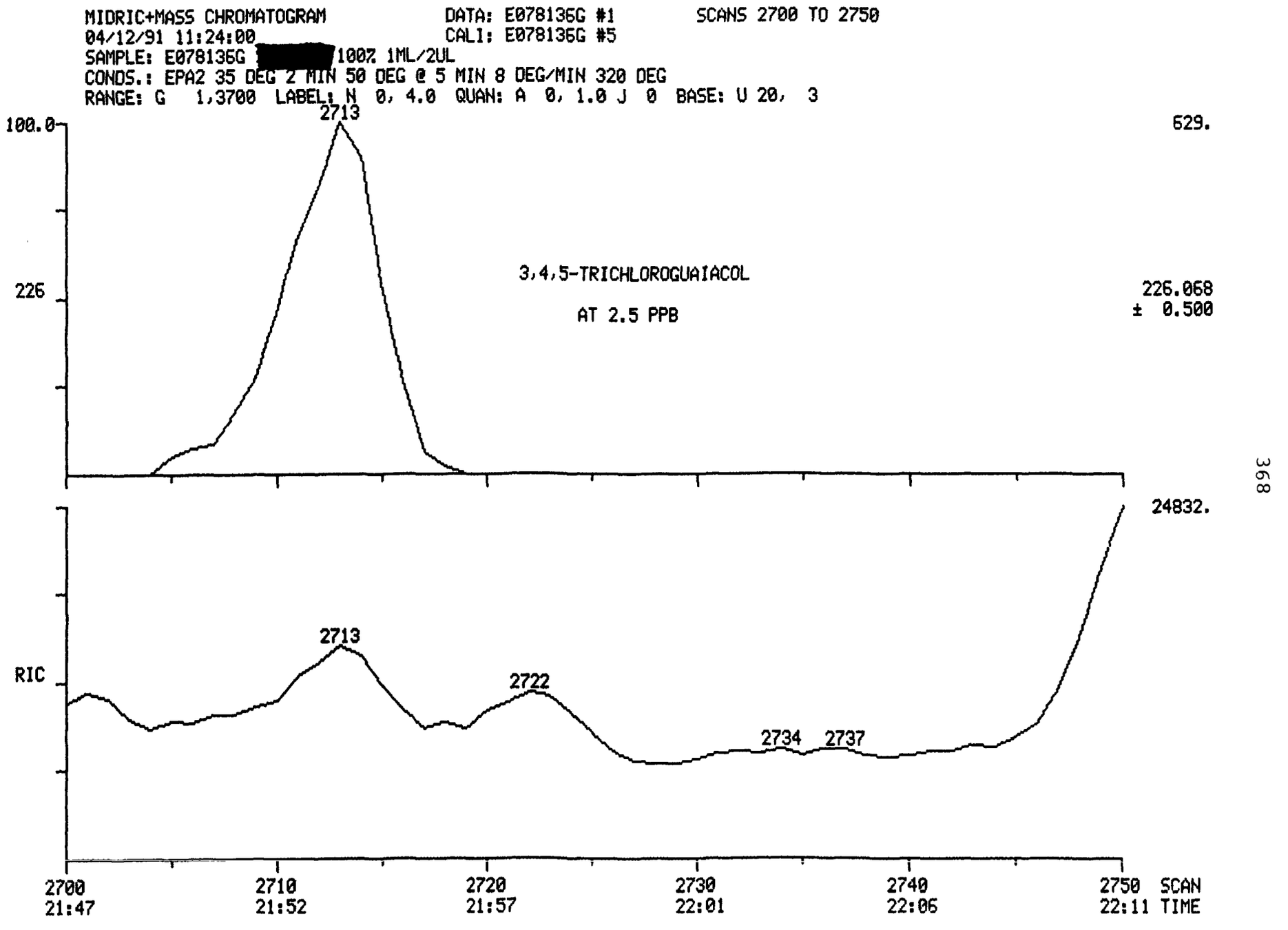
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22:11
SCAN
TIME

Table 6240:V. Single-Laboratory Bias and Precision for Chlorinated Phenols in Pulp Mill Effluents and Receiving Waters******

	Bias as average recovery	RSD	N
Phenol	87.8	24.2	18
2-Chlorophenol	88.8	20.0	18
2,4-Dichlorophenol	96.8	11.9	18
2,4,6-Trichlorophenol	98.2	10.2	16
2,4,5-Trichlorophenol	99.6	7.0	18
Pentachlorophenol	91.	17.3	18
Guaiacol	93.4	15.6	16
4-Chloroguaiacol	101	7.2	18
4,5-Dichloroguaiacol	99.0	15.9	18
3,4,5-Trichloroguaiacol	102	8.6	16
4,5,6-Trichloroguaiacol	99.8	9.1	18
Tetrachloroguaiacol	95.5	14.3	18
4,5-Dichlorocatechol	88.5	20.5	16
3,4,5-trichlorocatechol	89.2	14.7	14
Tetrachlorocatechol	83.9	18.4	16
6-Chlorovanillin	95.7	23.0	10
5,6-Dichlorovanillin	123	35.5	10
Trichlorosyringol	104	19.2	18

MR. TELLIARD: Good morning. We'd like to get started this morning, please. If the folks in the lobby could bring in your strawberry and sit down.

Our session this morning will start off with a subject that we've heard a lot from you over the last few years on methods consolidation and efforts along that line. Every time we've had a discussion along that line, there's always some young person in the audience who says, geez, why don't you guys get your act together and bring the message together...showing complete lack of understanding of the government.

But in an attempt to do that or the appearance of an attempt to do that, which is even more important in government, the agency has formulated, as usual, a committee...when in doubt...to look at methods consolidation, laboratory certification and along that lines and we're going to discuss some of those issues this morning.

Our first speaker is the Secretary of the Environmental Monitoring Management Council. Ramona Trovato has been with the agency 13 years...14 years?

MS. TROVATO: Eighteen years.

MR. TELLIARD: Eighteen years. So, Ramona is going to talk about the EMMC this morning and then we'll follow it by two presentations on methods consolidation.

MS. TROVATO: Thanks, Bill. I worked in an EPA Regional Laboratory for 13 years and I really loved it. About five and a half or six years ago, I decided to move to headquarters. About a year ago the new Deputy Administrator, Hank Habicht, was contacted by EPA's Region 111 Administrator, Ted Erickson, who raised the question of methods consolidation and recommended the formation of a committee to address these issues.

Regional Administrator Erickson recommended that we establish a group to coordinate agency-wide policies concerning all environmental monitoring issues. This recommendation was an important step. The Deputy Administrator valued data quality and was willing to set uup an agency-wide committee to address monitoring issues.

The Section 518 Report, which dealt with the adequacy, availability and comparability of testing methods provided a road map for establishing the environmental monitoring management committee. The EMMC is co-chaired by the Assistant Administrator for Research and Development and a Regional Administrator. The establishment of the EMMC is exciting since it addresses cross-program method issues. I was especially interested because after having worked 13 years in a lab; having to do certain things for RCRA and certain things for Superfund and other things for drinking water and yet other things for NPDES and not really thinking the quality of the data was much different from method to method or program to program, I was looking forward to some cross-program consolidation. At this time, the Deputy Administrator asked me to serve as the Executive Secretary.

The EMMC charter includes seven charges.

The first is to coordinate agency-wide environmental methods research and development needs; they have started doing that. Second is to foster consistency and simplicity in methods across media and programs. Third is to coordinate long and short term strategic planning and implementation of method development needs. Fourth is to promote adoption of new technology and

instrumentation. Fifth is to coordinate development of quality assurance and quality control guidelines. Sixth is to evaluate the feasibility and advisability of the National Environmental Laboratory Accreditation Program. The seventh one is a catch-all: Any other activities that influence environmental monitoring programs. So that sort of gives us a free hand to get involved anywhere the committee identifies issues for resolution.

The EMMC is structured to allow the Deputy Administrator to decide any issues that we can't resolve ourselves. The Deputy Administreator gets at least an annual update on what we're doing and what progress we've made.

The Policy Council identifies and addresses monitoring issues. The Steering Committee goes ahead and starts looking into the details of what we need to do and the ad hoc panels are the actual people who are doing the work. Right now, we have five ad hoc panels.

The Policy Council is co-chaired by the Assistant Administrator for Research and Development since EPA's Office of Research and Development plays such a key role in all of the methods development issues, by Ted Erickson the Regional Administrator from Region III. The members consist of our Deputy Assistant Administrators, Deputy Regional Administrators, and Office Directors.

This is the first time in the 20 years of the Agency that we've had this kind of attention focused on the methods issues, so we're very excited and believe that we have an opportunity to make a difference in the way things are working.

The Steering Committee is run by the Director of our Office of Modeling, Monitoring Systems and Quality Assurance.

The Executive Secretary of the Steering Committee is David Friedman. Many of you may know him from his work on SW846. The members of the Steering Committee are division directors and branch chiefs from our regional and headquarters offices.

The five panels that are set up right now include: The quality assurance services panel which will focus on funding of

quality assurance activities includings performance evaluation samples.

The Methods Integration Panel is looking at developing uniform test procedures across programs.

The Automated Methods Compendium Panel is developing an Agency-wide data base of our analytical methods-called EMMI.

The Analytical Methods and Regulatory Development Panel will ensure that our methods are factored into our regulatory development process, earlier, so that we can have the method ready to go when it's time to implement the regulation.

Last of all, the National Lab Accreditation Panel will look into the advisability and feasibility of a national environmental lab accreditation program.

The quality assurance services group is struggling with the budget issues. They are addressing: How are we going to fund QA and once we do get some funds, how are we going to prioritize where the money goes? We were hoping to have a budget initiative for FY '93, but it looks like it's not going to be ready until FY '94.

The issue of National Environmental Lab Accreditation was raised because the private lab community said that they are being audited by states and they said that this is costing them a fortune and it's taking a lot of time. The laboratories feel that the audits aren't that different and that there could be a better way. It was also recommended in the Section 518 Report that EPA investigate the feasibility and advisability of national environmental laboratory accreditation. We believe that it could benefit the agency's programs to have a National Lab Accreditation program. The next question to address is its advisability? And the advisability question revolves around a number of issues. One is, are the states willing to adopt reciprocity. I see that as one of the very big, important steps that we have to come to agreement on.

One of the others is how are we going to administer the program and how will it be funded? That's one of the things that

the panel is now looking into and we're in the process of setting up a Federal Advisory Committee so that we can have industry associations and industry members join us in making recommendations on the design of a program and how it should be administered. Jeanne Hankins is going to be the Executive Director of that group, and we plan to have our first meeting sometime this summer.

All of you know Bill Telliard. Fred Haeberer is here also. They both chaired the Automated Methods Compendium Panel. This grew out of the list of lists that Bill has been running on a shoe string for a long time. Bill and Fred made a presentation to the panel about what they've been doing and what the system included and the panel decided to adopt it as the agency's Automated Compendium of Methods. Each of the programs agreed to contribute to its support and update. Bill's the lead on taking care of the Compendium. Again, this is the first time that the agency has had in any one place all of our methods pulled together. Bill was telling me that he's planning on having it available in September of this year and I think that it's going to make a big difference to us in all of our methods consolidation efforts because it will show us where we have methods overlap now. It's going to show us some of the precision, bias, and detection limit information on each of our methods. So I think this is a major step forward and a major accomplishment for this group. It couldn't have happened if Bill hadn't already been working on it for all of these years.

When I was in the lab, oftentimes I would be told, we're going to start up this priority pollutant program or RCRA's going to roll or whatever, and I would turn around and go try and find the method that I was supposed to use, pull it off the shelf, start trying to set it up, and one or another of a number of things could happen to me. First, maybe I couldn't find a method at all. If I found a method, it couldn't get the detection limit I needed. Sometimes, I couldn't get it to work at all. So, one of the things we thought was very important was

to get the methods development activities included early in a regulatory development process. We will begin by asking: Are methods available? Are methods already in existence that we can use? If they're already in existence, then we are one step along the way of consolidation. This will allow us to use what we already have so that each program doesn't develop their own methods unnecessarily.

Inclusion of methods development in the regulatory development process has just started. We're going to try it for a year and then at the end of the year, we're going to evaluate how well it worked and see if we need to make any changes to make it work better.

The last panel I want to talk about is methods integration. Joan Fisk, who is up next, is going to talk in detail about this, but I'll just say that generally this is the group that's taking a look at what methods we have now, where the possibility for consolidation exists and then recommend that all of the programs adopt, perhaps, an existing method or make minor modifications to an existing method so that it will be acceptable to all.

They're looking at five methods right now including: VOCs, metal digestions, ICP, semi-volatiles and microwave digestion. They're hoping to have some results this fall and Joan will be able to tell you more in detail about that.

So, with that, if there are no questions, I'll just turn it over to Joan and she can get into the specific methods integration activities that we're addressing right now.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions? We have a question.

MR. MYERS: My name is Harry Myers. I'm from Keystone Environmental Resources. My question is, is there going to be any opportunity for industries analysts to participate in this?

MS. TROVATO: In the Federal Advisory Committee, once we get that set up for laboratory accreditation, that will include folks from the laboratory industry, laboratory associations, users of lab data like industries, states, federal government and other federal agencies. In some of the other panels... Right now, the Methods Consolidation Panel only includes representatives from EPA and other federal agencies. We start to get into a real problem anytime we try to include industry folks because when we're writing regulations, industry folks can't help us write them. And so, the only way we can get there specific input is to ask them to give us a factual presentation or, if we set up a Federal Advisory Committee, then they can give us advice. But that is the only way that we can do that legally. So right now, the only panel that's going to have industry input, in the form of advice, is going to be the lab accreditation panel.

MR. MYERS: I appreciate what you've said, but also I believe there are good folks out there in industry that know best the kinds of things they have to look for with respect to their own waste waters and I suspect that they have methods that might be useful to you that aren't presently recognized.

MS. TROVATO: Yes, there's no doubt about it, I'm sure. Ron Hites is here and he's going to talk about one of the opportunities where we did have industry involved.

MR. HITES: Sure.

MS. TROVATO: Yes, I thought so. I

wasn't real involved with this. My husband, who also works in the chemistry lab, was involved in this and they had a real wonderful approach to coming up with which methods could be consolidated, which ones we should skip, which ones we should keep, and...

You're going to talk in detail about that right?

MR. HITES: At length.

MS. TROVATO: At length, yes. He's going talk at length, so I don't need to say anymore. But, yes, we did have some industry...

MR. TELLIARD: Fred brought up an interesting point. If there are some methods out there that people are using in an industrial category, we'd certainly like to reference them at least in the list of lists and have them available as far an information source. So, if you want to make that available to us, we'll be glad to look at that since ours isn't really a regulation; it's an information system. We could do that.

NO SLIDES AVAILABLE

FOR THIS PRESENTATION

MR. TELLIARD: Our next speaker is Joan Fisk. Joan used to work in the Office of Water and then she lost religion and went some place else. Joan used to be much taller when she worked in the Office of Water, but now she's in Superfund and you know how that stuff will hurt you.

Joan's going to talk about the Methods Consolidation Panel and where the agency is presently standing.

MS. FISK: Thank you, Bill. I have the illustrious Dr. Fred Haeberer helping me with my slides. I decided I had to go very high in the agency, in order to assure the quality of the turning of my slides, so I've gone to the Quality Assurance Management Staff.

The first thing I want to mention is that I did hear a little riddle the other day about something that happened in Cleveland. For those of you who don't know, this is where Bill Telliard hails from. It's about a busy corner in Cleveland and there were four people standing on that corner. One was Santa Claus, one was the Easter Bunny, one was the perfect man and the other, the perfect woman. The riddle is, on this corner in Cleveland, which of these four people crossed the street first?

I thought the answer was real easy, myself...the perfect woman. The others are just a figment of your imagination!

The first slide shows the first three tenets of the charter for EMMC as previously described by Ramona.

The next slide has the rest of them. I have six, though there are several versions of them. Sometimes it shows six and sometimes it shows seven. So, I pulled a couple of the redundant ones together.

See, there's the first three tenets. What I'm pointing out here are the ones that have an X next to them. Those are the ones that I consider the methods integration panel as being involved in. I think it's pretty clear that if you're coordinating methods research and development, the method integration panel must be involved. This is it's primary function - fostering consistency and simplicity.

In order to coordinate methods research and development, we must focus on consistency and simplicity if we're going to be doing a better job and improving our methods.

The next one is "promoting and facilitating adoption of improved and new instrumentation and technologies." We are doing this with other government agencies.

The gentleman who asked Ramona the question before about whether the industry would have any participation in this, Ramona was correct in that the panel and the work group do not have any contractors or industry people involved. However, there will be at some point in time mechanisms for contractor participation.

The next one is "coordinating development of QA/QC guidelines." I wouldn't call that QA/QC. I would say QC. The quality control that we put in our methods in order to make sure that they meet our needs is an intrinsic part of the methods that we write, and while it may vary from program to program, it is within the methods. So this also part of the charge of the Methods Integration Group.

The next one is the only one without an X in front of it and that's Ramona and Jeanie's charge of evaluating the feasibility of a National Lab Accreditation Program. The methods integration really would not be concerned about that at all.

And the last one, as Ramona said, is that kind of bureaucratic one that allows us to do pretty much anything we need or want. Definitely the Methods Integration Panel is doing that.

Presently there are two ongoing efforts in the Methods Integration Panel. Obviously, we have this plethora of methods that Ron will be probably be showing you much more graphically than I'm going to do, and figuring out how to integrate them is one important part of the panel's job.

One of the things the panel did do to help with this is establish a work group. I believe it's the only one of the panels that actually has gone to another level.

As you can see from Ramona's description EMMC is kind of hierarchical. I remember at the original panel meetings we talked about a core work group that would be a panel who had enough authority that they could make decisions and didn't have to go several levels above to make final decisions. We also said we needed rotating subgroups tailored to the different methods

that we deal with. Now, I have not seen that show up in most of the summaries of meetings, but this is the design we did have in mind.

The other thing, of course, as was already mentioned is there is interaction.

The other effort of the Methods Integration Panel is probably the one I consider even more important because we're coming together on our own to make the plethora of methods go away. That's how we're going to do things in the future so we do not have everybody doing their own thing, driving you people in the industry crazy.

One of the things the panel decided to do, and the work group agreed upon, was in order to sell our ideas that we really wanted this to work, we thought that we would deal with some of the easier situations first. We want to have early successes to show Hank Habicht and Ted Erickson and all of the other people who initiated EMMC that it was a good thing to do.

The three methods that were originally dealt with were the digestion procedure for solids, which our air people at AREAL/RTP did, integrating the various digestions that were around. EMSL, Cincinnati, did the capillary GC/MS method for volatile organics and EMSL, Las Vegas did the ICP spectroscopic method for elements. Ultimately the validation of the ICP and the digestion will occur together in that they are related. In order to check out your digestions, you do have to do some analysis and so we all felt that it made good sense to do a coordinated validation of the two methods.

As far as the capillary column GC/MS, right now EMSL Las Vegas is looking into the volatiles in soils and AREAL/RTP is looking into the volatiles in air analysis. Cincinnati did take the lead to do this with water and now the other procedures have to be added.

The work group has chosen six other methods. We said that we could do about six integrations a year. Ron Hites will probably give you an idea of the number of methods that have to

be integrated or can be integrated. We say this has a finite end, and I'm not sure when that finite end is when we will have resolved all of the issues with multiple methods.

One of the things that was decided also was that as we start getting these methods integrated, we will no longer support the cold methods after a period of time. We will be starting Federal Register notices and give everybody time to be aware of what's coming down the pike before we actually make these the methods that should be approved cross programs whenever possible. After methods are integrated and so forth, they would be approved by the panel, the Steering Committee and ultimately the Policy Council and would become the integrated method. One thing I do want to mention here is if it can be justified to have more than one version of a method, the panel feels very strongly that this will be allowed. No one is going to tell Bill that he can't use isotope dilution anymore, because there is a need for him to do something different than what we in Superfund are doing. Therefore, there would certainly be allowances for different variations of methods to do the same thing when there is, say, a regulatory impact or a regulatory need, a need for, say, better precision, recovery, whatever. So, there could actually end up being more than one version of an analysis when there is a need.

Okay, the next group that was proposed to the Steering Committee to be looked into were also ones that I think are all very well-known to all of you, the semi-volatile organics by capillary GC/MS. We're talking about Method 625, Method 8270, the CLP Method. 8270 and the CLP Method are pretty much identical now. While they don't look the same, they are literally. If you follow procedures in the lab, they are exactly the same.

Microwave digestion, this is one, again, where there are a few different versions out there and continuous liquid-liquid extraction. These three are already started; they are in process. Here, I would think logically when we went through the

validation, we would combine the continuous liquid-liquid extraction and the semi-volatile organics by capillary column. That certainly makes good sense.

Later on in the year, at the end of FY '91, we would be looking into the organochlorine pesticides and PCBs. The dioxin/furans by high res GC/high res mass spec. We're not talking about the low res mass spec method. And last, graphite furnace AA with a selection of elements.

The Steering Committee has been thinking about how the Methods Integration Panel could be improved. One of the things they are proposing is to have multiple work groups. It was my understanding in the beginning to have tailored groups for the different methods, such as separate workgroups for water, soil and air aith tailoring to deal with spinfus (such as organic or inorganic, simple preps, etc.). Also, we reiterated the need to do the easy integrations first, the ones we that we can do quickly and get the successes out there. The last thing, which I think is very, very important is we should be emphasizing pollution prevention. We should be looking into things like solid phase extraction, micro extractions, things where we're getting rid of our solvents or as much as possible in the process and prevention of lab waste. This is a very, very important piece that the Methods Panel has to be thinking about all the time.

Future methods development. Here's where we're going to have possibly a little bit of, shall I say, politics involved? There are many programs in EPA. Every program is very possessive. We all work very hard and we come up with what we, ourselves, think are the best ways to do things and this is why we have this plethora of methods and this is why we now have EMMC to make this plethora of methods go away. There's been a couple of options proposed on how to deal with methods development in the future. I, myself, believe personally and I believe that the other people on the panel agree that we can go with a couple of different options and use them all and use them all effectively.

The first option I've mentioned up there...and it will go onto the next overhead in just a second, is one that really has ORD, the Office of Research and Development, pretty much in control of the process from beginning to end, with the work group participation, of course, coming from the programs and the regions and so forth. This would be where a priority setting process would be developed and then these priorities for chemical, physical, immuno-assay and sampling methods would be addressed by these various work groups. We would need to add people with a bio assay background to help in prioritizing because this is something...we do not haverepresented now.

It is important to identify regional needs for methods. There is a lead region who does a needs survey and I don't know if they do this every year, but they do it quite routinely and this is done from the Office of Regional Operations and State and Local programs. We within Superfund have always...and also OSW...tried to get this information. In fact, Ramona was our source of this information for several years...to try to keep apprised of where we needed to be going for Superfund. We had lots of other ways of doing this, too. We look into our Special Analytical Services requests to see where our contractor, Viar, who does subcontracting to do special things for Superfund through the CLP, to see where we are getting large volumes of needs demonstrated. That's how we came up with the dioxin/furans and the air toxic, radionuclides and things of that nature.

We also go to our clients on a routine basis. We examine the ARARs. That's the "Applicable, or Relevant and Appropriate Regulations to see where other legislations are forcing us to perhaps make some changes to our methods or add methods. Anyway, we look into all of those kinds of things and these are certainly the kinds of things I think this work group will look into, just as we do. This process would ultimately implement these priorities as we've come up with them.

The other thing that has been proposed, and the panel liked it, would still provide a little bit of ownership and pride

of ownership to the various programs. E.G. The program has a burning need. It does not want to sit around and wait for the Office of Research and Development to get it prioritized and have ORD address it. What we've proposed is that when we have a need...something we really need badly...OSW does...water does...pesticides...whoever...that they could go forward and take the lead, but get EMMC...to coordinate participation in the development of the method and make sure that we have all of the right people there, the right Federal agencies, etc., and help us coordinate that process and still be able to carry it through in the same kind of work group manner that Superfund has been using traditionally.

This is where I want to answer the question that the gentleman asked before. We in Superfund have always included the contractor community in our methods development work groups because we always have believed that you are the guys who knows what works in a lab if you're doing research versus what happens in a large volume laboratory. It's a lot different if you're trying to push 200 or 300 samples out a month than it is in a more researchy-type atmosphere. We would like to think that we can continue that process because we do have the attention of upper management with EMMC, we would be able to get all of the right people in the agency to participate to make sure all of their needs were recognized.

Ultimately, after we have our work group product, we would put it through the panel and Steering Committee for approval, going through the Federal Register process and so forth. We do believe that these two things are complementary and that ORD certainly should be taking the lead in any of the ones that are really, really researchy. But the problems themselves, when it comes to just revisions or things to update or adapting things, we really believe that this can be done with the program in the lead.

The next thing I wanted to mention is that RCRA and Superfund have worked very well together for about four or five

years now. We are in the same office, the Office of Solid Waste and Emergency Response. And we kind of made a pact. We found that some of these little differences were driving our community nutty. We decided to avoid redundancy in the methods development effort and by avoid the redundancy, we were able to get more methods developed. Instead of ORD working on just say, for example, a volatile capillary method for Superfund and another one for RCA, they could do the volatile capillary one for both of us and then they could be working on a pesticide method for both of us, too. This also, we felt, would be a tremendous relief to our laboratory community so that they didn't have to keep their RCRA samples and their Superfund samples separate all of the time because they were changing temperatures or changing surrogates or whatever.

That's why we decided to do it. We thought it made sense. Now, how do we do that? We do our Research Committee process together. We sit down together on and off over many, many, many weeks and identify our common needs. Both programs have research committee monies. You cannot mix our monies; So we'll say, okay, here's all the stuff we need. Why don't we recommend that we do all of X, Y, Z methods, using Superfund money and we'll use RCRA money for all of these other methods over here on this side and then we both kind of monitor the progress of ORD together.

We also do methods development that does not involve Research Committee monies. We pay for it directly out of our program funds and this can be either to ORD contractors who do methods development or our own contractors. Here again, we sit down and we decide who's going to take the lead on each one. It was kind of like, really, which one do you want to do? Which one do you think is more fun? And then we just again kept each other completely in the process, knowing what was happening.

We do have RCRA participation in all of our work groups and we in the Analytical Operations branch have been participating for many years on the RCRA SW846 work group.

These are some of the things that we have done together. There's a much longer list, but these are the ones that came to my mind.

The first is the low res dioxin/furans the lead being Superfund's Operations Branch. We're going to have an Invitation For Bid out on the street within days right now and OSW is in the process of rewriting it in their own format. The method will not be different, but it will be in the SW846 format.

We also have what we call our Quick Turn-around GC methods. This is for a 48 hour turn-around, once the samples hit the laboratory. These are all kinds of streamline/methods so that our clients can get the answers a lot faster.

The organochlorine pesticides, we did a lot of updating and rewriting the methods for wide bore capillary columns.

The radionuclides and mixed wastes is a new effort we have ongoing right now because we've got 116 odd sites on the national priority list that are federal facilities, many DOE, and some are EPA leads. This is something we're having to address.

Air toxics, which is a real big thing, particularly with the Clean Air Act being reauthorized. We added new analytic to the target compound list.

The last one, I didn't mention on the slide is field development efforts methods. The majority of the field analytical methods are being funded by Superfund and we are the ones developing a compendium of methods. This is something that RCRA is, of course, very interested in also.

RCRA has taken the lead on some of the, shall I say, more sophisticated things. The LCMS, both thermospray and particle beam. In fact, RCRA did a really fine job coordinating the efforts. They've actually got the vendor community...different members of the vendor community doing different pieces, the different EMSL laboratories, everybody doing their own part and I think it's worked very well. They're also taking the lead in supercritical fluid extractions and have been able to give many papers about their progress and I think

we're going to probably have something working in the near future.

The microwave digestion is kind of divided. There is a soil and water digestion. We've got the lead on the water and RCRA on the soil. RCRA is taking the lead on cations and also on the high res mass spec for dioxin/furans. This is one where we did try to coordinate and keep as much similar in the low res mass spec methods as possible.

There are many others. As I said, RCRA has lots and lots of methods that we don't need and we really only would want to be kept informed of some of the things they're doing. We certainly would want to have the methods available to us and would not think about changing them if these were things that we suddenly came up with a need for. We certainly don't plan on going out and doing our own TCLP.

That's it. Any questions?

QUESTION AND ANSWER SESSION

MR. TELLIARD: Questions?

MS. FISK: I'd like to thank Dr. Haeberer for the quality assurance of my slides.

SPEAKER: I have a question. I'd like to know if you are...

MR. TELLIARD: Could you tell us who you are and who you are with?

MS. ASHCRAFT: Oh, I'm Merrill Ashcraft, with the Navy Public Works Center. I would like to know if you have privileged information as to when the new addition to SW846 is being published?

MS. FISK: No, I don't. I think possibly, if Jeanie Hankins is in the audience, she may know. Is Jeanie here?

Jeanie, do you have an answer to the question?

MS. HANKINS: Well, we had all hoped that it would be ready before the symposium in the second week in July, but it looks like it may be coming out later this summer.

MS. ASHCRAFT: Thank you.

MS. FISK: Anymore?

MR. TELLIARD: Thanks, Joan. Thanks, Fred.

ENVIRONMENTAL MONITORING MANAGEMENT COUNCIL

METHODS INTEGRATION PANEL OBJECTIVES AND

SUPERFUND/RCRA METHODS INTEGRATION SUCCESSES

by

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EMMC CHARTER ADDRESSES FOLLOWING ISSUES:

X o *Coordinating methods research and development (including short and long term strategy).*

X o *Fostering consistency and simplicity in methods across all media.*

X o *Promoting and facilitating adoption of improved and new instrumentation and technologies in cooperation with other federal agencies, universities, industry, and other interested parties.*

EMMC CHARTER (Cont'd)

X	*o*	*Coordinating development of QA/QC guidelines as they apply to specific measurement methodologies.*
	o	*Evaluating the feasibility of a national laboratory certification program*
X	*o*	*Other activities impacting environmental monitoring programs*

X Means Methods Integration Panel/Workgroup are involved.

There are two distinct efforts of the MI Panel

(1) Integration of existing methods (by medium)

- *Methods Integration Workgroup established*

- *Interagency participation (FDA, USDA, DOD, DOE, NOAA, USGS)*

(2) Future Method development efforts

Integration of Existing Methods

- *Early successes desired*

- *Three methods integration projects prioritized/piloted*

  - *Digestion procedure for solids (AREAL/RTP)*
  - *Capillary column GC/MS method for volatile organics (EMSL-Cincinnati)*
  - *ICP spectroscopic method for elements (WMSL-LV)*

INTEGRATION (Cont'd)

- ***Six methods to be integrated/year, as prioritized by the workgroup***

  - ***As approved by workgroup, Steering Committee, & Policy Council, a Federal Register Notice will be developed to propose application of the method in all Agency programs.***

- ***Finite end when integration of existing methods is complete***

Next Group of Methods for Integration

(to be proposed to Steering Committee and Policy Council)

Immediately

- *Semivolatile Organics by Capillary GC/MS*
- *Microwave digestion*
- *Continuous liquid-liquid extraction*

End of FY'91

- *Organochlorine pesticides & PCBs*
- *Dioxins/Furans by HRGC/HRMS*
- *GF AA (to include a suite of analytes)*

<u>Improving Process</u> - MI Panel is considering

- ***Multiple workgroups***

  - ***more participation by bench people***
  - ***easy integrations first***
  - ***pollution prevention emphasis***

Future Methods Development

- *MI Panel will begin work on how to address new methods development.*
  - *Market Survey good idea for identifying methods development needs.*
- *Proposed at workgroup meeting (1/23/91) - Option 1.*
  - *Develop priority-setting process & recommend annual priorities for chemical, physical, immunoassay, & sampling methods.*
  - *Establish bioassay workgroup to assist with setting priorities.*

Future Methods Development (cont'd)

- *Integrate with Research Committee & Regional Needs Identification Initiative.*

- *Implement new priority-setting process*

(Implies OMMSQA control).

o *Proposed at MI Panel meeting (10/25/90)-Option 2.*

- *Program lead when a strong need exists.*

- *EMMC Methods Integration Panel assists in coordinating the effort for program lead with all Agency & (other agencies) Programs with an interest/need.*

Future Methods Development (cont'd)

- *Program lead workgroup would function in a TQM manner as presently is done in Superfund methods development.*

  - *o Workgroups include all EPA Programs & other government Agencies, EPA Regions, ORD, Headquarters, & the contractor laboratory community.*

- *EMMC approval process would follow.*

Both Options could be used.

Superfund/RCRA Methods Integration Initiatives

Why?

As sister offices in OSWER we decided to merge our methods development efforts as much as possible

- ***avoid redundant effort***
- ***reduce number of method variations labs must implement***
- ***allow for more methods to be developed***

How?

- ***Prioritization of Research Committee projects done jointly so that both our needs could be met between both programs allotted dollars/FTEs, (eg., RCRA resources used for some joint projects and Superfund resources for others)***

- ***For non Research Committee methods development, RCRA & Superfund negotiated who would take the lead and oversight (Program resources determined lead on Research Committee Projects)***

- ***RCRA participates in all Superfund methods workgroups and Superfund on SW 846 workgroup.***

- ***communicate routinely on status.***

WHAT?

Superfund lead	***RCRA lead***
Dioxins/Furans (HRGC/LRMS)	***LC-MS (thermo spray & particle beam)***
GC-Quick turnaround	***SFE***
Organochlorine pesticides (cap. column)	***Microwave digestion***
Radionuclides/mixed waste	***Cations***
Air toxics	
Field methods	***Dioxins/Furans (HR)***

MR. TELLIARD: I think that you can see there are a lot of efforts and a lot of things haven't gelled yet, mainly because we've only been at it a few months.

Along the same line, we've kind of initiated an effort to try to consolidate, at least in a small way, part of the program and that is in the water methods. Ron Hites is with us from the University of Indiana and he did a study, which we affectionately refer to as the Hites Report. That could become infamous. It's going to describe a little bit of what they went through and how they did it.

I think that if you look at the methodologies that we have been dealing with here, we've all kind of used the same instruments. If you're using SW846 or 500 or 600 series methods, when you get to the mass spectrometer or the ICAP or the AA, it's pretty much the same. Where we find that there's a large discrepancy is in the QA and QC and I think that's one of the biggest areas where we're going to try to come to closure.

Since we know that QA/QC is pure science, which means it's negotiable, that's going to be probably the biggest area of work over the next year or two, to come to closure on some of that. And that all ties into Ron's paper and I'd like to say right now that it was the first shot at this effort and I think if you haven't seen the report, if you want a copy or something, we'll try to get them to you. Ron?

THE U.S. EPA'S ANALYTICAL METHODS FOR ORGANIC COMPOUNDS IN WATER AND WASTEWATER: THE NEXT GENERATION

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HISTORY

By the late 1970's, it had become clear to the U.S. Environmental Protection Agency (EPA) that organic compounds were polluting many of the nation's waters. By 1977, as a result of a lawsuit by several environmentally concerned plaintiffs, the EPA had focused on a list of 114 "priority" organic pollutants (*1*). These included such compounds as the trihalomethanes (by-products of the water chlorination process), polycylic aromatic hydrocarbons (well-known human carcinogens), and numerous compounds of industrial significance (nitroaromatic compounds, for example).

The EPA's first task was to assess the prevalence of these compounds in both wastewater and drinking water. Their long term goal was the regulation of specific compounds that were found to pose significant environmental problems, a daunting task.

Tens of thousands of samples needed to be measured by hundreds of different laboratories. Clearly, there were concerns about the comparability of data among laboratories. The result was a series of laboratory-based analytical "methods".

These EPA methods are detailed, step-by-step directions (recipes) that describe everything the analyst needs to know to complete a satisfactory analysis. Analysts must have basic chemistry laboratory skills, which are not covered in the methods. The methods include sample collection, preservation, shipment, and storage; instrumentation, apparatus, glassware and reagents; analytical calibration and quality control; and the calculation and reporting of results. In most cases, the methods are directed toward specific environmental matrices, for example, industrial wastewater. This approach is similar to that used by standard-setting organizations (for example, "Standard Methods for the Examination of Water and Wastewater" published by the American Public Health Association). The EPA felt that their methods would eventually be used for regulatory purposes; thus, a tightly focused set of directions would best serve the regulator and regulatee and minimize disputes about analytical results.

During the 1970's, the first set of methods were developed; these were the "600 series" methods for the analysis of organic compounds in wastewater. Some of these methods are applicable to a relatively small set of compounds (for example, Method 606 is aimed at 6 phthalate esters), while others are aimed at a much larger set of analytes (for example, Method 625 focuses on a list of 72 compounds which can be extracted from water with methylene chloride). The 600 series methods are now required for monitoring effluents under National Pollution Discharge Elimination System permits and were promulgated in the regulations under Title 40 of the Code of Federal Regulations (40 CFR) Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" under the Clean Water Act (2).

In 1979 and in the 1980's, a set of "500 series" methods, focusing on drinking water, was developed. For example, Methods 501.1, 501.2, and 501.3 are for the 4 trihalomethanes, and Method 525 is for 43 compounds that can be isolated from water by liquid-solid extraction. The 500 series of methods was developed in response to the requirements of the Safe Drinking Water Act (SDWA). Many of these methods are mandatory test procedures under National Primary Drinking Water Regulations (40 CFR, Parts 141 and 142) (*3*), and a number of other 500 series methods have been proposed for future regulations under the SDWA (*4*). The complete 600 series methods are printed in the Federal Register (*2*), and the 500 series methods are available from the National Technical Information Service (*5*).

Another series of methods, the "1600 series", has evolved over the last several years. Methods 1624 and 1625 are both described in the Federal Register rule of 1984 (*2*). These two methods are the same as their lower numbered cousins (624 and 625), except for the isotope dilution calibration procedures, which require an isotopically labeled standard for each analyte. These standards are available, but they are expensive (a complete set costs $2500-3000). These methods are particularly useful for extremely complex samples (such as sewage sludge). For this reason, they should be retained in their present form, and we will not consider them further.

By now, many of the 500 and 600 series methods are in wide-spread use, and it is clear that there are considerable overlaps among the methods in terms of both procedures and analytes. For example, Methods 524.1, 524.2, and 624 have 30 out of 62 analytes in common, and they all use similar purge and trap gas extraction procedures.

There are also considerable differences between these methods. They reflect various levels of analytical technology because of the different times at which the methods were developed. There are also differences in the detection limits of the methods; the drinking water methods generally have lower detection limits than the wastewater meth-

ods. There are also some trivial variations among the methods. For example, gas extraction times and flow rates vary for the different purge and trap methods; there is a large range of initial and final sample volumes; there is a bewildering array of maximum storage times for the samples; mass spectrometric scan rates and mass ranges vary widely. These differences have proven to be troublesome for analytical labs that must faithfully execute these procedures. In some cases, this means having different sets of equipment to analyze virtually the same set of compounds. This is both expensive and wasteful.

In response to these concerns, Section 518 of the Water Quality Act of 1987 directed the EPA to study the availability and adequacy of field and laboratory test procedures and methods to support the provisions of the Act. This study resulted in a report to Congress titled "Availability, Adequacy, and Comparability of Testing Procedures for the Analysis of Pollutants Established Under Section 304(h) of the Federal Water Pollution Control Act" (*6*). The report included the finding that "Improved coordination is needed in the Agency's methods development program to avoid duplication in the development and standardization of test procedures and inconsistencies in quality assurance and quality control guidelines." As a result of this finding, Indiana University was asked by the EPA to consider the question "Is it possible to revise or eliminate some of the 500 and 600 series methods and effect a savings of time and money?" This and related questions were studied and recommendations were developed.

Our study considers only the fifteen 600 series methods and twenty-four 500 series methods given in Table I. These methods were selected because these are the methods that are either mandated in the regulations or were recently proposed for inclusion in the regulations under the SDWA. The EPA's Office of Emergency and Remedial Response (Superfund) contract laboratory program (CLP) uses several methods that are derived from 500 and 600 methods. While these methods are well-known because of the requirements of numerous EPA contracts, the unnumbered CLP methods are not part of any

regulatory requirement; therefore, they were not considered in this study. Similarly, the methods published by the EPA's Office of Solid Waste in the manual "Test Methods for Evaluating Solid Waste" (*7*) contain many numbered methods that are derived from the 600 series methods, but the SW-846 methods are generally not mandatory in the Resource Conservation and Recovery Act regulatory program; therefore, they were not included in this study either. Although inclusion of the CLP and SW-846 methods is beyond the scope of the current study, they should be included in a broader-based, consolidation study that might be done in the future.

ISSUES

As we began our task, we had several concerns in mind. First, many of the methods are somewhat out of date in terms of analytical technology. For example, capillary gas chromatographic columns are rarely specified in the 600 series methods. Hydrophobic traps are not used in the purge and trap methods. In some cases, hazardous solvents and preservatives are specified; for example, diethyl ether and arsenic and mercury salts are required in some methods. It seemed clear that a revision of these methods should bring them in line with modern analytical technology.

Our second concern centered on the different sizes and types of laboratories which use these methods. These include "Mom and Pop" and large contract laboratories and small and large drinking and wastewater treatment plant laboratories. Some laboratories are concerned with only one or two methods, while other laboratories are concerned with virtually all of the methods. As we considered this issue, it seemed clear that revisions of these methods should not make it prohibitively expensive for the small laboratory with limited resources to meet their needs, while at the same time, the revisions should be extensive enough to streamline the operations of large laboratories.

Third, we were concerned with the great level of detail now specified in these analytical methods. We wondered if this was necessary, either to produce good data or to facilitate the operations of the laboratories.

Because our laboratories at IU or the EPA do not routinely use these methods, we convened an expert panel of 24 "method users." This panel met for one and a half days, and the discussions ranged over all aspects of the methods. This panel helped us form the recommendations which follow. Despite their valuable assistance, we should make it clear that the recommendations that follow are our own and are not necessarily the consensus of the panel.

RECOMMENDATIONS

Ground-rules. There are several advantages to revising and eliminating various 500 and 600 series methods: The total number of methods would be less; thus, there would be fewer methods with which the various laboratories would need to be familiar. This would lead to less paperwork and result in cost savings for everyone. With fewer methods, there would be more uniformity, and presumably, data quality would improve.

Consolidation should not be taken to its extreme. Rather, methods should be consolidated *only* as needed to reduce redundancy. Let us explain. The complexity of a method increases dramatically as the number of analytes the method is designed to cover increases. This is illustrated in Figure 1; complexity is plotted in arbitrary units against the number of analytes (note that this is a log-log plot). Two lines are shown in this plot. One is for methods based only on gas chromatography (GC) and the other is for methods based on gas chromatographic mass spectrometry (GC/MS). This graph shows that a GC/MS method reaches its maximum complexity when one attempts to measure about 120 analytes at the same time. A GC method which does not use mass spectrometry

reaches its maximum complexity at about 40 analytes. The numbers on this graph are somewhat arbitrary, but they were derived from discussions with the panel mentioned above. The lesson from this graph is that existing methods should not be consolidated in a way that pushes the number of analytes beyond about 40 for a GC-only method or about 120 for a GC/MS method.

Another issue affected our thinking. The 500 and 600 methods can be broadly divided into three groups: (**a**) those which use GC with a selective detector (such as an electron capture detector), (**b**) those which use GC/MS, and (**c**) those which use high performance liquid chromatography (HPLC). The last group represents only a very few methods, but it is a group that will grow in the 1990's as more attention is focused on non-volatile compounds. As we considered the pros and cons of the GC-only methods, it became apparent to us that these were valuable methods, and they should be retained. There were two reasons for this decision. First, these methods are useful as screening methods. It makes no sense to use a relatively expensive mass spectrometer to analyze a sample that has virtually no analytes in it. GC-only methods can screen out those samples which do not require a follow-up. Second, GC-only methods can be useful in small laboratories, which measure only a few analytes in well characterized samples. For example, until recently, small drinking water utilities only needed to measure the four trihalomethanes. There was no need for these laboratories to invest in more sophisticated equipment when a GC-only method would meet their requirements.

Despite our acceptance of GC-only methods, laboratories which use them are cautioned that the analytes must be properly identified. The only qualitative data that GC-only methods produce is the analytes' retention times and responses on selective GC detectors. This is frequently not enough information for an exact compound identification. Additional qualitative data can be obtained by rerunning the sample on a GC column with a truly different liquid phase. Another possibility is the simultaneous use of two or more

selective GC detectors. For example, Method 502.2 specifies a photoionization detector followed by an electrolytic conductivity detector. The ratio of detector responses helps to identify a compound. Of course, if the sample were more complex than anticipated, GC-only methods would not produce satisfactory results, and GC/MS would be essential.

As mentioned above, most 600 series methods do not specify capillary GC columns; rather, they provide detailed instructions for the use of packed columns. Packed columns do, in fact, have several advantages: They are less expensive than capillary columns (both the GC instrumentation and the column itself). Packed columns are also simpler to operate, have a higher on-column analyte capacity, and sometimes allow for faster analysis times. On the other hand, capillary columns have considerably higher resolution per unit time. Thus, retention times can be measured more accurately and precisely, and many more compounds can be distinguished from one another based only on their retention times. Using wide-bore capillary columns, on-column analyte capacities can be reasonably high, and analysis times can be reasonably low. Once a laboratory changes over to capillary columns, analysts usually find that these columns are no more complicated to operate than packed columns. Thus, we recommend that all methods should use capillary columns. The only exception might be in cases where a screening method is needed. If it is expected that a large fraction of the samples will be blank, then screening these samples with a packed column could be acceptable.

Specific Recommendations. Having laid out the ground rules of our strategy (a minimal consolidation to keep the number of analytes relatively low and retaining GC-only methods), we can now present our specific recommendations. These are summarized in Table II.

Our first recommendation is to eliminate Methods 501.1, 501.2, and 501.3. These vintage methods use packed GC columns to measure the four trihalomethanes. Because current drinking water regulations require monitoring for a broader group of volatile

organic compounds than just the trihalomethanes and because these compounds are covered adequately by other, more general methods (see below), these old methods are no longer needed.

Methods 502.1, 502.2, 503.1, 601 and 602 are GC-only, purge and trap methods, which use photoionization or electrolytic conductivity detectors. A total of 63 analytes are covered by these five methods; 58 analytes are in two or more of these methods. Clearly, considerable consolidation of the 5 methods is possible. In practice, we recommend that this consolidation be done by simply keeping Method 502.2, which is already a consolidation of Methods 502.1, 503.1, 601, and 602. These latter four methods are based on packed GC columns while Method 502.2 uses capillary GC columns. While the number of analytes (60) covered by Method 502.2 is above our implied limit of 40 (see Figure 1), these are simple compounds which should be easily distinguished from one another on capillary GC columns serviced by two different detectors.

Methods 524.1, 524.2 and 624 are also purge and trap methods, but they use GC/MS as the detection system. These can be consolidated to form one method. This new method would have a total of 62 analytes, 42 of which are in two or more of the existing methods. Again, this represents a major reduction of overlapping methods. This consolidation is a *fait accompli*; Method 524.2 is the capillary column upgrade of Methods 524.1 and 624. Thus, we recommend dropping these latter two methods and retaining 524.2; this is a paper exercise that requires no further research.

Methods 515.1, 552 and 604 are for the measurement of halogenated acids such as 2,4,5-trichlorophenoxyacetic acid or 2,4,5-trichlorophenol. They all start with liquid-liquid extraction followed by derivatization to form methyl esters or ethers. They represent a total of 31 different analytes, only 4 of which overlap among the methods. Nevertheless, because of the similarity of the extraction and derivatization procedures, we recommend that these 3 methods be combined into one. This is a case where laboratory work is

needed to develop a revised method. The major experimental issues are: **(a)** Diazomethane is used in Methods 515.1 and 552, but it may not work for the less acidic phenols of Method 604, some of which chromatograph well without derivatization. **(b)** Some of the phenols now covered by Method 604, which specifies a flame ionization GC detector, may not respond well in the electron capture detector specified in Methods 515.1 and 552. **(c)** Method 515.1 uses diethyl ether, a hazardous solvent; this must be omitted without sacrificing the quality of results. **(d)** It is not clear whether the volatile haloacetic acid methyl esters (covered in Method 552) and the phenoxyacetic acid methyl esters (covered in Method 515.1) can be separated in a reasonable amount of time on the same column. Given these problems, it is entirely possible that these 3 methods could only be consolidated into 2 methods.

Methods 525 and 625 address a total of 93 compounds; these methods start with an extraction step followed by GC/MS. There is some overlap between the methods: 22 compounds appear in both. Unfortunately, simply combining these two methods is fraught with difficulties: Method 525 is an integrated liquid-solid extraction, capillary column GC/MS method that works well with particulate-free water. There are data in the recent literature that suggest that this method will fail even with particulate-free water containing large amounts of dissolved humic acids (*8*). This method could be modified by adding the much more robust methylene chloride extraction for wastewater and particulate-laden waters and the cleanup sections of Method 625. This would probably result in an excessively complex method which would be more difficult to implement than the current ones. As a result of this thinking, we recommend keeping Method 525 as it is and revising Method 625 so that it includes all the modern features of Method 525 but retains the methylene chloride extraction and cleanup features of the old Method 625.

Phthalate esters are measured by Methods 506 and 606, and virtually all of the analytes overlap between the two methods. These compounds are also covered by Meth-

ods 525 and 625. Furthermore, phthalates are frequently laboratory artifacts. It requires heroic efforts to make sure that these compounds are really in the sample at the levels measured. For these two reasons we recommend that both of these methods be dropped.

Polycyclic aromatic hydrocarbons are measured by Methods 550, 550.1 and 610 using HPLC with UV fluorescence detection. The analyte lists for these 3 methods are identical. We recommend that Method 610 be dropped; it is badly out of date. Unfortunately, Methods 550 and 550.1 probably cannot be combined. Method 550.1 is limited to particulate-free water with low humic acid content, while Method 550 is for particulate-laden water. For this reason, both of these methods should be retained.

A total of 39 chlorinated pesticides are measured by Methods 508 and 608. There is considerable overlap between the methods: 24 compounds appear on both lists. These are both GC-only methods using electron capture detection. Method 608 should probably be dropped in favor of Method 508; of course, the latter would need to be recertified for wastewater use. This will probably require including the cleanup procedures from Method 608.

Methods 551 and 612 have no compounds in common. Nevertheless, we recommend combining these two methods. Methods 551 and 612 both deal with chlorinated organic compounds; they both use liquid-liquid extraction and electron capture GC. Method 551 is a microextraction method, but 612 is not. Microextraction methods use very small volumes of sample and solvent; typically 35 mL of water and 2 mL of the extraction solvent. We suggest that the combined method should be a microextraction method, having a total of 27 analytes, a number that can easily be handled by a GC-only method. Clearly laboratory work is needed to be sure that all of the 27 analytes can be separated from one another and be precisely measured.

A variety of other methods have problems. They should probably be dropped and the analytes which are left uncovered should be added to some other, more modern

method. Method 603 for acrolein and acrylonitrile is a purge and trap method at an elevated water temperature. This results in large amounts of water vapor entering the analytical system, which in turn, results in poor method performance. Clearly, more research is needed to develop a satisfactory analytical method for these two compounds. Methods 605, 607, 609, and 611 deal with benzidines, nitrosamines, nitroaromatics, and haloethers, respectively. The analyte lists cover a total of 14 compounds. These methods have serious problems: For example, Method 605 uses chloroform, a solvent which many laboratories are not permitted to use, and it uses an electrochemical detector which requires specialized skills to operate. Research is needed to incorporate these 14 "orphaned" compounds in other, existing methods.

Methods 504 and 505 are GC-only microextraction methods for halogenated pesticides and polychlorinated biphenyls, which use electron capture detection. There is no overlap with any 600 method. These microextraction methods should be retained, and as discussed below, given more emphasis.

Methods 513 and 613 both focus on only one compound: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD). Method 613 is about 15 years old. This method is out of date, and it should be dropped--there is little to salvage. Method 513 is a high resolution mass spectrometric method, which was adapted from Method 8290 (*7*). This latter method covers all of the dioxins and dibenzofurans containing between 4 and 8 chlorines. Method 513 was adapted lifted from the more comprehensive and complex Method 8290. This is an approach which should be repeated in the future.

There were several 500 series methods that have no parallels in the 600 series. These include Methods 507 and 531.1. Both of these methods are for nitrogen- and phosphorus-containing pesticides, a compound class which is not addressed by any 600 series method. Therefore, both of these methods should be retained. Methods 547, 548, and 549 are for glyphosate, endothall, diquat, and paraquat, compounds which are not

addressed by any 600 series method. These compounds present unusual analytical difficulties, and these 3 methods should be retained.

Other Recommendations. Beyond the specific revisions outlined above, we have several other recommendations. First, we recommend that the EPA should standardize the format of official methods throughout the entire Agency and that the process of writing new methods be modularized. Each method should incorporate all necessary modules to be complete.

Sampling needs to be addressed in a module. Specifications on the sample container should be included; toxic preservatives such as mercury and arsenic salts should be avoided; and the minimum set of sample preservation specifications (including holding times) should be given.

An extraction module should specify the physical procedures for extracting the sample. These could include a continuous liquid-liquid extraction system or shaking or stirring the sample with the extraction solvent. Liquid-solid extraction should also be considered in this module. Micro-extraction methods could be included as options for screening in each method.

A clean-up module should explain how the extract is fractionated so that the analytes of interest can be measured without interference. Beyond the existing liquid-solid chromatography, this module could include gel permeation chromatography as an option for samples that are especially "dirty". HPLC is also a useful clean up procedure and could be included where appropriate.

The analysis module should specify how the isolated extract is to be measured for the various analytes. It should give exact GC and GC/MS procedures. It should also be clear about identification criteria for the analytes. For example, it should specify how a compound is to be identified from its mass spectral or gas chromatographic data. Of

course, the identification criteria should be no less rigorous for an analyte measured by gas chromatography than by mass spectrometry.

The calibration module must specify how the raw data from the analytical instrument (either the GC or GC/MS system) are to be converted into concentrations. In general, an internal standard for each analyte is the optimum calibration, but when this is not feasible, a 3 to 5 point external standard working curve may be suitable. This working curve should be defined by a regression analysis, and it need not be linear. It is, however, important to bracket the analyte's concentration by the standard's concentrations. It is not justifiable to extrapolate a working curve too far above or below the highest or lowest measured concentration. Other issues that the calibration module should address are calibration frequency and the acceptance criteria for the calibration. For example, the maximum scatter of the data about the calibration working curve could be specified, perhaps as a standard error of the estimate.

A reporting module is needed. The specifications on quantitation limits should be given here. In a method for both drinking water and wastewater, the quantitation limits will be different depending on the matrix. In a drinking water sample, which is presumably much cleaner than a wastewater sample, it should be possible to measure analytes at much lower concentrations. We suggest that each method include a "practical quantitation level" which is defined as the sensitivity for a given analyte in a given type of matrix that a competent lab could routinely achieve (*3*). There would be different "practical quantitation levels" for each compound in each matrix encountered.

The reporting module should address another issue: All of the 500 and 600 methods focus on a set of target analytes. On occasion, mass spectral or chromatographic data may be obtained indicating that a compound in the sample is abundant, but it is not one of the target analytes. If the abundance of these compounds are high, their presence should be reported even though their identity is not known. It would be a shame for a laboratory

to report that all of the target analytes' concentrations are low but not to report that some other, unknown compound's concentration was very high. This information should be reported back to the organization that requested the analysis, and it should be their responsibility to decide what to do next.

The last module should be the quality assurance and quality control (QA/QC) module. This should include a section on the demonstration of competence with the method and a section on reproducibility and accuracy. It is important, however, that the quality assurance and quality control procedures be as simple as possible and thus maximize the ratio of data quality to cost. It does no good to have QA/QC procedures that routinely take up 30-50% of the cost of running these methods. A way must be found to minimize the cost of QA/QC, while at the same time assuring the regulator and regulatee that the data are of sufficient quality to meet their needs. The QA/QC module should include specifications and acceptance limits for all of the QA/QC data that are required. For example, field duplicates are now required by QA/QC, but the methods do not tell the laboratory how to interpret the data. The same problem exists for laboratory fortified blanks and spikes.

Data should be continually gathered on the usage of the various methods. This could be done by an annual survey or questionnaire sent to laboratories using the methods. Data could also be gathered in connection with annual performance evaluation studies which are required for certification under the SDWA regulations. By gathering data in these ways, the EPA can keep track of which methods are most important and focus development efforts on those methods. Methods which are seldom used over a period of 2-3 years should be proposed for decommissioning.

We recommend that all revised and new methods should have expiration dates. When a widely-used method is about to expire, the EPA would need to recertify it, which would allow for public comment on the method. An expiration date would ensure that the

most recent analytical technology would be considered for the method. Expiration dates might cause an additional expense if many methods need to be extensively revised, but we are convinced that the benefits outweigh the cost.

Before we address the issue of recipe-based versus performance-based methods, let us define what we mean by a performance-based method. Rather than having an exact specification of how all of the details should be carried out, the method simply specifies the goals of the various parts of the method. For example, a large number of extraction possibilities could be given, and the analyst allowed to choose among the various procedures as long as a certain percent recovery is achieved. The advantages of performance-based methods include flexibility and the ability to add new analytical technology as it develops. The disadvantages include a need for a significantly higher level of chemical skill and knowledge on the part of the method user. We have no firm recommendation on which is better, but we do suggest that new methods should include ample options so that an experienced method user can take advantage of technological improvements. "Ad hoc" improvements, which eventually prove to be effective can be incorporated in the next version of the method, presumably when it is recertified after its expiration.

Revisions to the EPA's analytical methods should aim to significantly reduce waste from laboratory operations, especially hazardous wastes. One of the EPA's goals for the 1990's is "pollution prevention". Unfortunately, millions of liters of methylene chloride are either evaporated up the hood or buried in the ground as a direct result of its use in official EPA analytical methods. Methods based on liquid-solid and supercritical fluid extraction, which can reduce solvent consumption by about 90%, can contribute to this goal of pollution prevention. For particulate-laden water samples, these extraction methods may not work; thus, we need to retain liquid-liquid extraction methods. In this case, microextraction methods have many advantages. These methods are excellent for screening samples; in some cases, they may be sufficient for the final measurement of relatively

clean samples. Microextraction methods use less solvent; therefore, they are less expensive and generate less waste than the "macro" methods. Furthermore, the micro methods are frequently much more rapid. For all of these reasons, we recommend that the use of microextraction methods be expanded.

In considering these issues and in developing the recommendations presented here, it became evident that the EPA faces a potential long-term problem: Where are the environmental chemists of the future going to come from? The development of new methods and the implementation of existing methods will require increasingly well-trained technical personnel. Unfortunately, the number of new scientists entering the work force continues to decline, in some cases (such as chemistry) dramatically. Clearly, a problem lies ahead, and it behooves the EPA to do something about it. We recommend that the EPA fund a system of training grants to academic institutions for the express purpose of increasing the flow of trained scientific personnel into the chemical work force.

SUMMARY OF RECOMMENDATIONS

1. Some existing 500 and 600 series methods should be revised and some others should be dropped. The set of changes that we recommend is given in Table II; the resulting methods provide for the determination of about 340 compounds and mixtures (such as PCBs).

2. Gas chromatography in any revised or new method should use capillary columns. This is necessary to provide sufficient resolution to distinguish analytes from one another, especially when they are measured *only* with gas chromatography.

3. The format of official EPA methods should be standardized throughout the Agency, and the *writing* of revised methods should be modularized. The different methods should then incorporate the appropriate modules. This would promote uniformity among

the methods and eliminate trivial but irksome differences.

4. A usage survey of the EPA's analytical methods should be conducted. This would help in the development of new methods, in dropping old methods, and in the revision of current methods.

5. Revised or new methods should have expiration dates. This would force the EPA to either drop the method or recertify it. Clearly, this would lead to the incorporation of the most up-to-date analytical technology.

6. The development of microextraction methods, using small volumes of sample and solvents should be encouraged. These methods can be excellent but inexpensive screening tests. They also prevent pollution.

7. The EPA should establish a system of training grants to help increase the pool of environmental chemists.

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TABLE I

LIST OF 500 AND 600 SERIES METHODS CONSIDERED

501.1 Trihalomethanes in finished water by the purge and trap method using gas chromatography with electrolytic conductivity detection. **4**

501.2 Trihalomethanes in drinking water by liquid-liquid extraction using gas chromatography with electron capture detection. **4**

501.3 Trihalomethanes in drinking water with gas chromatographic mass spectrometry and selected ion monitoring. **4**

502.1 Volatile halogenated organic compounds in water by purge and trap gas chromatography with electrolytic conductivity detection. **40***

502.2 Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detection in series. **60**

503.1 Volatile aromatic and unsaturated organic compounds in water by purge and trap gas chromatography with photoionization detection. **28**

504. 1,2-Dibromoethane and 1,2-dibromo-3-chloropropane in water by microextraction and gas chromatography with electron capture detection. **2**

505. Organohalide pesticides and commercial polychlorinated biphenyl products in water by microextraction and gas chromatography with electron capture detection. **24**

506. Phthalate and adipate esters in drinking water by gas chromatography with photoionization detection. **7**

507. Nitrogen-and phosphorus-containing pesticides in water by gas chromatography with nitrogen-phosphorus detection. **46**

508. Chlorinated pesticides and polychlorinated biphenyls in water by gas chromatography with electron capture detection. **38**

513. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in drinking water by gas chromatography and high resolution mass spectrometry. **1**

515.1 Chlorinated acids in water by methylation and gas chromatography with electron capture detection. **16**

524.1 Purgeable organic compounds in water by packed column gas chromatographic mass spectrometry. **48**

524.2 Purgeable organic compounds in water by capillary column gas chromatographic mass spectrometry. **60**

525. Organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatographic mass spectrometry. **43**

531.1 N-methylcarbamoyloximes and N-methylcarbamates in water by direct aqueous injection HPLC with post column derivatization. **10**

547. Glyphosate in drinking water by direct aqueous injection HPLC with post-column derivatization. **1**

548. Endothall in drinking water **1**

549. Diquat and paraquat in drinking water by high performance liquid chromatography with ultraviolet detection. **2**

550. Polycyclic aromatic hydrocarbons in drinking water by liquid-liquid extraction and HPLC. **16**

550.1 Polycyclic aromatic hydrocarbons in drinking water by liquid-solid extraction and HPLC. **16**

551. Chlorination disinfection byproducts and chlorinated solvents in drinking water by microextraction and gas chromatography with electron capture detection. **18**

552. Haloacetic acids in drinking water by liquid-liquid extraction and gas chromatography with electron capture detection. **8**

601. Purgeable halocarbons in municipal and industrial wastewater by gas chromatography with electrolytic conductivity detection. **29**

602. Purgeable aromatics in municipal and industrial wastewater by gas chromatography with photoionization detection. **7**

603. Acrolein and acrylonitrile in municipal and industrial wastewater by heated purge and trap gas chromatography with flame ionization detection. **2**

604. Phenols in municipal and industrial wastewater by gas chromatography with flame ionization detection. **11**

605. Benzidines in municipal and industrial wastewater by gas chromatography with special electrochemical detection. **2**

606. Phthalate esters in municipal and industrial wastewater by gas chromatography with electron capture detection. **6**

607. Nitrosamines in municipal and industrial wastewater by gas chromatography with nitrogen selective flame ionization detection. **3**

608. Organochlorine pesticides and PCBs in municipal and industrial wastewater by gas chromatography with electron capture detection. **25**

609. Nitroaromatics and isophorone in municipal and industrial wastewater by gas chromatography with flame ionization and electron capture detection. **4**

610. Polycyclic aromatic hydrocarbons in municipal and industrial wastewater by high performance liquid chromatography. **16**

611. Haloethers in municipal and industrial wastewater by gas chromatography with electrolytic conductivity detection. **5**

612. Chlorinated hydrocarbons in municipal and industrial wastewater by gas chromatography with electron capture detection. **9**

613. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in municipal and industrial wastewater by gas chromatographic mass spectrometry. **1**

624. Purgeable organic compounds in municipal and industrial wastewater by gas chromatographic mass spectrometry. **31**

625. Basic, neutral, and acidic organic compounds in municipal and industrial wastewater by gas chromatographic mass spectrometry. **72**

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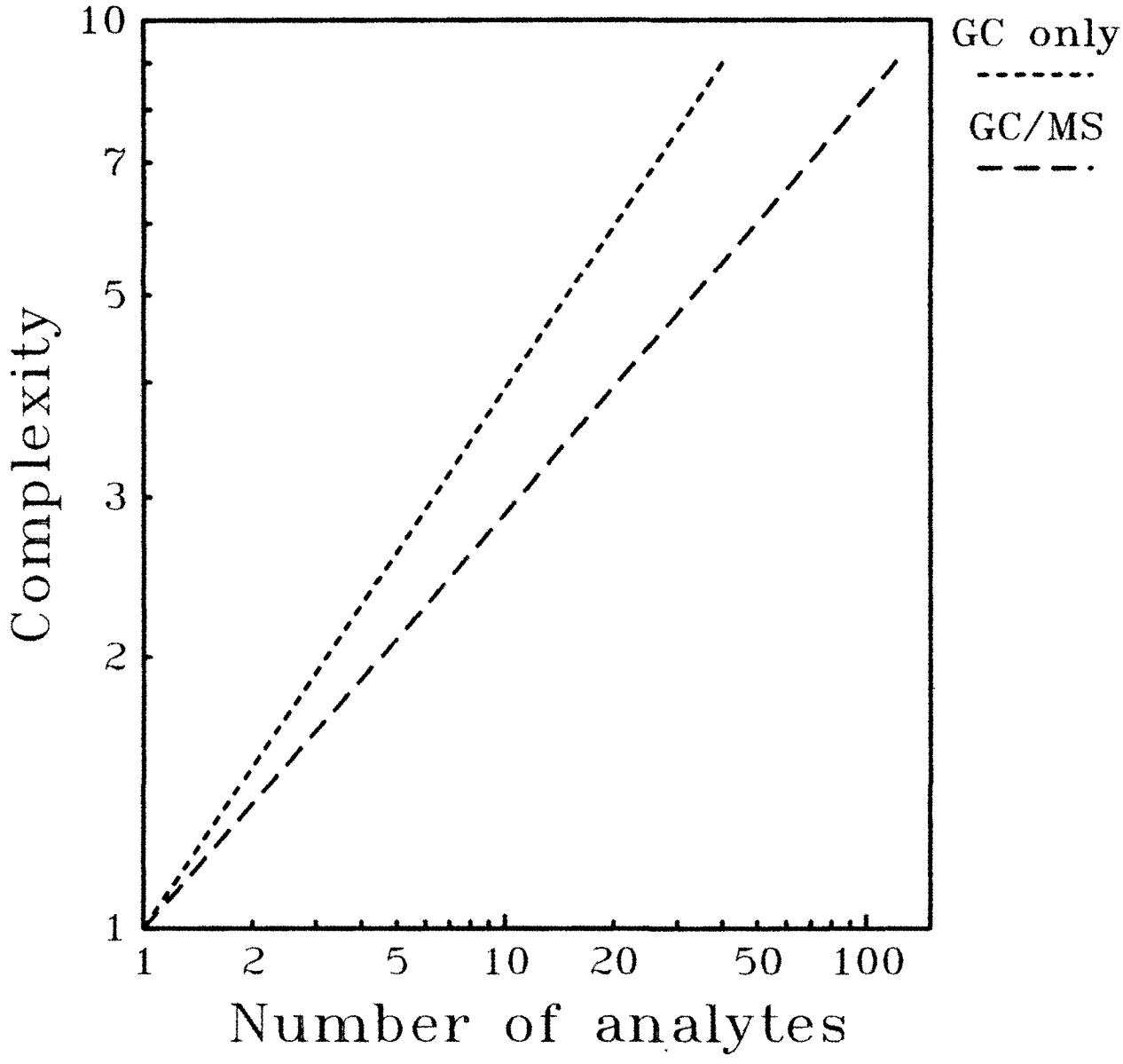
* The bold faced number is the total number of analytes on the target list of a given method.

TABLE II

PROPOSED METHOD REVISIONS

		Number of analytes	Number of duplicates	Recommendations
501.1, 501.2, 501.3	Trihalomethanes	4	4	Drop all three
502.1, 502.2, 503.1, 601, 602	Purge and trap by GC-only	63	58	Keep 502.2, drop all others
524.1, 524.2, 624	Purge and trap by GC/MS	62	42	Keep 524.2, drop all others
515.1, 552, 604	Haloacids by GC	31	4	Combine into one method
525, 625	Extractables by GC/MS	93	22	Keep 525, revise 625
506, 606	Phthalates by GC	7	6	Drop both
550, 550.1, 610	PAH by HPLC	16	16	Keep 550 and 550.1, drop 610
508, 608	Chlorinated pesticides by GC	39	24	Revise 508, drop 608
551, 612	Misc. chloro compounds	27	0	Combine into one method
603	Acrolein and acrylonitrile	2	-	Drop
605, 607, 609, 611	Nitrogen compds. & haloethers	14	0	Drop all four
504,505	Halogenated compds.	26	0	Keep both
513, 613	2378-TCDD	1	1	Keep 513, drop 613
507, 531.1	Nitrogen & phos. pesticides	56	0	Keep both
547, 548, 549	Unusual pesticides	4	0	Keep all three

Figure 1


10
7
5
3
2
1
Complexity
1
2
5
10
20
50
100
Number of analytes
GC only
GC/MS

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions for Ron? Good morning, George.

MR. STANKO: Good morning, Bill. George Stanko, Shell Development Company.

In keeping with the past history of this conference, I've been asked to inject some controversy. I think the time is opportune.

Ron, it seems to me...I don't know if this is a case of the committee or yourself or your students, but there's a general bias towards the 500 series methods. If the bias towards the 500 series is for the more comprehensive quality control, I think we can concur that that was a good decision. If the bias towards the 500 series methods was because it has, I must say, unrealistically low detection limits, then we think that is wrong and we have some concerns there.

You may not have been given all the facts, but I would like to tell you that all of the criteria that was developed and reported in the 500 series was actually done on the 600 series methods and it's a mystery to me how you can have a lower detection limit using the same data set. But that can happen. One other thing that's obvious to me is that none of the methods in ASTM, which are consensus standards, were ever shown on any of your slides or did not appear to be even considered. ASTM has the consensus standard methods for low molecular weight chlorinated compounds which covers trihalomethanes, which is an excellent method. It is an environmentally accepted method because it's a mini-shake procedure and it's used by a lot of drinking water plants. It's a very cost effective method, environmentally acceptable method. I would like to have seen that one considered.

Another thing, there's a PCB method in ASTM that is also a consensus standard method and EPA was party of the round robin and EPA, Cincinnati, is on Committee D1906 that had a major impact on that method itself. One advantage of the ASTM methods

is they are re-certified on a five year cycle. This is one of the things you recommended.

Currently, Method 524.2 is being considered for a round robin in ASTM D1906. In fact, there's a Shell person who is a task group chairman and industry and trade organizations have supported the ASTM activity towards elevating Method 524.2 to a consensus standard method. But nothing...either you weren't given all the information about the ASTM activity in this area and I think it really needs to be considered.

MR. HITES: Let me respond to three points. The ASTM area is, in fact, one that we deliberately avoided. We were told to focus only on the 500 and 600 series methods and, of course, we weren't in a position to say, oh, we should do much more than that. I think that's probably a more important policy issue for the agency as a whole and, in fact, commended. I think if ASTM is going to do round robin studies on official methods, that's absolutely great.

Let me respond to the issue of the 500 versus 600. We did not discriminate against the 600 based on detection levels. We recognize that the detection levels are going to be vastly different between the two methods because the matrix is vastly different and so we did not discriminate on that basis. We did not discriminate on the basis of QA/QC. I hate QA/QC; it's just too boring. So, we didn't even pay much attention to that. We discriminated on the basis of age. The 600 level methods are old technology. The 500 methods are...and this is an oversimplification...the 500 methods are newer technology and that's it. We recommend newer analytical technology.

MR. STANKO: Ron, I have one further comment. Not only should you drop the methods for phthalates, you really ought to drop the phthalates.

MR. HITES: I agree.

MR. VINOPAL: My name is Howard Vinopal from the Army Environmental Hygiene Agency and I'd like to say that in general I agree with your recommendations. One

area, though, that I'd like to get a little comment from EPA on... At a recent meeting, I talked to some people and they felt that they weren't going to pursue the microextraction procedures much further and I hear that you're recommending them, such as 505, which is a microextraction method. I think we need a little better direction from EPA in this area because we're considering some method development efforts in microextraction, in improvement of the 505, which is a somewhat weak method in the way that it extracts compounds. You must spike the samples with standards and carry them through the procedure in order to overcome deficiencies in recoveries. I would like to see a little more direction on whether microextraction is what we should be spending more effort on.

MR. TELLIARD: I think from the Office of Water standpoint, it is something we're looking at and, again, it's in relationship to the pollution prevention effort. If we don't need a 55 gallon drum sample and then have to dispose of it... And, of course, it's very dominant in the dioxin issue where we have laboratories sitting around with whole storerooms full of trash that they can't get rid of. So, we're going to pursue it. In fact, this coming year we're going to fund some efforts, both in the contract lab program and also with some of our regional labs to look at not only microextraction, but additional pollution prevention of solvent substitution and along that line. So, it is something we're concerned about and we are intending to move that way.

MS. FISK: I can second that for Superfund and some of the research committee money. I was talking before about the mystery process. A lot of that is diverted now toward pollution prevention. I don't know where you got your information because I don't think it's true.

MR. TELLIARD: The gentleman over here.

MR. MOYE: Yes, good morning. Anson Moye, University of Florida.

Ron, in your considerations on how to reduce costs and time in combining and doing away with some of the 500, 600 methods, one of the criteria has to be sample throughput yet you did not mention that in your discussion. Did you have sample throughput criteria, and if so, what were they?

