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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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

FIFTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT
MAY 6 & 7, 1992

FOREWORD

The Engineering and Analysis Division of the USEPA Office of Science and Technology sponsors an annual meeting to provide a forum for the presentation of new ideas and advances in the determination of environmental pollutants. These proceedings document the Fifteenth Annual Conference on the Analysis of Pollutants in the Environment. The speakers delivered 24 technical and policy presentations on subjects as diverse as solvent reduction and enzyme immunoassay.

The fifteenth annual conference was a resounding success. The conference was attended by nearly 300 scientists from industry, consulting firms, environmental laboratories, and state, local, and federal government agencies.

We would like to thank Jan Sears of Ogden Environmental for coordinating the conference, Harry McCarty of Viar for his assistance in arranging the technical program, the speakers for their outstanding efforts, and all the others who helped make the fifteenth annual conference a success. We are looking forward to your attendance at the sixteenth annual EPA conference in May of 1993.

W. A. Telliard

FIFTEENTH ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

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

May 6-7, 1992
Norfolk, Virginia

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PROCEEDINGS

May 6, 1992

MR. TELLIARD: Good morning. I would like to welcome you to the 15th annual Norfolk symposium on analytical chemistry in the environment. This meeting is sponsored by the Office of Water, and I am Bill Telliard, and I am from EPA, and I am here to help you. This morning, we are going to be embarking on two days of discussions.

As you know, over the last few years, the Environmental Protection Agency and, specifically, the Office of Water, have developed a number of programs to regulate the discharge of pollution into the environment. Typically, through the Clean Water Act and the Safe Drinking Water Act, the Agency has set forward standards of performance and had installed technologies to remove pollution and to mitigate existing pollution through the use of treatment technologies.

Over the last 24 months, the Agency has undertaken a program of pollution prevention in an attempt to reduce at the source those pollutants that we are presently trying to clean up in the environment. Through the use of either product substitution, manufacturing process alteration, or whole new manufacturing techniques, it is attempting to reduce at the source those pollutions of concern to the environment, thereby reducing both risk and exposure to the American public.

We in the laboratory community kind of accept the exposure to chemicals as part of our everyday life, but we do have also a responsibility to see that this mandate of pollution prevention is taken to heart.

So, we are going to address a number of issues today that deal with either mitigation through product substitution or, in a smaller sense, either reduction or recycle/reuse in an attempt to reduce both exposure and also discharge to the environment. And we are going to talk about some technologies that use less solvents or use different solvents or enable us to reclaim or reuse solvents.

So, with that kind of an open introduction, we would like to start our program. The first speaker this morning is Craig Markell from 3M Corporation, and he

is going to talk about a new system that is going to address part of this question of solvent reduction and also, in a sense, solvent reuse, because it is amenable to that approach.

Craig?

MR. MARKELL: Thank you, Bill.

What I really got a kick out of was this is my name badge, and if you take a look at your name badge, there is an obsolete piece of equipment on here. It is a separatory funnel. We are going to replace separatory funnels, because we don't want to use all those solvents, and we don't want to shake so much anymore.

Could I have the first slide, please? Now, how many of you can read that? (Slides are backwards.)

You know, I will just say a few words here before we get going. Leonardo da Vinci always did everything backwards so you had to read it in a mirror, and that way, nobody could steal his ideas. I don't want any of you folks stealing my slides here.

What I really want to do today is talk a little about some new technology. It is something we have developed at 3M, and it is, indeed, a substitute for the separatory funnel, something we came up with about three or four years ago. It is actually a fairly new technology, and what we have done is, as the title says "Extending the Range of Solid Phase Extraction," and that is what we are trying to do is go from drinking water which is where we started out into all kinds of matrices.

I can hear the slides clicking away back there, being corrected.

Well, at any rate, let me describe the first slide. It is two chromatograms, and they are very historic chromatograms. In fact, it is the first time anyone ever ran an Empore™ pore disk and water, and there are some features about it I want to tell you about.

There are two chromatograms. We have a blank, and we have one with a few peaks in it. There are six pesticides that we spiked into Mississippi River water. The river water was a fairly clean matrix, but we learned something about the extraction from that.

First of all, we have very good recoveries for five of the six analytes we spiked, quantitative recoveries. We were very impressed with that, even though it was the first time we had tried one of these strange solid phase extraction disks.

Thanks. Great things go on behind curtains sometimes. (Slides are now corrected.)

Here it is. Okay, and the point is that on the left, we have a real sample, about 1 part per billion spiked in. On the right is the blank, and there actually was something in that river water.

Well, again, the point is we got good recoveries of five of the six analytes, but we also learned something else. It was a fairly slow filtering sample, and I will describe the technology a little more, but the water plugged the disk. We only got a half a liter through a 47 millimeter disk, and it plugged.

Secondly, there was a low recovery from one of the analytes, and it was one of the polar analytes which is fairly water soluble, and that was a problem.

So, the very first time we did one of these extractions, we found two problems. One was plugging and the second was the loss of polar analytes just because the partition ratios aren't right.

And we have been researching for the past three years or so to get around that problem. That will be the focus for the rest of my talk.

Now, there is something else I want you to take note of. I hope you can all read it. At the bottom, you will see a couple of dates. They really were inadvertently put on, but it says January 25, 1901.

Now, Greg Junk is sitting up here in the front row who is considered by many the founder of solid phase extraction. I just want to point out to Greg that our work predates his by about 70 years, I think. Always had a little problem putting slides in and also setting dates on these doggone integrators.

Well, I just wanted to take a couple of slides to describe the technology to you. These are solid phase extraction disks. Here is one, and it is a 47 millimeter circle by 0.5 millimeter thick. I is 90 percent by weight solid phase extraction particles, 8 micron particles, and, you filter your sample through, and the hydrophobic analytes are extracted out by the disk just like a liquid-liquid extraction. Then, when you are finished you go to elute it off.

We are using a typical all-glass filtration apparatus with a test tube inside to collect the eluant. This has been replaced by some slicker apparatus in the meantime, but that is part and parcel of what the process is.

The efficiency comes from the 8 micron particles. Really, everything is very efficiently caught right up at the top of the disk.

So, the features are speed and efficiency. You can filter a liter of water through this somewhere in the range of maybe 5 to 10 minutes per liter, and get a very efficient extraction of the hydrophobic analytes.

So, if you look at the whole process and think about separatory funnel extractions, you use a lot less solvent, over 90 percent less solvent. It is not a labor intensive process. It is filtration. And, finally, you can do samples very quickly, thus the faster turnaround times.

Now, when we first looked at this, we looked at it in relation to Method 525.

525 was developed at the Cincinnati EMSL lab as a solid phase extraction technique. It was a great method. It was the first time solid phase extraction had been officially installed in the EPA methodology, and it was really a landmark method.

Well, the way we did it with disks was a 47 millimeter C18 bonded silica disk. We extracted a 1 liter sample of drinking water, eluted with three 5 milliliter portions of dichloromethane, and, finally, you dry that and concentrate it down to a milliliter. You are ready to go into the GC mass spec. Pretty straightforward method.

Just summarizing some results, we see very good numbers. I have broken these down. There are about 50 analytes. I have broken them down into several categories, and really the recoveries are quantitative. They are as good as you would expect with a liquid-liquid extraction.

So, with this solid phase extraction, our environmental analysis was off and running, but, of course, it was directed at drinking water and hydrophobic analytes.

This diagram will get you thinking a little about the mechanism of what is going on during an extraction. You have C18 chains bonded to the silica substrate. You have your analyte here designated by a dipole type of structure, R being a hydrophobic end, X being a hydrophilic end. And, of course, you are in an aqueous matrix.

Now, it will work great as long as the hydrophilic end of the molecule, the X group, whatever it is, isn't a strong hydrogen bonder or something that will have a

dipolar interaction with the water. For example, if that molecule was phenol, you would get a low recovery. You have a ring, and that interacts well with the C18.

The problem is that the other end of the phenol is the hydroxyl group. That hydrogen bonds very well with the water, and that is a stronger interaction than the hydrophobic C18 interaction. So, phenol is a tough compound to do.

That is the problem with extractions of polar compounds. What we have done is a lot of research looking at the priority pollutant phenols, because it is as tough of a class of compounds as any there is.

Think about polynuclear aromatics. Chemically, they are all very similar, a piece of cake to extract. Think about PCBs, ditto. Very easy to do as a class.

But when you look at the phenols doing an extraction, you have a wide range in terms of water solubility, from phenol which is about 10 percent water soluble to pentachlorophenol, which is substantially insoluble in water.

In addition, the water solubility is also a function of whether or not the phenol is ionized. So, for example, if you have 4-nitrophenol that is neutral, it is less water soluble than the ionized 4-nitrophenol. A tough group of compounds to extract.

pK is all over the map as well. Phenol has a pK up around 10, and pentachlorophenol probably down around 2 to 3.

So, it is a tough group of compounds. These are the analytes we have chosen as a basis for our work to see how we can do on these.

Now, the sorbent we decided on is the styrene-divinylbenzene. It, in fact, was the sorbent chosen by Greg Junk in that early work and a very good sorbent.

It has a lot of aromatic character, about 75 percent. In addition, it has got some aliphatic functionality.

The other nice thing about styrene-divinylbenzene is that there is no silica here. It is 100 percent organic. So, it has a lot of extracting power. C18 silica is really mostly silica by weight.

Now, when we look at the sorbents, on the left you see C18 silica; on the right you see the polystyrene-divinylbenzene.

Particle sizes are similar. The functionality of the C18 is all aliphatic,

whereas the styrene is about 75 percent aromatic.

If you look at the final row, you have the weight of actual organic material in the disk. This is the stuff that does the extracting, and the more of it there is, the better off you are. It is just like in a separatory funnel, if you put in twice as much organic solvent, you will get more of your analyte extracted out of the water.

So, you see that when you look at a single disk, you have got about 100 mg of C18 silica, whereas when you go to the styrene-divinylbenzene, 230 mg. So, a lot more organic material, and that is amplified, perhaps, with the aromatic interactions you get with the phenolics.

So, it should be a good sorbent for these phenolic compounds.

Just got a couple of micrographs showing you what this material looks like in the disk matrix. This is .5 mm top to bottom, and we will just zoom in here a little bit. Here is a close-up shot. What you are seeing here is the individual particles, with a little bit of a size distribution, and that is not bad, because you can pack more of it per unit volume.

Finally, you can start to see some of the teflon fibrils which hold the matrix together. And here are some single particles, with a good shot of the fibrils. That is really what the teflon matrix does for you. It holds everything together, with absolutely no chance of channeling. That is what the styrene looks like in disk form.

Well, here we have a comparison. This is a .5 liter sample. A little about the conditions. There is no pH adjustment of this sample. It is essentially neutral water, D.I. water, and you can see the C18 column and the styrene-divinylbenzene columns are the two to the right, and the analytes.

What we are seeing here is under those conditions, the styrene is clearly a better choice to extract polar analytes out of water. When using the C18, we have recoveries as low as about 3 percent for phenol out of .5 liter, not very acceptable.

You are going up to about 97 or 98 percent for the big trisubstituted phenolics, and that seems to be what we are seeing. If you use conditions like this, once you get up to trisubstituted phenols, now you have a quantitative extraction.

In fact, the bottom one, pentachlorophenol, is an analyte in Method 525.1,

and it works very well, but we have got to get the other recoveries up, and as you can see, the styrene recoveries don't look too bad, even under these conditions.

But we can do a little better. One thing you have got to think about, again, is the fact that the phenolic can be either neutral or ionized. If it is neutral, you can extract it into an organic solvent. It is less water soluble, so the partition coefficient is in your favor.

What you have to do, then, is adjust the pH so your phenolics are neutral, and here we have pH 2. Now, the last one I showed you was at neutral pH. This is pH 2.

We have got 100, 300, and 500 ml samples at pH 2 using a styrene disk. Not bad looking results at 100 ml. We have got 66 percent for phenol. Arguably, that is quantitative.

From there, of course, it goes up. As you get out, though, to higher volumes, your recovery drops off, and the reason for that is you have exceeded the break-through volume.

You have got to think of these as a little HPLC column. Your analytes are actually chromatographing through as you are extracting the sample, and sooner or later, they come out the bottom, and you start losing your analyte. Your recovery goes down.

So, it is very good if you can work below the break-through volume for your analytes, and at 100 ml, we are below the break-through volume for everything but phenol.

Now, take a look at 300 ml. We are below the break-through volume for everything but 4-nitrophenol, and even at 500 ml, that holds true. So, just by changing the pH, we have done a better job on several of these analytes.

At pH 2, we are looking at a comparison between the C18 and the styrene-divinylbenzene. Again, the first table I showed you had C18, but it was at neutral pH.

Here is what happens if we drop the pH. C18, is a bit of a disaster for several of the analytes even at pH 2. These are 100 ml samples. And, of course, the styrene results I just showed you. 66 percent is our lowest recovery.

100 ml is unrealistically low for a lot of analyses. You just can't get the

detection limits you need.

This is what we finally came up with. What we are seeing is a .5 liter sample through a styrene disk. The samples are at pH 2, and in addition, they contain 10 percent sodium chloride.

Now, there is nothing so bizarre about adding salt to a sample if you are doing a liquid-liquid extraction. Here, we are just doing it on solid phase extraction, and it turns out to be pretty effective.

We have done some studies of what happens if you go up to 20 or 30 percent sodium chloride. It seems as though, from a few experiments, what we are seeing is that when you get to about 10 percent, you start leveling off in a plot of percent versus recovery.

You can get better results if you go up to 25 percent, but that is a lot of salt. That can cause other problems with the extraction. So, 10 percent looks like a pretty good number.

And these results are good. We are looking at 25 percent on phenol with good RSDs. In fact, the next speaker is going to show you some more, and the RSDs are under 10 percent at that 25 percent recovery.

The rest of the analytes quantitative extractions.

So, the styrene does look like a good bet for samples with polar analytes, and that is what we are talking about here - extending the range of these disks to be able to do things that are more polar than the Method 525 list.

Now, the next topic I just want to wrap up with is dirty water. How about if your water is what we call dirty water, has all kinds of garbage in it? You can have anything from algae - very low quantity of suspended solids but very effective at plugging filtration media, all the way to things like sand and so on, up to 20 grams per liter. What can you do about that?

Here is an actual sample that I did in my lab, and what we are doing here is filtering some water through the disk. We are measuring the volume of filtrate as a function of time.

What you are seeing here is that the first 200 ml went through very well, 12

minutes for 200 ml. So ar, so good.

The problem is, then the curve starts dropping off pretty rapidly. In fact, in the upper right, you see 3.5 days per liter. That is a real number. It did actually take 3.5 days per liter.

And what you are seeing is that the particles in the sample are coming into the pores, and plugging the matrix, and that is all there is to it. What can you do about it?

Well, again, you can use a smaller sample. 200 ml would have been a great sample size here. 12 minutes to extract your sample, and you are off and running.

Another thing you can do, and this has been used pretty effectively by some people, is to take and put a pre-filter right down on top of the disk. In that way, you are making a little depth filter. You are catching some of the bigger particulates before they get to the actual disk.

The disk is an incredibly effective filter. It has got a very small pore size such that there is nothing larger than about .1 micron coming out the bottom. It is a really good filter which also means that it can really plug quickly.

Here, what you are doing is catching some of those particles before they get to the disk, and this is what we found to be about as effective as anything is one of the Whatman glass fiber filters. It is a depth filter with a 1 micron base and a 10 micron top.

That will buy you maybe a factor of 3, maybe a factor of 5, maybe even up to a factor of 10 faster filtration, but if you are talking 3.5 days per liter, that is still not great.

Well, we tried all kinds of things to filter some of these difficult samples. We even tried putting a little propeller, little stirring mechanism into the reservoir to keep the sample stirred up and so on. Didn't work worth a darn.

The only way to do this is brute force. Here, what we are showing is a 47 mm disk compared to a 90 mm disk. Now, when you look at the actual area that is exposed to the flow and not clamped in the glassware, we are using a 38 mm and 81 mm, and if you do the mathematics, those come out to areas such that the 90 has about 4.5 times the surface area.

That means it has 4.5 times more pores to plug up, and when you think of our 200 ml in 12 minutes, now that translates to almost a liter in 12 minutes. Starting to look pretty good.

Just a couple of the other features here. With a 90 mm disk, you can filter a liter in 2.5 minutes or less...in fact, some of the data you are going to see from the next speaker is down to about a minute per .5 liter, with good extraction efficiencies.

Remember, the bigger your disk, the lower the linear velocity through that disk as well.

Look at the capacity. 90 mm disks have a lot more capacity, and that is good if you have dirty samples where you might need that capacity to handle some of your analytes or interferences in the sample.

The bottom line is the sediment thickness. Now, this gets into a situation where you are eluting through a bed of mud, essentially. If you have a larger disk, that bed of mud is thinner, and that will help you out in the elution, too, to soak the analytes off of the particles if you have got things like PAHs or PCBs which we know spend some of their time sorbed to the particles.

So, 90 ml looks like it should work pretty well for dirty samples. Here is a picture of the two disks and the apparatuses.

This is the last slide. What we have done here is taken a number of typical samples from Minnesota and, indeed, the water is not frozen year-round like some of you think, just about ten months out of the year, and that is really hard to filter, by the way.

What you are seeing here is 47 mm disk on the left and a 90 on the right. In this case, we talk about a pre-filter. It is a thin glass fiber pre-filter, not the thick depth filter.

When we look at some of these real samples, we see that on the 47 with a pre-filter is very slow. Some samples took more than 8 hours for a liter. That is just not acceptable.

When you go to the 90 with a pre-filter, which is the right column, what you are seeing are very attractive flow times. 55 minutes per liter from pond water was

the worst we saw.

It seems to be the biological material that really causes the plugging. Sand isn't a big deal. Sand is actually a pretty good filter bed, but when you get to the small biological things, that is what causes the problems. So, a stagnant pond was the worse.

Since this work, we have seen one sample that is worse. It took about 2 hours per liter, and it was from an EPA laboratory in Duluth, Minnesota, and it looked like chocolate milk only with chunks in it.

At any rate, what I hope to have done here is just given you a flavor for how we have extended the solid phase disks from drinking water into being able to do some more polar analytes, also looking at getting into dirty water, such as wastewaters.

We think there is no reason in the world that you can't use solid phase extraction for a whole variety of samples. We are seeing people use them now for soils where they extract the soil with an organic solvent, filter it, water it out to the point where it is mostly aqueous, and then extract it with a disk.

We think that there are a lot of applications for the technology. I hope this has given you an introduction for the other papers you are going to see this morning.

That concludes what I have to say. Thank you very much for coming.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions? Good morning, George.

MR. STANKO: Good morning, Bill. George Stanko, Shell Development Company.

One of the things that is done in Method 625 and 8270 is that once you transfer your sample from the 1 liter container to the sep funnel, you actually rinse the inside of the container with your extraction.

MR. MARKELL: Yes.

MR. STANKO: Now, how do you account for recovering the material that is adsorbed onto the glass with your procedure?

MR. MARKELL: Good question, because it is a problem. You are right. If you have got things that are especially hydrophobic like polynuclears, those are the worst.

Basically, what we like to do is rinse the inside of the sample bottle and the reservoir, the filtration reservoir, which were the only two pieces of glassware the sample ever saw, with the elution solvent and then run it through.

Any other questions? Yes, sir?

MR. TELLIARD: Could you go to the microphone, please, and would you give us your name and your affiliation so that these people over here can take it down and won't break my knees?

MR. RAMARUMO: My name is Maurice Ramarumo from the Suny Research Foundation.

We have tried the C18 disks, and one of the things which we found was with Florisil, you tend to get...with Florisil in your sample, it will clean up chromatograms.

Now, in your method, you didn't mention that fact. I wonder if maybe that was just an oversight.

MR. MARKELL: I apologize, I didn't quite catch the question. Could you repeat it, please?

MR. RAMARUMO: Do you clean your samples through Florisil after extraction or not?

MR. MARKELL: Okay. So far, we haven't found any need to do it. Now, I don't know if that means you are accomplishing a cleanup or if simply the fact is we haven't tried any samples dirty enough yet. I think, in fact, one of the other speakers here has tried some real wastewaters, and I don't believe Florisil is necessary for those, either.

So, the answer is we haven't used Florisil.

MR. RAMARUMO: I was just sharing my experience that with Florisil, we got cleaned up chromatograms.

MR. MARKELL: Thank you.

MR. TELLIARD: Anyone else? (No response.)

MR. TELLIARD: Thank you.

Extending the Range of SPE Disks: Styrene/Divinylbenzene Sorbent

Craig Markell, 3M

Benefits of SPE Disks

- **Less Solvent Used**
- **Not Labor Intensive**
- **Faster Turnaround**

Method 525.1

- 47 mm C18 Disk
- Extract 1 Liter Sample
- Elute With 3 x 5 ml $MeCl_2$
- Dry and Concentrate

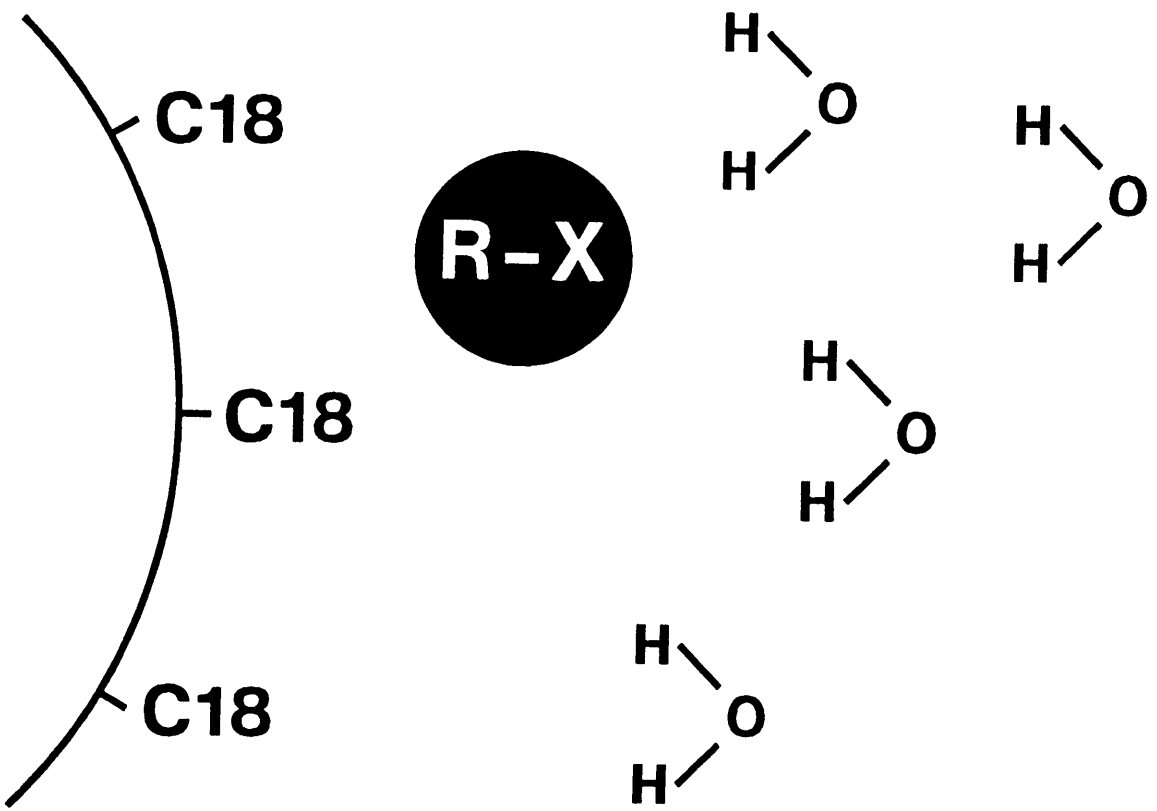
Method 525.1

Analyte Class	Average Recovery (Ave. RSD)*	
Phthalates and Adipates	102%	(5.5)
PAH´s	87	(9.4)
OCP´s and PCB´s	94	(8.4)
Other (4)	108	(7.5)

*n=9

B

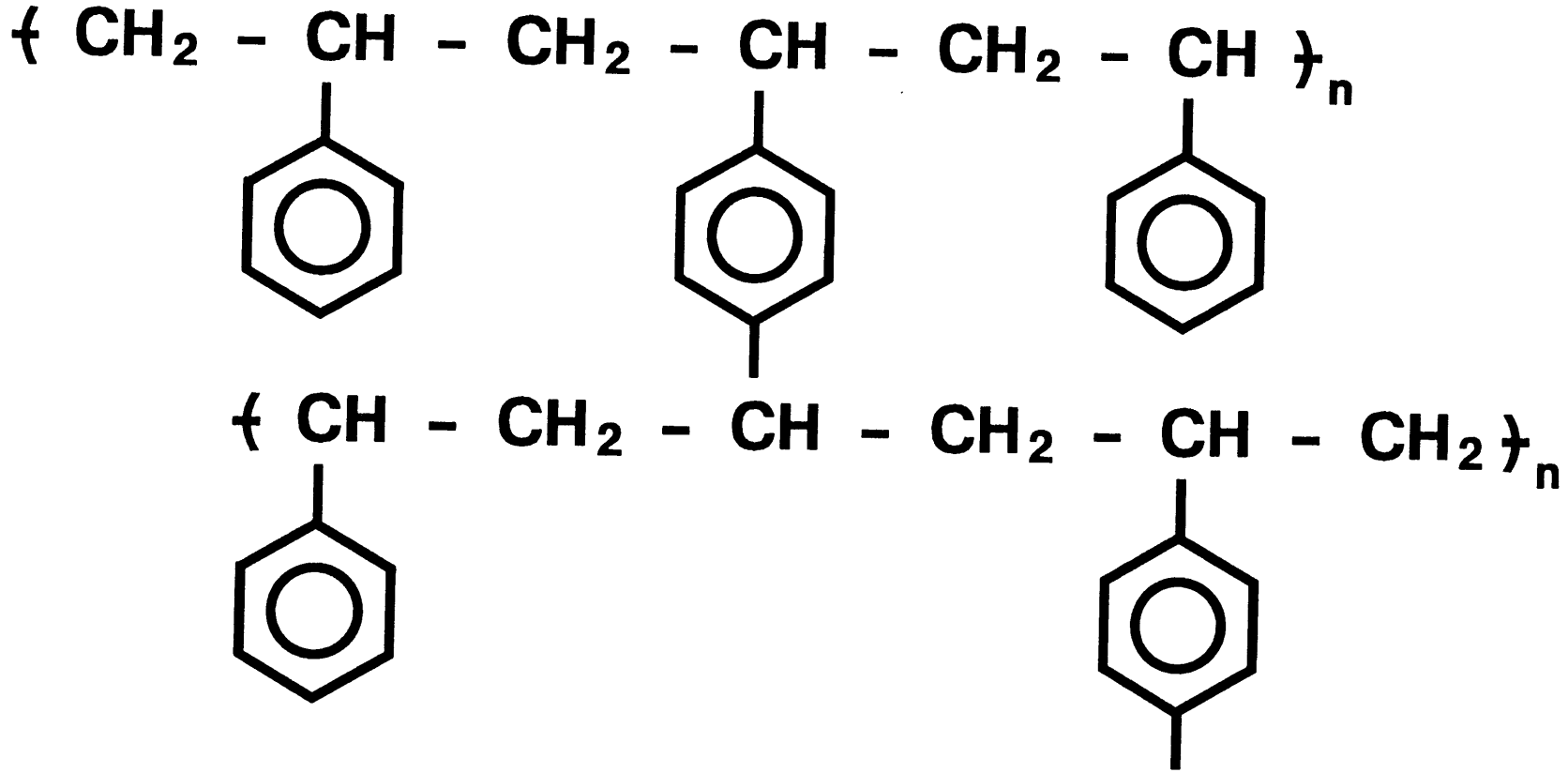
Solid Phase Extraction for Environmental Analysis - Hydrophobic, Reverse Phase Interactions



Priority Pollutant Phenols

- Phenol
- 2-Nitrophenol
- 4-Nitrophenol
- 2-Chlorophenol
- 2,4-Dinitrophenol
- 2,4-Dichlorophenol
- 2,4-Dimethylphenol
- 4-Chloro-3-Methylphenol
- 2,4,6-Trichlorophenol
- 2-Methyl-4,6-Dinitrophenol
- Pentachlorophenol

Poly (Styrene-Divinylbenzene)

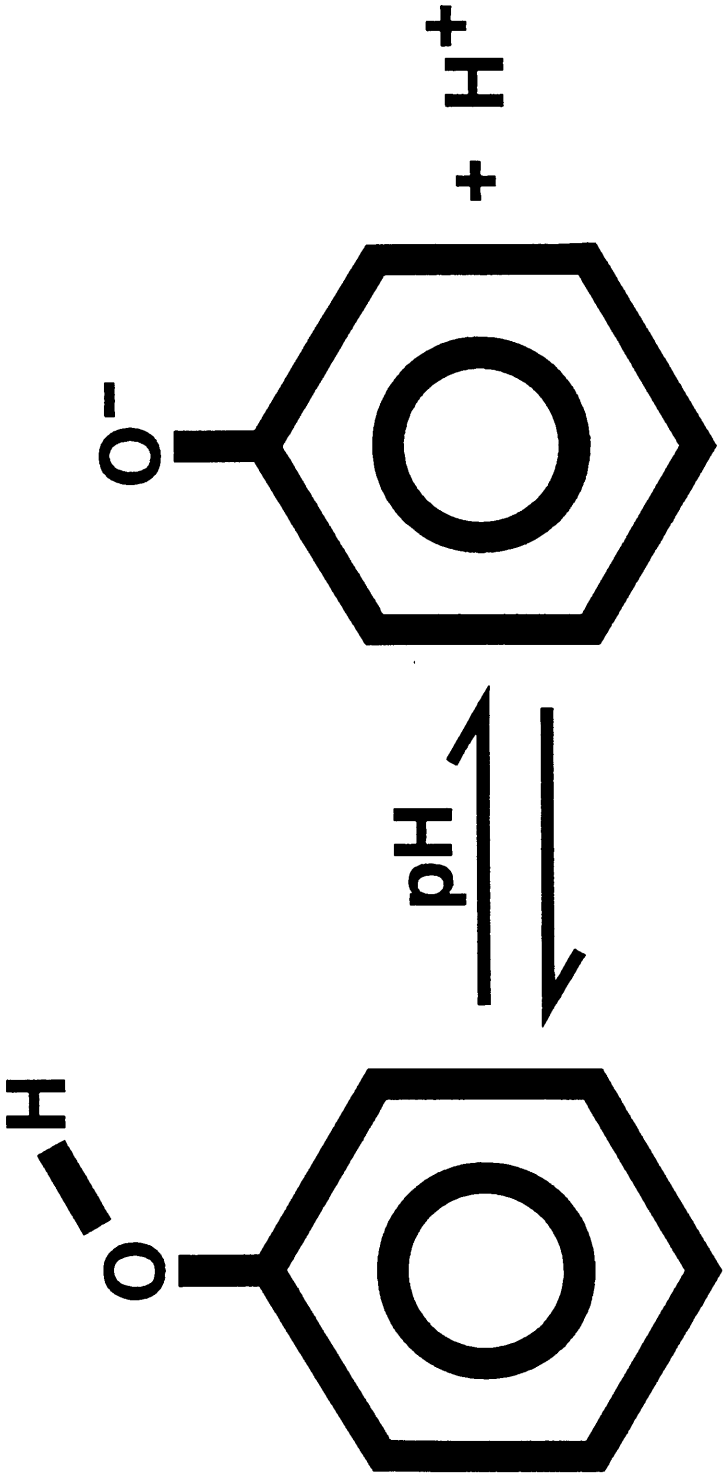


Sorbent Comparison

	C18 Silica	CH Silica	SDVB
Particle Size (μm)	8	8	8
Functionality	Aliphatic	Aliphatic	Aliphatic + Aromatic
% in Disk	90	90	80
% Organic	20	15	100
Wt. of Organic in 47 mm Disk (mg)	100	75	230

500 ml Results, % Recovery (RSD, n=3)

Compound	CH	C18	SDVB
Phenol	2.0 (16.6)	2.8 (7.3)	9.2 (13.6)
2-Nitrophenol	8.9 (8.2)	15.4 (5.2)	93.0 (2.7)
4-Nitrophenol	5.2 (6.1)	6.8 (5.8)	33.1 (12.9)
2-Chlorophenol	8.9 (6.9)	10.7 (5.2)	71.6 (5.9)
2,4-Dinitrophenol	0.8 (19.7)	1.6 (5.3)	22.2 (11.6)
2,4-Dichlorophenol	34.4 (12.6)	47.5 (4.8)	91.8 (0.6)
2,4-Dimethylphenol	21.6 (18.4)	37.1 (6.7)	95.9 (1.3)
4-Chloro-3-Methylphenol	35.7 (20.5)	60.5 (7.9)	100.3 (2.9)
2,4,6-Trichlorophenol	86.7 (9.3)	97.0 (1.4)	97.8 (1.6)
2-Methyl-4,6-Dinitrophenol	6.3 (11.0)	11.7 (4.3)	85.1 (1.5)
Pentachlorophenol	98.7 (1.1)	98.2 (1.8)	98.2 (0.1)


+
H+
O-
pH
H
O

Results - SDB Disks*

Compound	Recovery (%)		
	100 ml	300 ml	500 ml
Phenol	66	18	10
4-Nitrophenol	102	78	42
2,4-Dinitrophenol	100	105	101
2-Chlorophenol	90	101	99
2-Nitrophenol	92	98	96
2,4-Dimethylphenol	91	103	99
4-Chloro-3-Methylphenol	105	102	100
2-Methyl-4,6-Dinitrophenol	93	100	98
2,4-Dichlorophenol	96	98	101
2,4,6-Trichlorophenol	92	103	101
Pentachlorophenol	96	106	101

*Samples at pH 2

Results - 100 ml Sample - C18 Vs. SDB*

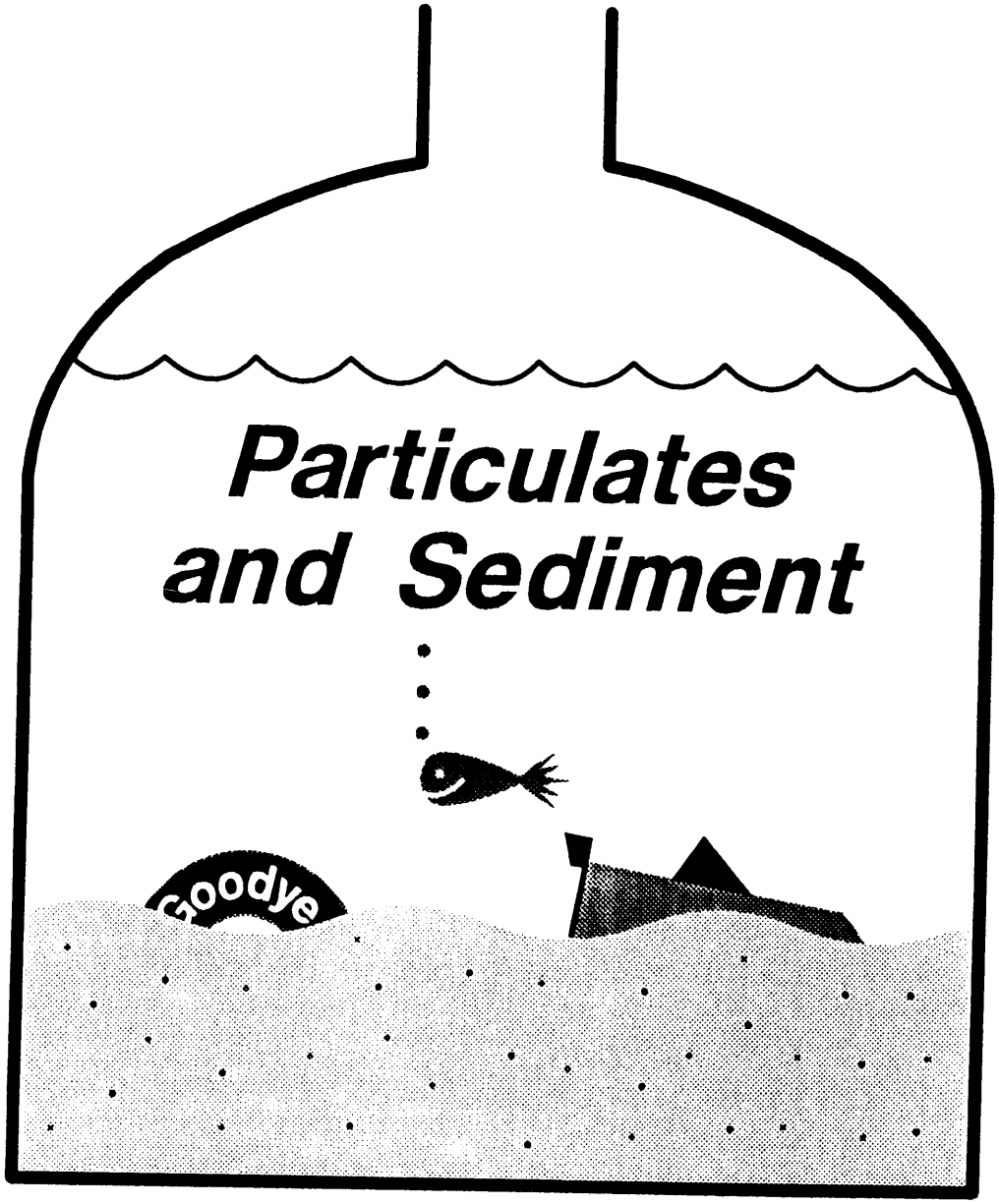
Compound	Recovery (%)	
	C18	SDB
Phenol	0	66
4-Nitrophenol	29	102
2,4-Dinitrophenol	80	100
2-Chlorophenol	47	90
2-Nitrophenol	79	92
2,4-Dimethylphenol	86	91
4-Chloro-3-Methylphenol	101	105
2-Methyl-4,6-Dinitrophenol	92	93
2,4-Dichlorophenol	90	96
2,4,6-Trichlorophenol	94	92
Pentachlorophenol	95	96

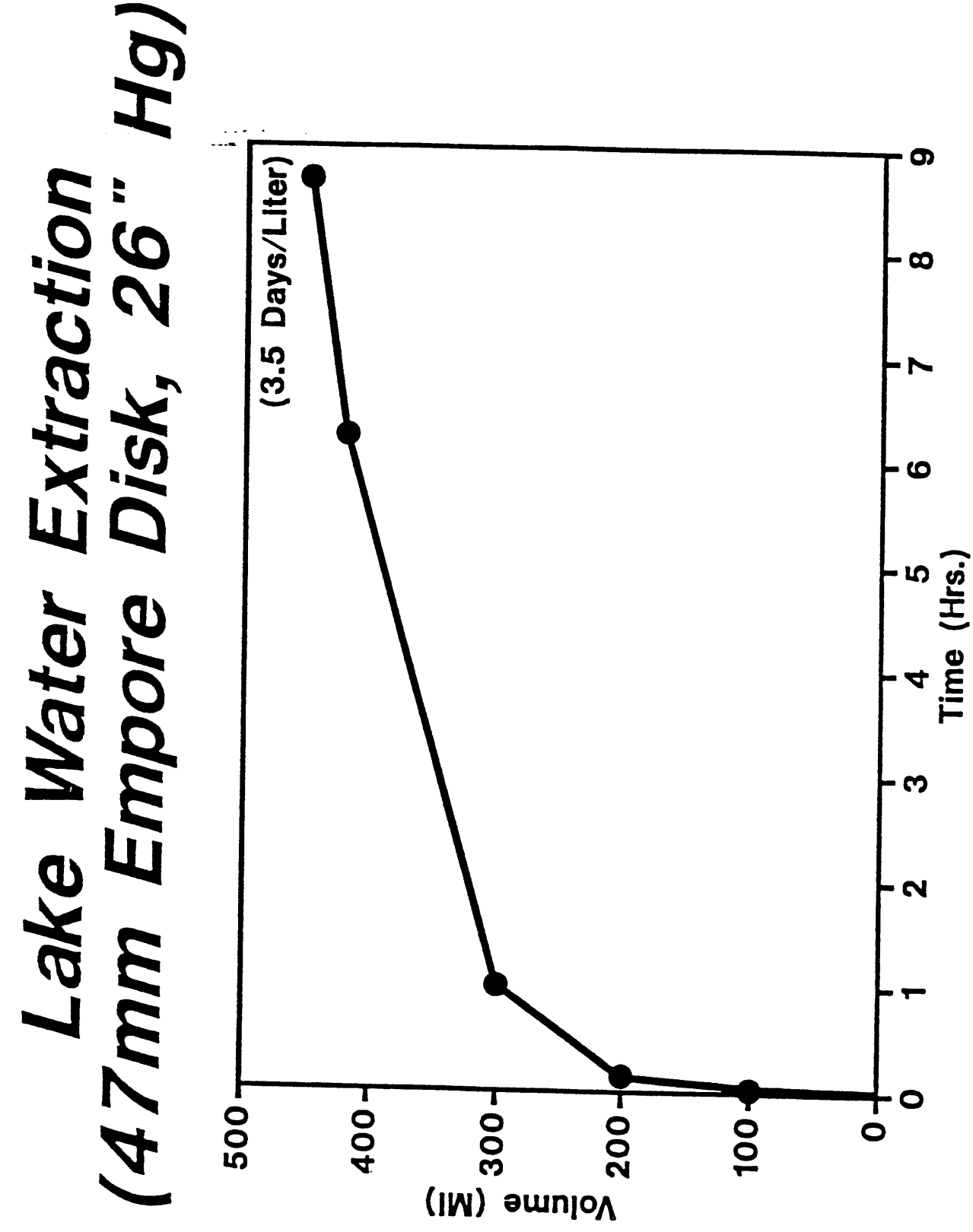
*pH 2

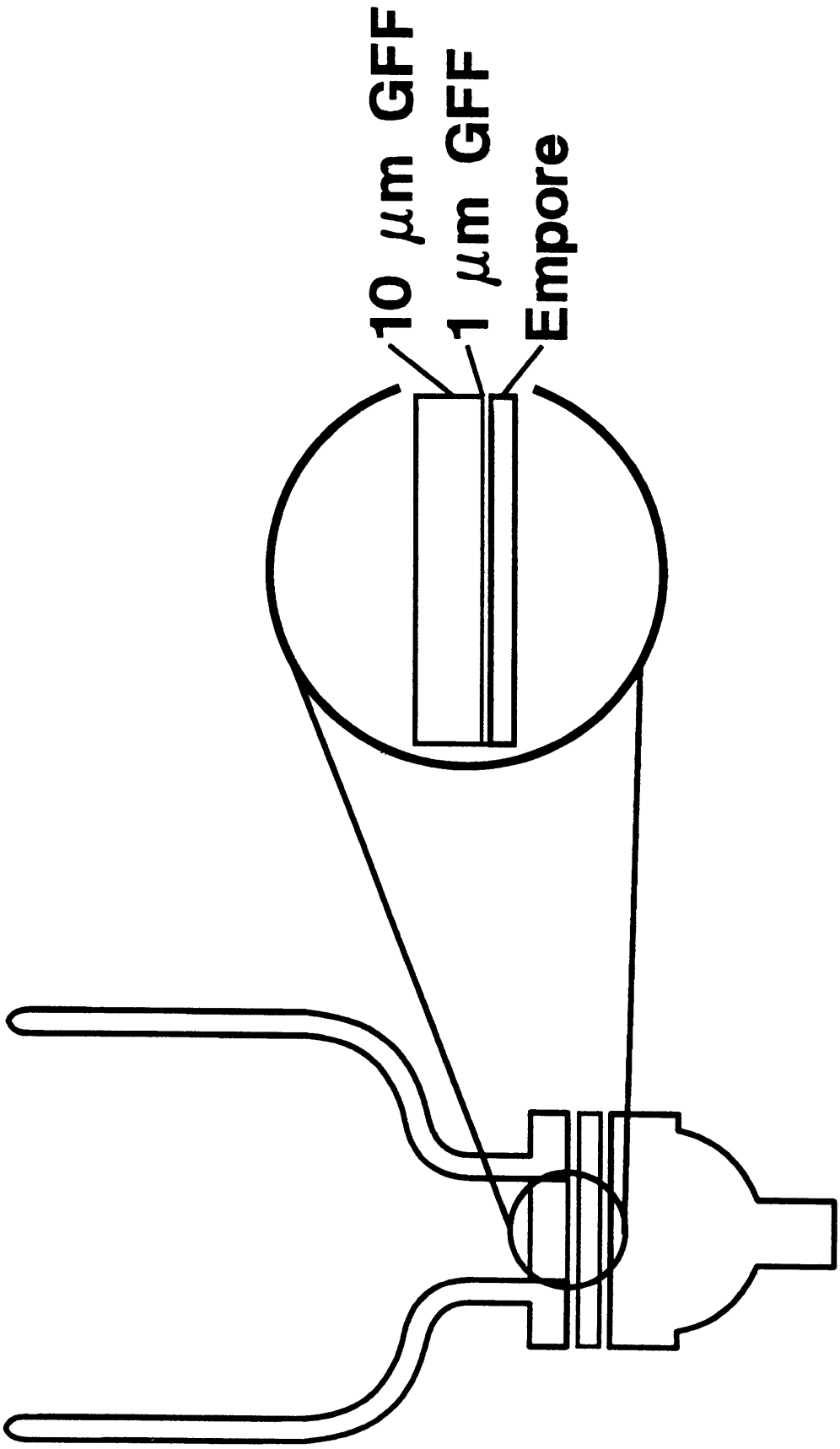
*Results - 500 ml Sample - SDB Disks**

Compound	Recovery (%)
Phenol	25
4-Nitrophenol	64
2,4-Dinitrophenol	99
2-Chlorophenol	96
2-Nitrophenol	92
2,4-Dimethylphenol	94
4-Chloro-3-Methylphenol	96
2-Methyl-4,6-Dinitrophenol	98
2,4-Dichlorophenol	98
2,4,6-Trichlorophenol	114
Pentachlorophenol	99

*Samples at pH 2, 10% NaCl


Particulates
and Sediment
Goodye


Lake Water Extraction
(47mm Empore Disk, 26" Hg)
(3.5 Days/Liter)
Volume (Ml)
500
400
300
200
100
0
0
1
2
3
4
5
6
7
8
9
Time (Hrs.)


10 μm GFF
1 μm GFF
Empore

	47mm	90mm
Active Diameter (mm)	38	81
Active Area (cm^2)	11.3	51.5
Flow Time/Liter (min)	10	2.2
Capacity (mg)	15	68
Void Volume (ml)	0.3	1.3
Sediment Thickness (mm)	2	0.4

Flow Time/Liter

	47 mm		90 mm	
	No Prefilter	With Prefilter*	No Prefilter	With Prefilter*
Reagent H_2O	8 Min.	8 Min.	2 Min.	2 Min.
Stagnant Pond	>8 Hrs.	>8 Hrs.	2 Hrs., 52 Min.	55 Min.
Lake 1	>8 Hrs.	>8 Hrs.	1 Hr., 33 Min.	39 Min.
Lake 2	>8 Hrs.	>8 Hrs.	27 Min.	21 Min.
Lake 3	>8 Hrs.	>8 Hrs.	15 Min.	15 Min.
River 1 Mississippi	>8 Hrs.	>8 Hrs.	20 Min.	9 Min.
River 2 St. Croix	7 Hrs.	5 Hrs., 57 Min.	11 Min.	9 Min.
River 3 Minnesota	4 Hrs., 44 Min.	4 Hrs.	12 Min.	6 Min.

*Prefilter Was Thin Glass Fiber Filter - Whatman 934-AH or GF/A. This Was *Not* the GMF Depth Filter Used Above, Which Probably Would Have Further Reduced the Times

MR. TELLIARD: Our following speakers are going to be talking about some environmental analysis that they have done using the solid phase extractor on some real world samples. Rick...and I am going to crucify this...Schrynemeeckers?

MR. SCHRYNEMEECKERS: That is close enough.

MR. TELLIARD: Good, Rick. He is from Enseco, and he is going to talk about some real world samples that he has done. Rick, would you like to come over?

MR. SCHRYNEMEECKERS: Good morning. I appreciate all you guys being here this morning.

I wanted to make a few acknowledgements before I get started this morning. I wanted to thank the folks at 3M. We have spent a lot of time over the last year working closely with these people and have developed a great deal of respect for them, and they have been instrumental in the development of this data.

I would also like to recognize Brett Vandelinder from SPL Environmental Laboratories who couldn't be here today. Mr. Vandelinder was instrumental in this study.

As we have seen the environmental market mature, we have seen the price per sample go down. We have seen the deliverables per sample go up. And all of this has made it very difficult for laboratories to remain profitable.

The environmental aspects of our business have come full circle.

Issues such as reusing solvents, redistilling solvents, recycling solvents, eliminating certain solvents like benzene and freon, and also the reduction of solvents has become a major concern. All of these factors are taking an active place in the environmental laboratory today.

Fortunately, innovations in technology are helping us deal with several of these issues, and one of those innovations is solid phase extractions. Obviously, solid phase extraction has been around for quite a while and is nothing new. It has been around for over 15 years, so why hasn't it been used previously for environmental analyses?

First of all, plugging has always been a significant problem. Even relatively clean samples have caused excessive plugging, using previous cartridge technology.

Also, very low recoveries for polar analytes has been a problem.

And the third issue which is more difficult to deal with, is organic analytes absorbing to particulates, consequently, adequate recovery of those compounds can be difficult due to reductions in extraction efficiencies.

So, how do changes in solid phase extraction technology address some of these issues?

The first issue, plugging causes the most concern. Plugging has been substantially reduced by moving to 90 mm solid phase extraction disks.

One of the things you see as you double the size of the disk you actually get a four-fold increase in the surface area that is available for the extraction process. The surface area of the disk is what allows you to perform the extraction on the sample.

I won't spend time talking a great deal about the low recoveries of polar analytes, because Craig has already stolen part of my talk, and I will discuss that with him later, but the third portion is analytes on particulates, and this is really a tougher issue to deal with, because if you look at the older style of solid phase extraction technology you have the column type beds, which have a very small surface area.

The problem with a small surface area is that you develop a mono-layer of sediment or particulates after only a few milliliters of sample. Consequently only a very small percentage of the particulates come in contact with the extraction media and are involved in the extraction process.

If the particulates and the organic material do not come in contact with the extraction media, they cannot be extracted. They will not be separated from the matrix.

Data indicates 200 ml of sample may elude through a 47 mm disk in about 12 minutes. 300 ml requires over an hour. 400 ml requires over 6 hours while 500 ml requires up to 3.5 days.

Additional studies indicate that a 47 mm disk requires approximately 20 minutes to elute deionized water. 90 mm disk require only 2 to 5 minutes to elude 500 ml of deionized water. Now, when you consider approximately 5 minutes for a liter of water, you are looking at some very acceptable times for extraction of your samples.

Let's talk about the particulate issue.

As this slide indicates, the typical sample contains more particulates than analytes of concern. As a result the older style of the column type packing becomes overwhelmed with particulates.

If you get several layers of particulates over your media, then the problem becomes every particulate above that monolayer doesn't come in contact with the media. If it doesn't touch the media, it is not separated or extracted from the matrix that you

are looking at.

You move to the 90 mm disk, you have a tremendous amount of surface area. With that additional surface area, you now have the ability to bring all those analytes and all those particulates in contact with the filter media. The result is a tremendous increase in extraction recoveries.

Let's move from the theoretical into the laboratory. If you are doing Method 625, you are going to take a liter of sample, adjust the pH, and extract with methylene chloride using a separatory funnel or continuous liquid-liquid extraction.

You will place the condensate K-D, heat it and finally take it down to 1 ml.

By the time you rinse your glassware and concentrate the sample, you are going to use anywhere from 400 to 1000 ml of methylene chloride to extract the sample.

Due to the large final volume, it will be necessary to heat this solvent to reduce the volume.

Here is the system we came up with for the disks. We started with 500 ml of sample. We adjusted pH to 2. We added salt so that we had a 10 percent sodium chloride solution, to change the ionic strength of the solution. Prior to use, all disks were subjected to a prewash with methanol, acetone, and a final rinse with methylene chloride which was the extraction solvent.

You elute the sample of 500 ml through the disk. The disk was then eluted with three 10-ml portions of methylene chloride, and taken to a volume of 1 ml.

A couple of items to note here. One is when you take this sample down, you now have 30 ml of solvent. You don't have 300 or 400. That makes a difference, because now you can blow down the extract. You don't have to heat the condensate, because you don't have an excessive volume of solvent.

This becomes important when considering some of the very volatile compounds, such as 1,4-dichlorobenzene or n-nitrosodimethylamine.

Another important point is the fact that you have a tenfold or more decrease in the amount of solvent that you are using. The solvent volumes seen in the slide are actually approximate volumes of solvent required for this extraction process.

For our study, these are the analytes that we decided to use. We decided to use the surrogates and the matrix spike components according to method 625 for several reasons. One they were easily available and two, the broad range of compounds gave a good representation of all the constituents encompassed in Method 625.

For example, you have some of the very volatile compounds like 1,4-dichlorobenzene. You also have the large PNAs like ace-naphthene and pyrene, as well as the acids. The acidic constituents include the problem child phenol as well as the large molecule of pentachlorophenol. So, we have a wide range of representative compounds that we are investigating in this select group of analytes.

Now, these are the preliminary studies that we did trying to hone our technique and find out what worked the best. It is a little difficult to read, but we were using different volumes and different elution orders. We used some with salt, some without, and here is what we found.

I should say this now. For all studies we used a glass fiber pre-filter.

In the first example, we used a single disk. We used a 1 liter sample, and performed two rinses with two 15 ml portions of methylene chloride.

It took approximately 3 minutes to soak the sample. In other words, after we had eluted the water through the sample, we allowed the extraction solvent of methylene chloride to sit on top of the filter for approximately 3 minutes to soak before we pulled that through using vacuum.

If you look at some of the recoveries for the base neutrals, you will observe excellent recoveries. Nitrobenzene 72 percent, trichlorobenzene 66 percent, and excellent recoveries on the remaining base neutrals constituents, which was very encouraging.

Similar results were observed for many of the acids. If you look at the water solubility and the distribution coefficient of phenol and 4-nitrophenol, you expect to see the poor recoveries.

We then went with a single disk and three 10 ml elutions with a 5 minute soak. We saw moderate improvement in the phenol and the 4-nitrophenol recoveries, and we saw a marginal improvement also in some of the base neutral compounds as

well, if you look at terphenyl-d14, ace/naphthene, pyrene, some additional constituents.

We used two 15 ml effluents, and we also used three 10 ml effluent or washes in figures 3 and 4. You really don't see a tremendous difference in these two slides. You do see an increase in the recovery of phenol and 4-nitrophenol, with a substantial increase in the recovery of 4-nitrophenol.

We then used two disks. We thought if one disk works well, maybe two disks will work better. At this point we were primarily focusing on the phenolic recoveries with this approach.

We then decided to go to two disks, and used a 10 percent sodium chloride solution in run 5, and you can see an increased recovery for phenol as well as 4-nitrophenol and 2-chlorophenol.

If you look at the base neutral recoveries, you really don't see a tremendous difference in any of these runs. You basically are getting a quantitative recoveries at this point.

In the final experiment we went with two disks, three 10 ml elutions, a 5 minute soak, and used 500 ml of sample as opposed to a liter. Using these conditions we obtained the highest recovery of the phenolics with a 43 and a 53 percent recovery of phenol.

If you also look at 4-nitrophenol, and we obtained almost a 100 percent recovery.

During the rest of the study, though, we finally decided to go to the one disk configuration even though we got the best conditions using two disks, because it would be so cost prohibitive to use two disks in this technology that we felt that that just wasn't going to be a viable alternative, especially when I found out from 3M how much they were going to charge for the disks.

Well, the issue comes up if you are going to use 500 ml of sample, from a laboratory point of view, the very first question that arises can you obtain the same detection limits when compared to a one liter sample with continuous liquid-liquid extractors. Indeed, you find that that is what you get.

We used 500 ml of deionized water. You see the spike amounts of 12.5

micrograms per liter for the base neutral compounds and 25 micrograms per liter for the acidic compounds. We attempted to spike at approximately five times the estimated detection limit.

We did seven replicates. We determined the standard deviation and then multiplied student "T" values times the standard deviation to get the method detection limits that you see here.

As you can see, excellent detection limits were obtained for the base neutral compounds. You are talking about 1 to 2 parts per billion for many of the compounds and 3.5 to 5 parts per billion for some of the other constituents.

When you look at the results for the acidic compounds, you also see excellent lower limits of detection. Phenol shows an MDL of 3.5 parts per billion. The highest detection limit observed was tribromophenol and pentachlorophenol.

When I looked at the chromatograms, the elevated detection limit for the acidic compounds seems to be more a function of the chromatographic conditions than the extraction process, because these were analyzed on an older column that had been used for extensive analytical runs in a normal environmental laboratory. The analytical column had been cut several times. The chromatogphraphy wasn't crisp and clean like you would really hope for.

So, I think the elevated acid detection limits are more a function of the chromatographic conditions as opposed to the extraction process.

Well, where do you go from here? This is all well and good, and what we have seen so far is really encouraging from our with deionized water. Results indicate that we had resolved many of the initial problems that we had previously seen, but all of this is just fluff if you can't take it to real world samples and start analyzing and extracting some samples with particulates and sediments.

So, these were the sources of the field waters that we chose to analyze, because these were sources that we commonly had available in the laboratory. We used POTW water. We used pesticide manufacturer effluent from the effluent from a pesticide manufacturing plant.

We looked at paper and pulp effluent. And we also looked at some

groundwater samples from groundwater monitoring wells from a petroleum refinery around the Baytown/Port Arthur area in Texas.

What we decided to do was we use the same matrix spike and surrogate compounds that we had used previously, so that we would be comparing apples to apples.

Of course, the first thing you are looking for is the possibility of reduced recoveries. The experiment must ascertain whether reduced recoveries were due to matrix effects or the extraction process?

So, we designed the experiments so that every set of samples that we did by disk, was also extracted by continuous liquid-liquid extractions.

We started with the DI samples, and this is some of the apparatus that we used, very simple, straightforward, nothing fancy. You can use a manifold for this process. These are the small 47 mm disks.

But, basically, you can see the samples that typically come in the 1 liter jars are very easy to use, because you simply take off the screw trap, turn it upside down, pour it into the reservoir and set it on top of the glassware.

So, you don't have any problems with...it is not manually intensive, and you can prepare a manifold system so that you can be extracting four, six, eight, ten samples, as many as you prepare an adequate manifold system for yourself to use.

Let's look at the first extraction process using continuous liquid-liquid extraction. LLE is liquid-liquid extraction, and then we have the disk extractions here.

All samples were done in quadruplicate. And one small note. It says that we spiked at 200 and 400 on the bottom corner. Actually, we spiked the base neutrals at 100 micrograms per liter, and the phenolics or acidic compounds were spiked at 200 micrograms per liter, according to the methodology.

What you see here is that for the acidic compounds...I mean, for the base neutral compounds, you got excellent recoveries in the 70 to 100 percent quantitative range for all the base neutrals. Really looked exciting for that. We were very encouraged here.

For the phenolics or the acidic compounds, for the continuous, obviously,

you got excellent recoveries. For some of the phenol recoveries and 2-fluorophenol, the recoveries were not as well, but you get into the 2-chlorophenol, the 4-chloro, 3-methyl and look at those recoveries, and you are talking in the 80 percent recovery range which was excellent for these samples.

What about real world samples, though? Here is the POTW water. Now, if you look at this, in the base neutral compounds, we actually got better extractions using the disk than we did using the continuous liquid-liquid extractors.

This really surprised us, but we had done the samples in quadruplicate, and you see that the RSDs for many of the base neutrals for the liquid-liquid, you are talking 17 percent, 18 percent. While a little bit high, they were reproducible, so it must have been a function of the matrix itself.

So, the disk technology actually worked better in this case for the base neutrals, and we got decent recoveries for the acidic compounds, and, of course, you still have a problem with phenol.

Let's look at the pesticide manufacturing plant. These samples had quite a bit of particulates in the samples. We got excellent recoveries for the base neutral compounds and similar recoveries for the acidic compounds.

If you look at 2-chlorophenol and larger, you are 93, 90 percent, 104 percent for pentachlorophenol. You have some excellent recoveries going on here.

By the way, if you look at pyrene for the liquid-liquid, you get 135 percent recovery which shows you that if you use liquid-liquid extractions, you can actually general target compounds which is a negative for continuous liquid-liquid extractors.

Let's look at the petroleum refineries. Now, these samples had a lot of particulates in them. These samples were not clean samples, and we had a little bit of problems with these samples. We were a little bit worried about what the results would look like.

But you look at the base neutral results, and you have excellent recoveries in the 85, 95 percent range for many of them, 100 percent for nitrobenzene-d5. You look at the acid compounds, again you are looking at 94 percent for 2-chlorophenol and the typical recoveries there.

But if you also look at some of the recoveries for phenol and 2-chlorophenol in the liquid-liquid, you are only getting approximately in the 80s and upper 80s for those constituents as well.

Now, the next sample we are looking at is the samples from the paper and pulp industry. Let me tell you about these samples. These were some nasty, horrible samples. These samples had all kinds of debris floating in them. They looked like watered down chocolate milk. These were nasty samples. We were really worried about what we were going to see here.

But we were very pleasantly surprised. The base neutral recoveries, again, were excellent, basically comparable to the liquid-liquid extractions. For the acids, you even note some reduced recoveries for the acids even in the continuous liquid-liquid extractors.

And here we have got 103 percent recovery for tribromophenol, excellent recoveries for the 4-chloro, 3-methylphenol and those guys, and for the phenol, of course, we have got the typical 20 percent recovery which was to be expected.

But believe me, if you had seen these samples, you would have been happy, first of all, to get anything through a disk and to recovery anything. So, we were very pleased with the results that we did.

I also want to tell you for these extractions on these compounds, we didn't pour the water samples on top of the disk, spike it, and then pull the water through there quickly. We actually took the 1 liter containers, we spiked it into the water, let it sit there for approximately 15 to 20 minutes so that you could have adhering to the particulates, any problems that would go on in the matrix.

We didn't just pour these real world samples in the filter apparatus and spike it as it was going down through the filter. That probably would have helped our recoveries, perhaps, but we didn't feel real comfortable with that.

Here are the flow times that we saw for many of these. Now, for the POTW water and all the others, we got approximately 1.5 minutes to 2 minutes for all these samples. The paper and pulp chocolate milk sample was only 9.5 minutes, and that is for 500 ml of sample. Let me tell you, for the paper pulp sample, we are excited

we got anything through the filter, and we were really surprised when it only took 9.5 minutes.

These times that you see are the average of the four replicates that we did, so it wasn't that we took the best time that we got out of each sample. This is the average that we obtained.

When you do these studies, you tend to be overly harsh and overly critical, I think, when you evaluate your data. If you look at this data that you see on the screen, what you are looking at is the average recovery that we got using reagent water for the compounds, some of the compounds that we did.

On the right are the acceptable criteria if you are doing method validation according to Method 625. As you see, every one of these, if you are using disk technology, every one of these samples would pass that criteria. All of the base neutrals would well be within the criteria, and even phenol would be well, not well within, would be acceptable according to Method 625 if you were trying to validate that method.

The reason I bring that up is, obviously, these windows were developed when some of the analyses first began years ago, and that is to show you that when you even first started with continuous extractors and liquid-liquid extraction years ago, you had a wide range of variability in the method.

I think you focus too much on the negative aspects, and if you look at this, only one of the recoveries was poor out of all these samples, and even that was within the acceptable limits as approved by the methodology itself.

In conclusion, we were really very pleased with the study and the results that we got. We had excellent recoveries on almost all of the compounds. The relative standard deviations were very small.

If you noticed on the slides, typically, you got much better reproducibility with the disk technology than you got with the liquid-liquid extractors even. Typically, the reproducibility in the studies for the disk was in the neighborhood of 5 to 8 percent where you are looking at 10 to 15 percent with the liquid-liquid extractors.

The MDL studies were actually better. You got better detection limits with using a smaller volume of sample, and for everything except phenol and perhaps 2-

fluorophenol, you got comparable results as with the liquid-liquid extractors.

There is a significant reduction in the solvent usage. As opposed to using 400 to 1000 ml of solvent, you are now using 50 ml of methylene chloride, and when you are talking about trying to reduce the cost in your laboratory and trying to work in conjunction with the EPA to reduce the solvents that you use and the recycling efforts, that is a significant difference.

When you do liquid-liquid extraction, you are talking 18 hours to extract the samples, and you are talking probably a couple of hours before you get the samples set up for K-D and concentration.

With the disk technology, you are looking at an hour. The longest sample took us a little bit less than 10 minutes to extract, and you are looking at a smaller volume to concentrate. So, it takes much less time to concentrate the sample, and you don't have to heat it which is a tremendous advantage when you look at some of the very volatile base neutral compounds that are of concern.

Also, we did a single extraction of base neutrals and acids at a pH of 2 without the problems inherent of adjusting the pH and worry did I adjust the pH on these samples and having to go back and re-extract from time to time, because in the midst of doing this, you forgot to adjust the pH during the course of your extraction process which is much easier.

Also, I think you need to realize not only did we accomplish these things, but where we started from the study, when we started this study, we didn't know if disk technology or even solid phase technology would work. So, we had to overcome things such as plugging factors. We had to consider did we overcome things like channeling, did we overcome the issues of the particulates issues.

And as you look, even in these real world samples that were heavily laden with particulates, we overcame all of those issues, and the only problem child we had was phenol.

The final comment I would like to make is we have come a long way with the solid phase extraction technology in the last year. Some of the things I think you need to realize, too, is the technology works extremely well for everything except the

very water soluble compounds, and I think that is going to be a function of just finding the right solid phase extraction material that can retain some of these more water soluble or polar compounds.

There is some great evidence on the market already that just preliminarily gives very high recoveries for phenol, but that is going to be a function of the manufacturers and do they really want to promote or resolve some of the technical issues that are associated with that.

Also right now, we are looking at solid phase extraction for total petroleum hydrocarbons using C^{18} disks because of the problems associated with freon and Method 418.1 and some of the other GC methods, and we feel like the disk technology will be very amenable to those analyses as well.

Do I have any questions? That ends my talk. Can I answer any questions for anybody?

QUESTION AND ANSWER SESSION

MR. JUNK: Greg Junk, Iowa State University.

I think, first of all, the speaker should be commended for carrying methods development beyond where many laboratories carry them, doing the test with reagent waters and then getting out and doing it with real waters, and then doing a comparison of the liquid-liquid extraction with the solid phase extraction with real waters.

The third step in method development, though, is to not spike the water with the reagent analytes as you did with the 20-minute aging but to take some real world samples that have real compounds like PAHs in it and then do liquid-liquid extraction and then solid phase extraction.

Have you done in your laboratory any of what I would call the third step in true analytical methods development?

MR. SCHRYNEMEECKERS: No, we haven't, as a matter of fact.

All of these samples that we analyzed were samples that had come into our own laboratory, and we were hoping that there would be naturally occurring constituents within the water itself, and that was one of the reasons...I didn't show it up here, but we did a blank, obviously, with every sample. We did no blank substraction in any of these analyses, and we also just did a blank where we looked at the sample. We did a distilled blank with the samples.

We also did a sample blank, because the thought occurred to us if we had naturally occurring constituents in the sample that that would skew our results, but, unfortunately, none of these samples that we chose had any naturally occurring constituents in them.

I mean, I think that is an excellent point, and that is obviously where you want to go next. You want to find some real world samples that have contaminants in them and then move on to expand the scope of your spiking study as well.

Yes, sir?

MR. MCCARTY: Harry McCarty from Viar and Company.

I echo the comments of the last commenter, a very nice piece of work.

The thing I am concerned about is the whole discussion of detection limits.

What you did was read two-thirds of the MDL procedure. If you read 40 CFR Part 136, appendix B, pages 198 and 199, which is where EPA has the MDL procedure, as you pointed out, you spiked at 1 to 5 times the estimated detection limit. The last third of the procedure is where your MDL is 1 to 5 times...within 1 to 5 times...your spiking limit within 1 to 5 times of your MDL.

Yours clearly weren't. Some of yours were 10 to 15 times. It means you spiked too high. 12.5 and 25 are too high a spike, particularly for the 1.5 kind of levels that you were showing, the 2.5.

Do you have any plans to go back and redo that at a more appropriate spiking level so that you get MDLs that look a lot like what you would expect?

MR. SCHRYNEMEECKERS: Right. That is as good point, and no, we didn't have the ability to do that at the time. We had considered doing that.

The reason we chose those levels is because we really had no idea where the detection limits were going to be. So, we typically...wetried to error a little bit on the high side purposely for that reason.

If we were to do the studies over again, obviously, we, having some base data now, we would actually go down and spike at a much lower level.

MR. MCCARTY: Not knowing is fine, and the procedure does give you a suggested way to account for that which is you start by taking two of those aloquats and seeing what happens.

MR. SCHRYNEMEECKERS: Right.

MR. MCCARTY: But, you know, there is that problem that if you spiked at 100, boy, you could have come up with some detection limits.

MR. SCHRYNEMEECKERS: You could have some great detection limits.

MR. MCCARTY: Yeah. Nobody is going to believe it, necessarily, but I think at these levels, I think you do need to go back and do that again.

MR. SCHRYNEMEECKERS: No, that is an excellent point, and I appreciate that comment.

MS. FAVERO: My name is Toni Favero, and I with the North Shore Sanitary District in Guerney, Illinois.

Can you tell me if the problem with the phenol recovery is being addressed and if EPA favors the obvious benefits of the disk extraction over the reduced recovery for phenol?

MR. SCHRYNEMEECKERS: That is an excellent question. Part of the reason I showed the slide on the various disk setups that we did...and we even did more studies than I showed up there, but I didn't want to bore you any longer than I already was...the 50 percent recovery was the optimum recovery that we were able to obtain using either C^{18} or styrene-divinylbenzene disks and using the duplicate, the disks back to back. That was the optimum recovery that we were able to obtain using any type of set-up or configuration.

In terms of where it is going, we found, no matter what we did, that was the best that we could get. So, we really stopped doing any further studies with the styrene-divinylbenzene disk.

I think, as I somewhat alluded to, to be able to enhance that recovery, you are going to have to do a few things like basically change the basic set-up of the solid phase extraction material that you are using. There are papers out that show enhanced recovery for the phenolics, but, unfortunately, those give up some of the recoveries of their other constituents like some of the base neutral constituents that you look at.

I know that 3M has done some very preliminary work using different types of solid phase extraction material and have gotten in the 85 percent range for phenolics, but that is so preliminary that, you know, I just don't...I don't think they even know at this point in time where they are going to go with that.

In terms of what the EPA deems, the second part of your question, how they view the tradeoff, I really wouldn't be able to answer for the EPA on that issue. That was something that Bill or maybe Harry could answer for you.

MR. TELLIARD: We have used and have recommended for use solid phase extractors for drinking water methods. We are presently looking at implementing these techniques based on data we are getting like what you saw today for

wastewater methods, particularly as it relates to, say, compliance monitoring or discharge permits.

We haven't got a complete data set yet. We have done some additional work, and Merlin is going to speak about additional industrial work we have looked at in developing one of our regs which is a pesticide reg which you will hear about today also.

So, we are close, but we are not over the wall yet as far as totalling endorsing it for wastewater.

MR. SCHRYNEMEECKERS: I think one of the things you have to realize, too, that two years ago, we were at the point where we couldn't even get samples through the filter. A year ago, we sat down and several people talked with 3M, several laboratories, and with industry input, we came up with variations in disk technology that allowed us to really get past a major hurdle.

So, all the work that you are seeing here today over the last year has really been some very exciting work and some really forefront work. So, a lot of the questions that you are asking, the natural next step is, obviously, what the laboratories are pursuing, but they are just really...you are seeing the data as we come out with it, basically.

So, many of the next steps that would naturally occur, we are just now getting to that, believe it or not. So, I mean, that is an excellent question.

Yes, sir?

MR. DAWSON: Tom Dawson, Union Carbide.

You guys were real good comparison on the differences between the total times for extraction for liquid-liquid versus solid phase.

MR. SCHRYNEMEECKERS: Yes, sir.

MR. DAWSON: Would you comment on any differences in actual technician time required for the two methods, that is, people saving times?

MR. SCHRYNEMEECKERS: Actually, we didn't do any, you know, mapped out studies, but we did notice even still a significant time. Obviously, with setting up the continuous liquid-liquid extractors, it is a time-consuming process. You adjust the rates, you transfer all the solvents, you are rinsing all the continuous

liquid-liquid extractors.

And I guess one thing I didn't point out here is that the cleaning of this glassware, such smaller glassware, it is much easier to clean, it is much faster to clean, and it is much faster to set up. So, you do get a significant reduction, even in your technician time.

I think one of the things that we saw also with the improved reproducibility is that you get a reduction in the variability due to technicians as well.

And the other issue I wanted to point out is we did most of our studies with just one or two glassware set-ups, because we weren't using it for high production needs, but it is very easily amenable to setting it up with a manifold system where you can set up quite a few apparatuses, and you just take the 1 liter bottle, sit it on top of the glassware, and let it drain in, and then turn on the vacuum.

So, it doesn't take a whole lot of effort, and it is really a nice, efficient method in that means.

MR. TELLIARD: George?

MR. STANKO: George Stanko, Shell Development Company.

Your work and the previous paper both had two different size filters, the 45 and the 90.

MR. SCHRYNEMEECKERS: Right.

MR. STANKO: My question is more directed towards 3M. Are we at the optimum size, or could we see a 150? And if we are not at optimum, how long do you think it is going to take before we get there?

MR. MARKELL: Well, you can always go bigger, but the question is, what is the magic between the particulate loading size and your sample.

MR. TELLIARD: Craig, they might not be able to hear you. You might want to go...

MR. MARKELL: Oh, I am sorry. Can you hear? No. I have got one of these famous Minnesota colds.

Right now, what we have done is we have looked at a number of different

samples on the 90 mm. Now, why did we choose 90 instead of 95? Because the apparatus is out there. You don't have to make custom apparatus.

It seems as though for a 1 liter sample, 90 mm is pretty good. It works for most of them. Rick used a half a liter, but we have gone up to a liter in many of them.

Certainly, they could be made bigger, and, of course, there is a cost impact there, a significant cost impact, and there is also an apparatus impact. There is really no currently available glassware. If you go to stainless steel or something, you have got all kinds of problems with interactions with the analytes.

So, that is kind of a roundabout answer to your question. We think 90 is pretty good for 1 liter samples.

MR. STANKO: My question was for the benefit of the laboratory industry, because if we are going to develop standard or EPA-approved methods based on this technology, we would probably like to have the optimum thing when the method is actually developed.

MR. SCHRYNEMEECKERS: You know, I think one comment in concern to your question, George, is that these were actual samples that were randomly picked to try to get as wide a variety of samples as possible, and for 90 mm disks, we got, on the average, about a 2 minute extraction process. You are not going to get a whole lot better than that. I mean, what is the difference between 2 minutes and, you know, 30 seconds?

The issue in terms of going to a larger disk I don't think is going to be that much of a concern, because, obviously, every technology is not amenable to everything. If you look at separatory funnels, you can't use separatory funnels for every single sample, and there obviously will be samples that may not be amenable to solid phase extraction.

As Craig made a mention of, samples that are stagnant ponds that have a tremendous amount of biological activity, those are going to be your troublesome samples, and I don't think even going to 150 mm disk is going to be a big help with that.

MR. TELLIARD: Question?

MR. REDDY: My name is Sushakar Reddy from Shrader

Labs in Detroit, Michigan.

I have a concern about these phenol recoveries. Did you do any more work to find out where these phenols are lost like in the filtrate or...

MR. SCHRYNEMEECKERS: Well, actually, you know, Craig may know more about this than I do, but I imagine what they are doing is they are just staying in the water and going straight through the filter. They are going through the filter, and then they are coming right out the other end of the filter.

Because the problem is the partition...if you look at the water solubility of phenol and 2-fluorophenol and also the partitioning coefficient between that and the styrene-divinylbenzene, it becomes crystal clear that it is just not favorable for the phenol to stay on the disk itself. It actually has more opportunity and it is easier for it to stay in the water and pass through the disk, and that is why it has such a small break-through volume. It is actually coming out the other end.

Isn't that correct, Craig?

MR. MARKELL: That is our guess. There is a possibility that you are seeing a little volatility from something like phenol where it is actually going into the headspace above your sample, but I think Rick is right. It is probably water solubility.

MR. TELLIARD: I have one question for Rick. That pulp and paper sample, that wasn't an effluent sample, was it?

MR. SCHRYNEMEECKERS: No, no, it wasn't.

MR. TELLIARD: Thank you. Thank you very much.

A Comparison of Conventional Liquid-Liquid Extraction Vs. Solid Phase Disk Extraction on Real-World Samples Using USEPA Method 625 Protocol

Rick Schrynemeeckers, Enseco - Houston Technical Service Center

Craig Markell, 3M I&E New Products Department

Brett VanDelinder, SPL Environmental Laboratories

Why Can't You Use SPE for Dirty Water?

1. Plugging
2. Low Recoveries of Polar Analytes
3. Analytes on Particulates

Why Can't You Use SPE for Dirty Water?

1. Plugging
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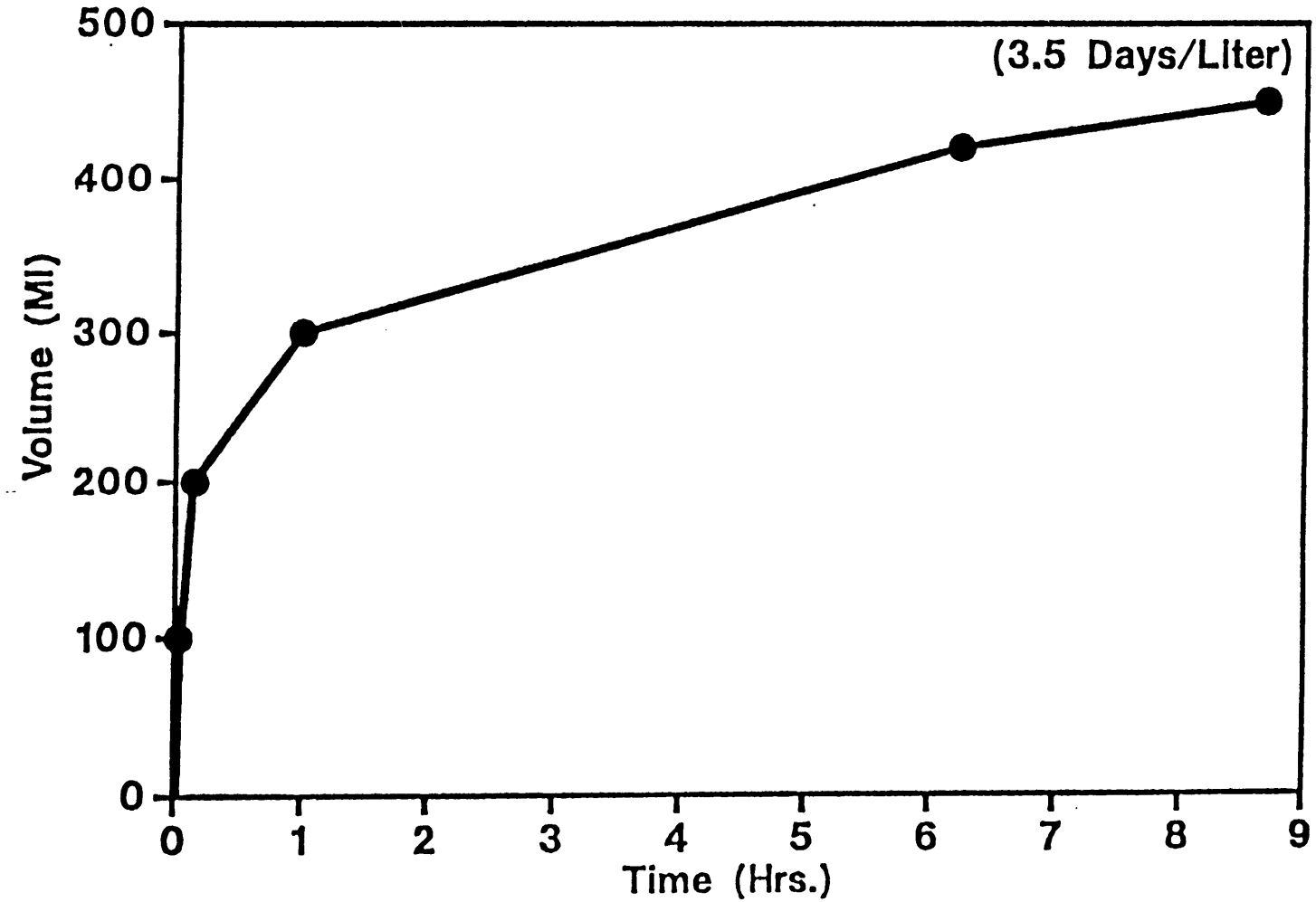
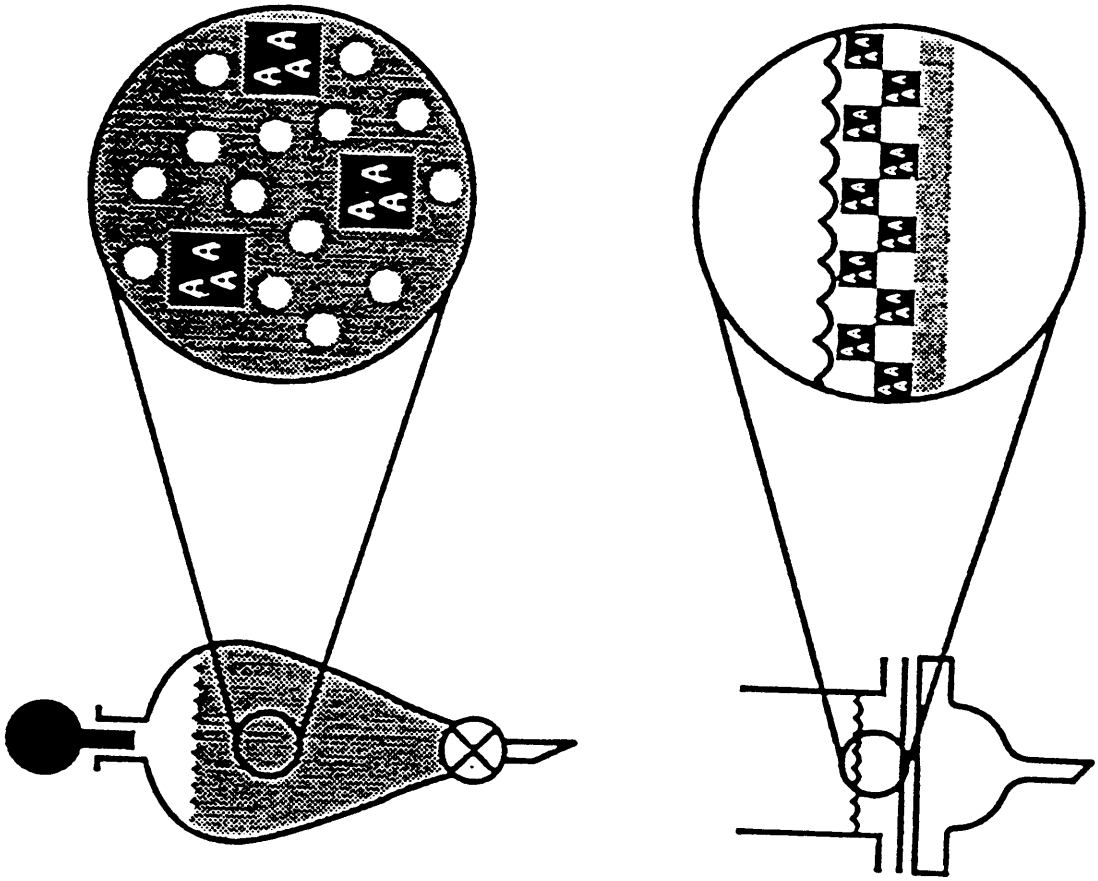
3. Analytes on Particulates

You Can, With New Technology

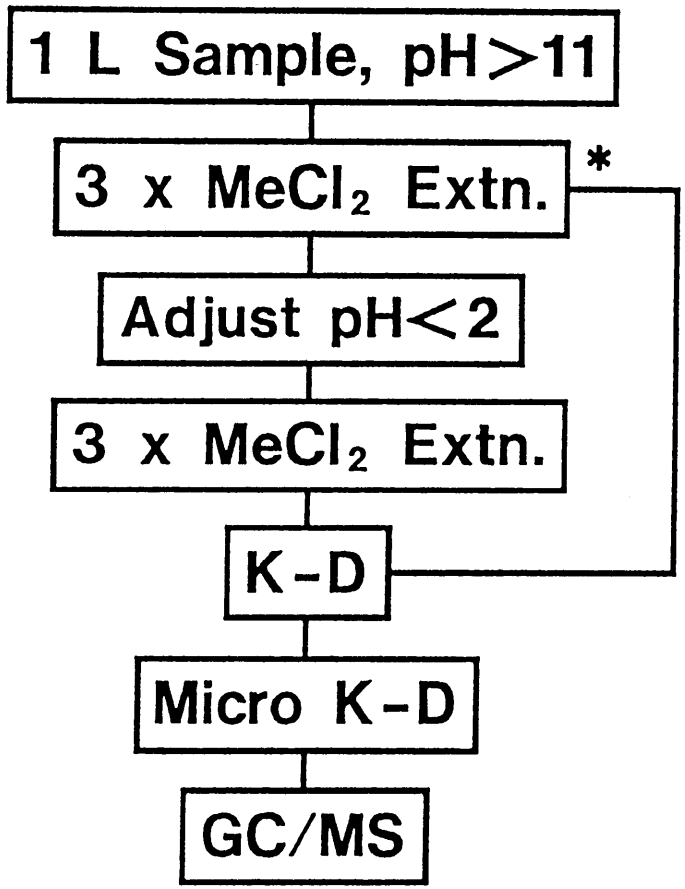
1. 90 mm SPE Disks
2. SDB Disks
3. Analytes on Particulates?

Lake Water Extraction (47mm Empore Disk, 26" Hg)





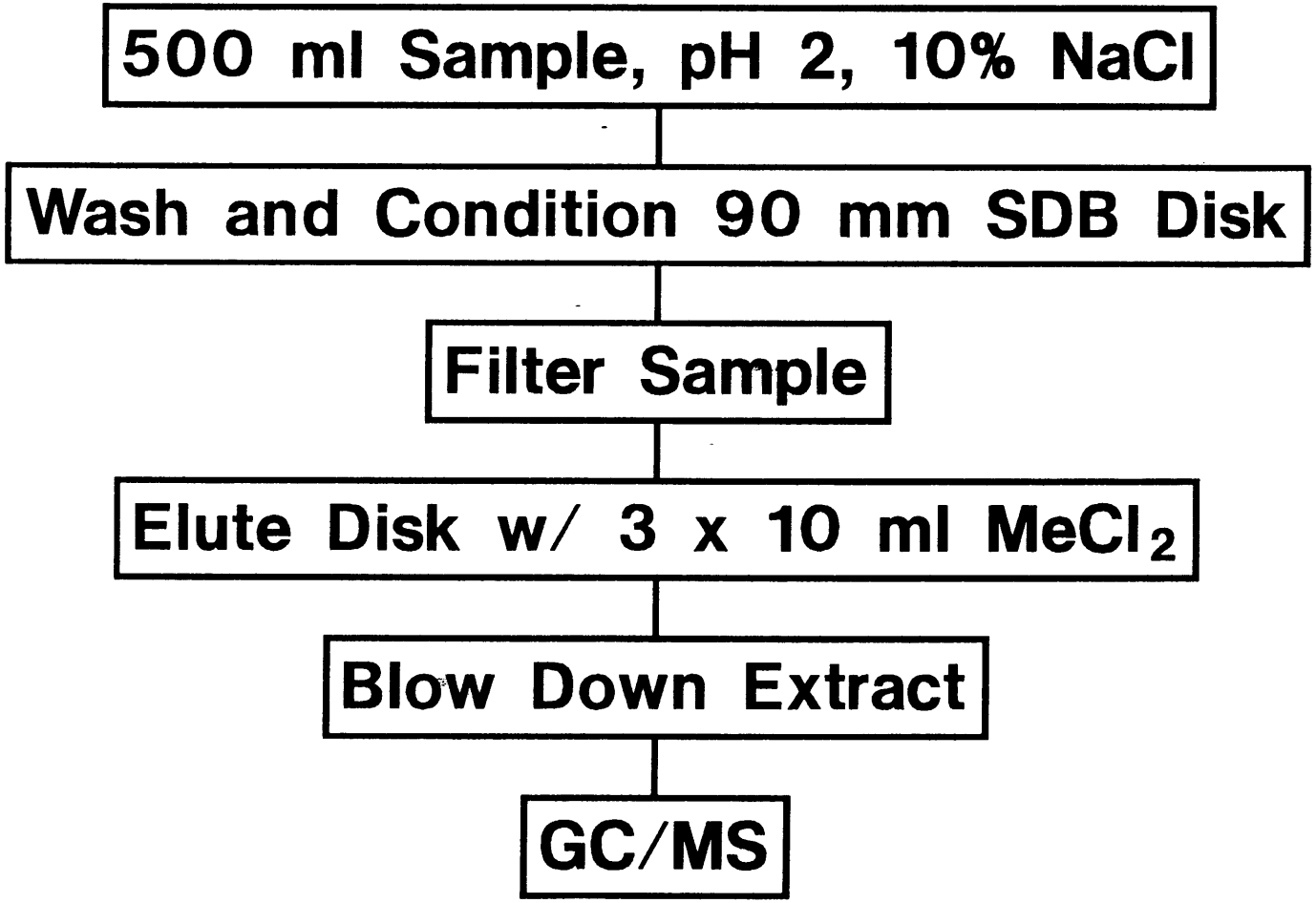
Method 625



400 - 1000 ml $MeCl_2$

*Continuous Extraction is an Option

Method 625 - Disk Modification



40 ml Acetone, 20 ml MeOH, 50 ml $MeCl_2$

Analytes

Base/Neutrals

Nitrobenzene - d5
2-Fluorobiphenyl
Terphenyl - d14
1,4-Dichlorobenzene
N-Nitroso-Di-Propylamine
1,2,4-Trichlorobenzene
Acenaphthene
2,4-Dinitrotoluene
Pyrene

Acids

Phenol - d5
2-Fluorophenol
2,4,6-Tribromophenol
Phenol
2-Chlorophenol
4-Chloro-3-Methylphenol
4-Nitrophenol
Pentachlorophenol

Recovery/Elution Study - Reagent Water, $MeCl_2$ Elution, Reagent Water (% Recovery)

Base/Neutral Compounds	1	2	3	4	5	6
Nitrobenzene-d5	72	83	84	70	78	74
2-Fluorpbiphenyl	79	92	89	67	67	63
Terphenyl-d14	82	99	114	98	76	87
1,4-Dichlorobenzene	62	66	59	59	61	56
N-Nitroso-Di-Propylamine	73	80	78	72	87	81
1,2,4-Trichlorobenzene	66	71	64	65	61	62
Acenaphthene	79	82	78	67	66	73
2,4-Dinitrotoluene	83	82	86	82	93	92
Pyrene	78	93	98	84	70	93
Acidic Compounds						
Phenol-d5	5	11	19	14	25	43
2-Fluorophenol	10	13	32	31	48	43
2,4,6-Tribromophenol	89	116	116	87	77	85
Phenol	6	7	15	15	29	53
2-Chlorophenol	46	70	76	66	77	77
4-Chloro-3-Methylphenol	84	91	81	73	85	77
4-Nitrophenol	14	31	85	56	76	114
Pentachlorophenol	93	91	96	71	76	99

1 - Single Disk, 2-15 ml Elutions, 3 Min. Soak, 1 Liter
2 - Single Disk, 3-10 ml Elutions, 5 Min. Soak, 1 Liter
3 - Double Disk, 2-15 ml Elutions, 5 Min. Soak, 1 Liter
4 - Double Disk, 3-10 ml Elutions, 5 Min. Soak, 1 Liter
5 - Double Disk, 3-10 ml Elutions, 5 Min. Soak, 1 Liter, 10% NaCl
6 - Double Disk, 3-10 ml Elutions, 5 Min. Soak, 500 ml, 10% NaCl

Method Detection Limits - Reagent Water - 90 mm SDB Disks

	MDL (ug/L)
Base/Neutrals*	
Nitrobenzene - d5	1.5
2-Fluorobiphenyl	1.7
Terphenyl - d14	5.6
1,4-Dichlorobenzene	1.3
N-Nitroso-Di-Propylamine	3.0
1,2,4-Trichlorobenzene	1.9
Acenaphthene	1.7
2,4-Dinitrotoluene	4.5
Pyrene	3.5
Acids**	
Phenol - d5	2.3
2-Fluorophenol	5.0
2,4,6-Tribromophenol	15.5
Phenol	3.5
2-Chlorophenol	1.8
4-Chloro-3-Methylphenol	6.0
4-Nitrophenol	9.8
Pentachlorophenol	10.3

*Spiked at 12.5 ug/L
**Spiked at 25 ug/L

Waste Water Types

- POTW
- Pesticide Manufacturer
- Pulp and Paper
- Petroleum Refinery

Reagent Water Results - 90 mm SDB Disks and Continuous LLE - % Recovery (RSD, n=4)

	LLE	Disk
Base/Neutrals*		
Nitrobenzene - d5	89 (2.7)	84 (5.4)
2-Fluorobiphenyl	94 (3.8)	90 (3.3)
Terphenyl - d14	103 (1.8)	103 (8.0)
1,4-Dichlorobenzene	80 (6.9)	72 (5.0)
N-Nitroso-Di-Propylamine	87 (6.4)	87 (5.2)
1,2,4-Trichlorobenzene	82 (10.2)	74 (7.2)
Acenaphthene	94 (6.6)	88 (2.0)
2,4-Dinitrotoluene	102 (6.6)	89 (0.9)
Pyrene	98 (5.8)	95 (4.5)
Acids**		
Phenol - d5	95 (2.8)	25 (7.3)
2-Fluorophenol	83 (2.8)	35 (9.6)
2,4,6-Tribromophenol	103 (2.5)	-- --
Phenol	85 (6.9)	23 (7.1)
2-Chlorophenol	86 (8.4)	84 (4.5)
4-Chloro-3-Methylphenol	93 (7.9)	82 (5.6)
4-Nitrophenol	107 (12.3)	51 (7.3)
Pentachlorophenol	108 (4.7)	82 (1.2)

*Spiked at 200 ug/L
**Spiked at 400 ug/L

POTW Results - 90 mm SDB Disks and Continuous LLE - % Recovery (RSD, n=4)

	LLE	Disk
Base/Neutrals*		
Nitrobenzene - d5	76 (16.5)	75 (8.0)
2-Fluorobiphenyl	73 (15.0)	81 (8.8)
Terphenyl - d14	94 (7.7)	94 (5.1)
1,4-Dichlorobenzene	56 (17.0)	63 (7.6)
N-Nitroso-Di-Propylamine	57 (16.5)	71 (2.9)
1,2,4-Trichlorobenzene	57 (16.7)	70 (6.7)
Acenaphthene	70 (18.1)	81 (5.6)
2,4-Dinitrotoluene	82 (17.8)	85 (9.6)
Pyrene	81 (11.6)	82 (2.6)
Acids**		
Phenol - d5	77 (17.5)	18 (18.7)
2-Fluorophenol	69 (14.7)	31 (10.5)
2,4,6-Tribromophenol	56 (13.2)	92 (21.6)
Phenol	80 (19.8)	19 (7.8)
2-Chlorophenol	76 (17.0)	71 (9.4)
4-Chloro-3-Methylphenol	81 (16.4)	83 (11.3)
4-Nitrophenol	99 (12.3)	76 (9.6)
Pentachlorophenol	68 (30.5)	76 (18.3)

*Spiked at 200 ug/L
**Spiked at 400 ug/L

Pesticide Manufacturer Results - 90 mm SDB Disks and Continuous LLE - % Recovery (RSD, n=4)

	LLE	Disk
Base/Neutrals*		
Nitrobenzene - d5	90 (7.4)	83 (8.1)
2-Fluorobiphenyl	82 (17.3)	75 (2.3)
Terphenyl - d14	160 (3.7)	101 (6.6)
1,4-Dichlorobenzene	68 (7.4)	74 (2.4)
N-Nitroso-Di-Propylamine	76 (3.3)	81 (4.1)
1,2,4-Trichlorobenzene	70 (6.9)	73 (2.4)
Acenaphthene	85 (3.5)	86 (3.5)
2,4-Dinitrotoluene	90 (4.6)	91 (2.8)
Pyrene	135 (3.7)	94 (5.5)
Acids**		
Phenol - d5	87 (5.5)	21 (15.2)
2-Fluorophenol	77 (22.4)	24 (17.3)
2,4,6-Tribromophenol	118 (7.0)	100 (2.9)
Phenol	91 (7.1)	20 (14.5)
2-Chlorophenol	91 (5.4)	93 (7.1)
4-Chloro-3-Methylphenol	81 (2.0)	92 (4.2)
4-Nitrophenol	89 (6.7)	61 (18.0)
Pentachlorophenol	116 (9.8)	104 (4.1)

*Spiked at 200 ug/L
**Spiked at 400 ug/L

Petroleum Refinery Results - 90 mm SDB Disks and Continuous LLE - % Recovery (RSD, n=4)

	LLE	Disk
Base/Neutrals*		
Nitrobenzene - d5	81 (6.6)	100 (12.5)
2-Fluorobiphenyl	76 (3.5)	107 (11.0)
Terphenyl - d14	74 (13.8)	86 (18.7)
1,4-Dichlorobenzene	54 (6.9)	84 (11.6)
N-Nitroso-Di-Propylamine	52 (11.3)	93 (8.4)
1,2,4-Trichlorobenzene	56 (6.7)	85 (10.0)
Acenaphthene	70 (2.0)	95 (9.7)
2,4-Dinitrotoluene	91 (4.7)	95 (14.0)
Pyrene	73 (6.4)	78 (17.2)
Acids**		
Phenol - d5	81 (7.1)	28 (19.4)
2-Fluorophenol	73 (5.4)	47 (21.2)
2,4,6-Tribromophenol	69 (8.5)	71 --
Phenol	85 (5.4)	28 (19.8)
2-Chlorophenol	82 (2.7)	94 (11.5)
4-Chloro-3-Methylphenol	88 (7.2)	83 (9.7)
4-Nitrophenol	112 (10.4)	56 (25.5)
Pentachlorophenol	64 (8.8)	76 (12.1)

*Spiked at 200 ug/L
**Spiked at 400 ug/L

Pulp and Paper Results - 90 mm SDB Disks and Continuous LLE - % Recovery (RSD, n=4)

	LLE	Disk
Base/Neutrals*		
Nitrobenzene - d5	81 (3.0)	81 (6.0)
2-Fluorobiphenyl	81 (3.0)	76 (10.6)
Terphenyl - d14	99 (8.7)	79 (16.5)
1,4-Dichlorobenzene	67 (5.0)	71 (7.6)
N-Nitroso-Di-Propylamine	73 (4.3)	84 (4.4)
1,2,4-Trichlorobenzene	70 (2.3)	73 (11.5)
Acenaphthene	83 (2.9)	84 (4.5)
2,4-Dinitrotoluene	86 (2.5)	91 (6.2)
Pyrene	96 (7.3)	89 (12.5)
Acids**		
Phenol - d5	75 (4.1)	21 (6.3)
2-Fluorophenol	58 (12.0)	27 (26.4)
2,4,6-Tribromophenol	118 (11.4)	103 (2.5)
Phenol	75 (4.5)	20 (4.9)
2-Chlorophenol	74 (2.3)	85 (5.1)
4-Chloro-3-Methylphenol	78 (4.0)	97 (11.6)
4-Nitrophenol	93 (12.3)	75 (7.0)
Pentachlorophenol	136 (3.3)	113 (4.4)

*Spiked at 200 ug/L
**Spiked at 400 ug/L

Flow Times - 500 ml

POTW	2 Min.
Pesticide Manufacturer	1.5 Min.
Pulp and Paper	9.5 Min.
Petroleum Refinery	1.5 Min.

Reagent Water Results Vs. QA/QC Limits - % Recovery

	Disk	Method 625 Acceptance Limits***
Base/Neutrals*		
1,4-Dichlorobenzene	72	37-106
N-Nitroso-Di-Propylamine	87	14-198
1,2,4-Trichlorobenzene	74	57-129
Acenaphthene	88	60-132
2,4-Dinitrotoluene	89	48-127
Pyrene	95	70-100
Acids**		
Phenol	23	17-100
2-Chlorophenol	84	36-120
4-Chloro-3-Methylphenol	82	41-128
4-Nitrophenol	51	13-107
Pentachlorophenol	82	38-152

*Spiked at 200 ug/L
**Spiked at 400 ug/L
***At 100 ug/L

Conclusions

- Recoveries, RSD´s, and MDL´s Are Very Comparable to LLE (Except Phenol)
- Significant Solvent and Time Savings
- Base/Neutrals *and* Acids Extracted at pH 2

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MR. TELLIARD: Carrying on with the same theme, this year, we have been working diligently on getting out a regulation on pesticide manufacturers, and part of the work was involved with attempting solid phase extraction, basically looking at Method 608.

Merlin Bicking from Twin Cities is going to talk about the work that they have done looking at the application of pesticides analysis.

I have always kind of thought it would be neat to be a chemist and have a first name like Merlin.

MR. BICKING: All right. Like Craig, I would like to acknowledge Greg Junk's contributions to solid phase extraction. I was a graduate student at Iowa State in the mid to late seventies, but when much of his work was going on, and I certainly remember Greg's contributions.

This presentation will discuss a modification to EPA Method 608, which is organochlorine pesticides and PCBs.

[SLIDE 2] We had several primary objectives. The first one was to evaluate EMPORE disks as a replacement for liquid-liquid extraction. The emphasis was on wastewater samples in this particular method. We were interested in the recovery of spiked samples. We were not analyzing native contamination levels in this particular study. We were simply looking at a recovery of spiked samples. Finally, because of the concerns that have been mentioned earlier, we are working with the 90 mm disks for samples which probably are going to contain particulates.

[SLIDE 3] There have been concerns about whether or not EMPORE disks could be used for wastewater samples. Certainly, disk plugging from high particulate samples is one of the primary concerns. If we can't get the sample through the disk, we are not going to do an analysis. The other issue with high particulate samples is adsorption of the analytes on the particulates. Most of these analytes have very low water solubility, and adsorption on a particulate is quite likely. The next issue is the level of interferences compared to the standard methods.

Then, if we can solve all of those three problems, the big question is: "does it work?" If it does work, is the precision comparable to what we get with, say, a methylene chloride extraction (or, at least, not any worse)?

[SLIDE 4] We split up the Method 608 analytes into four groups, a pesticide "A" and "B" mix, simply for convenience. We chose two PCBs, the lower level of chlorination, Aroclor 1016, and then the upper end, Aroclor 1260. Toxaphene was evaluated separately. We chose four peaks in each of those patterns. We used decachloro-biphenyl as a surrogate. In this case, while we are trying to follow Method 608 as closely as possible, we also considered the CLP protocols, which employed a surrogate, and wanted to adopt some of those procedures as well, or at least evaluate

them at the same time.

[SLIDE 5] This study was divided, like Gaul, into three parts. The initial evaluation simply was a qualitative evaluation of the matrices we were working with: do they go through the filters, through the disks, and what are the levels of interferences?

The full method validation consisted of five replicates at approximately 100 times the MDL and one control or unspiked sample. We used three different procedures, as you will see in the following tables; the Method 608 procedure which involved methylene chloride extraction in a separatory funnel, and the two EMPORE procedures. The "EMPORE-Baker" and the "EMPORE-Varian" refer to the manufacturers of the C_{18} particles. We evaluated both sets of disks, and in this paper, we are going to discuss those two disks separately.

Four matrices were evaluated: POTW, pulp and paper effluent, a pesticide manufacturing effluent (from a facility that does not manufacture organochlorine pesticides) and, finally, a petroleum facility effluent. We have completed this phase for the first three matrices. We are just beginning the petroleum matrix and do not have any data for that at this time. The other thing I should note is our pulp and paper sample was as bad as the others you have heard about today, although ours looked like a vanilla milkshake rather than a chocolate milkshake. Finally, the last phase is an MDL study with the replicates. We have not completed this yet and won't be talking about that today.

[SLIDE 6] For those of you who may not be intimately familiar with the EMPORE disks and method 608, I thought I would provide a little more detail on the actual performance of this method. All of our spikes were into a 1 liter glass container. This procedure was used for all three methods. In our case, we allowed the sample, after spiking and shaking, to equilibrate for one to two hours. This was a suggestion from EPA. It certainly represents a worst case scenario for studying the adsorption on particulates problem.

The liquid-liquid extraction approach is conventional separatory funnel extraction, K-D techniques for concentration, solvent exchange to hexane, and ECD quantification.

[SLIDE 7] The EMPORE procedure involves a disk preparation step. You assemble the apparatus. (We used the disk and glass fiber filters from Whatman.) You condition the disk, essentially cleaning it with the elution solvent, which is methylene chloride in this case, allow it to soak, and then pull that solvent through. Then the disk is conditioned with methanol, by soaking.

At this point, it is very important that you not let the disk dry out. Leave some methanol on the surface. We believe this affects the wetting process, and allows the water to go through the disk.

The sample extraction or filtration, depending on your terminology, required about 20 minutes to filter a 1 liter sample. The range was probably 10 to 30 minutes for these matrices. The pulp and paper sample was particularly difficult in the early work, and we discovered, much to our surprise, that if we adjusted the pH to about 2, it would filter much more readily. At neutral pH, I think we set the new record for the 90 mm disk. It would have gone past Craig's three and a half day limit, but at a pH 2, it filtered quite nicely, and all of our data for pulp and paper will be at that lower pH.

[SLIDE 8] In the final step, we eluted with three 15 mL portions of methylene chloride, allowing the portions to soak 3 minutes each time, and then pulling them through the disk. The rest of the process is just like the conventional 608 procedure: solvent exchange and GC/ECD.

[SLIDE 9] Now, it is time to talk about the data. We have talked a lot about what we think the EMPORE disk can do. Now, we can have a chance to see what they actually can do.

[SLIDES 10-12] This is the kind of slide that will make your eyes glaze over when you see it. I really don't intend you to read it. It is just up there to show that we have done the work. These are real data points, and I will have another graph which is a little easier to comprehend.

We have four or five data points for each analyte. We have looked at the individual replicates, performed statistical tests to reject the outliers, and then looked at the final sets. We have recovery, or accuracy, and precision data, then, for all three experiments (liquid-liquid extraction, Empore-Baker, and Empore-Varian).

[SLIDE 13] We feel it is much easier to evaluate the two techniques using a graphical approach. The X-axis on this plot is the percent recovery for each analyte for the liquid-liquid extraction method (Method 608). That is plotted against the recovery for that analyte with the two EMPORE disks. The "square" is for the Baker disksand the "pluses" are for the Varian disks.

If the recoveries are equal for each of those analytes using the two techniques, all points should fall on that 45-degree line. You can see that there is a cluster of points around that 45-degree line, weighted a little bit below it. That means that the EMPORE recoveries are a little bit lower than the corresponding liquid-liquid recoveries, and there are obviously some scattered points. However, it looks like the points are clustering near the 45-degree line and are within about 10 percent of the liquid-liquid recoveries. We are very encouraged by this result. For a large number of data points, we see a good match in recoveries.

[SLIDE 14] This is a plot for the pulp and paper matrix. You can see there are many points in the lower right part of the plot, where the EMPORE disk recoveries are lower than the liquid-liquid recoveries. Most of the problems occur with the PCBs and toxaphene. We are not sure why this happens, but 3M has indicated that the PCBs are more difficult than the rest of the conventional organochlorines.

[SLIDE 15] The next graph gives the same type of presentation for the pesticide effluent. Again, we see a pretty good cluster around the 45-degree line, but a little bit lower for the EMPORE experiments.

One of the other important things to note here is that you do see a general trend along the 45-degree line. In other words, if you have lower recoveries for the Method 608 procedure, you also get lower recoveries for the EMPORE procedures. This is telling us that whatever the reasons are for those recovery losses, they are the same for either procedure. In other words, there have been concerns that we are going to lose analytes on particulates with the EMPORE approach that we would normally extract with the liquid-liquid approach. The fact that we are seeing a general trend rather than a complete scatter tells me that that is not the case. Whatever the sources of the recovery losses are, they are independent of the EMPORE step itself. This

conclusion is important in evaluating the performance of the EMPORE disks.

[SLIDE 16] There were so many data points that we wanted to take a more formal approach to evaluating it, and we really thought statistics offered a convenient way to do that.

[SLIDE 17] This slide summarizes two statistical tests for the data. The first test, a t-test, is shown in the left two columns. This test compares the means, or the average recoveries, for liquid-liquid and the two different EMPOREs. This is really answering the question: "are the average recoveries different for the two data sets or being compared?" A "NO" means there is no difference, and that is good in this case. A "YES" means there is a statistical difference between the two means. For the POTW matrix, you see there are more NOs than YESs, and that is good. In other words, there are no statistical differences for most of the data sets.

The right two columns summarize the results from an F-test on the variance. This test is answering the question: "is there a difference in the variance or, ultimately, the precision, for these two methods?" You can see that in most of those cases, there are NOs in the table and that means that the variances are not statistically different. In other words, we can expect comparable precision for the two techniques.

[SLIDE 18] This table gives a summary in more absolute terms. Where there is a statistical difference, what is the difference in those recoveries? For the first two columns, the numbers are the average recovery differences. If you see a minus sign, it means that the EMPORE recovery is lower, and statistically different from liquid-liquid recovery. Most of the numbers are in the 10 to 20 percent range lower. So, even when there is a statistical difference, the difference is only 10 to 20 percent for the EMPOREs. There are a few cases where the EMPORE recoveries are actually higher.

The third and fourth columns indicate where there was a significant difference in the variances, which of the variances were smaller. In some cases, the EMPORE procedures had a statistically significant smaller variance (or precision).

I think this result is encouraging news. It tells us that, from a precision standpoint, the EMPORE disks are going to provide results which are comparable to the standard procedure.

[SLIDE 19] Similar results were observed for the pulp and paper matrix, except we see more YESs here. For some reason, we had some low recoveries in the EMPORE procedures. We are not sure why. This is the worst sample we have worked with, although most of the variances were still comparable between the procedures. We seem to have problems with the pesticide "A" and "B" mixes which are the top sets in the table. We are not sure why at this point.

[SLIDE 20] The next slide is in a similar format. Where there are significant differences, the magnitudes are listed in the table. These differences tend to be a little larger, 20 to 30 percent, and for the top group, the liquid-liquid extraction procedure is giving better precision. For the other sets, the variance test indicates mixed results, with either technique showing a smaller varience, depending on the analyte.

[SLIDE 21] This table shows results for the pesticide effluent. There was a split between whether or not there was a significant difference in the average recoveries, although there were very few differences in the variances.

[SLIDE 22] We see a few larger differences in recovery, but many of them are pretty close. Again, recognize taht the blank spots are cases where there are no statistically significant differences between the data sets, and all of those recoveries are usually within 10 percent of each other. Again, on the right two columns where there are blanks, that means that the variances are not statistically different.

[SLIDE 23] A final comparison on solvent usage is provided in this table. We reduced total volume from over 300 to under 140 mL. That reduces our purchase cost by more than a factor of 2. It certainly helps with disposal costs also. So, EMPORE is certainly doing one of the things that it is claimed to do, and that is significantly reduce our solvent use in the laboratory.

[SLIDE 24] In conclusion, we feel we have demonstrated that we are going to get comparable results between the two techniques. The recoveries are usually within 15 percent, and even where there are statistically significant differences, many of the recovery differences are less than 20 percent. Precision is comparable in most cases with the exception of the pulp and paper matrix.

In general, the extracts from EMPORE disks have fewer interferences. We

did not evaluate any cleanup steps for these samples. That is one important aspect to remember. We found no substantial differences in interferences but somewhat lower levels of interferences using the EMPORE disks. And I should note that all of the recovery values we have are corrected for levels in the unspiked sample, so they are all blank corrected. Certainly, solvent use is reduced, as we have demonstrated.

We have had no problems with plugging from the 90 mm disks. Extractions are rapid, with the exception of that first set of pulp and paper samples at pH 7 to 8.

We are also looking at other procedures which will further reduce solvent use. For example, supercritical fluid extraction (SFE) can be used to remove analytes from the disks, and that will eliminate much of the solvents, and take the total solvent usage down to less than 50 mL total.

[SLIDE 25] I would like to leave you with a parting comment (and warning) about statistics. Certainly, we have generated a lot of statistical information here. I don't want to go overemphasize in our use of statistics, but I think they do provide a valuable tool for us in evaluating these two procedures.

[SLIDE 26] I would like to acknowledge Craig and George at 3M, who have been working with us closely on the experimental design and the operational considerations. Bill and Harry have been also heavily involved in the planning stages and the early execution and have had substantial input into the experimental design.

I would be happy to answer any questions.

QUESTION AND ANSWER SESSION

MR. STANKO: George Stanko, Shell Development Company.

In your studies in the pulp and paper industry, your recoveries were lower. Was there any effort to look in what came through the filter to see of the actual analytes were in there, and is there a possibility that there were other polar solvents like DMSO or acetone that may have accounted for this?

MR. BICKING: No, we have not looked at that issue. That is certainly a good suggestion. Our primary objective was to see how total recoveries compared between the techniques. I think now we have to go back and look at where recoveries were different and find out why.

Another issue is that the type of particulates in the pulp and paper sample are fibrous. I have concerns about whether or not there is some swelling or shrinking that goes on when that organic solvent contacts the particulates in the elution step. It could be that analytes are on the particulates or on the fibers, and when you add methylene chloride, something happens that traps them. That is another possibility.

MR. PERTUIT: Bob Pertuit, PPG Industries.

When you are running garbage samples through these disks, is the water coming out of the disk still turbid, showing that you are passing some ultrafine particulates through the disks?

MR. BICKING: In almost all cases, the filtrate is clear. In most cases, we remove any color with the disks also. So, we don't see any turbidity.

MR. PERTUIT: I have had some experience working with these ultrainsoluble compounds like PCBs, and they are going to find anyplace besides the water to reside. They are going to get out of solution.

If they attach to particulates, they will pass through a moderately porous system on the particulates, and you won't be able to find them. I would suggest that you look on the glass in the bottle and in the filtrate for your PCBs to see if they either stayed in the bottle on the walls or have gone through with the particulates.

MR. BICKING: That is a good comment. I didn't mention that we rinsed the sample container with the methylene chloride that we used for elution, and we also

rinsed down the sidewalls of the glass reservoir. All of the glass contact surfaces have seen methylene chloride at least once, and in the case of the reservoir, usually two or three times. So, I hope that isn't an issue. Now, if an analyte adsorbs to a particle which is smaller than about 0.1 microns, then you are right. Then the analyte is going to go right through.

In looking at the extraction from particulates issue, if you consider the amount of time that the solvent is in contact with the particulate, it is actually longer with the EMPORE procedure than with conventional separatory funnel extractions. With the particulates, it is soaking, in our case, three times for 3 minutes each. So, it has a total of 9 minutes of contact time, (direct contact) between organic solvent and particulates. That is substantially higher than you are going to get from a separatory funnel shake which is, at best, maybe 2 minutes for each step.

MR. PERTUIT: Thank you, sir.

MR. WESTON: Charlie Weston from ETC.

What significance level did you use in your statistical comparisons?

MR. BICKING: 95 percent. Alpha equals .05.

MR. WESTON: Thank you.

MR. LAW: Peter Law with Tighe & Bond Laboratory in Westfield, Mass.

Could you clarify the initial pHs for your sample? Was the pulp and paper the only one at 2, everything else at neutral?

MR. BICKING: We checked the pH of all the samples, and they were adjusted as specified in the method (7 to 9), to make sure they were in the range specified by the method.

MR. LAW: But the pulp and paper was at 2?

MR. BICKING: That sample was initially at a higher pH, but we adjusted it to a pH of 2 for all of the studies we reported here.

MR. TELLIARD: Thanks, Merlin.

All right, it is break time. For all of those who are still napping, would you please go out, get your coffee, your strawberry, and get back in here in ten minutes so that we can continue on. Thank you very much.

(WHEREUPON, a brief recess was taken.)

[SLIDE 1]

EVALUATION OF A MODIFICATION TO EPA METHOD 608 USING SOLID-PHASE EXTRACTION DISKS

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[SLIDE 2]

OBJECTIVES

- Evaluate Empore disks as a replacement for liquid-liquid extraction in wastewater analysis.

- Evaluate recovery of organochlorine pesticides and PCBs from spiked samples.

- Evaluate 90 mm disks with glass fiber filters for samples containing particulates.

[SLIDE 3]

QUESTIONS/CONCERNS ABOUT THE USE OF EMPORE DISKS FOR WASTEWATER SAMPLES

- Disk plugging from high particulate samples, resulting in slower filtration rates.
- Adsorption of analytes on particulates, resulting in lower recoveries.
- Level of interferences.
- Accuracy (Does it work?)
- Precision (Is it any better than methylene chloride, or at least not any worse?)

[SLIDE 4]

EPA METHOD 608 ANALYTES

PESTICIDE "A" MIX
ALDRIN
HEPTACHLOR EPOXIDE
ENDOSULFAN I
DIELDRIN
ENDOSULFAN II
ENDRIN ALDEHYDE
DDT
DCBP(SURROGATE)

PCBs
AROCLOR 1016-1
AROCLOR 1016-2
AROCLOR 1016-3
AROCLOR 1016-4
AROCLOR 1260-1
AROCLOR 1260-2
AROCLOR 1260-3
AROCLOR 1260-4
DCBP(SURROGATE)

PESTICIDE "B" MIX
A-BHC
B-BHC
D-BHC
A-CHLORDANE
DDE
ENDRIN
DDD
DCBP(SURROGATE)

TOXAPHENE
TOXAPHENE-1
TOXAPHENE-2
TOXAPHENE-3
TOXAPHENE-4
DCBP(SURROGATE)

[SLIDE 5]

EXPERIMENTAL DESIGN

INITIAL EVALUATION

Evaluate filtration rates.
Qualitatively evaluate level of interferences.

FULL METHOD EVALUATION

Five replicates at approximately 100X MDL.
One control (unspiked) sample.
Procedures:
- EPA Method 608
- Empore-Baker
- Empore-Varian

Matrices:
- POTW Effluent
- Pulp/Paper Effluent
- Pesticide Manufacturing Facility Effluent
- Petroleum Facility Effluent

MDL STUDY

Eight replicates at three- to -five times the estimated MDL (reagent water).
Two control (unspiked) samples.

[SLIDE 6]

PROCEDURE

- **SPIKING**

  Spike a 1 L water sample with Method 608 analytes. Allow to equilibrate 1 - 2 hours.

- **LIQUID-LIQUID EXTRACTION (LLE)**

  Extract three times with methylene chloride. Dry using Na_2SO_4.

  Concentrate extract using K-D.

  Solvent exchange to hexane. Adjust final volume to 2 - 5 mL.

  GC/ECD using 0.53 mm X 30 m DB-608 column. Quantification using external standard method.

[SLIDE 7]

PROCEDURE (cont.)

- **EMPORE DISKS**

Disk Preparation

Assemble filtration apparatus with 90 mm disk and glass fiber filter.

Condition disk with 20 mL elution solvent (methylene chloride). Soak 3 minutes. Pull solvent through disk for 1 minute.

Condition with 20 mL methanol. Soak 3 minutes. Pull most of solvent through disk.

Sample Extraction

Add 1 L sample to reservoir. Filter at approximately 50 mL/minute. Draw air through disk for approximately 5 minutes.

[SLIDE 8]

PROCEDURE (cont.)

- **EMPORE DISKS (cont.)**

  Sample Elution/Concentration

  Add 15 mL methylene chloride to reservoir (rinse sides). Soak 3 minutes. Pull through disk into test tube.

  Repeat with 2 additional portions of methylene chloride. Dry combined methylene chloride portions using Na_2SO_4.

  Solvent exchange to hexane.

  GC/ECD using 0.53 mm X 30 m DB-608 column. Quantification using external standard method.

[SLIDE 9]

"Get your facts first and then you can distort 'em as much as you please."

Mark Twain

[SLIDE 10]

SUMMARY OF SPIKE RECOVERIES FOR POTW MATRIX

Analyte	Spike Level, µg/L	Recovery, percent					
		LLE		Empore-Baker		Empore-Varian	
		n	Ave. (s.d.)	n	Ave. (s.d.)	n	Ave. (s.d.)
G-BHC	1	5	86.3 (8.9)	5	84.3 (2.6)	5	87.0 (5.2)
Heptachlor	1	5	81.6 (8.8)	5	72.6 (8.9)	5	61.4(11.0)
Aldrin	1	5	63.6 (6.6)	5	55.8 (5.9)	5	56.0(10.0)
Heptachlor Epoxide	1	5	86.7 (6.1)	5	78.9 (4.7)	5	76.8(10.1)
Endosulfan I	1	5	96.0 (6.9)	5	87.8 (4.9)	5	77.6 (9.5)
Dieldrin	2	5	93.1 (6.4)	5	82.5 (5.0)	5	78.7(10.2)
Endosulfan II	2	5	79.8 (5.2)	5	74.3 (3.0)	5	74.7(11.4)
Endrin Aldehyde	2	5	105.0 (5.8)	5	81.1 (5.8)	4	85.5(14.3)
DDT	2	5	82.9 (9.3)	5	80.6 (4.3)	5	80.4(10.0)
DCBP (Surrogate)	3	5	97.2 (4.0)	5	86.1 (4.2)	5	80.1 (7.8)
A-BHC	1	5	83.6 (4.3)	5	82.9 (3.6)	5	87.9 (2.9)
B-BHC	1	5	104.6 (9.0)	5	103.1 (6.8)	5	109.9 (5.0)
D-BHC	1	5	113.8 (7.3)	5	116.3 (7.6)	5	123.0 (3.6)
A-Chlordane	2	5	69.9 (6.7)	5	85.9 (5.7)	5	94.5 (3.2)
DDE	2	5	83.1 (6.0)	5	81.8 (5.3)	5	88.5 (4.3)
Endrin	2	5	130.9 (7.2)	5	131.4 (6.1)	5	140.6 (3.8)
DDD	2	5	103.3(15.4)	5	112.5(12.5)	5	111.6 (8.0)
Endosulfan Sulfate	2	5	79.3 (6.5)	5	85.0 (4.0)	5	89.0 (3.3)
Endrin Ketone	2	5	78.8 (6.2)	5	82.6 (5.0)	5	86.0 (3.4)
DCBP (Surrogate)	3	5	106.9 (4.4)	5	105.8 (5.0)	5	109.2 (9.2)
Toxaphene-1	24	5	129.2 (8.6)	5	113.1 (5.9)	5	102.3(18.6)
Toxaphene-2	24	5	126.2(16.2)	5	116.5(14.1)	5	114.5(12.3)
Toxaphene-3	24	5	110.7(11.1)	5	103.4 (8.1)	5	100.8(11.7)
Toxaphene-4	24	5	102.3(10.1)	5	95.2 (7.8)	5	94.8 (8.0)
DCBP (Surrogate)	3	5	80.2 (8.7)	5	83.3 (1.5)	5	83.7 (2.9)
Aroclor 1016-1	4	5	78.4 (3.0)	5	52.6 (4.2)	4	15.5 (6.2)
Aroclor 1016-2	4	5	93.8 (8.3)	5	79.6 (3.6)	5	80.9 (3.8)
Aroclor 1016-3	4	5	129.0 (3.9)	5	76.8 (4.8)	5	97.0(15.6)
Aroclor 1016-4	4	5	101.1 (6.0)	5	90.5 (7.9)	5	82.9(12.3)
Aroclor 1260-1	4	4	81.5 (1.5)	5	63.8(12.8)	5	58.2 (5.1)
Aroclor 1260-2	4	5	97.5 (6.1)	5	65.0 (7.0)	5	76.2 (2.5)
Aroclor 1260-3	4	5	88.5(11.3)	5	74.5(14.9)	5	81.6 (6.0)
Aroclor 1260-4	4	4	95.4 (3.2)	5	84.8(22.7)	5	79.3 (7.6)
DCBP (Surrogate)	3	5	84.0 (5.0)	5	65.5 (3.5)	5	75.8 (2.7)

[SLIDE 11]

SUMMARY OF SPIKE RECOVERIES FOR PULP/PAPER MATRIX

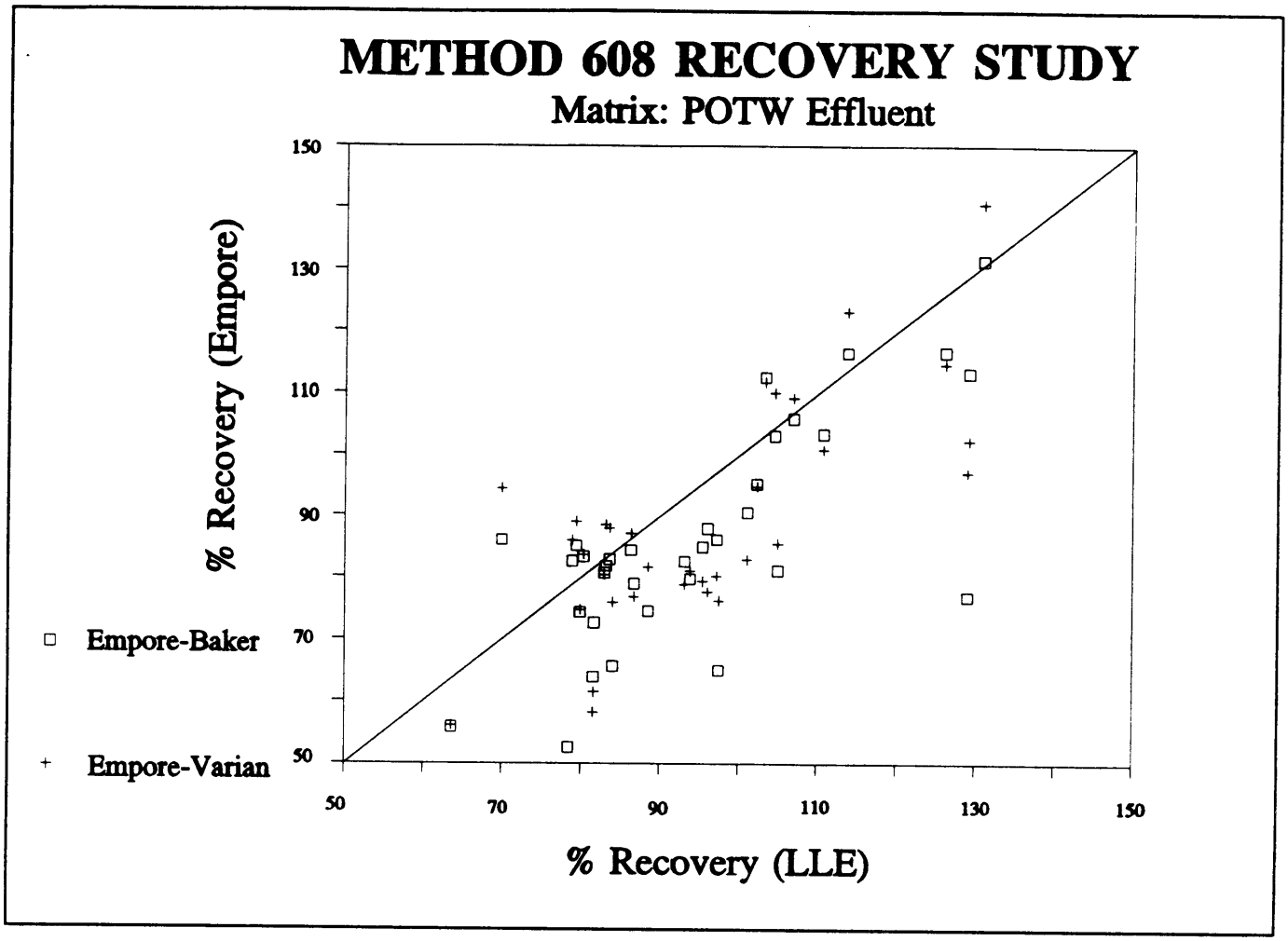
Analyte	Spike Level, µg/L	Recovery, percent					
		LLE		Empore-Baker		Empore-Varian	
		n	Ave. (s.d.)	n	Ave. (s.d.)	n	Ave. (s.d.)
G-BHC	1	5	99.2 (1.3)	5	65.8(12.9)	5	65.7(10.8)
Heptachlor	1	5	86.9 (1.5)	5	60.9 (7.0)	5	51.2 (7.4)
Aldrin	1	5	77.8 (1.4)	5	53.0 (6.6)	5	42.9 (6.5)
Heptachlor Epoxide	1	5	111.7 (2.5)	5	75.1(14.0)	5	64.6(11.9)
Endosulfan I	1	5	92.6 (1.1)	5	63.8(10.6)	5	57.9(10.5)
Dieldrin	2	5	89.0 (2.0)	5	61.9 (9.1)	5	47.7 (8.2)
Endosulfan II	2	5	90.2 (2.1)	5	62.1(12.1)	5	48.7 (8.0)
Endrin Aldehyde	2	5	116.7 (2.5)	5	86.3(15.5)	5	66.5 (9.9)
DDT	2	5	67.7 (1.1)	5	54.2(11.9)	5	43.6 (6.7)
DCBP (Surrogate)	3	5	78.1 (1.3)	5	55.5 (5.2)	5	46.6 (6.9)
A-BHC	1	5	81.9 (7.5)	5	78.4 (3.5)	5	86.7 (4.7)
B-BHC	1	5	95.0 (7.7)	5	100.3 (6.8)	5	110.4(12.7)
D-BHC	1	5	101.6 (8.6)	5	96.2 (6.0)	5	104.4 (5.7)
A-Chlordane	2	5	75.5(19.2)	5	39.2 (3.8)	5	55.8 (6.6)
DDE	2	5	89.5(10.6)	5	44.6 (5.1)	5	64.3 (8.7)
Endrin	2	5	98.3 (9.4)	5	78.9 (4.3)	5	92.9(10.1)
DDD	2	5	111.8 (9.6)	5	63.7 (6.7)	5	87.1 (7.5)
Endosulfan Sulfate	2	5	86.9 (9.4)	5	75.6 (3.3)	5	84.3 (5.7)
Endrin Ketone	2	5	79.7 (9.8)	5	71.5 (2.9)	5	77.7 (4.8)
DCBP (Surrogate)	3	5	48.1(13.0)	5	12.4 (4.6)	5	26.2 (4.9)
Toxaphene-1	24	5	63.7 (4.3)	5	50.5(15.3)	3	69.7(21.6)
Toxaphene-2	24	5	82.3 (4.4)	5	36.1 (5.7)	3	50.4 (4.8)
Toxaphene-3	24	5	62.8(12.7)	4	21.7 (5.8)	3	45.9 (2.3)
Toxaphene-4	24	5	98.6 (3.3)	5	92.5(10.0)	3	93.3(26.2)
DCBP (Surrogate)	3	5	63.8(19.4)	5	44.9(17.4)	3	72.1 (3.7)
Aroclor 1016-1	4	5	52.9 (5.5)	4	48.2 (7.5)	4	29.1 (5.2)
Aroclor 1016-2	4	5	55.1 (8.3)	4	59.3(11.0)	5	32.3(11.2)
Aroclor 1016-3	4	5	96.8(11.9)	4	83.7 (9.0)	5	44.1(17.7)
Aroclor 1016-4	4	5	98.5 (9.5)	5	100.1(10.5)	5	65.4(16.8)
Aroclor 1260-1	4	5	80.0 (8.6)	4	41.2 (5.3)	4	14.9 (1.0)
Aroclor 1260-2	4	5	85.1 (8.8)	4	44.8 (4.9)	4	12.6 (5.2)
Aroclor 1260-3	4	5	60.9 (6.6)	4	30.4 (1.8)	4	12.9 (2.6)
Aroclor 1260-4	4	5	91.4(10.5)	4	52.6(14.9)	5	33.9(17.0)
DCBP (Surrogate)	3	5	99.7(10.7)	4	81.9(11.1)	4	27.0 (6.6)

[SLIDE 12]

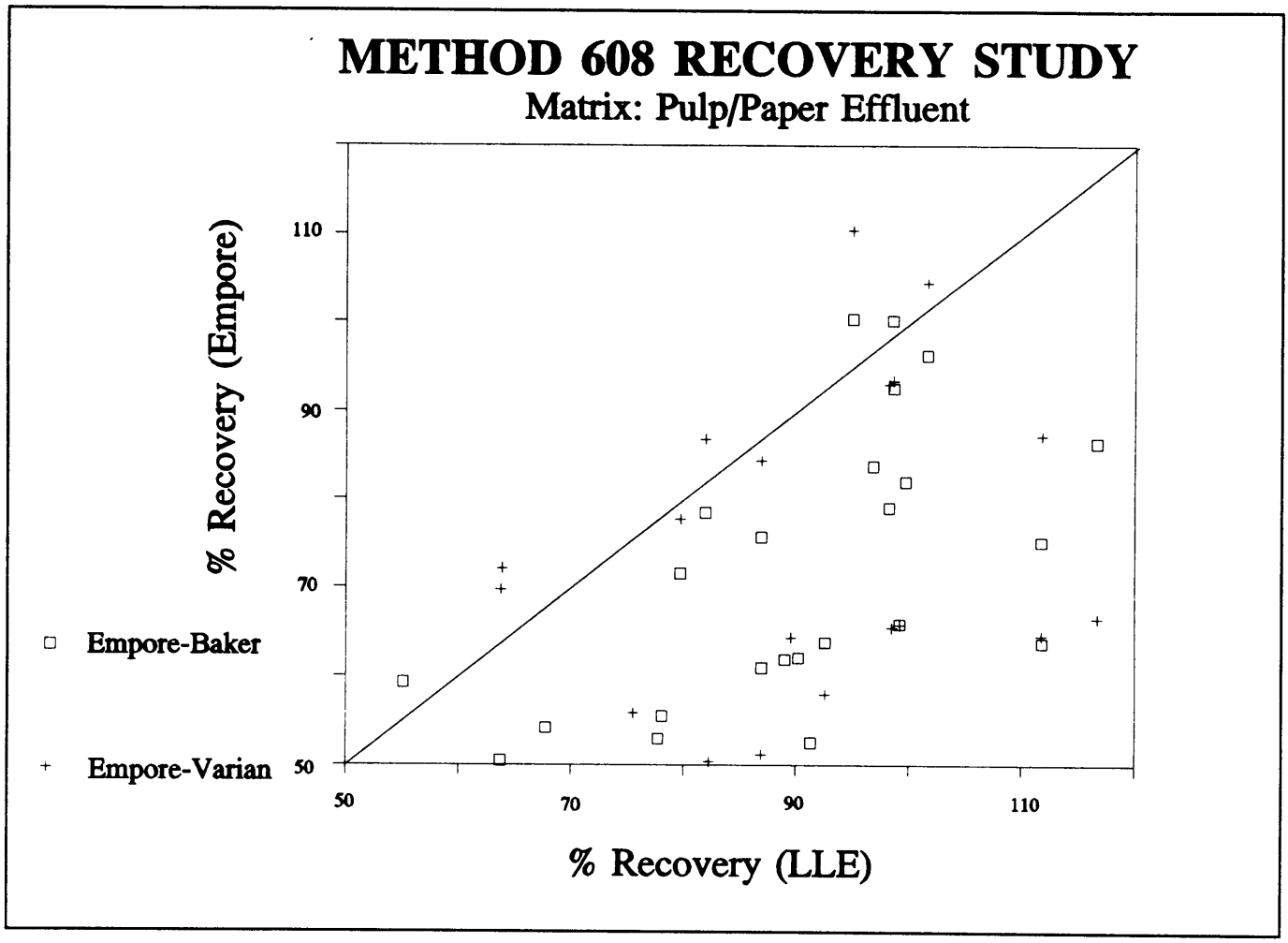
SUMMARY OF SPIKE RECOVERIES FOR PESTICIDE EFFLUENT MATRIX

Analyte	Spike Level, µg/L	Recovery, percent								
		LLE			Empore-Baker			Empore-Varian		
		n	Ave.	(s.d.)	n	Ave.	(s.d.)	n	Ave.	(s.d.)
G-BHC	1	5	99.1	(2.7)	5	92.3	(5.6)	5	91.7	(2.3)
Heptachlor	1	5	67.0	(5.2)	5	69.1	(5.7)	5	67.4	(1.6)
Aldrin	1	5	65.8	(4.8)	5	61.7	(5.1)	5	58.1	(1.7)
Heptachlor Epoxide	1	5	88.0	(1.8)	5	85.6	(3.7)	5	78.0	(2.3)
Endosulfan I	1	5	87.9	(2.0)	5	83.1	(3.2)	5	74.5	(2.2)
Dieldrin	2	5	95.4	(2.0)	5	84.8	(2.3)	5	82.5	(2.9)
Endosulfan II	2	5	99.0	(3.3)	5	91.3	(5.5)	5	86.1	(2.2)
Endrin Aldehyde	2	5	123.2	(5.3)	4	90.0	(6.8)	5	91.1	(3.8)
DDT	2	5	95.8	(3.9)	4	89.4	(3.3)	5	89.9	(4.4)
DCBP (Surrogate)	3	5	89.3	(3.8)	5	81.2	(4.1)	5	92.4	(3.1)
A-BHC	1	4	104.7	(2.5)	5	94.0	(3.0)	4	97.7	(1.3)
B-BHC	1	5	119.5	(4.4)	5	105.9	(3.7)	5	111.9	(5.1)
D-BHC	1	5	117.7	(3.6)	5	104.5	(4.1)	5	108.8	(4.4)
A-Chlordane	2	5	89.2	(0.9)	5	82.2	(8.2)	5	96.4	(1.5)
DDE	2	5	115.6	(5.7)	5	93.2	(8.2)	5	98.5	(5.8)
Endrin	2	5	156.3	(5.4)	5	135.4	(5.0)	5	140.4	(2.7)
DDD	2	5	121.4	(8.2)	5	102.3	(7.0)	5	112.2	(12.2)
Endosulfan Sulfate	2	5	89.6	(3.7)	5	87.8	(1.1)	5	92.1	(4.1)
Endrin Ketone	2	5	88.7	(1.0)	5	88.5	(5.2)	5	88.9	(2.8)
DCBP (Surrogate)	3	5	83.6	(2.2)	5	71.2	(4.8)	5	71.7	(3.1)
Toxaphene-1	24	5	97.2	(4.7)	5	72.3	(6.4)	5	60.6	(7.8)
Toxaphene-2	24	5	95.3	(4.1)	5	77.3	(9.1)	5	51.2	(20.3)
Toxaphene-3	24	5	109.7	(6.5)	5	51.2	(10.4)	5	94.9	(31.8)
Toxaphene-4	24	5	105.0	(7.6)	5	98.3	(11.0)	5	76.6	(13.3)
DCBP (Surrogate)	3	5	106.1	(3.6)	5	81.5	(4.0)	5	77.2	(10.8)
Aroclor 1016-1	4	5	3886.2	(186.8)	4	3338.6	(434.8)	5	3162.3	(268.8)
Aroclor 1016-2	4	5	84.6	(5.5)	5	99.6	(22.2)	5	88.3	(6.4)
Aroclor 1016-3	4	5	191.1	(24.4)	5	147.5	(45.8)	5	128.4	(9.1)
Aroclor 1016-4	4	5	76.7	(8.7)	5	82.4	(23.2)	5	62.7	(6.8)
Aroclor 1260-1	4	5	143.7	(7.4)	4	101.3	(13.4)	5	98.5	(8.7)
Aroclor 1260-2	4	5	100.7	(9.2)	5	86.1	(8.5)	5	87.1	(7.6)
Aroclor 1260-3	4	5	115.1	(15.6)	4	103.7	(11.0)	5	115.6	(17.7)
Aroclor 1260-4	4	5	115.7	(40.3)	4	81.5	(15.5)	5	160.6	(38.9)
DCBP (Surrogate)	3	5	85.0	(1.5)	5	62.1	(7.9)	5	66.7	(3.6)

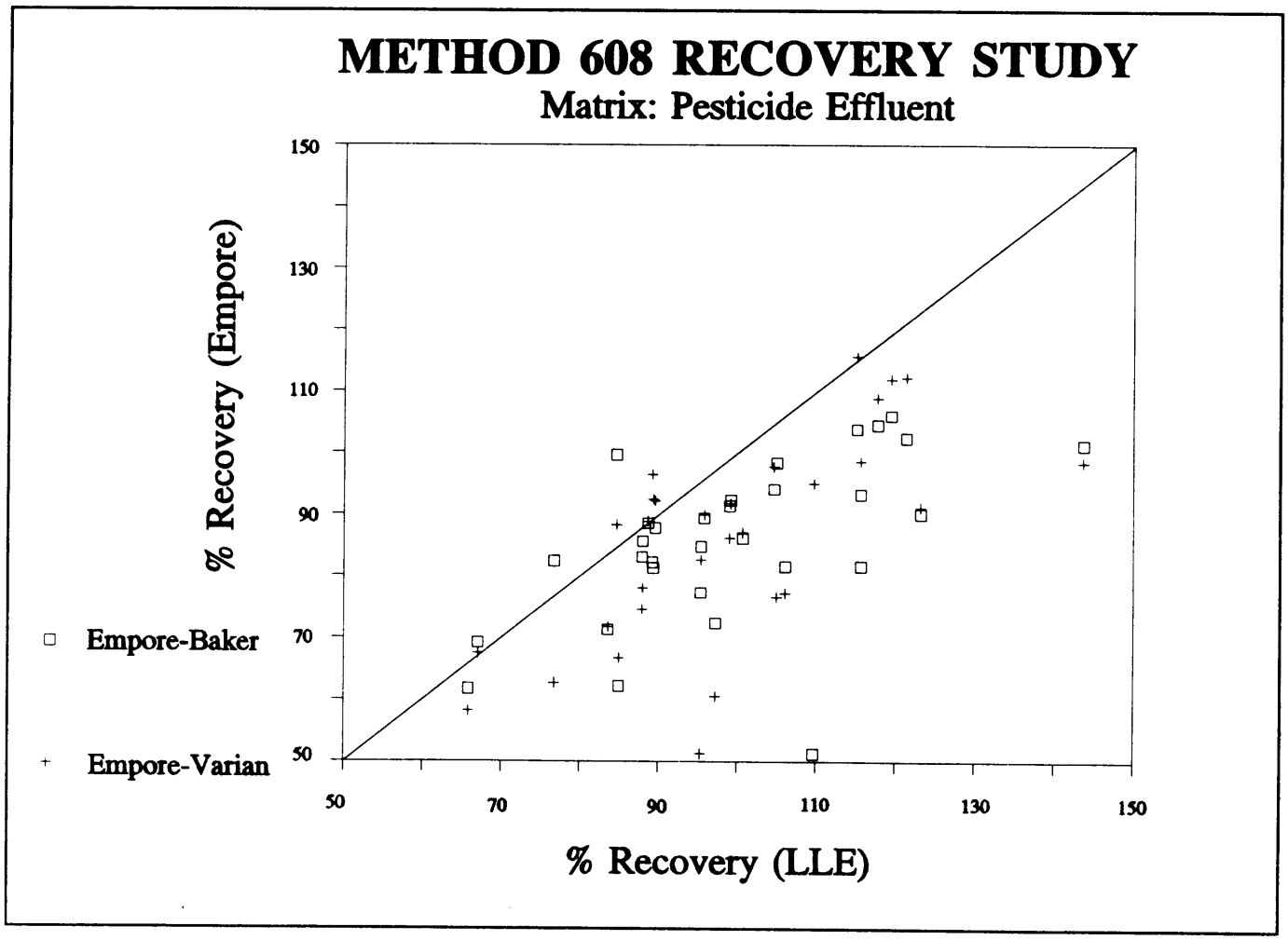
[SLIDE 13]


METHOD 608 RECOVERY STUDY
Matrix: POTW Effluent
% Recovery (Empore)
% Recovery (LLE)
Empore-Baker
Empore-Varian
150
130
110
90
70
50
50
70
90
110
130
150

[SLIDE 14]


METHOD 608 RECOVERY STUDY
Matrix: Pulp/Paper Effluent
% Recovery (Empore)
110
90
70
50
50
70
90
110
% Recovery (LLE)
Empore-Baker
Empore-Varian

[SLIDE 15]


METHOD 608 RECOVERY STUDY
Matrix: Pesticide Effluent
% Recovery (Empore)
% Recovery (LLE)
150
130
110
90
70
50
50
70
90
110
130
150
Empore-Baker
Empore-Varian

"There are three kinds of lies: lies, damned lies, and statistics."

Benjamin Disraeli

[SLIDE 17]

SUMMARY OF STATISTICAL TESTS FOR POTW MATRIX

Analyte	t-Test, α = 0.05		F-Test, α = 0.05	
	LLE/Empore-BAK	LLE/Empore-VAR	LLE/Empore-BAK	LLE/Empore-VAR
G-BHC	NO	NO	YES	NO
Heptachlor	NO	YES	NO	NO
Aldrin	NO	NO	NO	NO
Heptachlor Epoxide	NO	NO	NO	NO
Endosulfan I	NO	YES	NO	NO
Dieldrin	YES	YES	NO	NO
Endosulfan II	NO	NO	NO	NO
Endrin Aldehyde	YES	YES	NO	NO
DDT	NO	NO	NO	NO
DCBP (Surrogate)	YES	YES	NO	NO
A-BHC	NO	NO	NO	NO
B-BHC	NO	NO	NO	NO
D-BHC	NO	YES	NO	NO
A-Chlordane	YES	YES	NO	NO
DDE	NO	NO	NO	NO
Endrin	NO	YES	NO	NO
DDD	NO	NO	NO	NO
Endosulfan Sulfate	NO	YES	NO	NO
Endrin Ketone	NO	NO	NO	NO
DCBP (Surrogate)	NO	NO	NO	NO
Toxaphene-1	YES	YES	NO	NO
Toxaphene-2	NO	NO	NO	NO
Toxaphene-3	NO	NO	NO	NO
Toxaphene-4	NO	NO	NO	NO
DCBP (Surrogate)	NO	NO	YES	YES
Aroclor 1016-1	YES	YES	NO	NO
Aroclor 1016-2	YES	YES	NO	NO
Aroclor 1016-3	YES	YES	NO	YES
Aroclor 1016-4	YES	YES	NO	NO
Aroclor 1260-1	YES	YES	YES	YES
Aroclor 1260-2	YES	YES	NO	NO
Aroclor 1260-3	NO	NO	NO	NO
Aroclor 1260-4	NO	YES	YES	NO
DCBP (Surrogate)	YES	YES	NO	NO

[SLIDE 18]

SUMMARY OF STATISTICAL TESTS
MATRIX: POTW

Analyte	Average Recovery Difference		Smaller Variance	
	LLE/Empore-BAK	LLE/Empore-VAR	LLE/Empore-BAK	LLE/Empore-VAR
G-BHC			EMPORE	
Heptachlor		-20		
Aldrin				
Heptachlor Epoxide				
Endosulfan I		-18		
Dieldrin	-11	-14		
Endosulfan II				
Endrin Aldehyde	-24	-20		
DDT				
DCBP (Surrogate)	-11	-17		
A-BHC				
B-BHC				
D-BHC		9		
A-Chlordane	16	25		
DDE				
Endrin		10		
DDD				
Endosulfan Sulfate		10		
Endrin Ketone				
DCBP (Surrogate)				
Toxaphene-1	-16	-27		
Toxaphene-2				
Toxaphene-3				
Toxaphene-4				
DCBP (Surrogate)			EMPORE	EMPORE
Aroclor 1016-1	-26	-63		
Aroclor 1016-2	-14	-13		
Aroclor 1016-3	-52	-32		LLE
Aroclor 1016-4	-11	-18		
Aroclor 1260-1	-18	-23	LLE	LLE
Aroclor 1260-2	-33	-21		
Aroclor 1260-3				
Aroclor 1260-4		-16	LLE	
DCBP (Surrogate)	-18	-8		

[SLIDE 19]

SUMMARY OF STATISTICAL TESTS FOR PULP/PAPER MATRIX

Analyte	t-Test, α = 0.05		F-Test, α = 0.05	
	LLE/Empore-BAK	LLE/Empore-VAR	LLE/Empore-BAK	LLE/Empore-VAR
G-BHC	YES	YES	YES	YES
Heptachlor	YES	YES	YES	YES
Aldrin	YES	YES	YES	YES
Heptachlor Epoxide	YES	YES	YES	YES
Endosulfan I	YES	YES	YES	YES
Dieldrin	YES	YES	YES	YES
Endosulfan II	YES	YES	YES	YES
Endrin Aldehyde	YES	YES	YES	YES
DDT	YES	YES	YES	YES
DCBP (Surrogate)	YES	YES	YES	YES
A-BHC	NO	NO	NO	NO
B-BHC	NO	YES	NO	NO
D-BHC	NO	NO	NO	NO
A-Chlordane	YES	NO	YES	YES
DDE	YES	YES	NO	NO
Endrin	YES	NO	NO	NO
DDD	YES	YES	NO	NO
Endosulfan Sulfate	YES	NO	YES	NO
Endrin Ketone	NO	NO	YES	NO
DCBP (Surrogate)	YES	YES	YES	YES
Toxaphene-1	NO	NO	YES	YES
Toxaphene-2	YES	YES	NO	NO
Toxaphene-3	YES	NO	NO	YES
Toxaphene-4	NO	NO	YES	YES
DCBP (Surrogate)	NO	NO	NO	YES
Aroclor 1016-1	NO	YES	NO	NO
Aroclor 1016-2	NO	YES	NO	NO
Aroclor 1016-3	NO	YES	NO	NO
Aroclor 1016-4	NO	YES	NO	NO
Aroclor 1260-1	YES	YES	NO	YES
Aroclor 1260-2	YES	YES	NO	NO
Aroclor 1260-3	YES	YES	YES	NO
Aroclor 1260-4	YES	YES	NO	NO
DCBP (Surrogate)	YES	YES	NO	NO

[SLIDE 20]

SUMMARY OF STATISTICAL TESTS
MATRIX: PULP/PAPER

Analyte	Average Recovery Difference		Smaller Variance	
	LLE/Empore-BAK	LLE/Empore-VAR	LLE/Empore-BAK	LLE/Empore-VAR
G-BHC	-33	-33	LLE	LLE
Heptachlor	-26	-36	LLE	LLE
Aldrin	-25	-35	LLE	LLE
Heptachlor Epoxide	-37	-47	LLE	LLE
Endosulfan I	-29	-35	LLE	LLE
Dieldrin	-27	-41	LLE	LLE
Endosulfan II	-28	-42	LLE	LLE
Endrin Aldehyde	-30	-50	LLE	LLE
DDT	-14	-24	LLE	LLE
DCBP (Surrogate)	-23	-32	LLE	LLE
A-BHC				
B-BHC		15		
D-BHC				
A-Chlordane	-36		EMPORE	EMPORE
DDE	-45	-25		
Endrin	-19			
DDD	-48	-25		
Endosulfan Sulfate	-11		EMPORE	
Endrin Ketone			EMPORE	
DCBP (Surrogate)	-36	-22	EMPORE	EMPORE
Toxaphene-1			LLE	LLE
Toxaphene-2	-46	-32		
Toxaphene-3	-41			EMPORE
Toxaphene-4			LLE	LLE
DCBP (Surrogate)				EMPORE
Aroclor 1016-1		-24		
Aroclor 1016-2		-23		
Aroclor 1016-3		-53		
Aroclor 1016-4		-33		
Aroclor 1260-1	-39	-65		EMPORE
Aroclor 1260-2	-40	-73		
Aroclor 1260-3	-30	-48	EMPORE	
Aroclor 1260-4	-39	-57		
DCBP (Surrogate)	-18	-73		

[SLIDE 21]

SUMMARY OF STATISTICAL TESTS FOR PESITICIDE EFFLUENT MATRIX

Analyte	t-Test, α = 0.05		F-Test, α = 0.05	
	LLE/Empore-BAK	LLE/Empore-VAR	LLE/Empore-BAK	LLE/Empore-VAR
G-BHC	YES	YES	NO	NO
Heptachlor	NO	NO	NO	YES
Aldrin	NO	YES	NO	YES
Heptachlor Epoxide	NO	YES	NO	NO
Endosulfan I	YES	YES	NO	NO
Dieldrin	YES	YES	NO	NO
Endosulfan II	YES	YES	NO	NO
Endrin Aldehyde	YES	YES	NO	NO
DDT	YES	NO	NO	NO
DCBP (Surrogate)	YES	NO	NO	NO
A-BHC	YES	YES	NO	NO
B-BHC	YES	YES	NO	NO
D-BHC	YES	YES	NO	NO
A-Chlordane	NO	YES	YES	NO
DDE	YES	YES	NO	NO
Endrin	YES	YES	NO	NO
DDD	YES	NO	NO	NO
Endosulfan Sulfate	NO	NO	YES	NO
Endrin Ketone	NO	NO	YES	YES
DCBP (Surrogate)	YES	YES	NO	NO
Toxaphene-1	YES	YES	NO	NO
Toxaphene-2	YES	YES	NO	YES
Toxaphene-3	YES	NO	NO	YES
Toxaphene-4	NO	YES	NO	NO
DCBP (Surrogate)	YES	YES	NO	YES
Aroclor 1016-1	YES	YES	NO	NO
Aroclor 1016-2	NO	NO	YES	NO
Aroclor 1016-3	NO	YES	NO	YES
Aroclor 1016-4	NO	YES	YES	NO
Aroclor 1260-1	YES	YES	NO	NO
Aroclor 1260-2	YES	YES	NO	NO
Aroclor 1260-3	NO	NO	NO	NO
Aroclor 1260-4	NO	NO	NO	NO
DCBP (Surrogate)	YES	YES	YES	NO

[SLIDE 22]

SUMMARY OF STATISTICAL TESTS
MATRIX: PESTICIDE EFFLUENT

Analyte	Average Recovery Difference		Smaller Variance	
	LLE/Empore-BAK	LLE/Empore-VAR	LLE/Empore-BAK	LLE/Empore-VAR
G-BHC	-7	-7		
Heptachlor				EMPORE
Aldrin		-8		EMPORE
Heptachlor Epoxide		-10		
Endosulfan I	-5	-13		
Dieldrin	-11	-13		
Endosulfan II	-8	-13		
Endrin Aldehyde	-33	-32		
DDT	-6			
DCBP (Surrogate)	-8			
A-BHC	-11	-7		
B-BHC	-14	-8		
D-BHC	-13	-9		
A-Chlordane		7	LLE	
DDE	-22	-17		
Endrin	-21	-16		
DDD	-19			
Endosulfan Sulfate			EMPORE	
Endrin Ketone			LLE	LLE
DCBP (Surrogate)	-12	-12		
Toxaphene-1	-25	-37		
Toxaphene-2	-18	-44		LLE
Toxaphene-3	-58			LLE
Toxaphene-4		-28		
DCBP (Surrogate)	-25	-29		LLE
Aroclor 1016-1	-548	-724		
Aroclor 1016-2			LLE	
Aroclor 1016-3		-63		EMPORE
Aroclor 1016-4		-14	LLE	
Aroclor 1260-1	-42	-45		
Aroclor 1260-2	-15	-14		
Aroclor 1260-3				
Aroclor 1260-4				
DCBP (Surrogate)	-23	-18	LLE	

[SLIDE 23]

COMPARISON OF SOLVENT USAGE

Solvent	Amount of solvent used, mL	
	Liquid-liquid	Empore-solvent
Methylene chloride	260	60
Hexane	60	60
Methanol	0	20
TOTAL VOLUME	**320**	**140**
PURCHASE COST	$4.19	$1.56

[SLIDE 24]

CONCLUSIONS

- Empore extraction disks are an acceptable alternative to liquid-liquid extraction for the determination of organochlorine pesticides and PCBs in wastewater:

  recoveries are comparable, usually within 15 % of the liquid-liquid extraction data
  precision is comparable
  extracts from Empore disks have fewer interferences
  solvent use is reduced.

- The 90 mm disks can process wastewater samples without difficulty, when used with a glass fiber filter.

- Empore disks can be used with other procedures, such as SFE, which further reduce solvent consumption.

[SLIDE 25]

"He uses statistics as a drunken man uses lamp posts - - for support rather than for illumination."

Andrew Long

[SLIDE 26]

ACKNOWLEDGEMENTS

3M Company

Craig Markell
George Schmitt

U.S. EPA/VIAR

Bill Telliard
Harry McCarty

[Blank Page]

MR. TELLIARD: Could we get started again, please? We would like to continue. I forgot this morning to announce that...after 15 years, my mind is going or has gone...the folks to my right are taking down the proceedings that end up on a publication that generally comes out two to three hours right after this publication or concurrently, you know, in about 11 months.

So, everything we are saying is being recorded for posterity. If for some reason you would like to make a comment, call somebody a name or something along that line, and don't necessarily want it in the record or the proceedings, simply state that when you get to the microphone, and we will be glad to turn off the women. Turning off women is one of my specialties. So, keeping that in mind, we will continue on.

Our next speaker is from Boise Cascade. They are the people who make those milkshakes that you heard about earlier this morning.

Sarah Barkowski is with Boise Cascade and has been doing some work on the analysis of dioxins and furans using solid phase extraction, and I hope she is using Method 1613, and she is going to talk a little bit about their success with using solid phase extraction.

Thank you.

MS. BARKOWSKI: I would like to start off the record. Our milkshakes are strawberry.

First slide, please. The analytes that I want to talk about are 2,3,7,8-tetrachlorodibenzodioxin and 2,3,7,8-tetrachlorodobenzofuran or just dioxin and furan for short.

As you guess from the structure of these compounds, they are very hydrophobic. They don't present for use the problems that we have seen earlier this morning with the phenols. 2,3,7,8-TCDD is an extremely toxic compound for certain animals, and, unfortunately for the pulp and paper industry, very small quantities of these compounds are made under certain bleaching conditions during the bleaching of pulp.

Naturally, then, the EPA being right on the ball, they have written some methods for analyzing for our effluents for these compounds at the part per quadrillion level. Other agencies have written similar methods, and they all follow the same sort of generic background.

Next slide, please. It is an isotope dilution method. A liter of sample is spiked with C^{13} labeled 2,3,7,8-TCDD and TCDF which I will refer to as the internal standard. When everybody writes a method, they all call these things different. They assign different names to all these standards, and I have always called these the internal standards.

The sample after spiking is then filtered, and the solids are Soxhlet extracted. Some methods use toluene and a Dean Stark trap on the Soxhlet. Other methods use a mixture of toluene and ethanol, and the air dry the sample. But the point is that the sample is filtered, and the solids are extracted separately.

The filtrate is extracted by all the methods using a separatory funnel, liquid-liquid shakes with methylene chloride. The sample bottles have to be rinsed, as we talked about this morning, with other analytes. Methylene chloride is used to rinse the sample bottle, and that just gets thrown in with the shakes.

These two extracts then have to be concentrated and combined, and then that gross extract is spiked with Cl^{37} labeled cleanup standard.

The extract then goes through a series of column chromatography steps which serve to purify the extract, and finally, it is concentrated to 10 microliters, and just prior to analysis by GD/mass spec, the extract is spiked with the C^{13} labeled recovery standard which has the chlorines in the 1,2,3,4positions.

You get five pieces of information from this process. Three of those are the internal standard and the cleanup standard recoveries.

The internal standard recoveries will reflect losses that occurred after spiking with internal standard and before spiking with recovery standard, whereas the cleanup recoveries will reflect only losses that occurred after the extraction procedure.

So, if you run a sample and you get lousy recoveries across the board with all these standards, you know that the losses occurred in the cleanup steps and not during extraction. Alternatively, if the internal standard recoveries are poor but the cleanup standard recoveries are good, then you know that the losses occurred during extraction.

The two other pieces of information that you get from this are, of course, the analyte concentrations, the 2,3,7,8dioxin and furan native to the sample.

As with any isotope dilution method, the measured analyte concentrations will be correct only if the internal standard is recovered at the same efficiency that the native is recovered. If both of these compounds are recovered at 10 percent efficiency, the measured concentration will be correct. If they are both extracted and recovered at 100 percent efficiency, the measured concentration will be correct. This is true with any isotope dilution method.

However, if for some reason the native is recovered at 100 percent and the internal standard is recovered at 50 percent, the measured concentration will be twice the actual concentration.

Now, you might ask how could you do this when the only difference between these compounds is that one is C^{13} labeled and one is just the native compounds. Well, back when you spiked the compounds or spiked the samples, there is no guarantee that the internal standard will get incorporated into the matrix in a way that mimics the native compounds.

So, for example, if the native is...whydon't you go ahead and go to the next slide. If the native is 90 percent attached to the solids and only 10 percent over there in the filtrate portion and the internal standard gets evenly distributed between those two phases, then if your Soxhlet extraction and filtrate extraction run at different efficiencies, then the internal standard recoveries in this example would be 75 percent which is generally accepted to be a good recovery, but the measured concentration will have inherent to it a 27 percent positive bias.

So, basically, there are some assumptions that the method makes that must be valid before the measured concentrations will be good.

Either the internal standard and native have to partition between these two phases in exactly the same way, or you have to extract these two phases at exactly the same efficiency, or else you will have an inherent bias in the procedure.

The reason that I wanted to bring attention to this feature of the method is because what I am talking about is making a change to the conventional liquid-liquid extraction part of the procedure, and it is very important when doing this, you know, you make a change like this, to validate this.

Matrix spikes or native spiked blanks are not a rigorous validation experiment. You have to run samples side by side, samples which contain measurable quantities of these compounds. Side by side. Do them by liquid-liquid shakes and do them by the alternative extraction procedure and compare the results.

We know that we can extract matrix spikes at the same recovery that we extract the internal standard, because they are in the same...you know, they are introduced in the sample in the same way.

The reason Boise Cascade decided to mess around with this procedure was because about two or three years ago, we had about 200 or 300 effluent samples that needed to be analyzed, and nobody in our lab had ever done a liquid-liquid shake on an effluent before.

When we started doing that, we found out right away that we formed emulsions, and not being experienced with handling these emulsions, we found ourselves extracting a couple samples in the morning and spending the rest of the day trying to

break up these emulsions. The backlog was not improving.

So, we abandoned our efforts altogether in analyzing the samples and just focused our attention in developing an alternative extraction method.

Why don't you go to the next slide, please. After failing miserably with some attempts at continuous liquid-liquid extractions, we started experimenting with some solid phase extraction methods. We started out with the pre-packaged columns and cartridges that were available. This is a couple years ago. They were plugging within less than 100 ml.

Then we went on to the 47 mm disks. This was at a time when the 90 mm weren't available. And we did get significantly more sample through. We could get 300 or 400 ml, depending on the sample, before it would plug, but they did plug before we got a liter through.

We did one of those long, drawn-out experiments, though, where we just let it drip and drip and drip and drip so that we could get a sample through the lab, and we did get good recoveries, and the analyte concentrations matched very well with the liquid-liquid shakes.

So, what that told us was that there is a good chance that the chemistry was right for doing solid phase extraction of effluents for dioxins and furans. We were just restricted by the physical limitations of the gadgets that were out at that time.

So, we had some conversations with the folks at 3M, and bearing in mind the hundreds of samples in our backlog, we decided to go ahead and put together a little homemade device.

Next slide please. This is a...it is kind of a poor man's disk. This is using the conventional glassware for the filtration assembly. We put a GFF glass fiber filter in the normal spot, and then we poured both phase RP silica on top and just leveled it out. It was 10 ml of silica.

And then we wedged one of those chubby GFDs on top of that and kind of made a sandwich out of it.

Next slide, please. These sandwiches didn't plug, so we went ahead and worked out the details of running the samples through, and we have done some

validation experiments.

The pre-extract steps that we used for the sandwich method was to adjust the sample pH to 1 to 2. Sample pH adjustment is one of those optional steps in some of the conventional methods, and we found that it was a necessary step in doing solid phase extraction.

The conventional methods, the spikes are usually transferred in acetone, and this is done in hopes to get that internal standard integrated into the matrix. Acetone is a little bit stronger solvent than ethanol, so we chose to go ahead with ethanol since we could get the spike dissolved in the ethanol, and we could get the ethanol dissolved into the sample. We figured it would accomplish the same thing.

We sonicate all our samples right after spiking for an hour, just a little added step that makes us feel better about getting that internal standard incorporated into the matrix.

The samples are then pre-filtered through a GFC and through a GFF, and the bottle rinse step which is normally done with methylene chloride, we were doing that now with methanol, and then that methanol gets added to the filtrate, and it makes, if you have got a 1 liter sample, it makes your filtrate 5 percent in methanol which will help maintain the activity of the silica.

The filtrate extraction steps, then, are to assemble the apparatus from the previous slide and then to pass methanol through the silica to activate it, and then pass the filtrate through before the silica...or before the methanol has all gone through, and then we were eluting with methylene chloride.

Next slide, please. We didn't optimize the parameters for this method because of the pressure to get the samples run through the lab, so we just went ahead with those and validated it.

To validate the method, like I said earlier, we didn't look at matrix spike recoveries and those sorts of things, because they really don't reflect...they don't address the issues that I talked about earlier where it is so important that the native and the internal standard be proportioned between those two phases in the same way and that the recoveries are the same through those two phases.

So, we just went ahead and compared measured concentrations from runs using the sandwich method to measured concentrations from runs using the liquid-liquid extraction method. Also, we did look at the internal standard recoveries.

And to test for break-through, we took the filtrate after it had been passed through the sandwich and did liquid-liquid shakes on that. So, I will show you some of the results from that as well.

Next slide. You can see here that we did 12 runs with liquid-liquid shakes and 12 runs using the sandwich method. All those sandwich runs were done at Boise Cascade. The liquid-liquid shakes were done mostly at two different outside labs, labs A and B, and then also some were done at Boise Cascade.

There are four samples in this experiment. These are all...well,they are not milkshakes, but they are real samples. They have been collected from four different Boise Cascade mills. Three of them are secondary effluents or effluents to the river, and one of them is an untreated effluent.

You can see that the lowest level sample we ran, sample number 4, is around 15 parts per quadrillion TCDD and that the highest level sample is about 130 parts per quadrillion TCDD. So, that is kind of the low end and the high end.

The calibration limit for the method is 10 ppq. Then, samples 1 and 2 kind of fall there in between.

Regardless of the statistical method that I came up with to look at these two sets of numbers, the two methods yielded results which were not significantly different at the 99 percent confidence limits. I ran these by lumping all the samples together, but what that tends to do is just increase the sigmas for the two sample sets because of the big differences in the samples.

So then I did it sample by sample, comparing the means of all the liquid-liquid runs for sample 1 to the mean of all the sandwich runs for sample 1, and for both analytes and for all four samples, the difference between the means was not statistically significant at the 99 percent confidence limit.

Next slide, please. The next slide looks at the internal standard recoveries for the two different runs. On the right-hand side is the average of the sandwich

methods and 95 percent confidence limits for that, and then the bar on the left-hand side is the average of the internal standard recoveries for the liquid-liquid shake method.

So, you can see that we got a little better recoveries. I think the point is that the recoveries were, in general, good.

There is another factor in this experiment because it crosses labs, you know.

If you go to the next slide, it shows a comparison of the furan internal standard recoveries for the liquid-liquid on left versus the sandwich on the right.

Next slide, please. We did get through our backlog using this method, but as you all know, 3M has come out with the 90 mm disk. This is a chromatogram from a standard, and I want to explain this so I can show you what we got in our test for break-through.

The top two peaks show the native analyte. The bottom two peaks are the C^{13} labeled peaks. The ones on the right-hand side which elute the same time as the native, that is the C^{13} labeled internal standard, and the one on the left-hand side is the 1, 2, 3, 4, the recovery standard that is put in. This is just what a standard injection looks like, the chromatogram.

Would you go to the next slide, please? When we did the liquid-liquid shakes on the filtrate after it had passed through the sandwich, this is a typical result of what we got. The peaks that you see there are due to the recovery standard.

The location of where the internal standard would be...could you raise that a little bit, a little higher? I put an arrow on there to show. That is where the internal standard would be if we had found some.

And then the two chromatograms on the top would show where the native...the native would be at the same place where the internal standard is.

So, basically, our tests for break-through on the solid phase extraction method pretty much all looked like this. There was no significant break-through.

With the 90 mm disks available now, though, there are a lot of limitations to this sandwich method, especially in comparison to the disk method. We are using 10 ml of the RP silica for our sandwich, and we are using it very inefficiently. We don't

have it packed into a little teflon matrix. That is why we have to use so much of it. You can get by with a lot less silica on a disk than you can with a sandwich.

It takes a lot of time to put the sandwiches together. The RP silica all has to be pre-extracted with methylene chloride. The two filters have to be cleaned. The top filter has to be trimmed. You know, it takes time to put all that together.

And the solvent used for the solid phase extraction method is not at all minimized. As I said earlier, we really didn't optimize for minimal solvent use. We optimized for the fastest method we could validate and run our samples.

The sandwich method worked very well in comparison to the liquid-liquid shake method, but in comparison to the disk method, there is a whole lot of opportunities that are in front of us there.

Next slide, please. The only differences between the pre-extract steps with the disk method and the sandwich method is that you only pre-filter through a GFC, and the methanol that is added, we reduced that from 50 ml to 5 ml.

In our tests for break-through on the disk method, we were seeing some early experiments, and we cut back on this methanol thinking that it might reduce that break-through, but I don't think it really had an effect.

The filtrate extraction steps, though, are a little bit different. We put a GFF on top of the disk so the filtration steps, whereas in the other method, you have two filtration steps, with the disk method, you also have two filtration steps, and the extraction of the filtrate gets accomplished in that second filtration step. So, it really streamlines the procedure.

Again, the 50 ml of methanol is passed through to activate the disk. And then we put a water step in between the methanol step and the filtrate, and that kind of helps make the method a little bit more user friendly.

If you add the methanol and then the sample, you have got to get that sample in before the methanol all goes through but not too much before, or else you will have a lot of methanol in there, and you will just be washing your analytes through. So, you can get a little bit sloppy about when you add these things if you put a water step in between.

Finally...could you raise that a little bit? The real streamlining of the procedure is in this last part here. The analytes are not eluted from the disk with solvent by passing it through the filtration assembly. Instead, we just take the disk and the GFF and the GFCs from the pre-filtration and throw the whole mess into the Soxhlet.

So, what we have...next slide, please...is the original method gets streamlined quite a bit, because you don't have two separate flasks that have to be rotovapped and combined. You know, the methylene chloride from doing shakes, you have to dry it with sodium sulfate, rotovap or concentrate it by whatever means and combine it, and all that is removed from the procedure.

I know everybody in our lab is delighted to run the disk method as compared to any of the other methods.

Next slide, please. Again, to validate the disk method, we did run, of course, you know, method blanks and spikes of the method blanks and spikes of samples, and all those results, you know, we got clean method blanks, and our spiked recoveries are all right around 100 percent, but just because you have accomplished that doesn't mean you have a method that will give a right answer. You have to compare the results of measured concentrations from liquid-liquid shakes compared to the disks, and again we did the tests for break-through.

Next slide, please. If you will start out by looking at just the first eight lines here, you can see that there were four runs with liquid-liquid shakes, four runs with the disk method. Sample number 3 is evenly distributed between each of those four runs and the same with sample number 1.

Again, statistical analysis of the concentrations for dioxin and furan show that there is no statistically significant difference at the 99 percent confidence limits, and the recoveries, again, for the disk method are very good in comparison to the liquid-liquid shake method.

The dioxin issue, though, it isn't over with a method that measures down to 10 ppq. The proposed compliance levels at some of the mills in our final effluents are well below the calibration limit in addition to being below, in some cases, the detection

limits.

So, some of the regions are looking into going into the mill back at a location where that dioxin is more concentrated and pulling a sample from there and measuring the dioxin.

So, the method, if they are going to do that, the method will need to be valid for samples other than just our final effluents.

Now, a final effluent really looks like a cup of tea, but a D-stage filtrate looks like espresso, and it is about a pH 10. So, we ran some of the espresso and other filtrates collected during the different stages of the bleaching process through the disks.

And we didn't...when we were running our final effluents, we didn't measure how long it took to run them through the disks. They ran through so fast it didn't matter.

But when the D-stage filtrates and the E-stage filtrates were run through, they were taking about 20 minutes.

What it kind of looks like when it goes through the disk, the first part that is coming through is colorless, but after a couple hundred ml have come through, colored compounds start breaking through, and by the time you get a liter through, you really can't tell if you have removed a significant amount of that color.

Now, with the D-stage filtrates, they look just as bad coming out as they do going in, but the analytes here, the dioxins and furans, are so hydrophobic as well as being particulate-bound that if you reduce the pH of the sample prior to running it through the disk, you will precipitate out a lot of these compounds, and then they will go through the Soxhlet extraction rather than the filtrate extraction.

For the first four runs of the purple compounds, those are all collected from one mill, and the recoveries were good for those samples, and the measured concentrations compared well to runs that we did using solid phase extraction.

The last three lines on this overhead show samples which were non-detect for dioxin. All the samples were. And there were some measured concentrations for furan.

These concentrations compared very well with those from liquid-liquid

shakes on the same compounds. I didn't include them in the statistical analysis, because it becomes a little difficult on how to work with non-detects.

You can see, though, that the furan recoveries for two of these samples were very low. They are down there in the 40 percent.

This was really kind of a puzzle, because you would normally expect the furan internal standard to be recovered at the same efficiency as the dioxin internal standard is. You can cut your cleanup steps wrong and lose some of your furan compounds relative to the dioxins, but if that were happening through our cleanup steps, you would think that it would happen to all the samples and not just two.

So, I really can't explain why, for two of our runs with the disk method, we got low furan recoveries for the E-stage filtrates.

Next slide. In our tests for break-through with the disk method, in our first experiments, we were seeing about 10 percent internal standard, and as I said, we changed some things in the pre-extract steps to help reduce that, but it wasn't until we ran a sample through at a reduced pH that we really got it down to where it is now. You can see just a little bit of internal standard in there, and there are obviously no peaks up in the native channels.

I guess, in summary, I think that the disk method is definitely an attractive alternative to liquid-liquid shakes. It reduces solvent consumption, and it makes the method much more efficient.

But there are a lot of things that will need to be done before you can validate something like this. In particular, those validation studies will have to include more work on bleach plant filtrates, the espresso type samples, and it will have to be work that compares the measured concentrations from the disk method to those from the liquid-liquid shake method.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MR. THOMAS: My name is Roger Thomas. I work for Viar and Company.

I notice that concerning your solid phase extraction, you noted that there is a pre-extraction step whereby you take 1 liter of sample plus your spiked compound which is your internal standard, and then you sonicate it for 1 hour.

Have you done any studies on improved recoveries due to sonication based on time of sonication, you know, like 15 minutes, 30 minutes, 1 hour, versus, you know, samples not going through the sonication process?

MS. BARKOWSKI: The answer is no, we haven't done any studies to compare the effects of sonicating and different lengths of time that you sonicate, but I would imagine that all we are doing in that sonication step is trying to get the internal standard integrated into a matrix which mimics the native.

If the recovery of the filtrate and the solids are both good, then the effects of sonication will not be seen in any studies, but if the filtrate is extracted at a lower efficiency than the solids, and if the sonication pushes the internal standard toward the solids, then you would see an effect.

MR. THOMAS: Okay, thank you, but my biggest concern was an additional hour of time being added, you know.

MS. BARKOWSKI: Well, during the time that the samples are being sonicated, we are setting up our glassware.

MR. THOMAS: Okay, thank you.

MR. HALVORSON: My name is Jeff Halvorson from Burdick & Jackson.

I had a question for you about the glassware that you are using. You mentioned that you take some special precautions when you are...for instance, the reverse phase silica and the materials you are using, you clean them and prepare them specially. I know looking at part per quadrillion levels, you are going to need to have clean glassware and everything.

Are there any problems that you noticed with the filtration apparatus itself, any problems cleaning that?

MS. BARKOWSKI: We just used B&J solvents to clean it.

MR. HALVORSON: That is nice to hear.

MS. BARKOWSKI: Is that what you wanted?

MR. HALVORSON: I was more concerned with the frit itself. There is a lot of surface area in there.

MS. BARKOWSKI: Yes, yes.

MR. HALVORSON: And these are.

MS. BARKOWSKI: That is a good point. The extractions that we did on the filtrate after it was passed through, anything that we found in there did not prove that we were getting break-through. Because the glassware goes through two filtration steps, the first time through, you run it through, and that frit gets exposed to the sample.

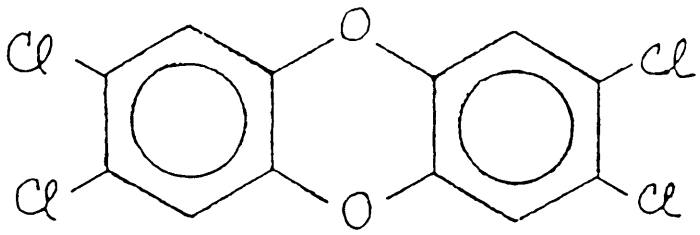
The second time through when you have a disk on there, of course, the first thing you run through the disk is methanol, and that sample that is stuck to the fritted glassware will then get washed through with methanol down there into that flask that we then take and test for break-through.

So, it could be that something like that is going on except for that wouldn't explain why we got different results for break-through from the sandwich method versus the disk method.

I think to solve the break-through with the disk method, it was important to lower the pH of the samples.

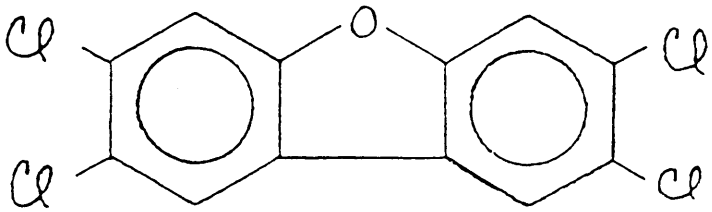
MR. HALVORSON: Thank you.

MR. TELLIARD: Thank you, sir.



2378-TCDD

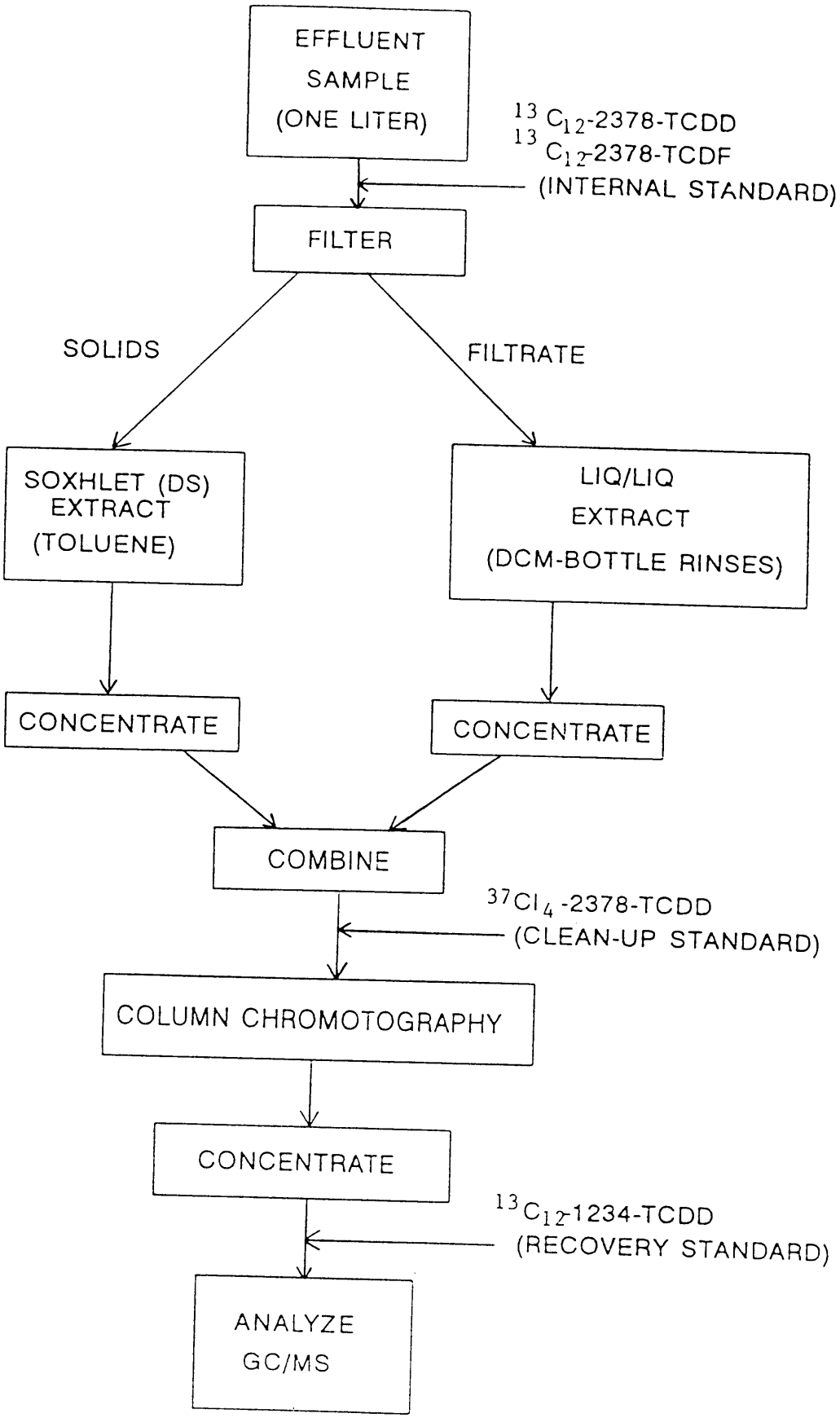
"DIOXIN"



2378-TCDF

"FURAN"

ppq = pg/L = 10^{-12} g/L


EFFLUENT SAMPLE (ONE LITER)
$^{13}C_{12}$-2378-TCDD
$^{13}C_{12}$-2378-TCDF
(INTERNAL STANDARD)
FILTER
SOLIDS
FILTRATE
SOXHLET (DS) EXTRACT (TOLUENE)
LIQ/LIQ EXTRACT (DCM-BOTTLE RINSES)
CONCENTRATE
CONCENTRATE
COMBINE
$^{37}Cl_4$-2378-TCDD
(CLEAN-UP STANDARD)
COLUMN CHROMOTOGRAPHY
CONCENTRATE
$^{13}C_{12}$-1234-TCDD
(RECOVERY STANDARD)
ANALYZE GC/MS

NATIVE ANALYTES PARTITION:	90% SOLIDS 10% FILTRATE
INTERNAL STANDARDS PARTITION:	50% SOLIDS 50% FILTRATE
SOXHLET EXTRACTION:	100%
FILTRATE EXTRACTION:	50%

(ASSUME 100% RETENTION THROUGH CLEAN UP.)

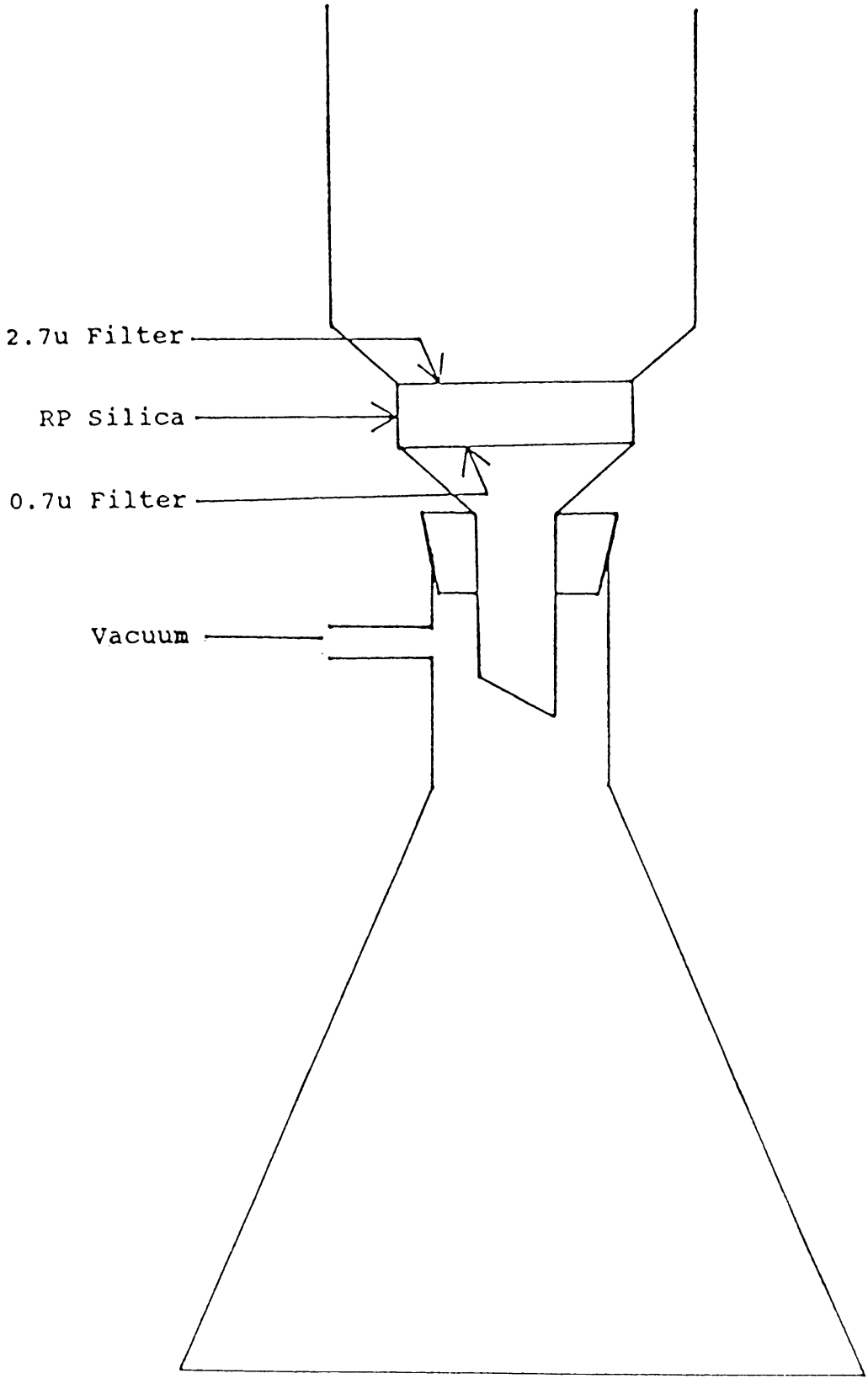
INTERNAL STANDARD RECOVERIES:	75%
MEASURED ANALYTE CONCENTRATIONS:	1.27 x ACTUAL

SPE METHODS

- PRE-PACKAGED COLUMNS AND CARTRIDGES
  - PLUGGED RAPIDLY
- 3M EMPORE DISK (47 MM)
  - PLUGGED
  - IF PATIENT, GOOD RESULTS
- HOMEMADE SANDWICH

BCC

Solid Phase Extraction Apparatus



SANDWICH METHOD

PRE-EXTRACT STEPS

- ADJUST SAMPLE pH TO 1-2
- SPIKE IN ETHANOL
- SONICATE 1 HOUR
- FILTER THROUGH GF/C AND GF/F
- RINSE BOTTLE WITH 50 ml METHANOL

FILTRATE EXTRACTION STEPS

- PREPARE SANDWICH:

  10 ML RP SILICA
  GF/F (BOTTOM); GF/D (TOP)

- PASS 30-50 ml METHANOL (TO ACTIVATE)
- PASS FILTRATE **BEFORE SILICA GOES DRY**
- ELUTE WITH 300 ml DCM

VALIDATION OF SANDWICH METHOD

- MEASURED ANALYTE CONCENTRATIONS:

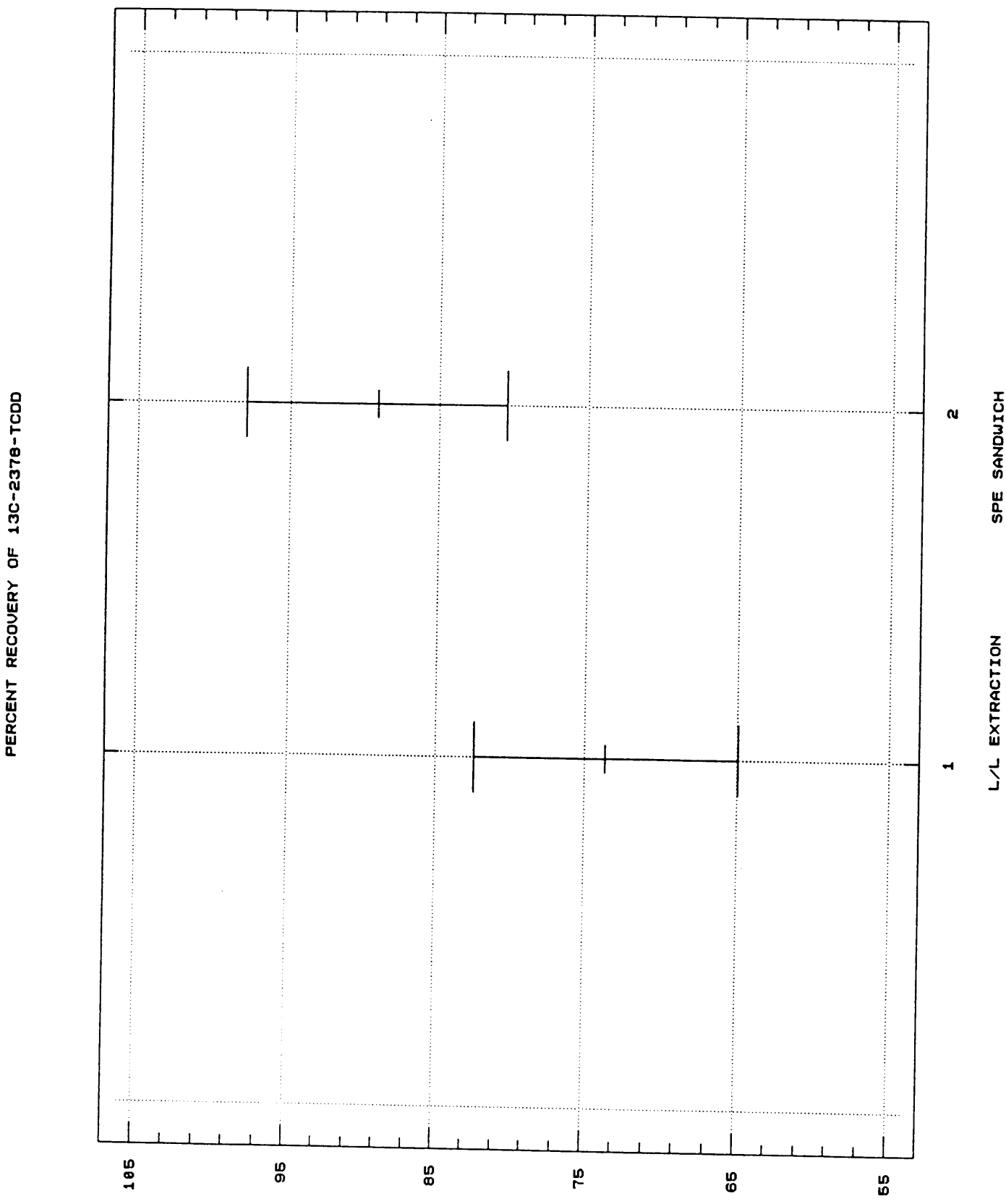
  SANDWICH VS. L/L

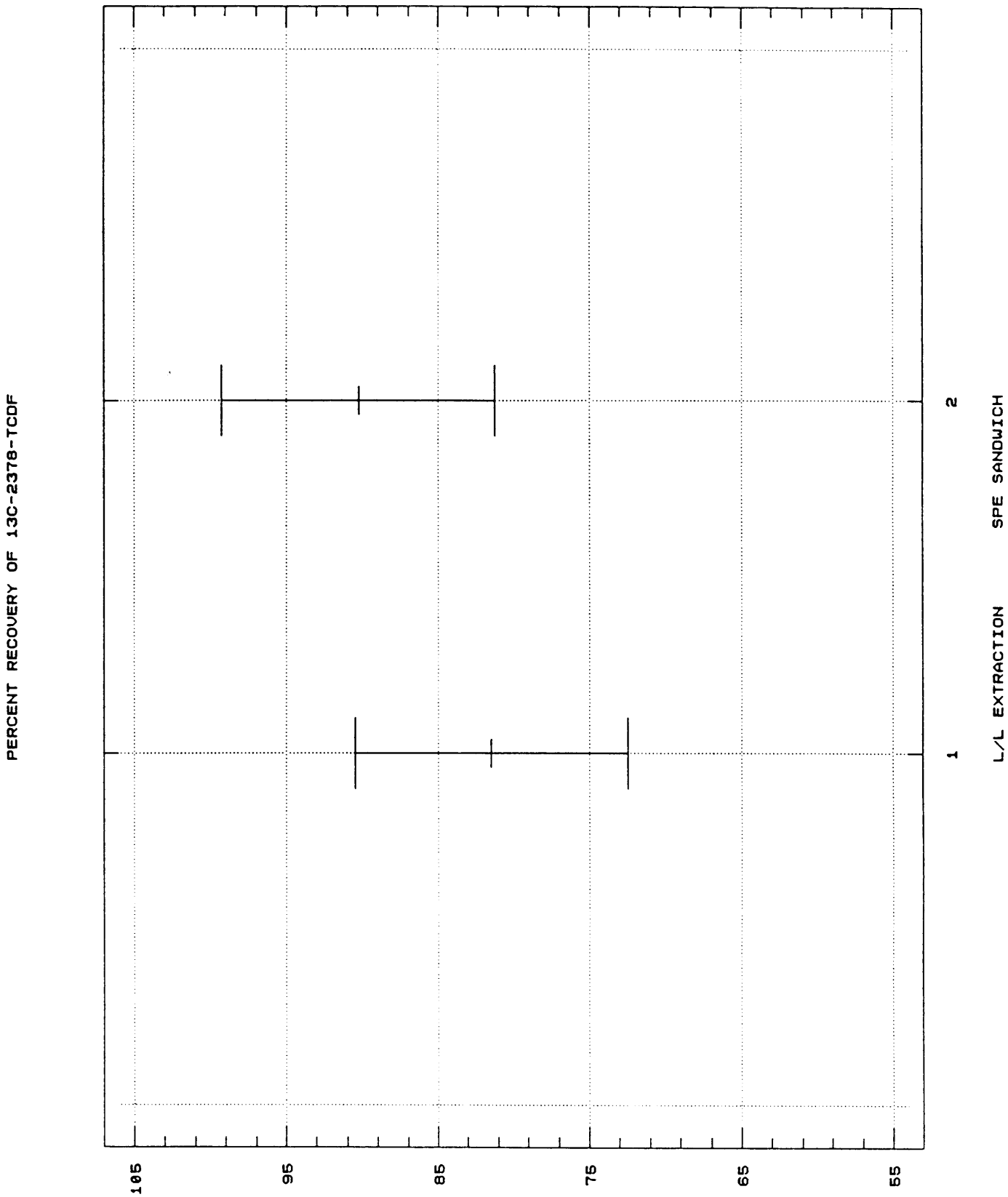
- INTERNAL STANDARD RECOVERIES:

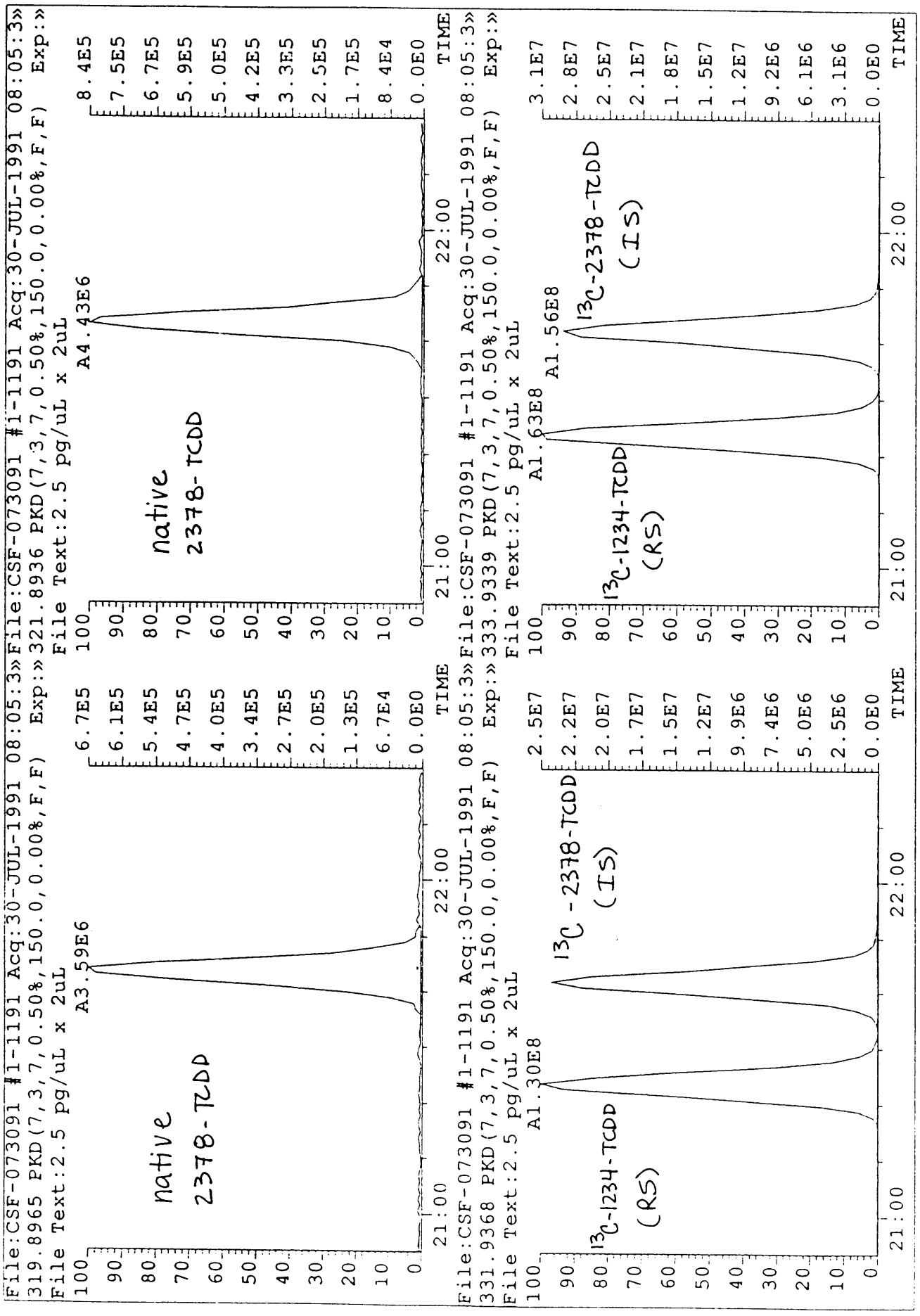
  SANDWICH VS. L/L

- L.L SHAKES OF FILTRATES AFTER PASSING THROUGH SANDWICH

METHOD	LAB	SAMPLE	TCDD	TCDF	ISD	ISF
L/L	B	1	68	250	62	88
L/L	B	1	76	260	42	56
L/L	A	1	75	310	78	70
L/L	A	1	76	300	71	67
L/L	B	2	36	220	71	72
L/L	B	2	41	230	65	78
L/L	BCC	2	40	280	89	106
L/L	BCC	2	49	240	104	114
L/L	B	4	13	70	69	81
L/L	A	4	16	84	70	73
L/L	A	5	120	770	75	81
L/L	A	5	140	750	88	92
SAND	BCC	1	68	319	108	83
SAND	BCC	1	73	330	95	76
SAND	BCC	1	65	337	97	73
SAND	BCC	1	70	351	94	83
SAND	BCC	2	43	190	70	104
SAND	BCC	2	44	260	78	112
SAND	BCC	2	40	260	67	96
SAND	BCC	2	45	280	87	112
SAND	BCC	4	15	73	107	84
SAND	BCC	4	15	70	97	88
SAND	BCC	5	120	820	94	95
SAND	BCC	5	130	850	76	77


PERCENT RECOVERY OF 13C-2378-TCDD
105
95
85
75
65
55
1
2
L/L EXTRACTION
SPE SANDWICH


PERCENT RECOVERY OF 13C-2378-TCDF
105
95
85
75
65
55
1
2
L/L EXTRACTION
SPE SANDWICH


native
2378-TCDD
native
2378-TCDD
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(IS)
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(IS)
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(RS)
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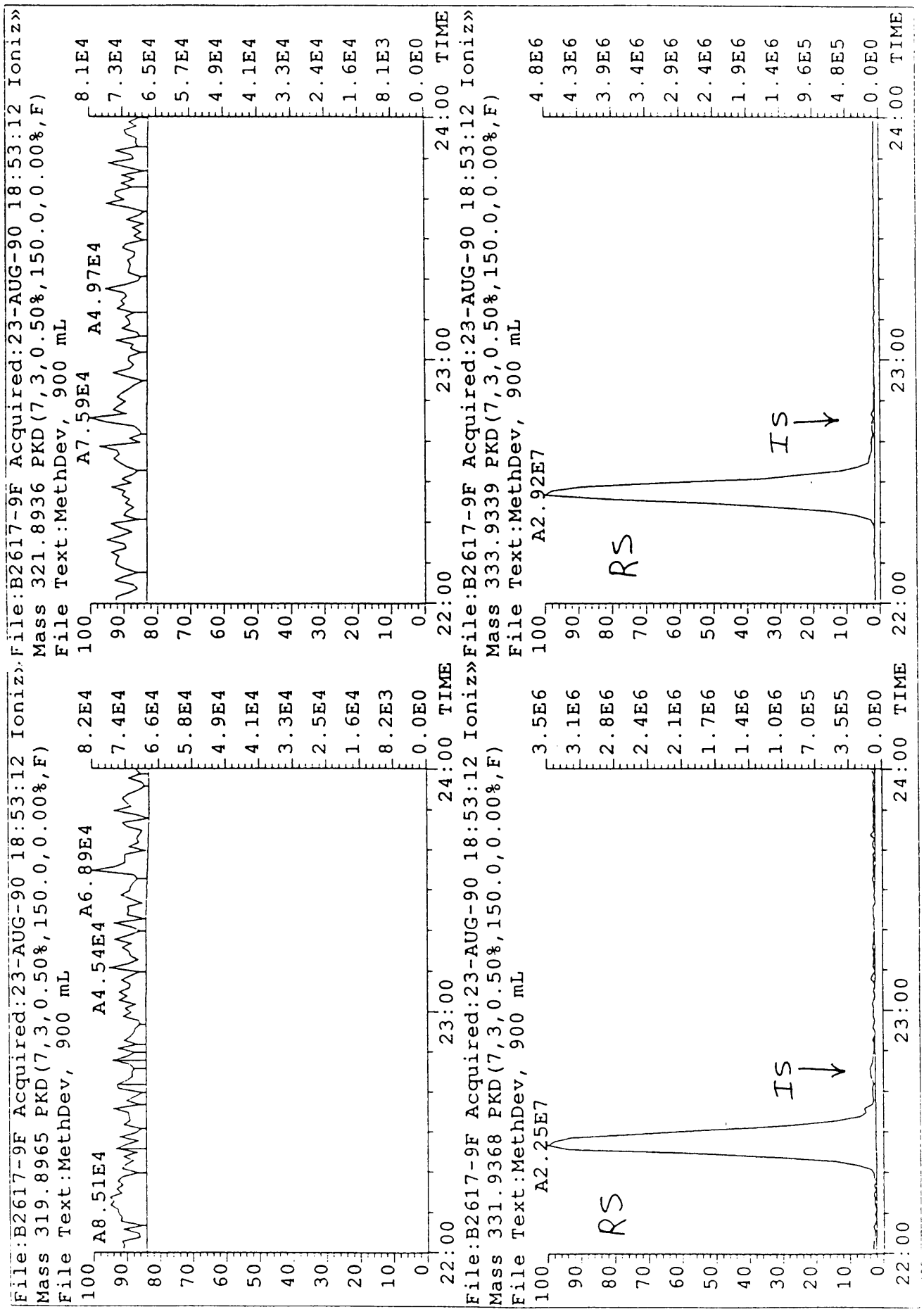
21:00
22:00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A4.54E4
A6.89E4
RS
IS
A2.25E7
22:00
23:00
24:00 TIME
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A2.92E7
RS
IS

LIMITATIONS OF SANDWICH METHOD

(AS COMPARED TO EMPORE DISK)

- INEFFICIENT USE OF EXPENSIVE RP SILICA
- PREPARATION OF SANDWICH
- SOLVENT USE NOT MINIMIZED

DISK METHOD

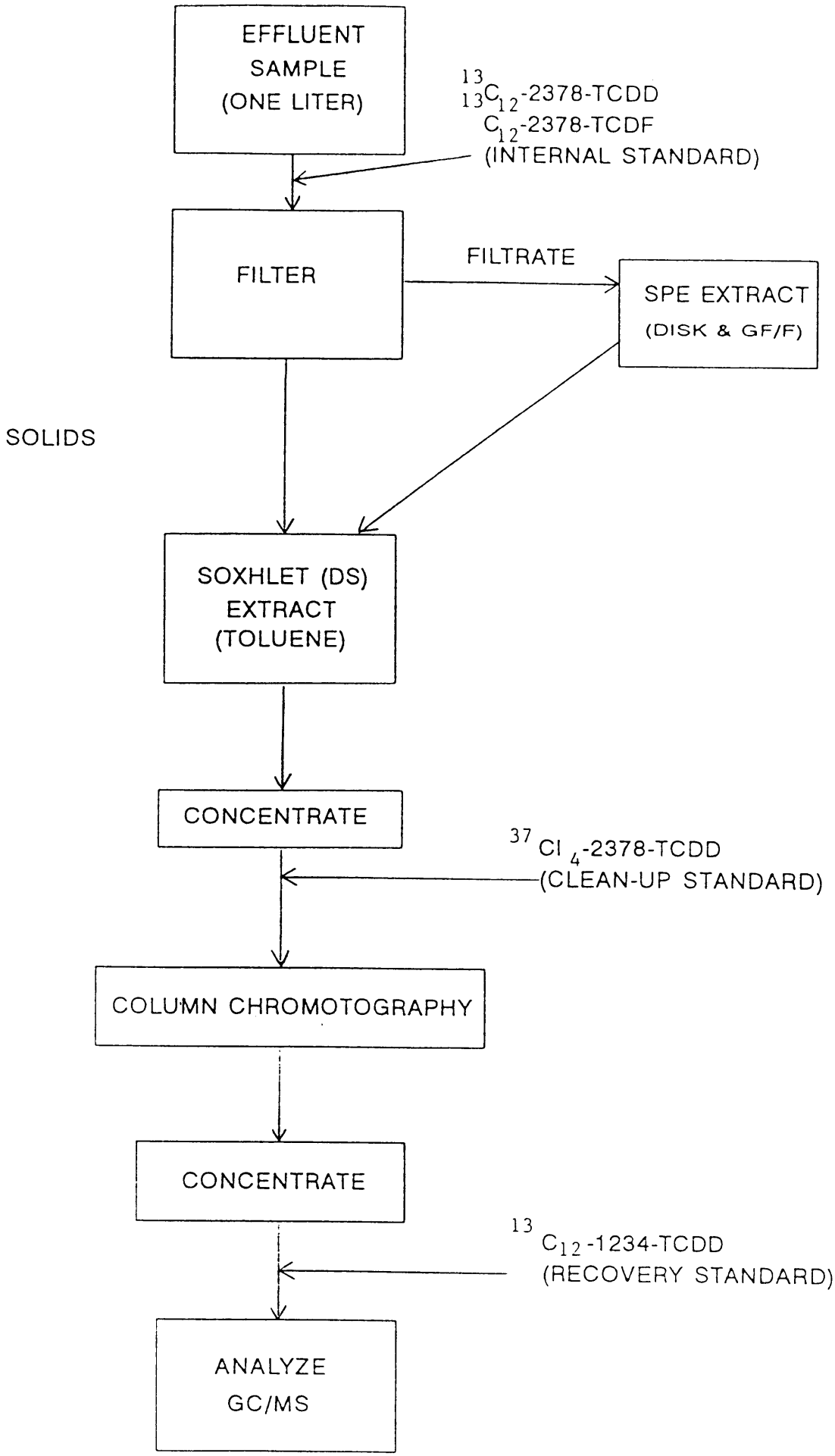
PRE EXTRACT STEPS:

- o ADJUST pH TO 1-2
- o SPIKE IN ETHANOL
- o ADD 5 ml METHANOL
- o SONICATE 1 HOUR
- o FILTER THROUGH GF/C
- o RINSE BOTTLE WITH 50 ml TOLUENE **(SOXHLET)**

FILTRATE EXTRACTION STEPS:

- o GF/F ON TOP OF 90 MM EMPORE DISK (C_{18})
- o PASS 50 ml METHANOL (TO ACTIVATE)
- o PASS 50 ml WATER **(BEFORE DISK GOES DRY)**
- o PASS FILTRATE **(BEFORE DISK GOES DRY)**
- o SOXHLET-DS EXTRACT WITH TOLUENE:

  ALL GF/Cs
  GF/F
  EMPORE-DISK


EFFLUENT SAMPLE (ONE LITER)
$^{13}C_{12}$-2378-TCDD
$^{13}C_{12}$-2378-TCDF
(INTERNAL STANDARD)
FILTER
FILTRATE
SPE EXTRACT
(DISK & GF/F)
SOLIDS
SOXHLET (DS) EXTRACT (TOLUENE)
CONCENTRATE
$^{37}Cl_4$-2378-TCDD
(CLEAN-UP STANDARD)
COLUMN CHROMOTOGRAPHY
CONCENTRATE
$^{13}C_{12}$-1234-TCDD
(RECOVERY STANDARD)
ANALYZE GC/MS

VALIDATION OF DISK METHOD

- MEASURED ANALYTE CONCENTRATIONS:

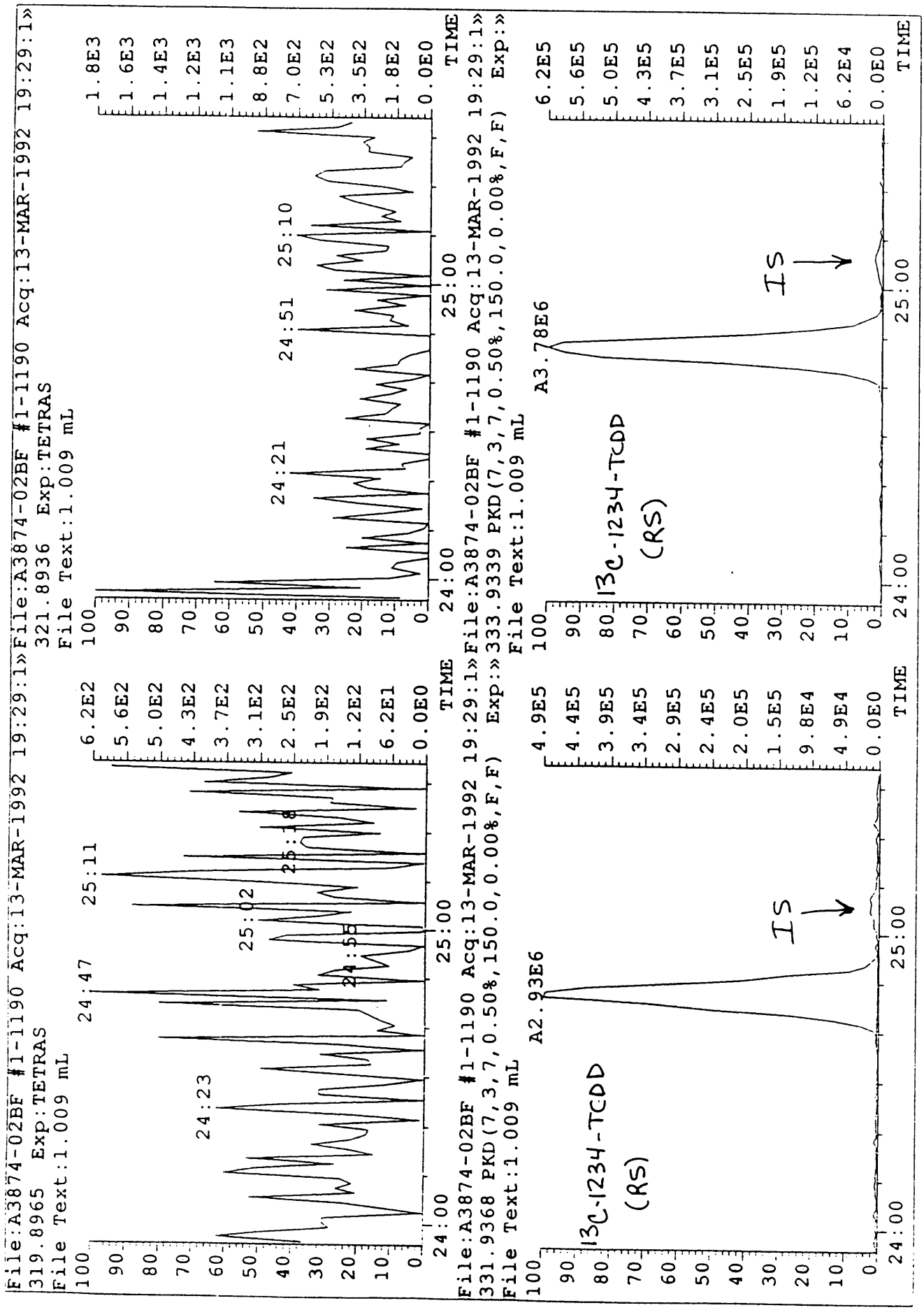
  DISK VS. L/L

- INTERNAL STANDARD RECOVERIES:

  DISK VS. L/L

- L/L SHAKES OF FILTRATES AFTER PASSING THROUGH DISK

METHOD	LAB	SAMPLE	TCDD	TCDF	ISD	ISF
L/L	A	3	54	290	88	88
L/L	A	3	53	280	93	98
L/L	A	1	75	310	78	70
L/L	A	1	76	300	71	67
DISK	BCC	3	49	297	71	87
DISK	BCC	3	52	305	72	89
DISK	BCC	1	69	296	79	81
DISK	BCC	1	76	306	89	98
DISK	BCC	6	130	390	106	114
DISK	BCC	7	140	270	84	94
DISK	BCC	8	17	50	92	110
DISK	BCC	9	1600	3300	74	76
DISK	BCC	10	0	0	74	42
DISK	BCC	11	0	5	80	46
DISK	BCC	12	0	3	72	77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File Text:1.009 mL
321.8936 Exp:TETRAS
File Text:1.009 mL
331.9368 PKD(7,3,7,0.50%,150.0,0.00%,F,F) Exp:»
333.9339 PKD(7,3,7,0.50%,150.0,0.00%,F,F) Exp:»
24:23
24:47
25:11
25:02
25:18
24:55
24:21
24:51
25:10
IS
13C-1234-TCDD
(RS)
A2.93E6
A3.78E6
TIME
24:00
25:00

MR. TELLIARD: Our next speaker comes from PACE Laboratories. Gabe is going to be talking about, again, solid phase extraction as it relates to the analysis for explosives. We have seen some data on this. We got a real big bang out of it.

MR. LE BRUN: First slide, please.

Good morning or good late morning. My name is Gabe Le Brun, and I am from PACE, Incorporated. Basically, what I am here to talk about today is the solid phase extraction disk method for the extraction of explosives from water.

Myself and Jim Madison developed this for the cartridge type technique about a year ago. We have been doing explosives by solid phase for about a year.

You may notice there is not on this list of credits, Craig Markell. If it wasn't to his dedication and perseverance and, mainly, his patience for my 6:00 a.m. phone calls and weekend phone calls, we wouldn't have been able to get the material that we were able to get for this particular presentation.

The first thing I want to do is I want to take a look at the analytes, the analytes of interest, and they were these particular compounds right here. HMX and RDX are, you may notice, the non-aromatic type compounds. TETRYL, the tri-nitrobenzene, the di-nitrobenzenes, the nitrotoluenes, the di-nitrotoluenes, and then the last two in the lower right-hand corner, PETN and nitroglycerin. You will notice that those are the two smaller molecules. Therefore, they needed to be analyzed at a different wavelength.

The two types of techniques that we have been utilizing, as I mentioned earlier, was the cartridge technique which is essentially a 6 ml type self-packed cartridge when we weren't able to get styrene divinylbenzene in actual cartridges.

And then the disk which I am not even sure if it is on the market as of right now, but at that particular time...that is why I was working so close with Craig, he said that he had disks for it. So, we were able to get some of these disks from Craig. We were using the 47 mm disks.

The biggest difference between these two methods is time. The amount of

time is unbelievable, as you will end up seeing from the following slides.

For the disk type technique, we analyzed groundwater, reagent water, and surface water. The groundwater went through in approximately 4 minutes. The reagent water went through in about 10 minutes.

You may be wondering why the difference between groundwater and reagent water. We think it is probably because in the groundwater, it has gone through a much more filtered type system. They are much cleaner than the actual reagent water. Kind of a scary thought, but it was much faster.

The surface water averaged about 70 minutes. We have heard about the milkshakes, and, actually, if this was given about a week ago, I would say that most of our samples have a little bit of particulate matter, but Thursday and Friday of last week, we had mosquito larvae swimming up and out, a lot of silicates, things like that.

I wish I could have had a slide, but believe me, I couldn't get it developed fast enough for this presentation.

The cartridge rate that we are currently using, and this is primarily to get the HMX recoveries that we need, is 1 to 2 ml a minute. Now, when you are doing 500 ml of water, that translates into 4 to 8 hours.

Those particular samples that I just mentioned with the high silicates and the biological, they were going the next day when I came in. So, there is problems with the cartridge technique, and I think that they can be eliminated with the disk technique with the glass fiber filter, as we have seen earlier.

This is the setup that we used for the cartridge technique. It is basically a homemade type apparatus, as you can probably see. I have got a manifold down there. We use the sep funnels. Craig, you want to get rid of the sep funnels? We think it makes a great container.

We can set this up for auto-flow. We are just stopping the top of the sep funnel, and it is just gravity feed. It goes into those 50 ml reservoirs. It flows down and, essentially, when the level goes down in the reservoirs, just enough is delivered that you can end up displacing with the air in the sep funnels.

When you are dealing with 8 hours, you only want it to be set up. So, that

is the particular technique that we used.

Here is just a little closer look. I am sorry about the overexposure, but you can see that the 50 ml reservoir is attached to the 6 ml cartridges, and then all of the water is collected right down in your suction flasks.

This is the disk manifold that we used. We obtained this from Craig. It is very effective. You notice that there are six set-ups.

Those are for the 47 mm disks. The question was automatically asked, what about the 90 mm disks when they end up becoming available? He goes well, then you just alternate every other one. So, your six position holder turns into a three position holder if you want to go to the 90 mm disks.

The disk technique, 75 to 125 ml a minute. I mentioned the item of time. When you are dealing with 75 to 125 ml a minute, that translates into 4 to 6 minutes.

This is for groundwater and for reagent water. I mentioned earlier that if you have a lot of particulate matter...we did not use the glass fiber filters for any of our stuff that we did. So, I would say that our 70 minutes would probably be drastically cut down, but on average for the groundwater and the reagent water, we are talking some very fast flow rates at 54 to 6 minutes for 500 ml of water.

Basically, what I want to do is I want to give you the opportunity to find out how the method was developed and what we actually did. I will be going into the disk preparation, the sample introduction. I will be touching briefly on the disk drying and the elution and concentration.

First, let's take a look at the disk preparation. The disk preparation was done in the following manner:

Essentially, what we were doing is we were adding acetone. We added 5 ml of acetone and brought through approximately 1 ml of it and allowed it to sit there for 3 minutes. The purpose of this is to shock the material so that it will release any of the contaminants.

I cannot emphasize enough how important this disk preparation is, and you will end up seeing that, believe me.

Next, what we did after bringing the acetone to air, we did the same thing

with the acetonitrile. 5 ml again, we brought 1 ml through, let it sit there for about 3 minutes, and then we brought that through to air. This was important, because that is what we are going to be eluting with.

Finally, we started making that transition so we could end up adding our aqueous. We added 5 ml of methanol, brought through about 1 ml, let it sit there for 3 minutes, and then we brought that down, at this point not allowing the disk to go dry.

We had about 1 ml there before we added 10 to 15 ml of water.

I mentioned that you can probably leave that there for about a minute which is kind of option, but, actually, if you are bringing it through slow enough, you can add an additional 15 ml and then you will be ready for your sample addition.

Here we go with sample addition. This is a real quick slide, and this is how it looks.

People have mentioned that it is real nice. You can just tip the bottle over. You may be able to see...I am not sure if you are able to see it. I can't see it from my angle. Maybe you can't see it, either, but there is actually water in those bottles. It is auto-feeding. You are essentially just going to set up the manifold very much like this. You turn over the bottle. You don't have to worry about the disk going dry.

In fact, when you get into the disk drying, you would like to leave it sit there for about 15 minutes. It can sit there an hour, it can sit there two hours. The dryer the disks are, the better off you are going to be, especially for these particular analytes.

As I mentioned, we go into disk drying, and I don't have a slide for this, but there are two means of doing it. Essentially, what we did, we first, in our first experiments, we were allowing it to dry for about 15 minutes.

What we found with the cartridge technique is that we essentially had to spin-dry it in a centrifuge. We were putting the 6 ml cartridges into a centrifuge and spinning the water off.

The disks, we actually took them off the manifold, and we dried them in a desiccator.

The problem is if you don't soak the disks to get rid of all of the

contamination levels, when you put it back on, inevitably, you are going to end up putting it in such a position that you are going to end up just getting a little bit of contamination from the disks. These disks, we found, were extremely dirty, and the disk preparation was crucial.

The elution in concentration, I have got a slide here, and I don't know how it is going to show up. It didn't show up very well in my room, but I am going to give it a shot. And it doesn't. What a deal.

Okay, essentially what we were doing is we were adding like a 30 ml VOA vial to the bottom of that manifold. We essentially took off the entire apparatus. We put that 30 ml VOA vial down below, and that is what we collected it into.

We were essentially taking 3 ml of acetonitrile three times. In some of our experiments, we took two 5 ml aloquats, but three 3 ml aloquats, we believed from the statistics that we read, 80 percent the first time, 80 percent of the remaining 20 percent, and so on and so on. Worked very effective.

At this point, we are putting it on an evap type system. We are taking that 9 ml, and we are bringing it down to approximately 1 ml. At that point, when we get it to 1 ml, we will bring it up to 1 ml with water in a 2 ml pipette.

And you have to have that type of a mixture, because if you have pure organic, your chromatography just does not look the way it should. You get a lot of tailing, and the compounds start running together.

These were the particular levels that we went after. We had a high spike, we had a mid-spike, and we did have a low spike. The low spike is at the detection limit.

I am going to show you a little later on some of the chromatography that we have got at the detection limit. You are going to see that it is much dirtier, but we were able to get some pretty good recoveries even at the low limit.

If anybody is familiar with Method 8330, we are approximately five to ten times lower than the 8330 detection limits which uses essentially a dilute and shoot type method.

If you are able to meet those particular detection limits, this is going to be

a godsend. You are going to get 250 times lower.

We did not try Method 8330. We are approximately, like I said, five to ten times lower. So, it has worked very well for us.

This is what we tried with one disk. This is a 47 mm disk using reagent water. We spiked it at the high. Those are the way our recoveries looked. As you can see, they are very encouraging.

Lowest one that we were able to have was 85 percent, I believe, for the 2- and the 4-nitrotoluene.

I mentioned that we did have a contaminant that ended up coming off with the 3-nitrotoluene, and that ended up accounting for some of our high recoveries. Especially in this 2 disk that we ended up using, notice the recoveries are a little bit better, but take a look at the 3-nitrotoluene, 3-nitrotoluene at 200 percent. That is primarily because of a contaminant.

This is the groundwater that we had, and I mentioned that we did do...this was the first run that we had through it, and, actually, Craig used this as some of the preliminary results.

We did not use this one on the manifold. This was before we got the manifold. We just wanted to have an idea of whether this had a potential of working. We essentially did one point at the high, and the recoveries were such that we were like hey, bring them on, bring on the disks, let's see what we can do here.

Now, if you are like me, like I was, I am like okay, what exactly were the recoveries like? What did the chromatography look like? Was it clean?

As you can see by the following, this is a groundwater high. Jim Madison did an excellent job on developing the HPLC type technique. This is at 254 nanometers.

Notice that the peaks are very, very well resolved. The highest peak in the chromatogram, not the first one which is essentially a solvent type peak, but the one in the middle, that is TETRYL.

Right after TETRYL, you will see a little blip down below. That is essentially your nitroglycerin. And then way on the end is your PETN.

The nitroglycerin and the PETN have to be absorbed at a different

wavelength, and this is the exact same sample at 210. Notice again how the separation. It really worked well for us.

Now, things weren't all glorious. Things were not all glorious, and if you got your chromatogram and you looked like that, you know you had some problem in your disk preparation.

This is essentially a slide of our disk preparation if we didn't do the disk preparation. Chromatography here had a little bit to be desired.

We essentially used a cyano column for confirmation. None of these peaks come out on the cyano column, but you have to have a confirmation type column.

And this is a slide right here that I am hoping will emphasize the importance of the disk cleaning technique. These disks, when you first get them, are extremely dirty, and if you can perfect the disk preparation technique, your recoveries and the rest of it is just a dream.

This particular slide indicates what the chromatography looked like at the detection limit. These were spiked at, if you remember the earlier slide where I showed you the three levels, this is a surface water which has got some contaminants to begin with right at the detection limit.

Notice the nitrotoluenes on the end. The contamination in the nitrotoluenes was primarily due to a disk problem in my inability to actually prepare them correctly.

We have been working at it, and we have gotten much better, and with a little bit of time and perseverance, you can bring that contaminant peak down to nothing, and you can essentially have real good recoveries.

That is at 254; this one is at 210. Notice that even though you have the contamination, the nitroglycerin, the PETN still very well resolved from all contaminant type peaks.

This is a look at a high of the surface water, and notice again here, even despite the biological type nature of the samples that you can have in there, chromatography is good not only at the 254 but also at the 210 nanometer wavelength.

In comparison, we have been doing the cartridge technique for a year now.

We got into the certification of this particular method for a client that we had. They cut off certification. We would love to go to the disks, and as soon as they open up that certification process, you can bet we are going to be doing that. We have a real good feel for it.

The percent d's, if you notice, very, very tight. It is almost equivalent. The only difference...and I mentioned this earlier and I will mention it again in summary...is the time issue. The amount of time to run these things through disks is almost nothing.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MR. LE BRUN: Not to cut anybody off on questions, I am just going to ask...I am going to give one little bit of information. I am sure that people are going to ask where did you get the standards.

Standards are tough to come by, and, actually, if you are not doing explosives for a particular part of the government, they are going to be very difficult to get. So, if that is what your question is, I can't help you.

MR. TELLIARD: Anyone?

(No response.)

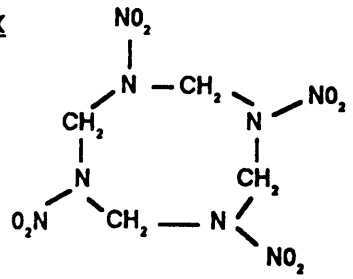
MR. TELLIARD: Thanks, Gabe.

A SOLID PHASE EXTRACTION DISK METHOD FOR THE EXTRACTION OF EXPLOSIVES FROM WATER

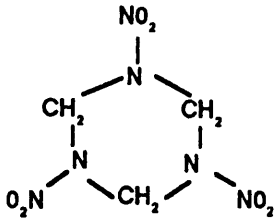
Gabriel LeBrun, Pat Rethwill, and Jim Matteson,
Pace, INC., 1710 Douglas Drive N., Minneapolis,
MN 55422

ANALYTES OF INTEREST

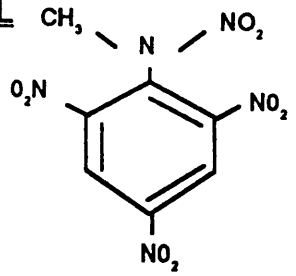
HMx



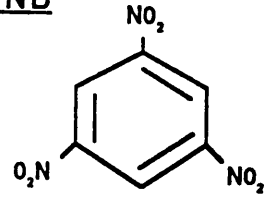
RDX



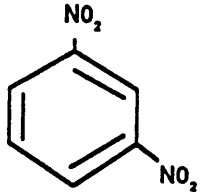
TETRYL



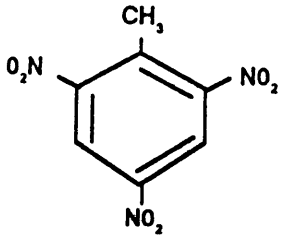
135TNB



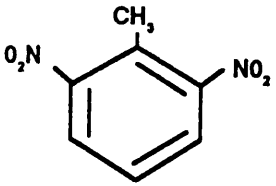
13DNB



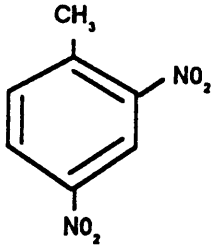
TNT



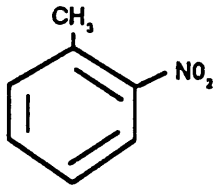
2,6DNT



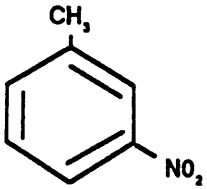
2,4DNT



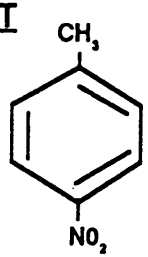
2NT



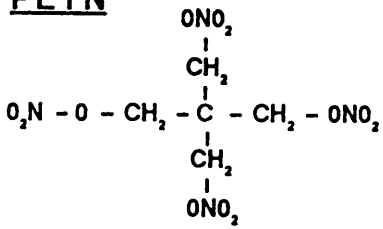
3NT



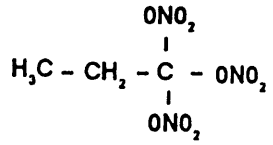
4NT



PETN



NG



SOLID PHASE EXTRACTION METHODS

CARTRIDGE

DISK

TIME

GROUND WATER FLOW RATES

- AVERAGED ABOUT 4 MINUTES

REAGENT WATER FLOW RATES

- AVERAGED ABOUT 10 MINUTES

SURFACE WATER FLOW RATES

- AVERAGED ABOUT 70 MINUTES

CARTRIDGE TECHNIQUE

1 - 2 mL / MINUTE

4 - 8 HOURS

DISK METHOD OVERVIEW

- DISK PREPARATION
- SAMPLE INTRODUCTION
- DISK DRYING
- ELUTION AND CONCENTRATION

DISK METHOD

- DISK PREPARATION
- SAMPLE INTRODUCTION
- DISK DRYING
- ELUTION AND CONCENTRATION

DISK PREPARATION

ACETONE - 3 MINUTE - AIR

ACN - 3 MINUTE - AIR

MeOH - 3 MINUTE - 1 mL

15 mL H_2O - 1 MINUTE (OPTIONAL) - 1 mL

15 mL H_2O - 1 MINUTE (OPTIONAL) - 1 mL

DISK TECHNIQUE

75 - 125 mL / MINUTE

4 - 6 MINUTES

EXPLOSIVE IN GROUND WATER

47 mm SDB Disk, 500 mL Reagent Water. 2 X 5 mL CH3CN Elutions,

About 4 Min/500 mL, Concentrations Ranged from 22 ug/L to 250 ug/L

Compound	Recovery
HMX	96%
RDX	89
1,3,5-Trinitrobenzene	88
1,3-Dinitrobenzene	91
Tetryl	87
2,4,6-Ttrinitrotoluene	92
2,6-Dinitrotoluene	87
2,4-Dinitrotoluene	89
2-Nitrotoluene	85
4-Nitrotoluene	85
3-Nitrotoluene	114*
Nitrotoluene	96
PETN	93

*An Impurity Coeluted With This Compound

SDVB EMPORE EXTRACTION STUDY
ANALYTES AND SPIKE LEVELS

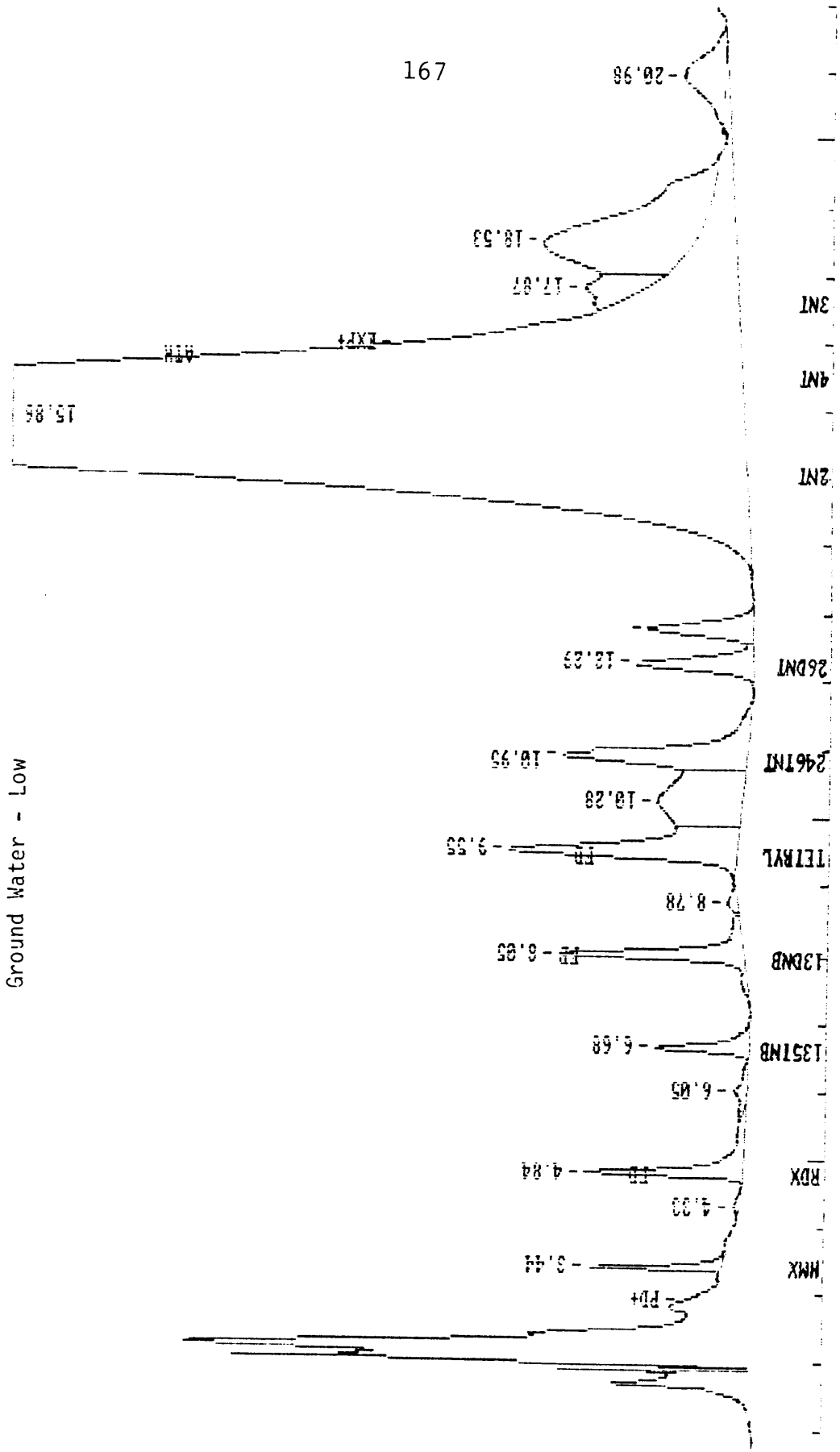
	HIGH SPIKE(ug/L)	MID SPIKE(ug/L)	LOW SPIKE(ug/L)
HMX	49.9	7.49	2.00
RDX	50.0	7.50	2.00
135 Trinitrobenzene	25.2	3.78	1.01
13 Dinitrobenzene	25.1	3.76	1.00
TETRYL	100	15.0	4.00
246 Trinitrotoluene	25.0	3.75	1.00
26 Dinitrobenzene	50.0	3.51	2.00
24 Dinitrobenzene	25.1	3.77	1.00
2 Nitrotoluene	50.2	7.53	2.01
4 Nitrotoluene	24.6	3.70	0.99
3 Nitrotoluene	25.2	3.79	1.01
Nitroglycerin	248	37.2	9.92
PETN	248	37.2	9.92

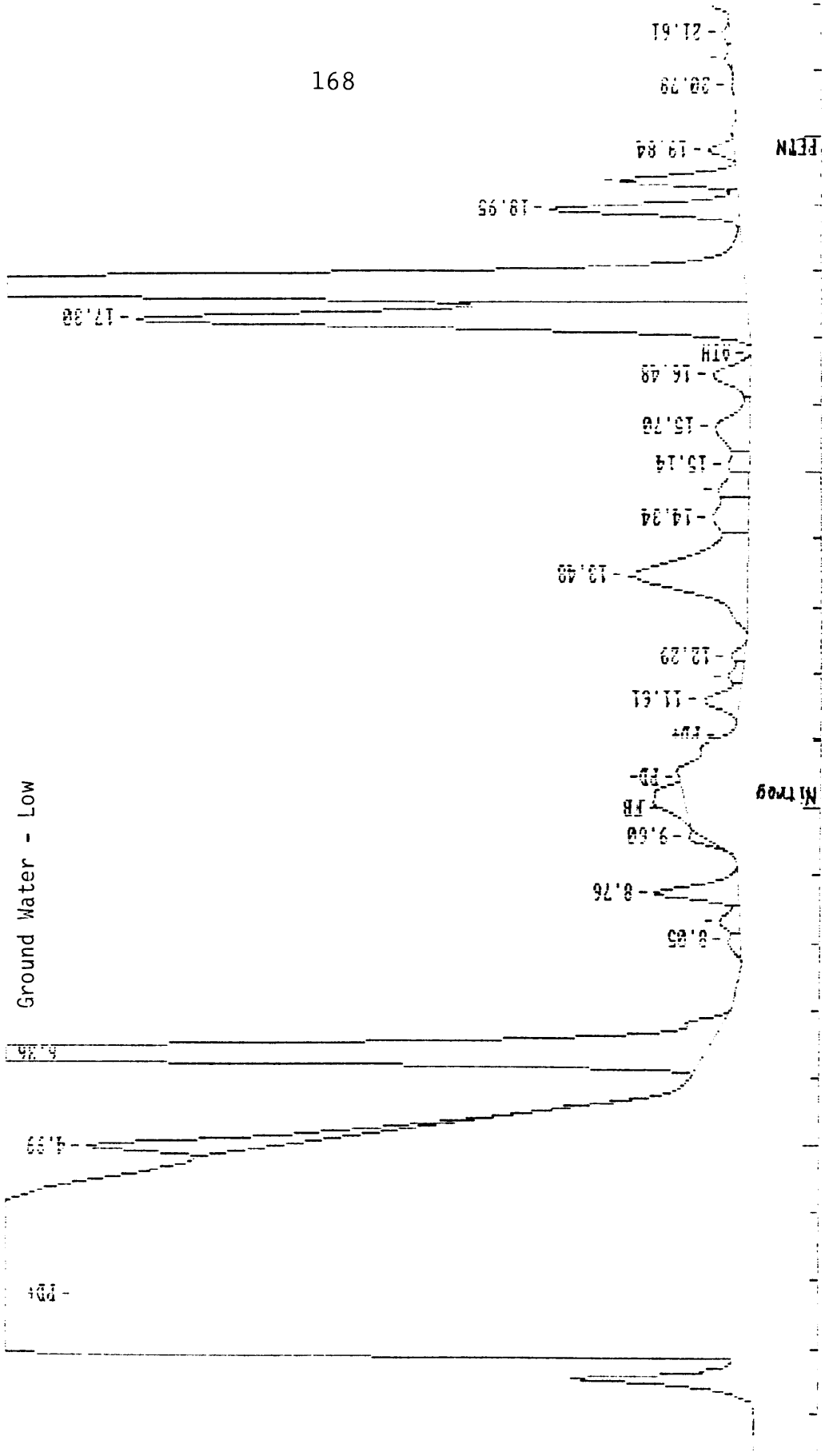
SDVB EMPORE - 1 DISK

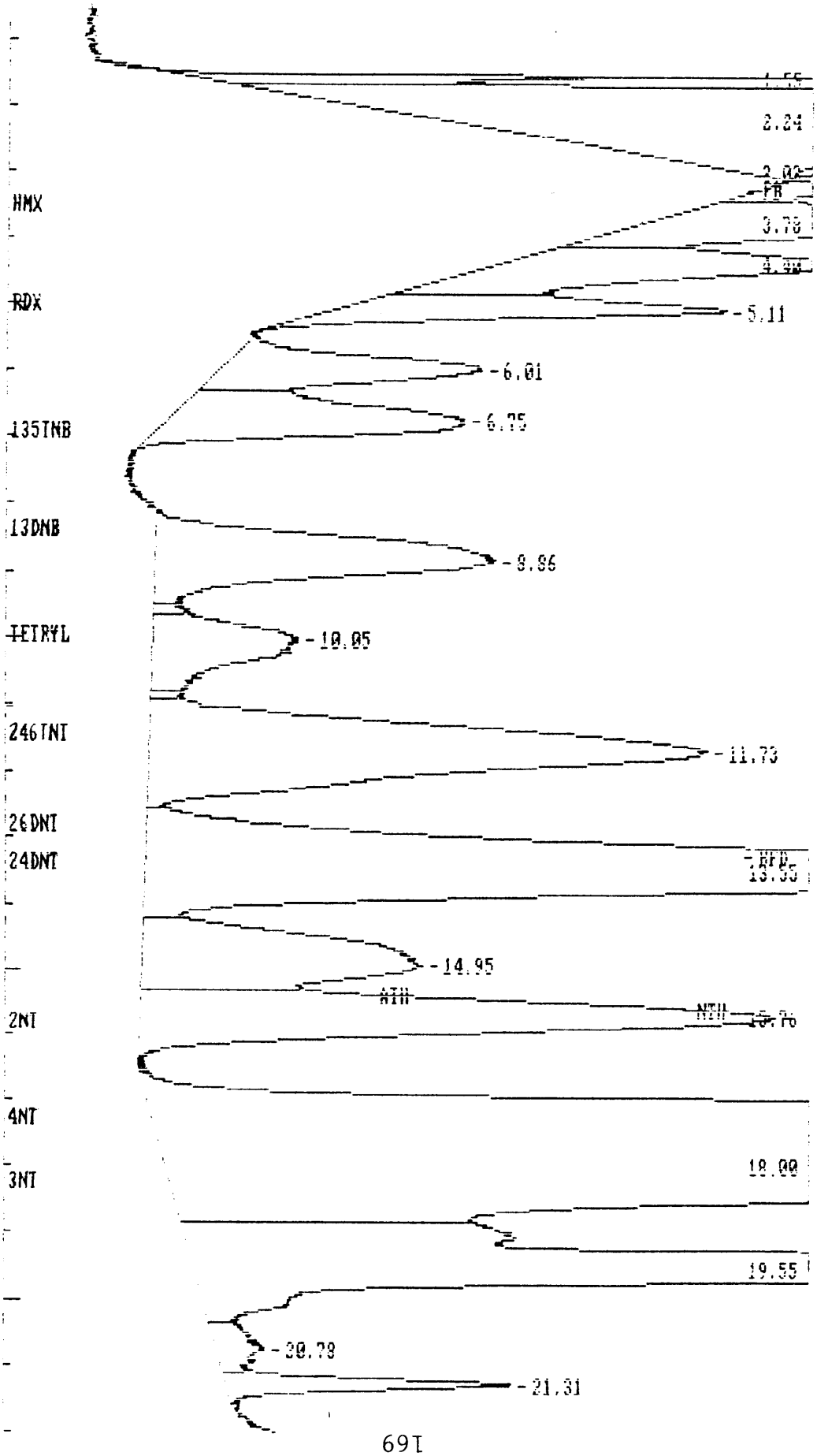
	SPIKED AMT	AMT RECOVERED	% RECOVERY
HMX	49.9	47.7	96
RDX	49.6	43.9	89
135 Trinitrobenze	25.6	22.5	88
13 Dinitrobenzene	24.8	22.6	91
TETRYL	99.8	86.7	87
246 Trinitrotoluene	23.7	21.8	92
26 Dinitrotoluene	51.1	44.7	87
24 Dinitrotoluene	23.1	20.7	89
2 Nitrotoluene	50.7	43.0	85
4 Nitrotoluene	22.0	18.6	85
3 Nitrotoluene	25.6	29.3	114
Nitroglycerin	250	240	96
PETN	250	232	93

SDVB EMPORE - 2 DISKS

	SPIKED AMT	AMT RECOVERED	% RECOVERY
HMX	49.9	48.9	98
RDX	49.6	43.1	87
135 Trinitrobenzene	25.6	20.1	78
13 Dinitrobenzene	24.8	20.3	82
TETRYL	99.8	77.2	77
246 Ttrinitrobenzene	23.7	19.1	80
26 Dinitrobenzene	51.1	40.4	79
24 Dinitrobenzene	23.1	18.4	80
2 Nitrotoluene	50.7	34.6	68
4 Nitrotoluene	22.0	15.2	69
3 Nitrotoluene	25.6	50.6	198
Nitroglycerin	250	212	85
PETN	250	204	82


Ground Water - Low
HMX
RDX
TETRYL
3NT
4NT
2NT
26DNT
246TNT
13DNB
135TNB
PID+
ATH
TXT+
15.86
20.98
18.53
17.87
12.29
10.95
10.28
9.55
8.78
6.85
6.68
6.65
4.84
4.33
3.44


Ground Water - Low
Nitrog
PETN
21.61
20.79
19.84
19.95
17.38
BTH
16.49
15.78
15.14
14.24
13.48
12.29
11.61
FLU
PD-
FR
9.60
8.76
8.65
6.26
4.59
PD+


HMX
RDX
135TNB
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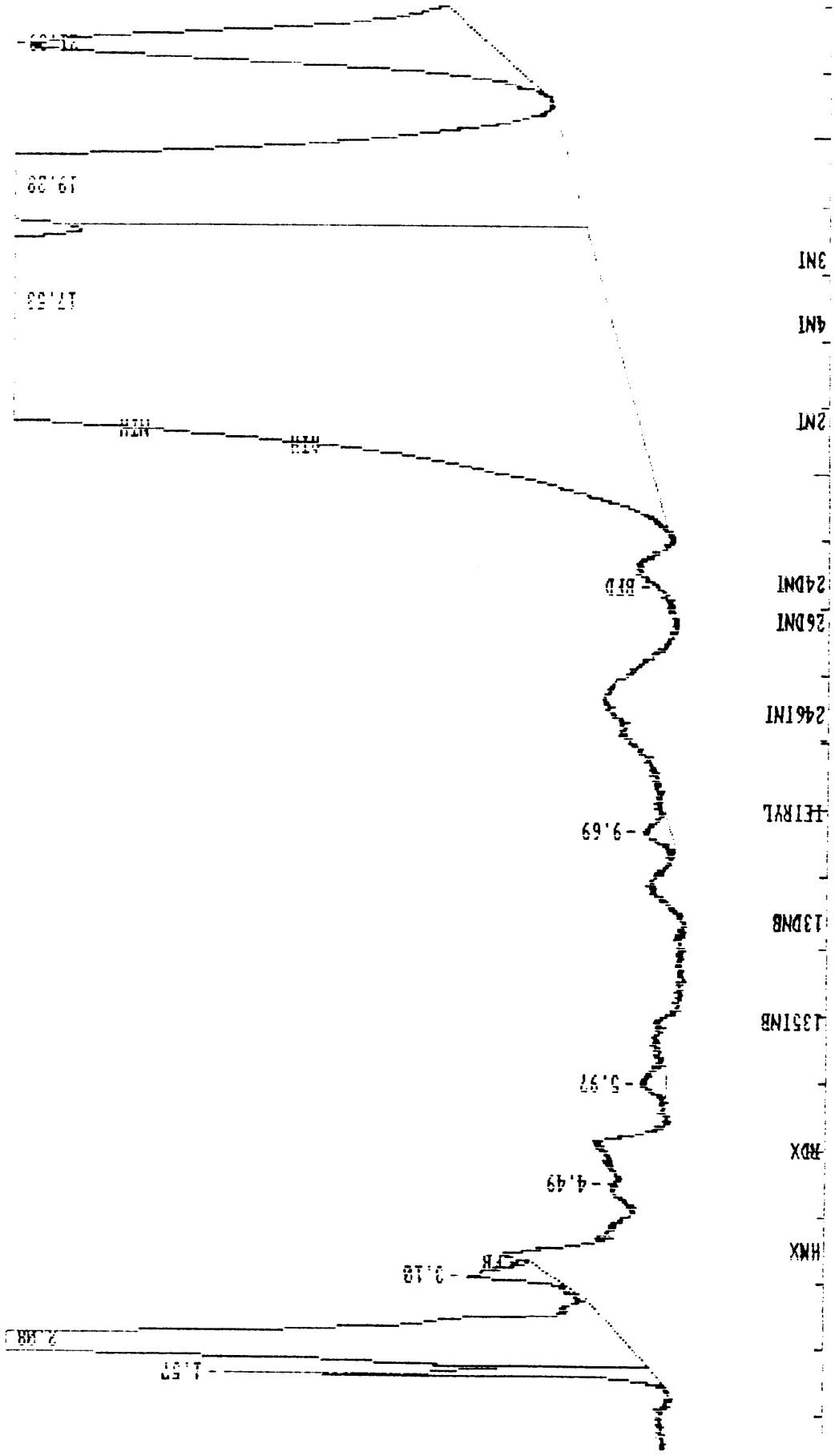
TETRYL
246TNT
26DNT
24DNT
2NT
4NT
3NT
2.24
FB
3.78
5.11
6.01
6.75
8.96
10.05
11.73
14.95
19.00
19.55
20.79
21.31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4NI
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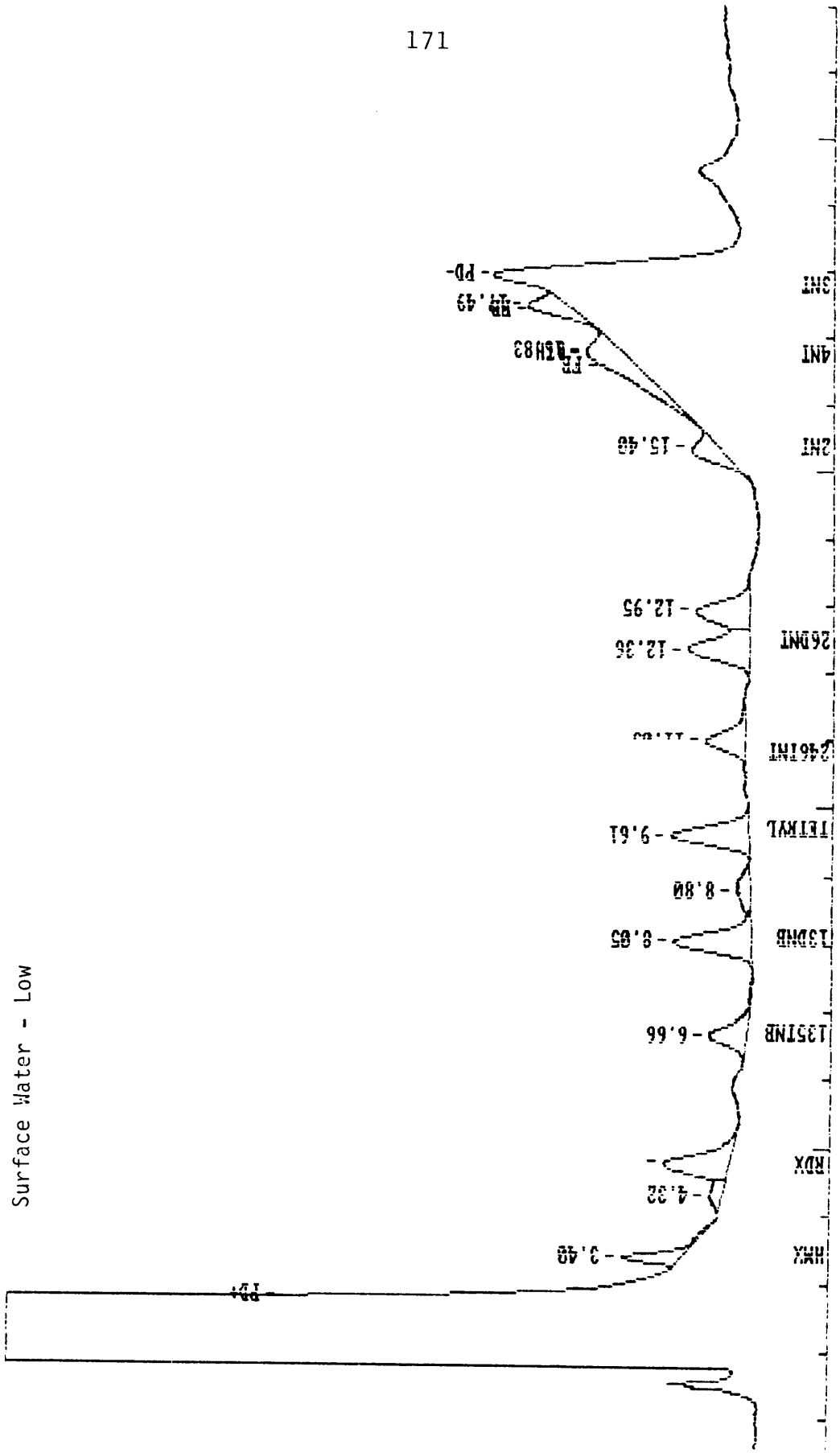
RDX
HMX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RDX
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TETRYL
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2NT
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4NT
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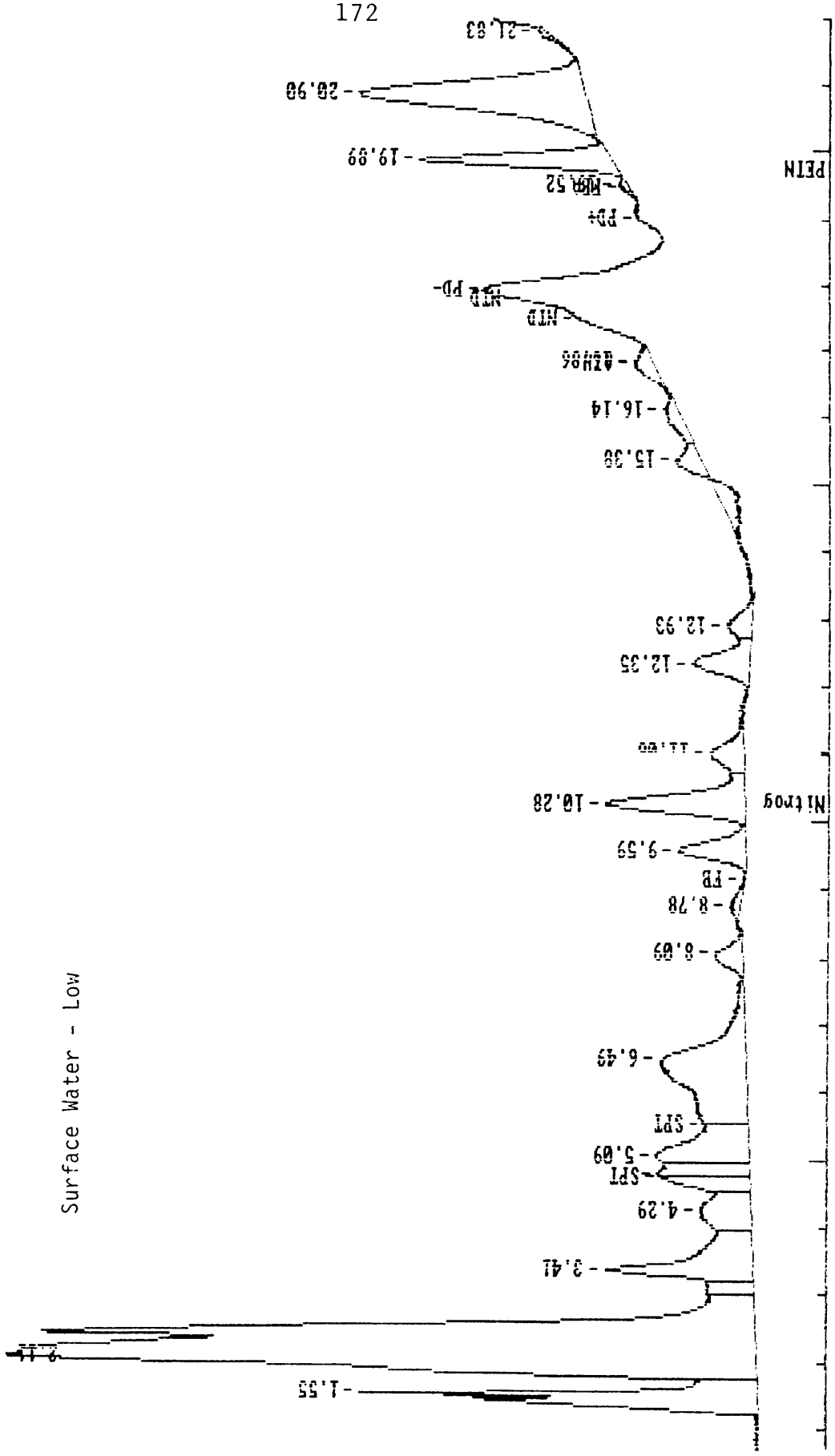
3NT
PD-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Nitrog
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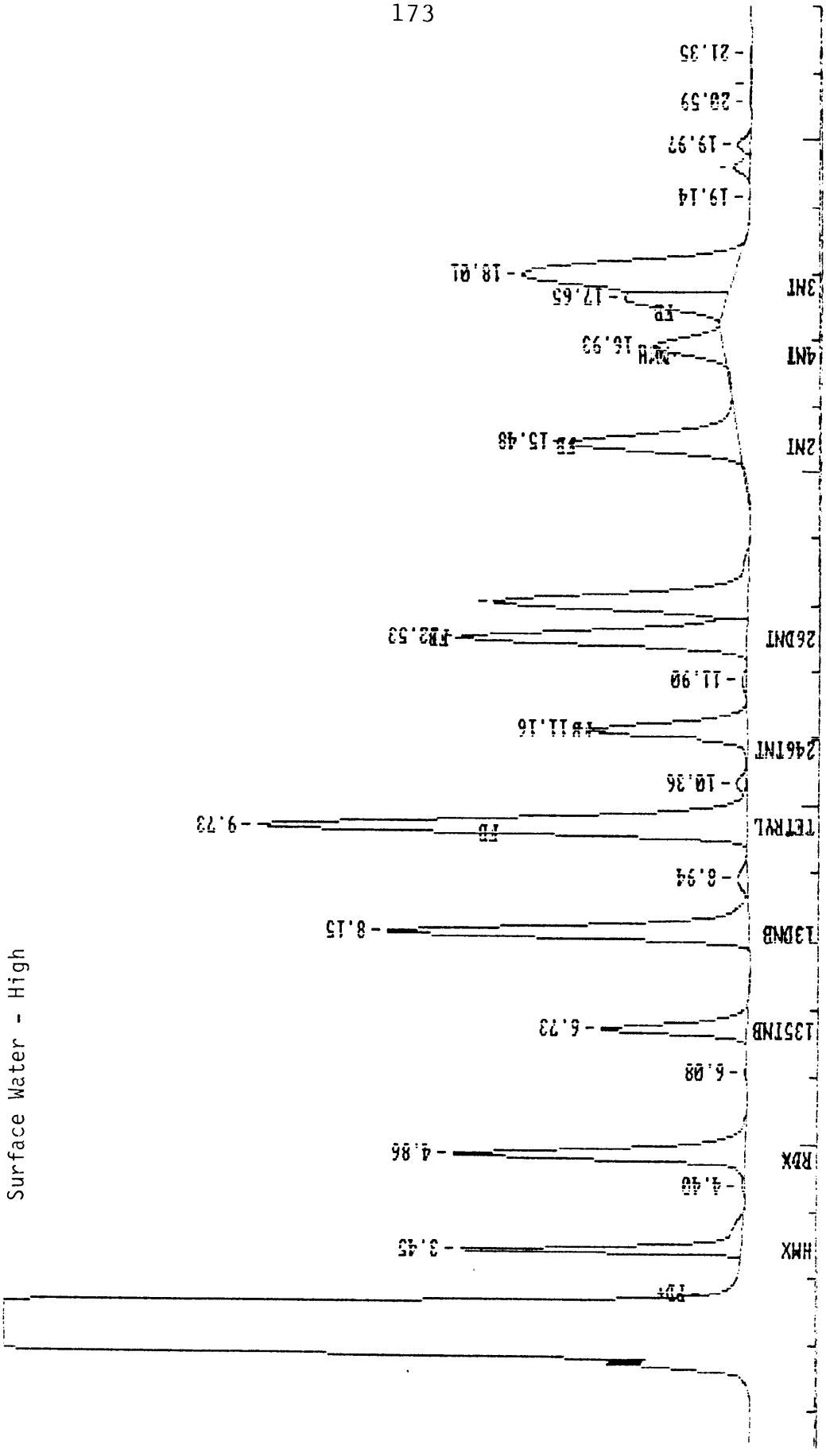
-3.41
-4.29
-5.09
SFT
-6.49
-8.09
-8.78
FB
-9.59
-10.28
-11.80
-12.35
-12.93
-15.38
-16.14
-AZHX86
-NTD
-NTD PD-
-PD+
-MDNA52
-19.99
-20.98
-21.83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RDX
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6.08
6.73
8.15
8.94
9.73
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17.65
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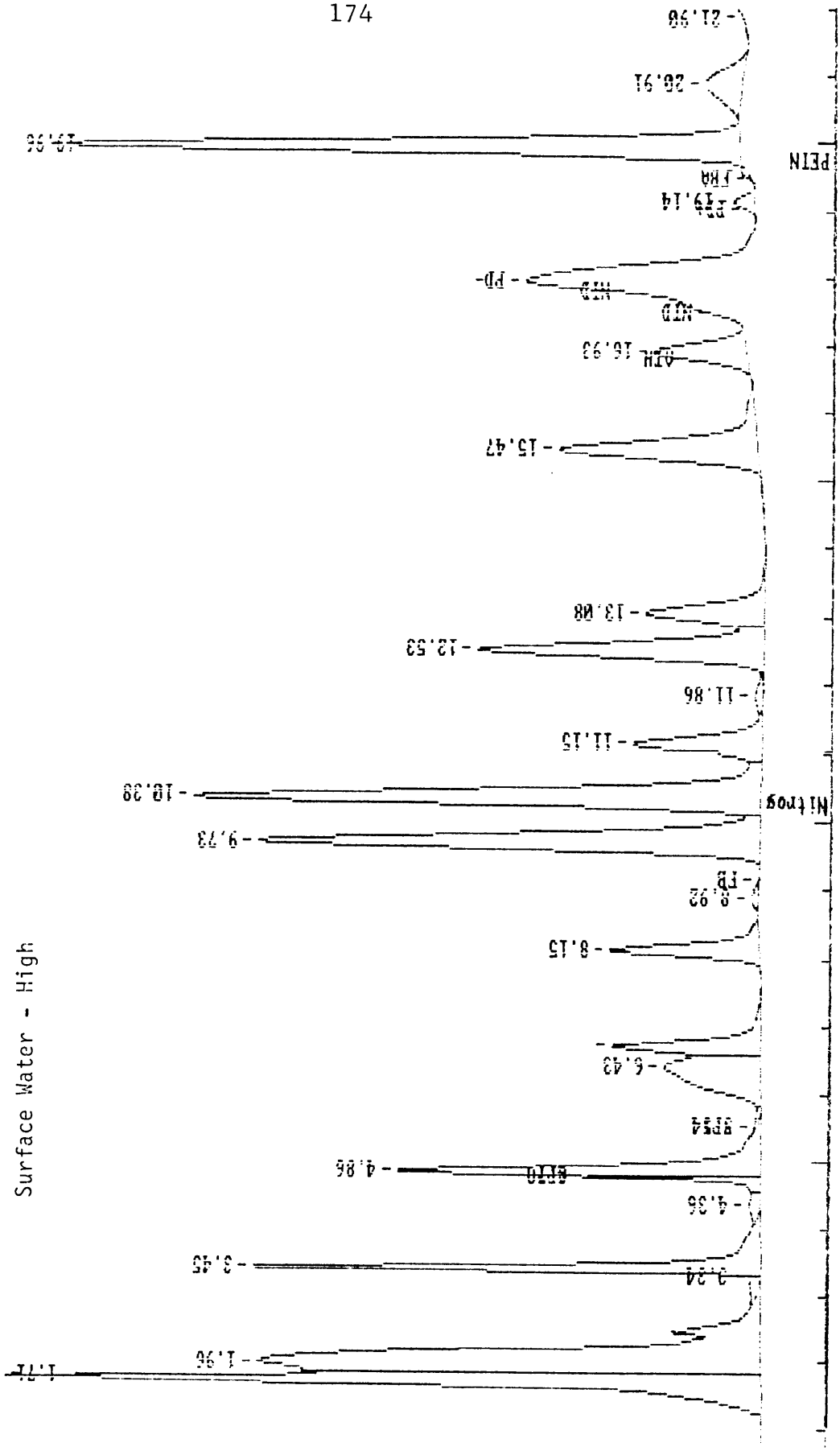
19.97
20.59
21.35


Surface Water - High
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9.73
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11.15
11.86
12.53
13.08
15.47
16.93
19.14
19.96
21.98
28.91
PETN

DISK - CARTRIDGE RECOVERY COMPARISON

Compound	SDVD DISKS Recovery	SDVB Cartridges	%D
HMX	96%	90	6
RDX	89	93	4
1,3,5-Trinitrobenzene	88	93	5
1,3-Dinitrobenzene	91	101	10
Tetryl	87	70	17
2,4,6-Ttrinitrotoluene	92	91	1
2,6-Dinitrotoluene	87	95	8
2,4-Dinitrotoluene	89	82	7
2-Nitrotoluene	85	96	11
4-Nitrotoluene	85	87	2
3-Nitrotoluene	114*	110	4
Nitrotoluene	96	103	7
PETN	93	104	11

*An Impurity Coeluted With This Compound

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MR. TELLIARD: As we have heard this morning, solid phase extraction offers a lot of flexibility in the laboratory. One of the questions that we are faced with is an ongoing issue of taking samples...and some of you have heard rumors...taking samples and sending them to the lab all at once. This is a rash lie.