MR. HITES: We didn't really have that as an explicit criteria. It seemed in reading over the various methods, the 500 and 600, there were not major differences in throughput between them. I agree with you. That certainly is an important consideration and I've got to believe that as we go to more and more modern technology, that it has to increase the sample throughput.

MR. MOYE: Well, I hope you're right, but there are certain steps that can be taken in the development of a method with old technologies that will greatly reduce sample throughput, particularly in the extraction end of the method, as you well know.

MS. ASHCRAFT: Merrill Anderson Ashcraft from the Navy Public Works Center.
This is really directed at the panel. I don't know if you can answer this question. I'm not someone who works a whole lot with organic matrices so I don't know what the detection limits are in those processes, but I do have to interpret a lot of data and use that data in environmental regulations and apply it to our industry. One of the problems that I've seen is, for example, like in metal analysis, hazardous waste limits for chrome is five. Well, I don't see a need to measure...

MR. HITES: Five what?

MS. ASHCRAFT: Five parts per million. I don't see a need to measure one part per billion if my limit is five. I would like to see a lot of the methods be directed at regulatory limits. Also, some of the actual organic species like tricholoethane, which is an F category waste, it says 10 percent solvent. Now, 10 percent is a large number and I would like to see some of the methods detection limits directed

at actually what the regulatory limits are so that you could do rough screenings and not worry about detection limits to find out whether or not you have a hazardous waste. That's my comment.

MS. FISK: One of the things that's happening at the agency, which you've probably all been hearing about for years, is data quality objectives and the user of the data is supposed to determine up front what quality of data he needs and one of the things he would be concerned with would be the detection or quantitation limits for whatever the regulation was or whatever his use and he should then be selecting the appropriate method or at least reviewing the data from the point of view of that method. It may be that the method may have a much lower detection limit than what you really need, but when you're looking at it from your data review perspective, all you're concerned about is the five parts per million. This is the kind of thing where we in Superfund are constantly trying to provide a gamut...a whole gamut of methods. Like I mentioned before, the quick turn-around GC. These are basically screening type things. Is there any of that junk in there or not? And kind of direct where you do your sampling. You may find hot spots and you say, okay, these are hot spots. There's going to be real high concentrations and then you may want to send samples on to a fixed laboratory and you would certainly not be asking the laboratory to look for two parts per billion if you knew these things were at two parts per million or 200 parts per million. It's an ongoing process in the EPA today.

MR. HODGESON: Jimmie Hodgeson, USEPA.

I was glad to hear most of your conclusions. Just one issue though. On the organic acids, Methods 515.1 and 552, I gave a talk on these yesterday on the research we're doing...not on combining the methods, but on methods for simplification by the use of solid phase extraction. They are not both for halo acids. 552 is for haloacetic acids which are components of chlorinated drinking water. 515.1 is for organic herbicides.

These are, in fact, quite different in their chemical and physical properties and the forms in which they are found. It may or may not be possible to combine them.

MR. HITES: I agree. That's a good point.

MR. TELLIARD: It's break time. I want to thank the panel for this morning. If you folks will get your strawberries and get back in here, we'll continue on. Thank you.

THE U.S. EPA'S ANALYTICAL METHODS FOR ORGANIC COMPOUNDS IN WATER AND WASTEWATER: THE NEXT GENERATION

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EPA's 500 AND 600 SERIES METHODS ARE NOW IN WIDE-SPREAD USE.

THERE ARE CONSIDERABLE OVERLAPS AMONG THE METHODS (BOTH PROCEDURES AND ANALYTES).

THERE ARE ALSO DIFFERENCES BETWEEN THESE METHODS (SOME IMPORTANT AND SOME TRIVIAL).

SECTION 518 OF THE WATER QUALITY ACT OF 1987 DIRECTED THE EPA TO STUDY THE AVAILABILITY AND ADEQUACY OF FIELD AND LABORATORY TEST PROCEDURES AND METHODS TO SUPPORT THE PROVISIONS OF THE ACT.

THIS STUDY RESULTED IN A REPORT TO CONGRESS TITLED "AVAILABILITY, ADEQUACY, AND COMPARABILITY OF TESTING PROCEDURES FOR THE ANALYSIS OF POLLUTANTS ESTABLISHED UNDER SECTION 304(H) OF THE FEDERAL WATER POLLUTION CONTROL ACT".

THE REPORT INCLUDED THE FINDING THAT "IMPROVED COORDINATION IS NEEDED IN THE AGENCY'S METHODS DEVELOPMENT PROGRAM TO AVOID DUPLICATION IN THE DEVELOPMENT AND STANDARDIZATION OF TEST PROCEDURES AND INCONSISTENCIES IN QUALITY ASSURANCE AND QUALITY CONTROL GUIDELINES."

AS A RESULT OF THIS FINDING, INDIANA UNIVERSITY WAS ASKED BY THE EPA TO CONSIDER THE QUESTION "IS IT POSSIBLE TO REVISE OR ELIMINATE SOME OF THE 500 AND 600 SERIES METHODS AND EFFECT A SAVINGS OF TIME AND MONEY?"

RECOMMENDATION 1. SOME EXISTING 500 AND 600 SERIES METHODS SHOULD BE REVISED AND SOME OTHERS SHOULD BE DROPPED. THE RESULTING METHODS PROVIDE FOR THE DETERMINATION OF ABOUT 340 COMPOUNDS AND MIXTURES.

PROPOSED METHOD REVISIONS

501.1, 501.2, 501.3
TRIHALOMETHANES

DROP ALL THREE

502.1, 502.2, 503.1, 601, 602
PURGE AND TRAP BY GC-ONLY

KEEP 502.2, DROP ALL OTHERS

524.1, 524.2, 624
PURGE AND TRAP BY GC/MS

KEEP 524.2, DROP ALL OTHERS

515.1, 552, 604
HALOACIDS BY GC

COMBINE INTO ONE METHOD

525, 625
EXTACTABLES BY GC/MS

KEEP 525, REVISE 625

506, 606
PHTHALATES BY GC

DROP BOTH

550, 550.1, 610
PAH BY HPLC

KEEP 550 AND 550.1, DROP 610

508, 608
CHLORO PESTICIDES BY GC

REVISE 508, DROP 608

551, 612
MISC. CHLORO COMPOUNDS

COMBINE INTO ONE METHOD

603
ACROLEIN AND ACRYLONITRILE

DROP

605, 607, 609, 611
NITROGEN COMPOUNDS & HALOETHERS

DROP ALL FOUR

504,505
HALOGENATED COMPOUNDS

KEEP BOTH

513, 613
2378-TCDD

KEEP 513, DROP 613

507, 531.1
NITROGEN & PHOSPHOROUS PESTICIDES

KEEP BOTH

547, 548, 549
UNUSUAL PESTICIDES

KEEP ALL THREE

RECOMMENDATION 2. GAS CHROMATOGRAPHY IN ANY REVISED OR NEW METHOD SHOULD USE CAPILLARY COLUMNS. THIS IS NECESSARY TO PROVIDE SUFFICIENT RESOLUTION TO DISTINGUISH ANALYTES FROM ONE ANOTHER, ESPECIALLY WHEN THEY ARE MEASURED ONLY WITH GAS CHROMATOGRAPHY.

RECOMMENDATION 3. THE FORMAT OF OFFICIAL EPA METHODS SHOULD BE STANDARDIZED THROUGHOUT THE AGENCY, AND THE WRITING OF REVISED METHODS SHOULD BE MODULARIZED. THE DIFFERENT METHODS SHOULD THEN INCORPORATE THE APPROPRIATE MODULES. THIS WOULD PROMOTE UNIFORMITY AMONG THE METHODS AND ELIMINATE TRIVIAL BUT IRKSOME DIFFERENCES.

RECOMMENDATION 4. A USAGE SURVEY OF THE EPA'S ANALYTICAL METHODS SHOULD BE CONDUCTED. THIS WOULD HELP IN THE DEVELOPMENT OF NEW METHODS, IN DROPPING OLD METHODS, AND IN THE REVISION OF CURRENT METHODS.

RECOMMENDATION 5. REVISED OR NEW METHODS SHOULD HAVE EXPIRATION DATES. THIS WOULD FORCE THE EPA TO EITHER DROP THE METHOD OR RECERTIFY IT. CLEARLY, THIS WOULD LEAD TO THE INCORPORATION OF THE MOST UP-TO-DATE ANALYTICAL TECHNOLOGY.

RECOMMENDATION 6. THE DEVELOPMENT OF MICROEXTRACTION METHODS, USING SMALL VOLUMES OF SAMPLE AND SOLVENTS SHOULD BE ENCOURAGED. THESE METHODS CAN BE EXCELLENT BUT INEXPENSIVE SCREENING TESTS. THEY ALSO PREVENT POLLUTION.

RECOMMENDATION 7. THE EPA SHOULD ESTABLISH A SYSTEM OF TRAINING GRANTS TO HELP INCREASE THE POOL OF ENVIRONMENTAL CHEMISTS.

MR. KING: The next session is on other methodologies. We're talking about everything from robotic BOD to LCMS and there could be a change of schedule with the LCMS. Bill Budde has a late arrival, so we're anticipating switching Henry Kahn's 1: 45 paper on analytical variability into the 11: 15 slot for playing purposes. So, with that, we'll get ready to start.

Wayne Michalik of Shell Oil is going to talk a little bit about automated BOD. Wayne has been working on laboratory automation and robotics for about six years now and is just trying to meet the limits and all of that good stuff that you guys are really familiar with.

AUTOMATION OF THE BIOCHEMICAL OXYGEN DEMAND (BOD) TEST FOR WASTE WATER

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SUMMARY

The procedure for determination of the Biochemical Oxygen Demand (BOD) of waste water given in Standard Methods 16th Edition (1985) has been automated with a Zymark Laboratory Automation System using a custom BOD workstation. The BOD workstation does all glassware and sample manipulations except movement of the filled BOD bottles to and from the incubator. The system handles all sample transfers, as well as the additions of dilution water, biological seed and phosphate buffer. Dissolved oxygen readings are made before and after incubation with a YSI Dissolved Oxygen Meter. The sample transfers and additions of dilution water are made with calibrated peristaltic pumps rather than using conventional pipets. In addition, the robotic system has a workstation to wash and rinse the BOD bottles after use.

The precision of the BOD results obtained with the robotics system has been equal to that obtained using the manual BOD procedure and has met the precision requirements prescribed in the standard method for the glucose/glutamic acid mixed primary standard.

Analyst involvement with BOD testing has been reduced by about 75% since the procedure has been automated.

INTRODUCTION

Most analyses of environmental samples such as waste water require a considerable amount of analyst time to do repetitive tasks such as sample transfers, sample dilutions, reagent additions and pH adjustments. The determination of the Biochemical Oxygen Demand (BOD) of waste water, as described in Standard Methods, 16th Edition (1), indeed requires a high level of analyst involvement and testing is often required 24 hours per day, seven days each week. The automation of BOD testing should allow an increase in laboratory productivity by freeing the analyst from routine analytical procedures.

The BOD of waste water is proportional to the amount (ppm) of soluble, biodegradable organic compounds present in the water, and as such, is an indication of the performance of an effluent biotreating system. Most operating refineries or chemical plants have maximum BOD levels for the waste water that they can discharge from the manufacturing facility which are stipulated by governing and controlling agencies, such as the Environmental Protection Agency. Thus, accurate measurement of the BOD is necessary to assure the quality of plant waste water.

The BOD method consists of completely filling a bottle with a waste water sample to exclude contact with air and incubating the bottle at 20 Degrees C for five days. The dissolved oxygen (DO) in the waste water is measured before and after incubation. Most waste waters contain more oxygen-demanding materials than the amount of DO in air-saturated water. Therefore, the waste water samples are diluted to several different concentrations before incubation in order to bring the DO demand and supply into appropriate balance. Active bacterial growth requires nutrients and a fairly narrow pH range. To supply these needs, a biochemical seed solution and phosphate buffer solution is added to each sample dilution before the incubation is started. The BOD (mg DO/L) is computed from the difference between the initial and final DO readings divided by the volume fraction of sample in the bottle.

To meet environmental testing requirements at the Shell Manufacturing Complex in Wood River, Illinois, BOD analyses are done four days each week on a number of different aqueous effluent streams. As many as seven dilutions are required for each waste water sample, and this amounts to an average of 30 sample preparations on each of the four days. The manual manipulations required for a BOD analysis consist of

transferring water samples to BOD test bottles, adding biological seed solution, buffer solution and dilution-water to the test bottles, taking dissolved oxygen (DO) readings on the resulting sample solutions and calculating the BOD for the sample. The time spent by an analyst doing these manual manipulations amounted to 16-20 hours of a 40-hour week. In addition, the analyst who prepared a series of BOD samples would often be working a different shift five days later when the samples were removed from the incubator. Thus, another analyst had to make the final DO determinations on the samples and calculate the BOD. Robotic automation of the BOD test (except for moving the BOD test bottles to and from the incubator) has significantly reduced the amount of analyst involvement with the test, and by repetition of each step in exactly the same manner, has removed inconsistencies that could have occurred when more than one analyst was involved in running the test.

This article describes the laboratory robotic system that performs these manual manipulations required for the determination of BOD in refinery waste water. The automated method adheres to the standard protocol specified for the manual procedure (1).

EXPERIMENTAL

A Zymark "Zymate II" Robotic Laboratory Automation system has been used to automate the BOD analysis of waste water. Since BOD analyses require multiple sample dilutions (with the addition of biological seed solution and phosphate buffer solution to each dilution), it was necessary to determine the most efficient way to do these multiple dilutions and reagent additions robotically. The Zymark Robotic Pipet Hand is accurate, but extremely slow when transferring volumes from 1 to 250 milliliters (ml). Since the sample load in our Environmental Laboratory averages 30 dilutions per day, parastaltic pumps and pinch valves were used to deliver sample and dilution water accurately and in a reasonable time period. Sample and dilution water transfer lines are 1/4-inch OD Tygon tubing.

The Zymate II Robotics System is installed on a mobile bench equipped with 5-ft x 7-ft upper and lower bench areas. A schematic of the equipment located on the upper bench is shown in Figure 1. This consists of a BOD bottle wash station, a BOD work station, a 15-bottle incoming-sample rack, two 15-bottle sample-dilution racks and a robotic-hand

parking station. The glass BOD bottles used with the system are conventional 300-ml volume BOD bottles with glass caps purchased from the Wheaton Glass Company.

The BOD bottle-wash station consists of the following:

- A BOD bottle holder with an optical sensor to confirm the bottle is in place.

- An aspirator for removal of sample from the bottle.

- A single-head variable-speed peristaltic pump to add soap solution to the BOD bottle.

- A dual-head variable-speed peristaltic pump to aspirate sample from the BOD bottle, add rinse water to the BOD bottle and to pump the drain of the wash station when adding soap solution or rinse water.

- A pinch valve to allow aspiration of sample from the bottle or draining the bottle holder.

- A pinch valve to control the addition of soap solution or rinse water to the bottle.

The pumps are located on the lower bench and the pinch valves on the upper bench near the bottle-wash station. Aspirating the sample from the BOD bottle, washing and then rinsing the bottle are being done while the final DO readings are being made after incubation. After the final DO reading is made on a sample, the BOD bottle is removed from the BOD work station holder, positioned under the wash station aspirator and the sample removed. The bottle is then inverted and placed in the bottle washing section, where the position of the bottle is confirmed optically. A strong, low-foaming soap solution is pumped into the bottle coating all surfaces on the inside. Rinse water is pumped into the bottle to remove the soap. While this process is being done, the DO reading is being taken on the next sample dilution.

The BOD work station consists of the following:

- A holder for BOD sample bottles, which includes a sample transfer cannula, cannula wash station and stirrer.

- A holder for empty BOD dilution bottles, which includes the YSI DO probe, nozzles for addition of the biological seed, buffer solution and dilution water, a level-sensing thermistor and an air line to remove water droplets from the thermistor.

- An apparatus to remove the glass stoppers from the BOD bottles and an optical sensor to confirm removal of the stopper.

- A 100 rpm fixed-speed peristaltic pump and pinch valve used to transfer sample from the original sample bottle into the BOD bottle.

- An AT&T personal computer, the System V controller for program operation and System control and an Okidata Microline 182 printer.

The sample-transfer pumping system is calibrated each day before analyses are started. The BOD work station dispenses the biological seed and buffer solutions using a Zymark MasterLab station. The MasterLab station is equipped with a 10-ml syringe for the seed solution and a 5-ml syringe for the phosphate buffer solution. Both solutions are added directly to each sample dilution.

The sample dilution water and DO probe rinse water are dispensed using a dual-head, 600 rpm, variable-speed peristaltic pump. One pump head dispenses dilution water and the other dispenses the rinse water. The rinse water flushes the DO probe between readings and washes the sample-transfer line and sample-transfer cannula. The dilution-water pump is calibrated before sample dilutions are started.

A low-temperature thermistor on the BOD work station is used to insure the proper amount of dilution water has been dispensed before initial DO readings are taken. After the initial aliquots of dilution water, biological seed solution and buffer solution have been dispensed, an initial amount of dilution water is added that is needed to bring the total volume of water in the BOD bottle to 306-ml (the average neck-full volume of the 300-ml BOD bottles). If the thermistor is not in contact with the water in the bottle after the initial amount of water has been added, dilution water is added in 1-ml increments until the thermistor contacts the liquid. This insures that there is an adequate amount of water in the bottle for the DO probe to make a proper reading, with no free air trapped in the bottle. The maximum volume of any of the BOD bottles used was found to be 315-ml and provisions were made in the control program so that no more than a total of 315-ml can be added to any bottle, regardless of the thermistor reading. The thermistor is also used after the DO reading is completed to insure that there is enough water in the bottle to make a water seal when the glass stopper is replaced.

The DO readings are obtained using the YSI Model 58 DO Meter equipped with a self-stirring BOD-bottle probe. This meter has been easy to calibrate and maintain. It is interfaced directly to the robotic system, which controls the stirrer and captures the DO readings in memory. The DO probe is placed in the BOD bottle and allowed to stabilize for 90 seconds. Then, DO readings are taken every 2 seconds until a stable reading of ± 0.05 mg/l is achieved. This final DO reading is captured in memory.

A schematic of the equipment on the lower bench is shown in Figure 2. This equipment consists of:

- Five 20-liter plastic reservoirs (three used for rinse water, one for soap solution and one for dilution water).

- All pumps and controllers except for the sample transfer pump.

- The MasterLab Station for adding the biological seed and buffer solutions to the diluted samples.

- The containers of the biological seed and buffer solutions.

- The Power and Event Controller.

- The Liquid Handling and Event Controller.

Dilution water is conserved by a loop arrangement. When the dual-head pump is moving rinse water to the BOD work station, the dilution water is circulated. While dilution water is being dispensed, rinse water is delivered to the two wash stations in the BOD work station. The three rinse water reservoirs have been plumbed together and a constant fill apparatus installed. The dilution water and soap solution reservoirs are filled independently. The cleaning solution is purchased from Baxter Scientific Products (Micro All-Purpose Liquid Cleaner).

Before sample preparation is begun, the analyst adjusts the pH of each waste-water sample (pH = 6.5 - 7.5) and places the samples in the designated locations in the incoming sample rack. Table 1 lists the basic steps of the BOD procedure.

TABLE 1

STEPS FOR ROBOTIC BOD ANALYSIS OF WASTE WATER SAMPLES

- CALIBRATE SAMPLE AND DILUTION WATER DELIVERY PUMPS.
- MOVE SAMPLE AND BOD BOTTLES FROM RACKS TO THE BOD WORK STATION.
- ADD 50 ML DILUTION WATER, 3 ML BIOLOGICAL SEED AND 1 ML PHOSPHATE BUFFER TO THE BOD BOTTLE.
- ADD NECESSARY AMOUNT OF SAMPLE TO THE BOD BOTTLE.
- FILL BOD BOTTLE WITH DILUTION WATER.
- TAKE INITIAL DO READING FROM THE BOD BOTTLE.
- STORE INITIAL DO READING IN MEMORY.
- REPLACE SAMPLE BOTTLE AND BOD BOTTLE IN THE RESPECTIVE RACKS.
- WHEN ALL SAMPLES HAVE BEEN DILUTED, THE ANALYST MOVES THE BOD BOTTLE RACK TO THE INCUBATOR.
- INCUBATE THE SAMPLES FOR 5 DAYS.
- AFTER 5 DAYS, THE ANALYST MOVES BOD BOTTLE RACK FROM THE INCUBATOR BACK TO ROBOTICS SYSTEM BENCH.
- TAKE FINAL DO READINGS FOR EACH BOD BOTTLE.
- CALCULATE AND PRINTOUT THE BOD READINGS FOR EACH DILUTION OF EACH SAMPLE.
- WASH AND RINSE EACH BOD BOTTLE AND REPLACE THEM IN THE BOD RACK.

Following is a more detailed step-wise procedure for calibration of the sample and dilution water dispensing systems, for sample preparation and DO determinations.

Step 1 : The program is started by the analyst. The BOD hand is retrieved and the DO Probe storage bottle (a) removed and placed in a reserved position in the incoming sample rack.

(a) The DO probe is stored in this bottle partially filled with water when not in use.

Step 2 : The analyst is asked by the system whether or not to do pump calibrations. The pumps are calibrated before each set of sample dilutions.

Step 3 : If calibration is desired, the analyst inputs the amount of time (120 seconds) to warm up the pumps before calibration.

Step 4 : After pump warm up, the analyst decides which pump to calibrate and enters (1) for the sample-transfer pump, or (2) for the dilution-water pump.

Step 5 : The transfer line is purged with dilution water and the analyst is prompted by the system to check for air bubbles trapped in the line. If no air bubbles are found, the calibration continues. If air bubbles are observed, further purging is done.

Step 6 : If pump calibration is required, the analyst places a 100-ml graduated cylinder under the proper water dispenser and informs the system that the cylinder is in place. Then, 50-ml of water are dispensed if calibrating the sample-transfer pump, or 100-ml of water are dispensed if calibrating the dilution-water pump. The analyst observes the amount of water dispensed into the cylinder.

Step 7 : The analyst inputs the volume of water that was dispensed and that value is saved in the system memory. Then, a calibration factor for that pump is calculated and is automatically entered into memory.

Step 8 : Steps 5 - 8 are repeated for calibration of the other pump.

Step 9 : After calibration of the pumps has been completed, initialization of the system is done automatically.

Step 10: Testing samples is started by removing the first sample bottle from the incoming-sample rack and placing the bottle on the appropriate sample holder at the BOD work station. The sample-transfer line is then purged with the sample.

Step 11: While purging the sample-transfer line with sample, the first dilution bottle is obtained from the dilution bottle rack, the glass stopper removed and the empty bottle placed into the dilution-bottle holder on the BOD work station.

Step 12: Next, 50-ml of dilution water, 3-ml of the seed solution and 1-ml of the phosphate buffer solution are dispensed into the BOD bottle. The designated volume of sample for the first dilution is transferred into the dilution bottle. The amount of dilution water that is needed to bring the total liquid volume in the bottle to 306-ml is added to the bottle. The level of water in the bottle is checked by the low-temperature thermistor to assure that an accurate DO reading can be obtained. If the water level is low, 1-ml increments of water are added until the correct level is obtained.

Step 13: The sample transfer line and the dilution water line are removed and the DO Probe is inserted into the BOD bottle for the initial DO reading.

Step 14: The DO Probe is given 90 seconds to stabilize before taking the first DO reading. Readings are then taken every 2 seconds until a stable measurement is achieved. This value is stored in memory.

Step 15: A check is also made to assure that enough water is in the bottle to obtain a proper water seal using the low temperature thermistor, as described previously.

Step 16: The dilution bottle is removed from the holder, the glass stopper inserted and the bottle placed into the same location in the dilution-bottle rack.

Step 17: Steps 10 - 16 are repeated for all dilutions required for each sample to be analyzed.

Step 18: After all samples have been diluted, the analyst is alerted by a flashing blue strobe light which means that the sample dilutions and initial DO readings have been completed.

Step 19: The analyst transfers these initial DO readings from memory to a disc file, places plastic caps on each BOD bottle to preserve the water seal and places the racks containing the diluted samples into the incubator, where they remain for five days.

Step 20: After the five day incubation period, the analyst replaces the racks containing the diluted samples on the robotics bench and the system is activated to make the final DO readings for each dilution of each sample. Each BOD bottle is washed after the final DO reading is completed.

Step 21: After all the final DO readings are completed, the BOD values are calculated for each dilution of each sample and the final report is printed. Washing of the BOD bottles is continued until all have been washed and replaced in the BOD bottle rack.

DISCUSSION

Since the BOD analyses has been automated with the Zymark II Robotic System, the time spent by an analyst in BOD sample preparation has been reduced from 16 - 20 hours per week to less than 5 hours per week. Lowering the amount of analyst involvement in BOD testing has resulted in at least 15 hours of additional analyst time each week that can be channeled into more involved, non-routine analytical procedures.

The accuracy and precision of the BOD test obtained with the robotic system has been equal to that obtained when running the BOD tests by the manual method. The prescribed standard for measuring the accuracy and precision of the BOD test given in the Standard Method (1) is a 50/50 mixture of glucose/glutamic acid. Acceptable performance of the BOD test for this standard mixture is an average BOD of 200 ± 37 mg/l. This standard mixture is routinely analyzed by the robotic system and was analyzed by the manual BOD method for comparison. For 40 analyses, the automated BOD analyses of this standard yielded an average value of 205 ± 31 mg/l BOD compared with values of 218 ± 34 mg/l BOD for the manual method. Thus, the automated BOD results obtained for the standard mixture have been more accurate at essentially the same level of precision.

Since the robotics system was installed in September 1989, good reliability has been obtained. However, a problem was encountered in delivering the correct amount of dilution water to the BOD bottles. The water volume dispensed into the bottles was 5-10 ml short of the 306-ml final volume required. It appeared that the thermistor for sensing the liquid level in the BOD bottles was malfunctioning. However, it was determined that short volumes of dilution water were being dispensed. The pinch valves were being opened at the same time the pumps were started, but the pumps require at least five seconds to attain full speed. As a result, smaller amounts of water were being dispensed than the pumps had been calibrated for. In this instance, the thermistor system for detecting the water level in the bottle did not continue to add water because the calibrated delivery system had already determined that the amount of water in the bottle exceeded the maximum volume (315-ml) that had been previously determined for the BOD bottles being used. Thus, with this low level of water in the bottle, the initial DO reading was in error because the DO probe was suspended in air, not in the water sample. Inserting a 5 second wait after pump start before starting to dispense the dilution water solved the problem.

After 5 months of operation, a dilution water line ruptured from fatigue of the Tygon tubing material. To assure that this does not occur again (and result in losing a substantial number of BOD measurements), the dilution water lines are replaced every two weeks. Further preventative maintenance procedures includes replacement of the YSI DO Probe membrane every two weeks and replacement of the sample transfer lines at least every 3 months.

CONCLUSIONS

The automation of the BOD procedure from Standard Methods (1) with the Zymark II Robotic Laboratory Automation System has been a success, resulting in accuracy and precision equal to that obtained when performing the test manually. Further, a 75% reduction in analyst involvement with the BOD test has been realized. Acceptance of the robotic system by the analysts has been good because it is easy to understand and operate.

REFERENCE

Standard Methods for the Examination of Water and Wastewater, 16th Edition, American Public Health Association, 1015 Fifteenth Street NW, Washington, DC, (1985), pp 526-531.

FIGURE 1

ROBOTIC SYSTEM UPPER BENCH

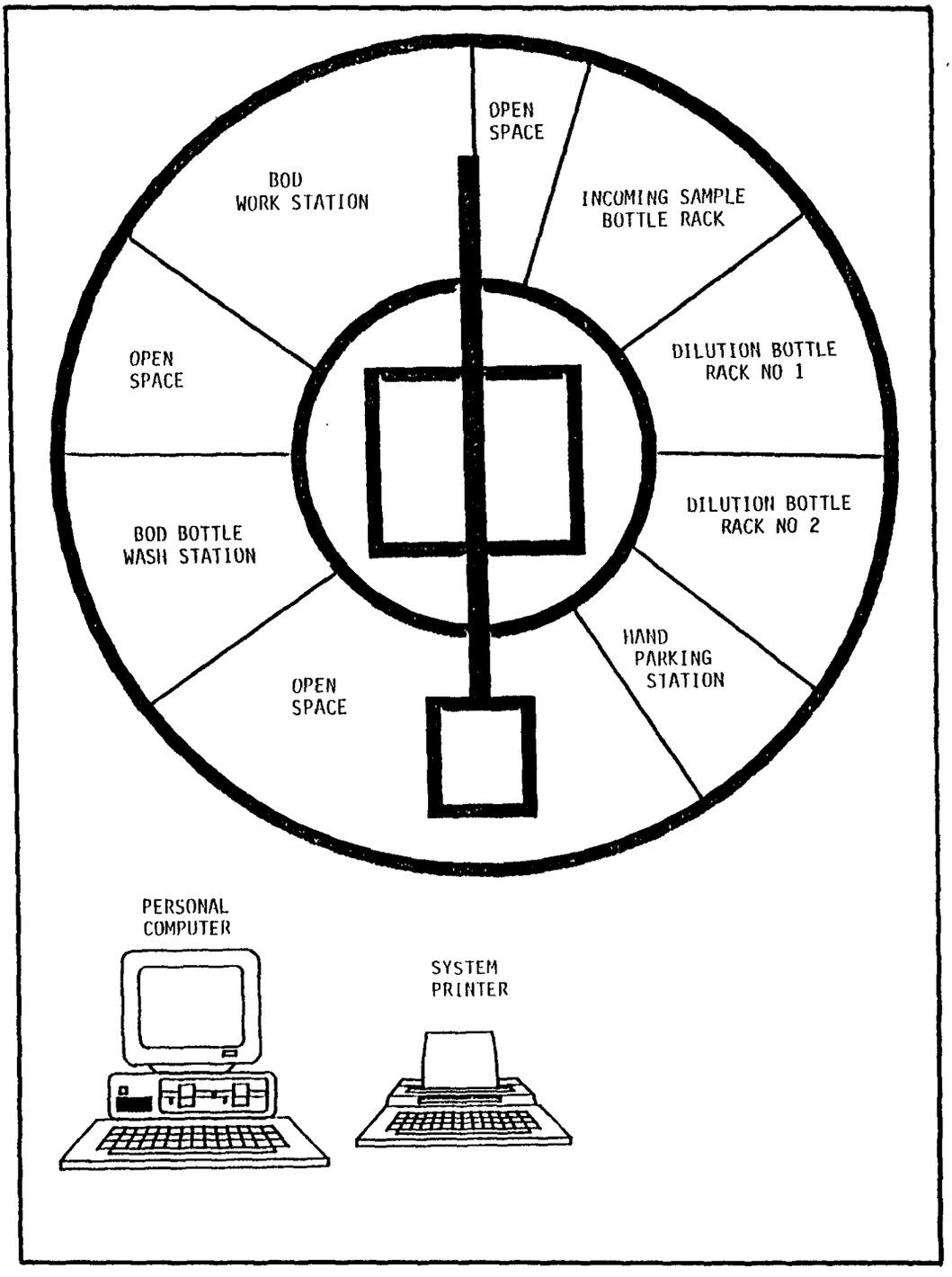
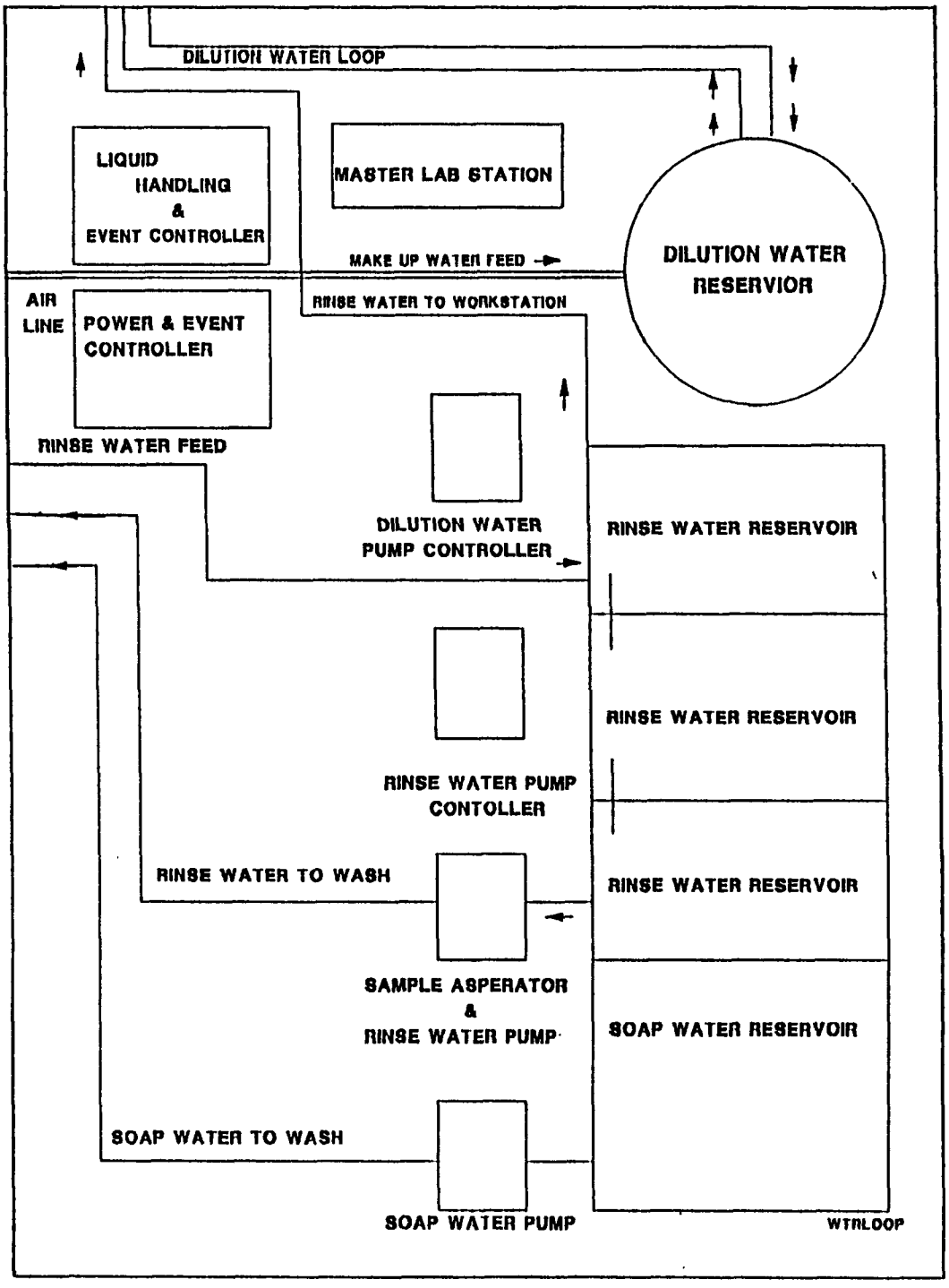


FIGURE 2

ROBOTIC SYSTEM LOWER BENCH



MR. KING: Our next speaker is Merlin Bicking. He's with Twin City Testing. He's currently the Manager of Research and Development there and he's going to talk a little bit about supercritical fluid extraction.

THIS IS AN UNEDITED VERSION OF THE PRESENTATION BY THE SPEAKER

MR. BICKING: We've got a slight audiovisual problem.

Okay, can you put the first one up...preferably the other way? Thank you.

When Bill and Harry called us earlier in the spring and asked if we could talk, we said, sure, I'd love to talk about SFE. And Harry's comment was, fine, as long as you don't say the same things you did two years ago. So, Harry, if you're out there, I've changed the title slide and a few other things since then.

Could I have the first slide, please, and the transparency can go off. Turn the transparency off for now. First slide, please.

Really, what I'd like to talk about is an experimental design approach that we've been using for optimizing supercritical fluid or SFE conditions for a number of environmental applications.

Next slide, please.

We have two primary objectives here. One is we're going to be using an experimental design approach for optimization. In keeping with our method development activities, we feel this is a better and more efficient approach to optimizing methodology and we'd like to use that information to look at some environmental applications.

Next slide, please.

SFE, if you're not familiar with it, is an extraction process that uses a supercritical fluid rather than a typical liquid solvent.

Next slide.

In terms of potential advantages, in general, you get faster extractions, with 15 to 16 minutes being typical extraction times versus an overnight soxhlet for many of our standard methods.

Your selectivity is different because we're using a different extraction medium and also because we have other modifiers we can add that will also affect our selectivity. In addition to that, we can vary the selectivity through the operating conditions, which are temperature and pressure. In other words, we really have almost... With these two factors here, we almost have the equivalent to an infinite number of solvents at our disposal.

Finally, the SFE approach is compatible with a number of other analytical techniques.

Next slide, please.

There are some concerns which you're probably already familiar with. Certainly, what are the optimum conditions for extraction? At this point in time, we have a limited database of applications. There are some excellent examples published where SFE works very well, compared to standard methodologies and, obviously, there are a number of conditions where SFE does not work well and, of course, those are generally never published. Certainly, if you can optimize the conditions, will your extraction efficiency be what you expect it to be? If you can get everything out, will you get out other things you don't want, the usual problems with selectivity and matrix interference. And finally, if you can get it out of your sample, can you collect it at some point?

These are really, I think, the four critical parameters that have to be solved or at least optimized if we're going to use SFE as a really viable extraction method.

Next slide.

We were using a statistical approach rather than trial and error for optimization and I'll discuss the central composite design in a minute.

Our approach is to simultaneously optimize two experimental values and in the process generate data over a wide range of operating conditions, with a relatively few number of experiments. This statement is actually incorrect. We are

fitting a mathematical model to the data, not the other way around.

Next slide.

As much as I'd like it to be the other way around, we're actually doing it the right way.

The central composite experimental design approach, also called a star square design, allows us to look at temperature and pressure and in this case, we will choose three levels in each factor, generating nine separate extraction conditions and then a regression using a full second order polynomial model involving six coefficients. We have first order terms in temperature and pressure and second order terms in temperature and pressure plus an interaction term.

Next slide.

This is a combination phase diagram and experimental design summary. Every talk dealing with supercritical fluids is required to have a phase diagram of carbon dioxide so here it is. This is one of the compulsories for SFE talks. If you're familiar with the critical point for carbon dioxide, 73 atmospheres 31 degrees centigrade... Above that point, we're in the supercritical fluid region or the supercritical region.

The nine dots there represent the central composite experimental design. It really is a combination of two techniques.

The star which you see in the middle is really the conventional one variable at a time optimization scheme. You set the, in this case, the temperature. By the way, the numbers here are...the first number is the temperature and the second number is the pressure. You set the temperature and you look at several pressures and then you set the pressures and you look at several different temperatures and that's really the way most of us have done our optimizations over the years.

Superimposed over this is a square or a box and that is a conventional factorial design where we're, through these four experiments simultaneously looking at high and low values for

each of the variables. If you throw all of those together, you get the central composite design and it does allow you to work with a full second order polynomial as a result.

Next slide, please.

Again, a summary, nine extraction conditions. We're using a dynamic extraction for 60 minutes. That is a continuous flow through the cell and we're collecting the sample in a vial which contains glass beads and a small volume of solvent and then we are using conventional analytical techniques for analysis. We are not using SFC.

Next slide.

These experiments were performed in a Super X SFE50.

Next slide.

The sample is held in this sample cell. We're using a 5 mL extraction vessel. There are some switching valves which control the pressurization of the system and the effluent exits from the top of the oven out through the restrictor area, which is shown on the next slide.

We've mounted our restrictors a 40 centimeter length of 50 micron fusilica capillary. It's simply a simple pressure restriction device. It's heated externally at about 50 degrees centigrade and then our collection is in the vial with glass beads here. The tip of the restrictor extends down into the glass beads.

Next slide.

There are a number of extraction cells available. This is an old Super X model. There's a new finger-type version which is available commercially and then this is marketed by Keystone Scientific, the TCT modification of the Keystone Scientific one.

This is what happens if you tell the technician to tighten it until it doesn't leak anymore.

The TCT modification will probably not be used in most laboratories.

Next slide, please.

We have two main applications. One of them is oil and

grease and the other is a subject that's dear to Bill Telliard's heart. That's the dirty, deadly and dangerous dioxins. Actually, you're looking at a suite of EPA methods here with oil and grease. There's a 413.1, in addition to the 413.2, and also a 418.1. Our reference mixture is hexadecane and chlorobenzene in this case and in both instances, we're using clay or celite or diatomaceous earth as our reference majors for our optimization.

Next slide, please.

This is a summary of the oil and grease methods, at least of 413.2, a 20 to 40 gram sample, a soxhlet for four to eight hours in freon. The sample or the extract is concentrated to 100 mLs and analyzed by FT-IR. This is an infrared method at 29-30 wave members so we're looking at aliphatic CH stretches. So it's a general screening tool for general...for aliphatic hydrocarbon contamination.

The 413.1 is simply a gravimetric analysis from this extract.

418.1 involves passing the sample with silica gel which removes the esters and leaves the petroleum hydrocarbons behind, the simple aliphatics and the 418.1, called the TPH or total petroleum hydrocarbons.

Our comparable SFE method uses a smaller sample size, about six mLs of freon and a 60 minute extraction versus four to eight hours. In this case, we dilute to 10 mLs, rather than concentrate and then again can do FT-IR.

Next slide.

Just as an overall summary of how these methods are working, our soxhlet procedure generated 97 percent recovery for four...actually in this case eight replicates. This was spiked hexadecane onto celite. We have a room temperature shaker method which we also use, which gives slightly lower recoveries and then the SFE method generated about 91 percent recovery. This is a summary of the 13 extractions performed for the experimental design. Not all of them optimized. So even including the non-optimum conditions, we still get a very high recovery with SFE.

Next slide.

If you pull out the results from the regression from the experimental design approach, we get a profile that looks like this in terms of temperature on this axis and pressure on this axis. It's a fairly flat response surface. But in this triangle in the lower left half, it's really the high recovery region. All of the recoveries in this area are in excess of 90 percent and the recoveries fall off a little at high temperature and high pressure. But basically over a wide range of conditions, we can get high recovery of hexadecane from celite.

We were very pleased with that result. It meant we probably had a fairly rugged method. We next evaluated SFE with several real samples and one low level soil by all three methods, the soxhlet, shaker and SFE approach. We found a very good agreement between the soxhlet and the SFE approach...comparable standard deviations. These are for a minimum of four replicates. High level soils...higher level, I guess...around 1,000 milligrams per kilogram. We find a little bit lower recovery in the SFE numbers, about 60 to 70 percent of the corresponding soxhlet number and somewhat better agreement with some of the shaker...one of the shaker numbers.

We're encouraged by this because we're certainly within a factor of two in each case for the SFE versus soxhlet.

Next slide. Could we have the transparency on now, please?

These are some more recent data we have which are a more rigorous comparison of the methods. Again looking at the gravimetric numbers, we actually have two different SFE experiments now, a dry collection which is simply allowing the CO_2 to evaporate into a volumetric in this case and then weighing the viable before and after and then collecting in freon and using the conventional EPA methods for a workup.

We see for the dry collection excellent agreement for the oil and grease number between those two methods. A little

bit low, but not too bad for the TPH number. The freon collection is just over half the oil and grease number and probably 70 to 80 percent of the TPH number. In this case, the SFE vial was actually heated to constant mass to make sure there was no water in that gravimetric determination and this sample was extracted as received in all experiments and these are summaries of at least four replicates in each case.

Next transparency, please.

This is a second sample which has somewhat higher levels. In this case, we get good agreement, again, between the SFE numbers and the soxhlet values by gravimetric means. The oil and grease value for the freon extract from SFE is very comparable...very good agreement with the soxhlet number. And again, the TPH numbers are also in good agreement. In this case, the dry collection seems to be a little bit low. I'm not exactly sure why. In think in general we're finding the SFE numbers vary between 50 and 100 percent of the corresponding soxhlet values. This sample was moist and it was mixed with sodium sulfate before extraction, which is the conventional procedure for soxhlet. We also used that same approach for the SFE experiments. But you can see in general we're generating comparable data sets with the SFE approach.

That's all for the transparency. If I could have the next slide, please?

The next thing we wanted to look at was a comparison of SFE with the conventional procedures and with our existing setup, we felt a single technician could prepare about eight soxhlet samples a day and roughly six SFE samples. We get high recovery in both cases. The cost of materials is weighted heavily in SFE's court there. Most of this cost...in fact, all in this case is the cost for freon. We're estimating with rinsing and glassware cleaning, it requires about 500 mLs of freon. Freon is presently costing us about $100.00 for four liters. The cost here for SFE are roughly 10 mLs of freon and about $1.25 for the

actual supercritical fluid, the supercritical CO_2. So, there's considerable savings in this case, especially when we're only charging about $30.00 for the analysis to begin with. To have half of it tied up in solvent costs means it's not a terribly profitable venture.

The SFE approach offers a lot of advantages there and this six per day is a very conservative estimate on the low side. This does not incorporate any automation which is going to be coming in the next generation of SFE instruments.

Next slide, please.

In summary, we've got excellent recovery from a model matrix over a broad range of operating conditions and the results, we feel, are comparable, probably realistically in the 50 to 110 percent range, compared to the soxhlet.

One of the big issues in environmental methods, we are minimizing the use of freon. We've eliminated 98 percent of the freon required for this method. We've reduced the use from 500 mils, roughly, to about 10. That's going to have a tremendous advantage in our waste stream. It has a tremendous advantage in the air quality since much of that 500 mLs is often evaporated during workup. And certainly, automation is going to improve things considerably.

Next slide.

I can't go away without talking about dioxins very briefly. EPA Method 8290 or 1613 involve soxhlet extractions and three column steps. We have worked on an SFE method which, in this slide, eliminates all of the column steps. That's probably unrealistic across the board. We expect that we'll probably have to incorporate the carbon column in a routine method, but we feel we can probably eliminate the silica gel and alumina steps.

Next slide.

If you look at the regression information from the experimental design, you get a much different profile for TCDD. Basically, we find optimum conditions for extracting TCDD are at

much higher temperatures than this conventional wisdom. Conventional wisdom has most people working up in this upper corner here where things are a more slower recovery. It partly explains why a lot of the work with TCDD and carbon dioxide has been very disappointing. In fact, some of our work we reported two years ago was disappointing because we were working in this region. We now have more information that temperatures are much more important....variable. Unfortunately for CO_2, we still don't get good recoveries with dioxins.

The next slide explains partly why that is. Looking at the recoveries as a function of time, you see up to two hours from some samples. We are still extracting samples out. In fact, they're just beginning out. So we have in this case a kinetic problem with extraction.

The next slide summarizes the same results for the furans and, again, we see at two hours we're just beginning to extract the majority of the materials. So, we think we have a kinetic problem with CO_2 that will probably prevent it from being used. Fortunately, we have some other alternatives. One of those is summarized in the next slide and that's another picture with a CO methanol mixture. This is, again, an experimental design summary. We get a different profile...more interesting, but still it's telling us that high temperature and pressure are probably the way to go in this system and we don't have corresponding dioxin extraction for that same matrix. I believe that kinetics will be faster here.

The next slide shows one other application we've developed and that's using the empore disks, which are marketed by 3M and Analytic M. They involve a C_18 matrix or C_18 particles which are embedded in a teflon membering matrix and you simply pass your aqueous sample through the membrane and the organics are trapped inside. We have spiked dioxins...the suite of dioxins into water samples, extracted with the empore disk and now we're looking at a supercritical fluid extraction of the

empore disk, rather than a soxhlet or convention solvent extraction. The results are summarized in the next slide.

We can see spiking at 160 picograms per liter for the tetra, hexa and octas. Spiking directly on the disk, we can get pretty much quantitative recoveries at the higher levels of chlorination. A little bit lower for the tetras, but probably within the range that we see for some of our other methods. If we actually do the spikes in water, we see recoveries drop a little bit, which could be due to a number of other factors. But basically, even at this spike level, we're getting most of it back at the higher levels of chlorination and with a little bit of fine tuning, we can probably improve the tetra numbers, too.

But again, we're doing the CO_2 methanol extraction of the empore disks. So in this case, we've eliminated the use of organic solvents except for the dissolution of the final extract for GC/MS analysis.

Next slide.

In summary, we've demonstrated slow extraction rates with CO_2 for the dioxins and furans. Our preliminary data indicate that CO_2 methanol is going to offer some improvement. There is information in the literature that nitrous oxide also may be even better. We feel for a number of samples we're able to reduce the analyte enrichment requirements, eliminating perhaps two or three of those open column steps. But certainly at this point, we need to do some more optimization.

Last slide, please.

I'd like to acknowledge my colleagues at Twin City Testing and Super X Corporation which has also provided partial support for this work.

Thank you.

MR. KING: Questions?

NO SLIDES AVAILABLE
FOR THIS PRESENTATION

MR. KING: Our next speaker is Bill Budde. He's found his way here from EMSL, Cincinnati. He's going to talk about recent work that EMSL has been doing on LC/Mass Spec.

MR. BUDDE: Thank you very much. I want to thank especially Bill Telliard. I don't know if Bill is in the room today. Is Bill here?

MR. KING: He's upstairs putting out a fire.

MR. BUDDE: Bill's upstairs putting out a fire, I was told.

Anyway, I am sure all of you know Bill Telliard and his enthusiasm for his work, his marvelous sense of humor, his dedication to environmental protection, and his friendly style at all times and I want to thank him for inviting me here and asking me to say a few words about liquid chromatography-mass spectrometry, which I refer to as an emerging technology for environmental analysis.

Before I go on and this is off the record, so please don't take this down. I wanted to show you a side of Bill Telliard that's not often seen. You all see him running around here organizing this symposium, doing his other work. You don't often see him back at his job where he works in Washington as a person who covers his in box well...covers his in box well and his out box. So, sometimes you might want to ask Bill about that.

Before I begin, I want to say that we've had a program of research to develop liquid chromatography-mass spectrometry and methods for environmental analyses for a number of years. Among other co-workers, I'd like to introduce Thomas Behymer who has been with us almost four years now. He received his PhD from Indiana University from Ron Hites, who was up here earlier this morning. Also, Thomas Bellar has been working on this project. Tom is the inventor of the purge and trap method for volatile organics in water. Jim Eichelberger has been working with me for about 19 years and we're still working together, believe it or not, and Jim Ho, a chemical engineer on our staff who is also working on this project. It gives you a little hint of what you might need to make liquid chromatography-mass spectrometry work;

that is, a PhD in chemical engineering.

I don't have pictures of all of the staff and all of my co-workers here, but here's certainly Tom Behymer, and for those of you who do not know him, Tom Bellar. Jim Ho and Jim Eichelberger are not on this picture and the other person there no longer with us...regrettably.

The objective of our work is to develop a broad spectrum liquid chromatography-mass spectrometry method for the simultaneous identification and measurement of what I would call non-gas chromatographable materials. In other words, we'll define non-volatile as being not amenable to gas chromatography toxic organic environmental pollutants. This would be the LC/MS equivalent of capillary column GC/MS. That is an ambitious goal, very ambitious, and we're not there yet, but perhaps we will be in a few years.

Why do we want to do this? We want to do this because there are a number of compounds which in some cases are marginal GC analytes and in other cases simply are not amenable to gas chromatography at all. I give you an example of the carbamate pesticides. Carbamates contain a carbonyl group...nitrogen on one side, oxygen on the other and often are a methyl carbamates because these compounds are derived from methyl isocyanate. If an R group was alpha naphthol the carbamate would be carbaryl. Carbamates are sensitive to temperature and to gas chromatographic injection system or column. They tend to lose the elements of methyl isocyanate.

Another group of compounds which are pesticides are the thio-ureas which contain a carbon sulfur double bond with a nitrogen on either side for example, ethylene thio-urea, which is not only a pesticide but a metabolite of other pesticides. Other compounds are the ureas with a carbonyl group and nitrogen on either side. A number of these are used commercially: diuron, linuron and siduron would be three examples.

I'm just showing you examples of the types of compounds. Another one which is rotonone, a natural product that

happens to be a pesticide also. It's been used to kill fish, if you want to get rid of all the fish in a pond. It's a very sensitive compound and has one, two, three, four, five ether linkages and unsaturation in a carbonyl group and in a gas chromatographic injection port of a GC column, this has no change whatsoever. It decomposes quite easily.

Another group of compounds are the benzidines. Benzidines are important for a reason which I'll give you in the next slide. Benzidine is basically a diphenyl system, two amino groups, and often substituted in the three and three prime positions with methyl, methoxy, chlorine and so on. Benzidines are important because they are used in a class of azo dyes. This happens to be one example. Color index Direct Red 2 is an azo dye, a sulfonated azo dye. But you see there's an azo group right here and an azo group right here and these azo groups are susceptible to reduction under anaerobic conditions as in anaerobic sediments, sewage, landfills and biological systems and reduction of this azo group here to form an amino, reduction of this azo group to form an amino here would release three, three prime dimethylbenzidine to the environment or to the biological system and that's a known human carcinogen. In fact, all of the benzidines I showed on the previous slide are known human carcinogens. So, the benzidines are of great interest because these azo dyes are widely used in large volume commercial chemicals and a number of them still incorporate the benzidine groups.

I think, before we proceed, I will just give you a little review of the status of liquid chromatography among EPA's approved analytical methods. I'm particularly referring to the drinking water methods, which would be the 500 series, waste water methods, the 600 series, and the 1600 series, perhaps.

If you look at what has happened over time, beginning in '79 up through about '89, for a 10 year period, these methods are the number of gas chromatography methods...just the number of methods which employ gas chromatography among those EPA approved

methods...and these are the number of methods which employ liquid chromatography for non-volatile compounds. As you see, there's been a tremendous growth over the years from something like 10 in 1979 to over 33 in 1989 and that's still grown a little bit until 1991 in gas chromatography, whereas liquid chromatography methods were rather dormant. We were stuck on two for a long time...recently jumped up to seven. I'm predicting that for the 1990s we'll see very little growth in gas chromatography methods. I think the compounds and the environmental interest that can be exploited and analyzed by gas chromatography has been pretty well accomplished. There will be continuing improvements in these methods, to be sure, but not many new methods. I think there will be a continuous and an accelerating growth in liquid chromatography methods as we look at more and more of these non-gas chromatographable compounds in environmental samples.

Let's see if I can focus here. I don't have a remote focus, do I? Can someone touch up that focus a little bit?

This is in the handouts, so you may not want to write it down, but I thought I would throw this up. This gives you an idea of some of the activity we've been engaged in, particularly journal articles published by EMSL, Cincinnati. This will be in the proceedings because I left it with the people who are publishing that. We had an article on thermospray in Analytical Chemistry in 1988, a very definitive article, I think, a wide-ranging evaluation of thermospray. Later, we switched our attention to the particle beam and the carrier effect, particle beam in another recently published paper, and a paper in Environmental Science & Technology, on thermospray. So these are the sources of more information about what I'm going to say this morning. I simply cannot cover all of the material and all of the information that's been developed in this short presentation. So, if you're interested in more information, I would suggest any of these articles.

The kind of liquid chromatography/mass spectrometry I want to discuss today has to do with sprays and aerosols. There

have been many different types of liquid chromatography/mass spectrometry interfaces proposed and studied over the last 10 or 15 years. Some of these have been more successful than others. The one that we have been concentrating on lately in our work has to do with sprays and aerosols and this picture is courtesy of Marvin Vestal of Vestec Corporation, who is one of the inventors of this type of interface. In effect, what you have with a spray on aerosol generator is a liquid chromatographic effluent coming out here and by some means or another, we convert this into a spray or an aerosol which is billions and billions of tiny droplets of the liquid phase. And, of course, the non-volatile analytes that are swimming around in these little droplets do not realize what has happened to them. They think they are still in a perfectly happy liquid state. They're dissolved; they're in solution. They don't know that they're flying through the air and about to become a gas phase analyte. That's why this type of interface actually is so attractive and why it works.

The ways to generate sprays and aerosols and there are...Four I've listed here for common ones. One is the pneumatic approach in which you use a gas...helium, for example, and mix that gas with your liquid, emerging from the liquid chromatograph and form a spray.

Another variation on that is the heated pneumatic in which you not only heat the liquid, but you also apply the gas.

A different version and really the first one...this one should have been at the top...is thermospray. Thermospray does not use a gas. It does not use a pneumatic approach. What it does is it heats the liquid chromatographic effluent. It heats the mobile phase and converts some of that mobile phase into a gas which then acts as the nebulizing agent to form the spray or the aerosol. Recently, we've seen some work published and some advances in using ultrasonic systems to form sprays or aerosols for liquid chromatography/mass spectrometry.

Most of the work I'm going to talk about is going to be concerned with the pneumatic and the heated pneumatic. I'm not

going to say a whole lot about these other, but in general, we can use any of these techniques to form an aerosol.

I want to take a little bit... If you could touch that up and see if that's a little better in focus there, I would appreciate it.

This is kind of a generalized schematic diagram of particle beam LC/MS interface. This is the mobile phase from the liquid chromatograph coming in under high pressure and an aerosol nozzle. If we're using a pneumatic system, that is, if we're using helium or a heated nebulizer to form a spray, then we need to supply that gas. If this was a thermospray or an ultrasonic nebulizer, we wouldn't need this supply here, but we'd need it over here anyway. This sprays into a chamber which is usually heated. We have our billions and billions of little droplets of mobile phase now in a spray or aerosol form and regardless of the type of nebulization we use here, we now have to...if we haven't added a gas here, we have to add it here, as in the case of thermospray or ultrasonic in order to provide a carrier effect to push these particles in the direction we want them to go, which is over here, which is the ion source of the mass spectrometer.

This nozzle or beam columnator, you might call it...a nozzle, separates this desolvation chamber from this chamber which is evacuated with a pump and a skimmer, which has a small hole in it, a second chamber, another vacuum pump, and finally, a chamber over here which leads directly into the ion source of a mass spectrometer. What happens, of course, is as we move these particles containing our non-volatile materials through this desolvation chamber which may be heated...usually it is and not very high...we get some evaporation of solvent. The particles as they move through the nozzle pick up speed because they're being pushed in this direction and we're pumping on this side. They may reach supersonic velocities over here. Because of the momentum of these particles, their mass and their velocity, they tend to move straight ahead whereas solvent vapor, helium and other gases entering this chamber tend to be pumped out. So, in

fact, from maybe slightly less than one Torr, you get down to 10 to the minus five over here and you have a beam of particles and these are little droplets of solvent containing our non-volatile materials. As they pass through these systems, more and more solvent evaporates.

Now there are many variations on this basic design commercially available. Usually the desolvation chamber walls are solid walls. They're metal and they're heated, as I pointed out. In one variation, however, by one company, in particular due to Marvin Vestal, these walls, in fact, are made of teflon or some other membrane and there's another gas on the outside sweeping along and sweeping away solvent and what happens is that the vapor and the solvent molecules pass through the membrane and are swept away and so we get some reduction in solvent in this chamber, as well as this chamber and this chamber. So there are several variations.

There's another device, I've heard, which uses a three stage momentum separator. This is the momentum separator region where you're separating the particles and the gases by their momentum. That's the basic design. Some of you would probably recognize that if you chopped off the momentum separator and threw it away, drilled a hole in the solvation chamber and stuck a mass spectrometer right here, you'd have the classic thermospray device. That's what a thermospray originally was as invented by Vestal. It didn't have the momentum separator on it. Putting the momentum separator on is merely a refinement to bring thermospray and these other methods of generating aerosols up to a higher state of performance.

The method which I'd like to discuss briefly is what we're calling Method 553. It's the determination of benzidines and nitrogen-containing pesticides, the ureas, thio-ureas and carbamates I mentioned, in water. We use both liquid-liquid extraction and liquid-sold extraction and I might also add that we're experimenting with the techniques similar to what was described by the previous speaker; that is, using the liquid-

solid extraction and then using supercritical fluid CO_2 to extract the cartridges or the disks in this particular methodology. We also use reverse phase high performance liquid chromatography particle beam mass spectrometry and we've been working with three different systems, three different designs of the basic particle beam interface. This happens to be rev 1 of this method which was made available in July of 1990. We expect to have rev 2, or maybe it's 1.2 or something like that...1.1...I'm not sure...available this October. As I mentioned before, Tom and Tom and Jim have all worked diligently on this and are responsible for most of the information that I'm presenting.

This is not a typical total ion current profile from our LC/MS particle beam system. This is absolutely the best one we have. There's no reason to show one of the ones that isn't the best. But so far, this is one of the best. This is done with a reverse phase C18 column packing by Waters, called Novapak. It is a very low bleed. It's very important to have a low bleeding column. We're seeing in liquid chromatography pretty much the same thing we saw in gas chromatography. In the beginning of gas chromatography, 20 or so years ago, when they used certain types of detectors, non-mass spectrometry detectors, they didn't realize the column packings bled. When someone put a mass spectrometer on, they found the bleed and then the manufacturers fixed that problem and got non-bleeding columns. The same thing in liquid chromatography. There's a lot of LC columns out there that have been used with UV detectors and no one knew they were bleeding until we put a mass spectrometer on it. We found the bleed and the problem with the bleed. Now we're seeing much advance in liquid chromatography columns and the bleeding problem is going away.

This is a group of about 15 compounds that are included in Method 553. As I mentioned, most of them are cleanly separated and identified by abbreviations in the slide but, for example, this is 3,3'-dichlorobenzidine and linuron and rotenone.

If you remember, rotenone is the natural product with a complex structure and five ether functions and a carbonyl and unsaturation.

In addition to this being a total ion current profile, this happens to be a gradient elution. In the early part of the chromatograph where you're running about 25 percent acetonitrile, 75 percent water, and as we go through the gradient elution, we end up with about 25 percent water and 75 percent acetonitrile. So, it's a gradient elution and we also have present 100th molar ammonium acetate in the solution in order to facilitate the liquid chromatography and do some other things, which I can't really go into at this time.

The mass spectra that you get though really do look like electron impact spectra. I know this isn't new information. It's been known for a few years that by whatever process that goes on, when these little particles enter the heated electron impact ion source of a mass spectrometer, they form...the solvent goes away, the ammonium acetate disappears and what you see are what appear to be classical electron ionization spectra.

In this particular case, for example, we're using 3,3' -dimethoxybenzidine, molecular ion at 244. There are no signs of ions here due to ammonium ions of any type, M minus 15 and then a loss of CO, presumably from this, a spectrum which looks very much like the spectrum that you would obtain from GC/MS. In this particular case, this compound is what we would call a marginal GC/MS analyte. It doesn't work very well, but you can actually get it through and compare the spectra and they pretty much look alike.

Let's see. Another example...well, here's rotenone, the one I was talking about before. You have no hope of getting rotenone through a gas chromatograph, but it's electron ionization spectrum is known, using a direct insertion probe and the spectrum from the liquid chromatography particle beam mass spectrometer is remarkably alike, similar to the direct insertion probe. They're even showing a little bit of a molecular

ion...about 10 percent at 394 and a major fragment at 392. So the spectra that we're getting from these systems, all of the systems that I've talked about, are real EI spectra.

As you might expect, we've investigated the possibility of finding a test compound, one that we could use to evaluate the performance of an LC mass spec system and we tried our favorite compound, which is decafluorotriphenylphosphine and that was simply too volatile for this system. But there is an oxide that forms from DFTPP which is really a very nice compound. It's a little bit more polar, liquid chromatographs very nicely, and I'll show you the spectrum of it later. I just put the masses in there. The molecular weight of the compound is 458 and we're calling it DFTPPO. I'll show you the composite spectrum of that in a few minutes.

Estimated detection limits using this methodology varies. Now in this particular case, we're showing three systems: System A, System B and System C. They're all commercial products and if anybody wants to know what they are, I'll be glad to tell them. Just see me after the talk. But the remarkable thing is that we've seen very similar performance with all three of the commercial particle beam systems. You can see ethylene thio urea, approximately five nanograms. This is amount injected in nanograms.

These are the estimated detection limits, based on a 3:1 signal to noise ratio for the quantitation ion. For many of these compounds, if you drew a line across here, you can see many of these compounds are well below that. Many of them are well below even 10 nanograms. In particular, the benzidines, although there are some differences in interfaces. Look at benzidine right here. System A and System B around five nanograms...System C up around 30 nanograms. That persists to this day and we don't quite understand this.

This is methylbenzidine. In that particular case, System A and System C did better than System B. I think this is methoxy. I'm sorry. This is 3,3'-methoxy. This is 3,3'-

dimethyl.

Here's the 3,3'-dichlorobenzidine. You see there's 30 nanograms here or so...20 nanograms here. But for System C, 100 nanograms. So there are some remarkable differences. Rotenone is an interesting one. You see, rotenone for System A requires almost 70 nanograms, System B, 40 nanograms. System C is a rotenone machine. It will do five nanograms. So, there's some differences here which we don't understand and this data is pretty reproducible. This doesn't represent just one experiment, but any number of experiments that are summarized on this graph.

For the reason that...a number of reasons...we conducted a small multi-laboratory study. It was actually conducted by our Quality Assurance Research Division and we concentrated only on benzidine, 3,3' dimethoxy, dimethyl and dichloro. We took the four benzidines and included them in the study and we did not include the extraction step in that particular multi-lab study. Again, I want to acknowledge our Quality Assurance Research Division in EMSL, Cincinnati, which orchestrated this study.

If you could focus that up, I would appreciate it.

The four benzidines were included and it was only the determinative step of the...that is, the liquid chromatography and the mass spectrometer. We didn't include extractions in this preliminary multi-lab study. However, we did include 13 laboratories. I think it should add up to 13. I didn't check it. When I made out the slide, there were four Hewlett-Packard systems, which were pure Hewlett-Packard particle beam LC/MS systems. There was one system using a Vestec interface and HP otherwise. There were two systems using an HP...I'm sorry, a Vestec interface and a hybrid Vestec HP spectrometer with a Techninet data system. There was one pure Extrel. There was sort of an Extrel interface with an Extrel spectrometer and somehow an Incos data system. I don't know who put that together. Some of you may know these labs by the strangeness of the combinations here; I don't. There's an Extrel interface with

a Finnigan TSQ spectrometer and an Incos data system and a VG with a Finnigan-MAT. That's a magnetic machine with an Incos and, finally, a General Electric interface. That's an ultrasonic with a Joel mass, a magnetic machine. So, there are some 13 laboratories that participated in this little study of the determinative step of Method 553 with only the four benzidines. We wanted to see how this would work on a multi-lab basis, and the answer is on the next slide.

This is the easy slide. This is multi-laboratory accuracy. I will say of the 13 laboratories, two laboratories' data had to be discarded because they were clear statistical outliers and it wouldn't be fair to average those numbers in with the other 11 because they were just screaming statistical outliers. Even I could accept that. But, if you take the remaining 11 sets of data and average them out...this is benzidine...this is methoxybenzidine...this is the dimethylbenzidine and this is the dichlorobenzidene...there were two different concentrations. The double crosshatch is 10 micrograms per liter and the other one is 100 micrograms per liter equivalent and the mean and multi-lab accuracy in measuring those four compounds is across here and you can see it's right around 97 percent or so. Those are mean accuracies again. That doesn't say anything about precision at this point. So, the accuracy we're very pleased with in terms of measuring those four compounds.

The precision is in this slide. Again, there are two bars because there's the 10 microgram per liter and the 100 microgram per liter equivalent. These are RSD numbers, relative standard deviations, going from zero to 22.

This is the multi-laboratory precision of the 11 facilities. You see if you draw a line across here, you'd see that, in fact, all of them at 100 micrograms per liter are under 10 percent. When you go to 10 micrograms per liter, even one of those...benzidine itself is under 10 percent. One of them gets up as high as 20 percent and the other ones are in this range.

Now, the statisticians that we have on our staff by some wondrous process that I don't understand are able to convert multi-laboratory precision data into single analyst precision data. That is, of course, an estimate of what a single analyst would get, based on the multi-lab data and you can see, again, the RSDs for these, if you draw the line across here, are all under 10 percent for a single analyst except this one measurement of...that would be 3,3'-dimethoxybenzidene at 10 micrograms per liter.

So we were very pleased with these results and, again, I think you'll be hearing more about this study as time goes on.

I also wanted to tell you a little bit about decaflurotriphenylphosphineoxide. This is not a single spectrum measured, but this is the composite spectrum measured by all 13 laboratories in the study. What we did is we simply averaged the intensities together of the ions that you see and this is the composite, a molecular ion at 458, about 25 percent...M minus...let's see that would be a loss of a fluorine, I think...38...58...no, it's HF...loss of HF. It must be knocking off one of these two HFs or M minus 20 at 438. Base peak generally at 271 and a number of ions and you can see why this compound is so attractive as a performance test compound. It has a range of ions of significant intensity, ranging all the way from mass 77, even mass 69, all the way through mass 458. We've looked at some ranges of reasonable performance and we've also found two correlations where if certain conditions are present, which are not desirable on the LC/MS, this ion will drop down like mad and this one will go up like mad. We also see other conditions here these ions will disappear and will get weighted down here. So we look like we have a good performance test compound and it's diagnostic for problem conditions in the system.

Conclusions: I would like to make, and I didn't show you any slides on this and you'll really have to consult some of the papers and the literature because we just don't have time to

go into all of these things, but there is a strong tendency towards non-linear calibration in this particular type of system. We used second order regressions for quantitative analysis. There are some alternatives. For example, isotope dilution analysis will straighten this out and make it linear.

There is a co-elution effect and that's the explanation for this. I won't go into this at this time. It's in the literature. We don't think this is necessarily true anymore. External calibration is certainly one option and that's what was used in the multi-lab study. But it looks like if the isotopically-labeled compounds are available and they were in a few cases that we've studied, you can use those very nicely and get a very linear calibration.

The performance of the three systems are similar for most compounds, but I did mention the fact that rotenone and there are some other exceptions where one or more other type of instrument may give you significantly improved performance.

The precision and detection limits have been improved significantly over the last three years or so by incorporation of method controls. Now, you've seen those method controls if you looked at any of the 500 or 600 series methods and in particular, one that I mentioned happened to be column bleed. Column bleed can have a significant effect on precision and detection limits.

Detection limits and short term precision are acceptable for environmental analysis and we think that long term stability will be improved and is being improved in the current commercial instruments.

So this is the end of my presentation. I have one more slide which is off the record again. I don't know if Bill Telliard has come into the room, but I want to congratulate Bill for this wonderful conference because he is not doing what is depicted on this slide, which says: Let's leave the public in the dark. It works for government; it should work for business. Bill doesn't do that and he has arranged a marvelous meeting here which I know is in its 17th year in which we all have the

opportunity to share some of the things we're doing with all of you folks in the public.

Thank you very much. I'll be glad to address any questions.

QUESTION AND ANSWER SESSION

MR. BICKING: Bill, the high res dioxin methods use a lock mass approach for monitoring performance during the run. Do you anticipate or have you looked into possible applications for lock mass with LC/MS?

MR. BUDDE: Lock mass is made capable by the fact that you do have a high resolution mass spectrometer.

MR. BICKING: Right.

MR. BUDDE: That's what makes it possible.

MR. BICKING: Right.

MR. BUDDE: We've been doing all of this work with a nominal mass resolution mass spectrometer and so we don't have that capability. But if we ever find another dioxin and it's not volatile, we can put an LC on a high resolution mass spectrometer and certainly that would be a viable approach.

DR. HAEBERER: Fred Haeberer, QAMS, EPA.

Bill, you very cavalierly addressed the ammonium acetate liquid phase modifier and said, it went away...it goes away. Yet in your spectrum of DFTPPO, I noticed a strong 77 MO ratio. Was that run with the acetate modifier in there? Is that what we're looking at? What's going on?

MR. BUDDE: Well, in that particular case, no. When I said ammonium acetate goes away, we don't see any trace...any ions in the spectra that are attributable to adduct ions from ammonium acetate. The 77 in that case is due to the unfluorinated phenyl ion. On DFTPP, there is one ring which does not contain fluorine and probably forms an ion and that's probably the reason for that ion.

Ammonium acetate is very important in these analyses and I didn't take the time to go into it.

DR. HAEBERER: I understand that completely.

MR. BUDDE: Yes, ammonium acetate facilitates chromatography, but more important, it does give us some enhanced signals for some of these compounds and we just don't have time to go into that. But, it's...

DR. HAEBERER: But you're not seeing it at all?

MR. BUDDE: No, there's no evidence that ammonium acetate participates in the mass spectra. However, it would be there, of course, in lower masses and we don't scan those masses. We don't scan much below 77.

DR. HAEBERER: Very good. Thank you.

MR. BUDDE: Thank you again for your attention. Let's go to lunch, I guess.

MR. KING: Thank you very much. Let's break for lunch and get back here promptly at 1:15. The statisticians are going to do their magic and I'm sure you don't want to miss any of that.

(WHEREUPON, a brief recess was taken for lunch.)

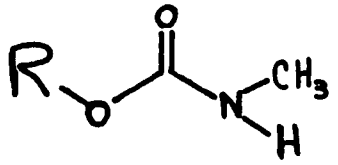
OBJECTIVE

TO DEVELOP A BROAD SPECTRUM LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY (LC/MS) METHOD FOR THE SIMULTANEOUS IDENTIFICATION AND MEASUREMENT OF NON-GAS CHROMATOGRAPHABLE (NON-VOLATILE) TOXIC ORGANIC ENVIRONMENTAL POLLUTANTS.

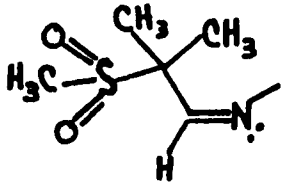
(THE LC/MS EQUIVALENT OF THE CAPILLARY COLUMN GC/MS METHODS)

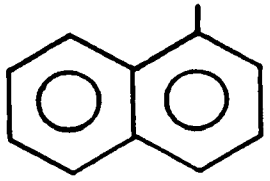
CO-WORKERS AT EPA

- THOMAS D. BEHYMER, PH.D.
- THOMAS A. BELLAR
- JAMES W. EICHELBERGER
- JAMES S. HO, PH.D.

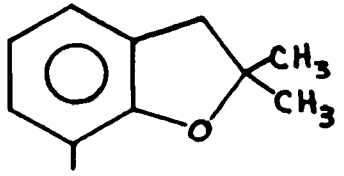


ALDICARB SULFONE

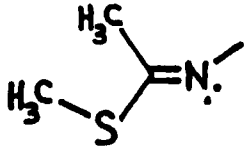




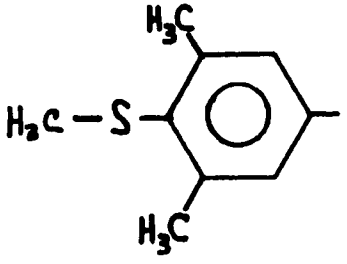
CARBARYL



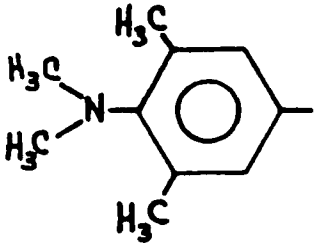
CARBOFURAN



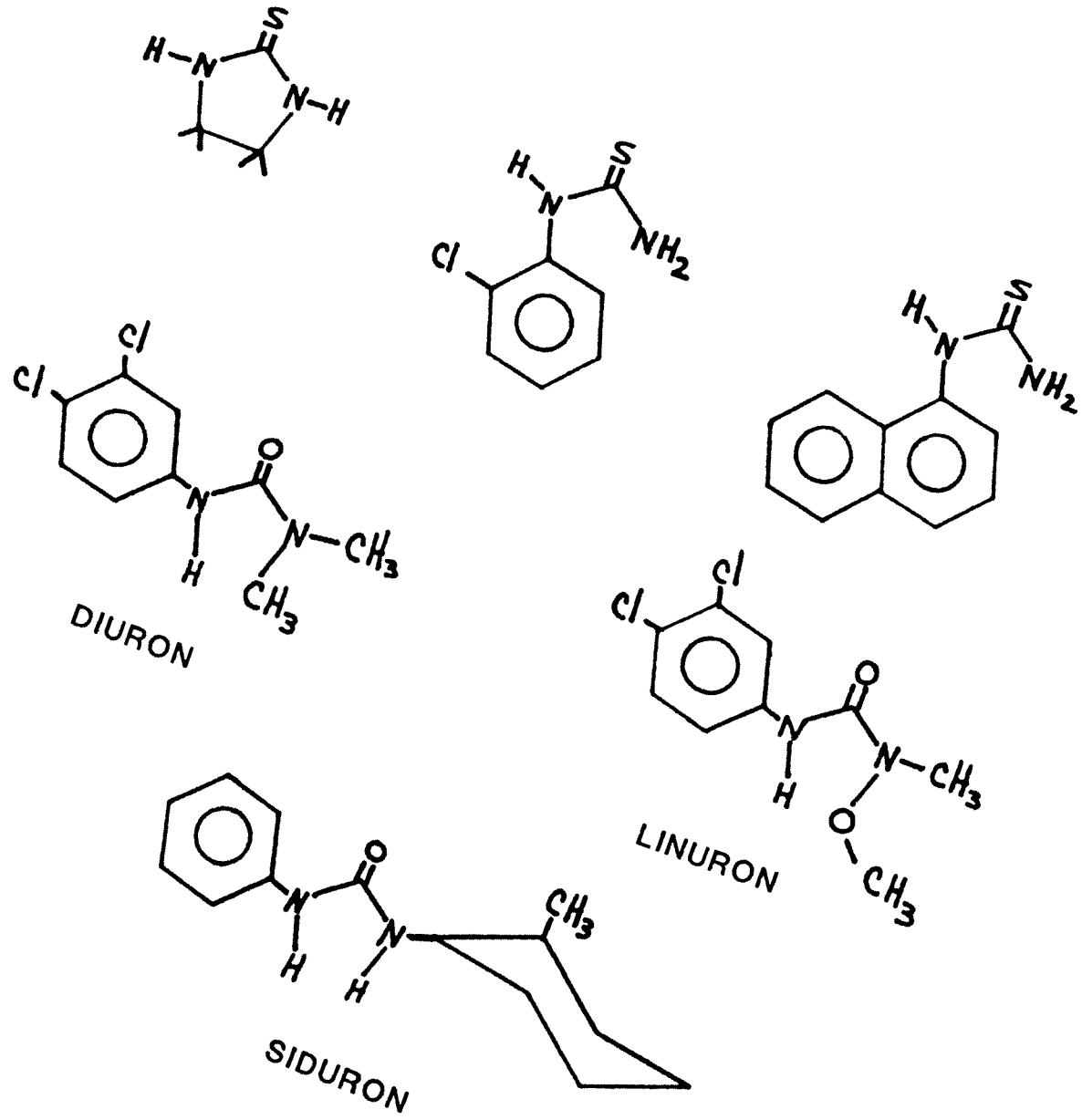
METHOMYL

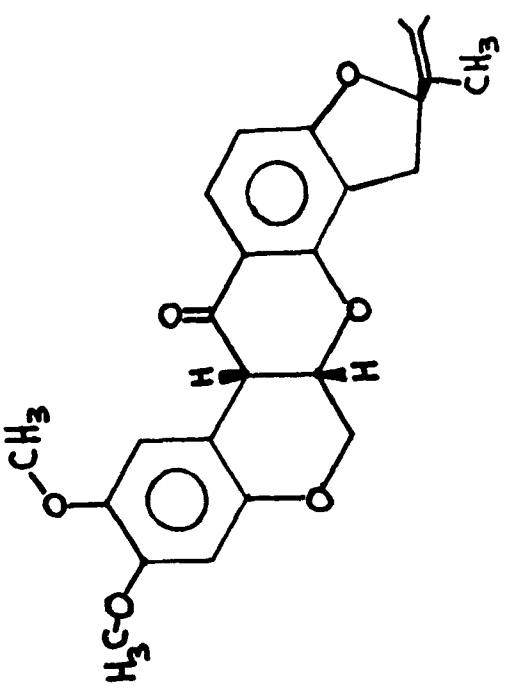


METHIOCARB

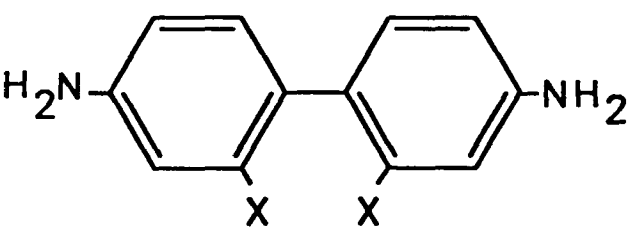


MEXACARBATE


DIURON
LINURON
SIDURON

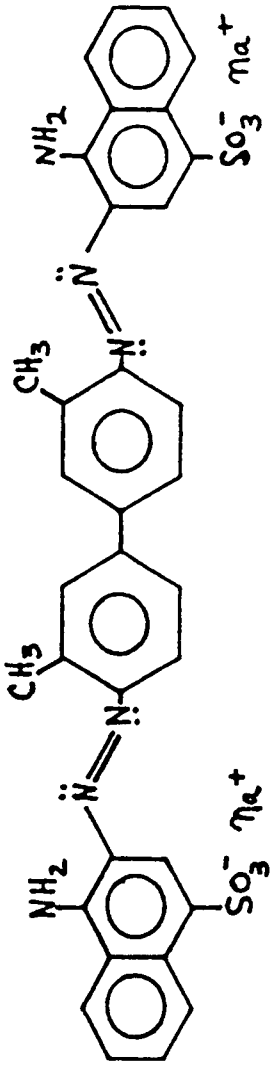


ROTENONE

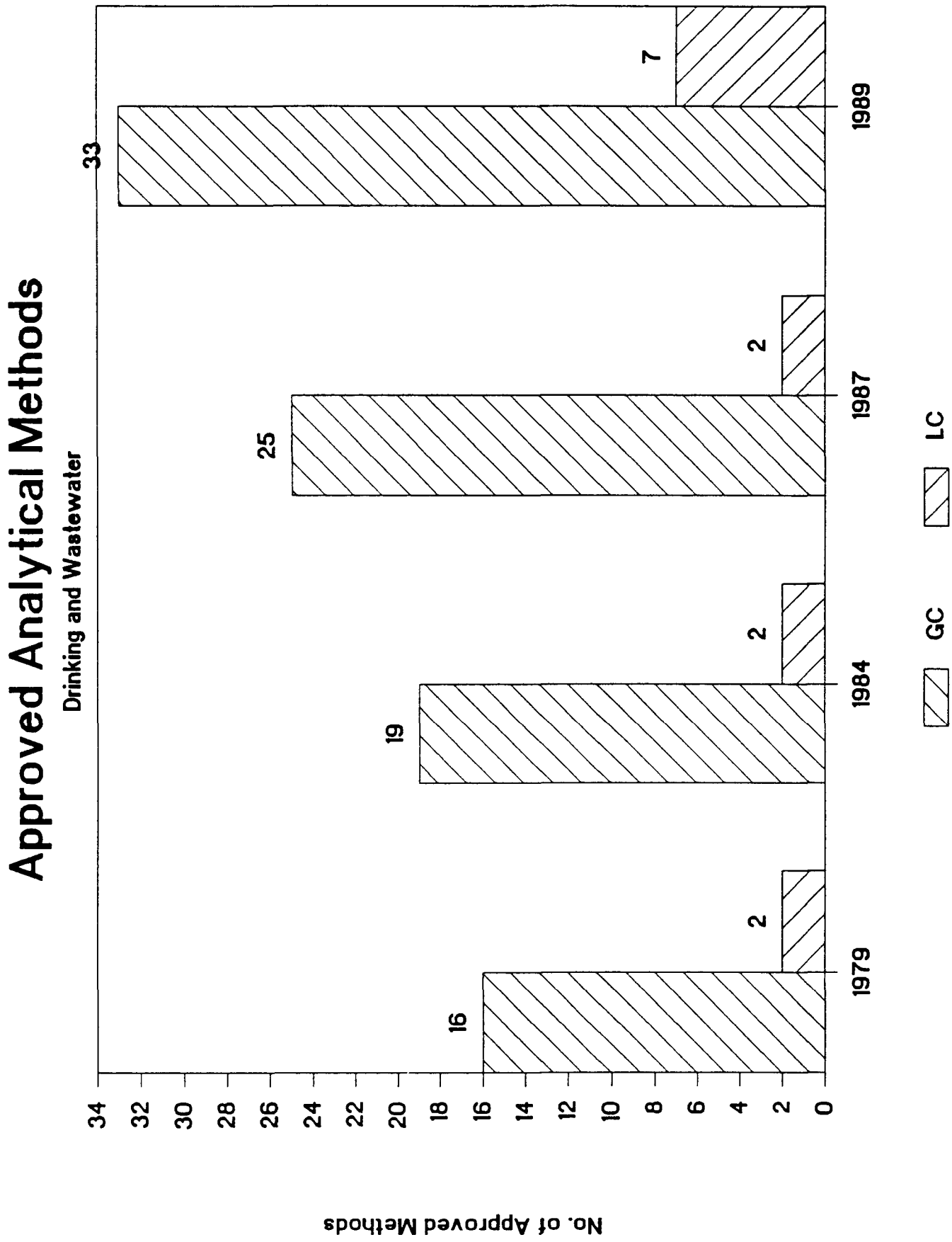


X = H, CH_3, OCH_3, Cl

Benzidines



C.I. DIRECT RED 2


Approved Analytical Methods
Drinking and Wastewater
No. of Approved Methods
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
16
2
19
2
25
2
33
7
1979
1984
1987
1989
GC
LC

METHOD 553

DETERMINATION OF BENZIDINES AND NITROGEN-CONTAINING PESTICIDES IN WATER BY LIQUID-LIQUID EXTRACTION OR LIQUID-SOLID EXTRACTION AND REVERSE PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/PARTICLE BEAM/MASS SPECTROMETRY

REVISION 1.0
JULY, 1990

THOMAS A. BELLAR
THOMAS D. BEHYMER
JAMES S. HO
WILLIAM L. BUDDE

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

EMSL-CINCINNATI LC/MS JOURNAL ARTICLES

- THERMOSPRAY: ANAL. CHEM., 1988, 60, 2076-2088.
- PARTICLE BEAM CARRIER EFFECT: J. AM. SOC. MASS SPECTROM. 1990, 1, 92-98.
- PARTICLE BEAM: ANAL. CHEM., 1990, 62, 1686-1690.
- PARTICLE BEAM: J. AM. WATER WORKS ASSOC. 1990, 82, 60-65.
- THERMOSPRAY: ENVIRON. SCI. TECHNOL. 1990, 24, 1748-1751.

SPRAY/AEROSOL GENERATORS USED WITH PARTICLE BEAM LC/MS

- PNEUMATIC
- HEATED PNEUMATIC
- THERMOSPRAY
- ULTRASONIC

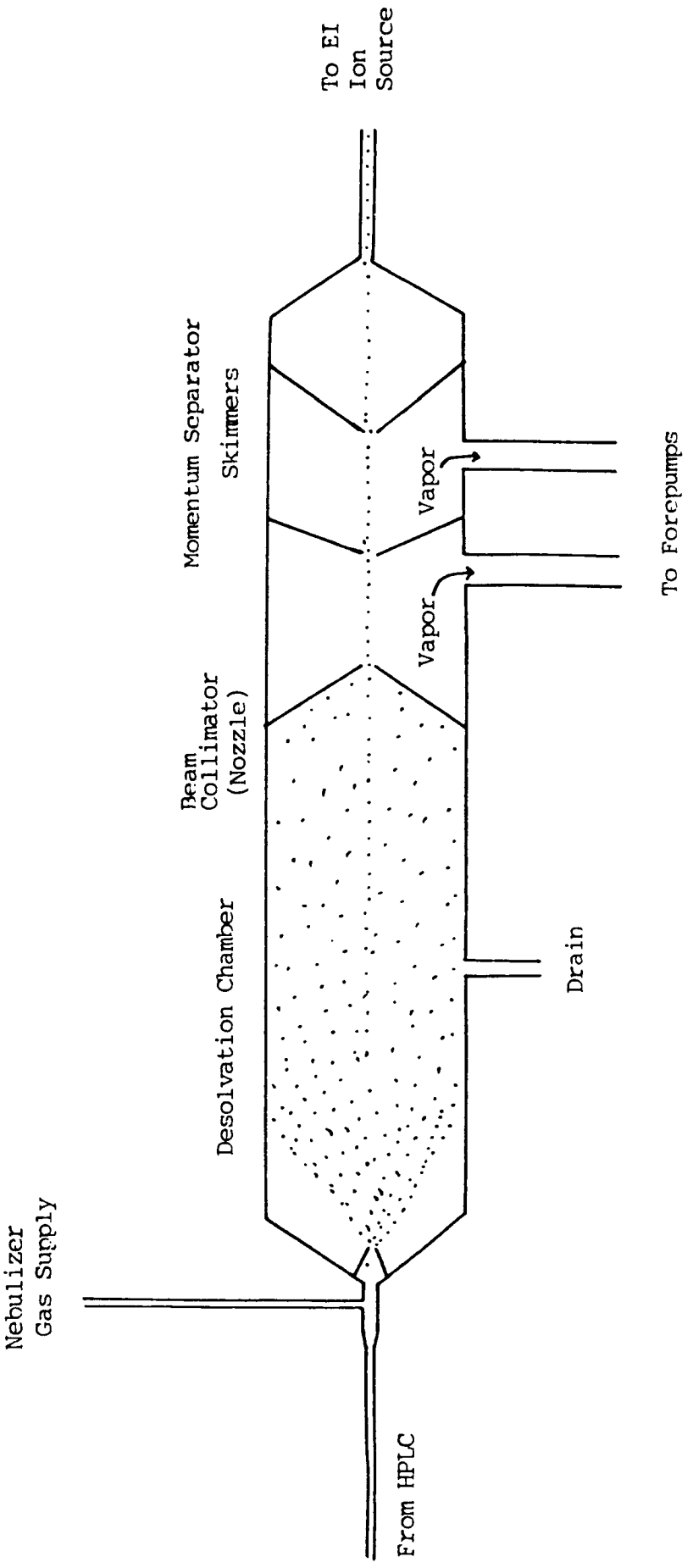
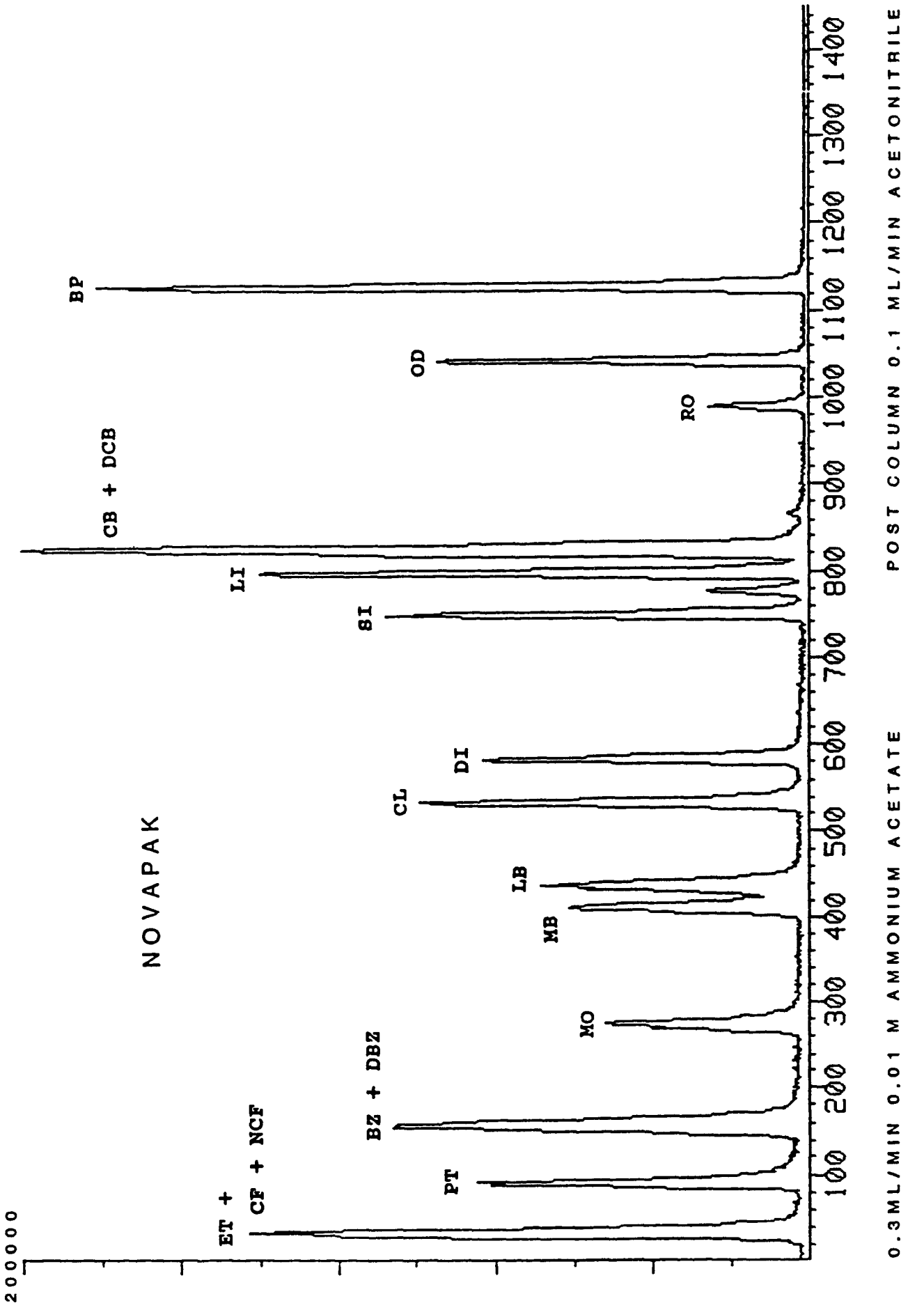
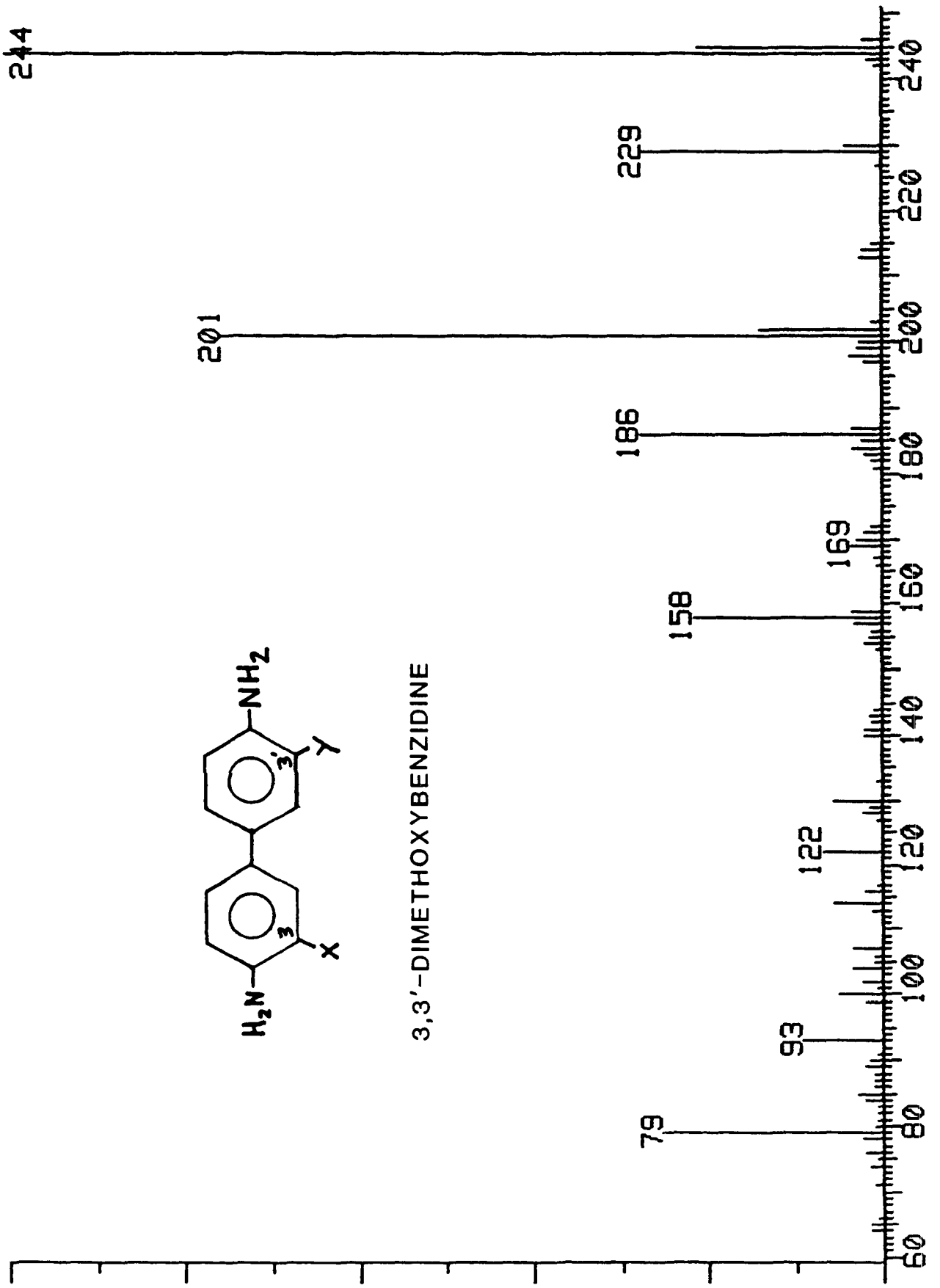
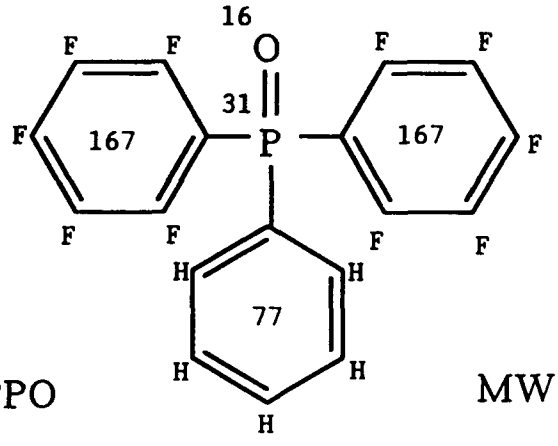


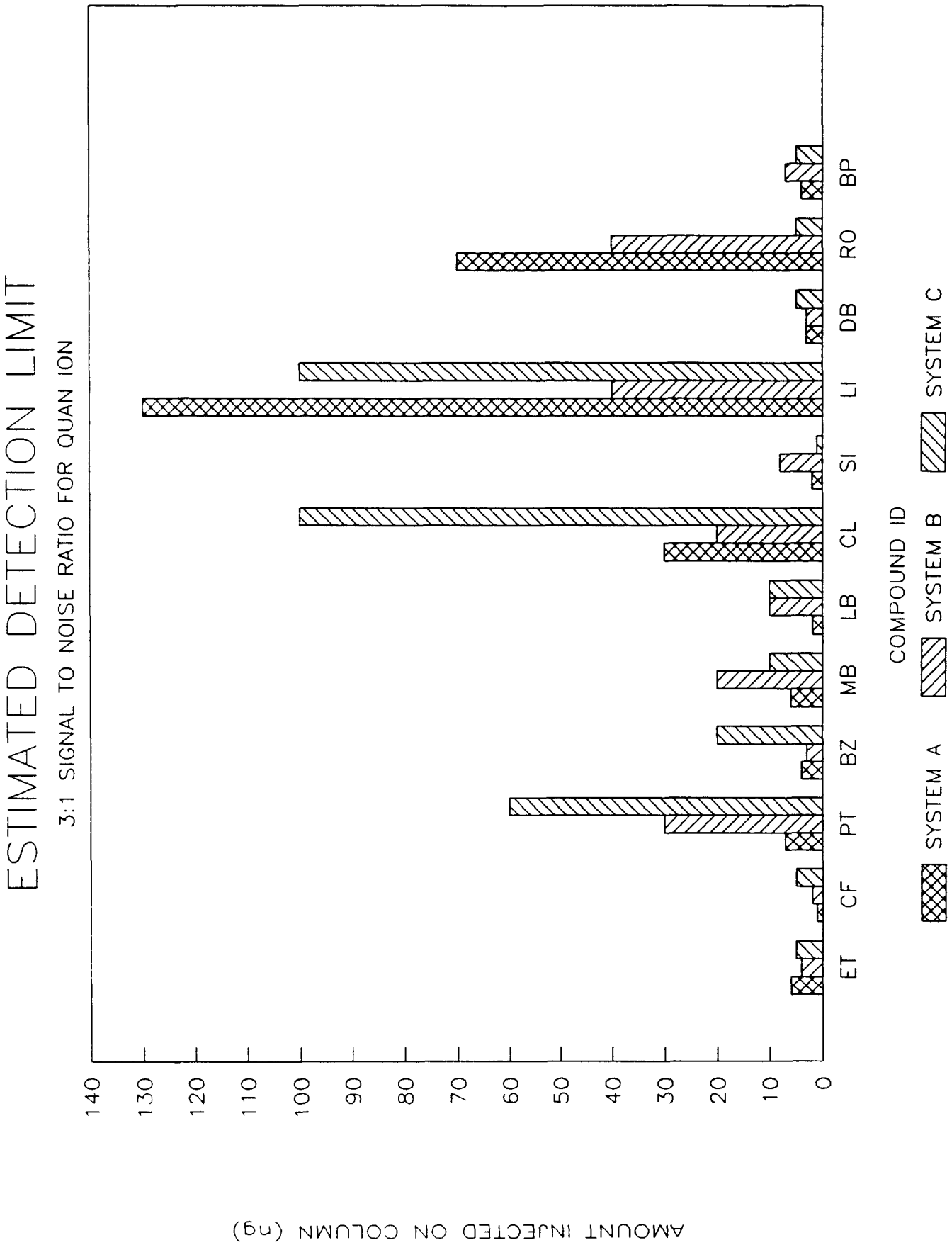
Figure 4. Schematic Diagram of a Particle Beam LC/MS Interface


1200000
ET +
CF + NCF
PT
BZ + DBZ
MO
MB
LB
CL
DI
SI
LI
CB + DCB
OD
RO
BP
NOVAPAK
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400
0.3ML/MIN 0.01 M AMMONIUM ACETATE
POST COLUMN 0.1 ML/MIN ACETONITRILE


244
229
201
186
169
158
122
93
79
60
80
100
120
140
160
180
200
220
240
NH2
3'
Y
X
3
H2N
3,3'-DIMETHOXYBENZIDINE



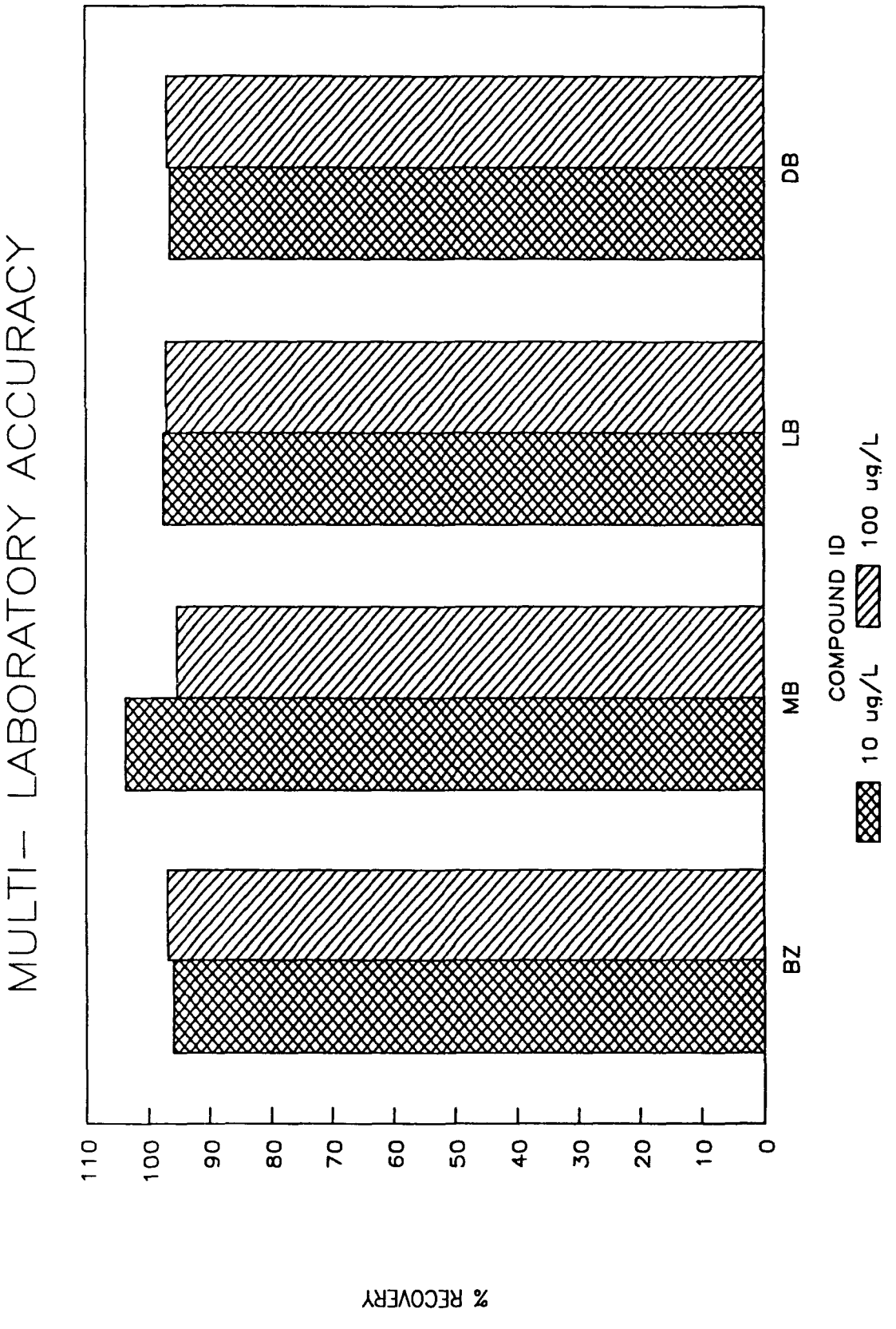
DFTPPO MW 458


ESTIMATED DETECTION LIMIT
3:1 SIGNAL TO NOISE RATIO FOR QUAN ION
AMOUNT INJECTED ON COLUMN (ng)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
ET
CF
PT
BZ
MB
LB
CL
SI
LI
DB
RO
BP
COMPOUND ID
SYSTEM A
SYSTEM B
SYSTEM C

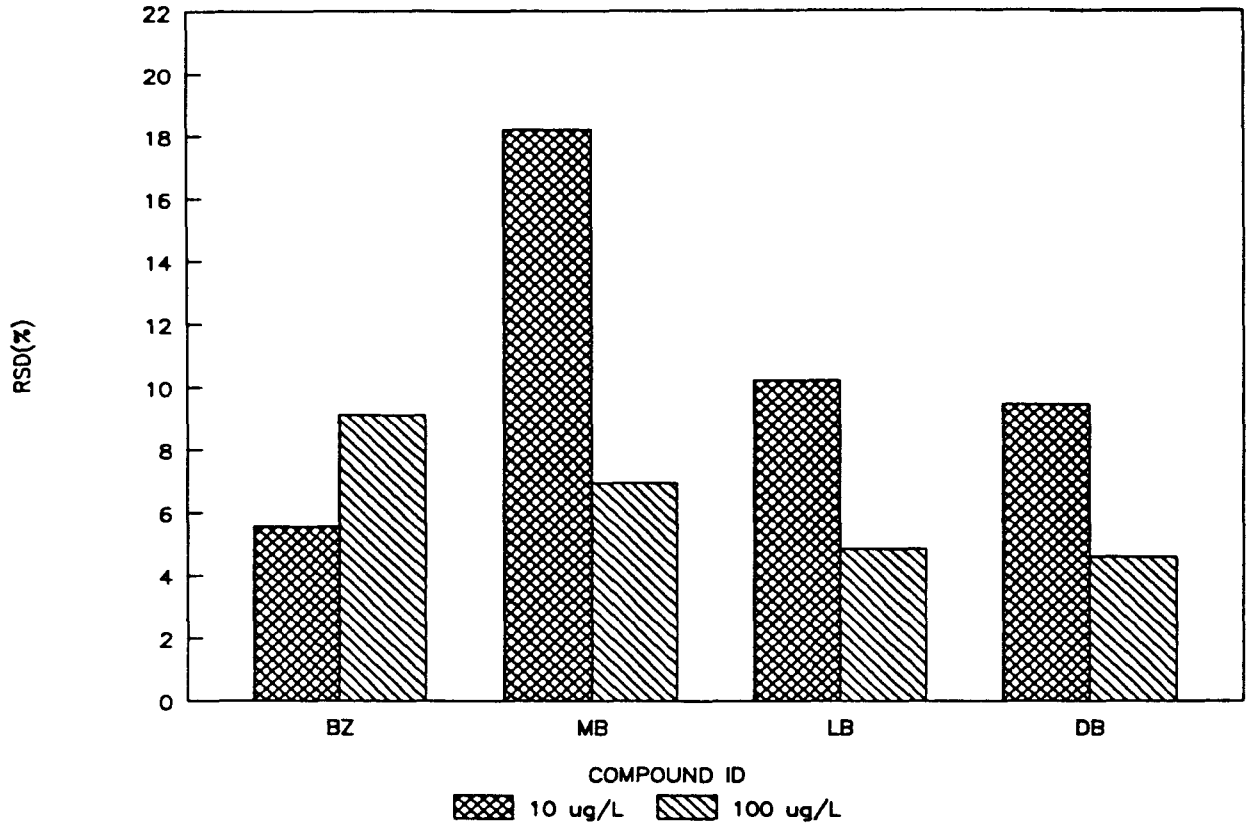
MULTI-LABORATORY LC/PARTICLE BEAM/MS STUDY

DIVERSITY OF EQUIPMENT

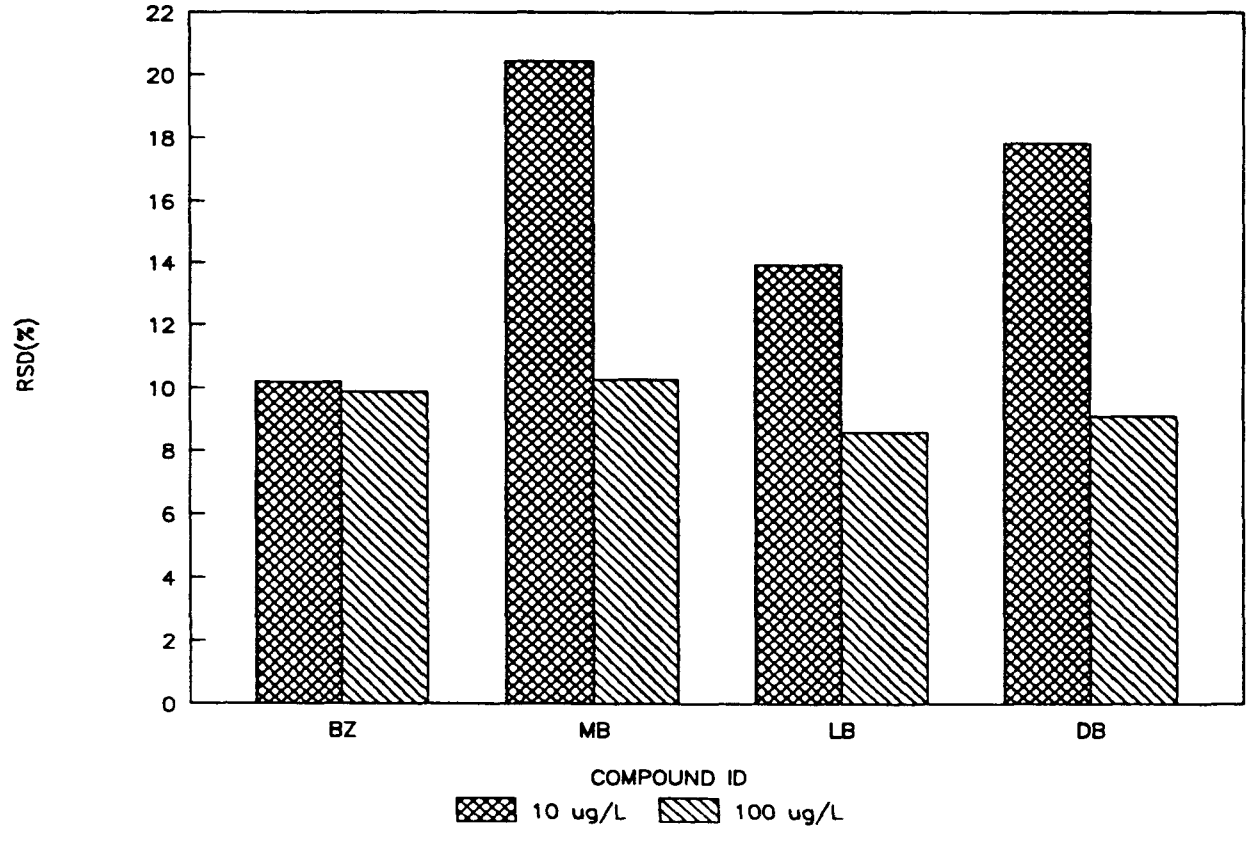
No.	Interface	Spectrometer	Data System
4	HP	HP	HP
1	Vestec	HP	HP
2	Vestec	Vestec/HP	Technivent
1	Extrel	Extrel	Extrel
1	Extrel	Extrel	Incos
1	Extrel	Finnigan-TSQ	Incos
1	VG	Finnigan-MAT	Incos
1	GE	Joel	Joel

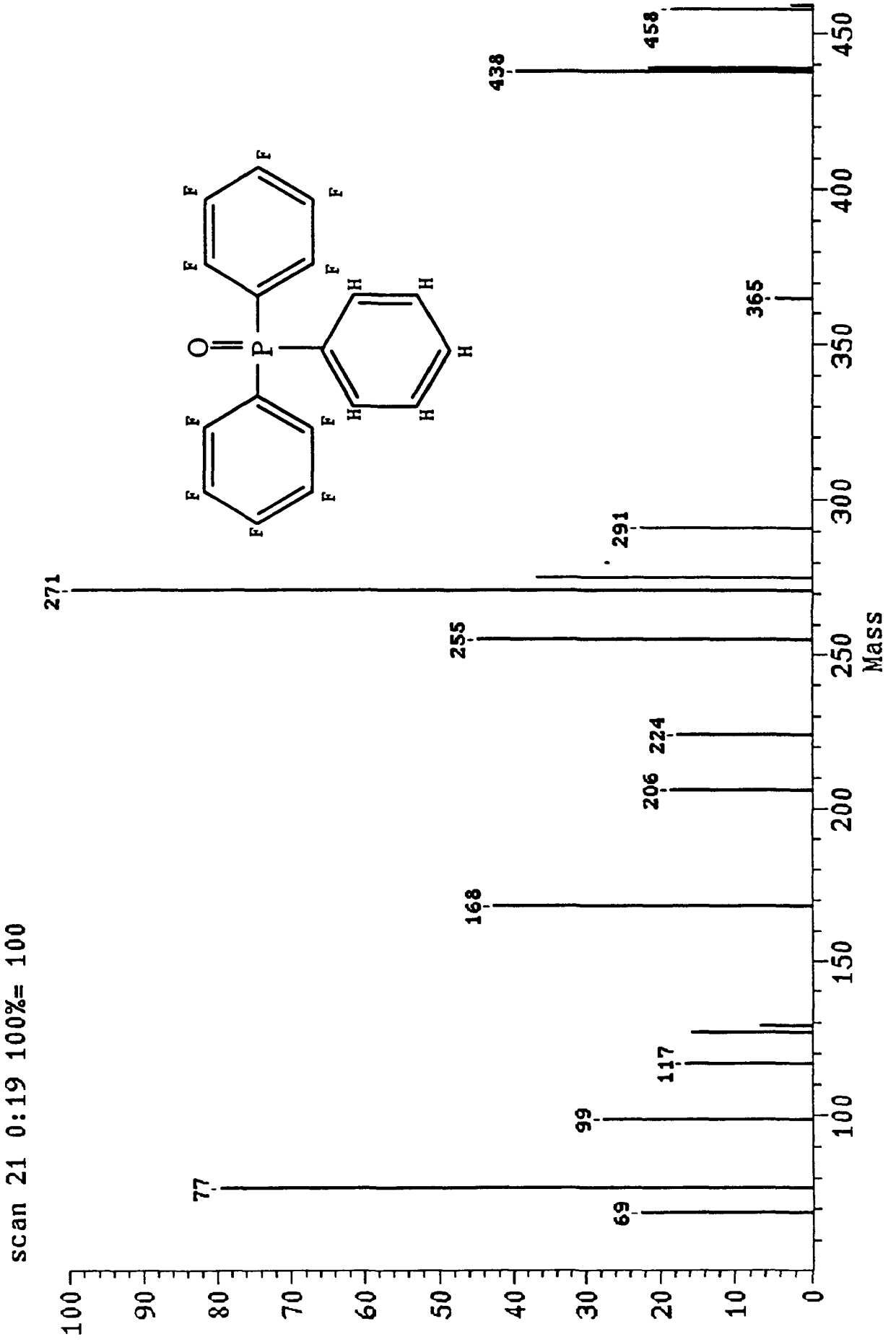

MULTI- LABORATORY ACCURACY
% RECOVERY
110
100
90
80
70
60
50
40
30
20
10
0
BZ
MB
LB
DB
COMPOUND ID
10 ug/L
100 ug/L

SINGLE ANALYST PRECISION



MULTI— LABORATORY PRECISION




scan 21 0:19 100%= 100
Mass
77
69
99
117
168
206
224
255
271
291
365
438
458

CONCLUSIONS

- STRONG TENDENCY TOWARDS NONLINEAR CALIBRATION (SECOND ORDER REGRESSION)
- COELUTION EFFECT (POSITIVE BIAS)
- EXTERNAL CALIBRATION PROBABLY REQUIRED
- PERFORMANCE OF 3 SYSTEMS ARE SIMILAR FOR MOST COMPOUNDS
- PRECISION AND DETECTION LIMITS HAVE BEEN IMPROVED BY METHOD CONTROLS
- DETECTION LIMITS AND SHORT TERM PRECISION ARE ACCEPTABLE FOR ENVIRONMENTAL ANALYSIS
- LONG-TERM STABILITY NEEDS IMPROVEMENT

MR. TELLIARD: Our first speaker today is Dr. Hau. He is Assistant Professor at the Center for Quality and Productivity Improvement at the School of Business at the University of Wisconsin in Madison. He's going to talk about an interesting paper that I saw about a year and a half or so ago on the use of statistics as it relates to...particularly has a lot of implications in the NPSD program down the road and I think you will find it very interesting.

DR. HAU: Well, I'm going to talk about a paper called, Judging Compliance and the Limit of Detection. This is a joint paper with Professor Mac Berthouex. He is a professor of Environmental Engineering at U of Wisconsin-Madison.

For the last two days I feel I am in a foreign country. It seemed like I'm in Japan. I'm Chinese anyway, so Japan is as foreign to you as to me. I heard names such as GC and MS and CFC and all of those terms and I don't know what they were. Well, just to feel closer to you, we changed our name actually. We changed our name to M-A-C and I-A-N. From now on, you can call me I-A-N and you can call Mac, M-A-C. It sounds more chemical.

Well, the problem we're going to talk about is about a detection limit. Recently, we have some regulation and the water quality limit is required even below the detection limit. As a consequence in that situation we will see a lot of cases where most of the measurements are reported as below detection limits. It looks like that if our effluent quality is below the detection limit, we can expect a lot of measurements below detection limits, i.e. only a very small portion of the numbers are reported. If we take a lot of samples, we see this kind of situation: we get a distribution on the effluent quality and only a very small part above detection limits. In that case, we really cannot talk about the average or the standard deviation. The only meaningful measure or statistic is the proportion of measurements above the detection limit.

Recently, we saw a regulation similar to this. I call this Regulation I that I want you to remember because we are going to refer to it a lot. "An effluent will be judged out of compliance if there is a measurement above detection limits." It looks like a very reasonable regulation because if the limit is below the detection limit, we should expect that not many of our measurements above detection limits. So this is a reasonable regulation...it seems like. However, the fact is that all effluents will be judged out of compliance under this regulation

no matter what!

We are to understand why this is so. I think most of you know better than me what is detection limit, but let's go through it quickly. Detection limit mostly is set to three standard deviation of the blank measurements. The idea is that we do not want to report any small number which we may get from measuring blank. How do we do that? We set the detection limit so that there is a very small chance for a blank measurement to exceed that limit. How small? One percent chance to see a measurement from blank falling above the detection limit. So if you actually see a number that is above the detection limit, then we are pretty sure that it is not coming from a blank.

So this is a graphic representation of the statement and if we measure the blanks, we get a distribution and we set the detection limit 3 standard deviations away from zero. The idea is make the tail area to be one percent which is very small chance. If we see a number out here, we are pretty confident that it is not coming from a blank.

To see why Regulation I has a problem, we use this example. Suppose we make 100 measurements on blank and by definition, each measurement has only one percent chance greater than detection limit. However, the chance of getting no detect out of 100 measurements is .99 to power 100 and that number actually decreases very fast. That number is in fact equal to .37. Although there is very little chance to get one detect out of one measurement, there's a very small chance to get no detect out of 100, or, in other words, the chance of getting at least one detect out of 100 measurements is very high, namely, 63 percent. Okay. And what we mean by this 63 percent was in computation of it. Well, remember this is the blank so this number means that under Regulation I, if you take 100 measurements of blank, there is a 63 percent chance that we would be declare blank out of compliance. And as you can see, if we increase the number of observations, there is a chance you'll get even higher chance and finally you'll get up to 100 percent.

An analogy: suppose you want to judge if a coin is fair or if a coin is balanced. What do we do? We toss the coin seven times. If we see all heads then we declare it fair. What's the rationale behind it? Well, we think that if the coin is fair, there is a very small chance to see seven heads in seven tosses and that's very reasonable. The problem is that we do this every week for the same coin, and this is the regulation similar to Regulation I. We perform this experiment to the same coin every week and whenever we see seven coins out of seven tosses, we declare them as fair and, as you expect, sooner or later we're going to see seven heads out of seven tosses just by chance and this is exactly the problem of the Regulation I. Although there is very little chance to see a detect in one measurement, but in the long run the chance is getting very high and eventually gets up to 100 percent.

So in the following, we are going to propose a regulation, a form of regulation that takes into account the variability of the measurements.

To review the situation, suppose we have effluent quality limit below the detection limit. Then, as we said before, the number that measures the quality of the effluent is the proportion of measurements expected to fall above the detection limit. This is actually a measure of the effluent quality. Graphically, it looks like that. This is the effluent quality and since this is below detection limits, most of the measurements we cannot or we won't report. So we use this shaded area, which is the probability that we just talked about. The area here is the proportion of the measurement above detection limits. For the blank, the P is one percent and if the effluent quality is not as good as blank, but below detection limits like this, the P is five percent as in the second figure. If we move the distribution to the right and the P will get higher. So the P is indication of the quality of the effluent. So we can write the permit in terms of P. For example, suppose we say that, when P is greater than 10 percent, then we'll declare noncompliance.

That is, if we see 10 percent of measurement of detection limits, then we'll declare noncompliance. Otherwise, when P is less or equal to .1, we'll declare compliance. This is the number to be determined by chemists as a lot of people here.

But however, P here is unknown. We cannot observe the P because we don't know the distribution and so this needs to be estimated by the sample proportion in a particular sample, or even more convenient, by the number of detects in a sample of observations.

So although the permit was written in terms of P, we need an operational rule that we can actually carry out which is based on the sample value. What is the sample value? We said that the number of detects is the statistic we want to use. What we need to do is to determine the critical value, CVu. If the number of defects is greater than CVu, then declare compliance.

We want to determine critical value so that if the number of detects is greater than this number, then we will declare noncompliance. For example, let's take the example where P is equal to .1. That means in the permit we just mentioned, it is in compliance. And how should we determine the upper critical values, CVu? Let's suppose we take a sample of 20 observations. Which number we should take as the upper critical value? Well, in that case we have to calculate the chance of seeing a different outcome in 20 observations. If P is really .1, we should expect to see two detects, (20 times .1.) However, it's quite likely that we can see three defects in a particular set of samples or it's also likely to see one detect. However, it's quite unlikely to see five or above. And actually, the chance of seeing five or above is less than five percent and that is the critical value we should set. That way the chance of seeing the number of detects above that critical value is very small and this chance we call the discharger's risk. This is the wrong decision we are making. And we want to minimize that risk and in this example we want to control that risk to be less than five percent. Then, according to this probability, we should set the

critical value to be five. That means the regulation is that if we see five or more detects, we will declare noncompliance. And the idea is to minimize the risk of making the wrong decision that we declare noncompliance when it is, in fact, in compliance.

For example, this is the probability of different outcome and P equal to .1 when we have 20 observations. As you can see, we have a 12 percent chance to see zero detects and so forth and, as you can see, the highest we have is 28 percent...which is the highest to see two detects and although it's not that weird to see one detect or three detects. But, as you can see here, we have only a three percent chance to see five defects and a very small chance to see six and so the chance of seeing five or above is less than five percent and this is the upper critical value we are choosing. The rationale is that we chose the critical value such that it discharges risk which is the probability of declaring noncompliance, when, in fact, in compliance.

In this example is the probability of the number of detects greater than the critical value when P is equal to .1, which is in compliance. We want to control the critical value such that the discharge's risk is small enough. How small is enough is a difficult question. It depends on our risk analysis.

When can we declare in compliance? Well, similarly, we define another critical value, the lower critical value, such that the regulator's risk is small. What is the regulator's risk? Well, this the probability of declare non compliance when in fact it is in compliance. What is the risk in this example? That is the probability of seeing the number of detects below the lower critical value when P=0.1. We want to control the critical value so that this risk is small enough.

If you see the graph again, this side, up about five...the area is small...and this side as low as we can get, at zero. When you calculate, the number is 12 percent. We are getting as low as we can get. You can make a regulation that we have to see no detects. The regulators still have ... of 12

percent making a wrong decision. But that's the lowest we can get so we have to set the lower critical value in that value, zero.

Well, to summarize, we can set the critical values according to what the value of P we require. So for each P, we can calculate the chance of seeing different outcomes. Take P equals .15 as an example. When P is equal to .15, that means we want the permit limit to require P to be less than .15 in order to be in compliance and above .15 to be noncompliance. When P is equal to .15 out of 20 observations, it's very little chance that we see zero detects and it's very little chance to see above six detects. So the upper critical value we should set is when we declare noncompliance, we receive six or more detects and we declare in compliance when we receive zero detects.

What should we decide if we see one, two, three, four or five detects i.e., between the two critical values. We can not declare noncompliance and we cannot in compliance. Well, when the number of detects is less than the upper critical value and above the lower critical value, then there's not enough chance (enough evidence) to declare either compliance or noncompliance because making either decision we will have high either regulator's risk or the discharger's risk. In that case, we should issue a warning. What does that mean? Well, that needs to be discussed in detail. The idea is to get more evidence by getting additional N samples. Okay. And if one detect is seen in that additional N sample, then we will declare noncompliance. Otherwise, we would declare in compliance. But what is N? That's the question.

Well, this is a table of what N should be. Of course, the N depends on the P that requires a proportion of value above detection limit. This is the P and, in most cases, we want the rule in the form: if we see one value above detection limits, we will declare out of compliance. In how many additional samples? Well, it depends on the P. When P is equal to .01, then we require six more samples. Let's take this as an example. When P

equals .05, then if we issue a warning, what it means is that we require to take five more samples. If we see receive one detect out of the five, then we'll declare noncompliance. How did we get these numbers? Well, these numbers come from the fact that we want to control the discharger's risk. This number is set so that the discharger's risk is small. So, you can calculate the chance of getting a detect out of N additional samples for different P. If that is small, then that's the number we want.

To summarize what the proposed regulation is, well, first, we have to determine the P value which is the expected proportion of detects you want to control and the limits should be in this form: when P is greater than (then we will declare in noncompliance and when P is less than equal to) then we declare compliance.

But in order to carry out this rule, we need an operation rule that depends on observation. If the number of detects is greater than the upper critical value, we would declare noncompliance and if the number of detects is less than the lower critical value, we declare in compliance and if it's in-between, then we issue a warning and additional N observations are required, and if we see at least one detect in the additional observations, then declare noncompliance. Those values, the upper critical value is determined so that the discharger's risk is small so that we don't wrongly declare it in noncompliance. The lower critical value is determined so that the regulator's risk is small so that we don't wrongly declare in compliance. When it's fuzzy, i.e. when we don't have enough evidence, we require more evidence and the additional number of sample N is determined so that the discharger's risk is small because we are going to make a decision based on N to declare noncompliance.

Of course, there are some issues that we haven't discussed such as how to determine P. Some other issues that we haven't discussed that is in the paper that Mac and I wrote. If you are interested, we can talk about it, afterwards.

So to summarize what I've done in this talk is, first,

to introduce the risk associated by regulations. Okay, that is the discharger's risk and regulator's risk and if we're not careful, by regulation I that looks like a very reasonable regulation. But is has actually not much meaning because we know that sooner or later we will be declare every discharger noncompliance according to that regulation. Also, we propose a form of regulation so that we can minimize or control the discharger's risk and also the regulator's risk.

QUESTION AND ANSWER SESSION

MR. HAU: Should I take questions up there?

MR. TELLIARD: Yes, come on up here. Questions?

MR. PRONGER: This is Greg Pronger, National Environmental Testing.

I'm not really certain who this question is for, but how do you differentiate between a natural variance in a waste stream discharge where you're going to be measuring which basically is steady state system and looking at the statistics around that or true variances in the concentration where you would have a positive hit because there's been a change in the outfall? As a regulating community, how do you differentiate between those two occurrences looking at an argument like this for the statistics? I can see where the Regulation I was possibly trying to approach the problem in the variances in the outfall itself where this is addressing the issue if it's a steady state outfall.

MR. HAU: This is an excellent question. I am not a regulator, so I'm not able to answer that.

DR. KAHN: That's a tough question. Basically, you'd have to make... I mean, the data that you would use to establish the compliance standard should be consistent with the rules that you use to measure compliance. I mean, that's the way that we try to do it. It doesn't always work out that way.

MR. WHITE: There's also a couple of different kinds of waste water regulations. There are waste water regulations that are based on water quality and there are waste water regulations that are based on technology. With the technology regulations, you would be assuming that there's a waste water treatment technology that can reduce pollutants to a certain level and you would not be allowing peaks. You would say that is the level at which you're going to regulate and even if

you're working on a batch process and every once in awhile you've got a heavy load of this chemical coming in, we say you've got a technology that can keep the pollutant concentrations down to this level. With the water quality standard, I don't work with those as much and I can't...

MR. TELLIARD: Did you get an answer?

MR. PRONGER: Thank you, I think so.

MR. HAU: I think this issue is about determining all sources of variations. It's really important and I think that we need to look more.

MR. HAEBERER: Fred Haeberer. While I understood about 20 percent of what you said and am in complete agreement with you, my observation is that perhaps a more efficient way of bringing reason to what we're doing would be to introduce more and more rationale risk assessment process and to develop methods that are more sensitive. We're going to have a very, very, very difficult time introducing those concepts into the regulatory process.

MR. HAU: Well, maybe I should clarify the difference here. The risk analysis, I think, should be done here. When we determine what is the expected proportion of detects we want, that is the risk analysis here. Once this is determined, what we are talking about is how to carry out this rule. So, I think it's two different issues. You can be stringent here, but because of the random errors, including the sampling error or the measurement error, there is some uncertainty involved that when we carry out this rule, if you're not careful, we are making a lot of mistakes on this regulation...on this part. But it's two different issues here. I think most of us are concerned with P, which is very important. If this was set wrong, it doesn't matter what you do afterwards, you won't correct the situation. But if this is set right here and still there is the random error that we should be careful how

to carry out this part.

MR. TELLIARD: Thank you. Any other questions? I can't see over there. Anyone over there? One more.

MR. PRONGER: How do you correlate this information with the different working ranges of a piece of measuring equipment where you have traditionally a detection limit...a range up to your limit of quantitation...the range. I think part of what I'm seeing as confusion is I'm trying to relate this to being an analyst. There's this grey area whenever you're running an instrument that's from your MDL to your LOD. It seems to me that this has some application in that range. Once you get above a limit of quantitation, you have a pretty sound measurement and it would seem unlikely that the statistics are on that bell curve. If you extrapolated that thing out infinitely, you could have an accidental discharge of a pH of two. That would be statistically possible, but hugely unlikely. There seems to be a factor in here that's being missed that takes into account that at some point, the probability just goes to zero, rather than looking at just possible hits. There also has to be a relation to the distance from the mean.

Am I making myself at all clear to anybody?

DR. KAHN: Let me try to respond to that, sort of partly in defense of Dr. Hau, who I think has provided us with a very interesting framework to look at what is really a general class of problems. What he's talking about, I think, can be extended to other situations. That is, where you're not just looking at detection limit compliance. In other words, you can see a P value that would correspond in compliance at any level. So, I think that would...some more work, some more generalization of what he's done, I think, could fit the situation that you're describing, although we could argue about that grey area between the so-called detection limit and the so-called LOQ.

MR. PRONGER: Whatever you wanted

to...

DR. KAHN: Whatever you want to call it.

MR. PRONGER: Just so you...

DR. KAHN: The PQL, the XYZ, whatever it is.

MR. HAU: I think that's right. I think the method is general. But, of course, when we talk about LOQ, then the probability has to be adjusted accordingly. I think the framework is general.

MR. TELLIARD: Thank you.

Regulation Design Related to Detection Limit

by

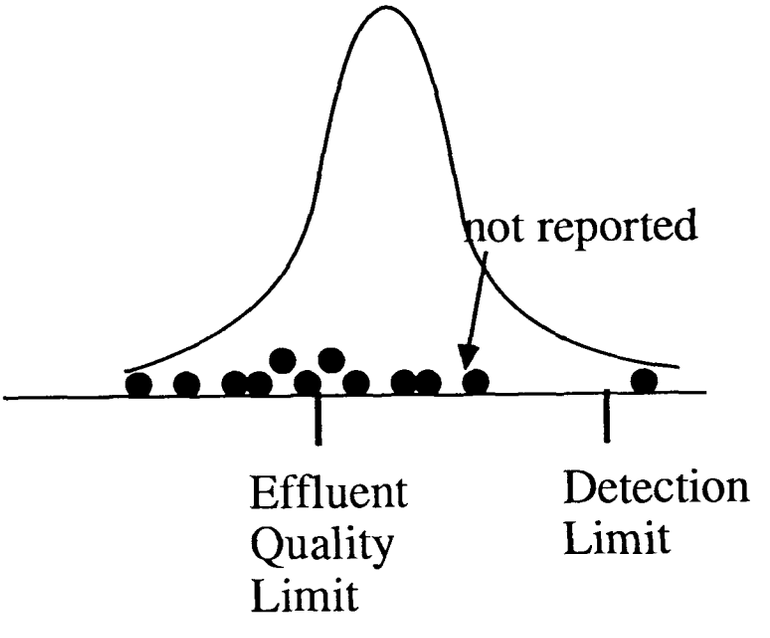
Dr. Ian Hau

Problem:

Water-quality limit is below the "Method Limit of Detection" (MDL)

Consequence:

Most measurements are not reported.



Regulation I

The effluent will be judged out of compliance if there is a measurement (the concentration of the restricted substance) above MDL.

Fact

Under Regulation I, all effluents (even "blank") will be judged out of compliance.

What is MDL:

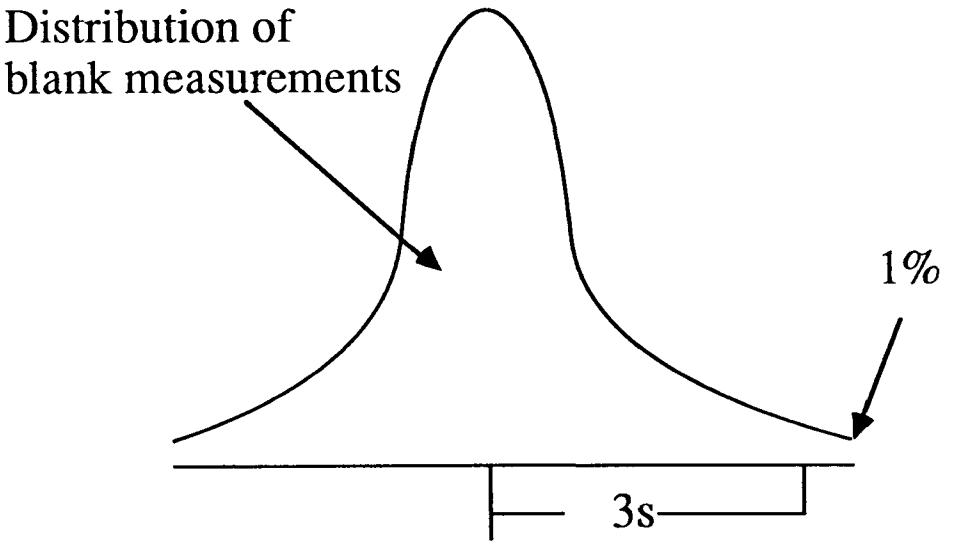
Let **s be the standard deviation of the repeated measurements on "blanks", where**

$$\mathbf{MDL = 3s}$$

Idea:

Do not want to report small numbers which we may get from measuring "blanks".

Set MDL so that there is only 1% chance to see a measurement from "blanks" falling above MDL.



Example:

≈ **100 measurements on "blanks"**

≈ **Each measurement has 1% chance greater than MDL.**

≈ **Chance of getting no detects out of 100:**

$$0.99^{100} = 0.37$$

≈ **Chance of getting at least 1 detect out of 100:**

$$1 - 0.37 = 0.63$$

i.e. The chance of wrongly declared an effluent (blanks) out of compliance when 100 measurements are taken is 63%.

Analogy:

Judge if a coin is "fair" by:

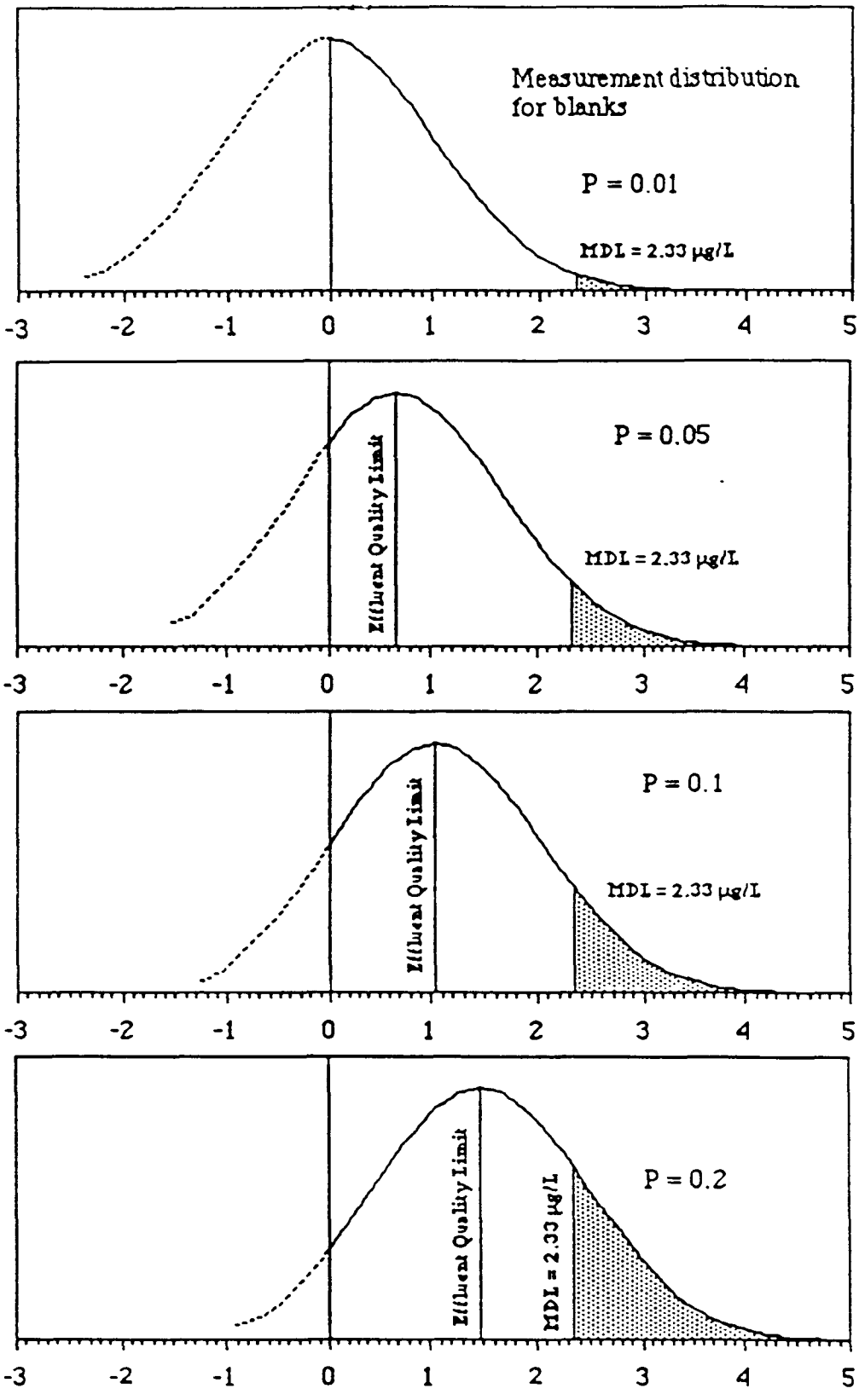
> **Tossing a coin 7 times, if all 'heads', then declare "unfair".**

Perform this test for the same coin once every week; whenever we get all 'heads', declare "unfair".

When the EQL < MDL, the parameter

> ***P*** **= proportion of measurements expected to fall above MDL**

is an indicator of an effluent's quality.The smaller the *P*, the better quality the effluent.


Measurement distribution for blanks
P = 0.01
MDL = 2.33 µg/L
-3 -2 -1 0 1 2 3 4 5
Effluent Quality Limit
P = 0.05
MDL = 2.33 µg/L
-3 -2 -1 0 1 2 3 4 5
Effluent Quality Limit
P = 0.1
MDL = 2.33 µg/L
-3 -2 -1 0 1 2 3 4 5
Effluent Quality Limit
MDL = 2.33 µg/L
P = 0.2
-3 -2 -1 0 1 2 3 4 5

Permit limit:

If $P > 0.1$,
then declare noncompliance.

If $P \leq 0.1$,
then declare compliance.

But P is unknown, it needs to be estimated by sample proportion OR the number of detects in a sample of n observations.

Operational Rule

Determine the critical values CV_u :

If the number of detects > CV_u,
then declare noncompliance.

Suppose $P = 0.1$, i.e. in compliance, calculate the probability of seeing different outcomes (# of detects) out of 20 observations.

$n=20$

s	$P=0.1$
0	0.12
1	0.27
2	0.28
3	0.19
4	0.09
5	0.03
6	0.01
7	<0.01

Choose CV_u such that the discharger's risk :

Probability (declare noncompliance when in fact in compliance) = Probability (S>CVu | P=0.1)

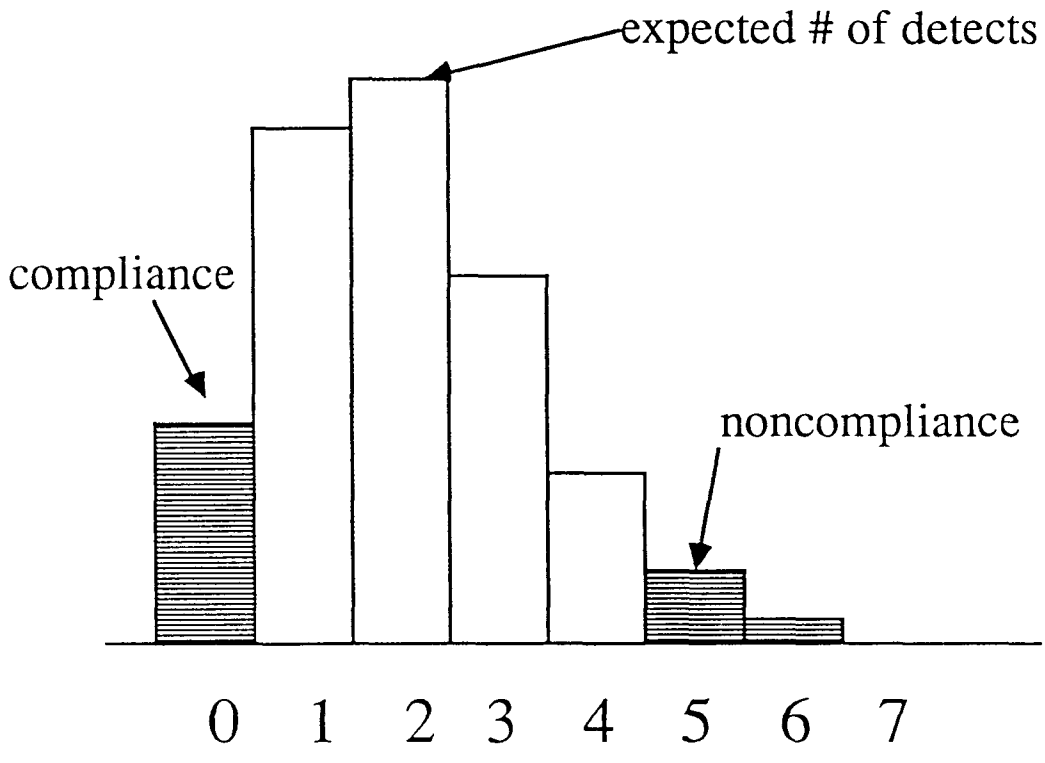
is small enough (say 0.05).

Similarly:

Choose CV_L such that the Regulator's risk :

Probability (declare noncompliance when in fact in noncompliance) = Probability (S<CV_L | P=0.1)

is small enough (say 0.05).


expected # of detects
compliance
noncompliance
0 1 2 3 4 5 6 7

What happen if ...

$$CV_L < \#\ \text{of detects} \leq CV_u$$

... then there is not enough evidence to declare either compliance or non-compliance.

Warning is issued. Additional N samples are required.
If a detect is seen, then declare non-compliance. Otherwise, declare compliance.

Summary of Proposed Regulation:

Determine the desired p_o s.t.:

If $P > p_o$, then in noncompliance;
If $P \leq p_o$, then compliance.