We send three or four a week all year long just to make them happy. However, in the summertime, we like to take a little more samples, because the water isn't frozen, and we ship them off to the lab, and there is sometimes a protect about getting 122 samples and having a 45-day turnaround time.

This shows a lack of real initiative and imagination on the laboratory's part. Some people would consider this a problem. Other people with more initiative would consider it a challenge. I generally get the guys who don't consider it a challenge.

One of the issues that we were looking at was the viability of using solid phase extraction for such things as field application and, for example, shipping a solid phase to the laboratory rather than 52 1-liter bottles in an ice chest rattling around Federal Express.

The other issue was, of course, when you get these high numbers of samples into the laboratory, could we extract them and then hold the samples on the filters and analyze them, as they usually do, at their own damn well rate, you know.

So, one of the issues that had come up was stability and storage of these samples as it relates to field application, and our next speaker is going to discuss that, Scott Senseman from the University of Arkansas.

STORAGE STABILITY OF SELECTED PESTICIDES ON MEMBRANEOUS SOLID PHASE EXTRACTION DISKS

S.A. Senseman, J.D. Mattice, T.L. Lavy, B.M. Myers, and B.W. Skulman

INTRODUCTION

The storage stability of various pesticides in water for prolonged storage periods is a concern of many environmental laboratories. With increasing numbers of samples being collected, it becomes important not only to be concerned with storage stability but storage space as well. With the emergence of solid phase extraction, alternative methods to resolve these problems may be available by concentrating the pesticide on a solid phase extraction disk directly after collection of a water sample.

Earlier applications of solid phase extraction in the cartridge form were shown to be successful, although limitations such as slow flow rate and bed channeling arose. To alleviate some of the limitations, more recent technology has been introduced that involves similar solid phase material but contained in a membrane filter or disk form. Figure 1 is a conceptual picture of a C-18 47 mm diameter Empore™ disk that was used as the storage media in our experiment. The disk consists of a teflon fibril network that suspends silica particles. These silica particles have carbon chains emanating from them which creates a non-polar environment. This non-polar environment is very conducive to "dissolving" non-polar pesticides. Also, by holding pesticides in the solid phase, it is

possible that some protection from hydrolysis and microbial decomposition over long storage periods might be achieved.

Consequently, by concentrating the pesticides on the disk, the problem of storage space could be greatly reduced in the laboratory while also giving rise to substantial reductions in mailing costs of analytical samples being sent from one laboratory to another. Past studies with SPE cartridges encourage this approach and have shown that some hydrocarbons were more stable when residing in an organic matrix (Green and Le Pape, 1987). However, the limitations of the cartridges influenced further studies with membranous filters.

The objectives of this experiment, therefore, were to compare the relative storage stability of some selected pesticides on solid phase extraction disks to the storage stability of pesticides in water and also to determine the chemical stability of these pesticides on solid phase disks under various temperature storage regimes.

MATERIALS AND METHODS

General. The fortification solutions were prepared by dissolving all of the pesticides of interest in methanol with the exception of captan which was dissolved in benzene for stability reasons. Prior to initiation of the experiment, it was determined that captan was unstable in methanol and is also subject to hydrolytic attack when stored in water. Consequently, it was decided that

benzene would provide a more stable chemical environment for captan. A 2500 μg/ml solution of captan in benzene was made and then added to water samples in a small quantity of 2 μL such that the concentration of benzene would be insignificant. The final fortified water sample contained 250 mls of deionized water, 1 ml of methanol with dissolved pesticides, and captan contained in 2 μL of benzene. All of these pesticides were fortified at 20 μg/L in water.

Storage treatments. The four storage treatments were replicated four times and included storage of pesticides in amber glass jars and refrigerated at 4 C representing the common method of storage for water samples. This treatment was compared to three disk storage treatments in which the water sample was fortified, filtered through a solid phase extraction disk, followed by storage of the disk at a predetermined temperature. The three storage regimes for the disk-stored treatments included frozen at -20 C, refrigerated at 4 C, and a combination of refrigerated for 24 hours then frozen at -20 C for the remainder of the storage period.

The rationale for the frozen regime was that the temperature was considered to be optimum for chemical stability. The disks stored at 4 C would show not only a comparison of temperatures on stability, but also a direct comparison between disk storage and storage in water. Including the combination of refrigerating and freezing treatments of the disk was representative of what a

water quality researcher might attempt when extracting pesticides from water in the field. This system might begin by filtration of the water sample to load the pesticides onto the solid phase allowing for temporary storage of the disk in an envelope at a cool temperature (approximately 4 C) until it could be more permanently stored at the laboratory in a freezer (-20 C).

All pesticide loaded disks were stored in plastic bags until the storage periods had expired. Upon expiration, the disk was taken out of the plastic bag, replaced back onto the filter apparatus on which the pesticides were first loaded, then, solvated with ethyl acetate which extracted the pesticide from the solid phase. The ethyl acetate solution was then used to further quantify using gas chromatography (GC) and liquid chromatography (HPLC). The pesticides stored in water were extracted at the termination of the storage period in the manner described above except the disk was not removed and stored after filtration of the water sample but rather immediately solvated with ethyl acetate after concentration onto the solid phase.

Storage periods. Five storage periods were included in the study including a time-zero where pesticides were extracted immediately after pesticide loading thus represented the extraction efficiency. The remaining storage periods included 3, 30, 90, and 180-day incubations.

Pesticides. The twelve pesticides included in the experiment are shown in Table I with retention times and method of quantification. The pesticides listed

cover a wide range of chemical families and were chosen because of their previous detections in surface or ground water. Also, it was known apriori that trifluralin and captan were relatively unstable under certain environments and that a direct comparison of disk storage versus water storage would be informative.

Statistical evaluation. The mean percent recoveries of the four treatments by five storage period factorial design from GC and HPLC analysis were statistically separated by the Least Significant Difference (LSD) at a 0.05 probability level.

Table I. Retention times (min) of compounds quantified in storage study.

Compound	GC-ECD ----- Column ----- SPB-5	GC-ECD ----- Column ----- SPB-608	HPLC-UV VARIABLE C-18 Column
	-------retention time, min-------		
alachlor	5.1	6.1	ND
atrazine	ND	ND	8.4
benomyl	ND	ND	2.5
captan	7.9	14.7	ND
fluometuron	ND	ND	7.1
methyl parathion	4.8	7.1	18.5
metolachlor	5.9	8.4	ND
norflurazon	16.9	24.9	ND
pendimethalin	6.5	10.7	ND
profenofos	11.0	15.9	ND
simazine	ND	ND	4.5
trifluralin	2.5	2.2	ND

RESULTS AND DISCUSSION

Benomyl, fluometuron, and atrazine showed no interaction between storage treatment and storage period (Figures 2, 3, and 4). In general, the highest percent recovery for these pesticides occurred when the disk was stored at -20 C; although, these recoveries did not always differ statistically from the other disk storage treatments. In all cases each pesticide stored at -20 C on the C-18 material gave better recovery than those stored in bottled water (Figures 2, 3, and 4). Moreover, the lowest recovery was for the pesticides stored in bottled water, but it was not always statistically different from the next lowest value within a selected disk storage treatment. The combination treatment gave the second highest percent recovery for each pesticide with the exception of atrazine (Figure 4). Atrazine showed no differences among disk storage treatments indicating that temperature treatment of the disk had no effect on the recovery of this compound. Statistical differences for pesticide recovery from disks were shown only for benomyl and fluometuron of the three pesticides. Thus the consistent differences in percent recovery do not occur between specific disk storage treatments among the pesticides tested. Nevertheless, these data show that these pesticides are at least as stable and often more stable when stored on solid phase material as compared to storing the pesticides in water over the same duration.

Trifluralin, alachlor, methyl parathion, metolachlor, pendimethalin, norflurazon, captan, and profenofos showed a significant interaction between storage treatment and time interval. The examples shown in Figures 5 and 6 are alachlor and trifluralin data after 180 days of incubation and are representative of data of the other compounds. After six months, alachlor and trifluralin were fairly stable and recovery significantly higher when stored on the solid phase disk. In most cases, the disk storage of pesticides was equivalent or superior to pesticide storage in water.

Two distinct cases of statistical differences between disk storage and water storage occurred in the trifluralin and captan data (Figures 6 and 7). The various storage treatments of trifluralin did not demonstrate any differences until the 180 day storage period. After 180 days of storage, there was 32% recovery with trifluralin when stored in bottled water while recovery from solid phase storage ranged from 54 to 64%, representing about a 50% loss of pesticide when stored in water compared with disk storage. This loss would double the sensitivity and detection limits of samples stored over this duration. Similar trends of pesticide loss were shown for alachlor, metolachlor, methyl parathion, pendimethalin, norflurazon, and profenofos, however, over the 180 days of storage in water their loss was not as great as found for trifluralin.

Captan demonstrated the most dramatic results (Figures 7-9). The recovery from water stored for 3 days at 4 C was 28% whereas the recovery

from disks stored at 4 C was 114%. The differences were more pronounced after 30 days when captan had all but completely dissipated in water while 32 to 54% was recovered from disk storage (Figure 8). This stabilizing ability of the C-18 material has been observed by other researchers who stated that materials bonded to a solid phase were more stable (Green and Le Pape). It is also apparent from this data that disk storage does not totally solve the stability problem of captan. Observation of the 30 and 90 day results for this compound display significant loss of the parent captan over that time span even when it was stored on the non-polar media of the solid phase (Figures 8 and 9). This loss may be due to hydrolysis by water that could not be totally removed from the disk by vacuum filtration. Therefore, captan would still be in an aqueous environment and susceptible to hydrolytic attack even while it resides in the non-polar matrix of the C-18 material. It may be possible to further stabilize these compounds by removing the residual water through desiccation, lyophilization, or blotting with anhydrous sodium sulfate prior to permanent storage.

Other limitations to disk storage may include microbial growth on the disks over longer storage periods. At the 90 and 180 day storage period, disks stored at 4 C exhibited some microbial growth. This may have been a factor in the slightly lower recoveries from these treatments. Microbial growth was not observed on the frozen disk-storage treatments, therefore, supporting the advantage to freezing the disk after loading the pesticides.

SUMMARY

The stability of these pesticides has been preserved and in most cases enhanced by concentrating the pesticides on C-18 material. Trends appear to favor storage of pesticides on the disk by freezing after extraction. These results offer promising possibilities that could alter the way water samples containing these pesticides are currently stored. The pesticides were both stabilized and extracted by the non-polar media of the disk. Therefore, water samples that formerly occupied the space necessary for 500 to 1000 ml bottles may be reduced to a 0.5 mm thick X 47 mm diameter pliable filter. The reduction in storage space is clearly and quickly realized. Field extraction using SPE disks appears to be the next logical step in developing and utilizing the potential of this technology. Through field extraction, pesticides could be both concentrated and stabilized on a disk while in the field. The disk could then be stored rather than a bulky glass jar. While increased time would be required for sample collection a part of the normal laboratory extraction procedure would have been performed in the field. Consequently, sample preparation time in the laboratory would be decreased, thereby, allowing a quicker overall analysis time. In addition, transport of pesticide samples through the mail from one laboratory to another may be easier and cheaper if disks are used as the storage container rather than bottles. Drawbacks of the this type of storage scheme, such as hydrolysis found in the case of captan, must be studied more

completely. Further studies need to explore more complete removal of water from the disks as a means of stabilizing the bound pesticides.

Acknowledgments.

The author would like to express his appreciation to Dr. Craig Markell of the 3M Corporation for his technical support in this endeavor. A special thanks goes to Mr. Benjamin Myers for his dedication and input that was so crucial to this project.

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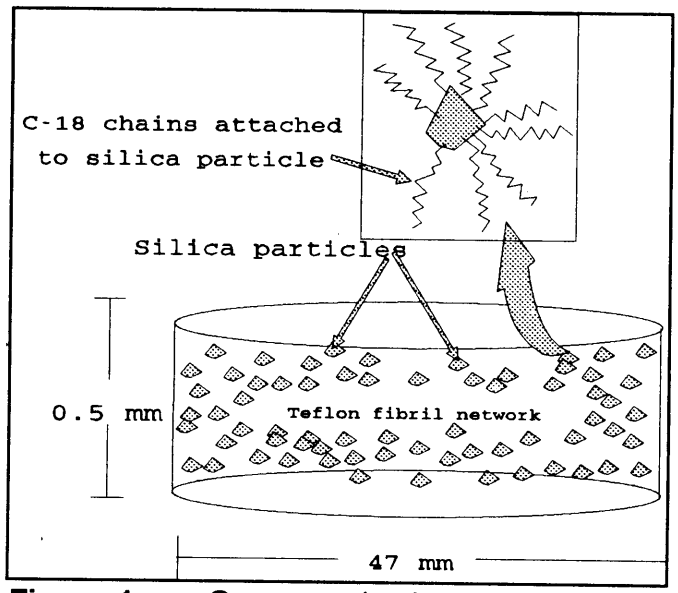

Figure 1. Conceptual drawing of C-18 Empore™ disk.

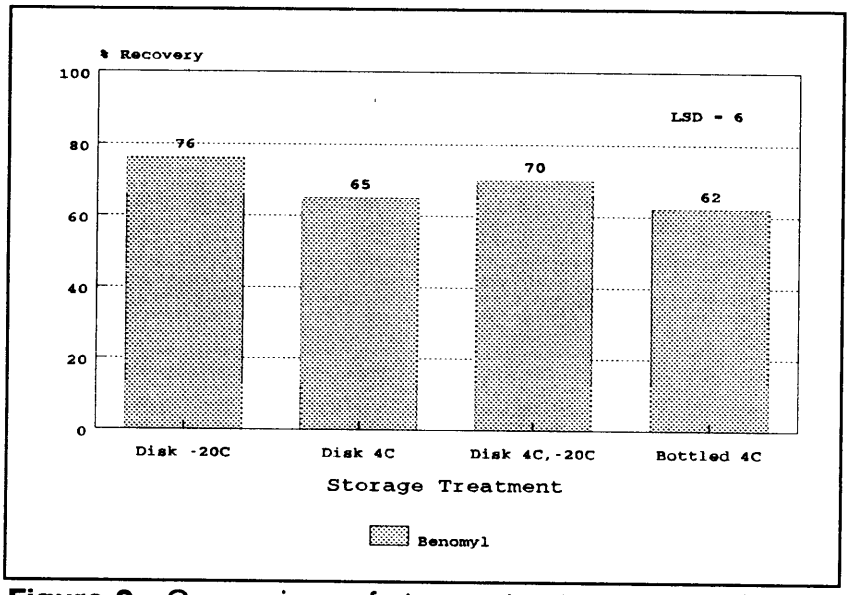

Figure 2. Comparison of storage treatment on stability of benomyl.

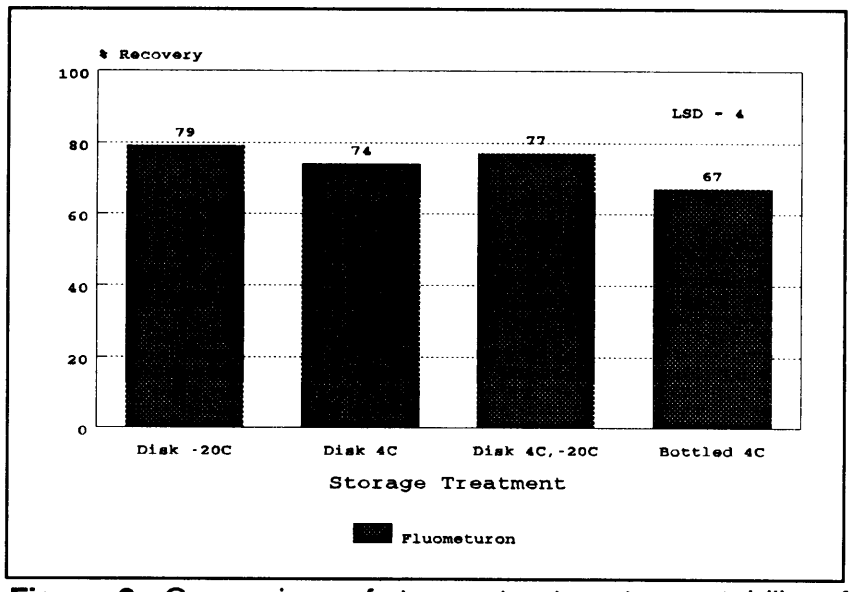

Figure 3. Comparison of storage treatments on stability of fluometuron.

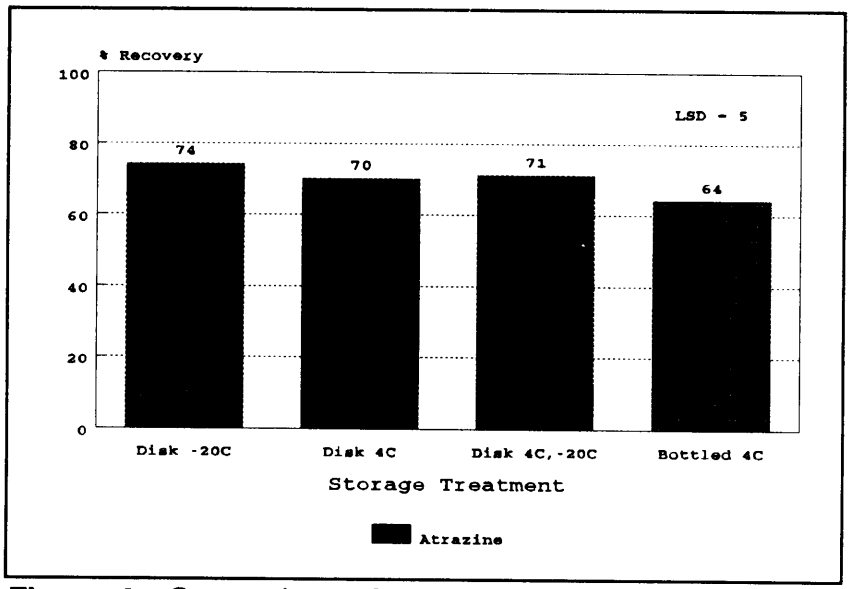

Figure 4. Comparison of storage treatment on stability of atrazine.

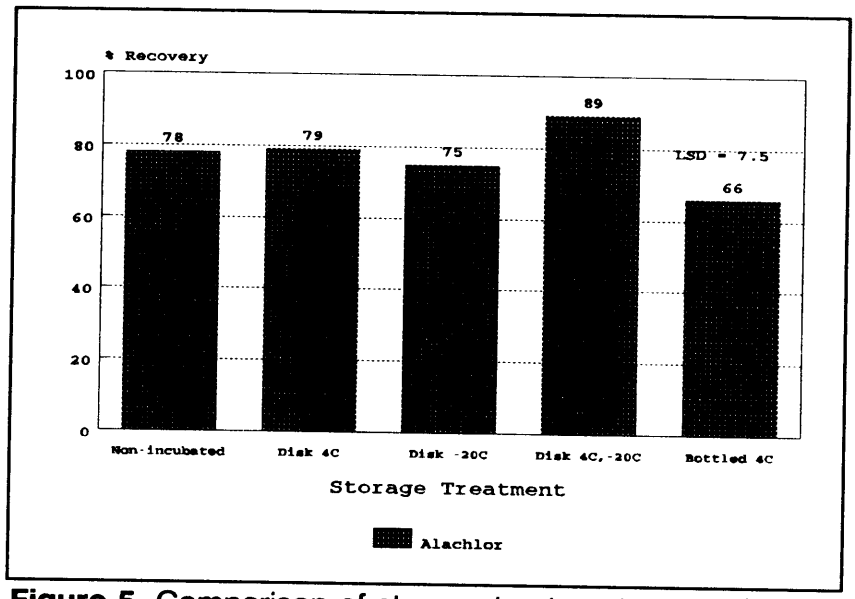

Figure 5. Comparison of storage treatments on stability of alachlor after 180 days of storage.

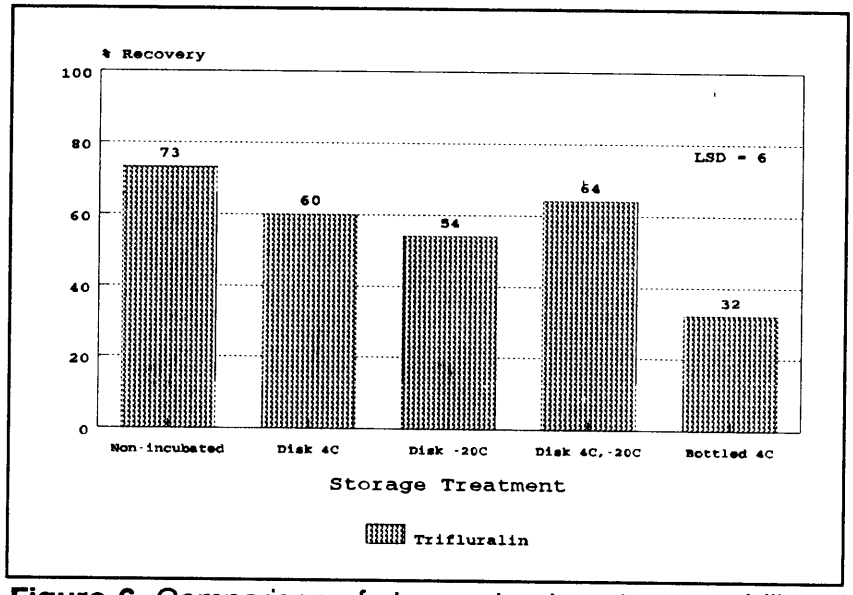

Figure 6. Comparison of storage treatments on stability of trifluralin after 180 days.

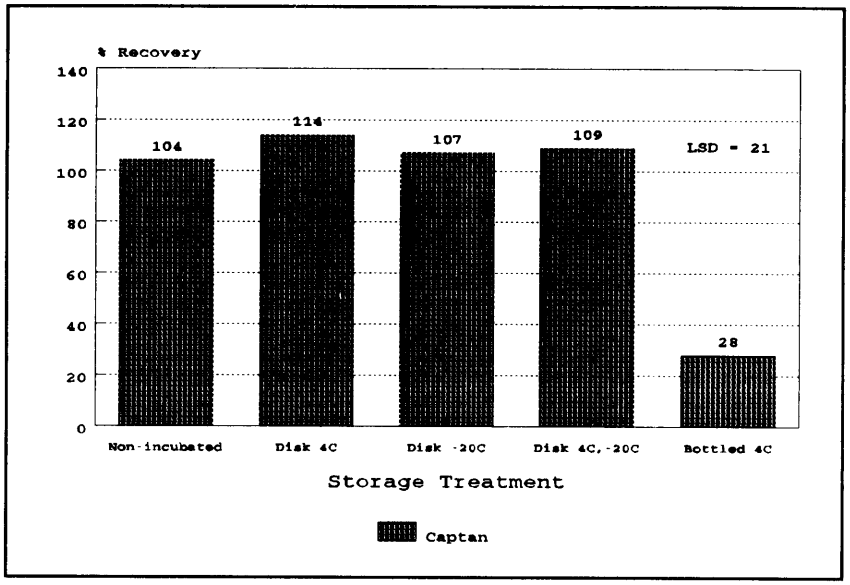

Figure 7. Comparison of storage treatments on stability of captan after 3 days of storage.

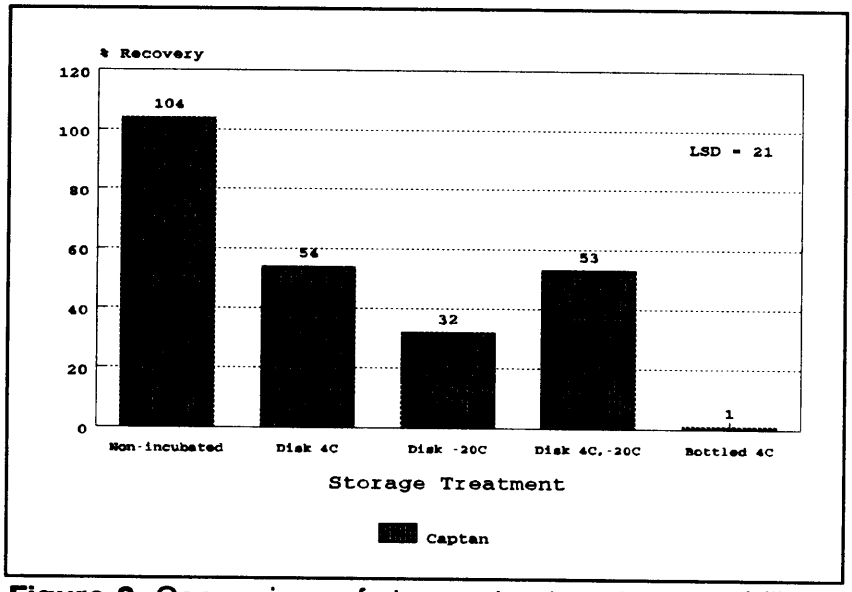

Figure 8. Comparison of storage treatments on stability of captan after 30 days.

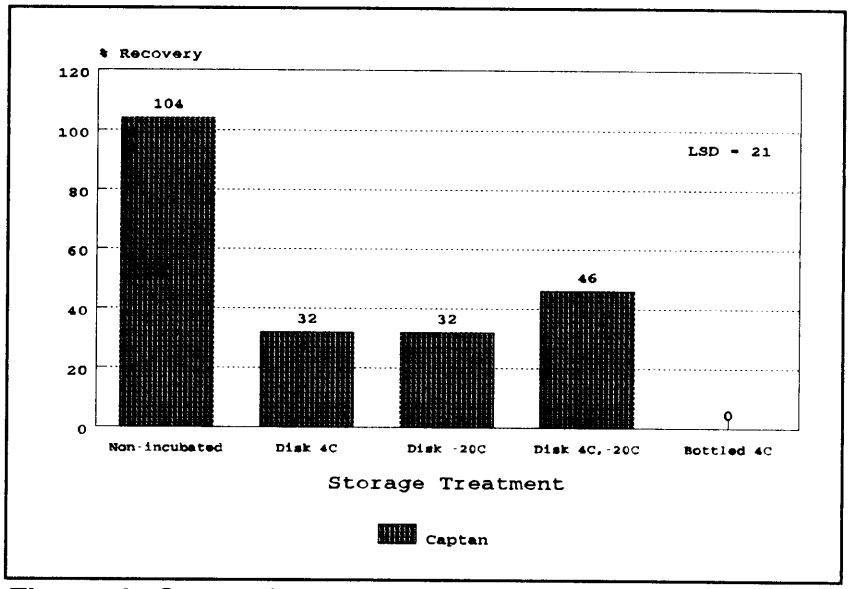

Figure 9. Comparison of storage treatments on stability of captan after 90 days.

QUESTION AND ANSWER SESSION

MR. BICKING: Merlin Bicking from Twin City Testing.

Two questions. Particularly in trifluralin after 180 days, you had 50 to 60 percent left. My first question is, did you see a steady linear decrease over time, or was it exponential? Did you see a rapid drop-off at the beginning?

And the second question is it appeared that the data labeled disk minus 20 which was, I think, frozen immediately always seemed to be lower than, for example, the one that was stored at 4 degrees centigrade for a day and then frozen. Is there any reason for that?

MR. SENSEMAN: There was an exponential decrease in trifluralin over the storage period in both water and when stored on the disk but the data has not been presented in terms of kinetics. The reason is because the main purpose of the experiment was to study relative stability not necessarily kinetics. However, the data is such that it could be used for a kinetic study.

MR. EPSTEIN: Paul Epstein, National Sanitation Foundation. Did you look at all at room temperature stability on the disks?

MR. SENSEMAN: No, we didn't. That is a treatment that should be studied. We felt that, in general, it would be just as easy, if we had the pesticides stored on a disk, it could very easily be stored in a cold room and, generally, be more optimum as far as stability of some of these pesticides is concerned.

MR. EPSTEIN: That is true, but if you have hundreds of samples in the laboratory, even the disks take up a lot of refrigerator space.

MR. SENSEMAN: Yes. No, we did not involve room temperature, but that could be future treatment in a similar study.

MR. EPSTEIN: Thank you.

MS. NOLAN: Lydia Nolan of Supelco, Incorporated.

My question is you alluded at the beginning of your talk to the fact that a lot of these studies had been done in years past with cartridges also, and I am wondering

if you are aware if the EPA is considering ever including this into their field methodology. Are they really going to take this seriously?

MR. SENSEMAN: I'll have to direct that question to Mr. Telliard.

MR. TELLIARD: As we build a data base, the answer is yes, if we can make it so that it cuts down on the shipping cost which, in our case, is quite extensive. When you go out to do a facility, you have 20 ice chests that you are mailing around the country. If you can get down to two boxes, that is going to be a significant cost savings.

For NPDS purposes for permit compliance, if the guy can do this at the facility, put it in a little canister, and mail it to L.J. Slink & Associates to run the analysis, that is going to be a cost savings.

So, as we build this data base and as we build the information, I think solid phase extraction, certainly as far as we see in drinking water, is applicable, and in wastewater, as we build a data base, will become more and more so.

MR. JUNK: Greg Junk, Iowa State University.

Relative to the previous question regarding stability at room temperature, we had very limited results with organophosphates which are very labile kinds of material. Phenotrion I remember specifically. At room temperature, we were able to preserve them for long periods of time, but the speaker mentioned something that is critical.

If that cartridge and/or disk is completely dry, there are good theoretical reasons for most of the lability that exists for these pesticides being some sort of sovolysis motivated. So, it is important for it to be perfectly dry.

But I do believe it requires further study, because if you don't have to refrigerate it, particularly in shipment, this is a very definite advantage.

MR. TELLIARD: George:

MR. STANKO: George Stanko, Shell Development Company.

The experiments that you did were with compounds that probably would not react with each other when they were next to each other. I would like to remind Bill back to Conference 2304. When we tried to do this with tenax traps on the purge and trap devices, we had very serious problems with the compounds reacting, disappearing,

forming humpograms.

In the case of 8270 type methodology where you had bases and acids, when you run them through this cartridge and you put them close to each other, I think you are going to have some real storage stability problems.

For pesticides, this probably might work, but for the rest of the things, I am not so sure it will.

MR. TELLIARD: We agree, George, and that is why we are trying to do some of these things to take a look at it. Again, too, remembering that it may not be...it is not a total panacea, but it may be, certainly, a field application, particularly if you have a permit where you have one or two or three analytes and you are not looking for a whole recipe here, that you could run it through and ship it off.

In our case, we were looking for everything creating by God and man. It sometimes creates a bigger problem. We agree.

MR. TELLIARD: Thanks, Scott.

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AFTERNOON SESSION

MR. TELLIARD: Continuing on with the same theme, we are going to discuss solid phase extraction and applications of the system. Our next speaker is Marie Brinkman from Battelle, Columbus.

MS. BRINKMAN: Before I start, I just want to make sure that everybody can hear me through the microphone. Can you guys hear me in the back? All right.

I also want to say that I had the bad form to have vertical slides, so what you are going to see on the screen is a little bit smaller version than the slides you saw this morning, because Randy needed to change the lens in order for us to see the full vertical slide. So, I apologize for that. If you all want to change your seats and come up to the front, feel free.

I also wanted to point out that everybody has been saying solid phase extraction, and I just wanted to mention that liquid-solid extraction is the same thing. We just call it liquid-solid extraction.

If I could have, let's see, the first slide here. I hope the people that expressed concerns about phenol recoveries are still here. I will be discussing a new liquid-solid extraction anion exchange technique for the extraction of phenols and acids from water that we developed in cooperation with USEPA-EMSL in Cincinnati.

This method includes the use of anion exchange resin and a novel derivatization method. So, I will also be giving some background information on both of those.

Our program goals are listed here. Our first two goals, reduce volumes of toxic solvents by applying liquid-solid extraction, tie in with the theme for this year's conference, pollution prevention in the laboratory. Our next two goals were to develop a single method for the analysis of diverse phenols and to achieve sensitive detection appropriate for drinking water levels.

Some of the concerns that we were faced with about the established methods included the fact that phenols are poorly extracted from water using liquid-

liquid extraction techniques. For example, EPA Method 625 and 625.1 which, as you know, are liquid-liquid extraction techniques, give recoveries for phenols as low as 25 percent.

Also, those procedures use about 400 to 500 ml of methylene chloride per sample, and non- or singly-chlorinated phenols, even when methylated, are detected on the order of 0.1 ng/ml, and we wanted to detect phenols at levels 10 and 100 times more sensitive than that.

Hence, our approach, liquid-solid extraction with anion exchange and pentafluorobenzyl bromide, or PFBBr, derivatization and GC/ECD.

Liquid-solid extraction is not new. We have been hearing about it all morning. There are many commercially available cartridges, and as discussed this morning, disks that contain different liquid-solid extraction media, including C18 and silica.

However, analytes can desorb or partition off of these media after large sample volumes are passed through the cartridge or over the disk. This behavior is especially common for phenols, because they are so soluble in water. Therefore, they are not strongly retained by these materials.

This phenomenon was discussed in a couple of the talks this morning.

Anion exchange solves this problem, because the phenols are retained by a chemical bond to the resin. This reaction can then be reversed in order to elute the analytes from the column.

One of the strong points for our method and, in fact, all liquid-solid extraction techniques is that minimal quantities of toxic solvents are used. We were able to reduce the amount of organic solvent used in our method to less than 20 ml per sample.

And by using PFBBr derivatization, we were able to detect analytes at the 1 pg/ml level.

The first important aspect of our method is the anion exchange resin itself. This slide is divided into three panels to show what is happening chemically between the AG MP-1 resin and the analytes during retention and elution from the column.

The resin has a polymeric backbone that is a styrene divinylbenzene co-polymer which is represented in this slide as an orange wave. However, the AG MP-1 resin has two distinct features, the chemically bound quaternary amine groups and an exchangeable anion which is the hydroxide bound to the amine.

We initially purchased the resin in the chloride form. We then exchanged the resin from the chloride to the hydroxide form to produce the strongest possible aqueous base, and that state is shown in the first panel in the slide.

As the water sample containing the phenols passes through the resin in the column, that hydroxide anion abstracts a proton from the analyte, and this results in the attachment of the analyte anion via an ionic bond to the quaternary amine functional group.

You can see in the middle panel that the phenol has lost its hydrogen and is now ionically bonded to the resin.

Neutral and basic molecules may be slightly retained by the polymeric backbone, but they can then be eluted using neutral solvents without removing the retained phenols.

Now, to elute the phenols from the column, a strong acid...and in this case we used hydrochloric...will displace the analyte from the resin. The phenols are eluted from the column and then collected as shown in the last panel there.

I would like to point out that this slide shows phenol as the only analyte for simplicity's sake only. The resin retains many types of phenols and carboxylic acids, and I will list the analytes we tested for this program a little later.

The second important aspect of our method, pentafluorobenzylbromide or PFBBr derivatization, is not new. It has been reported in the literature many times.

PFBBr reacts with phenol in the presence of potassium carbonate and heat to produce the derivatized analyte, thereby attaching five ECD-sensitive fluorine groups to the analyte of interest.

And, again, only phenol is shown for simplicity's sake. The bottom of the slide shows an ECD chromatogram of the diverse phenols derivatized with PFBBr for this program.

With those two main concepts introduced, I move on to our program design. Looking back to the derivatization reaction shown in the previous slide, we evaluated the effects of reaction temperature and duration, potassium carbonate concentration, and trace amounts of water in the reaction solution on the formation of PFBBr derivatives.

In addition, we evaluated the strong anion exchange resin, AG MP-1, for collection of phenols and acids from water. Because AG MP-1 is an organic resin, we needed to evaluate methods to remove residual organics from the resin prior to its use.

We were then able to measure recoveries of analytes spiked into 1-liter and 100-ml volumes of water.

These are the compounds we evaluated in this study. We included both weak acids, the alkylphenols, and strong acids, dichloroacetic acid and 2,4-D. We also evaluated mono through pentachlorinated phenol.

This slide shows a schematic representation of a typical experiment.

First, we suspended the resin in the chromatography column. The resin was then exchanged from the chlorine to the hydroxide form using a sodium hydroxide solution. We then put the resin through the washing procedure to remove any residual organics.

We exchange and wash the resin after it is already in the chromatography column to minimize passive sampling.

The syringe in the slide represents the spiking of 0.1 mg per analyte which we spiked into varied water volumes for various experiments, 30 ml, 100 ml, and 1 liter. The resin itself is pictured in the right-hand insert.

Once the aqueous sample is passed through the column and the analytes are then chemically bound to the resin, we come to the analytical procedure depicted in this slide.

I realize this is a complex slide with arrows going all over the place, so I will start at the upper right-hand corner and go slowly.

Again, the sample has already been passed through the column, and the analytes are now bound to the resin. We then eluted the analytes from the resin using a 2 percent hydrochloric solution of methanol/methylene chloride into a separatory funnel.

The organic layer was then partitioned against an acidic aqueous solution. The aqueous layer is discarded, and the organic layer containing the analytes is dried using a sodium sulfate column. It is then concentrated to 1 ml by Kuderna-Danish, the internal standards are added, and the extract is separated at this point.

900 ml branching to the left is solvent exchanged to methyl t-butyl ether, methylated with diazomethane, and analyzed for acids using GC/ECD. 100 ml branching to the right is solvent exchanged to acetone and diluted to 1 ml.

This is then derivatized using PFBBr and analyzed for phenols using GC/ECD.

To isolate the issues, we focused on one pathway at a time per sample. I will explain later why the extract is split and one derivatization technique is used for acids and a different derivatization technique is used for phenols.

This graph shows analyte recoveries for 1 mg/analyte spiked into two different water volumes. In general, recoveries are greater than 75 percent.

These results also show that the sample volume passed through the resin does not affect analyte recovery. This is because of the ionic bond formed between the resin and the analyte.

In fact, the recoveries are a little higher when the analytes were spiked into 1 liter of water, because silanized glassware was used for that experiment.

Because this was our first evaluation of the resin, we chose a spike level amenable to methylation and GC/FID. Later, I will show results for lower phenol spike levels using PFBBr derivatization and GC/ECD.

I should mention that each experiment was performed in triplicate and included method blanks.

As I said before, numerous PFBBr derivatization methods have been reported in the literature for selected phenols and acids. Our experience with these methods is summarized by the top chromatogram which shows numerous artifacts in addition to the three derivatized analytes highlighted in pink.

The bottom chromatogram demonstrates that it is possible to achieve similar derivatization efficiency of those same three analytes without excessive artifacts.

I should point out that the GC/ECD temperature programs are different for those two chromatograms, and that is why the analytes don't exactly line up.

The original PFBBr derivatization procedure that we developed included four steps. We start with 1 ml that contains all of the phenols and acids in acetone. At the completion of step 2, the acids and pentachlorophenol are the only species derivatized, and they are shown in the top chromatogram.

At the completion of step 4, phenols are derivatized, as shown in the bottom chromatogram. However, the highly alkaline conditions of steps 3 and 4 hydrolyze the acid derivatives, so these species are no longer detected at this point.

Here we show that even at one of our lowest concentration levels, the 2.5 pg/ml per microliter standard shown in the bottom chromatogram, derivatized phenols are still discernable from minor ECD detectable artifacts. The analytes are highlighted in the pink rectangles, and this unhighlighted version allows you to see the baseline a little bit more clearly.

These are examples of the calibration curves for one of the analytes, pentachlorophenol, in the derivatized mix of 20 phenols and acids. Note the linearity over the range of 1 to 100 pg/ml per microliter. All phenols and acids in the derivatized mix exhibited similar linearity.

Now that I have shown you our standards, this is a chromatogram of the phenols recovered from water using the anion exchange resin and subsequently derivatized with PFBBr. As you can see, the resin does yield some other detectible species. Remember, it is an organic resin. Yet, these species do not interfere chromatographically with the analytes.

Again, the analytes are highlighted in pink here, and this unhighlighted version lets you see the baseline.

This chromatogram shows the recovery of the acids from water using the anion exchange resin. The blank below shows minimal interferences and artifacts, however, 4-chlorobenzoic and dichloroacetic acid, had to be blank subtracted for the analysis shown here.

These analytes were methylated prior to analysis; they were not derivatized

using PFBBr.

Although we were able to derivatize acid standards using PFBBr, we were not able to apply this technique successfully to resin extracts. We believe that this is due to small quantities of HCl that are carried through from the final partition step in the separatory funnel.

This acidic environment did not appear to adversely affect methylation. For this reason, we split the extract, and the two derivatization techniques are applied for acids versus phenols.

In subsequent work, we have been able to identify slightly different PFBBr derivatization conditions to compensate for this analytical procedure.

Shown here are the overall method recoveries for the phenols spiked into water. These data represent recovery of 0.1 mg spike with PFBBr derivatization and GC/ECD. The reason why we say simulated 0.1 mg/L is because we spiked 0.1 mg of material into 30 ml or 100 ml volumes rather than a liter. This was done for experimental efficiency.

Remember, the analytes are retained by an ionic bond to the resin, and our experimental results, presented in a previous slide, showed that recoveries are comparable whether analytes are spiked into water volumes of 100 ml or 1 liter.

These data show that overall recoveries are good, generally better than 70 percent. The exception is 1-naphthol, which is on the far right side there, which was slightly less than 50 percent. We believe that that was due to its chemical instability.

I would also like to point out the large deviation for phenol, which is the farthest bar on the left, was due to phenol contamination of the laboratory air from roofing tar being applied to the roof near our hood exhaust. We would expect the phenol standard deviation to be similar to the other analytes under normal conditions.

We would like to define and use a new term for the evaluation of liquid-solid extraction media. We call this term LSE efficiency, and it describes the efficiency of the collection onto and the subsequent release off of the resin.

This number isolates and defines the performance of the resin alone. This involves isolating a portion of the analytical method which we call the post-resin method

which is shown here in the green box.

In the post-resin method, the analytes are not spiked into the water sample but directly into the separatory funnel and then carried through the rest of the analytical procedure.

In the analytical method which is shown here in the purple box, the analytes are spiked into the water sample. The sample is run through the resin, the analytes are eluted from the resin into the separatory funnel, and on down through the rest of the post-resin method.

To calculate an analyte's LSE efficiency, we divide its recovery value from the entire analytical method by its recovery value from the post-resin method, and multiply by 100 to get a percent value. An analyte's method recovery is the same as its recovery from the entire analytical method.

If the method recovery for an analyte is low, the next number to look at is the analyte's LSE efficiency. If the LSE efficiency is high, that means that the resin is performing well and that losses are due to problems with the extractions or derivatizations in the post-resin method.

However, if the LSE efficiency is low but the post-resin method recovery is high, then that indicates that the resin is not retaining and eluting that analyte efficiently.

This graph shows the calculated LSE efficiencies for the phenols. They are very high, averaging 92 percent. These data show that the AG MP-1 resin collects and releases these analytes efficiently.

This slide shows the overall method recoveries and the LSE efficiencies for the acids and two selected phenols. The post-resin method recoveries were nearly 100 percent for all of these acid analytes.

Because overall analytical method recoveries averaged about 80 percent, we calculated LSE efficiencies that averaged 80 percent. It appears that the AG MP-1 resin's performance is slightly lower for the retention and elution of the acids.

Our data from this program for liquid-solid extraction with anion exchange resin is listed on the left-hand side. Published data using liquid-liquid extraction techniques are listed on the right side.

For the acids, our recoveries are comparable, and our spike levels were approximately the same. For the phenols, our recoveries are, again, comparable, and our spike levels were almost 100 times lower than those used for the published data.

In conclusion, our method recoveries are comparable with those given using liquid-liquid extraction techniques, and our method uses less than one-tenth the amount of toxic extraction solvent used by liquid-liquid extraction methods. Also, PFBBr derivatization gives more sensitive detection and will allow us to detect phenols at drinking water levels.

Thank you. Any questions?

QUESTION AND ANSWER SESSION

MR. TELLIARD: Bill?

MR. BUDDE: My name is Bill Budde. I work for EPA in Cincinnati.

I want to congratulate the speaker for using the terminology liquid-solid extraction which, I believe, is a slightly more scientifically correct than the equally useful solid phase extraction.

I would also just like to point out...I don't have any questions, but I wanted to point out that this work which was sponsored by EMSL-Cincinnati is continuing, and one of our goals is to eliminate entirely the use of solvents such as methylene chloride, and one of the new approaches that we are looking at now is to use supercritical carbon dioxide to elute the cartridges and disks and resins.

Thank you.

MS. BRINKMAN: Thank you.

MR. TELLIARD: Anyone else like to make an advertisement?

MR. BUDDE: We hope to report on that result with supercritical carbon dioxide at the SFE meeting which is later this month in Cincinnati. If anyone would like to know about that, I will be glad to tell you.

MR. MCCARTY: Harry McCarty, Viar and Company. I don't have anything to advertise.

Two questions. What were you using for internal standards, and how many relative to the number of analytes you had?

MS. BRINKMAN: The number of analytes totalled 18, and we had 2 internal standards, 4-chlorobenzoic acid for the acids and 3,4-dimethylphenol for the phenols.

MR. MCCARTY: As I understood it, you added those after you went through the resin and eluted it off. Would the addition of the internal standards prior to passing it through the anion exchange resin eliminate the need to calculate the efficiency factors? I mean, basically, you have some correction for the loss that was going on in that efficiency process.

MS. BRINKMAN: That is a very interesting idea, and we refer to that as a surrogate, and that sounds like an excellent experiment to do. We didn't do any work doing that, though.

MR. MCCARTY: Well, I am suggesting that you not use it as a surrogate. A surrogate is what you would put in and say okay, we got this, we probably got as much of everything else.

If you put it in and you use it for quantification, if it was a labeled compound, you would call it isotope dilution, but what I am suggesting is it might eliminate the need to even worry about the efficiency of the LSE itself and separate out that step which might save, looking at other compounds, it might save a lot of time. All you would need to do is find a compound that resembles the ones you are looking for.

MS. BRINKMAN: It is true calculating the LSE efficiency does involve two separate experiments. Thank you.

Anion Exchange Liquid-Solid Extraction of Phenols and Halogenated Carboxylic Acids from Water

Marcia G. Nishioka, Marielle C. Brinkman, and Mary Lou Briner
Battelle

Jimmie W. Hodgeson
US EPA

Program Goals

- reduce volumes of toxic extraction solvents

- apply liquid-solid extraction (LSE)

- develop single method for diverse phenols

- achieve sensitive detection appropriate for drinking water analyses (0.01 - 0.1 ug/L)

Concerns

- Phenols are poorly extracted from water with LLE
- LLE procedures employ large solvent volumes
- Drinking water levels of many phenols not detectable using methylation with GC-FID or GC-ECD

Approach

LSE with anion exchange

PFBBr derivatization, GC-ECD

Approach

LSE with anion exchange PFBBr derivatization, GC-ECD

- LSE efficiency depends on reversible chemical bond rather than partition efficiency

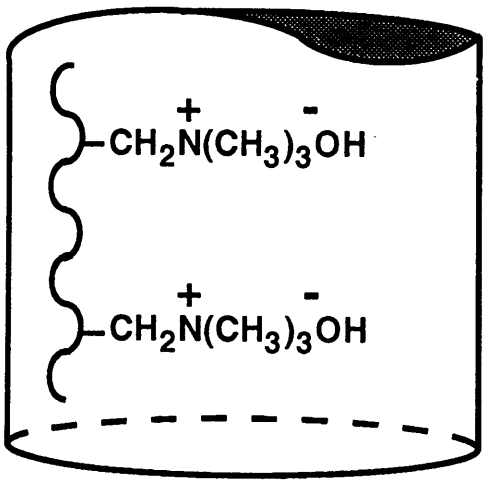
- LSE uses minimal quantities of toxic solvents

- PFBBr derivatization offers possibility of sensitive detection for diverse phenols using GC-ECD

Retention and Elution of Phenols and Organic Acids from Anion Exchange Resin (AG MP-1)

Initial State

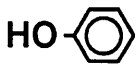
Suspend AG MP-1 in solvent in open chromatography column

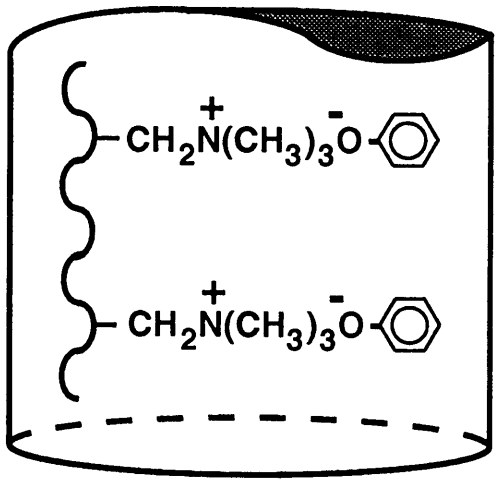


Retention

Attach phenol or acid to AG MP-1

Added Material:





Eluted Material:

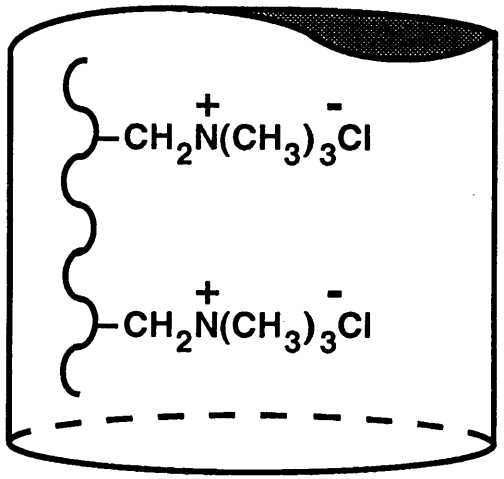
- H_2O
- Neutral molecules
- Basic molecules

Elution

Remove phenol or acid from AG MP-1

Added Material:

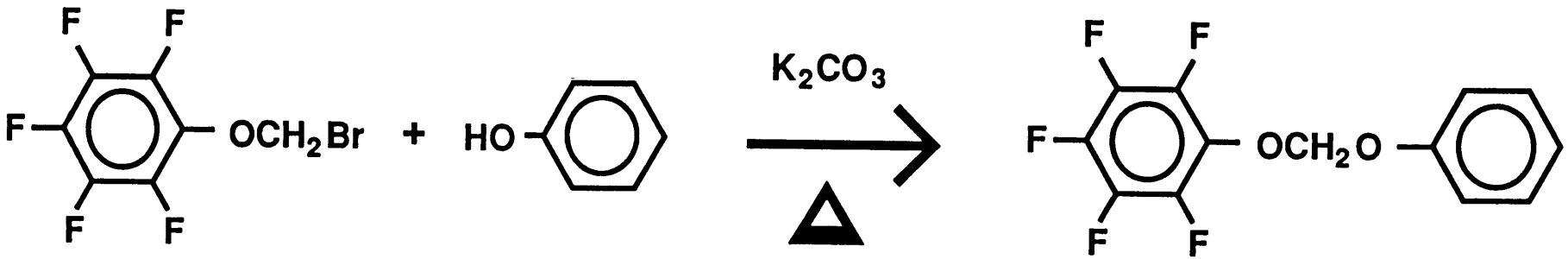
$HCl : MeOH : MeCl_2$



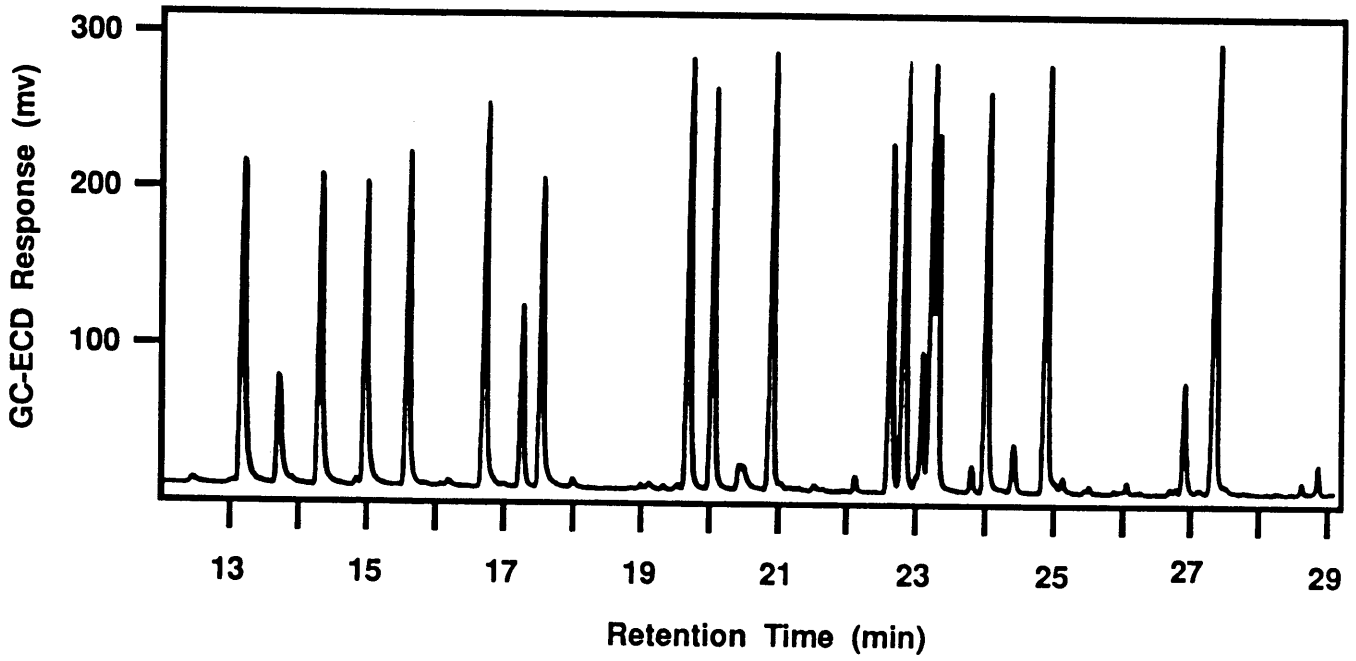
Eluted Material:

- Excess HCl
- MeOH, $MeCl_2$

Pentafluorobenzylbromide (PFBBr) Derivatization



PFBBr Phenol Derivatized Phenol



pfbpix1H α

Program Design

Evaluate parameters which effect PFBBr derivatization:

- Reaction temperature and duration
- K_2CO_3 concentration
- Trace amounts of water in reaction solution

Evaluate strong anion exchange resin AG MP-1:

- develop resin cleaning method to produce clean blanks and reduce passive sampling
- compare analyte spike recoveries from 1 L and 100 mL water

Analytes Evaluated

Alkylphenols

phenol
2-CH_3-phenol
4-CH_3-phenol
2,6-diCH_3-phenol

Nitrophenols

2-NO_2-phenol
4-NO_2-phenol

Chlorophenols

2-Cl-phenol
4-Cl-phenol
2,3-diCl-phenol
2,4-diCl-phenol
2,5-diCl-phenol
2,4,5-triCl-phenol
pentachlorophenol

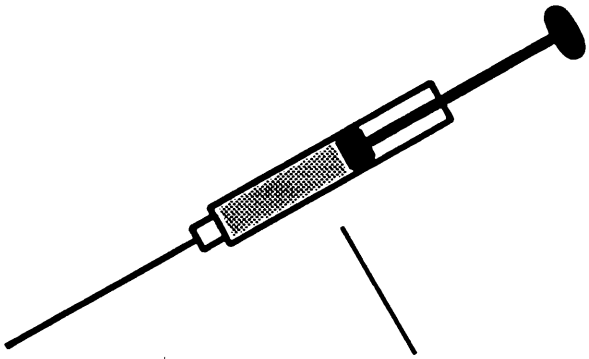
Naphthols

1-Naphthol
2-Naphthol

Halogenated Carboxylic Acids

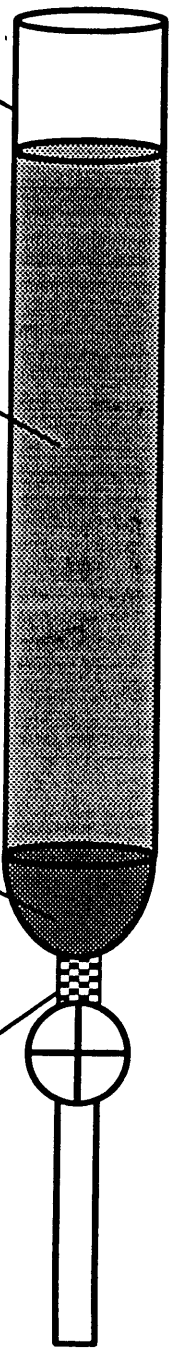
diCl-acetic
2,4-diCl-benzoic
2,4-D
2,4,5-T

LSE of Phenols and Acids from Water



1 mL of 0.1 ug/mL analyte mix in MeOH

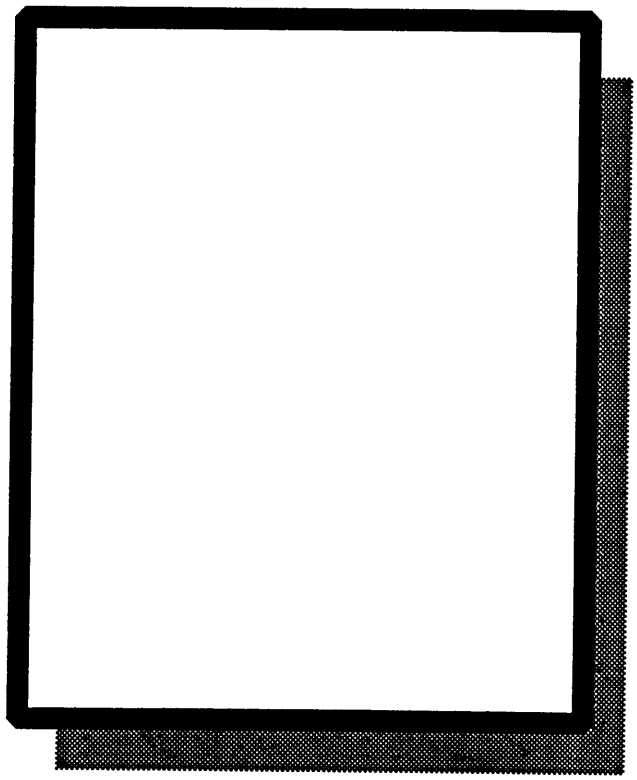
Silanized glass chromatography column



H_2O

0.5 g AG MP-1

Silanized glass wool



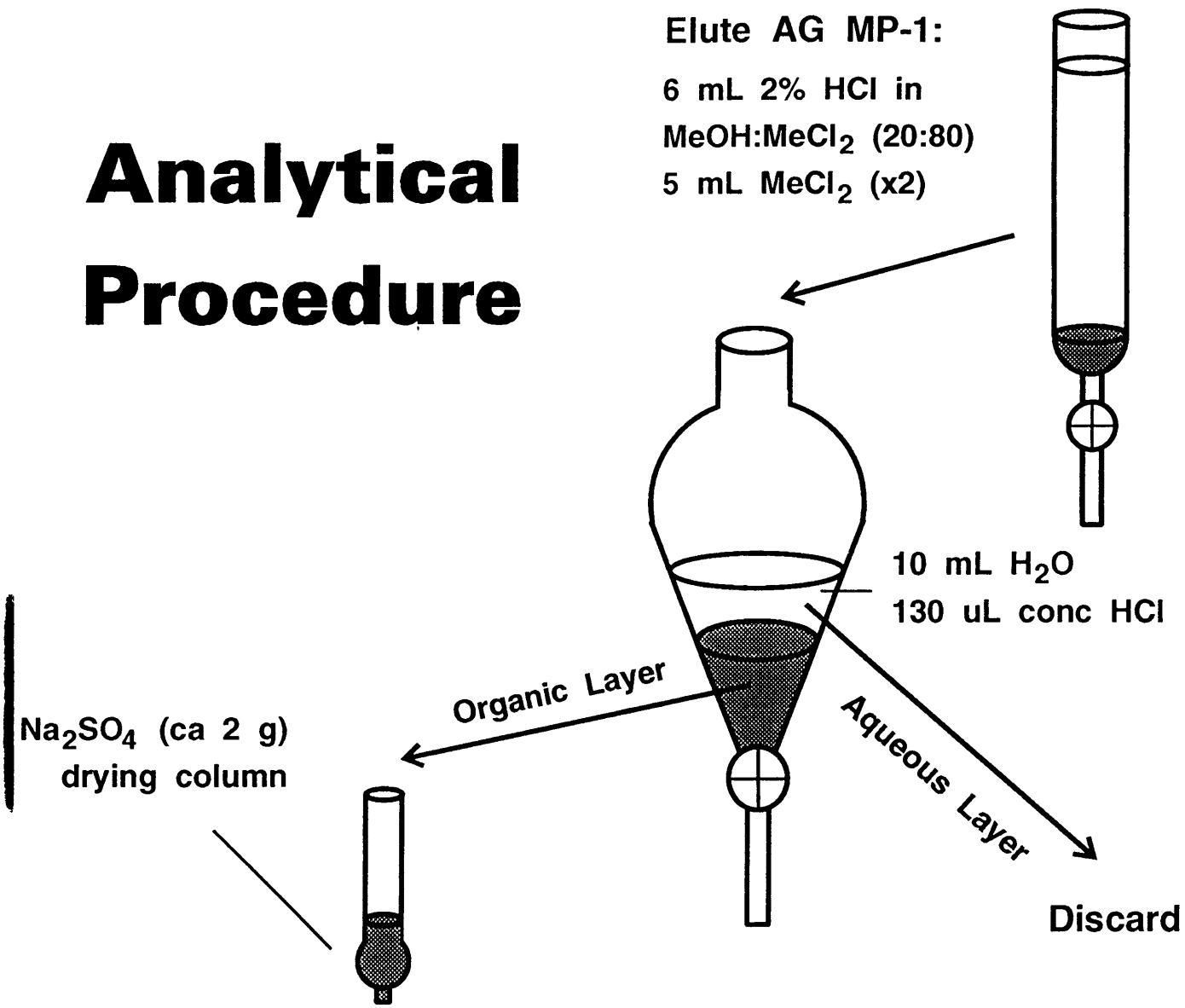
BioRad AG MP-1

100-200 mesh resin

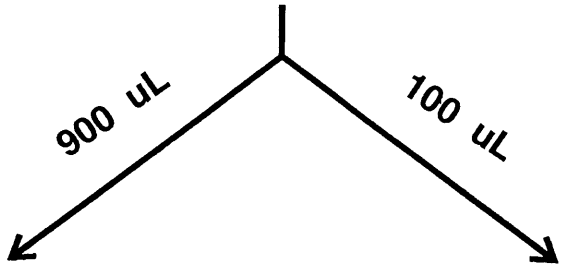
70-150 um, chloride form

CD\Recov1H

Analytical Procedure



- K-D concentration
- Add IS: 3,4-diCH_3-phenol for phenols
  4-Cl-benzoic acid for acids



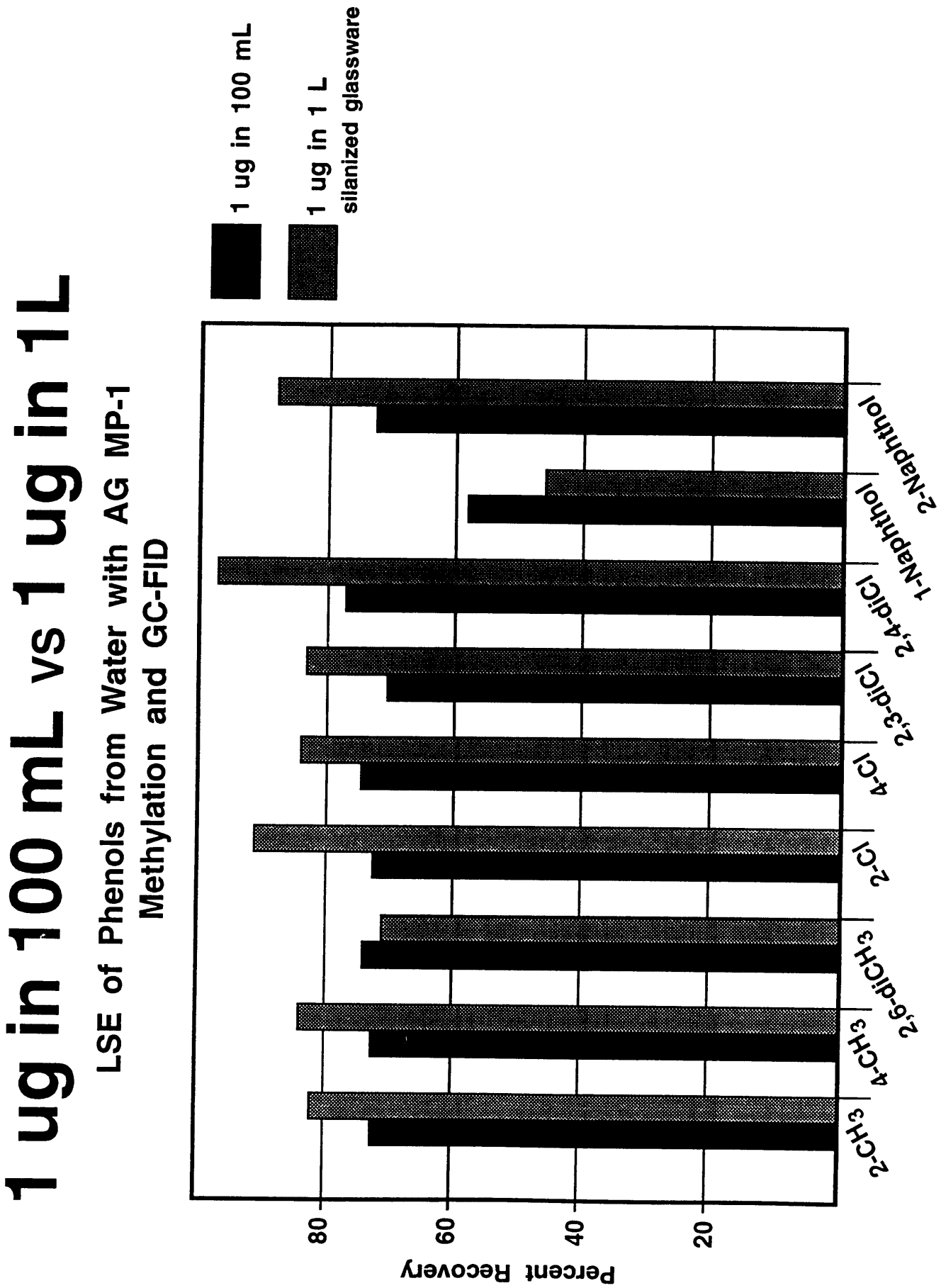
Acids

- Solvent exchange to MTBE
- Methylate
- GC-ECD

Phenols

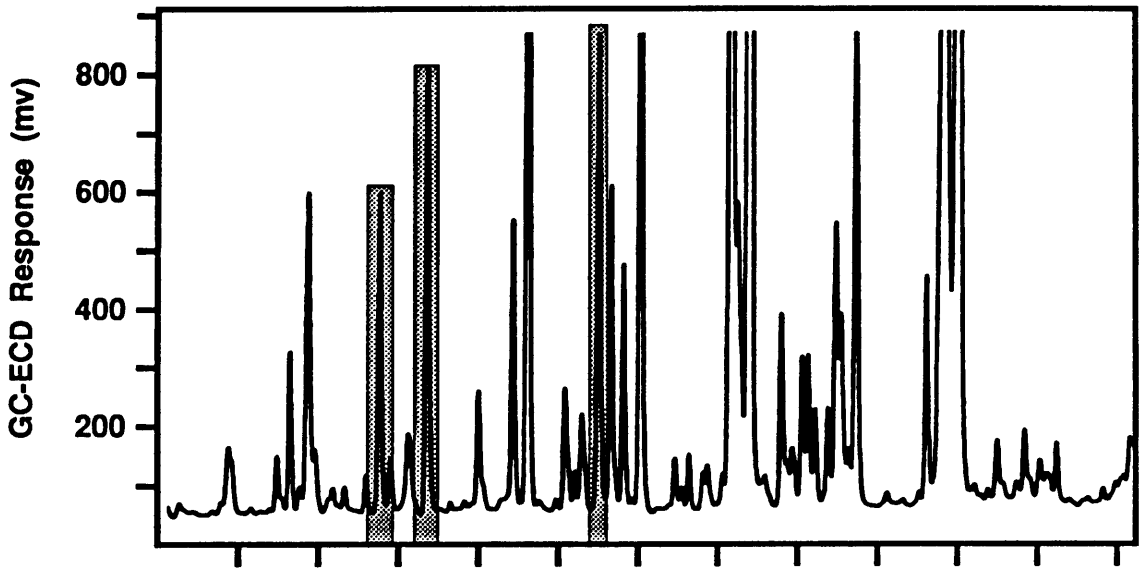
- Solvent exchange to acetone, dilute to 1 mL
- PFBBr derivatization
- GC-ECD

procedur.cdr


1 ug in 100 mL vs 1 ug in 1L
LSE of Phenols from Water with AG MP-1
Methylation and GC-FID
1 ug in 100 mL
1 ug in 1 L
silanized glassware
Percent Recovery
80
60
40
20
2-CH3
4-CH3
2,6-diCH3
2-Cl
4-Cl
2,3-diCl
2,4-diCl
1-Naphthol
2-Naphthol

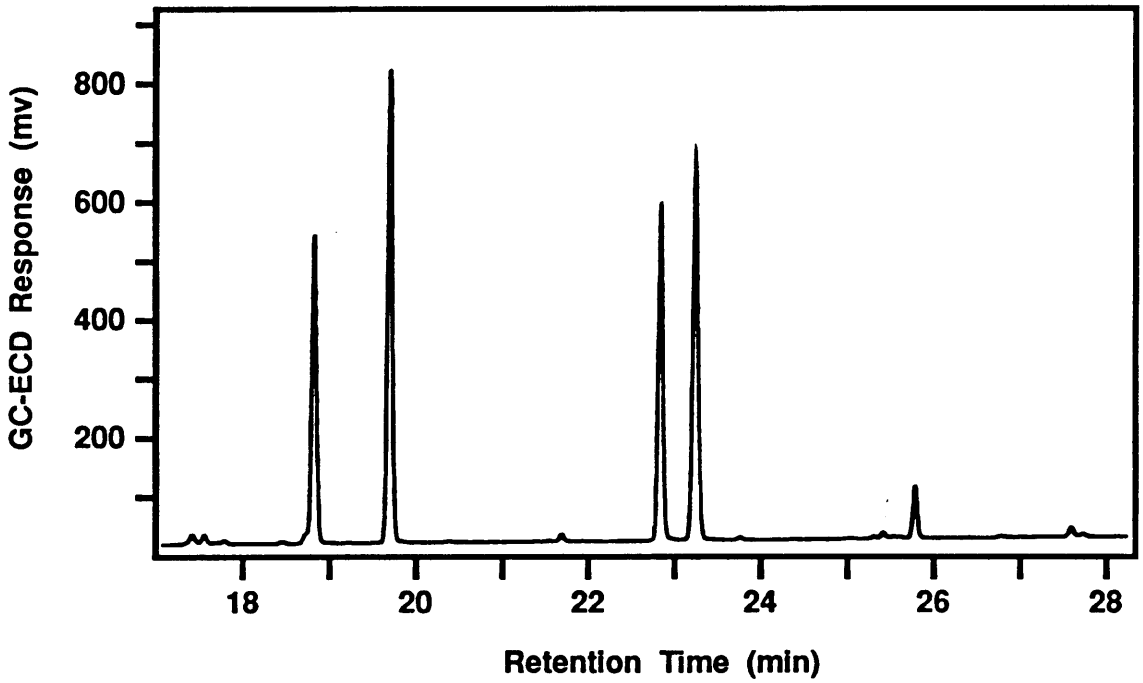
Battelle PFBBr Method vs Literature

Literature Method*



**J Chrom* 469, 351-9, 1989

Battelle Method



4-Step PFBBr Derivatization Method

Step 1

0 ug K_2CO_3
95°C for 1hr

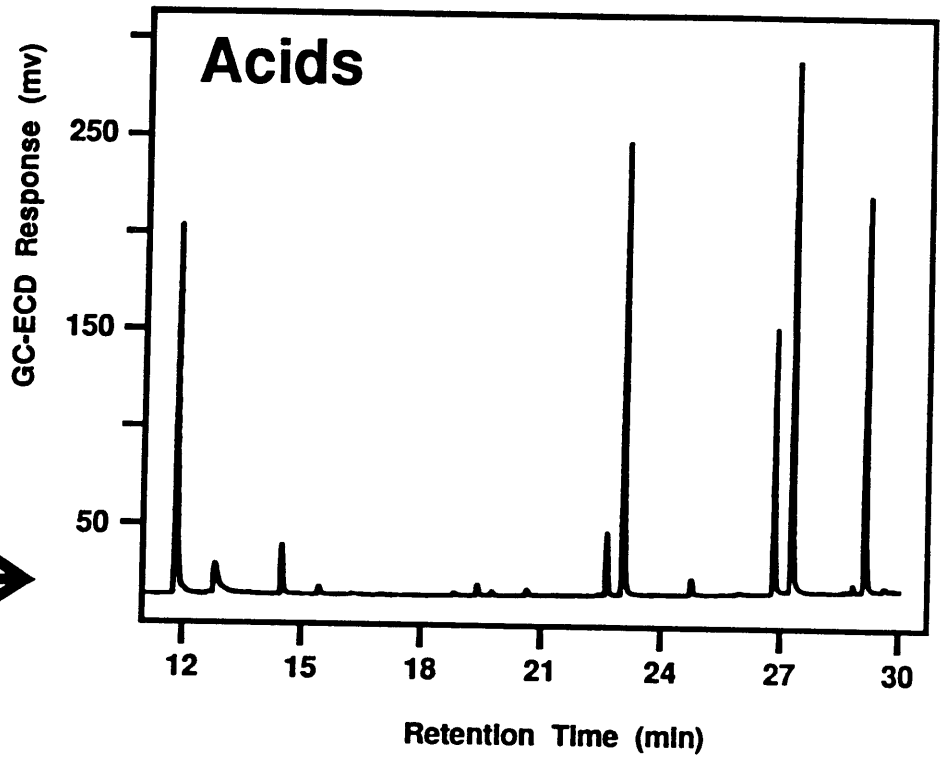
Step 2

0.1 ug K_2CO_3
95°C for 20 min

250 uL

750 uL

GC-ECD

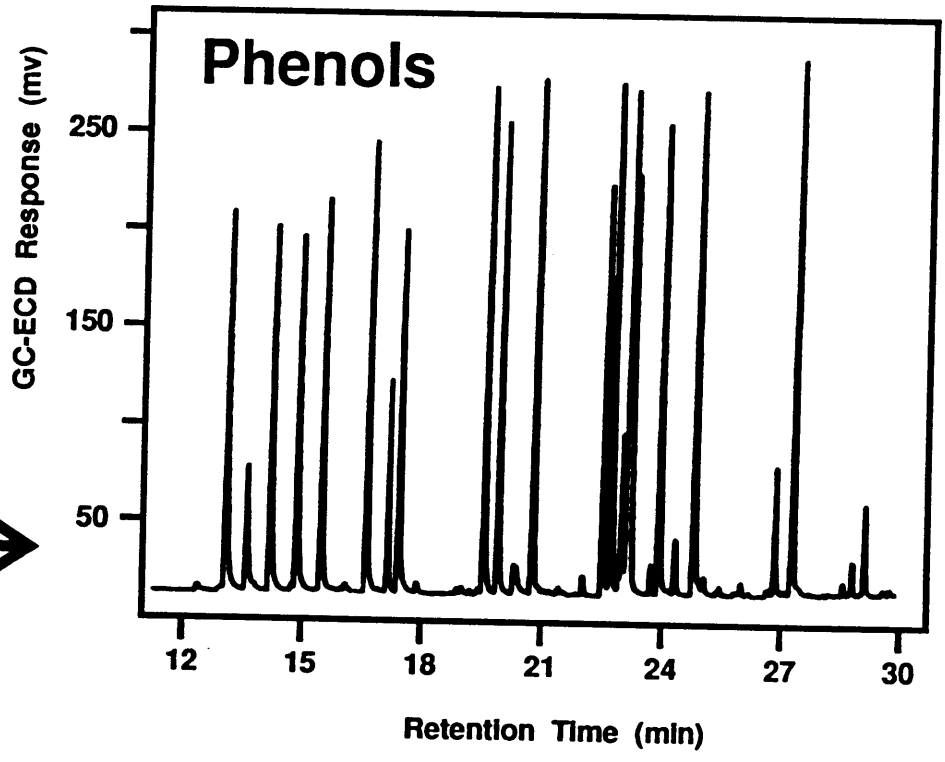


Step 3

2 ug K_2CO_3
95°C for 20 min

Step 4

100 ug K_2CO_3
95°C for 20 min



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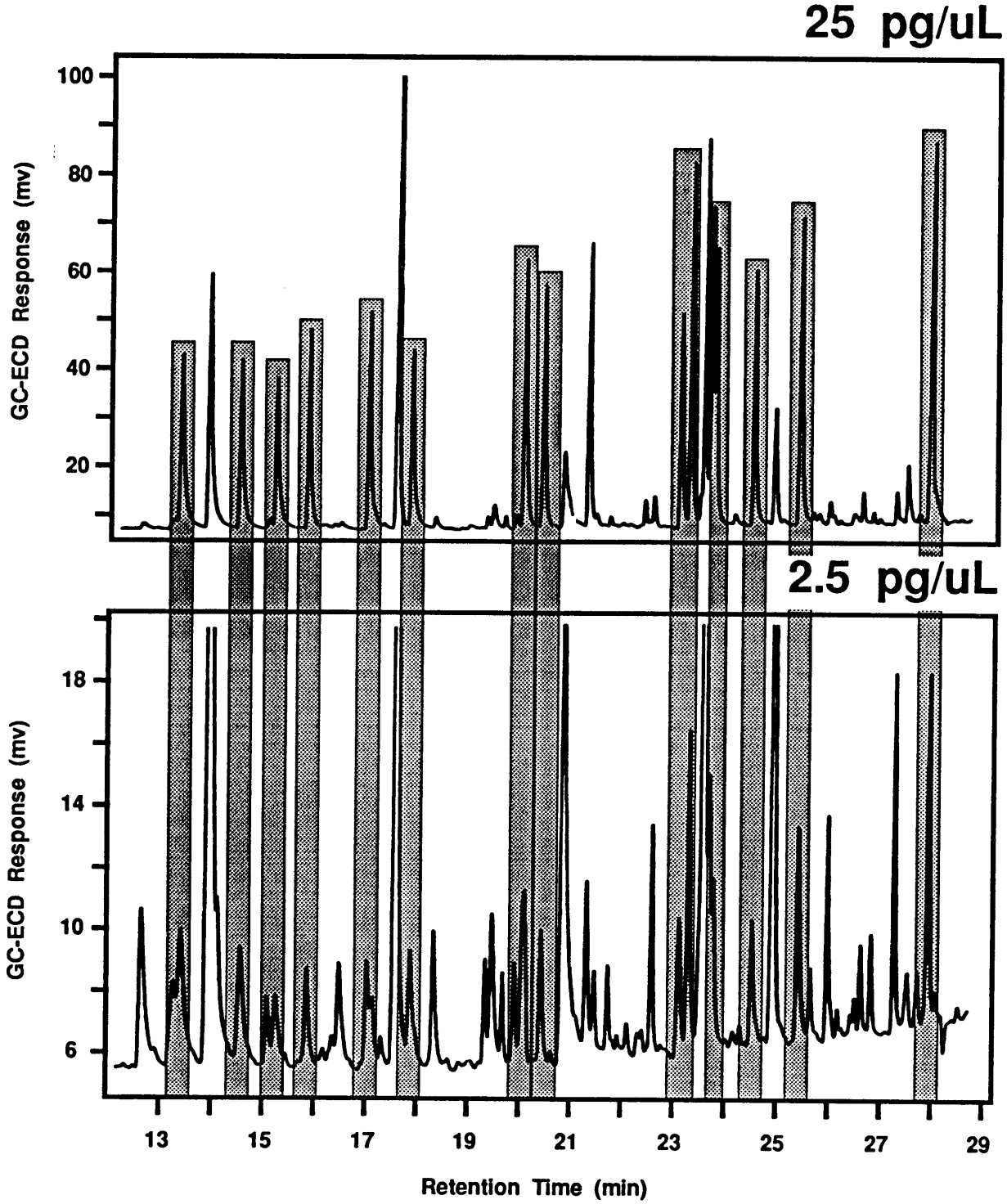
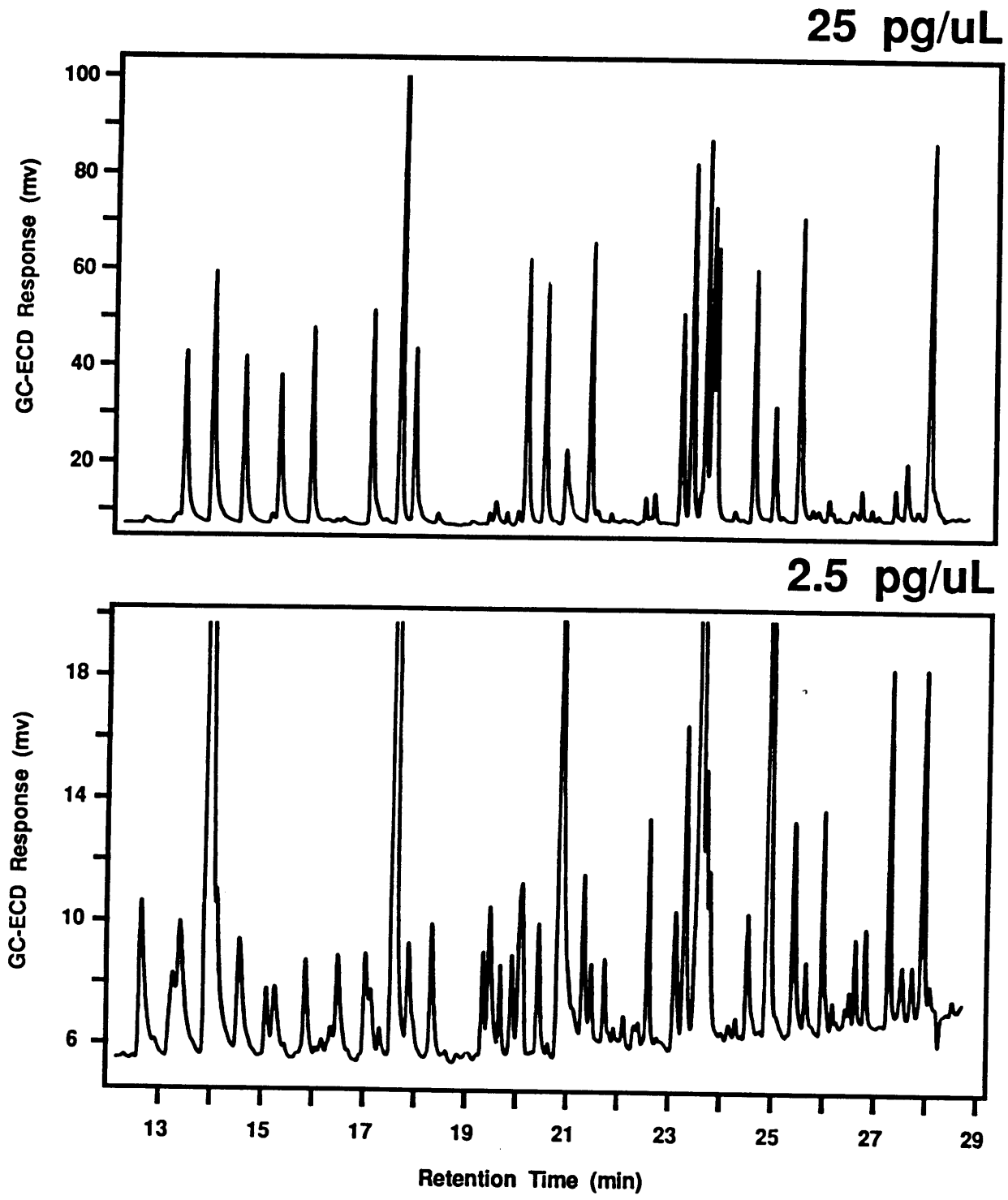
PFBBr-Derivatized Phenols by GC-ECD



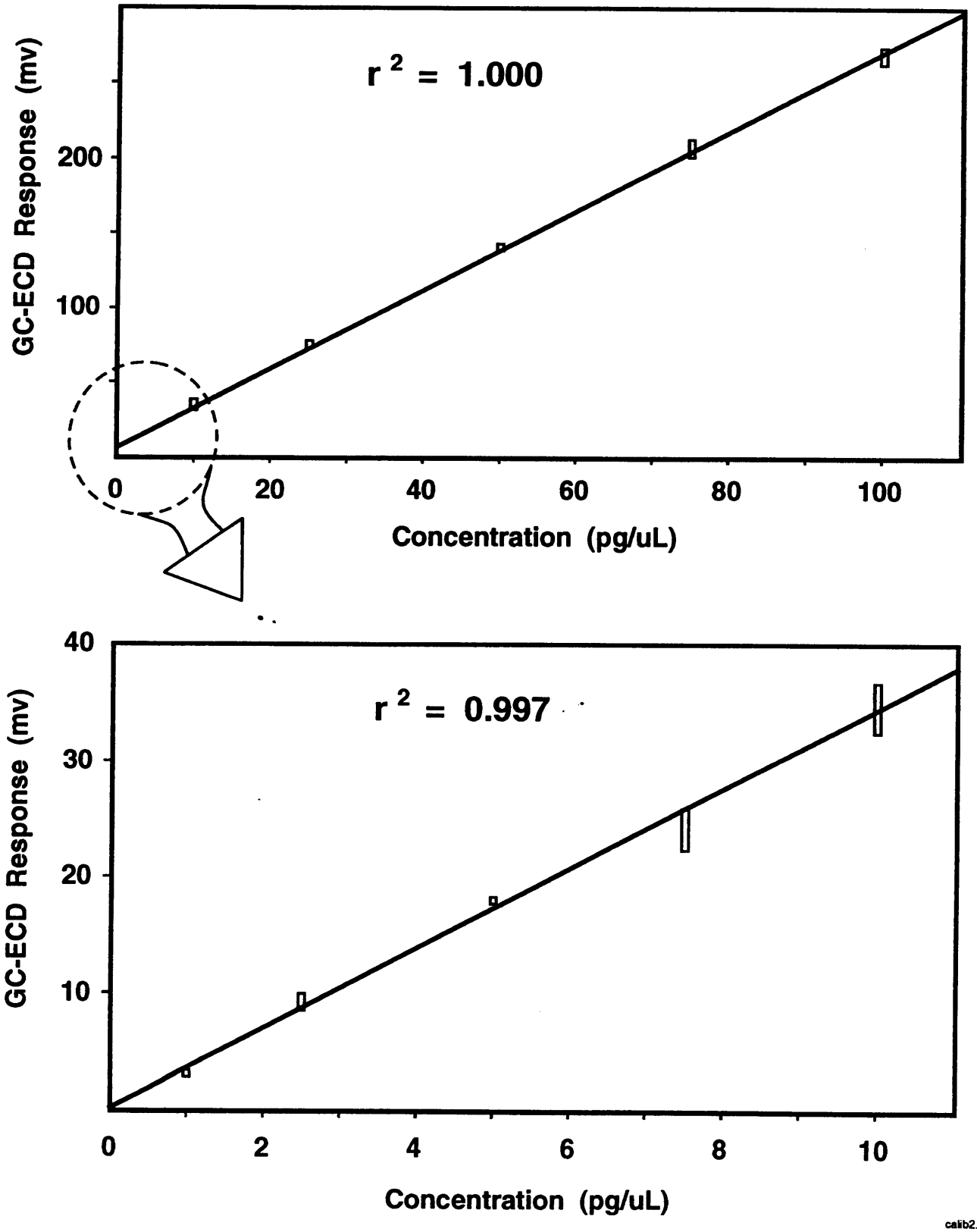
phenstlc

PFBBr-Derivatized Phenols by GC-ECD



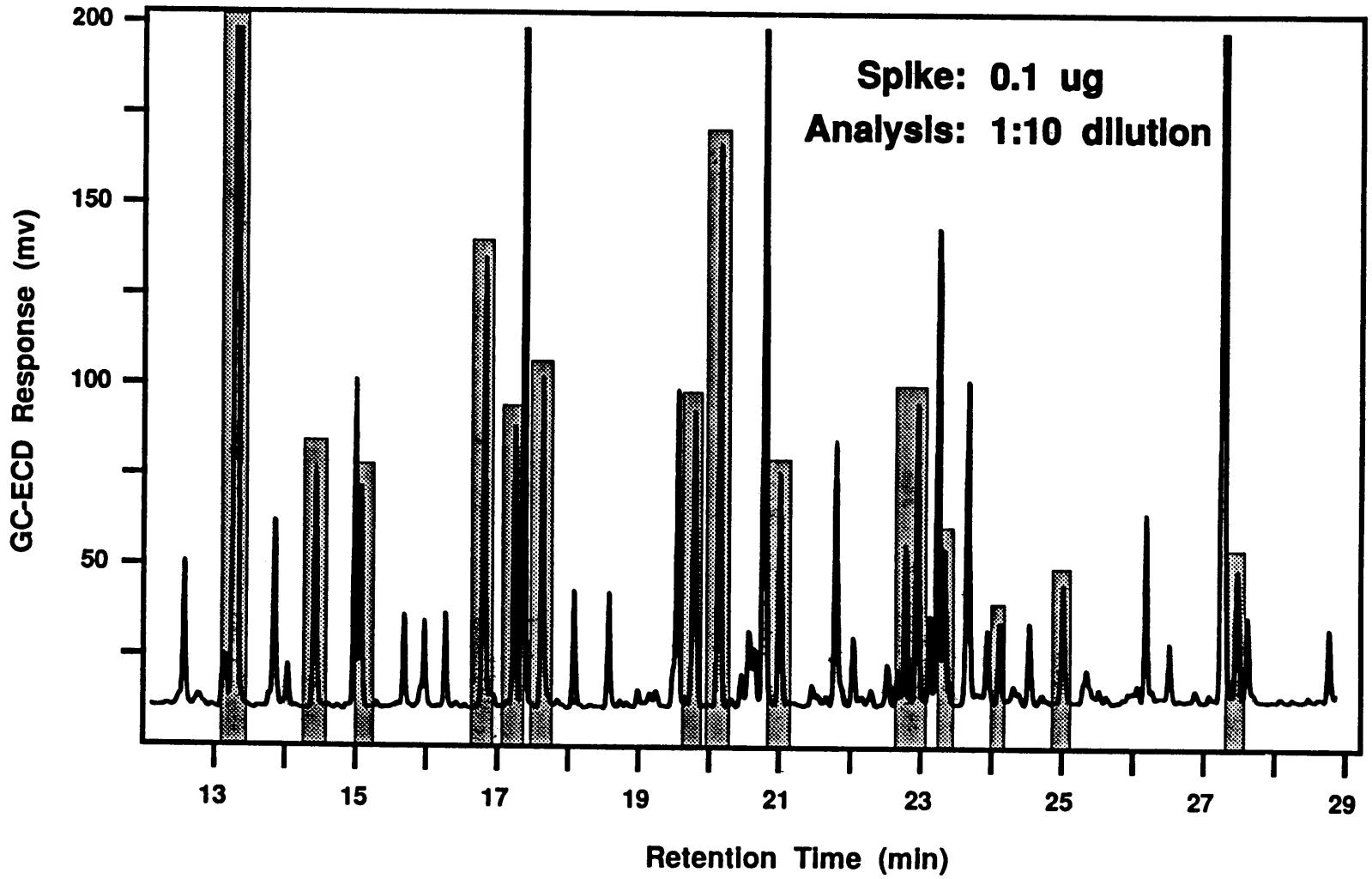
phenstic

GC-ECD Calibration Curve for PFBBr-Derivatized PCP

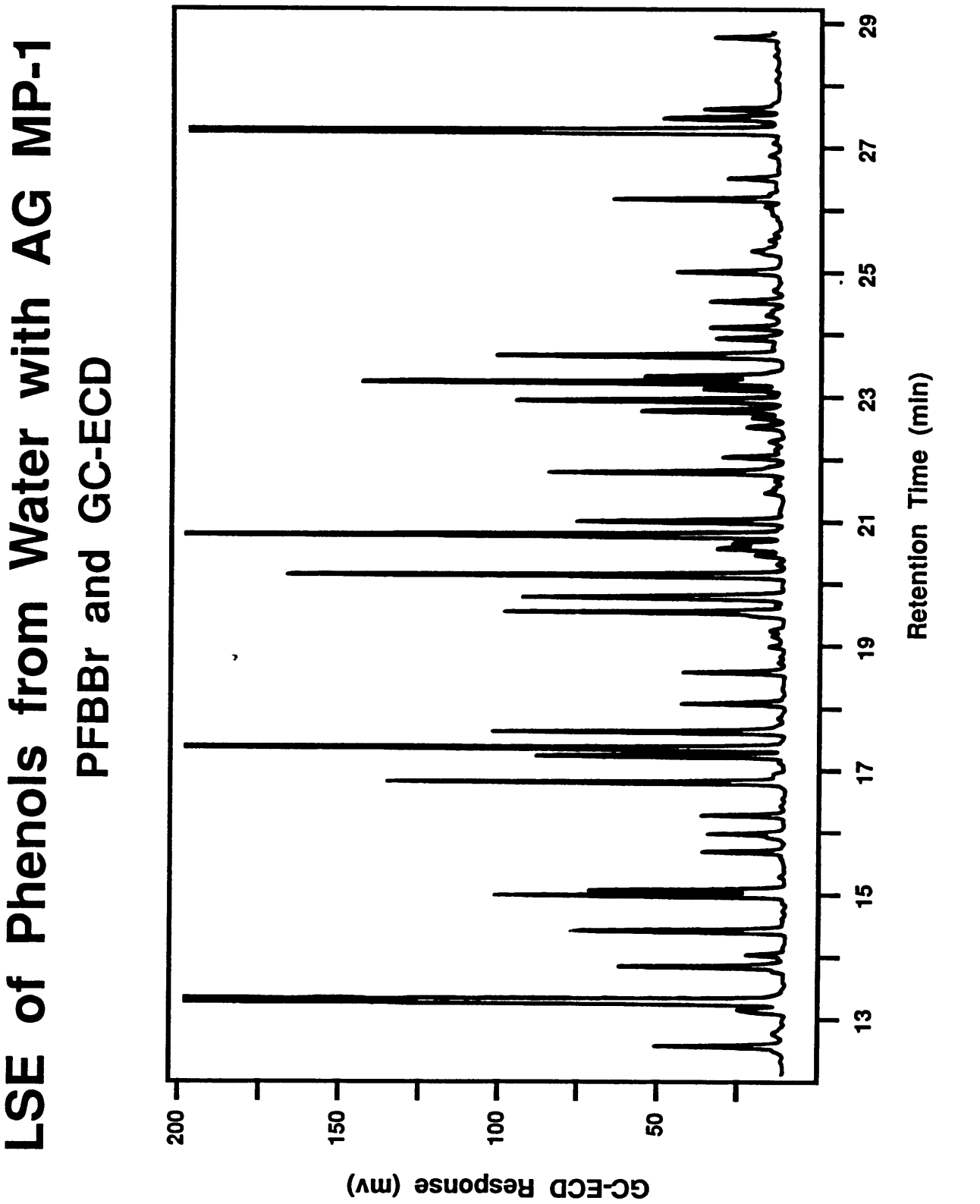


LSE of Phenols from Water with AG MP-1

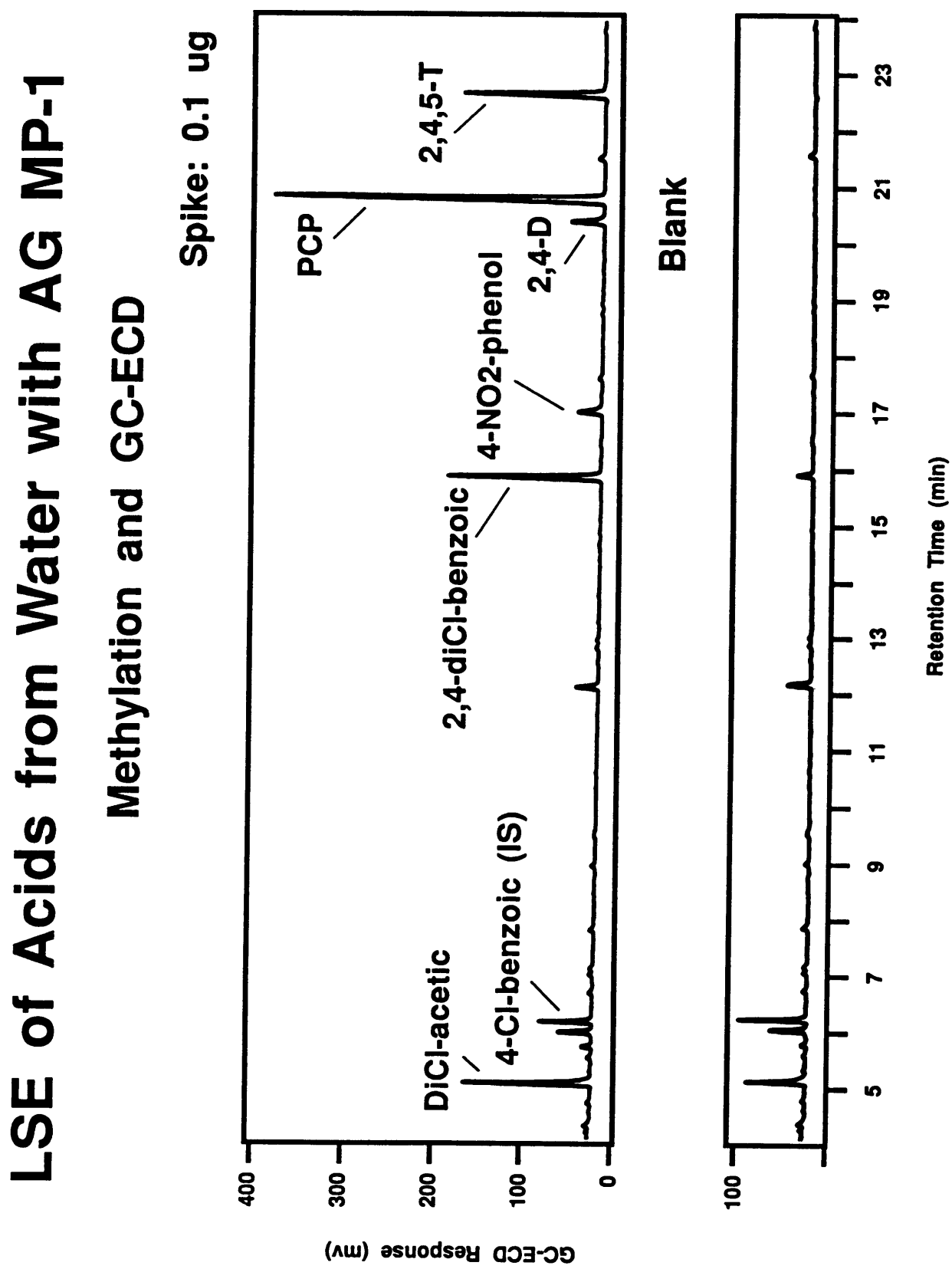
PFBBr and GC-ECD



CDALSE2H

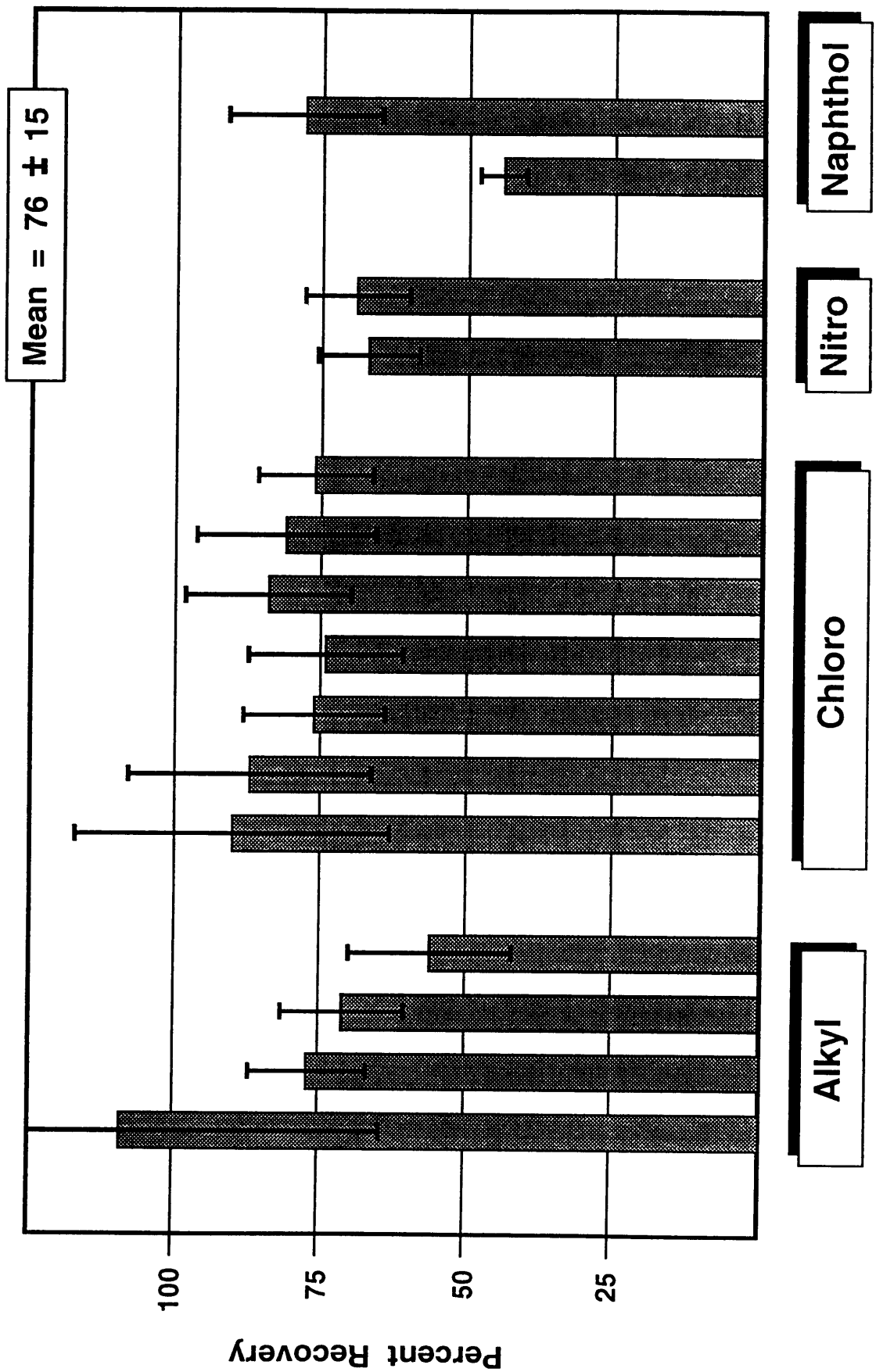

LSE of Phenols from Water with AG MP-1
PFBBr and GC-ECD
GC-ECD Response (mv)
200
150
100
50
13
15
17
19
21
23
25
27
29
Retention Time (min)

COLSE2A


LSE of Acids from Water with AG MP-1
Methylation and GC-ECD
Spike: 0.1 ug
PCP
2,4,5-T
2,4-diCl-benzoic
4-NO2-phenol
2,4-D
DiCl-acetic
4-Cl-benzoic (IS)
400
300
200
100
0
GC-ECD Response (mv)
Blank
100
5
7
9
11
13
15
17
19
21
23
Retention Time (min)

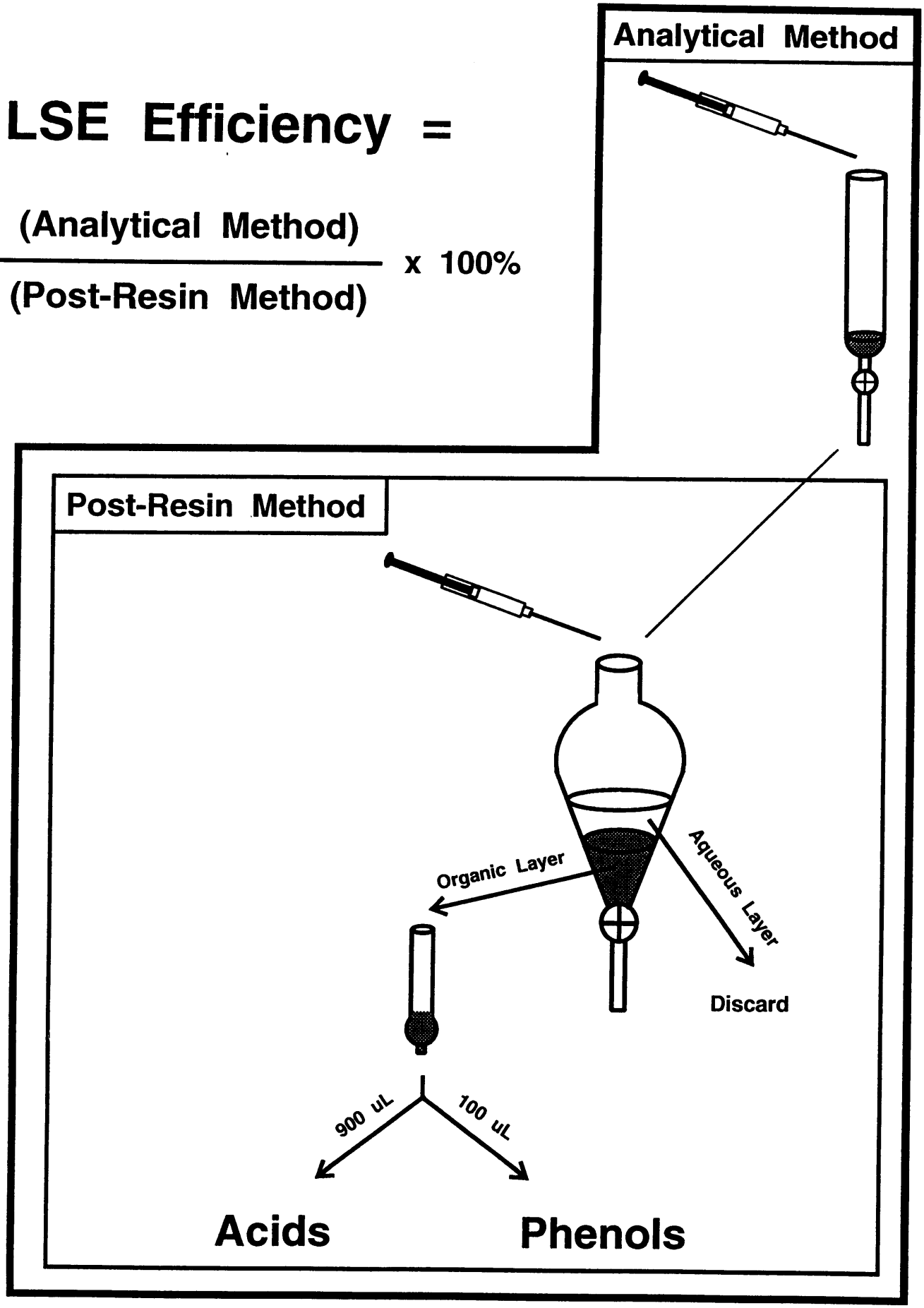
LSE Method Recovery for Phenols

Simulated 0.1 ug/L Drinking Water, PFBBr and GC-ECD



LSE Efficiency =

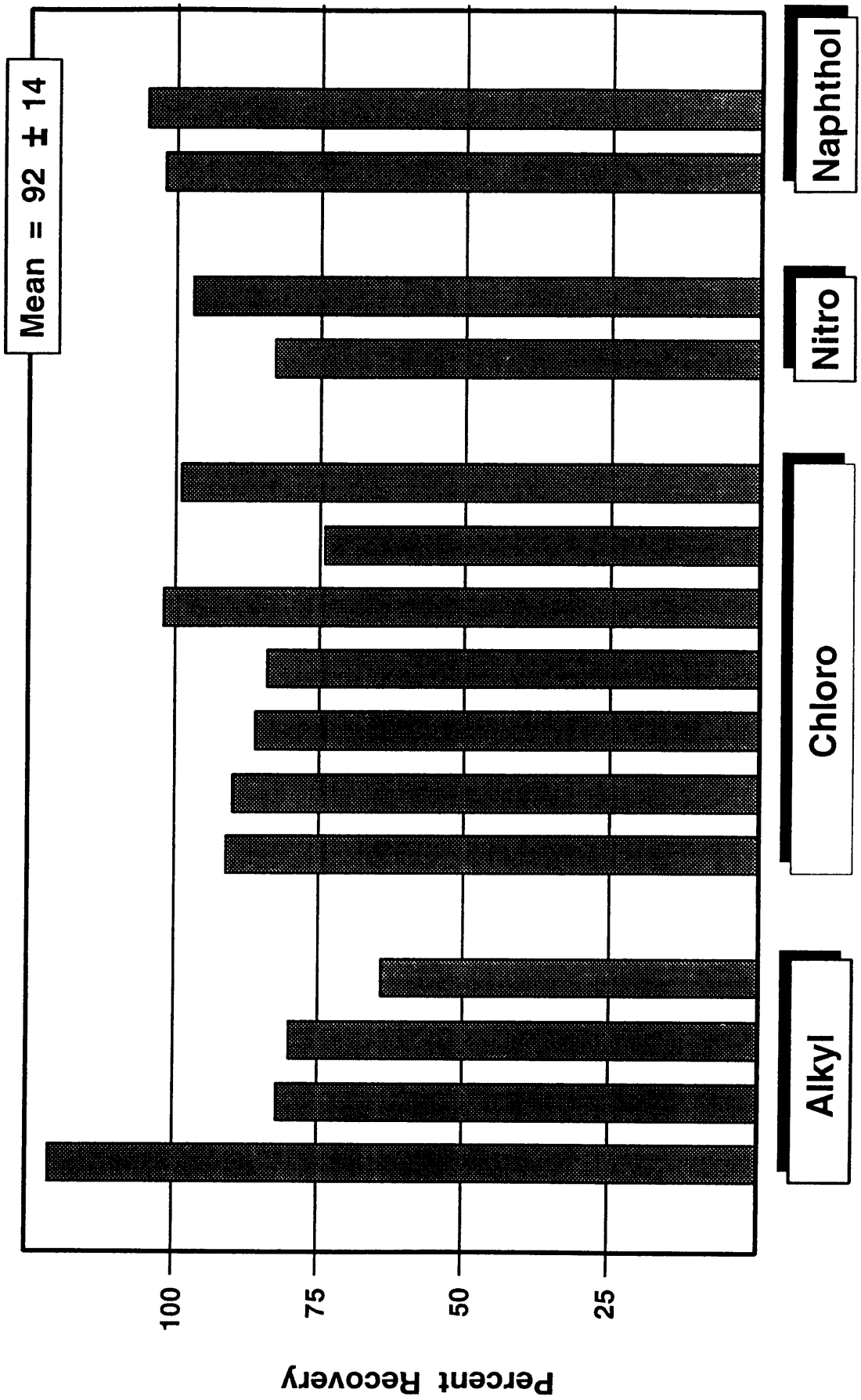
$$\frac{\text{(Analytical Method)}}{\text{(Post-Resin Method)}} \times 100\%$$



lse.cdr

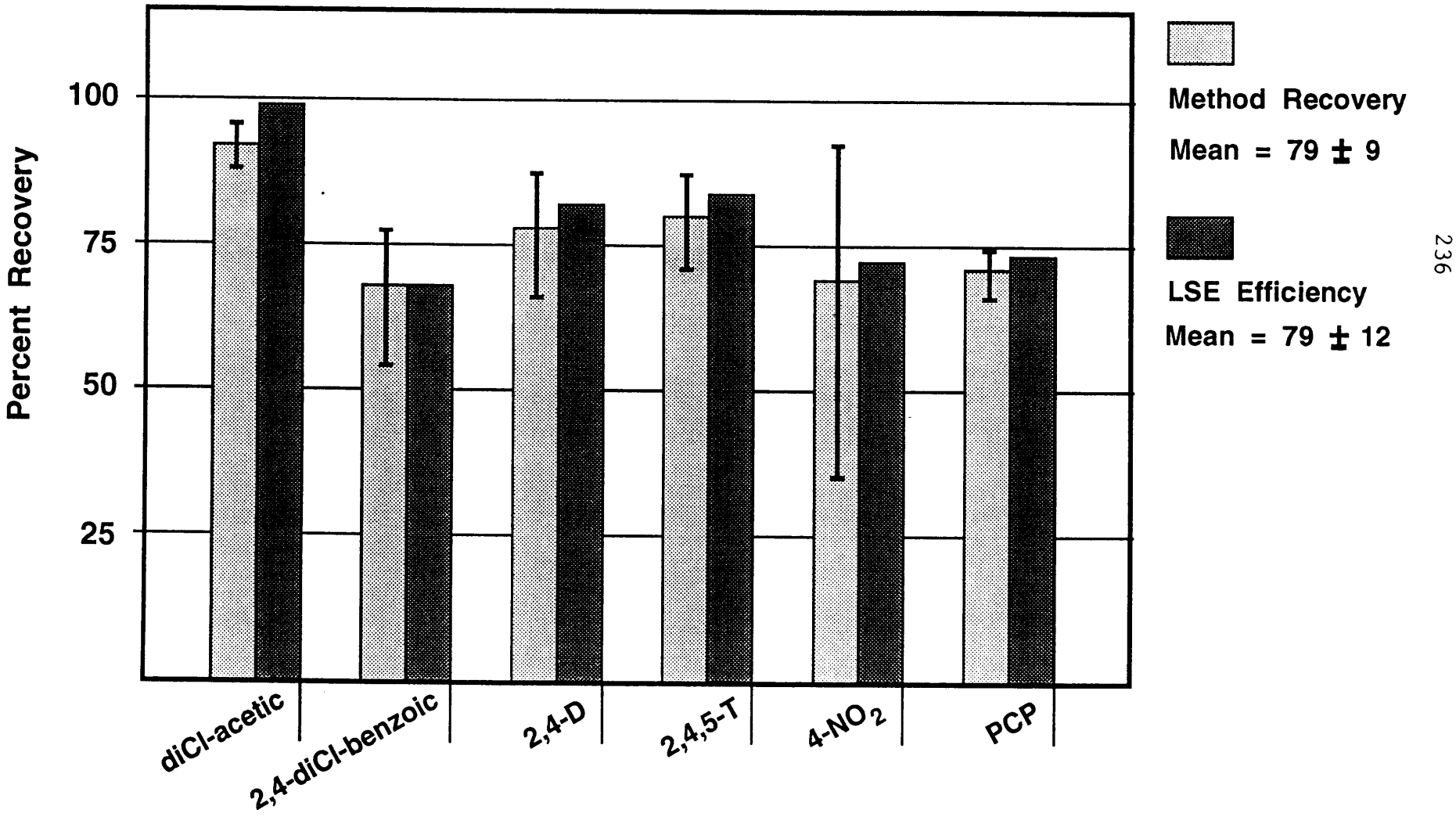
LSE Efficiency of AG MP-1 for Phenols

Simulated 0.1 ug/L Drinking Water, PFBBr and GC-ECD



Method Recovery and LSE Efficiency of AG MP-1 for Acids

Simulated 0.1 ug/L Drinking Water, Methylation and GC-ECD



LSE vs LLE

% Recovery

	LSE	LLE
Acids	68 - 92 (0.1 ug in 0.1 L)	69 - 130 (~0.1 ug in 1 L)
Phenols	44 - 109 (0.1 ug in 0.1 L)	25 - 78 (~8 ug in 1 L)

Conclusions

- Recovery of Phenols and Acids using LSE with Anion Exchange AG MP-1 is equivalent to LLE recovery

- PFBBr allows detection of phenols at drinking water levels (0.01 - 0.1 ug/L)

Acknowledgement

Battelle acknowledges support
for this work from
US EPA Contract No.
68-CO-0003

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MR. TELLIARD: Our next speaker is going to present data on some groundwater analysis, using microextraction procedure, and Cathy Arthur from Waterloo University.

MS. ARTHUR: Good afternoon, ladies and gentlemen. My presentation to you this afternoon is on both the theory and mostly the practice of solid phase microextraction.

The focus of the research in our group is not to reduce solvent in sample preparation; we want to eliminate it entirely. That gives us some advantages as far as solvent recovery and solvent expense. We also would like to see it very fast, and we would like to see it automated.

For solids, we are using supercritical fluid extractions, and for liquids, we feel that solid phase microextraction meets these objectives.

Solid phase microextraction is similar to solid phase extraction in that we are taking the organic analytes out of the aqueous phase and onto a stationary phase, but instead of the usual support, we have a stationary phase coated on a fused silica optical fiber. The fiber has a diameter of about 200 microns. [SLIDE TWO]

The stationary phases that we are using right now are mostly polymethyl siloxine which you can buy directly from the manufacturer. We have also used polyimide, which doesn't work very well, uncoated fibers, carbowax, and liquid crystal polyacrybite.

At present, we are also working with Supelco, because they have licensed this technology, to put GC stationary phases on the outside of the fiber.

There is one other major difference between microextraction and SPE, and that is that we do not exhaustively extract the analytes. Instead, we form an equilibrium between the aqueous phase and the stationary phase.

200 micron fibers are a little bit difficult to handle, so we have developed what we call a solid phase microextraction device [SLIDE THREE], and what we have done is we have inserted this fiber, 200 microns in outer diameter, inside 30 gauge stainless steel. 30 gauge stainless steel runs up through the needle and the plunger of a Hamilton 7000 series syringe, and we put a blob of epoxy at the end of the steel so that we can move the fiber up and down through the needle at any time we wish.

When we do this technique, we draw the fiber into the needle, pierce the septum of your sample vial, and drop the fiber into the sample. We leave it there until it equilibrates. That takes about 5 minutes.

We then draw it back up into the needle, transfer it over to our GC, put it in the injector, and thermally desorb it. You can use a split/splitless, a SPI, or an on-column injector. Those are the ones we have tried. If you have got others, please try it, and we will be interested to hear what happens.

One other nice aspect of SPME relative to, for example, purge and trap...and I will mostly be talking about volatiles today...is that you can use any column you like. You are not stuck to larger bore columns because of the high flow rates that come with purge and trap devices.

I have mentioned several times that we form an equilibrium in a large volume, and by that I mean above 25 ml. The amount that is absorbed on the fiber is related to K, the distribution constant, the volume of the stationary phase V_s, and the aqueous concentration C_{aq}. It is linear over four orders of magnitude.

This is what we call an equilibration time profile [SLIDE FOUR] or an absorption time profile. This was for the compounds benzene, toluene, ethyl benzene, and the xylene isomers, and virtually everything that I talk about today will refer to the BTEX compounds.