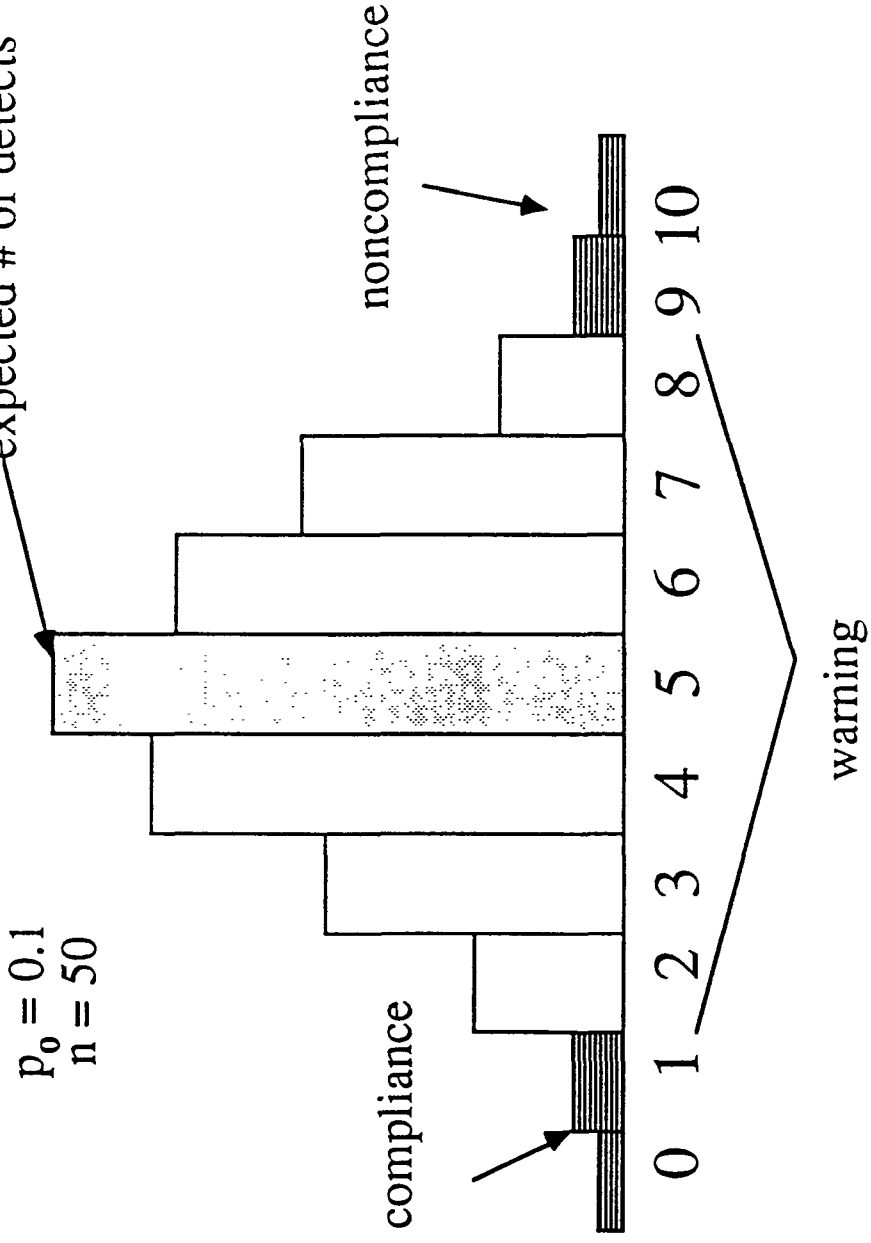
Operational Rule:

If # of detects $> CV_U$,
declare noncompliance;

If # of detects $\leq CV_L$,
declare in compliance

If $CV_L <$ # of detects $\leq CV_u$,
issue warning. Additional
N observations are required.
If see at least 1 detect,
declare noncompliance.

Determine CV_U so that Discharger's Risk is small.
Determine CV_L so that Regulator's Risk is small.
Determine N so that Discharger's Risk is small.


expected # of detects
noncompliance
$p_o = 0.1$
$n = 50$
compliance
0 1 2 3 4 5 6 7 8 9 10
warning

Issues need to considered further:

- **defination of MDL**
- **definition of "blanks"**
- **determine p_o**
- **serial correlation**

MR. TELLIARD: Our next speaker is Henry Kahn. Dr. Kahn is a chief of the statistical section in the Engineering and Analysis Division in the Office of Water.

DR. KAHN: It just seems that way, Bill.

MR. TELLIARD: Henry is going to talk on some work that he did looking at analytical variability in a study that was carried out regarding the discharge of dioxins and furans from the pulp and paper industry.

Assessment of Analytical Variability of Dioxin and Furan Measurements in Environmental Samples From Bleached Pulp Mills

Henry D. Kahn and Marla D. Smith
Office of Water, EPA
Kirk Cameron
Science Applications International Corporation

Presented at the 14th Annual Environmental Protection Agency Conference on Analysis of Pollutants in the Environment, May 8-9, 1991, Norfolk, Virginia

ABSTRACT

Assessment of analytical variability of dioxins and furans in environmental samples from bleached pulp mills

Henry D. Kahn and Marla D. Smith, US EPA, and Kirk Cameron, Science Applications International Corporation

This presentation considers data collected in 1988 by EPA and the paper industry as part of a cooperative study to evaluate the discharge of dioxins and furans from mills in the United States that bleach wood pulps with chlorine or chlorine derivatives. Bleaching wood pulp with chlorine has been shown in other studies to be a source of dioxins and furans. The study included the measurement of 2,3,7,8-TCDD and 2,3,7,8-TCDF in samples of effluent, pulp and sludge taken at all mills in the United States that bleach pulp (referred to as the "104 Mill Study"). The analyses of the samples were conducted using an analytical method developed by the paper industry known as Method 551. The data are used in a number of statistical analyses which are discussed in this presentation. These analyses include an assessment of analytical measurement variability and the combined effect of analytical measurement variability and field sampling variability using components of variance analysis. Both these components of variability are shown to be small relative to other components of the total variability in the data. Other analyses of the data discussed include distributional properties of detected measurements, distributions of reported detection levels and the effect that different amounts of chlorine usage and chlorine dioxide substitution have on levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

In 1988, the Environmental Protection Agency and the paper industry conducted a cooperative study to evaluate the discharge of dioxin and furan from all 104 mills in the United States that bleached wood pulps with chlorine or chlorine derivatives; the study is referred to as the "104-Mill Study". These mills were the subject of investigation because other studies demonstrated that the bleaching of wood pulp with chlorine is a source of dioxins and furans. An important objective of the 104 Mill Study was to measure dioxin and furan levels in samples of effluent, sludge, and pulp from the mills. The measurements were performed using a high resolution GC/MS and isotope dilution analytical procedure (known as Method 551) developed by the paper industry for the most toxic of the dioxin and furan congeners: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF). The effluent samples were obtained from treated wastewater at the mills. Very few untreated wastewater samples were obtained in the study. The sludge samples were obtained from semi-solid residue from the treatment system. The pulp samples were cellulose fibers after conversion from wood chips. Most of the effluent, sludge, and pulp samples were collected in mid to late 1988. Paper industry representatives managed the collection of the samples, coordinated the laboratory work and forwarded the analytical results to EPA. The Engineering and Analysis Division in EPA's Office of Water coordinated quality control reviews with industry representatives, constructed computer files containing the data and performed analyses that include the results described here. The data and a thorough description of the statistical analyses are contained in references [1] and [2].

Information useful in preparing this paper was provided in paper industry reports (references [4] and [5]) and EPA documents (references [3] and [6]).

This paper will concentrate on a number of results and conclusions based on our analysis of the 104 Mill data. Of primary interest is the analysis of a number of laboratory and field replicates collected in the study which demonstrates that for effluent, sludge and pulp: (1) variability in the data due to analytical measurement is small; and (2) the combined variability in the data due to analytical measurement and field sampling is small. For (1) and (2), only the results based on analysis of effluent data will be presented here; the results for sludge and pulp are similar. Also of interest are: (3) greater chlorine use is associated with higher TCDD and TCDF discharges from the mills when combined mill output from effluent, sludge and pulp is analyzed; and (4) increased chlorine dioxide substitution for chlorine is associated with slight reductions in TCDD and TCDF. For (3) and (4) only the results for TCDD are presented. Results for TCDF are similar. Also, as part of our analysis we determined that, for effluent, sludge, and pulp: (5) detected values are approximately lognormally distributed; and (6) detection levels of 10 ppq for effluent and 1 ppt for sludge and pulp are achievable based on reported detection levels reported (these detection levels were established as goals at the beginning of the study). For (5) and (6), only the results for effluent will be presented here.

As part of the cooperative agreement, industry agreed to collect

the data and send the results to EPA. The National Council of the Paper Industry for Air and Stream Improvement (referred to as NCASI) managed the program for industry. NCASI provided guidance on taking the samples, developed the laboratory method for 2,3,7,8-TCDD and 2,3,7,8-TCDF, submitted the samples to labs and reviewed the results before forwarding them to EPA. The Engineering and Analysis Division (formerly the Industrial Technology Division) in EPA's Office of Water was responsible for coordinating the submission of data from NCASI to EPA and data quality control reviews, entering the data into computer files and performing a variety of analysis tasks including the work described here.

Data

Each mill was required as part of the agreement to provide one sample from each of effluent, sludge, and fully bleached pulp from each bleach line at the mill. These samples were composite samples taken over a 5-day period. This generated about 400 samples with about 80 additional samples for QA/QC. The mills also submitted process information corresponding to the dates of sampling. EPA also received from NCASI a limited amount of QA/QC information (recoveries and ion ratios). The paper industry used only two labs for all of the laboratory analyses. Both labs did some samples from each of effluent, sludge, and pulp; however, the bulk of the analyses for any particular matrix was limited to one lab. The two labs were Wright State University in Dayton, Ohio which did about 80% of the pulp analyses. Enseco-California Analytical Laboratories in West Sacramento, California was the other laboratory and did 89% of the effluent samples and 81% of

the sludge samples. None of the effluent or sludge samples were analyzed by both laboratories. Since there were only a few pulp samples done by both labs, inter-laboratory variability could not be estimated.

The emphasis in this paper is on the results for TCDD measurements in effluent at kraft mills. There are several reasons we chose to focus on effluent. The primary reason is that the conclusions based on analyses of effluent data are similar to those based on sludge and pulp data. In addition, there were confounding factors in the measurements of sludge and pulp which are not present in effluent. In some cases, the sludge samples were difficult to obtain physically, and the results may not reflect completely the effectiveness of the treatment system. Pulp is the final product rather than a by-product as are effluent and sludge. However, the pulp was sampled before going through the drying process and the water from this drying process became part of the effluent which was then sampled. This may have resulted in some double-counting of TCDD and TCDF levels between pulp and effluent.

We also decided to focus on the results for TCDD for this paper because TCDD and TCDF are highly correlated and, accordingly, the results for TCDD and TCDF are similar. Figure 1 (Figures and Tables are located at the end of this paper) shows the strong relationship between TCDF and TCDD for effluent from kraft mills. The linear regression of the data shown in Figure 1 yields an R^2 of 79% for detected measurements of TCDD and TCDF.

In addition, we are focusing on kraft mills for a number of

reasons. The processes at kraft and sulfite mills are very different and, in our analysis, we found a significant difference in the data from the two types of mills. Sulfite mills would be expected to produce less TCDD and TCDF because they use less bleaching than kraft mills and in fact most of the measurements from sulfite mills were reported to be close to detection level. In addition, sulfite and kraft mills tend to use different types of wastewater treatment so that mill type and treatment type would be confounded in the data. There were also some difficulties with the TCDD and TCDF analyses of samples from sulfite mills. Part of this was apparently due to the low levels of TCDD and TCDF in the sulfite samples, and part was due to analytical interferences.

Lognormal Data: In general, we found that the detected measurements are approximately lognormally distributed across mills. This finding is not surprising but important in that it provides the basis for the use of logarithms of the detected measurements in our analyses. The probability plot in Figure 2 demonstrates the approximate normality of the Kraft mill effluent TCDD data.

Non-Detect Measurements: Measurements reported as non-detect constitute an important segment of the data; for example, 28% of the effluent samples in kraft mills were non-detects for TCDD. Because all of the mills had detected concentrations in either effluent, pulp, or sludge for TCDD or TCDF, we concluded that a non-detect was more likely to be an amount too small to measure rather than an indication that the TCDD and TCDF were not in the sample.

On the basis of the reported data, we concluded that a detection level of 10 ppq for TCDD and TCDF in effluent was reasonable. The use of 10 ppq for effluent was established as a goal at the beginning of the cooperative study. There were 30 effluent measurements for TCDD from both kraft and sulfite mills that were reported as detection level values. The minimum detection level is 3 ppq, the maximum 17 ppq, the mean 7.7 and the median 7.5 ppq. The cumulative distribution (Figure 3) shows that about 80% of the non-detect measurements were reported at or below the target detection level of 10 ppq. In addition, after completion of the 104 Mill Study, EPA received new data from industry which report almost all detection levels as less than 10 ppq for effluent. Reports developed by NCASI (reference [5]) now support the use of detection levels of 10 ppq.

For the analyses presented in this paper, we considered two possibilities for treatment of the non-detect measurements: substituting of a value equal to one-half the detection level or substituting a value equal to the detection level for measurements reported as non-detect. The choice of substituting a value of one-half the detection level for non-detects offered a reasonable "middle ground" approach and the results did not differ much from substituting the detection level.

Analytical and Field Sampling Variability: Evaluation of analytical and field sampling variability was possible using a number of laboratory and field replicate sample measurements collected as part of the study. A statistical procedure referred to as components of variance analysis (see, e.g., [7]), we were able to estimate: (1) the component of variation in the data due to analytical variability

utilizing the laboratory replicate measurements; and (2) the component of variation due to the combined effect of field sampling and analytical variability utilizing field replicate sample measurements. The results of the components of variance analysis demonstrated that the contribution to the total variability in the data due to analytical variability and field sampling variability was low as measured by laboratory and field replicates.

Laboratory replicates are individual samples that are split in the laboratory to form separate aliquots of the same sample; the separate aliquots are then analyzed to generate separate measurements of the concentration of the sample. Variation in the replicate measurements is attributable to variation in the analytical measurement process. Repeated laboratory measurements on the same samples (i.e., laboratory replicates) may be used to estimate variability in concentration measurements due to analytical measurement variability.

Field replicate samples are physically distinct samples collected at the same time using identical field sampling and handling protocols. Measurements on distinct field replicate samples may be used to estimate variation due to the combined effect of field sampling techniques and analytical variability.

In this study, about 30% of all samples were either field or laboratory replicate samples. For TCDD concentrations in effluent, there were 107 samples from 84 kraft mills of which 34 were replicate samples from 15 mills. The number of combined laboratory and field replicates from each of these 15 mills varied from 2 to 3 samples. (Not all mills provided replicate samples.) There were 15 laboratory

replicates from 6 mills and 19 field replicates from 9 mills.

We examined analytical and field sampling components of variability because we intended to average the replicates to determine mill specific values for use in other analyses and we wanted some indication of the effect that this averaging would have. In addition, a paper industry study (reference [8]) had asserted that the analytical variability in measuring TCDD and TCDF is high. This assertion is not supported by a components of variance analysis which provides a specific estimate of the component of variance in the data attributable to variation in analytical measurement.

Components of variance analysis may be used to examine any components or sources of variation given the availability of appropriate data. In this case, for instance, examination of variability of inter-lab effects and variability due to field sampling alone would be desirable. However, there were not enough data to evaluate the variability due to inter-laboratory effects because only a few samples were analyzed by both laboratories. Also, evaluation of variability due to field sampling alone was not possible because no lab replicates of field replicates were analyzed.

A plot of the laboratory replicate effluent TCDD measurements for kraft mills is shown in Figure 4. A pair of replicate measurements that agree perfectly would be plotted on the diagonal dashed line. To show the approximate variability, the figure also shows a 95 % confidence ellipsoid for the data. The correlation coefficient between replicates

is 0.98. In performing the analysis, we assumed the data are approximately lognormally distributed and set non-detect measurements equal to one half the detection level. The data for field replicate effluent TCDD for kraft mills are shown in Figure 5 and demonstrate similarly good results. The correlation coefficient is 0.99. The results for sulfite mills were not as good (correlation coefficient of 0.73) although there were only five laboratory replicates for TCDD. The laboratory effluent TCDD replicates for sulfite are shown in Figure 6. There was only one field duplicate pair from sulfite mills.

The results of the components of variance analysis are summarized in Table 1. The amount of variability due to analytical measurement was small, 1.4% of the total variability. The amount of variability due to the combination of field sampling and analytical error is also small, 0.8% of the total. Some assurance that these small percentages are valid throughout the range of the data obtained in the 104 Mill Study is provided by the plot shown in Figure 7. The plot shows the cumulative distribution of TCDD effluent measurements by replicate type for the kraft mill data. There are more non-replicate measurements but, as shown in the plot, the range covered by non-replicate and replicate measurements is virtually the same.

The following conclusions are supported by the components of variance analysis: (i) the component of variability in the data due to laboratory analytical measurement variability, or analytical variability, is small; (ii) the component of variability in the data due to the combined effect of field sampling variability and analytical

variability is small; (iii) given (i) and (ii), it was reasonable to average replicates to determine mill specific values for use in other analyses; and (iv) analytical variability or field sampling variability alone are not sufficient to explain the variability observed in the TCDD and TCDF data. These results suggest that the observed variability in the data may be due to differences among the mills in production, manufacturing processes and other factors that could be controlled at a specific mill.

We were able to examine some other sources of variability in the bleaching operations. This analysis examined the combined output of TCDD from effluent, sludge, and pulp with output adjusted for the amount of pulp production in each mill. The results are not strong and tend to support working hypotheses generally accepted in the industry concerning relationships among plant operations and generation of TCDD and TCDF. The data collected in this study were not intended to support an analysis of what factors would account for increases in TCDD and TCDF. However, we were able to examine two factors that were presumed to influence TCDD and TCDF levels using the available data. These factors were chlorine usage and chlorine dioxide substitution for chlorine usage.

Chlorine Usage: Chlorine is important because it is used in bleaching to whiten the pulp and other studies have shown that most TCDD and TCDF are produced in the chlorination stage. Different amounts of chlorine are required in bleaching to produce different products. For example, high grade writing paper requires more bleaching than diapers.

Using the 104 Mill data it is possible to demonstrate a weak positive relationship between the chlorine use and TCDD formed. A plot of the data is shown in Figure 8 overlaid by the estimated regression line and a 90% confidence band about the estimated regression line. This relationship accounts for only about 30% of the variation in the data. One problem may be that over-chlorination in the chlorination stage even for a very short period of time may lead to excess TCDD and TCDF although the overall chlorination may remain about the same as usual (see reference [3]). This problem may provide a partial explanation of the relative weakness of the estimated relationship. In Figure 8, the vertical axis is the total TCDD in lbs/ton of air-dried brownstock pulp adjusted for amount of production. The horizontal axis is the amount of chlorine in lbs/ton of air-dried brownstock pulp. The estimated regression equation is

$$\log_{10}(\text{total TCDD}) = -0.449 + 0.010 * Cl_2$$

with an R^2=32%. The plot shows an upward trend in the data although the relationship is not well defined.

Chlorine Dioxide Substitution: Chlorine dioxide is substituted for chlorine in bleaching to improve effluent quality and to reduce TCDD and TCDF (reference [3]). Very few mills substituted chlorine dioxide for more than 30% of their chlorine usage (most substituted between 0 and 20 %) and not all mills substituted. In the 86 kraft mills, 59 bleach lines out of the 165 bleach lines did not use any substitution. Regression analysis of data from mills that practice substitution demonstrated a relationship which accounted for at most 16% of the

variation in the data. The increased use of substitution produced slight reductions in TCDD formation. The data are shown in Figure 9. The estimated regression equation is

$$\log_{10}(\text{total TCDD}) = 1.145 - 0.693 * \%ClO_2\text{substitution}$$

with R^2=16%. The plot in Figure 9 shows the weak relationship between the total TCDD and the percent ClO_2 substitution, which accounts for the low R^2.

Analysis of chlorine and chlorine dioxide substitution separately is problematic. The order that these chemicals are added in the bleaching process may affect the amount of TCDD and TCDF formed. Adding the chemicals in stages instead of in one dose may reduce TCDD and TCDF. In laboratory and field studies, it has been found that there is competition between the chlorine and chlorine dioxide and this competition may increase the amount of chlorine related to the formation of TCDD and TCDF (reference [5]).

EPA is continuing to collect data and study the pulp and paper industry to support the development of water pollution control regulations. We are aware that the industry is dynamic and responding to the challenge of reducing and controlling TCDD and TCDF discharges. The situation represented by the data collected in 1988 is changing. Preliminary analysis of some post-1988 data indicate some changes in the amounts of TCDD and TCDF in effluent, pulp and sludge from paper mills have may occurred. Changes in the levels of TCDD and TCDF discharged should not, however, affect the conclusions based on the 1988 data presented here. EPA is sampling a number of mills (total of 16 to 19 mills) with 4 or more of these planned for long term sampling. In these

sampling episodes, EPA is collecting TCDD and TCDF concentrations at more places in the process than were collected in the 104-Mill Study. This should provide a more complete database and support the evaluation more factors influencing variability in TCDD and TCDF measurements. In addition, a detailed questionnaire has been mailed to these facilities. Additional self-monitoring data and process information should be provided with the completed questionnaires which will add substantially to the base of information available to support evaluations of the industry and the Record for EPA's rulemaking activities.

REFERENCES

[1] USEPA/Paper Industry Cooperative Study, The "104-Mill Study", Statistical Findings and Analyses, U.S. EPA, Washington, D.C., July 13, 1990.

[2] Preliminary Draft Report, Follow-up Analysis of Analytical Data from the 104 Mill Study, U.S. EPA, Washington, D.C., July 31, 1990.

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[8] A Study of the Variability of 2,3,7,8 - TCDD and 2,3,7,8-TCDF in Bleached Kraft Mill Pulps, Sludges and Treated Wastewaters, Technical Bulletin No. 568, National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York, July, 1989.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MR. KAHN: Larry, no questions?

MR. BERTHOUEX: Not to ask a question, but to add a comment.

My name is Mac Berthouex from the University of Wisconsin.

I like this kind of a study very much and I wish there were more analysis of variance studies made. I'll just briefly tell of a similar experiment that was done in Denmark on dioxin and furan emissions from incinerators, a designed experiment with loading rate to the incinerator, operating temperature of the incinerator, type of waste going in and so on. When it was all designed, they found out they didn't have enough samplers of the same kind to study all of the incinerators in the study. So, just as a matter of chance, they were forced to add one variable to the experiment which was the kind of a sampler. Both samplers were widely used and approved and when all of the data was in, it turned out that the most significant variable of all the things under study was this sampler. The difference between samplers explained more variation than analytical procedures which were done in different laboratories and a lot of other things.

I suspect if we saw more studies of this kind, we would find out that very often we may blame the chemist for variations in the data which is really not their fault and it is coming from other sources and it's very important for us to know what the sources are.

MR. TELLIARD: He's a damn engineer.

MR. BERTHOUEX: I am an engineer. You can blame the engineers if you like.

MR. TELLIARD: Thank you.

MR. KAHN: Well, I think that's part of the message to this group. It's when you see these high levels of variability, it's not the chemist's fault, it's somebody else.

MR. TELLIARD: Thank you, Henry.

FIGURE 1

TCDD VS. TCDF: EFFLUENT SAMPLES

KRAFT MILLS

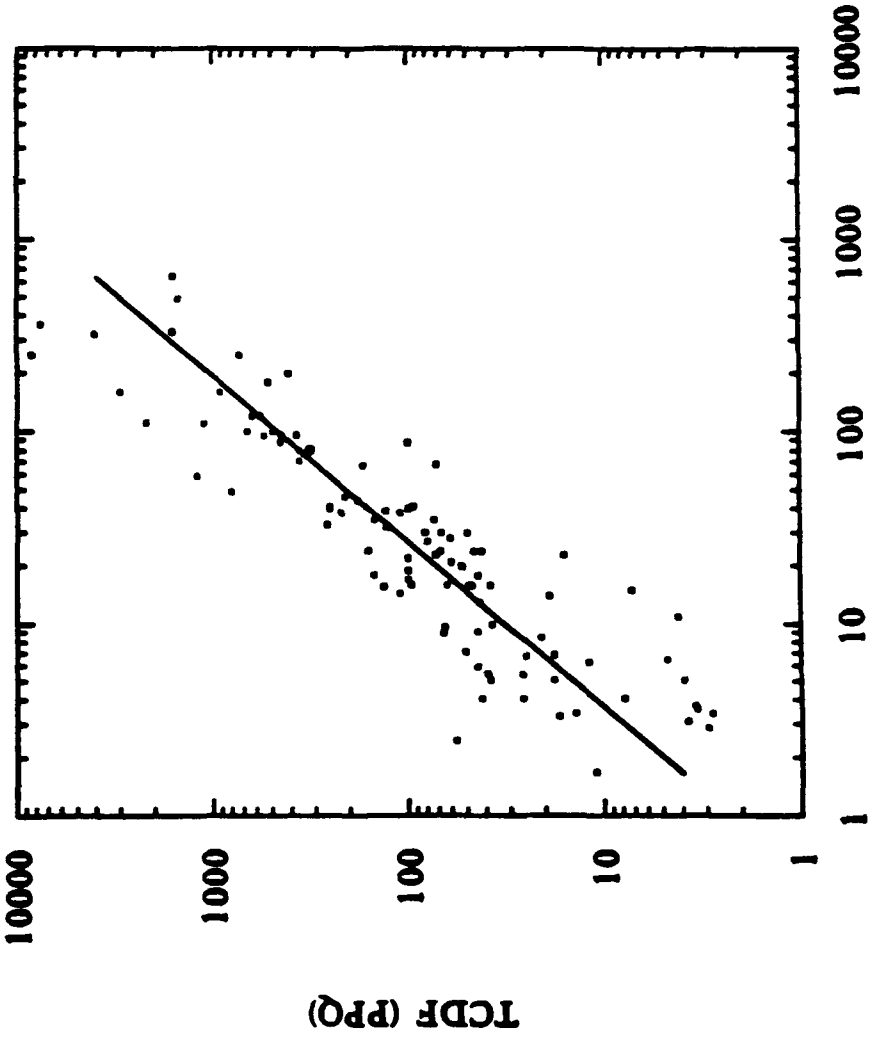


FIGURE 2

PROBABILITY PLOT: EFFLUENT TCDD

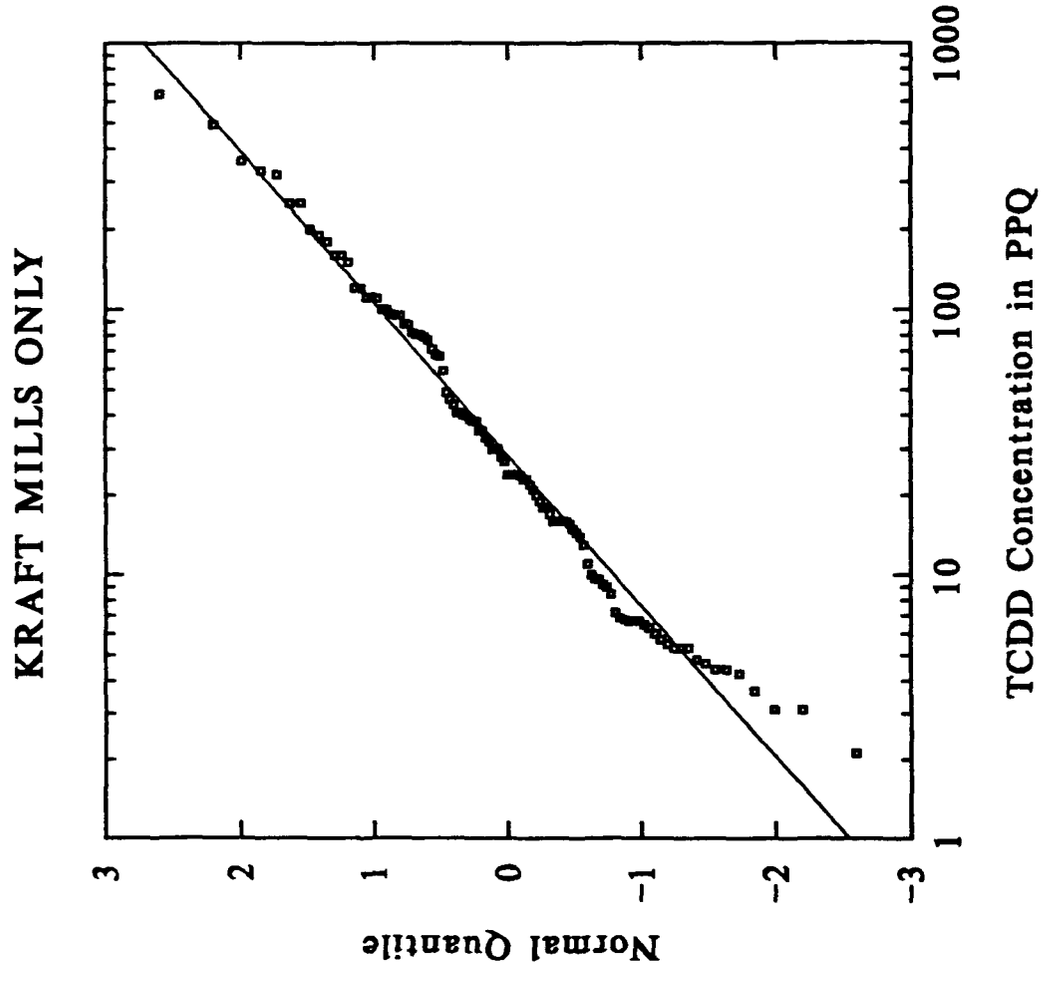


FIGURE 3

EFFLUENT TCDD DETECTION LEVELS
SAMPLE CUMULATIVE DISTRIBUTION GRAPH

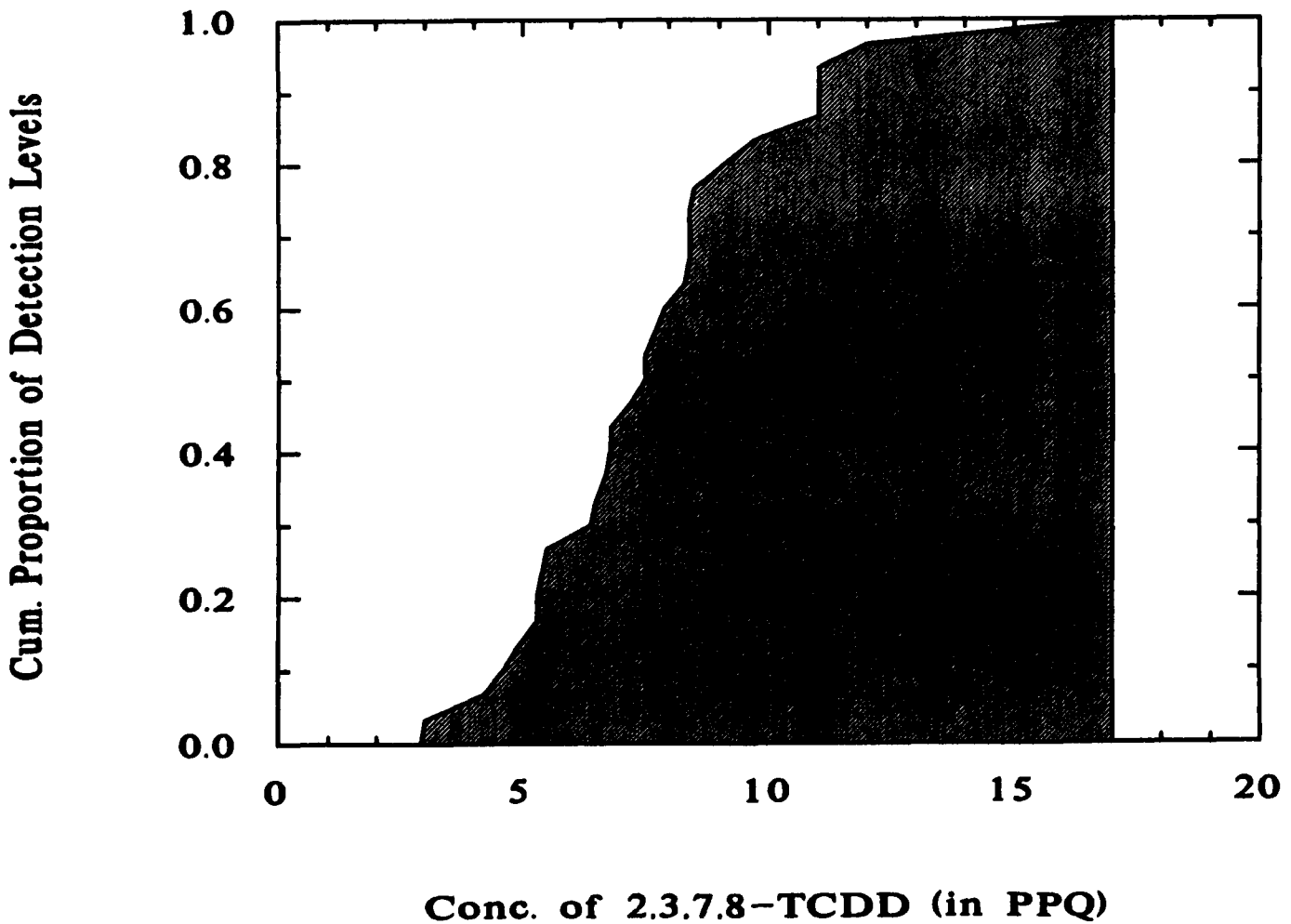


FIGURE 4

TCDD: EFFLUENT LAB REPLICATES

KRAFT MILLS ONLY

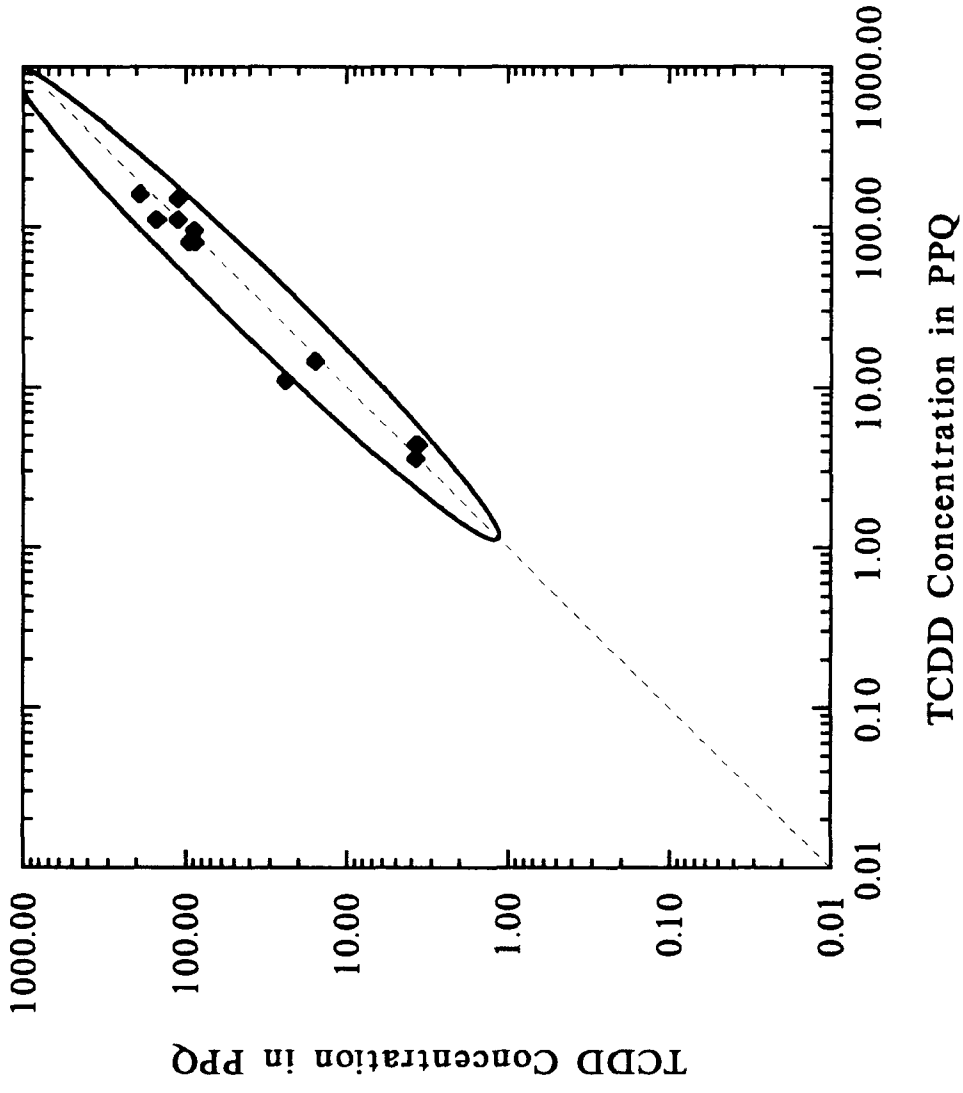


FIGURE 5

TCDD: EFFLUENT FIELD REPLICATES

KRAFT MILLS ONLY

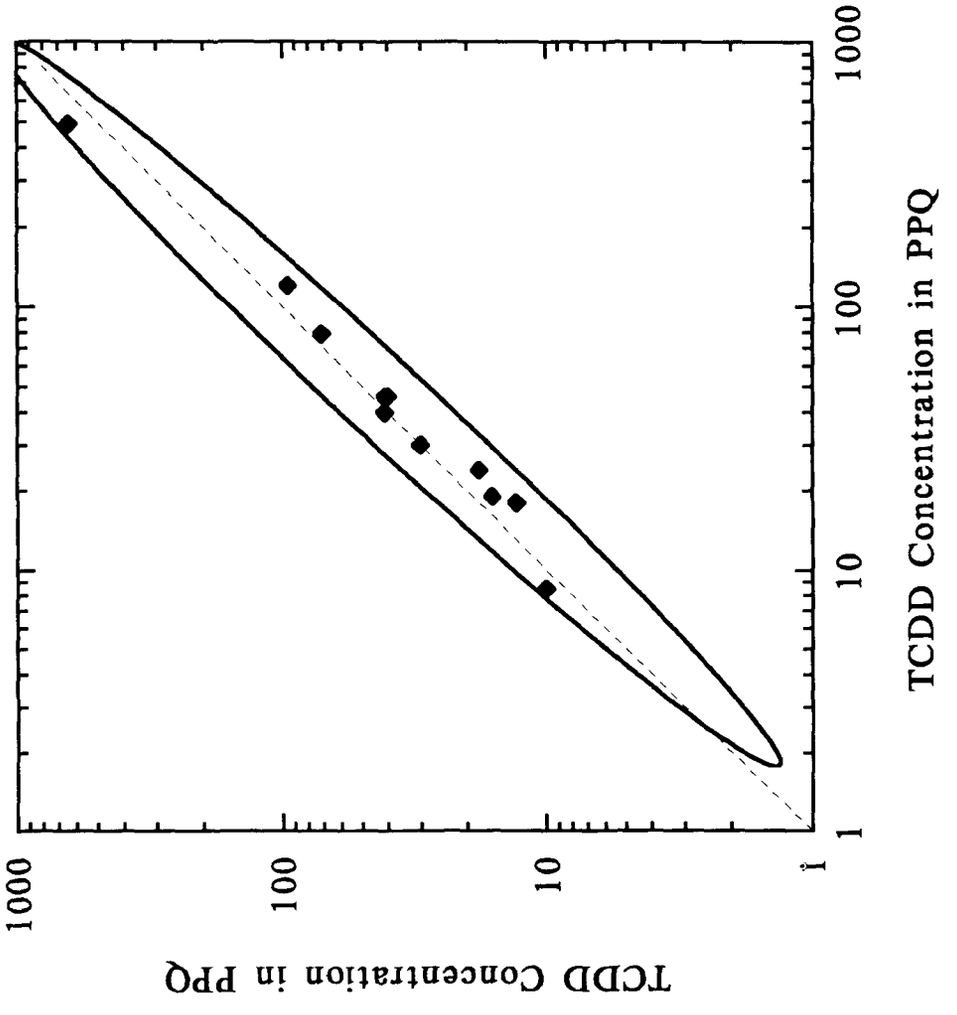


FIGURE 6

TCDD: EFFLUENT LAB REPLICATES

SULFITE MILLS ONLY

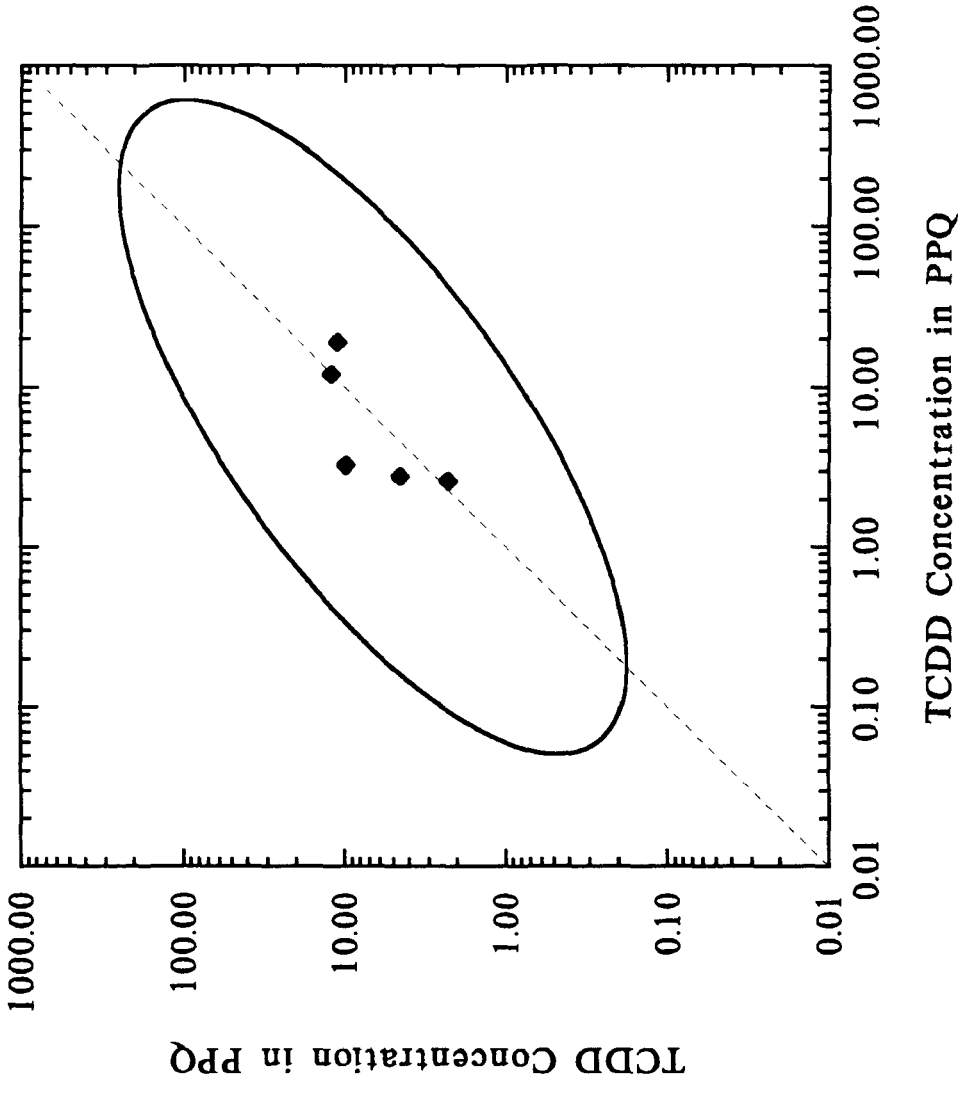


FIGURE 7
CUMULATIVE DISTRIBUTION OF TCDD EFFLUENTS
KRAFT SAMPLES ONLY
BY REPLICATE TYPE

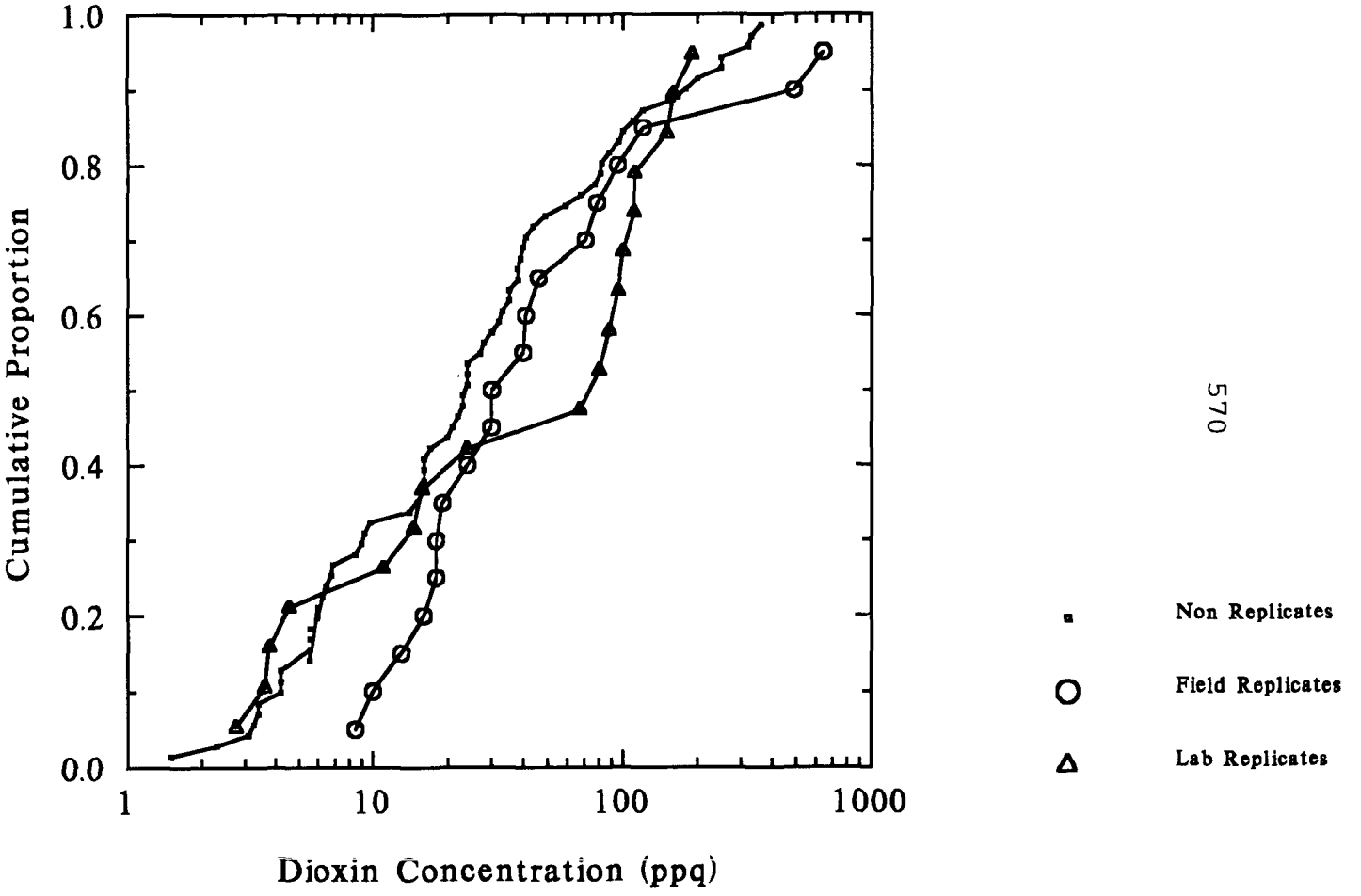


FIGURE 8

Cl_2 vs. ADJUSTED TOTAL TCDD

KRAFT MILLS ONLY

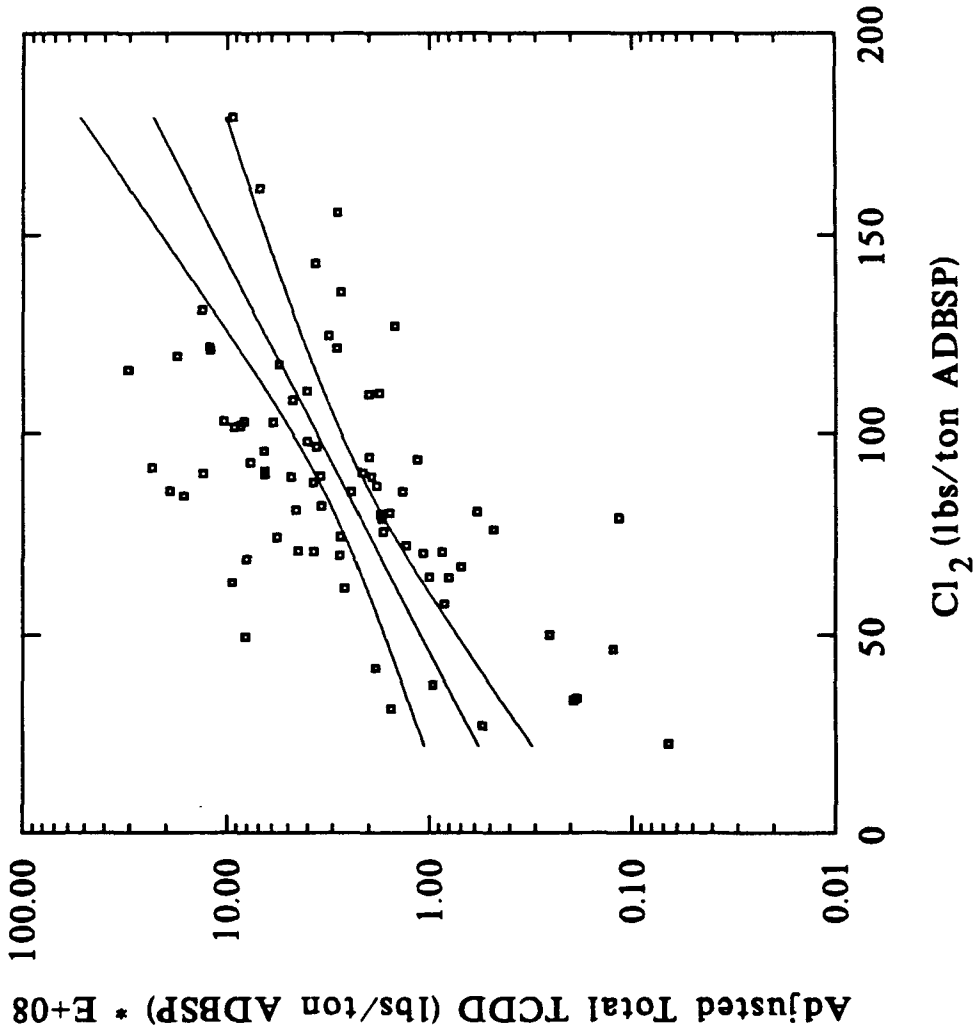


FIGURE 9

% ClO_2 SUBSTITUTION vs. ADJUSTED TOTAL TCDD

KRAFT MILLS ONLY

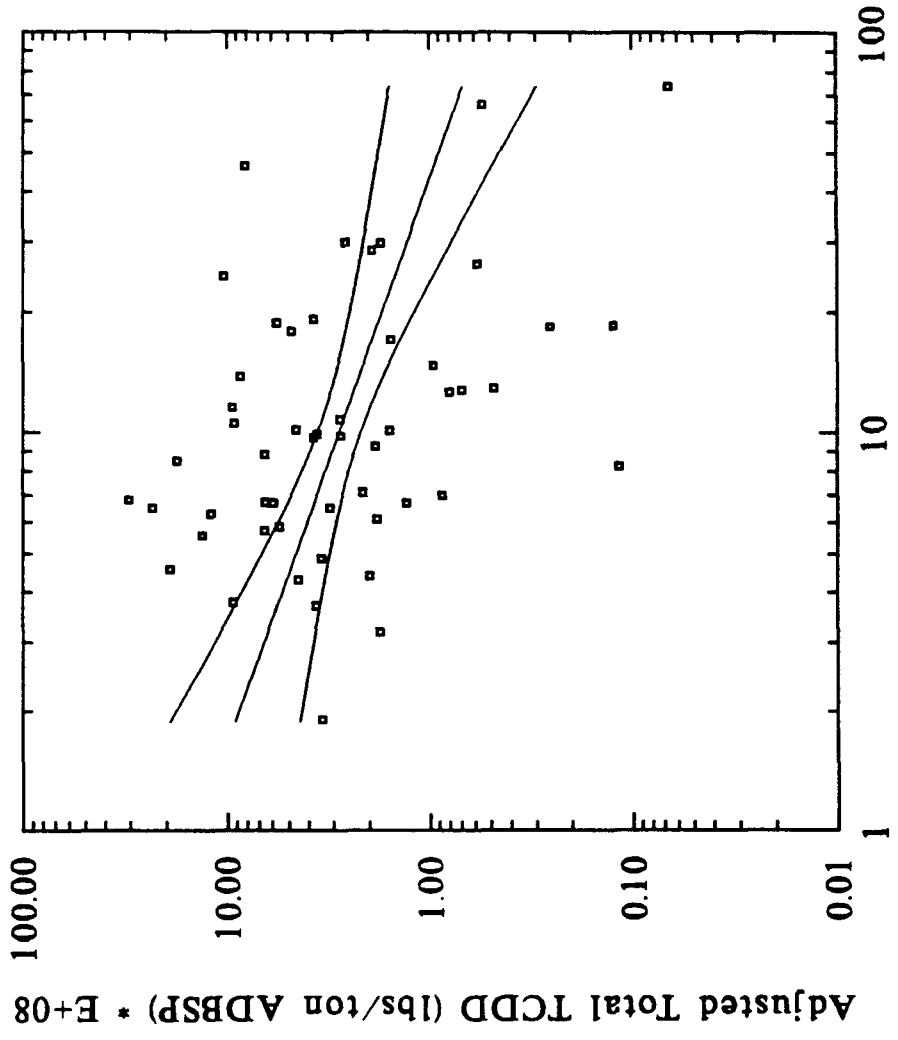


TABLE 1

COMPONENTS OF VARIANCE RESULTS
EFFLUENT REPLICATE SAMPLES FROM KRAFT MILLS

	N	SS1	SS1%	SS2	SS2%
Lab Replicates					
Log_{10} (TCDD)	15	5.57	98.6	0.08	1.4
Field Replicates					
Log_{10} (TCDD)	19	4.75	99.2	0.04	0.8

SS1 = Between replicate set sum of squares, i.e., the sum of the squared deviations of the replicate set means from the overall mean

SS2 = Within replicate set sum of squares, i.e., the sum of the squared deviations of individual sample measurements from their respective replicate set means

N = Number of replicate sets

SS = Total Sum of Squares = SS1 + SS2

SS1% = (SS1/SS)*100

SS2% = (SS2/SS)*100

MR. TELLIARD: Our next speaker is Chuck White. Chuck is also with the Office of Water.

Chuck is going to talk about a study that we did a year ago...almost a year and half ago...on a national evaluation of domestic sewage sludge from some 180-something publicly-owned treatment plants and he's going to address a multi-approach to the various analytes that were analyzed in that study.

Chuck?

STATISTICAL ANALYSIS OF ANALYTE CONCENTRATIONS IN MUNICIPAL SEWAGE SLUDGE WITH MULTIPLE DETECTION LIMITS

Chuck White, USEPA
Henry Kahn, USEPA
Kathleen Stralka, SAIC

Presented at
The Fourteenth Annual EPA Conference on
Analysis of Pollutants in the Environment
May 9, 1991

Statistical Analysis of Analyte Concentrations in Municipal Sewage Sludge with Multiple Detection Limits

Chuck White, USEPA
Henry Kahn, USEPA
Kathleen Stralka, SAIC
Washington, D.C.

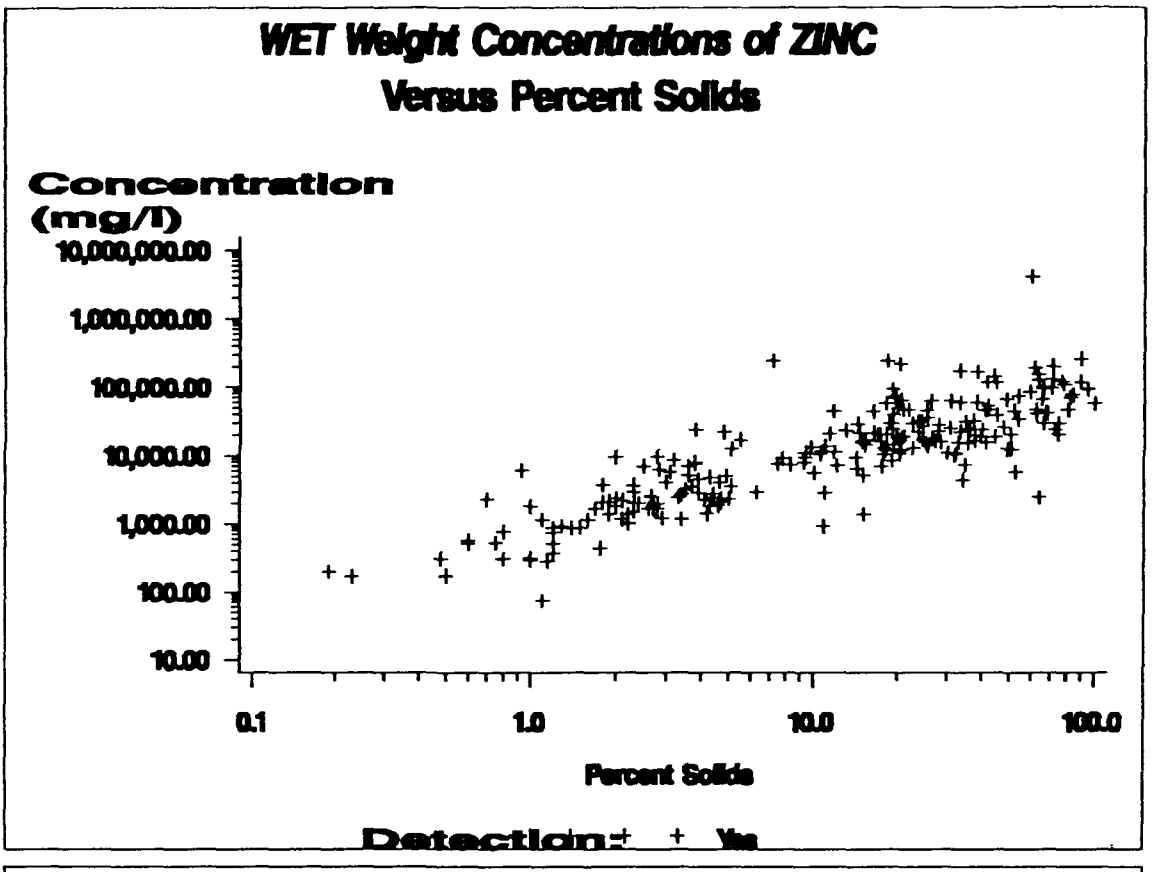
This paper will present the current analysis approach to multiple "detection limits" contained within physical analytical data from the National Sewage Sludge Survey (NSSS). The term "detection limit" generically describes an analytical response where it has been determined that the concentration of an analytical material, e.g., zinc concentration, is below a certain level although a single numeric estimate for that concentration is not produced. We will provide basic background for the survey, our motivation to seek out innovative methods of statistical analysis, describe some of the methods we considered, present selected results of our analyses, and discuss the usefulness of the selected statistical approach to the analysis of these NSSS data.

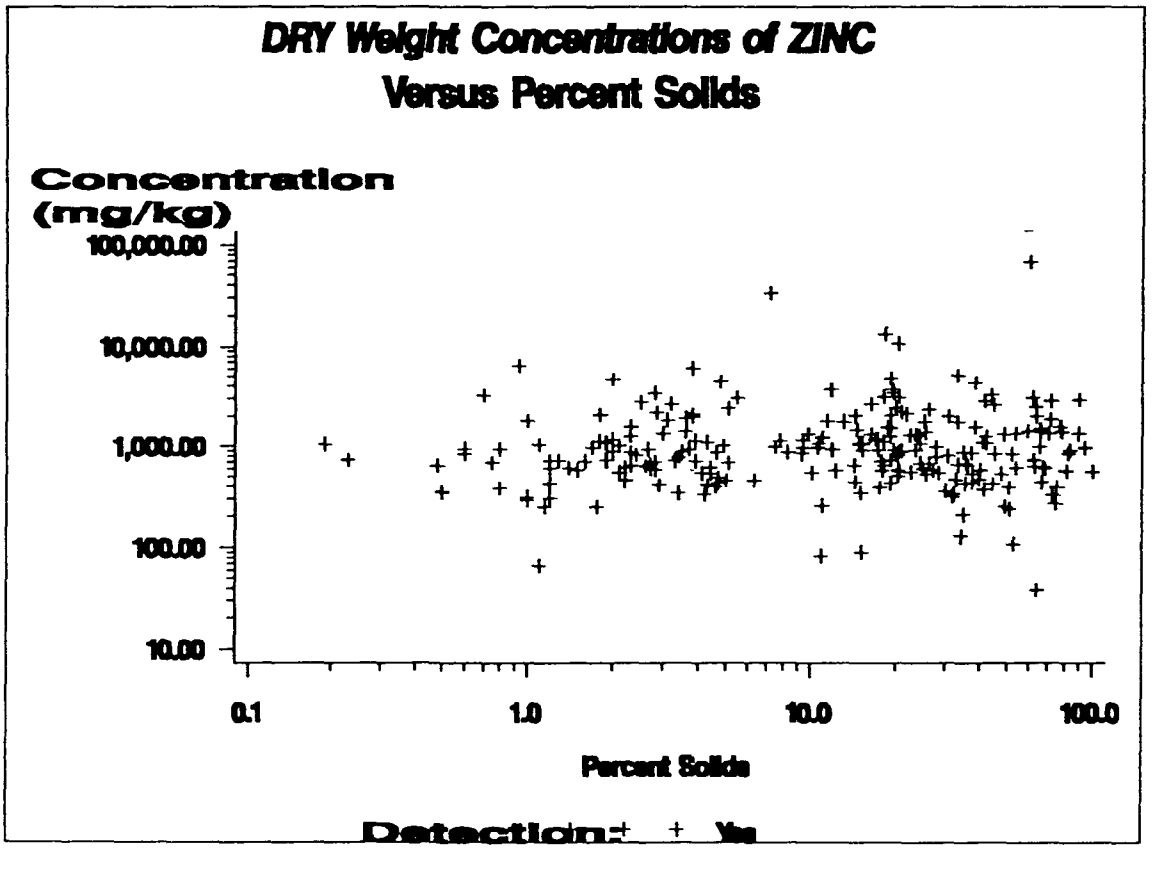
Background on the Survey

The NSSS was conducted in order to obtain technical, economic, and chemical analytical data that will support analyses required for the development of sewage sludge use and disposal regulations under the Clean Water Act. These analyses include the regulatory impact analysis and the aggregate risk analysis. The regulatory impact analysis will estimate the cost and potential for closures of Publicly Owned Treatment Works (POTWs). The aggregate risk analysis will estimate the health impact of current use and disposal practices.

The survey included questionnaire and physical analytical portions. The questionnaire portion requested both physical process and economic condition information. The physical analytical portion physically sampled final process sewage sludge and analyzed these samples for 412 analytes. In order for the Agency and the Public to better understand the potential risk associated with sludge use and disposal practices, the current statistical analysis has focused on estimating national distributions for 28 pollutants of concern identified by analyses of previous data collections.

The NSSS was restricted by design to POTWs that practice secondary or better wastewater treatment. The population of POTWs practicing secondary or better treatment was determined from responses to the 1986 NEEDS Survey conducted by EPA's Office of Municipal Pollution Control. For the physical analytical portion of the survey, this population of 11,407 POTWs was divided into strata by four flow groups. These four flow groups were:


WET Weight Concentrations of ZINC
Versus Percent Solids
Concentration
(mg/l)
10,000,000.00
1,000,000.00
100,000.00
10,000.00
1,000.00
100.00
10.00
0.1
1.0
10.0
100.0
Percent Solids
Detection: + Yes


DRY Weight Concentrations of ZINC
Versus Percent Solids
Concentration
(mg/kg)
100,000.00
10,000.00
1,000.00
100.00
10.00
0.1
1.0
10.0
100.0
Percent Solids
Detection: + Yes

Flow < = 1 Million Gallons per Day
1 MGD < Flow < 10 MGD
10 MGD < Flow < = 100 MGD
100 MGD < = Flow

A stratified probability sample of 208 POTWs was then selected from within these strata. This probability design provides the basis for calculating unbiased national estimates with calculable sampling variability. However, the stratification used in the design requires that the sampling fraction for each stratum be taken into account when calculating such unbiased national estimates. The sampling fraction was the probability that a particular POTW within a particular stratum would be selected for participation in the survey.

Characteristics of the Physical Analytical Data

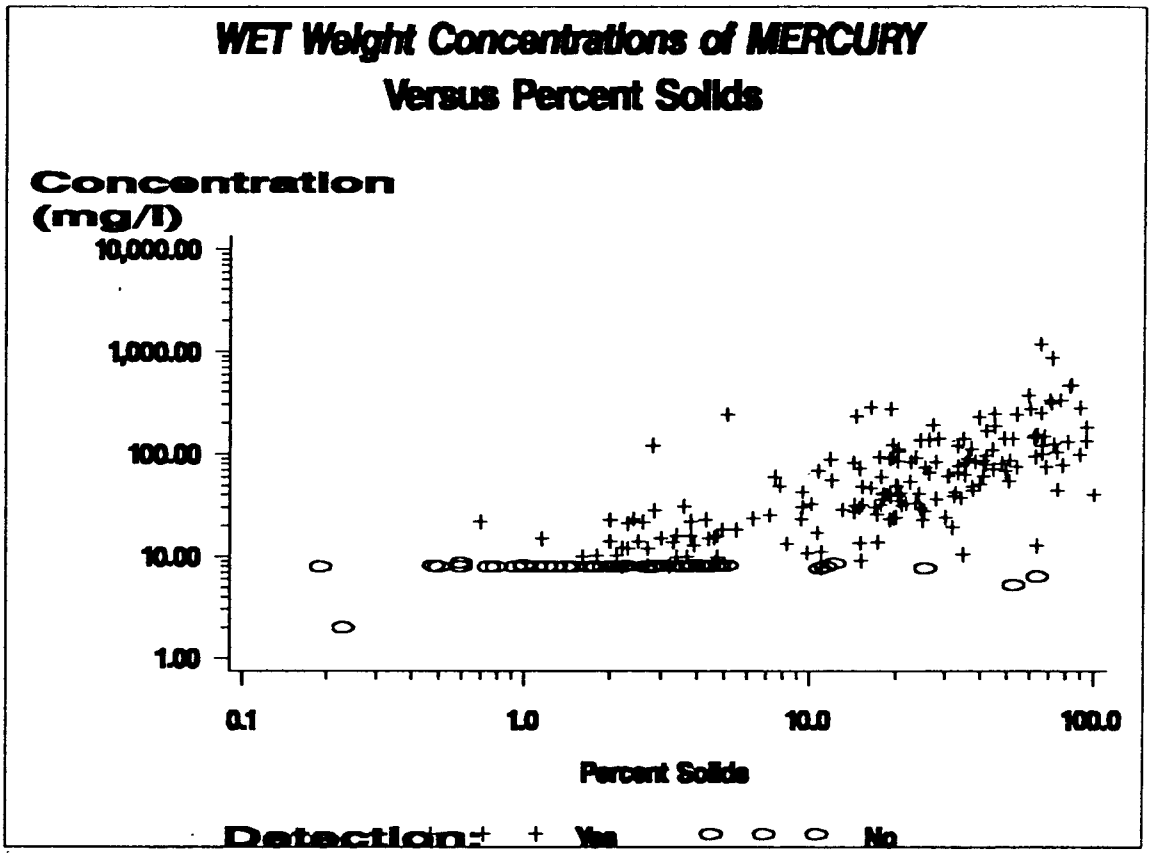
Innovative statistical techniques were adopted because of the chemical analytical results obtained in the survey. Relevant characteristics of these results were caused by a combination of the percent solids correction required to compare analyte concentrations in sludges and by the behavior of the "detection limits" reported from the survey samples.

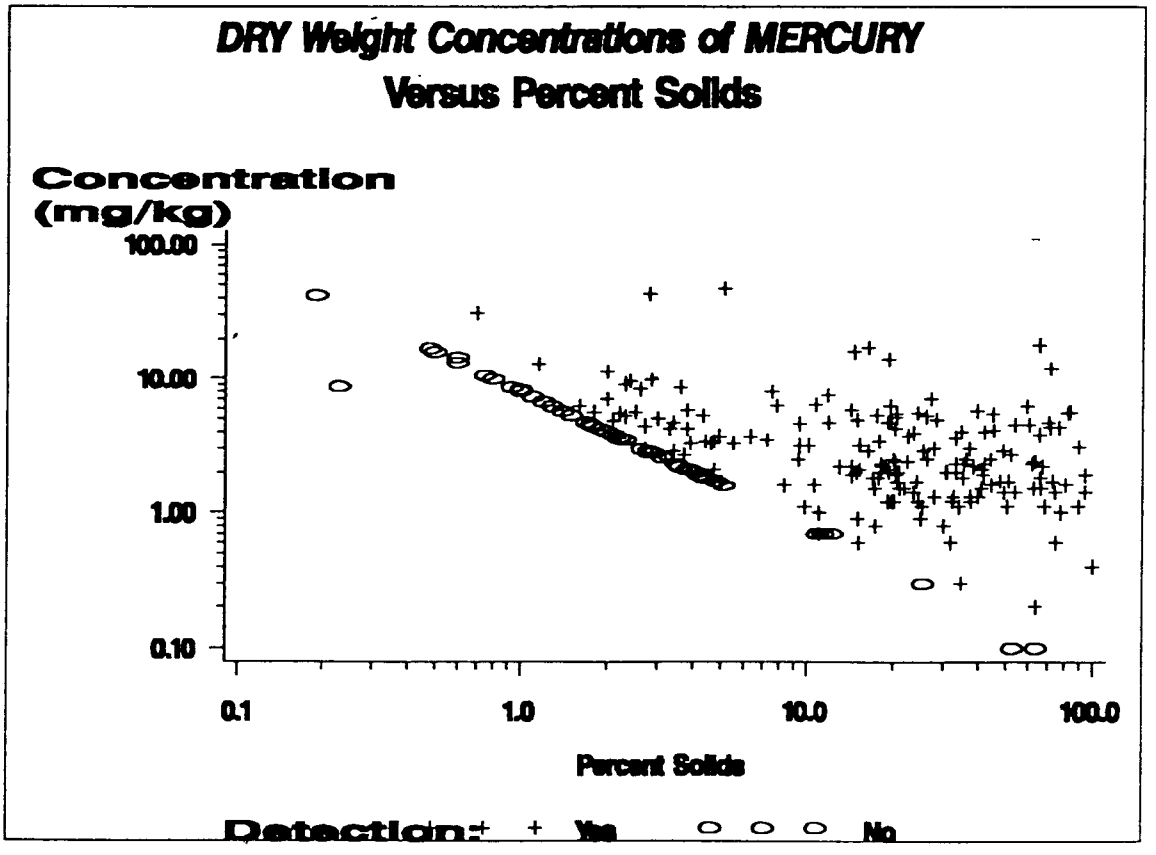
In general, there is an increasing relationship between whole sample concentrations of pollutants and the percent solids in a sewage sludge sample. This relationship is illustrated by the plot titled *Percent Solids of NSSS Samples Versus Wet Weight Concentrations of Zinc*. However, converting all sample results to a dry weight basis removes this relationship. The plot titled *Percent Solids of NSSS Samples Versus Dry Weight Concentrations of Zinc* illustrates that this trend is removed by the dry weight conversion. This log-log plot shows dry weight Zinc concentrations varying in a random fashion about some median concentration value independently of percent solids.

The form of "detection limit" used in the NSSS is called a Minimum Level. The Office of Science and Technology in EPA's Office of Water defines the Minimum Level to be the lowest acceptable concentration level used to establish the calibration relationship. That relationship describes the response of the measurement system to analyte concentrations. The plot titled *Percent Solids of NSSS Samples Versus Wet Weight Concentrations of Mercury* illustrates the whole matter concentration results and Minimum Levels for a pollutant where a noticeable portion of the sample results were reported to be below the Minimum Level. The plot titled *Percent Solids of NSSS Samples Versus Dry Weight Concentrations of Mercury* illustrates the mixture of quantified values and Minimum Levels that required the search for innovative statistical methods. In particular, notice that Minimum Levels for this analyte occur throughout the same range of concentrations as the quantified values.

Estimating the Frequency Distribution for Pollutant Concentrations within a Flow Group

The occurrence of "detection limit" observations in environmental data is not unusual and there are a number of statistical methods for analyzing such data. Several computationally simple methodologies and the Agency's current methodology for most analytes in municipal sewage sludge are discussed briefly.


WET Weight Concentrations of MERCURY
Versus Percent Solids
Concentration
(mg/l)
10,000.00
1,000.00
100.00
10.00
1.00
0.1
1.0
10.0
100.0
Percent Solids
Detection: + Yes o No


DRY Weight Concentrations of MERCURY
Versus Percent Solids
Concentration
(mg/kg)
100.00
10.00
1.00
0.10
0.1
1.0
10.0
100.0
Percent Solids
Detection: + Yes o No

Computationally Simple Methodologies

We will discuss four computationally simple methodologies for estimating the frequency distribution within flow groups for pollutant concentrations when data from a particular pollutant contains several "detection limit" values. The first two of these methods will be used in illustrating the estimates calculated by EPA's current method.

One method is to assign the Minimum Level ("detection limit") value to sample results reported below the Minimum Level. However, the true concentration value could be anywhere between zero and the Minimum Level. Hence, the method of assigning the maximum possible concentration value for the sample will result in overestimates for the frequency of occurrence for concentrations of the pollutant at the reported Minimum Levels.

Another method is to assign the sample results reported below the Minimum Level to the value zero. This method is likely to underestimate the frequency of occurrence for concentrations of the pollutant that are actually between zero and the Minimum Level.