There are two things I would like you to note from this. First of all, there is a lot more xylene absorbed than there is of the benzene. The topmost curve is double, because meta and para co-elute on our column. More xylene is absorbed than benzene because of the difference in the distribution constant of those compounds from each other.

The second point I would like to make is that the benzene has stabilized in about 1 minute, and the xylenes took about 5 minutes. This is not, in fact, what mathematical theory predicts, and we have developed the mathematics to describe the process. They predict 15 seconds for a perfectly stirred solution, and 2 hours for an unstirred solution, the difference being the time it takes to diffuse through water.

We have this difference from the ideal 15 seconds, because we have yet to figure out how to perfectly stir a solution. We do not have mixing that would come from

pouring through a cartridge or a disk, so we have to stir our samples.

Instead, what we feel happens is we have a stationary layer of water next to the fiber, so our mixing is effective to a large degree, but the analytes come up, hit that stationary layer, and have to diffuse through. It takes longer for the xylene than it does for the benzene, because we have to flux more of the xylenes through that stationary layer than we do the benzene.

Well, I hope I have teased your interest enough to find out how sensitive it is, but before we could do that, we had to figure out how precise it was, because, initially, we were having 20, 25 percent relative standard deviations, and that is not acceptable.

There are three factors that are particularly important in this. The first is the desorption temperature and time. [SLIDE FIVE]

The xylenes in this mix are the highest boilers. They boil at 145 or so. We can desorb at 150, so we don't have to worry as much about thermal degradation of either our fiber or of our analytes. Because of the very simple geometry of that fiber, we don't have to go to very high temperatures.

It takes 30 to 60 seconds at 150 degrees to desorb our materials back out of the fiber. This is not a problem as long as you cryofocus your oven, because 30 seconds, 60 seconds is long relative to your peak width. So, we cryofocus, in this case, at minus 5. You can go up to zero degrees centigrade, but I like to hedge my bets, so we use minus 5.

The last factor that we have found was very critical was the time between exposing your sample in the vial and taking it over to your GC. If you go to your very worst case which is an uncoated fiber, your benzene has gone 30 seconds after you have taken it out of the sample, even though it is sheathed inside the needle.

If you have 56 microns of methyl silicone sitting on your needle, your benzene is good for 2 minutes. Your xylenes are good for 5 minutes. Go to a thicker film, it is stable for even longer.

Two minutes is more than enough time to go from your sample to your GC, but you have to be aware of the fact that the problem may exist.

With the flame ionization detector, we can see limits of detection of 0.3 to 1 part per billion on a weight by volume basis [SLIDE SIX]. This is with a 56 micron coating.

The linear range is almost four orders of magnitude, and we have a relative standard deviation that averages around 5 percent, and this is over six grad students. So, I am reasonably confident of that number.

If you go to a more sensitive detector, such as an ion trap mass spectrometer, you can go down to 50 parts per trillion of benzene and still see it with a signal to noise ratio of about 10 to 1 [SLIDE 7]. Here again, your signal to noise ratio is even higher for your toluene and your xylene because of the difference in the K values.

When you compare for these five compounds to the method detection limits for EPA 524.2, we are well within those method detection limits [SLIDE 8]. At the 50 part per trillion level, our relative standard deviation is a little bit higher at about 7 percent, but it is still, I think, more than good enough for most people.

The other thing I would like you to notice off this Table is I have compared the log of the distribution constant with the log K_{ow}. That is the octanol/water partition coefficient, which is quite widely tabulated for a whole range of compounds, and they are very similar.

So, if you wish to develop a method and you want to know is it going to be sensitive enough, you can use log K_{ow} as an initial estimate of what your distribution constants will be if you are using the methyl silicone film. If you go to different films, of course, your K values are going to be different, but this is not a bad initial guideline.

Well, the technique seems to be precise, and it has low limits of detection in very nice clean reagent grade water. The question then comes what happens in the real world when you have things like organic contaminants, salt, varying temperatures, and all that sort of thing.

So, since we had good precision, we went on to look at matrix effects. These are things that will change the distribution constant.

Above 1 percent methanol, we see a decrease in the amount absorbed [SLIDE 9]. Below 1 percent, there is no discernable effect on the amount absorbed by the fiber.

This can, in fact, be predicted by calculating out what the change in the distribution constant would be using solvent selectivity parameters according to those equations in the reference if you are interested. They would predict a 6 percent change in K,

which we cannot see with the 5 percent RSD. So, you are good up to about 1 percent methanol.

Similarly with salt [SLIDE 10]. If you go up to 1 percent salt, we are not seeing any influence on the amount that is absorbed. Above 1 percent, you see a big increase in the amount absorbed, because your well known salting out effect is kicking in.

In fact, for these compounds, if you go up to a saturated salt solution, you will increase the amount absorbed by a factor of ten. You also, however, increase the analysis time by a factor of two to five, depending on the compound.

We also looked at the effect of temperature [SLIDE 11]. The top graph is a 5 minute equilibration time, and we sampled our spikes at anywhere from 0 degrees up to 55 degrees, and you see an apparent influence on the amount absorbed.

What you are seeing is not a change in the distribution constant but a change in the rate of diffusion through water. So, if you go to a 30 minute equilibration time, which eliminates the effect of diffusion, you do not have any noticeable effect on temperature except maybe a slight decrease at higher temperatures which suggests to us that we have an exothermic reaction and it is shoving the equilibrium back in favor of the aqueous phase.

We have also looked at pH, and between pH 4 and 10, there is no influence on the amount absorbed. Below pH 4, you are starting to dissolve the methyl silicone film.

That is all well and good. We also like automated methods. We are not in the business of doing routine analysis, but we know most people are.

So, we adapted a Varian 8100 autosampler to work with the fiber method. What we have done is taken out the Varian autosampler syringe and mounted our syringe about 3 cm higher in the carriage so that the needle heights are identical. Otherwise, you are going to smash out your inserts.

We also extended the plunger by about 1.5 cm so that it will fit nicely into their device.

The other major change that we made is we had to add a stirrer, because our samples must be stirred. And you see a little black box down at the bottom with a piece of white tape on it. That is a microstirres that you can buy from Cole-Parmer. It is about 2 by 2 inches and .5 inches thick, and you can mount it where the wash cup normally is, and the

carriage will, in fact, move and up and down in front of it.

The whole thing is controlled through Lab View software on a McIntosh, and it allows us to adjust the plunger movement so that the fiber is always contained in the needle whenever it needs to pierce a septum, and it also controls the sampling time in the vial so you can have whatever sampling time you choose.

Quite often, incidentally, even if we only need 5 minutes to equilibrate, if we have a 20 minute analysis run on our GC, we just let the fiber sit in the sample for 20 minutes, because sampling time makes no difference once you have reached equilibrium.

One disadvantage to using an autosampler is that you only have a 2 ml sample vial, and this fiber actually sucks up enough material that you will significantly exhaust the vial. This, again, depends on the distribution constant of your compound.

So, for the xylenes, you are seeing a significant drop after two or three injections, and I am using significant to be more than 5 percent, whereas with the benzene, you can do 100 injections, and you are not going to exhaust the sample [SLIDE 12].

Oh, one other thing on that slide. We have calculated out what the actual amount is. That is shown up in the middle of that slide. So, if you are using small volumes, you can calculate out how much you are going to be extracting.

If you play around with that formula mathematically, you can work it so you can calculate the number of injections you can do for a specific volume for a specific K value, so you know how far you can go before you are going to exhaust your sample. [SLIDE 13]

On the right-hand column, you can see that for compounds with a K of about 1000, which is typical of xylene, you can only do less than one injection before you are pulling out 5 percent. If you go to benzene which has a K of about 126, then you can do 2 injections per autosampler vial.

The converse side of this coin is if you are going up to compounds with a K of 10,000 or more which would be typical of PCBs and PAHs and you want to extract that...if you want to exhaust that vial, you can hold your oven at a cryotemperature, sample your vial, desorb it in the hot injector, cryofocus and trap it in your column, and go back and do a second injection, and you have got all your stuff out of your vial. So, you have done an

exhaustive extraction.

So much for theory. What does it do in the real world? Well, I don't have any "milkshakes" to analyze, but what we could do is we went out in the middle of January to a nice culvert after a snowfall and got parking lot runoff.

As you can see, [SLIDE 14] we picked up the BTEX isomers and trimethylbenzene and some naphthalene which is all well and good. We expected that. What we were actually looking for was carry-over, because it is very easy to have a nice clean sample and not see carry-over, but what happens if you get to a real sample?

And the lower RICs show you that we did not get carry-over on this particular sample. So, for at least this sample and, presumably, for a lot of surface waters, carry-over is not going to be a problem.

We went to a somewhat nastier sample [SLIDE 15]. This is a coal gasification wastewater sample that someone sent us from New Jersey. I have no idea exactly where.

As you can see, we got everywhere from benzene all the way up to acenaphthalene which just happens to be the length of our chromatographic run.

This technique, while I have focused so far on volatiles, works just as well for the semi-volatiles, so that for all those analyses where you are doing liquid-liquid extractions, you can replace it with the fiber technology and eliminate your solvents.

We didn't tackle semi-volatile, before this, because BTEX is a nice, fairly simple range of compounds to study before we get into the 60-odd that the EPA is interested in.

In summary [SLIDE 16], solid phase microextraction for BTEX compounds is a whole lot less expensive than your solvents and your purge and trap device, and it is very portable. One thing I didn't mention earlier is that because we are independent of sample volume above about 25 ml, if you want to go field sampling, you do not have to measure the volume of water. If it is a stream that is flowing fast, you don't even have to stir it, because you depend on concentration, not total amount.

We have completely eliminated solvents from the sample preparation. We have completely automated it so you do not have to handle it once it has been collected, assuming it is collected in an autosampler vial or manual vial.

We have a very short sampling time with excellent limit of detection with either an FID or, if you want to do drinking water standards, you can go and use an ion trap mass spec.

It is linear over four orders of magnitude. Incidentally, our mass spec is also linear over four orders of magnitude.

We have shown it is independent of salt and organic solvents if those are both below 1 percent. Also pH and temperature.

Lastly, I would like to acknowledge funding from all of these companies which have contributed to our research program [SLIDE 17].

Any questions?

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3. Arthur, C.L.; Killam, L.M.; Motlagh, S.; Potter, D; Pawliszyn, J.; J. Env. Sci. Technol. 1992, 26, 979.

4. Louch, D.; Motlagh S.; Pawliszyn, J.; Anal. Chem. 1992, 64, 1187.

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QUESTION AND ANSWER SESSION

MR. TELLIARD: Questions?

MR. SOLOMON: You mentioned you used different injectors in the analyses that you did. Could you go into a little bit of detail on the differences you saw between the split/splitless, the SPI, and on column?

MS. ARTHUR: Yes. Most of the stuff has been done on the SPI, because our GCs get muddled around between both fiber and regular syringe injections, and we like the SPI.

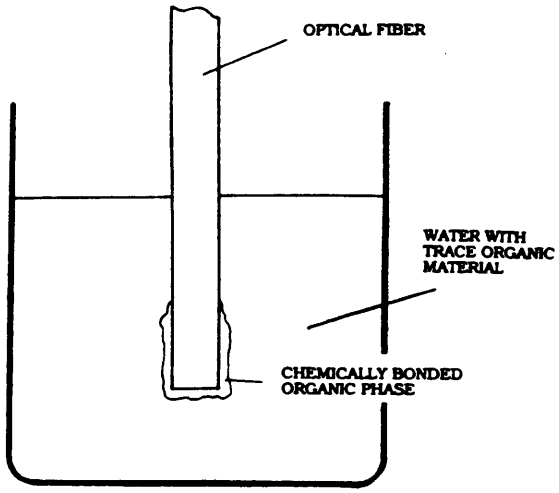
The difference in them is largely that the split/splitless is nicer because the gauge on these needles is about 24 gauge, and you tend to core septa. So, with a split/splitless, you are not plugging the restriction that occurs on a SPI injector, and that is about the only difference we have seen.

MR. TELLIARD: Thank you, Cathy.

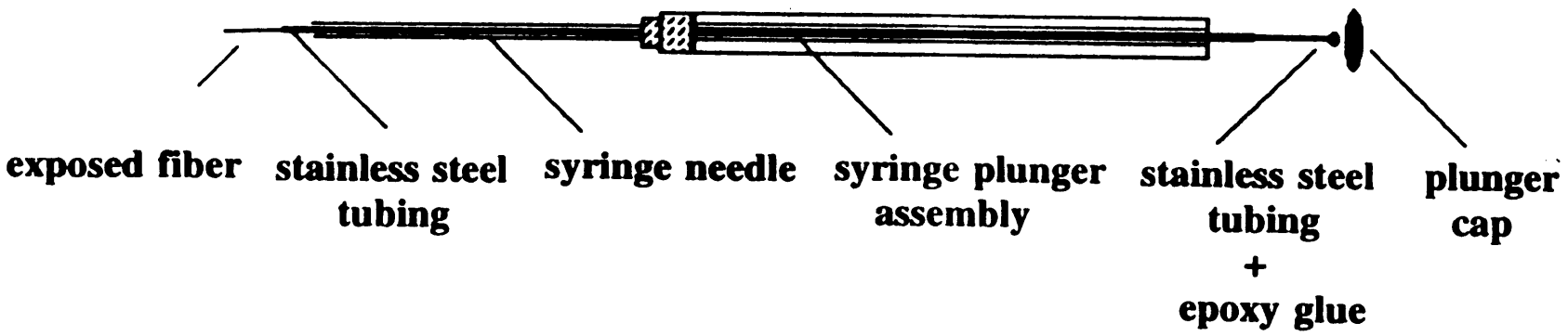
Practical and Theoretical Aspects of Solid Phase Microextraction for the Direct Analysis of Groundwater

Catherine L. Arthur, Lisa Killam, Karen D. Buchholz, David Potter, Janusz Pawliszyn, The Guelph-Waterloo Centre for Graduate Work in Chemistry and the Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

John R. Berg, Varian Associates, 2700 Mitchell Dr., Walnut Creek, California, U.S.A. 94598

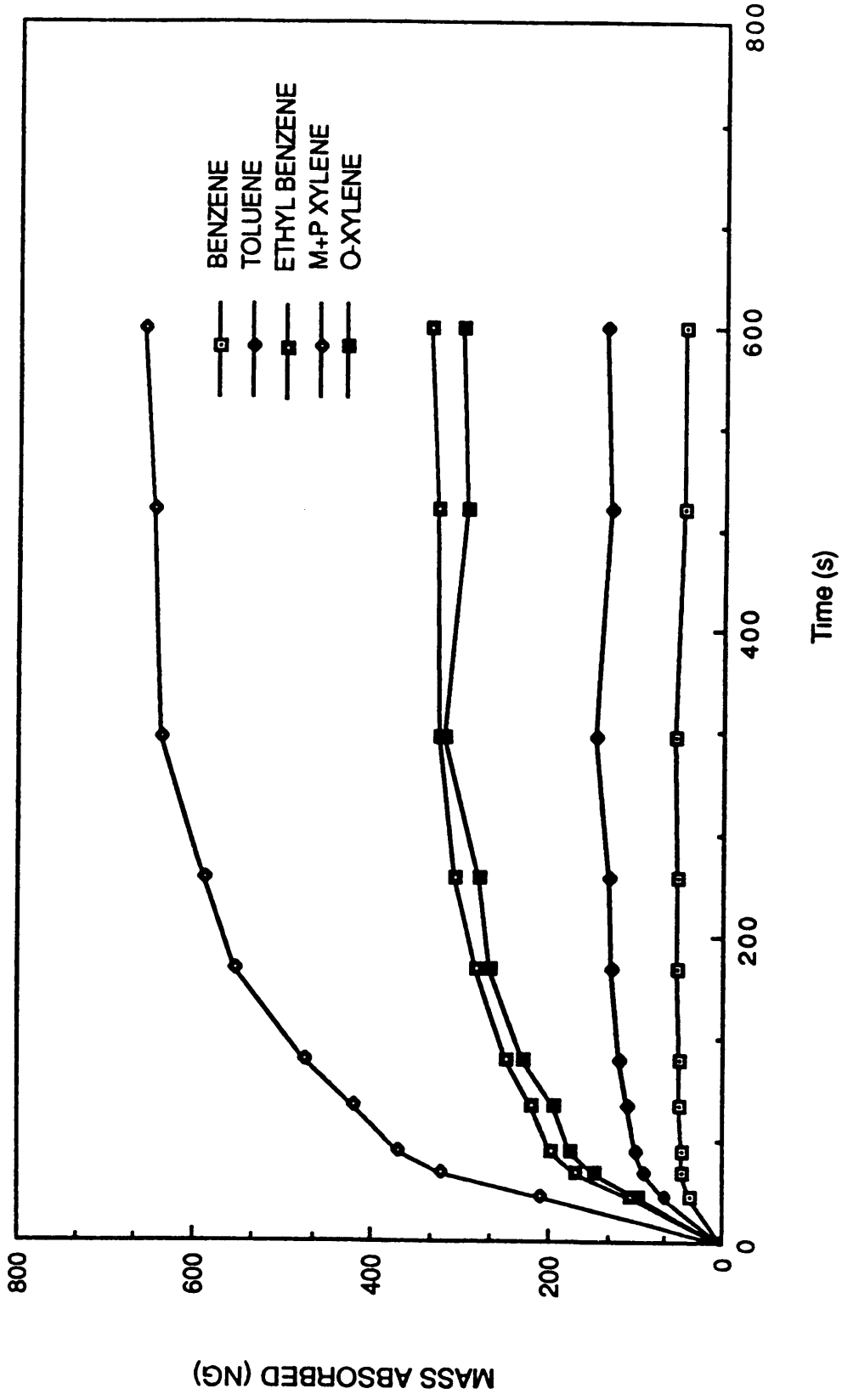

OPTICAL FIBER
WATER WITH
TRACE ORGANIC
MATERIAL
CHEMICALLY BONDED
ORGANIC PHASE

A SOLID PHASE MICROEXTRACTION DEVICE



BASIC EQUATION FOR SOLID PHASE MICROEXTRACTION

$$n_s = KV_sC_{aq}$$


BENZENE
TOLUENE
ETHYL BENZENE
M+P XYLENE
O-XYLENE
MASS ABSORBED (NG)
Time (s)
0
200
400
600
800

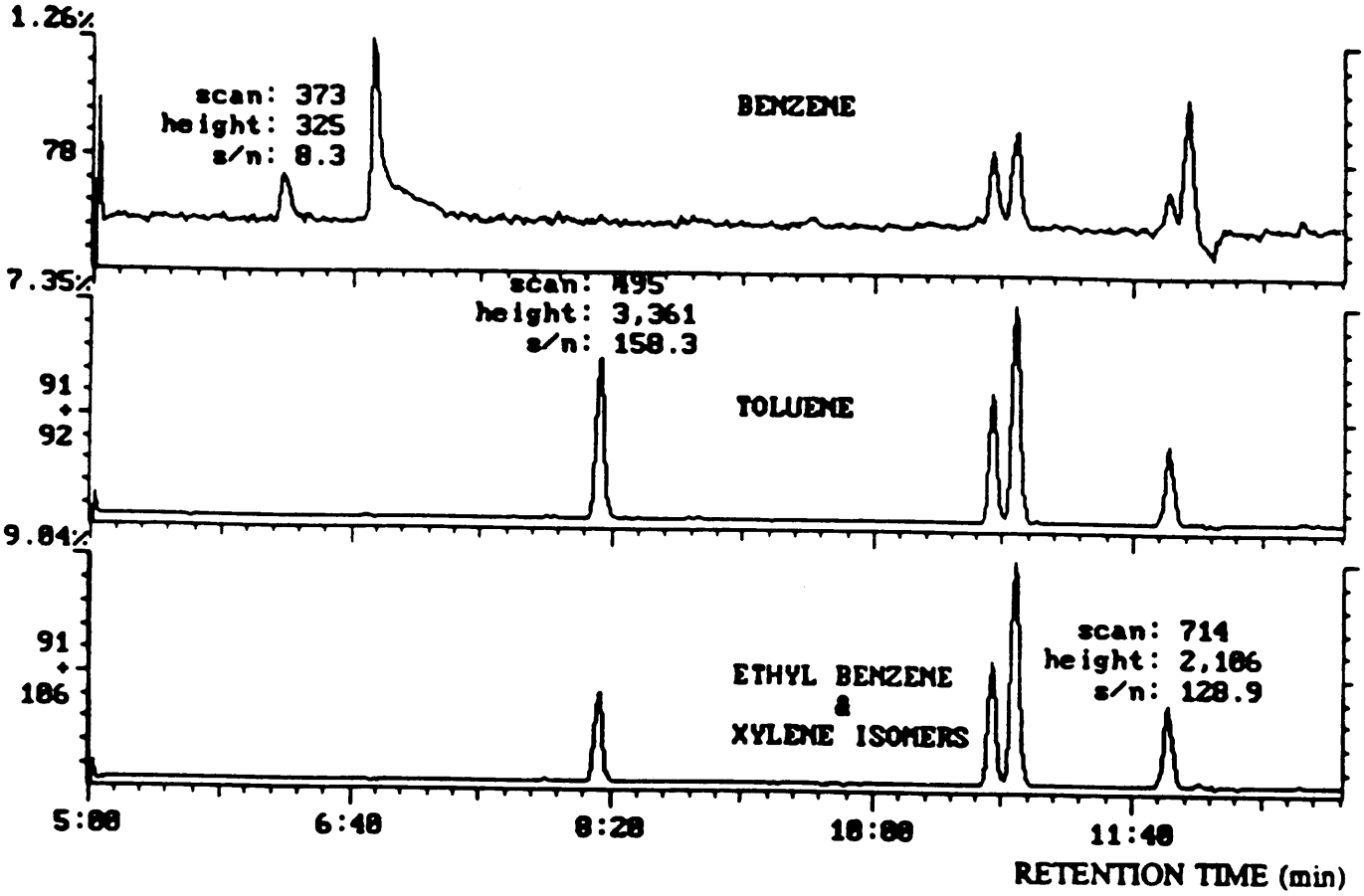
Factors Affecting Precision

- desorption temperature and time
- cryofocus temperature
- time between absorption and desorption

Optimized Precision with Spiked Reagent Water and Flame Ionization Detector

Analyte	LOD (µg/L)	Linear Range (µg/L)	RSD (%)
toluene	1	1-8000	6
ethyl benzene	0.5	1-8000	3
m,p xylene	0.3	1-8000	6
o-xylene	0.3	1-8000	6

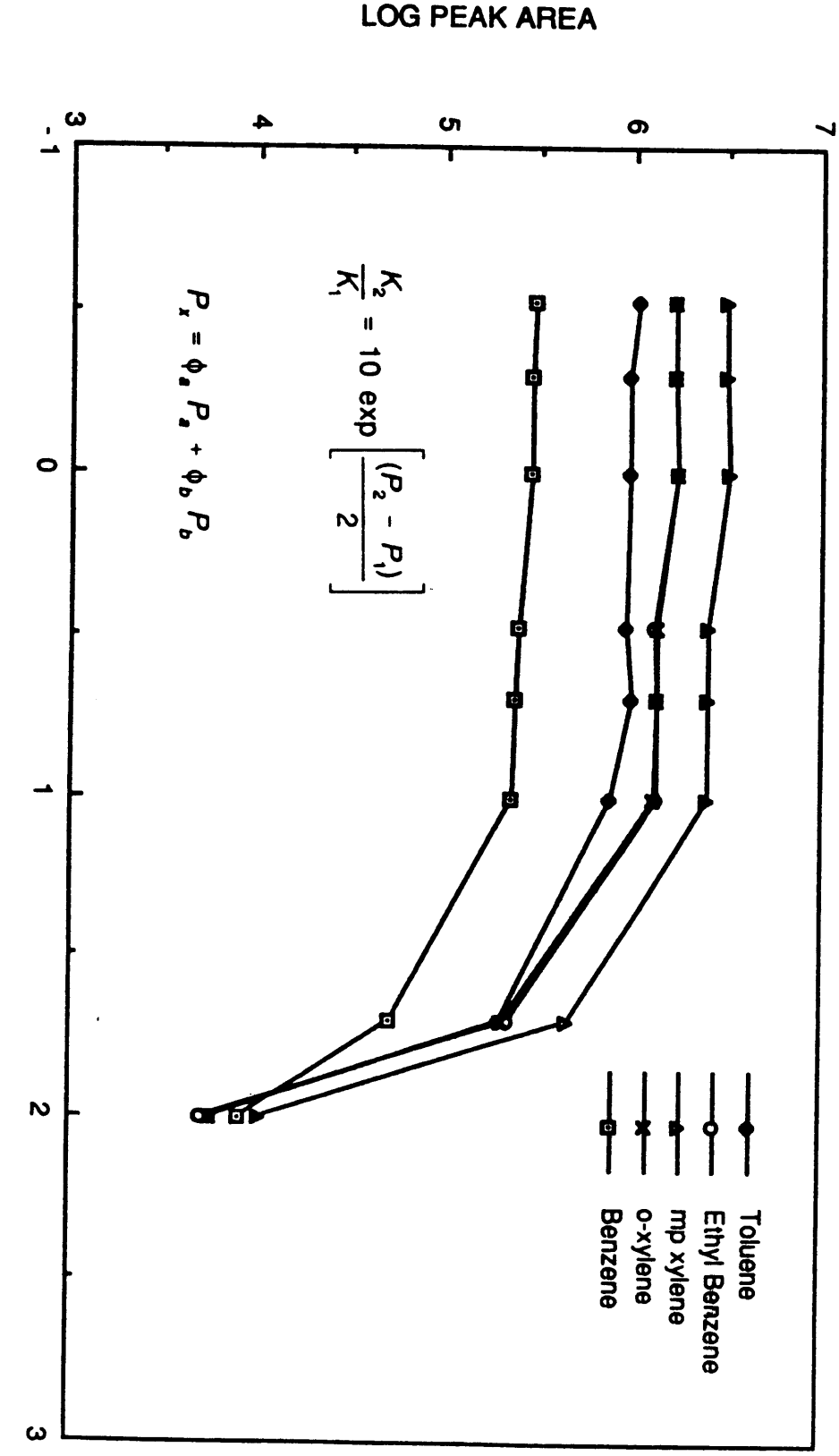
50 PPT BTEX IN WATER



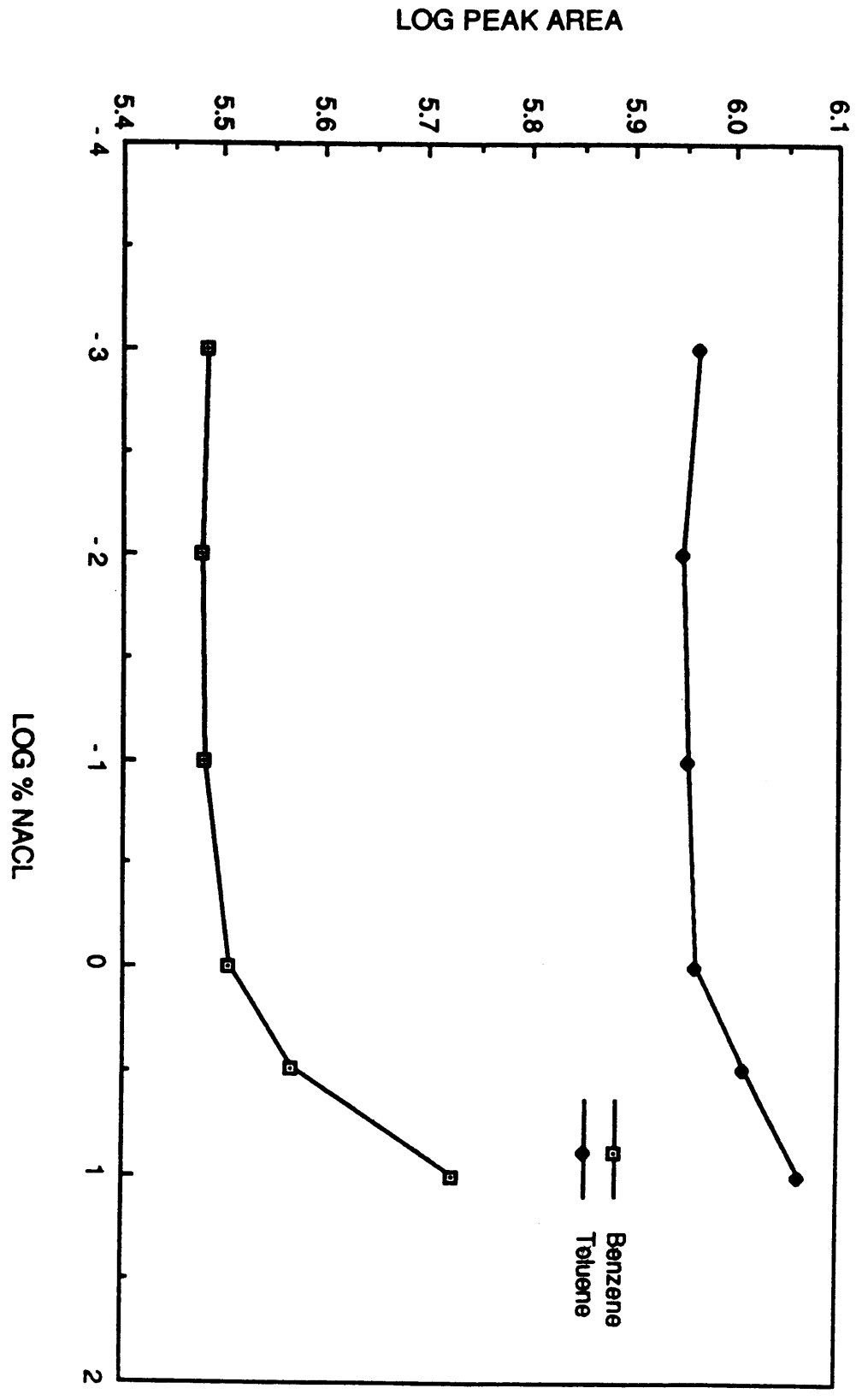
Distribution constants, limits of detection, limits of quantitation, precision of SPME, K_{ow}'s, and method detection limits as required by MISA and EPA regulations.

	$\log_{10}K^1$	$\log_{10}K_{ow}$	LOD (ppt)	LOQ (ppt)	Precision (50 ppt)	Precision (15 ppb)	MDL (MISA) ppt	MDL (EPA) ppt
benzene	2.30	2.13	15	50	7.3%	5.3%	500	30
toluene	2.88	2.69	5	15	6.7	3.2	500	80
ethyl benzene	3.33	2.84	2	7	7.2	3.6	600	60
m,p - xylene	3.31	3.20 meta 3.15 para	1	4	6.5	6.5	1100	90
o - xylene	3.26	2.77	1.5	5	5.5	2.7	500	60

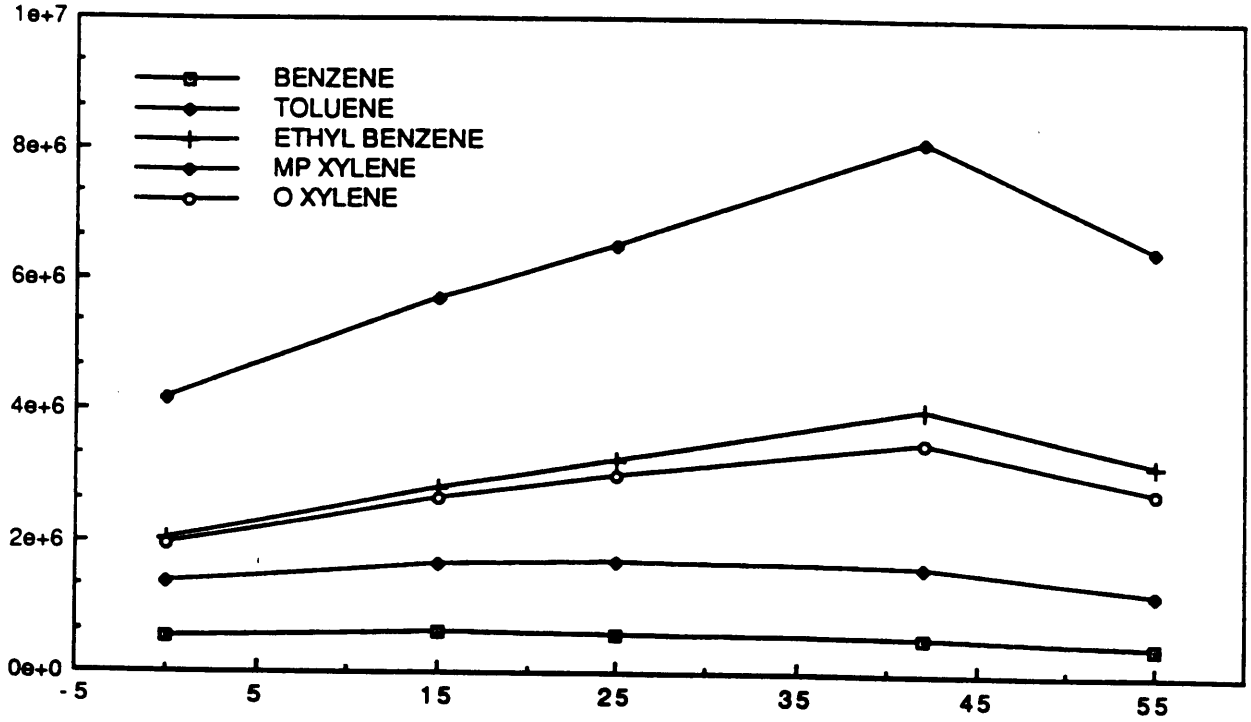
1. Experimentally Determined



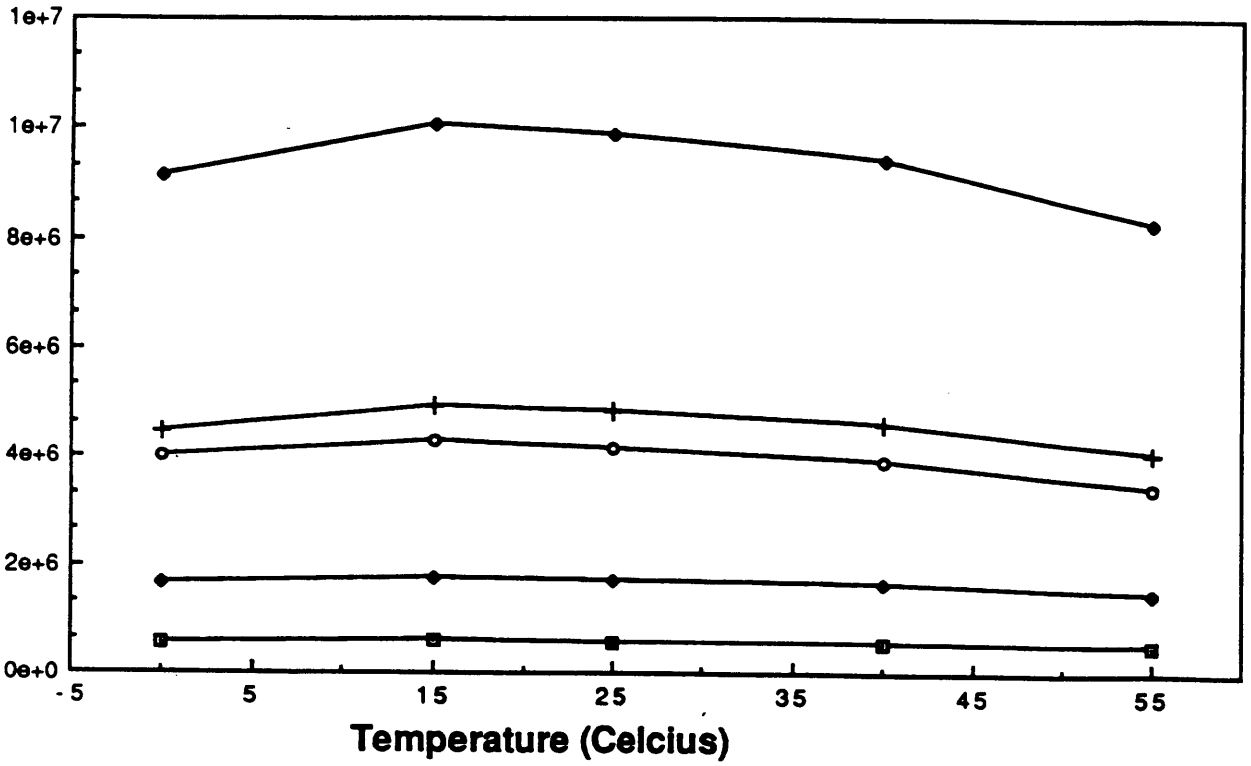
Snyder, L.R.; *J. Chrom. Sci.* **1978** *16*, 223.

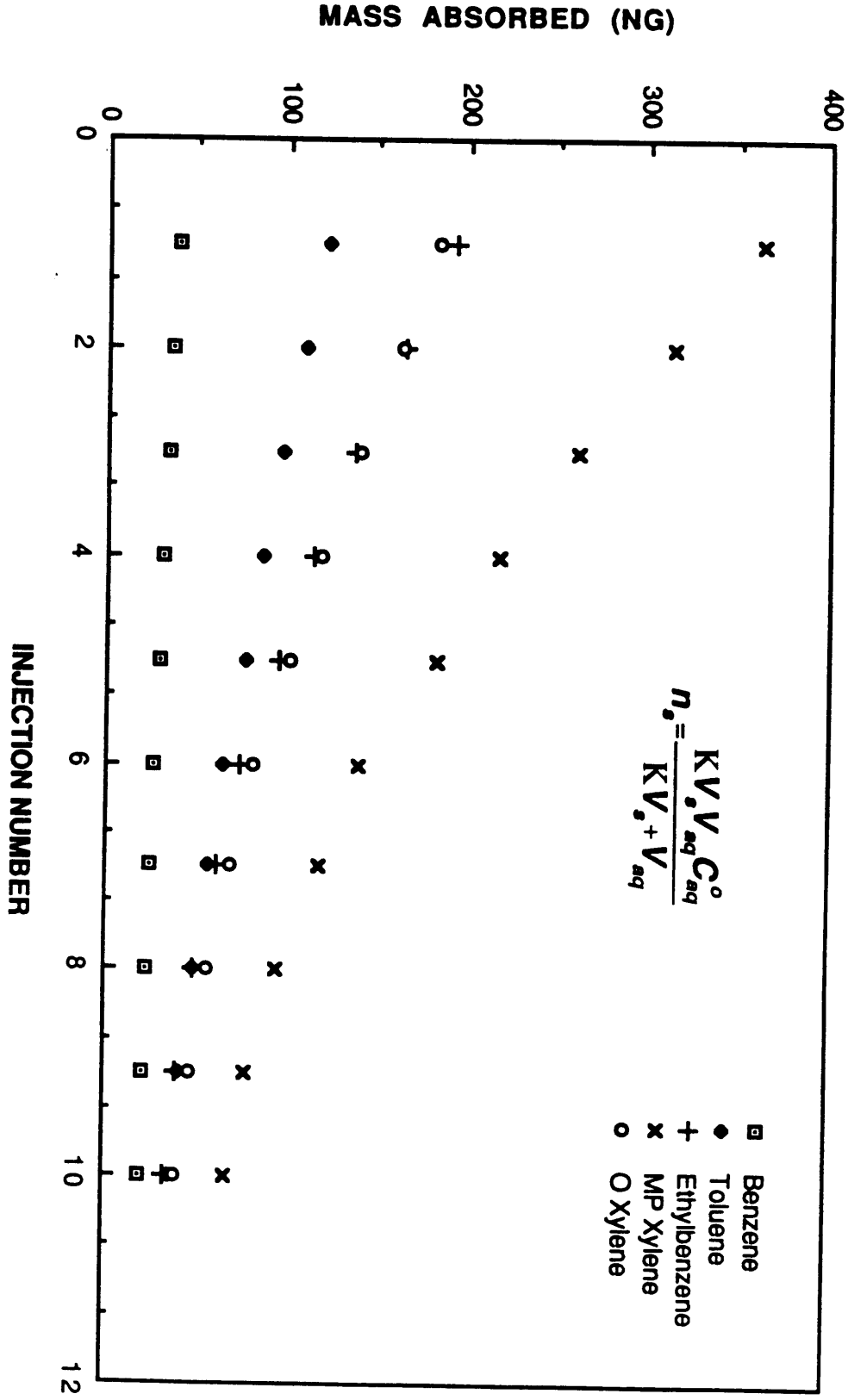

LOG PEAK AREA
5.4
5.5
5.6
5.7
5.8
5.9
6.0
6.1
-4
-3
-2
-1
0
1
2
LOG % NACL
Benzene
Toluene

5 MINUTE EQUILIBRATION TIME



30 MINUTE EQUILIBRATION TIME



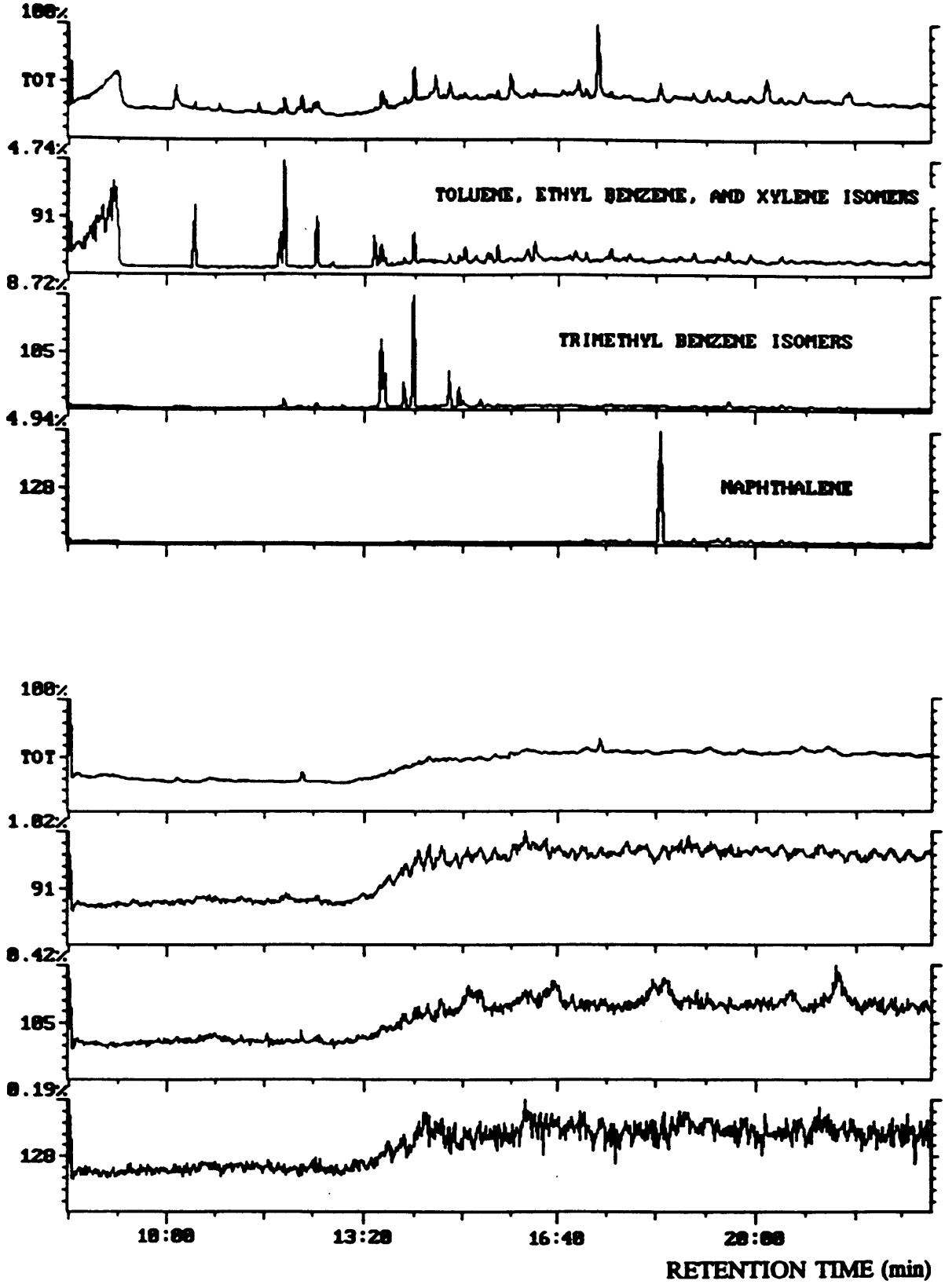

MASS ABSORBED (NG)
0
100
200
300
400
INJECTION NUMBER
0
2
4
6
8
10
12
$n_s = \frac{KV_s V_{aq} C^o_{aq}}{KV_s + V_{aq}}$
Benzene
Toluene
Ethylbenzene
MP Xylene
O Xylene

$$F = \frac{C_2^j}{C_2^o} \qquad j = \frac{\log(1/F)}{\log[K(V_1/V_2)+1]}$$

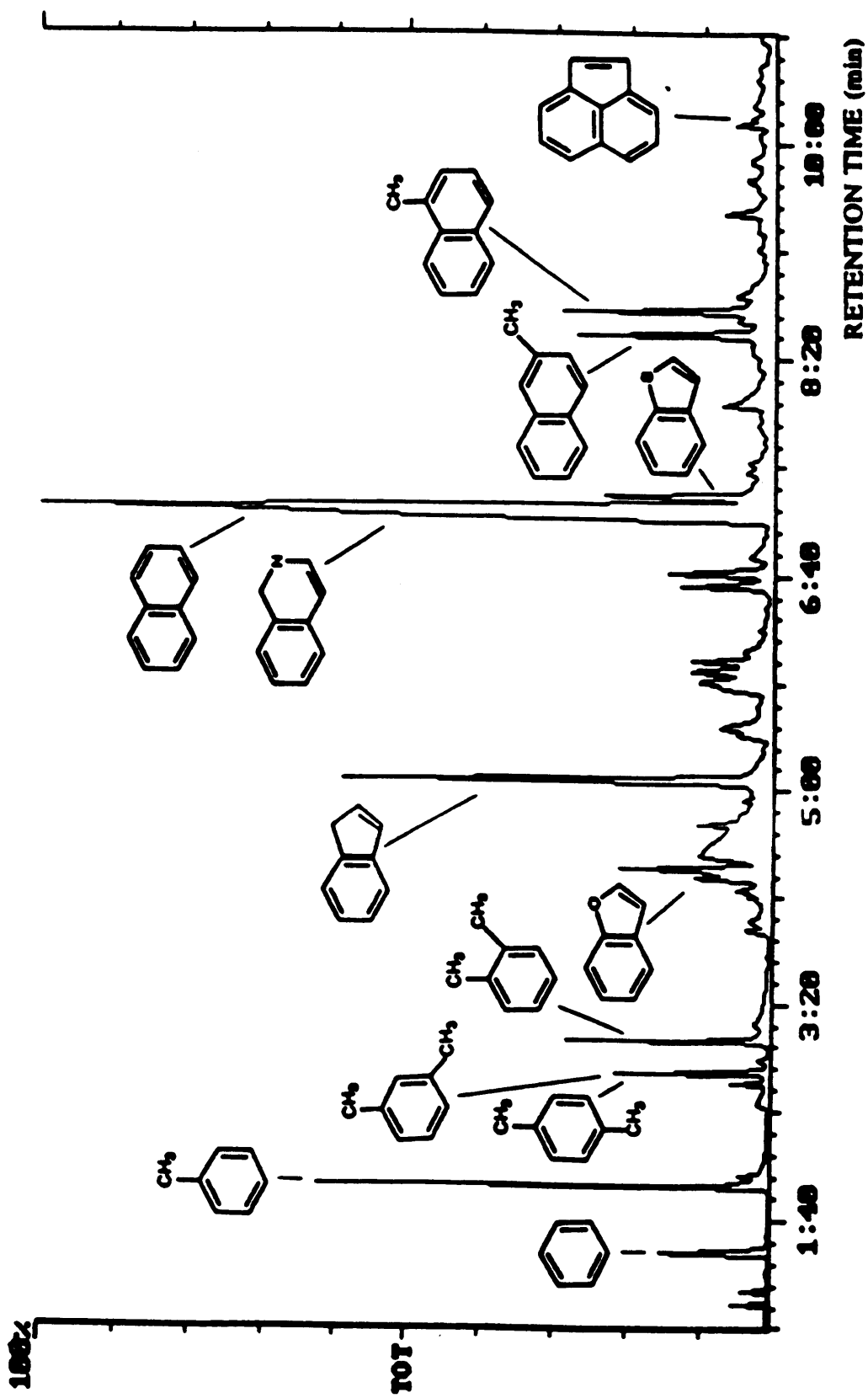
Distribution Constant	# injections to remove 95%	# injections to remove 5%
10	1016	22
100	103	2
1000	11	<1
10000	2	<1

for a 1.7 mL autosampler vial.

ORGANICS EXTRACTED FROM PARKING LOT RUNOFF WATER



ORGANICS EXTRACTED FROM A COAL GASIFICATION WASTEWATER SAMPLE



Solid Phase Microextraction of BTEX Components from Water

- inexpensive and portable
- solvents completely eliminated
- 2-5 minute sampling time
- LOD with FID 0.3 - 1 μg/L
- linear range 1-8000 μg/L
- independent of salt, organic solvent if < 1%
- independent of pH 4 - 10
- independent of temperature 0-40 °C
- fully automated sample preparation
- meets EPA 524.2 and MISA requirements with ion trap mass spectrometer detector

Acknowledgements

Natural Sciences and Engineering Council of Canada

Varian Canada

Varian Associates

Supelco Canada

Imperial Oil Canada

University Research Incentive Fund

Apple Canada

MR. TELLIARD: That concludes our ramblings on solid phase extraction. A number of questions came up at lunchtime on okay, or when can we use it and when will EPA approve it.

I think we are all interested and excited about getting this procedure accepted for wastewater. Drinking water, I have had the insight to move ahead and get it into their methods. We would like to come back here next year and be able to use solid phase extraction. I can't promise that, but we are going to try moving on that path.

George Stanko pointed out earlier that extraction in wastewater matrices, could present problems, and we certainly have to build a data base before we give it a blessing, but the data you have seen today looks very, very promising, and we think it might be the way to go.

It relieves us of our solvent problem to a lesser extent. It also gives us some more flexibility as far as field application is concerned, and I was very impressed with what was presented in the storage studies.

So, we are hoping that, by next year, we will be able to see this in more of our methods, and I am sure drinking water will continue on this path.

The Office of Solid waste have already mentioned that they are incorporating solid phase extraction.

So, with that, I would like to introduce our next speaker. Jeanne Hankins is presently Secretary of the methods consolidation group of the Environmental Monitoring Methods Council. For those of you who don't know what all that is, the Environmental Monitoring Methods Council is an agency-wide council which is dealing with issues of methods consolidation, laboratory certification, quality assurance, and quality control issues.

Jeanne, as Secretary, is going to be talking a little bit about what is going on with the EMMC and, more specifically, what is going on with lab certification.

UPDATE: COMMITTEE ON NATIONAL ACCREDITATION OF ENVIRONMENTAL LABORATORIES

Jeanne Hankins
Executive Director
Committee on National Accreditation of Environmental Laboratories

The Environmental Protection Agency (EPA) has initiated an effort to investigate the concept of a national program for accreditation of environmental laboratories. This effort started with the Environmental Monitoring Management Council (EMMC) and its *Ad Hoc* Panels. The Federal Advisory Committee on National Accreditation of Environmental Laboratories (CNAEL), established on the recommendation of the EMMC, has expanded the number and range of interests of the involved parties. The history, accomplishments and plans for the future of these two groups are summarized in the following discussion.

The seed for this effort was planted early in 1990 by EPA's Science Advisory Board (SAB). The SAB observed that the development and direction of EPA programs have been established in response to concerns of the public and Congress. As a result, there is not necessarily coordination between programs and therefore, implementation of Congressional statutes is not always efficiently accomplished. This lack of uniformity is reflected in the monitoring requirements. Under Deputy Administrator Hank Habicht, a committee of top managers was assembled into the Environmental Monitoring Management Council to look at comprehensive multi-media solutions to environmental monitoring. (Environmental monitoring has an all encompassing definition in this instance and covers one-time sampling and analysis, as well as routine monitoring of a relatively stable situation.) The EMMC recommended that coordinated Agency-wide policies on environmental monitoring issues be established. The goal is to enable the Agency to operate more efficiently and effectively. In this way it will be possible to improve the monitoring data which is a linchpin in the decisions which are made in the Agency everyday.

EMMC

The EMMC structure (see diagram) consists of a Policy Council, a Steering Committee, and several *Ad Hoc* Panels. The Policy Council is composed primarily of deputy administrators of the EPA program and regional offices, and is chaired by the Assistant Administrator of Research and Development Eric Bretthauer and the Regional Administrator of Region III Ted Erickson. Ramona Trovato serves as the Executive Secretary. The Steering Committee members are mainly division directors from the program and regional offices and represent the position on the technical and scientific policies of their offices. The *Ad Hoc* Panels were established to address specific issues at the implementation level. The Panels provide background information, and are a source of technical expertise, and inter-agency input.

The EMMC is charged with examining several issues. Several specific issues were identified for investigation and were initiated in 1990. Five separate *Ad Hoc* Panels were established to investigate 1) the development of integrated methods, i.e. methods that can be used to generate data for any EPA program; 2) a comprehensive computerized library of information on methods which are suitable for use in complying with EPA regulations; 3) the institution of a process in regulation development that assures consideration of monitoring requirements; 4) a system for assuring EPA program offices continued support for quality assurance (QA) services and quality control (QC) samples; and 5) the feasibility and advisability of a national program for accreditation of environmental laboratories.

AD HOC PANEL ON ENVIRONMENTAL LABORATORY ACCREDITATION

The *Ad Hoc* Panel on Environmental Laboratory Accreditation completed Phase I of its task, which was to evaluate the feasibility of a national multi-media program. After approximately six months of deliberations the Panel determined that there are numerous feasible options for a national laboratory accreditation program and that it was advisable for EPA to examine the spectrum of possible options in depth and to evaluate alternative solutions.

The Panel made several specific findings. First, the growing number of non-reciprocal state and private sector accreditation programs indicates the need for national accreditation. Each program is aimed at determining the capability of a laboratory to perform analysis in accordance with EPA or state regulations. The manner in which this is determined, the range of analyses covered, and the rigor applied to the evaluation of the capability varies with the accrediting organization. Therefore, there is extreme reluctance to grant reciprocity among the multiple accrediting organizations. Costs for these programs range from the indirect costs of the time and effort of the laboratory staff to comply with the requirements, to over a hundred thousand dollars in accreditation fees.

Second, there is significant evidence suggesting that laboratory accreditation contributes to overall improvements in performance. These improvements are most likely a result of information acquired during on-site inspections, specifically: 1) an improved understanding of methods requirements (both understanding which method to use and understanding how best to interpret and implement the published method), 2) improvements to quality assurance programs and quality control practices, and 3) improved data management practices.

Thirdly, the laboratory industry is promoting national accreditation as one mechanism for addressing recent problems with laboratory performance and professional ethics. Some professional organizations are making efforts to improve the industry's reputation and strengthen the public's and government's confidence in its work. National environmental laboratory accreditation is cited by these organizations as one tool for achieving this goal. One group has approached both EPA and Congress to request that a government sanctioned national program be created.

The benefits of a national program were also examined by the EMMC *Ad Hoc* Panel. Primary among the benefits was that a national program might help strengthen the credibility and integrity of EPA's monitoring and compliance programs. Public confidence is an important factor in the success of EPA's program, particularly those that involve remediation of environmental contamination or control of point sources of pollution. Although accreditation does not provide the public with guarantees concerning laboratory performance, it would provide uniform baseline assurance that practicing laboratories meet certain minimum capability standards.

A national accreditation program may help to reduce the potential for misapplication of EPAs' monitoring methods. The on-site examination of laboratory facilities, equipment, personnel, etc. provide the laboratory personnel with an opportunity to seek clarifications regarding performance requirements. Therefore, accreditation can provide an effective mechanism for ensuring that environmental laboratories are appropriately applying EPA's required methods.

Users could be provided with assistance in selecting appropriate and qualified laboratories under a national program. The majority of users currently rely, at best, on available information from existing programs, their ability to interpret the information, and on their own experience with laboratories. A national program would provide such users with and up-to-date indication of laboratory capability and a source of information concerning historical laboratory performance.

The economic and operating burdens imposed by the existing multitude of non-reciprocal accreditation and certification programs could be reduced. A strong national program with technical implementation at the state level should increase reciprocity among state program, potentially reducing costs for laboratories and some accrediting organizations.

The Panel recommended that steps be taken to further evaluate the usefulness of a national program. Their recommendation to establish a Federal Advisory Committee was based on the need to determine the needs and effects on the entire environmental community. The EMMC concurred with this suggestion and the Committee on National Accreditation of Environmental Laboratories (CNAEL) was established by Mr. Habicht in July, 1992.

Next steps for the Panel will be to develop an independent cost estimate for current programs and proposed options. Emphasis will be on that portion allocable to EPA. An optimal program will also be developed which will take into consideration EPA and state capabilities and responsibilities.

COMMITTEE ON NATIONAL ACCREDITATION OF ENVIRONMENTAL LABORATORIES

The charter for CNAEL directs the committee to counsel the EMMC Policy Council, Deputy Administrator Habicht, and Administrator Bill Reilly on the advisability

of a national accreditation program for environmental laboratories. This program would include any laboratory which provides services and analyses of environmental samples which are collected in order to comply with federal and state environmental statutes and regulations.

The objective of CNAEL is to advise EPA on whether a national environmental accreditation is the most beneficial approach and, if not, what alternative solution would best meet the needs. During this investigation, CNAEL is charged with characterizing the needs of the affected community, including the laboratories, EPA, the states, the regulated community, and the public. In addition, the committee is to identify and evaluate alternate solutions which will satisfy those needs. The committee has also been directed to provide a design outline for the selected program, to recommend modes to implement the program, and to suggest appropriate roles for EPA participation.

The Committee on National Accreditation of Environmental Laboratories was established following the requirements of the Federal Advisory Committee Act. The composition of the members must fairly represent the affected community. In this case, members were selected from state governments, trade associations for both environmental laboratories and EPA's regulated community, public environmental interest groups, academia, and other federal agencies, including EPA. All meetings, proceedings, and correspondence are open to the public. The public is encouraged to provide written comments for consideration by the committee members or to make an oral presentation during one of the meetings. Meeting dates and locations are announced in the Federal Register at least two weeks prior to the meeting. To further disseminate information, a mailing list has been set up which provides basic information on meetings as well as minutes of any meetings.

CNAEL has accomplished several of the tasks which were designated by EPA. First among these was the description of the needs of the laboratories, regulatory agencies, and laboratory users. The scope of any program was defined in terms of the regulations covered, the media of concern, and the type of analytical procedures. A total of fifteen alternative approaches were identified and ranked. Finally the committee identified multiple options for implementing a program which will be evaluated in relation to the selected alternatives.

The primary concern of all parties was to obtain data of the needed quality in a cost effective manner. This takes into account the concept that the quality of the data may vary, depending on the use. Purely qualitative information may be needed in a confirmative analysis, while extremely precise and accurate data with low detection limits may be needed when evaluating whether a particular source can be used for drinking water. The goal of achieving the quality needed must take into consideration the most efficient means for obtaining the data in order to avoid overburdening the reservoir of capable laboratories in the face of expected increases of environmental analyses in the coming years.

Some of the specific needs identified, which stem from this overall goal were 1) reciprocity among states, international organizations, private programs, and federal programs; 2) standardization of sampling, analytical methods, and quality control; 3) an objective means of evaluating laboratory performance in various sample matrices (including provision of materials); 4) a comprehensive yet flexible program to cover all environmental regulations and 5) elimination of technical redundancy and inconsistency such as exists in the current system.

CNAEL recommends that the scope of the program would encompass testing to serve all existing EPA monitoring, enforcement or other functions which are mandated by statutes and pursuant regulations, including those which have authority and responsibility invested in the states. Monitoring under the Resource Conservation and Recovery Act (RCRA), the Comprehensive Emergency Response, Compensation and Liability Act (CERCLA or Superfund), the National Pollutant Discharge Elimination System (NPDES), the Safe Drinking Water Act (SDWA), the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), the Toxic Substances Control Act (TSCA), etc. would be included within the scope of a national program.

All types of environmental media would be within the scope, to include water, soil, air, sludge, solid waste, liquid waste, and related samples, such as biological tissue, body fluid, food and neat chemicals. Analytical procedures ranging from simple routine analyses (such as turbidity determinations) to complex procedures (such as identification and measurement of organic components using GC/MS) would be included within the scope.

In addition, emerging technology and new environmental regulations would need to be accommodated within the scope of any program. Flexibility is critical to allow for adaptation to the rapidly changing rules and methodology.

One of the difficulties that surfaced in discussing a national accreditation program was that there was disagreement on what constituted the elements of such a program. For clarification purposes the committee defined the basic elements of a program for the laboratory and the accreditation organization. Some of the critical items for the laboratory would be performance evaluation samples, on-site audits, QA program documentation, equipment maintenance, calibration, and record keeping. Accreditation organization elements included, among others, record keeping requirements, a directory of accredited laboratories, an appeals process, standard auditing methods, and a technical advisory committee. The specifics for each category have not been completely defined, pending the selection of the best alternative, but there was general agreement that consideration of International Standards Organization (ISO) Guides should be given high priority.

One important portion of the charge to CNAEL was to identify alternatives to a national environmental laboratory accreditation program. The committee identified 15 alternatives, including accreditation, which were then evaluated. Some of the identified alternatives were 1) analyst certification, 2) product certification, 3) resident inspectors,

4) performance bonds, 5) reciprocity agreements among states, and 6) training for analysts, lab managers, and/or auditors. In order to determine the benefits and disadvantages, each alternative was evaluated in how well it met the identified needs of the various affected parties. Using a matrix and a numerical scoring system the committee graded each alternative and ranked them according to their individual merits.

After evaluation of the alternatives it was decided that the selection would require a combination of some of the alternatives in order to obtain the best solution. Therefore, the following three alternatives were selected as the top choices: 1) national environmental laboratory accreditation, 2) a combination of performance testing and certification of the QA program and the laboratory process (on-site audit), and 3) a combination of performance testing and certification of the QA program and the product (e.g. spot inspection of data records).

The means to implement any program on a national scale were discussed at length. Various speakers informed the committee of what was currently being practiced in similar areas, e.g. the clinical laboratories, the fastener industry, and weights and measures, which is coordinated by NIST. Six implementation options were identified. Within each of option there were various minor sub-categories. Those options were 1) a centralized program operated by the federal government, 2) a program with federal oversight but daily operation by states and/or private organizations, 3) a program operated independently by states/private sector with guidelines provided by the federal government, 4) a completely state run program with full reciprocity, 5) a private sector program with input from the federal and state governments through an advisory/oversight committee, and 6) a completely private sector program with no government involvement at either state or federal level.

The next steps for the committee will be to examine the final three alternatives under the six different implementation scenarios. The feasibility of each option and the impact on current systems will be considered and weighed in the selection process yielding a 6 X 3 matrix. The eighteen possibilities will be winnowed down to a more reasonable number for recommended action to EPA.

Information on costs for operating an accreditation program and costs for participating in such a program are currently being collected from the CNAEL members. Extrapolating from these costs an estimate will be made for each of the alternatives selected. This cost analysis is designed to compare the status quo with each alternative and identify any savings or additional expenditures,

An overall evaluation of the pros and cons of each alternative will be compiled. This will include not only cost to establish and operate the program, but also the ease of implementation and the ability to apply an objective scientific process for evaluation. In looking at the effects on the current systems in place special emphasis will be placed on the effects on enforcement of regulations. Equitable disposition of any cases coming to litigation would be a high priority for all parties.

A final report with recommended action will be prepared. This report will outline the selected alternatives, the recommended operating systems, and a complete documentation of the benefits and costs for each plan. This counsel from the Committee on National Accreditation of Environmental Laboratories will be considered by Administrator Reilly, Deputy Administrator Habicht and the EMMC in developing their plan for action. This report is expected to be presented in mid-summer, 1992. Additional input will be provided from the *Ad Hoc* Panel on Environmental Laboratory Accreditation, especially regarding estimated costs to EPA for implementation of any program.

The public is encouraged to attend and participate in the advisory committee process. The next meeting will be in the Washington, DC area on June 1-2, 1992. The meeting location has not been finalized but will be available in the Federal Register and, additionally, to all who have been enrolled on the mailing list.

Everyone is invited to provide written comments to the committee. These should be submitted two weeks prior to the meeting in order that the committee members will have sufficient time to consider the comments before discussion begins. A limited amount of time is also available for any member of the public who would like to make an oral presentation to the committee. Again, notification two weeks prior to the meeting is needed to assure sufficient time on the agenda. Frequently during committee meetings members of the public are requested to make comment when their expertise is recognized by one of the members.

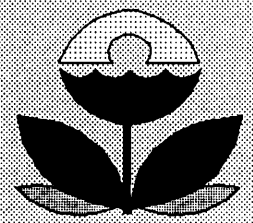
Anyone wishing to be included on the mailing list need only call Jeanne Hankins at (202) 260-8454 or send a business card or brief written request to:

Jeanne Hankins
US EPA; (WH-550G)
401 M St. SW
Washington, DC 20460

Portions of this presentation were extracted from the "First Interim Report of the Environmental Monitoring Management Council *Ad Hoc* Panel on the Feasibility of a National Environmental Laboratory Accreditation Program", the "Summary of the February 4 and 5, 1992 Meeting of the Committee on National Accreditation of Environmental Laboratories", and unpublished paper "Environmental Monitoring in the 90's: Meeting the Information Needs of Environmental Programs".

COMMITTEE ON NATIONAL ACCREDITATION OF ENVIRONMENTAL LABORATORIES (CNAEL)

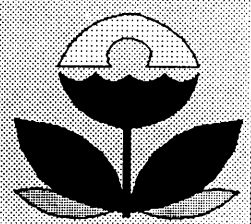
Jeanne Hankins
Executive Director, CNAEL
U.S. Environmental Protection Agency
Washington, D.C.



EMMC
Deputy Administrator
Policy Council
Steering Committee
Ad Hoc Panels

EMMC

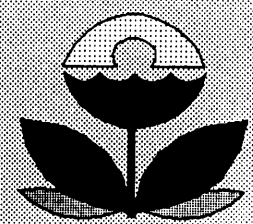
Recommend Coordinated Agency-Wide Policies Concerning Environmental Monitoring Issues



EMMC

Environmental Laboratory Accreditation

Co-Chairs	Jim Finger, Environmental Services Director, Region IV Ramona Trovato, Office of Water
Charter	Explore the Feasibility of a Uniform National Accreditation Program for Laboratories Performing Environmental Testing Procedures
Accomplishments	Phase I Study of Benefits and Potential Issues Complete Recommendation accepted for establishment of Federal Advisory Committee
Next Steps	Design optimal program and critically evaluate recommendations of CNAEL



CNAEL

Goal

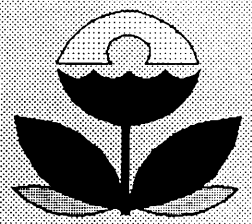
Advise and counsel the Administrator, Deputy Administrator, and the EMMC on a national accreditation program for environmental testing laboratories which provide services related to compliance with federal and state environmental statutes and regulations

CNAEL

Composition

Members from state governments, trade associations for environmental laboratories and EPA's regulated community, public environmental groups, academia, and federal agencies

All meetings are open to the public



CNAEL

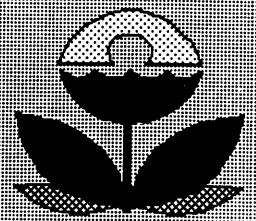
Objectives

Advise EPA on:

Need for a national environmental accreditation program

Alternatives to an accreditation program

Appropriate role for EPA



CNAEL

Accomplishments

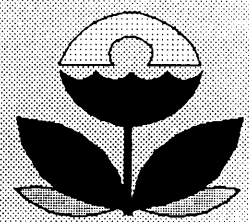
Definition of needs of all affected parties

Definition of the scope

Identification of alternative approaches

Description of elements of an accreditation program

Identification of implementation options

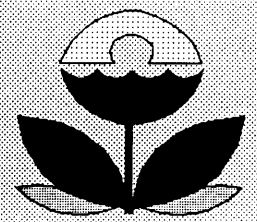


CNAEL

Needs

Obtain date of the needed quality in a cost effective manner

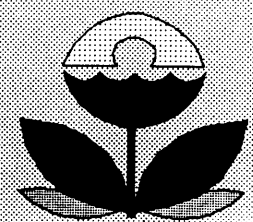
Several objectives were defined clarifying the concerns and issues of all parties



CNAEL

Scope

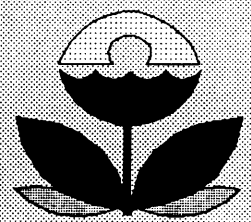
All media for all EPA regulated programs (e.g. air, water, soil, sludge, solid waste regulated under such programs as SDWA, RCRA, NPDES, CERCLA)



CNAEL

Program Elements

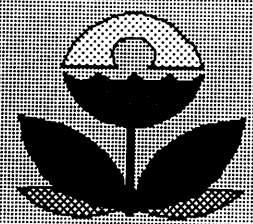
International Standards Organization (ISO) criteria for accredited laboratories and accrediting organizations were deemed a suitalbe model for the purpose of a uniform national environmental laboratory accreditation program



CNAEL

Alternatives

Fifteen different alternatives were identified and evaluated against the criteria established under the definition of needs



CNAEL

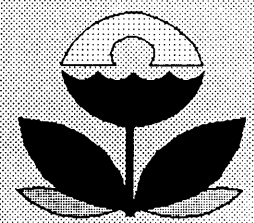
Selection of Alternatives

Selection of three top alternatives:

National Environmental Laboratory Accreditation

Performance Testing; QA Systems Certification; Lab Process Certification

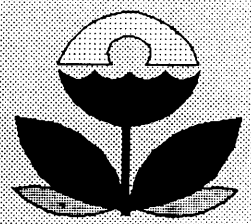
Performance Testing; QA Systems Certification; Product Certification



CNAEL

Implementation Options

Administrative options were identified which ranged from a centralized federal operation to a system free of governmental control and operated by private accrediting bodies



CNAEL

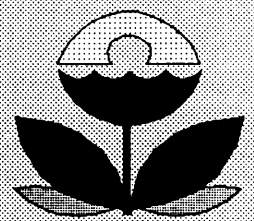
Next Steps

Evaluation of the three alternatives administered under different implementation options

Cost analysis of selected options vs. status quo

Pros and cons of each alternative

Final report to EPA



CNAEL

Public Participation

CNAEL meeting on June 1-2, 1992

Written comments and oral presentation

Mailing List

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Status of EPA Studies on a Replacement Solvent for Freon for the Determination of Oil and Grease

William A. Telliard

Analytical Methods Staff
Engineering and Analysis Division
Office of Science and Technology
USEPA Office of Water

Introduction

The United States, as a party to the Montreal Protocol on Substances that Deplete the Ozone Layer and as required by law under the Clean Air Act Amendments of 1990 (CAAA), is committed to controlling and eventually phasing out CFCs as well as other listed chemicals, because the chlorine in CFCs has been shown to be a primary contributor to the depletion of the stratospheric ozone layer. Under both the Montreal Protocol and the CAAA, CFCs will be phased out by the year 2000.

To be consistent with its commitment on CFCs, EPA proposed on July 3, 1991 (56 FR 30519) to amend certain analytical methods under the Clean Water Act (CWA) and the Resource Conservation and Recovery Act (RCRA) to allow the use of alternative solvents in lieu of CFCs that are mandated in these methods. Of the CFCs to be regulated by EPA, only CFC 113 (Freon 113) is used in laboratory testing.

The analytical methods that EPA proposes to amend include Method 413.1 in 40 CFR Part 136 and Methods 9070 and 9071A in 40 CFR Parts 260-270 (EPA Publication SW-846 by reference). At issue will be the possible effects of amending analytical procedures that are presently required for monitoring under the authority of the National Pollution Discharge Elimination System (NPDES) and the Resource Conservation and Recovery Act (RCRA).

Method 413.1 is used in the CWA programs to determine total oil and grease content in surface and saline waters and in industrial and domestic wastes. This gravimetric method involves the acidification of the sample, followed by serial extraction of the oil and grease with Freon 113 into a separatory funnel, evaporation of the solvent from the extract, and weighing of the residue.

Method 9070 is used in programs administered under RCRA and is essentially the same as Method 413.1. RCRA Method 9071A is used to recover low levels of oil and grease from sludges, soils, other solid matrices, biological lipids, and some industrial

wastewaters. The method involves acidification or drying, extraction of oil and grease with Freon 113, and weighing of the residue after evaporation of the solvent.

In all three methods described above, the result, termed "total recoverable oil and grease," is a method-defined parameter. Therefore, any changes to the specific analytical protocols will change the manner in which the analytical result is derived and potentially change the numerical value of the results for a given sample.

The Agency's initial efforts to find a suitable replacement solvent for Freon 113 have been conducted by the Office of Research and Development's Environmental Monitoring Systems Laboratory in Cincinnati, Ohio (EMSL-Ci). EMSL-Ci first used laboratory-prepared, synthetic samples containing materials that represent "oil and grease" compounds covering extremely wide boiling ranges, such as No. 2 fuel oil, No. 6 fuel oil, Prudhoe Bay crude, animal lard, and wheel bearing grease. Reagent water was fortified with these materials dissolved in an organic solvent to simulate real-world samples. These samples were then extracted using several different solvents in place of Freon 113, and the residue was determined gravimetrically. Subsequent evaluations used a limited number of actual industrial waste samples. It was on the basis of this work that EPA proposed the amendment of the methods in question.

In response to comments on the July 3, 1991 *Federal Register* notice, EPA will publish another notice that withdraws the proposed rule to amend the methods. That notice will:

- Allow laboratories to continue to use Freon 113 in the immediate future.
- Strongly recommend that laboratories reclaim and/or reuse the Freon 113 rather than vent it up a hood.
- Give the details of the Draft Study Plan for Sampling and Analysis Activities to Support the Freon Replacement Study.

Draft Study Plan

The study of possible replacement solvents for Freon 113 will be run jointly by the Office of Water, the Office of Solid Waste, and the Office of Air and Radiation. The focus of the study is to:

- Determine a solvent/extraction system that provides equivalent performance to the current Freon 113 method across a rang of effluent and sludge sample types.
- Determine the solvent/extraction system that poses the least potential risk to stratospheric ozone.
- Provide clear direction for further study of one or two of the solvent/extraction systems across and even broader range of effluents and sludge sample types that are regulated under NPDES or RCRA.

Five solvents in addition to Freon 113 will be examined. They are:

- Methyl tertiary butyl ether (MTBE) and n-hexane in a 20/80 mixture
- n-Hexane
- Dupont-123, a hydrochlorofluorocarbon alternative to CFCs
- Methylene chloride (dichloromethane)
- Perchlorethylene

A total of four different extraction procedures will be employed, depending on the sample matrix. Aqueous samples will be extracted by all six solvents using traditional separatory funnel procedures. Samples representing final effluents will also be extracted using solid-phase extraction cartridges. Solid samples will be extracted with all six solvents using traditional Soxhlet procedures and by sonication as well. Each sample will be extracted in triplicate by each solvent/extraction system.

The types of sample matrices to be included in this study will represent wastes from a diversity of industrial categories and activities, and will involve a wide range of oil and grease concentration levels. The intent is to select wastewaters and solid waste matrices that are applicable for investigating the subject oil and grease methodologies.

Table 1 presents a list of suggested sample sources and types based on these recommendations. A total of 15 solid wastes and 12 wastewater effluents have been selected for study. Final site selection should also take into consideration the following:

- accessibility of waste streams,
- limited commingling of wastes,
- EPA's previous experience at selected facility,
- cooperation of facility personnel, and
- willingness to conduct voluntary self-sampling to minimize labor and travel costs.

Because the purpose of the study is to compare the six extraction solvents, and not to develop interlaboratory performance statistics, the number of laboratories will be limited. The Region III Central Regional Laboratory will perform the SPE work. A single laboratory will be contracted for the aqueous sample separatory funnel samples, and a single laboratory for the solid samples.

Data Evaluation

The statistical approach to the evaluation of the data from the study will be consistent with the complete block design. Each of the solvent/extraction combinations will be statistically compared to the Freon 113 data. As the objective of the study is to determine a

suitable replacement for Freon 113 in the context of a NPDES monitoring method, the null hypothesis for the statistical comparisons will be that the solvent/extraction systems are not equal. Thus, solvent/extraction systems that achieve higher or lower results than the Freon 113 will be identified and may be eliminated from consideration. Although achieving higher results than the Freon 113 method might be seen as a method "improvement", such enhanced recovery of an operationally-defined parameter such as oil and grease presents significant problems for implementation of the "improved" method under NPDES, as thousands of existing NPDES permits contain oil and grease limits based on the present Freon 113 methodology.

Any solvent/extraction systems that have performance equivalent to that of the Freon 113 will be candidates for further evaluation. Given the complete block design of the study, the data may be compared across all sample types and within sample types as well. As a result, EPA can identify those sample types which pose the greatest analytical challenge for any of the solvent systems, and thereby direct further research efforts to the evaluation of those sample types.

Follow Up Actions

After the completion of the first phase of the study, EPA will publish a notice in the *Federal Register* of the availability of the results. EPA will also sponsor a workshop to discuss and take comments on the study results.

The second phase of the study, evaluating the one or two most promising alternatives, will begin following the workshop.

TABLE 1

SUGGESTED SAMPLE SOURCES FREON REPLACEMENT METHOD STUDY

	Industrial Category	Possible Location	Wastewater Stream	Solid Waste
1.	POTW	Region 2	Final effluent	Municipal sewage sludge
2.	Petroleum Refining	Oil Refinery, Reg 3	API separator effluent	API separator sludge
3.	Organic Chemicals	Polymer Plant, Reg 2	Final effluent	Polyoxyalkaline sludge
4.	Timber Products	Wood Preserving Plant, Reg 3	Oil/water separator effluent	Sludge from creosote operation
5.	Iron & Steel	Coke Plant, Reg 3	Oil/water separator effluent	Sludge from coking operation
6.	Oil & Gas	Coastal Production Facility, Reg 6	DAF effluent	Used drilling mud
7.	Pulp & Paper	Paper Mill, Reg 3	Bleach plant filtrate	Dewatered sludge
8.	Meat Packing	Rendering Plant, Reg 7	Final effluent	Rendering/cooking waste (chicken fat)
9.	Meat Packing	Slaughter House, Reg 7	Final effluent	Slaughter house sludge
10.	Leather Tanning	Tannery, Reg 1	Primary effluent	Tannery sludge
11.	Misc. Foods	Margarine Plant, Reg 5	Primary effluent	Vegetable oil waste
12.	Coil Coating	Can Manufacturing Plant, Reg 3	Oil/water separator effluent	Oil/water separator sludge
13.	Restaurant	Region 2	none	Filter cartridge from vegetable oil use
14.	Soil	Prepared by OSW	none	Contaminated with synthetic motor oil
15.	Soil	Prepared by OSW	none	Contaminated with motor oil

QUESTION AND ANSWER SESSION

MR. TELLIARD: Hi, Merlin.

MR. BICKING: Hi, Bill. I guess the obvious question is, are you assuming that SFE is not going to be a viable alternative in the near future and that is why it has been left off the list?

SPEAKER: What about 418.1, TRPH?

MR. TELLIARD: I am sorry?

SPEAKER: The TRPH, total recoverable petroleum hydrocarbons, the 418 series which is the IR methods, any work on those?

MR. TELLIARD: I am not that familiar with that method. Can somebody help me? Joe?

Oh, okay. No, we have not looked at that. That is an option. I talked to somebody at lunchtime about IR. Right now, what we are trying to do is maintain the standard method that we have in place and just look for a, quote, "solvent substitution".

MR. SCHRYNEMEECKERS: Rick Schrynemeeckers, Enseco.

I was curious as to when you think the workshop is going to be and how will you be announcing that.

MR. TELLIARD: We can do it a couple of ways. We will probably publish it, certainly, in the Federal Register, but we have the mailing list from this meeting and if you are really interested, we can just send you a flyer.

MR. SCHRYNEMEECKERS: Approximately when do you think that will be?

MR. TELLIARD: End of summer, November.

MR. SCHRYNEMEECKERS: Okay.

MR. TELLIARD: I hope earlier than that, but knowing all the other trash we have on our plate, that will probably be it.

Hi.

MS. ROTHMAN: Hi. Nancy Rothman from Enseco.

This might be a real naive question, but are we also looking at the permitting process to determine why we need oil and grease numbers, or can we change that process and eliminate freon that way?

MR. TELLIARD: Thank you for asking that. Thank you very much. I think that would be a wonderful idea.

Getting rid of this measurement would probably be a giant step forward for science, but there are a whole group of people who went to school to get sanitary engineering degrees who just would not know what to do without this number.

So, we have to come up with something. Now, there is TOC and COD and AOXs and MMLSSs, you know. I think that has certainly got to be a viable option. No one wants to hear that, but I think it is. I think there are so many other ways that we can measure whatever the hell we are measuring, because no one knows, that I think that would be a wonderful idea.

MS. ROTHMAN: How do we get it going?

MR. TELLIARD: Well, we are going to have to get phase one done to show...because there are people who believe that if you mix a little blue and a little green, you will end up with a freon that will work just the same. So, that is part of this. You have to preface that by saying fine, we looked, and there isn't, you know, and put that on the plate.

That has been whispered in the halls but not spoken very loudly.

How are you doing?

MR. LEVY: Hi, Bill. Nathan Levy, A&E Testing.

As long as we are throwing out methods, can I put in my order to throw out the BOD test? It is almost as worthless as the oil and grease.

I do have a question, though, and another comment. Let's not use n-hexane, because that is going to increase the labor considerably, since it is going to float on top of the water.

But my other question was on the liquid-liquid. Is your study going to really include some liquid-liquid, or are they all going to be separatory funnel extractions with those solvents?

MR. TELLIARD: On the first shot through for the five that we are looking at, we are going to use separatory funnel. Then, when we narrow it down, if we do narrow it down, to one or two, we have archived a number of these samples, and then we will run continuous liquid-liquid extraction on those to see what type of comparability we get.

I don't envision that liquid-liquid would be a problem as an alternative.

MR. LEVY: Well, the time factor may be. Right? You know, it is going to...liquid-liquid for the organics extraction is 18 hours. What do you expect a liquid-liquid on a grease would be?

MR. TELLIARD: Don't know yet.

MR. LEVY: All right, thanks.

MR. THOMAS: Hello, Bill. How are you doing?

MR. TELLIARD: Hi.

MR. THOMAS: My name is Roger Thomas. I am from Viar and Company.

I was wondering in the solvent selection process, have you taken into consideration the boiling points of the solvents that you are selecting?

The reason why I said that is because if it is a high boiler, you have to boil down the solvent at a higher temperature, thereby losing some of the low boiling oils and greases and fats.

MR. TELLIARD: Right. You are absolutely right. No, we didn't.

MR. THOMAS: Okay.

MR. TELLIARD: Running concurrently with this study, the Canadians are doing a similar study, and we met by accident in Colorado, and it turned out we all had the same solvents which shows that this is a real warped community.

We are going to share data with them. So, you figure that we will end up with about 30 different types of matrices. So, we will have a fairly substantial data base.

They are out sampling also at this present time using the same sets of solvents. So, it looks like we will have a fairly stable data base to work from.

Thank you very much for your attention.

MR. TELLIARD: Our next speaker is Joe Raia from Shell Development. Joe and I did a similar dog and pony show in Colorado about a month and a half ago, but Joe is going to again be talking about solvent substitution for freon.

MR. RAIA: I just want to say I am really glad to be able to have the dialogue that we do with Bill Telliard, and that his sense of humor is a real help in all of this work.

The work that I am going to present here, as Bill said in the introduction, I have presented in part at a recent API meeting in Colorado. I will also present some additional new data today.

We are looking at alternative methods for oil and grease which includes the use of different solvents, and we have also looked at some solid phase extraction techniques.

As you have heard before, what we have to do is replace freon in the oil and grease tests. This has been dictated by the Montreal Protocol and the timeline by the Montreal Protocol was by the year 2000.

The Clean Air Act Amendments, though, also require the same thing by law, and recently, the President moved that deadline up some because of data from NASA aircraft probes which reportedly showed a more serious problem with ozone depletion.

The thing is the amount of solvents...the amount of freon used in laboratory tests probably account for a very small portion of all the freon used out there. I think the Federal Register notice that EPA issued estimated on the order of 1 percent.

I am not sure how you come up with a number like that, but if, while trying to find this alternative method we do solvent recycling, that will essentially cut down on any freon emissions from laboratory testing to something that we would not be able to even measure.

Now, the number of EPA methods that are really involved in freon use, are those that I have outlined up there on the slide under both the Clean Water Act and RCRA. The gravimetric 413.1 is the main one that we have talked about here. in which

you extract by separatory funnel and then weigh the oil and grease.

The IR method, 413.2, is really not a promulgated method, but it is in the EPA Methods Manual and is used in some testing.

The TPH method someone just asked about is 418.1, and that is the method where silica gel is used to treat the oil and grease extract, and then you finish the test with an IR analysis. Freon works very well with that, because it has no absorption in the IR region where the aliphatic hydrocarbons absorb.

The other methods, and I won't go through all of them, are shown up there in the slide. Under RCRA solids, there is the Soxhlet extraction gravimetric finish, and in the next slide, I will mention some concerns we have with changing the solvent away from freon in that type of a procedure.

Now, I will say industry, and I know that this has been expressed in API comments to the Federal Register notice that came out in July of '91 and then a later one in October, the industry supports EPA and the need to comply with the Montreal Protocol and the Clean Air Act Amendments to phase out and eliminate CFCs.

Alternatives need to be found, and the solvent change concerns are equivalency, NPDES compliance, and RCRA methods. For RCRA, I am speaking again about the Soxhlet method primarily. For the solvent mixture, hexane/MTBE, that was proposed in the Federal Register notice, there was only a limited amount of data on RCRA methods, and we wonder how such a mixture will really work in a Soxhlet type apparatus.

The petroleum hydrocarbon methods use silica gel treatment to remove polar organic compounds leaving the hydrocarbon fraction. When you change solvents, what effect will that have on the silica gel treatment and how will it change that number?

The safety and human health concerns have already been mentioned. This includes flammability of the non-freon type solvents, such as hexane, and the human health concerns of these solvents. methylene chloride toxicity, for example, and hexane has some toxicity concerns in terms of nerve ending effects.

We need to have a cooperative and focused research effort with EPA and

industry and vendors and anyone else interested in helping to solve this problem, and we need to get it done at an accelerated pace to select the alternative methods.

The potential areas for research are alternative solvents testing of test samples of different industrial categories, such as Bill has mentioned in EPA's work plan. This includes produced water, wastewater, and solid waste.

Solid phase extraction, certainly, is a viable option, and it shows a lot of promise, and we have seen a lot of data earlier today on that.

Petroleum hydrocarbon methods really come under this also,-the silica gel method and also GC/FID methods for petroleum hydrocarbons. At the Colorado conference, there were a lot of papers presented on the many different ways that petroleum hydrocarbons were measured by GC/FID.

Supercritical fluid extraction is something that we should consider especially for solid phase matrices.

And then, direct oil in water analyzer development. Wouldn't it be really neat to not have to use an extraction solvent at all for an oil and grease type measurement, if we are indeed going to have to make oil and grease measurements? There is some work out there that is being done, but very preliminary at this point. There are some commercial analyzers available, but all of these have not been evaluated completely and really proved reliable in operations in a lot of different applications.

In the meantime, solvent recovery is what we need to be doing.

The work plan that we followed and that I will show data on here is shown up there in the next slide. We compared solvents: freon, normal hexane, the hexane/MTBE mixture, and dichloromethane.

We looked at liquid-liquid extraction, and by that I mean the separatory funnel extraction and not continuous liquid-liquid extraction, and solid phase extraction using an envirelute column type material that is available from Varian.

We looked at the solvent removal temperature effect on freon extracts and dichloromethane extracts at 70 degrees C, which is the temperature used in the standard method, and at 90 degrees C, which is the temperature that we used for removing normal hexane and normal hexane/MTBE solvents.

We did some characterization of the extracted oil and grease fractions. The samples that we looked at in Shell were produced waters and some of our refinery and chemical wastewaters. The objective here is to share this data with API and EPA in providing input into the method selection.

The liquid-liquid extraction schematic is shown there in the next slide, where you take 1 liter of the water, acidify it, extract with your solvent three times, evaporate the solvent, and then weigh the residue.

In solid phase extraction, this was the column technique, take 1 liter water sample, acidify, pass it through the solid phase, elute the captured oil and grease with the solvents that we were testing, evaporate the solvent and weigh.

This shows the glassware that we used for the solid phase extraction. We simply put the sample in the sep funnel and let that percolate through the cartridge, and then rinse the bottle...well. Next, move the column cartridge to the other apparatus on the right side of the slide and carry out your elution step, and then rinse the oil and grease out of the bottle onto the cartridge in that elution step.

These results show comparisons of the different solvents with the samples tested. The slide shows the solvents pretty much in the order of the polarity of the solvent from hexane through dichloromethane. The lowest numbers there that you see are for the refinery and chemical wastewaters. The right-hand slide shows levels for produced water.

The trend, generally is the more polar the solvent, the more oil and grease you extract. This is for the liquid-liquid extraction.

The next slide shows the same kind of results for solid phase extraction. You will note that for the sample W, there were a couple of high oil and grease numbers that we got for the non-polar solvents. We wondered about whether that was just a sampling inconsistency or whether there was something else going on. We wanted to take a look at that.

So, we looked at the oil and grease extract by GC/mass spec and found some silane material contributing to the weight. Typically, the blank levels from the solid phase cartridges were quite low, actually, on the order of 1 to 2 milligrams, but in

that particular case, there was a lot more blank material that was contributing to the weight, and it was identified by GC/mass spec to be silane. A large portion of the weight was due to silane, a material evidently used in the manufacture of the column.

So, an important consideration that we are going to need to keep in mind if we are going to use solid phase is to have high quality or appropriate quality columns of consistency.

This one is a vertical slide. We got our statistics people to take a look at the data. The top slide is for solid phase, and the bottom illustration is for liquid-liquid extraction for the refinery and wastewater data. I am sorry, this is for produced water data. The next slide will be for the refinery and wastewater data. Box plots are used here to compare the results.

Now, for these box plots, basically, let's take the first one up there on the dichloromethane. You can see this bottom whisker which represents 25 percent of the data. The total box itself contains 50 percent of the data, and the top whisker would be another 25 percent of the data. The line in the middle of the block is the median of the values.

Those data are not for duplicate analyses but for all of the samples tested which included different locations.

This slide shows results for the refinery and chemical plant wastewaters, and in the case of freon on the top portion of the slide, the stars represent outliers.

Now, what does all this mean? We tried to make a summary of these results in this next slide, - the top portion being the produced water data and the bottom portion the refinery and chemical plant data.

The dashed line represents the freon value that you get with liquid-liquid extraction, and the other solvents and techniques show how well or how different they compare to the freon value and also gives you some notion about the variability between the different matrices that we looked at in produced water locations and in refinery and chemical plant locations.

Actually, the hexane liquid-liquid extraction, in the case of produced water, comes out quite close to the freon liquid-liquid extraction. The more polar solvent,

dichloromethane, is higher and shows more variability as does the hexane/MTBE mixture.

The other two plots at the right of the slide are for the hexane/SPE and hexane/MTBE/SPE. The hexane/SPE is not that different from the hexane liquid-liquid extraction. So, hexane/SPE may be a viable alternative if we have to go to hexane.

Now, this next slide shows a comparison of the effect of the evaporation temperature. If we start at the top and look at W70 and W90 for Freon, this compares the effect of evaporation at 70 degrees and at 90 degrees, which shows a decrease in the oil and grease value.

The other side of the slide shows a sample from the same location that was tested with dichloromethane. These are all liquid-liquid extraction results.

In general, the trend of the slide shows, as you would expect, that if you have to go to 90 C to remove your solvent, you are going to have a lower oil and grease number, if you have volatile oil and grease present. These samples show varying amounts of volatile oil and grease.

This next slide shows some characterization work that was done on a produced water sample. The oil and grease was treated with silica gel. The non-polar fraction is essentially total petroleum hydrocarbon done in the standard way.

The polar fraction was obtained by washing the polar material off of the silica gel column and getting a weight on that. The heavy polar material represents the difference number of oil and grease that was not able to be washed back off the silica gel column.

Essentially, this shows that a more polar solvent is going to have a large effect on an oil and grease value, for samples with different kinds of oil and grease present.

This is data for a refinery wastewater done in a similar way which compares freon, either by solid phase or liquid-liquid, with dichloromethane.

In solid phase extraction, this next slide shows a standard that was made up containing mineral oil, hexanoic acid, and ortho-cresol, and this slide shows what each of the solvents was able to do with the different type of organic compounds present. Again,

as we have seen earlier today, the phenolic type compounds are not recovered well.

To summarize results, this study, with the limited samples that were examined, shows all of these parameters will affect the oil and grease value: the extraction solvent polarity; the extraction method; the oil and grease type, non-polar and polar; and the solvent removal temperature.

The trend was that the oil and grease values increased with solvent polarity, and that was observed by both LLE and solid phase extraction. The order was dichloromethane was greater than hexane/MTBE, greater than or equal to freon, greater than or equal to hexane.

The oil and grease values by solid phase extraction were greater than by liquid phase extraction with the higher polar solvents like dichloromethane. The oil and grease values are lower with higher solvent removal temperature.

SPE can yield column artifacts and consistent quality columns are necessary to use these materials for the oil and grease tests.

Another observation in this work was that the non-freon solvents tended to have interferences from salt to a greater extent than did freon.

I would like to thank and acknowledge other people in Shell who have contributed to this work. Some of these folks are here today. Tom Randolph is here with Shell Offshore Environmental Affairs. George Stanko is here, and these other people shown on the slide are from Shell Development Company who helped either with statistics or other analytical work. Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Any questions?

MR. SCHRYNEMEECKERS: Joe, I guess this is a question for both Joe and Bill. Is the purpose of the search for the missing solvent, so to speak, is part of the mission to really find a solvent that, quote/unquote, is going to give the same numbers? Because I know when you deal with certain permitting regulations and offshore oil and grease numbers, a lot of things are driven off the number that you get being above a certain level.

So, is the purpose of the substitute solvent one issue to try to find a solvent that gives satisfactory numbers or similar numbers, and if you can't find one, what are your thoughts on where we are going to go with that?

MR. RAIA: I think the purpose is to see if you can find one. Whether or not that is going to happen I don't think any of us know yet, although we have seen some data, limited data, here in a couple of industrial categories, that would show that hexane might be a solvent that will come close to freon. Actually, hexane was used for oil and grease up until about 1978.

How close we have to come to say that it is equivalent, I am not sure how that is going to work out. Bill may have some input here on whether we may have to go in and adjust permits.

MR. TELLIARD: I think one of the answers is that you have a situation where normal hexane was our substitute for carbon tet way back in the dark ages, and then, right away, we switched over almost immediately to freon.

Normal hexane will probably give you a lower number, thereby not driving too many people into non-compliance. That is an assumption. But then again, we are looking here at oil and grease in the sense of petroleum hydrocarbons. That is why we are out looking at meat packers and margarine plants and rendering plants as to what happens to mineral and animal fat when you get into this thing. We don't know.

Where do we go? We go have a meeting this fall and talk about it, because I don't know. There is a hope that we are going to come close enough, quote,

for government work. I am not sure that that is going to happen.

MR. SCHRYNEMEECKERS: Thank you.

MR. YOUNG: I am John Young with Westinghouse.

I have got a question about the use of more polar solvents. Would you not expect a significant contribution by pH of the sample influencing whether you would extract the acidic compounds or the basic compounds?

MR. RAIA: Yes, you would.

MR. YOUNG: Yes. Are you going to try to control that?

MR. RAIA: In all this work, we adjusted the pH to less than 2.

MR. YOUNG: Okay.

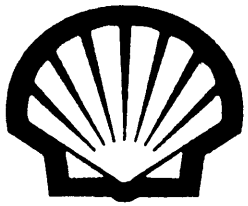
MR. RAIA: As you do in the standard method.

MR. YOUNG: Thanks.

MR. TELLIARD: Thanks, Joe.

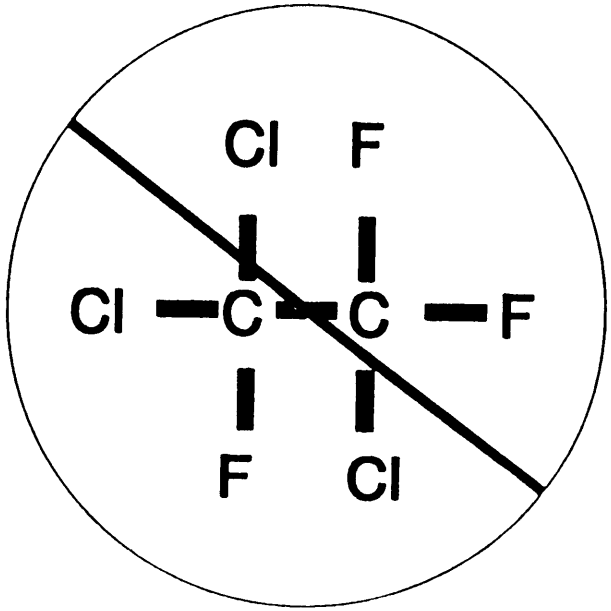
ALTERNATIVE METHODS FOR OIL AND GREASE ANALYSIS WHICH USE NO CHLOROFLUOROCARBONS

J. C. RAIA, D. K. LEE, P. J. STALEY
SHELL DEVELOPMENT COMPANY
HOUSTON, TEXAS



15TH ANNUAL EPA CONFERENCE
ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT
Norfolk, Virginia
May 6-7, 1992

REPLACE FREON-113 IN OIL & GREASE TESTS
1,1,2 Trichloro-1,2,2 Trifluoroethane

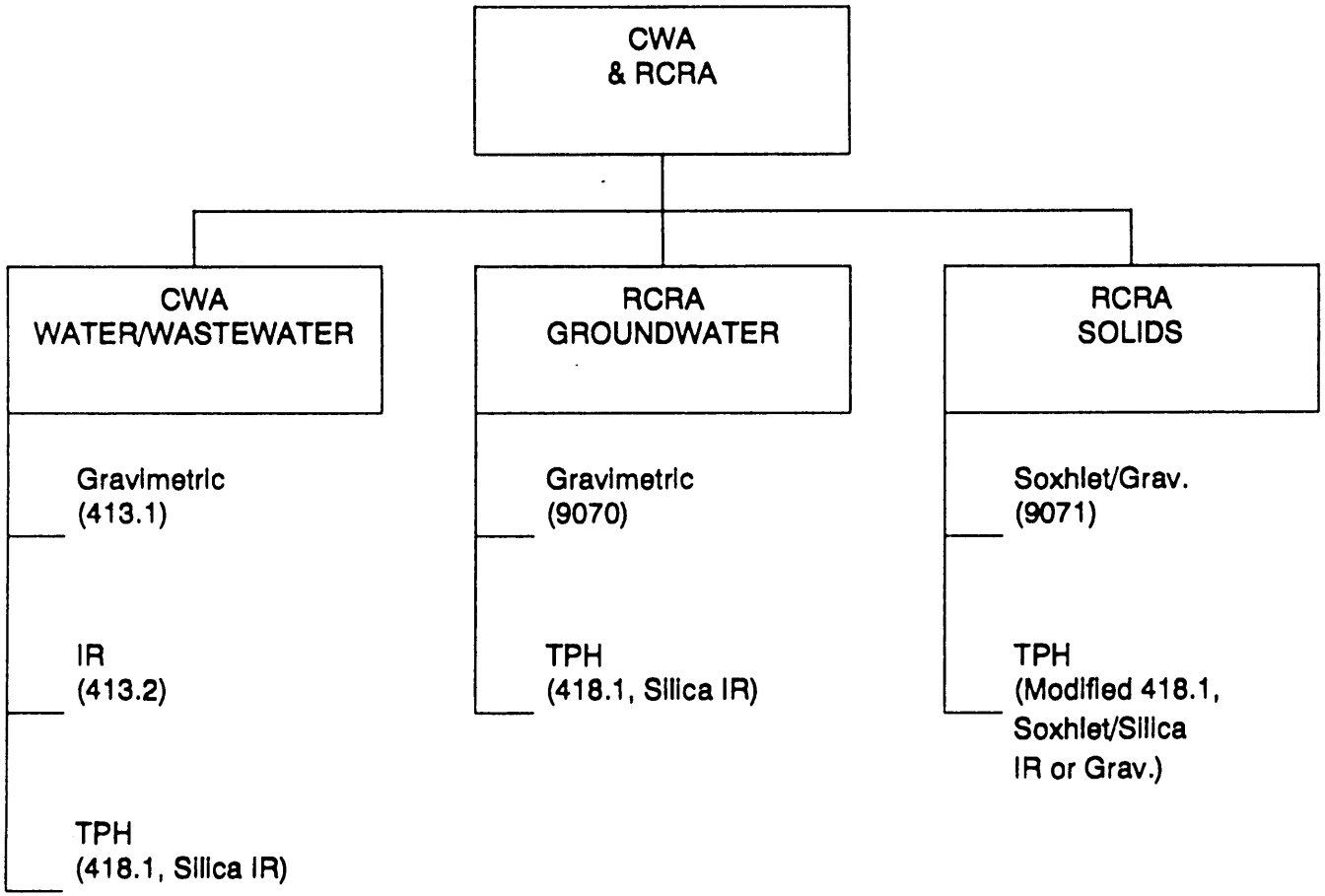


Montreal Protocol No CFC's by year → 2000

CAAA → 2000

U.S.(Bush) → 1996

EPA O&G METHODS & SAMPLE TYPE



OIL & GREASE ANALYSIS METHOD CHANGE CONCERNS & NEED FOR COOPERATIVE WORK

* INDUSTRY SUPPORTS EPA IN THE NEED TO COMPLY WITH THE MONTREAL PROTOCOL AND CLEAN AIR ACT AMENDMENTS TO PHASE OUT & ELIMINATE CHLOROFLUOROCARBONS (CFC's)

* ALTERNATIVES TO FREON-113 MUST BE FOUND FOR ANALYTICAL TEST METHODS FOR OIL & GREASE

* SOLVENT CHANGE CONCERNS

  - Equivalency & NPDES Compliance
  - RCRA Methods
  - Petroleum Hydrocarbon Methods
  - Safety & Human Health

* COOPERATIVE FOCUSED RESEARCH WITH EPA & INDUSTRY PARTICIPATION IS NEEDED AT AN ACCELERATED PACE TO DEVELOP & VALIDATE THE ALTERNATIVE METHOD

OIL & GREASE METHOD CHANGE
POTENTIAL COOPERATIVE RESEARCH AREAS

* ALTERNATIVE SOLVENTS TESTING OF TEST SAMPLES FROM INDUSTRIAL CATEGORIES

  Produced Water
  Wastewater
  Solid Waste

* SOLID PHASE EXTRACTION

* PETROLEUM HYDROCARBON METHODS

  Silica Gel Method

  GC-FID Method

* SUPERCRITICAL FLUID EXTRACTION

* DIRECT OIL IN WATER ANALYZER DEVELOPMENT

Interim Action is Solvent Recovery

WORK PLAN
ALTERNATIVE OIL & GREASE METHOD TESTING

* Compare Solvents

  Freon-113
  n-Hexane
  n-Hexane/MTBE Mixture (80:20)
  Dichloromethane

* Compare Extraction Methods

  LLE and SPE

* Test Solvent Removal Temperature Effects

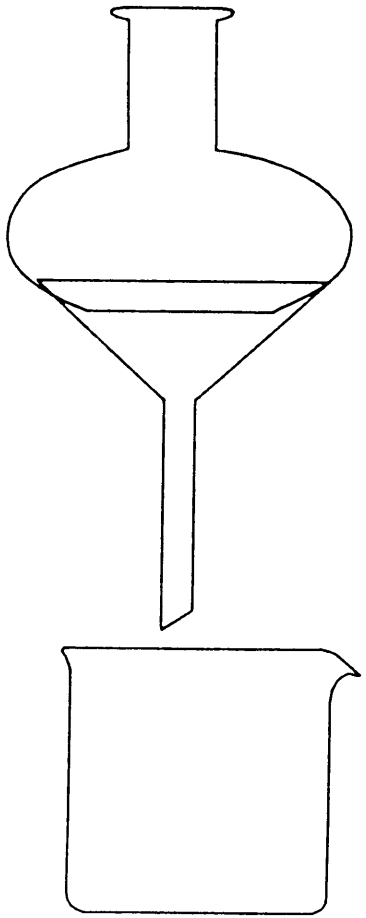
  70 C & 90 C

* Characterize Extracted Oil & Grease Fractions

* Test Produced Waters and Refinery & Chemical Wastewaters

* Share Shell's Data with API and EPA for Method Selection

LIQUID / LIQUID EXTRACTION
OIL & GREASE ANALYSIS PROCEDURE



1 LITER
WATER SAMPLE

↓

ACIDIFY

↓

EXTRACT WITH SOLVENT

↓

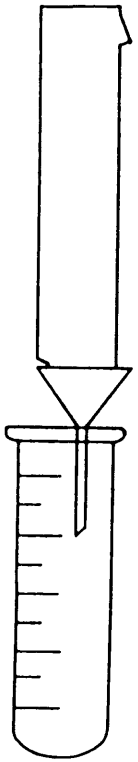
EVAPORATE SOLVENT

↓

WEIGH RESIDUE

SOLID PHASE EXTRACTION (SPE)
OIL & GREASE ANALYSIS

RAPID ANALYSIS & REDUCED WASTE ADVANTAGES



1 LITER
WATER SAMPLE

↓

ACIDIFY

↓

SOLID PHASE EXTRACTION

↓

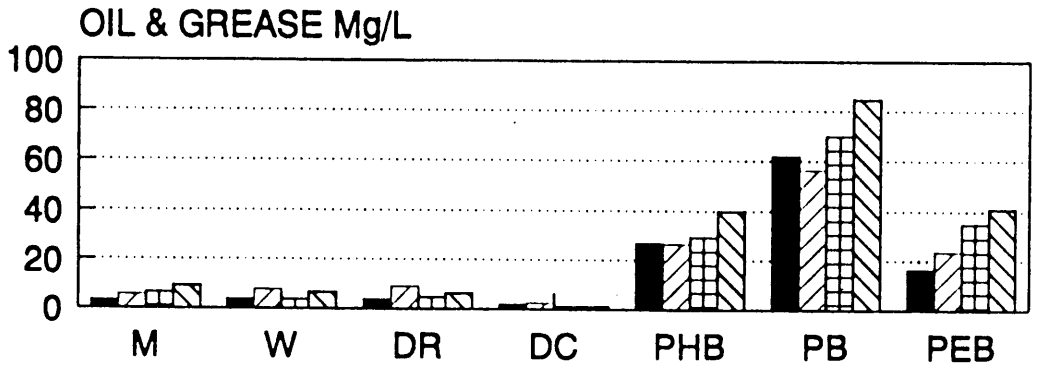
ELUTE CAPTURED O&G

↓

EVAPORATE SOLVENT

WEIGH RESIDUE

OIL & GREASE ANALYSIS RESULTS
ALTERNATE SOLVENTS COMPARISON
BY LIQUID/LIQUID EXTRACTION

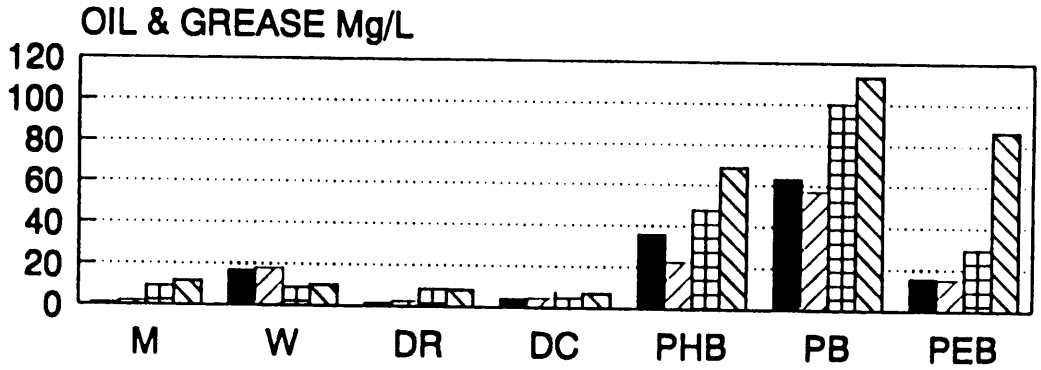


	M	W	DR	DC	PHB	PB	PEB
HEXANE	3.3	4	3.9	2.1	26.8	61.8	16.5
FREON-113	5.7	7.8	9.2	2.6	26.5	56.5	23.8
HEXANE/MTBE	6.9	4	5	1.3	29.5	70.2	34.9
DICHLOROMETHANE	9.3	6.8	6.4	1.2	39.8	84.7	40.9

SOLVENT TYPE

HEXANE
FREON-113
HEXANE/MTBE
DICHLOROMETHANE

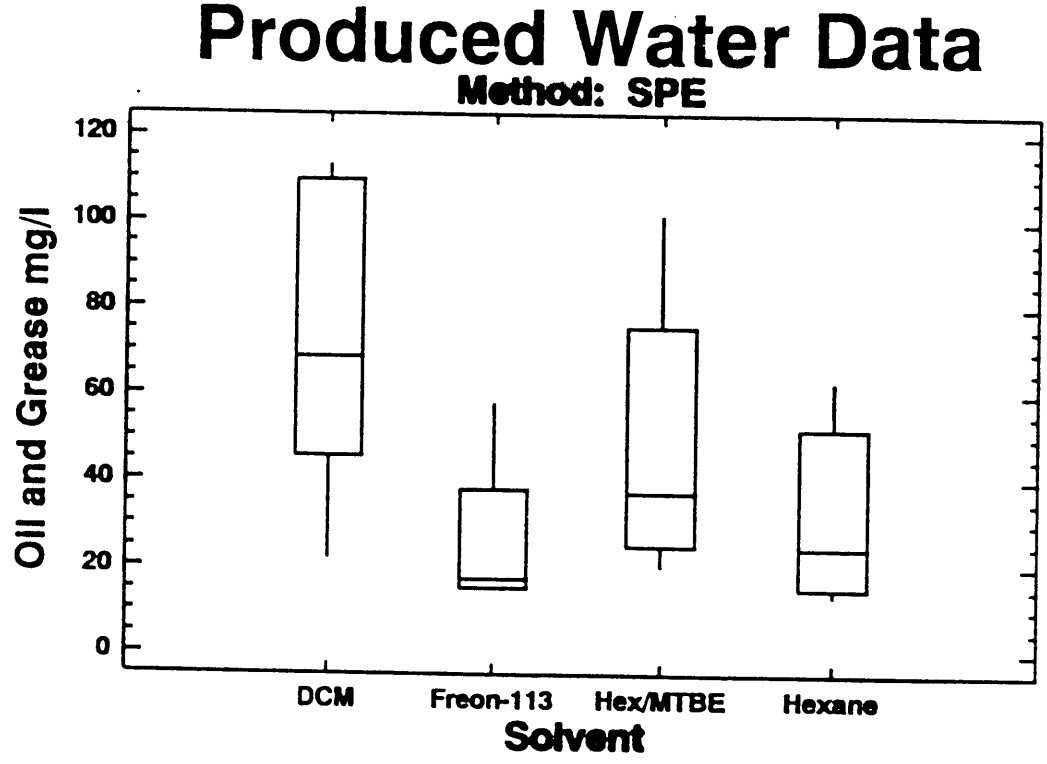
OIL & GREASE ANALYSIS RESULTS
ALTERNATE SOLVENTS COMPARISON
BY SOLID PHASE EXTRACTION

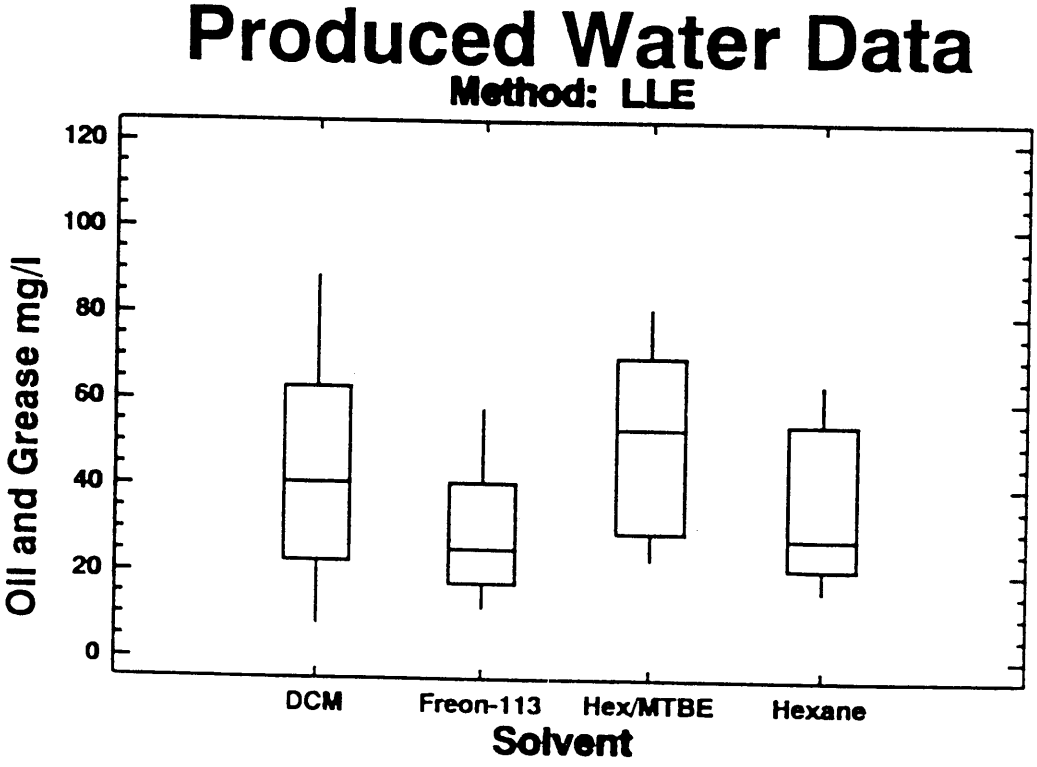


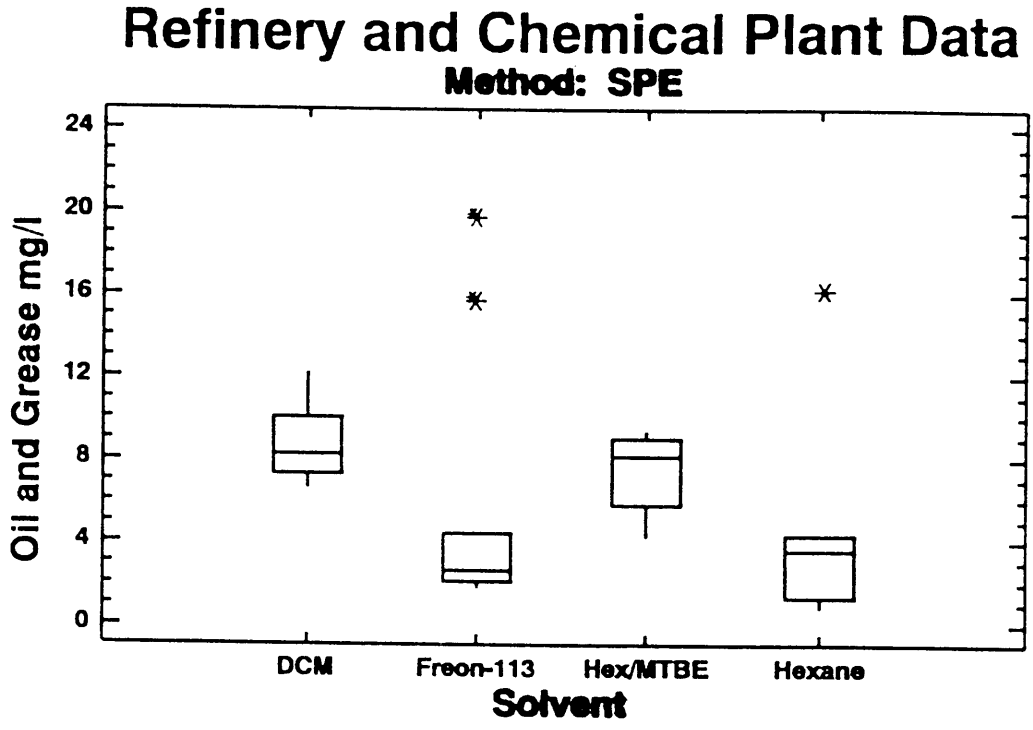
	M	W	DR	DC	PHB	PB	PEB
HEXANE	1	16.7	1.6	4.2	35.8	62.8	15.2
FREON-113	1.8	17.8	2.4	4.3	22.5	57.1	14.9
HEXANE/MTBE	9.2	8.8	8.4	4.6	47.9	100	29.5
DICHLOROMETHANE	11.7	10	8	6.9	68.6	113	86.3

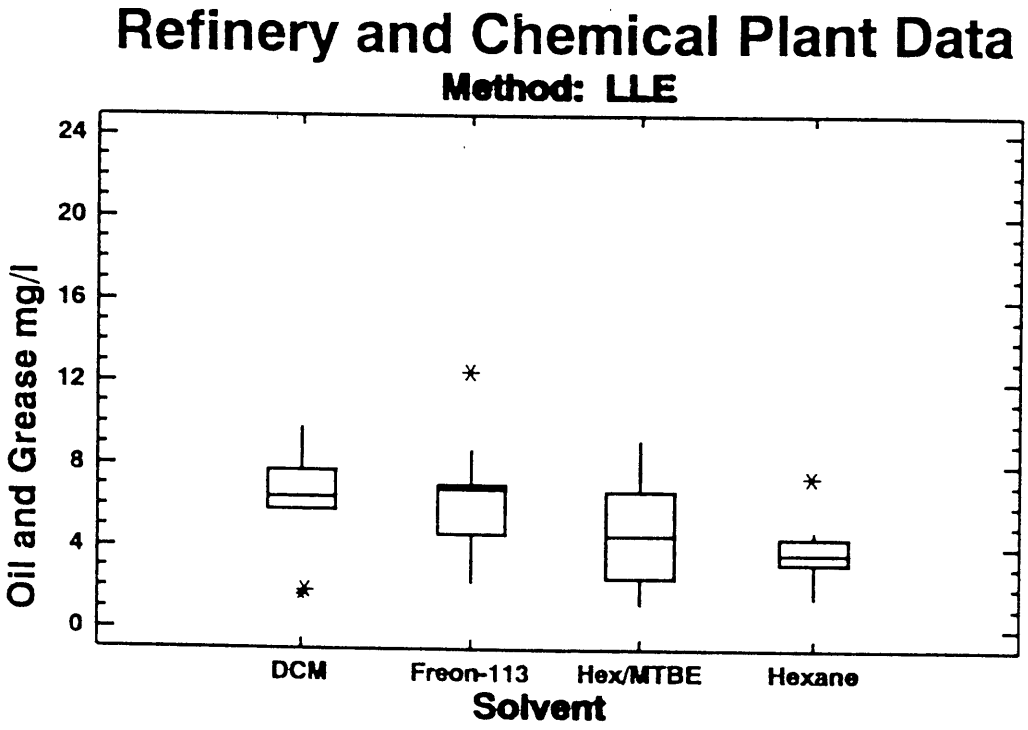
SOLVENT TYPE

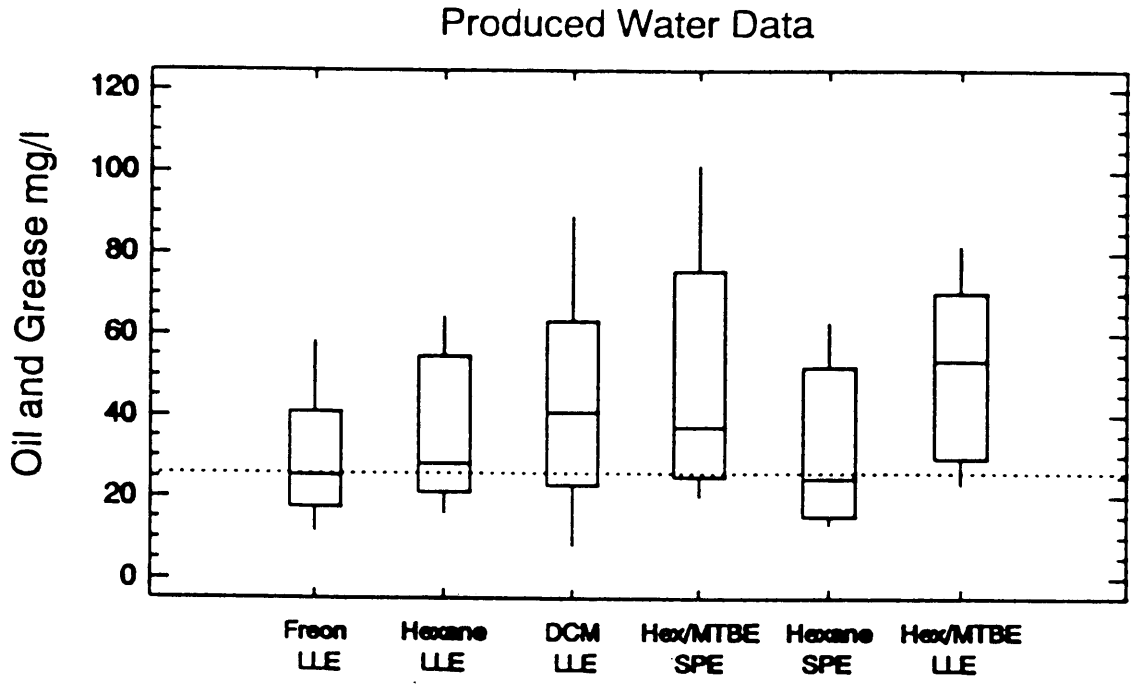
HEXANE
FREON-113
HEXANE/MTBE
DICHLOROMETHANE

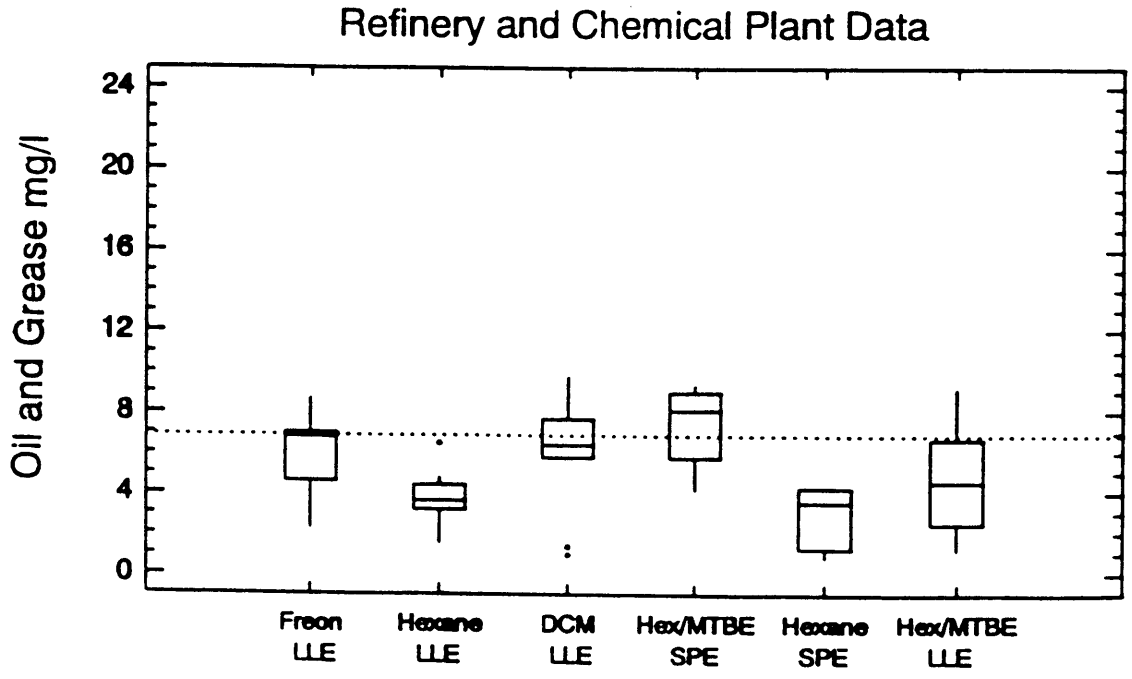

Produced Water Data
Method: SPE
Oil and Grease mg/l
120
100
80
60
40
20
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent


Produced Water Data
Method: LLE
Oil and Grease mg/l
120
100
80
60
40
20
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent

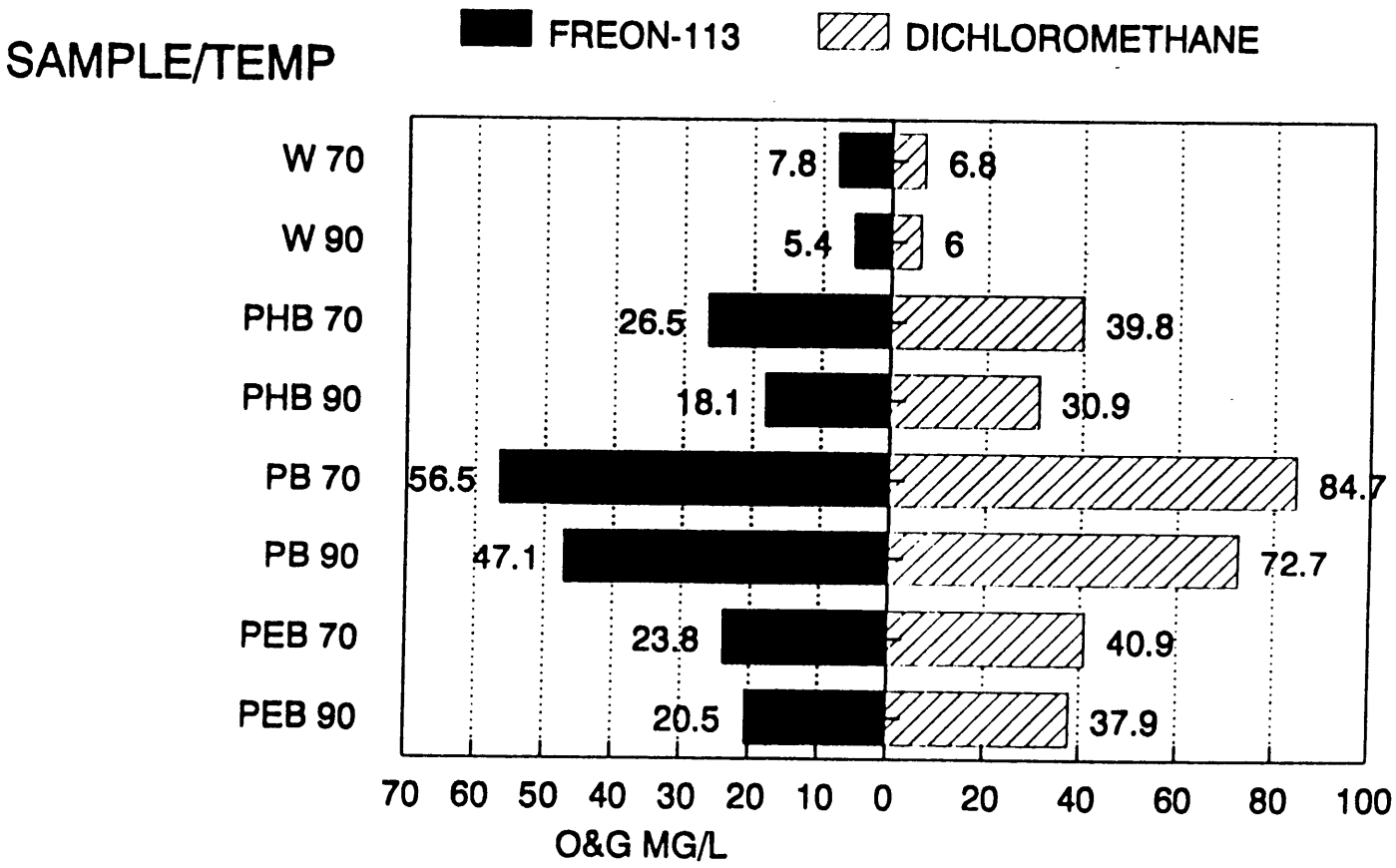

Refinery and Chemical Plant Data
Method: SPE
Oil and Grease mg/l
24
20
16
12
8
4
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent


Refinery and Chemical Plant Data
Method: LLE
Oil and Grease mg/l
24
20
16
12
8
4
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent

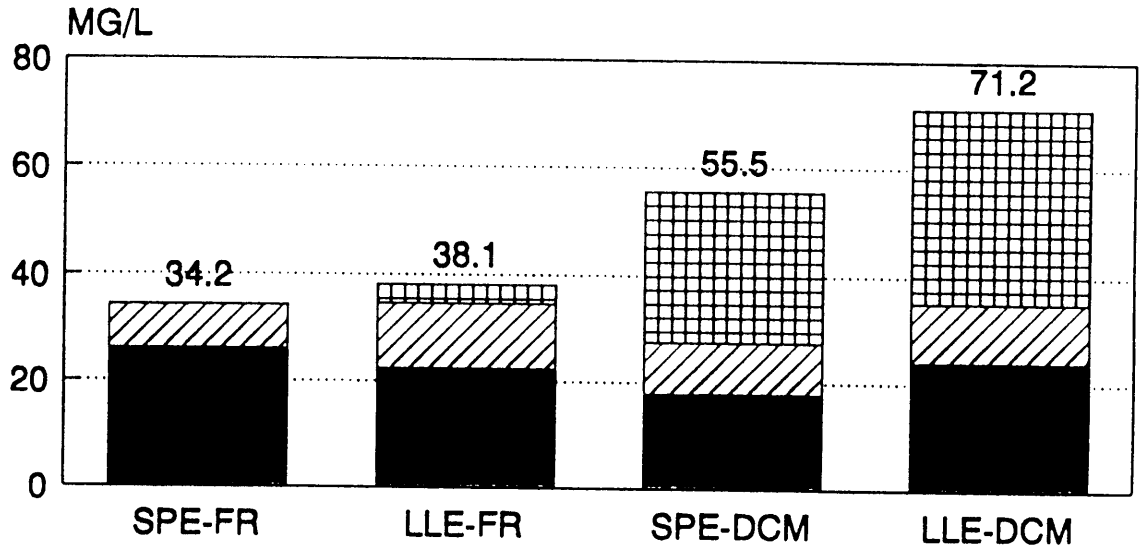

Produced Water Data
Oil and Grease mg/l
120
100
80
60
40
20
0
Freon LLE
Hexane LLE
DCM LLE
Hex/MTBE SPE
Hexane SPE
Hex/MTBE LLE


Refinery and Chemical Plant Data
Oil and Grease mg/l
24
20
16
12
8
4
0
Freon LLE
Hexane LLE
DCM LLE
Hex/MTBE SPE
Hexane SPE
Hex/MTBE LLE

OIL & GREASE ANALYSIS RESULTS BY LLE
EFFECT OF SOLVENT REMOVAL TEMPERATURE
AT 70 C & 90 C



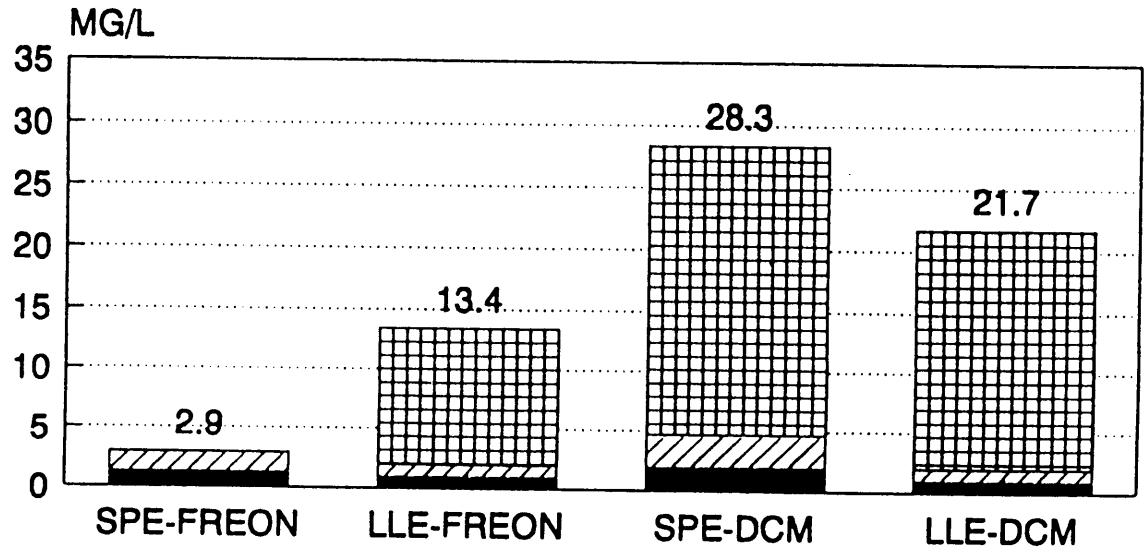
OIL & GREASE CHARACTERIZATION
SILICA GEL TREATED FRACTIONS
PRODUCED WATER EB



	SPE-FR	LLE-FR	SPE-DCM	LLE-DCM
HEAVY POLAR	0	3.5	27.9	36
POLAR	8.2	12.2	9.8	11.1
NON POLAR	26	22.4	17.8	24.1

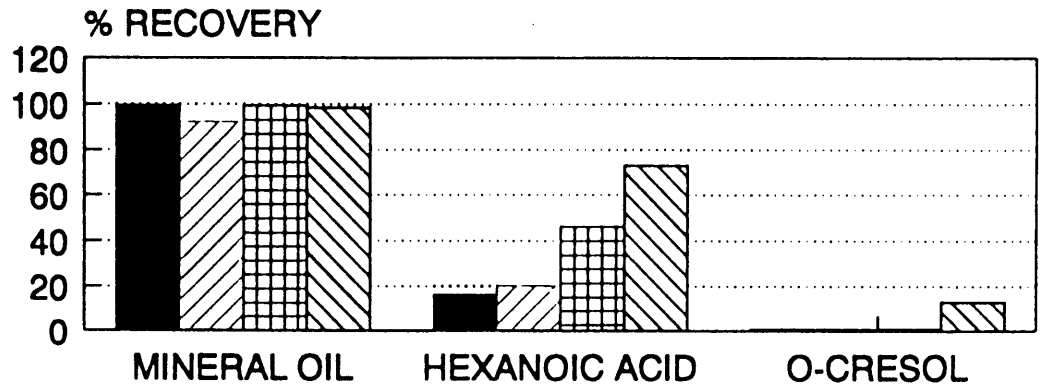
NON POLAR POLAR HEAVY POLAR

OIL & GREASE CHARACTERIZATION
SILICA GEL TREATED FRACTIONS
REFINERY WASTEWATER M



	SPE-FREON	LLE-FREON	SPE-DCM	LLE-DCM
HEAVY POLAR	0	11.4	23.6	19.7
POLAR	1.6	1	2.7	1
NON POLAR	1.3	1	2	1

OIL & GREASE ANALYSIS RESULTS
SOLID PHASE EXTRACTION
MINERAL OIL, HEXANOIC ACID, O-CRESOL



	MINERAL OIL	HEXANOIC ACID	O-CRESOL
HEXANE	99	16	1
FREON-113	92	20	1
HEXANE/MTBE	99	46	1
DICHLOROMETHANE	98	73	13

25 MG/L ACID OR CRESOL
50 MG/L MINERAL OIL

RESULTS SUMMARY

* OIL & GREASE MEASUREMENT DEPENDS ON

  EXTRACTION SOLVENT POLARITY
  EXTRACTION METHOD (LLE, SPE)
  OIL & GREASE TYPE (NONPOLAR, POLAR)
  SOLVENT REMOVAL TEMPERATURE

* O&G VALUES INCREASE WITH SOLVENT POLARITY
  BY BOTH LLE & SPE

  DCM > HEXANE/MTBE >/ FREON >/ HEXANE

* O&G VALUES BY SPE > LLE WITH HIGHER POLAR SOLVENTS

* O&G VALUES ARE LOWER WITH HIGHER SOLVENT
  REMOVAL TEMPERATURE

* SPE CAN YIELD COLUMN ARTIFACTS (SILANE)
  CONSISTENT QUALITY COLUMNS ARE NECESSARY

* INCREASED SALT INTERFERENCE OBSERVED WITH
  NON FREON SOLVENTS IN BOTH LLE & SPE

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E. E. KETTL, Statistics, Shell Development Co.

T. FAN, Analytical, Shell Development Co.

G. R. BEAR, Analytical, Shell Development Co.

ALTERNATIVE METHODS FOR OIL AND GREASE ANALYSIS WHICH USE NO CHLOROFLUOROCARBONS

Authors: J. C. Raia
D. K. Lee
P. J. Staley

Shell Development Company
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Norfolk, Virginia
May, 6-7, 1992

ABSTRACT

Because the Environmental Protection Agency (EPA) must phase out the use of chlorofluorocarbons (CFCs) in laboratory test methods, substitutes for CFCs or alternative test methods need to be adopted. In July, 1991, the EPA issued proposed analytical methods under the Clean Water Act (CWA) and the Resource Conservation and Recovery Act (RCRA) to allow the use of alternative solvents in place of chlorofluorocarbons (CFCs) in EPA test methods. EPA proposed an 80:20 mixture of n-hexane and methyl tertiary butyl ether (MTBE) solvent to replace Freon-113 in oil and grease tests. In October, 1991, EPA issued a second notice which addressed the need for additional research before a suitable replacement solvent can be selected for oil and grease tests.

In anticipation of the EPA method change to eliminate Freon-113 in the analysis for oil and grease, work was initiated by Shell Offshore Inc. (SOI), and Shell Development Company Westhollow Research Center (WRC) to evaluate alternate extraction solvents and also alternate procedures for the oil and grease test. This effort included the analysis of produced water samples from the Gulf of Mexico and west coast, and also samples of wastewater effluents from refinery and chemical plant locations.

Samples were analyzed for oil and grease by EPA Method 413.1 and with modifications to allow comparison of different solvents which included Freon-113, n-hexane, dichloromethane, and the new EPA proposed 80:20 n-hexane/MTBE solvent mixture. Data were also developed for a potentially new technique for oil and grease, solid phase extraction (SPE). The SPE method offers solvent waste reduction advantages.

Results of this continuing work are presented, which show that the oil and grease measurement will give values which will depend on the extraction solvent polarity, extraction method, and type of oil and grease present. This poses a true challenge in finding an equivalent solvent to Freon-113 for NPDES monitoring, since all existing permits have limits based on the Freon-113 method. Further work is needed at an accelerated pace with joint industry and EPA participation to evaluate and select the most suitable test method for oil and grease which uses no chlorofluorocarbons.

ALTERNATIVE METHODS FOR OIL AND GREASE ANALYSIS WHICH USE NO CHLOROFLUOROCARBONS

by

J. C. Raia, D. K. Lee, P. J. Staley

INTRODUCTION AND SUMMARY

There continues to be increasing concern that the emission of chlorofluorocarbons (CFCs) into the atmosphere causes significant depletion of the stratospheric ozone layer. In 1987, a multi-nation treaty called the Montreal Protocol was signed to control and reduce the production and use of ozone-depleting substances. In June 1990, the United States and some 100 other countries agreed to amend and strengthen the Montreal Protocol and to phase out and eventually ban the production and use of CFCs, halons, and carbon tetrachloride by the year 2000 [1,2]. The Clean Air Act Ammendments (CAAA) enacted in November 1990 (PL 101-549), by law require control and phaseout of CFCs and other listed chemicals by the year 2000, similar to and in some cases more stringent than the Montreal Protocol. Congress has recently enacted an excise tax on all ozone-depleting chemicals listed in the Montreal Protocol and in the 1990 CAAA. The phaseout is now being accelerated because of findings by recent aircraft probes of the northern stratosphere by the National Aeronautics & Space Administration.

Because the Environmental Protection Agency (EPA) must phase out the use of CFCs in laboratory test methods, substitutes for CFCs or alternative test methods need to be adopted. On July 3, 1991, the EPA issued proposed analytical methods under the Clean Water Act (CWA) and the Resource Conservation and Recovery Act (RCRA) to allow the use of alternative solvents in place of chlorofluorocarbons (CFCs) in EPA test methods (56 Fed. Reg. 30519). EPA proposed an 80:20 mixture of n-hexane and methyl tertiary butyl ether (MTBE) solvent to replace Freon-113 in oil and grease tests [3]. On October 8, 1991, the EPA issued a second notice (Fed. Reg. 50758) which acknowledged the public comments to the earlier notice, and need for additional research before selecting a suitable replacement solvent for Freon-113 in oil and grease tests.

In anticipation of the EPA method change for oil and grease, work was initiated by Shell Offshore Inc. (SOI), and Shell Development Company Westhollow Research Center (WRC) to evaluate alternate extraction solvents and also alternate procedures for oil and grease measurement. This effort included the analysis of produced water samples from the Gulf of Mexico and west coast, and also samples of wastewater effluents from refinery and chemical plant locations.

Results of this continuing work are presented in this paper, which show that the oil and grease measurement will give values which will

depend on the extraction solvent, extraction method, and type of oil and grease present. This poses a true challenge in finding an equivalent solvent to Freon-113 for NPDES monitoring, since all existing permits have limits based on the Freon-113 method. Further work is needed at an accelerated pace with joint industry and EPA participation to evaluate and select the most suitable test method for oil and grease which uses no chlorofluorocarbons.

EVALUATION OF ALTERNATE OIL AND GREASE METHODS

Samples were analyzed for oil and grease by liquid/liquid extraction (LLE) by EPA Method 413.1 [4], and with modifications to allow comparison of different solvents which included Freon-113, n-hexane, dichlormethane (DCM), and the new EPA proposed 80:20 n-hexane/MTBE solvent mixture. Data was also developed for a potentially new technique for oil and grease, solid phase extraction (SPE). The SPE method requires no CFC and offers solvent waste reduction advantages.

The boiling points of the different solvents tested required different temperatures for solvent removal from the extracts: 70 C was used for Freon-113 and dichloromethane, and 90 C for n-hexane and n-hexane/MTBE mixture. The effect of solvent removal temperature on the oil and grease value was tested.

The extracted oil and grease fractions were characterized and compared according to their non polar and polar content. The hydrocarbon (non polar) fractions were measured using silica gel treatment as in Standard Method 5520F (Standard Methods for the Examination of Water and Wastewater, 17th edition). The polar fractions were obtained as material recoverable from the silica gel by washing with methylene chloride; the heavy polar fraction was non recoverable material as determined by difference.

TEST RESULTS FOR PRODUCED WATERS AND REFINERY AND CHEMICAL PLANT WASTEWATERS

Results comparing the Freon-113 standard method with different solvents by liquid/liquid extraction (LLE) and solid phase extraction (SPE) are summarized for the samples shown in Figures 1 and 2. The data represent the mean of duplicate analyses and reflect the combined variabilities for the sampling and the analysis. Comparisons were difficult for some samples because the oil and grease values were near or below the detection limit of the method. A statistical analysis of all the data was made using a complete block design. Data comparisons are shown in box plots in Figures 3-5. The produced water data set were grouped separately from the refinery and chemical wastewater data set.

The results show that generally oil and grease values by both LLE and SPE increase with solvent polarity in the order dichloromethane > hexane/MTBE >= Freon-113 >= hexane. A solvent system based on n-hexane may be a suitable alternative to Freon-113. The single solvent gave better

precision than the solvent mixture. Oil and grease values by SPE were higher than LLE with higher polar solvents.

Sample W by SPE was atypically high for the less polar solvents relative to dichlormethane. Further analysis of this sample's hexane and freon extractable oil and grease fractions by gas chromatography-mass spectrometry revealed a substantial contamination of silane material. Blank runs of the SPE columns were generally in the 1-2 mg residue range. A consistent acceptable quality of SPE material will be a necessary requirement for application of this technique to the oil and grease analysis.

The oil and grease results reflect the temperature used to remove the solvent from the extract. Figure 6 illustrates the decrease in oil and grease with increased temperature in the solvent removal step using 70 C and 90 C.

The polar and non polar character of the oil and grease in a sample will influence the oil and grease value. Produced water and refinery wastewater samples were extracted and the oil and grease fraction then treated with silica gel. The hydrocarbon (non polar) fraction and polar fractions were measured as shown in Figures 7 and 8. The results show the more polar solvent, dichloromethane, extracts more of the very heavy polar oil and grease than does the less polar freon solvent. The amounts of hydrocarbon and polar material are more comparable by each solvent by both LLE and SPE.

FUTURE WORK

This study has shown that the oil and grease measurement will give values which will depend on the extraction solvent, extraction method, and type of oil and grease present. Because the solvent change can impact compliance to existing permit limits under the CWA, sufficient data should be collected over time for permitted discharges using the replacement solvent and method selected. Permit limits could be adjusted if necessary to account for any bias caused by the solvent change.

RCRA test methods which require the soxhlet extraction of solids such as sludges and soils need to be tested with the replacement solvent [5]. Data are also needed to determine any effect of a solvent change on the use of silica gel in oil and grease methods - Method 418.1 for Total Petroleum Hydrocarbons (TPH), and Method 5520F (Standard Methods for the Examination of Water and Wastewater, 17 th ed.).

Gas Chromatography techniques which use no CFC should also be standardized for TPH analysis.

New solvents need to be found which are compatible with IR analysis methods for oil and grease. Direct oil in water analyzers which require no solvent extraction need to be evaluated and further developed if necessary with improved reliability.

The SPE technique, which does not require CFC and has reduced waste solvent advantages, shows promise as a potential alternate technique for oil and grease but needs further testing and optimization. Consistent SPE cartridge performance is a necessary requirement.

The safety and human health concerns of alternate solvents need to be addressed.

This work is needed at an accelerated pace with joint industry and EPA participation to evaluate and select the most suitable test method for oil and grease which uses no chlorofluorocarbons.

ACKNOWLEDGMENTS

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REFERENCES

1. 56 Fed. Reg. 30519, July 3, 1991: Guidelines Establishing Test Procedures for the Analysis of Pollutants; Identification and Listing of Hazardous Wastes; Test Methods

2. Chemical and Engineering News, July 9, 1990 pp. 6-7.

3. A Report on Additional Work Done by the Environmental Monitoring Systems Laboratory-Cincinnati To Find the Most Suitable Solvent to Replace Freon-113 for the Gravimetric Determination of Oil and Grease, October 22, 1990.

4. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 March 1979, Revised March 1983.

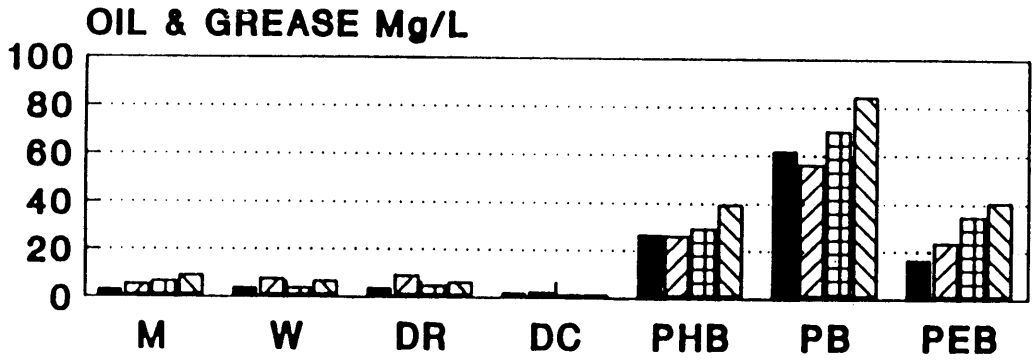
5. Test Methods for Evaluating Solid Wastes Chemical/Physical Methods, SW-846, 1986.

6. Sax, N. I. Dangerous Properties of Industrial Materials, 7th ed., Van Nostrand Reinhold, New York, 1989.

7. Proctor, N. H., et. al. Chemical Hazards of the Workplace, 2nd ed., J. B. Lippincott, Philadelphia, 1988.

FIGURE 1

OIL & GREASE ANALYSIS RESULTS
ALTERNATE SOLVENTS COMPARISON
BY LIQUID/LIQUID EXTRACTION



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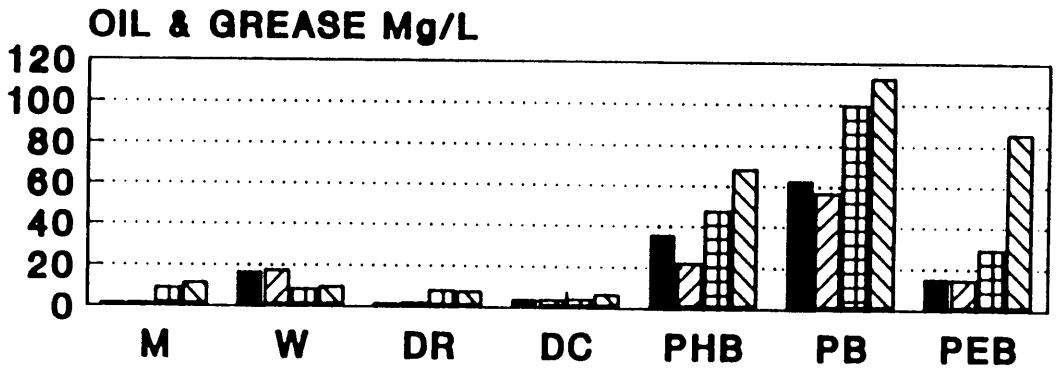
DICHLOROMETHANE	9.3	6.8	6.4	1.2	39.8	84.7	40.9

SOLVENT TYPE

HEXANE
FREON-113
HEXANE/MTBE
DICHLOROMETHANE

FIGURE 2

OIL & GREASE ANALYSIS RESULTS
ALTERNATE SOLVENTS COMPARISON
BY SOLID PHASE EXTRACTION



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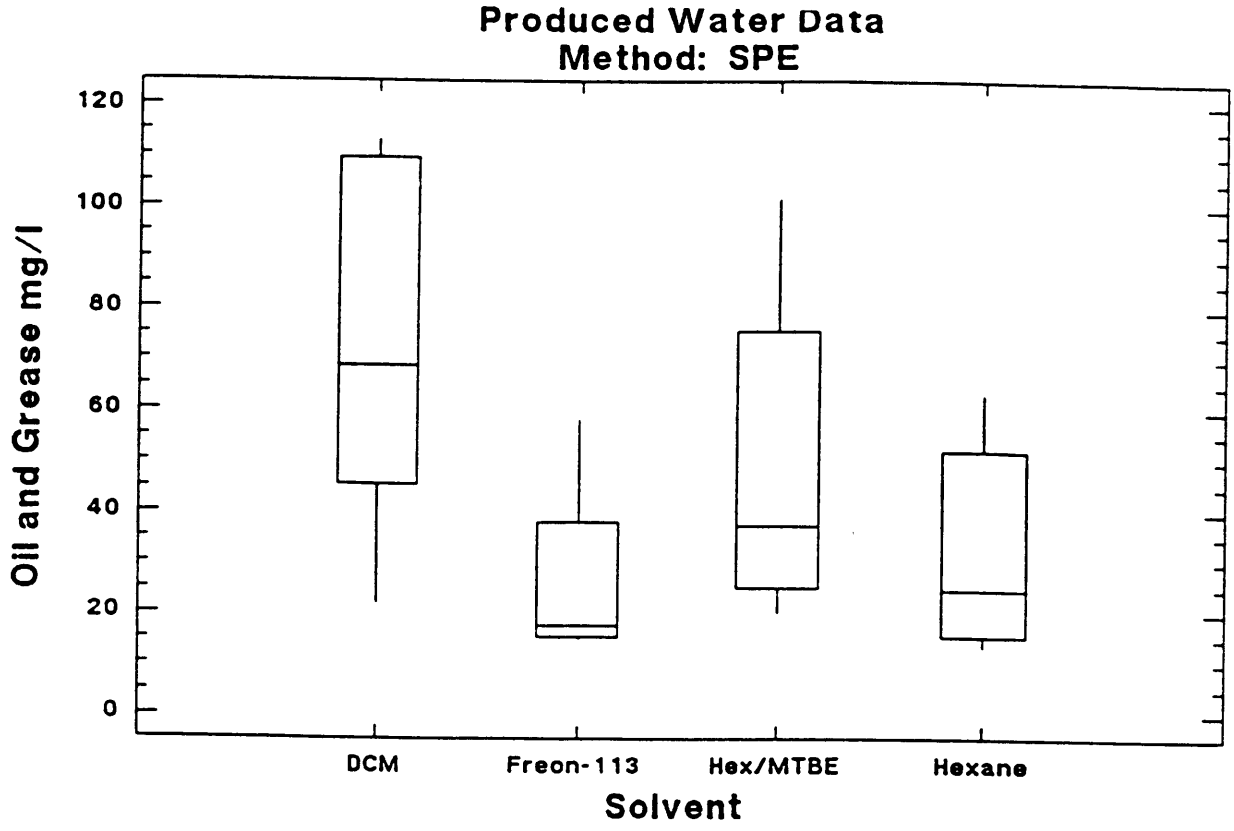
DICHLOROMETHANE	11.7	10	8	6.9	68.6	113	86.3

SOLVENT TYPE

HEXANE
FREON-113
HEXANE/MTBE
DICHLOROMETHANE

FIGURE 3

335


Produced Water Data
Method: SPE
Oil and Grease mg/l
120
100
80
60
40
20
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent

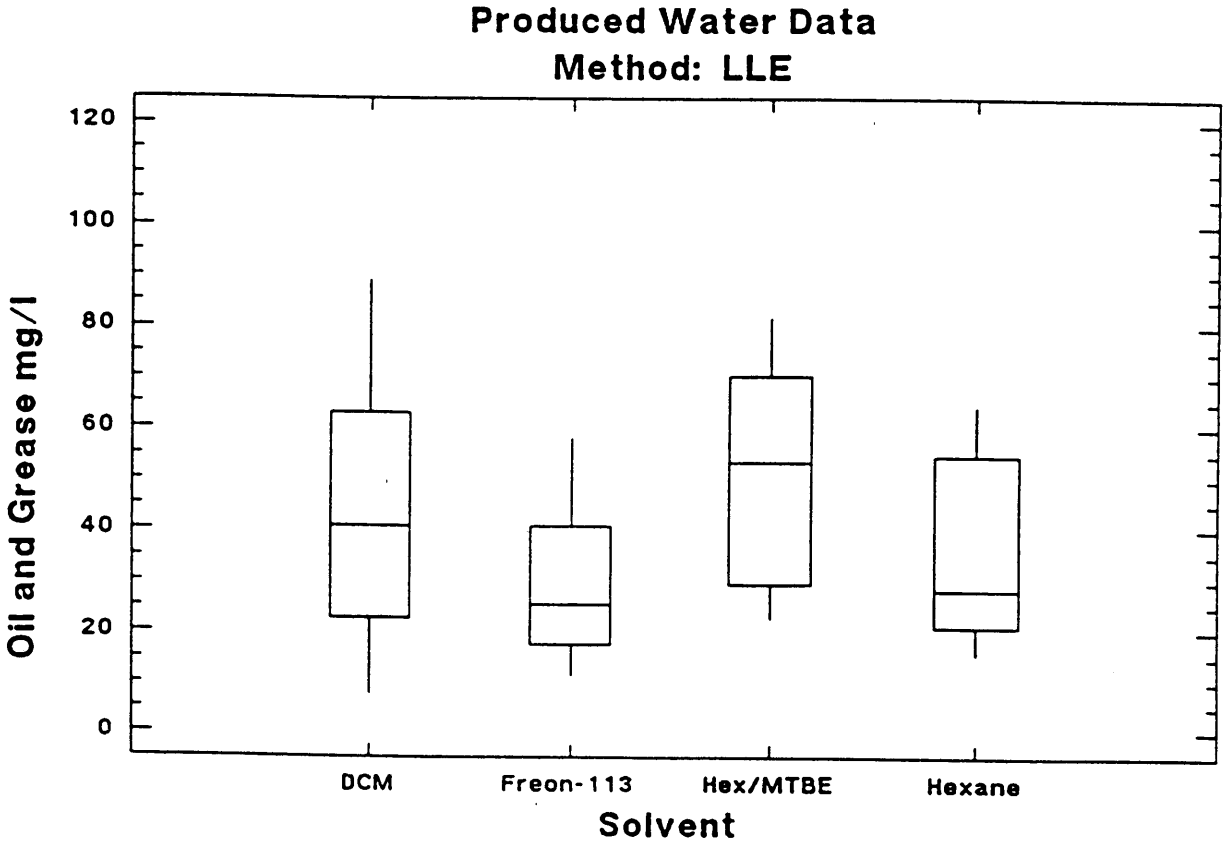
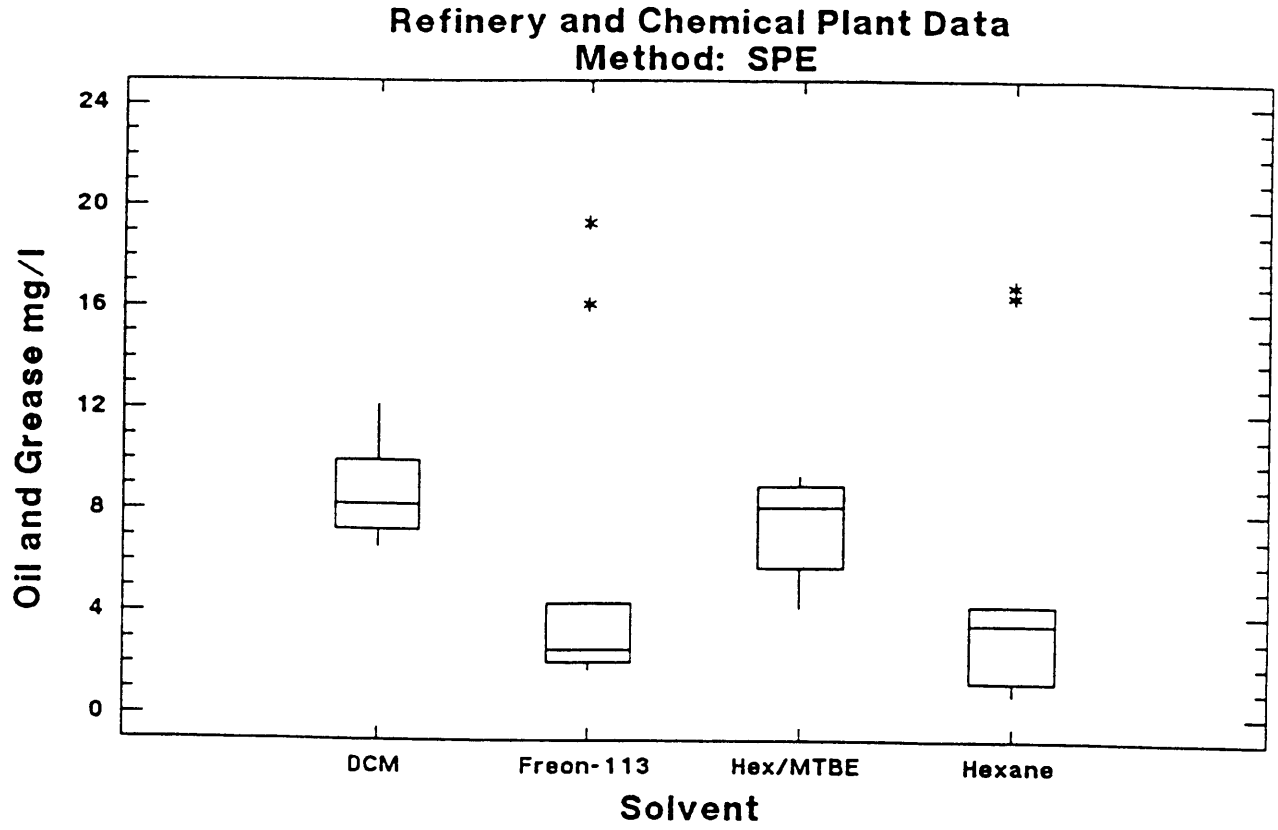

Produced Water Data
Method: LLE
Oil and Grease mg/l
120
100
80
60
40
20
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent

FIGURE 4


Refinery and Chemical Plant Data
Method: SPE
Oil and Grease mg/l
24
20
16
12
8
4
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent

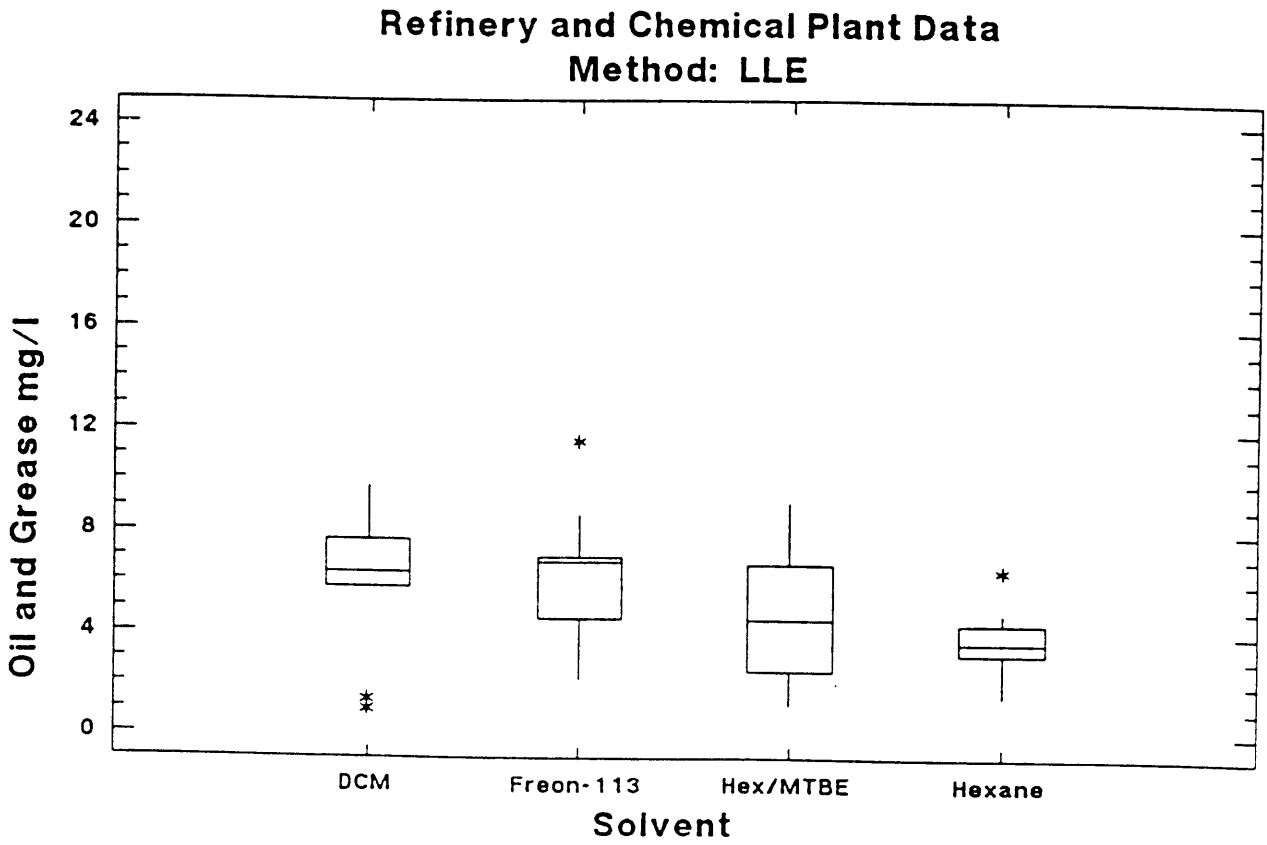
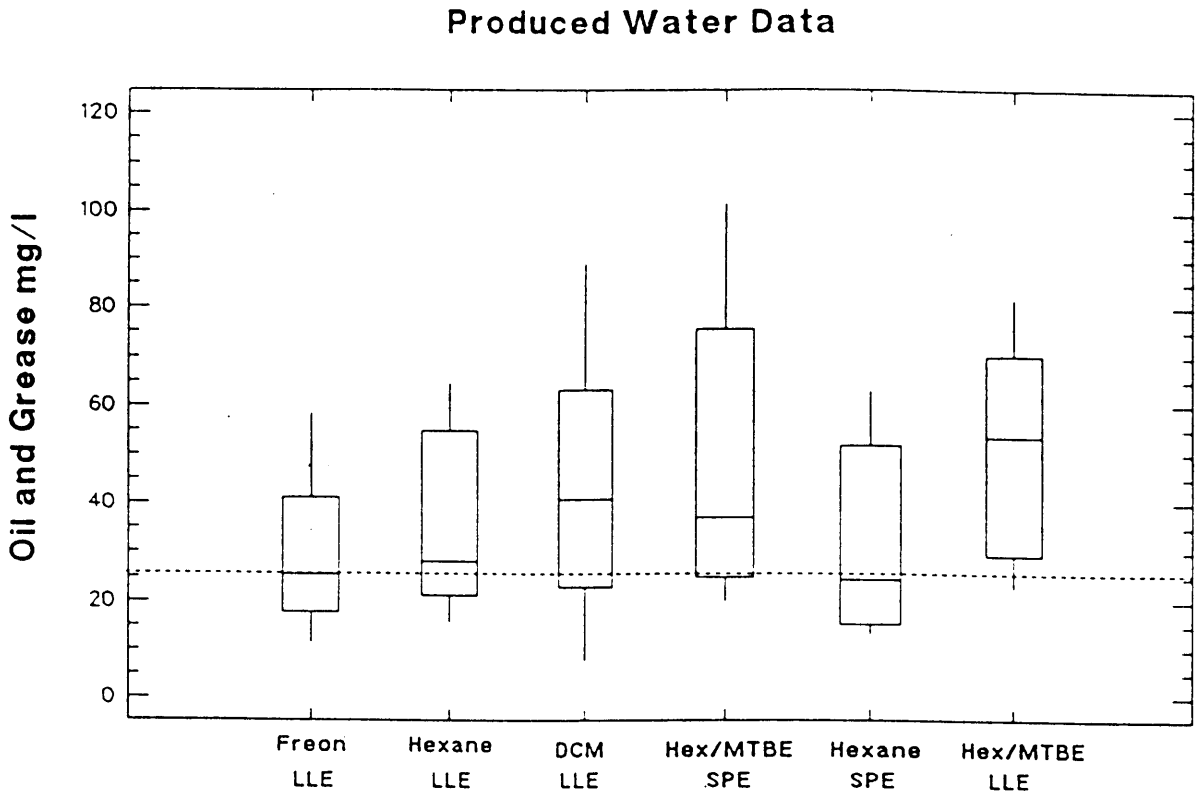

Refinery and Chemical Plant Data
Method: LLE
Oil and Grease mg/l
24
20
16
12
8
4
0
DCM
Freon-113
Hex/MTBE
Hexane
Solvent

FIGURE 5


Produced Water Data
Oil and Grease mg/l
120
100
80
60
40
20
0
Freon LLE
Hexane LLE
DCM LLE
Hex/MTBE SPE
Hexane SPE
Hex/MTBE LLE

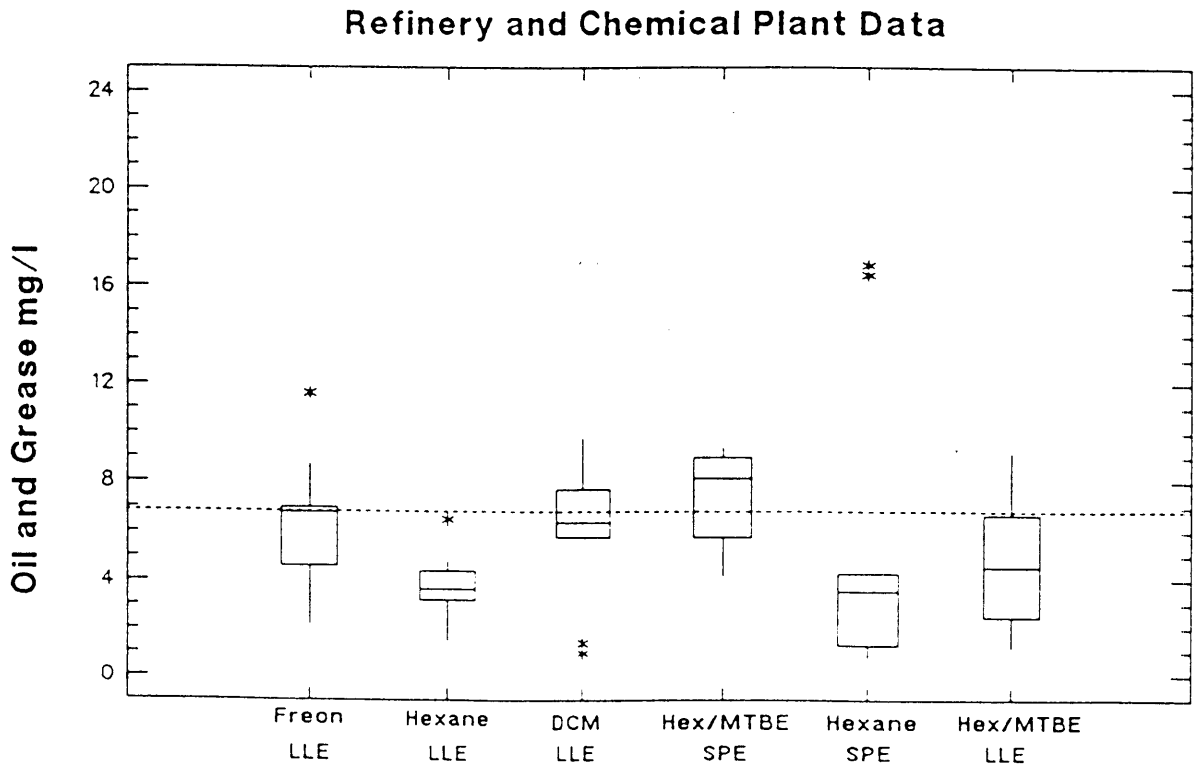

Refinery and Chemical Plant Data
Oil and Grease mg/l
24
20
16
12
8
4
0
Freon LLE
Hexane LLE
DCM LLE
Hex/MTBE SPE
Hexane SPE
Hex/MTBE LLE

FIGURE 6

OIL & GREASE ANALYSIS RESULTS BY LLE
EFFECT OF SOLVENT REMOVAL TEMPERATURE
AT 70 C & 90 C

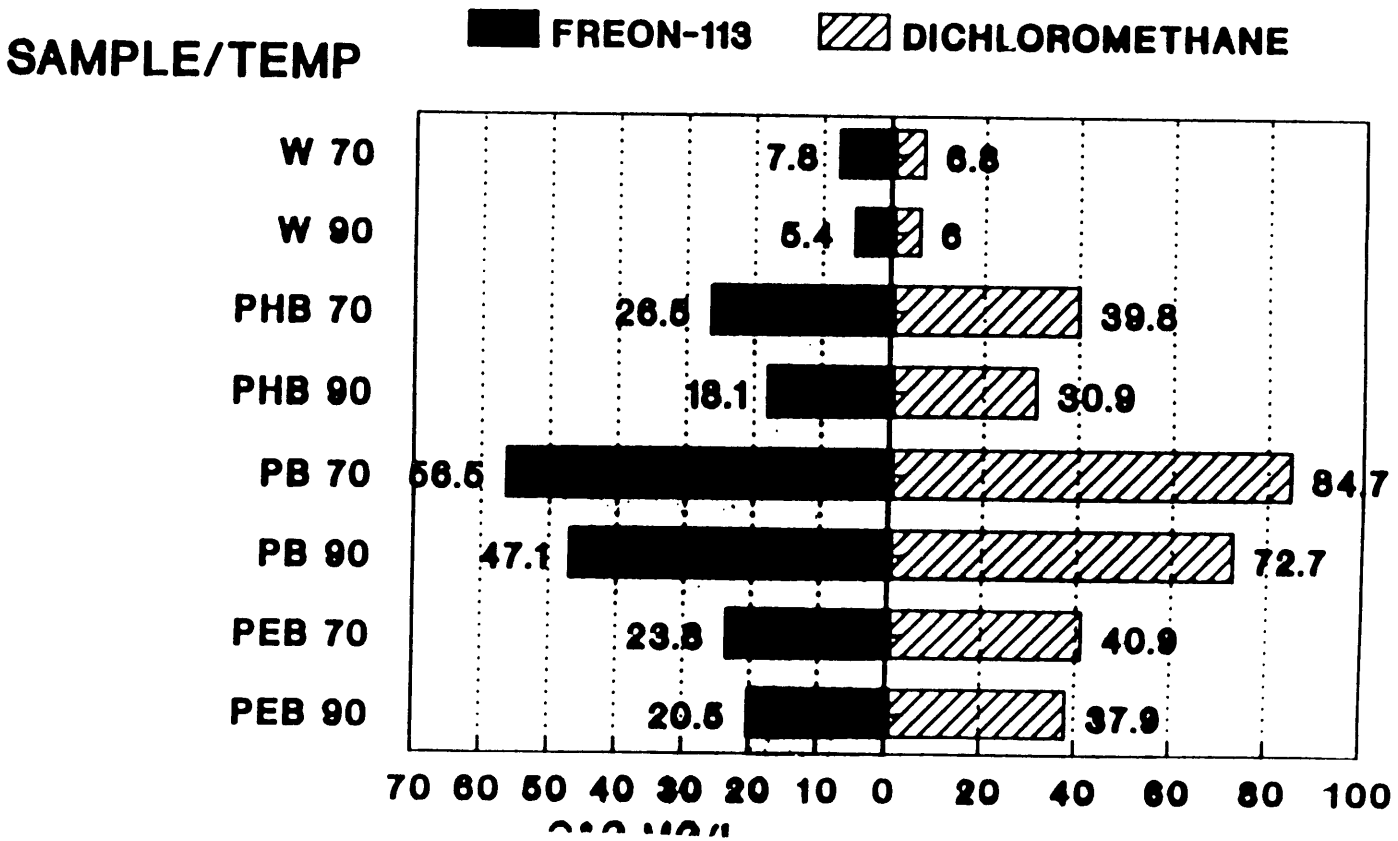


FIGURE 7

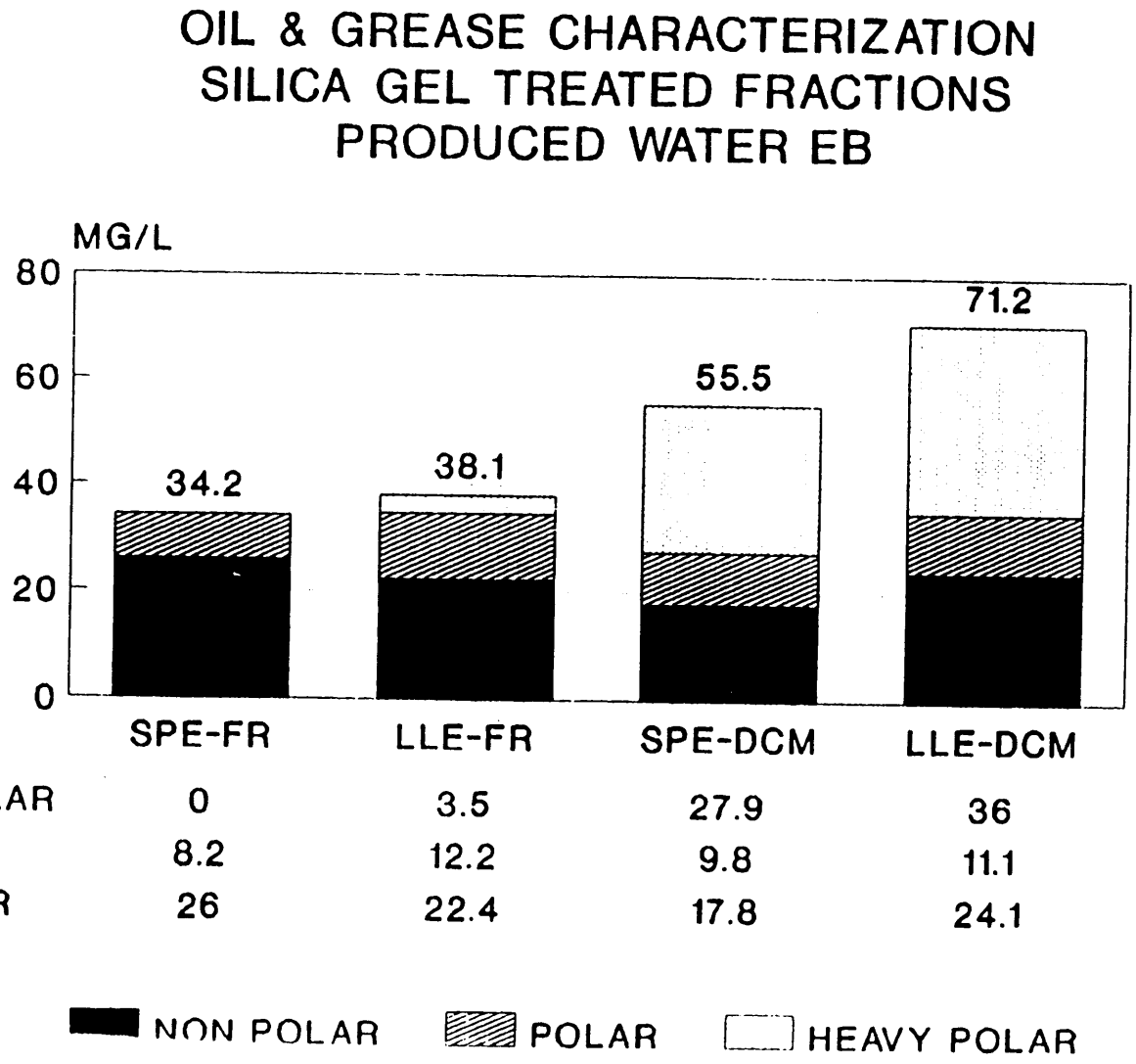
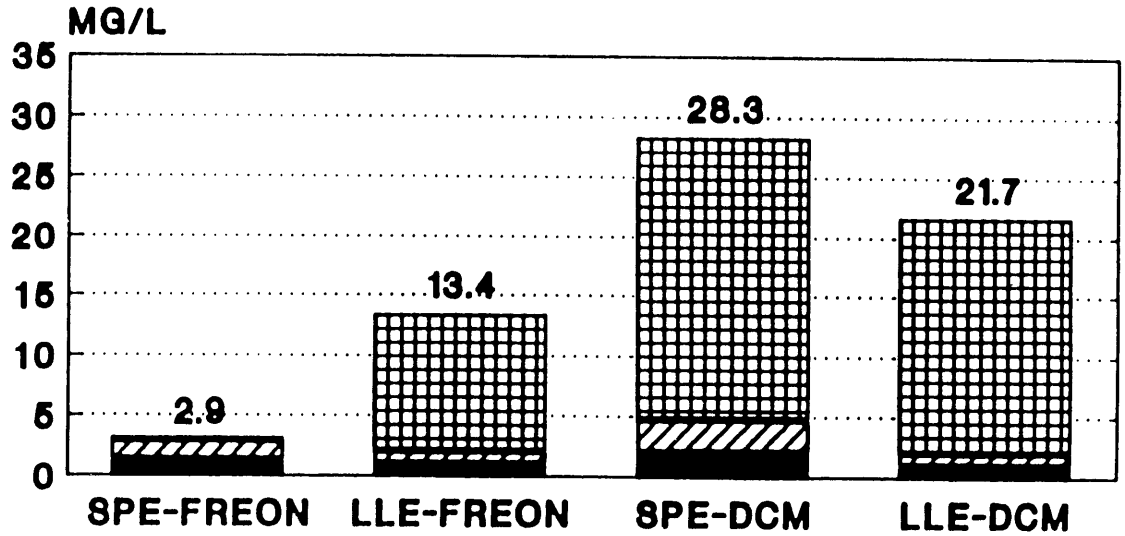

OIL & GREASE CHARACTERIZATION
SILICA GEL TREATED FRACTIONS
PRODUCED WATER EB
MG/L
80
60
40
20
0
34.2
38.1
55.5
71.2
SPE-FR
LLE-FR
SPE-DCM
LLE-DCM
HEAVY POLAR 0 3.5 27.9 36
POLAR 8.2 12.2 9.8 11.1
NON POLAR 26 22.4 17.8 24.1
NON POLAR
POLAR
HEAVY POLAR

FIGURE 8

OIL & GREASE CHARACTERIZATION
SILICA GEL TREATED FRACTIONS
REFINERY WASTEWATER M



	SPE-FREON	LLE-FREON	SPE-DCM	LLE-DCM
HEAVY POLAR	0	11.4	23.6	19.7
POLAR	1.6	1	2.7	1
NON POLAR	1.3	1	2	1

NON POLAR POLAR HEAVY POLAR

MR. TELLIARD: One of the approaches that we are looking at is also a reduction in solvent use by micro or semi-micro extraction. Paul Epstein is going to talk about that now and see where it goes. Paul?

MR. EPSTEIN: When we started using the term microextraction, the first thing that came to mind is an itty-bitty separatory funnel. We don't do that.

I would also like to say before I get into the body of the talk is that the organization I represent used to be called the National Sanitation Foundation. It was always referred to as NSF, however, we finally changed our name legally to NSF International which causes some confusion with that other NSF that works out of Washington, but we had the initials first.

I will be describing the analysis of several unused compounds compared to what people have been talking about today. NSF runs a program called the Drinking Water Additives Program.

In 1988, EPA turned over to a consortium led by NSF this program to certify and test possible health effects of either chemicals or any indirect or direct additives put into drinking water. This little cartoon kind of illustrates the process that we go through.

The judge sitting up at the top represent the regulatory agencies. The tap at the end is the public water supply, and in between, you have people putting chemicals into the water, people manufacturing pipes, and NSF examining everything that goes on.

We consider our client base to be tri-fold. It is the regulatory agencies, the public, and the manufacturer of the items that we test and certify.

Just some quick definitions. An additive, a term which I will be often, is any chemical added in any form to drinking water; and a contaminant is any physical, chemical, biological, or radiological substance that is in water. That is the definition from the Safe Drinking Water Act.

We deal in two types of additives. Direct additives are additives that are added deliberately in the water treatment process. Indirect additives are contaminants that may come out of the drinking water transmission process from the pipes, materials,

coatings, paint, anything at all that comes into contact with drinking water.

We have two standards that deal with these additives. Standard 60 covers the direct additives; Standard 61 covers the indirect additives. These standards, again, examine only potential health effects. We don't test the performance of products. Everything is driven by health effects, and it is all driven by a toxicology department.

I am going to give you some quick examples of additives. I don't want to dwell on this, because there are many products. The direct additives include coagulation, flocculation chemicals, scale, corrosion, softening, pH control, disinfection and oxidation (ozone and chlorine), chemicals, and also possible additives in well drilling muds, and antifreeze.

The indirect additives provide a much broader scope of products that we test. We test these products to see if they are adding anything to the drinking water. Again, we are not testing the products for performance. We don't care how well they do what they say they are supposed to do. We are testing to see if there is anything at all leaching out as the drinking water passes by these products.

There are many different categories of indirect additives. There is pipes and related products, protective barrier materials, joining and sealing materials. The protective barrier and the joining and sealing materials generate many unusual chemicals that we have to identify, and later on in the talk, you will see the table of chemicals that we have worked on in the past few months.

There are also process media that go into water purification. These are generally media that are used at water treatment plants. And there is mechanical devices. There are feeders, pumps, valves, meters.

There are two new sections to the standard that haven't been accepted yet. Section 9 which is getting close to acceptance will be looking at faucets, valves, and anything of that type, any mechanical valve material.

And there is a new section that we are looking at that doesn't affect that many people. EPA asked us to go ahead and start working on it. This section covers rainwater catchment materials for people who get their water from rain. There are sections of the country where that is important. So, we will be testing paint that is put

on roofs that the water runs down before it gets caught by cisterns.

Our process includes a complete formulation review by the toxicology department. They get formulation information from the manufacturers and, in some cases, go two and three levels deep. If a manufacturer submits a product, they may look at it and say well, that product is manufactured, so we need that manufacturer's submission.

This particular process sometimes can take anywhere up to a year to get complete formulation information. Once the toxicology department has this formulation, they select analytes that they want the laboratory to test, and this is where the fun really starts for the laboratory.

We then get the products, and we try and simulate real world use of the product. We call this simulation an exposure. We treat the product with a very aggressive water. It is usually either a pH 5, 8, or 10 buffered water that hss similar characteristics to standard drinking waters, but it is as aggressive as possible toward the analytes of interest.

When we are looking for metals, we use the high and low pH water; when we are looking for organics, we use the pH 8 water.

The laboratory then reports back its results to the toxicology group who then takes these results and normalizes them based on expected usage and determines what the potential human exposure is at the tap from that chemical.

Potential analytes include metals, screens, and organics. The organics include anything that you can imagine that goes into any plastic or metal product; anything that comes into contact with drinking water.

We are testing a whole series of coatings now that are used to coat the inside of water storage tanks. We test barrier materials. A hot issue right now is the concrete that goes into concrete pipe, since there are some concerns that some of the concrete is manufactured by burning hazardous waste in the concrete kilns.

The typical expected MDLs that the toxicology group asks us to provide are 1 to 20 parts per billion. These are adjustable, because we have some control over the amount of sample that we can expose. If we can't get a low enough detection limit,

we try and raise the surface area to volume of the sample exposure.

We get 1 to 2 requests per week from toxicology to analyze for new chemicals that we have never done before. They are usually not amenable to the standard methods.

There are two groups in our lab. There is the group that performs all the regular methods and runs similar to a commercial laboratory.

Then we have the small group that does method development and tries to do method development on a production line basis.

The resources of this particular group are limited to one full-time senior chemist. She has limited resource available to her at all times. We try and develop methods that are amenable to GC/FID and GC/EC.

The bright side of what we do is that we are not in the real world, and greater than 95 percent of our samples are potable water or something that looks like potable water. We don't test sludges, we don't test soils, we don't test oil and grease, we don't test any of the things that people have been complaining about all day. So, there are some advantages to doing our type of work.

The disadvantages are what we call the analytes from hell, the water soluble glycol ethers and amines that we are trying to determine down at the low part per billion level. We struggled with these for about a year and came up with the methods that I am going to talk to you about which coincidentally use very small solvent volumes and fit in with the topics that we are talking about today.

We have three different procedures. The glassware involved is usually a 40 ml volatiles vial. We don't have to clean sep funnels. We don't have to worry about cross contamination, because we throw the vials away when we are done.

This is a neutral extraction method. It is really something we used to call a shake and bake when I was in commercial labs where you just add a small amount of solvent, shake it very hard for a couple of minutes. In some cases, for example, the amines, we add sodium hydroxide to raise the pH. We add sodium chloride to salt it out. We extract with 1 ml of methylene chloride. After 2 minutes, we take the methylene chloride out with a Pasteur pipette and analyze it directly by GC/FID.

It is a very simple method. You can test anywhere from 5 to 10 samples an hour. It gives us the detection limits that we need, and in order to generate a high confidence that the numbers are correct, we prepare what we call "standards prepared as samples."

We will do our linearity set by spiking the standards into the same type of water that we are extracting, whatever the buffer is, extracting the standards and then doing external standard GC quantitation.

We also occasionally analyze 100 ml sample volumes in which case we get a slightly greater concentration effect, but we found that, for the purposes of the detection limits we need to reach, it doesn't make that much of a difference.

The primary aliphatic and aromatic amines were compounds that were difficult to analyze. Again, the toxicology group wanted 1 to 20 parts per billion, and the best we were able to do was about 1 to 5 parts per million by direct water injection GC/FID.

One of the nice things about having somebody fresh out of school working for you is that they come in with a totally different perspective on the world. Never having done environmental chemistry, Kris Kurtz who is one of the co-authors, just started to do real chemistry and looked for some possible derivatives of the aliphatic amines that would solve the problem we were having, they just would not extract out of the water.

We had tried some solid phase extraction, and what we found there was that once it was on the column, you just couldn't elute it off. It was too polar and too strong a hydrogen bonding material.

Kris went ahead and did some bookwork and came up with a benzaldehyde derivative which is also a very simple technique. You add 20 ml of benzaldehyde and allow it to react, and it forms an imine. I will show you the chemistry on the next slide.

You salt it out, extract it with methylene chloride, allow it to settle, and sample the methylene chloride layer.

The only problem with this method is it is not very hardy. The derivatives don't last a whole long time, so you really need to do your extraction and inject the

sample as soon as possible.

The chemistry is fairly simple. If you take your primary amine, react it with benzaldehyde, you get an imine which is a lot less water soluble and, therefore, extractable.

Here are some chromatograms. The benzaldehyde derivatives are in the upper right-hand corner. The one on the left is a n-butylbenzene sulfonamide which is a neutral, underivatized example.

These are detection limit chromatograms. We consider our detection limit the low standard. We don't do statistical detection limits, because we need to guarantee to the toxicology group that if we need to see something at a level that they have said is toxicologically significant, we could have seen it if it were present in the sample.

The other method that we use for primary aromatic amines is based on the OSHA 57 method for methylenedianiline. It is a heptafluoro-butyric acid anhydride derivative (HFAA). Again, it is a very simple method. It is also performed in a 40 ml VOA vial.

We add 1 ml of half-normal sodium hydroxide, extract with 2 ml of toluene, allow the toluene layer to separate, pull it out, add 25 microliters of the HFAA reagent directly to the sample, add 1 ml of pH 7 buffer, shake, and then analyze the extract by GC/ECD.

The big difference between this and the benzaldehyde method is that the primary aliphatic amines are derivatized before they are extracted. These compounds which are a little less soluble in the water can be extracted first and then derivatized.

This is a series of three injections of 5-chloro-ortho-toluidine using the HFAA method. The first one is at 3.5 parts per billion. This middle one is at 1.8 parts per billion, and the last one which is actually below our reported detection limit is .7 parts per billion. We report this one at a 1 part per billion detection limit.

I have got several slides now showing you some of the compounds that we have analyzed in the last few months. They are not the normal compounds that you see in environmental chemistry, but they are significant, because they are in products that might be in the water transmission system.

There are several glycol ethers which have a typical detection limit of 20 parts per billion. The one that is a fairly low boiler has a detection limit at 50. The butylphenylglycidyl ether has a detection limit of 5 parts per billion.

Hydroxymethylpentanone is 50. That is a compound that can be analyzed by other methods, but we chose to analyze it by this method.

The n-butylbenzenesulfonamide had a detection limit of 10 parts per billion.

These are some of the amines that are done by straight extraction. On the next slide, I will show you some of the benzaldehyde derivatives.

We have analyzed some pure hydrocarbons, the vinylcyclohexane, and vinylcyclohexane dioxide. Again, you can see the third column over has the detection limits, and they are anywhere from 1 to 50 parts per billion. Most of them are under 20.

These are the derivatized samples. We have done ethylenediamine, 1,6-hexanediamine, and isopheronediamine...by the benzaldehyde method, and we get detection limits of either 5 or 50.

The last five compounds were all done using the heptafluoro-butyric acid anhydride derivative. All five of those have detection 1 part per billion.

Again, this derivatization method is based on OSHA 57 for 4,4/methylene dianiline which is basically the same method. It is collected, I believe, either on a tube or a filter, desorbed into water, and then derivatized and extracted.

That is the end of my talk. These methods are just one more tool in our toolbox of different techniques. It has turned out to be very valuable, because, other than the fact that it is quick, it does use a very small amount of solvents, it doesn't use expensive glassware, one person can prepare the samples and analyze them fairly quickly, and as you can see from the list, we developed methods for about 20 compounds in the last 6 months using this technique.

Anybody have any questions?

MR. TELLIARD: Questions?

(No response.)

MR. TELLIARD: Thank you, Paul.

MICROEXTRACTION: A GENERAL SAMPLE PREPARATION METHODOLOGY FOR PPB LEVEL DETERMINATIONS OF ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY.

P.S. Epstein, K.S. Kurtz, and F. Forozesh
NSF *International*

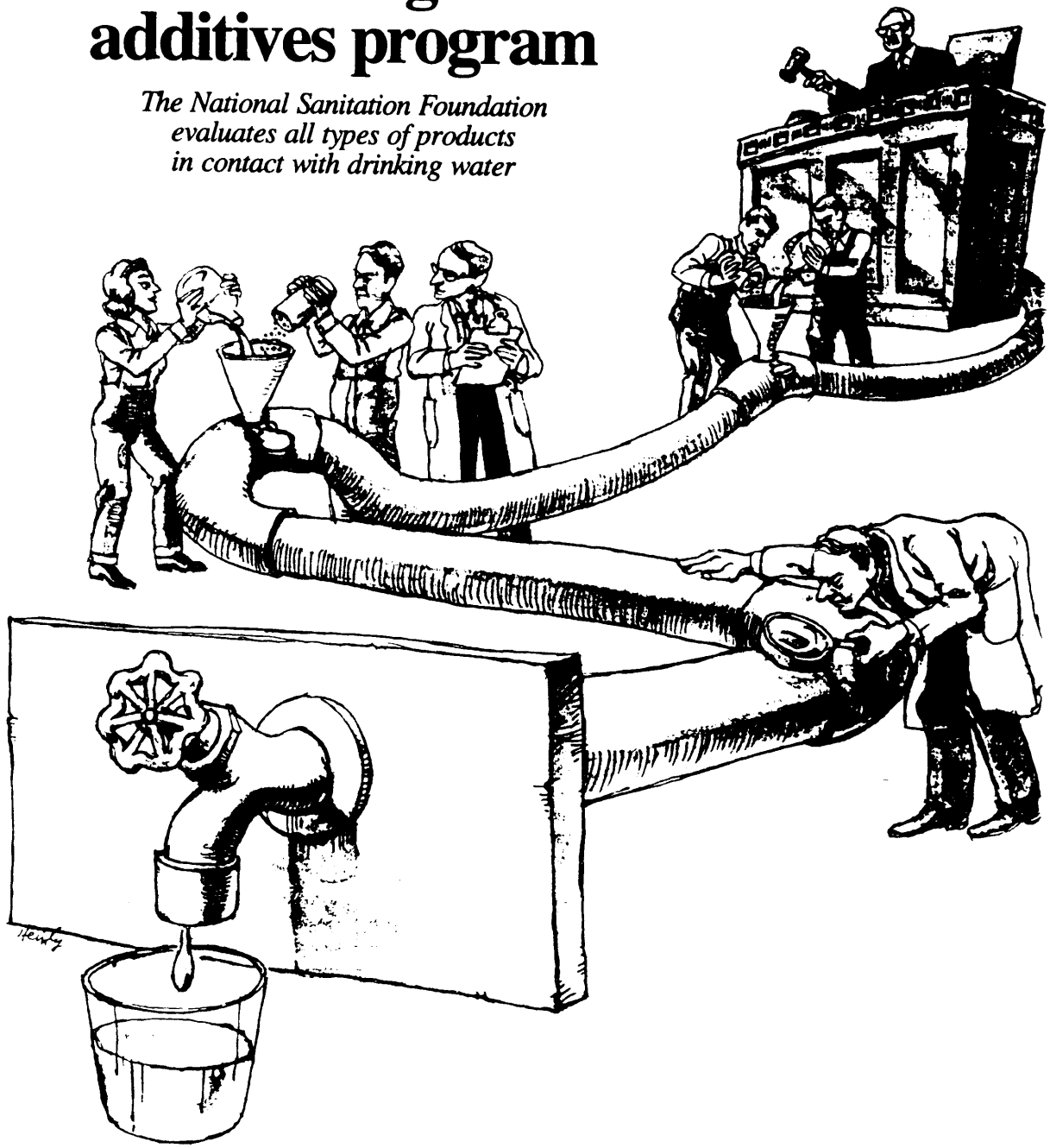
3475 Plymouth Road, Ann Arbor, MI 48105
Phone: (313) 769-8010, Fax: (313) 769-0109

DEFINITIONS

Additive	Any chemical added in any form to drinking water.
Contaminant	Any physical, chemical, biological, or radiological substance or matter in water.
Direct Additive	Contaminants added to water in the production of drinking water.
Indirect Additive	Contaminants that are introduced to drinking water through contact with surfaces of materials or products used for its treatment, storage, transmission, and/or distribution.

The drinking-water additives program

The National Sanitation Foundation evaluates all types of products in contact with drinking water



NSF *International* has two Standards (ANSI/NSF 60 & 61) that relate to real and potential health effects associated with products used to treat, store, and distribute drinking water.

EXAMPLES OF INDIRECT ADDITIVES

Pipes and Related Products	Fittings Couplings Pipes Tubing Well Screens
Protective (Barrier) Materials	Coatings/Linings - Vehicles, Pigments, Solvents, Additives Concrete Admixtures Concrete Release Agents Concrete Sealers Diaphragms - Bladders Sheet Liners Thermoset and Thermoplastic Polymers Rubber and Rubber Chemicals
Joining and Sealing Materials	Adhesives Brazing Materials Solders - Fluxes Caulks Gaskets Grouts Lubricants O-Rings Packing Primers Sealers

EXAMPLE OF INDIRECT ADDITIVES (CONT.)

Process Media

Adsorption Media Activated Alumina Aeration Packing Material
Carbonaceous Resins Chelating Polymers Granular Activated
Carbon Powered Activated Carbon
Filtration Media Aluminum Silicates Anthracite Diatomaceous Earth
Garnet Gravel Ilmenite
Ion Exchange Resins
Oxidative Media
Sand
Synthetic Media

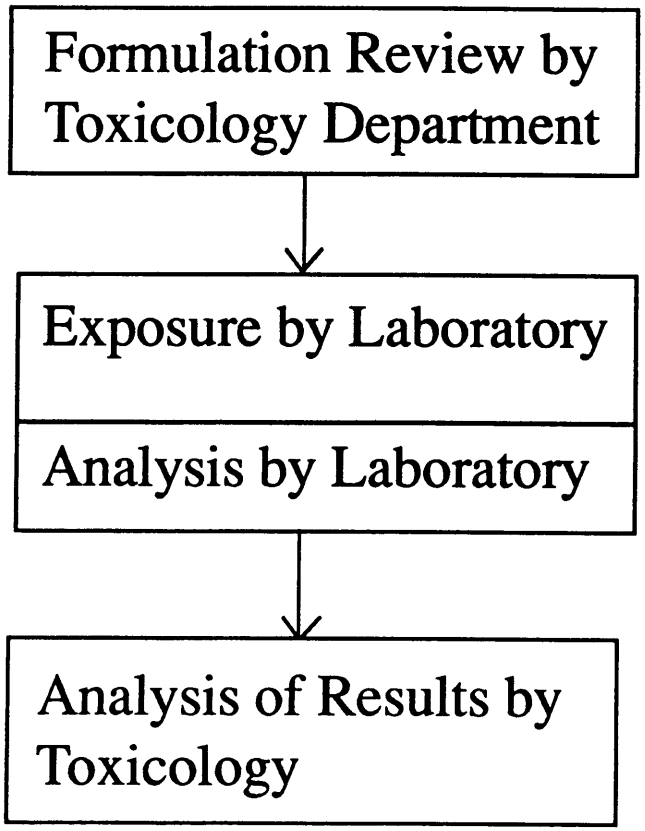
EXAMPLE OF INDIRECT ADDITIVES (CONT.)

Mechanical Devices	Feeders
	Pumps
	Disinfection Generators
	Wire and Switches on Submersible Pumps
	Valves and Fittings in the Distribution System
	Process Treatment Devices Aeration, Clarification, Filtration, etc.

EXAMPLES

Direct Additives	Coagulation and Flocculation Chemicals
	Scale, Corrosion, Softening, pH control, Disinfection and Oxidation, Well Drilling chemicals, Anti-freeze

THE PROCESS



Selects analytes for testing

Simulate Real World use of the product

Normalization based on usage. What is potential human exposure at the tap

POTENTIAL ANALYTES

Metals

Screens (TKN, TOC, Total Phenolics)

Organics - Anything you can imagine

Typical Expected MDLs are 1 - 20 ppb.

One to two requests per week from toxicology.

Usually not amenable to one of the standard methods -
524 - 525 - 624 - 625 - 502.2

Resources are essentially limited.

One full time senior level chemist.

One small (5 foot hood) available.

Try to develop GC/FID and GC/ECD methods when possible with GC/MS confirmation if necessary.

The bright side is that all (>95%) of our samples are potable water - from in house exposure sequences.

Water Soluble Compounds

"The analytes from Hell"

Glycol Ethers

Amines

At ppb MDL's

PROCEDURES

Microextraction - (Standards prepared as Samples)

35 mL Sample Volume - 35 >1 mL Concentration

35 mL of sample is prepared in a 40 mL VOA vial

Add 0.5 mL of 1N NaOH for polar analytes and mix well.

(Optional for non polar analytes)

Add 6g NaCl and shake to dissolve.

Extract with 1 mL of CH_2Cl_2 by shaking vigorously for 2 minutes.

Allow CH_2Cl_2 layer to settle for approximately 2 to 3 minutes.

Sample the CH_2Cl_2 layer and analyze by GC/FID.

PROCEDURES (CONT.)

100 mL Sample Volume - 100 >1 mL Concentration

100 mL of sample is prepared in a 125 mL flask

Add 1.5 mL of 1N NaOH for polar analytes and mix well.

(Optional for non polar analytes)

Add 18g NaCl and shake to dissolve.

Extract with 1 mL of CH_2Cl_2 by shaking vigorously for 2 minutes.

Allow CH_2Cl_2 layer to settle for approximately 2 to 3 minutes.

Sample the CH_2Cl_2 layer and analyze by GC/FID.

PROCEDURES (CONT.)

Primary Aliphatic Amines - Benzaldehyde Derivative.

35 mL of sample is prepared in a 40 mL VOA vial.

Add 0.5 mL of 1N NaOH.

Add 20 mL of Benzaldehyde and allow to react for 50 minutes with periodic shaking.

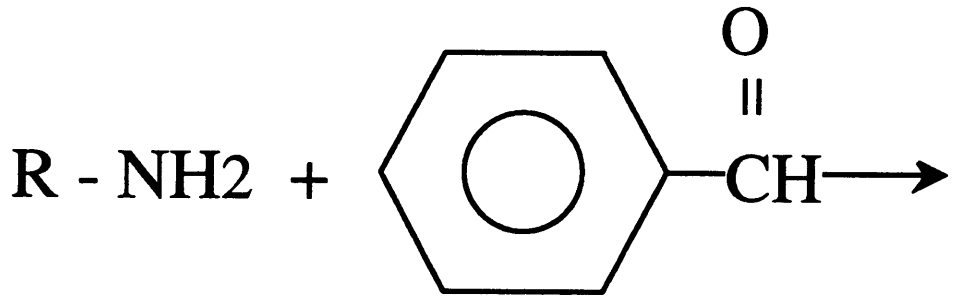
Add 6g NaCl and shake to dissolve.

Extract with 1 mL of CH_2Cl_2 by shaking vigorously for 2 minutes.

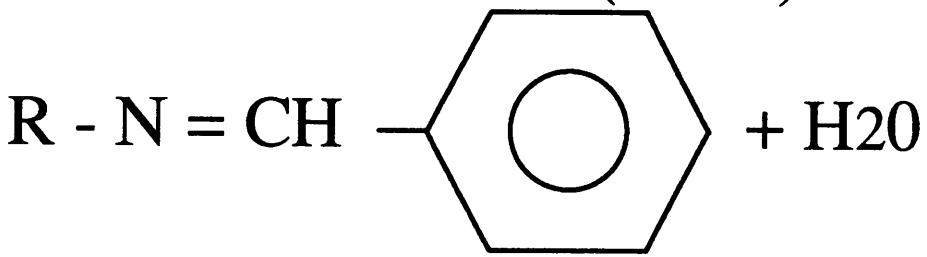
Allow CH_2Cl_2 layer to settle for approximately 2 to 3 minutes.

Sample the CH_2Cl_2 layer and analyze by GC/FID.

(sample extracts stored at 4°C until injected)



(imine)



PROCEDURES (CONT.)

Aromatic Primary Amines - Heptafluorobutyric Acid Anhydride (HFAA) Derivative. (Pierce Catalog # 63164)

35 mL of sample is prepared in a 40 mL VOA vial.

Add 1 mL of 0.5N NaOH and mix well.

Extract with 2 mL of toluene by shaking vigorously for 10 minutes.

Allow toluene layer to separate for approximately 2 to 3 minutes.

Transfer toluene layer (extract) to an 8 mL vial.

Add 25 uL of HFAA reagent to the extract and shake vigorously for 10 seconds.

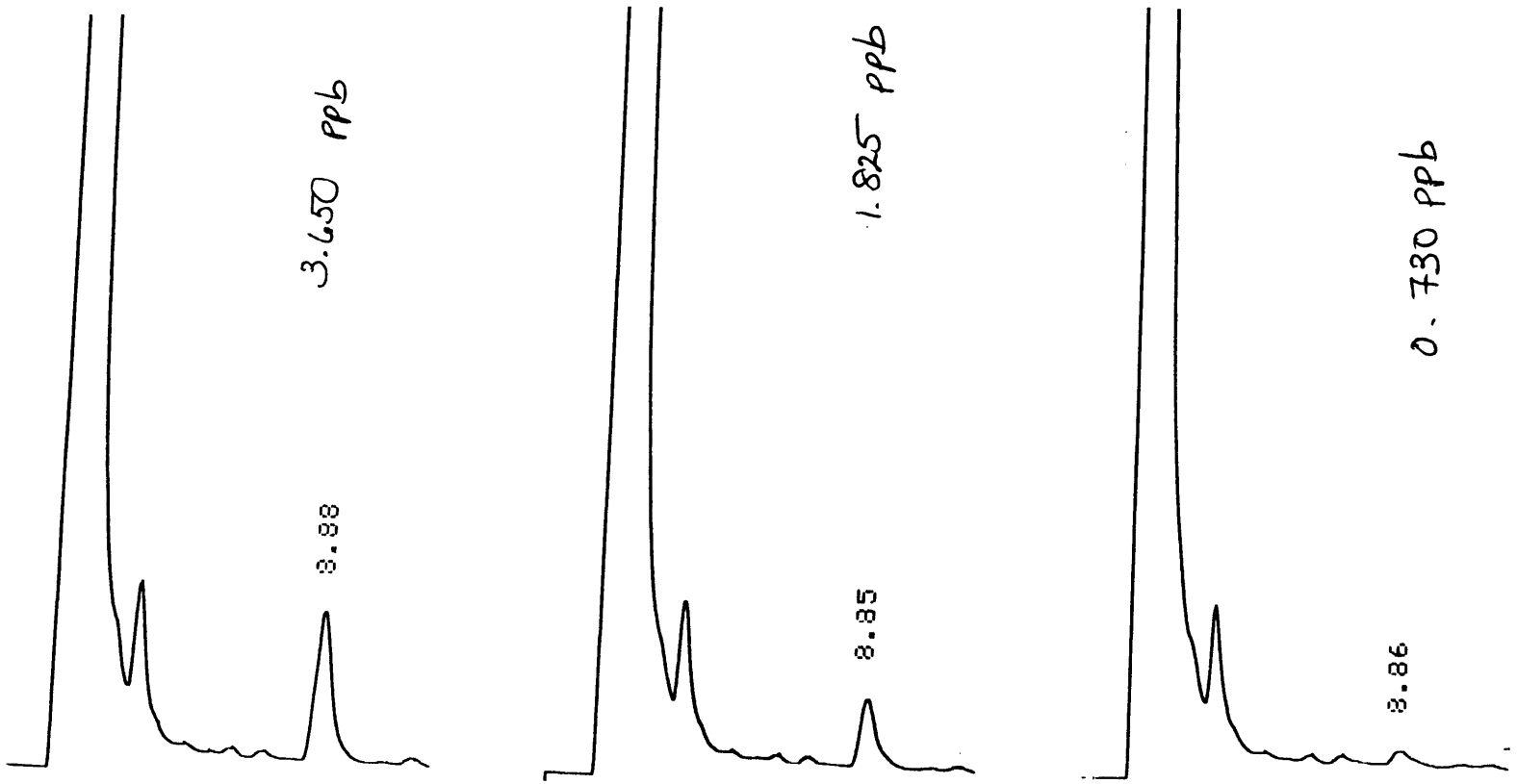
Add 1 mL of 1M KH_2PO_4 buffer (pH 7) and shake for 10 seconds.

Sample toluene layer and analyze by GC/ECD.

MICROEXTRACTION METHODS

Compound	Concentration	Boiling Pt. °C	MDL (ug/L)	Recovery (%)
dipropylene glycol monomethyl ether	35:1	90/12 mm	50	15
diethylene glycol monobutyl ether	35:1	231	20	71
propylene glycol monobutyl ether	35:1	169	20	94
p-t-butylphenylglycidyl ether	35:1	165/14 mm	5	130
4-hydroxy-4-methyl-2-pentanone	100:1	166	50	-
N-butylbenzenesulfonamide	35:1		10	139

5-CHLORO-O-TOLUIDINE
HFAA DERIVATIVE GC/ECD



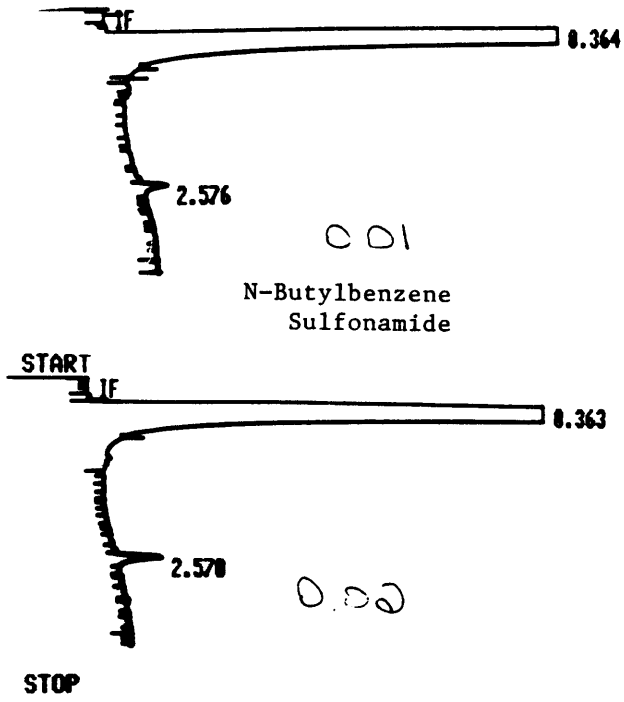
DERIVATIZED MICROEXTRACTION METHODS

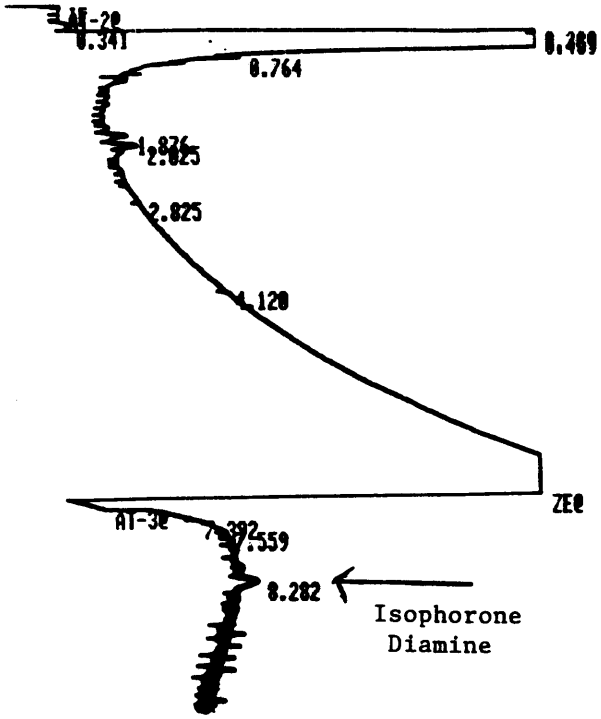
Compound	Concentration	MDL (ug/L)
Ethylene diamine (Benzaldehyde)	35:1	50
1,6 Hexanediamine (Benzaldehyde)	35:1	50
Isophoronediamine (Benzaldehyde)	35:1	5
o,p-toluidine (HFAA)	35:2	5
aniline (HFAA)	35:2	1
Dimethylanilines (HFAA)	35:2	1
4,4'-methylene dianiline (HFAA)	35:2	1
5-chloro-o-toluidine (HFAA)	35:2	1

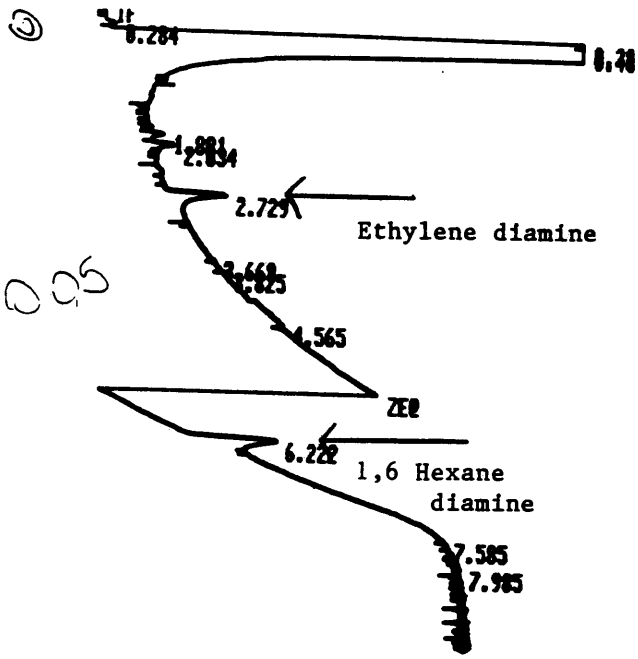
HFAA derivatization based on OSHA method #57 for 4,4'-methylenedianiline (GC/ECD)

MICROEXTRACTION METHODS

Compound	Concentration	Boiling Pt. °C	MDL (ug/L)	Recovery (%)
4,4'-Methylene bis-cyclohexylamine	35:1	-	50	118
B-naphthylamine	100:1	306	1	-
N,N-dimethylbenzylamine	35:1	183	10	129
Crotonaldehyde	35:.7	104	10	-
4,4'-dichlorodiphenylsulfone	35:1		50	-
Benzothiazole	100:1	230	5	-
t-butylacrylamine	35:1		20	67
4-vinylcyclohexane	35:1	126	10	97
4-vinyl cyclohexene dioxide	35:1	227	20	103


0.364
2.576
N-Butylbenzene
Sulfonamide
START
0.363
2.570
STOP


0.341
0.764
2.825
2.825
4.120
ZERO
8.282
Isophorone
Diamine


2.729
Ethylene diamine
4.565
ZERO
1,6 Hexane
diamine
7.585
7.985

MR. TELLIARD: Our last speaker for the day is from Columbia Analytical Services, Inc. out in Oregon. That is true. They all look the same, trees, water, grass, no delis, you know. And Mr. Anderson is going to discuss a system they have installed for solvent recovery in the laboratory.

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SOLVENT RECOVERY

presented by Jon Anderson
Columbia Analytical Services, Inc.
May 6, 1992
The 15th Annual EPA Conference
on
Analysis of Pollutants in the Environment

The goal of the solvent recovery program at Columbia Analytical Services, Inc. (CAS) is to recycle the solvents used in our extraction procedures and those used for rinsing glassware. At CAS we are averaging 2,000 - 2,500 semivolatile extractions for our semi-volatile laboratory, so the amount of solvent used and its cost was a factor in our interest in recycling. The extraction procedures commonly employed at CAS are 3510, 3520, 3540, 3550 with Soxhlets, separatory funnels, continuous liquid-liquid extractors and sonic horn. These extraction procedures and methods call for the use of the solvents: methylene chloride, which will be abbreviated DCM; acetone; hexane; and freon. It is these solvents that CAS is reclaiming and reusing.

We start out by segregating the solvents. The methylene chloride used in rinsing glassware and that collected from the S-evaps must be segregated from the methylene chloride waste. We also must segregate the 1:1 solvents used in our soil extractions, methylene chloride/acetone and hexane/acetone, which are collected from the S-evaps during the concentration procedure. Another solvent that we reclaim and reuse is the freon from Method 418.1, the oil and grease methods, and that used in rinsing glassware. We collect, distill, and reuse the acetone used to dry glassware. We do not reuse any of our solvents in sample extracts.

We make use of six Organomation S-evaps for solvent collecting during the concentration procedure from the KD apparatus. We also have four stills, one 22-liter still for DCM, one 22-liter still for the one-to-one solvents, one 12-liter still for freon, and a small 3-liter still for acetone.

The reclaimed and then distilled 1-to-1 solvents passed preliminary mass spectroscopy tests, so we are in the process of redistilling almost fifty cases of reclaimed 1-to-1 solvent.

For the collection of the solvents to be recycled, we have clearly marked, color-coded, and labeled 5 gallon and 2.5 gallon cans. We also use 2 liter nalgene beakers in our hoods to collect the methylene chloride that is used to rinse glassware. The color\coding used is: red for reclaimed, but not yet distilled solvents; yellow for distilled, but not yet tested for purity; and green for solvents ready to be used in the laboratory. Yellow and red are used on solvent containers that did not pass our testing procedures.

We have found that the segregation and clear labeling is the key to making this system work.

For DCM reclamation, we discard the first 500 ml that comes over the still. The distillate is collected in clean, rinsed 4-liter bottles, which are labeled and stored for testing. These bottles are very important. We have found that the primary cause of contamination in the distillate is the collection containers, not the distilling process. We then collect 100 ml from four of these bottles, place it in a clean KD and concentrate it to 1 ml for GC/MS testing. Our acceptance criteria for the reclaimed

solvent is that there is no detection of any of the target compounds tested for in Method 8270, and that the total area for all non-target peaks is less than 10 percent of the area of the internal standard. If no interferences are present, the DCM is then labeled for use in the lab.

Hydrocarbon testing and the GPC cleanup procedure are a two tests we do not used reclaimed DCM for:

We test the 1-to-1 solvents by Method 8270 using the same acceptance criteria as we use for the DCM. We then dilute 10 microliters in one milliliter of iso-octane and run it on the FID to determine the percentage of acetone versus DCM and hexane in order to adjust it back to a 1-to-1 mixture. It can then be used for soil extractions.

To distill and test the Freon, we first filter off any silica gel, then collect and discard the first 500 ml that comes from the still, collect the rest in 4-liter bottles and then run an aliquot from each bottle on the IR. The pass criteria is less than 2 ppm of hydrocarbons by Method 418.1 procedure.

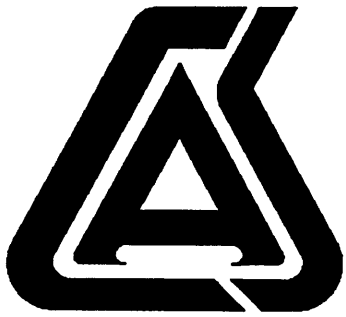
In our glasswashing areas, we have installed a small still for the glasswashers to distill the acetone they use to dry glassware. After distillation, they reuse the acetone.

For all of these reclaimed solvents we keep daily and monthly records of the reclaimed solvent batches and the test results.

The system cost:

22-liter still	$3,500
12-liter still	$3,000
Organomation S-evaps, KDs, condensers, various glassware	$5,000/each
5-gallon stainless steel cans	$ 200/each

During an average month we reclaim and distill approximately 30 cases of four, 4-liter bottles of DCM, 15 cases of freon, 30 cases for 1:1 solvent at a total savings of $8,300. In one year we have saved approximately $100,000. However, our reclamation and distillation is on the increase, so we will be seeing even greater savings.



COLUMBIA ANALYTICAL SERVICES, INC.

SOLVENT RECOVERY PROCEDURE

GOAL

To reclaim and reuse solvents used in extractions and glassware rinsing for Methods SW-846; EPA Methods 3510, 3520, 3540, 3550, 413.1, and 418.1.

Methylene Chloride; Acetone; Hexane; and Freon.

SOLVENT SEGREGATION

A. Methylene Chloride

1. Used in rinsing glassware.
2. Collected from S-Evap.

B. 1:1 Methylene Chloride: Acetone and Hexane: Acetone

1. Collected from S-Evap.

C. Freon

1. Used in 418.1 hydrocarbon method.
2. Collected from S-Evap.
3. Used in glassware rinsing.

D. Rinse Acetone

1. Used for rinsing glassware.

Solvents from each are collected in 5 or 2½ gallon stainless steel cans. Clearly marked.

APPARATUS

A. 2 L Nalgene beakers to collect rinse solvent (i.e., DCM, Acetone, Freon).

B. Organomation S-Evap for collecting solvent off K-D concentrators.

C. Stills:

1. DCM: Kontes 22L distillation apparatus.

2. 1:1 Solvents: Kontes 22L distillation apparatus.

3. Freon: Kontes 12L distillation apparatus.

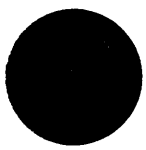
4. Acetone: Simple 3L heating mantle/column use for glassware rinsing.

LABELLING

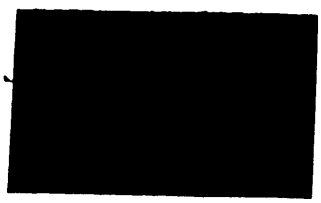
All canisters, bottles,
and boxes will be labeled accordingly:

RECLAIMED DCM
(includes RINSE, to be distilled, canisters)

DISTILLED DCM
Waiting to be Tested



OK FOR USE
Passed GC/MS Testing



RE-DISTILL
Did not Pass GC/MS Test

DISTILLATION AND TESTING

DCM

1. Collect and discard the first 500 mL that is collected after filling still.

2. Collect in clean, rinsed 4 L bottles, label and store until after testing.

3. Testing - Collect 100 mL from 4-4 L bottles and place in clean, rinsed K-D and concentrate to 1.0 mL for GC/MS testing.

4. If no interferences are present, label for use in lab.

Redistilled DCM is not used for GPC. Redistilled DCM is not used for volatile hydrocarbon testing on water samples.

DISTILLATION AND TESTING

1:1 Solvents
DCM/Acetone/Hexane use in Soil Extractions

1. Collect and discard the first 500 mL that is collected after filling still.

2. Collect in clean, rinsed 4 L bottles, label and store until after testing.

3. Testing:

   A. Collect 100 mL from 4-4 L bottles. Place in clean, rinsed K-D and concentrate to 1.0 mL for GC/MS testing.

   B. Dilute 10 μL into 1.0 mL of isooctane run on GC/FID to determine percent acetone vs DCM and hexane, in order to adjust to 1:1 mixture.

DISTILLATION AND TESTING

FREON

1. Filter off any silica gel present from 418.1.

2. Collect and discard the first 500 mL that is collected after filling still.

3. Collect in clean, rinsed 4 L bottles, label and store until after testing.

4. Run an aliquot from each bottle, if solution concentration of hydrocarbons is < 2.0 μg/mL by IR techniques, then the bottle is posted and ready for use.

DISTILLATION AND TESTING

ACETONE

Collect redistilled and use for rinsing glassware after washing.

IMPORTANT NOTES

1. Good, clear, labeling system.

2. Solvents to be redistilled, tested, and used must be kept separate.

3. Daily and monthly records of batch testing and use must be kept.

SYSTEM COST

Kontes 22L still with 2 Columns	$3,500
Kontes 12L still with 2 Columns	$3,000
Organomation S-Evap with Glassware	$5,000
5-Gallon Stainless Steel Cans	$200

One Technician to run system(s)
30 to 40 hours per week.

SYSTEM SAVINGS

DCM Average 30 Cases/Month	$2,000
Freon Average 15 Cases/Month	$4,200
Acetone Average 50 Gallons/Month	$300
1:1 Solvent Average 30 Cases/Month	$1,800
Total Average Savings/Month	$8,300

Average Yearly Savings - Approximately $100,000

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PROCEEDINGS

May 7, 1992

MR. TELLIARD: Good morning. We are going to start out this morning's session with a number of papers discussing immunoassay techniques for analysis. This particular procedure is quite common in the medical field, but it has just in the last few years become more and more prominent in the environmental area.

Office of Water have done some work with immunoassay and we think it shows promise. It could have application for field monitoring and for such things as non-point source discharge monitoring programs.

Our first speaker is Kevin Carter, and Kevin is going to present data on some of the basic field methods.

MR. CARTER: I am going to talk today about the performance of some immunoassays for polychlorinated biphenyls and pentachlorophenol. I would like to first thank Bill and the rest of the conference organizing crew for recognizing the potential value that immunoassays have in the environmental field and including a session on immunoassays. Immunoassay methods can address a wide variety of contaminants ranging from industrial contaminants, like I am going to talk about, to pesticides, which are the subject of the next three or four talks.

The orientation of my talk will be around field methods. We feel that the mitral application of immunoassays in the environmental field is probably best directed toward field methods, because adequate laboratory methods already exist for the kinds of compounds that we are talking about.

That is not to say that immunoassays can't be used in the laboratory, because they certainly can be, but that the field is a better place to start.

To begin, I want to talk a little bit about the typical hazardous waste site cleanup progression, going through four phases. Field analysis is valuable in a few of the phases. It is really most valuable where many samples are collected and have to be

analyzed.

Field methods can be used most valuably in the field to help you make field decisions. Field analysis and laboratory analysis are complimentary activities. If you use each where it provides the necessary level of information, the most value for the dollar, you are optimizing your analytical efficiency on environmental projects.

One of the places where field analysis has a lot of value is in site assessment or contaminant mapping. Whether you are working with soil to locate "hot spots" or with water to follow a plume of contamination in groundwater, field testing can help you cost-effectively increase your understanding of contaminant distribution. Through the use of directed sampling more useful site assessment data can be obtained. One of the greatest challenges in characterizing a contaminated site is taking samples that are really representative of the site that you are trying to address and using field analysis, you can do a better job of doing that.

I have heard it said that a greater number of measurements of lower resolution, meaning field analysis methods, results in higher confidence with regard to decisions that have to be made in the field. That has certainly proven to be true in the projects that we have participated in.

The results of field analysis can be used in the area of site assessment and contaminant mapping for several things. You can use them on-site for attempting to define the actual site boundaries, not the property boundaries, but the contamination boundaries. You can use them to define hot spots, clean areas, or both, depending on what the goals of the project are. And you can certainly use them to optimize further sample collection for laboratory confirmation. Obviously, it is not particularly valuable to choose many samples from areas that contain either very low levels of contamination or very high levels of contamination. Because you are trying to map the gradient across the site. So, choosing the correct samples for laboratory analysis can be aided by field analysis.

In addition, estimating the volume of contaminated soil can be done very conveniently in the field using field analysis. You can take many samples, both laterally and vertically, to get an idea of how much soil would have to be treated or how much

water would have to be treated in a remediation project. This helps you establish a remediation approach, as well as estimate a cost and time frame.

Another area where many samples are collected is in the pursuit of remediation of a site. In the case of remediation, the same principles apply, but, in many cases, when you are remediating a site, the thing that is of most value is knowing when an area is clean. You want to know that what you have left at the site is actually clean.

Now, there are some specific areas, where field analysis can play a role in remediation: testing of influent soil to ensure that you are only remediating dirty soil;

Monitoring remediation efficiency; Verifying the completeness of remediation; And guiding the collection of samples that will be needde for the closure permitting process.

Throughout this process, QA is extremely important, and part of QA, as I think I have already referred to indirectly is laboratory confirmation of a portion of the samples. People who are using these techniques in the field are doing a certain amount of laboratory confirmation to back up the results that they get from field analysis.

At this point I want to go further and identify the characteristics that would be advantageous for a field analytical technique. It is highly desireable for the test to be specific to the analyte that is doing the clean-up.

The test needs to be sensitive, because the kinds of limits that have to be measured against these days are generally not getting higher, they are getting lower.

It needs to be easy to use, because in the field, conditions aren't optimum for analytical techniques. It needs to be rapid, because, of course, the desired response is quick decision making.

Finally, it is important that field analysis techniques, just as laboratory analysis techniques, not be significantly affected by the matrix that is being analyzed.

There needs to be a lack of interferences so that when you think you are measuring, for example, PCBs, you are not measuring something else.

Well, all of these criteria are met by immunoassay-based analytical methods. I think that you will see as we go through the field performance data and see

some of the data presented in subsequent talks in this session that these tests very useful for field analytical purposes.

What is an immunoassay, for those of you who don't know? An immunoassay is simply an analytical method that uses a biological molecule, an antibody, which is simply a protein, to detect and quantify compounds in a test sample.

There is something special about the antibody in that it can be tailored to specifically bind to the compound of interest that you are analyzing for. As well as binding in a specific fashion, the antibody does so at very low analyte concentrations, and that is what confers the specificity and sensitivity on immunoassays.

Now, I would like to review a generalized model of how an immunoassay works. There are many formats for immunoassays. Some of them involve various other components, but the most common type that is used and the kind that you will most often find in environmental tests is the so-called competitive enzyme immunoassay. You will see what competitive means in a second. The word ELISA is an acronym for enzyme linked immunosorbent assay. Two components are necessary for the test. You see on the bottom of the tubes, tubes 1, 2, and 3; a little Y-shaped figure. That is a representation of an antibody. An antibody has two "arms" that contain two individual analyte binding sites. Those correspond to the two arms of the Y that are sticking out into the tube. In the way that we run immunoassays the antibody is actually immobilized to a plastic test tube.

You also need what is referred to as an enzyme conjugate. The enzyme catalyzes a color-forming reaction that serves as the reporting or reading result in the test. Each enzyme molecule has several analyte molecules chemically bound to the outside surface of it.

Now, a practical immunoassay test for the environmental field is realized in the following fashion. The tests I am going to be talking about are semi-quantitative tests in which at the same time as you test samples that contain the analyte of interest, you run a standard that contains the same analyte of interest. You compare the color formed at the end of the test period with the standard to that developed with the sample to determine whether the sample contains less than or greater than the amount of

analyte that is present in the standard.

So, you get a presence/absence indication relative to a preset quantitative level.

Referring abck to the slide, you test a standard which is represented in tube 1 on the left where you add enzyme conjugate and standard. In sample tubes, you add processed sample, as well as enzyme conjugate.

Once you have added these and mixed them, the analyte that is bound to the outside of enzyme competes with the analyte that originated from the sample for antibody binding sites.

It is easy to see that in samples that contain a greater amount of analyte that originated in the sample, such as tube 3, that you get analyte from the sample bound at a higher level to antibody immobilized on the tube.

In the case of tube 2, there was no analyte in the sample. Therefore, the only thing that can bind to antibody is enzyme conjugate.

In the standard, which has an intermediate amount of analyte present, you get both enzyme conjugate and analyte bound to the antibody.

So, at the point at which the equilibrium has been nearly established after an incubation period and incubations typically range from 2 or 3 minutes to upwards of 30 minutes at ambient temperature...you stop the incubation by rinsing out the antibody-coated tubes.

In doing so, you wash out all unbound materials. Only analyte and enzyme conjugated analyte that are bound to antibody stay in the tube. Following the wash the substrates for the color forming reaction are added. Color formation is catalyzed by the enzyme part of the enzyme conjugate.

In our tests, we use an enzyme called horseradish peroxidase which, in the presence of tetramethylbenzidine and hydrogen peroxide, catalyzes the formation of a blue color, the starting substrates being colorless.

A short incubation proceeds, again, usually on the order of either seconds or minutes up to 2 or 3 minutes. During this time, any enzyme conjugate that is immobilized to the antibody catalyzes the formation of color, using the substrates.

In the standard tube where there were a few molecules of enzyme conjugate bound, a medium color intensity develops.

In a negative sample...and it doesn't show up very well in this slide where only enzyme conjugate is bound, a deep color results.

In a positive sample that contains no enzyme conjugate bound because there was so much analyte, you observe virtually no color development.

At the end of the incubation period, you stop the reaction through the addition of acid which kills the enzyme activity, and compare samples and standards in some kind of a colorimetric reader. A differential photometer is commonly used. There are battery-powered instruments that can be used in the field very conveniently, set at a fixed wavelength.

In cases where assays are in a multiple well plate format there are automatic readers, which will scan several wells and give you a readout for each well, but the principle is the same. It is reading the amount of color in the sample.

If you were to make a plot of the color intensity that was present at the end of reaction versus the concentration, you would see over a certain range a log linear response. This kind of a test is very capable of being used as a quantitative test.

But to make the tests field-usable, we employ a semi-quantitative approach, to do this we set the standard in the middle of the linear range, as you see portrayed in this slide, and then determine whether sample that has been processed through the assay yields tubes with greater or lesser color. As you can see, this is an inverse relationship, so less color implies more analyte; more color implies less analyte.

In a real world implementation, there are some things that I have left out of the discussion so far. The first thing that I have left out is that, obviously, you need to do some sample processing, because you can't dump soil into a coated tube and expect an assay to work.

So, coupled to the immunochemistry that you have seen, there is also a simple sample processing step that involves taking a weighed amount of soil, extracting it with a solvent which is compatible with water, and then doing serial dilutions on the sample extract to adjust the sensitivity to the appropiate semi-quantitative level.

By making further dilutions on the sample extract one can actually use semi-quantitative tests to range sample concentrations.

Immunoassay-based tests can be used very effectively as semi-quantitative tools to zero in on analyte concentrations in samples in the field.

Now, I am going to switch gears and talk about some data that has been generated in field trials for PCB and pentachlorophenol assays that use this technique.

The objective for field trials of these products was to document the performance on a real world situation with real world samples using people, geologists, engineers, and chemists that collect samples in the field.

There is also some data presented from spiked samples that were run in a laboratory.

For the PCB soil test, two sets of data will be presented. First, a trial was carried out at the Department of Energy's facility at Oak Ridge in their organic chemistry analytical division.

And, second, the Gas Research Institute sponsored a trial of the PCB test that was conducted by Roy F. Weston Analytics Division to assess its applicability to gas pipeline sites where PCBs had gotten into the soil as a result of being used in compressors.

In the case of the DOE trial, they had several objectives in looking at field analytical methods. They were interested in documenting the degree of correlation that could be obtained with the standard EPA GC Method 8080; looking at potential matrix effects relative to various DOE sites; determining repeatability from test to test with the same sample; and determining the degree of user variability that might have an impact on the accuracy and precision of the results.

DOE took a soil from one of their facilities, the Rocky Flats facility, and spiked it with several levels of Aroclors, 1254 and 1260, and had two different operators run the immunoassay and compared the results with the spiked values.

What they found was 85 percent correlation between the results of the semi-quantitative immunoassay and the spiked values.

In the cases where correlation wasn't observed, they observed that the

immunoassay over-estimated the amount of PCBs in the sample. In fact, that happened only 15 percent of the time. There were no false negative or underestimated results.

That has significance, because in the field when you are making decisions based on a field analytical method, you don't want to say that something is clean that isn't clean.

The user variability was shown to be very minor with this test in that operators 1 and 2 both got similar false positive percentages when they ran the test.

There was also little variability with duplicate analyses. That variability was all correlated with the false positive results.

They also analyzed contaminated samples that came from the Oak Ridge area, samples of soil and sediment that had PCB contamination from historical operations there. With these samples, almost 90 percent of the immunoassay results agreed with the GC-ECD analyzed results.

Again, in this case, there were no false negative results. In this case, the user variability was virtually nil. Duplicates also agreed well.

For the Gas Research Institute trial, 30 samples were collected from 6 different pipeline sites throughout the country. They represented several soil types, to try to identify potential matrix effects.

All of the soils were analyzed for PCBs using EPA Method 8080, as well as with the immunoassay-based test. GRI and Weston found that for nearly 90 percent of the samples, the two methods agreed, and where they didn't agree, again, false positives predominated over false negatives.

In fact, there was only one false negative result in this trial, and that was a 55 ppm sample that tested negative relative to a 50 ppm level. Given the standard precision achievable with Method 8080, this is a questionable false negative.

Similar validation data have been generated for pentachlorophenol tests that were applied to contaminated soil. The first trial was done in conjunction with Mississippi State Forest Products Lab.

Mississippi Forest Products laboratory is associated with Mississippi State University and focuses on the State's forestry industry and applications of timber to

various uses. One of those applications is treated wood products using pentachlorophenol to make a range of products, principally telephone poles.

As a result, they had an interest in the remediation of sites that are contaminated with wood treating products and, as such, they have developed a very good laboratory skilled in analyzing for pentachlorophenol by EPA Method 8270.

They conducted the immunoassay test in their laboratory. They also did the GC/MS analysis to determine the pentachlorophenol concentration in a variety of soil samples that they collected from various contaminated wood treating sites throughout the U.S. Again, the goal was to get a number of samples that were representative of a wide variety of soil types to examine potential matrix effects.

The other trial that was conducted with the pentachlorophenil testing product was one that was conducted in conjunction with the EPA's Environmental Response Team who, last summer, conducted the first phase of a removal action at a number of pentachlorophenol contaminated wood treating plants, primarily in the Southeast.

They needed a screening test that would allow them to look at these big sites, document contamination, where it was and where it wasn't, and get an order of magnitude idea of contamination levels.

To do this they used the EnSys pentachlorophenol soil test out in the field to screen about 1000 samples for pentachlorophenol contamination. They compared these results to GC analysis performed in a mobile lab. I will show you a summary of the results of about 200 of those samples that were run at the Brunswick wood treating plant in Brunswick, Georgia, by the EPA's contractor.

In the case of the Mississippi Forest Products lab trial, a high correlation was observed between the GC/MS results run under Method 8270 on the soil samples and the immunoassay results The immunoassay overestimated the amount of pentachlorophenol in only one sample.

In the case of the Brunswick wood treating trial, 176 samples were tested using both methods. The results for 84 percent of the samples agreed between the immunoassay and their field lab. Where there was disagreement, there was about a 3:1

ratio of false positives to false negatives in the field.

I think, in summary, it can be said that immunoassays, as field screening methods, have very promising application and that with real world samples in the hands of real world users, results that correlate very highly with conventional analytical techniques operated back in the laboratory can be obtained.

These tools, present an opportunity for the environmental community to use them selectively in field work and money on the analysis side where, instead of spending $150, $200, $300 for a lot of laboratory analysis, do some of the testing in the field and back that up with laboratory analysis.

But perhaps of greater value than that is the ability to delineate contaminated areas in the field and make decisions in the field with no delay. Most of the benefit that is going to accrue from a time and money standpoint will be had there.

Thank you very much.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Questions, please?

While they are getting to the microphone, I have one, Kevin. A lot of times when you take a sample like we are talking about for water, the old bugaboo about colorometric problems in that you have either a discolored sample or a lot of turbidity, could you expand a little bit about how the color doesn't interfere with your...with this type of analysis?

MR. CARTER: Yes. Actually, for water samples, this kind of a test presents a unique tool in that because you are binding the analyte to the antibody and washing the rest of the unbound sample out of the tube, you are also washing any color out of the tube that you have placed in it.

I know in working in these wood treating sites, many of the water and soil samples are essentially black because of the creosote contamination that is present in concert with pentachlorophenol contamination. While that would interfere with a normal colorometric method, it doesn't interfere with these colorometric methods because of the wash step.

MR. TELLIARD: Thank you. Yes?

MR. YOCKLOVICH: Steve Yocklovich from Burlington Research.

I just wanted to get a clarification. Were all the samples you were talking about that were tested contaminated, or was it a blind or double blind study where they had some uncontaminated samples to compare against? Were they expecting them to be contaminated and they found it?

MR. CARTER: Well, for the most part, these were single blind experiments. Obviously, some of them were done in the field where nobody knew what was in the samples, whether they were contaminated or not.

Laboratory investigations, such as the Mississippi Forest Products lab trial and DOE trial were set up to have a mix of uncontaminated and contaminated samples, and the contamination range was chosen so that the samples were contaminated, in the concentration range close to the decision levels that were being tested.

We restricted the choice of samples to things that were in range as opposed to either outrageously contaminated or predominantly clean. So, it was a mixture of the two intentionally.

In the case of the field trials where work was actually done in the field, there was no way of knowing. But as is typical with field situations, a large percentage, perhaps half or more, of the samples you collect are actually contaminated below the action level, and that was the case with the Brunswick trial. I would say roughly 60 percent of those samples were below the action level that they were interested in and perhaps half of those were non-detects by the GC method.

MR. YOCKLOVICH: Thank you.

MR. SCHRYNEMEECKERS: Rick Schrynemeeckers with Enseco Corporation.

The question I have for you is twofold. One, when you say you had like an 88 or 85 percent agreement between the GC and the immunoassay tests, is that for an agreement on the concentration or just an agreement on whether it is or isn't a hit?

And the second question is, is the response variable to the PCB Aroclor that you are looking for, or do you get basically the same response no matter what Aroclor you are looking for?

MR. CARTER: Well, in response to the first question, it was kind of a mixture between the two alternatives that you gave me, because we ran the tests, in this case, in a ranging fashion, meaning that each sample was tested, in the case of PCBs, at 5 ppm and at 50 ppm.

So, if the GC result was 33 ppm and the immunoassay test said it was greater than 5 and less than 50, then that I counted as an agree.

MR. SCHRYNEMEECKERS: All right.

MR. CARTER: If the immunoassay test said it was greater than 50 but it actually tested at 33 with the GC, then that was a false positive.

MR. SCHRYNEMEECKERS: Okay.

MR. CARTER: In answer to the second question, the test is relatively insensitive to which Aroclor you are testing.

In the case of this test, Aroclors 1248, 54, and 60 test with essentially identical sensitivity. When you step down to 1016 and 1242, you get a decrease in sensitivity such that if you were testing at a standard semi-quantitative level at 5 for 1260, you would be testing at a semi-quantitative level of 10 in the same test for 1242.

And as you get down to something like 1221 which really is very rarely found as an environmental problem, the sensitivity drops fairly drastically because of the low chlorine content and resulting poorer recognition by the antibody of that group of congeners.

MR. SCHRYNEMEECKERS: For a specific analyte like pentachlorophenol, what would you perceive the problem to be in just using a UV/VIS spec and running a curve using your test as opposed just to show/no show at specific concentrations?

MR. CARTER: There is really no issue in doing that. It certainly can be done. There is a range about a tenfold or twenty-fold concentration range, over which there is a linear relationship between absorbance and log concentration, and one could certainly measure the color generated by the enzyme and correlate that to standards that one runs in the test.

MR. SCHRYNEMEECKERS: Thank you. Appreciate it.

MR. PERTUIT: Your immunoassay is very...

MR. TELLIARD: Could you identify yourself, please?

MR. PERTUIT: Pardon me?

MR. TELLIARD: Could you tell us who you are and who you are with?

MR. PERTUIT: Oh, I am Bob Pertuit, PPG Industries, Lake Charles.

MR. TELLIARD: Thank you.

MR. PERTUIT: Immunoassay is generally specific to one particular compound. Have you determined which one of the PCB isomers that the assay is actually reacting to?

MR. CARTER: Well, this particular antibody was developed against one of the pentachloro congeners that is present as a predominant component of Aroclor 1254, but there is enough vagueness in its response with regard to recognition of, 4, 5, or 6

chlorine containing congeners that, in fact, it has relatively broad specificity as a result.

MR. PERTUIT: But for something like decachlorobiphenyl or monochlorobiphenyl, it would probably be totally insensitive?

MR. CARTER: Yes, I suspect that is true. We have not actually tested that, but the results with Aroclor 1221 bear that out.

MR. PERTUIT: Okay, thank you.

MR. WITHAM: Mark Witham, Bio-Tek Instruments.

A two-part question. With the false positives, did you do anything to look at the reason behind the number of false positives, number one? And number two, in your field versus laboratory work, were the same methods used including the methods and instruments for washing and doing the actual end reading?

MR. CARTER: I will answer the second question first. We used exactly the same setup in the laboratory and in the field. All of the instruments, the washing setup, everything was the same.

In answer to the first question, in most cases, we didn't go any further with samples that were false positives. In some percentage of those cases, it is simply analytical error or analytical imprecision, I should say, in the GC or GC/mass spec results, because with real samples, you know that if you send off samples to two different labs, you get two different results within some kind of an error window.

So, that was responsible for part of them. Part of them were probably due to matrix interferences, things in the soil that resulted in an overestimation.

One of the properties of these tests that is useful is the way they respond to interferences. Because of the inverse relationship of color and concentration, if you have something in the sample that inhibits the formation of color in the assay in some way, that results in less color and, therefore, a falsely positive reading.

So, failure modes with respect to matrix interferences give you false positives.

MR. MYERS: Harry Myers from Keystone Environmental Resources.

A couple of questions ago, there was a question related to developing a curve for using a spectrometer to get a more quantitative result. With the test kit that

you have, the color development is time dependent. So, everything would have to be done within the same time frame, all the operations of the tests to make use of a calibration curve.

In the field, you can't always do those kinds of things. Therefore, the fact that you develop a color from a standard for some finite number of samples every time and you are comparing back and forth between the sample and the standard makes it useful in the field.

MR. CARTER: Well, that was exactly the reason that we used in setting this up as a field analytical method that was semi-quantitative. I mean, you certainly could run a 3 or a 5 standard line and then use this quantitatively, but because all the samples are timed and because, typically in the field, you are under adverse conditions, it is just not very easy to get accurate and precise results under the circumstances.

MR. TELLIARD: Joe?

MR. VITALIS: Joe Vitalis, EPA.

More of a comment than a question. The history of the names of Aroclor go back to the production process so that if you had an arochlor 1260, it really is 12.60 percent chlorine by weight in the manufacturing process.

This means that those are the...that would be a more stable pentachlorophenol...I am sorry...a biphenyl than if you had a 1021.

So, also the congeners that you get depend on how much chlorination and also the process and when the biphenyls were actually made. I think you made a good selection in using the 1254.

MR. CARTER: Thank you.

MR. TELLIARD: Can we wrap this up? One more, and then we will get on to our next speaker.

MR. BOTNICK: Eric Botnick from Electro-Analytical Laboratories in Ohio.

A couple of questions with the color development. Is there any temperature dependency as far as the development of the color goes at the time?

MR. CARTER: Yes.

MR. BOTNICK: As in as the temperature goes up, the color development increases, or have you established a...

MR. CARTER: And that is why you run a standard at the same time as you run a sample, to basically cancel that effect out.

MR. BOTNICK: Okay. Once the color has been developed and you have stopped that development with the acid, is that color stable, and if so, how long is it stable for?

MR. CARTER: It is highly stable over an hour's period of time. We haven't actually tested it longer than that, but I hear tell that it is stable for upwards of 12 hours.

MR. SMITH: At least two hours.

MR. CARTER: There is user comment.

MR. TELLIARD: Thank you.

THE PERFORMANCE OF IMMUNOASSAY-BASED FIELD METHODS FOR PENTACHLOROPHENOL AND PCBs

ENSYS INC.

Kevin R. Carter

HAZARDOUS WASTE SITE CLEAN-UP

ENSYS INC.

Project Phase	Samples Collected	Analysis Methods
Characterization	Few	GC, GC/MS, HPLC
Mapping	Many	GC, GC/MS, HPLC Field Methods
Remediation	Many	GC, GC/MS, HPLC Field Methods
Closure Monitoring	Few	GC, GC/MS, HPLC Field Methods

SITE ASSESSMENT AND MAPPING

- Determining actual site boundaries
- Defining clean areas
- Identifying "hot spots"
- Optimizing further sample collection
- Estimating the volume of contaminated soil
- Establishing a remediation approach
- Accurately assessing remediation costs and timeframe

REMEDIATION

Testing influent soil

Monitoring remediation efficiency

Verifying the completeness of remediation

Guiding the collection of samples required for closure permitting purposes

ATTRIBUTES OF IMMUNOASSAY-BASED ANALYTICAL METHODS

- Highly specific
- Sensitive
- Easy to use
- Rapid (< 30 minutes)
- Not affected by sample matrix
- Few interferences

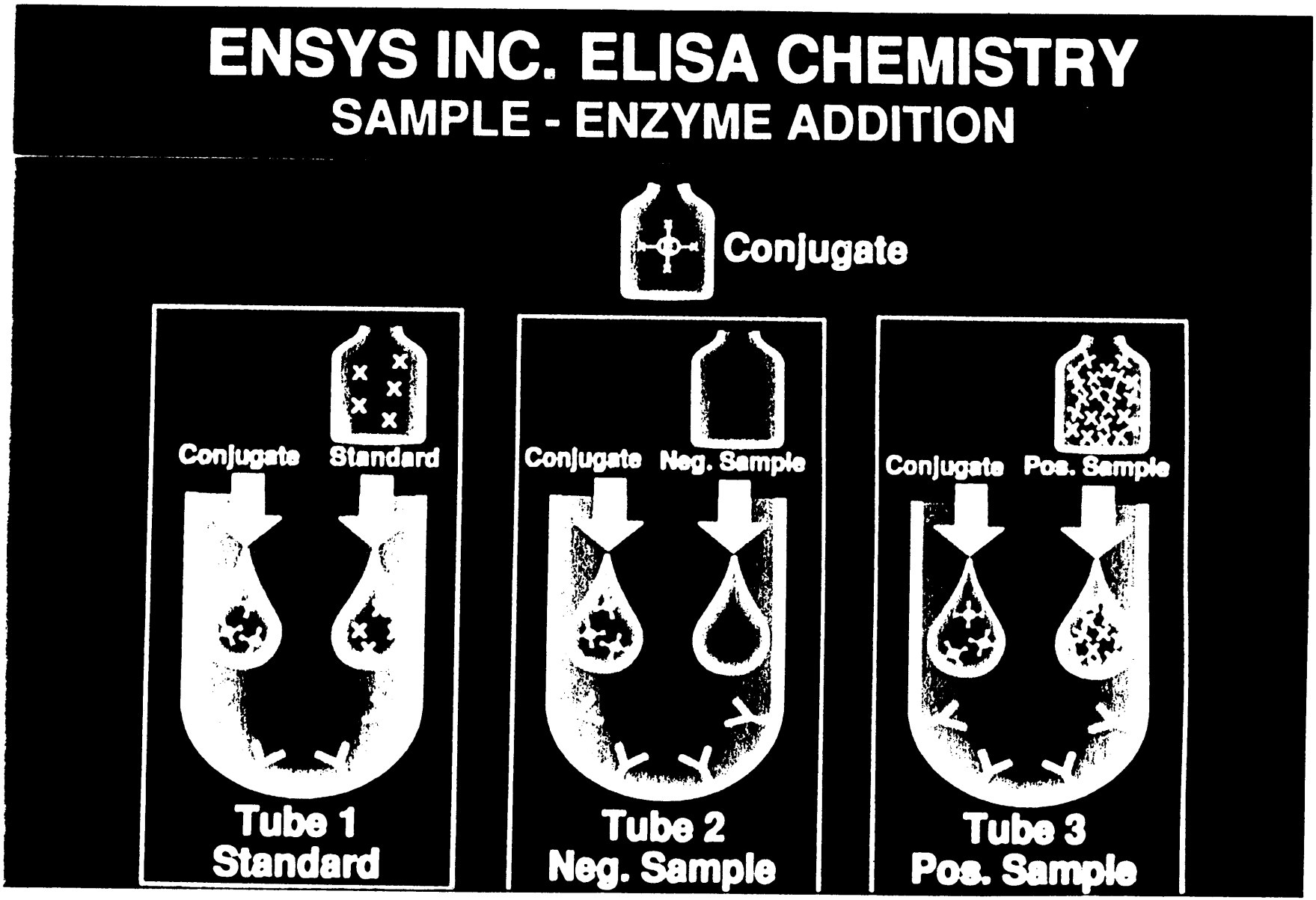
IMMUNOASSAY

- An analytical method that uses an antibody molecule to detect and quantify compounds in a test sample.