A third method is to discard sample results reported below the Minimum Level. This method will overestimate the frequency of occurrence within the flow group for higher concentrations of the pollutant because pollutant concentrations for pollutants not detected at low levels will be treated as if they do not exist. This method discards valuable information contained in the survey results and is not recommended.

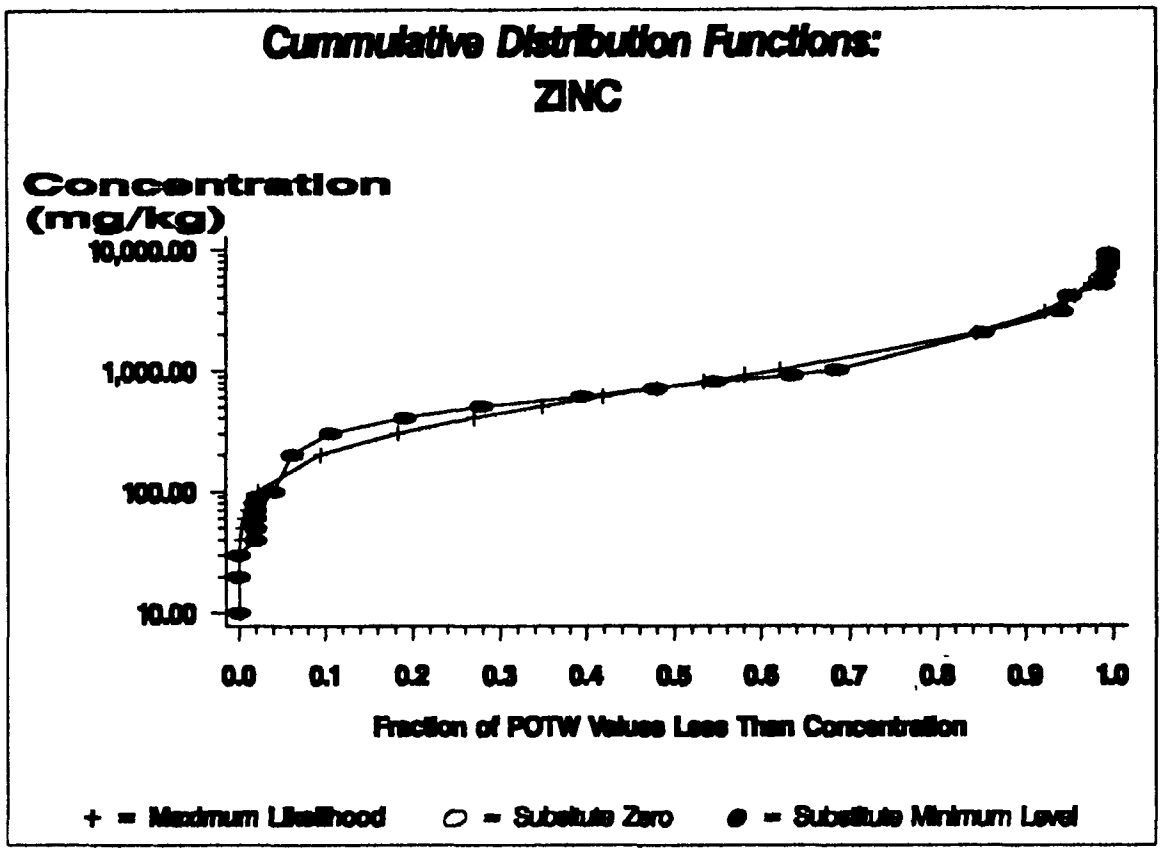
The fourth method is to assign sample results reported as below the Minimum Level to some fraction of the Minimum Level. This method requires a policy decision as to what fraction to use and the precision of any estimates produced from this procedure will depend on how well the chosen fraction models the true concentration values censored by the detection limit. This method is commonly used as a computatuionally simple manner for analyzing censored data.

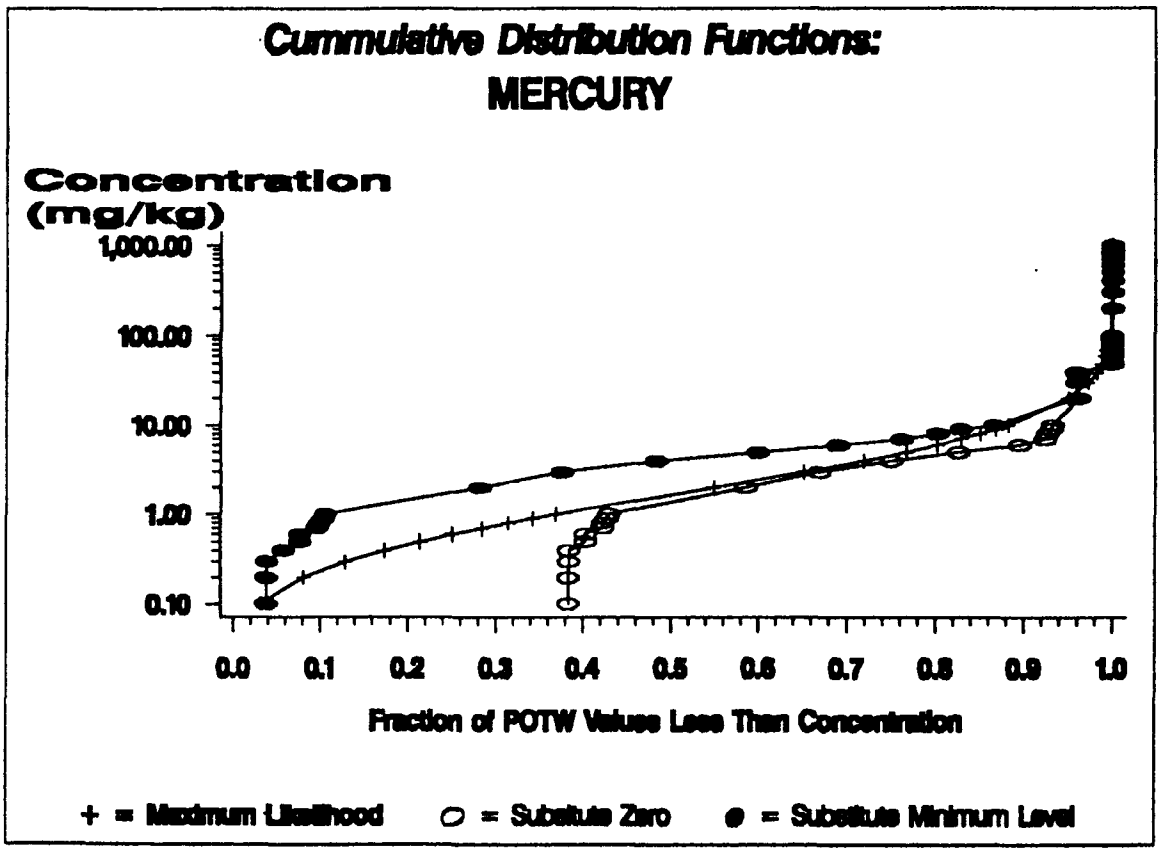
EPA's Current Methodology

EPA's current methodology for sewage sludge concentration data was adopted in order to maximize the use of information contained within the available data. It uses quantified observations, assumptions about the shape of the curve that will describe the frequency distribution for the pollutant concentrations, and Minimum Levels in order to pick the optimum estimate for the scale of the curve with the assumed shape. The assumed shape of the curve is that of the lognormal distribution and the optimum estimate for the scale of the curve is expressed as a combination of the log mean and the log variance for the distribution represented by the curve. This statistical method, called Maximum Likelihood Estimation for Left Censoring Points, was developed for use with the normal distribution and single "detection limits" by Cohen in 1959. Cohen and others have extended this method to multiple "detection limits" and other distributions through a series of papers published in the 1970's and 1980's. An explicit description of how EPA has used this method with the NSSS is provided in the *Technical Support Documentation for Part I of the National Sewage Sludge Survey Notice of Availability.*

Estimating the National Distribution of Pollutant Concentrations

Flow group means and variances were combined in the usual fashion for calculating overall mean and variance estimates from a stratified probability design for sampling. This usual method requires knowledge of the probability for selecting a POTW during the design of the survey in order to weight that POTWs response


Cummulative Distribution Functions:
ZINC
Concentration
(mg/kg)
10,000.00
1,000.00
100.00
10.00
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Fraction of POTW Values Less Than Concentration
+ = Maximum Likelihood
= Substitute Zero
= Substitute Minimum Level


Cummulative Distribution Functions:
MERCURY
Concentration
(mg/kg)
1,000.00
100.00
10.00
1.00
0.10
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Fraction of POTW Values Less Than Concentration
+ = Maximum Likelihood
= Substitute Zero
= Substitute Minimum Level

when calculating national estimates. These combined mean and variance estimates were then assumed to be the mean and variance for a lognormal distribution of pollutant concentrations across the nation. In particular, the estimated distribution is used to represent the distribution among publicly owned treatment works of pollutant concentrations in dry weight sewage sludge that is ready for disposal and that is generated by secondary or better treatment of wastewater.

Fit of the Estimated Distribution

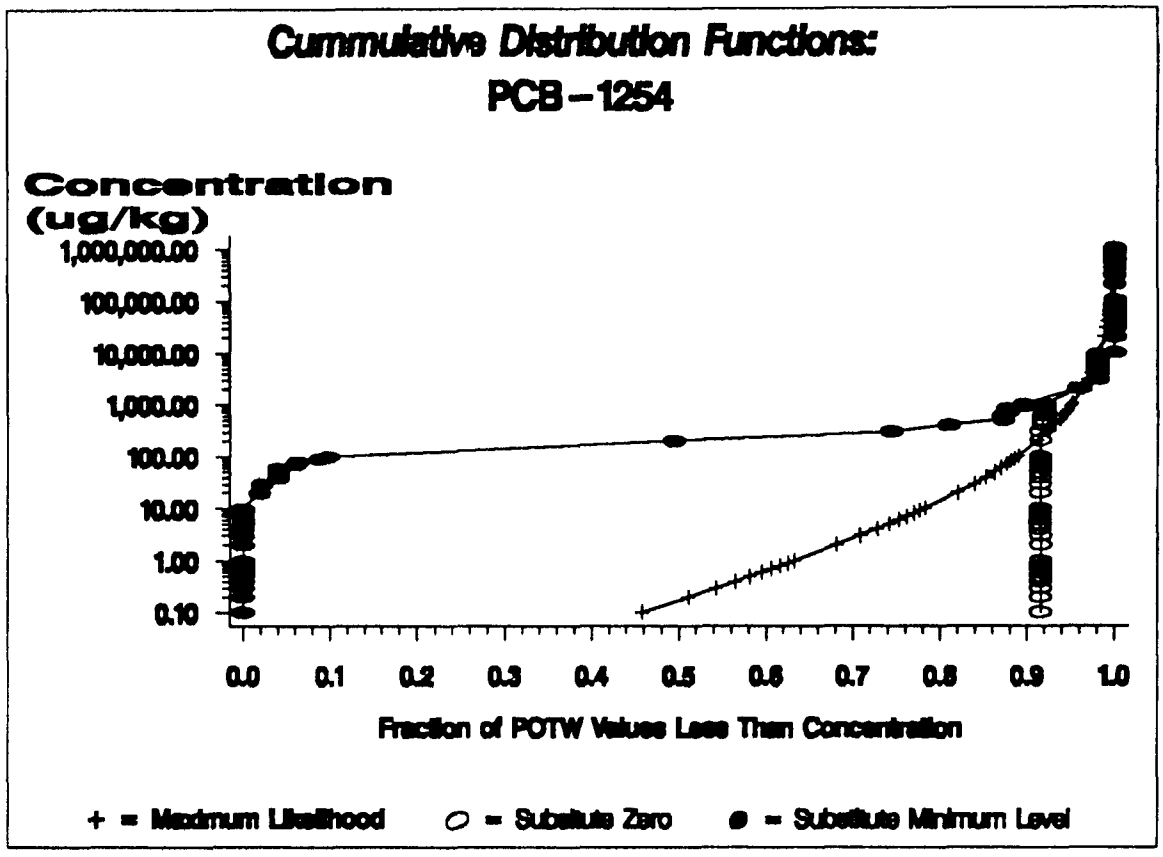
Since the true underlying distribution of pollutant concentrations is unknown, it is difficult to evaluate the fit of the maximum likelihood estimates. However, using two substitution methods, it is possible to approximate upper and lower bounds for each pollutant's cumulative frequency distribution. The upper bound is obtained by assigning the value of the Minimum Level to samples reported below the Minimum Level and then calculating percentiles of the observed distribution in the usual fashion for data from a stratified probability design. The lower bound is obtained by assigning the value of zero to samples reported below the Minimum Level followed again by the usual calculation for percentiles of the observed distribution.

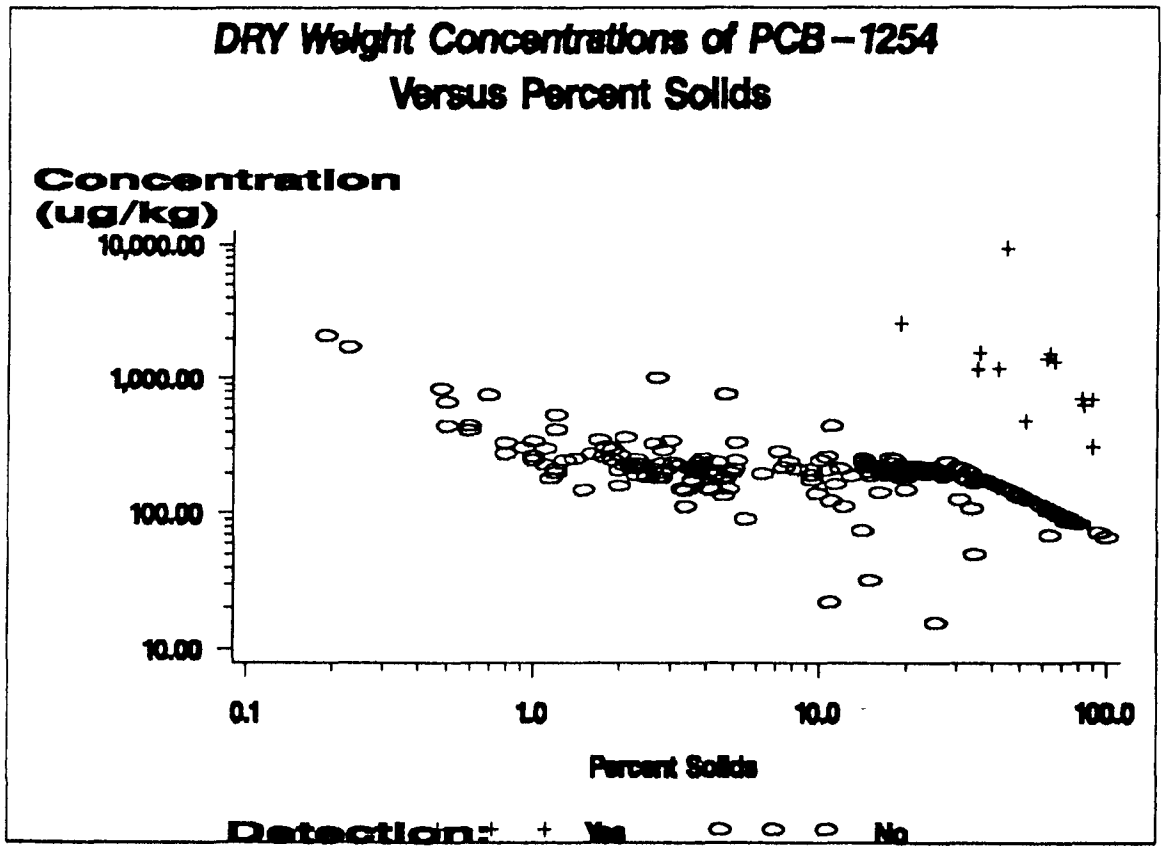
The plot titled *Cumulative Distribution Functions: Zinc* illustrates the curve estimated by these three procedures when all sample results are reported above the Minimum Level. A point on a curve indicates what percentage of the POTWs across the nation have pollutant concentrations below the concentration quantified on the left axis. The curve accented with solid circles is the frequency of occurrence for Zinc concentrations reported in the survey and as adjusted for POTW membership in each appropriate design flow group. Since all sample results are reported above the Minimum Level, this curve illustrates the results from both substitution methods. The curve accented with cross marks is the curve estimated by the maximum likelihood methodology. This estimate appears to model the observed distribution quite closely.

The plot titled *Cumulative Distribution Functions: Mercury* illustrates the curve estimated by this procedure when a noticeable portion of the sample results are reported as below the Minimum Level. The top curve is the frequency of occurrence for Mercury concentrations reported in the survey, as adjusted for POTW membership in each appropriate design flow group, and where the concentration value for a sample reported as below the Minimum Level is set equal to the Minimum Level. The bottom curve is the frequency of occurrence for Mercury concentrations reported in the survey, as adjusted for POTW membership in each appropriate design flow group, and where the concentration value for a sample reported as below the Minimum Level is set equal to zero. This maximum likelihood estimate, generated in the presence of multiple "detection limits," appears to be reasonable.

However, it is important to note that there are at least two cases where this maximum likelihood method does not work with these sludge data. In the first case, if there are no sample concentration values quantified above the Minimum Level for any one of the survey design flow strata then no national estimates will be produced. In the second case, if the data do not approximately follow the lognormal curve than national pollutant concentration, estimates will tend to be unreasonable.

The plot titled *Percent Solids of NSSS Samples Versus Dry Weight Concentrations of PCB 1254* illustrates a pollutant that does not appear to follow a lognormal distribution. In particular, the log-log plot does not show the uncensored dry- weight PCB-1254 concentrations varying in a random fashion about some median concentration value. The plot titled *Cumulative Distribution Functions: PCB-1254* shows that the curve estimated by the current methodology falls between those extreme curves estimated by the substitution methodologies. However, the curve produced by the maximum likelihood estimates does not appear to be reasonable. In particular, the inflection point at the 50th percentile, i.e., the log mean, of the estimated lognormal distribution does not appear on the plot. It does not appear on a plot that shows the range of all observed values and "detection limits" recorded from the survey for this pollutant. Additionally, the gap between the


Cummulative Distribution Functions:
PCB-1254
Concentration
(ug/kg)
1,000,000.00
100,000.00
10,000.00
1,000.00
100.00
10.00
1.00
0.10
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Fraction of POTW Values Less Than Concentration
+ = Maximum Likelihood
= Substitute Zero
= Substitute Minimum Level


DRY Weight Concentrations of PCB-1254
Versus Percent Solids
Concentration
(ug/kg)
10,000.00
1,000.00
100.00
10.00
0.1
1.0
10.0
100.0
Percent Solids
Detection: + Yes No

quantified values and the recored minimum levels provides evicence that this PCB does not vary log symetrically about some median value as would be expected if these data followed a lognormal distribution.

Mean Pollutant Concentration Estimates

The table titled *National Pollutant Concentrations for the National Sewage Sludge Survey Using Lognormal Maximum Likelihood and Arithmetic Substitution Estimation Procedures* presents mean pollutant concentration and standard deviation estimates for zinc, mercury, and PCB-1254. The mean estimates for zinc are consistent with the assumptions of lognormality since the lognormal mean estimate is "close" to the arithmetic estimate. Mean estimates using a methodology specific to the lognormal distribution are expected to be lower than those generated by an arithmetic methodology since the arithmetic methodology allows for more influence from unusually high concentration values. The mean estimates for Mercury are as desired since the lognormal mean estimate is between the arithmetic estimates. However, mean estimates for PCB-1254 provide evidence that the lognormal model does not fit the data for this pollutant. In particular, the estimated mean of the log normal distribution is three orders of magnitude greater than either arithmetic mean and in fact exceeds the highest PCB-1254 concentration value reported in the survey.

National Pollutant Concentrations for the National Sewage Sludge Survey using Maximum Likelihood and Arithmetic Substitution Methods

ANALYTE	UNITS	PERCENT DETECT	ESTIMATION PROCEDURE	MEAN	STANDARD DEVIATION
			Substitue Zero	1,320.34	3,820.82
Zinc	mg/kg	100	Maximum Likelihood	1201.88	1554.42
			Substitute Minimum Level	1,320.34	3,820.82
			Substitute Zero	3.90	8.78
Mercury	mg/kg	63	Maximum Likelihood	5.22	15.54
			Substitute Minimum Level	6.58	8.94
			Substitute Zero	281.33	1,347.08
PCB-1254	ug/kg	8	Maximum Likelihood	118,118,762.55	81,514,762,398.43
			Substitute Minimum Level	515.86	1,324.97

Conclusion

The maximum likelihood procedure for left censoring points allows, in many cases, the calculation of national estimates for pollutant concentration distributions that are more accurate than simpler methods. When the data approximately follow the lognormal distribution and the lognormal dis-

tribution is the model then the maximimum likelihood method method provides excellent results. However, this method does not work in cases where there is an extreme departure from the model distribution. In these cases it is useful to investigate other models since the general maximum likelihood method can be used with other probability models and it is quite powerful. The Office of Water continues investigage appropriate methods to use with data from the NSSS.

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QUESTION AND ANSWER SESSION

MR. TELLIARD: Are there any questions?

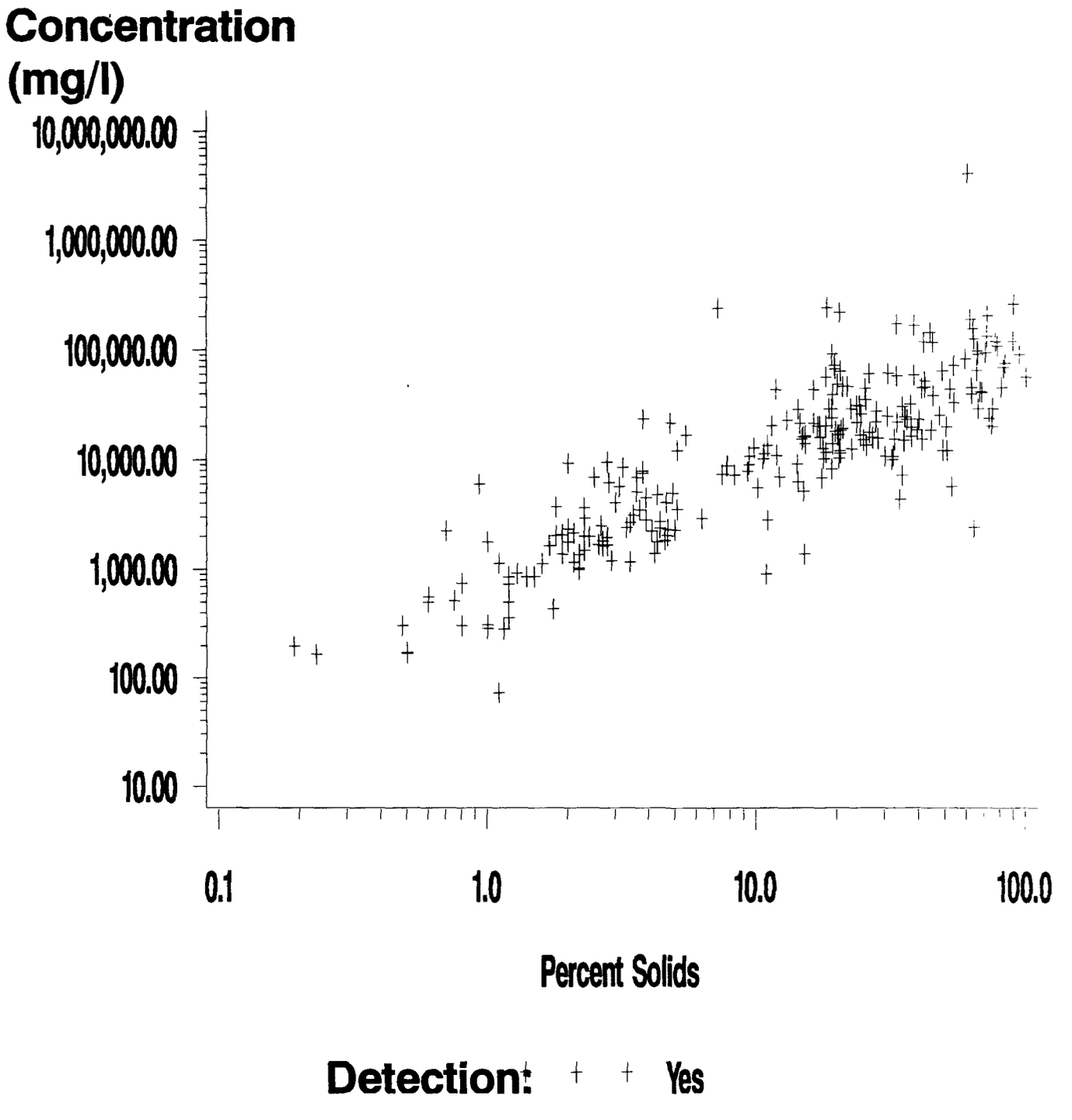
(No response.)

MR. TELLIARD: It's break time. If you could get your coffee and your cookie and come on back in here on time, we will try to keep it moving.

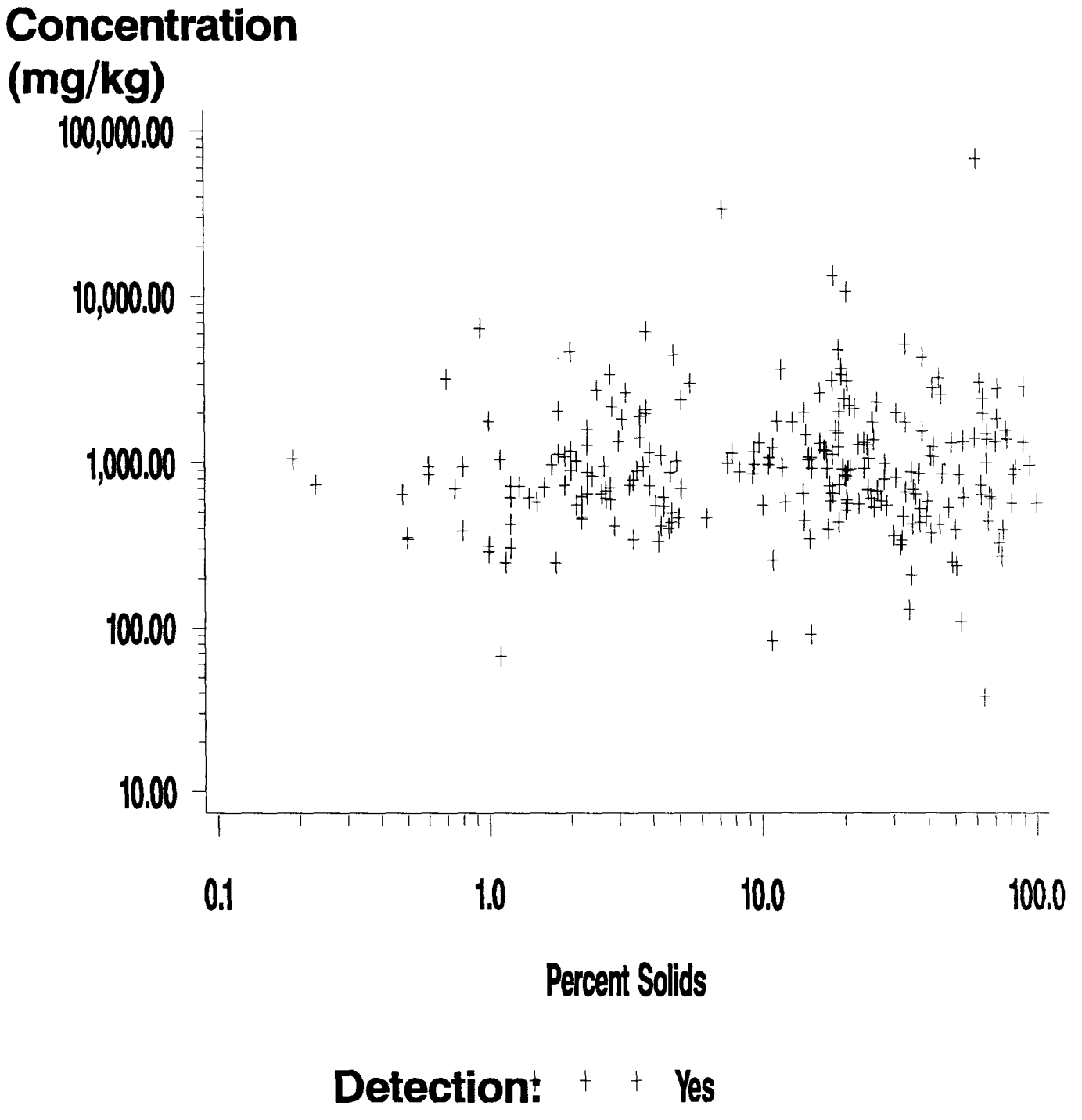
National Pollutant Concentrations from the National Sewage Sludge Survey Using Lognormal Maximum Likelihood and Arithmetic Substitution Estimation Procedures

Analyte	Units	Percent Detect	Estimation Procedure	Mean	Standard Deviation
Zinc	mg/kg	100	Substitute Zero	1,320.34	3,820.82
			Maximum Likelihood	1,201.88	1,554.42
			Substitue Minimum Level	1,320.34	3,820.82
Mercury	mg/kg	63	Substitute Zero	3.90	8.78
			Maximum Likelihood	5.22	15.54
			Substitute Minimum Level	6.58	8.94
PCB-1254	ug/kg	8	Substitute Zero	281.33	1,347.08
			Maximum Likelihood	118,762.55	81,514,762,398.43
			Substitute Minimum Level	515.86	1,324.97

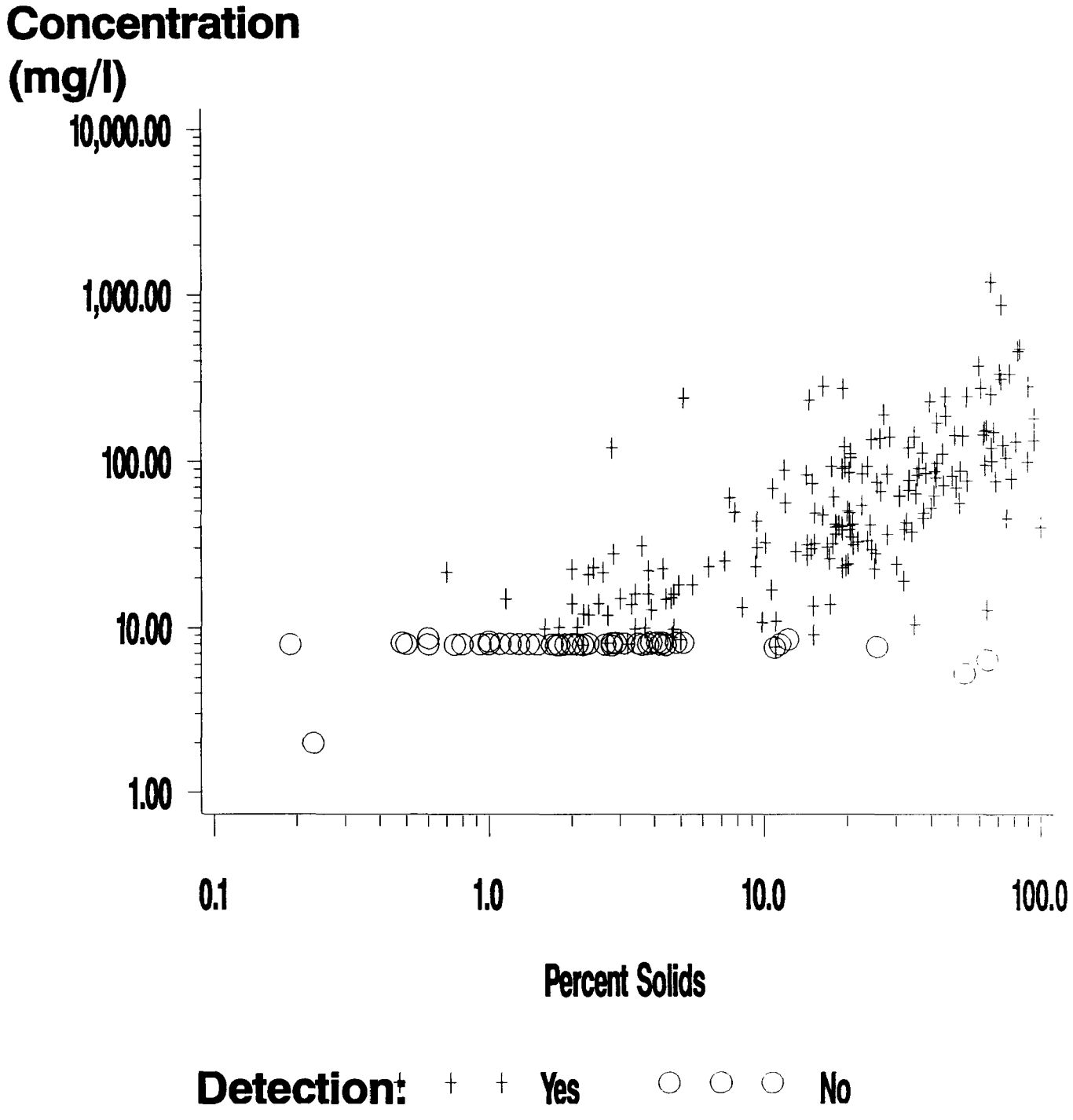
WET Weight Concentrations of ZINC
Versus Percent Solids



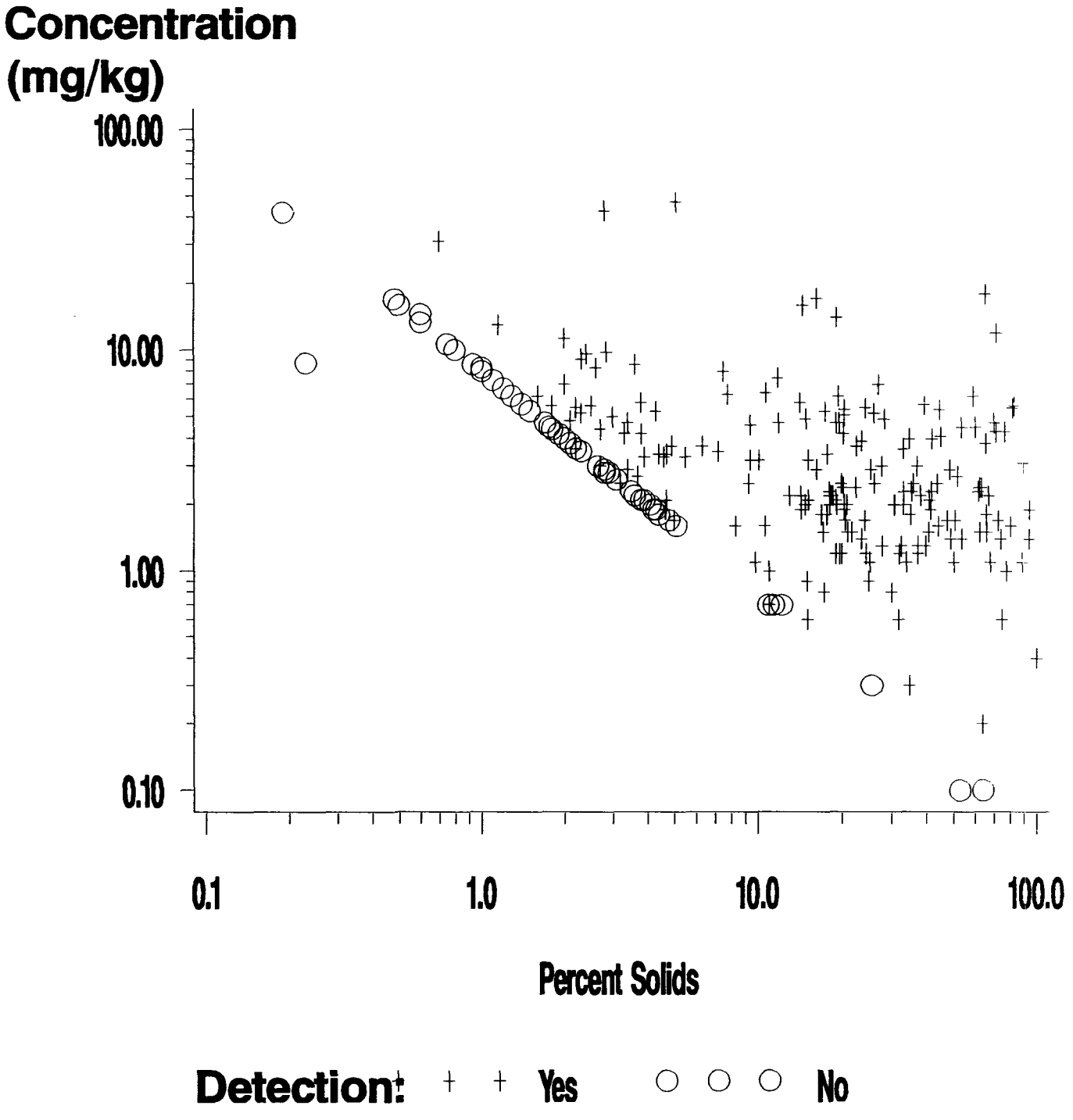
DRY Weight Concentrations of ZINC Versus Percent Solids



WET Weight Concentrations of MERCURY Versus Percent Solids

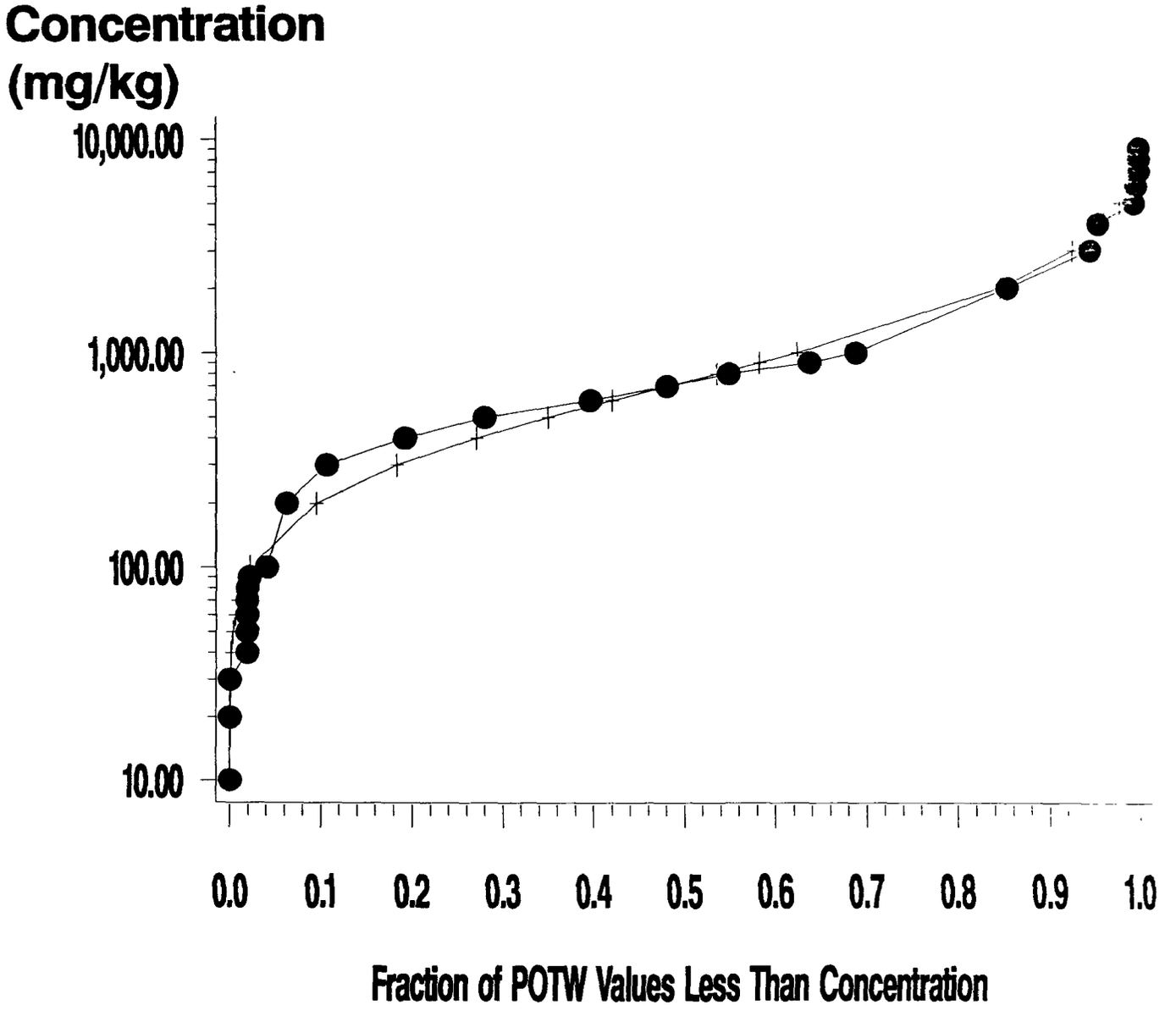


DRY Weight Concentrations of MERCURY Versus Percent Solids



Cummulative Distribution Functions:

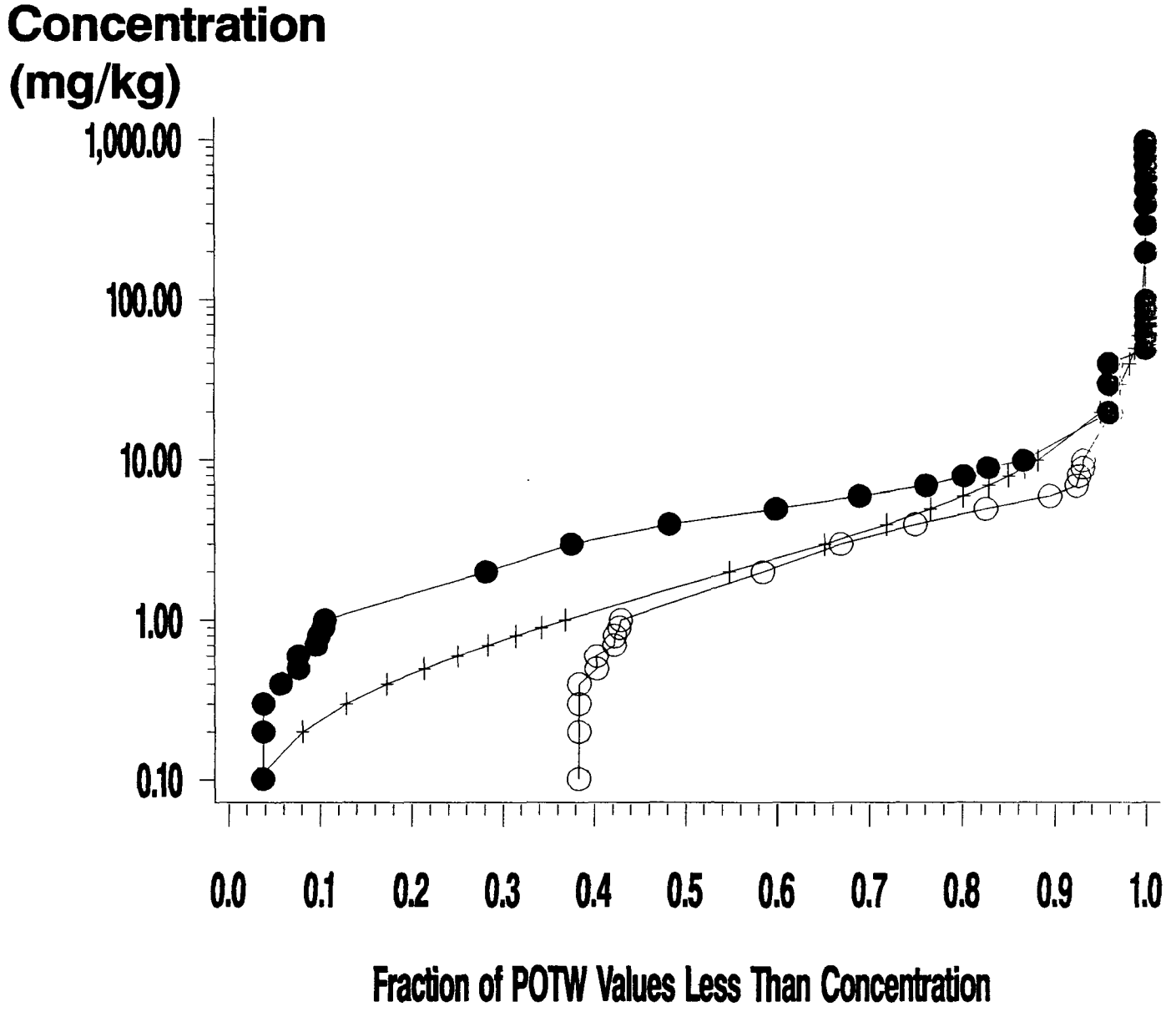
ZINC



+ = Maximum Likelihood ○ = Subsitute Zero ● = Substitute Minimum Level

Cummulative Distribution Functions:

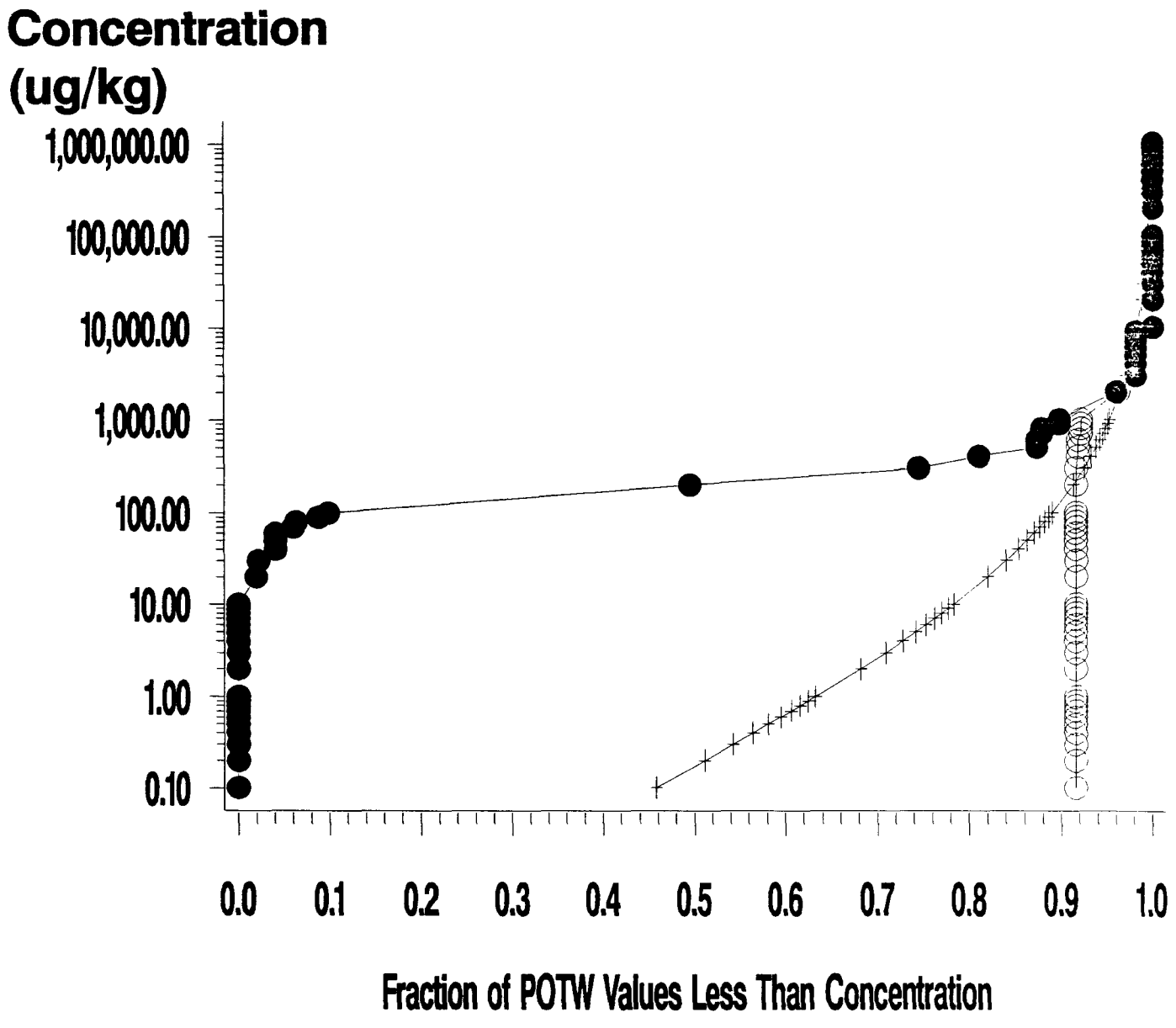
MERCURY



+ = Maximum Likelihood ○ = Subsitute Zero ● = Substitute Minimum Level

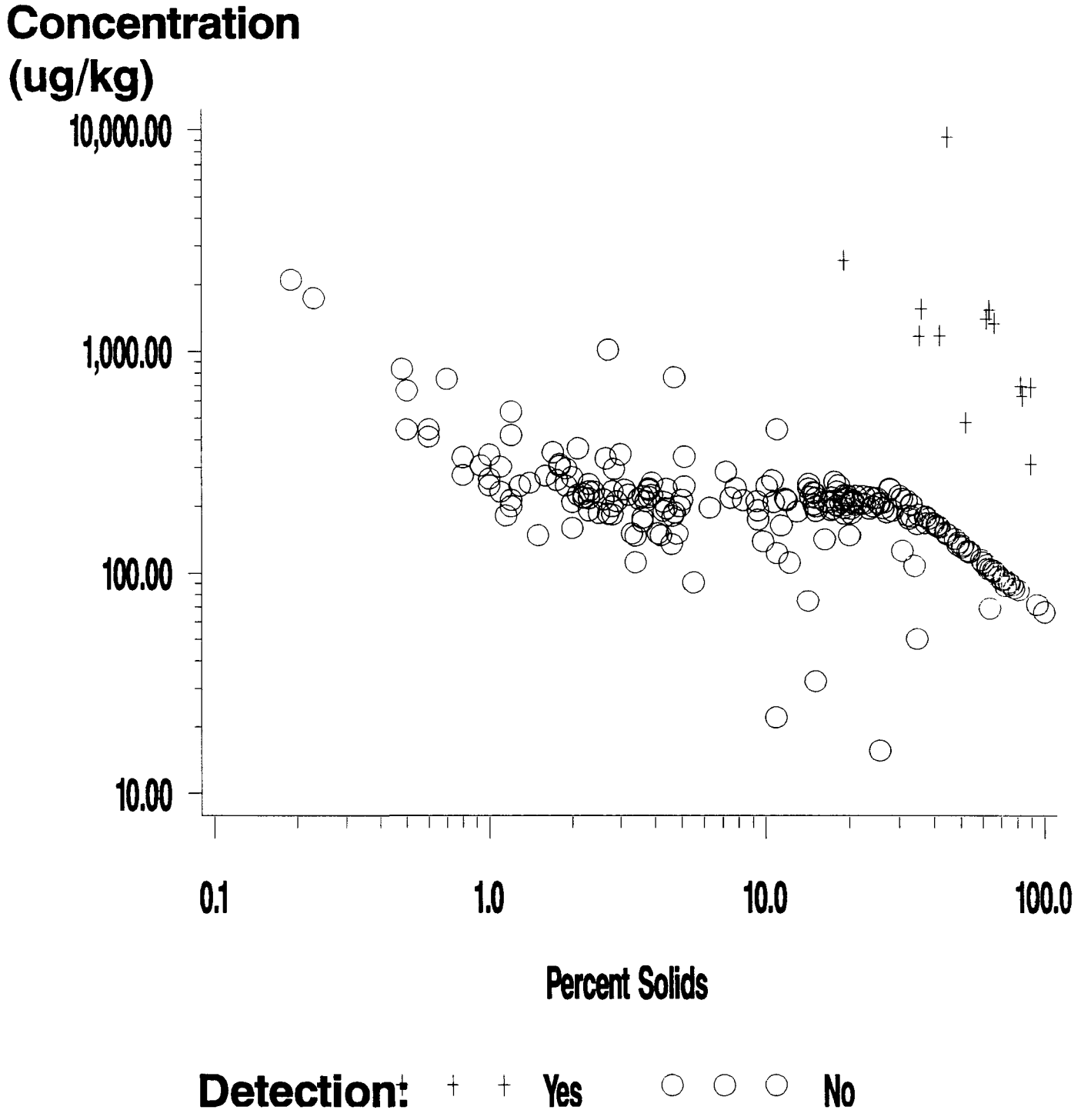
Cummulative Distribution Functions:

PCB-1254



+ = Maximum Likelihood ○ = Subsitute Zero ● = Substitute Minimum Level

DRY Weight Concentrations of PCB-1254 Versus Percent Solids



MR. TELLIARD: We'd like to get started, please. Could we get the folks in from the back a little bit? Have them bring their cookies.

Our afternoon session is on quality assurance. Our first speaker is Rick Johnson. Rick is with the Environmental Protection Agency's...this is good...Science Systems Staff in the Office of Information Research Management...wow. Basically, he's an OIRM down in RTP.

MR. JOHNSON: Can everybody hear me okay?

I want to thank Bill for inviting me to talk today. This is going to be kind of a different talk for you all. One thing I promise is you won't see a chromatogram. You won't see a piece of instrumentation or equipment and you probably won't hear a chemical name said unless I slip one out by accident. This is an entirely different arena from most of the stuff that was talked about today. However, I think it's a very serious and important part of a laboratory operation. As I move through the talk, I'll try to give you a feel for why.

I've given this talk to USDA, FDA and EPA laboratory auditors, North Carolina Quality Assurance Group, Contract Laboratory Data Management, CAUCUS and ORD's retreat recently. How many people have heard this before so I don't repeat?

(No response.)

Oh, good, I can tell the joke then. Fred, pardon for having to hear it over again.

There were two computer salesmen who had landed a rather lucrative contract in a city which they had never been to before. They went out celebrating that night and went sort of bar hopping and in the course of it, had a little bit too much to drink. Trying to make their way back to their hotel room, unbeknownst to them, they wandered into the city zoo and they're sitting on one of the benches in the zoo. Suddenly, there's a roar of a lion and the one computer salesman gets up and he starts to run away and the other one is still sitting there on the bench waiting and kind of curious. Then one turns around and says, well, aren't you leaving? The other one says, no, man, I'm staying to see the movie. So, with that in mind, I'd like you to kind of stay and bear with me for a few minutes.

My purpose here is to describe to you our program for assuring integrity of data in laboratories as they automate. I'll try and give you sort of a feel for what happened and why we went about it and what we found out and where we are today.

As Bill has indicated, the document is in review. There are about 500 copies that have been distributed to date. My name and address are in the speaker book, so if you want to get a hold of me or would like a copy later, I'll certainly be glad to make one available to you. We're currently having more copies made. I expect them to be out of the print shop at the end of next week forward.

I put this up here because I spent a lot of time with two folks on contract that said it couldn't be done. This was done on computer with computer graphics and computer coloring and all that. They said they couldn't put the circle around it and couldn't do the coloring and there was one reason or another and we just worked with it for a day and half. So, just to show it can be done, I wanted to put it up to show you that you can do things like this.

In a nutshell, where my organization is, you can see here there is the administrator. Under the administrator are the major offices of Research and Development, Pesticides and Toxic Substances, Program Planning and Evaluation, Office of Administration and Resource Management and Office of Air and Radiation. Unfortunately, I forgot another key one in here, OSWER, which Joan reminded me at the last meeting. The point is that there are numerous different folks reporting to the administrator and we basically are under the Office of Administration and Resources Management in what's called the Scientific Systems Staff.

Basically, the mission of our office is really threefold to essentially deal with hardware and software technology to improve the information flow and management in the agency, develop and manage the agency's information assets, and promote data sharing and integration. I think this project nicely fits under what I would consider to be data sharing...quality data sharing.

Why did we get into this program in the first place? There were a couple of things about two and half years ago that

led us down the road of thinking we might need to look at laboratory practices as they now exist and with automation moving into the laboratory.

First, as many of you know, automation is moving into the laboratory. We're steadily replacing one person after the other one, body after the other, with one kind of piece of software or hardware or combination thereof.

Secondly, problems were beginning to surface. We were seeing some problems that ultimately wound up in fines, disbarments, and a number of other penalties on folks who were doing business with the agency because they were beginning to tamper with data in an electronically-oriented environment.

Third, our laboratory auditors for years have been operating with laboratory notebooks and principles thereof and folks at the same time were moving to automate and it became clear that the auditors...there now becomes a generation gap between the auditors and what they know and also with what's going on in the laboratory and the movement to automation. Many of our auditors when they go into labs and you mention the computer, they simply just turn around and walk away from it. They are virtually computer illiterate. So, another reason, an indication of why we wanted to do this was to help bring our auditors into the 21st century with some updating for them.

Third, in spite of EPA having all kinds of edicts and we have all kinds of measurement requirements and monitoring methods and all of that, we did not have one single set of uniform principles in one place to guide laboratories as they move to automate. As a result, in the course of this talk, I'll show you numerous laboratories that made a lot of mistakes in trying to automate their labs because they didn't have appropriate guidance from the agency.

Finally, to add to all of this, there were a number of requirements underway or being developed in a variety of different areas in the agency that seemed to be kind of scattered about and they needed to be brought together. So, with these

things in mind, we started this project on a shoestring about two and a half years ago.

What we did was, first of all, we worked in a couple of different areas. One, we wanted to go out and find out what the current situation was in laboratories. Was it, in fact...

Are we getting an echo here? Maybe it's me. The trip last night, I guess, on the boat.

First, we wanted to find out what the condition in the laboratories was. We've had some indications that there were problems and we wanted to go out firsthand and see for ourselves so we conducted many site visits across the country at laboratories that provide data to the agency, either through contract programs or through requirements to generate data for the agency to decide whether or not a chemical should be registered for pesticide use or for introduction into the environment as a new chemical.

Secondly, we wanted to look at what kinds of procedures already existed in a lot of places that were already there to guide people into automating. Automated financial systems have been around for many years. Many of you folks use the teller machine and the principles and understandings of data exchange through that kind of electronic media have all been established and several court cases settled a lot of different disputes about different issues related to electronic data transferring stuff. We felt like it was imperative on us not to reinvent the wheel, but find out what lessons were learned in that arena.

Third, clinical laboratories have been moving to automation very rapidly over the last 15 years, particularly your forensic toxicology labs, your drug testing programs and all of that. There were lessons there to be learned, so we also looked into the clinical arena.

Then we decided to look at hardware and software. There are a number of different changes going on in the hardware and software arena. Maybe there are lessons. Maybe there are some fixes there that probably could straighten this thing

out...that you really have a very simple fix available.

Fourth, there are lessons from EPA's Good Laboratory Practices, guiding principles for management when they generate data for the agency.

Finally, there were requirements being developed that we also felt like we needed to track.

So this is basically the seven methods or ways we went about looking and putting this thing together.

What we found out in a nutshell through about 150 different surveys sent out and 10 different laboratory visits and some other voluntary submissions was in a nutshell that physical security in laboratories was lacking. People could walk in and out of automated laboratories without much chance of running into any kind of a problem. System access was not protected. Joe Doe could get on the computer right behind Joe Schmoe and make data changes and Joe Doe would never have known it and the data becomes corrupted.

Third, and probably one of the key things was data verification. People were manually entering data, keying it in, and where a lot of the problems in laboratories were coming in were not necessarily the corruption...intentional corruption of data, but rather the fact that errors were occurring in data input that were not being caught because there were not proper data verification procedures going on or some type of way to determine, in fact, that the data that were being entered manually were, in fact, correct. I'll speak to that a little bit in a minute.

Documentation was very sketchy. In a number of cases, people couldn't tell what version of the software was used to create what data set. They didn't even have the version of software around. A sad story on this to illustrate how poignant this situation can be, one of our sister agencies, whose name I shall not mention but who deals a lot in outer space, has lost some one and a half billion dollars worth of data because, while the data are there in resident on computer tapes, the software

that was used to create it is gone and they can't read it. They have no way of knowing what the data are. They are lost for future use. So, what I'm leading up to is that private industry is not alone in some of these problems.

There were several other problems, too, that I will not go into now.

When we looked at financial systems, we found a number of things in place that we thought were lessons there to be had to be put into the automated laboratory environment.

First of all, they always do a security risk analysis. Whenever a company puts in...typically, a large company puts in an automated financial system, they evaluate where their security risks are, where their problems are, where there may be some reasons to suspect that there could be some corruption or misrepresentation of dollars since they're coming back and forth through transmission lines and they evaluate that and put together a portfolio of where all the different problems are.

Secondly, they implement... Based on that report, they implement what's called a risk management program and some of the things that typically go into a risk management program include system access management programs where tellers come and go from the organization. Their passwords are automatically taken out. People move on to other jobs and their passwords are changed and so on and so forth. Depending on the level and the type of person, they have access to further levels of security within the system.

There are verification procedures, typically double entry. Somebody will enter the data from a strip chart or something like that or it comes off of a roller from a register and they'll enter it and somebody will come in behind and re-enter it to double check it or they may have double verification going on at the same time. The point is, anytime data are entered manually, there always is some type of verification procedure in place.

Third, audit trails. Whenever data are changed in a

computer system in the financial arena, there is a trail to indicate, number one, that data have been changed; number two, who changed it; number three, when they changed it and the reason why they changed it, and the original data are still there to be able to see. This is an important point because one of the things we found out in our laboratory visits and also through the survey were a number of people had been sold what they thought was an audit trail that really amounts to a transaction log. What I mean by that, without getting into a lot of detail, is data are dumped onto another tape and the new data replaces it so that they don't know per se that the data have been changed and there is no direct link between the new data and the original data to satisfy the conditions that I just mentioned. Which reminds me, what's the difference between a... Pardon me, anybody, if I hurt anybody's feelings here, but what's the difference between a computer software salesman and a used car salesman? The used car salesman knows when he's prevaricating.

Finally, hard copy retention. This is an important point that I found out kind of oddly enough through the course of this. You know the little receipt you get when you do a mini-bank transaction? That is your official legal copy of your transaction and if anything happens or if any error occurs with that, that is your actual legal tender to prove anything about that transaction. I've been throwing them away. I started keeping them after I found this out.

When we looked at hardware and software technology, a couple of things: One, there were no breakthroughs in hardware or software to guarantee data integrity. Nobody had come along with a great software system or nobody had come up with an optimum hardware fix to be able to ensure integrity in automated laboratories and this kind of surprised me. There were no established software standards to ensure data integrity. The business I just mentioned audit trail, there was never any official proclamation from any organization or the other that, here, these are the conditions that constitute an acceptable

audit trail and in order to be able to be selling this as an audit trail, you should follow these conditions. There isn't such a thing in place. But, however, software can be customized much like the software salesman I mentioned. They will sell you about anything you want. They can do it about any way you want. The only thing is, let the buyer beware.

Audit trails can be provided. They are now being provided in some cases, I think, as a large result and password protection is pretty well standardized.

There are some interesting hardware advances that some of you in your laboratories may be already moving to: Optical scanners, such as you have in the grocery store. They're now being used in some labs. Magnetic ink readers, such as that kind that are on your checks. You know, your checks are now all standardized across the country. That's why when you write a check in California, by the time you get back home, you may find to your surprise it's already cleared your account. Electronics is a marvelous thing when it comes to taking money away from you.

Finally, smart cards. This is something that is just now coming along. We all have those magnetic strips on the back of our credit cards and all. Well, technology is moving in such a way now that you virtually can put almost an entire person's life history on the back of it. Some hospitals are doing this, for example, for patient history in certain cases and the patient is carrying it around. This also has incredible application in the laboratory. It's not really a forefront technology as it sounds like. It's on its way in and we found some innovative laboratories moving to use it, too.

With any of these things I might mention, what you're doing is reducing the need for verification because you're reducing the need for manual entry. You're enhancing the reliability of the electronic environment. But again, as I'll mention, there does need some caution with this.

Finally, when we looked at our own good laboratory practices requirements that are in place in a number of offices,

we found several things out. One, you can use whatever data you want...whatever median you want in a laboratory and call it raw data with the one proviso that wherever the data are first recorded, that ergo is the median for the raw data. Without getting into a lot of legalese and stuff about this, some of which I don't even know, if, for example, you're typically recording data and you're reading it off of an instrument and you write it down to a piece of paper, that instrument isn't actually recording it, itself, but that piece of paper is the raw data. When you go to enter it into the computer system, that data are not considered the raw data, but the original data written on the piece of paper are and they typically have to be retained under the conditions of our GLP.

Secondly, wherever a computer is used during the course of a study, it also is part of and subject to the conditions of good laboratory practices. Anytime a computer is used in the course of data generation in a laboratory, it must also follow the things that are required of other instruments through the good laboratory practices, such as maintenance requirements and a log if the system goes down or problems occur and what corrective actions were taken and so on and so forth. I'll speak about those a little bit in a minute.

Finally, documentation requirements of personnel qualifications for the computer system are also, therefore, under the aegis of the GLP.

Oversight of a quality assurance unit... Many of you have had the quality assurance people, I'm sure, up and down your backs. I'm sure you are all good buddies by now.

And SOPs must be in place.

When we started looking at our own requirements that were underway, there were several things we found. One was there's an electronic transmission standard whereby people can electronically transfer data to the agency directly. That needed to be factored into this and our own information resource management policy that we lean heavily on that I'll show you in a

minute.

Finally, there were a number of things under development. The Federal Electronic Reporting Standards, Federal Computer Security Act and our own System Design Developed Guidance, all of those had to be factored into this, too.

So, what we ended up with through all of this was clearly... It looked like there was a need for the agency to come out with a standard set of good automated laboratory practices and as a companion to that, implementation guidance for how people can successfully implement any one of the practices that we would put in and, finally, guidance for laboratory auditors to determine if a lab is in compliance.

So, we published December 28th and actually distributed February 13th The "Good Automated Laboratories Practises"- GALP. There were some very important issues that arose between the December 28th date and the February 13th distribution date. One of them was, is it appropriate to put acknowledgments in the document? We spent about a week discussing this issue. There is a quote in the document by Francis Bacon. Another week and a half passed discussing whether or not it was proper to put a quote in a government publication. And then there was about a three or four day discussion about what it meant. People couldn't seem to grasp it. At any rate, nonetheless, it went out on the 13th of February.

All of these things I've mentioned...all of these things come into it. In a nutshell, its got two basic elements that it relies heavily on: Good laboratory practices and our IRM policy that relates to the development of hardware and software and implementation thereof, stress testing and so on and so forth, some of which I'll go through in a minute, and then several other statutes come into play and are brought into it, as well.

National Archives and Records Administration is mentioned up here. They have guidelines out for dealing with such things as...if you're data are on magnetic tape, how often

should that magnetic tape be refreshed? If it's on optical disks, how often and so on and so forth... Those requirements are all effected in here, too. There are statutory requirements from each one of the other federal EPA statutes that we deal with that are referenced through in here and must be dealt with...the Computer Security Act and then a couple of other things, as well.

What I'm going to do real quickly here is just run through the different areas that the GALP speaks to and I'll show you...and then I'm going to focus in on one of them in particular...the data change requirement, to show you basically how and what's going on in the document.

There are several areas and within each one of these areas, there are several different subgroups of specifications that are stated.

Personnel requirements. Those things relate to such things as the documentation of the training of the personnel. Are the personnel adequate? Are there sufficient personnel to handle the computer and stuff like that.

Laboratory management responsibilities that they have are under the aegis of the GALP.

Responsible person. He's a character who can be anybody in the organization chain, including management, but he is somebody who has certain very specific charters within the GALP and would be able to sort things out and identify them. So he's the guy who you kind of point to, to be able to say he's the one who is responsible, typically like a system manager or something like that...has those kinds of roles.

Quality assurance unit. Their responsibilities are not only relative to the laboratory and its manual operation, but also certain things when automating the laboratory. There are about eight or 10 different specifications for the quality assurance unit.

Facilities. Certain requirements on the facilities to assure that the facilities are adequate to accomplish the need of the automated laboratory.

Equipment Requirements.

Security. There are four or five different areas of security standard operating procedures. It specifies about six or eight different standard operating procedures that must be maintained as you automate a laboratory. In doing this, for example, and also consistent with the software requirements, if they were in place, we probably wouldn't have this problem with about three and a half billion dollars worth of data sitting around unable to know what to do with.

Date entry requirements a set of procedures, mostly surrounding data verification and the like and transmission of data, documentation, and who entered the data and so on and so forth.

Raw data requirements. We could spend an entire career dealing with the whole idea of raw data. We try and deal with it in two pages in the GALP.

The bottom line, interestingly enough without getting into a whole lot of detail on it, probably is a legal issue in the long run. There was a recent court decision where Dalkon Shield was being sued by somebody because apparently something didn't work right and the company claimed that they kept the raw data consistent with the federal FDA requirements and that they threw it away after the requirement mandate had expired and they were using that as justification in their case for not having to be prosecuted any further and the judge threw that out and said the FDA requirements did not supersede common sense in certain situations. So what this kind of means, unfortunately for a lot of the industry, is they're basically keeping everything as long as they can. I don't know what to say about that except to say that if it wasn't on paper and it was on an electronic media, there might be a little more room in the house for other things.

Records and archives. That deals with record retentions and the like and archiving of software and hardware, as well...software and hardware maintenance records and so on and so forth.

Reporting requirements and finally the last thing, comprehensive ongoing testing that periodically...and again this is up to the lab, but probably no more than every 24 months, but there should be a periodic stress test done of the system or, if there are any changes in the hardware or software configuration of the system in the interim, there should be a stress test done following those changes. But at the minimum, certainly no more than 24 months, regardless.

What I'd like to do now is kind of focus in on one area in particular, the data entry requirement which I mentioned before. This is the one in particular.

These are the two different groupings under the data entry requirements: Integrity, the tracking person, the tracking equipment, data change and data verification. So this is one of the 13 different elements. There's a total of 82 sub-elements within the GALP so this one particular element has four or five.

What I'd like to do now is just focus in on the data change requirement. I think that does it for that...yes.

This is a specific element from the GALP, the data change requirement. I'll read it for those of you that can't see it in the back of the room.

> When the laboratory uses an automated data collection system in the conduct of a study, the laboratory shall ensure integrity of the computer-resident data collected, analyzed, or maintained on the system. The laboratory shall ensure that in automated data collection system:
>
> 1. The individual responsible for the direct data input shall be identified at the time of data input.
>
> 2. That the instrument transmitting data to the automated data collection system shall be identified and the time shall be documented.

And three, the one that seems to have given a lot of trouble over the years:

> 3. Any change in automated data entry shall be made so as not to obscure the original entry, shall indicate the reason for the change, shall be dated, and shall identify the person responsible for the change.

In addition to identifying these requirements in the GALP, we also provide guidance in the GALP on how to implement each requirement.

The implementation guidance is set up much like this for each one of the 82 standards and in a nutshell up in the upper left corner, there is an icon directing your attention to the particular category that it sits in, the fan for the facilities, the responsible person with a little RP on his or her chest, a checklist for standard operating procedures and the like. I got into that because I have a Mac and Macs are heavily icon-oriented and I thought it would be a good idea.

Finally, then the specification...the exact statement from the GALP about what the requirement is or what the specific standard is.

Then there is an explanation of what it means...what it's all about, an example of how one might be in compliance with the specification. And then there are codes that relate to two things. One, the person...the operational role. There are six operational roles. Without getting into a lot of detail, there are six operational roles and it relates to who probably should be in charge of that specific...this specific GALP entry and the principle...the underlying principle behind why this standard was put out in the first place. There are six of those basically.

And any special considerations... The thing I just mentioned before about the Dalkon Shield thing in the raw data definition, that thing was elucidated and brought out and spelled out so as to give the reader, when they get through with this thing, a full feel for the spectrum of issues and ideas and concepts that are going into each one of these things.

And finally, there is a notes section where you can put in any other additional information or reference other things that you see fit.

Let me show you how this works for one in particular. Here is our little beast, the data change requirement. Do you see the icon in the top left? We chose something that attemps to look like a PC.

Next a restatement of the GALP requirement followed by an explanation of the need for this requirement.

The data change requirement is nothing new. This has been in place for many years in accounting. It's been in the FDA Good Laboratory Practices since the '70s and it was considered and drafted into the EPA draft GLP back in the '80s. It's interesting that a lot of software houses somehow or another decided that their data change specifications probably could be different from this. I have no other explanation for that.

Next we have an example of how to comply with the principle. The codes down here show the responsible person. In this case, the responsible person is suggested to oversee data changes and probably be the one to do it. Next we have the underlying principle behind this requirement.

Finally, here's a special consideration in this case. Laboratories may consider adopting a policy by which one

individual may be authorized to changed data rather than implementing a system that records the name of any and all individuals making data changes.

For example, in this case, the responsible person would be the only one authorized to make a data change and you might have the software set up in such a way as to do that.

And here... This is from the manual, as well. It's kind of a pictorial of what...one picture is worth 1,000 words, so the picture had better be good. We worked on this one for awhile. I think it kind of tells the story of what you mean by a successful data change.

And then this notes section at the bottom here is in each one of the GALP guidance areas to allow people to be able to go back to and find other information relative to it to be able to determine if they want more information or need to have a further understanding of what's going on.

In most cases, this audit trail requirement is mentioned in all of the background documents that were prepared that I mentioned earlier because it's something that comes out of the automated financial systems. It's something that comes out of the clinical laboratory area. It's something that comes out of a lot of different places. It does not come out of chemical laboratories right now for some reason.

Finally, in a nutshell, none of this is new. Most everything that I mentioned here is already requirements that have been in place for a number of years in different places. They just never were put together.