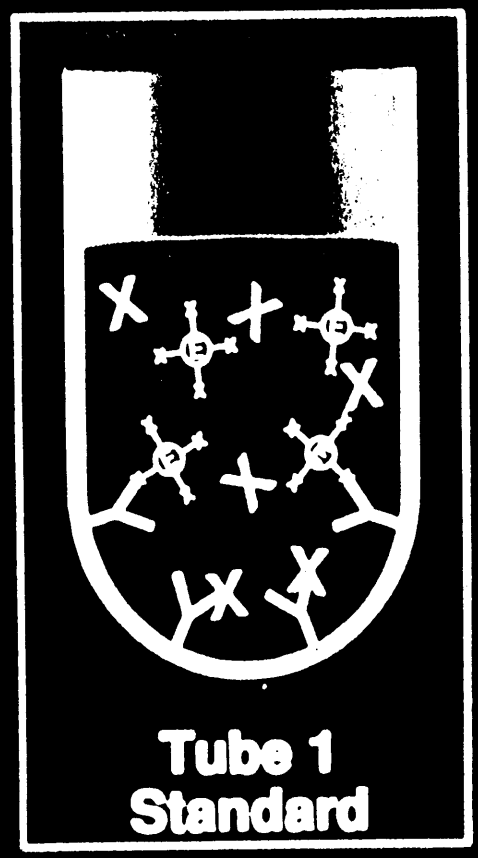
ENSYS INC. ELISA CHEMISTRY
COMPONENTS
Conjugate
Tube 1
Tube 2
Tube 3

ENSYS INC. ELISA CHEMISTRY

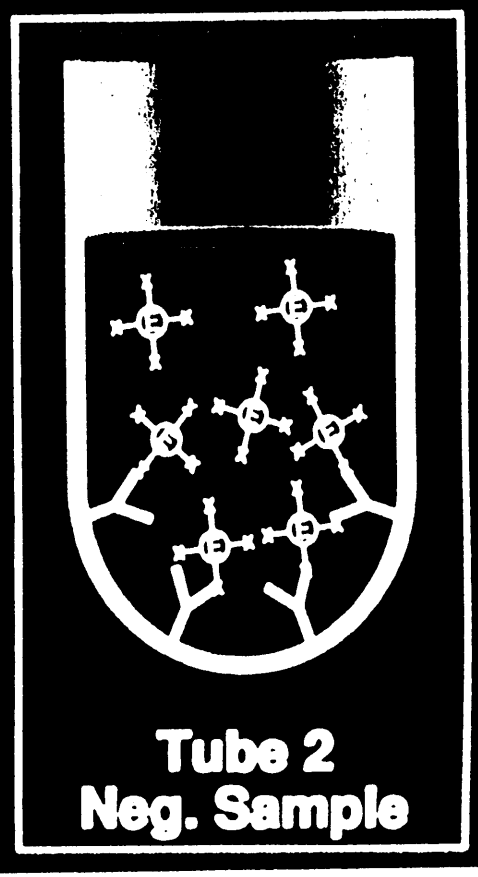
SAMPLE - ENZYME ADDITION



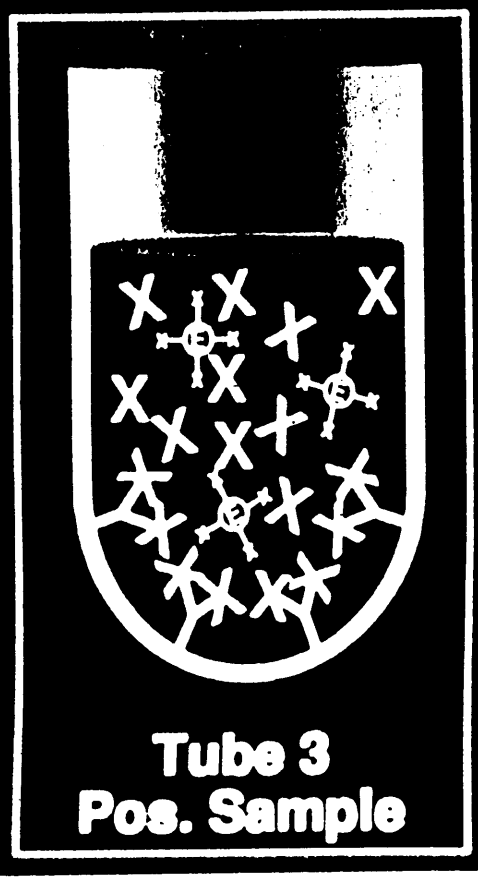
ENSYS INC. ELISA CHEMISTRY
INCUBATION/COMPETITIVE BINDING REACTION



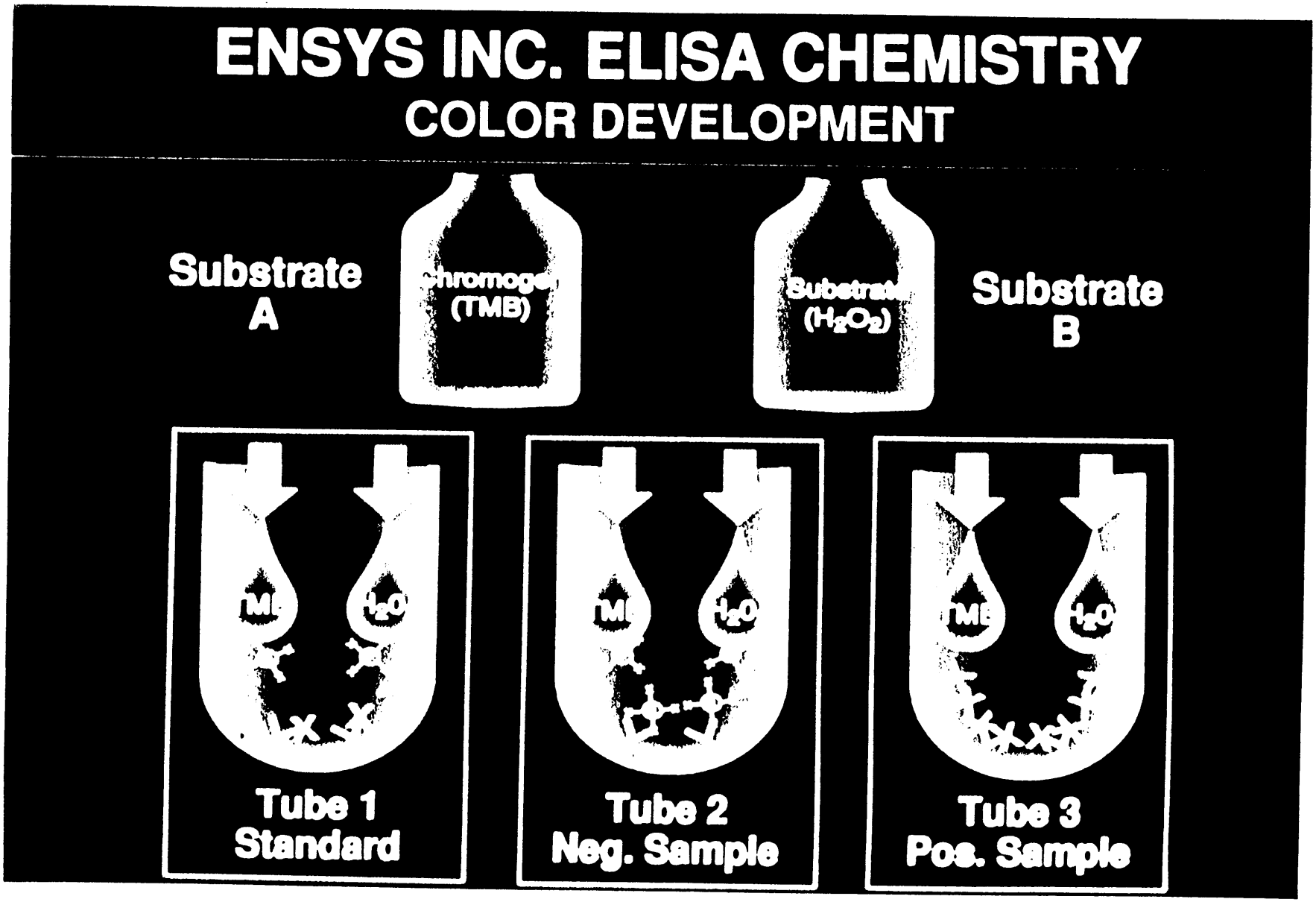
Tube 1
Standard



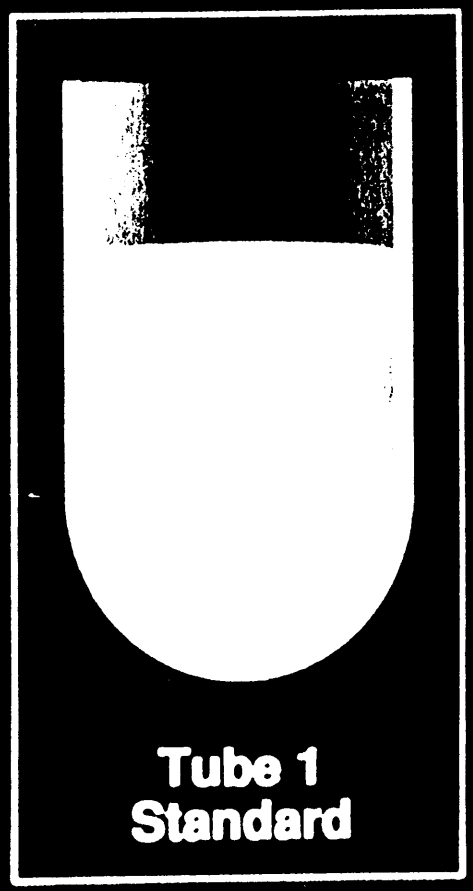
Tube 2
Neg. Sample



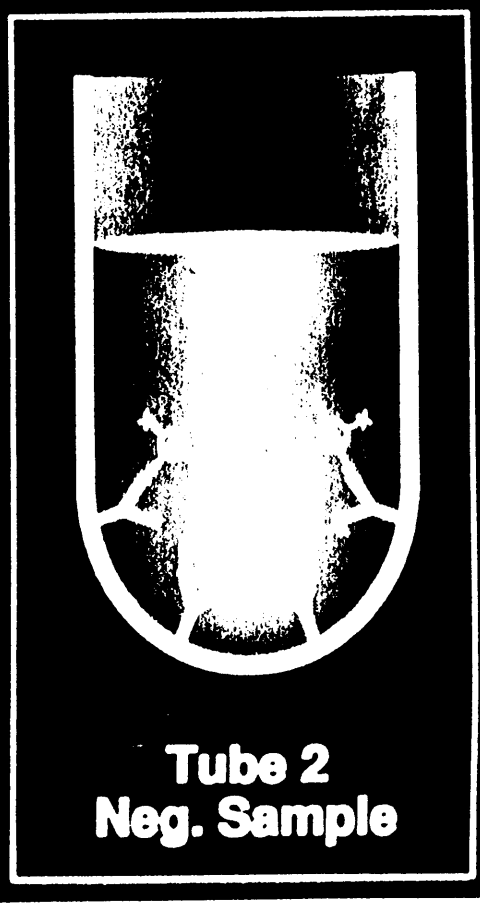
Tube 3
Pos. Sample


ENSYS INC. ELISA CHEMISTRY
COLOR DEVELOPMENT
Substrate A
Substrate B
Tube 1 Standard
Tube 2 Neg. Sample
Tube 3 Pos. Sample

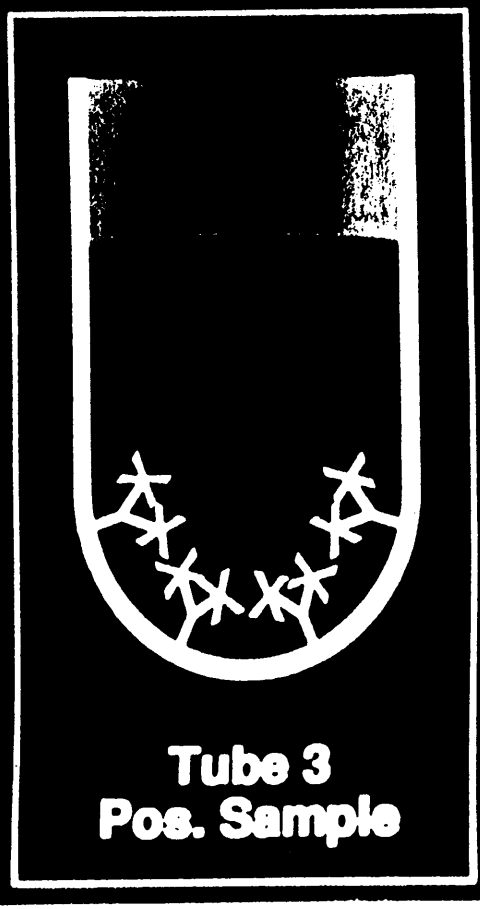
ENSYS INC. ELISA CHEMISTRY
COLOR DEVELOPMENT



Tube 1
Standard

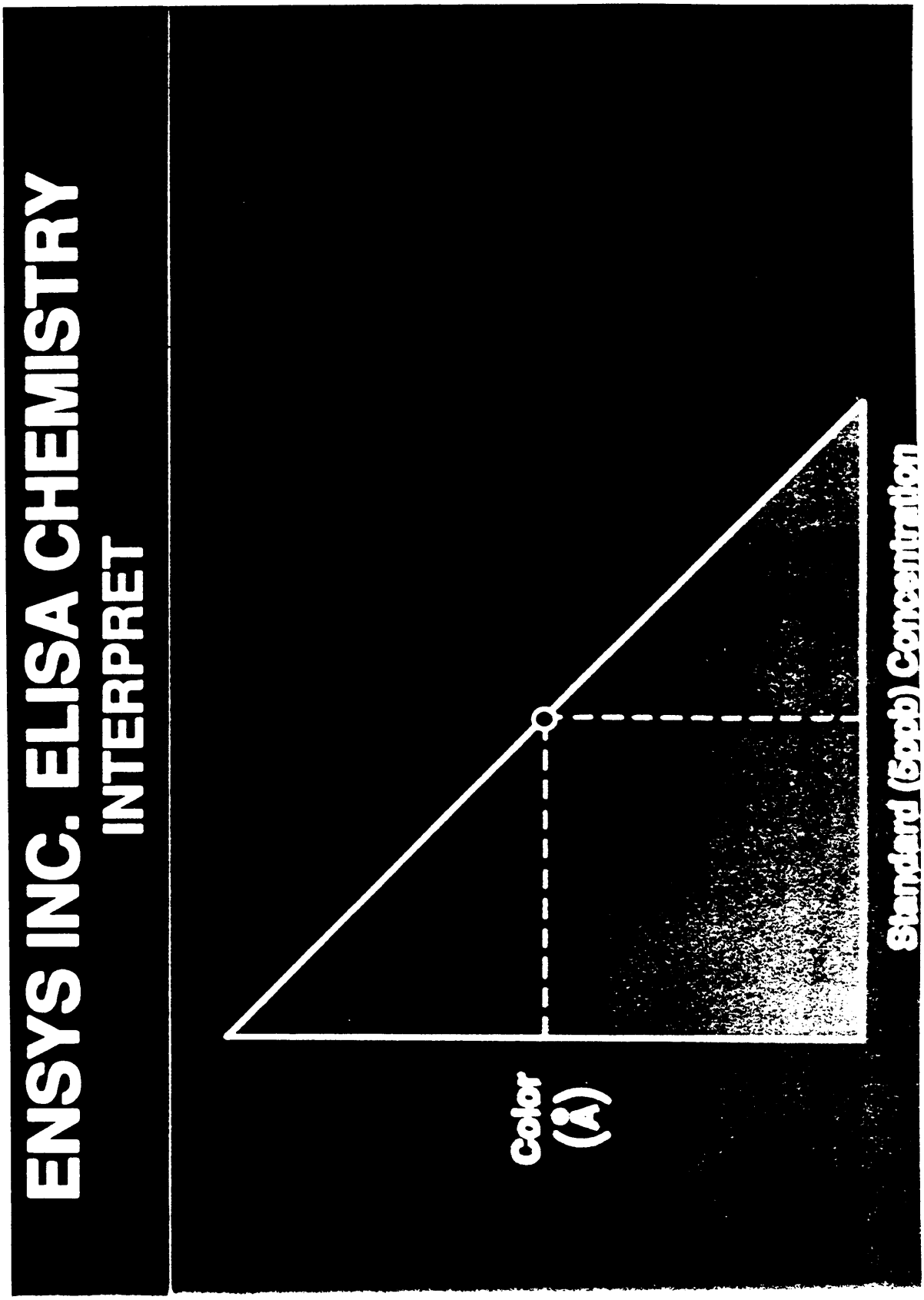


Tube 2
Neg. Sample



Tube 3
Pos. Sample

ENSYS INC. ELISA CHEMISTRY
READ
Standard
Sample


ENSYS INC. ELISA CHEMISTRY
INTERPRET
Color
(A)
Standard (Goat) Concentration

RISc™ SOIL TEST FIELD TRIALS

Objective

To document performance of immunoassay-based field analytical method

- **Potential users as operators**
- **Soil samples from actual contaminated sites**

DOE-ORNL TRIAL

ENSYS INC.

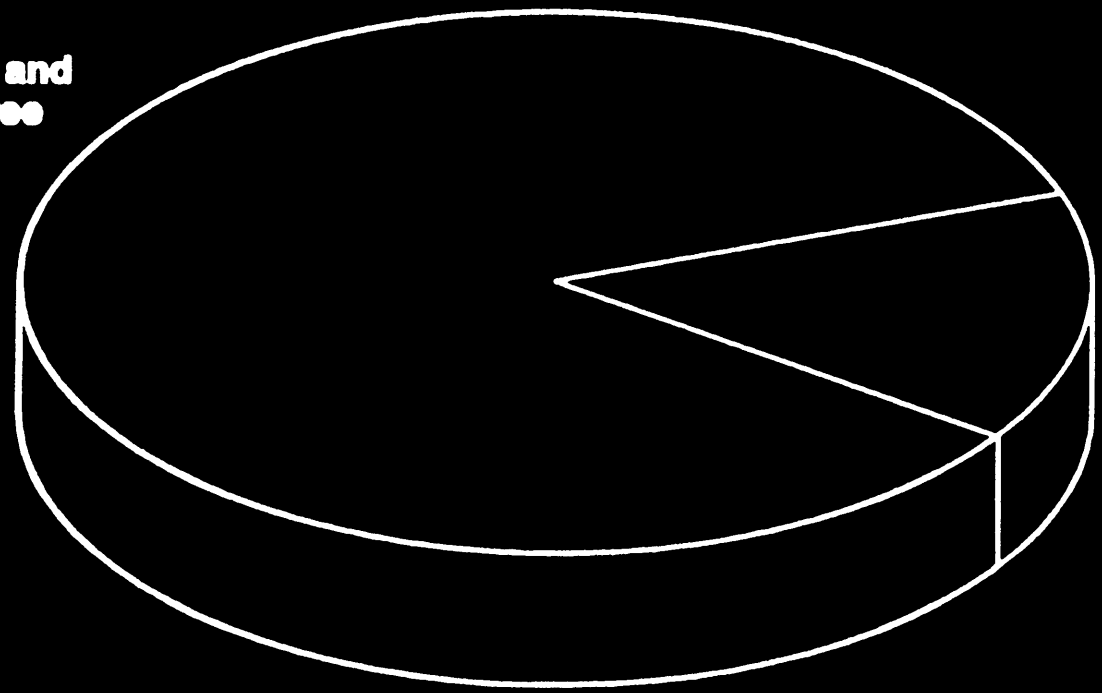
Identify usable field analytical methods for application to DOE site clean-up efforts

- Document degree of correlation with EPA method (3540/8080)
- Examine matrix effects with samples from DOE sites
- Determine repeatability
- Establish lack of user variability

DOE - ORNL TRIAL

ENSYS INC.

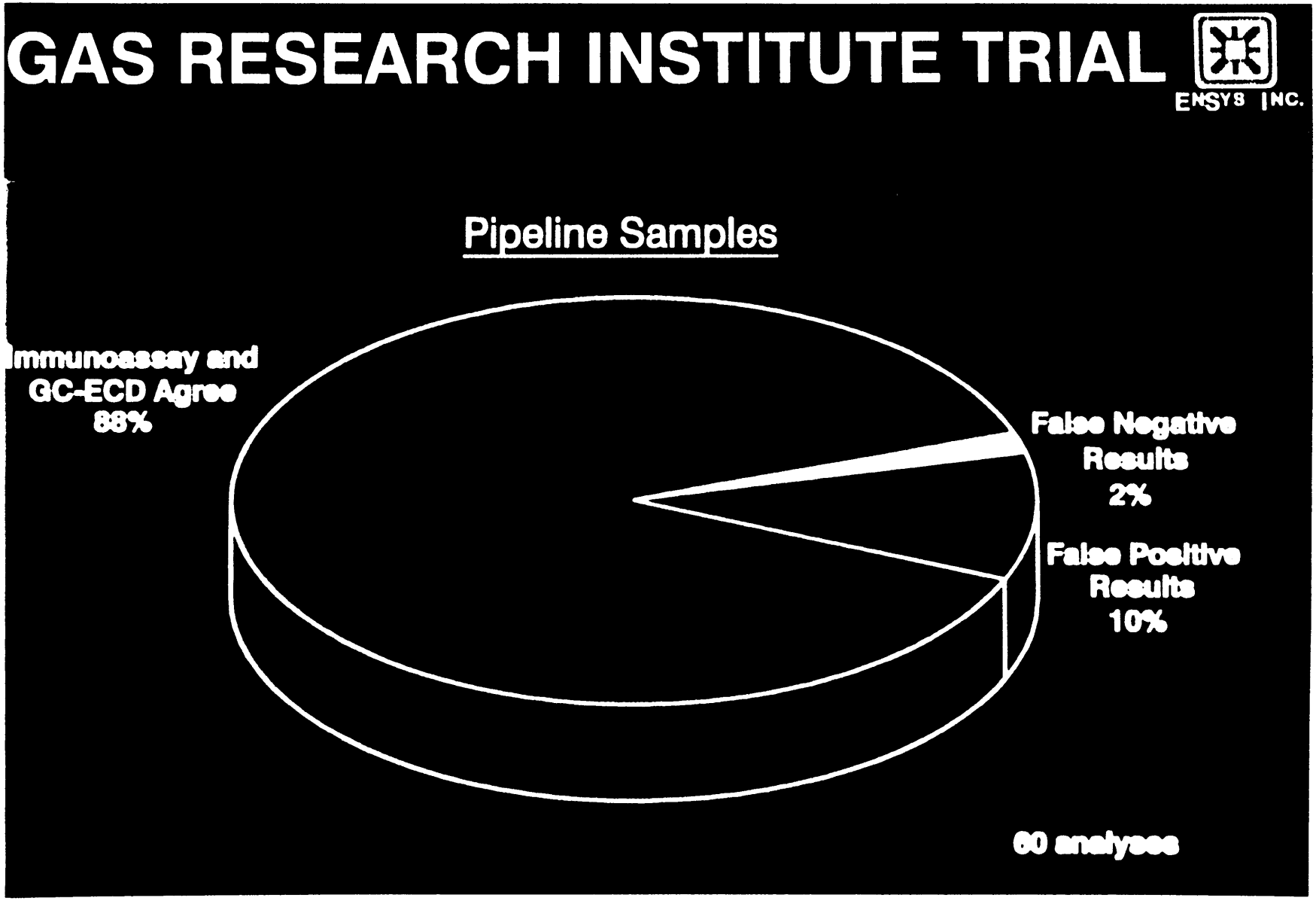
PCB-Spiked Samples



84 analyses

GAS RESEARCH INSTITUTE TRIAL

ENSYS INC.



PENTACHLOROPHENOL RISc™ SOIL TEST FIELD TRIAL

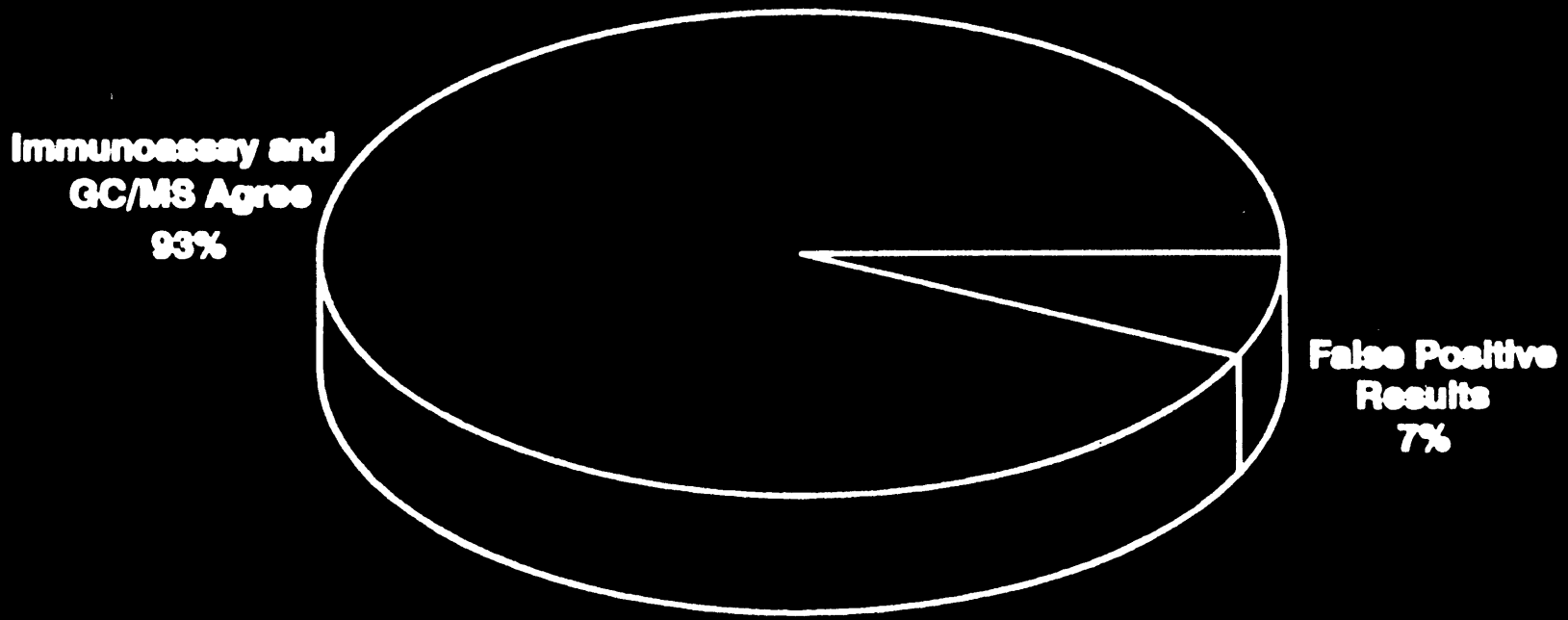
Mississippi State Forest Products Laboratory

Brunswick Wood Treating

ENSYS INC.

MISSISSIPPI FOREST PRODUCTS LAB TRIAL

Pentachlorophenol - Contaminated Soil Samples

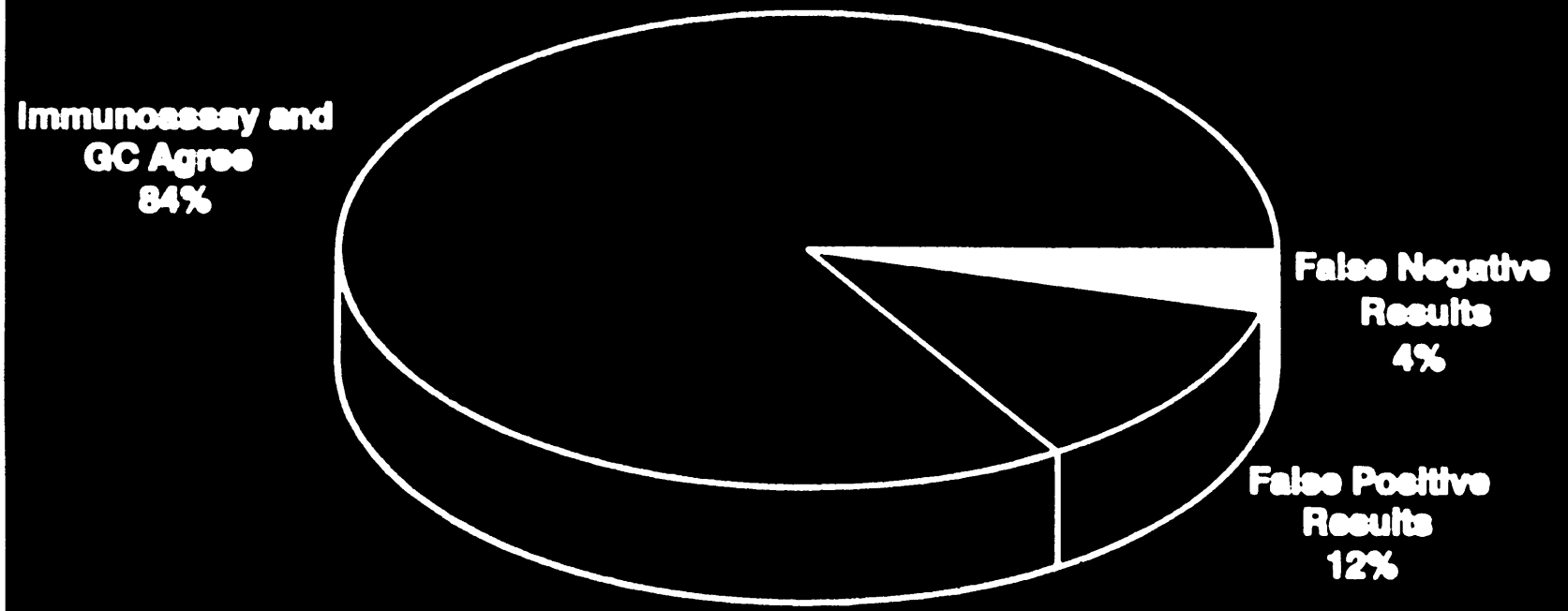


15 samples

BRUNSWICK WOOD TREATING TRIAL

ENSYS INC.

Pentachlorophenol - Contaminated Soil Samples



176 analyses

MR. TELLIARD: Our next speaker is an old timer here. Jim Smith has been an ongoing presenter at this meeting. He is going to discuss the analysis of PCBs and an economic analysis using immunoassay methods for PCB's.

MR. SMITH: This is all real world stuff. You are going to get the numbers.

I am going to give you a little site history. It is going to be a very small place. We haven't got much money. We are going to have a lot of fun.

We are going to attack it normally by gridding the small site. I am going to give you the results. I am going to tell you what successes and failures we had and what we are trying to do to work on other sites with this assay.

The site is about an acre and a half. It is owned by a family. It was used for storing heating oil.

They wanted to sell it. The first thing they did was take down the above-ground heating oil tanks, and they were in the small berm to the left-hand side of the site. You can see the outline of the berm with the right-hand side torn out. Those tanks are now gone.

To the bottom toward the fence next to those above-ground tanks were six very small, 500 to 1000 gallon gasoline underground storage tanks. They were also removed.

In the site assessment, soil samples were taken to conform with New Jersey's regulations. In so doing, you take VOCs, the infamous total petroleum hydrocarbons, and base neutrals, and, of course, for the base neutrals, you look for the PAHs.

That is nice. Fairly clean site. Ready to roll. And some idiot had to look at the TICs.

In that bottom corner where the gasoline tanks were, there was as TIC named 1,1-prime-biphenyl-2,2-prime-3,4-prime tetra...and there wasn't enough space for the rest of the answer. No problem. We have those all the time.

Well, it doesn't take too much to look at the mass spectrum and say oh-oh,

we have got problems here.

Well, if you tell a husband and a wife whose cash flow is not very great on their heating oil business "you have PCBs out there and you own them," you get a lot of tears, gnashing of teeth, calling of lawyers, and the next phase is, what are you going to do for us now that you have given us this good information?

We decided to do some surface samples to find out where the PCBs were. Use the immunoassays, because they don't cost as much as laboratories, they go a lot faster, we can be very selective on site. We are going to work on that hot corner where the gasoline tanks were.

There was an electrical substation next door. We thought we would work along that border. The rest of them we will do at random, a little here, a little there, and see what is dirty and what is clean.

Oh, yes, one must have quality control samples somewhere just to make sure it works. We decided to take out a field GC and use Tom Spittler's Region I quick and dirty PCB analysis just to keep us in the ball park, and then, of course, a laboratory GC method to tell us whether anything we did was right.

If it worked, maybe we could clean up the site if the owners had money.

We gridded it. Nothing difficult there. Quality control. We used blanks out of our back yard soil. We tested it to make sure there were no PCBs in our own back yard. This is aa added benefit of running such things.

We then made a spike of our back yard soil sample. We thought we would do some replicates and, of course, the field GC and the laboratory GC.

We are on site. We have three days. One of the days it rained. So, therefore, we are working inside and outside of the back of a pickup truck with a cap.

The person doing the analysis, both the GC and all the immunoassays, is a high school graduate who has worked in industry for 26 years in a GC lab. He is no dummy, but he certainly is not a Ph.D., either. Of course, that doesn't prove much, does it?

We are using a test for positive PCB above 5 ppm in soil on an as is, not dry weight, basis. All the blanks, and that is 2 a day, show positive numbers, and positive

numbers mean that PCBs are not found by the immunoassay.

This made us very happy. Our blank spikes, 20 ppm, as determined by GC, spiked into our back yard soil should give us all negative numbers which means that it is above 10 ppm for PCB 1242, and we do get negative numbers in each case. As a matter of fact, the technician was so happy with this result, he didn't run the last one, because he was supposed to run 2 a day. But when you are happy and things are going right, why not run an extra GC at the same time?

The replicates looked pretty good except for K1, and he kept running it and running it and running it until he gave up. It just gave us fits. We don't know whether it meant it was positive or was negative.

Field GC, Tom Spittler's method. It is a beautiful method if you want not to use very much solvent or very much sample. One gram of dirt. You put in 2 mL of solvent, shake like the devil, pull a microliter and shoot.

You use a 1-point calibration curve and hope like heck all your peaks are on your chart paper. If not, you have got to go through a dilution, but even with dilutions with a syringe, you never have more than 10 mL of solvent.

The solvent that we used is 1 part water, 4 parts methanol, and 5 parts hexane.

These are the hits, 9 of them. Looks pretty good. Happiness reigns.

The clean samples, 7 of them. Happiness still reigns, except we ran 20 of them. 9 and 7 still doesn't make 20. So, we have 4 that we just don't understand very well.

Apparently, K1 is going to give us fits forever. I would dig up that one and haul it out just for fun. The rest of them seem to be false positives.

Let's go to the lab work. The lab tells me it is 1248 and 1260, mostly 1248. Again, the hits, and note that the highest hit is very close to 1000 ppm which is about 10 times the total concentration of PCBs on the TIC page for the same location.

So, it is a hint. If you see PCBs, as TICs, add up the J values, multiply by 10, and you are going to be fairly close to what is actually in that sample.

The clean ones, 10 of them. Looks very nice. Please note as we have gone

through the numbers, the pluses and the minuses from the immunoassay system that it doesn't look as if it is quantitative. Some answers give you very negative values with very high amounts; some give you very negative values with very low amounts. It does not appear to be quantitative.

Oh, yes, we still have the infamous 4, except these 4 are 2 different ones from the field GC work. So, if you like, we now have 6, and again, they apparently are false positives.

Note that for all of these, whether it be field GC or laboratory GC work, we are dealing with the values near the go/no go level of 5 ppm. There is no major disaster there.

What did we do in three days? By the way, the technician told me if I said they were 8-hour days, I had to pay him time and a half for the rest of it. So, therefore, they were closer to 12-hour days.

One hundred seventy-two runs on the assay system, 20 on the field GC, and he worked hard. It would be much simpler to have two people working the system and setting up each. You would get a lot more done a lot faster without burnout.

Twenty-one samples were sent to a laboratory with full CLP-like data packages.

Was it successful? The map again. The red X's are the hits for the immunoassay. The red solid squares are hits for either the field or laboratory GC. The green X's are the clean, and the fukk green boxes are laboratory or field clean samples by GC.

The spot that seems to be most contaminated is where they dug up the gasoline tanks. I have yet to hear anyone mention that PCB is a new additive for gasoline.

When they dug up the dirt, guess where they placed it? On the concrete right next to it, and, of course, that is the next place that is most contaminated.

And where did they push the concrete after they cleaned up some of the soils they took out when they were removing the gasoline tanks? Well, down by S, about two or three or four, and the S mark is where you will find the concrete pieces.

So, it makes sense that the system worked very well in the field. We know where the contamination is.

How did the contamination get there? The previous owner was a supplier of fuel oil. He was also a hazardous waste hauler. New Jersey did indict him, so it is said, for hauling fuel oil laced with PCBs to be burned in New York City apartment buildings. Who knows? But the PCBs are certainly there where the gasoline tanks were.

It cost approximately $12,000 to do all the tests on site. That comes down to about $30 on an immunoassay test and the technician's time. The field GC was free. It was his time anyway.

The laboratory confirmation cost about as much as the 172 tests that we made on site, and they came in about two weeks later.

This does not count the time and effort put in by the sampler whom we kept very busy. The amount we saved is approximately an equal amount to what was spent. If we had gone to a laboratory and received just sample results sheets, the cost would have been about $25,000.

The success is that it worked. I think we did map the problem. It is a success if you can do that and save money.

If there is a failure, it is the false positives and possibly a false negative that occurs near the detection limit of the system.

Presently, we are trying to get approval to use the system on a Superfund site to help guide test borings to determine where the PCBs are on about a 3-acre Superfund site in New York State. We are trying to lower the detection limit, because the United States EPA developed a ROD for a 1 ppm cleanup. We think we have accomplished that.

We are not sure of the extraction efficiency which uses methanol on very wet samples. We think it works well. We have just never tested it.

The other thing we would like to do is to compare, side by side in the field, various companies' systems. They are not exactly the same, but we would like to compare them to see which one is easier to run, which one works better at the detection limit and gives the fewer false positives, and which one would be most cost effective to

do a screening analysis for a site for PCBs.

I thank you for your attention. We had fun. I suggest you try it. It works.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Questions? Are you going to let him off?

Okay, thanks so much. Oh, hold it. Got you.

MR. THOMAS: Yes, my name is Roger Thomas. I am from Viar and Company.

I had a question concerning the false positives and false negatives. The majority of times, false positives and false negatives are usually attributed to interferences, and the way to remove interferences is through various cleanup procedures.

Have you done any studies concerning various cleanup procedures both for the field GC analysis and the colorimetric procedure that you used in your immunoassays? Like, for example, you have a wash procedure that removes interferences prior to performing the colorimetric procedure. Have you tried various types of washes?

MR. SMITH: No.

MR. THOMAS: Okay, thank you.

MR. TELLIARD: Thanks, Jim.

MR. TELLIARD: Our next speaker is going to discuss some work that the Office of Water sponsored looking at the implications of immunoassay.

Harry?

COST EFFECTIVE PCB INVESIGATION

UTILIZING IMMUNO ASSAY

By:

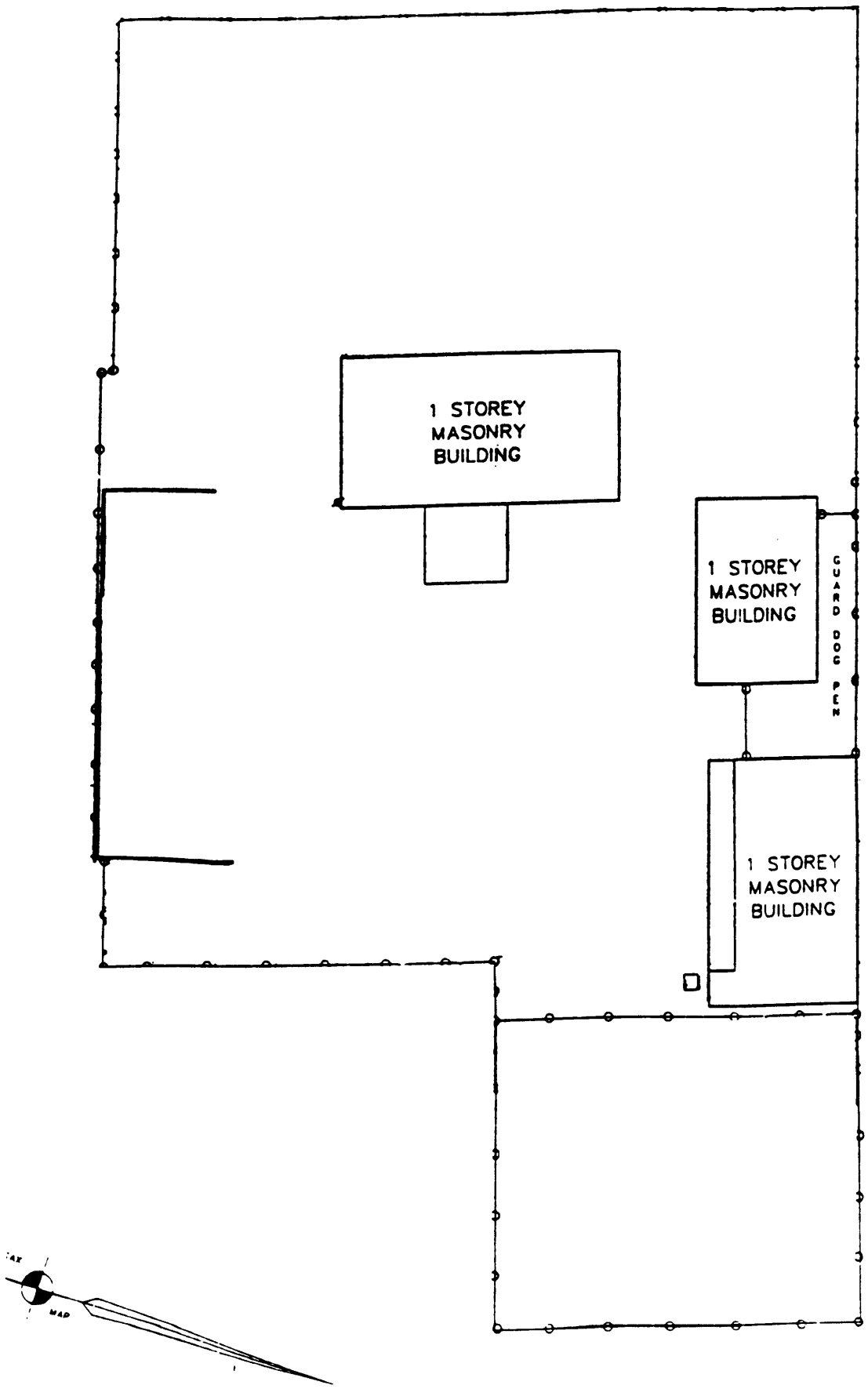
Jim Smith and Gene Brozowski
Trillium, Inc.

and

John Rhodes
Rhodes Engineering

PRESENTATION OUTLINE

1. *Site History*
2. *Plan of Attack*
3. *Results*
4. *Successes and Failures*
5. *Tomorrow*


1 STOREY
MASONRY
BUILDING
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BUILDING
GUARD DOG PEN
1 STOREY
MASONRY
BUILDING

PLAN OF ATTACK

1. *Surface Samples*

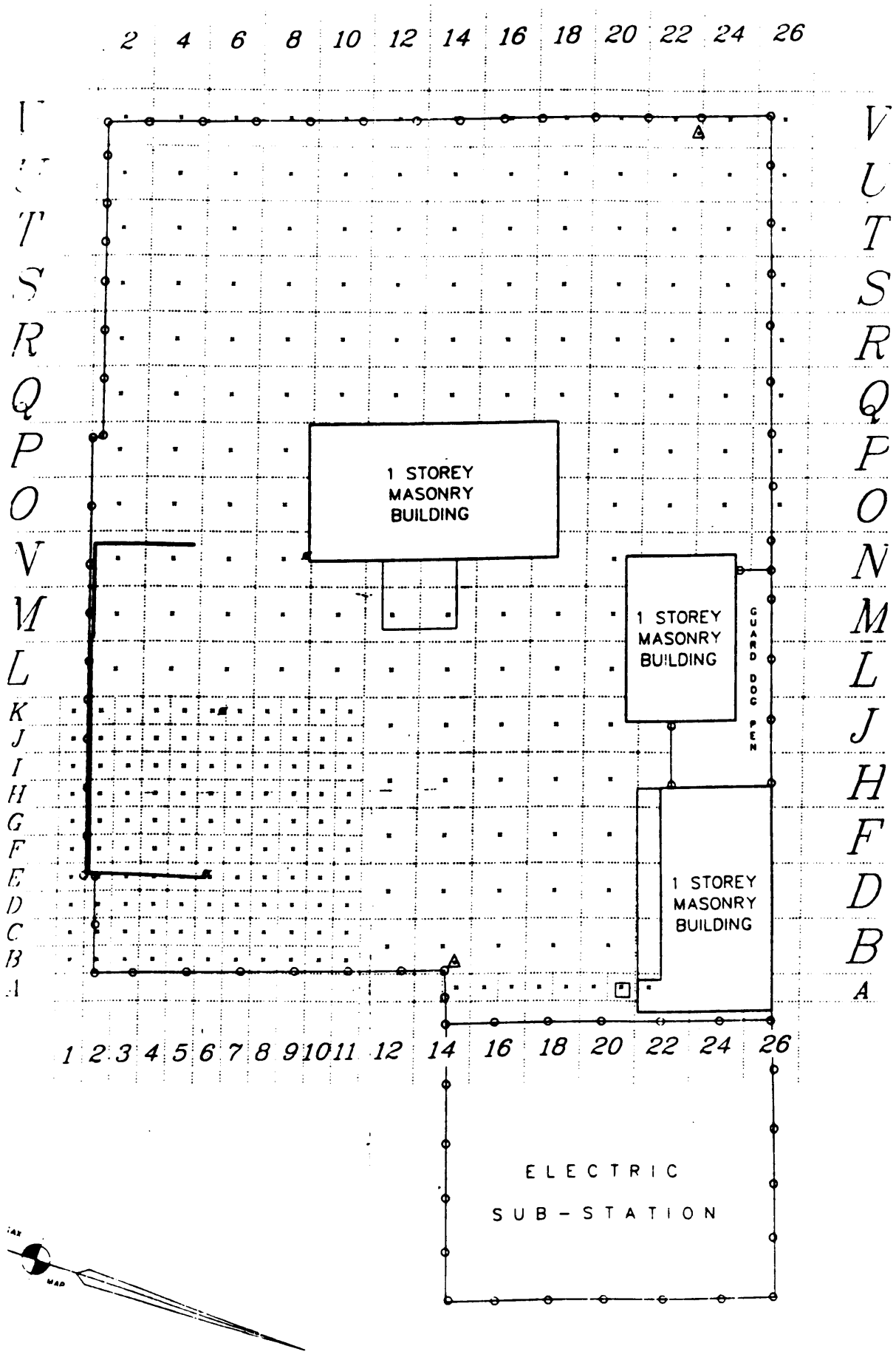
2. *Immuno Assay*

   - *Hot corner*
   - *Electric substation*
   - *Random*
   - *Quality control (QC) samples*

3. *Field Gas Chromatograph (GC)*

4. *Laboratory GC*

5. *Option of Cleanup or Depth Profile*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V U T S R Q P O N M L K J I H G F E D C B A
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1 STOREY MASONRY BUILDING
GUARD DOG PEN
1 STOREY MASONRY BUILDING
1 2 3 4 5 6 7 8 9 10 11 12 14 16 18 20 22 24 26
ELECTRIC SUB - STATION

QUALITY CONTROL

1. ***Blanks***
2. ***Blank Spikes***
3. ***Replicates***
4. ***Field GC***
5. ***Offsite Laboratory GC***

BLANKS

All positive sample values indicate a "not detected" (ND) with a detection limit of 5 parts per million (ppm) PCBs.

Blank No.	*Value*
1	*+0.18*
2	*+0.14*
3	*+0.32*
4	*+0.30*
5	*+0.27*
6	*+0.05*

BLANK SPIKES

20 mg/Kg (Air Dried) PCB 1242

All negative sample values indicate that the sample contains 5 mg/Kg or more of PCBs.

Blank Spike No.	*Value*
1	*-0.33*
2	*-0.16*
3	*-0.11*
4	*-0.10*
5	*-0.23*

REPLICATES

(Co-located)

	Values				
Sample Location	***Run 1***	***Run 2***	***Run 3***	***Run 4***	***Run 5***
D-9	***+0.04***	***+0.22***			
G-10	***- 0.12***	***- 0.07***			
H-3	***+0.15***	***+0.22***			
H-14	***+0.24***	***+0.28***			
K-1	***- 0.01***	***- 0.01***	***+0.22***	***+0.09***	***+0.01***
K-5	***- 0.43***	***- 0.25***			
K-10	***+0.17***	***+0.21***			

Positive values: <5 mg/Kg (wet weight)
Negative values: >5 mg/Kg (wet weight)

FIELD GC

"HITS" (Negative Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (wet wt.)*
D-6	*-0.47*	*>400*
F-9	*-0.09*	*16*
E-1	*-0.55*	*100*
J-5	*-0.39*	*18*
J-4	*-0.56*	*120*
I-7	*-0.23*	*24*
D-7	*-0.42*	*40*
D-4	*-0.51*	*400*
I-5	*-0.60*	*150*

FIELD GC

"CLEAN" (Positive Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (wet wt.)*
D-10	*+0.06*	*ND*
B-6	*+0.36*	*ND*
C-8	*0.00*	*2*
B-10	*+0.07*	*ND*
B-8	*+0.38*	*2*
H-20	*+0.37*	*ND*
J-14	*+0.28*	*ND*

ND is not detected with a detection limit of 1 mg/Kg (wet weight).

FIELD GC

"OOPS"

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (wet wt.)*
G-10	*-0.12 and -0.07*	*ND*
K-1	*-0.01 and -0.01 and +0.22 and +0.09 and +0.01*	*6 and 8*
K-9	*-0.01*	*1*
D-8	*-0.06*	*4*

3 False Positives
1 False Negative

ND is not detected with a detection limit of 1 mg/Kg (wet weight).

LABORATORY RESULTS
(Sum of PCB 1248 and PCB 1260)

"HITS" (Negative Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (dry wt.)*
B-1	*-0.51*	*730*
D-4	*-0.54*	*960*
D-6	*-0.47*	*700*
E-1	*-0.55*	*640*
H-6	*-0.45*	*210*
J-5	*-0.39*	*36*
S-4	*-0.22*	*5*

LABORATORY RESULTS
(Sum of PCB 1248 and PCB 1260)

"CLEAN" (Positive Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (dry wt.)*
A-15	*+0.32*	*0.4*
A-16	*+0.33*	*0.8*
A-17	*+0.37*	*ND*
A-18	*+0.06*	*2.7*
A-26	*+0.34*	*0.5*
B-6	*+0.36*	*1.3*
B-10	*+0.07*	*0.6*
L-14	*+0.15*	*0.6*
O-24	*+0.67*	*ND*
V-12	*+0.63*	*ND*

ND is not detected with a detection limit of 0.1 mg/Kg (dry weight).

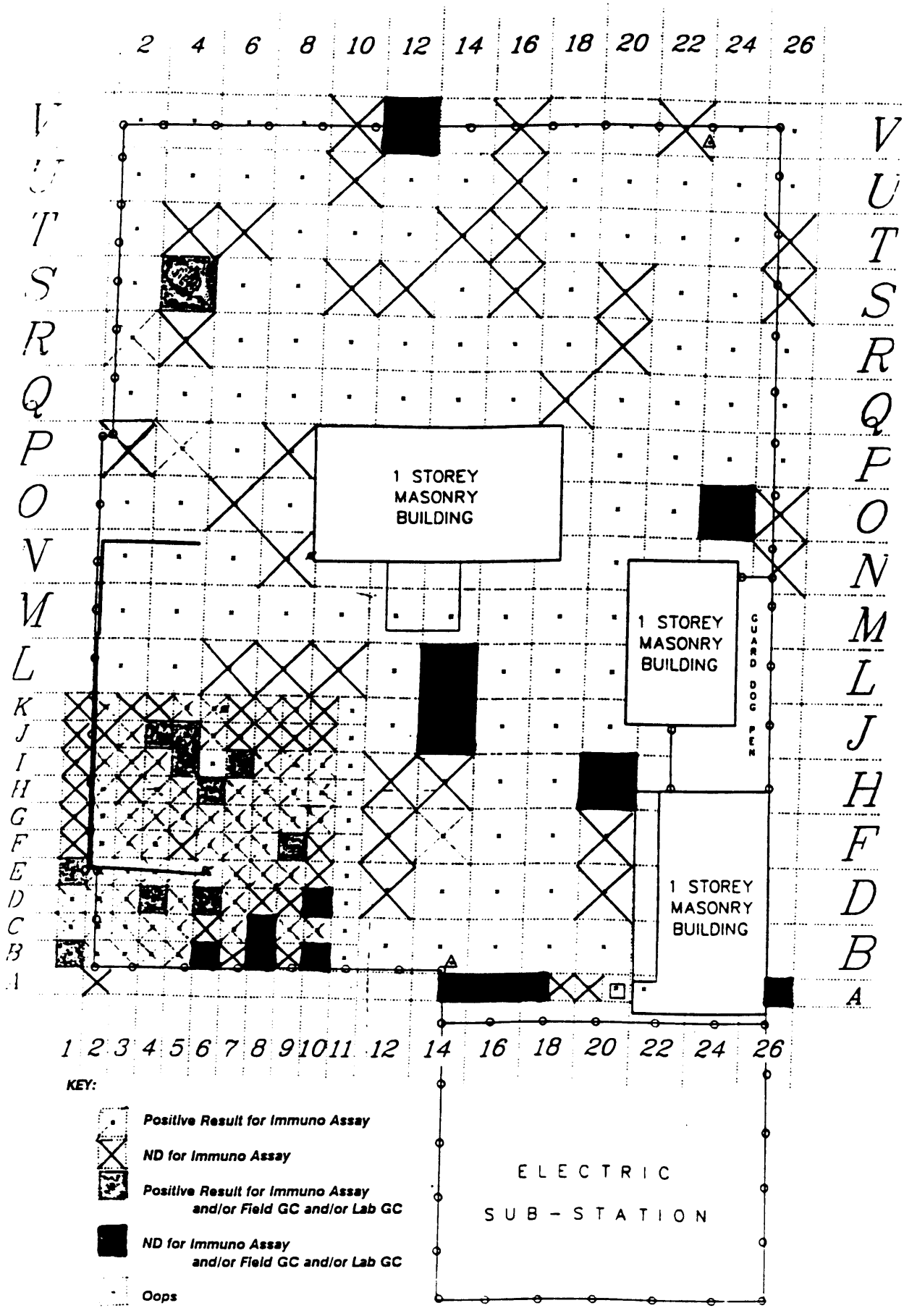
LABORATORY RESULTS
(Sum of PCB 1248 and PCB 1260)

"OOPS"

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (dry wt.)*
G-10	*-0.12 and -0.07*	*ND*
K-1	*-0.01 and -0.01 and +0.22 and +0.09 and +0.01*	*1.5*
K-9	*-0.01*	*1.4*
P-2	*-0.23*	*1.7*

3 False Positive Values
1 False Negative Value

ND is not detected with a detection limit of 0.1 mg/Kg (dry weight).


2 4 6 8 10 12 14 16 18 20 22 24 26
V U T S R Q P O N M L K J I H G F E D C B A
1 STOREY MASONRY BUILDING
1 STOREY MASONRY BUILDING
GUARD DOG PEN
1 STOREY MASONRY BUILDING
1 2 3 4 5 6 7 8 9 10 11 12 14 16 18 20 22 24 26
KEY:
Positive Result for Immuno Assay
ND for Immuno Assay
Positive Result for Immuno Assay and/or Field GC and/or Lab GC
ND for Immuno Assay and/or Field GC and/or Lab GC
Oops
ELECTRIC SUB-STATION

SUMMARY

SAMPLES ANALYZED

Immuno Assay (3 Days)

# Samples:	*151*
# Blanks:	*6*
# Blank Spikes:	*5*
# Replicates:	*10*
Total:	*172*

Field GC

# Samples:	*20*

Laboratory GC

# Samples:	*21*

SUMMARY

SAMPLE COSTS

Immuno Assay	*$ 5,160*
Field GC Analyses (including technician for field GC)	*2,560*
*Laboratory GC Analyses**	*4,050*
Total Analytical Invoice:	*$11,770*

**Includes 2 duplicates, 2 matrix spike/matrix spike duplicates, and data package.*

SUCCESSES AND FAILURES

Successes

1. *Surface PCBs Mapped*
2. *Money Saved*

Failures

1. *False Positives and False Negatives*

TOMORROW

1. *Compare immuno assay systems*
2. *Lower detection limit to 1 mg/Kg (ppm)*
3. *Determine extraction efficiency versus sample water content*
4. *Field test at a Superfund site*

MR. MCCARTY: Good morning, folks. I would like to thank you for hanging around for Thursday.

I would like to make three points real quick. One, I am not Bill Telliard. Two, contrary to popular confusion, I am not with EPA, and three, I am not here to help you.

[FIRST SLIDE] I am also not Cindy Simbanin, but I figured you could figure that one out on your own. Cindy couldn't make it today to give you this presentation. She asked me to give you her apology, and if Bruce is in the audience somewhere, she particularly wanted to be remembered to Bruce Colby. Not sure why.

As Bill mentioned, we are going to talk a little bit about the work that was done in conjunction with the pesticide effluent guideline work that Bill's office has been doing in this past year or so. We looked at the traditional gas chromatographic methods in concert with some immunoassay techniques that have become available.

[SECOND SLIDE] By way of introduction for those of you who haven't been regulated yet or don't know what an effluent guideline is, under the authority of the Clean Water Act, EPA develops guideline limitations for the 64 industrial categories, in the U.S. that discharge wastewaters into surface waters of the United States.

The current slate of guidelines include the development of guidelines for the pesticide manufacturing industry and the formulators and packagers, the people who take what somebody else manufactures, mix it together, add the 87 percent inert ingredients, and put it in a bottle that you can't get the cap off unless you are a five-year-old.

[THIRD SLIDE] As a result of trying to develop these guidelines, EPA collects a large amount of data. The number of samples will vary from facility to facility and, certainly, is dependent upon the industry, but there are a large number of compounds that they look for at any one time.

At a minimum, we are talking about looking for things on the priority pollutant list which brings it up to about 126 compounds.

The sample types span the range of what is produced in an individual

industry. The obvious importance of the final effluent that is being discharged is pretty evident, but also, they look at the in-process waste streams, in part, to look at treatment technology. If you have got a lot of it in your process and you end up with very little at the end, then you have got a good treatment process, and there is some measure of that treatment efficiency.

[FOURTH SLIDE] In terms of analytical methodologies, and traditional methodologies in particular, you are talking about the need for relatively high sensitivity, sub-ppb levels for the pesticides in particular. We are talking about a wide range of concentrations, because you are dealing with not only final effluents that are supposed to be pretty clean, but also in-process samples.

Given the matrix effects you would expect in in-process samples, you are going to have to be able to deal with those kinds of challenges to the technique itself.

[FIFTH SLIDE] For the traditional GC approach, you are talking about some sort of a solvent extraction. For the herbicides in particular and other related compounds, you are often talking about a derivatization step which helps deal with some of the matrix effects.

There are various cleanup techniques including florisil alumina, and silica gel column cleanups, GPC in certain cases, etc.

And then the analysis is typically dual column GC with one of several detectors, EC, the Hall or electrolytic conductivity, or an NPD (nitrogen/phophors) kind of detector.

[SIXTH SLIDE] As any of you who have ever run those analyses know, there is a whole suite of problems associated with those analyses. While an individual analysis may not appear particularly costly, the cost to EPA for a large number of samples adds up.

Waiting 35 to 40 days, in some cases, to get the data back is certainly an issue in terms of going out and making sure that you have collected the right samples from the right part of the industry.

The wide range of concentrations that you find complicates the problem for both the agency and the laboratory. You often end up running a large number of

dilutions to get 1 of 27 compounds in range for this dilution and 2 others at a higher dilution, et cetera.

For the laboratory, certainly, you can easily contaminate your instruments and other samples or the sample processing glassware by having really nasty, ugly, dirty samples come in that didn't look that bad when you took them out of the bottle. And this often leads to down time in the laboratory and, from the perspective of EPA, or Viar and Company as one of their contractors, it leads to a certain amount of down time as we wait to get the data back, and then determine that the lab was supposed to have run another dilution.

So, we are looking at ways to get around these problems in a cost effective manner. We are looking at the promotional material that has been available for immunoassay for the past couple years. I know I get it. I have seen it in Bill's office, and most of the rest of you probably get swamped with 3rd class mail around the time of the Pittsburgh conference, and occasionally you read some of it.

[SEVENTH SLIDE] We have talked with a number of the vendors for immunoassay materials in the past year, and are looking at some of the materials that were available, and the advantage that we could see was, obviously, as you have heard already this morning, they are quick. They can be highly selective, depending on what analytes you are looking at and what matrices.

They are relatively simple to use. We could even teach engineers to do this, I suspect.

They are portable, or fieldable. You could carry some of the immonoassay kits in a knapsack if you needed to go out in the field, but, certainly, given all the other things that are being lugged around in coolers, this technology presents no problem in terms of getting it to the site.

[EIGHTH SLIDE] The purpose of this specific study was to provide a rapid, cost effective comparison of immunoassay techniques with traditional gas chromatographic techniques on what everyone else here has been talking about, real world samples. Nasty, ugly, awful, effluent and in-process samples.

If you know how to read the buzz words, rapid and cost effective, we are

talking quick and cheap. Quick because we wanted to do it in concert with the existing schedule for the pesticide manufacturing, packaging and formulating work that was going on out of Bill's office; cheap because we didn't have a lot of money to do it.

[NINTH SLIDE] We designed a study, again, piggybacked on the existing sampling plans for these industrial facilities. So, it had to be done on the fly in that regard, and we were fortunate in that it didn't take a lot of work to set up something for immunoassay. It doesn't present any difficult problems in terms of sampling.

We were already using or getting ready to use the traditional GC methods, and we added to that what we are calling the tube and plate immunoassay materials. We were dealing with commercially available materials from Millipore.

Their tube kit looks very much like the material that Kevin Carter was talking about this morning. I want to thank him for putting up the nice slides, because I certainly didn't have the facility to do the diagrams specifically of the process.

There was some discussion of the plate kit. It is a little well kit like you would see in a medical testing laboratory. 96 wells to a plate, 8 by 12, something like that, and there is a reader that will do a quantitative, or certainly much more quantitative, measure of the color development and give you a better number.

The tube kits, again, we used as a semi-quantitative screening tool. It is essentially a 1-point calibration.

We were using a calculator-sized, you can stick it in your pocket, color comparator that Millipore has. It will give you an instrumental reading much as Jim Smith was showing, (minus point something to plus point something) which can be related to concentration.

[TENTH SLIDE] The tube kits were run in duplicate, which is also a recommendation from the manufacturer.

For the tube kits, we started out saying, we know this is semi-quantitative, let's not go overboard on running 17 replicates of all of these things. We decided to run a duplicate if running of a duplicate, and use that to figure out what level of dilution of the sample was most appropriate to move forward with for the plate kit, which is alleged to be a lot more quantitative. It certainly was in our case.

As a result, we ran the plate kits in triplicate once we figured out the best level of dilution using the tube kit, rather than going through the whole process again to determine what is the best level of dilution. We said the immunoassay procedure is the same regardless of the form of the kit, whether it is the plate or the tube. Therefore, once we had established, through the use of the tube kit, how many hundreds of times you had to dilute some of these samples to get them in the range you want, we just went ahead with that level of dilution and ran the plate kit in triplicate.

The GC methods were performed as traditionally is done; as a single analysis. We took the ERL Athens, Georgia approach " Anybody who runs a sample more than once gets exactly what they deserve. "

We looked started with either a neat analysis for GC and then diluting down, or making an intermediate level of dilution as a first estimate, and then going back and either reconcentrating or diluting, in most cases, much further, in order to get all of your analytes within the range of the GC method.

All the GC results were confirmed by a second column analysis.

All of this work was done in a commercial laboratory under contract to Viar and Company, under our EPA contract.

As was discussed earlier this morning, these materials are fieldable, but we wanted to have a single set of operators essentially doing everything.

[ELEVENTH SLIDE] We were looking at four specific analytes by GC that were amenable to the immunoassay techniques that were commercially available. The metolochlor, atrazine, the two endosulfans, and 2,4-D were the analytes that we picked from the GC method and came up with corresponding immunoassay kits.

As you can see for the first three, you are not talking about a compound-specific immunoassay. There are a lot of triazines out there. We were concerned about atrazine because of the facilities we were working in.

There is an even larger suite of possible cyclodiennes compounds that the immunoassay is sensitive to. 2,4-D was very convenient because it is a compound-specific immunoassay.

[TWELTH SLIDE] Again, the work was all done in a single commercial

laboratory. The sampling crews went out in December of '91 and February of this year to sample two facilities, based on knowledge of what was going on at the planned time of sampling.

We were looking at 2,4-D, atrazine, and metolochlor in the first facility. There were four of what the facility called treated effluents. These were typically materials that had been through some level of bulk carbon column cleanup or some other treatment technology to which a final finish was applied before you got to the final effluent.

We looked at two in-process wastewaters from the first facility, and then one raw water, which is essentially their well water or city water, whichever it is that is coming into the facility.

[THIRTEENTH SLIDE] At the second facility we were concerned about endosulfan in particular, because of what they were doing. With packagers and formulators in the pesticide industry, what they are doing this week may be radically different from what they did last week or what they do next week, or even what they do two days from now.

The second facility had five of what they call untreated wastewaters, two of these partially treated effluents, and then three different final effluents that we looked at at that facility.

The tests were all done at a single contract laboratory, which had little experience with immunoassay techniques. We got the materials to them a couple weeks ahead of time, and they played around with them and got some experience using some leftover sample volume that they had in the laboratory.

They reported back some potential problems to us and some specific concerns from the standpoint of the work we were trying to do.

We worked with the manufacturer, Millipore, at that point, to try to resolve some of these issues so that we didn't start work on real samples with a bunch of laboratory people who were essentially rookies at the technique. I want to thank Millipore for their responsiveness to our time frame in getting answers back to the laboratory. We were acting, in part, as intermediates here on the issues of the

technology itself.

[FOURTEENTH SLIDE] I am actually going to present some real data. These are the data as received from the laboratory. One of the biggest problems is we forgot to tell the laboratory to treat the immunoassay data like everything else and not give us every decimal place they could generate on an 8 bit computer chip.

So, as a result, 937 probably isn't a real significant number there, but I did not make any attempt to round off these data.

The 2,4-D results; the first column of results is the results from the duplicate tube kits. That is a mean of the two results and a relative percent difference in parentheses. The second column is for the plate kits. It is the mean of the three replicates and a relative standard deviation. The third column the GC is a single value reported to essentially two significant figures there.

Some of these samples are pretty highly contaminated. For the in-process waste streams at the bottom, I did not put the commas into the GC results on that last one, but we are talking about percent levels of 2,4-D in the process itself.

The answer by any one of these techniques for the in-process samples, there is a hell of a lot of 2, 4-D there. You are not going to discharge that, so from a compliance monitoring standpoint, it doesn't matter if it is really, 33365 or 40,000, or whatever. It is a lot of material, certainly.

If you look at the raw water results, there was very little, if any, 2,4-D found. The GC detection limit is probably on the order of 0.1 ppb in this analysis.

So, you have a detectable level of 2,4-D there. It is confirmed quite well in the plate test. For the tube test, it simply was not there below a 1 ppb level. All these values are in ppb, micrograms per liter.

For the first of the various treated effluents, there is not very good agreement at all among the tube results, the plate results, and the GC results. With a 29 percent RSD, there is a fair amount of overlap there, certainly.

For the second treated effluent, the tube and the plate come into closer agreement; the GC results look to be higher. I am not going to make apologies or excuses or explanations about these data at this point, but I think there is a fair amount

of agreement, certainly, between the two immunoassay techniques and the GC results. In particular, the 2,4-D results look fairly similar.

[FIFTEENTH SLIDE] For atrazine, the biggest problem we found was we could not find it by the GC method because of sensitivity. The limit on the atrazine method, as run, was about 20 parts per billion, and we weren't seeing it there. By doing a little bit of work on the raw water, we were able to get down to a lower concentration and confirm a number around 1 ppb.

The tube and the plate kits look fairly close, certainly within a factor of 2 to 3 for the triazines. If we had run the tube in triplicate, as opposed to duplicate, we could have even done a T test and maybe shown a little bit better agreement.

[SIXTEENTH SLIDE] The metolochlor results are shown here. Again the basic problem is that it was not detectable by the GC method. We came up with quite close agreement for most of these samples. For the raw water, we couldn't detect it in the tube kit. It was below the sensitivity of that, but we got reasonably decent plate kit results there with a 10 percent RSD at a low level.

[SEVENTEENTH SLIDE] Endosulfan was another one where there was clearly a lot of it out there. Huge results in some of these untreated effluents for the tube and the plate kits. But if you look over at the GC results, you will notice very quickly that the GC does not confirm, in many cases, either the presence of endosulfan I or II, or the concentration. I will talk a little bit more about this later.

As you can see from this slide, this is the worst of it. There are the untreated effluents, the five of them, and some of those are pretty heavily loaded.

[EIGHTEENTH SLIDE] For the treated effluents, clearly you got lower results with the GC than with either the tube or the plate kit.

The first of the final effluents had non-detects by any one of the techniques. In the second final effluent, the plate kit came up with a 12 ppb level where the GC method did not confirm it.

[NINETEENTH SLIDE] Basically, there is a lot of comparison between the techniques for certain analytes and certain samples. The cleaner samples were clearly better. Looking at final effluents, and at raw water, where you have not got

significantly elevated concentrations of any of these analytes, there was pretty good agreement. Based on the reports from the laboratory there seemed to be a lot fewer problems with the samples.

This is certainly consistent with the results that other people have shown for agricultural runoff, for drinking water, things like that.

You don't expect a lot of problems with samples that are on the order of 10 ppb or less. These techniques are all relatively sensitive there, and you get good reproducibility.

The tube kits are semi-quantitative by design. Nobody advertises them to be significantly different. As we heard earlier this morning, the quantitation is based on a 1-point calibration.

One could go out, presumably, and develop a multi-point calibration, but given you are looking at a color development reaction in the field, I don't know that it would really make a lot of sense.

In a fixed laboratory, you would have a lot more possibility to do that, but you also have the possibility to do the plate kit, which is certainly intended to be more quantitative.

[TWENTIETH SLIDE] Both the tube and the plate kit results gave pretty good precision, judged by RPDs or RSDs, for some of these samples and some of the analytes. For other samples and analytes, there is poor agreement. There is no hiding that.

The 2,4-D results probably are the best, and, again, that is the instance where we are talking about a compound-specific analysis. As one might expect, when you get to higher concentrations, the agreement is worse, in part because of the dilution.

We are talking about samples that were diluted by a factor of 500,000 to 1 to be analyzed by almost any one of these techniques. Given percent levels of endosulfan or some of these other compounds, you are going to have to dilute the hell out of these samples to put them on a GC without blowing it and the laboratory away.

The typical dilution factors for the immunoassay kits were on the order of 100 to 1000 just to get a sample run. Even some of the treated effluents had to be

diluted fairly heavily to get the analytes within range.

If you have got that kind of a dilution factor, you are going to have a fair amount of error associated simply with the dilution. If you are doing it by three different techniques, each of those samples was a separate sample, so you have a compounded error there.

[TWENTY FIRST SLIDE] The agreement was clearly worse for the atrazine and the endosulfan results where you are not talking about a compound-specific immunoassay. Any one of the triazine compounds could have produced some level of positive response in that kit. We were looking for specific compounds.

The kit that does the endosulfan is designed for any one of the cyclodienes, and given the materials that could be in these samples that we were not specifically targeting by the GC method, there is a significant possibility of false positive results.

[TWENTY SECOND SLIDE] We did look at the possibility that the GC results were false negatives due to severe matrix effects in the in-process samples. So far, from the evidence we have, we don't think that is the case.

We looked at matrix spike data and blank spike, (OPR) data from the GC method, and there is no indication of false negatives at all. If you look at the spike sample data for the tube and the plate kit results, we are getting recoveries on the order of 700 percent for the atrazine or the endosulfan in some cases.

Obviously, there are other compounds in those samples that are providing a positive response and that we are not measuring by the GC technique itself.

We were a little bit surprised by the metolochlor results. The samples were too low to be quantitated by the GC technique, but we got very consistent results between the tube and the plate kit. Certainly within a factor of 3 or better, between a technique that is designed as semi-quantitative and one that is designed as a quantitative technique.

So, we were fairly pleased with the results for metolochlor and for the 2,4-D. Again, the metolochlor is not a compound-specific analysis, but either because of the facility we were sampling, or the particulars of the immunoassay test, we did not seem to have a lot of variability in those data.

[TWENTY THIRD SLIDE] We set out to look at a relatively rapid comparison of the techniques in the constraints of what effluent guidelines development needs for analytical work, what Bill Telliard's program is going to do in terms of field sampling.

We think the immunoassay kits worked reasonably well on some of the effluents that we looked at. We certainly think they worked better for the less contaminated samples than for the highly contaminated samples.

The compound-specific test kits clearly have an advantage when compared to GC results. There is a lot better agreement there.

We think that one of the biggest uses of immunoassay kits in the context of Bill Telliard's work is to identify those high concentration, awful, nasty, samples that you only discover three days after they go to the lab and somebody calls up and says, "do you realize we are not going to be able to analyze anything for a week until we get the lab clean?" Some of the labs we deal with routinely know the kind of samples we are talking about, the ones that crap up the columns and the glassware and everything else.

Even with the ability to do a quick "shake and shoot" solvent extraction in the laboratory, that takes a lot more time than the 30 minutes to an hour that an immunoassay would take to tell you that this is the really hot sample.

[TWENTY FOURTH SLIDE] Certainly, in the context of using them in the field, the tube kits would be relatively straightforward for a field sampling crew to deal with in the course of processing samples.

You don't require a large sample volume, so you do not have to take a whole another one liter bottle of sample in order to do the test. As you heard earlier today, you put the sample in a test tube, you add a couple of reagents. These come in little squeeze bottles. It is not unlike doing a home swimming pool chlorine test in some respects.

If you can live with a "presence or absence" kind of number, you don't even need to use the small color comparator that you can get for these materials. You could readily determine which samples were likely to be highly contaminated and which were likely to be relatively clean.

The plate kits could easily be used in a fixed laboratory for a screening technique, the advantage being you are not talking about using solvents (which is one of the things we would like to get away from where possible) and having to go through the aggravation of extracting industrial effluents.

These are samples that cause emulsions that break about three and a half days later. (By that time, you could have got the sample through the EMPORE disk.) The immunoassay techniques ought to be a lot quicker, ought to be a lot more easy to set up in the laboratory if you are going to do it on a routine basis.

The advantage to the laboratory, obviously, is to avoid unnecessary time spent running diluted samples and the costs associated with contaminating the glassware and the instrumentation.

From the standpoint of the Office of Water, we think that there will be an advantage in terms of not only cost, but in the timeliness of the results that come back to EPA.

[TWENTY FIFTH SLIDE] This is strictly a personal opinion, but I don't think you are ever going to replace traditional GC methods with an immunoassay in terms of developing a data base for an effluent guideline. I think either there is going to have to be a lot more development of the quantitative results for these techniques and the compound specificity or Bill is going to still be paying for an awful lot of traditional GC analysis.

There is some potential, from my point of view, for compliance monitoring at an individual facility if you are talking about compound-specific immunoassays.

In terms of the cost issues, if you have to use seven different immunoassay kits to do your compliance monitoring for a suite of analytes for which you are permitted on under NPDES, the cost isn't going to be as advantageous as if you can get away with a single kit that is compound-specific. If you are talking $300 for a GC analysis and maybe a half to two-thirds of that for immunoassay, there is probably not going to be a rush to go out and use those techniques for compliance monitoring.

But, certainly, I can see a number of instances where it could be very helpful.

[TWENTY SIXTH SLIDE] Finally, I would like to acknowledge Don McCarthy and Barbara Young at Millipore, in particular, who were not only very helpful in terms of getting us information and getting us the materials we needed when we needed them, but who were very responsive to the questions that we were having to transmit to them from the laboratory.

And the analytical work was all done at Analytical Technologies in Fort Collins, Colorado. Steve Workman was heading up that work and spent a lot of time working the bugs out from his laboratory's end of how to do the immunoassays. We actually were able to get some feedback from the laboratory that Millipore found very helpful in terms of what a production laboratory is going to expect out of any sort of technology, and we owe a lot to Steve for the time he spent doing all of this.

Thank you.

QUESTION AND ANSWER SESSION

MR. TELLIARD: Questions? You know, a little historic note here, on April 10th, 1992, the proposed reg went out for pesticides formulators or manufacturers. We are looking at formulators and packagers at the present time.

Over the next 24 to 36 months, what we would like to do is generate a data base that is large enough that when we go final with these rules allows for the purpose of compliance monitoring, again figuring that your permit will not have 92 pesticides in it but perhaps 3 or 4, that this type of technique...again, understand the agency can live with a false positive.

I mean, people out in the field can't, but we don't care about you. We can live with a false positive because what it says to us is then you have to do the whole rigmarole. You have to run the GC/FID, LC/MS, whatever you are going to do.

So, what we are looking at here is trying to start building into the regulations an opportunity to cut down on the compliance monitoring costs, and, of course, since it will be $1.38, that means you can do it every hour which will save a lot of money. Right?

But we are looking at...we don't want to overload all these commercial labs with samples, you know. They are constantly having to push them off the benches. This way, on a routine basis, you can turn the sample around. If you get a positive hit, then you are required.

And that is kind of the thinking here. The in-process streams that Harry was referring to here, I mean they basically when you sample these things and you send them to the lab. They kind of rattle in the jar, and we affectionately refer to them as water samples.

So, that is kind of the thinking, and a lot of this, as you notice, is preliminary. So, we are going to, over the next 24 months, be spending a lot more time trying to work on this data base as it relates to, again, treated industrial effluents is what we are looking primarily at.

Got a question?

MR. HARRISON: A comment first and then a question. My name is Bob Harrison. I am from ImmunoSystems which manufactures the kits that they were using.

The comment first is that the cross reactivity issues that you were addressing fairly well are significant to comment on here. The difference between the metolochlor and the atrazine that you were seeing may be due to the fact that the alachlor kit is cross reactive with a series of compounds. It is a very small group, actually, about three or four. And the triazine kit is cross reactive with as many as a dozen.

The presence of small amounts of several of that dozen may actually account for the significant variation between the GC and the immunoassay results.

Another factor that may come in here...and I would like you to comment on this...isthe dilution factor. Your alachlor detection level, I think, was 20 ppb and you couldn't reach that, or you couldn't reach the level that the samples were at with the GC.

Can you comment on how the dilution factor might account for, for example, the difference between the metolochlor and the cyclodienes where you had a profound dilution?

MR. MCCARTY: We have gone back and tried to look at the whole issue of diluting the samples and the sensitivity of the GC method. I will confess it has been a low priority at some level simply because we wanted to get some of this information out in the context of this conference.

The GC analyses were all done under what was then called Method 1618, which is the Office of Water combined organochlorine/phenoxy acid/herbicide/pesticide method.

Each of the three individual pieces of that method has a series of surrogate compounds that have method-specified recovery limits. If you can't meet the recovery limits in the analysis, and some of these samples were clearly well outside the expected surrogate recoveries, you are instructed to dilute the sample itself, not the extract, but dilute the sample itself, re-spike it, and go back and do another analysis.

Because of some matrix effects, we noticed a relatively high number of samples that needed to be diluted, and I think that ties into our inability to get down to

those levels. If you dilute the sample itself to achieve acceptable surrogate recoveries, you have a corresponding loss of sensitivity for the analytes of interest.

We did not spend a lot of time in this study going back and saying "well, what can we do." The traditional cleanup techniques were certainly applied to these samples, but we didn't go back and go an extra mile on any of these in order to achieve the lowest possible detection limits.

That is certainly an aspect in the work that Bill is talking about in the next two years or so, going back and looking at that more carefully.

We think that there is a significant problem with the lack of specific requirements for the immunoassay kits. That is not to say that you don't get good reliable results, but you are working with a system that has a lot fewer constraints on what someone was going to accept as data.

In some cases, if you get a number, that is probably, the end of the quality control. We got an answer; we wrote it down.

We looked at what we needed to do to add additional quality assurance to those immunoassay techniques. We added the requirement that the laboratory perform what we call the initial precision and recovery tests, blank spikes, essentially, at a specified level. Those results certainly looked reasonable, so we went on from there.

The dilution issue is essentially, you have 14 percent recovery of DBC or some surrogate, and the method says it has got to be above 37 percent (or whatever happens to be in the method.) So, when you get in that situation, you have got to go back and run a diluted analysis.

Part of the problem is that most laboratories tend to run order of magnitude serial dilutions, when, in some cases, you might have gotten away with a 1:2 dilution instead of a 1:10. Therefore, the loss of sensitivity can be much more profound than you would expect simply based on the matrix.

MS. CRANE: I don't have a question. I have just a comment.

MR. MCCARTY: Would you identify yourself, please?

MS. CRANE: My name is Laura Crane. I am with J.T. Baker.

Just a general comment and a word of caution to those of you who are

presenting these studies. This is a very new technology in this particular field, and I think it is extremely valuable to get specific experimental studies reported.

I think it is very dangerous to draw sweeping generalizations about the capabilities or limitations of the technology based upon the limited experimental data and studies that are presented so far. I think the limitations will become apparent as the technology matures, but there are very large differences in assay format, in assay approach, in antibody specificity among the kits and assays that have been developed so far and will be developed in the future.

So, just a word of caution about making very broad generalizations about the technique. I think it is just too premature to do that.

MR. TELLIARD: Thank you. Anybody else?

MR. MCCARTY: We had also discussed looking at other formats and vendors, but given the time frame, that wasn't a possibility. That is also down the line. Thank you.

MR. TELLIARD: Thanks, Harry.

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Comparison of Immunoassay and Traditional Gas Chromatographic Methods for the Determination of Selected Organochlorine Pesticides and Herbicides in Wastewater Samples

Cynthia A. Simbanin and Harry B. McCarty
Viar & Company

Introduction

- Under the authority of the Clean Water Act, EPA has a responsibility to develop Effluent Guidelines for US industries discharging wastewater in US surface water
- EPA is currently developing or revising guidelines for a variety of industries, including:
  - Pesticide Manufacturers
  - Pesticide Formulators and Packagers

Data collection activities associated with these guidelines involve:

- Collection of a large number of samples from a number of facilities
- Analysis for a large number of compounds
- Sample types that range from final effluents to in-process
- Waste streams

Analytical challenges include:

- Need for sensitivity (sub-ppb for pesticides)
- Wide range of expected concentrations
- Great likelihood of matrix effects, especially for the in-process samples

Traditional analytical approach involves:

- Solvent extraction
- Derivatization where feasible
- Cleanup techniques (column chromatography, etc.)
- GC analysis with selective detectors (EC, ELCD, NPD)

Traditional problems:

- Costly
- Time-consuming
- Complicated by wide range of concentrations found
  - Dilutions
  - Instrument and sample contamination
  - Down-time

Potential advantages of immunoassay techniques:

- Quick
- Can be highly selective
- Simple to use
- Portable

Purpose of Study

To provide a rapid, cost-effective comparison of the capabilities of immunoassay techniques to supplement traditional techniques for the analysis of effluent matrices

Study Design

- Piggy-backed on existing plans for sampling and analysis of pesticide manufacturing and pesticide formulating and packaging industries
- Involved use of traditional GC methods plus the "tube" and "plate" immunoassay materials commercially available from Millipore
  - Tube kits were used as a semi-quantitative screening tool
  - Tube kits were run in duplicate

Study Design (cont'd)

- Tube kit results were used to determine most appropriate dilution of sample to use for plate kit analyses
- Plate kits were run in triplicate once the dilution level was established
- GC methods were performed as a single analysis of each sample, with subsequent dilution of samples and/or extracts as needed to achieve traditional results
- Confirmation of GC results utilizing a second GC column

Compounds for GC Analyses	Corresponding Immunoassay Kits
Metolachlor	Alachlors
Atrazine	Triazines
Endosulfan I and II	Cyclodienes
2,4-D	2,4-D

Sampling

Two industrial facilities were sampled in December 1991 and February 1992. Based on knowledge of products being manufactured or packaged at that time, the samples were analyzed for:

2,4-D, Atrazine, and Metolachlor at the first facility in:

- 4 treated effluents
- 2 in-process waste waters
- 1 raw water

Sampling (cont'd)

and Endosulfan at the second facility in:

5 untreated waste waters

2 treated effluents

3 final effluents

2,4-D results (in ug/L)

Sample Type	Tube (RPD)	Plate (RSD)	GC
Treated effluent	937 (25%)	23585 (29%)	18000
Treated effluent	2471 (18%)	3297 (23%)	7400
Treated effluent	2162 (74%)	4177 (38%)	4200
Treated effluent	2038 (42%)	7992 (10%)	8800
Raw water	< 1.0	0.22 (14%)	0.19
In-process	33365 (65%)	382105 (50%)	380000
In-process	679808 (19%)	864046 (60%)	1400000

Atrazine Results (in ug/L)

Sample Type	Tube (RPD)	Plate (RSD)	GC
Treated effluent	386 (81%)	154 (7%)	< 20
Treated effluent	36 (25%)	131 (16%)	< 20
Treated effluent	71 (25%)	118 (15%)	< 20
Treated effluent	72 (13%)	165 (12%)	< 20
Raw water	4.2 (26%)	10 (16%)	1.2

Metolachlor results (in ug/L)

Sample Type	Tube (RPD)	Plate (RSD)	GC
Treated effluent	0.76 (22%)	2.0 (32%)	< 20
Treated effluent	0.68 (3%)	0.9 (17%)	< 20
Treated effluent	0.83 (6%)	1.3 (16%)	< 20
Treated effluent	0.96 (4%)	1.0 (12%)	< 20
Raw water	< 0.1	0.2 (10%)	< 0.2

Endosulfan results (in ug/L)

Sample Type	Tube (RPD)	Plate (RSD)	GC
Untreated effluent	52000000 (4%)	18500000 (34%)	50000
Untreated effluent	872000 (8 %)	221000 (49%)	1044
Untreated effluent	69000 (4%)	12200 (14%)	< 10
Untreated effluent	67600 (6%)	11400 (10%)	< 10
Untreated effluent	6060 (14%)	683 (45%)	16

Endosulfan results (in ug/L) (cont'd)

Sample Type	Tube (RPD)	Plate (RSD)	GC
Treated effluent	410 (48%)	50 (5%)	5
Treated effluent	732 (10%)	130 (30%)	9
Final effluent	4660 (0%)	920 (50%)	1.4
Final effluent	< 10	< 5	< 0.2
Final effluent	< 10	12 (15%)	< 0.1

Discussion

All three techniques are comparable for the majority of low level (<10 ppb) samples studied here (final effluents and raw water). This is consistent with the results shown by other investigators for drinking water samples, agricultural run-off samples, etc.

The tube kits are semi-quantitative, but still provided good agreement with the plate kits and the GC analyses for some samples. Similarly, the tube kits gave good precision for some analytes and some samples.

Discussion (cont'd)

For other samples and analytes, there is poor agreement between the tube and plate kit results.

Excellent agreement of the plate kit and GC results for 2,4-D

Differences between the three techniques are generally worst at the highest concentration levels (> 1000 ppb), where dilution of the sample is necessary for all three techniques.

Dilution factors ranged as high as 500,000 for some samples using the immunoassay kits, but were typically 100 to 1000.

Discussion (cont'd)

Agreement was worst for the Atrazine and Endosulfan results, where the immunoassay kits are not compound-specific.

The tube and plate kits generally had higher results for Atrazine and Endosulfan, relative to the GC results, and these higher numbers may be the result of "false positives ".

However, given the lack of specificity of these test kits for the single GC analyte, the higher results may be due to the presence of other triazines or cyclodienes that were not targeted by the GC method.

Discussion (cont'd)

Alternatively, the GC results may be false negatives due to severe matrix effects for the in-process samples.

The Metolachlor results represent the other end of the spectrum

The levels in these samples were generally too low for quantitation by the GC method.

The immunoassay kits gave results for these samples that were consistent with a factor of 3 or better.

Conclusions

- Immunoassay techniques work reasonably well on some of the industrial effluents studied here
- Immunoassay techniques performed best for low level samples
- Better agreement with GC results for test kits that are compound-specific than for kits that test for a class of related compounds
- Immunoassay kits are potentially very useful for identifying those samples with high concentrations of analytes or interferences

Conclusions (cont'd)

- Tube kits are probably reasonable to be used by sampling crews at an industrial facility for screening of samples and refinement of sampling plans
- Plate kits would be readily used by a fixed laboratory to screen samples prior to extraction and analysis, thereby protecting the instrumentation and the laboratory environment from contamination by particularly dirty samples. They would allow laboratory to segregate highly contaminated samples from low level samples

Conclusions (cont'd)

- Given the need to analyze a variety of in-process waste streams as well as final effluents, kits are not likely to replace traditional GC methods for regulatory guideline development work
- Kits may have utility for compliance monitoring purposes if they are compound-specific, and the monitoring involves a relatively small number of analytes

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ANALYSIS OF ALACHLOR-ETHANE SULFONIC ACID IN WELL WATER

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ANALYSIS OF ALACHLOR-ETHANE SULFONIC ACID IN WELL WATER

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Abstract

Screening of ground water samples by Enzyme ImmunoAssay (EIA) for a panel of common herbicides led to the identification of a major metabolite of alachlor, 2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid (alachlor-ESA), in several wells. Some water samples giving consistent positive results by alachlor EIA were consistently negative when analyzed for alachlor by GC and HPLC. These samples were further analyzed using a high-performance liquid chromatography (HPLC) method developed specifically for the analysis of alachlor-ESA. Quantitative correlation of alachlor-ESA concentrations determined by HPLC and EIA was demonstrated by using an alachlor-ESA standard for calibration of the EIA. Immunoreactivity of the HPLC purified material was confirmed by EIA analysis of HPLC fractions, indicating the presence of an alachlor-like structure. Absolute structural confirmation of the EIA positive HPLC peak was obtained by HPLC/MS/MS. The above work is briefly summarized in the following paper; a more extensive account is in press in J. Agric. Food Chem. (Macomber et al., in press).

Introduction

In recent years Enzyme ImmunoAssay (EIA) has become a valuable tool for screening of environmental water samples. Commercial kits for a variety of pesticides have become available (Fleeker and Cook, 1990; Van Emon and Lopez-Avila, 1992) and numerous groups have developed cost-effective screening programs using such kits as the first component of a comprehensive testing system (Goolsby et al., 1991; LeMasters et al., 1989; Thurman et al., 1990; Thurman et al., 1991). As numerous reviews have emphasized (Harrison et al., 1988; Jung et al., 1989; Hammock et al., 1990; Van Emon and Lopez-Avila, 1992), there are important differences between immunochemical methods and chromatographic methods which support their complementary use. One of the most critical and possibly the most undervalued of these differences is the potential of EIA methods for class-wise specificity, including metabolite recognition (Thurman et al., 1991). The design of QA procedures, primarily in the form of confirmatory analysis by approved methods, must take into account the class-wise specificity and metabolite recognition of the EIA's used. Specific crossreacting substances, such as metabolites or related parent compounds, behave differently in a panel of EIA's than non-specific interferences, such as pH or humic materials. It is important for the EIA user to understand these differences and react appropriately. The study summarized here illustrates this point and confirms the effectiveness of EIA for screening of ground water samples.

Materials and Methods

Methods for sampling, HPLC-UV, and HPLC/MS/MS have been described (Macomber et al., in press). Kits for EIA were obtained from Millipore (manufactured by ImmunoSystems). All EIA testing was performed according to the kit inserts.

Results and Discussion

Heidelberg College of Tiffin, Ohio, has for the past few years offered a well-water testing service using EIA screening for a panel of common pesticides, followed by GC confirmation as necessary. During 1991, it became apparent that the Alachlor EIA Kit was demonstrating an unusually high positive rate in comparison to the positive rate of the Triazine EIA Kit, prior use of the same Alachlor EIA Kit, and expected alachlor concentrations based on past use patterns and survey results. For more than 4400 samples tested by the Alachlor EIA Kit during 1991, 22 (0.5%) were over 2.0 ppb, 145 (3.3%) were over 0.2 ppb, and 236 (5.3%) were over 0.2 ppb. In a selected subset of over 3400 of these samples which were also tested with the Triazine EIA Kit, the frequency of high and mid-range positive samples for the Alachlor EIA Kit was about sixfold higher than the rate for the Triazine EIA Kit (Table 1).

Table 1. Frequency of Positive Samples (total n > 3400) for Two EIA Kits.

Kit	middle range (ppb)	high range (ppb)
Alachlor	3.2% (0.2-1.0)	0.6% (≥2.0)
Triazine	0.6% (0.3-1.0)	0.1% (≥3.0)

This pattern varies significantly from the expected pattern because of the lesser use and lower environmental persistence of alachlor. Selected samples from this set were tested for alachlor using an approved GC method and shown to be negative. Many of these samples were retested by both GC and EIA, confirming prior results. Because of the geographic clustering of some of these apparent false positive samples, a metabolite of alachlor was suspected to be responsible, rather than a non-specific interference. Matrix effects did not appear to be a plausible explanation because of the lower rates for the Triazine EIA Kit as shown in Table 1. Nonspecific matrix effects would be expected to affect the two kits roughly equally and to be more geographically homogeneous.

Because the false positive results appeared to be kit specific, a sample of the alachlor metabolite 2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid (alachlor-ESA) was obtained and an HPLC method was developed for this compound (Macomber et al., in press). Seventeen false positive samples were selected for more extensive follow-up. These were analyzed by HPLC for alachlor and shown to be negative. The same 17 samples were then analyzed by three labs using the newly developed HPLC method for alachlor-ESA. The samples were found to have a peak matching this metabolite in retention time and UV spectrum. Quantitation for these samples was performed by comparison to the alachlor-ESA standard. Aliquots of these 17 samples were analyzed again with the Alachlor EIA Kit, but using the alachlor-ESA standard, rather than alachlor, to create a standard curve for quantitation. Partial results of both EIA and HPLC for these 17 samples are shown in Figure 1. The regression equation for the ISI EIA data against the U of Maine HPLC data (both from Figure 1) was $y = 0.8x + 8$ ppb, with a correlation coefficient of 0.94.

For verification that the Alachlor EIA Kit was detecting the alachlor-ESA in water samples, the metabolite peaks from 6 of these 17 samples were collected and analyzed by the kit. Immunoreactivity of the captured peaks was confirmed and approximate quantitation correlated with both HPLC results and Alachlor EIA Kit results from direct analysis of the original samples. Absolute confirmation of the identity of the metabolite was obtained for six samples by HPLC/MS/MS. The mass spectra of all of the immunoreactive peaks closely matched the spectrum of the alachlor-ESA standard. All spectra demonstrated a molecular ion at 314 and major fragments at 79, 120, and 160 m/z. These and other data supporting the identification of alachlor-ESA in the samples tested are summarized in Table 2.

Table 2. Summary of Data Supporting the Presence of Alachlor-ESA in Well Water

1. HPLC peaks of standard and samples match in retention time and UV spectrum

2. Correlation of HPLC and EIA using water samples with an alachlor-ESA standard

3. Correlation of HPLC and EIA using captured HPLC peaks with an alachlor-ESA standard

4. HPLC/MS/MS results
   a. correlation of concentrations with HPLC-UV
   b. molecular ion at 314, fragments at 79, 120, and 160
   c. match to alachlor-ESA standard

Conclusions

This study illustrates the importance of understanding immunoassay crossreactivity in general principle and for the specific test being used. The Alachlor EIA Kit described in this study performed well, as validated by the extensive follow-up work described. The metabolite alachlor-ESA is easily detected by this kit, at levels near the detection limit of the kit for alachlor. These results indicate that the presence of alachlor-ESA should be suspected in areas of high alachlor use and that EIA results should be treated accordingly. Thus confirmation by GC or other approved methodology is essential for any effective monitoring program for alachlor or any other pesticide.

All EIA methods have the potential for crossreactivity to a wide range of metabolites and other compounds related to their targets. Not all EIA kits are equal in their ability to detect metabolites or related compounds, not will all of these potential crossreactants necessarily be detected. Each kit should be tested individually, preferably by the manufacturer in the kit validation process. Ideally this testing should include metabolites identified during the registration process, many of which may be unavailable except through the registrant. Thus the cooperation of pesticide manufacturers in evaluation of immunoassay crossreactivity is critical to proper use of EIA kits. The ideal situation is to anticipate potential problems due to metabolite crossreactivity and provide the maximum data with the kit.

As for the case described above, it is critical to the successful use of all EIA kits that crossreactivity considerations be understood by the user and that proper confirmatory analyses be done to follow up positive results. Regardless of the methods used, the best results come from thorough knowledge of the capabilities and limitations of all methods, whether immunochemical or chromatographic. This study shows that when positive EIA results are confirmed by approved methods, EIA can be a valuable tool for water quality monitoring. Even in situations where only metabolites with unknown health effects or with no legal limits are found, EIA still may be an important tool for assessing well or aquifer vulnerability.

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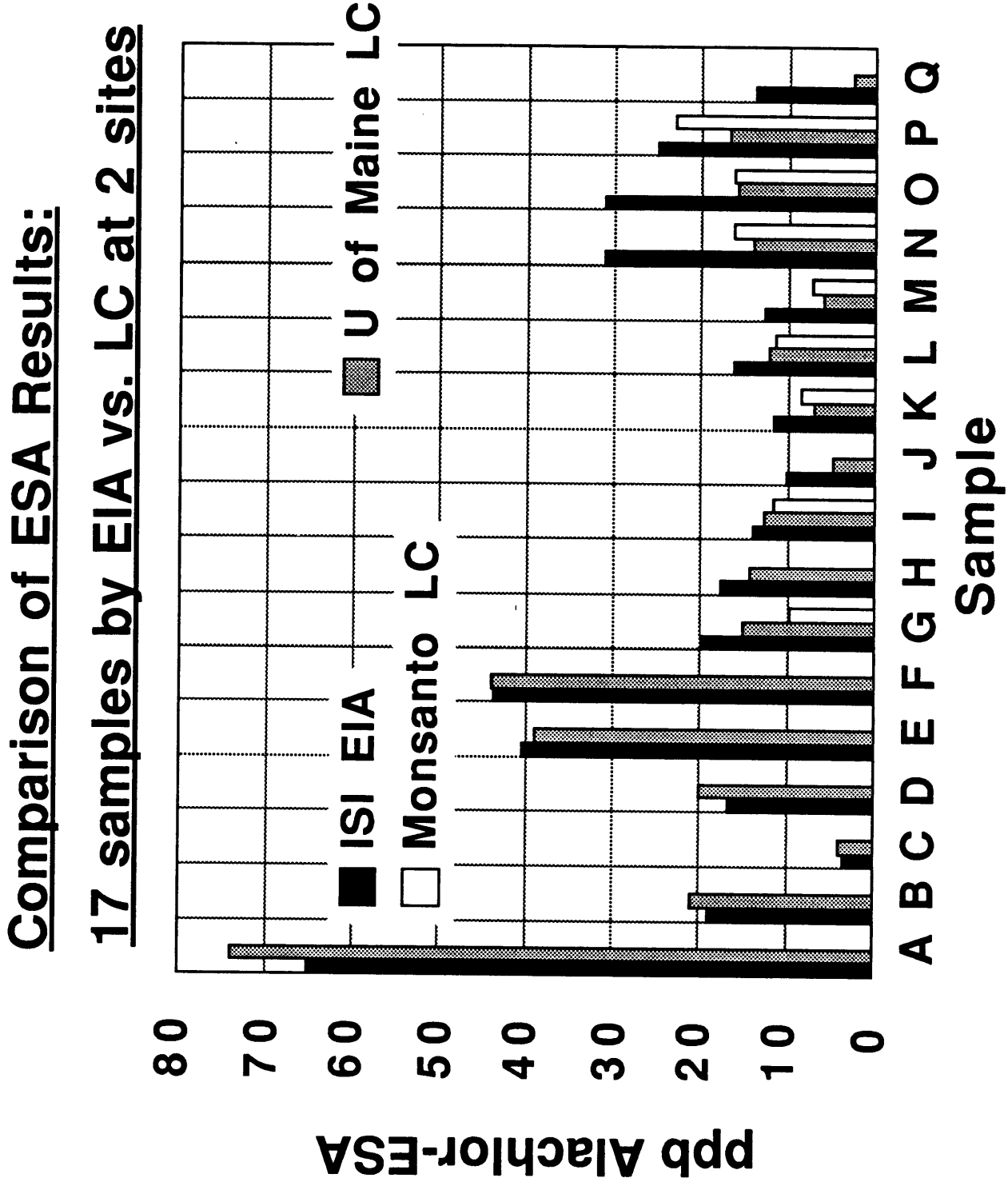
Comparison of ESA Results:
17 samples by EIA vs. LC at 2 sites
ISI EIA
Monsanto LC
U of Maine LC
ppb Alachlor-ESA
80
70
60
50
40
30
20
10
0
A B C D E F G H I J K L M N O P Q
Sample

MR. TELLIARD: Our next speaker this morning is Ken Robillard from Kodak and a little change of pace. He is going to present data on the analysis of silver, Ken?

MR. ROBILLARD: Thanks, Bill. The subject of my talk is the analysis of bioavailable metal ions in waste waters. This truly is a multi-disciplinary area of research, utilizing knowledge of analytical, inorganic and aquatic chemistry and environmental toxicology. I will focus particularly on the speciation of silver and the measurement of free silver ion. Developing an analytical method that can selectively analyze free silver ion at concentrations below a part per billion has been a formidable challenge. We have been working on this project for approximately twelve years. Several analytical approaches have been tried; but very few have shown the requisite sensitivity and selectivity. Often it seemed that trying to find the proverbial needle in a very large haystack would have been much simpler.

Our story isn't without chapters of success, and it is those successes that I wish to share with your this morning. I will begin by providing the credits, which I do to emphasize where credit is due. A tremendous amount of creativity and hard work went into the efforts which I am going to describe. Some of this work was done at Eastman Kodak Company in Rochester, New York, by Mr. James Chudd and Drs. Deniz Schildkraut and Edwin Garcia. And, development work was done at the New Mexico State University by Dr. Joseph Wang and his colleague, Dr. Ruiliang Li. What I will do now is describe to you the Why, the What, and the How of this project.

Why did we get involved in this project? (FIGURE 1) Because, for metals (M) like silver there is usually a relationship between their chemical speciation and their environmental toxicity. The water quality criteria data that exist for silver were derived from laboratory tests with silver nitrate, a soluble form of silver that provides exposure to the free silver ion. However, silver as well as many other metals and some organics exist in a variety of forms in water (M_a, M_b,...). Silver does not exist just as the free metal ion, but in complexed and adsorbed forms. There have been a number of efforts over the years to describe the speciation of metals using both analytical

procedures as well as mathematical modeling.

In terms of toxicity, if each species of the metal (e.g. free ion, absorbed, complexed, etc.) has its own unique toxicity (represented as $T_a \cdot C_a$, $T_b \cdot C_b$,...),then the relationship between speciation and toxicity can be conceptualized as the summation of individual toxicities. (FIGURE 1) This is a very simple description which assumes additive toxicities for all the metal species. In fact, the relationships can become very complicated both conceptually and mathematically if synergistic, antagonistic or non-additive behavior occurs.

Mother nature may have anticipated the limits on our ability to deal with these multiple and interactive variables. She made things somewhat easy for us by often associating a higher level of toxicity to the free ionic form of metals as opposed to their complexed or absorbed forms. (FIGURE 2) This isn't true in all cases. But, it certainly is true in a large number of them. Available data indicate that it is particularly true for silver.

Free silver ion is extremely reactive. There is ample evidence in the literature to show that when placed into an aqueous solution that contains organics, inorganic ions, sediment and particulates, ionic silver will rapidly associate with these other chemicals and forms a variety of compounds. (FIGURE 3) The toxicities of these silver compounds have been studied to a limited extent. The most extensively studied silver species, other than free silver ion, are silver thiosulfate, silver chloride and silver sulfide. Silver sulfide is the most commonly occurring form of silver in the environment. Silver chloride is a prevalent species of silver in marine waters. And, silver thiosulfate is the most prevalent form of silver in photoprocessing effluents. FIGURE 4 presents the results of acute and embryo-larval aquatic effects tests in which fish were exposed to these different species of silver. The differences in acute and chronic toxicities amongst these species of silver varied from two to six orders of magnitude. In fact, no toxicity was ever evident for silver sulfide. Referring back to the relationship shown in FIGURE 1, we should be able to ignore any of the toxicity terms beyond that of the free silver ion.

<u>What</u> we have tried to accomplish with this project is to develop one or more analytical methods that respond selectively to the principal toxic form of the

analyte, e.g. free silver ion. FIGURE 5 shows algebraically that the response should be proportional to the concentration of the free metal ion. We have examined a number of approaches, and subsequently focused on electrochemistry. Two electrochemical techniques constitute the How of our story: potentiometry, using an ion selective electrode; and, anodic stripping voltammetry (FIGURE 6)

The potentiometric methods is based on the Nernst relationship that the potential of the electrochemical cell is proportional to the log of the activity of the analyte. (FIGURE 7) The activity of the analyte is equal to the activity coefficient times the concentration. Using the Nernst relationship and solutions containing known amounts of free silver ion, it is possible to construct a calibration curve. (FIGURE 8) The calibration procedure involves the use of both silver nitrate and silver nitrate with various complexing agents. By adjusting the concentration of silver nitrate and of the complexing agents, one can alter the activity of the free silver ion in the solution. The activity of the free silver ion in each solution can be calculated using known equilibrium constants and a knowledge of the amount of each added reagent. By analyzing each of the standard solutions, we construct a calibration curve that is linear and quite reproducible. Following calibration of the electrodes, the activity of free silver ion in the test sample(s) can be measured. The electrodes are placed in the sample and the cell is allowed to come to equilibrium. The measured potential is converted to a pAg value using the calibration curve. Generally, we assume the activity coefficient in the sample is unity, and therefore the numerical value of the activity is equal to the numerical value of the concentration. This is a good approximation for a monovalent ion such as free silver ion, especially if the sample does not have a high salt loading.

We have been using this potentiometric method for about 10 years at our facilities in Rochester as well as at some selected wastewater treatment facilities in other locations. FIGURES 9 and 10 contain data from a field study that was performed using this analytical technique. We selected six wastewater treatment plants, dividing them into three categories. Two plants received known quantities of photographic effluent; two plants received effluent which contained some non-photographic industrial silver; and two treatment plants received some silver from non-industrial non-photographic

sources. In all cases there was some measurable amounts of total silver in the influents and effluents of the treatment plants. When we used the potentiometric technique to measure the free silver ion, we saw extremely small amounts. These results were consistent with previous knowledge on the fate of silver during biological treatment. Most of the silver is accumulated in the sludge. Any silver remaining in the aqueous phase is believed to be present in complexed or colloidal forms. In this study and in other work, the potentiometric method for measuring free silver ion has been useful and informative.

I should mention that the ion selective electrode we used initially was a silver wire. We are now using a commercial silver sulfide thin layer electrode, which works very well, and is a bit more durable that the silver wire.

The potentiometric analytical method, like all analytical methods, has its limitations. The diagram in FIGURE 11 is an attempt to graphically portray the working boundaries of the method. On the right-hand side of the S-shaped curve (Region A), you see a single flat line. This represents the situation where the concentration of free silver ion is large enough to maintain a steady state (constant) potential across the electrodes. This condition exists when the concentration of free silver ion is greater that 50 parts per billion. On the left-hand side (Region B), there is a series of flat lines, which represents the presence of ligands and ions which complex strongly with ionic silver. In the presence of these complexing agents, the activity of silver is buffered. When this buffering capacity is sufficiently large, one sees a constant and reproducible potential across the electrodes. This is exactly analogous to the conditions present in the standard silver chloride, silver bromide, silver iodide and silver thiosulfate solutions that are used to obtain the calibration curve. The series of lines in this region represent varying activities of free silver ion. Each separate activity is determined by the concentration and strength of the silver-complexing agents that are present in the solution.

The difficulty comes when you approach the vertical incline (Region C), where the concentration of free silver ion is less than 50 parts per billion and where there is insufficient silver-complexing materials present. Under these conditions, the

measurement does not work well. The analogy is trying to measure the pH of distilled water. It is extremely difficult to do, and the results are very seldom reproducible.

We recognized the limitations of the potentiometric method and set about to develop a supplemental or alternative method. The selectivity and sensitivity of anodic stripping voltammetry prompted us to pursue this as an alternative analytical approach.

FIGURE 12 shows the heart of the anodic stripping instrument, the cell in which the measurement takes place. Anodic stripping is very similar to the technique of microextraction, which we heard about yesterday. Only in this case, the driving force for the collection of the silver is not a difference in fugacity but, rather, an applied potential across the electrodes. A reducing potential is applied initially which forces the silver (or whatever metal ion you are analyzing for) to plate out on the tip of the electrode. After a period of extraction ranging from a few seconds to several minutes, the voltage is changed to an oxidizing voltage, thereby forcing the metal ions to oxidize and return to the solution. This oxidation creates a current that is proportional to the amount of metal on the surface of the electrode. FIGURE 13 shows the process in graphical form. As we change the voltage from a reducing to an oxidizing voltage there is some point where the voltage will be appropriate to cause oxidation.

One of the first field trials of this method took place over a year ago, in collaboration with the Department of Natural Resources, State of Michigan. They provided us with samples from several wastewater treatment plants. These samples were analyzed for free silver ion using the anodic stripping technique and for total silver using a conventional atomic absorption method. The results are presented in FIGURE 14. In most cases, we found the total silver was less and 0.5 parts per billion. I believe this was pleasing to the operators of the treatment plants as well as to the Michigan Department of Natural Resources. The free silver ion measurements by anodic stripping voltammetry were performed in Dr. Joseph Wang's laboratory at New Mexico State University. They reported an analytical detection limit of 50 parts per trillion.

After the initial analyses for free silver ion, the samples were spiked with silver nitrate. The amount of silver nitrate added should have given a peak of about 30

millimeters in height if the silver persisted as free silver ion. As expected, the samples that were not preserved with nitric acid maintained a high buffering capacity for silver. When spiked, the free silver ion was quickly complexed. Whereas, those samples preserved with nitric acid, showed a much lower complexing capacity for ionic silver. Many of the ions and atoms that bind strongly to silver, such as nitrogen, sulfur and oxygen, become protonated in acidic solution and are no longer active (or adsorptive) for the cationic free silver ion.

The most recent results I wish to share with you were obtained during the past few months in our laboratory in Rochester. The anodic stripping voltammetry method developed by Dr. Wang required trace amounts of mercuric ion. We found that the reproducibility of the analysis could improve by eliminating mercury. FIGURE 15 shows examples of the traces that one would typically see when analyzing a series of standards ranging from 0.3 to 3 nanograms per milliliter (parts per billion) of free silver ion. An important observation we made, which confirmed similar observation reported by others, was the plated silver was capable of being stripped from the electrode as a series of peaks Sometimes we saw just one peak, sometimes two, and occasionally we have even seen three peaks. Eliminating the mercury helped us to overcome some of the early reproducibility problems. FIGURE 16 shows the results of analyzing two effluent samples containing free silver ion. The curves on the left are for the effluent samples. The curves on the right were obtained from calibration standards.

FIGURE 17 shows a typical calibration curve obtained using the anodic stripping technique. The calibration is linear between 0.2 and 1 part per billion with a good correlation coefficient.

FIGURE 18 provides information on the precision of the anodic stripping method. These results were obtained by pooling the data from several of the calibration curves. One sees a standard deviation of about 2 percent at the 1 part per billion level. The standard deviation is only 12 to 17 percent at concentrations as low as 0.2 parts per billion.

FIGURE 19 lists results for six separate effluent samples analyzed by anodic stripping voltammetry and by the potentiometric method. In each sample, anodic

stripping showed that the concentration of free ionic silver was less and 0.2 parts per billion. The two analytical techniques gave consistent results for all six samples. Because of the high silver-complexing strength in these effluent samples, the potentiometric method was able to give more precise values for the concentration of free silver ion. We spiked one of the samples with 10 part per billion of silver nitrate. After spiking, the anodic stripping analysis showed the concentration of free silver ion remained less than 0.2 parts per billion. As expected, the complexing strength of the effluent was sufficient to essentially adsorb all of the added silver ion.

FIGURE 20 shows the results of spiking an effluent sample with varying amounts of silver nitrate. The bottom curve (#1) is the sample before any silver is added. We began adding silver nitrate, starting with a nominal concentration of 5 parts per billion, and continuing up to a nominal concentration of almost 500 parts per billion. For comparison, curve #6, shows the response for a standard solution containing 0.2 part per billion concentration of free silver ion. Even after adding almost 500 parts per billion of silver nitrate to this effluent sample, the concentration of free silver ion barely exceeded 0.2 parts per billion. These are the type of results we would expect based upon biological effects testing of effluent samples spiked with silver nitrate. Some effluent samples can be spiked with considerable amounts of silver nitrate without any resulting toxicity. This indicates the added silver was converted from free silver ion to other relatively non-toxic forms of silver.

Presently, we continue to work on improving the anodic stripping method. We would like to make it easier to use and more reproducible at sub-parts per billion concentrations. And, we would like to encourage other laboratories to become familiar with this analytical procedure.

Future work will include validating the anodic stripping method by collecting a variety of effluent samples and analyzing them using the anodic stripping and potentiometric methods, as well as analyzing them for total silver. Our overarching goal of this work is to achieve a recognized and approved method for measuring free silver ion in samples of effluent and receiving water. We believe the appropriate approach to environmental protection for silver (and for many other metals) is to regulate the specific

toxic form(s) of the metal, notably the free metal ion, and to monitor compliance on that basis. **THANK YOU.**

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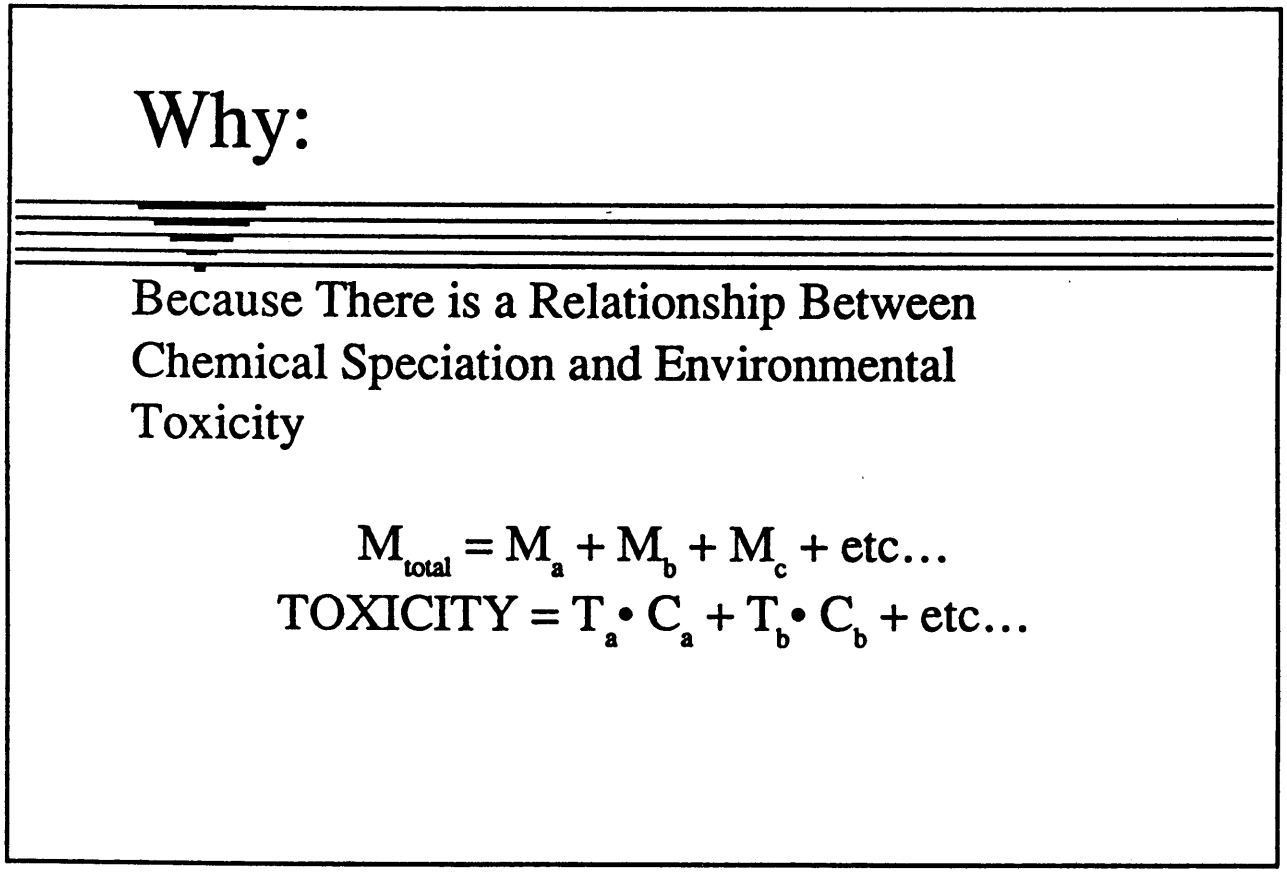

Why:
Because There is a Relationship Between Chemical Speciation and Environmental Toxicity
$M_{total} = M_a + M_b + M_c + etc...$
$TOXICITY = T_a \bullet C_a + T_b \bullet C_b + etc...$

FIGURE 1

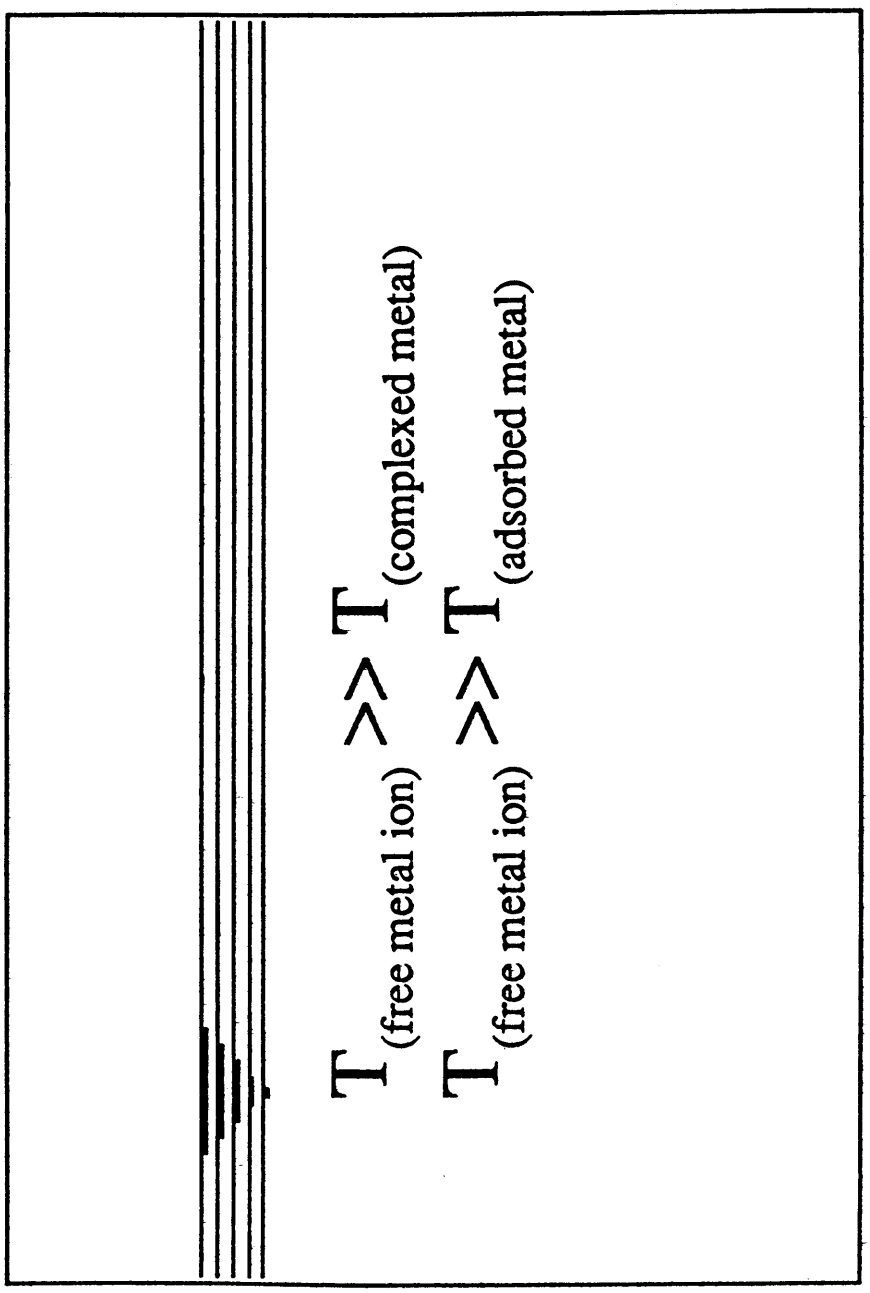

$T_{(free\ metal\ ion)} >> T_{(complexed\ metal)}$
$T_{(free\ metal\ ion)} >> T_{(adsorbed\ metal)}$

FIGURE 2

Different Environmental forms of Silver

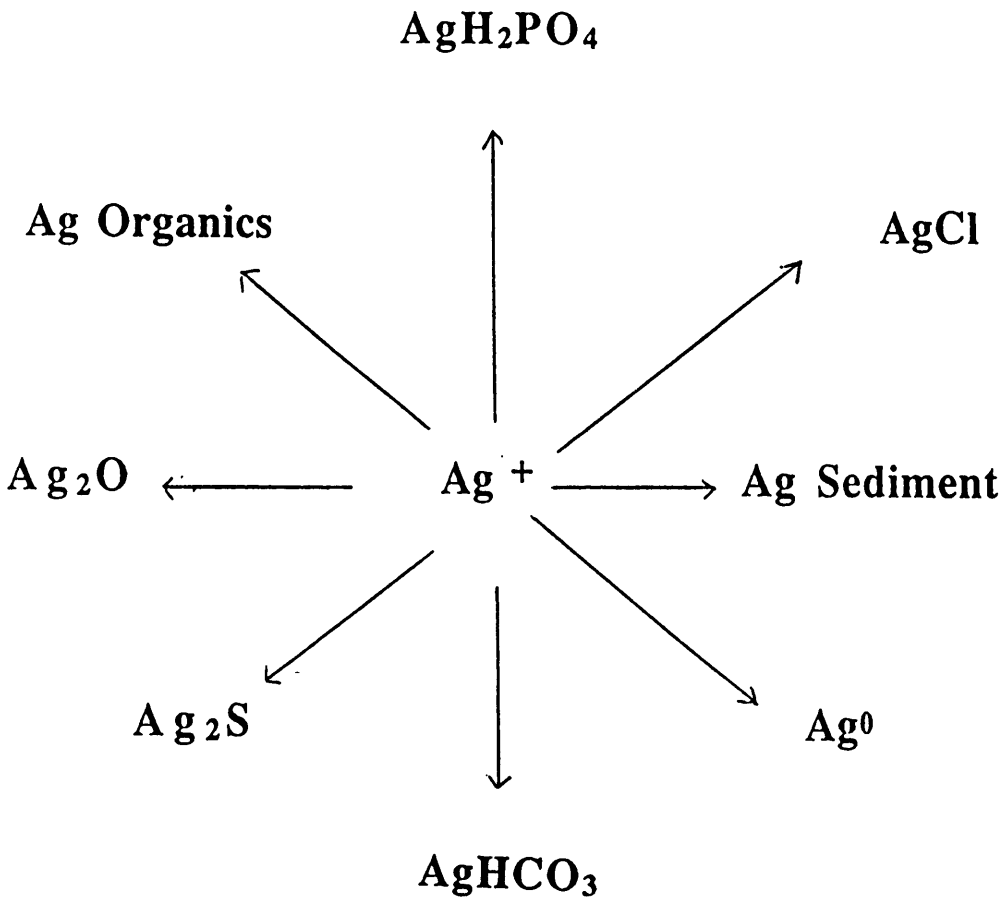


FIGURE 3

COMPARISON OF MINIMUM THRESHOLD CONCENTRATION FOR SOME SILVER SPECIES

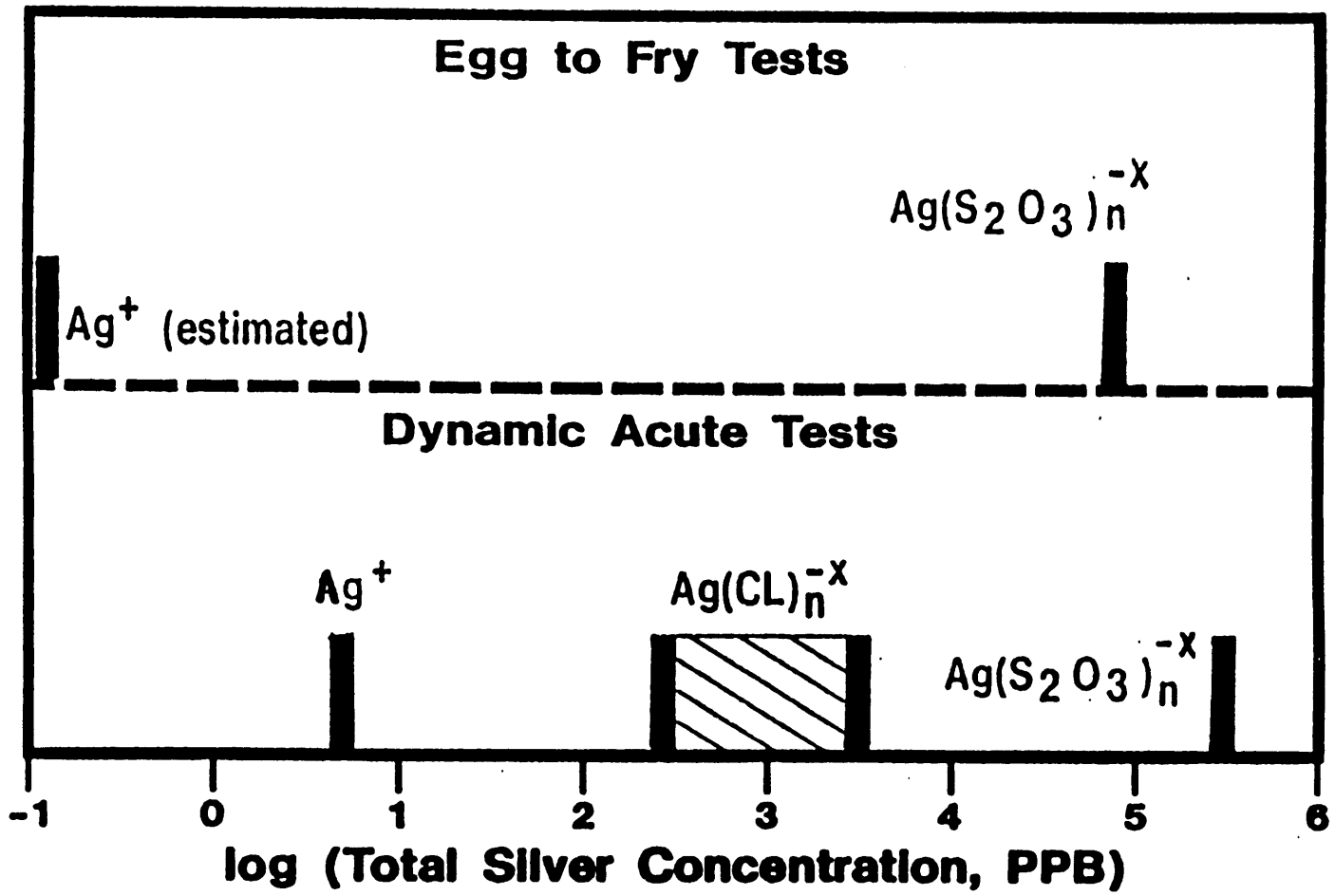


FIGURE 4

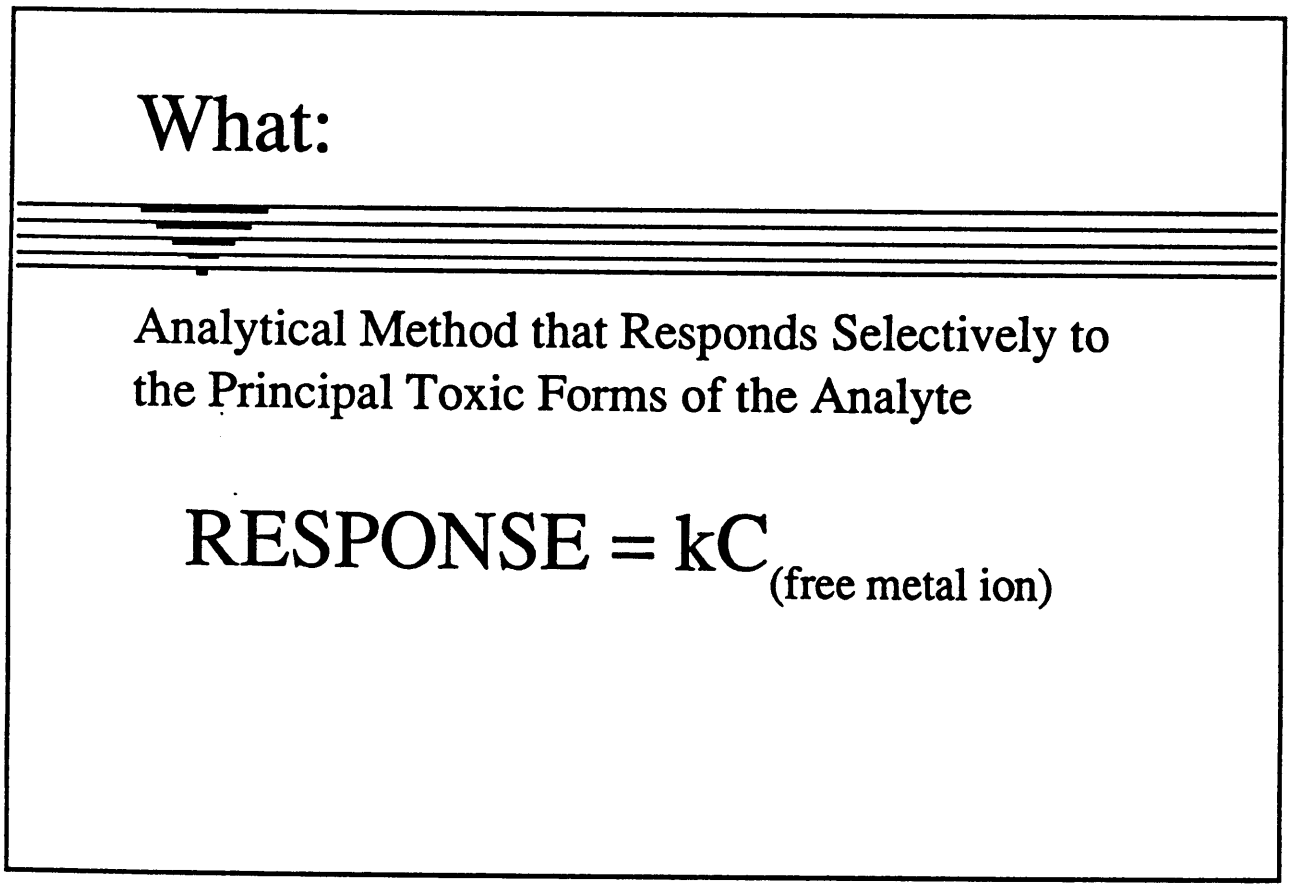

What:
Analytical Method that Responds Selectively to the Principal Toxic Forms of the Analyte
RESPONSE = kC(free metal ion)