In the case of facilities and all the various statutes that have been in place, they just never were all brought together...and so on and so forth for those areas and procedure software documentation and the like...and things related to

software backup and recovery and all of that. All of these things have been around for some time. There's really nothing new in it.

It looks like we have time for one or two questions.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MS. ASHCRAFT: Merrill Ashcraft from Navy Public Works Center.

Is there a documentation number? Is this document available?

MR. JOHNSON: Yes, if you'll write to me or call me. My phone number and address are all on the speaker list in the book. I'll be glad to get one to you. Unfortunately, there aren't any now. There will be some by the middle of next week. We ran out. We had 500 made. We only had 250 people on the original mailing list and now they're all gone. But we'll have more and I'll be glad to make you a copy...have a copy for you.

MR. TELLIARD: Rick, is this intended to become a rule?

MR. JOHNSON: No, let me explain, too. Thanks, Bill. These are recommendations from our office to EPA programs and to all people developing data to provide to the agency. They are not requirements that are being laid on anybody. It is going to be up to each one of the program offices within the agency to decide how and what they want to do with them and how they want to implement them. Part of the reason for that is... One of the biggest reasons for that is I'd like to get onto working on something else within the next 10 years and the second reason is that each one of the different programs has different constraints that... They may, in fact, want to go beyond this or they may already have this and some of these elements in place in their individual programs. So rather than pick and sort through all of that and try and come down to a core minimum set of requirements, we put these out as recommendations to the programs and to folks doing business with the agency in the hopes that each one of them would come to grips with one or the other of them and deal with them accordingly. For example, the Contract Lab Program, Joan, you might just mention very

quickly where you all stand with it.

MR. TELLIARD: Joanie, we're running late.

MS. FISK: You know I'm a man of few words. As far as the Contract Lab Program is concerned, the CLP is very anxiously awaiting this document. They are aware of it because Rick has spoken at our meetings in the past and our perspective right now is some of the things we consider absolutely critical, we are going to put into the contracts and have in some cases. We have included a lot of data management requirements in personnel and, as we learn more, we certainly intend to do more. Don't think we would ever make it a contractual requirement that this document an actual piece, but we would certainly intend our laboratories to use it. But we would expect them to use it as guidance. They may find other ways that work better for them to implement it and we would want them to monitor that, track it, write SOPs, the whole bit.

The other thing that we did want to do is we've talked to Rick about helping us in setting up better audit procedures so that we can learn more about the people's automated systems up front.

MR. JOHNSON: One of the things I might mention along that line of personnel procedures, we have put into the 1992 budget... We have put together a planning program for personnel, a training program or some sort of a program ...

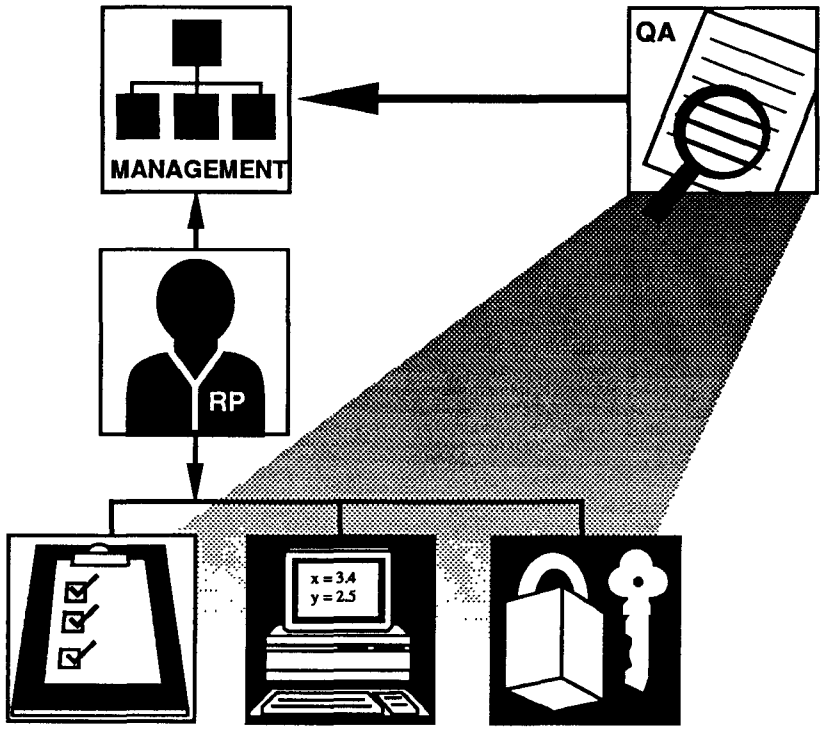
MR. TELLIARD: Thank you.

14th Annual
EPA Conference on
Analysis of Pollutants
in the Environment
May 8-9, 1991

GOOD AUTOMATED LABORATORY PRACTICES

EPA'S RECOMMENDATIONS FOR ENSURING DATA INTEGRITY

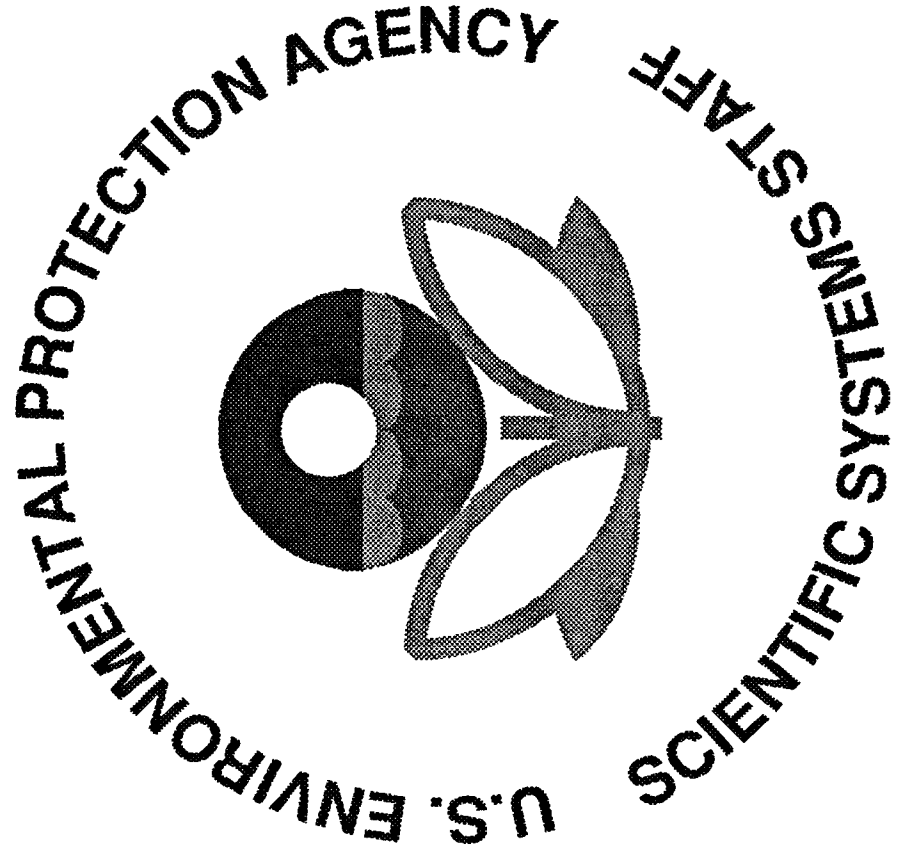
IN AUTOMATED LABORATORY OPERATIONS
WITH IMPLEMENTATION GUIDANCE



Purpose

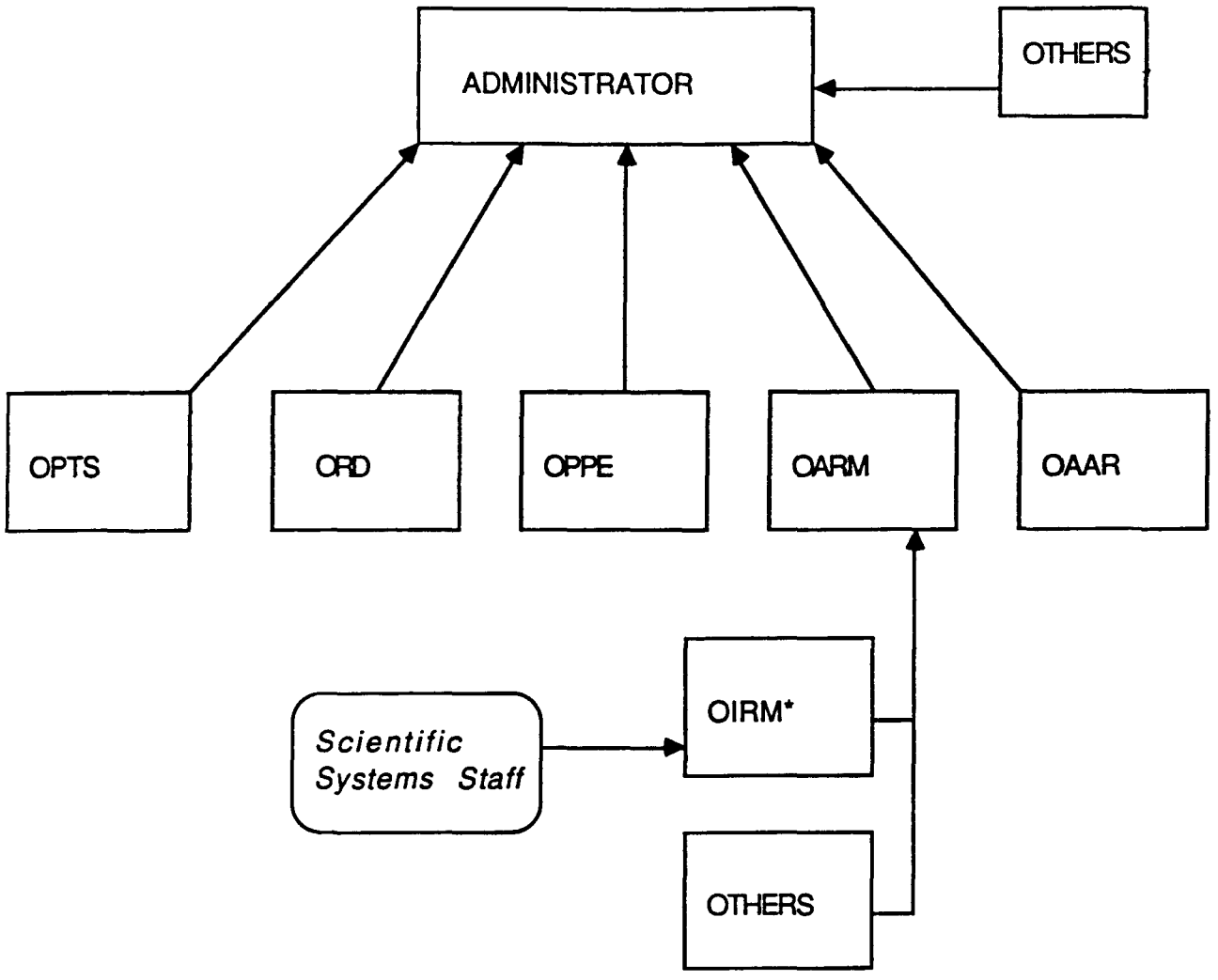
Describe EPA's Program for Ensuring Integrity of Computer Resident Laboratory Data

"GOOD AUTOMATED LABORATORY PRACTICES"


U.S. ENVIRONMENTAL PROTECTION AGENCY
SCIENTIFIC SYSTEMS STAFF

OIRM Mission

- **Provide Reliable, State-of-the-Art Information Technology and Services**
- **Develop and Manage EPA's Information Assets**
- **Promote Data Sharing and Integration**



* Office of Information Resources Management

Why

- **Rise of Automation**
- **Problems Surfacing**
- **Assistance for Auditors**
- **No Uniform EPA Principles**
- **Several Requirements exist/under development**

Methods

- Assess current laboratory procedures
- Examine existing procedures
    - automated financial systems
    - clinical laboratories
- Survey state-of-the-art hardware and software

Methods

- Analyze EPA's Good Laboratory Practices
- Incorporate existing requirements
- Track requirements being developed

Current Laboratory Conditions

- Physical Security Lacking
- System access not protected
- Data verification problems
- Documentation sketchy
- Several others

Automated Financial Systems

- Security Risk Analysis performed
- Risk Management Program implemented
    - System Access Management Program
    - Verification Procedures
    - Audit Trails
    - Hardcopy Retention

Hardware/Software Technology

- No breakthroughs to guarantee data integrity
- No established software standards for data integrity
- Software can be customized for needs
    - Audit trails
    - Password Protection, etc.

Hardware/Software Technology

- Hardware advances
    - Optical scanners
    - Magnetic Ink readers
    - "Smart Cards"

Assessment of Good Laboratory Practices

- **"Raw data may include … computer printouts, magnetic media, … and recorded data from automated instruments."**

  (54 CFR 158 & 160.3 (FIFRA) and ibid *792.3 (TSCA))*

- **"Testing facility encompasses … those operational units that are being or have been used to conduct studies.**

  ibid

Assessment of Good Laboratory Practices

- GLP requirements apply when automated systems are used, ergo:
    - Documentation of personnel qualifications
    - Oversight of QA unit
    - SOPs, etc.

Existing Requirements

- **EPA's *Electronic Transmission Standards***
- **EPA's *Information Resource Management Policy***

Requirements under Development

- EPA's implementation of *Federal Electronic Reporting Standards*
- EPA's implementation of *Federal Computer Security Act*
- EPA's evolving *System Design and Development Guidance*

Major Program Components

1 Registry of Principles

2 Implementation Guidance

3 Compliance Guidelines

United States Environmental Protection Agency

Office of Administration and Resources Management

Draft
December 28, 1990

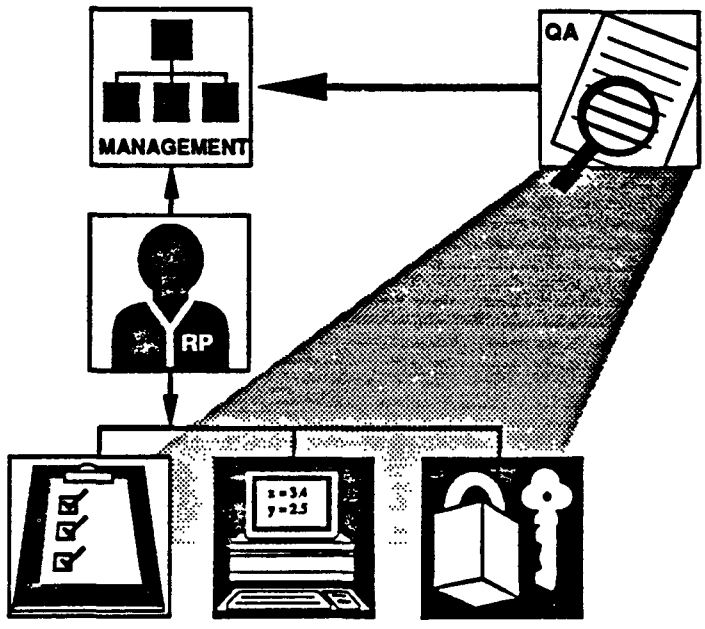
EPA

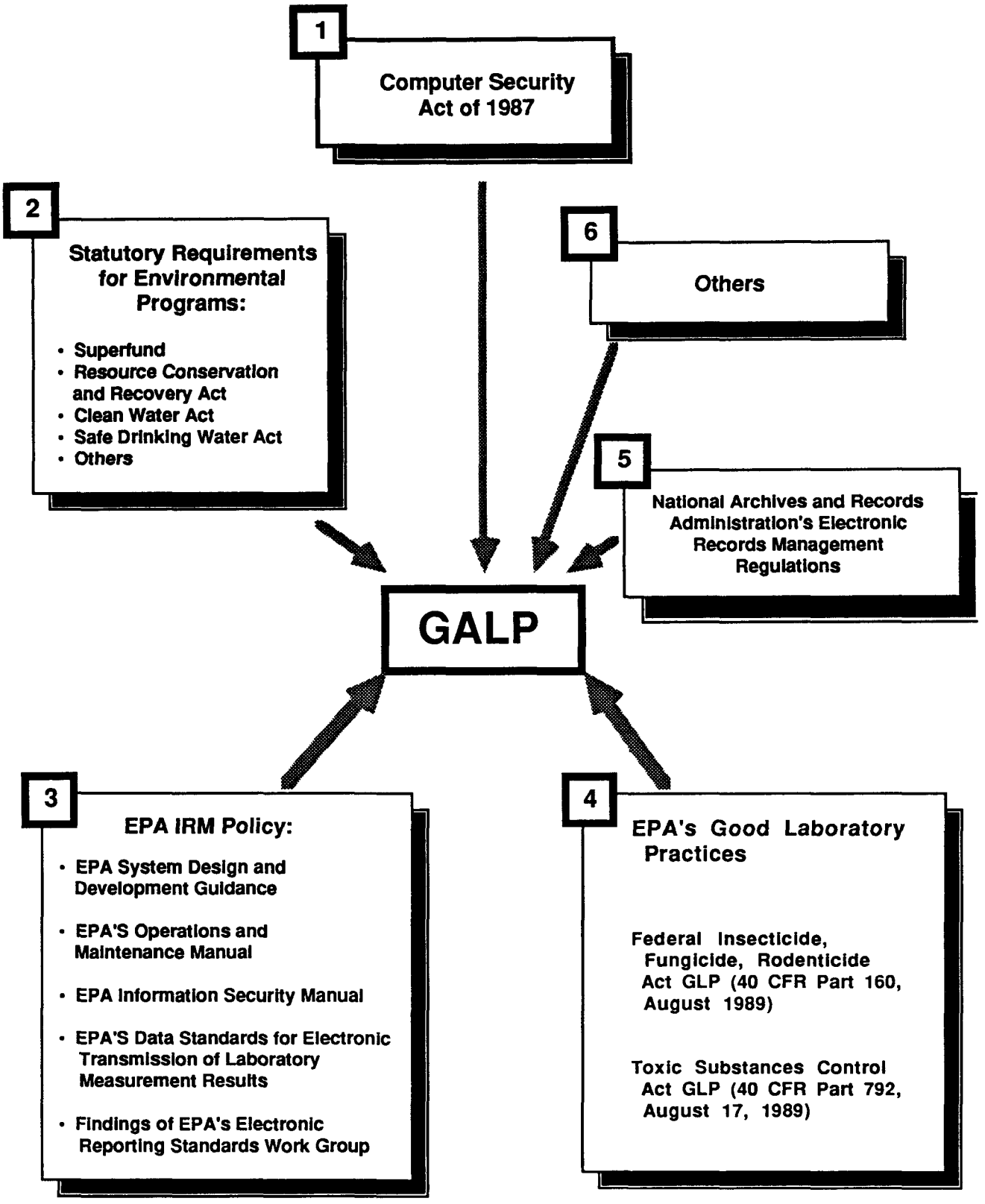
Good Automated Laboratory Practices

DRAFT

Recommendations For Ensuring Data Integrity In Automated Laboratory Operations

with **Implementation Guidance**




1
Computer Security Act of 1987
2
Statutory Requirements for Environmental Programs:
• Superfund
• Resource Conservation and Recovery Act
• Clean Water Act
• Safe Drinking Water Act
• Others
6
Others
5
National Archives and Records Administration's Electronic Records Management Regulations
GALP
3
EPA IRM Policy:
• EPA System Design and Development Guidance
• EPA'S Operations and Maintenance Manual
• EPA Information Security Manual
• EPA'S Data Standards for Electronic Transmission of Laboratory Measurement Results
• Findings of EPA's Electronic Reporting Standards Work Group
4
EPA's Good Laboratory Practices
Federal Insecticide, Fungicide, Rodenticide Act GLP (40 CFR Part 160, August 1989)
Toxic Substances Control Act GLP (40 CFR Part 792, August 17, 1989)

APPENDIX A: INVENTORY OF COMPLIANCE DOCUMENTATION

RECORD	PURPOSE	SUBSECTION	REFERENCE
Organization and Personnel			
Personnel Records	Ensure competency of personnel	7.1	FIFRA GLPs 160.29 TSCA GLPs 729.29
Quality Assurance Inspection Reports	Ensure QA oversight	7.4	FIFRA GLPs 160.35 TSCA GLPs 792.35
Facility			
Environmental Specifications	Ensure against data loss from environmental threat	7.5	FIFRA GLPs 160.43 TSCA GLPs 792.43
Equipment			
Hardware Description	Identify hardware in use	7.6 7.12	FIFRA GLPs 160.61 TSCA GLPs 792.61 EPA Information Security Manual for Personal Computers
Acceptance Testing	Ensure operational integrity of hardware	7.6 7.12	System Design and Development Guidance
Maintenance Records	Insure on-going operational integrity of hardware	7.6 7.12	FIFRA GLPs 160.63 TSCA GLPs 792.63
Laboratory Operations			
Security Risk Assessment	Identify security risks	7.7	Computer Security Act
Standard Operating Procedures	Ensure consistent use of system	7.8	FIFRA GLPs 160.81 TSCA GLPs 792.81
• Security Procedures	Ensure data integrity secured	7.8	Computer Security Act
• Raw Data Definition	Define "computer-resident" records subject to GLPs	7.8	FIFRA GLPs 160.3 TSCA GLPs 792.3

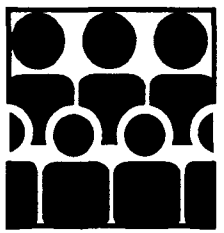
APPENDIX A: INVENTORY OF COMPLIANCE DOCUMENTATION

RECORD	PURPOSE	SUBSECTION	REFERENCE
• Procedures for data analysis, processing	Ensure consistent use of system	7.8	FIFRA GLPs 160.87, 160.107 TSCA GLPs 792.81, 792.107
• Procedures for data storage and retrieval	Ensure consistent use of system	7.8	FIFRA GLPs 160.81 TSCA GLPs 792.81
• Procedures for backup/recovery	Ensure consistent use of system	7.8	EPA Information Security Manual for Personal Computers
• Procedures for maintenance of computer system hardware	Ensure consistent use of system	7.8	FIFRA GLPs 160.63 TSCA GLPs 792.63
Standard Operating Procedures			
• Procedures for Electronic Reporting	Ensure consistent use of system	7.8	Transmissions Standards Electronic Reporting Standards Workgroup
• SOPs at bench/ workstation	Ensure consistent use of system	7.8	FIFRA GLPs 160.81 (c) TSCA GLPs 792.81 (c)
• Historical Files	provide historical record of previous procedures in use	7.8	FIFRA GLPs 160.81 (d) TSCA GLPs 792.81 (d)
Software Documentation			
Description	Identify software in use	7.9	FIFRA GLPs 160.81 TSCA GLPs 792.81 Computer Security Act
Life Cycle Documentation	Ensure operational integrity of software	7.9	System Design and Development Guidance
• Design Document/ Functional Specifications	Ensure operational integrity of software	7.9	see above

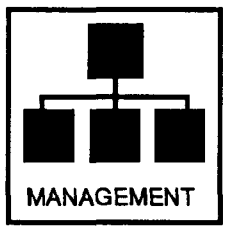
APPENDIX A: INVENTORY OF COMPLIANCE DOCUMENTATION

RECORD	PURPOSE	SUBSECTION	REFERENCE
Life Cycle Documentation			EPA Information Security Manual for Personal Computers
• AcceptanceTesting Testing	Ensure operational integrity of software	7.9	see above
• Change Control Procedures	Ensure operational integrity of software	7.9	see above
• Procedures for Reporting/Resolving Software Problems	Ensure operational integrity of software	7.9	see above
• Historical File (version numbers)	Ensure reconstruction of reported data	7.9	FIFRA GLPs 160.81 TSCA GLPs 792.81
Operations Records/Logs			
Back-up/Recovery Logs	Protection from data loss	7.12	EPA Information Security Manual for Personal Computers
Software Acceptance Test Record	Ensure operational integrity of software	7.12	System Design and Development Guidance
Software Maintenance (Change Control) Records	Ensure on-going integrity of software	7.12	see above

GALP



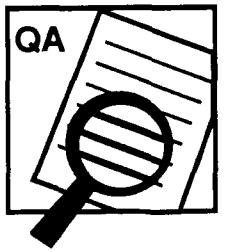
7.1 Personnel



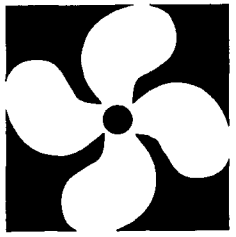
7.2 Laboratory Management

7.3 Responsible Person

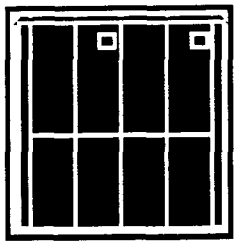
GALP



7.4 Quality Assurance Unit



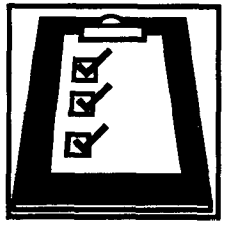
7.5 Facilities



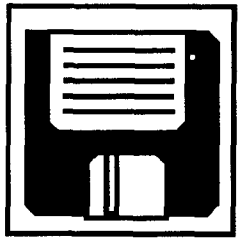
7.6 Equipment

GALP

7.7 Security

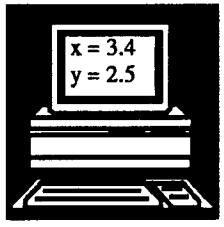


7.8 Standard Operating Procedures

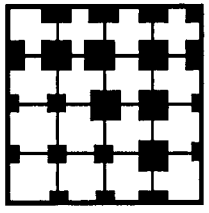


7.9 Software

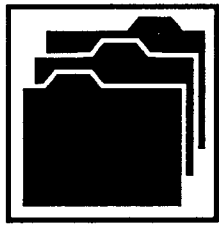
GALP



7.10 Data Entry

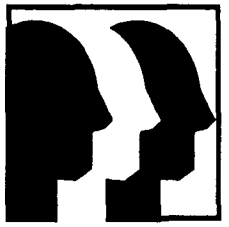


7.11 Raw Data



7.12 Records and Archives

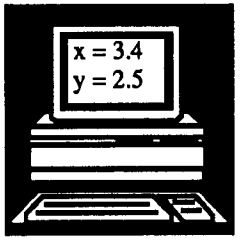
GALP



7.13 Reporting

7.14 Comprehensive Ongoing Testing

GALP



7.10 Data Entry

1 Integrity of Data

1.1 Tracking Person

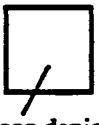
1.2 Tracking Equip, Time, Date

1.3 Data Change

2 Data Verification

GALP IMPLEMENTATION GUIDANCE

This section is intended as a key to using the Guidance. The model below, with commentary footnotes, illustrates the implementation guidelines provided for each of the standards.



GALP Category Name
GALP subsection

Icon depicting the GALP category

Specific and officially approved wording of the particular GALP standards.

In cases where a GALP has general specifications with distinct subsections or subspecifications, the general specification will always appear with each subspecification with two or three pages of discussion of that subspecification; the next subspecification will repeat the general specification, and follow with its discussion.

EXPLANATION — A paragraph exposition defining the key terms of the standards and explaining the intent of the standards.

EXAMPLE — Discusses the kind of compliance evidence that might be gathered or acceptable ways in which the standards has been or may be met.

CODE — Two codes are provided: the RESPONSIBILITY code identifying the role (or persons(s) assigned the role) expected to implement the standards; and the PRINCIPLES code; providing general guidance into the theoretical intent of the standard.

SPECIAL CONSIDERATIONS — Provides potentially relevant facts or noteworthy factors that may be relevant for certain laboratory settings, computer equipment, EPA statutes, or court decisions that may take precedence.

NOTES: The GALP Guidance is a working document. An area on the right-hand page is provided to allow annotation as needed. The size of this area is determined by the space available to complete a page. This variation is not meant to imply any difference in the extent of comment anticipated. Sources for additional guidance are also listed here.

7.10 Data Entry

1) Integrity of Data

3) Data Change

When a laboratory uses an automated data collection system in the conduct of a study, the laboratory shall ensure integrity of the computer-resident data collected, analyzed, processed, or maintained on the system. The laboratory shall ensure that in automated data collection systems:

3) Any change in automated data entries shall not obscure the original entry, shall indicate the reason for change, shall be dated, and shall identify the individual making the change.

EXPLANATION

When data in the system is changed after initial entry, an audit trail must exist which indicates the new value entered, the old value, a reason for change, date of change, and person who entered the change.

EXAMPLE

This normally requires storing all the values needed in the record changed or an audit trail file and keeping them permanently so that the history of any data record can always be reconstructed. Audit Trail reports may be required and, if any electronic data is purged, the reports may have to be kept permanently on microfiche or microfilm.

CODE

Responsibility: Responsible Person
Principle: 3. Audit

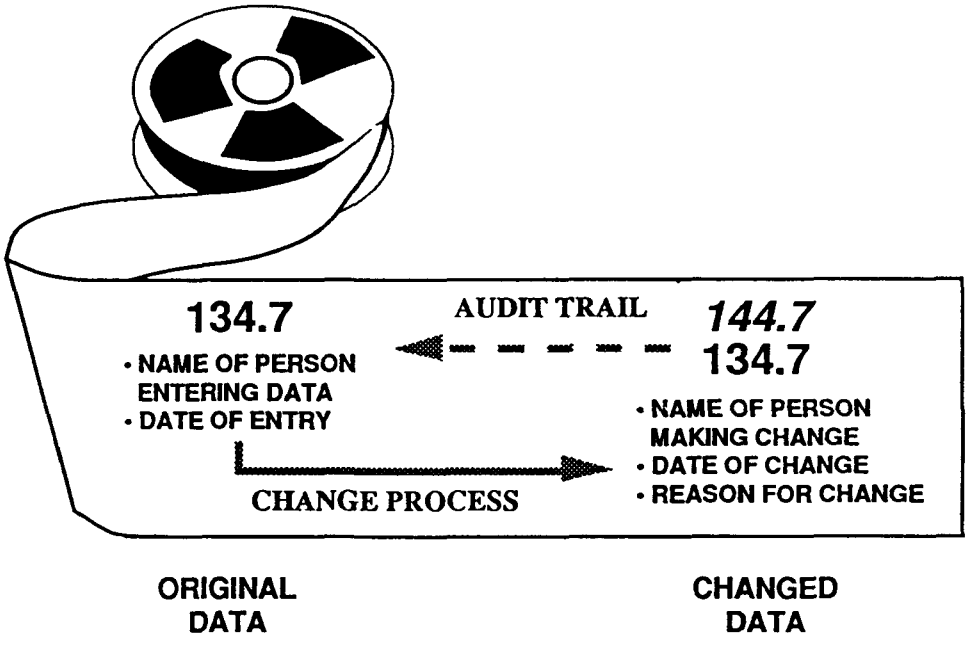
SPECIAL CONSIDERATIONS

Laboratories may consider adopting the policy by which only one individual may be authorized to change data, rather than implementing a system that records the name of any and all individuals making data changes.

7.10 Data Entry

1) Integrity of Data

3) Data Change



Notes...

For additional guidance, see: *FIFRA GLPs 40CFR 792.130(e); TSCA GLPs 40CFR 160.130(e); Automated Laboratory Standards: Evaluation of Good Laboratory Practices for EPA Programs, Draft (June 1990); Automated Laboratory Standards: Evaluation of the Standards and Procedures Used in Automated Clinical Laboratories, Draft (May 1990);* and *Automated Laboratory Standards: Evaluation of the Use of Automated Financial System Procedures (June 1990).*

MR. TELLIARD: Our next speaker probably doesn't need any introduction. It's George Stanko from Shell Development. George has probably the dubious honor of having been to as many of these conferences as I have. In fact, I think you outrank me by one.

George is going to talk about one of his favorite subjects: Contract laboratory performance. George has taken this on as a personal trust and is going to save the world.

PERFORMANCE EVALUATION STUDY OF ENVIRONMENTAL ANALYTICAL CONTRACT LABORATORIES

Author: G. H. Stanko

Shell Development Company
Houston, Texas

Presented at: 14TH Annual EPA Conference on Analysis of Pollutants in the Environment

Norfolk, Virginia
May 8,9, 1991

ABSTRACT

A performance evaluation (PE) study of environmental analytical contract laboratories used by Shell was conducted. Spiked groundwater samples were blindly submitted to 24 laboratories for analysis by GC/MS Method 8240 for volatile organics, ICP metals, and selected general parameters. Samples for the study were prepared by a contractor who also made arrangements to have the samples analyzed. Sampling kits were obtained from laboratories and returned for analysis. The results of the performance evaluation study were used to assess the performance of commercial laboratories from initial contacts; receiving and returning sampling kits; analysis of samples; and through final reporting of data. A second contractor was employed to statistically analyze the data and to evaluate the results for the study. The study was also designed to gain a better understanding for recovery correction of environmental data and to determine the qualitative and quantitative performance of commercial laboratories for non-target analytes commonly called "tentative identified compounds" (TIC's). The results for the PE study are presented in the paper.

PERFORMANCE EVALUATION STUDY OF ENVIRONMENTAL ANALYTICAL CONTRACT LABORATORIES

INTRODUCTION

A performance evaluation study of 24 environmental analytical contract laboratories was conducted in late 1990. To accomplish this, a contract was negotiated with a third party to contact the laboratories; make arrangements for receipt and shipment of sampling kits; prepare spiked matrix samples for the study; and to compile the data and significant information resulting from the study. The study was conducted with real matrix samples and the samples were submitted to the commercial laboratories without identifying them as performance evaluation samples. PE studies conducted in such a manner reflect actual real-time performance at commercial laboratories.

The current PE study was designed with one major goal and two secondary goals. The major goal was to assess the performance of a select group of laboratories for the analysis of groundwater samples for volatile organics, metals, and a limited number of general parameters. The secondary goals were to determine how well commercial laboratories can identify and quantify non-target analytes by GC/MS and to gain a better understanding for recovery correction of analytical data as proposed in the draft version of the new Chapter 1 of SW-846. These non-target analytes are commonly referred to as "tentative identified compounds" or "TIC's". To minimize bias for the study's major and secondary goals, a second firm was hired to statistically analyze and evaluate the resulting data for the PE study and to summarize the findings in a report to Shell. This paper includes the information and results reported by independent contractors to Shell.

PERFORMANCE EVALUATION STUDY

Twenty-four laboratories plus Shell's Westhollow Research Center were included in the PE study. Each of the laboratories were contacted by an engineering firm where arrangements were made to have some groundwater samples from a cleanup site analyzed for volatile organics and TIC's, oil and grease, BOD, pH, COD, TOC and ICP metals. EPA Method 8240 was specified for the organics and TIC's. ICP was specified for the metals and EPA approved methods were specified for the general parameters. To a limited extent, laboratories were given the impression that the engineering firm was doing an investigation associated with a leaking service station.

Laboratories were evaluated on their response and the help provided to the customer and how knowledgeable they were with respect to the customer's needs. Since Shell relies on contract engineering firms to do a lot of this type work, the resulting information was important. Sampling kits were requested and shipping instructions were obtained.

The program was arranged so that all of the laboratories eventually received their samples within one day of the same time.

The groundwater used to prepare the PE samples was a real groundwater matrix collected from a site with well characterized groundwater. The PE samples were prepared to simulate the kind of background matrix one might expect from a service station with leaking storage tanks. Some target analytes of interest were also present in groundwater and this was accounted for in the theoretical concentrations or made-to values. Three samples for organics were prepared with varying concentrations of nine target analytes and nine TIC's. The target analyte concentrations ranged from 5 to 68 ppb and the TIC's concentrations ranged from 15 to 270 ppb. The target analytes were prepared so two of the samples represented duplicates and the third was 2X the duplicates concentrations. These were randomly done with the three samples. The TIC's were prepared at 1X, 3X, and 6X concentration levels and these were also randomly done. The volatile organics and TIC's samples were designated MW-1, MW-2, and MW-3.

MW-4 and MW-5 were designated for ICP metals and a limited number of general parameters. Six of the target metals were present in the groundwater matrix. The background levels were accounted for in the made-to values for these analytes. A total of 11 metals were designated as target analytes for the study. These two samples were prepared to represent Youden[1] pairs to assess laboratory performance

MW-4 and MW-5 were also designated for the general parameters. Separate containers were used for metals, BOD and pH, TOC and COD, and oil and grease since different preservation steps were involved. The oil and grease samples were prepared by delivering a known quantity of oil and grease into the sample bottles provided by each laboratory and diluting to a known volume. Slight variations in the amount of oil and grease put into each container made the sample concentrations slightly different for each laboratory.

Table 1 is a tabulation for the made-to values for all the performance evaluation study samples. Essentially all of the samples were prepared to minimize any possible bias on the part of the laboratory and to disguise the samples from being associated with a PE study. It would have been difficult for anyone to establish any kind of pattern or that these were PE samples. All coolers were shipped to the laboratories by Federal Express on the same day.

LABORATORY INTERACTION

Records were maintained for all laboratory interaction between the engineering firm and each laboratory in the study. Such items as how helpful and knowledgeable the contacts at the laboratories were with respect to sampling requirements and analytical methodology were documented. The adequacy of the sampling kits, cost of analyses, turn-around time, and the degree of difficulty that was experienced in

trying to obtain missing information and verify some results were all documented. Most of this information was included in the individual laboratory evaluation reports provided by the contractor. These individual laboratory evaluation reports have since been sent to the laboratories along with the raw data reports for their samples. All this was done as part of the quality improvement process and has allowed laboratories to initiate corrective action where appropriate prior to complete statistical evaluation of the entire database.

Sampling Kits

There was a wide range of sampling kits that were provided by the laboratories. These ranged from a cardboard box containing bottles to well designed ice chests with labeled containers and blue ice included. Many of the bottles contained acid preservatives and some of these had leaked during shipment. It was obvious that there was a lot of room for improvement at many of the laboratories. One cannot expect precise and accurate data for samples that are collected and shipped with sampling kits that are inadequate.

Cost of Analysis

Laboratory pricing practices varied considerably depending on whether you wanted hard copies of the data, supporting QA/QC, and the raw data. Some laboratories were quite willing to provide CLP data packages for the analyses and based their bid on that basis. Other charges were quite confusing as well as the final billing. In one instance we were not billed for all analyses. There was approximately a 2X range of costs from the laboratories in the study. Because of the complex nature of the pricing practices it was not possible to estimate some average cost.

Turn-around Time

It was discovered that there are at least two major components for turn-around time problems. The first of these is that of holding times specified for most of the analyses. Only two laboratories did not meet the 10-day CLP holding time for volatile organics but did analyze samples within 13 days. The mean and median analysis times were 5 days for the study. For metals, the mean and median analysis time were 17 and 14 days, respectively. Because of the short holding time for the general parameters, no delays in reporting data resulted from these analyses.

Reviewing the raw data for when the data were available at the laboratory and when the data were actually sent to the customer, it was discovered that on the average it takes 35 days for a laboratory to report the data after the analyses are completed. This component of turn-around time leaves a lot of room for improvement. Essentially, this indicated that turn-around time delays are not caused by instrument limitations or delays but by clerical and/or quality assurance review.

The fastest and slowest laboratories sent out their data in 15 and 58 days, respectively. Unfortunately, this did not complete the laboratory

portion of the study. Five laboratories amended their reports to include forgotten data -- metals, raw data packages, and volatile organic TIC's data. These five reports were not completed from 51 to 103 days after the laboratories had received the samples. It should be noted that these five laboratories did not know their reports were not complete until they were contacted -- in some cases several times. Some information was never obtained after many attempts so a closing date was set for the study.

LABORATORY PERFORMANCE

There are a number of acceptable ways to assess laboratory performance. Two of the common parameters are precision and accuracy (recovery). EPA has also included precision and accuracy criteria in many of their analytical methods published in SW-846 or 40 CFR Part 136. Youden plots are another way to assess performance. Both common practices were employed to assess laboratory performance.

Outliers

It was not necessary to employ statistical tests to identify specific outliers. Simple visual comparisons and initial Youden calculations were sufficient in finding the most extreme outliers. The outliers also became quite obvious from the bar charts prepared for the data. Data that were seen as outliers were omitted from some of the calculations because of the obvious bias they would have given to the data group as a whole. Where any data were omitted from calculations, outliers were identified in the various tables and figures and usually enclosed in boxes.

Accuracy and Precision

The discussion of accuracy and precision is presented by analyte group -- volatiles, metals, and general parameters. Within each group, the discussion begins with Youden plots because they give a quick visual review of the data. A scorecard of laboratory performance was then made from the initial conclusions from these plots. Subsequently, tables and figures were prepared to give more details for laboratory performance. It was noted that these tables and figures were entirely consistent with the initial conclusions from the Youden plots.

Volatiles

The Youden plots for the nine target volatile analytes are shown in Figures 1 and 2. Noted on each plot are the laboratory numbers that fall outside the region of values where 95% of a single laboratory's results are expected to fall (the circle). A scoring system was devised to summarize the results from the Youden plots in Table 2. As can be seen in Table 2, there are four possible areas where a laboratory may fall on a Youden plot.

Before the 95% circle was determined for each Youden plot, preliminary areas were drawn using the data from all laboratories. Those that fell well outside the 95% area were then designated as outliers and deleted from the calculation of sample averages and intralaboratory precision that are used to draw the 95% circles shown in Figures 1 and 2. Those laboratory numbers that were considered outliers are enclosed within boxes in the Youden plots.

Some laboratories reported observations for analytes as less-than values and in some instances no values were reported. These reported observations could not be used in the Youden plots. Where laboratories reported less-than values in a sample pair, the symbol "X" was used in Table 2 for the observation. Where a laboratory did not report any data for an analyte, the letters "nr" were used for "not reported" in Table 2.

To get an overall picture of each laboratory's performance for the volatiles as an analyte group, the number of times a laboratory fell into a particular region were counted as well as the number of times a laboratory reported less-than values. This information is shown in Table 2 as the "performance summary". The best possible score would be a value of 9 for falling within the 95% circle for all analytes. Lab-15 and Lab-23 did have scores of 9. Other laboratories that most often fell within the 95% region were Lab-3, Lab-4, Lab-5, Lab-10, Lab-12, Lab-19, and Lab-25.

Laboratories that had a tendency towards higher than average recoveries were Lab-2, Lab-8, Lab-9, Lab-11, Lab-14, and Lab-17. Higher than average recoveries do not necessarily mean poorer performance for the volatiles. In most instances, the recoveries were actually closer to the made-to values. The made-to values for each sample pair are shown in the Youden plots in Figures 1 and 2. Judging from the position of the made-to values shown in the Youden plots, only Lab-2 has a clear problem with high recoveries that places it well outside the performance of the other laboratories. As noted in the Youden plots, Lab-2 was identified as an outlier in the group of laboratories used to calculate the 95% performance region for five of the nine volatiles.

Laboratories that had a tendency towards lower than average recoveries were Lab-1, Lab-16, Lab-20, Lab-21, and Lab-24. Lower than average recoveries are indicators of poorer performance as shown by the positions of these labs and the made-to values shown in the Youden plots. Some of these laboratories were also identified as outliers in the group of laboratories used to calculate the 95% performance regions. Boxes on the Youden plot identify these outliers.

Table 3 summaries the recovery of volatiles for all the laboratories and for each of the analytes. This is just another way to summarize the accuracy data. The outliers identified in the Youden plots were not deleted from the calculations of mean recoveries shown in Table 3 because they had little effect on the mean values. Table 3 also summarizes the mean recoveries for all nine analytes for each laboratory. In fact,

Table 3 was rank ordered by mean recovery from lowest to the highest. The mean recoveries ranged from 55% for Lab-20 to 117% for Lab-2.

Among the individual volatiles, the mean for all laboratories ranged from 59% for carbon tetrachloride to 105% for methylene chloride. The mean recovery of 88% for trichloroethylene is somewhat misleading. Nearly half of the laboratories could not detect trichloroethylene in the 5 ug/L samples (MW-2 and MW-3) although all 25 laboratories reported a detectable concentration for the 10 ug/L sample. The fact that most laboratories did report less-than values but had no problem with the 10 ug/L sample suggested that the detection limit for trichloroethylene is indeed somewhere above 5 ug/L. Given the number of less-than values reported for trichloroethylene, the mean recovery for all laboratories would be less than the 88% shown in Table 3.

Bar charts of mean recovery were prepared with the same data and these are presented in Figures 3, 4, and 5. The bar charts were prepared with all the data; however, outliers were removed for mean calculations. Both presentations represent additional ways of assessing the same recovery data. Another way of looking at the data in Table 3 is through range charts that show the high, mean, and low mean recoveries by laboratory and analyte. The range chart shown in Figure 6 shows the variability of each laboratory in analyzing volatiles with the laboratories ranked by overall mean recovery. The high value shown is the highest mean recovery among the nine volatiles for each laboratory and the low is the lowest mean recovery. The mean is the overall mean for all nine volatiles. In judging laboratory performance, if the mean recovery for volatiles as a group is acceptable, the laboratory with the narrowest performance range indicates overall consistency for the analyte group. For example, Lab-3 has a mean recovery of 86% compared with 84% for the group average and the range was 71 to 107% for all analytes.

Figure 7 is a range chart showing the variability in mean recoveries by volatile analyte. The analytes were ranked in order of increasing mean recovery starting with carbon tetrachloride at 59% and ending with methylene chloride at 105%. Toluene showed the most variability between high and low recovery which ranged from 61% for Lab-21 to 286% for Lab-19. The next highest value for toluene recovery was 124% if one considers the 286% value an outlier. The new range would be 61% to 124% which is more in line with the other analyte recovery ranges. This suggests the 286% recovery value for toluene is an outlier.

Intralaboratory precision was calculated for each laboratory from the duplicate samples for each of the nine target volatiles. These precision values were then compared with EPA expected single analyst precision (intralaboratory precision), calculated from the method performance equations found in Method 8240 from EPA's SW-846 Methods Manual[2]. Table 4 is a summary of these comparisons. As noted in the table, the comparison was not made for xylenes because there are no precision equations for this analyte in the method. In the last column of Table 4, the number of times that a laboratory met the EPA expected method performance is summarized. A value of 8 indicates meeting EPA criteria

for all analytes where comparison was possible. Laboratories that met the method criteria for all eight volatiles were Lab-3, Lab-4, Lab-14, Lab-15, and Lab-17. Other laboratories that did well were Lab-11, Lab-12, Lab-23, and Lab-25 which met the criteria for seven of the eight analytes. Laboratories that were on the poor performance end with meeting EPA criteria for three or less out of the eight volatiles were Lab-2, Lab-6, Lab-13, and Lab-21.

Interlaboratory precision was used to calculate the EPA expected recovery range that a laboratory should fall within. Again, EPA performance equations from SW-846 Method 8240 were used as the criteria. These results for interlaboratory precision are summarized in Table 5 using the same nomenclature as with Table 4. Again, because equations for xylenes are not given in the method, no comparison was made for this analyte. Only Lab-9 and Lab-14 met the recovery range criteria for all eight volatiles. Other laboratories that did nearly as well were Lab-3, Lab-4, Lab-5, Lab-8, and Lab-17 which met criteria for seven of eight analytes. Only Lab-21 did poorly meeting the criteria for three or less volatiles.

It appears from the number of times that the laboratories failed to meet the criteria for 1,1,1-trichloroethane, carbon tetrachloride, and trichloroethylene, that the EPA's criteria are not representative of general laboratory performance at the concentration levels used for this study and may be too restrictive (although the study concentration were within the applicable range of EPA's equations, 5-600 ug/L). Carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene had mean recoveries of 59%, 69%, and 88%, respectively over all laboratories for this study. The recovery equations for Method 8240 indicate recoveries greater than 100% for all three of these analytes which the 24 laboratories could not meet.

Metals

Youden plots for the eleven metals that were spiked into MW-4 and MW-5 are shown in Figures 8 and 9. As with the volatiles, preliminary Youden plots were made first to visually identify outliers. These outliers again were then omitted from the calculations of the circular area in the plots that represent where 95% of a single laboratory's results are expected to fall. The outliers were identified in the Youden plots by boxed-in laboratory number. All values for Lab-9 were omitted from the calculations because it appeared that the laboratory had switched sample numbers in reporting the results (MW-4 values were reported for MW-5 and vice versa). It could not be established prior to the closing date that this mistake had indeed been made. One exceptional outlier was the sample pair of Lab-18 for sodium. The values of this pair were an order of magnitude over the made-to values (1,800 and 1,700 mg/L reported for a made-to value of 176 mg/L for both samples). It is likely that the laboratory misplaced a decimal in calculating the sample concentration; however, no information was obtained from the laboratory to refute the reported values. The sodium data from Lab-18 were omitted from calculations for the 95% region.

A summary of the Youden plots for metals is shown in Table 6 using the same symbols and criteria described previously for volatile analytes. Again, the performance summary column shows the overall picture of each laboratory's performance for the metals. Lab-7, Lab-11, and Lab-14 results all fell within the 95% region for all metals. Other laboratories that most often fell within the 95% region included Lab-2, Lab-3, Lab-5, Lab-6, Lab-12, Lab-13, Lab-18, Lab-22 and Lab-24. Laboratories that had a tendency towards higher than average recoveries were Lab-10, Lab-20, Lab-21, and Lab-25. Laboratories with a tendency towards lower than average recoveries included Lab-8, Lab-16, Lab-17, and Lab-19. Lab-8 appeared to have a particular problem with recurring low recoveries for 9 of the 11 metals. Laboratories that had a tendency towards poorer than expected precision were Lab-1 and Lab-23.

Table 7 summarizes the mean recoveries for all analytes and laboratories. Again, a summary of the mean recoveries for all metals is shown in the last column of Table 7. The laboratories in Table 7 are ranked in increasing mean recoveries for all metals. The overall mean recovery for all eleven metals was 97%. Among the individual metals, the means for all laboratories ranged from 89% for cadmium to 107% for zinc.

Recovery bar charts were prepared for each of the metals and all data from all laboratories were included; however, the mean recoveries calculated excluded the outliers. These bar charts are shown in Figures 10 and 11. This is just another way to illustrate outlier data that were omitted from calculating the 95% circular regions of the Youden plots.

Range charts of the high, mean, and low mean recoveries by laboratory and analyte are shown in Figures 12 and 13. These charts do not show the range with the outliers included because they tend to distort the overall view of the data. The range chart in Figure 12 shows the variability of each laboratory in analyzing metals, with the laboratories ranked by overall mean recovery. The high value shown is the highest mean recovery among the eleven metals for each laboratory, the low is the lowest mean recovery, and the mean is the overall mean for all eleven metals.

Many laboratories showed a fairly narrow range between high and low recoveries. These were Lab-6, Lab-10, Lab-11, Lab-12, Lab-13, Lab-14, and Lab-16. The range of mean recoveries for these laboratories was from 90 to 103%.

Figure 13 is a range chart showing the variability in mean recoveries by metal. The metals were ranked in order of increasing mean recovery. Again all of the data were included and essentially this chart confirms those metals where some laboratories had generated exceptionally high recoveries (outliers).

There were no duplicate samples for metals, except for sodium, that could be used to compare performance with EPA method performance criteria for intralaboratory precision. Therefore, only interlaboratory precision was evaluated using the performance equations in EPA Method 200.7 for ICP metals analysis. It should be noted that some laboratories really did

not use ICP, but because this was the method requested to analyze the samples, it was used as the basis for comparison. In some instances, it was difficult to establish that ICP was not actually used. Interlaboratory precision was used to calculate the expected recovery range that a laboratory should fall within. Table 8 summarizes the overall (interlaboratory) precision for the 11 metals with respect to meeting EPA criteria.

For calcium, all laboratories met the EPA criteria. No laboratory was able to meet the expected recovery range for all 11 metals, primarily because of their performance with barium. Oddly enough, the recovery equation for total digestion of barium in Method 200.7 predicts an unusually low recovery (67%) for this metal that was not experienced by the laboratories included in this study. The mean recovery for all laboratories actually was 100%. This predicted low recovery when coupled with the interlaboratory precision estimate actually gives an upper limit of recovery range that is below the made-to concentration. This problem with the barium equations did not affect the relative performance among the laboratories, so it was merely noted here. It does suggest that laboratories can do much better in the recovery of barium than the method equations would predict.

Many of the laboratories did well by being within the expected recovery range for at least 8 out of the 11 metals. Lab-8, Lab-17, and Lab-25 did poorly in only meeting the recovery range for less than half the metals. Review of the tabulated data shown in Table 7 for individual mean recoveries for each metal as well as each individual laboratory suggested excellent performance by all laboratories with only a few outliers being observed; however, when one counts the number of times EPA criteria were not met in Table 8, one has a different impression. It suggests that the EPA criteria may be too restrictive in the case of metals. This possibility has not been thoroughly explored.

General Parameters

Youden plots for the five general parameter analytes are shown in Figure 14. Preliminary Youden plots were made first to visually identify outliers. These outliers were omitted from the calculation of the circular area in the plots that represent where 95 percent of a single laboratory's results are expected to fall. These outliers are identified in the plots by a boxed-in laboratory number. In total, only 6 sample pairs were considered outliers. There was no one laboratory that had persistent outliers; all 6 outliers came from different laboratories. It is interesting to note that all 6 outliers were in the BOD, COD, and TOC, analytes that address in different ways the organic content of a sample.

A summary of the Youden plots for general parameter analytes is shown in Table 9 using the same symbols and criteria described for volatile analytes. An overall picture of each laboratory's performance for these analytes as a group is shown in the performance summary column of the Table 9. The performance summary is the number of times a laboratory fell

in a particular region of the Youden plots as well as the number of times the laboratory reported less-than values.

Laboratories that always fell within the region expected for 95 percent of a single laboratory's results were Lab-6 and Lab-16. Other laboratories that most often fell within this region were Lab-5, Lab-11, Lab-13, Lab-17, Lab-18, and Lab-21.

Laboratories that had a tendency towards higher than average recoveries were Lab-1, Lab-9, Lab-12, Lab-20, and Lab-22. There is no explanation for the over 900 percent recovery shown by Lab-9 for TOC as the quality control sample analyzed by the laboratory had acceptable recovery near 100 percent.

Laboratories that had a tendency towards lower than average recoveries were Lab-2, Lab-4, and Lab-19. Lower than average recoveries are indicators of poorer performance as shown by the positions of these laboratories and the made-to values shown in the Youden plots. Lab-2 and Lab-19 were the poorest performers for oil and grease as shown in the Youden plot of Figure 14. They reported only about 10 percent of the made-to concentrations in the sample pairs. Lab-13 also had a greater deviation in pH from the true measurement (about 1.0 SU).

No laboratory showed a particular tendency towards poorer precision. Lab-8, Lab-20, Lab-23, and Lab-24 fell in the Youden plot regions of poorer precision only once each. No one analyte predominated as all four laboratories fell in these regions for a different analyte.

Laboratories that often reported less-than-values were Lab-14 and Lab-15. Among the four organic-related analytes, less-than-values were limited to BOD, COD, and oil and grease; TOC was always reported above detectable levels. (Analyses for pH would not be reported as less-than-value given the nature of the analysis.) Lab-9 had an abnormally high detection limit reported for BOD (60 mg/L). The laboratory's explanation was that they did not expect the BOD to be at such low concentrations and they set their dilutions too high for the analysis. Given that the true concentrations for the sample pair were typical of treated wastewater effluents (32 and 19 mg/L), the laboratory should have had no problem in setting up the dilutions correctly. Setting the dilutions too high is evidence of poor laboratory practice.

The laboratory performance shown in the Youden plot summary of Table 9 is reflected again in the mean recoveries shown in Table 10 and the recovery bar charts of Figures 15 and 16. The outliers identified in the Youden plots of Figure 14, were not included in any of the calculations of overall laboratory or analyte mean recoveries shown in Table 10 and the recovery bar charts because they distorted the overall means too much.

The mean recovery for each laboratory is shown for individual analytes in Table 10, along with the laboratory's overall mean for all general parameter analytes. The laboratories are ranked in the Table 10 according to these overall means. Lab-3, Lab-9 and Lab-15 reported

less-than-values for a few samples and so the mean recoveries for these labs could not be included in the overall mean calculation.

The range in overall mean recoveries for the five general parameters was 55% (Lab-19) to 115 percent (Lab-11). Among the individual analytes, the mean for all labs ranged from 59% (oil and grease) to 104% (TOC).

The bar charts of mean recovery shown in Figures 15 and 16 tell the same story as the numbers in Table 10, but highlight the differences among labs more dramatically. Range charts of the high, mean, and low mean recoveries by laboratory and analyte are shown in Figures 17 and 18. The range chart in Figure 17 shows the variability of each lab in analyzing general parameter analytes, with the laboratories ranked by overall mean recovery. The high value shown is the highest mean recovery among the five analytes for each laboratory, the low is the lowest mean recovery, and the mean is the overall mean for all five analytes.

Laboratories showing the most narrow range between high and low recoveries in Figure 17 were Lab-6, Lab-12, and Lab-21. The overall mean recovery for these laboratories was 94% to 109%. The other laboratories fall somewhere in between the wide and narrow range groups. In judging laboratory performance, the laboratory with a narrow performance range indicates overall consistency for this analyte group.

Figure 18 is a range chart showing the variability in mean recoveries by general parameter. The analytes are ranked in order of increasing mean recovery starting with oil and grease at 59 percent and ending with TOC at 104 percent. Again, the outliers were not used in these mean recoveries although they are noted on the range charts. COD showed the most variability between high and low recovery (185% for Lab-4 and 23% for Lab-19). The mean recovery for pH showed the most narrow range (95-113%) not surprisingly given the nature of the test and ease of measuring this parameter.

The general parameters do not have method performance equations that can be used for precision comparisons like the volatiles and metals. Instead, a recovery range was assumed of ±40% of the made-to concentration in order to make a performance comparison among laboratories. The ±40% level was selected because EPA[3] has previously used it in data evaluations of laboratory performance (specifically the PQL concept for volatile organics in drinking water).

The comparison of laboratory performance based on this recovery range is shown in Table 11. Four laboratories were able to met this criterion for all five conventional analytes -- Lab-6, Lab-12, Lab-20, and Lab-21. Laboratories that did rather poorly, meeting the criterion for only 2 of the 5 analytes, were Lab-2, Lab-4, Lab-10, Lab-19, and Lab-23.

Performance Summary

A lot of detail has been presented in various ways on laboratory performance in accuracy and precision, so much that it becomes difficult

to get a clear picture of one laboratory's performance relative to another. To present the data in a more concise form, a scoring system was created to rate each laboratory's performance in each analyte group -- volatiles, metals, and general parameters. The performance for TIC's was also included in summary table. The system was divided by analyte group because some laboratories had definite strengths in one or two groups, but may have been weak in others, so it was not appropriate to combine performance across these groups.

Each laboratory's score is shown in Table 12. The method of scoring is as follows:

Volatiles Accuracy

The performance within EPA expected recovery ranges for SW-846 Method 8240 shown in Table 5 was the basis of accuracy scoring. The number of times that a laboratory met the EPA criteria was given these scores:

Excellent -- 8
Good -- 6 to 7
Fair -- 4 to 5
Poor -- 3 or less

Volatiles Precision

The performance against EPA expected single analyst (intralaboratory) precision for SW-846 Method 8240 shown in Table 4 was the basis of precision scoring. The number of times that a laboratory met the EPA criteria was given these scores:

Excellent -- 8
Good -- 6 to 7
Fair -- 4 to 5
Poor -- 3 or less

Metals Accuracy

The performance within EPA expected recovery ranges for 40 CFR 136 Method 200.7 shown in Table 8 was the basis of accuracy scoring. The number of times that a lab met the EPA criteria was given these scores:

Excellent -- 10
Good -- 8 to 9
Fair -- 5 to 7
Poor -- 4 or less

Metals Precision

Unlike the volatiles, there were no duplicate samples for laboratories that could be used to calculate intralaboratory precision and compare each laboratory against the EPA criteria of Method 200.7. Instead, the performance of the laboratory in the Youden plots that were summarized in Table 6 were used to score precision. The number of times that a

laboratory fell into the poor precision region of the Youden plot was given these scores:

Excellent -- 0
Good -- 1
Fair -- 2 to 3
Poor -- 4 or more

General Parameters Accuracy

General parameters do not have EPA performance equations like volatiles or metals that can be used to judge accuracy. Instead a criterion of being within ±40% of the true concentration was used to judge accuracy performance. The number of times that a lab fell within the ±40% range (shown in Table 5-11) was given these scores:

Excellent -- 5
Good -- 4
Fair -- 3
Poor -- 2 or less

In assessing laboratory performance based on Table 12, the most important criterion is accuracy because if the laboratory cannot come close to the made-to concentration, the analysis is of little value no matter how precise it may be. If a laboratory's accuracy is satisfactory, one should then look for good precision. When a laboratory has good accuracy, but poor precision, it means that on average, its analyses are right on target, but any single analysis may be way too high or way too low. So one should look for both good accuracy and good precision in a laboratory.

Some of the best overall laboratories were Lab-12 and Lab-14. These two laboratories did good to excellent work in all three analyte groups. No laboratory did poorly in all three analyte groups. Each laboratory rated at least a "good" in one or more analyte groups.

Within individual analyte groups, the best and worst performers were:

	Best	Worst
Volatiles	Lab-3	Lab-2
	Lab-4	Lab-6
	Lab-14	Lab-13
	Lab-15	Lab-21
	Lab-17	
Metals		
	Lab-11	Lab-1
	Lab-12	Lab-3
	Lab-14	Lab-8

General Parameters

Lab-6	Lab-2
Lab-12	Lab-4
Lab-21	Lab-10
	Lab-19
	Lab-23

Two other points that stand out clearly in the table can be made. One, more laboratories achieve excellent precision for metals and general parameters, than for volatiles. Two, where a laboratory does quite poorly in one group, it may be very strong in another. For example, Lab-21 and Lab-6 did poorly in analyzing volatiles, but did excellent work in general parameters. Knowing a laboratory's strength and weaknesses can be useful if samples can be split according to analysis and sent to the laboratory that does the better job; although, the prime quality goal is to improve performance for all environmental analyses. Results from this study can direct a laboratory to improve in those weaker areas.

TENTATIVE IDENTIFIED COMPOUNDS

When one requests that a laboratory analyze a sample for volatile organics by Method 8240, it is implied that only the analytes listed in the method are to be reported. In some instances, a laboratory may be asked to report additional analyte peaks identified by the mass spectrometer on the basis of computer matching of the spectra. These additional analytes are commonly called "tentative identified compounds" or TIC's. As their name suggests, the reliability of the analyses is less than that for specific target analytes listed in the method.

There are many misconceptions concerning the ability of GC/MS methodology and instrumentation to identify and quantify non-target analytes or TIC's in environmental samples. This has been one of the major selling points for GC/MS methodology. The current investigation for TIC's could be considered biased to demonstrate the best that one might expect. Method 8240 utilizes the purge and trap concentration technique which not only concentrates volatile organics by a factor of 1000, but also separates these volatile organics from the other less volatile (extractables) organics present in most samples. The purge and trap technique is also a cleanup step. By limiting the study to volatile and purgeable-type organics the total number of possibilities was also reduced. From an analytical point of view, the method employed and procedures used were the most ideal one could select for TIC's.

The selection of the TIC analytes for the study was also conservative. All of the compounds were present in some samples that a number of these laboratories had previously analyzed for Shell and had been routinely reported at a number of cleanup sites. The concentrations spiked into samples were at levels to yield chromatographic peaks easily

distinguished above the matrix background. It was our intent to make the TIC's easy to pick out which should have improved the qualitative and quantitative probability.

The results for TIC's indicated most laboratories do not do very well with TIC's. Not a single laboratory qualitatively identified the presence of all nine TIC's. Table 13 shows the qualitative performance of the laboratories based on the percentage of samples that had reportable values (any values over the laboratories reporting limit). Methyl ethyl ketone (MEK) had the highest number of reportable values with 84% of the samples correctly identified for this analyte. In contrast, tertiary butyl alcohol (TBA) was not found by any of the laboratories. The only other TIC that was found in at least 50% of the samples was diisopropyl ether (DIPE) (59%). All other TIC's had less than 25% or less reportable values.

Reportable values would be expected to increase as the concentration of the analyte is the sample increases. The TIC's were spiked into samples at three levels. The percentages of reportable values at individual spike concentration are shown in Table 14. Methyl ethyl ketone, the analyte with the highest percentage of reportable values, shows a clear trend of increasing percentage with increasing concentration as the percentage reportable values increased from 72% to 96% with concentration increases from 30 ug/L to 180 ug/L. If 95% reportable values was chosen as the level at which the presence of an analyte could be reliably identified, then the quantitative level for methyl ethyl ketone for this study is around 180 ug/L.

The other eight TIC's showed a general trend of increasing percentage with increasing concentration but the concentration range did not extend far enough to show this clearly, nor to estimate at what concentration 95% of the values would be reportable. Based on the highest spiked concentration for these TIC's in Table 14, the concentrations at which 95% of the values would be reportable with Method 8240 would be greater than 90 ug/L for cyclohexane, MTBE, DIPE, napthalene, iso-octane, and THF; greater than 180 ug/L for TCB; and, greater than 270 ug/L for TBA.

The overall laboratory performance in identifying TIC's was evaluated, and the performance for each laboratory is shown in Table 15. This table shows the number of reportable values for each laboratory for each TIC. If a laboratory found an analyte in all three samples where it was spiked, then the number of reportable values for that TIC would be three. If a laboratory found every TIC in every sample, the maximum number of reportable values would be 27. The highest number of reportable values was 13 for Lab-25 which is a little less than a 50% identification rate. Other laboratories that did nearly as well with 10 to 12 reportables were Lab-2, Lab-10, Lab-13, Lab-15, Lab-17, Lab-19, and Lab-22. Laboratories that did poorly, reporting 3 or less values, were Lab-1, Lab-5, Lab-9, Lab-18, Lab-20, Lab-21, and Lab-23.

Table 15 also shows the number of analytes found at least once by each laboratory. The highest number of analytes found was only five out of

nine TIC's in the samples. Laboratories that found at least five TIC's were Lab-13, Lab-16, Lab-17, Lab-19, and Lab-25. The five TIC's found by these laboratories were not the same for each laboratory.

The number of laboratories that reported a TIC at least once is shown at the bottom of Table 15. The number of laboratories ranged from zero (TBA) to 24 (MEK). Lab-1 was the only laboratory that did not find methyl ethyl ketone in any of the three samples.

With such poor qualitative performance, one could not expect the quantitative performance to be good. Table 16 gives the mean recoveries for each TIC for each laboratory. The laboratories were ranked by overall mean recovery for all nine TIC's. The range in overall mean recoveries was much wider than those for the target volatiles, 41% to 344% as compared to 55% to 117% for the target volatiles. The range for each laboratory was also wider, for example, compare the TIC range of 87% to 933% for Lab-7 with its 54% to 99% range for target volatiles.

The overall mean recoveries in Table 16 cannot be used very well to judge each laboratory's performance with respect to the other laboratories because of the variability in the TIC mean recoveries and the number of TIC's that the laboratory actually identified. For example, the performance of Lab-21 is deceiving since its overall mean recovery was 101%, but this was based on only one sample in which it found methyl ethyl ketone. Since it only reported a single value the laboratory really had poor performance for TIC's.

To better judge laboratory performance for TIC's, the criteria shown in Table 17 were used. There are four levels of recovery performance that were arbitrarily chosen and are shown in Table 17. The table shows the majority of observations were less-than values or not reported at all. Of the reportable values, 14% were found within plus or minus 40% of the made-to values; 5% were between plus or minus 40% to 70% of the made-to values; and, 7% were more than plus or minus 70% of the made-to value.

RECOVERY CORRECTION

The most recent drafts of SW-846 Chapter 1 requires recovery correction of all environmental data. Recovery correction is currently mandated by regulations for some tests such as TCLP. Some in the analytical community have opposed recovery corrections and have provided EPA with very explicit comments on why recovery correction should not be mandated. However, it has been EPA's position that recovery correction always biases the data more closely to the true value. If this were actually true, it would be difficult to argue against. The current status of recovery correction is that EPA is rewriting Chapter 1 to remove the requirement.

While Method 8240 data are already recovery corrected on the basis of how the method is run, the data resulting from this current PE study can be and was used to gain a better understanding for recovery correction. The

target analytes were prepared as duplicates and the third sample was 2X the concentration of the duplicates. One could consider the 2X level sample as the matrix spike upon which each of the duplicates could be recovery corrected. Recovery correction calculations were performed following EPA prescribed procedures on the organic target analytes. We did not include the TIC's data for obvious reasons. Since the true values were known for our samples, it was possible to test the EPA hypothesis that the procedure always biases the data more closely to the true value.

The effects of recovery correction on the nine target volatile analytes are summarized in Table 18. Table 18 lists the analyte, the percentage of analyses that were improved by recovery correction (bought closer to the true value), percentage of those that were not, and the total number of analyses available for comparison among all the laboratories. These recovery-correction effects are also shown graphically in the bar chart of Figure 19.

The key for interpreting these recovery-correction effects in the bar chart is included in Figure 19 (the interpretation of the numbers in Table 18 is similar). As shown in the key, if the bar is all the way to the left, all of the values (100 percent) are improved by recovery correction. As the bar shifts to the right, fewer values are improved by recovery correction. When the 50/50 split between improved versus not improved is reached, one would say that recovery correction has no advantage whatsoever. In other words, recovery correction would not be useful because half the time it improved the values while the other half of the time, it made the values worse (or did not improve them at all in a very few cases). Continuing to the right past 50 percent, recovery correction becomes a disadvantage as more and more values are found not to be improved by recovery correction. Finally, arriving at the far right of the chart, none of the values are improved by recovery correction. Therefore, for recovery correction to be considered advantageous at all, more than 50 percent of the values must be improved. If there were an improvement for 60% of the values this would not represent much of an improvement overall since the remaining 40% would not be improved.

Seven of the nine volatile organics had greater than 50% of the values improved by recovery correction. Of the seven that were improved, the greatest improvements were for ethylbenzene (96% improved); carbon tetrachloride (86% improved); and 1,1,1-trichloroethane (86% improved). Lesser improvements were found for methylene chloride (65% improved); benzene (62% improved); xylenes (61% improved); and chloroform (61% improved). Two analytes that were less than 50% improved were toluene (48% improved) and trichloroethylene (19% improved). As a group the average improvement for these nine volatile organics was 65%, with 35% of the values not improved by recovery correction. For all practical purposes, recovery correction did improve observations for ethylbenzene, carbon tetrachloride, and 1,1,1-trichloroethane, but for the remaining six analytes there was marginal or no improvement at all.

The amount of improvement due to recovery correction, however, is negated in part by the percentage of values that are not improved. Subtracting the percentage not improved by recovery corrections yields the net improvement which is summarized for these nine analytes in Table 19. The net improvement among the nine analytes ranged from negative 62 percent for trichloroethylene to positive 92 percent for ethylbenzene with an average of plus 30 percent for the entire group. The negative percents for trichloroethylene and toluene mean that there was no net improvement, but rather that a net of 4% of the values for toluene and 62% for trichloroethylene were made worse.

Looking at recovery correction only as a percentage that was improved or not improved does not show how much the actual analytical values were changed. In other words, is the change a significant improvement? Statistical tests on the interlaboratory means (improved vs. not improved) were made for each analyte, using the Student's t-test. The results of these tests are summarized in Table 20 which lists the calculated "t" along with the two means and pooled deviations for each analyte. As shown in Table 20, recovery correction did not make a significant difference in the mean analytical value among the 25 laboratories for chloroform and methylene chloride. This indicated that the percentage improvement for these two analytes shown in Table 19 is not significant. For the other seven analytes in Table 20, the change in mean made by recovery correction either for better or for worse, would be considered significant.

In summary, recovery correction for volatile analytes improved the analytical values by bringing them closer to the true value for seven of the nine analytes tested in this study; however, two of the seven improvements were not considered statistically significant. Of the remaining five considered statistically significant, the net improvement by recovery correction (after subtracting the percentage of not improved values) ranged from 22% for xylenes to 92% for ethylbenzene. Recovery correction did not improve values for two of the nine analytes. Combining all effects for the nine analytes, recovery correction improved a net of 30% of the analytical values. The results from this study also show that the effects for recovery correction are different for each analyte and this fact needs to be considered should EPA find it necessary to mandate recovery correction for all environmental programs.

For metals data by ICP it was possible to review the results in Figure 12 which summarizes the range of recovery for all laboratories for all metals. Figure 12 shows that the mean recovery for all laboratories was 97 percent. The tabulated data for Figure 12 is found in Table 7.
Table 7 shows that the mean recovery for all laboratories was 97%. The means for each metal that resulted in the 97% mean value are listed on the bottom of Table 7. The individual means ranged from 89% to 107% which again illustrates the good performance of the laboratories involved. When one considers the mean recovery for all laboratories and the narrow range of recoveries for each of the laboratories and the fact that the study was done blindly, one wonders what would be accomplished

by attempting to recovery correct such observations.

CONCLUSIONS

The laboratories included in the performance evaluation study meet EPA method criteria for volatile organics and ICP metals with few exceptions. Performances for general parameters such as oil and grease, pH, BOD, etc. were disappointing. Considering that the PE study was conducted to reflect day to day operations and that the samples were blind to laboratories, one would expect similar performance for most compliance monitoring samples. We need to more closely monitor the nature of sampling kits provided by commercial laboratories to ensure the integrity of samples submitted for analysis. One cannot expect quality data on poorly collected or preserved samples.

The laboratories included in the blind PE study all were laboratories with considerable GC/MS experience. The method selected (8240) and the compounds investigated would be expected to bias the performance for TIC's toward good performance. Unfortunately, the results clearly show how poorly we perform on TIC's both qualitatively and quantitatively for groundwater samples. The performance would be expected to be even poorer for extraction-type methods (8270) and for solid or sludge samples. It is time we stop fooling ourselves on the ability of commercial environmental laboratories to routinely identify and quantify TIC's in environmental samples.

Recovery correction as proposed by EPA simply does not always bias results more closely to the true value. It was also discovered that in some cases just the opposite is true and that the effects of recovery correction may depend on the specific analyte. The results from the study for ICP metals clearly show recovery correction would do little to nothing to observations because of the extremely good precision and accuracy of the method. If there really is a need for recovery correction some discretion must be exercised. The results from this study clearly indicated recovery correction for organics would be complicated and for analytes such as the metals recovery correction really is not needed. This may be true for other analytes as well.

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1. W. J. Youden and E. H. Steiner, "Standard Manual of the AOAC", 1975, Published by the Association of Official Analytical Chemists, P.O. Box 540, Benjamin Franklin Station, Washington, DC 30044.

2. United States Environmental Protection Agency, "Test Methods for Evaluating Solid Wastes Physical/Chemical Methods" Office of Solid Waste and Emergency Response, Washington, DC 20460, November 1986, SW-846 Third Edition.

3. Preamble to Promulgated Rule Revisions for Ground Water Monitoring for Hazardous Waste Facilities, 40 CFR Part 264 (53 FR 3872).

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions for George?

MR. SCHUMACHER: Del Schumacher, Lancaster Laboratories.

Your oil and grease, did you specify which method, whether a gravimetric or infrared?

MR. STANKO: We specified an EPA approved method.

MR. SCHUMACHER: Which some of the spread of results could have been due to the fact that you did have volatiles in your sample?

MR. STANKO: It could be due to the fact that the contract laboratory did not use an EPA approved method, yes.

MR. SCHUMACHER: The gravimetric method is an approved method.

MR. STANKO: Gravimetric is not an approved method?

MR. SCHUMACHER: No, it is an approved method.

MR. STANKO: It is an approved method. That's what was specified...an EPA approved method.

MR. SCHUMACHER: But the IR method is also an approved method. One of them is going to give you volatiles results and the other one is going to slight your results.

MR. STANKO: That may be possible. In this particular case, I think it would more than implied that it was a gravimetric procedure as the EPA approved procedure. There has been some follow-up work since this time and we have discovered that, yes, they were pipetting 10 mLs of the sample. They were not extracting the bottle and the oil was always on the glass. The IR method will not give you the right answer if you can't get the oil off the glass. There was some zero percent

recoveries which is difficult to explain by any method.

MR. LANG: Ken Lang from the Army Toxic and Hazardous Materials Agency.

George, did you determine the error in the preparation of the samples that were sent out for analysis, especially the volatiles?

MR. STANKO: We are quite experienced at doing this and there were only two of the target analytes that were actually in the background matrix and we did account for that. Very carefully...it was done very carefully to make sure that the volatiles were prepared properly, as well as all the samples. There were double checks and balances and to our knowledge, we believe that the samples actually contained what we call the made-to values. If you looked at some of the average recovery, like for all the volatiles, it was about 84 percent. Why the data were biased low was because there were a couple of labs who did not perform as well. They were not outliers, but they did bias the data towards 84 percent.

MR. LANG: You also mentioned that many of the bottles that were shipped out contained acid. Were all the volatiles acid-preserved or were some not and some were? What was the...

MR. STANKO: Where they provided bottles that had acid in, we left the acid in. We did not add acid to ones that did not have it because the samples would have been analyzed in sufficient time not to exceed the holding times.

To give you an illustration of the extremes, one of these 43 mL vials had 20 mLs of hydrochloric acid. It's a little overkill.

MR. LANG: Yes, I'd just point out that the holding time study that was conducted by Oak Ridge National Lab would cast some doubt on those holding times, especially for the non-preserved samples which account for some of the variability in the volatiles data. That's why I was wondering whether or not they were all preserved or just some and

not others.

MR. STANKO: I know at least a half of these were.

MR. LANG: Okay.

MR. STANKO: But we were trying to simulate what an engineering firm would do once they got the kit. If it was there, they normally don't carry acid in the field. But if the acid was in the bottle, they just don't have much in the way of an option. They have to put what's in there. So that's what we did. There were some samples, oil and grease samples, where the sulfuric acid had eaten through the lid and also into the box.

MR. LANG: Okay. I have one last question. Did any of the labs report analytes that weren't in the samples?

MR. STANKO: We had no false positive. That was unusual. But I think we doctored this program up that the TICs should have stood out taller than the target analytes, so that may be the reason. Actually, the concentration of the TICs were higher than our target analytes. But that didn't seem to help them any.

MR. LANG: Okay.

MR. STANKO: But there were no false positives. Nobody reported something that wasn't there.

MR. LANG: Thanks.

MR. TELLIARD: One more.

MR. VINOPAL: I just have one question. I wonder on the TICs, did you verify if the laboratories had authentic standards for all of the TICs that you put in there or did they attempt to identify these without the aid of authentic standards?

MR. STANKO: It's not required to use authentic standards, but all of the laboratories in this study had analyzed samples from Shell at some point in time that contained these TICs and they were identified by at least one or

two or maybe three labs. So, in other words, our list of TICs were geared for samples that actually had them. So some of these labs should have seen them before.

MR. VINOPAL: Okay.

MR. TELLIARD: Thank you, George.

MR. STANKO: Thank you.

Figure 1
Youden Plots
Benzene, Toluene, Ethylbenzene, Xylenes

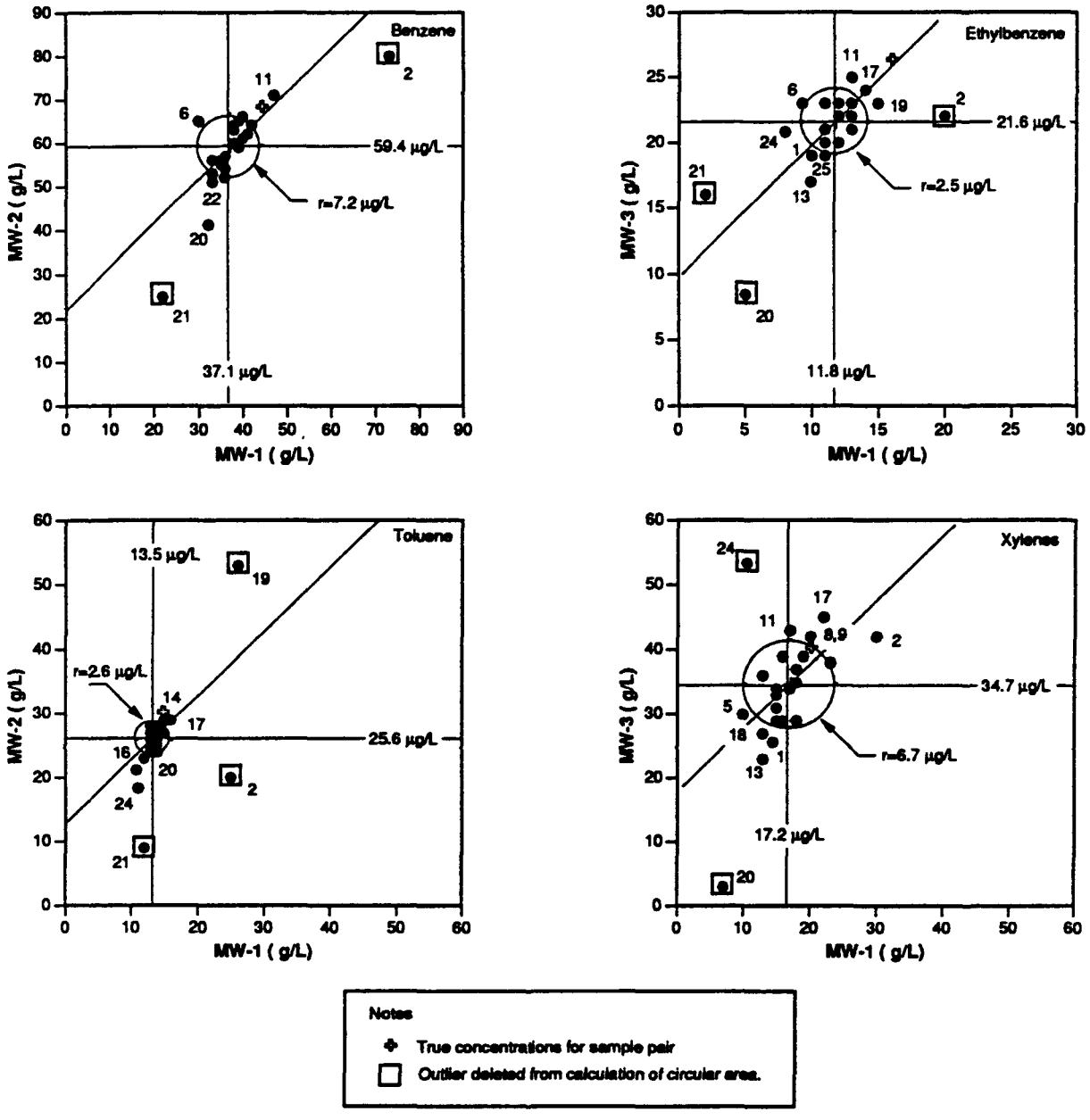
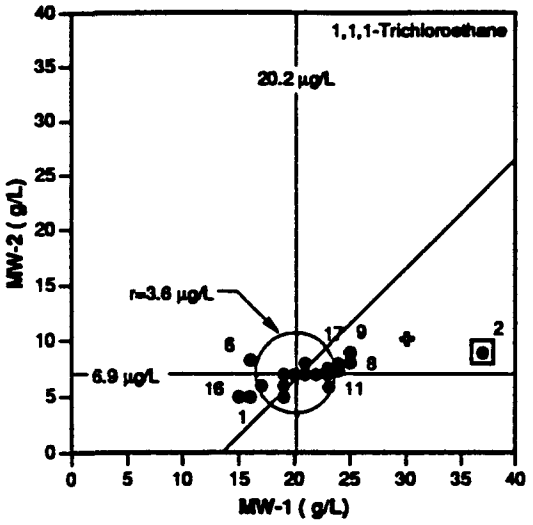
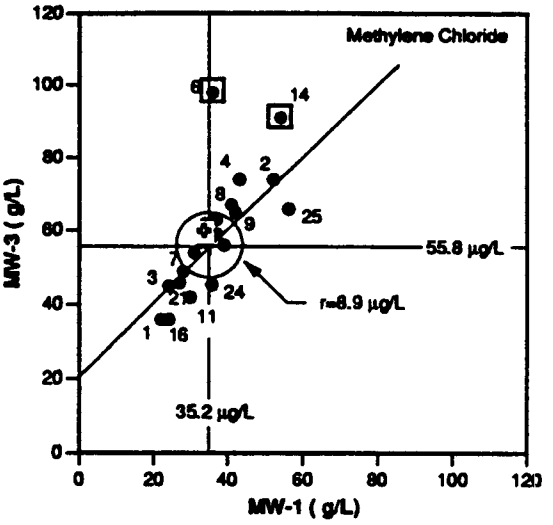
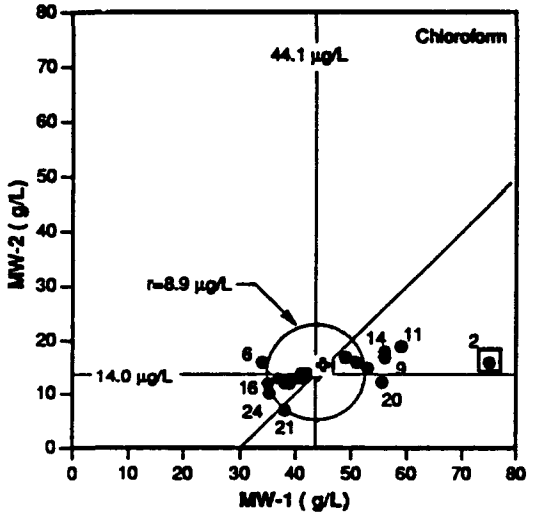
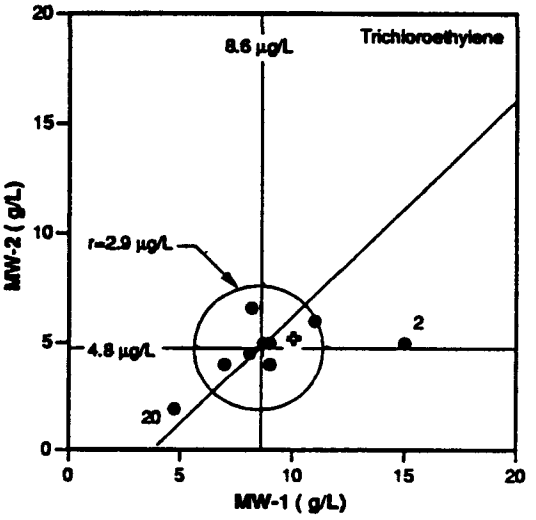


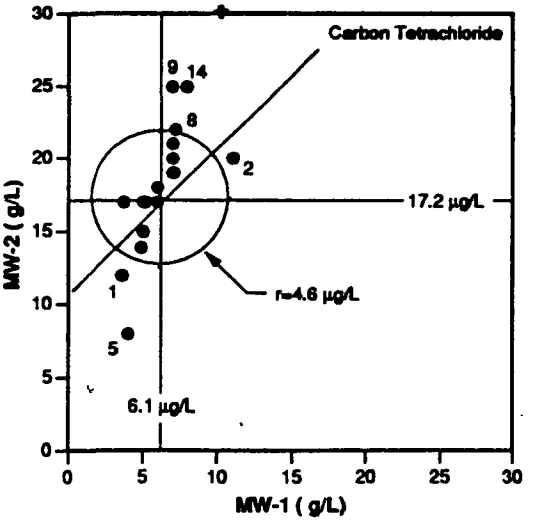
Figure 2
Youden Plots
TCA, Chloroform, Carbon Tetrachloride, Methylene Chloride, TCE





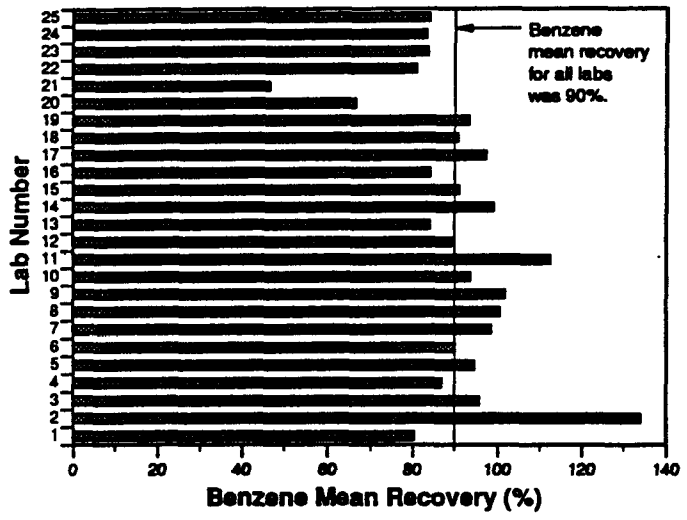


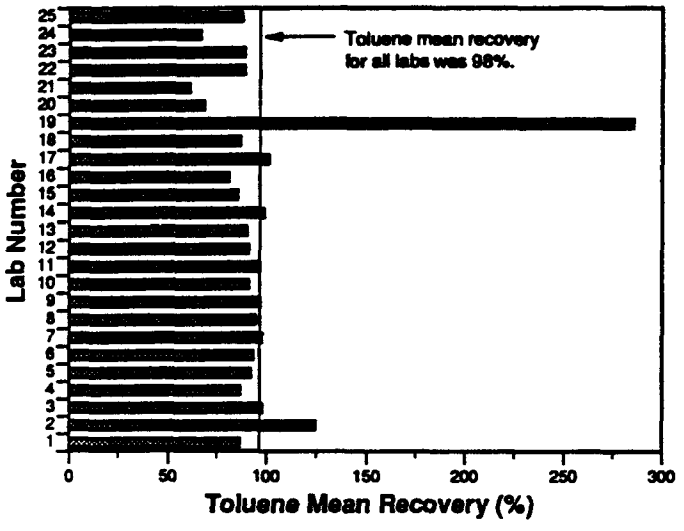


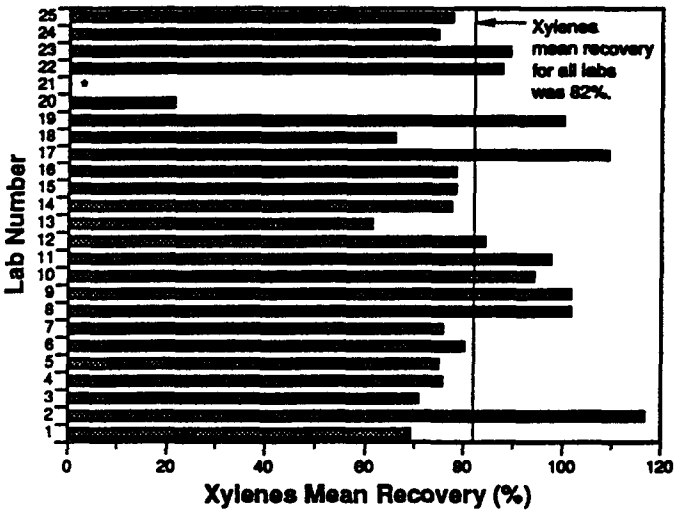


Notes
✣ True concentrations for sample pair
□ Outlier deleted from calculation of circular area.

Figure 3
Recovery Bar Charts
Benzene, Toluene, Xylenes



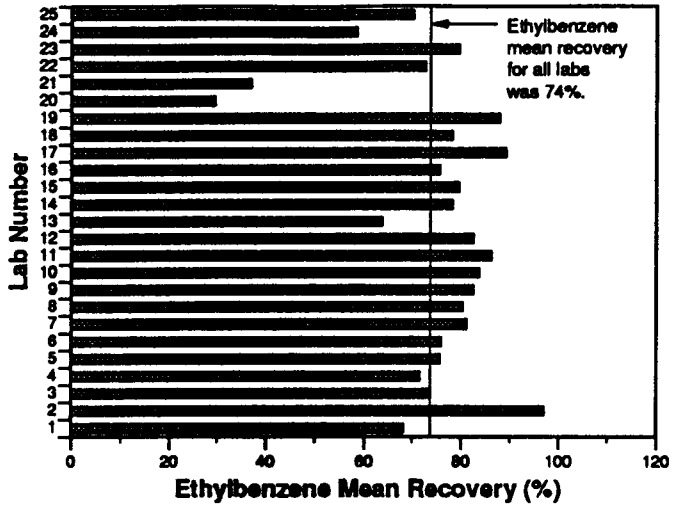


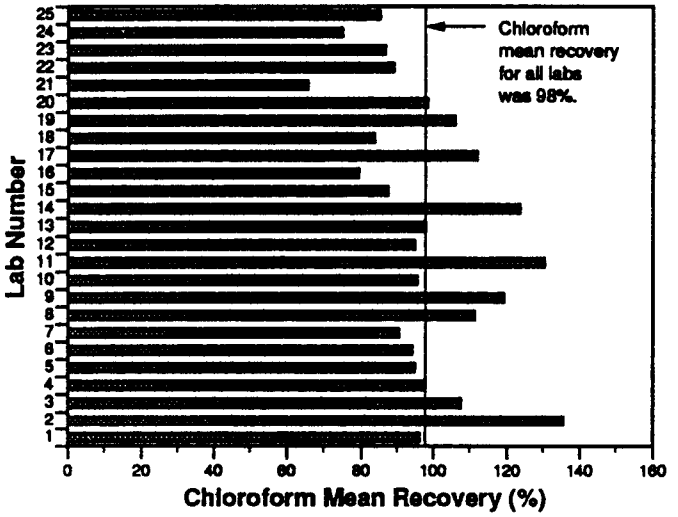


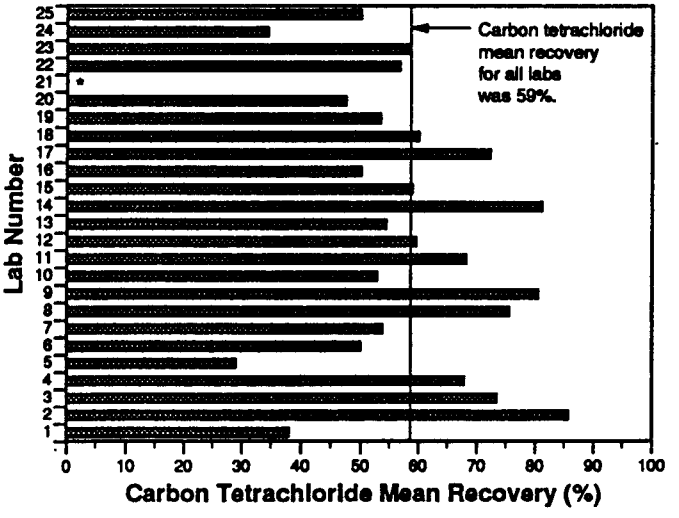
Notes

* Lab reported nondetects or below detection limits for all samples

Figure 4
Recovery Bar Charts
Ethylbenzene, Chloroform, Carbon Tetrachloride



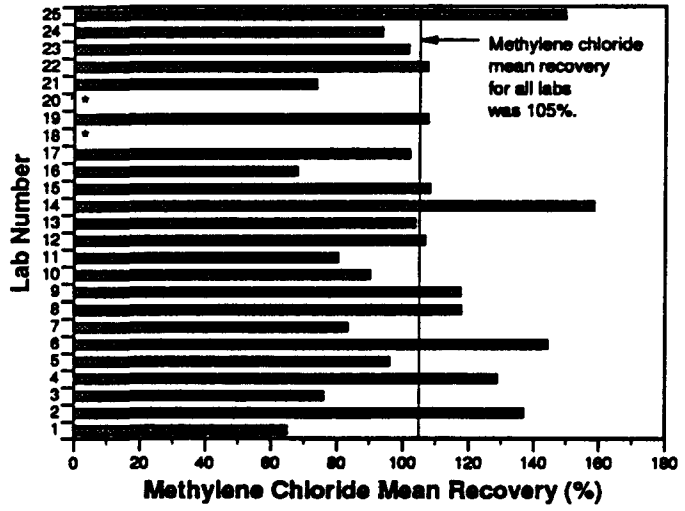


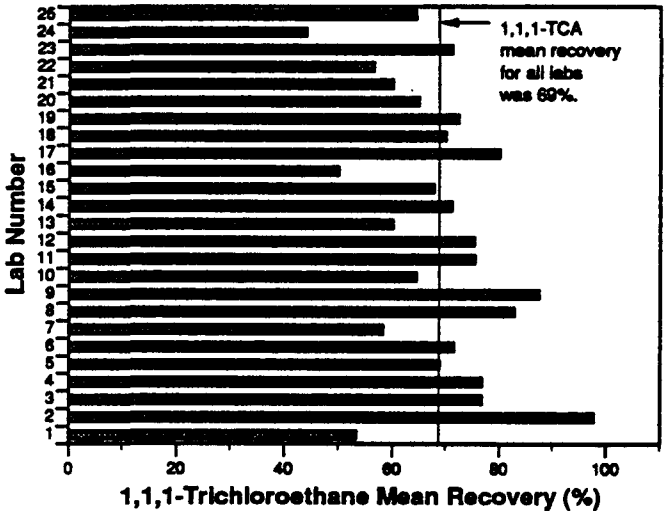


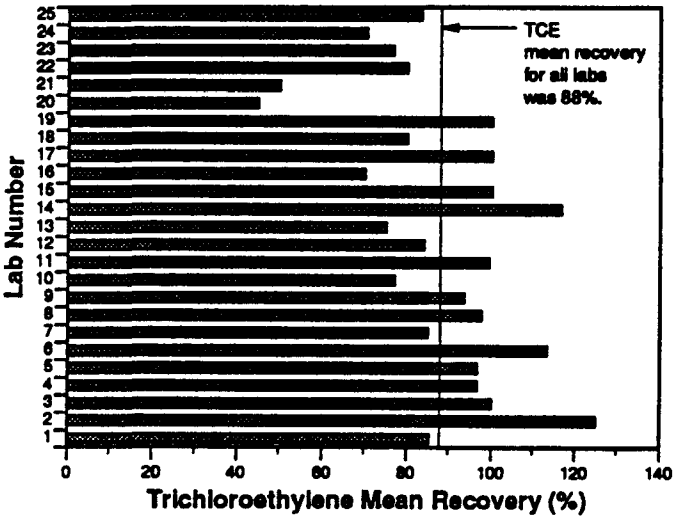
Notes

* Lab reported nondetects or below detection limits for all samples

Figure 5
Recovery Bar Charts
Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene







Notes

* Lab reported nondetects or below detection limits for all samples

Figure 6
Range in Recovery by Laboratory—Volatiles

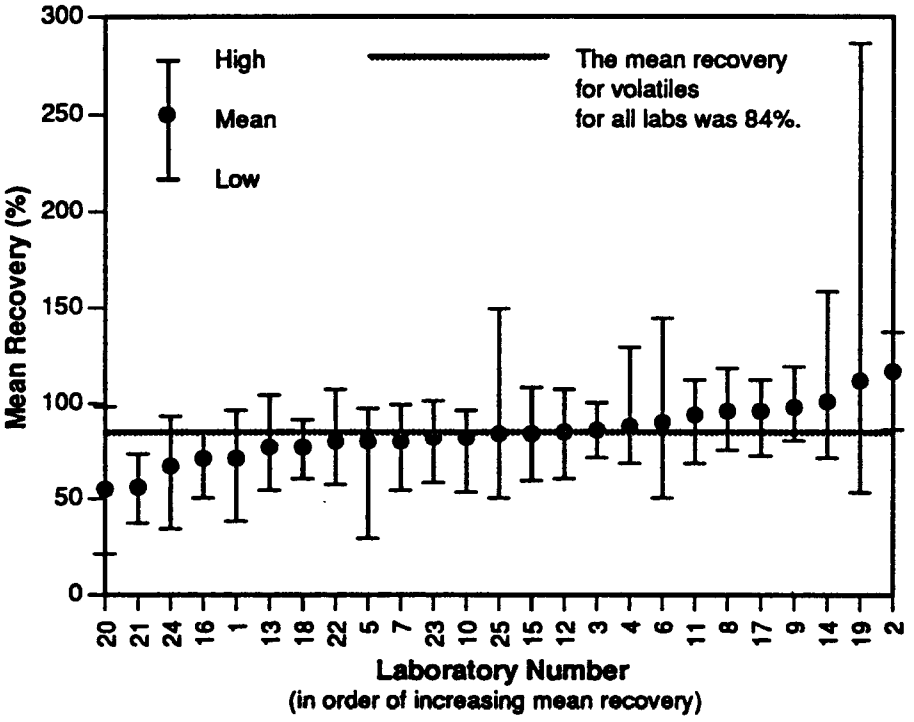


Figure 7
Range in Recovery by Analyte—Volatiles

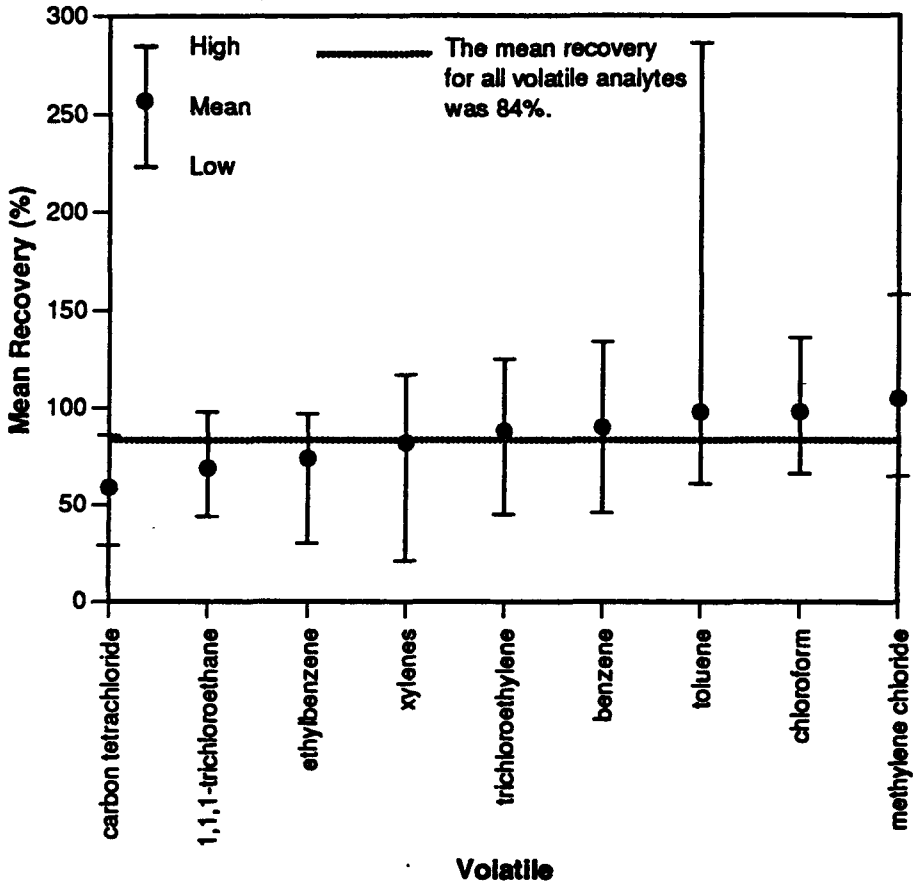


Figure 8
Youden Plots
Barium, Cadmium, Copper, Lead, Nickel, Zinc

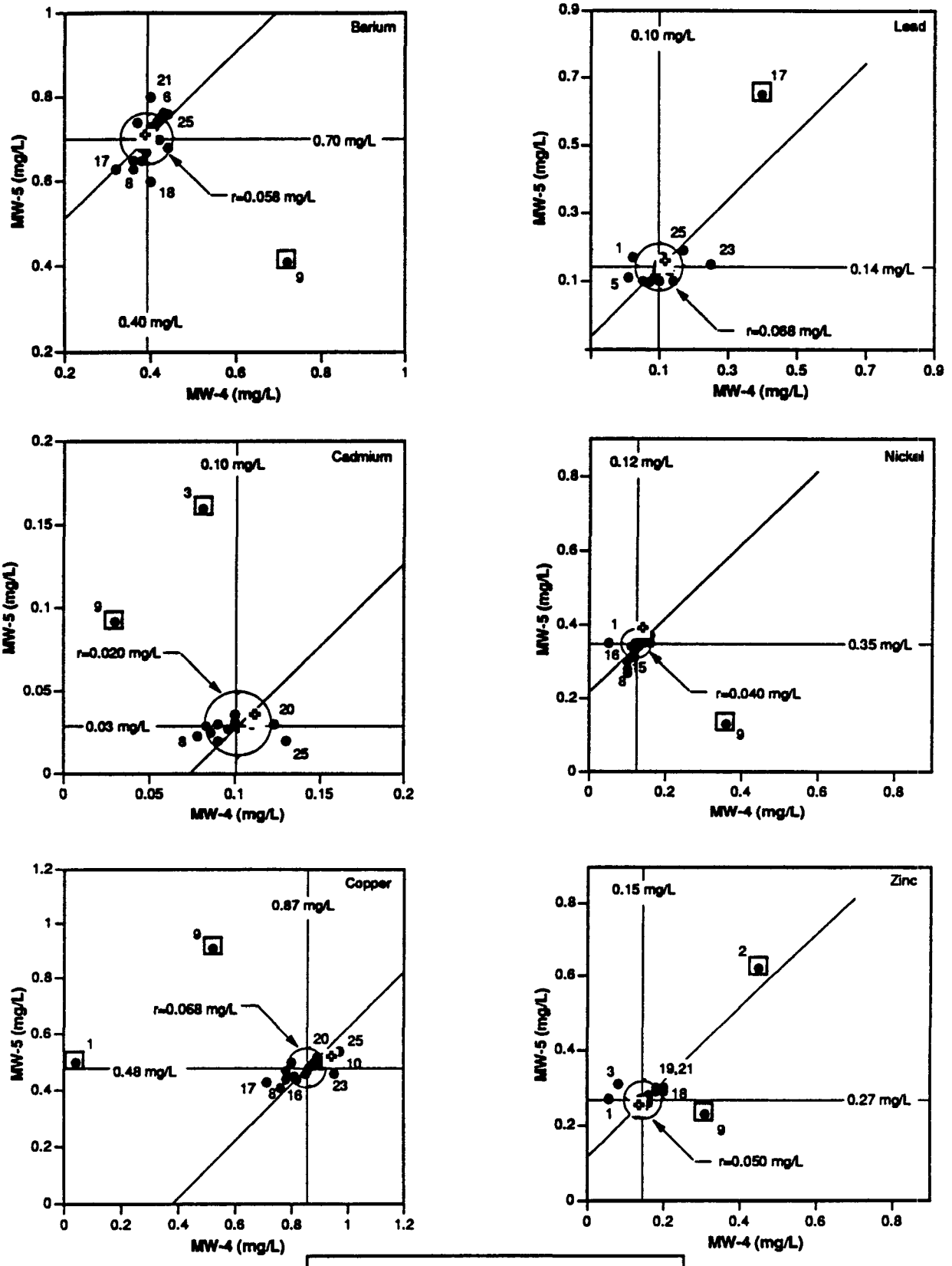
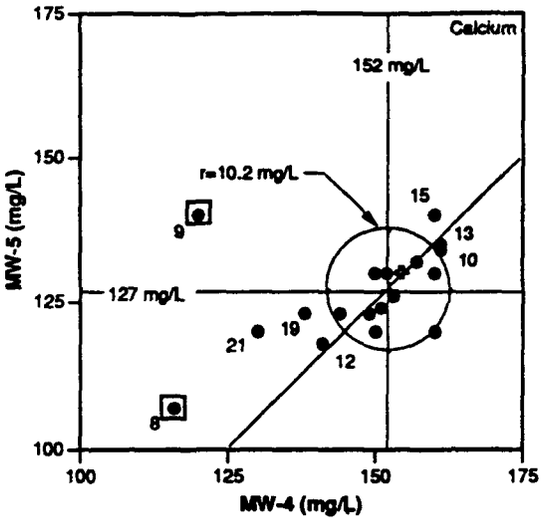
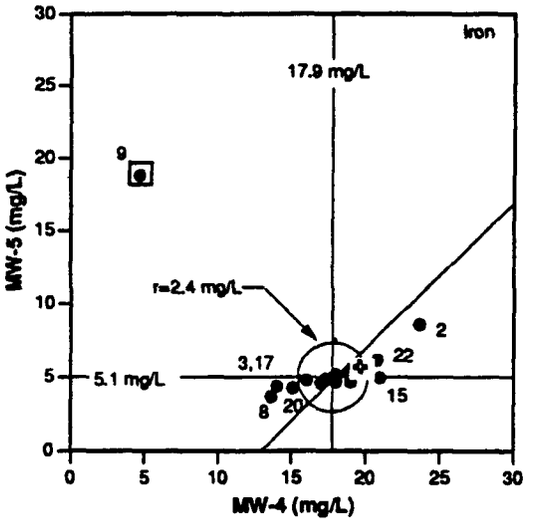
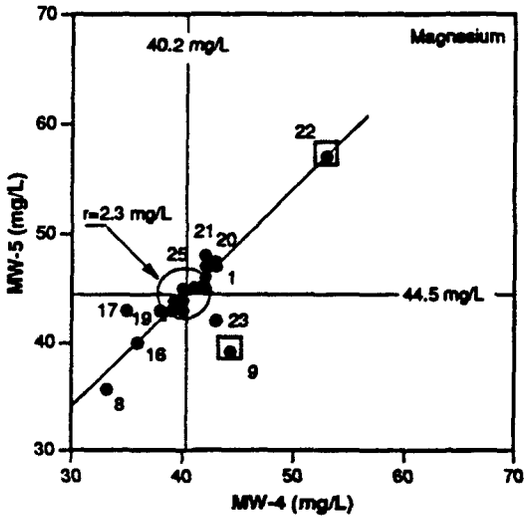
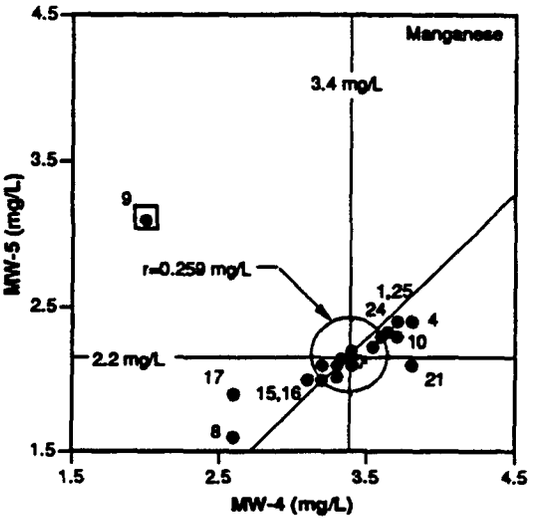


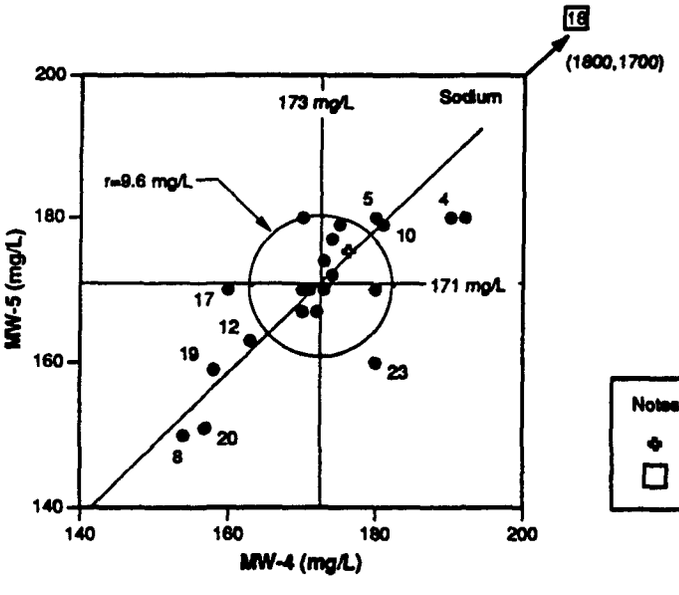
Figure 9
Youden Plots
Calcium, Magnesium, Sodium, Iron, Manganese





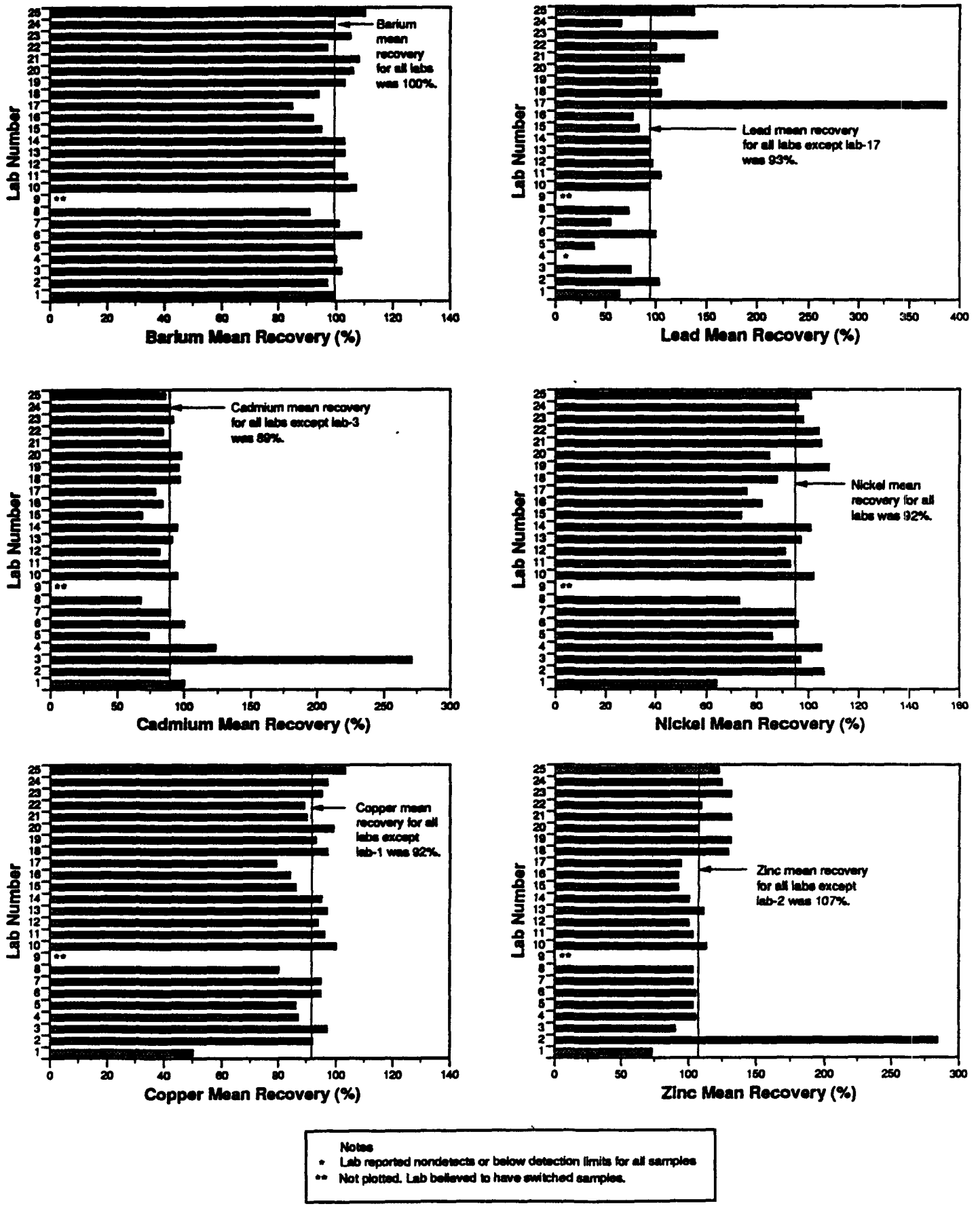






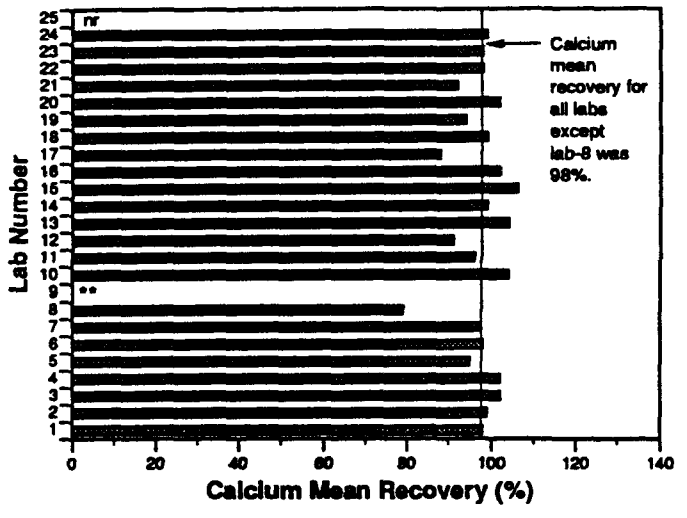
Notes
- ✥ True concentrations for sample pair
- □ Outlier deleted from calculation of circular area.

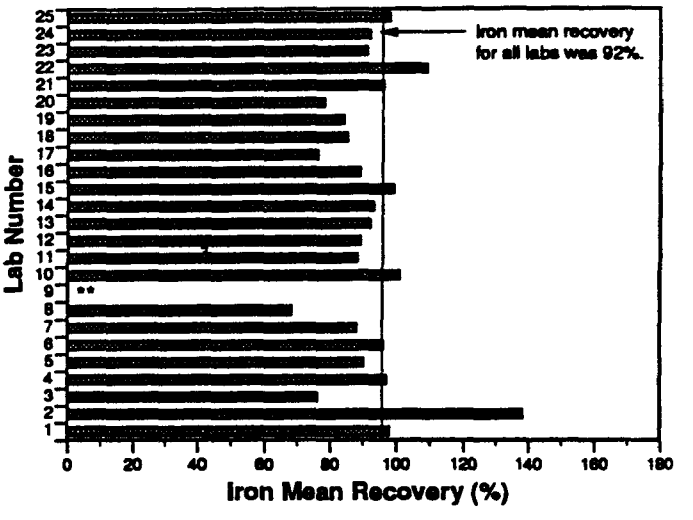
Figure 10
Recovery Bar Charts
Barium, Cadmium, Copper, Lead, Nickel, Zinc

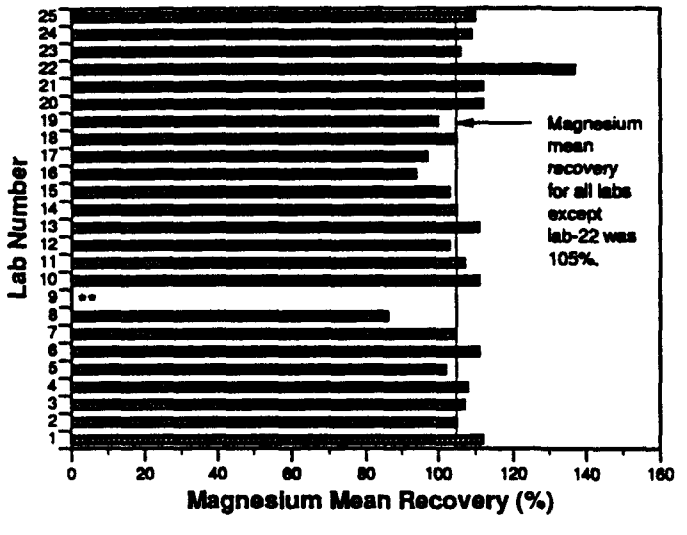


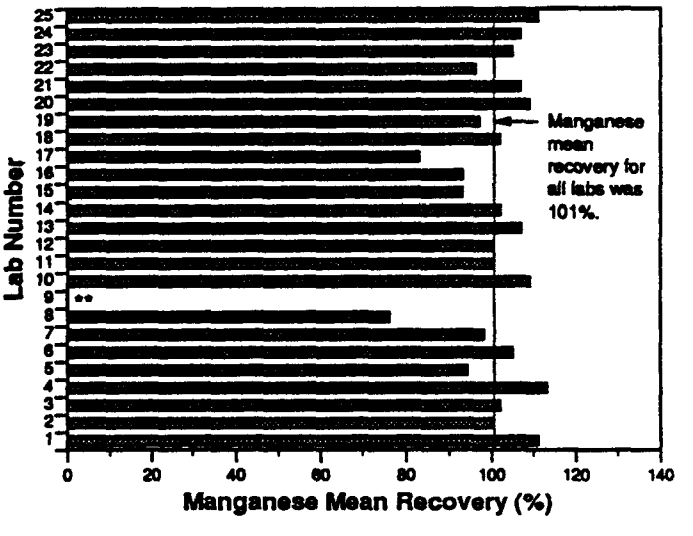
Notes
* Lab reported nondetects or below detection limits for all samples
** Not plotted. Lab believed to have switched samples.

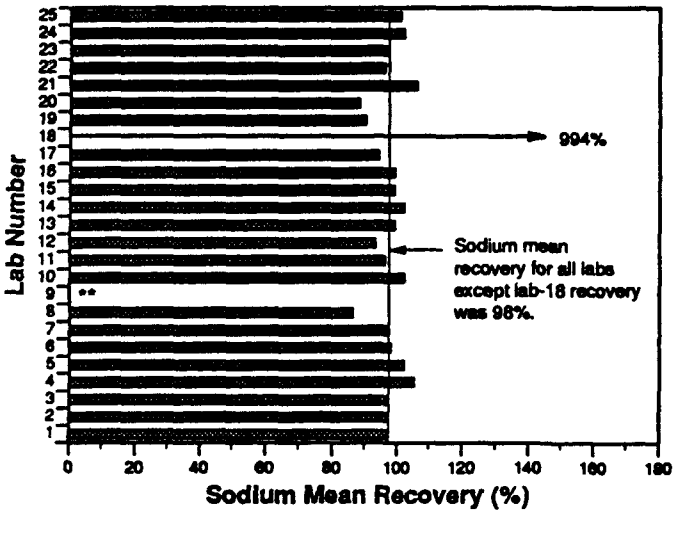
Figure 11
Recovery Bar Charts
Calcium, Magnesium, Sodium, Iron, Manganese











Notes
* Lab reported nondetects or below detection limits for all samples
** Not plotted. Lab believed to have switched samples.
nr No data reported.

Figure 12
Range in Recovery by Laboratory—Metals

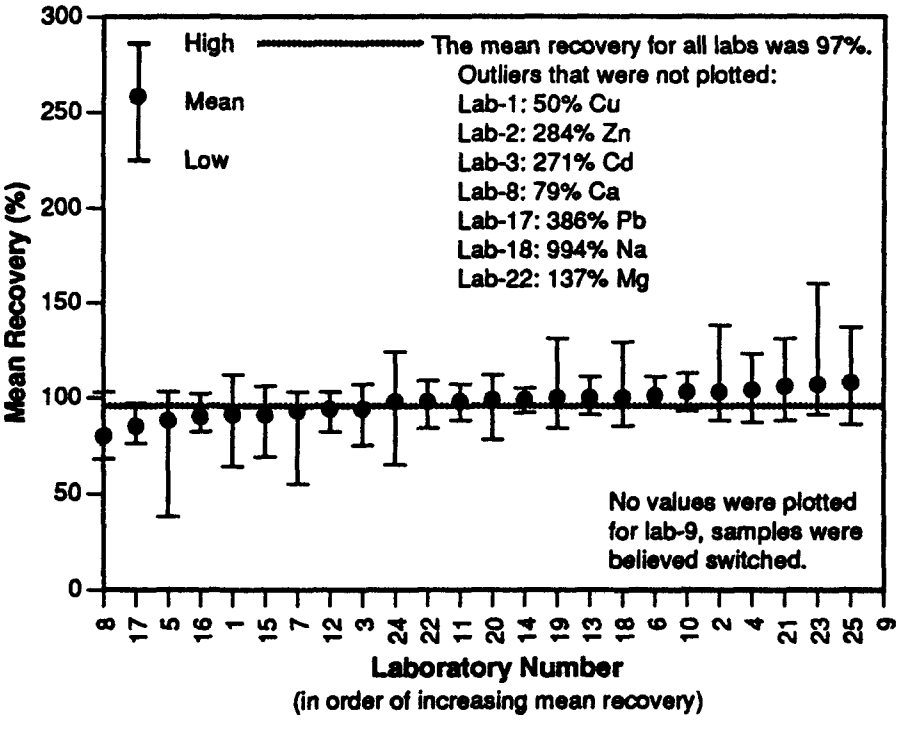


Figure 13
Range In Recovery by Analyte—Metals

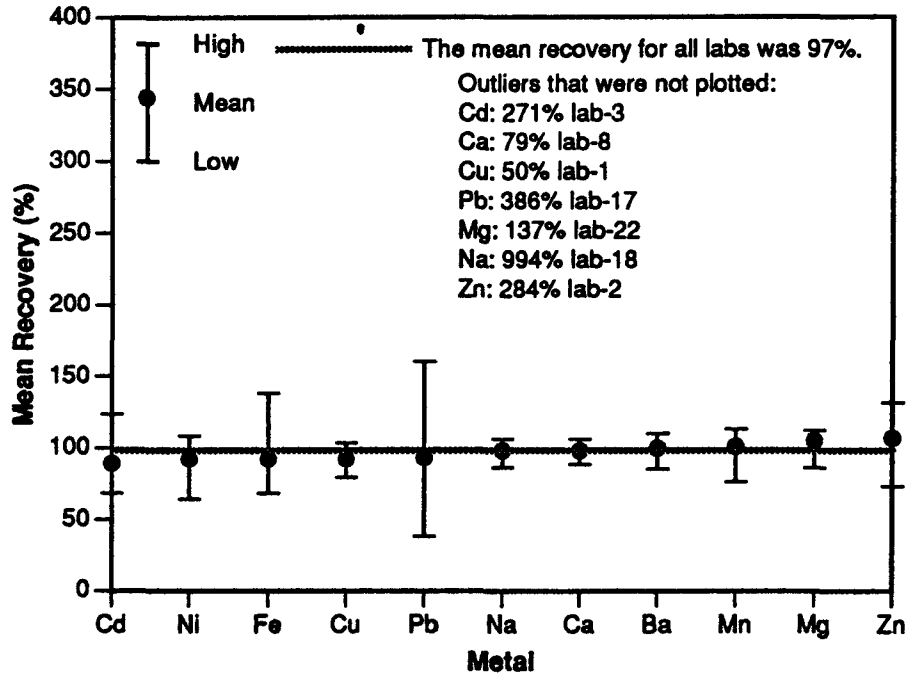
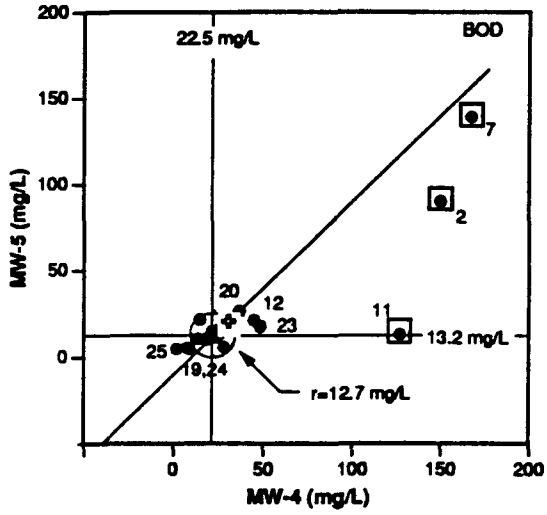
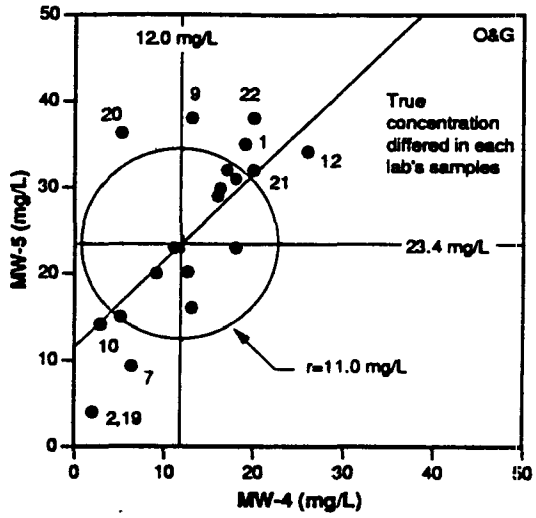
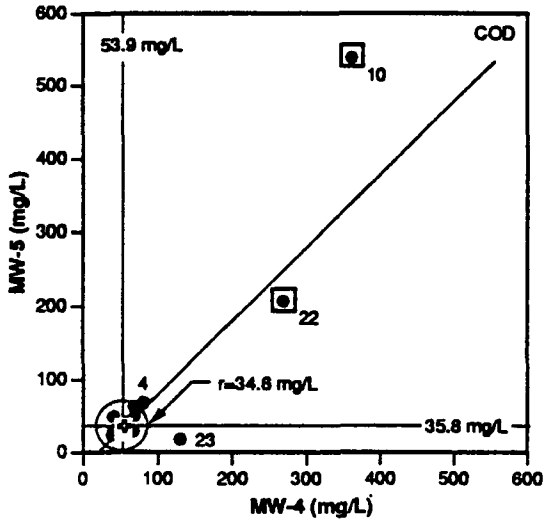
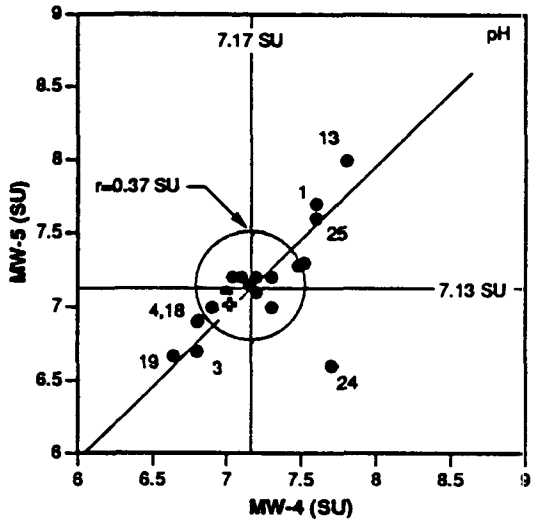


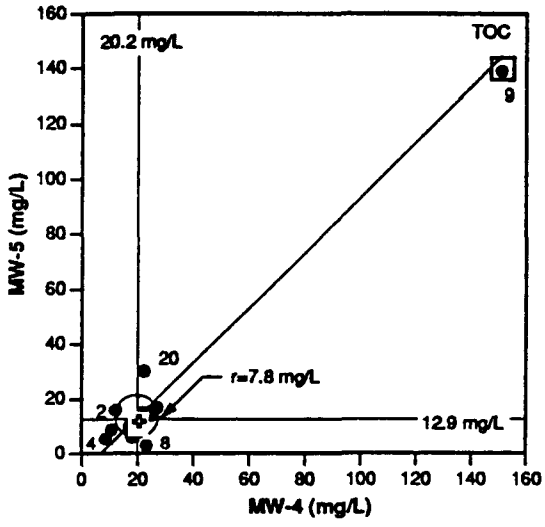
Figure 14
Youden Plots
BOD, COD, TOC, O&G, pH





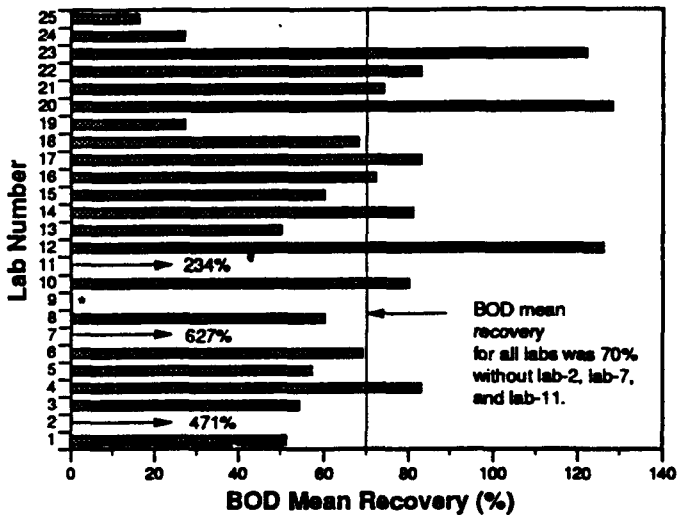


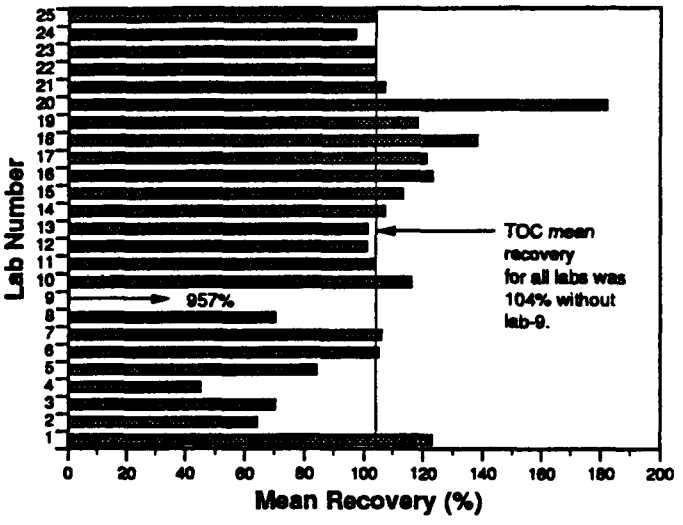


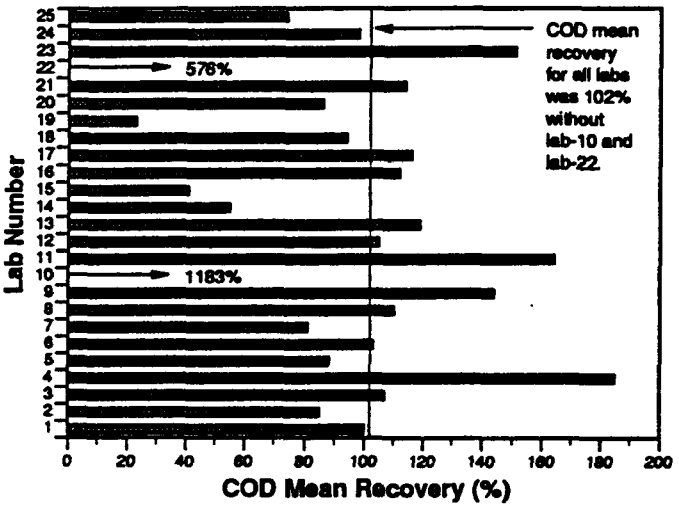


Notes
- ✥ True concentrations for sample pair
- □ Outlier deleted from calculation of circular area.

Figure 15
Recovery Bar Charts
BOD, COD, TOC



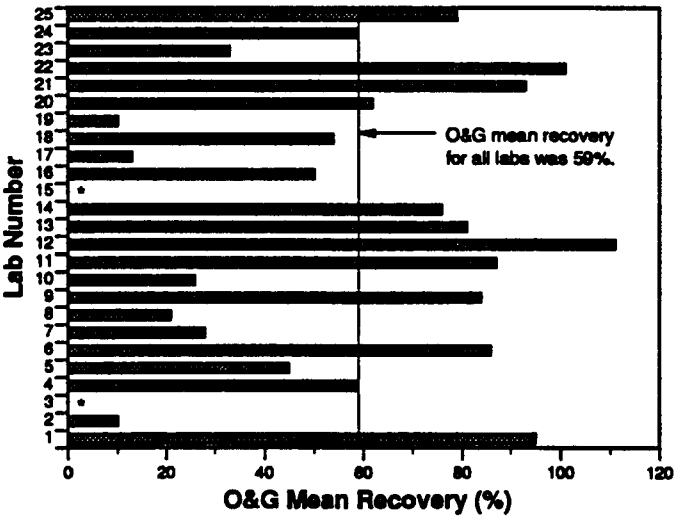


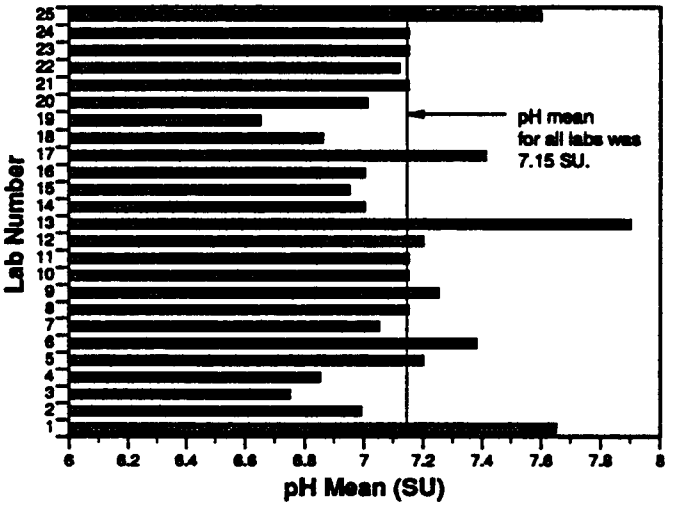


Notes

* Lab reported nondetects or below detection limits for all samples

Figure 16
Recovery Bar Charts
O&G, pH





Notes

* Lab reported nondetects or below detection limits for all samples

Figure 17
Range in Recovery by Laboratory—General Parameters

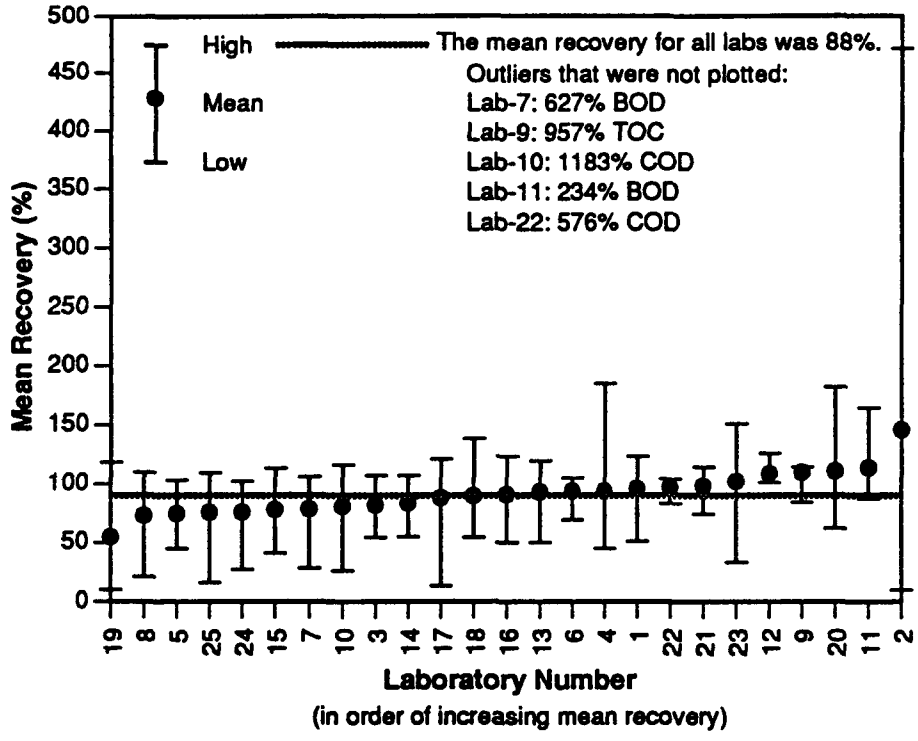


Figure 18
Range in Recovery by Analyte—General Parameters

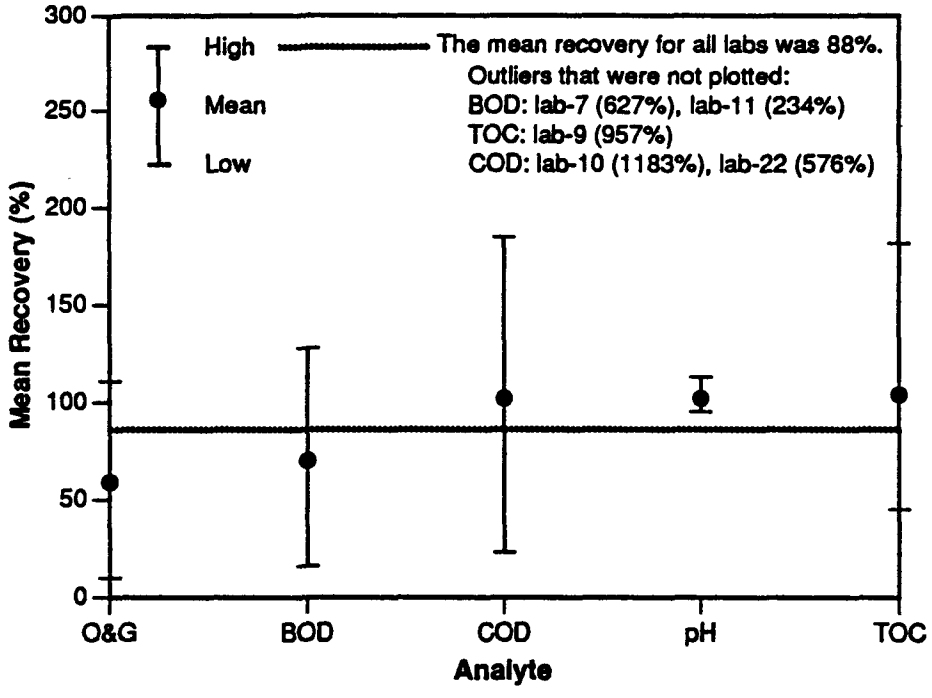


Figure 19

Effects of Recovery Correction
Volatiles

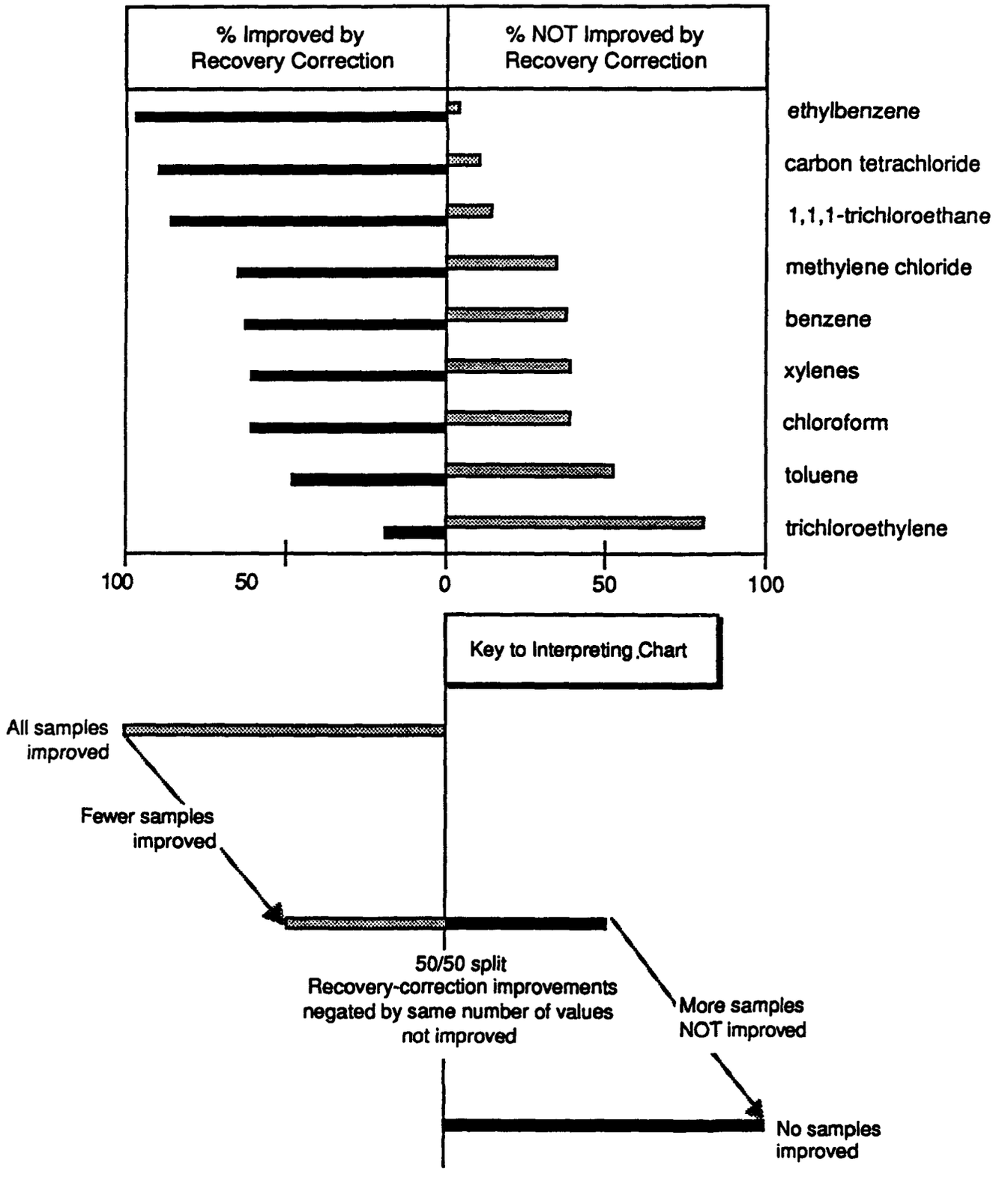


Table 1
Sample Concentrations
Target Volatiles and TICs

Analyte	Background Matrix* (µg/L)	Sample Concentration After Spiking (µg/L) MW-1	MW-2	MW-3
Target Volatiles				
benzene	18	43	68	43
carbon tetrachloride	-	10	30	10
chloroform	-	45	15	15
ethylbenzene	6	16	16	26
methylene chloride	-	33	33	59
toluene	-	15	30	15
1,1,1-trichloroethane (TCA)	-	30	10	10
trichloroethylene (TCE)	-	10	5	5
xylenes	-	20	20	40
Tentatively Identified Compounds (TICs)				
cyclohexane	-	15	45	90
diisopropyl ether (DIPE)	-	45	90	15
isooctane	-	15	45	90
methyl ethyl ketone (MEK)	-	30	90	180
methyl tert-butyl ether (MTBE)	-	45	90	15
naphthalene	-	90	45	15
tert-butyl alcohol (TBA)	-	45	270	135
tetrahydrofuran	-	15	45	90
1,1,1-trichlorobenzene (TCB)	-	90	180	30

* Groundwater contaminated with benzene and ethylbenzene was diluted with reagent water for the background sample matrix. The values for benzene and ethylbenzene were calculated from the original analysis of the groundwater and the dilution ratio. A '-' indicates that this analyte was not found in the groundwater source used to make the sample matrix.

Table 1, cont'd
Sample Concentrations
Metals

Analyte	Background Matrix* (mg/L)	Sample Concentration After Spiking (mg/L)	
		MW-4	MW-5
barium	0.384	0.384	0.72
cadmium	-	0.114	0.034
calcium	129	155	129
copper	-	0.939	0.522
iron	-	19.6	5.5
lead	-	0.111	0.158
magnesium	37.9	37.9	42.7
manganese	2.09	3.44	2.09
nickel	-	0.134	0.382
sodium	176	176	176
zinc	0.045	0.138	0.256

* Groundwater from an uncontaminated well was used as the background matrix for the spiked samples.