FIGURE 5

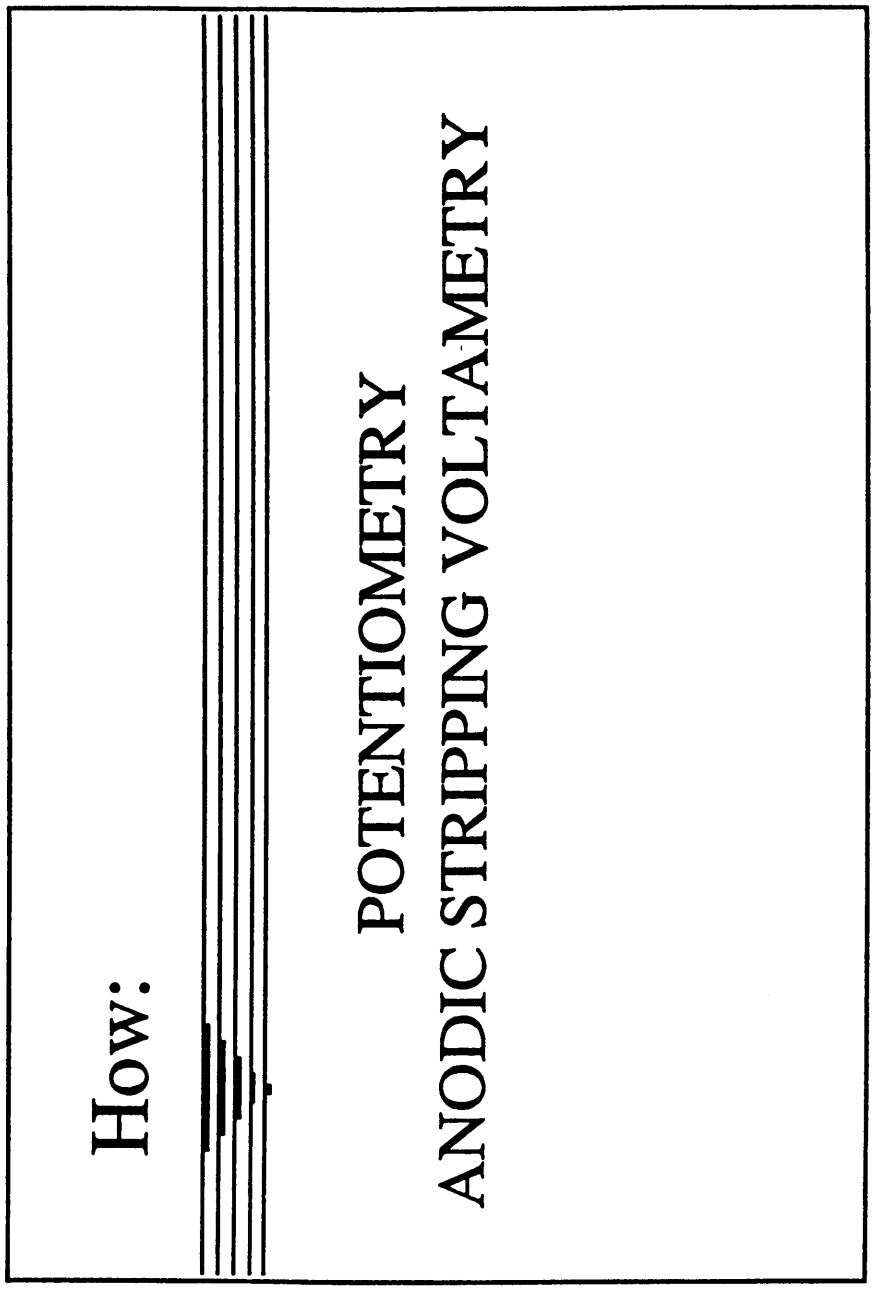


FIGURE 6

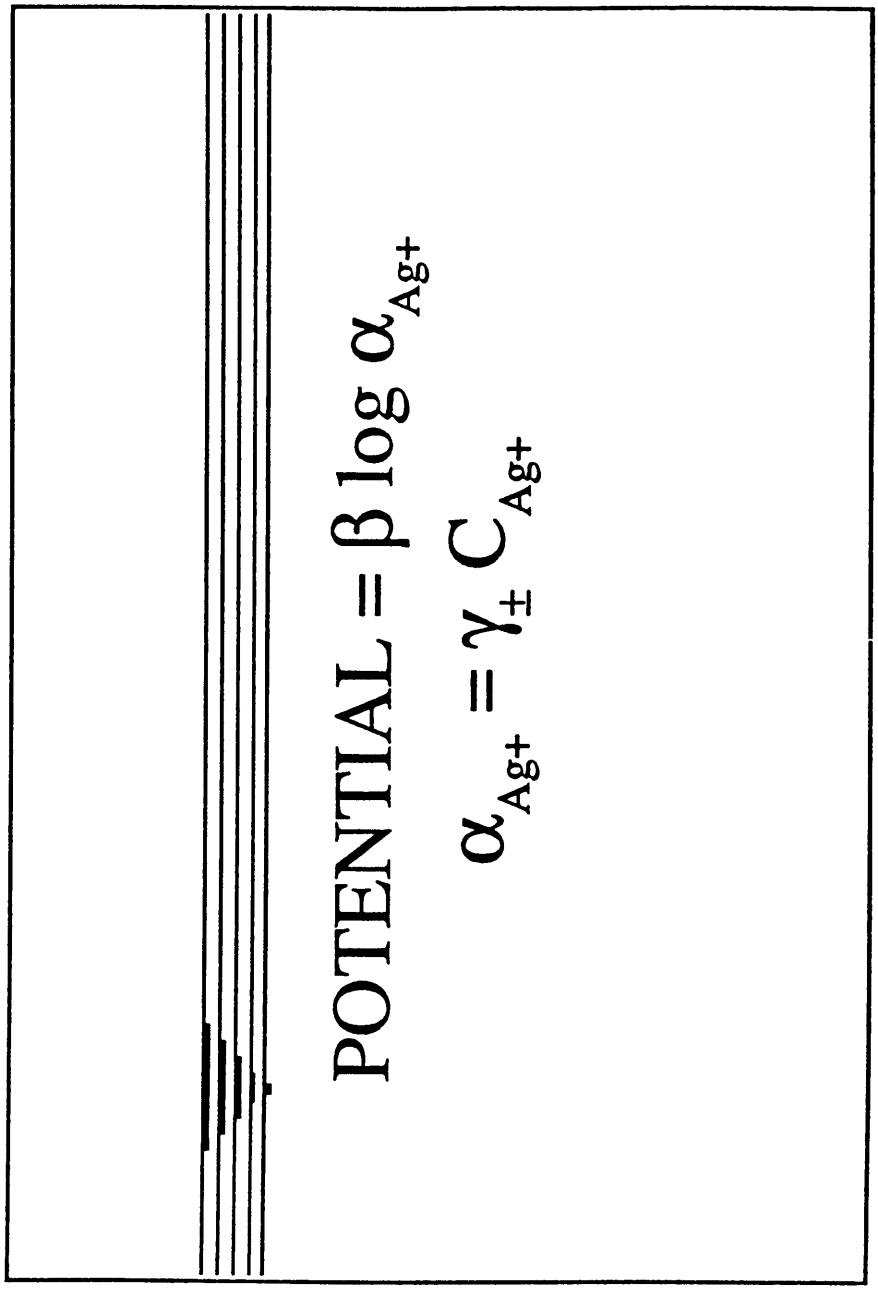


FIGURE 7

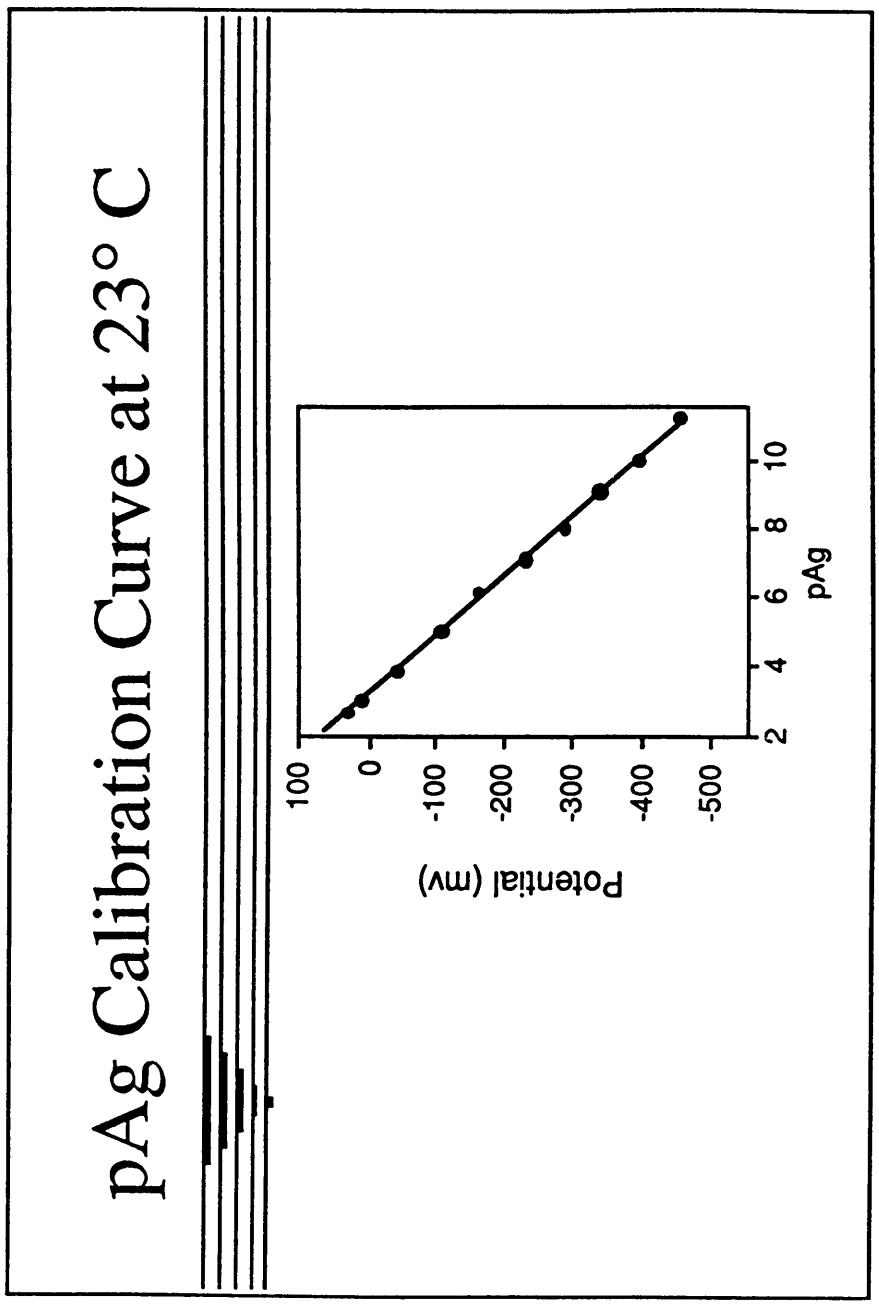

pAg Calibration Curve at 23° C
Potential (mv)
100
0
-100
-200
-300
-400
-500
2
4
6
8
10
pAg

FIGURE 8

Total Silver (µg/L) in POTW Influent, Effluent

POTW Category	Plant No.	Influent	Effluent
No industrial or photoprocessing sources	1	6 (5-7)	4 (3-5)
	2	8 (5-10)	3 (2-4)
Industrial silver sources	3	26 (22-30)	4 (<1-7)
	4	10 (8-13)	2 (2)
Photoprocessing silver sources	5	2,000 (1700-2200)	200 (120-300)
	6	713 (460-930)	4 (2-6)

FIGURE 9

Ionic Silver (µg/L) in POTW Influent and Effluent

		Influent		Effluent	
POTW Category	Plant No.	Ag^+ activity	pAg	Ag^+ activity	pAg
No industrial or photoprocessing sources	1	0.009	10.1	0.03	9.6
	2	0.009	10.1	0.001	11.0
Industrial silver sources	3	0.0002	11.7	0.07	9.2
	4	0.0007	11.2	0.007	10.2
Photoprocessing silver sources	5	0.00003	12.6	0.004	10.4
	6	0.0002	11.7	0.004	10.4

508

FIGURE 10

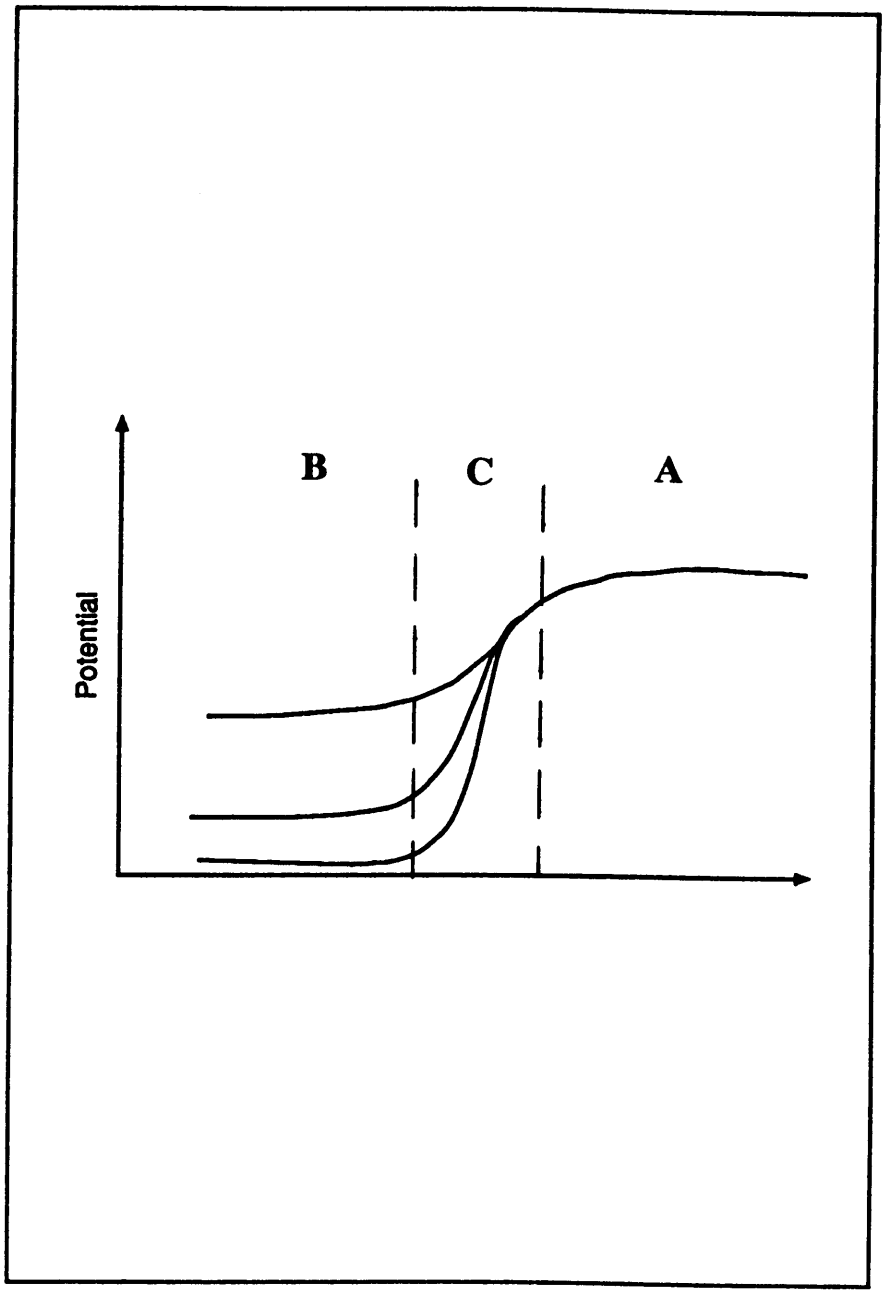


FIGURE 11

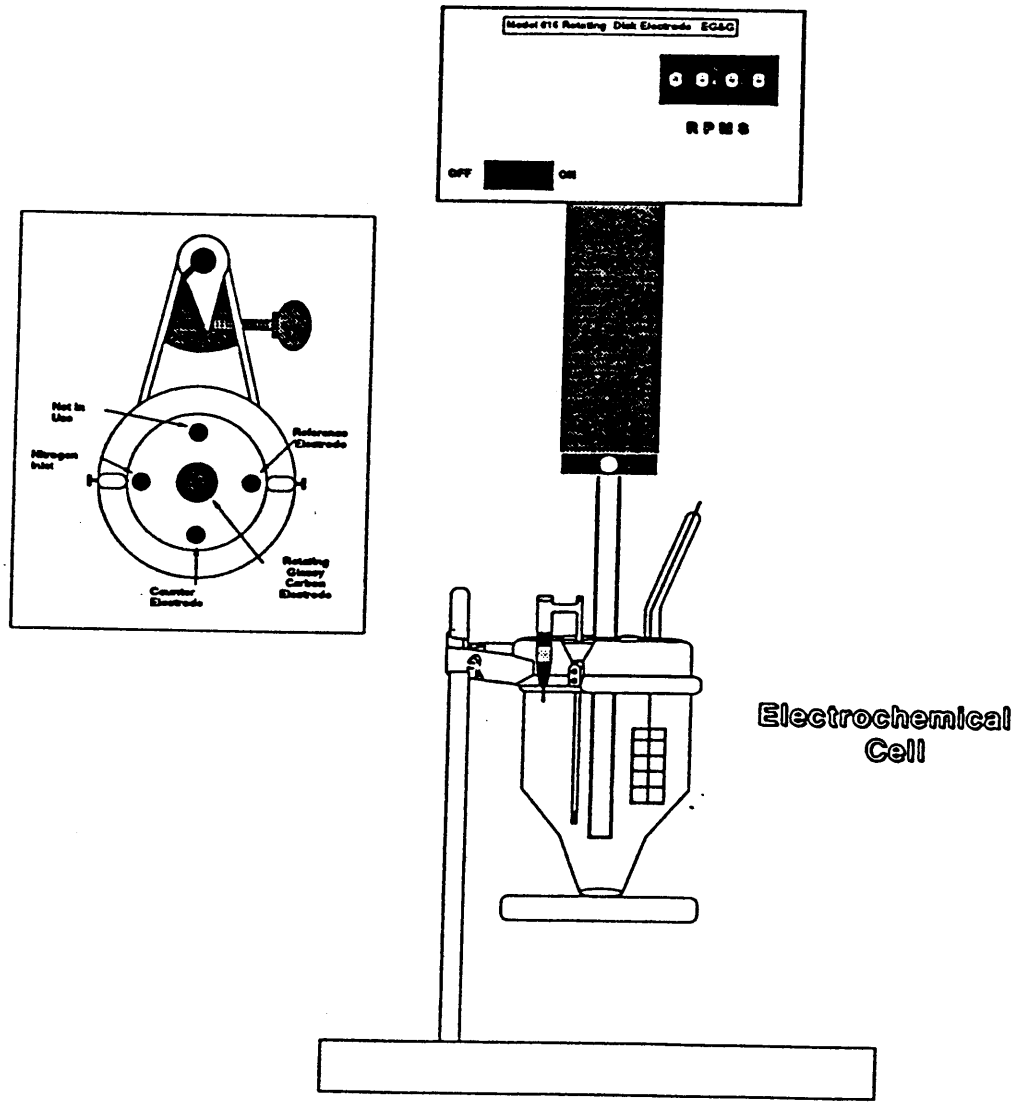


FIGURE 12

GRAPHICAL REPRESENTATION OF STRIPPING PROCESS

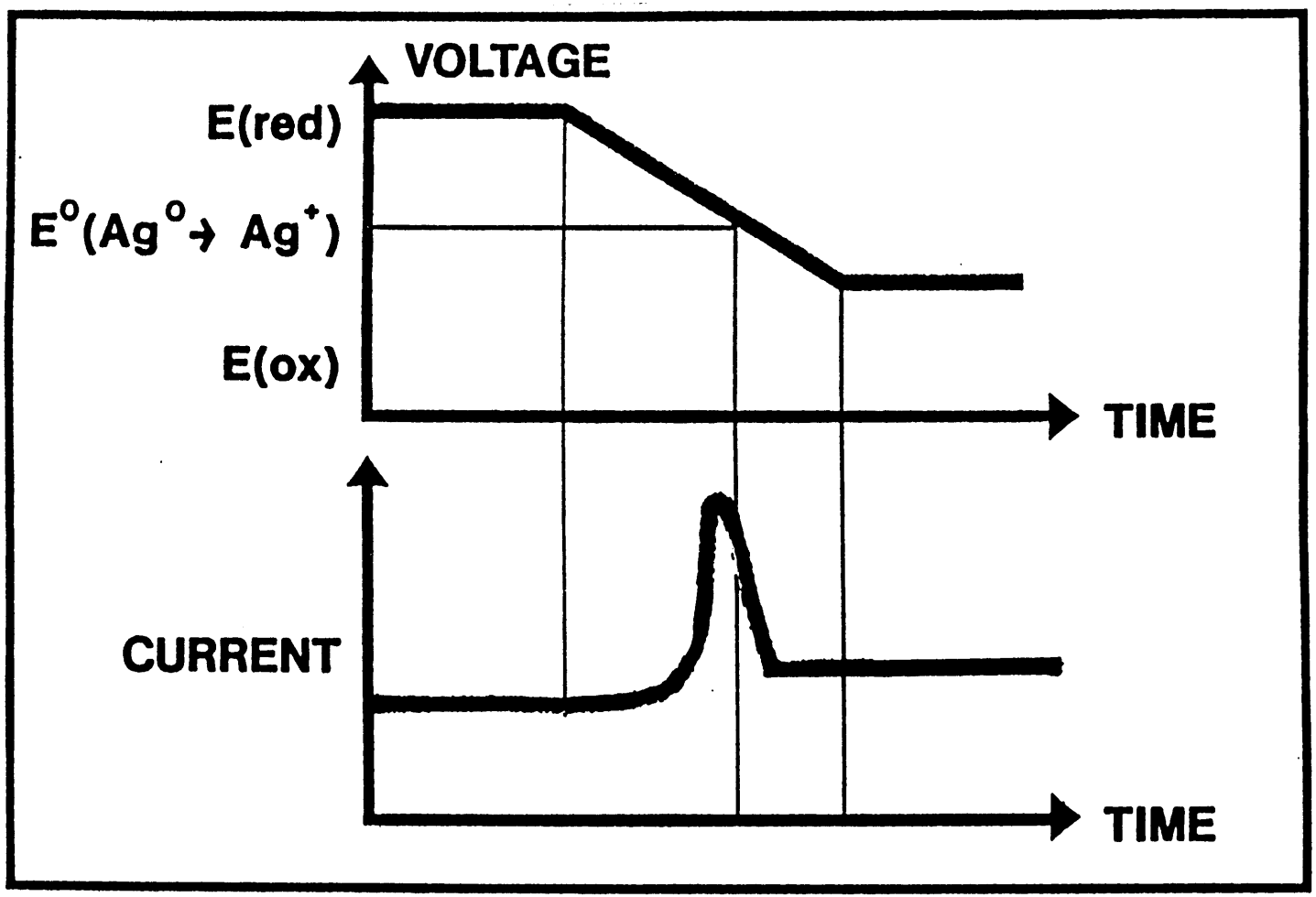


FIGURE 13

Sample ID (date)	Preservative	Silver (µg/L) Total	(Ag+)	Silver Spike Peak Ht. (mm)
1A	yes	<0.5	<0.05	36
(7-10-89)	no	--	<0.05	27
1B	yes	0.94	<0.05	30
(7-26-89)	no	--	<0.05	1
2	yes	<0.5	<0.05	38
(7-10-89)	no	--	<0.05	20
3	yes	<0.5	<0.05	40
(7-17-89)	no	--	<0.05	18
4	yes	2.3	<0.05	32
(7-24-89)	no	--	<0.05	7
5	yes	<0.5	<0.05	32
(7-26-89)	no	--	<0.05	20
6	yes	2.1	0.5	73
(7-10-89)	no	--	0.5	80
7	yes	<0.5	1.0	220
(7-17-89)	no	--	<0.05	16

FIGURE 14

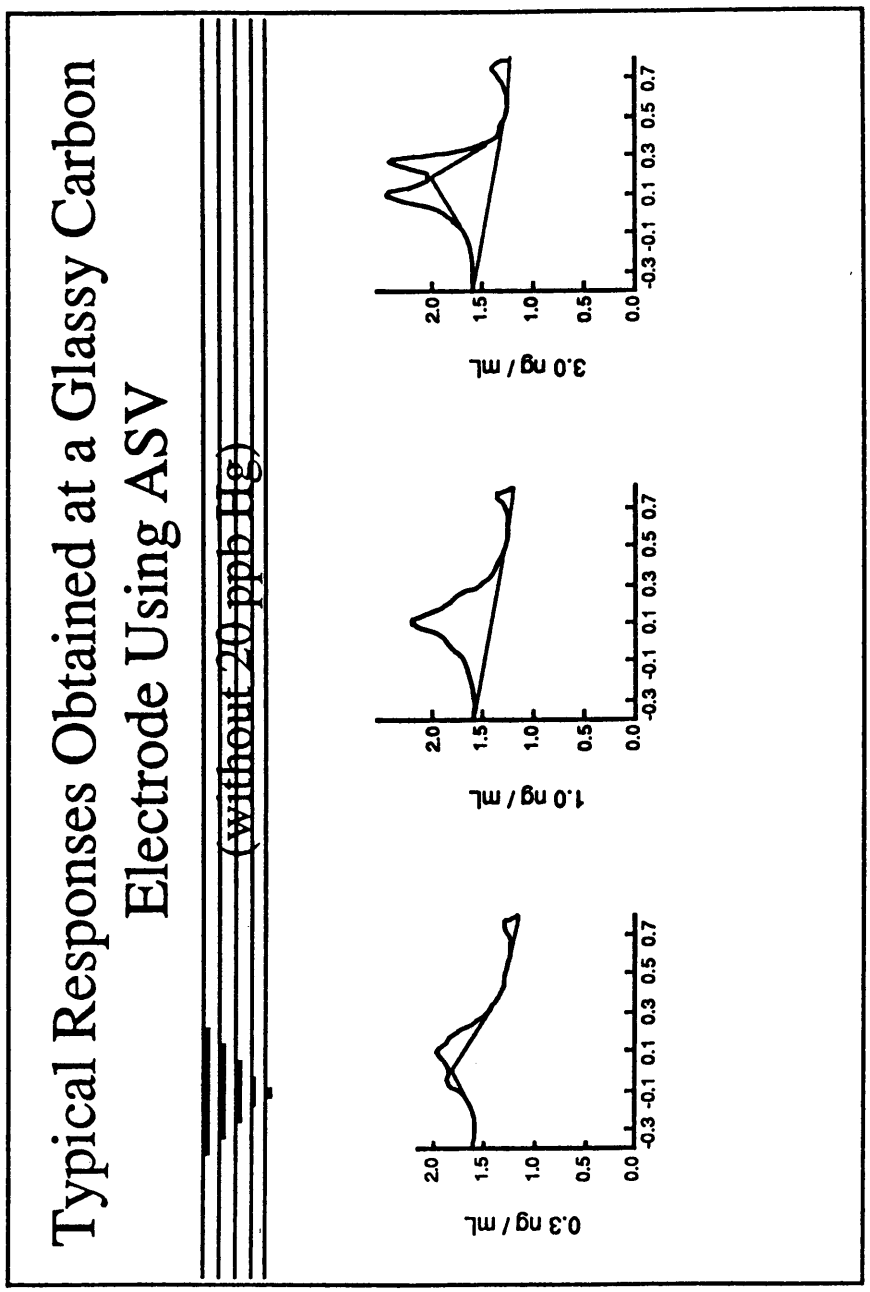

Typical Responses Obtained at a Glassy Carbon Electrode Using ASV
(without 20 ppb Hg)
0.3 ng / mL
1.0 ng / mL
3.0 ng / mL
2.0
1.5
1.0
0.5
0.0
-0.3 -0.1 0.1 0.3 0.5 0.7

FIGURE 15

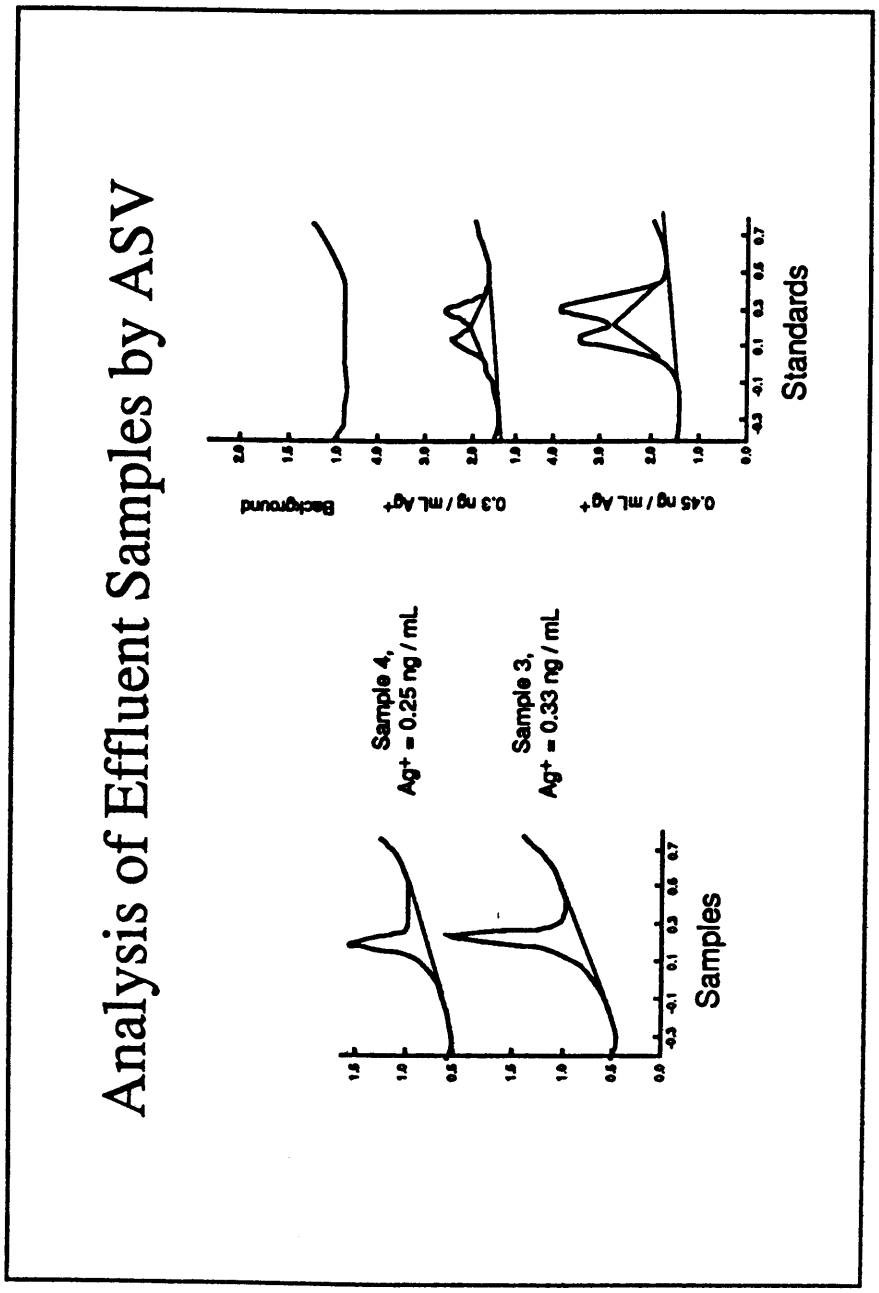

Analysis of Effluent Samples by ASV
Sample 4,
Ag+ = 0.25 ng / mL
Sample 3,
Ag+ = 0.33 ng / mL
Samples
Background
0.3 ng / mL Ag+
0.45 ng / mL Ag+
Standards

FIGURE 16

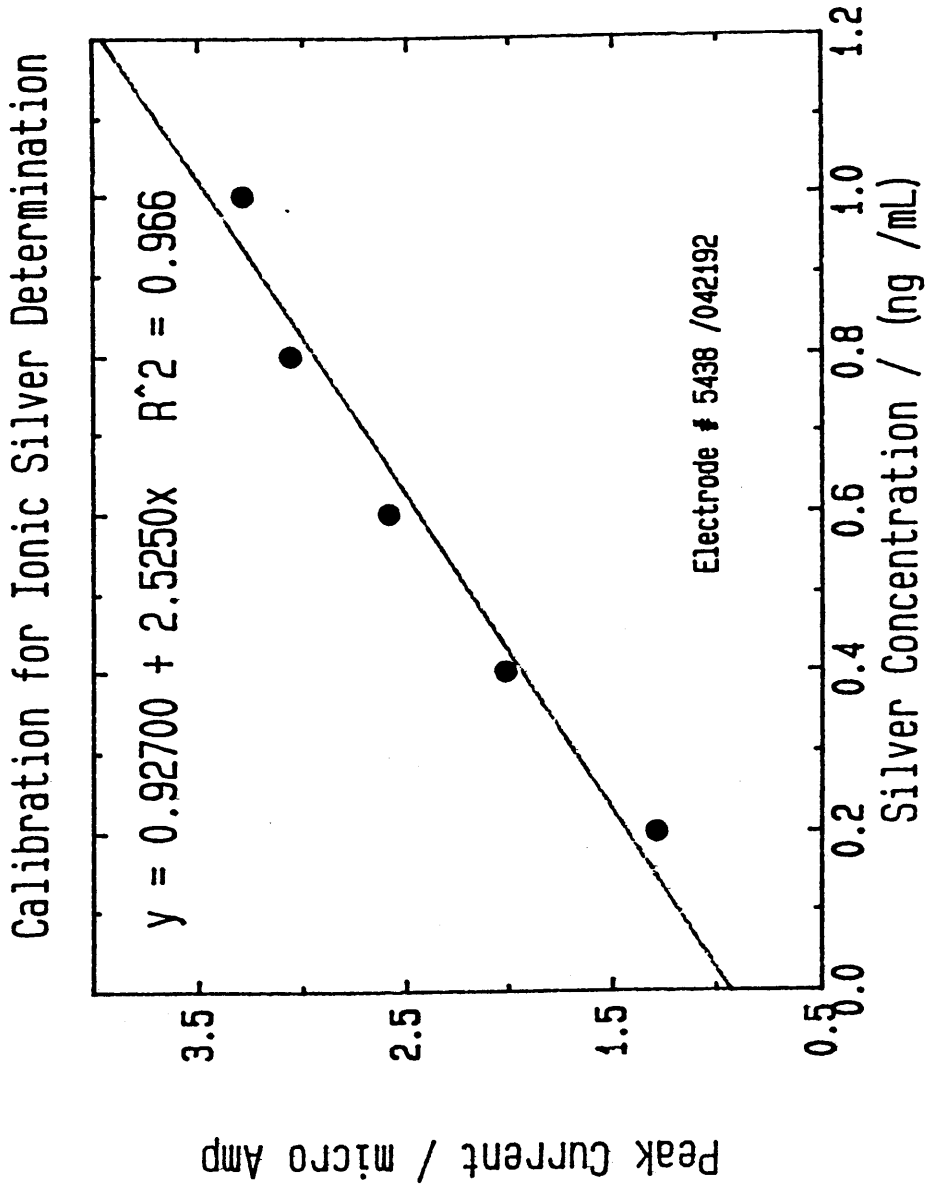

Calibration for Ionic Silver Determination
y = 0.92700 + 2.5250x R^2 = 0.966
Electrode # 5438 /042192
Peak Current / micro Amp
Silver Concentration / (ng /mL)
0.5
1.5
2.5
3.5
0.0
0.2
0.4
0.6
0.8
1.0
1.2

FIGURE 17

Summary of Reproducibility of Ionic Silver Analysis Results

based on silver standard solution analysis

Concentation of Ionic Silver ng / mL	Relative Standard Deviation of Response %
0.2	12.4
0.3	17.4
0.4	6.9
0.6	2.0
0.8	2.3
1.0	1.6

FIGURE 18

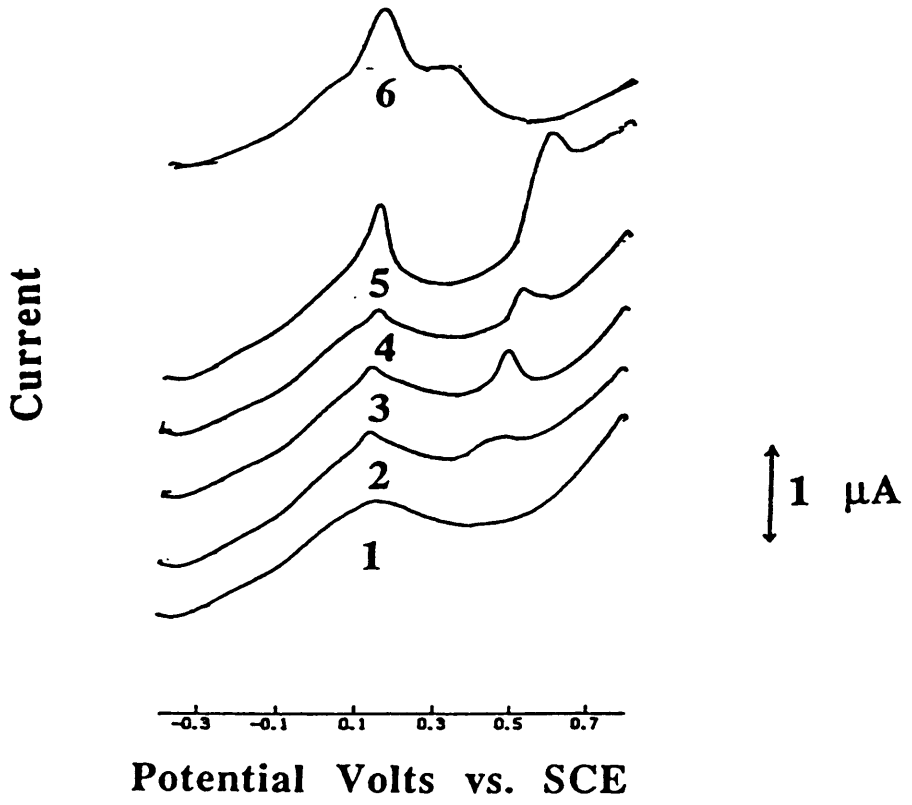
Summary of Results Obtained from Environmental Water Samples

Sample #	Silver ng/ mL by pAG	Silver ng/ mL by ASV	amount of spiked Ag, ng/mL	Total Ag ng/mL with spike by ASV	Comments
1A	0.003	< 0.2	0	NA	
2A	0.0146	< 0.2	0	NA	high
3A	0.0084	< 0.2	10	< 0.2	complexing
4A	0.0075	< 0.2	0	NA	ability
5A	0.0078	< 0.2	0	NA	
6A	< 0.010	< 0.2	0	NA	

Note: The historical TOTAL SILVER concentration in type A samples between 01/03/91 and 12/18/91 was 76 ng / mL.

FIGURE 19

Example of a Type A water sample



Type A sample, after addition of: (1) 0 ppb, (2) 5 ppb, (3) 10 ppb, (4) 200 ppb, (5) 465 ppb silver ion, and (6) 0.2 ppb silver standard.

FIGURE 20

MR. TELLIARD: I would like to thank the morning speakers. Continuing with pollution prevention, let's look at a pollution prevention solvent recovery system. Jim Stunkel with ABC Laboratories is going to tell us about a recovery system he has used.

MR. STUNKEL: Solvent purification by spinning band distillation with specific emphasis on purification of methylene chloride is the subject of my discussion today. I would first like to start out by reviewing some basic vapor-liquid equilibrium concepts as well as different types of distillation.

Shown at right is a graphical representation of a mixture of two solvents which I will designate as components A and B. As you know, the composition of the vapor above the mixture is dependent upon the relative volatilities of the two components.

Shown at upper left is Raoults law which allows us to calculate the vapor pressure of a component above a mixture. In words, this equation says that the vapor pressure of component A above the mixture is equal to the mole fraction of component A in the mixture times the saturation vapor pressure of component A.

If a mixture displays the type of behavior predicted by Raoults law exactly, then it is considered to be an ideal mixture.

In order to calculate the actual composition of the vapor, we can use the equation shown at bottom left. This equation states that the mole fraction of component A in the vapor is equal to the mole fraction of component A in the mixture times the saturation vapor pressure of component A all divided by the total pressure above the mixture caused by all components.

The more volatile components, of course, have a greater tendency to be in a greater abundance in the vapor phase due to their greater tendency to evaporate.

Now, the vapor in equilibrium with this initial mixture has at this point been enriched in the more volatile component by one evaporation stage. Now, if these vapors are condensed and the resulting liquid allowed to come to equilibrium with its

own vapor, we would find that the vapor has again favored the more volatile component.

By repeating similar condensation and evaporation stages multiple times, one can eventually obtain a small amount of condensed liquid that will be very rich in the more volatile component.

Now, if we construct a diagram of vapor composition versus liquid composition for each of these stages, we obtain a diagram similar to the isobar shown here for a mixture of benzene and toluene. In this diagram, the top curve represents the composition of the vapor; the bottom curve is the composition of the liquid.

Each stair step inside of the curve corresponds to one equilibrium stage.

Now, in some distillation columns, each one of these stages is an area in the column where actual condensation and evaporation can be seen to occur, while in other columns, each one of these stages is a more theoretical type more closely resembling those in gas chromatography.

There are two basic types of distillation. The first type, called simple distillation, involves a single equilibrium stage directly from the solvent flask to the condenser. The liquid formed during condensation is then directed away from the system in this type of operation.

The second type of distillation, called countercurrent distillation, on the other hand, redirects a specific portion of the condensate formed to the column where it flows back down to the solvent flask. The quantity of material returned to the column, referred to as reflux, must then be re-evaporated in order to reach the top of the column again.

Shown here is a rotary evaporator which is an example of simple distillation. Again, this type of instrument essentially utilizes one evaporation stage directly from the solvent flask to the condenser, and the condensate is then directed to the receiving flask.

This type of system is not a very efficient type of a separating mechanism and so is used primarily for evaporation of bulk solvent after sample extraction steps, for example.

Here is a photograph of a Kuderna-Danish concentrator equipped with a

Snyder column. This type of system represents a rudimentary form of countercurrent distillation.

This particular example shows a 3 ball column, each ball joint representing an actual equilibrium stage. Vapors rising up through the column are forced to come into close contact with the condensate formed at each ball joint, and the more volatile component is thereby enriched at each stage, and, more importantly, your analytes of interest are left behind.

In addition, a small amount of condensate formed at each Ball joint had a tendency to drip back one stage and results in countercurrent type distillation.

This is the system that I have been using to collect data that I am going to present here today. This is a spinning band column, distillation system. The basic components of the system from bottom to top are an electrically heated solvent flask, a spinning band distillation column which is the silver portion of the system.

There is a column head and condenser, and then up at the top, there is a motor which spins the spinning band which you will be able to see more clearly in the next slide, and then over on the right, there is a small box which is a microprocessor controller used to control the operating conditions of the system.

This is a closeup of the column head. I don't know whether you can see it very well from where you are at or not, but there is a reflux valve on the top surface of the silver portion of the column which is used to control the amount of reflux returned to the column.

Now, unlike the Snyder column, this column does not depend on distinct physical separating or equilibrium stages to achieve separation. Instead, this system uses a helically-shaped teflon band through the length of the column which is spun at about 2200 rpm during system operation.

Several things occur due to the spinning action of the spinning band. First of all, the band generates a lot of mixing throughout the column in the horizontal sense. This gives fairly rapid vapor-liquid equilibrium of the components in the mixture.

Second, vapors attempting to rise up out of the solvent flask are pumped downward by the spinning band which gives a longer residence time of the vapors in the

column and helps ensure complete equilibration.

Thirdly, there is a tendency for the spinning band to scrape the inner surface of the column, and this gives fresh surface area for liquid film formation.

Now let's move on to actual requirements for pesticide grade methylene chloride. This data was taken from the Reagent Chemicals Handbook published by the American Chemical Society and essentially lists all the parameters that they consider important in order for methylene chloride to qualify as pesticide grade.

In this study that I am presenting today, we concentrate primarily on total assay at the top right corner which must be greater than 99.5 percent. This essentially shows the presence of other solvents in the mixture.

For our studies, we use flame ionization detection for this test.

The other thing that we concentrated on was total chlorinated hydrocarbon content which is under the GLC interference category at bottom left. This was done by electron capture detection, and it must be not greater than 10 nanograms per liter for pesticide grade methylene chloride.

We did a series of experiments, actually. The first of these involved a test mixture which was composed of methylene chloride and four chlorinated pesticides. The top chromatogram shows an electron capture analysis of the test mixture diluted 100-fold and exchanged hexane for analysis.

The first major peak you see is lindane, the second is 4,4-prime DDE, the third large peak is 4,4-prime DDD. There are also multiple toxaphene components which are seen as small peaks throughout the chromatogram.

Each one of these chlorinated pesticides was added at approximately 93 million nanograms per liter when quantitated against heptachlor epoxide.

The bottom chromatogram shows a flame ionization detector analysis of the test mixture, also added some acetone at .6 percent by volume, which is the very small peak on the trailing edge of the solvent front. The FID analysis was undiluted.

These are the operating parameters that we programmed into the microprocessor controller to purify this test mixture. We programmed the distillate to be collected in two fractions.

The first fraction was collected when condensate temperature at the head of the column was between 28 and 39.3 degrees C.

Unwanted low boiling components were to be eliminated during this fraction by directing the distillate to a waste container. It turns out that these parameters did not come into effect during this particular experiment, indicating the absence of any low boiling components and also total suppression of the fortified acetone.

The second fraction was collected between 39.3 and 39.7 degrees C. This is the fraction during which we collected purified methylene chloride.

Other important parameters include the mantle rate and the reflux ratio which I will talk about in more detail later on.

These two chromatograms compare an FID analysis of the purified test mixture and Burdick & Jackson methylene chloride. Again, this test essentially is intended to show the presence of any other solvents, and in this case, any FID detectable compound.

Both of these solvents gave greater than 99.9 percent of total assay.

The top chromatogram is a chromatogram of the purified test mixture, and the bottom chromatogram a sample of Burdick & Jackson methylene chloride. In both instances, the samples were concentrated 100-fold using a Kuderna-Danish concentrator and exchanged to hexane for analysis.

In the top chromatogram, we see some carryover problems from the chlorinated pesticides. The second major peak in the top chromatogram is lindane carried over. The third and fourth chromatogram peaks are 4,4-prime DDE and 4,4-prime DDD respectively.

These three peaks amounted to about 196 nanograms per liter of carryover contamination.

The bottom chromatogram of Burdick & Jackson methylene chloride had about 59 nanograms per liter of ECD detectable contamination.

ACS specifications required less than 10 nanograms per liter.

Now, I realize that we are substantially over the ACS requirements, but

please keep in mind that we started out with a very concentrated mixture, and we did manage to bring contamination in the mixture down from 93 million nanograms per liter each to a total of 196 nanograms per liter.

After this experiment, we designed another series of experiments. We decided to dilute the test mixture 500-fold because of the carryover contamination problems that we experienced in the last experiment. Also, we decided that the most valuable information would be obtained if we optimized mantle heating rate and reflux ratio.

The first factor, mantle heating rate, is simply the percentage of time that the heating mantle is receiving power from the controller. This, in turn, controls the boiling rate of the solvent in the flask and the amount of vapor being loaded onto the column.

The second factor, reflux ratio, is related to the rate at which reflux and distillate are being produced. As was stated earlier, reflux is the quantity of the material returned to the column after condensation. Distillate, on the other hand, is the quantity of material taken off as final product.

So, reflux ratio is equal to the reflux rate divided by the distillate rate.

Now, if we add reflux rate and distillate rate, we obtain another important factor called column loading. This is simply the total amount of vapor passing through the column in unit time.

This table shows four experiments that we did in an attempt to optimize reflux ratio and mantle rate. By manipulating these two factors to produce opposite effects, we were able to maintain a fairly constant distillate rate of about 520 ml per hour for the first three experiment while, at the same time, reducing the amount of vapor loaded onto the column.

The fourth experiment was done at a slightly higher distillate rate of 685 ml per hour.

And I will just run quickly through these chromatograms. The top one is the chromatogram for the 35 percent mantle rate and 4:1 reflux ratio. We do have some carryover problems here although less than what we had from the original undiluted test

mixture.

The bottom chromatogram done at 28 percent mantle rate and 3:1 reflux ratio also has some carryover but in reduced amounts. So, reducing the mantle rate appears to have helped us.

This is really fairly unusual, since the higher the reflux ratio, generally, the greater the purity of your final product.

These are the two chromatograms for the last two experiments. The top one represents results from a 21 percent mantle rate and 2:1 reflux ratio, and here we have very good results, really not very much carryover contamination at all.

Then, in experiment 4, we were back up to a 28 percent mantle rate, and, correspondingly, the crossover contamination also increased.

This table summarizes the conditions and results from this series of experiments. Over in the far right-hand column we have carryover which you can see steadily decreases as the heating rate goes down.

I would like to call particular attention to experiments 2 and 4. Again, generally, as the reflux ratio goes up, your purity also goes up. Well, we see here that even though we lowered the reflux ratio from 3:1 in experiment 2 to 2:1 in experiment 4, we obtained almost exactly the same results.

So, what this shows us is that at least for chlorinated pesticides, achieving greatest purity is, by far, dominated by the heating rate of the solvent flask.

In experiment 3, we actually managed to achieve less than 10 nanograms per liter of contamination.

The last experiment we did was to recover actual used solvent and re-purify it to pesticide grade. This slide shows a chromatogram of GPC solvent which was used in the analysis of pesticides in corn oil. You see there is a fairly substantial contamination in that.

This chromatogram is an unconcentrated electron capture analysis of that solvent. It has simply been exchanged to hexane.

And these are the operating parameters. These parameters are identical to the parameters which gave best results during optimization of reflux ratio and heating

mantle rate.

These are the chromatograms of the final, purified GPC solvent. The top chromatogram shows a 100:1 concentration with exchange to hexane. The bottom slide shows hexane used for the solvent exchange concentrated 50:1. We concentrated the hexane 50:1 because that is the quantity of hexane we used for the solvent exchange.

As you can see, almost every peak in the GPC solvent is also present in the hexane used for solvent exchange. So, we found nothing in the purified solvent at all.

In conclusion, I would first like to say that we were very pleased with the performance of the system. We had no problems in achieving pesticide grade methylene chloride from actual recovered used material.

However, for extremely high levels, we may have to resort to double distillation, meaning that we take the purified product and put it through the same process again.

There is another possibility. We might try some pre-treatment such as using activated charcoal or other adsorbents to remove some of the pesticides before distillation.

We believe that tolerance for chlorinated hydrocarbons in the starting mixture is around .18 ppm for a single distillation operation. Optimum system efficiency is, without a doubt, achieved at low mantle rates and low reflux ratios, at least for this type of mixture.

The spinning band system produces high quality solvent from actual used material, and we were able to produce purified product at at least 520 ml per hour.

And an important lesson that I learned is that no matter how well your distillation system is working, if you are not extremely careful during the quality control steps, it doesn't do you any good. It is very easy to accidentally introduce contamination at the levels that we are working at.

Are there any questions?

QUESTION AND ANSWER SESSION

MR. PIWONI: My name is Marv Piwoni. I am with Illinois Hazardous Waste Research and Information Center.

I don't really have a question. I guess a commendation, first of all, for your efforts, but I have a sort of a comment of a philosophical nature perhaps.

MR. STUNKEL: All right.

MR. PIWONI: The recovery process requires two components, that is, gathering of the material that you are using in the lab, and we saw that demonstrated in the presentation yesterday, and then the trickier part, I think, is the marketplace for using that solvent.

You demonstrated here, I think, that you can with the spinning band still which is on the order of $10,000 or $12,000, I think, from BR Instruments, you can generate solvent to reuse, but I have more trouble envisioning every lab in the country doing this than I have them perhaps gathering the solvent in the first place.

I guess the comment maybe to Bill or to any solvent vendors in the audience, if they are still around, is are there alternatives once you gather that solvent in your little 4-liter jars to trying to process it in lab yourself?

The solvent manufacturers are equipped to do this, and if we could figure out some mechanism to return that solvent to them, I think we would all benefit, and we would benefit from the economies of scale, obviously. The still people don't like that, but we would benefit, I think.

MR. STUNKEL: Thank you.

MR. HALVORSON: My name is Jeff Halvorson from Burdick & Jackson.

I just thought I would make a comment on the last person's observations. B&J, I know, and my area...

MR. TELLIARD: Could you get closer to the microphone?

MR. HALVORSON: B&J is the solvent producer that a lot of people use, and I am not really in that area, so I am not completely familiar with all the processes involved, but I do know that they are very reluctant to take recycled solvent, because

there is no history behind reclaimed solvents in most cases. We don't know what they were used for, and we don't really know what clients are going to need to use it for once it is recycled.

So...

MR. STUNKEL: Excuse me. Did you say they were reluctant to take used solvent?

MR. HALVORSON: That is my understanding right now.

MR. STUNKEL: Okay.

MR. HALVORSON: There are companies that do recycle solvents, though, not necessarily for laboratory use but for industrial use, so it is not necessarily something that has to be disposed of.

MR. STUNKEL: Okay.

MR. HALVORSON: I had one question for you as well, though. I wondered if you had done any calculations on the number of theoretical plates you have for that distillation apparatus.

MR. STUNKEL: Yes, that is right. I did forget to say that. Under ideal conditions, this system produces about 50 theoretical plates.

MR. HALVORSON: Thank you.

MR. STANKO: George Stanko from Shell.

Did you by any chance look at any of the other analytes in, say, Method 625 or 8270 with respect to recovering the methylene chloride?

MR. STUNKEL: No, we didn't.

MR. TELLIARD: Anyone else?

(No response.)

MR. TELLIARD: Jim, thanks as lot.

Solvent Purification For Analytical Laboratories

Vapor Composition Above a Mixture

Raoults Law and Vapor Pressure

$$P_a = X_a \times P_a^o$$

Vapor Composition

$$X_a(vap) = \frac{X_a \times P_a^0}{P_{total}}$$

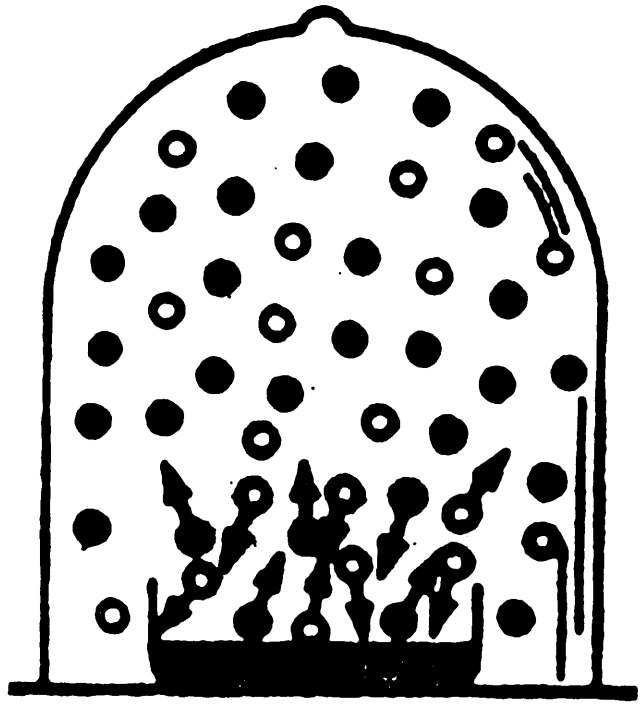


Figure from: R.H. Petrucci, General Chemistry: Principles and Modern Applications, Macmillan, NY (1982).

Equilibrium Curve For A Binary Mixture

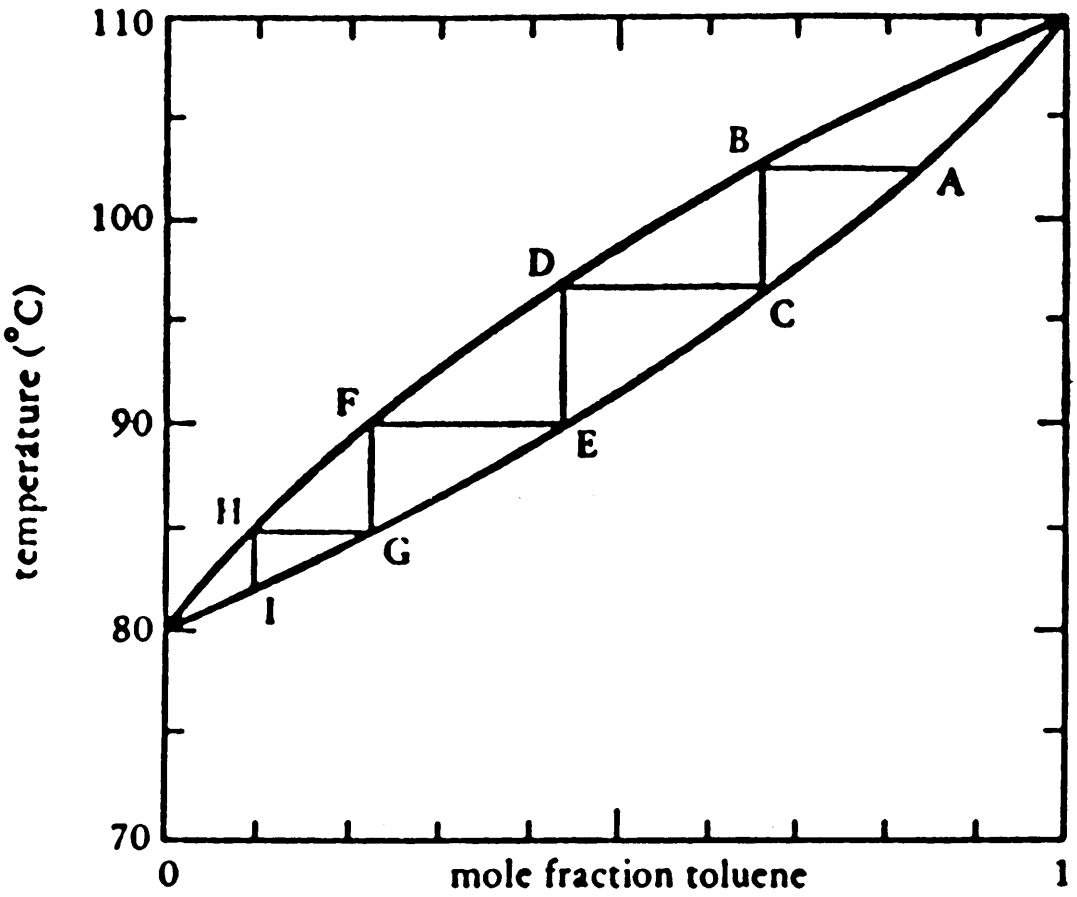


Figure from: Addison Ault, Techniques and Experiments for Organic Chemistry, Allyn and Bacon, Boston (1983).

Simple vs. Countercurrent Distillation

Simple Distillation	Countercurrent Distillation
Condensate Removed	Condensate redirected to column (reflux)
One Evaporation Step	Multiple evaporation steps

Effects of Spinning Band Rotation

Action	Effect
Horizontal Mixing	Rapid Vapor-Liquid Equilibrium
Downward Pumping	Long Vapor Residence Time
Scraping	Fresh Surface for Liquid Film Formation

ACS Specifications For Pesticide Grade Methylene Chloride

General Use

-Appearance: Clear
-Color (APHA): ≤10
-Residue After Evaporation: ≤0.002%
-Free Halogens: To pass test

-Assay: ≥99.5%
-Water: ≤0.02%
-Titratable Acid: ≤0.0003 meq/g

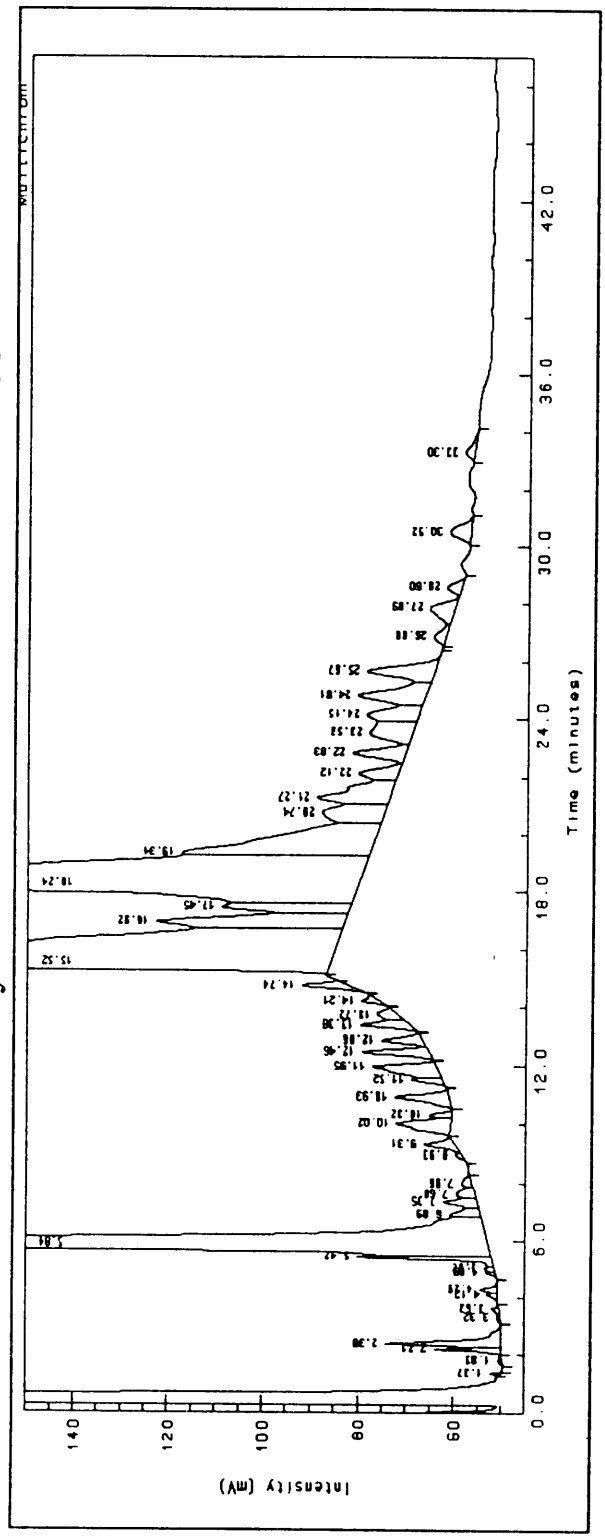
HPLC and UV Spectrophotometry

-Absorbance: To Pass Test

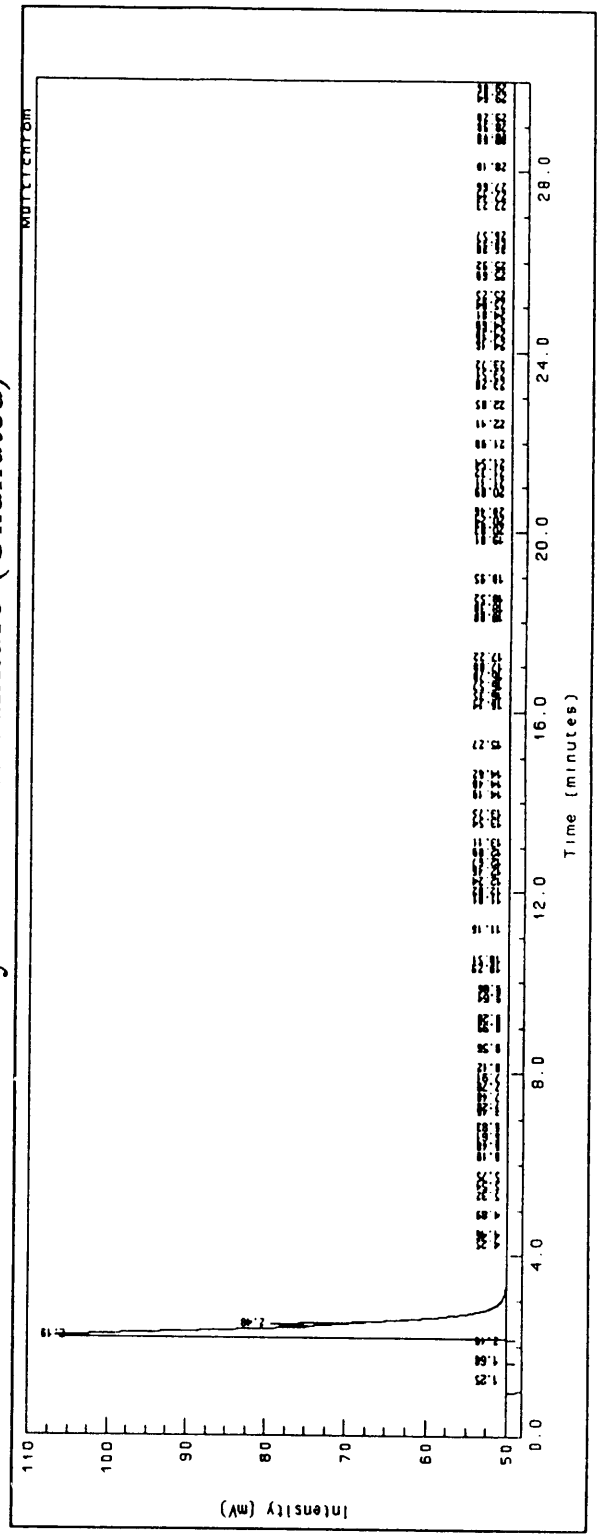
GLC Interference

-Chlorinated Hydrocarbons (as Heptachlor Epoxide): ≤10 ng/L
-Phosphorus (as Parathion): ≤100 ng/L
-Sulfur (as Parathion): ≤500 ng/L

ECD Analysis of Test Mixture Diluted 1:100



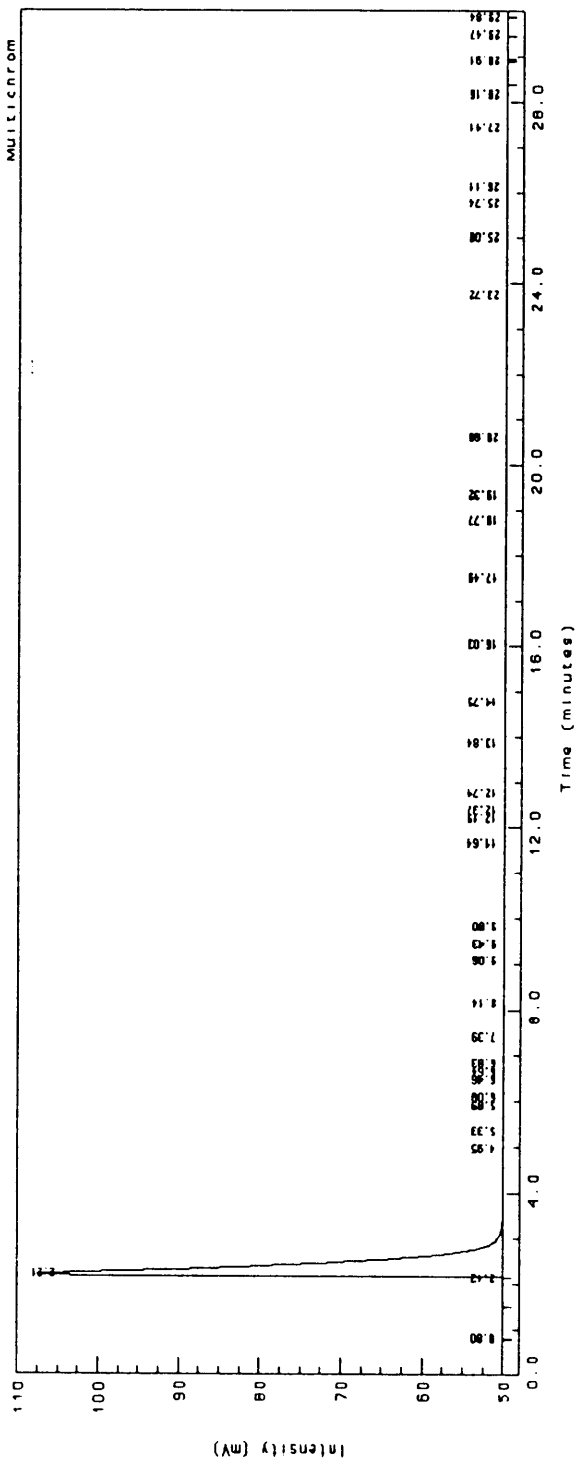
FID Analysis of Test Mixture (Undiluted)



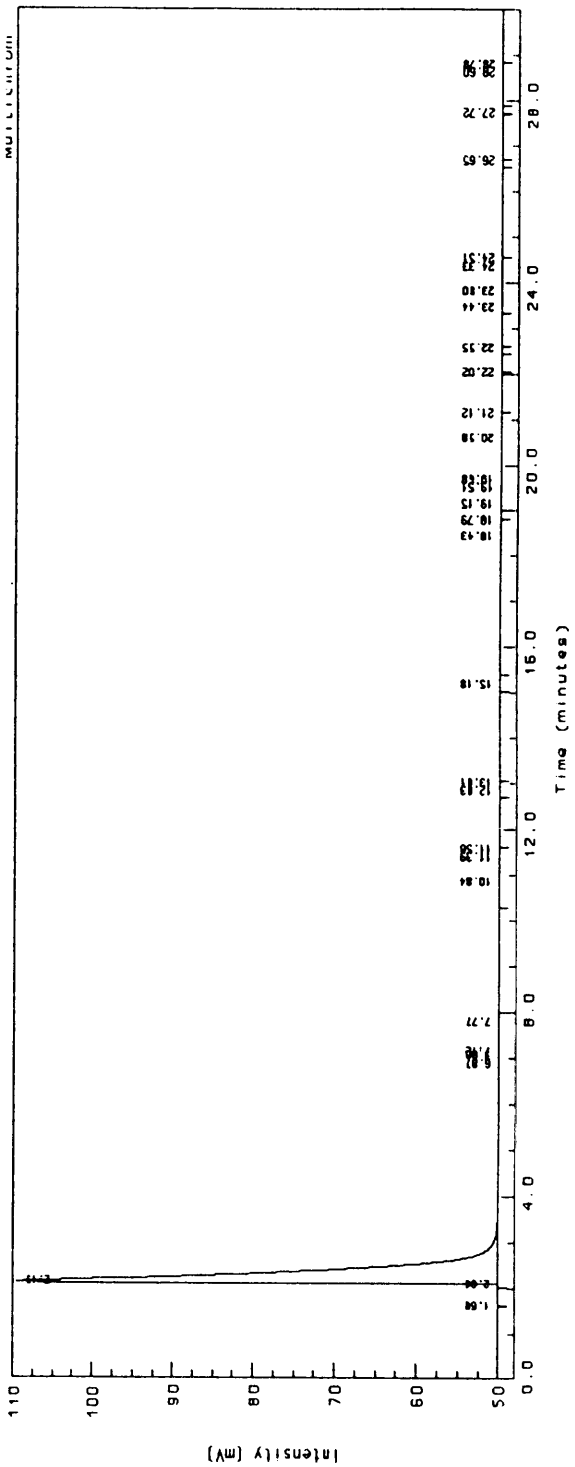
Distillation Parameters Used For Test Mixture

Parameter	Fraction 1	Fraction 2
Open Temperature	28.0 ^{0}C	39.3 ^{0}C
Close Temperature	39.3 ^{0}C	39.7 ^{0}C
Mantle Rate	21%	21%
Reflux Ratio	30:1	2:1

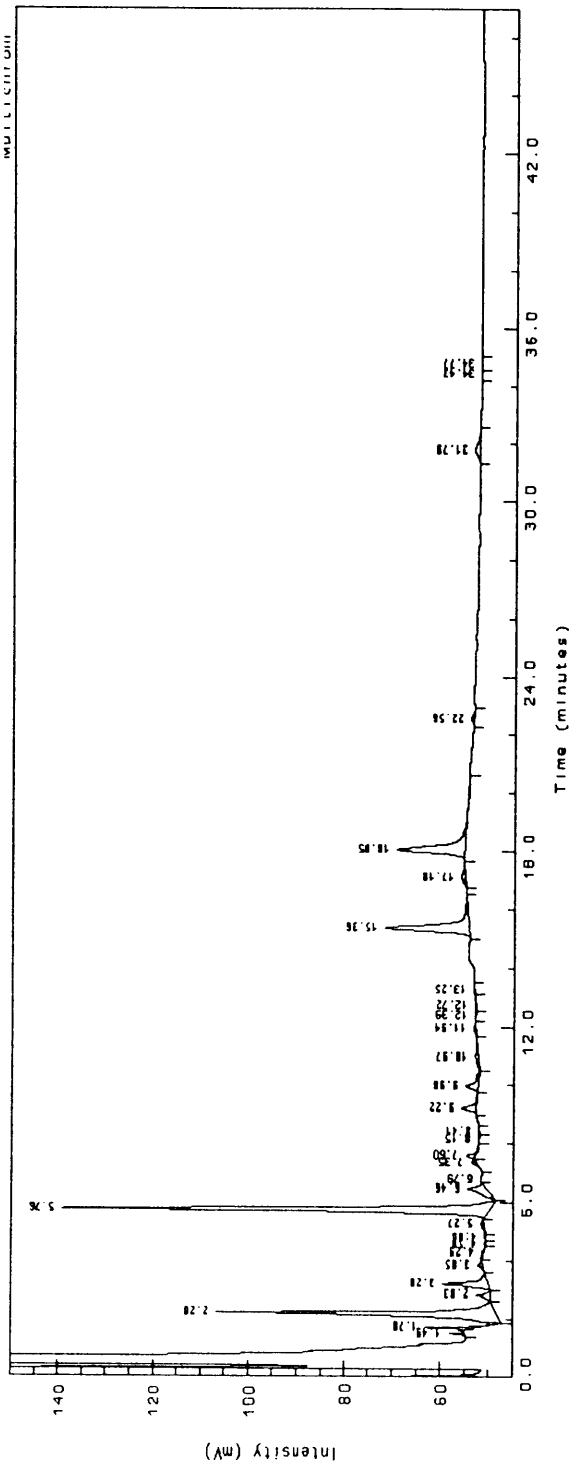
FID Analysis of Purified Test Mixture



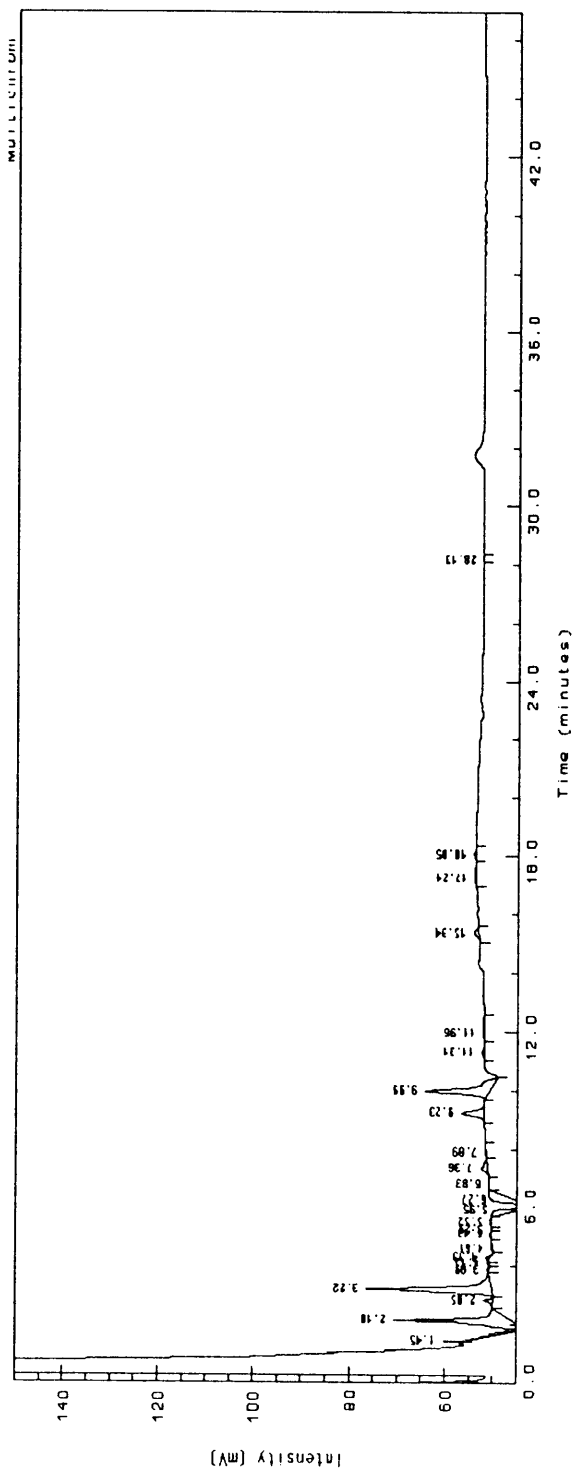
FID Analysis of Burdick and Jackson Methylene Chloride



ECD Analysis of Purified Test Mixture Concentrated 100:1



ECD Analysis of B&J Methylene Chloride Concentrated 100:1



Optimization of Operating Parameters - Mantle Rate vs. Reflux Ratio

$$Mantle\ Rate = \frac{Time\ On}{Total\ Time} \times 100\%$$

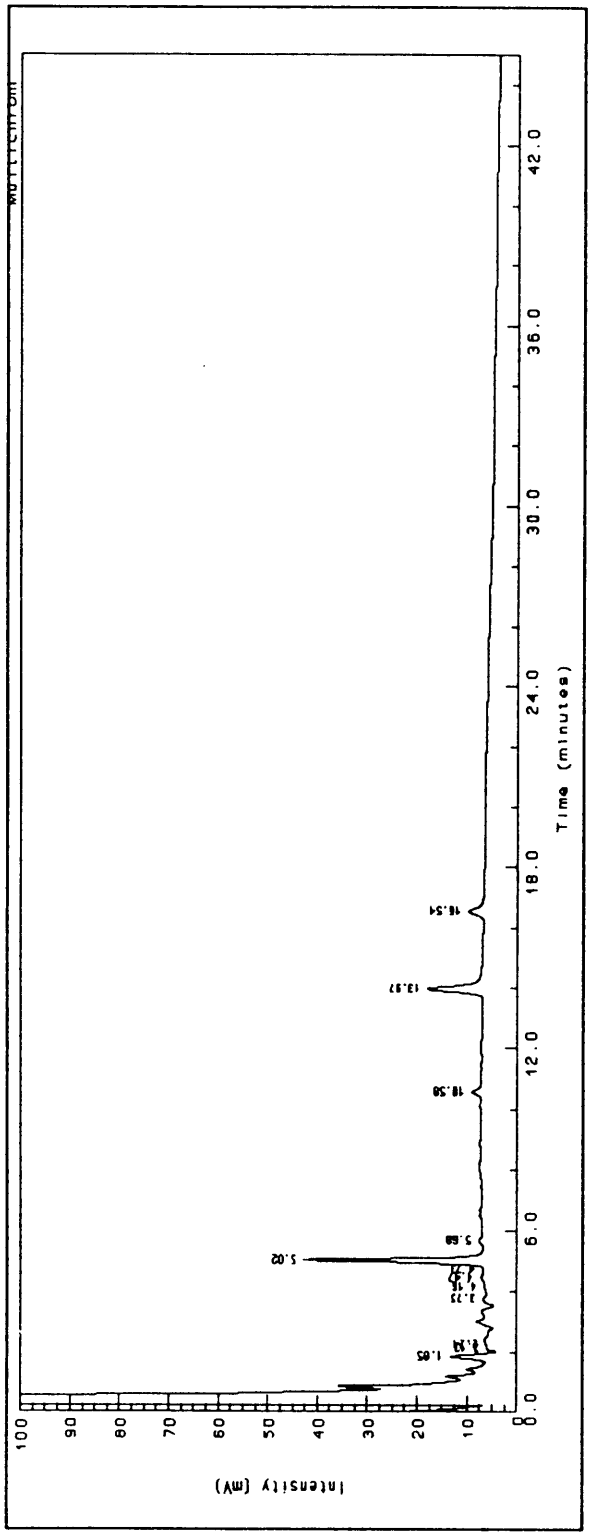
$$Reflux\ Ratio = \frac{Reflux\ Rate}{Distillate\ Rate}$$

$$Column\ Loading = Reflux\ Rate + Distillate\ Rate$$

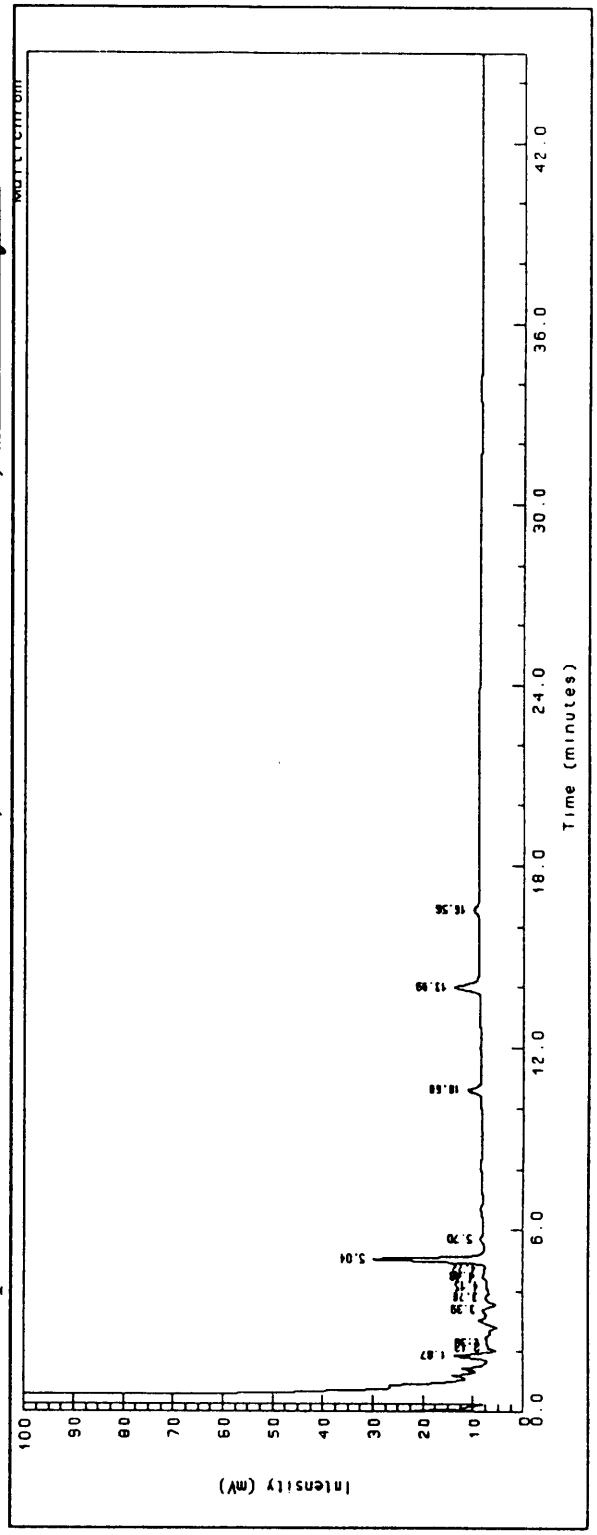
Optimization of Reflux Ratio and Mantle Rate - Operating Parameters

Experiment	Mantle Rate	Reflux Ratio	Distillate Rate
1	35%	4:1	524 ml/hr
2	28%	3:1	536 ml/hr
3	21%	2:1	510 ml/hr
4	28%	2:1	685 ml/hr

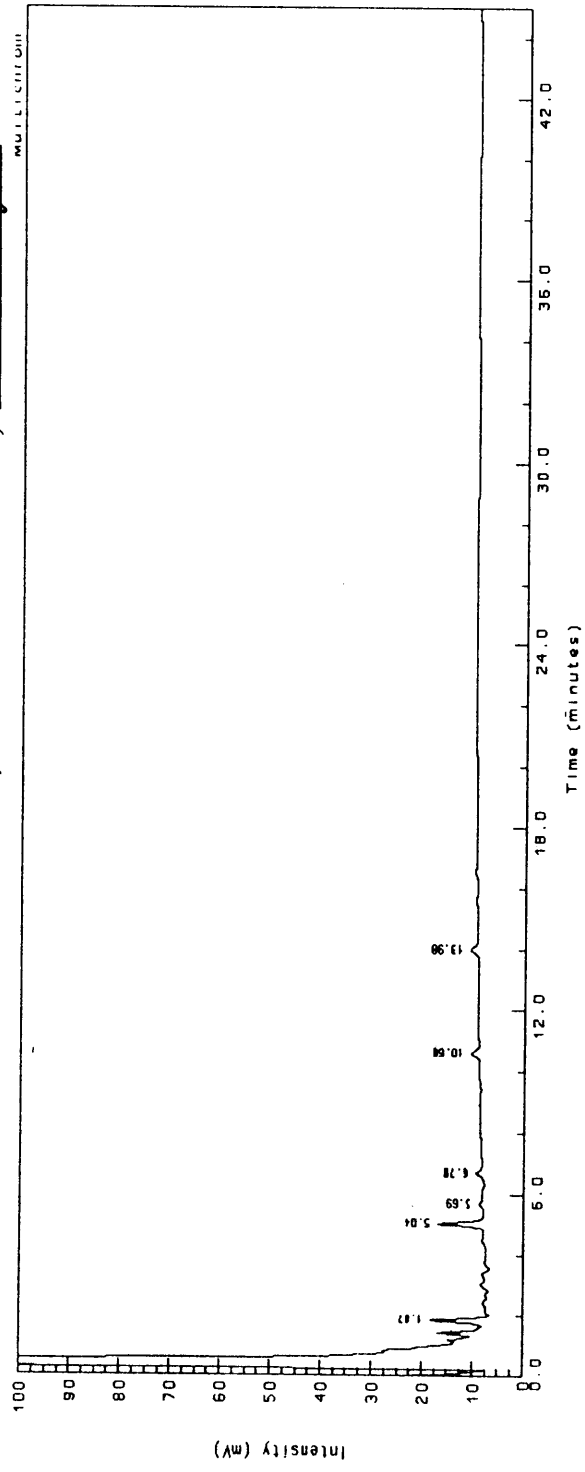
Experiment 1. 35% Mantle, 4:1 Reflux Ratio, ECD Analysis



Experiment 2. 28% Mantle, 3:1 Reflux Ratio, ECD Analysis



Experiment 3. 21% Mantle, 2:1 Reflux Ratio, ECD Analysis



Experiment 4. 28% Mantle, 2:1 Reflux Ratio, ECD Analysis

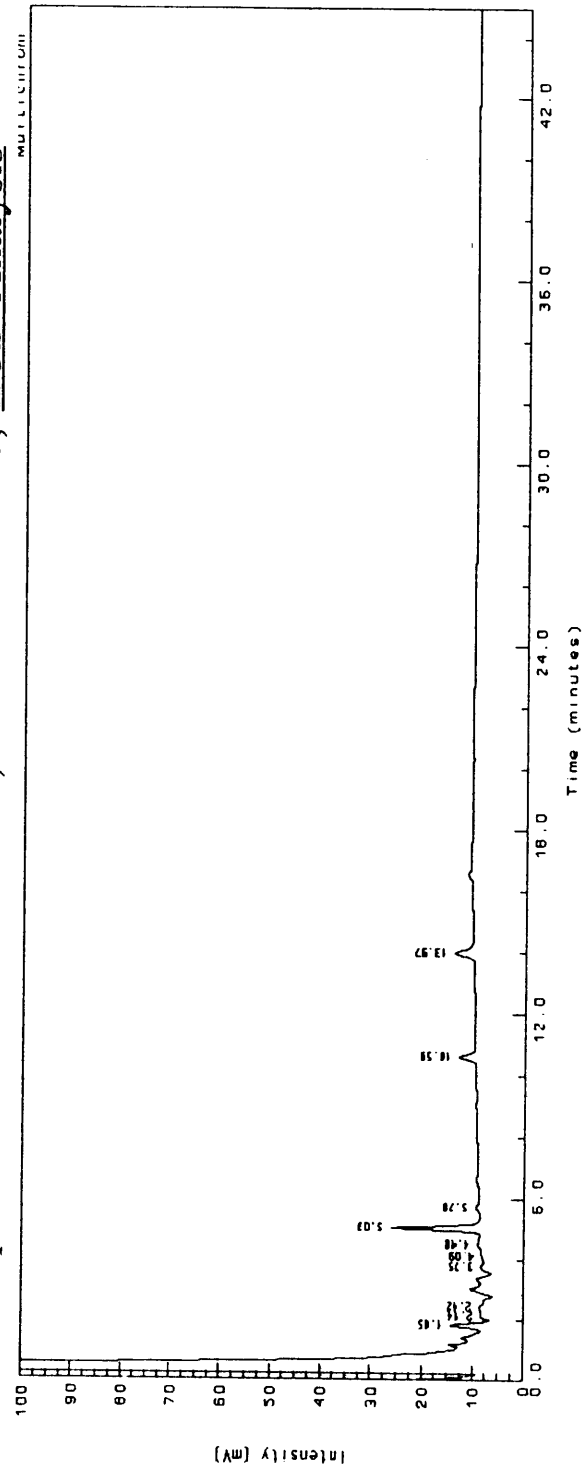
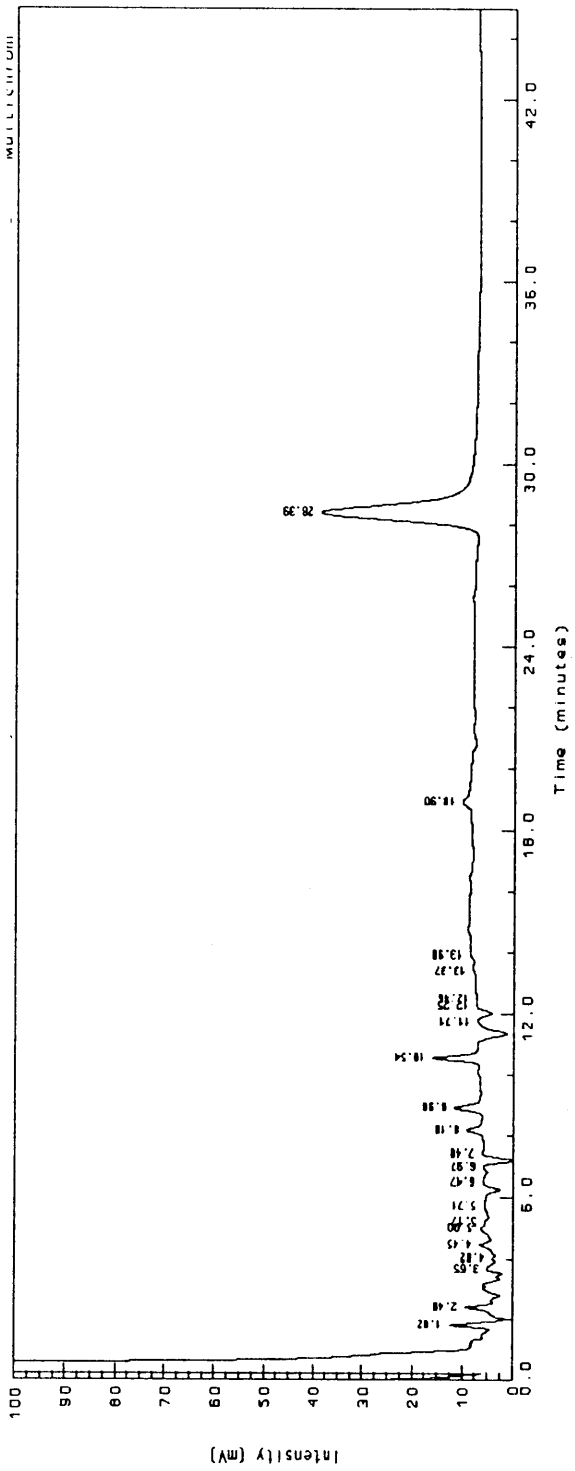


Table of Results For Reflux Ratio vs. Heating Rate

Experiment	Mantle Rate	Reflux Ratio	Distillate Rate	Carry Over
1	35 %	4:1	524 ml/hr	48.1 ng/L
2	28 %	3:1	536 ml/hr	25.6 ng/L
3	21 %	2:1	510 ml/hr	9.5 ng/L
4	28 %	2:1	685 ml/hr	25.2 ng/L

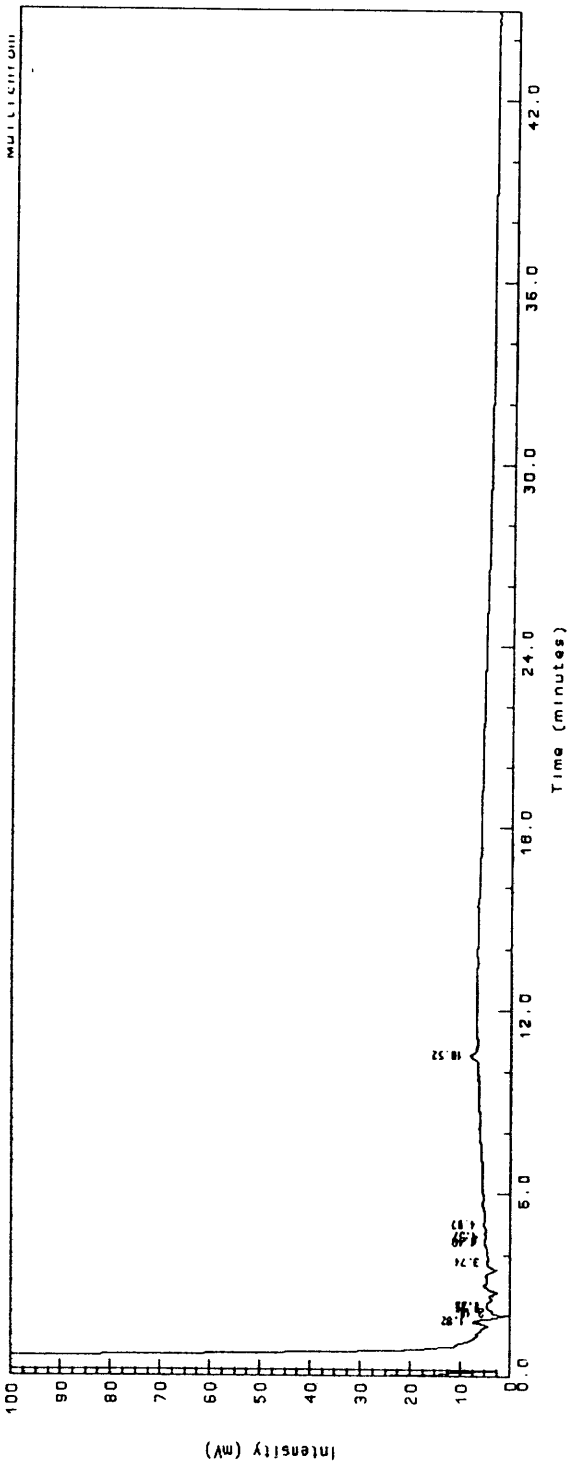
Recovered GPC Solvent Unconcentrated ECD Analysis



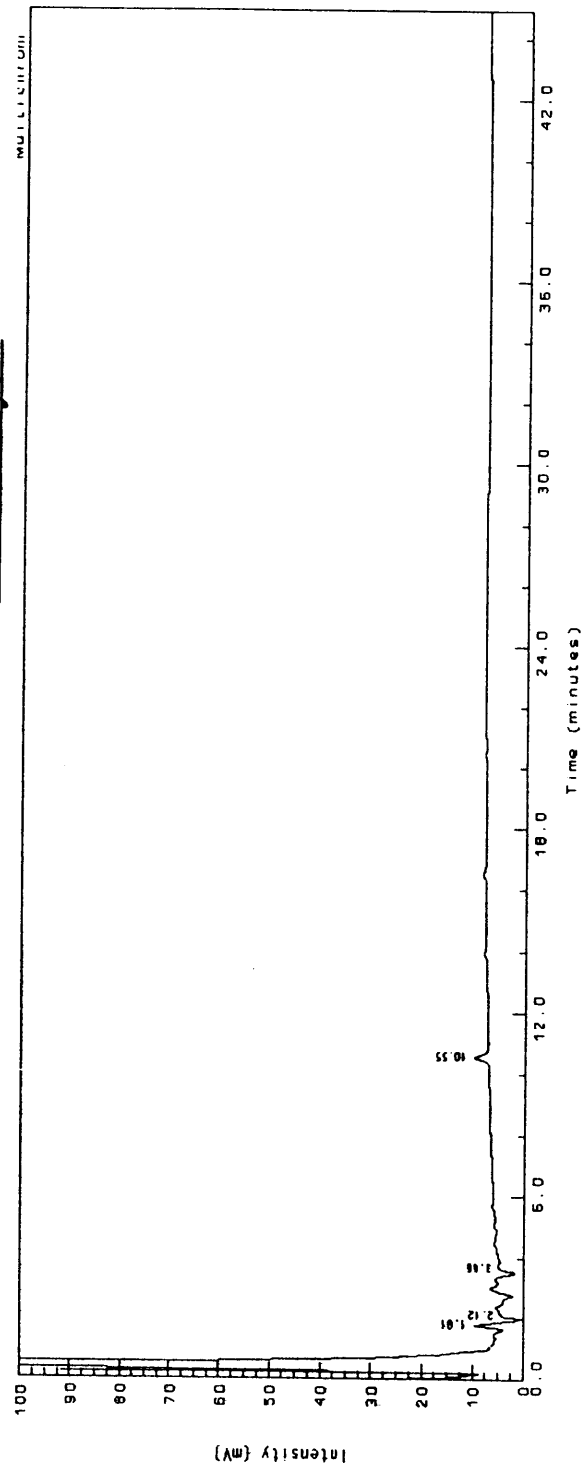
Operating Parameters For Purification of Recovered GPC Solvent

Parameter	Fraction 1	Fraction 2
Open Temp.	30.0 °C	38.0 °C
Close Temp.	38.0 °C	39.0 °C
Mantle Rate	21%	21%
Reflux Ratio	30:1	2:1

Purified GPC Solvent Concentrated 100:1 ECD Analysis



Hexane Concentrated 50:1 ECD Analysis



Conclusion

A. Extremely high contaminant levels may require double distillation.

B. Tolerance for chlorinated hydrocarbons in starting mixture is ~ 0.18 ppm for single distillation.

C. Optimum system efficiency achieved at low mantle rates and reflux ratios.

D. Spinning band system produces very high quality solvent from actual used material.

E. Purified solvent produced at ≥ 520 ml/hr.

F. Accurate QC is critical.

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MR. TELLIARD: Our next speaker is Greg O'Neil. He is from Tekmar, the man who has purged you for years. I am sorry. Going to talk about some headspace analysis work that they have done as soon as he masters the microphone.

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Analysis of Volatile Organic Compounds in Soil Using Static Headspace Extraction

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Paul Kester
Denise Sherman
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Cincinnati, OH 45242-9576

INTRODUCTION

There is a need to develop a better analytical method for the analysis of volatile organics in soil. This study isolates the problems associated with soils analysis. These difficulties can be overcome by using static headspace techniques.

Currently, soils analysis is performed with purge and trap/gas chromatography. There are fundamental differences between purge and trap and static headspace. Purge and trap is a continuous gas extraction where an exhaustive purge of the sample transfers the analytes from the sample to the trap, which is then desorbed to the GC column. Quantitation is based on recovery of internal standards, as is typical within EPA methods as shown in equation 1:

$$(C_X) = (A_X)\ (C_{IS}) \ / \ (A_{IS})\ RF \qquad \text{Eq. 1}$$

Where A_X = Area of Compound
A_{IS} = Area of Internal Standard
C_X = Concentration of Compound
C_{IS} = Concentration of Internal Standard

Static headspace is a discontinuous gas extraction where the analytes partition between the sample and the headspace. When the rate of the analytes leaving the sample is equal to the rate of the analyte returning to the sample from the headspace, an equilibrium condition exists. At this time an aliquot of the headspace is removed and analyzed by GC. It is very important within static headspace methodologies to heat samples to constant temperatures and for uniform periods of time. This ensures a fixed volume of the headspace is injected, resulting in reliable quantitation.

The equation typically used for static headspace quantitation is shown in equation 2:

$$C_S = C_G\ [K + (V_G \ / \ V_M)] \qquad \text{Eq. 2}$$

Where C_S = the concentration of the analyte in the sample
C_G = the concentration of the analyte in the gas phase

K = the partition coefficient (C_S/C_G
V_G = the volume of the gas phase
V_M = the volume of the matrix

There are two important characteristics of this equation. The first is the partition coefficient (K), and second is the phase ratio (V_G/V_M). The partition coefficient is the ratio of the concentration of the analyte in the gas phase (C_G) to the concentration of the analyte in the sample (C_S) phase. Phase ratio is the ratio of headspace volume to the volume (or matrix) of the phase in the vial. When K is very small the phase ratio becomes extremely important. When K is large the phase ratio is relatively unimportant.

In static headspace, the sample is placed in a vial and sealed with a teflon-faced septum, and a crimp cap. The vial is placed in the heated zone of the 7000 and allowed to equilibrate over time. The vial is slightly overpressurized with pressurization gas, typically helium, to the vial. The sample loop is then filled by opening a vent valve downstream of the sample loop. The pressure in the headspace drives the sample through the loop, filling the loop. Sample loop pressure is controlled with a Variable Injection Pressure Regulator (VIPR), set to a value approximately 2psi less than the vial pressure. This increase in pressure exerts a certain backpressure in the loop, compressing the sample during loop fill. The contents of the loop are then swept into the GC injection port.

Figure 1 shows the process of equilibrating a two-phase sample. As heating time increases, the concentration in the gas phase (X_G) increases over time until equilibrium is reached, represented by the flat portion of the curve. This is where the rate of the analytes leaving the sample equals the rate of the analytes re-entering the sample, giving maximum sensitivity and precision. After some point in time a loss of response through degradation will occur. This degradation is a result of a combination of factors: thermal degradation, leaks from the septum, and adsorption of analytes to the septum and walls of the vial.

Table 1 shows a series of partition coefficients for various analytes. These are literature values showing very low partition coefficients for alkanes, olefins, and aromatics, and much higher partition coefficients for polar compounds, such as ketones, aldehydes, and alcohols. The equation for the partition coefficient is:

$$K = (C_S) \ / \ (C_G) \qquad \text{Eq. 3}$$

Where K = the partition coefficient
C_S = the concentration of the sample matrix
C_G = the concentration of the gas phase

For sensitivity reasons, a large analyte concentration in the gas phase is desired. As that concentration increases, the partition coefficient becomes very small. Therefore, the lower the partition coefficient, the easier it is to get the analyte into the gas phase

and analyze by static headspace.

For polar compounds, such as alcohols, it is a typical analytical procedure to add salt to change the partition coefficient to a small value, driving the analyte into the headspace. This technique is called "salting out". In the homologous series of the alcohols, as the aliphatic character of the alcohol increases the partition coefficient decreases.

EXPERIMENTAL

This work was performed with a Tekmar 7000/7050 Headspace Autosampler equipped with a GC/FID. Experimental parameters appear as Tables 2 and 3.

The soil samples were weighed into a 22ml vial to which a matrix modifying solution and internal standards were added.

The matrix modifying solution is an aqueous solution saturated with sodium chloride adjusted to pH2 with phosphoric acid. It is important that the salt selected be a non-buffering salt to ensure the pH remains low. The salt chosen should not be a calcium salt, as this can complex methanol. This complexation is detrimental if methanol is an analyte of interest.

The main purpose of the matrix modifying solution is to control sample to sample matrix variations which may induce quantitation errors. By forcing the conditions of the sample to become constant, results from sample to sample become reliable.

RESULTS and DISCUSSIONS

Figure 2a shows equilibration of aromatic compounds in water, without mixing. A water sample was placed in a vial, heated to 85°C and allowed to equilibrate over time. An excess of one hour was required for the equilibration to occur. By mixing the sample with Optimix (Figure 2b), the time required to reach equilibrium was vastly reduced to less than 10 minutes.

Optimix involves mixing the sample by tapping the vial with a mixing rod from the outside. The sample tumbles in the vial so analytes more easily reach the gas/liquid interface, which is required for an extraction to occur.

Table 4 shows that area counts are increased and RSD values are improved with mixing. These improved results occur due to minimized thermal exposure time.

Standardization of the instrument was performed using the full evaporation technique (FET) to produce a gas phase standard for which response factors are generated. This was created by injecting 1-20 microliters of a liquid phase methanolic standard into a headspace vial, followed by heating the vial to 85°C. On a daily basis a full evaporation check standard was run to ensure

that the instrument was not drifting, and results had to be within 20% of initial values from the beginning of the study in order to continue operation. The standard used was an AccuStandard 502.2A standard. The internal standards/surrogates used for quantitation were dibromofluoromethane, toluene-d_5, and bromofluorobenzene.

A soil sample was placed in a vial, along with a matrix modifying solution that is equilibrated over time (Fig. 3a). This curve was completely unlike that observed for an aqueous sample in Fig. 1. Upon initial heating there was a rapid rise in the concentration of the headspace, followed by a rapid loss, and then a very unstable horizontal path along the plot, not really approaching equilibrium. The total sample equilibration time was 1.5 hours. Mixing the sample reduced the equilibration time to approximately one hour as evidenced by a more horizontal path along the plot (Fig. 3b). However, there was still a significant difference in the appearance of the equilibration curve observed in figure 1. The rapid rise followed by the rapid fall was attributed to the three-phase system contained in the vial.

Initially the analytes spiked into the soil partitioned into the liquid phase of the matrix modifying solution, subsequently analytes partitioned also into the headspace. There was a rapid loss of the analyte from the spike on the surface of the soil sample. The soil was broken up with mixing, increasing its surface area. This increased surface area improved the efficiency of the absorptive nature of the soil, shifting the partitioning to the solid phase. This was represented by the rapid drop in response at about 20 minutes. Eventually the analytes formed an equilibrium with the three phases as shown in Figure 3b.

Quantitation was performed with the use of multiple internal standards which tracked the pattern of their associated spiked analytes very closely. Response factors for the internal standards were derived using the full evaporation technique. Use of internal standards in this fashion produced reliable, quantitative, and reproducible results across the entire range of USEPA Method 502.2 analytes. Further, these internal standards were added prior to headspace extraction and thus served as true surrogate compounds.

SOIL MATRIX VARIATIONS

The most significant challenge with analyzing soil samples is the large number of variables involved. Seven have been identified. Each soil sample can have a wide range of conditions within each of the variables. Therefore soils can have a large number of permutations and combinations of characteristics.

The first condition is ionic strength. Salt content of a soil changes the partition coefficient, primarily of polar compounds. Therefore as this partition coefficient changes, the concentration of the analyte in the headspace changes. In order to control this aspect of the analysis, a saturated salt solution is added to the sample to control its ionic strength, making it constant for each

of the samples to be analyzed.

The second variable is the pH. The pH is adjusted low to prevent dehydrohalogenation reactions which occur spontaneously at 85°C within a sample when pH is at 9 or greater. The matrix modifying solution forces the pH to remain at 2 to prevent dehydrohalogenation reactions. These reactions are the loss of hydrochloric acid across a chlorinated alkane to form a halogenated alkene.

The third variable is biological activity. Biological activity within the sample can cause degradation of analytes during the storage time. Samples are required to be maintained at a temperature of 4°C. The lowering of the pH to 2 acts as a preservative. Salt content of the matrix modifying solution also acts to inhibit biological activity by killing bacteria.

The fourth variable is moisture. Samples vary in moisture content as they come in from the field. The way to compensate for this is to drive the concentration of water in the sample to remain constant by saturating it with an aqueous matrix modifying solution. The sample and headspace go to a consistent concentration of water due to maintaining a constant temperature within the sample and the headspace.

The fifth variable is to take the sample to a constant surface area. Samples have a variety of surface areas, depending on their composition. Some may be clumped, while others may be very fine particulate. By mixing, the sample is broken apart, increasing the surface area. This can be achieved by mixing within the instrument and/or pre-sonicating the sample. Driving the samples toward constant surface area reduces the average distance an analyte travels to be extracted from the sample. This improves extraction efficiency and reproducibility.

The sixth variable parameter is soil density. The soil density will cause a vast difference in the phase ratio. A highly dense material, such as a sandy soil, occupies a very small volume within the vial, leaving an extremely large headspace. An equal mass of a low density soil, such as top soil, occupies a large volume within the vial, with a comparatively small volume of headspace. If an analyte has a very low partition coefficient, this variation in phase ratio between soil densities becomes extremely important. Therefore, different results for non-polar organics in soil samples can be obtained if phase ratios are not controlled. The addition of the matrix modifying solution brings the samples to a more constant phase ratio. The effect of density of three types of soils with and without a matrix modifying solution is shown as Table 5. Without a matrix modifying solution there is an 8-fold difference in the phase ratio. By adding an equal volume of the matrix modifying solution to each sample, in this case 10ml, only a 2-fold change in the phase ratio occurs between high and low density soil samples.

The last variable which affects soil samples results is the organic content of the sample. Humic materials, such as top soil, tend to be very absorptive for organic compounds, as opposed to sandy soils which are inorganic and tend not to absorb. Comparable amounts of sample containing equal concentrations of analytes would give significantly different results. The way to control this is to improve the extraction ability of the matrix modifying solution with an organic modifier. This increases its solvating strength, removing the volatile organics from the soil itself. Once the anlaytes are in the liquid phase they are easily partitioned into the gas phase.

Figure 4 shows the effects of the soil matrix type on partitioning. The sandy soil shown at the bottom of the figure shows the best response for all analytes. The middle chromatogram is the clay soil, which shows somewhat similar recoveries although not quite as good at the higher molecular weights, such as naphthalene and hexachlorobutadiene. The top soil shows extremely low recoveries across the entire range of analytes due to its absorptive nature. The remaining factor to be established within the matrix modifying solution is to select the appropriate organic modifier. Once selected, the conditions for all sample matrices will be driven to equivalency resulting in reliable data from any sample type.

CONCLUSIONS

There are seven variables which have been identified that affect the partitioning of organic analytes out of soil samples. These variables occur in many combinations which make it difficult to get reliable data for soil samples. Use of a matrix modifying solution combined with heated mixing/sonication can force the conditions of the sample to become equivalent and override the inherent differences of soil samples. This allows analysis of the analytes within the samples to be accomplished successfully, reliably, and with good precision and accuracy. The use of multiple internal standards which act as true field surrogates combined with the matrix modification produces quantitative and reproducible results.

The next step in this research project is to finalize the organic modifier for the matrix modifying solution and to develop a diffused standard for analytes and finalize the field test sampling kit and procedures for its use. GC/MS BFB tuning will be automated using the full evaporation technique. The end result will be a reliable method for collecting and analyzing soil samples, where the sample is handled once in the field and the vial is never opened again. This will prevent loss of analytes through volatilization or addition of impurities from the lab air.

Acknowledgements:

Mike Markolov, BP Research, Cleveland, OH

Tom Herman, Northern Lake Services Laboratory, Cramden, WI

Tom Bellar, USEPA EMSL, Cincinnati, OH

Pedro Flores, TAI, Cincinnati, OH

TABLE 1.

PARTITION COEFFICIENTS FOR CLASSES OF ORGANICS IN WATER AT 50°C

PARAFFINS:	K
PENTANE	.023
HEXANE	.015
HEPTANE	.011

OLEFINS:	
BUTENE-1	.093
PENTENE-1	.068
HEPTENE-1	.030

AROMATICS:	
BENZENE	2.5
TOLUENE	2.1
o-XYLENE	1.3

ALCOHOLS:	K
METHANOL	1670
ETHANOL	1150
n-PROPANOL	770

ALDEHYDES:	
ACETALDEHYDE	99
PROPIONALDEHYDE	63
n-BUTYRALDEHYDE	44

KETONES:	
ACETONE	190
METHYLVINYLKETONE	154
METHYLETHYLKETONE	11

TABLE 2. 7000/7050 SOILS PARAMETERS
Static Equilibration Study

Vial Pressurization:	7 psi
V.I.P.R.:	5 psi
Loop Size:	2 ml
Sample Size:	2g soil/10 ml salt solution (spiked to 600ppb/soil)
Platen Temperature:	85°C
Platen Equilibration:	0 min
Sample Equilibration:	10 min-160 min in 10 min increments
Vial Size:	22.5 ml
Mixer:	OFF
Mix:	OFF
Mix Power:	OFF
Stabilize:	OFF
Pressurize Time:	0.08 min
Pressure Equilibration:	0.05 min
Loop Fill:	0.10 min
Loop Equilibration:	0.05
Inject:	1.0 min
Valve Temperature:	85°C
Line Temperature:	85°C
Injection per vial:	1

TABLE 3.

GC CONDITIONS
Soils VOC Analysis By Headspace Extraction

Carrier Gas:	Helium at 7 ml/min
GC:	Varian 3300
Detector:	Flame Ionization Detector
Column:	J&W DB-624 75m x .53 mm ID x 3.0 udf
Initial Temperature:	35°C; Hold 5 minutes
Rate:	Ramp 3°C/minute
Final Temperature:	180°C; Hold 2 minutes
Injection Temperature:	200°C
Detector Temperature:	230°C

TABLE 4.

REPRODUCIBILITY OF AROMATICS IN WATER

	Without Mixing			With Mixing		
	Mean	SD	RSD	Mean	SD	RSD
Benzene	326	18	5.4	372	5	1.3
Toluene	336	20	5.9	411	4	1.0
Ethylbenzene	353	18	5.2	472	8	1.7
o-Xylene	324	13	4.1	400	7	1.8
Bromobenzene	213	11	5.2	220	5	2.1
1,3-Dichlorobenzene	225	13	5.6	255	5	2.1
1,2,4-Trichlorobenzene	207	9	4.2	225	6	2.5

TABLE 5.

EFFECTS OF MATRIX MODIFICATION/PRESERVATIVE SOLUTION VOLUME ON PHASE RATIO

2g each in a 22.5ml Vial	Soil only Phase Ratio	Soil + Solution Phase Ratio
Topsoil (0.45 gl/ml	4.06	0.56
Clay Soil (1.8g/ml)	19.20	1.03
Sandy Soil (3.0g/ml)	33.00	1.11
	Δ Change = 8x	Δ Change = 2x

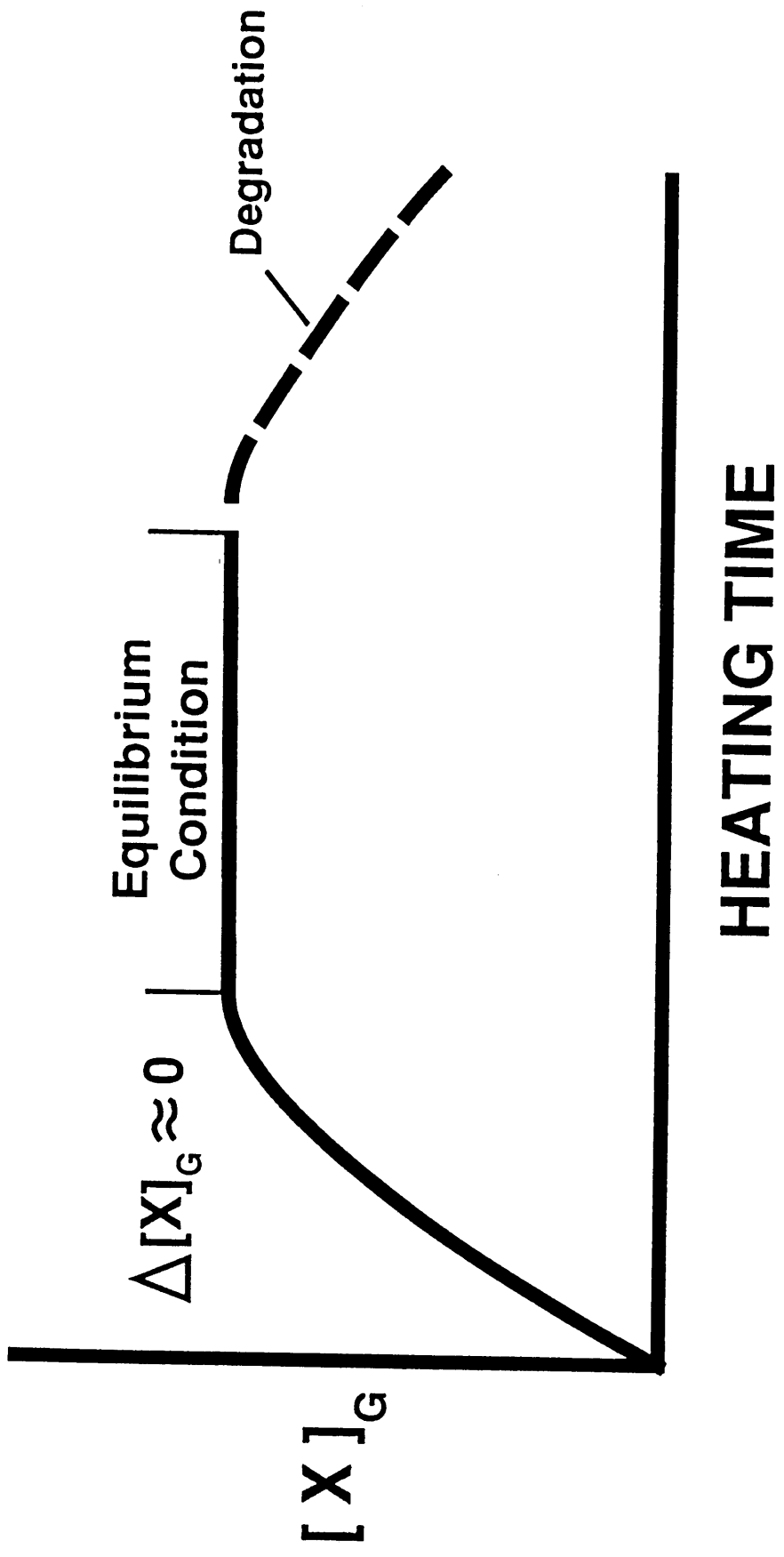

Degradation
Equilibrium Condition
$\Delta[X]_G \approx 0$
$[X]_G$
HEATING TIME

FIGURE 1.

FIGURE 2a.

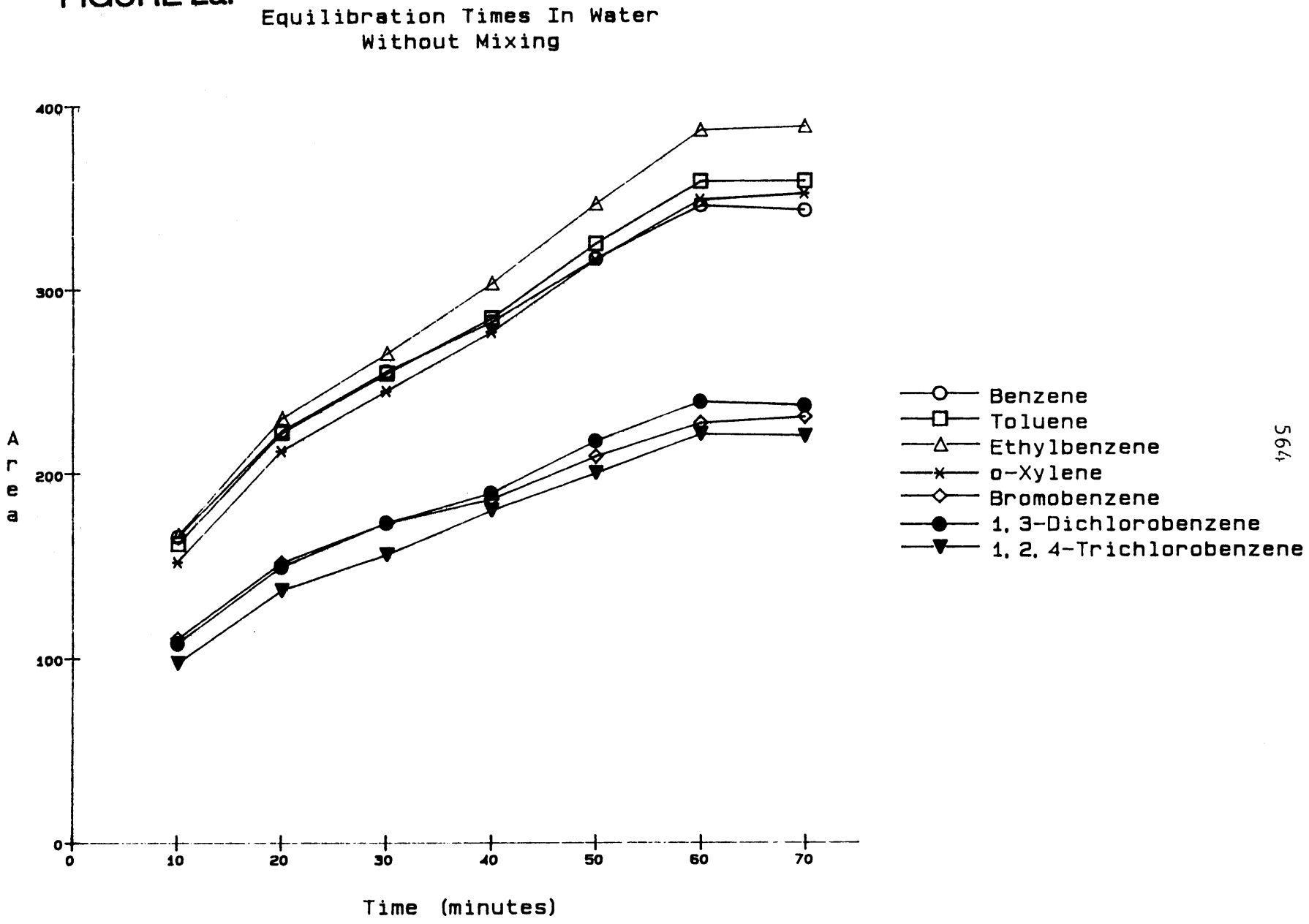

Equilibration Times In Water
Without Mixing
Area
400
300
200
100
0
0
10
20
30
40
50
60
70
Time (minutes)
Benzene
Toluene
Ethylbenzene
o-Xylene
Bromobenzene
1, 3-Dichlorobenzene
1, 2, 4-Trichlorobenzene

FIGURE 2b.

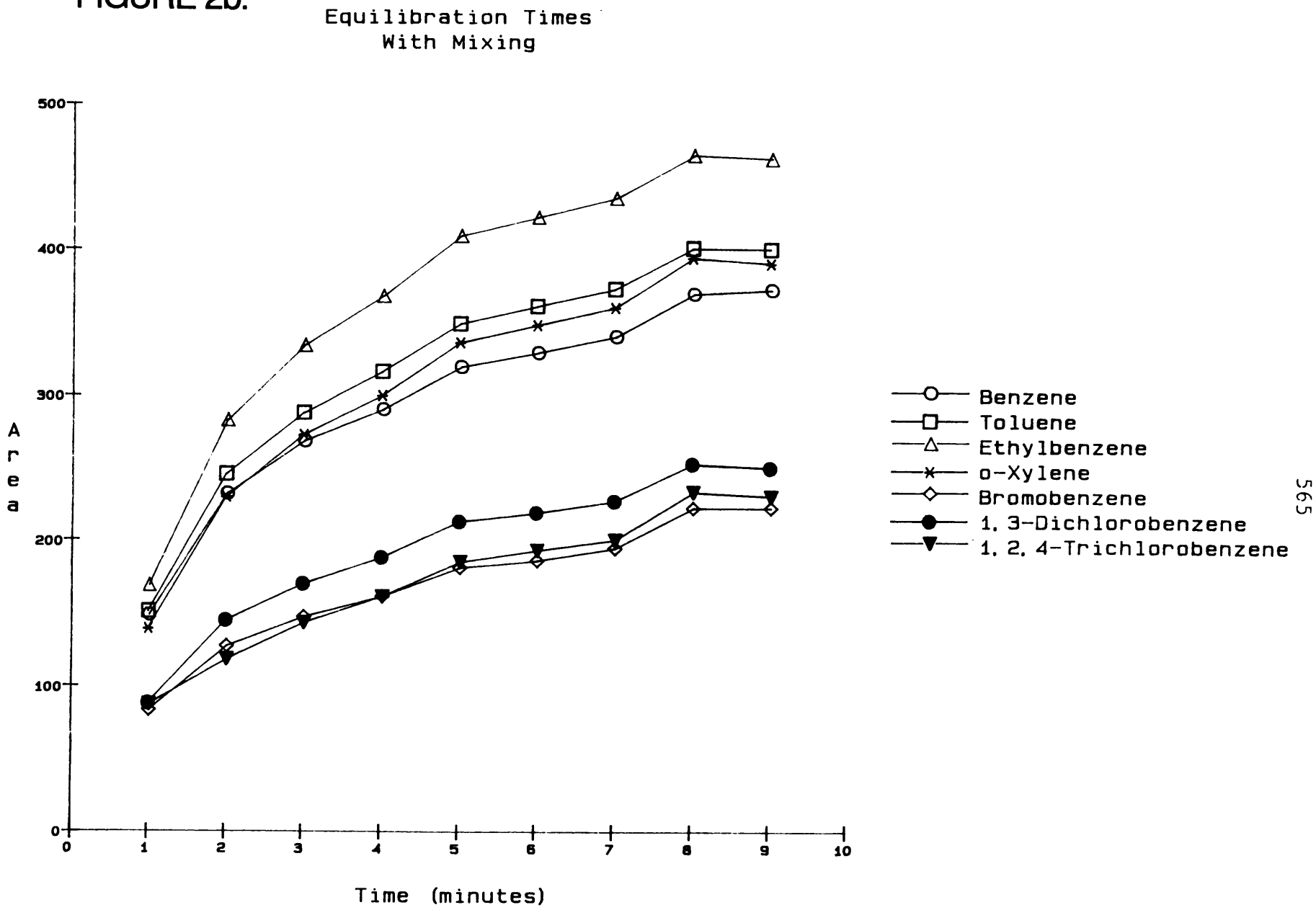

Equilibration Times
With Mixing
500
400
300
200
100
0
Area
0
1
2
3
4
5
6
7
8
9
10
Time (minutes)
Benzene
Toluene
Ethylbenzene
o-Xylene
Bromobenzene
1, 3-Dichlorobenzene
1, 2, 4-Trichlorobenzene

FIGURE 3a.

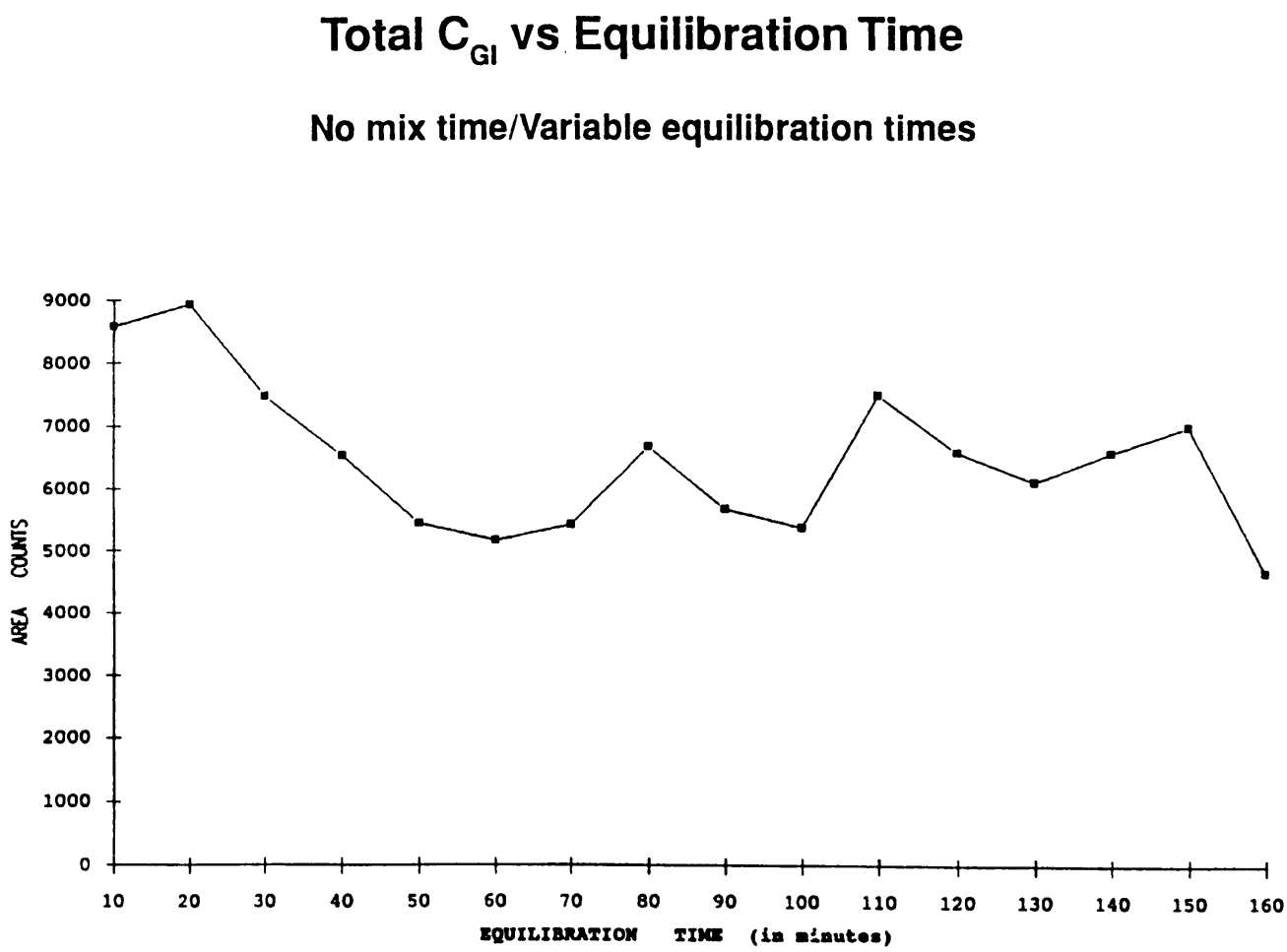
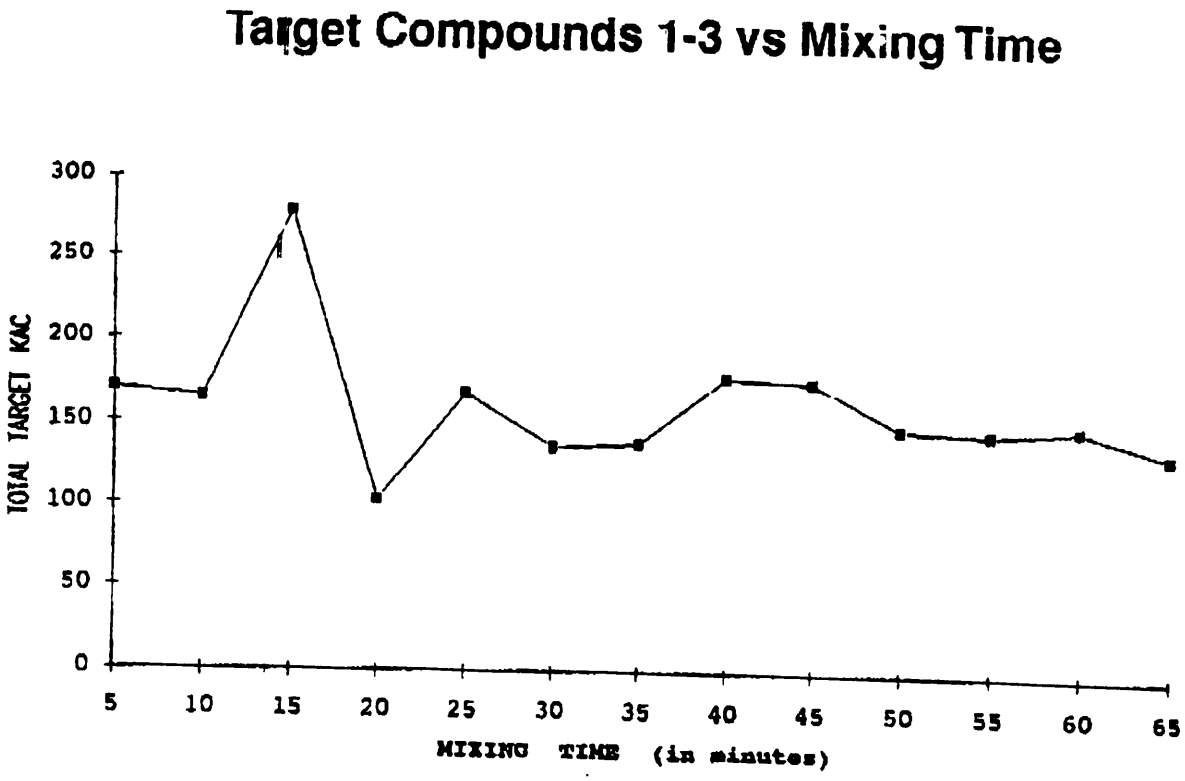

Total C_{GI} vs Equilibration Time
No mix time/Variable equilibration times
AREA COUNTS
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
EQUILIBRATION TIME (in minutes)

FIGURE 3b.