Table 1, cont'd

Sample Concentrations
BOD, COD, TOC, pH

Analyte	Sample Concentration after Dilution (mg/L)*	
	MW-4	MW-5
BOD	32	19
COD	53	32
TOC	20	12
pH	7	7

* Lab standard was diluted with deionized water to prepare samples

Table 1, cont'd

Sample Concentrations
Oil and Grease

Lab Number	Sample after Dilution (mg/L)*	
	MW-4	MW-5
1	20.0	37.0
2	22.2	41.8
3	20.3	39.8
4	19.8	39.7
5	19.5	39.3
6	19.7	38.7
7	18.5	34.6
8	21.8	41.9
9	20.5	41.7
10	19.0	35.0
11	18.8	36.8
12	20.0	36.6
13	20.0	37.0
14	19.3	33.8
15	20.1	36.4
16	21.1	39.4
17	21.7	42.8
18	20.7	38.8
19	19.7	37.8
20	19.8	38.8
21	19.9	38.1
22	19.8	38.0
23	20.6	38.2
24	17.1	26.5
25	20.3	37.0

* Each sample for oil and grease was made individually in each lab's containers. Variations in the amount of oil and grease added made for slightly different concentrations among the labs.

Table 2
Youden Plot Summary
Target Volatiles

Lab No.	Volatile Analytes (see list at bottom of table) 1	2	3	4	5	6	7	8	9	Performance Summary ●	Δ	∇	○	×
1	●	●	∇	∇	∇	●	∇	∇	●	4	0	5	0	0
2	Δ	○	Δ	Δ	Δ	Δ	Δ	Δ	Δ	0	8	0	1	0
3	●	●	●	●	●	●	●	∇	●	8	0	1	0	0
4	●	●	●	●	●	●	●	Δ	●	8	1	0	0	0
5	●	●	●	∇	●	●	∇	●	●	7	0	2	0	0
6	○	●	○	●	○	○	●	Δ	●	4	1	0	4	0
7	●	●	●	●	●	●	×	∇	×	6	0	1	0	2
8	×	●	●	Δ	Δ	●	Δ	Δ	×	3	4	0	0	2
9	×	●	●	Δ	Δ	Δ	Δ	Δ	●	3	5	0	0	1
10	●	●	●	●	●	●	×	●	×	7	0	0	0	2
11	Δ	●	Δ	Δ	Δ	Δ	●	∇	×	2	5	1	0	1
12	●	●	●	●	●	●	●	●	×	8	0	0	0	1
13	●	●	∇	∇	×	●	●	●	×	5	0	2	0	2
14	●	Δ	●	●	●	Δ	Δ	Δ	●	5	4	0	0	0
15	●	●	●	●	●	●	●	●	●	9	0	0	0	0
16	●	∇	●	●	∇	∇	×	∇	×	3	0	4	0	2
17	●	Δ	Δ	Δ	Δ	●	●	●	●	5	4	0	0	0
18	●	●	●	∇	●	●	●	nr	×	6	0	1	0	1
19	●	Δ	Δ	●	●	●	●	●	●	7	2	0	0	0
20	∇	∇	∇	∇	●	○	●	×	∇	2	0	5	1	1
21	∇	∇	∇	×	×	∇	×	∇	×	0	0	5	0	4
22	∇	●	●	●	●	●	×	●	×	6	0	1	0	2
23	●	●	●	●	●	●	●	●	●	9	0	0	0	0
24	∇	∇	∇	○	×	∇	×	○	×	0	0	4	2	3
25	●	●	∇	●	●	●	●	Δ	●	7	1	1	0	0

List of Analytes

1–benzene	4–xylenes	7–carbon tetrachloride
2–toluene	5–1,1,1-trichloroethane	8–methylene chloride
3–ethylbenzene	6–chloroform	9–trichloroethylene

● Within 95% circle representing values where 95% of single lab's results are expected to fall
○ Outside 95% circle showing tendency towards poor precision
Δ Outside 95% circle showing tendency toward higher than average recoveries
∇ Outside 95% circle showing tendencey toward lower than average recoveries
× Not plotted because at least one value was reported as less-than-value
nr No data reported
□ Values that were considered outliers and omitted from calculation of the circular region representing 95% of a single lab's results

Table 3
Mean Recovery—Target Volatiles

Lab No.	Mean Recovery (%) of Volatile Analytes (see list at bottom of table)									
	1	2	3	4	5	6	7	8	9	Mean
20	66	69	30	21	65	98	47	*	45	55
21	46	61	37	*	60	66	*	73	50	56
24	83	67	58	75	44	75	34	93	71	67
16	84	81	76	78	50	79	50	68	70	71
1	80	87	68	69	53	96	38	65	86	71
13	84	90	64	61	60	98	54	104	75	77
18	91	87	78	66	70	84	60	nr	80	77
22	81	89	73	88	57	89	57	107	80	80
5	94	92	76	75	69	95	29	96	97	80
7	99	98	81	76	58	90	54	83	85	80
23	84	89	79	89	71	87	58	101	77	82
10	93	91	84	94	64	96	53	90	77	82
25	84	88	70	78	64	85	50	149	83	84
15	91	86	79	78	68	87	59	108	100	84
12	89	91	82	84	75	95	60	107	84	85
3	96	98	73	71	77	107	73	76	100	86
4	87	87	71	76	77	97	68	129	97	88
6	90	93	76	80	71	94	50	144	113	90
11	112	97	86	98	75	130	68	80	100	94
8	101	94	80	102	83	111	75	118	98	96
17	97	101	89	109	80	112	72	102	100	96
9	102	97	82	102	87	119	80	118	94	98
14	99	99	78	78	71	124	81	158	117	101
19	93	286	88	100	72	106	53	107	100	112
2	134	124	97	117	98	136	86	137	125	117
Mean	90	98	74	82	69	98	59	105	88	84

List of Analytes

1–benzene	4–xylenes	7–carbon tetrachloride
2–toluene	5–1,1,1-trichloroethane	8–methylene chloride
3–ethylbenzene	6–chloroform	9–trichloroethylene

* Not calculated because lab reported "below detection limits" for all samples

nr No data reported

Table 4
Single Analyst Precision (Intralaboratory) Compared to Method 8240 Performance Criteria

Lab No.	Analytes (see list at bottom of table) 1	2	3	4	5	6	7	8	9	Number of Times Criteria Met √
1	√	√	√	-	no	√	*	√	*	5
2	no	no	no	-	√	√	no	√	*	3
3	√	√	√	-	√	√	√	√	√	8
4	√	√	√	-	√	√	√	√	√	8
5	√	no	√	-	√	√	no	√	√	6
6	no	no	no	-	√	√	no	no	√	3
7	√	√	√	-	√	√	*	√	*	6
8	*	√	√	-	√	√	√	√	*	6
9	*	√	√	-	√	√	no	√	*	5
10	√	√	√	-	no	√	*	√	*	5
11	√	√	√	-	√	√	√	√	*	7
12	√	√	√	-	√	√	√	√	*	7
13	√	no	*	-	*	√	*	√	*	3
14	√	√	√	-	√	√	√	√	√	8
15	√	√	√	-	√	√	√	√	√	8
16	√	√	√	-	*	√	*	√	*	5
17	√	√	√	-	√	√	√	√	√	8
18	√	√	√	-	√	√	√	*	*	6
19	√	no	√	-	√	√	*	√	√	6
20	√	no	√	-	√	√	√	*	√	6
21	√	√	*	-	*	*	*	no	*	2
22	√	no	√	-	*	√	*	√	*	4
23	√	√	√	-	√	√	*	√	√	7
24	√	no	√	-	*	√	*	√	*	4
25	√	√	√	-	no	√	√	√	√	7

List of Analytes

1–benzene	4–xylenes	7–carbon tetrachloride
2–toluene	5–1,1,1-trichloroethane	8–methylene chloride
3–ethylbenzene	6–chloroform	9–trichloroethylene

√ Met EPA performance for single analyst precision

no Did not meet EPA performance for single analyst precision

* Could not be determined because lab reported less-than-values for at least one sample

\- No EPA method performance equations for single analyst precision

Table 5
Expected Recovery Range for Volatiles Compared to Method 8240 Performance Criteria

Lab No.	Analytes (see list at bottom of table) 1	2	3	4	5	6	7	8	9	Number of Times Criteria Met √
1	√	√	√	-	no	√	no	√	no	5
2	√	no	√	-	√	no	no	√	√	5
3	√	√	√	-	√	√	no	√	√	7
4	√	√	√	-	√	√	no	√	√	7
5	√	√	√	-	√	√	no	√	√	7
6	√	√	√	-	no	√	no	no	no	4
7	√	√	√	-	no	√	no	√	√	6
8	√	√	√	-	√	√	no	√	√	7
9	√	√	√	-	√	√	√	√	√	8
10	√	√	√	-	no	√	no	√	no	5
11	√	√	√	-	√	no	no	√	√	6
12	√	√	√	-	√	√	no	√	no	6
13	√	√	√	-	no	√	no	√	no	5
14	√	√	√	-	√	√	√	√	√	8
15	√	√	√	-	no	√	no	√	√	6
16	√	√	√	-	no	√	no	√	no	5
17	√	√	√	-	√	√	no	√	√	7
18	√	√	√	-	√	√	no	*	no	5
19	√	no	√	-	√	√	no	√	√	6
20	√	√	no	-	√	√	no	*	no	4
21	no	no	no	-	*	√	*	√	no	2
22	√	√	√	-	no	√	no	√	no	5
23	√	√	√	-	√	√	no	√	no	6
24	√	no	√	-	no	√	no	√	no	4
25	√	√	√	-	no	√	no	√	√	6

List of Analytes

1–benzene	4–xylenes	7–carbon tetrachloride
2–toluene	5–1,1,1-trichloroethane	8–methylene chloride
3–ethylbenzene	6–chloroform	9–trichloroethylene

√ Met EPA performance for recovery range

no Did not meet EPA performance for recovery range

* *Could not be determined because lab reported less-than-values for at least one sample*

\- No EPA method performance equations for recovery range

Table 6
Youden Plot Summary—Metals

Lab No.	Metal											Performance Summary				
	Ba	Cd	Cu	Pb	Ni	Zn	Ca	Mg	Na	Fe	Mn	●	Δ	∇	○	×
1	●	×	○	○	○	○	●	Δ	●	●	Δ	4	2	0	4	1
2	●	●	●	●	●	Δ	●	●	●	Δ	●	9	2	0	0	0
3	●	○	●	●	●	○	●	●	●	∇	●	8	0	1	2	0
4	●	×	●	×	×	●	●	●	Δ	●	Δ	6	2	0	0	3
5	●	●	●	∇	●	●	●	●	Δ	●	●	9	1	1	0	0
6	Δ	●	●	●	●	●	●	●	●	●	●	10	1	0	0	0
7	●	●	●	●	●	●	●	●	●	●	●	11	0	0	0	0
8	∇	∇	∇	●	∇	●	∇	∇	∇	∇	∇	2	0	9	0	0
9	Not used. All sample pairs appeared to be switched in lab reports.															
10	●	●	Δ	●	●	●	Δ	●	Δ	●	Δ	7	4	0	0	0
11	●	●	●	●	●	●	●	●	●	●	●	11	0	0	0	0
12	●	●	●	●	●	●	∇	●	∇	●	●	9	0	2	0	0
13	●	●	●	●	●	●	Δ	●	●	●	●	10	1	0	0	0
14	●	●	●	●	●	●	●	●	●	●	●	11	0	0	0	0
15	●	●	●	●	∇	●	Δ	●	●	○	∇	7	1	2	1	0
16	●	●	∇	●	∇	●	●	∇	●	●	∇	7	0	4	0	0
17	∇	●	∇	Δ	●	●	●	∇	∇	∇	∇	4	1	6	0	0
18	○	●	●	●	●	Δ	●	●	Δ	●	●	8	2	0	1	0
19	●	×	●	×	●	Δ	∇	∇	∇	●	●	5	1	3	0	2
20	●	Δ	Δ	●	●	●	●	Δ	∇	∇	●	6	3	2	0	0
21	Δ	×	●	×	×	Δ	∇	Δ	Δ	●	○	2	4	1	1	3
22	●	●	●	●	●	●	●	Δ	●	Δ	●	9	2	0	0	0
23	●	●	○	Δ	●	●	●	○	○	●	●	7	1	0	3	0
24	●	●	●	●	●	●	●	●	●	●	Δ	10	1	0	0	0
25	Δ	○	Δ	Δ	●	●	nr	Δ	●	●	Δ	4	5	0	1	0

● Within 95% circle representing values where 95% of single lab's results are expected to fall
○ Outside 95% circle showing tendency towards poor precision
Δ Outside 95% circle showing tendency toward higher than average recoveries
∇ Outside 95% circle showing tendencey toward lower than average recoveries
× Not plotted because at least one value was reported as less-than-value
nr No data reported
□ Values that were considered outliers and omitted from calculation of the circular region representing 95% of a single lab's results

Table 7
Mean Recovery—Metals

Lab No.	Mean Recovery (%) of Metals											All Metals
	Ba	Cd	Ca	Cu	Fe	Pb	Mg	Mn	Ni	Na	Zn	
8	91	68	[79]	80	68	73	86	76	73	86	103	80
17	85	79	88	79	76	[386]	97	83	76	94	94	85
5	99	74	95	86	90	38	102	94	86	102	103	88
16	92	84	102	84	89	77	94	93	82	99	92	90
15	95	69	106	86	99	83	103	93	74	99	92	91
1	99	100	98	[50]	98	64	112	111	64	97	73	91
7	101	89	97	95	88	55	104	98	94	97	103	93
12	99	82	91	94	89	97	103	100	91	93	100	94
3	102	[271]	102	97	76	75	107	102	97	97	90	94
11	104	88	96	96	88	105	107	100	93	96	103	98
24	99	88	99	97	92	65	109	107	96	102	124	98
22	97	84	98	89	109	100	[137]	96	104	96	109	98
20	106	98	102	99	78	103	112	109	85	88	106	99
14	103	95	99	95	93	92	105	102	101	102	100	99
19	103	96	94	93	84	101	100	97	108	90	131	100
18	94	97	99	97	85	105	105	102	88	[994]	129	100
13	103	91	104	97	92	93	111	107	97	99	111	100
6	109	100	98	95	96	100	111	105	96	98	105	101
2	97	88	99	92	138	103	105	100	106	97	[284]	103
10	107	95	104	100	101	93	111	109	102	102	113	103
4	100	123	102	87	97	*	108	113	105	105	105	104
21	108	88	92	90	96	127	112	107	105	106	131	106
23	105	92	98	95	91	160	106	105	98	97	131	107
25	110	86	nr	103	98	137	110	111	101	101	122	108
9	Not used. All sample pairs appeared to be switched in lab reports.											
	100	89	98	92	92	93	105	101	92	98	107	97

* Not calculated because lab reported "below detection limits" for all samples

nr Lab did not report any analyses for this analyte

[ ] Boxed-in values are not included in calculations of overall means.

Table 8
Expected Recovery Range for Metals Compared to Method 200.7 Performance Criteria

Lab No.	Metals											Number of Times Criteria Met √
	Ba	Cd	Ca	Cu	Fe	Pb	Mg	Mn	Ni	Na	Zn	
1	no	*	√	no	√	√	√	no	√	√	√	7
2	no	√	√	√	no	√	√	√	√	√	no	8
3	no	no	√	√	no	no	√	√	√	√	no	6
4	no	no	√	no	√	*	√	no	√	√	√	6
5	no	no	√	√	√	no	√	√	√	√	√	8
6	no	√	√	√	√	√	√	no	√	√	√	9
7	no	√	√	√	√	no	√	√	√	√	√	9
8	√	no	√	no	no	no	no	no	no	√	√	4
9	Not used. All sample pairs appeared to have been switched in lab reports.											
10	no	√	√	√	no	√	√	no	√	√	√	8
11	no	√	√	√	√	√	√	√	√	√	√	10
12	no	√	√	√	√	√	√	√	√	√	√	10
13	no	√	√	√	√	√	√	no	√	√	√	9
14	no	√	√	√	√	√	√	√	√	√	√	10
15	√	no	√	√	no	√	√	√	no	√	√	8
16	√	no	√	no	√	no	√	√	no	√	√	7
17	√	no	√	no	no	no	√	no	no	√	√	5
18	√	√	√	√	√	√	√	√	√	no	√	10
19	no	√	√	√	√	√	√	√	√	√	no	9
20	no	√	√	√	√	√	no	no	√	√	√	8
21	no	√	√	√	√	no	no	no	√	√	no	6
22	no	no	√	√	no	√	no	√	√	√	√	7
23	no	√	√	√	√	√	√	no	√	√	no	8
24	no	√	√	√	√	no	√	no	√	√	no	7
25	no	no	-	no	√	no	√	no	√	√	√	5

√ Met EPA performance for recovery range
no Did not meet EPA performance for recovery range
* Could not be determined because lab reported less-than-values for at least one sample
- No data reported for analyte

Table 9
Youden Plot Summary—General Parameters

Lab No.	General Parameters					Performance Summary				
	BOD	COD	TOC	O&G	pH	●	Δ	∇	○	×
1	●	●	●	Δ	Δ	3	2	0	0	0
2	□Δ	●	∇	∇	●	2	1	2	0	0
3	●	●	●	×	∇	3	0	1	0	1
4	●	Δ	∇	●	∇	2	1	2	0	0
5	●	●	●	×	●	4	0	0	0	1
6	●	●	●	●	●	5	0	0	0	0
7	□Δ	●	●	∇	●	3	1	1	0	0
8	●	●	○	×	●	3	0	0	1	1
9	×	●	□Δ	Δ	●	2	2	0	0	1
10	●	□Δ	●	∇	●	3	1	1	0	0
11	□Δ	●	●	●	●	4	1	0	0	0
12	Δ	●	●	Δ	●	3	2	0	0	0
13	●	●	●	●	Δ	4	1	0	0	0
14	×	×	●	●	●	3	0	0	0	2
15	●	×	●	×	●	3	0	0	0	2
16	●	●	●	●	●	5	0	0	0	0
17	●	●	●	×	●	4	0	0	0	1
18	●	●	●	●	∇	4	0	1	0	0
19	∇	×	●	∇	∇	1	0	3	0	1
20	Δ	●	Δ	○	●	2	2	0	1	0
21	●	●	●	Δ	●	4	1	0	0	0
22	●	□Δ	●	Δ	●	3	2	0	0	0
23	Δ	○	●	●	●	3	1	0	1	0
24	∇	●	●	●	○	3	0	1	1	0
25	∇	●	●	●	Δ	3	1	1	0	0

● Within 95% circle representing values where 95% of single lab's results are expected to fall
○ Outside 95% circle showing tendency towards poor precision
Δ Outside 95% circle showing tendency toward higher than average recoveries
∇ Outside 95% circle showing tendencey toward lower than average recoveries
× Not plotted because at least one value was reported as less-than-value
□ Values that were considered outliers and omitted from calculation of the circular region representing 95% of a single lab's results

Table 10
Mean Recovery—General Parameters

Lab No.	General Parameters					All General Parameters
	O&G	BOD	pH	COD	TOC	
19	10	27	95	23	118	55
2	9	[471]	100	85	64	64
8	18	60	102	110	70	72
5	46	57	103	88	84	76
25	79	16	109	74	103	76
15	*	60	99	41	113	78
7	31	[627]	101	81	106	80
24	75	27	102	98	97	80
10	28	80	102	[1183]	116	82
3	*	54	96	107	70	82
14	81	81	100	55	107	85
17	12	83	106	116	121	87
18	52	68	98	94	138	90
16	47	72	100	112	123	91
13	81	50	113	119	101	93
6	84	69	105	103	105	93
4	57	83	98	185	45	93
1	95	51	109	100	123	96
22	101	83	102	[576]	104	97
21	92	74	102	114	107	98
23	32	122	102	151	103	102
9	77	*	104	144	[957]	108
12	112	126	103	105	101	109
20	60	128	100	86	182	111
11	90	[234]	102	164	104	115
	59	70	102	102	104	88

* Not calculated because lab reported "below detection limits" for all samples

[ ] Boxed-in values are not included in calculations of overall means.

Table 11
Recovery Comparison
General Parameters

Lab No.	Analyte: BOD	COD	TOC	O&G	pH	Number of Times Criteria Met √
1	no	√	√	√	√	4
2	no	√	no	no	√	2
3	no	√	√	*	√	3
4	√	no	no	no	√	2
5	no	√	√	*	√	3
6	√	√	√	√	√	5
7	no	√	√	no	√	3
8	√	√	√	no	√	4
9	*	√	no	√	√	3
10	no	no	√	no	√	2
11	no	√	√	√	√	4
12	√	√	√	√	√	5
13	no	√	√	√	√	4
14	√	no	√	√	√	4
15	√	*	√	*	√	3
16	√	√	√	no	√	4
17	√	√	√	*	√	4
18	√	√	√	no	√	4
19	no	no	√	no	√	2
20	√	√	√	√	√	5
21	√	√	√	√	√	5
22	√	no	√	√	√	4
23	no	no	√	no	√	2
24	no	√	√	√	√	4
25	no	√	√	√	√	4

√ Within ±40% of true concentration
no NOT within ±40% of true concentration
* Could not be determined because lab reported less-than-values for sample

Table 12
Lab Performance Summary

Lab No.	Volatiles		Metals		General	
	A	P	A	P	A	P
1	⊙	⊙	⊙	○	⊗	●
2	⊙	○	⊗	●	○	●
3	⊗	●	⊙	⊙	⊙	●
4	⊗	●	⊙	●	○	●
5	⊗	⊗	⊗	●	⊙	●
6	⊙	○	⊗	●	●	●
7	⊗	⊗	⊗	●	⊙	●
8	⊗	⊗	○	●	⊗	⊗
9	●	⊙	data not used		⊙	●
10	⊙	⊙	⊗	●	○	●
11	⊗	⊗	●	●	⊗	●
12	⊗	⊗	●	●	●	●
13	⊙	○	⊗	●	⊗	●
14	●	●	●	●	⊗	●
15	⊗	●	⊗	⊗	⊙	●
16	⊙	⊙	⊙	●	⊗	●
17	⊗	●	⊙	●	⊗	●
18	⊙	⊗	●	⊗	⊗	●
19	⊗	⊗	⊗	●	○	●
20	⊙	⊗	⊗	●	●	⊗
21	○	○	⊙	⊗	●	●
22	⊙	⊙	⊙	●	⊗	●
23	⊗	⊗	⊗	⊙	○	⊗
24	⊙	⊙	⊙	●	⊗	⊗
25	⊗	⊗	⊙	⊗	⊗	●

● Excellent
⊗ Good
⊙ Fair
○ Poor

A — Accuracy
P — Precision

Table 13
Summary of Percent Reportable Values
TIC's

Analyte	Percent Reportable Values Overall*
Cyclohexane	15
MTBE	21
DIPE	59
Napthalene	16
TBA	0
Isooctane	4
MEK	84
TCB	24
THF	12

* Over the entire set of samples (75, 3 samples analyzed by 25 labs)

Table 14
Percent Reportable Values by Concentration
TIC's

Analyte	Spiked Concentration (µg/L)	Percent Reportable Values
Cyclohexane	15	8
	45	20
	90	16
MTBE	15	16
	45	24
	90	24
DIPE	15	56
	45	56
	90	64
Napthalene	15	12
	45	20
	90	16
TBA	45	0
	135	0
	270	0
Isooctance	15	0
	45	0
	90	12
MEK	30	72
	90	84
	180	96
TCB	30	32
	90	16
	180	24
THF	15	4
	45	16
	90	16

Table 15
Number of Reportable Values
TIC's

Lab No.	Number of Reportable Values (see key and analyte list at bottom of table) 1	2	3	4	5	6	7	8	9	Total Reportable Values	Number of Analytes Found
1	0	0	1	0	0	1	0	0	1	3	3
2	0	0	3	3	0	0	2	3	0	11	4
3	0	0	0	2	0	1	3	3	0	9	4
4	0	0	2	0	0	0	3	0	0	5	2
5	0	0	0	0	0	0	3	0	0	3	1
6	3	0	3	0	0	0	3	0	0	9	3
7	1	0	3	0	0	0	2	1	0	7	4
8	0	0	0	0	0	0	3	2	0	5	2
9	0	0	0	0	0	0	3	0	0	3	1
10	0	0	3	3	0	0	3	3	0	12	4
11	0	0	3	0	0	0	3	0	0	6	2
12	0	0	1	0	0	0	3	0	0	4	2
13	0	2	3	0	0	1	3	3	0	12	5
14	0	3	3	0	0	0	3	0	0	9	3
15	2	0	3	0	0	0	3	0	2	10	4
16	1	3	2	2	0	0	1	0	0	9	5
17	0	1	3	0	0	0	3	1	2	10	5
18	0	0	0	0	0	0	3	0	0	3	1
19	1	2	3	0	0	0	3	0	2	11	5
20	0	0	0	0	0	0	3	0	0	3	1
21	0	0	0	0	0	0	1	0	0	1	1
22	1	2	3	0	0	0	3	0	2	11	4
23	0	0	0	0	0	0	2	0	0	2	1
24	0	0	2	2	0	0	1	0	0	5	3
25	2	3	3	0	0	0	3	2	0	13	5
Total Reportable Values	11	16	44	12	0	3	63	18	9		
Labs with Reportable Values	7	7	17	5	0	3	24	8	5		

List of Analytes

1–cyclohexane	4–Napthalene	7–MEK
2–MTBE	5–TBA	8–TCB
3–DIPE	6–Isooctane	9–THF

3 Found analyte at all three spiked concentrations
2 Found analyte at two of three spiked concentrations
1 Found analyte at one of three spiked concentrations
0 Did not find the analyte at of the three spiked concentrations

Table 16
Mean Recovery by Lab—TIC's

Lab No.	TIC Mean Recovery (%) (see list at bottom of table) 1	2	3	4	5	6	7	8	9	Mean
3	*	*	*	22	*	11	73	59	*	41
9	*	*	*	*	*	*	60	*	*	60
5	*	*	*	*	*	*	63	*	*	63
18	*	*	*	*	*	*	78	*	*	78
25	37	86	105	*	*	*	80	97	*	81
24	*	*	121	43	*	*	82	*	*	82
6	18	*	127	*	*	*	104	*	*	83
20	*	*	*	*	*	*	89	*	*	89
23	*	*	*	*	*	*	90	*	*	90
1	*	*	260	*	*	20	*	*	12	97
21	*	*	*	*	*	*	101	*	*	101
22	73	102	204	*	*	*	113	*	23	103
4	*	*	133	*	*	*	84	*	*	109
19	227	22	179	*	*	*	109	*	34	114
13	*	69	265	*	*	20	116	109	*	116
10	*	*	191	87	*	*	84	119	*	120
16	41	77	227	161	*	*	100	*	*	121
14	*	120	168	*	*	*	80	*	*	123
17	*	160	221	*	*	*	48	240	19	137
15	83	*	411	*	*	*	113	*	27	158
12	*	*	156	*	*	*	193	*	*	174
11	*	*	279	*	*	*	80	*	*	179
2	*	*	830	89	*	*	77	146	*	286
8	*	*	*	*	*	*	57	528	*	293
7	87	*	213	*	*	*	142	933	*	344
Minimum	18	22	105	22	*	11	48	59	12	
Maximum	227	160	830	161	*	20	193	933	34	

List of Analytes

1–cyclohexane	4–Napthalene	7–MEK
2–MTBE	5–TBA	8–TCB
3–DIPE	6–Isooctane	9–THF

* Did not find the analyte in any of the three spiked samples

Table 17
Overall Recovery by Lab
TIC's

Lab No.	Recovery Performance Number of Samples			
	NC	±40%	>±40% to ±70%	>±70%
1	24	0	0	3
2	16	6	2	3
3	18	4	2	3
4	22	4	1	0
5	24	2	1	0
6	18	4	2	3
7	20	2	2	3
8	22	2	2	1
9	24	2	1	0
10	15	9	1	2
11	21	3	0	3
12	23	0	1	3
13	15	8	0	4
14	18	7	1	1
15	17	5	1	4
16	18	5	2	2
17	17	0	5	5
18	24	3	0	0
19	16	6	1	4
20	24	1	2	0
21	26	1	0	0
22	16	6	0	5
23	25	2	0	0
24	22	3	2	0
25	14	9	4	0
Total Samples	499	94	33	49
Percent Samples	74%	14%	5%	7%

NC	Not calculated because lab reported no data or less-than-values
±40%	Within ±40% of spiked concentration
>±40% to ±70%	Between ±40% and ±70% of spiked concentration
>±70%	More than ±70% difference from spiked concentration

Table 18
Effects of Recovery Correction
Volatiles

Analyte	% Improved	% Not Improved	Total Number of Analyses
benzene	62	38	48
carbon tetrachloride	89	11	36
chloroform	61	39	49
ethylbenzene	96	4	48
methylene chloride	65	35	46
toluene	48	52	50
1,1,1-trichloroethane	86	14	42
trichloroethylene	19	81	27
xylenes	61	39	46
Average	65	35	

Table 19
Net Improvement by Recovery-Correction

Analyte	% Net Improved*
benzene	24
carbon tetrachloride	78
chloroform	22
ethylbenzene	92
methylene chloride	30
toluene	-4
1,1,1-trichloroethane	72
trichloroethylene	-62
xylenes	22
Average	30

* Net improved is the difference between percentage improved by recovery-correction minus the percentage not improved.

Table 20
Recovery-Correction Test of Means

Analyte	Mean (Interlaboratory) No Recovery-Correction	Mean (Interlaboratory) With Recovery-Correction	Standard Deviation for Test of Means	Calculated "t"
benzene	39.5	46.2	1.37	-4.88
carbon tetrachloride	6.3	10.7	0.41	-10.67
chloroform	14.6	14.7	0.48	-0.04
ethylbenzene	11.5	14.3	0.57	-4.77
methylene chloride	35.4	35.6	1.56	-0.13
toluene	15.4	18.2	1.64	-1.67
1,1,1-trichloroethane	7.1	10.1	0.30	-10.10
trichloroethylene	4.8	5.3	0.31	-1.66
xylenes	16.3	20.5	1.84	-2.26

Boxed-in "t" shows which means are NOT significantly different. For simplicity, a z-factor instead of Student's t was used to decide if the means were significantly different (z-factor of 1.645 at 95% significance level).

MR. TELLIARD: Our last speaker today is Dr. Fred Haeberer from Quality Assurance Management Staff. Are you going to work from up here or down there?

DR. HAEBERER: Up here. Thanks, Bill.

An observation, maybe it's apocryphal, but QA/QC is bringing up the rear again, Bill.

MR. TELLIARD: Who said it was boring? Anyway...

DR. HAEBERER: Well, it's boring to those people who let their egos get in the way.

MR. TELLIARD: Oh.

DR. HAEBERER: Like Joan Fisk and Ramona Trovato, I used to have a real job working in laboratories but as younger people came into the laboratory, brighter younger people with backgrounds in such esoteric areas as statistics and scientology, I knew it was time to get out and consequently I moved to headquarters, thereby raising the IQ levels of both organizations.

I'm going to tell you about a project that we have been kicking around for, oh, a couple of years now. The basic background of it is that, as we all know, there are error distributions associated with measurements and each operator introduces his own level of random errors and even systematic errors. Specifically, we have developed, through statistical means, a program for compensating for the difference between laboratories or analysts' performances; that is, through replication by the individual laboratories or analysts participating in a study, they are able to compensate for the differences in their performance.

Let me say that this program addresses only measurement errors. It does not address sampling errors and, as I understand it, the major share of total error is generally due to sampling design, sampling and sample preservation and sample handling. Also, this program is ideally suited for homogeneous matrices. One is looking at soils from a Superfund site where not only the individual sample may be non-homogeneous, but gross sample matrix differences may be encountered when sampling as close as three

feet apart, this program would have to address additional complexities.

Slide 1 illustrates if one has a series of measurements with an associated error distribution and averages these measurements, the error distribution of the end result, will be considerably tighteri.e., the averaged result will be more precise. That's what I've tried to indicate here with the yellow distribution "curve".

Slide 2 addresses that this program also addresses the issue of adjusting for bias. It adjusts sample analytical results for the method bias that a particular operator or laboratory incurs when performing matrix spike analyses The program takes into consideration that the error distribution of the adjusted result will be broader. This is shown here by the curve on the right representing the "adjusted" error distribution, which is somewhat broader than the left curve, the error distribution associated with the unadjusted results.

In implementing this program the agency would develop replication plans which would be based on the specific data quality goals that a particular program or data user required. Slide 3 is a representation of one such replication plan to achieve a specific data quality constraint. An operator that typically is incurring three percent relative standard deviation could get away with a one, one replication plan. That is to say, he would have to replicate his analysis once and he would have to do one matrix spike analysis for the purpose of bias adjustment. As relative standard deviation increases, replication requirements increase.

We have heard several people refer to data quality objectives today. Data quality objectives STET it really refers to a process. Slide 4, represents that process in diagram form. We're talking about holding the data user's feet to the fire and, through an iterative process, make that data user bite the bullet and communicate the level of total error that he or she is willing to tolerate in the environmental data that's to be used

for decision making. Once that total acceptable error is communicated, it is aportioned to field and laboratory operations. The major portion should be allocated to sampling the big lump has got to go over there and a portion to and a lesser amount to measurement activities. The laboratory portion is translated into measurement quality constraints i.e., analytical precision and bias.

The intra-laboratory QC approach to achieving these measurement quality constraints is depicted schematically on Slide 5. In implementing this program a laboratory or an operator would initially estimate the variability incurred either by examining available historical data, from the analysis of very similar type samples, or by doing a special study using the sample nmatrix to be analyzed to establish what his/her variability is. Then, taking that variability, the analyst would go to the agency provided replication plans, select the appropriate replication, perform the analyses, adjust the results, that is, average of the results and then adjust for bias or matrix spike recovery. If a significant change in precision has occurred, a different replication plan is selected for subsequent analyses. The adjusted data are then used for decision making.

An organization approached Quality Assurance Management Staff (QAMS) because it had noted significant performance differences in the results that it was receiving from a group of commercial laboratories. Slide 6 presents their zinc data.

There is a mistake in this illustration. It should read "micrograms per kilogram" along the abscissa.

This organization had been providing Performance Evaluation (PE) samples to its family of contract laboratories, over a relatively short time and noticed that the laboratories performance was quite variable and the organization didn't know whether the performance of these laboratories actually met their data quality constraints. QAMS took the results from these PE studies, and derived the error distributions depicted in this

slide.

QAMS entered into a dialogue with the organization, and got them to, in effect, to establish its data quality constraints. Slide 7 illustrates what we are calling jocularly the "discomfort curve". The organization defined its action limit is at 1.2. times the regulatory limit. Below 1.0 it could tolerate a 10 percent false positive error rate and above 1.4 times the regulatory standard for ambient stream water quality. It could tolerate a 20 percent false negative error rate. This input was presented to the statisticians and they developed the data quality constraints illustrated in slide 8.

The data quality constraints are depicted here as a "required performance envelope". The envelope is skewed because the acceptable error rates were skewed, 10 percent acceptable false positives, 20 percent acceptable false negatives. Acceptable performance is defined as bounded by the triangle. A laboratory with zero percent bias can provide the desired data quality, i.e.,the desired false negative and false positive rates, with a relative standard deviation ranging as high as 14 percent while a laboratory that has a negative bias of 14 percent would have to be dead-on in terms of deviation in order to meet those error bounds. Similarly, a laboratory having positive bias of 20 percent would also have to have zero percent relative standard deviation.

We entered into a pilot study with the organization to establish the actual variability of the participating laboratories. The essentials of that pilot study are presented in slide 9. A bulk sample was collected from a stream meeting the ambient water quality standards. That is to say, the concentration of copper, iron and zinc were below 5, 300 and 30 micrograms per liter. That bulk sample was divided in half, and one portion spiked with copper, iron and zinc at the ambient water quality standard levels. That is to say, if a concentration of N was contained in the original sample, after spiking it contained N plus the standard concentration. Both

spiked and unspiked samples were submitted to the contract laboratories as routine samples with no other specific information provided other than copper, iron and zinc analyses were desired. Each laboratory received 10 unspiked and 10 spiked samples.

The results obtained by the participating laboratories were analized for precision and matrix spike recoveries. The percents bias and the percents relative standard deviation achieved bu the participants is presented in slide 10. Laboratory A had a significant drift in their analytical results for copper. When graphed chronologically, one can see their results deteriorating and consequently their copper data couldn't be used. But looking at these results, one can see that some of the labs performed acceptably for some of the analytes. None of the laboratories performed acceptably for all analytes.

Slide 11 compares these performance results with the required performance envelope. Only STET those three data points within the triangle are acceptable. The five outside of the triangle for either reasons of bias or relative standard deviation would not meet the program's data quality constraints.

Based on those performance results, our statisticians then calculated the replication plans that would be required to meet the needed performance constraints. No replication plans greater than 10, 10 were calculated since clearly such plans would be economically unworkable. Consequently, you see here 10 plus, 10 plus plans listed for several of the poorer performing labs.

Slide 13 p[resents how the adjusted results obtained with various replication plans would compare with the required performance envelope, if the laboratories continued to perform as previously indicated. If we one plots the results, adjusted for matrix spike recovery against the required performance envelope, the results would all fall on the zero percent bias line. None of the 10,10 replication plans would result in acceptable performance from the poorer laboratories, or for outlier

analytes.

This is as far as we have gotten with this study. We have begun the next phase. Those laboratories with performance requiring 10,10 plans are being drawn into participating. We're not asking any of the labs to go beyond a 5,5 replication plan; the program won't pay for it. It's my gut feeling that once laboratories know that their precision and bias results are actually being utilized, they will focus on those aspects of their work and their precision and bias characteristics will suddenly improve.

The conclusions that we can make from phase 1, presented on slide 14, are as follows: (1) no single lab is meeting the data quality constraints for all the analytes, (2) expect the ILA, the intra-laboratory approach to succeed in allowing labs with differing performance characteristics to meet defined data quality goals, in some cases, yes, it's going to be cost-prohibitive. (3) the program will probably have to relax its data quality requirements unless it is really willing to bite the bullet and pay for a significantly greater number of analyses.

Slide 15 presents some of the planning for Phase 2. We hope to have all three laboratories participating in it for all three analytes. The laboratories would monitor and adjust for performance changes. When we conclude phase 2, we intend to take a look at the error rates that are incurred with the ILA versus the error rates that are incurred with the current approach, the current approach being one matrix spike and duplicate per batch of 10 or batch of 20, as the case is currently with this program.

Any questions?

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions for Fred? Thank you.

(No response.)

Achieving Predefined Laboratory Data Quality Levels

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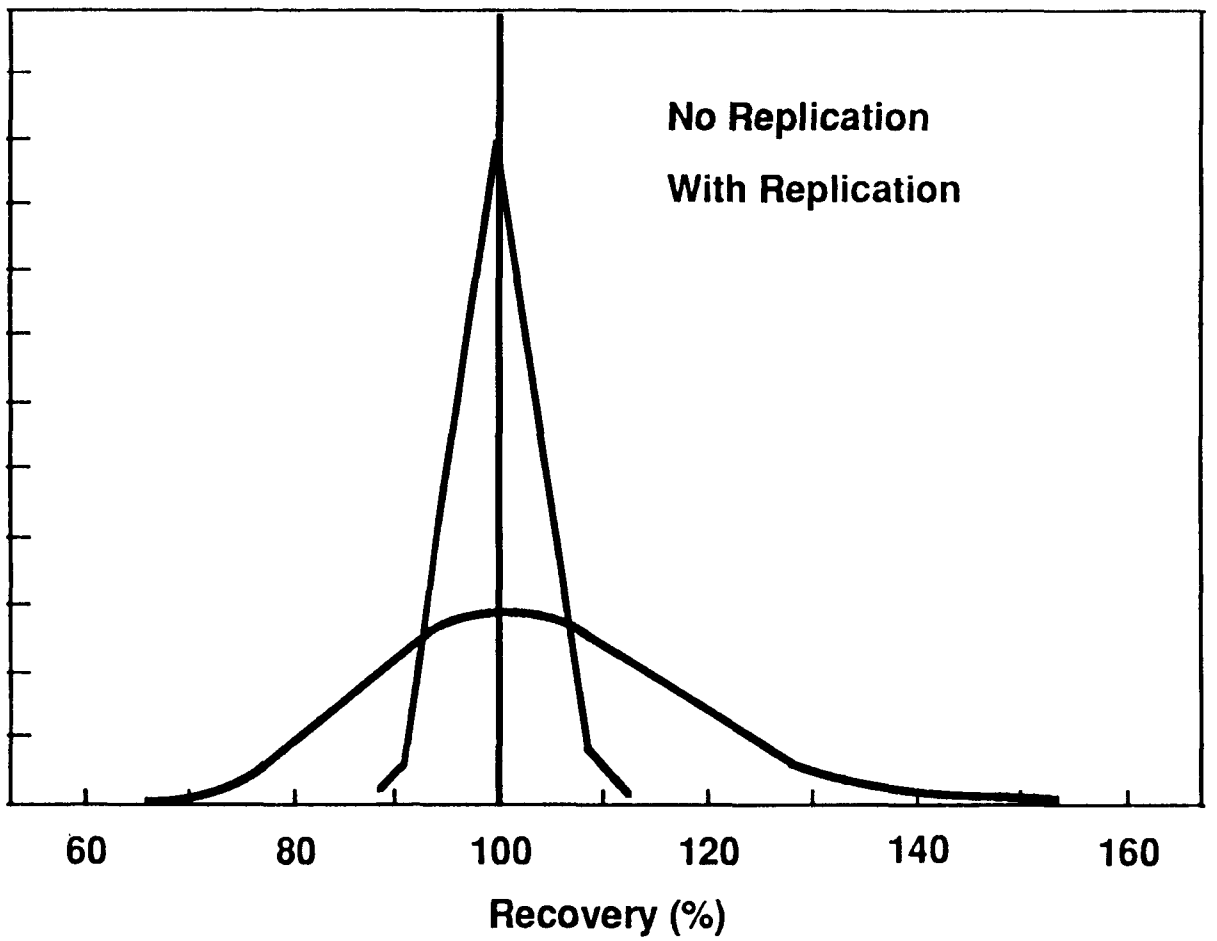
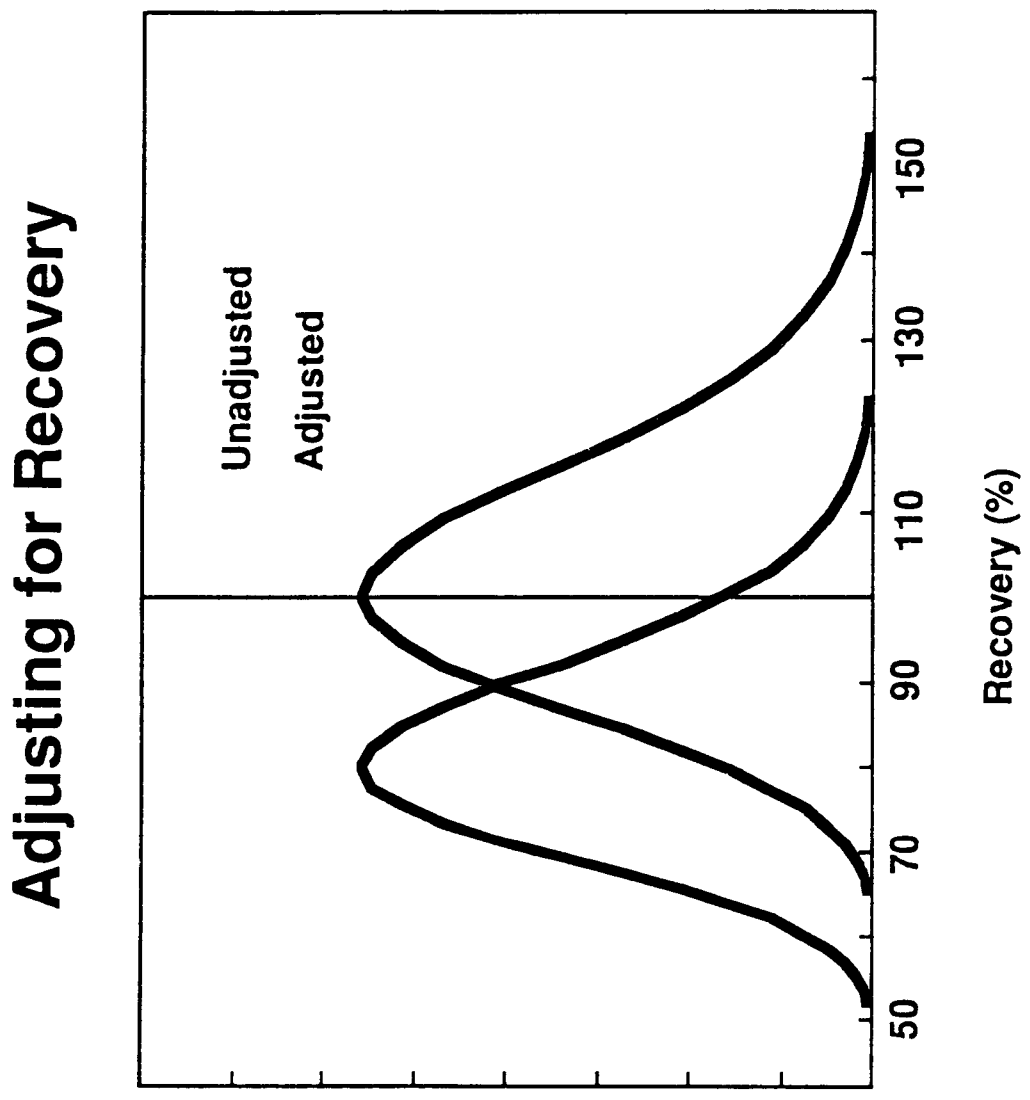
Replication and Averaging to Reduce Imprecision



SLIDE 1


Adjusting for Recovery
Unadjusted
Adjusted
50
70
90
110
130
150
Recovery (%)

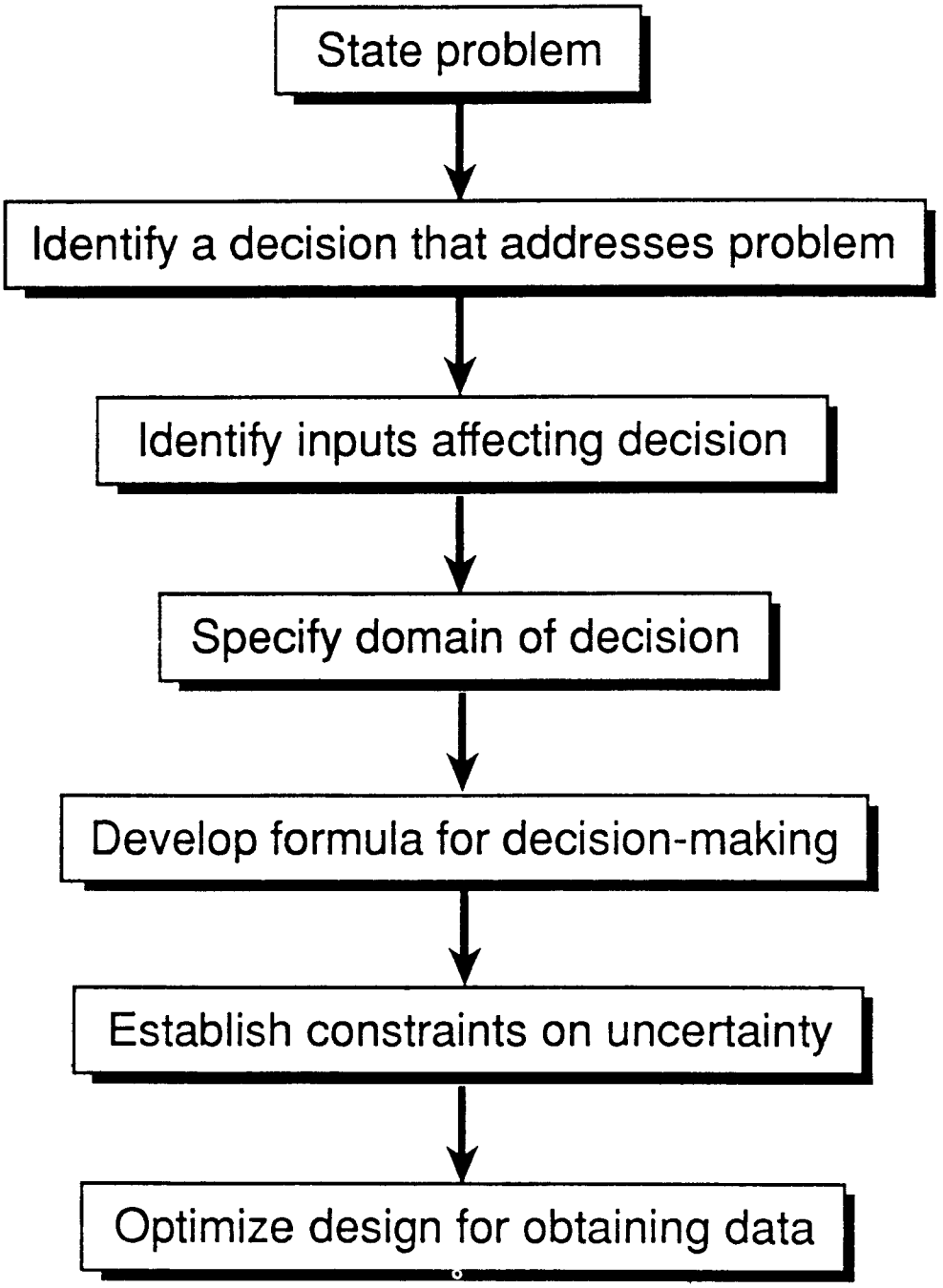
SLIDE 2

Replication Plans for Achieving Desired Objectives

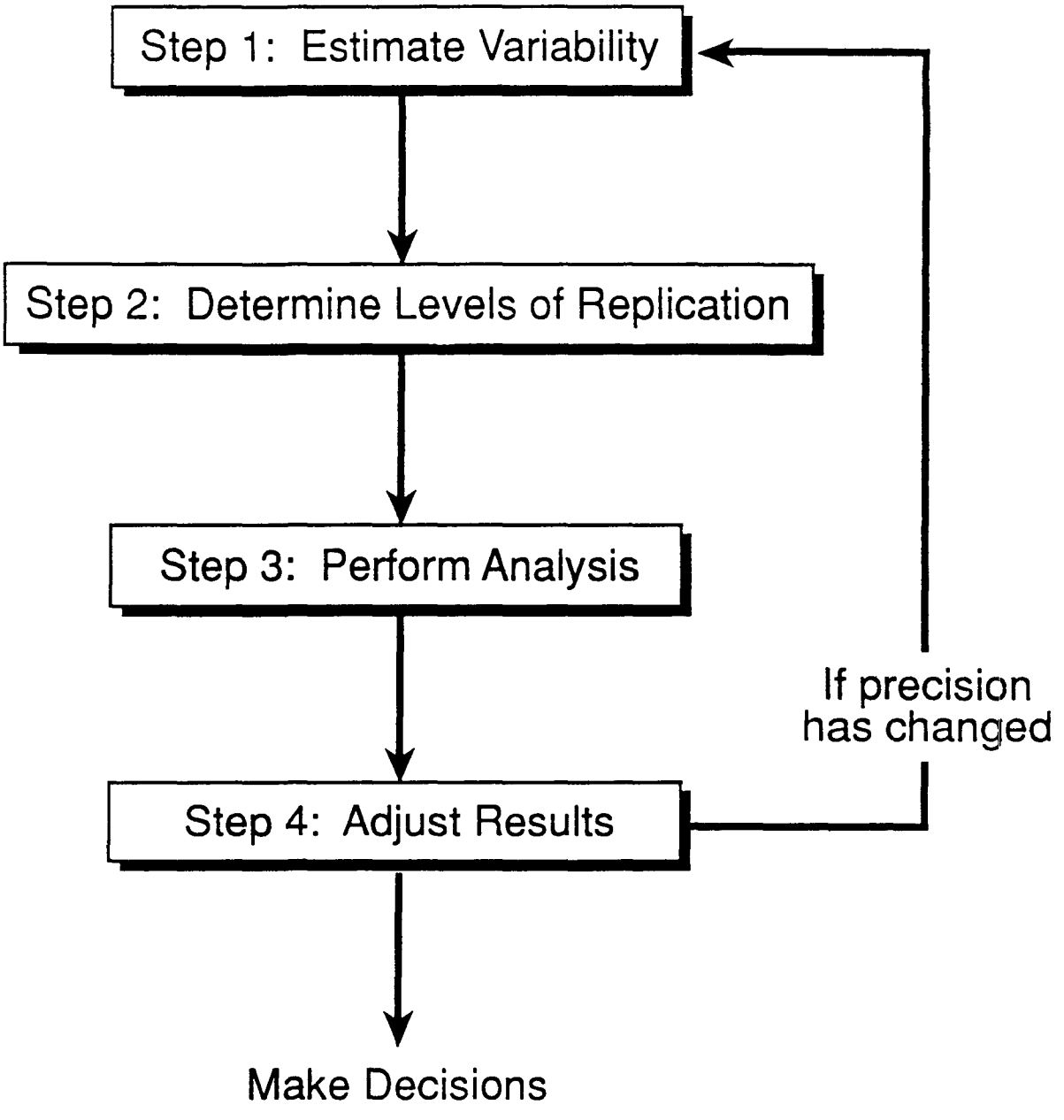
RSD (%)	Number of Spikes	Number of Replicates
3	1	1
6	2	2
10	5	4

SLIDE 3

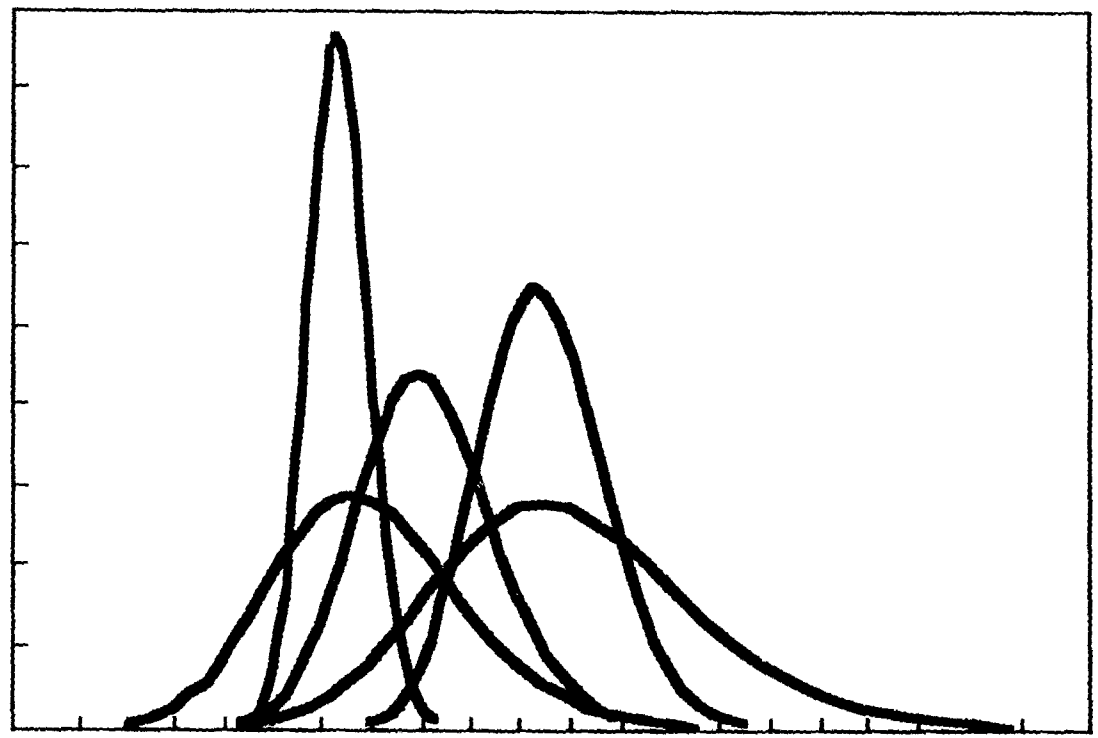
Data Quality Objective Process
(Logic Flow)



Steps of Intralaboratory Approach (ILA)

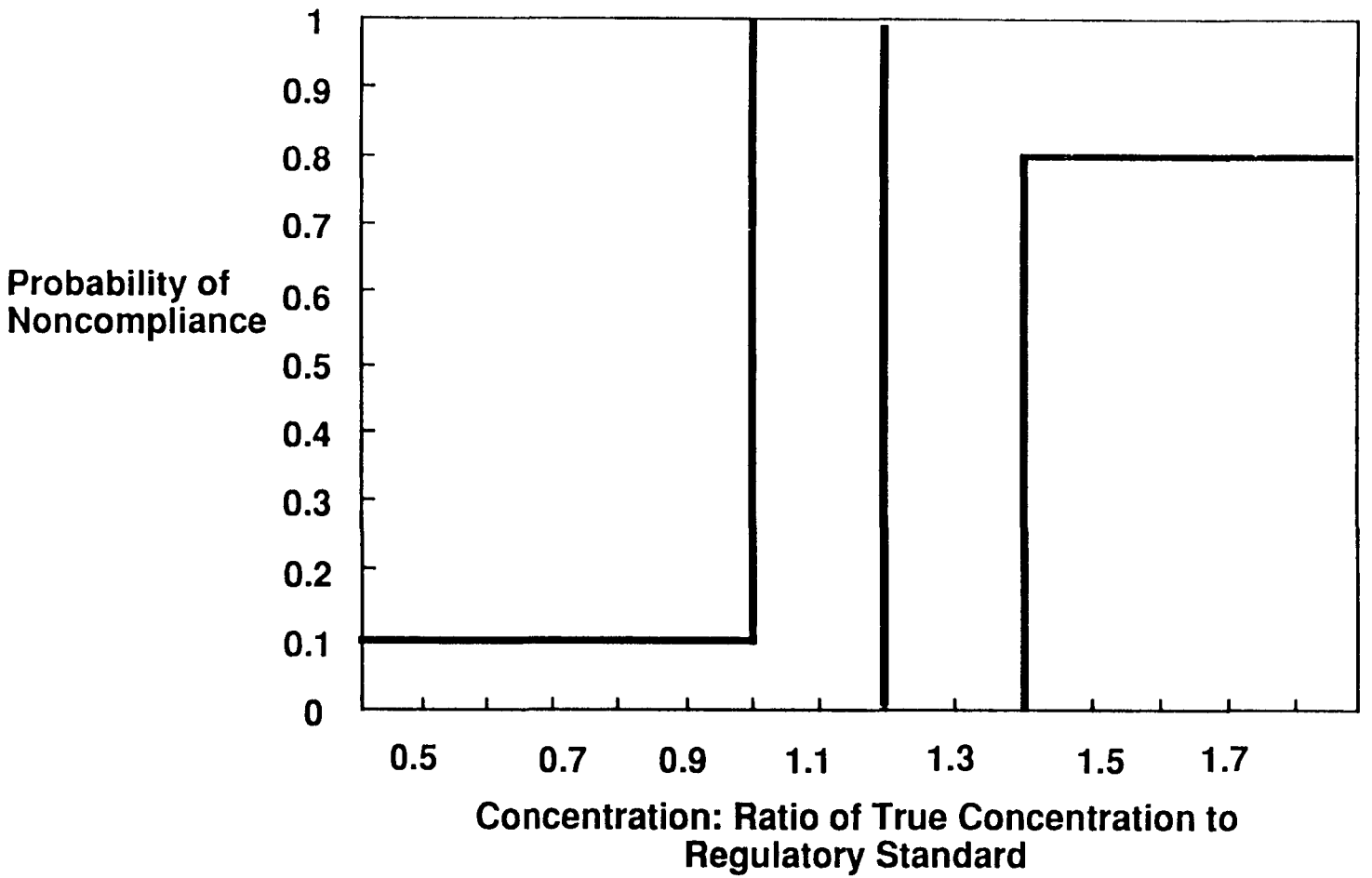


Original Program Data - Zinc
Lognormal Probability Distributions

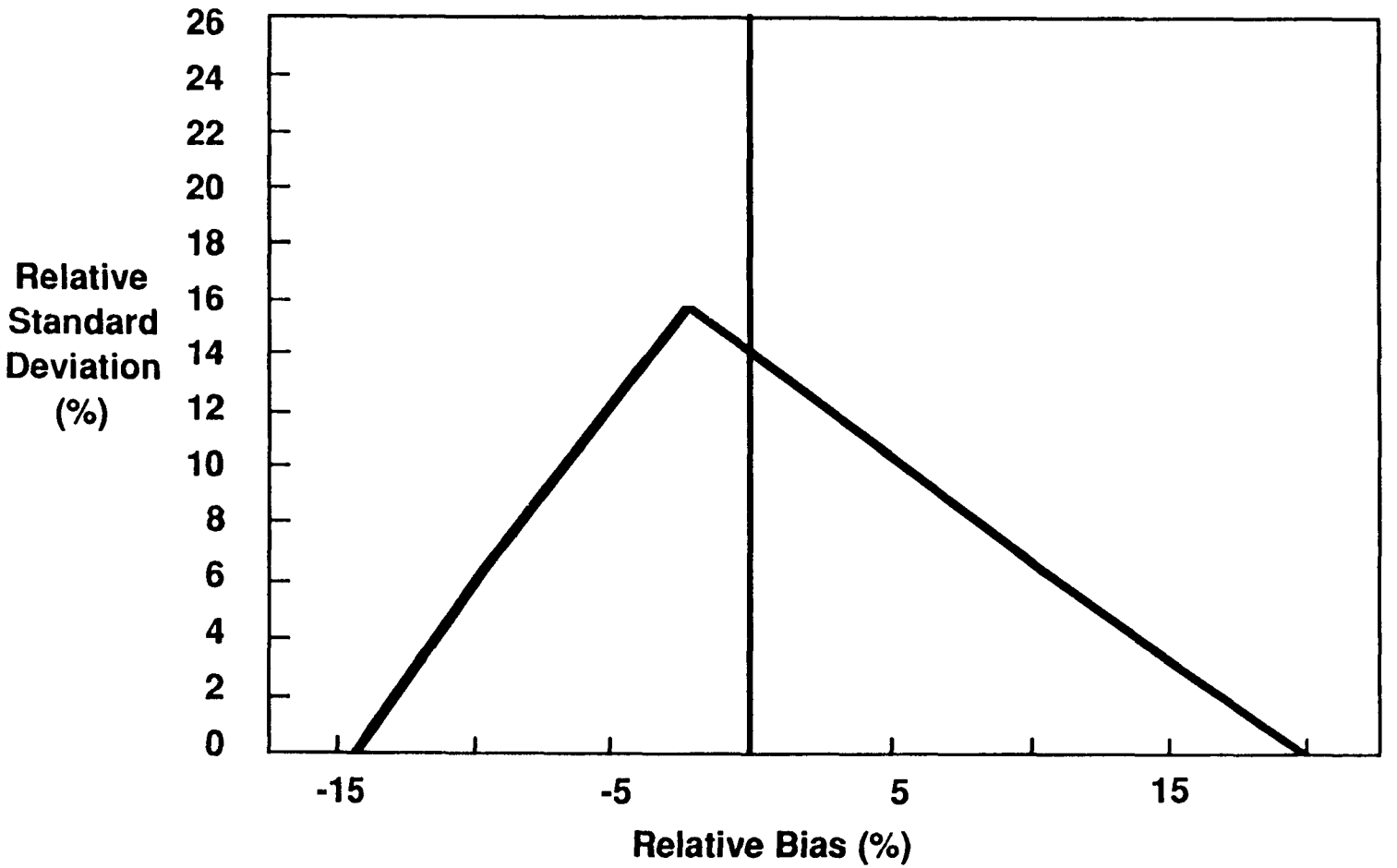


SLIDE 6

Program Data Quality Objectives for Compliance Test



Required Laboratory Performance Envelope



SLIDE 8

Pilot Study – Phase 1

Objectives: Characterize performance of different laboratories
Determine replication plans under ILA

Matrix: Surface water

Analytes: Copper, iron, and zinc

Ambient Water Quality Standards (µg/L):

Copper	5
Iron	300
Zinc	30

Expected Concentrations: Below ambient water quality standards

Spiking Levels: Equal to ambient water quality standards

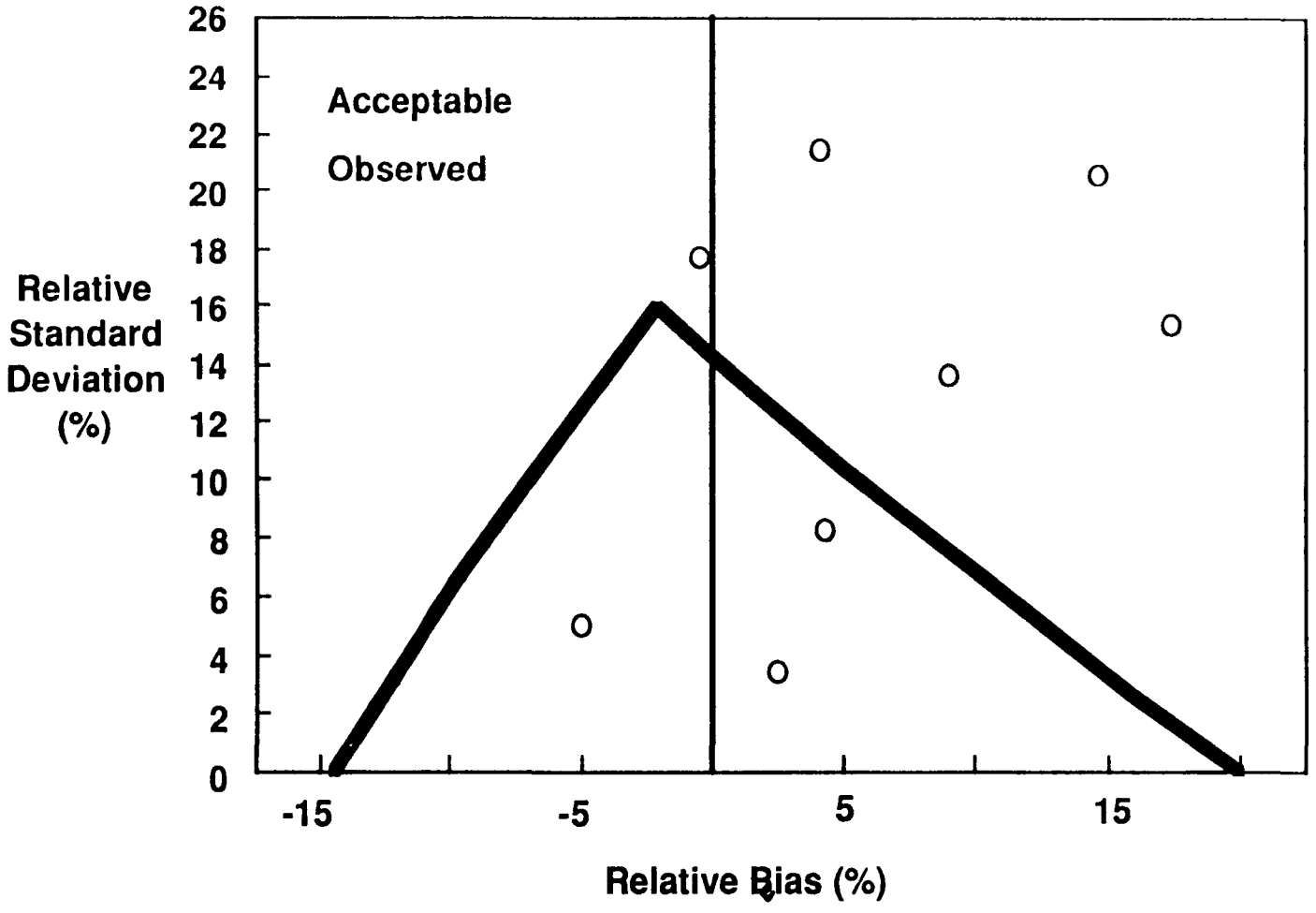
SLIDE 9

Performance Results of Phase 1

	Performance (% Bias, % RSD)		
Laboratory	Copper	Iron	Zinc
A	NA	(2.5, 3.4)	(9.0, 13.6)
B	(17.6, 15.4)	(-0.5, 17.7)	(4.5, 8.1)
C	(14.7, 20.6)	(-4.9, 5.1)	(4.2, 21.3)

SLIDE 10

Achieved Laboratory Performance, Phase 1



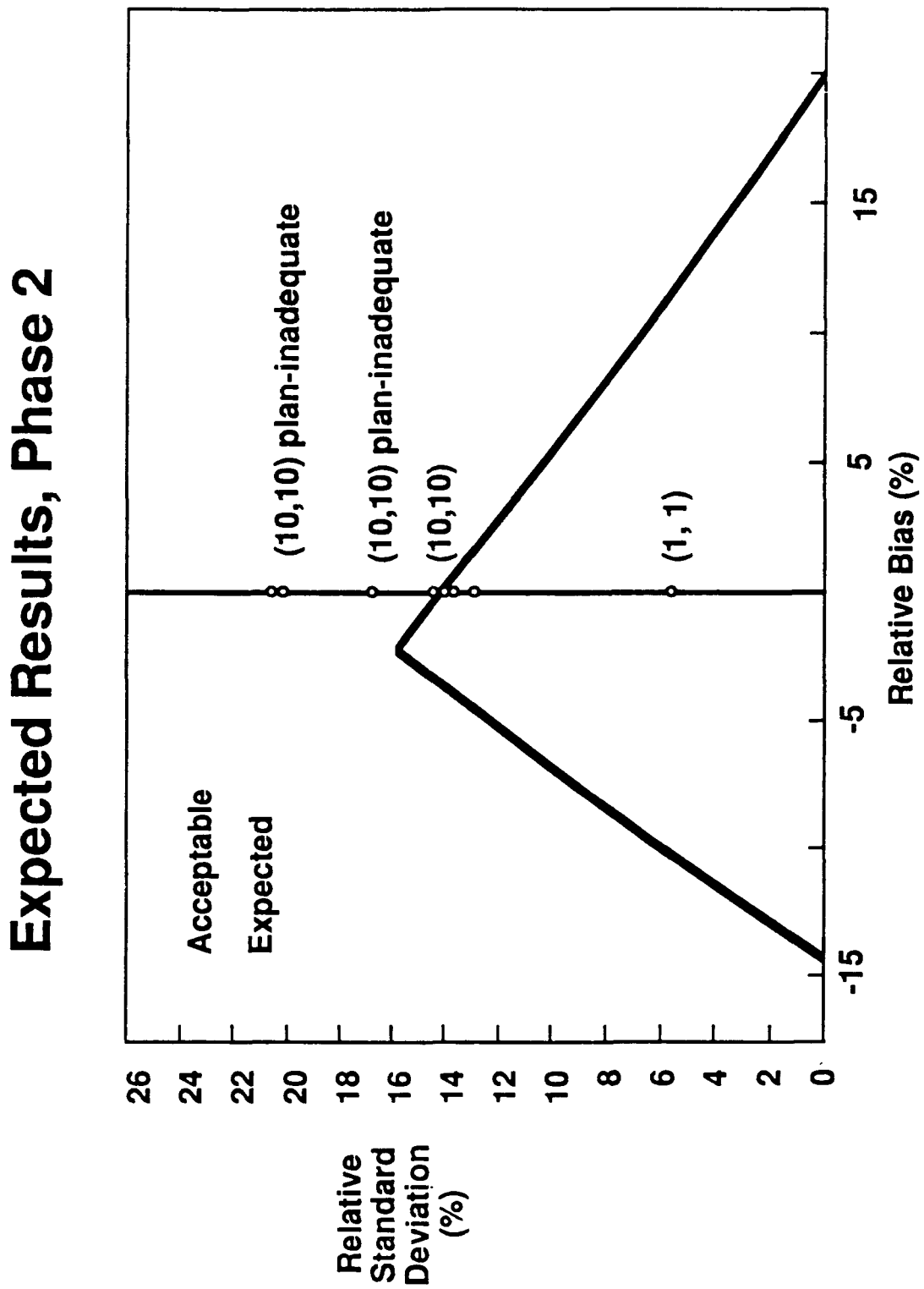
SLIDE 11

Required Replication Plans (n, r)

n = number of spikes, r = number of replicates

Laboratory	Copper	Iron	Zinc
A	NA	(1, 1)	(8, 8)
B	(10+, 10+)	(10+, 10+)	(3, 3)
C	(10+, 10+)	(2, 1)	(10+, 10+)

SLIDE 12


Expected Results, Phase 2
Acceptable
Expected
(10,10) plan-inadequate
(10,10) plan-inadequate
(10,10)
(1, 1)
Relative Standard Deviation (%)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
-15
-5
5
15
Relative Bias (%)

SLIDE 13

Phase 1 – Conclusions

- No single laboratory can meet DQOs for all analytes.
- ILA is expected to succeed in allowing laboratories to meet DQOs, but
- ILA appears to be cost-prohibitive in some cases.
- The program will need to consider relaxing its DQOs if it is unwilling to pay the higher costs of ILA.

Pilot Study – Phase 2

- Selected laboratories implement replication plans.
- Laboratories monitor and adjust for changes in precision.
- Error rates are estimated for ILA.
- Error rates are estimated for the current approach.

MR. TELLIARD: Thank you for your attention. I'd like to thank the speakers.

Any of you who would like to talk on a subject, please give me a call or drop me a line for next year. If there's something you'd like to talk about at one of these meetings and we haven't talked about it, drop me a line. If there is some area you think would be interesting either to you or your colleagues, we'd like to hear from you and see if we can work it in. We're always looking for new ideas.

I'd like to thank the court reporters for putting up with all of the strange names.

I'd like to thank Jan. What happened to Jan? Did you escape again? Jan Sears is the one who puts this thing together;

I'd like to thank Harry McCarty and Dale Rushneck for working on the speakers' program.

I'd like to thank you for your attention and hopefully we'll see you next year.

Thank you very much.

14th ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

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