Target Compounds 1-3 vs Mixing Time
TOTAL TARGET KAC
300
250
200
150
100
50
0
5
10
15
20
25
30
35
40
45
50
55
60
65
MIXING TIME (in minutes)

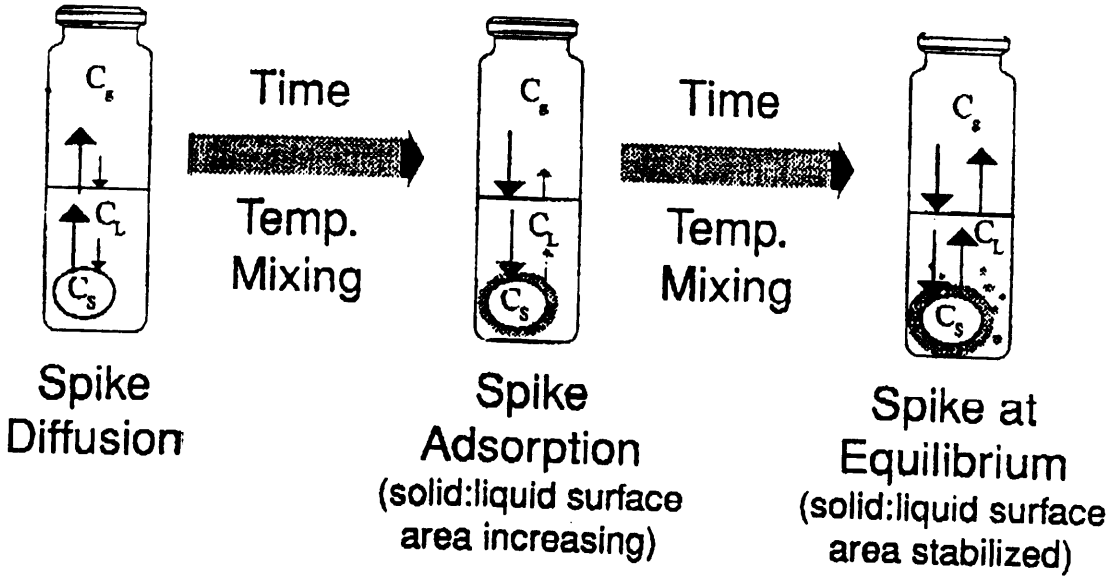
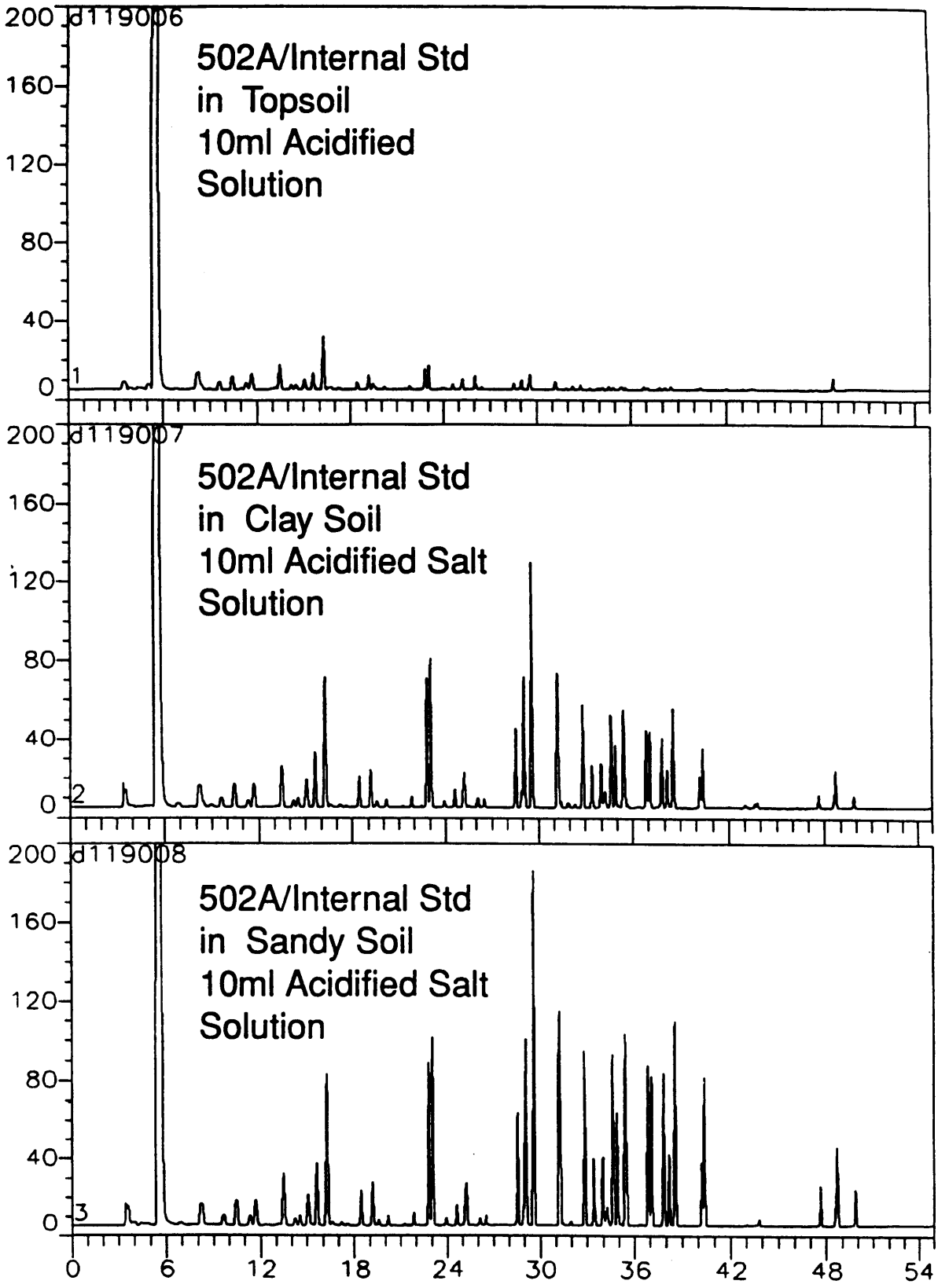

Time
Temp.
Mixing
Time
Temp.
Mixing
Spike
Diffusion
Spike
Adsorption
(solid:liquid surface
area increasing)
Spike at
Equilibrium
(solid:liquid surface
area stabilized)

FIGURE 4. **Effect of Soil Matrix Type Upon Partitioning**



Analysis of Volatile Organic Compounds In Soil Using Static Headspace Extraction

(Preliminary Study 5/92)

Greg O'Neil, Tammy Cappel
Tekmar Company

GC CONDITIONS
Soils VOC Analysis By Headspace Extraction

Carrier Gas:	Helium at 7 ml/min
GC:	Varian 3300
Detector:	Flame Ionization Detector
Column:	J&W DB-624 75m x .53 mm ID x 3.0 udf
Initial Temperature:	35°C; Hold 5 minutes
Rate:	Ramp 3°C/minute
Final Temperature:	180°C; Hold 2 minutes
Injection Temperature:	200°C
Detector Temperature:	230°C

7000/7050 SOILS PARAMETERS
Static Equilibration Study

Vial Pressurization:	7 psi
V.I.P.R.:	5 psi
Loop Size:	2 ml
Sample Size:	2g soil/10 ml salt solution (spiked to 600ppb/soil)
Platen Temperature:	85°C
Platen Equilibration:	0 min
Sample Equilibration:	10 min-160 min in 10 min increments
Vial Size:	22.5 ml
Mixer:	OFF
Mix:	OFF
Mix Power:	OFF
Stabilize:	OFF
Pressurize Time:	0.08 min
Pressure Equilibration:	0.05 min
Loop Fill:	0.10 min
Loop Equilibration:	0.05
Inject:	1.0 min
Valve Temperature:	85°C
Line Temperature:	85°C
Injection per vial:	1

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOIL USING STATIC HEADSPACE EXTRACTION

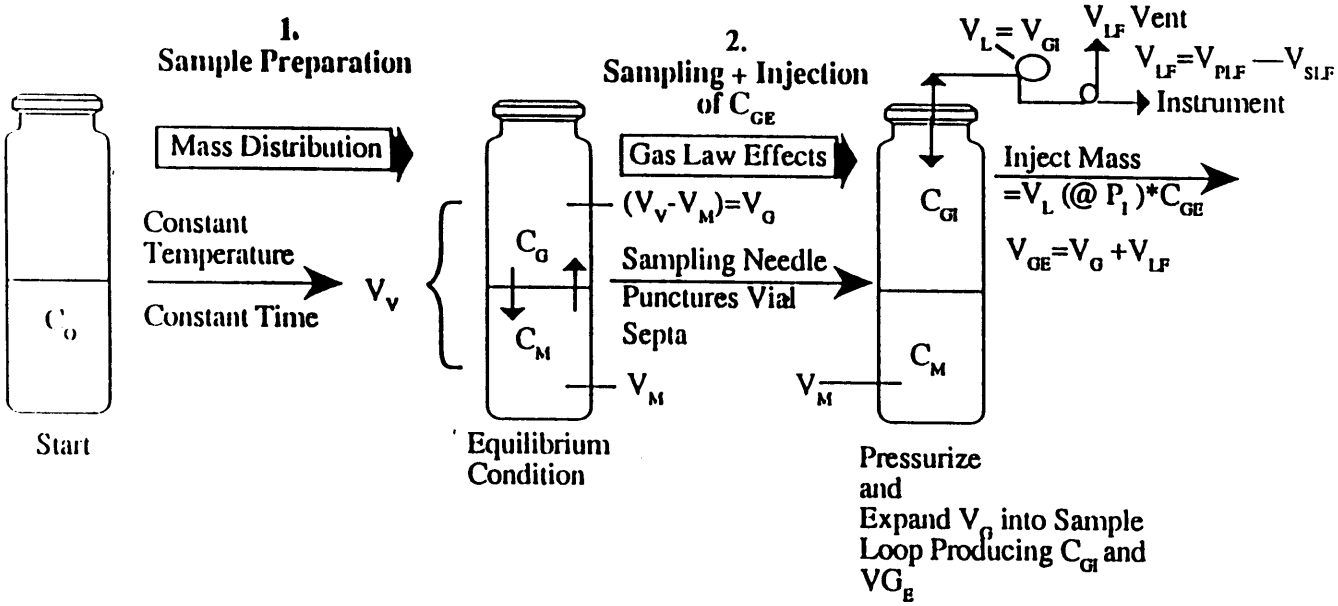
METHOD DEVELOPMENT SCOPE AND APPLICATION

A) Define the range of compounds which may be accurately and reproducibly analyzed from a wide range of soil matrices using static headspace extraction.

B) Define the method detection limits using various headspace extraction parameters as well as separation and detection techniques.

C) Test the method using field sampling procedures and devices.

STATIC HEADSPACE ANALYSIS
QUANTITATION



Tekmar™

5/5/92

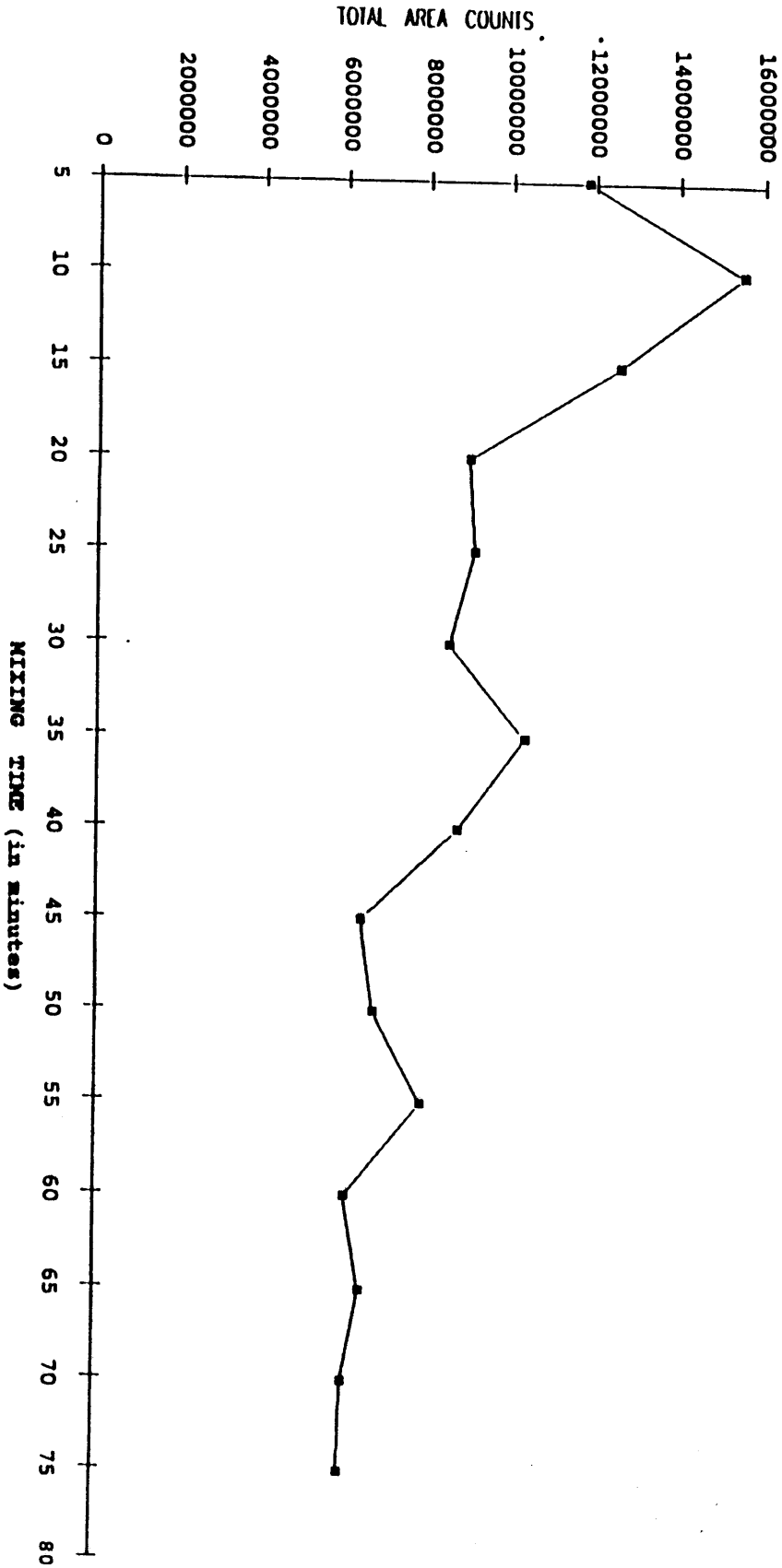

Total C_{GI} vs Mixing Time
NO EQUILIBRATION TIME / VARIABLE MIXING TIMES
TOTAL AREA COUNTS
16000000
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
MIXING TIME (in minutes)

Figure 1

CONCENTRATION CALCULATIONS

SOLUTION SPIKE

C_{LO} = Original concentration of standards in the liquid phase (water or m.m.s.) after spiking.

$$C_{LO} = \frac{\text{NG spiked into the liquid phase}}{V_M} = \frac{\text{NG}}{\text{ML}} = \text{ppb}$$

$$C_{LO} = \frac{\dfrac{\text{(200 NG) (6ul spiked into soil)}}{\text{(ul)}}}{\text{12 ml}} = \frac{\text{1200 NG}}{\text{12 ml}} = 100 \text{ ppb wgt}$$

V_M = Sample Matric Volume (liquids) or $V_M = \dfrac{\text{GMS Sample}}{\text{Density}}$

CONCENTRATION CALCULATIONS

SOLUTION SPIKE

C_{SO} = Original concentration of standards in the solid soil sample after spiking.

$$C_{SO} = \frac{\text{NG spiked into soil}}{\text{GMS Soil}} = \frac{\text{NG}}{\text{GM}} = \text{ppb}$$

$$C_{SO} = \frac{\dfrac{\text{(200 NG) (6ul spiked into soil)}}{\text{(ul)}}}{\text{2 GMS Soil}} = \frac{\text{1200 NG}}{\text{2 GMS}} = 600 \text{ ppb wgt}$$

Determining unknown sample concentrations using full evaporation technique (FET) gas phase response factors (GRF)

1) Determine a known GRF using an FET standard

   a) Inject no more than 10µl standard volume into a 22.5ml vial and then seal vial

   b) Run under FET standard conditions

   c) Note the AC response of the compound to be quantified

   d) Calculate the GRF:

$$GRF = \frac{C_{GE}^{FET}}{AC}$$

Example: 2µl of a 20ppm Parachlorobenzoic acid (in methanol) measured before injection was 15ml. The injection produced a detector response of 5.192 KAC

$$C_{GE}^{FET} = \frac{\text{MASS IN VIAL}}{V_V \; V_{LF}} = \frac{40\ ng}{22.5ml + 15ml} = 1.070ppb = .00107ppm \text{ Parachlorobenzoic acid}$$

$$GRF = \frac{C_{GE}}{KAC} = \frac{.00107ppm}{5.192\ KAC} = .00021\ ^{PPM}/_{KAC}$$

Concentration Calculations
Full Evaporation Technique (FET)

Full Evaporation Technique (FET) provides gas phase response factors, C_{GE}/FET calibration curves as well as target peak retention times for each analyte in the standard.

$C_{GI/FET}$ Concentration of gas phase analytes which are injected into the analytical system

V_V Internal volume of the sealed vial

V_{LF} Volume of gas expanded from the vial during loop fill

$$C_{GI/FET} = \frac{\text{ng analyte injected into vial}}{V_V\text{ml} + V_{LF}\text{ml}} = \frac{\text{ng}}{\text{ml}} = \text{ppb}$$

Example:

$$C_{GI/FET} = \frac{\left(\frac{200\text{ng}}{\mu\text{l}}\right)\left(2\mu\text{l}\right)}{22.5\text{ml} + 3.5\text{ml}} = \frac{400\text{ng}}{26\text{ml}} = 15.4\ \text{ppb}$$

Advantages of Static Headspace Extraction

1) Non polluting extraction method

2) Rugged procedure:

   a) Practical field sampling technique
   b) Not subject to contamination
   c) Wide range of sample concentrations

3) Techniques are available within this method to account for variables in sample matrices while producing both precise and accurate data

4) Potential lower cost/sample through increased capacity and shorter analysis turnaround time

Initial Selection of Analytes, Internal Standards

1) Full evaporation technique was used to produce gas standards of known concentration ($C_{GE/FET}$)

2) Analyte standard – 502.2A

   Internal standard – DBFM, Tuluene-d8, BFB

3) Separation conditions were set to track three target peaks and a non coeluting internalstandard. The values derived for R.T. and R.F. were used as a check standard.

FET Standard Conditions
7000/7050 Parameters

2µl of Standard Injected (200ppm each component)
Producing a $C_{Cl/FET}$ of 15.4ppb

Vial Pressurization:	7 psi
V.I.P.R.:	5 psi
Loop Size:	1 ml
Sample Size:	400ng
Platen Temperature:	85°C
Platen Equilibration:	0 min
Sample Equilibration:	30 min
Vial Size:	22.5 ml
Mixer:	OFF
Mix:	OFF
Mix Power:	OFF
Stabilize:	0.5 min
Pressurize Time:	0.08 min
Pressure Equilibration:	0.05 min
Loop Fill:	0.10 min
Loop Equilibration:	0.05
Inject:	1.0 min
Valve Temperature:	85°C
Line Temperature:	85°C
Injection per vial:	1

7000/7050 SOILS PARAMETERS
Mixing Equilibration Study

Vial Pressurization:	7 psi
V.I.P.R.:	5 psi
Loop Size:	2 ml
Sample Size:	2g soil/10 ml salt solution (spiked to 600ppb/soil)
Platen Temperature:	85°C
Platen Equilibration:	0 min
Sample Equilibration:	0 min
Vial Size:	22.5 ml
Mixer:	ON
*Mix:	5 min-65 min in 5 min increments
Mix Power:	7
Stabilize:	0.5 min
Pressurize Time:	0.08 min
Pressure Equilibration:	0.05 min
Loop Fill:	0.10 min
Loop Equilibration:	0.05
Inject:	1.0 min
Valve Temperature:	85°C
Line Temperature:	85°C
Injection per vial:	1

*M.O.M.Parameter

F.E.T. CHECK STANDARD

PASS = ± 20% OF INITIAL VALUES

	RT	RF
Target 1	10.4	0.16
Target 2	13.4	0.10
Target 3	22.8	0.79
Bromofluoromethane IStd	16.2	1.0

$$RF = \frac{(A_X)\ (C_{IS})}{(A_{IS})\ (C_X)}$$

A_X = Area of Compound

A_{IS} = Area of Internal Standard

C_X = Concentration of Compound

C_{IS} = Concentration of Internal Standard

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOIL USING STATIC HEADSPACE EXTRACTION

PRELIMINARY METHOD OVERVIEW

II. Lab Analysis

Sample information will include site I.D., date, time and temperature when sampled.

A) Trip Blank - (Internal standards in MM/P solutions) to determine transport integrity
- contamination, degradation check, R.T., R.F.
(GC/MS: primary quantitation ions)

B) Field Blank - (Internal standards in MM/P solutions) to determine sampling integrity
- contamination, degradation check, R.T., R.F.
(GC/MS: primary quantitation ions)

C) Dry Weight Sample - Determine sample dry weight and use for sample concentration calculations.

D) Analytical Sample - Run groups of target analytes against appropriate internal standards. Calculate original analyte concentration in sample $\left(\frac{\text{ng} \rightarrow \text{ug Analyte}}{\text{gm Sample}}\right)$

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOIL USING STATIC HEADSPACE EXTRACTION

PRELIMINARY METHOD OVERVIEW

I.Field Sampling

A) Triplicate samples are taken with a soil plug gun and placed into a screw top headspace vial. Two samples are analytical duplicates and the third sample is used for dry weight determination.

B) A matrix modification solution with preservative and internal standards is delivered from a constant volume/zero headspace dispenser into the two analytical duplicates and one field blank. All vials are sealed with screw top septa caps.

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOIL USING STATIC HEADSPACE EXTRACTION

METHOD DEVELOPMENT SCOPE AND APPLICATION

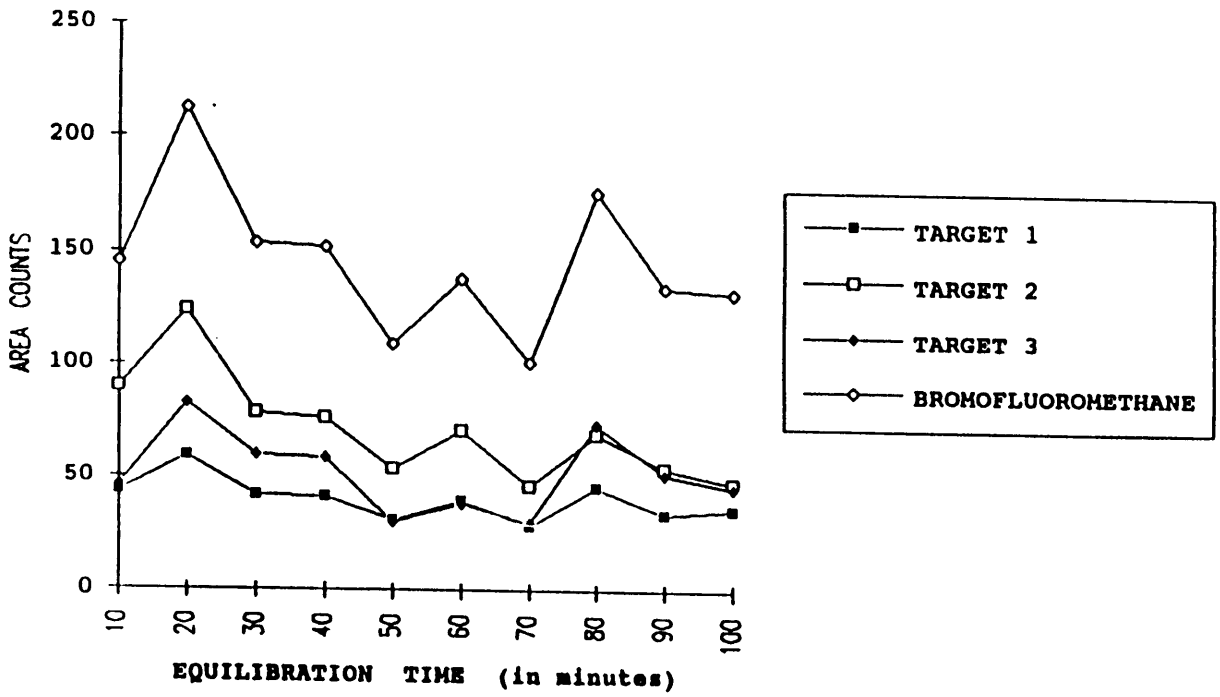
A) Define the range of compounds which may be accurately and reproducibly analyzed from a wide range of soil matrices using static headspace extraction.

B) Define the method detection limits using various headspace extraction parameters as well as separation and detection techniques.

C) Test the method using field sampling procedures and devices.

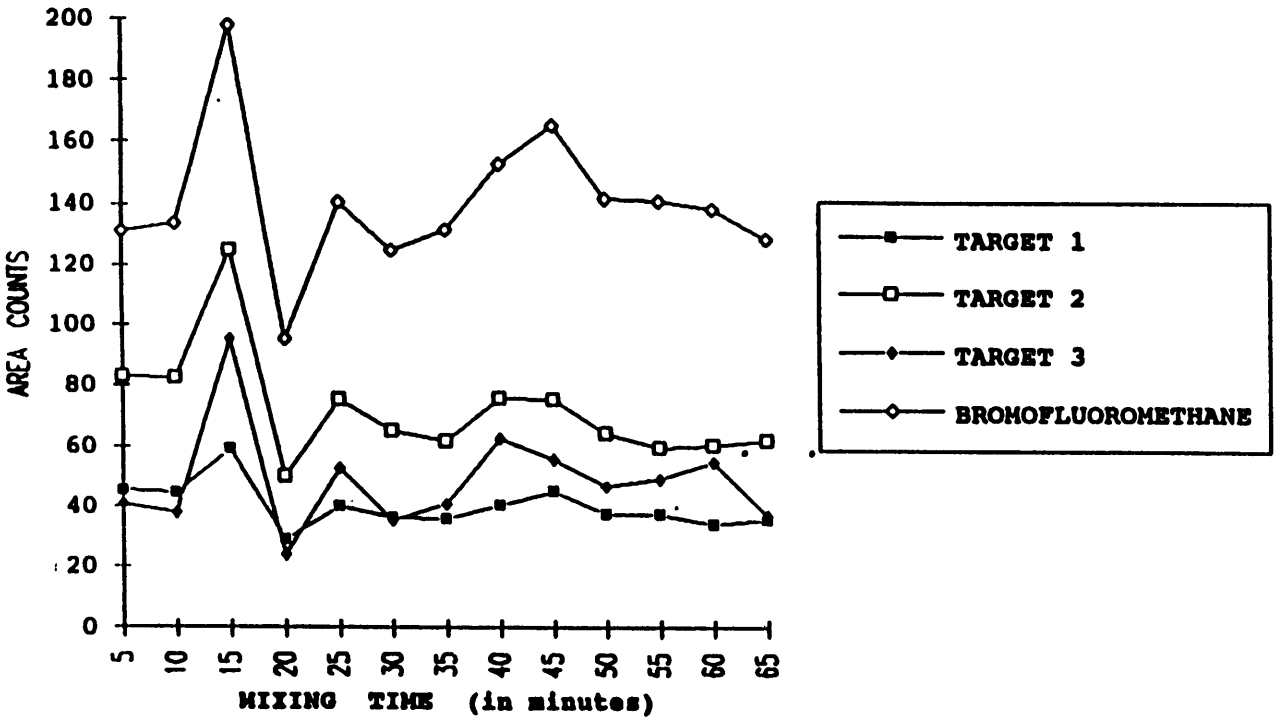
Target C_{GI} vs Equilibration Time

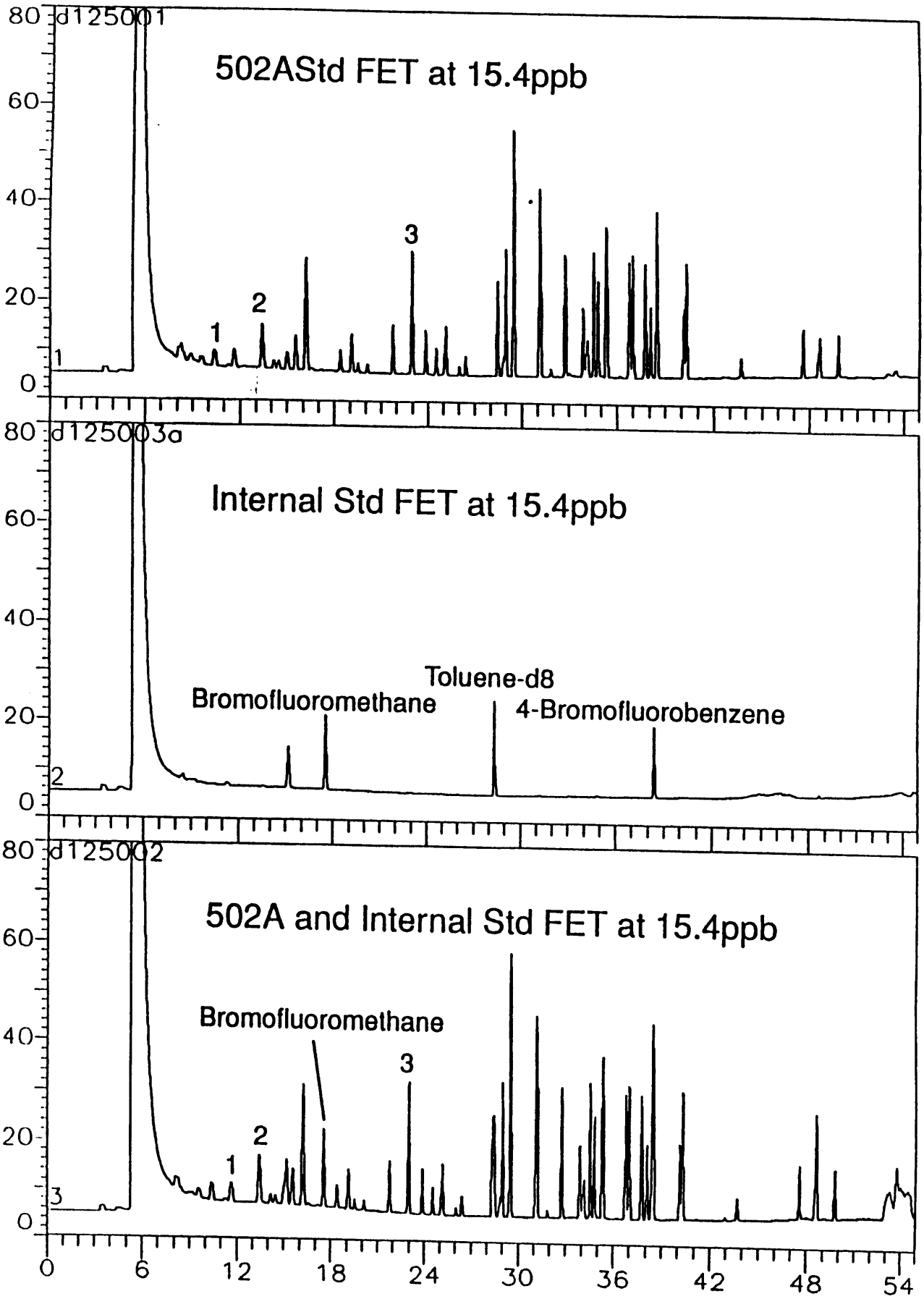
No mixing time/Variable equilibration time



Target CGI vs Mixing Time

No equilibration time/Variable mixing times




d125001
502AStd FET at 15.4ppb
1
2
3
d125003a
Internal Std FET at 15.4ppb
Bromofluoromethane
Toluene-d8
4-Bromofluorobenzene
d125002
502A and Internal Std FET at 15.4ppb
Bromofluoromethane
0
6
12
18
24
30
36
42
48
54

[Blank Page]

MR. TELLIARD: Our next presenter is going to talk about Method 524.2 which is presently undergoing a methods consolidation effort for the agency method for VOAs, and Jean is going to talk about how successful they were at applying the VOA method to the additional list of analytes.

MS. MUNCH: Today, I will be presenting the evaluation of 48 candidate compounds using USEPA Method 524.2. As an introduction, I will give an overview of the current method. [SLIDE 1ONE]

Currently, the method is used for the analysis of 59 volatile organic compounds in water. It isolates those compounds by purge and trap, and then the analytes are separated, identified, and measured using capillary column GC/MS. [SLIDE 2]

The equipment we used for this particular project was a Saturn ion trap system equipped with a purge and trap unit with a moisture control module. We used a 5 ml sample volume and the standard three-stage trap that is already outlined in the method. [SLIDE 3]

We used capillary GC with a 75 meter DB624 megabore column. At the end of the column, we had an open split interface set to split the column effluent at 20:1 before going into the ion trap detector.

The test compounds were selected because they are regulated or have the potential to be regulated. Many of them are on the 1991 drinking water priority list, and many of those are water soluble compounds that are particularly difficult to analyze in a water matrix. [SLIDE 4]

The steps we went through in the evaluation process were first, to create a calibration curve for each potential analyte and assess its linear range. We then looked at the chromatography, because potentially there could be 100-plus analytes in this single method. Additional steps were to evaluate purging efficiencies, calculate method detection limits, and do a time storage study in real environmental samples to see if the sample holding times would be valid for the new analytes, and take a look and see if

there were any potential matrix effects. [SLIDE 5]

The first thing we did in calibrating was to attempt to run a six-point calibration curve for all of the potential analytes. The concentration range was from .2 to 100 parts per billion.

The first part of the calibration step really acted as a screening procedure, because the first thing we found out was that 18 of the original 48 analytes gave no response at 100 parts per billion or less. As we look at this list, there are amines, alcohols, and high boiling compounds. So, it wasn't really a surprise that these didn't work very well. [SLIDE 6]

Therefore, at this very first step, they were eliminated from any further study.

Also during the calibration phase, we observed that 2 analytes had extremely short half-lives in water, propylene oxide and bis-2-chloroethyl sulfide. So, they too were eliminated from any further study. [SLIDE 7]

Finally, you get a look at a partial list of the compounds that we kept for further study. As you can see, there are ketones on this list that are on the drinking water priority list. Also of special interest was methyl-tertiary-butylether. [SLIDE 8]

All of these compounds worked surprisingly well in the initial calibration. They were all linear over at least two orders of magnitude.

1,4-dioxane and vinyl acetate had some non-reproducible data, but we will talk more about them later.

Here is the second page of compounds that were kept for further study. Of special interest on this list is acrylonitrile which is targeted for regulation in Phase V1 B of the Safe Drinking Water Act. [SLIDE 9]

Again, all of these compounds were linear over at least two orders of magnitude and showed generally good response during the calibration.

One observation during the calibration phase of the project was that some of the standards didn't hold up very well in methanol which is the prescribed solvent for Method 524.2. [SLIDE 10]

These particular five analytes were found to need weekly standard

preparation and, of course, to be stored refrigerated. It causes a little bit more work, but it is not really a problem, because we already have a number of analytes in the method that require weekly standard preparation.

The next step after the calibration was to take a look at the chromatography. Even though we were using mass spec, we wanted to minimize the number of co-eluting peaks. When you are talking about possibly close to 100 analytes in a method, you really want to minimize multiple co-eluting peaks. [SLIDE 11]

We had already decided at the beginning of the study that we were going to use the 75 meter column to try to give ourselves a little more room to minimize the number of co-eluting peaks, and we used cryogenics, because it gave better overall performance for the existing analytes and for the analytes that we were attempting to add, although it may not strictly be necessary. [SLIDE 12]

Starting at minus 10 degrees C and using a multi-ramp temperature program that lasted approximately 40 minutes, we ended up with seven pairs of co-eluting peaks and only one case where three analytes eluted together. In each case, the mass spectra of the co-eluting analytes were sufficiently different to allow independent quantitation using unique quantitation masses.

Now that we had verified the chromatography that we were going to use, we wanted to look at purging efficiencies. Although this information isn't strictly needed, it has traditionally been used as a diagnostic tool and as a measure of how rugged the method is for certain classes of analytes. [SLIDE 13]

In order to calculate the purging efficiency, we ran a series of standards at a particular concentration and kept track of the raw peak areas. Then we took the trap out of the purge and trap unit and spiked that same standard directly onto the trap, reinstalled the trap, put reagent water in the purging device and ran the sample as usual.

Then, by dividing the peak area of the purged analyte by the peak area of the standard spiked on the trap, we obtained a direct measure of purging efficiency.

These are the results of the purging efficiency experiments. The range was 1 to 100 percent for the compounds we were looking at. The mean and the median were both around 50 percent, indicating that maybe half of the proposed analytes were really

good candidates, and the other half could have potential problems with precision. [SLIDE 14]

At this point, it was time to do our traditional calculation of method detection limits. For this, we used a series of seven replicates analyzed at the estimated detection limit. Because we already had all the data from the original calibration steps, it was fairly easy to choose a concentration at which to run the MDL study. [SLIDE 15]

The range of the method detection limits was .02 to 1.9 micrograms per liter with a mean of .36 and a median of .18 micrograms per liter. The mean is brought up somewhat by the very few compounds that had MDLs greater than .5 micrograms per liter. [SLIDE 16]

I believe there were only four compounds that had MDLs above .5. When we look at the purging efficiencies of those compounds, their somewhat higher MDLs are directly related to their low purging efficiencies. But for some of the compounds we are talking about, chloroacetonitrile and THF, for example 2 parts per billion isn't bad.

One of the final experiments was to do a time storage study for the 28 analytes remaining in the study in some real environmental matrices. We needed to find out whether or not we could meet the sample holding times allowed in the method and if there would be any problem with the preservation techniques. [SLIDE 17]

Currently, the method allows a 14-day holding time when the samples are acidified, dechlorinated, and stored at 4 degrees C. The matrices we selected for the time storage study were a raw surface water and a chlorinated drinking water preserved and dechlorinated according to the method directions. [SLIDE 18]

Only two analytes showed losses during the 14-day holding time allowed in the method. These were benzyl chloride and acrolein.

This particular slide is from the tap water data, but we saw a similar loss in the raw water data. So, these two compounds were eliminated as candidates for the method. [SLIDE 19]

During the time storage study, we observed two analytes with poor day-to-day precision: vinyl acetate, because, as it turned out, we were actually outside its linear range and for 1,4-dioxane, because it had 1 percent purging efficiency and a response

factor of .001, both of which can cause precision problems. [SLIDE 20]

The last thing we wanted to look at in this evaluation process was to see if there were any apparent matrix effects, and because we had all of the data from the time storage study in raw water and chlorinated tap water, it was kind of easy to do a review of that data. [SLIDE 21]

What I did was to bring together the precision and accuracy data from the preparation day of the matrices from the time storage study. The grand mean of the precision and accuracy were calculated for each matrix from four replicates. We also calculated the grand mean of the precision and accuracy for the calibration standards which were prepared in reagent water.

The mean precision data didn't make it on this slide, but for each individual matrix, the grand mean for all 24 remaining analytes was less than 6 percent. [SLIDE 22]

The accuracy data which you see on the slide, the grand mean for 24 analytes was 97 percent for reagent water, 107 percent for raw water, and 105 percent for tap water.

These data seem to be very comparable, and there is no apparent matrix effect for these analytes.

In summary, we were pleased to find that 24 of the 48 compounds tested appeared to be suitable for inclusion into Method 524.2. The purging efficiencies of the suitable candidates ranged from 5 to 100 percent. The MDLs ranged from .02 to 1.6 parts per billion. There was no apparent matrix effect, and we were able to select chromatographic conditions that minimized the co-elution of analytes. [SLIDE 23]

The next step will be to include these compounds into interlaboratory validation studies so that we can evaluate the ruggedness of the method for each of the analytes and, to compare this single laboratory data with data that we can get from typical multiple laboratories.

Thank you. Questions?

QUESTION AND ANSWER SESSION

MR. STANKO: George Stanko, Shell Development Company.

Method 524.2 has undergone ASTM round robin testing. Were these analytes included in that round robin testing, or will this have to be done in the future?

MS. MUNCH: Most of the preparation for the round robin study was done in advance of these experiments. Some of these compounds of particular interest, for example, the ketones that are on the drinking water priority list and methyl-tertiary-butyl ether were included in the recent round robin study, and we are currently evaluating the data.

Most of that data for the analytes that were included and are common to these studies turned out very well.

MR. STANKO: The other thing is I would like to make a comment that Method 524.2 was being round robin tested as part of the method consolidation effort of the EPA to be used across all matrices, including Clean Water Act effluents and also RCRA groundwater.

The matrices that you studied here are very simple and would have little impact on the purging efficiency. I think if you find when you have more complex matrices like an effluent or some groundwater samples, you are going to find that the purging efficiency changes, and not only does it change, it is quite variable depending on what else is present in the sample.

MS. MUNCH: That may very well be true. As I said, some of these compound have already been in the recent study, and that did not appear to be the case for those particular analytes, but when these go to round robin, all matrices will be checked to see if there is a matrix effect.

This is simply single laboratory data to give us a starting point.

MR. TELLIARD: George, the issue was addressed Tuesday in a methods consolidation meeting, and we feel that probably this data is certainly supportable for ambient water and...perhaps ambient water and drinking water. We don't feel that the data supports any effluents or in-process streams.

Any further inclusion of those into the method would require additional testing.

MR. WESTON: Charlie Weston from ETC.

I have two questions. Number one, could you tell me what the spiking level was for your MDL study, and, number two, did the Saturn ion trap give the option of using a jet separator instead of a straight split?

MS. MUNCH: Okay. The MDL studies were done at different levels tailored to the estimated detection limit that we had calculated from the calibration studies. Most of them were done at .2 or 2 parts per billion.

The Saturn ion trap, at the time we purchased it and, I believe, also at this point in time, does not come with a jet separator option. We have not hand any problem with the open split option, and it has worked very well for us.

MR. WESTON: Okay, thank you.

MR. THOMAS: My name is Roger Thomas. I am from Viar and Company.

I notice with 524.2 that you had the ketones as part of your 48 compounds, the 2-hexanone, the 2-butanone, the 4-methyl-2-pentanone, and the acetone. Historically, those compounds have poor purging efficiency when you switch from the regular 5 ml to the 25 ml purging.

Is there anything in particular that you have done to improve their purging efficiency? And, number two, did the ion trap significantly improve your response factors for those compounds and your low response factor compounds?

MS. MUNCH: You are right. We observed purging efficiencies for the ketones in the neighborhood of 25 to 30 percent, with a 5mL sample. Traditional wisdom would have it that they would not have sufficient precision for the method.

It is my personal opinion that the quality of purge and trap devices over the years has gotten better, so that low purging efficiency compounds may now demonstrate acceptable precision and accuracy.

This is single laboratory data, but we did not take any special pains to obtain this data. We just ran the system as we would normally run it.

The ion trap is a very sensitive system, and its use contributed to the low MDL's achieved for poorly purged analytes.

MR. THOMAS: Okay, thank you.

MR. TELLIARD: Thanks, Jean.

EVALUATION OF FORTY-EIGHT CANDIDATE COMPOUNDS USING U.S. EPA METHOD 524.2

Jean W. Munch

U.S. Environmental Protection Agency
Environmental Monitoring and Systems Laboratory

U.S. EPA METHOD 524.2

- Currently used for the analysis of 59 VOCs in water
- Analytes isolated by purge and trap
- Analytes are separated, identified and measured using capillary column GC/MS

EQUIPMENT

Varian Saturn I Ion Trap System

- Tekmar LSC 2000 Liquid Sample Concentrator with Moisture Control Module, using 5mL sample volume and 3 stage sorbent trap
- Varian 3400 GC with cryogenic capability
- 75m X 0.53 mm DB 624 capillary column
- Open split interface (20:1)
- Ion Trap Detector

SELECTION OF TEST COMPOUNDS

- Compounds were selected for evaluation because they are regulated or have potential to be regulated.
- Many are on the 1991 Drinking Water Priority List or are of special interest to other environmental programs.
- Many are water soluble compounds that are difficult to analyze in a water matrix.

STEPS IN THE EVALUATION PROCESS

- Calibration/Linear Range
- Chromatography
- Purging Efficiencies
- Method Detection Limits
- Time Storage Study in Environmental Matrices
- Matrix Effects

NO RESPONSE AT 100 PPB

chloral hydrate
2-chloroethanol
1,3-dichloro-2-propanol
1,3-dichloropropanone
diethanolamine
1,2:3,4-diepoxybutane
2,4-dinitrotoluene
2,6-dinitrotoluene
isophorone
malononitrile
N-nitrosodimethylamine
N-nitrosodipropylamine
2-picoline
propargyl alcohol
B-propiolactone
n-propylamine
pyridine
o-toluidine

EXTREMELY UNSTABLE IN WATER

Half-life less than 30 minutes

propylene oxide

bis-(2-chloroethyl)sulfide

COMPOUNDS FOR FURTHER STUDY

Carbonyl compounds,alcohols,esters,ethers

acetone
acrolein
2-butanone
1,1-dichloropropanone
1,4-dioxane
diethyl ether
ethyl methacrylate
2-hexanone
methylacrylate
methyl methacrylate
4-methyl-2-pentanone
methyl-t-butyl ether
tetrahydrofuran
vinyl acetate

COMPOUNDS FOR FURTHER STUDY

Nitriles,alkyl halides,sulfur and nitro compounds

acrylonitrile
allyl chloride
benzyl chloride
carbon disulfide
chloroacetonitrile
1-chlorobutane
t-1,4-dichloro-2-butene
hexachloroethane
methacrylonitrile
methyl iodide
nitrobenzene
2-nitropropane
pentachloroethane
propionitrile

COMPOUNDS REQUIRING WEEKLY STANDARD PREPARATION

acrolein
acrylonitrile
iodomethane
methyl acrylate
vinyl acetate

STEPS IN THE EVALUATION PROCESS

- Calibration/Linear Range
- Chromatography
- Purging Efficiencies
- Method Detection Limits
- Time Storage Study in Environmental Matrices
- Matrix Effects

CHROMATOGRAPHY

- 75m X 0.53 mm DB 624 column used in conjunction with cryogenics, resulted in good peak shapes and a minimum of coeluting peaks
- 7 pairs of coeluting peaks; 1 case of three analytes eluting together
- In each case, the mass spectra of coeluting analytes were sufficiently different to allow independent quantitation using a unique quantitation mass for each analyte.

STEPS IN THE EVALUATION PROCESS

- Calibration/Linear Range
- Chromatography
- Purging Efficiencies
- Method Detection Limits
- Time Storage Study in Environmental Matrices
- Matrix Effects

PURGING EFFICIENCIES

- Range 1-100%
- Mean 47%
- Median 44%

STEPS IN THE EVALUATION PROCESS

- Calibration/Linear Range
- Chromatography
- Purging Efficiencies
- Method Detection Limits
- Time Storage Study in Environmental Matrices
- Matrix Effects

METHOD DETECTION LIMITS

- Range 0.02-1.9 ug/L
- Mean 0.36 ug/L
- Median 0.18 ug/L

STEPS IN THE EVALUATION PROCESS

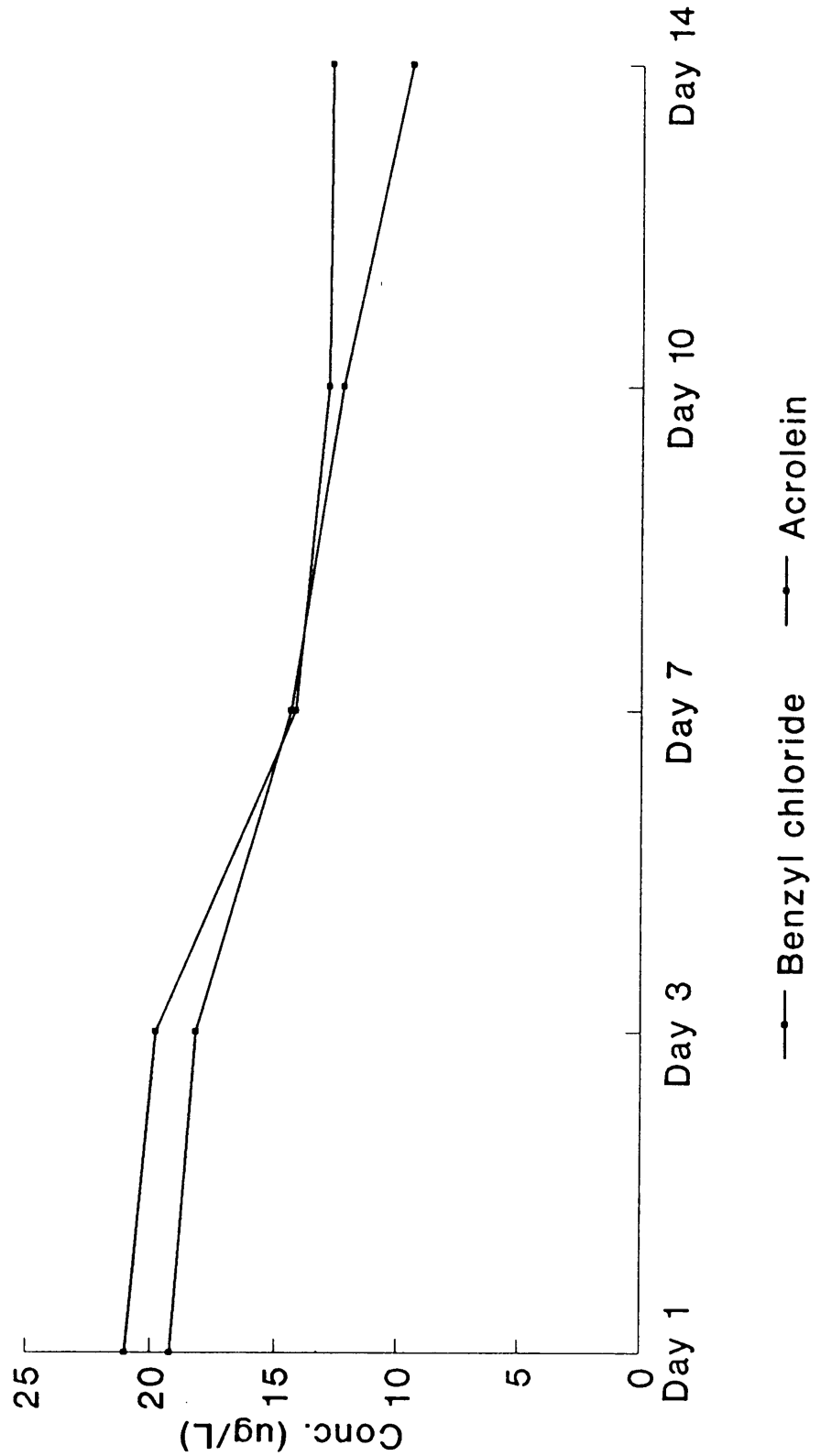
- Calibration/Linear Range
- Chromatography
- Purging Efficiencies
- Method Detection Limits
- Time Storage Study in Environmental Matrices
- Matrix Effects

TIME STORAGE STUDY

- Method 524.2 Rev. 3.0 permits a 14 day holding time, when samples are acidified, dechlorinated (if necessary), and stored at 4° C.

- Matrices selected for this study were
  -Raw surface water (acidified to pH2 with HCl)
  -Chlorinated drinking water (dechlorinated with ascorbic acid, and acidified to pH2 with HCl)

LOSSES OBSERVED IN THE TIME STORAGE STUDY



ADDITIONAL COMPOUNDS ELIMINATED

- Vinyl acetate - insufficient linear range

- 1,4 Dioxane - 1% purging efficiency, response factor = 0.001

STEPS IN THE EVALUATION PROCESS

- Calibration/Linear Range
- Chromatography
- Purging Efficiencies
- Method Detection Limits
- Time Storage Study in Environmental Matrices
- Matrix Effects

COMPARISON OF MEAN ACCURACY IN THREE MATRICES

Reagent	Raw	Tap
97%	107%	105%

Grand mean for 24 analytes

SUMMARY

- 24 of 48 compounds tested, appear to be suitable for inclusion into Method 524.2.
- Purging efficiencies of suitable candidates ranged from 5-100%.
- MDLs ranged from 0.02 - 1.6 ug/L.
- There is no apparent matrix effect.
- Chromatographic conditions selected minimized coelution of analytes.
- The next step is interlaboratory validation.

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MR. TELLIARD: Our next speaker is, I guess, a founding father of this conference. He was here when we opened the meeting, and he has been here ever since.

George Stanko is from Shell Development. He is going to talk a little bit about a project they have developed on TQM which we all know means that there is a threshold quality of misery. But George is going to talk about how he applies it on the contract lab program.

MR. STANKO: I probably won't need the microphone, as usual. I want to dispel a rumor that has been going around. Bill and I are really not twins.

I would like to share with you the results of an environmental analytical contract laboratory study where the quality improvement process was used to correct problems and to improve performance. This is something unusual for me. I usually come here and complain how bad things are. This is the first time I have come here and said how we have improved something.

A blind performance study of 24 environmental contract laboratories was conducted late in 1990, and this study was conducted on a real matrix sample, a bunch of samples, and they were submitted to these commercial labs, a select group, totally blind to them. Dummy engineering firms were set up, and the samples had a real background matrix. We put a little gasoline in it just to make things a little interesting.

The major goal of this PE study was to assess the performance of a select group of laboratories for the analysis of groundwater samples for volatile organics by GC/MS, metals by ICP, and also a select group of general parameters, the BODs, the oil and grease, and pHs.

Results of that study were reported at the Norfolk conference last year.

Results showed that there were really no problems with the ICP metals analyzed by these 24 laboratories. The precision and the accuracy for the ICP metals was outstanding for all participants, and the overall mean recovery for all 11 metals was 97 percent.

Among the individual metals, the mean of all laboratories ranged from 89

percent to 107 percent, and with such good precision, no corrective action was really needed for any ICP metals analyses.

Most of the labs that were included in the study performed well for the volatile organics by GC/MS, but there were some problems noted at two particular laboratories. Both laboratories did not find approximately half of the analytes that were spiked in the samples. These would be considered false negatives, and we consider false negatives important.

The problem was such that we contacted the labs by phone, provided them the necessary information they needed to go back to their raw data, and to search out what we identified as the root cause for their poor performance.

One of the labs quickly responded after they had reviewed their raw data and identified the problem that the sample had been diluted on the basis of their sacrificial lamb. They normally screen all samples with a GC/FID technique, and because we put a little gasoline in these samples, they saw the humpogram, and they calculated a dilution factor based on the humpogram and totally ignored what was totally in the samples.

They were the only laboratory out of 24 that found it necessary to dilute samples.

That identifies the root cause, and the corrective action, the samples should not be diluted unless it is absolutely necessary, and if it is necessary to dilute samples, the quantification levels should be adjusted according to the dilution factor.

We also had some concerns about what dilution might do to samples. There is very little information in the literature to indicate what that might do to analytical variability.

What we did internally in Shell is to devise a study to measure the impact of diluting samples for GC/MS analysis using the purge and trap technique. These are the particular analytes that were selected for the study, and here again, you have seen these before, and MTBE is one of them.

That is one we heard from a previous speaker, and there is an ether included in there. And these were some of the analytes that were originally spiked

blindly into the sample.

Special care was taken with the samples, and no other samples were run on the instrument during the time of this study. The spike levels are indicated at the bottom of the slide.

To reduce all the variability we could in this study, we used one particular analyst from start to finish.

These are the tabulated data for the study that we did on the dilution. Across the top, the compound concentration, and we show on the slide the mean recovery as well as the standard deviation.

This is the result of eight particular runs. Why not seven? Why not ten? For some reason, we chose eight runs.

The last sample which is the diluted 40 part per billion sample had a nominal 2 parts per billion of each of the analytes. For the statisticians who are still up in the audience, these are the corresponding coefficients of variations in large enough numbers so everyone can read.

We also had our statistician look at each individual analyte and compound, and we did some additional figures that appear in the paper. After this talk is concluded, I have approximately 100 copies of the paper available, so you can pick them up when that occurs.

The results for the 5, 10, 20, and 40 part per billion samples and the spiked samples showed purge and trap method has the capability to measure concentration of the eight selected analytes with good precision and accuracy in the distilled water matrix. The coefficient of variation for all concentrations and analytes were less than 10 percent, with toluene being the only exception.

Based on the observed CVs for this study, one would conclude that the method is quite capable of measuring the concentrations of these analytes down to the 5 part per billion level, and the analytical variability is relatively constant over a range and under the ideal conditions of this study.

I often told Bill Telliard it would be a cold day in Norfolk before he would ever hear me say that. I think today qualifies.

MR. TELLIARD: Is a cold day, right.

MR. STANKO: We observed in the last two columns of the previous slide the estimated mean standard deviation shown for the diluted samples from table 1. The actual diluted sample analytes contained only the 2 parts per billion levels of the analytes. The corresponding coefficient of variation shown in table 2 are also on the same basis.

Comparison of the means for the 40 part per billion spiked sample and the diluted sample for each of the analytes revealed that in every instance, the mean from the diluted sample were biased higher. Comparison of the estimated standard deviations also showed a similar bias with toluene being the only exception.

Since the spiked and the diluted samples should be compared for each compound, the statistician told me this is a paired comparison. A two-tailed sign test can be performed to assess the probability of observing eight out of eight higher means and seven out of eight higher standard deviations purely by chance.

The test results indicated that the chance probability or the p value for the means is less than .01 for the standard deviations and less than .05...or.01 for the means and .05 for the standard deviations. Thus, we concluded that diluting of samples prior to analysis resulted in less precise and accurate results.

The reason for this less precise and accurate results is quite simple. In the case of the 40 part per billion spiked sample, all the concentration estimates were calculated from response levels that were near the center of the calibration curve.

The uncertainty and the inaccuracy associated with establishing the location of the calibration curve are at a minimum near the center and increases considerably at the two extremes. The response level for the diluted sample which was a nominal 2 parts per billion was close to the one extreme or 1 part per billion standard.

There is another important consideration associated with the dilution of samples. In the above study, all of the concentration levels were designed to be within the calibration range.

For real samples or unknown samples, one never knows what the concentrations of these materials are, and in the case of lab number 1, they diluted the

sample and diluted the concentrations of the analytes below the detection limit.

In the second laboratory that had problems with organic volatiles by GC/MS, it was more complicated. The first response we got from the laboratory said that they had reviewed all their raw data, and they had concluded that their reason for missing more than half of the analytes that were spiked into these samples was that they missed the holding time by two days.

I had a little difficult time accepting that as the root cause for their poor performance. They assured me that that was their root cause, and now they are back in analytical control, would I please send them another sample.

With great delight, I sent them another sample and let them fall flat on their face.

Following their second poor performance, because the lab was deemed to be essential to certain operations, we opted to send two analytical chemists to the location to work with the lab for two days to establish what the root cause for their poor performance was and to get it corrected.

In this particular case, there wasn't a root cause. There were 13 root causes, and I will not go through the list. I will only zero in on one.

They were using a muffle furnace to clean their syringes, and when you check the calibration of the syringes, that can throw you off by 1 ml. In the 5 ml sample, that could introduce 20 percent error before they do anything else wrong.

The two Shell analysts worked with the laboratory to correct each individual root cause here to a point when they finally left this laboratory, the laboratory could at least get the correct answers on the standards that were prepared by our people.

The laboratory also agreed to analyze whole volume samples that are commercially available from ERA and to provide Shell with the data so that we could be assured that they were in analytical control at that time and for the next year.

I can report that the laboratory has performed well, and there have only been a few minor problems that they have had using these ERA standards.

The results for the blind study for the general parameters was rather disappointing, for those of you who recall, particularly the oil and grease, pH, and things

like that. In general, the performance was so poor at more than half of the labs that we didn't know exactly how to address this on a one-on-one situation.

Instead, what we thought we would do is propose a voluntary program where Shell would pay for whole volume samples from ERA that would be sent to the labs three times every other month, and the laboratory would analyze the samples at their expense and share the data with Shell and ERA so the data could be statistically analyzed.

All 24 labs agreed to participate in the voluntary program, and their response really indicated that laboratories are concerned with data quality and do try to improve performance. They are also willing to be active participants in programs that should lead to improved performance, and it also demonstrates the use of the quality improvement process where the laboratory and the laboratory customer work together to achieve some mutually agreed upon goal. In this case, it was improved performance.

The performance from the initial blind study which I reported on here last year was used as the benchmark for the voluntary program. The results from the initial blind study for the three whole volume samples were statistically analyzed, and the data were plotted in a number of ways.

The number of outliers for all these data is shown in the next slide. The data were further summarized with outliers removed into the next table. This table compares the results from the blind study or, as we call it, before, to the after which was the voluntary program. It also included on this slide, it shows the average recovery from all laboratories and the standard deviations for the means.

The question, was there a significant reduction in the variability, was a yes for all parameters, and the corresponding p values are shown in the final column and were included in this table along with a definition of what p stands for on the bottom. I don't want to explain it. For the benefit of the statisticians, that is how we derived the p values.

There are a number of ways to plot this data, and here again, I think a picture is worth a thousand words. The statistician initially did it for me, and she says which format do you like. I said I like all three formats, and will show you them.

This particular format is called the box plot with whiskers. Essentially, what is in the box is 50 percent of the observations are within a box. The line that goes through the box identifies the median value, and the whiskers identify the 25 percent above and below the boxes. This is for BOD.

If you compare the two blue boxes on the left which don't show that well to the three red boxes, you can see that there is an improvement in the mean recovery for BOD, and the boxes get smaller which is an indication of improved precision.

This is a similar plot for COD, and it is quite dramatic. This is the difference for COD, and here again, you look at the size of the boxes and the size of the whiskers, and that is an indication of improved precision as well as accuracy.

In this case, we have poorer accuracy but closer to 100 percent, or lower accuracy, I would say, but the precision was a very good improvement.

This is my old friend, oil and grease, which I was really concerned about the last time. If you look at the size of the boxes and the size of the whiskers before, the left two, compared with the three on the right, you can see that we are in analytical control, and there was a tremendous improvement in both precision and accuracy.

This is for pH, and I would like to have you remember those four dots on the bottom in the last column. That was the last performance evaluation sample. I will get back to that, but just remember where they are.

This is another format that the statistician came up with, and this actually plots each data point for each lab for every observation. We calculated the 95 percent confidence interval for the before or the blue color and for the red or the after, three samples.

You can see in this case the 95 percent confidence interval shrinks considerably, and, more importantly, the mean recovery goes from about 65 percent all the way up to about 95 percent. This is for BOD.

This is the corresponding format for the COD recovery, and here again, it is the same typical story. It is taking that same data that I showed in that table and showing you in different formats, and each format tells you a little bit something different.

This is TOC, and this is my old friend, oil and grease. You can see right now where I think the oil and grease recoveries and precision at these laboratories is quite acceptable, and now Bill Telliard wants to screw it up by changing the solvent on me.

This is the similar plot for the pH values. If you look...I told you to look at those dots on that previous format. This is what we term in East Texas as backsliding.

And for the real pure statistician in the group, I just had to show you histograms with curves superimposed over them. The top of the chart, the red, is the before situation or the blind study that I reported on last year, and the bottom or the blue is the result from the performance evaluation follow-up where we demonstrate the improved performance.

In this case, the top doesn't even look like a distribution, and now the bottom is starting to look like a normal curve. That is for BOD.

This is for COD. This is for TOC. Look how tight that thing gets, and here again, just like I say, it is the same data presented in different formats. Each format gives you a little different view of what you really accomplished.

And here is oil and grease. It is starting to look like a normal distribution.

MR. TELLIARD: Yeah, we are going to fix that, George.

MR. STANKO: This is the particular format that I like to show our backsliding. You see those four guys on the left? It is the same point, but here again, it points out something just a little differently.

The examples presented in this paper demonstrate the us of the quality improvement process to determine the root cause for analytical problems and the nature of the corrective action that may be required. In some instances, the root causes may be difficult to establish and require thorough on-site investigations and assistance, but root causes can be identified, and proper corrective action can be taken.

The follow-up investigation to assess the effects of sample dilution revealed that there are two important considerations associated with the dilution of samples. For real samples, the possibility of false negative observations is an important consideration.

The study also revealed that the dilution of samples down to the detection

limit or away from the middle of the portion of the calibration curve may result in less precise and accurate results, and these are beyond the control of the analyst. There is nothing he can do about it.

Based on the two problems that can result from the dilution of samples for organic volatiles by GC/MS purge and trap, it is recommended that samples should not be diluted unless it is absolutely necessary, and when dilution does occur, one should bump up the detection limit or quantification limit to reflect the degree that the sample was diluted.

For the voluntary and cooperative program for the general parameters, statistical analysis followed by innovative ways to depict the statistical information resulted in a clear understanding of what had been achieved through the quality improvement process. The bottom line is that there was considerable improvement for all general parameters with few exceptions.

The willingness on the part of laboratories to improve their performance, to participate in voluntary and cooperative programs with well-defined goals should be noted. The work presented also illustrates the importance of good communications between contract laboratories and their customers for mutual benefit.

I would like to give recognition to Lesa Rice-Jackson who is a co-author of this paper. She was also the individual involved in going to the laboratory, and she also was responsible for conducting the dilution study.

Joyce Wellman is my favorite statistician at the moment. She is a co-author, and she did all the analysis and plotting of the data in the different formats.

Ron Claybon is an analyst. He ran the GC/MS dilution study. He was also the analyst that went to the laboratory that had the particular bunch of problems.

And Lillian Thompson is my secretary who prepared the slides for the talk.

Thank you. Any questions?

QUESTION AND ANSWER SESSION

MR. MCCARTY: Harry McCarty from Viar and Company.

George, I want to thank you, too, for coming and saying something nice about something Bill Telliard did.

I am concerned, though, because in October of last year at the IATO meeting in Denver, I saw a presentation by Mark Carter, and about two-thirds of the way through, Mark had not identified the client for whom he was doing it, but it became very apparent it was the same round robin study.

At that point, he let on some of the details of how the study was done.

The problem I see in what you have presented here is that the base problem in this whole study was that you never or not you but the dummy company that Mark set up with dummy letterhead and checks, et cetera, never specified what they wanted the labs to do beyond I need volatiles, I need metals.

As Mark explained the story, he bought what the lab offered. Of the 24 labs, a significant portion, probably on the order of half, had a customer service type person who said well, why do you want volatiles? Oh, it is for NPDES monitoring or it is for groundwater monitoring? And talked whoever was on the phone through the selections, the choices, the menu, if you will, of what they could get.

Other laboratories said sure, send us the sample. Apparently, the labs were asked to provide shipping containers. Some of them came in cardboard boxes wrapped in tissue paper and were subsequently broken. There was a wide range of service that was offered.

The other problem is that, apparently, there was no specification whatsoever of deliverables as to what the client expected to get.

Not that your quality improvement process didn't help, but I think the root cause of the problems is you didn't ask for anything very particular in this study. When people know you want 524.2 or 624 or 1624 or any one of a number of other methods, they either do that, or they say you do it, and then you deal with the fact well, they really ran 8260 not 624 or something like that, and you go back and you can deal with those

kinds of problems.

But when you don't tell them what you want, it is kind of tough to beat on the labs for giving you what they felt like sending out that week if you didn't think to ask.

I am not exonerating the labs for not being good client relations type people, but I think a lot of the problems that you talked about last year and a lot of the root causes you are talking about here may be related to the fact that you didn't ask for something in particular.

MR. STANKO: The response to that is, first, Shell has never identified the public domain who had done the work, and we choose not to.

MR. MCCARTY: Oh, no, I am not asking that. I am just saying Mark didn't identify you in his presentation.

MR. STANKO: Okay. Shell has never identified who actually did this study for us.

The situation was that the study was set up to mimic a filling station that had leaking storage tanks. The engineering firm who contacted the laboratories told them or more than implied that this was a cleanup operation around a filling station for a client. That is why we spiked in gasoline in the samples. Any laboratory has probably run a lot of gasoline samples, because this happens quite often.

The other thing in defense of what we did, we think what we did was defined well enough, because we had no problems with the ICP metals.

We had very few problems with the GC/MS for volatiles. There was only two laboratories, and if you look at the root causes, that had nothing to do with who we talked to at the lab. These were laboratory problems associated with running the methodology itself and nothing with defining what was required for the program.

When it comes to the general parameters, the general parameters have been run for the last 20 or so years, and no one thought we ever had problems with things like BOD and COD and pH and our friend oil and grease. Anybody in the petroleum refining industry lives and dies with oil and grease. We didn't know the study was going to turn out that poorly.

Here again, I don't think there was anything we could have said to the labs in the way of being more specific of what our data quality objectives were to improve their performance. I think what we got is what you would get on every-day samples, and this is how it is done every day when engineering firms do work for Shell.

I wanted to assess the data that we have to look at and interpret at times, and which is very difficult, under realistic conditions. We think that the study that I reported on last year was conducted in a realistic fashion to really represent what we have to go through on a daily basis.

MR. MCCARTY: I won't argue that some aspects of it weren't realistic. My concern is that if your engineering firms that are actually doing work for you aren't specifying or knowing what methods they expect to get back, whether it be a gasoline, you know, distribution system that has got to use an underground storage tank type method from RCRA or a compliance monitoring method for Clean Water Act, if the engineering firms don't know that, then that is clearly a problem, because if you go in and tell somebody what you want, you have at least got a better shot, from my point of view, of getting what you are intending.

MR. STANKO: Most engineering firms don't know to ask for method 8240 or 8260 when they are looking for volatiles. They tell the lab they are interested in volatile organics for a cleanup operation at a Shell filling station someplace.

That is the best you are going to get from the engineering firms. Not all of them. Some of them are more knowledgeable than others, but that is the real situation that you face.

I am looking at it from the lab point of view. If somebody says this is a groundwater sample associated with a cleanup site, that clearly identifies this as RCRA, and there should be no ambiguity about whether you are using Method 524.2, 624, 1624, or 8240, or 8260. This is clearly RCRA.

MR. MCCARTY: I would argue...

MR. STANKO: You are not putting the responsibility on the laboratory.

MR. TELLIARD: Excuse me.

MR. MCCARTY: Yes, I am not going to belabor the point.

MR. TELLIARD: Time is precious here. We are not going to belabor the point, but let's point out the fact that, Harry, you just reviewed a whole bunch of documents from New Jersey all of which were sent in for NPDES, and they all ran SW846 methods which is against the law. Okay?

MR. MCCARTY: Yes.

MR. TELLIARD: And we told them they were water samples, guys. Now, this is not the cutting edge of science. This is called economics, outside of the scope of this conference. Thank you very much.

Moving on.

MR. STANKO: Marlene?

MR. TELLIARD: Hi.

MS. MOORE: I don't know if I can follow this. I am Marlene Moore with Advanced Systems.

MR. TELLIARD: Hi.

MS. MOORE: George, I know that some of the earlier studies that one of the things we thought of is that since these samples originally were blinds, I assume that the WPs and the 02, 03, 04 were knowns to the labs? They knew that these were essentially performance evaluations of some type?

MR. STANKO: They were known, but they were whole volume samples. We did not choose to go with concentrates.

So, the only difference between the whole volume samples and the blind samples is the blind samples had a little clay and dirt and a little gasoline thrown in it. These samples were still water with the same type of material spiked in. That is the only difference.

The laboratories did know they were performance evaluation samples, and there is always some possibility that they put their best people on it.

MS. MOORE: That is what I am concerned about, of course. One of the things is when a laboratory knows you are paying attention to it and that a particular client is paying attention to it, it will do very good work for a short period of time.

I am wondering if we can look forward to another blind survey next year at

this conference with some more statistics.

MR. STANKO: We feel that the blind performance evaluation studies conducted the way we have done them is the most effective way to assess what the laboratories that you are using for routine analysis are doing. That is the only way you can assess their performance.

MS. MOORE: Should we look for some more next year?

MR. STANKO: I hope so.

I would like to make one comment and one pitch. We have heard a lot about solid phase extractors and immunoassay, the leading edge. I really wish EPA would promulgate a paper method for pH. Narrow range pH paper is still the best way to measure pH, and I have no idea why we can't get it on the books.

MR. TELLIARD: Thank you. Thanks, George. Thanks so much.

THE QUALITY IMPROVEMENT PROCESS AND ENVIRONMENTAL ANALYTICAL CONTRACT LABORATORIES

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ABSTRACT

A performance evaluation (PE) study of environmental analytical contract laboratories used by Shell was conducted late in 1990 and the results from the study were reported at the "14th Annual EPA Conference on Analysis of Pollutants in the Environment" on May 9, 1991. The major goal of the PE study was to assess the performance of a select group of laboratories for the analysis of groundwater samples for volatile organics by GC/MS, metals by ICP, and a limited number of general parameters. Results from the PE study revealed no problems with ICP metals analyses by any of the 24 laboratories. Problems were noted at two laboratories for the analysis of volatile organics by GC/MS and performances for general parameters such as oil and grease, pH, BOD, etc. were disappointing. Results from the PE study were shared with the laboratories to assess their performances and to initiate corrective action. Using the quality improvement process, the root causes for the problems at the two laboratories with volatiles analysis by GC/MS were established and corrective action was taken. The quality improvement process was also followed to develop a voluntary and cooperative program with all 24 laboratories to improve performance for the five general parameters. The results from the cooperative program showed dramatic improvement in precision for most parameters and improvements in accuracy for some parameters. Details for the resolution of analytical problems using the quality improvement process are presented in the paper.

THE QUALITY IMPROVEMENT PROCESS AND ENVIRONMENTAL ANALYTICAL CONTRACT LABORATORIES

INTRODUCTION

A blind performance evaluation study of 24 environmental analytical contract laboratories was conducted in late 1990. The study was conducted with real matrix samples and the samples were submitted to the commercial laboratories without identifying them as performance evaluation samples. The major goal of the PE study was to assess the performance of a select group of laboratories for the analysis of groundwater samples for volatile organics by GC/MS, metals by ICP, and a limited number of general parameters. Results from the study were reported at the "14TH Annual EPA Conference on Analysis of Pollutants in the Environment" on May 9, 1991.[1]

Results from the PE study revealed that there were no problems with ICP metals analyses by any of the 24 laboratories. The precision and accuracy for the ICP metals was outstanding for all participating laboratories. The overall mean recovery for all eleven metals was 97%. Among the individual metals, the means for all laboratories ranged from 89% to 107%. With such good performance, it was not necessary to take action to improve performance at these laboratories for metals analysis by ICP.

Most of the laboratories included in the study performed well for the volatile organics by GC/MS, but some problems were noted at two laboratories. Both laboratories did not find a number of the target analytes in the blind samples. These would be considered false negative observations. The problem was serious enough to require immediate corrective action. The laboratories were contacted by phone and told of their poor performance. They were also provided with the necessary sample identification and the true values for the blind samples.

Volatile Organics - First Laboratory

One of the laboratories quickly established the root cause for their poor performance. Their review of the raw data revealed that the samples were screened using a GC/FID method and a decision was made to dilute the samples prior to GC/MS analysis. The laboratory routinely screens samples and dilutes them to reduce instrument contamination and associated analytical problems. The blind samples used for the study were prepared in such a way to have a natural background that was picked up by the GC/FID screening procedure; however, these samples should not have been diluted. This was the only laboratory that had diluted the samples prior to analysis. In this instance, the laboratory had diluted the samples to a point where the analyte concentration was near detection limits and in some instances below detection limits. The root cause for the false negative observations was that the laboratory diluted sample to a level where approximately half of the analytes were below their detection limit.

Dilution Study

The problem with dilution of samples for volatile organics by GC/MS was of concern to Shell. A study was designed and conducted to determine if there were other problems that could result from dilution of samples. It has been widely recognized that there is some degree of analytical variability associated with all measurements. As the analyte concentration approaches the detection limit, the analytical variability, expressed as the coefficient of variation (CV) (Note: CV = 100 x standard deviation/mean), usually increases at a rapid rate. While dilution of samples is allowed by EPA approved protocol[2], little information was available to assess how dilution might impact laboratory performance or analytical variability.

Eight common volatile analytes were selected for this study. The analytes were methyl-tert-butyl ether (MTBE), diisopropyl ether (DIPE), chloroform, benzene, toluene, ethylbenzene, para-, meta- and ortho-xylene. Spiked solutions of the analytes in distilled water were prepared at 5, 10, 20 and 40 ppb concentration levels. The 40 ppb spiked solution was diluted by a 1/20 dilution factor to represent the "diluted" sample. Each concentration level was analyzed eight consecutive times, and the mean, standard deviation, and coefficient of variation were calculated for each set. Systematic errors were minimized as much as possible. Only one trained technician performed all the analyses.

Special care was taken with the samples and no other samples were run on the instrument during this study. The calibration curves used for the study were prepared using calibration standards at the 1, 5, 10, 20, 50, 100, 150, and 200 ppb levels. The concentrations of all samples were within the calibration curve including the "diluted" sample.

The data from the study are summarized in Tables 1 and 2. The means and standard deviations of the analytes are given in Tables 1. The coefficients of variation are listed in Table 2. As can be seen from Table 2, the CV's are all < 10% except that of toluene. Unusual problems with toluene have previously been noted during several PE studies and no adequate explanation has been found for its unusual behavior [1,3,4,5].

To better illustrate the trends observed, comparative plots of the data are shown in Figures 1 and 2. In Figures 1a and 1b, the results for MTBE are shown. As expected, the estimates of the standard deviation increase with increasing concentration. However, for the corresponding CV plot, no particular trend was observed. This means that precision, when expressed as a percent of the mean, is fairly constant over the concentrations used for the study.

Figures 2a and 2b show similar trends for benzene, except for the 5 ppb standard. The 5 ppb points did not seem to fit as well. In this case, the estimate for CV was less than those calculated for the three higher concentrations. This is not what is normally observed or expected [6]. The observed estimate of CV for the 5 ppb point may have resulted from the greater uncertainty in both the estimate of mean and standard deviation which led to a somewhat lower CV.

The results for the 5, 10, 20, and 40 ppb spiked samples show that the purge and trap GC/MS method has the capability to measure the concentrations of the eight selected analytes with good precision and accuracy in the distilled water matrix. The coefficients of variation for all concentrations and analytes were less than ten percent with toluene being the only exception. Based on the observed CV's from this study, one would conclude that the method is quite capable of measuring the concentrations of these analytes down to the 5 ppb level and the analytical variability is relatively constant over this range and under the ideal conditions of the study.

The estimated means and standard deviations shown for the "diluted" sample in Table 1 were on the basis of observations that were corrected for the dilution. The actual "diluted" sample contained nominal 2 ppb levels of the analytes. The corresponding CV's shown in Table 2 are also on the same basis.

Comparison of the means (see Table 1.) for the 40 ppb spiked sample and the "diluted" sample for each of the analytes revealed that in every instance the means for the "diluted" sample were biased higher. Comparisons of the estimated standard deviations also showed a similar bias with toluene being the only exception. Since the spiked and diluted samples should be compared for each compound, this is a paired comparison. A 2-tailed sign test can be performed to assess the probabilities of observing 8 out of 8 higher means and 7 out of 8 higher standard deviations purely by chance (see Table 1.). The test results indicate that the chance probability (p-value) for the the means is less than 0.01 and for the standard deviations is less than 0.05. Thus, we concluded that diluting of samples prior to analysis resulted in less precise and less accurate results.

The reason for the less precise and less accurate results is quite simple. In the case for the 40 ppb spiked samples, all of the concentration estimates were calculated from response levels that were near the center of the calibration curve. The uncertainty and inaccuracy associated with establishing the location of the calibration curve are at a minimum near the center and increase considerably at the two extremes. The response levels for the "diluted" sample were all very close to the lower extreme (1 ppb) of the calibration curve.

There is another important consideration associated with dilution of samples. In the above study, all concentration levels were designed to be within the range of the calibration curve. For real samples or for the blind samples used for the recent PE study[1], the concentration of analytes are rarely the same. What actually was observed in the PE study was that a laboratory had diluted the sample to the point where some of the target analytes were present in the diluted samples at concentrations below the detection limits. In these cases the laboratory had false negative observations because of the dilution. For real samples the possibility of false negative observations is an important consideration.

It was concluded from the results from this limited study that the analytical variability was relatively constant over the concentration range studied and with the conditions of the study. The study also

revealed that the dilution of samples down to the detection limit or away from the middle portion of the calibration curve may result in less precise and less accurate results for reasons that are beyond the control of the analyst. A second problem associated with the dilution of samples is the possibility of diluting the sample to a point where target analytes are at concentrations below the laboratory detection limit. Based on these two problems that can result from dilution of samples, it is recommended that samples for volatile organics by purge and trap GC/MS analyses should be diluted only when it is absolutely necessary because of a matrix or interference problem. When dilution of samples is necessary, the quantification limits need to be adjusted by the dilution factor to reduce the possibility of false negative observations and to reflect the true capability of the analysis.

Volatile Organics - Second Laboratory

Establishing the root cause for problems with the volatile organics analysis at the second laboratory was much more complicated. The laboratory reported they had reviewed their raw data and had established the reason for the false negative observations was that the holding time had been exceeded by two days. Their corrective action was to make sure to analyze samples within holding times. This explanation was not acceptable to Shell. In discussions that followed Shell agreed to provide some additional spiked standards so the laboratory could demonstrate they had established the root cause and was now back in control. The performance of the laboratory for the standards was just as poor as with the blind samples.

Shell agreed to have two of their analysts visit the laboratory in an effort to establish the root cause of the poor performance and to assist the laboratory get back into analytical control. The two analysts were on-site for two days and did eventually establish a long list of root causes. Improper vials were used to store standards. Only one set of standards was available and the set did not have all analytes. Poor technique was employed to load the volatile samples. The samples were not at room temperature when loaded. Improper syringes were used and these were not calibrated. Errors from 0.5 to 1.0 mL were noted. Too many files were in the data system which led to confusion. Calibration and quantification files contained different response factors and the wrong procedure file was being used to update response factors. Variation in response factors as high as 60% were observed. The calibration range was too large (20 to 800 ppb). Poor judgement was used when a calibration should be updated. There were problems with missing peaks which had to manually be identified and this was not always being done. Reviewing and reporting of results was inadequate. There was a general lack of QA/QC which would have eliminated many of the observed problems.

The two Shell analysts worked with the laboratory analyst to correct the numerous problems to a point where the laboratory could achieve acceptable results for known standards. The laboratory agreed to include whole-volume PE samples from Environmental Resource Associates (ERA) into their QA program and to share the results with Shell. Results from these PE samples have demonstrated analytical control over the past year with a

few minor problems being noted. This example of the quality improvement process demonstrated the extent of involvement that may be required to achieve data quality objectives particularly if a given laboratory has been recognized as being essential for Shell's operations.

General Parameters

The results for the PE study[1] for the general parameter were disappointing. In general the performances at many of the laboratories for parameters such as pH, oil and grease, BOD, TOC, and COD were sufficiently poor to require corrective action to eliminate the obvious problems and to improve the overall performances of all laboratories for these parameters. Because of the number of laboratories involved and the total number of general parameters where poor performance was observed, it was decided to ask laboratories to participate in a voluntary and cooperative program where Shell would pay to have whole-volume PE samples shipped directly from Environmental Resource Associates (ERA) to the laboratories for analysis, and the laboratories would cover the cost of the analyses. Both Shell and the laboratories would share the resulting data which would be statistically analyzed by ERA. The program would run for six months and the PE samples would arrive every other month. The overall objective of the program was to allow laboratories the opportunity to establish root causes for poor performance and allow them to take the appropriate corrective action necessary to improve performance. Hopefully, the third PE samples would establish good performance at all laboratories.

All 24 contract laboratories agreed to participate in the voluntary program. Their response indicated that laboratories are concerned with data quality and do try to improve their performance. They are also willing to be active participants in programs that should lead to improved performance. It also demonstrates the use of the quality improvement process where the laboratory and laboratory customer work together to achieve some mutually agreed upon goal. In this case, the goal was improved performance.

The performance from the initial blind study was used as the benchmark for the voluntary program. The results from the initial blind study and the three whole-volume samples were statistically analyzed and the data were plotted in a number of different ways. The number of outliers for all of the data are summarized in Table 3. The data were further summarized (outliers removed) in Table 4. Table 4 compares the results from the blind study (Before) with the results from the voluntary program (After). Table 4 shows the average recoveries for all laboratories and the standard deviations for the means. The question of whether there was a significant reduction in variability was yes for all parameters and the corresponding "P" values were included in Table 4.

There are a number of ways to plot the data and each way provides some perspective for laboratory performance. The data were plotted as "boxplots" and Figures 3 to 7 illustrate the data in that format. A boxplot divides the data into quarters. Fifty percent of the values fall in the interval between the lower and upper edges of the box, with 25% of

the data above (and 25% below) the horizontal line within the box. One fourth of the values are below the lower edge of the box. This format summarizes the performance for all laboratories for each of the five samples. The boxplots showed improved performance for the "Before" and "After" comparison.

Another way to show the results is by plotting the percent recovery for each observation for the five samples. For example, percent recoveries for BOD are displayed in Figure 8. Note that this is not a control chart, but it is an effective display of the improved performance of the laboratories after corrective action was taken. It provides a more detailed visual comparison of the variability of the laboratory results before and after corrective action as well as portraying any shift in mean recovery (accuracy) that may have occurred. Figures 8 to 12 show the data for each of the general parameters. Also shown on the plots are the means and 95% confidence intervals that were calculated on a "Before" and "After" basis. Again, there is clear evidence of improved performance.

The data were also plotted as histograms with normal distribution curves superimposed onto the histograms. Figures 13 to 17 show the data in that format. Again, the comparison was made on a "Before" and "After" basis.

CONCLUSIONS

The examples presented in this paper demonstrate the use of the quality improvement process to determine the root causes for analytical problems and the nature of the corrective action that may be required. In some instances, the root cause(s) may be difficult to establish and require thorough on-site investigations and assistance, but root causes can be identified and proper corrective action can be taken.

The follow-up investigation to assess the effects of sample dilution revealed there are two important consideration associated with dilution of samples. For real samples the possibility of false negative observations is an important consideration. The study also revealed that the dilution of samples down to the detection limit or away from the middle portion of the calibration curve may result in less precise and less accurate results for reasons that are beyond the control of the analyst. Based on the two problems that can result from dilution of samples, it is recommended that samples for volatile organics by purge and trap GC/MS analyses should be diluted only when it is absolutely necessary because of a matrix or interference problem. When dilution of samples is necessary, the quantification limits need to be adjusted by the dilution factor to reduce the possibility of false negative observations and to reflect the true capability of the analysis.

For the voluntary and cooperative program for general parameters, statistical analysis followed by some innovative ways to depict the data resulted in a clear understanding of what had been achieved through the quality improvement process. The bottom line is that there was considerable improvement for all general parameters with few exceptions. The willingness on the part of laboratories to improve their performance

and to participate in voluntary and cooperative programs with well defined goals should be noted. The work presented also illustrates the importance of good communications between contract laboratories and their customers for mutual benefit.

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TABLE 1. MEANS AND STANDARD DEVIATIONS OF COMPOUNDS FROM 8 RUNS

Compound	Concentration (ppb) 5.0		10.0		20.0		40.0		40.0(dil)	
	X	s	X	s	X	s	X	s	X	s
MTBE	5.19	0.24	9.70	3.37	17.77	0.66	34.66	1.09	39.51	1.54
DIPE	4.76	0.07	8.69	0.63	17.15	0.64	33.00	0.86	37.28	1.45
CHLOROFORM	8.30	0.15	13.40	0.80	24.47	0.83	44.28	1.28	49.42	1.60
BENZENE	6.33	0.09	11.43	0.70	21.52	1.20	41.92	1.79	52.94	2.62
TOLUENE	7.55	0.75	13.46	2.22	24.12	1.16	49.81	5.19	60.33	4.11
ETHYLBENZENE	6.88	0.13	12.44	0.77	24.00	1.17	45.40	1.52	52.54	2.60
P & M - XYLENE	5.84	0.13	10.53	0.83	20.43	1.23	38.33	1.14	45.30	1.43
O-XYLENE	5.80	0.12	10.66	0.68	20.59	1.13	39.60	1.04	42.08	1.54

TABLE 2. COEFFICIENT OF VARIATION (%)

CONCENTRATION (PPB)

Compound	5.0	10.0	20.0	40.0	40.0(dil)
MTBE	4.62%	3.81%	3.71%	3.14%	3.90%
DIPE	1.47%	7.25%	3.37%	2.61%	3.88%
CHLOROFORM	1.81%	5.97%	3.39%	2.89%	3.24%
BENZENE	1.42%	6.12%	5.58%	4.27%	4.95%
TOLUENE	9.93%	16.49%	4.81%	10.42%	6.01%
ETHYLBENZENE	1.89%	6.49%	4.88%	3.35%	4.95%
P & M - XYLENE	2.23%	7.88%	6.02%	2.97%	3.16%
O-XYLENE	2.07%	6.38%	5.49%	2.63%	3.58%

TABLE 3

Outliers by Study and Substance

	BLIND1	BLIND2	ERA-WP02	ERA-WP03	ERA-WP04
BOD	3	2	0	1	1
COD	3	2	1	0	0
TOC	1	2	1	1	0
O&G	0	0	3	3	2
pH	0	0	1	0	0

TABLE 4

Summary Results (Outliers Removed)

Test	Study	# of Samples	Avg. % Rec.	SD	Significant Reduction in Variability	p-value*
BOD	Before	42	69.9%	32.2%	yes	<0.000001
BOD	After	66	96.8%	15.7%		
COD	Before	42	103.4%	36.8%	yes	<0.000001
COD	After	69	95.9%	11.9%		
TOC	Before	47	101.0%	25.1%	yes	<0.000001
TOC	After	68	99.4%	5.2%		
O&G	Before	43	61.6%	32.6%	yes	<0.000001
O&G	After	70	89.8%	10.7%		

Test	Study	# of Samples	Avg. Diff.	SD	Significant Reduction in Variability	p-value*
pH	Before	50	0.15	0.30	yes	0.000005
pH	After	74	0.02	0.17		

* P-value is from testing the hypothesis that the variance Before is equal to the variance After. A small p-value (typically less than 0.05) means that it is highly unlikely that the variances are the same. The smaller the p-value, the stronger the evidence that the variance of the lab results After is smaller the variance Before.

FIGURE 1

Figure 1a
Standard Deviation vs. Conc. of MTBE

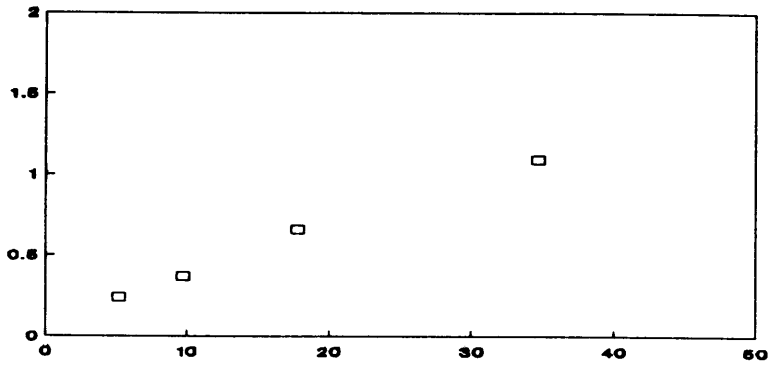


Figure 1b
Coefficient of Variation vs. Conc. of MTBE

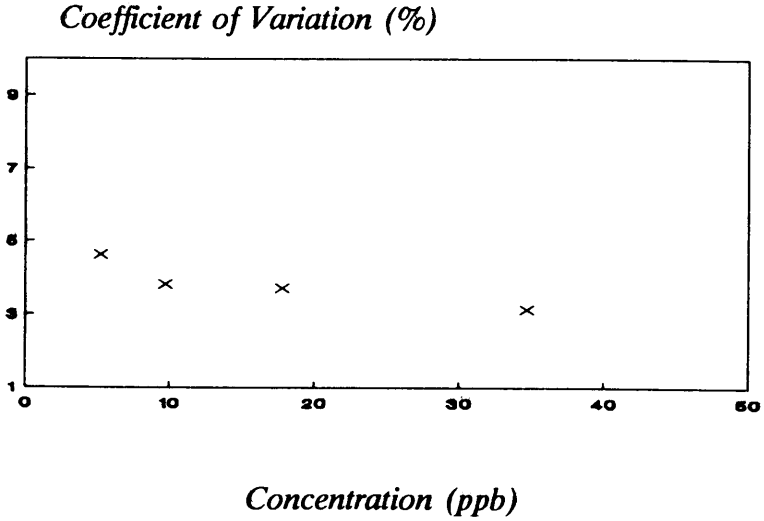
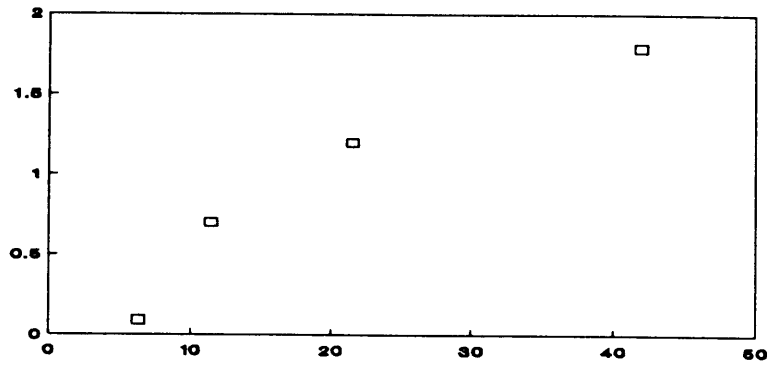


FIGURE 2

Figure 2a
Standard Deviation vs. Conc. of Benzene

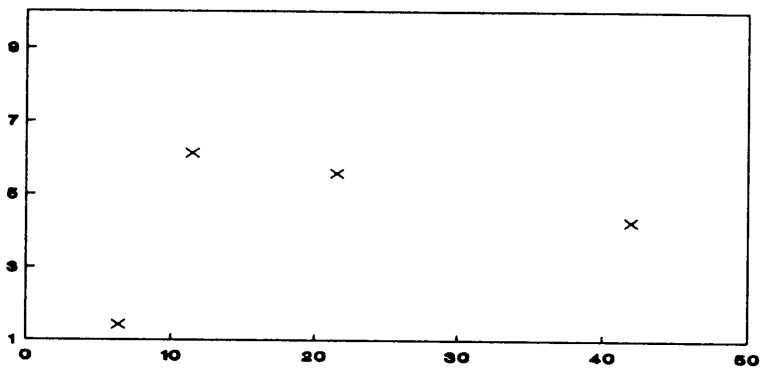
Standard Deviation (ppb)



Concentration (ppb)

Figure 2b
Coefficient of Variation vs. Conc. of Benzene

Coefficient of Variation (%)



Concentration (ppb)

FIGURE 3

BOD Recovery Percentages
Comparisons Study

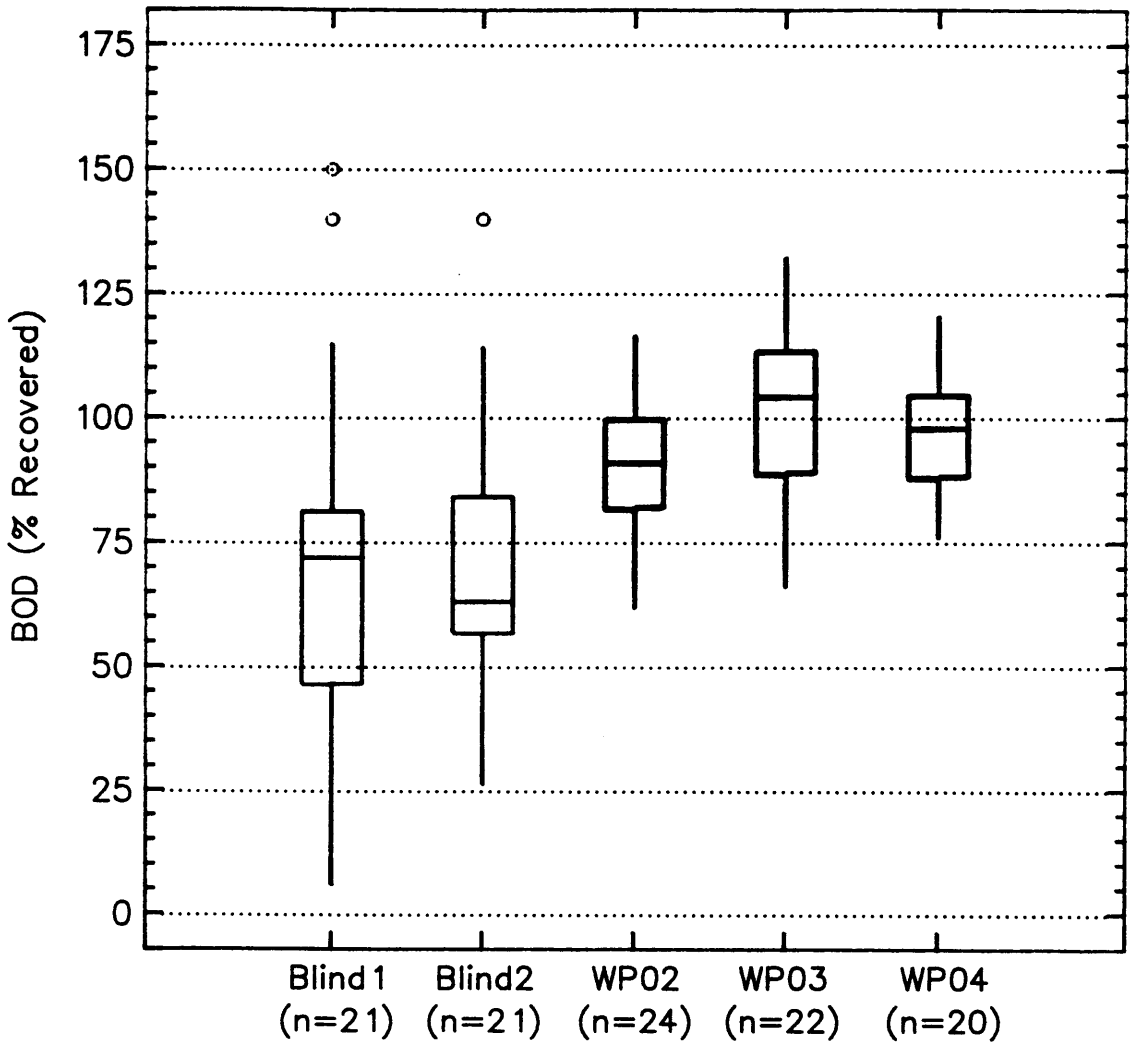


FIGURE 4

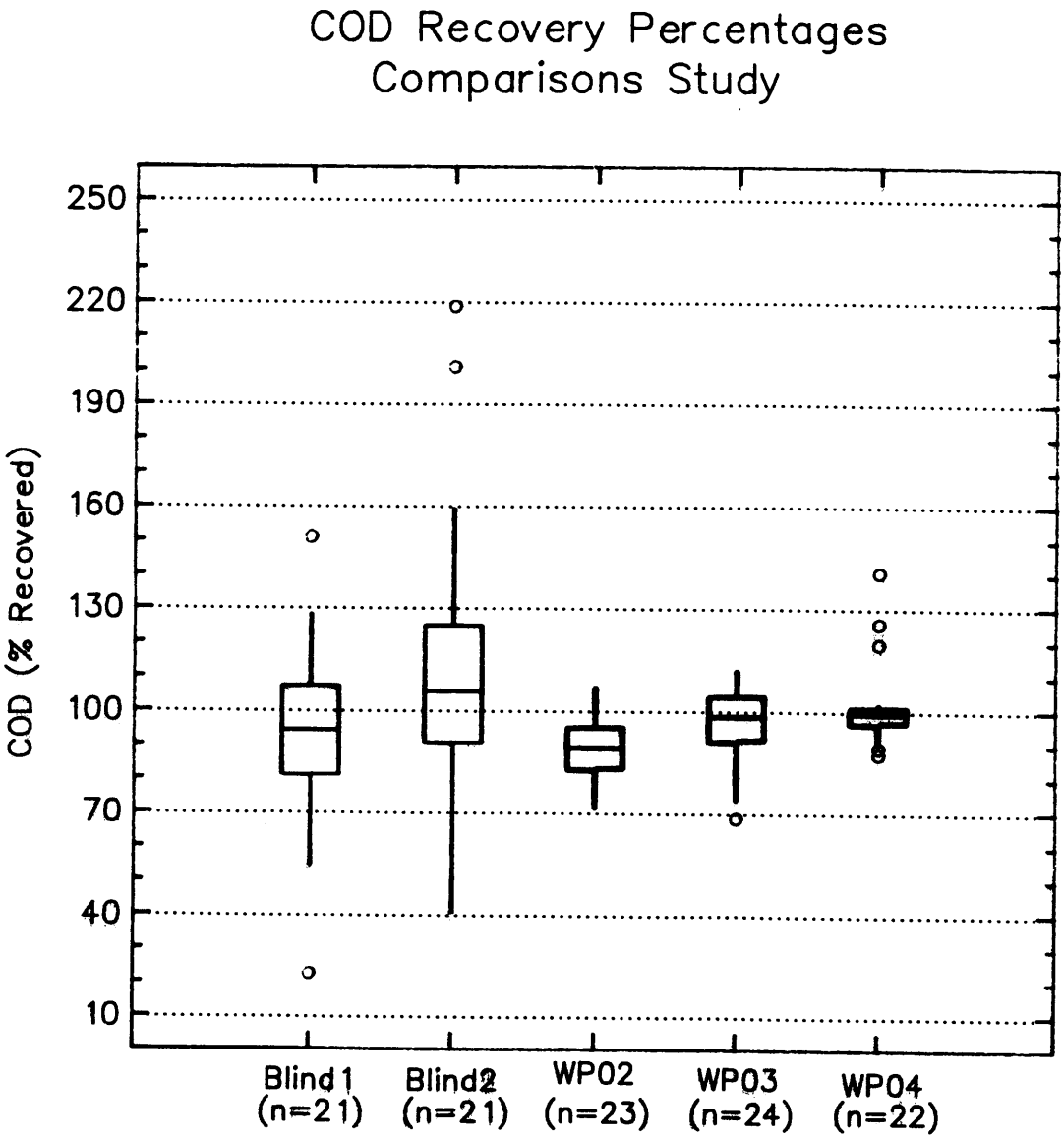

COD Recovery Percentages
Comparisons Study
COD (% Recovered)
250
220
190
160
130
100
70
40
10
Blind1 (n=21)
Blind2 (n=21)
WP02 (n=23)
WP03 (n=24)
WP04 (n=22)

FIGURE 5

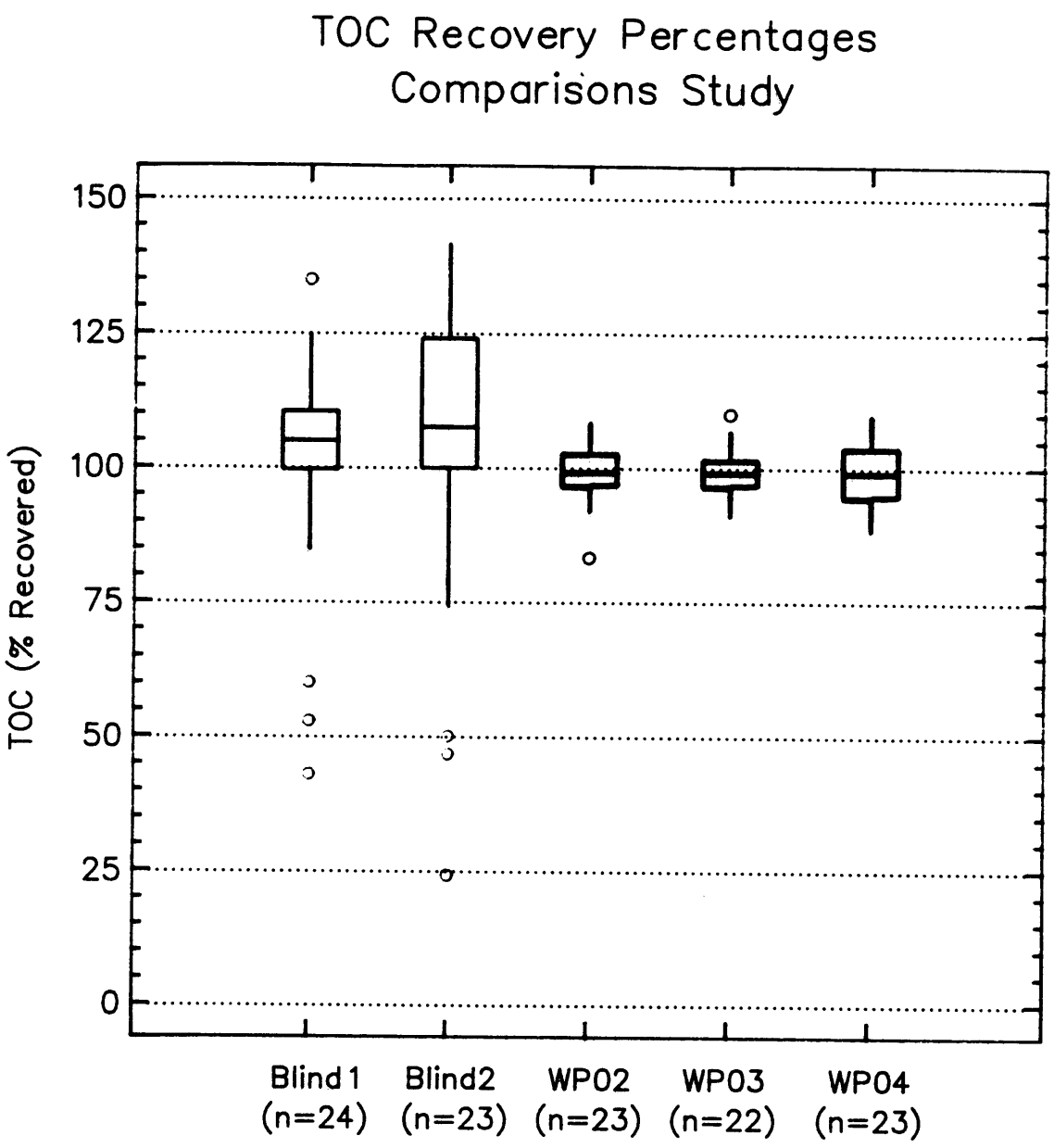

TOC Recovery Percentages
Comparisons Study
TOC (% Recovered)
150
125
100
75
50
25
0
Blind 1 (n=24)
Blind2 (n=23)
WP02 (n=23)
WP03 (n=22)
WP04 (n=23)

FIGURE 6

Oil and Grease Recovery Percentages
Comparisons Study

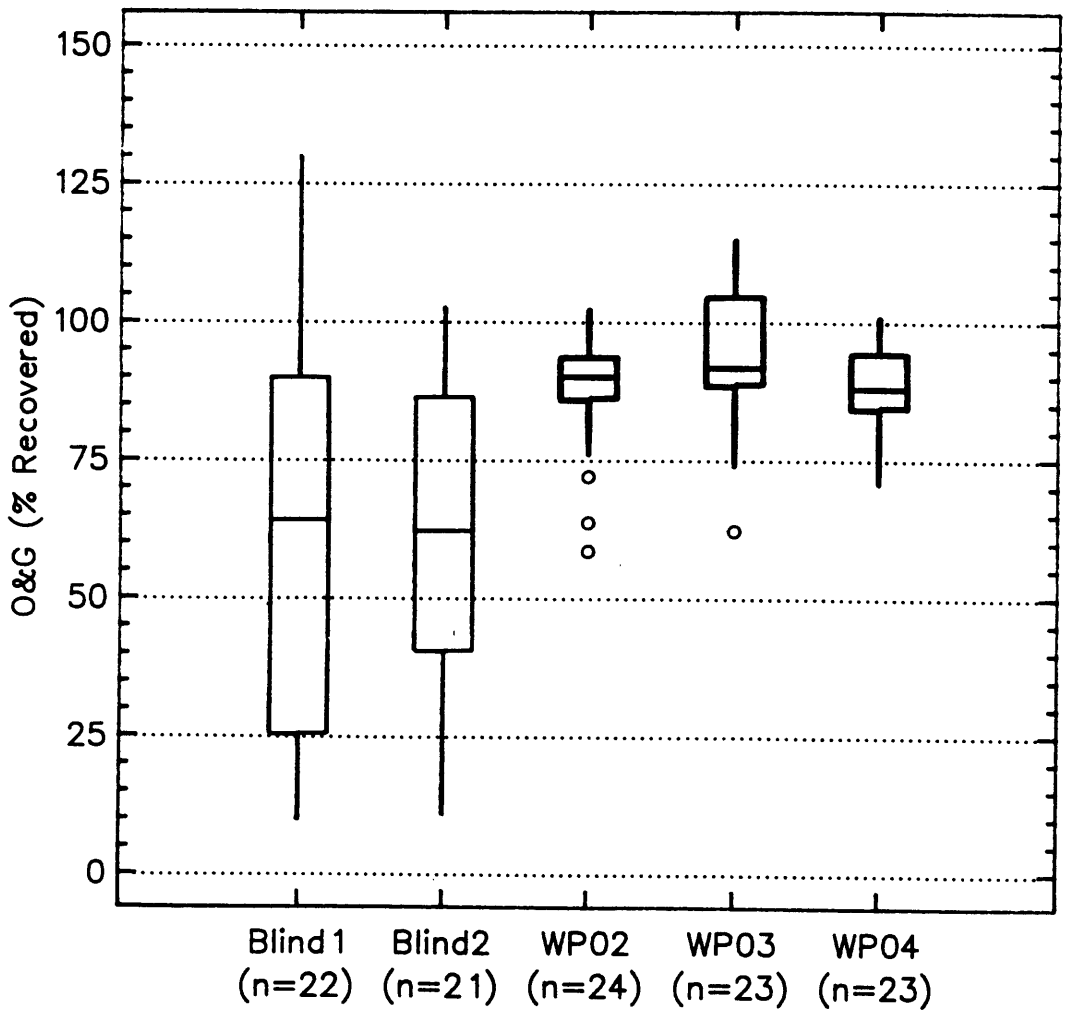


FIGURE 7

pH Differences Between Observed and Made–To Values
Comparisons Study

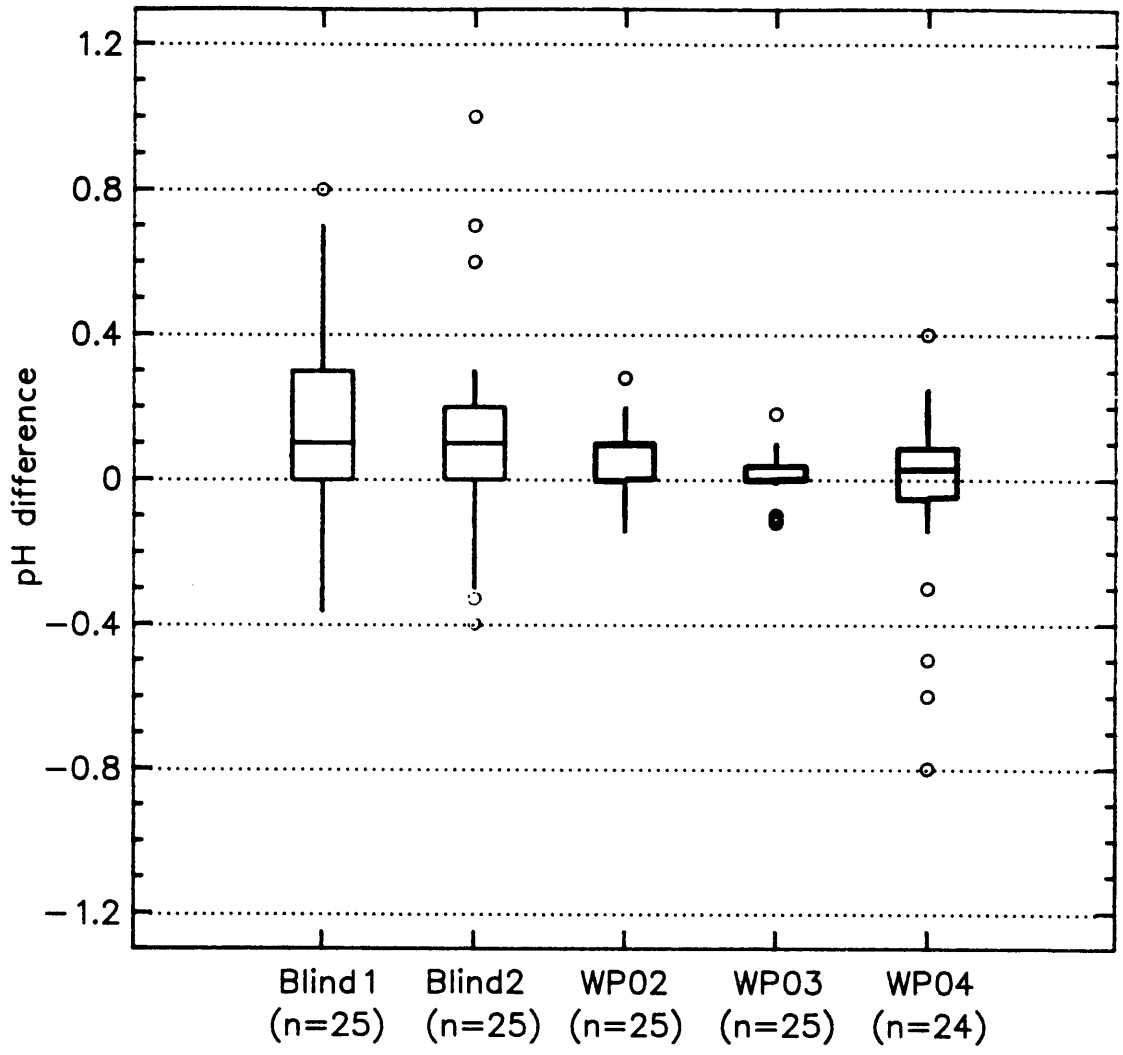
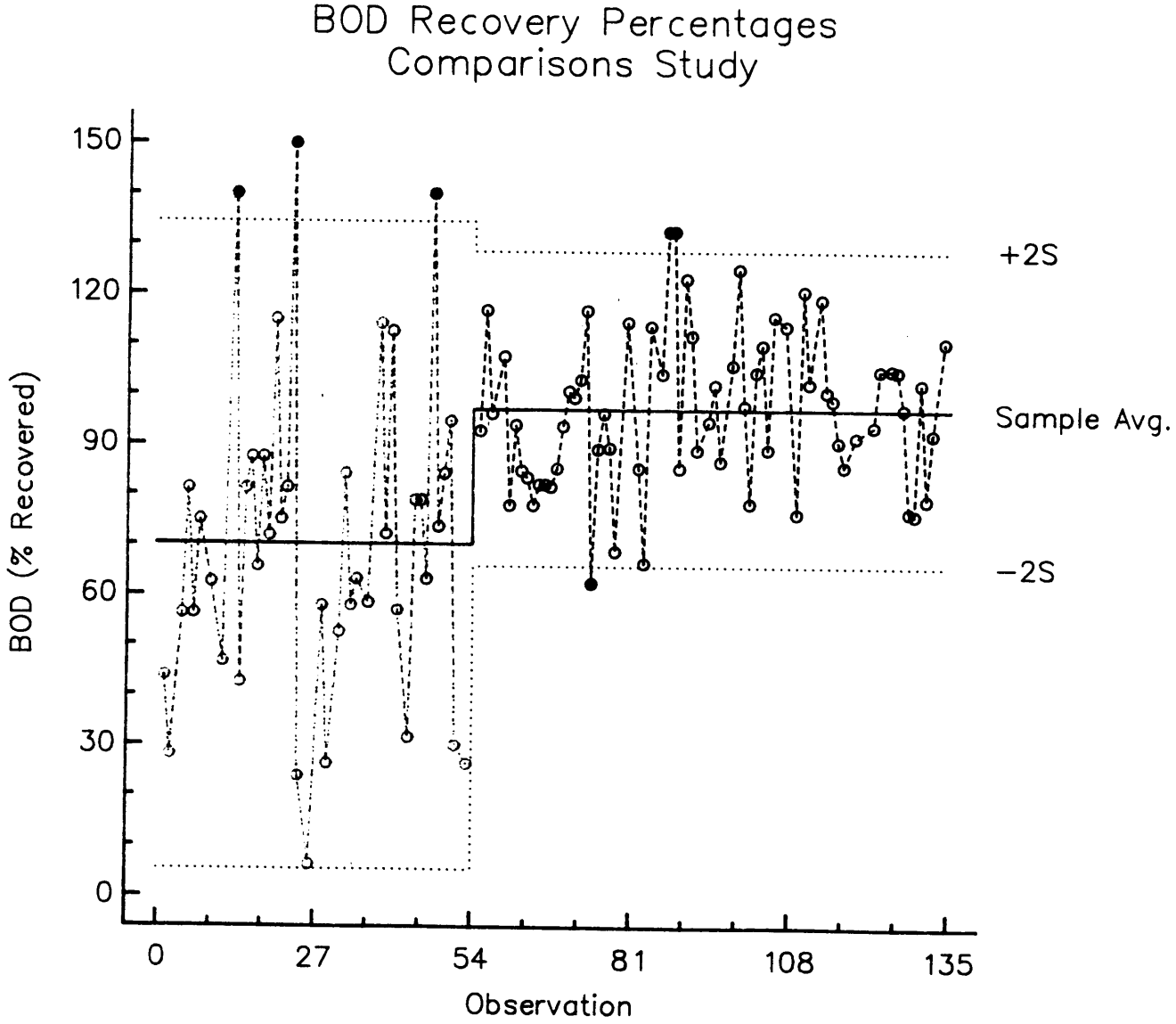
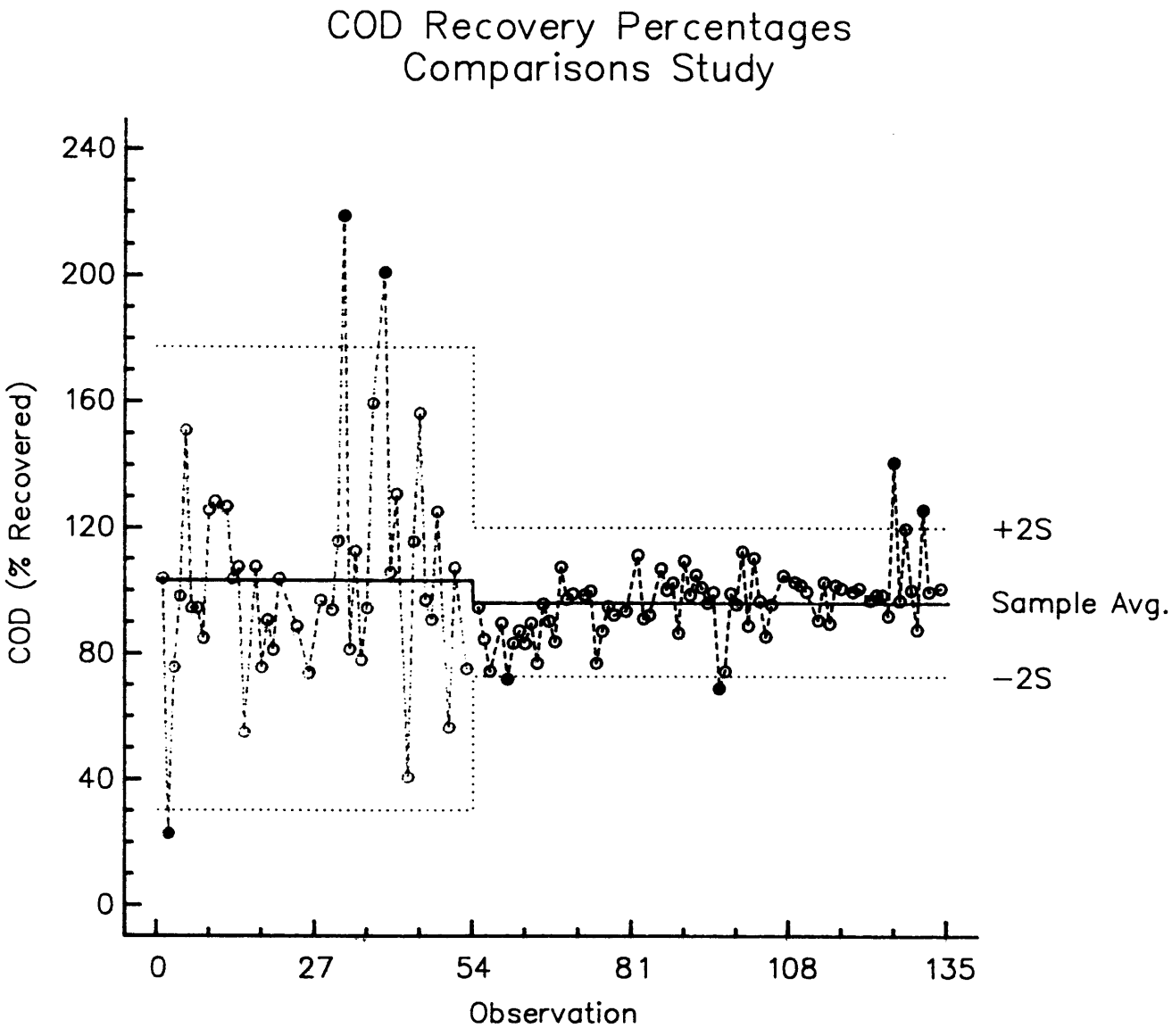


FIGURE 8



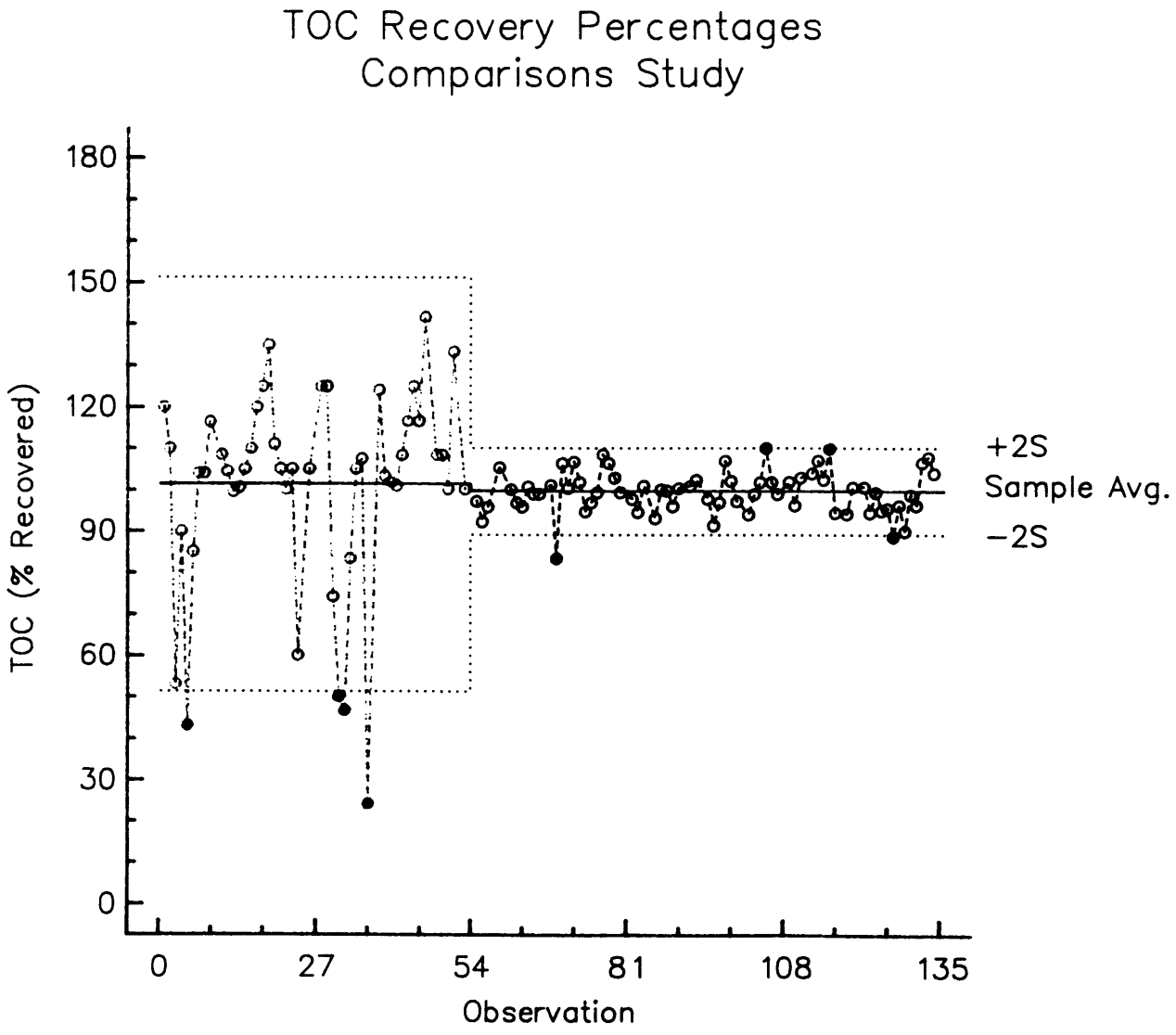
Blind1: Obs. 1–27
Blind2: Obs. 28–54
WP02: Obs. 55–81
WP03: Obs. 82–108
WP04: Obs. 109–135

FIGURE 9



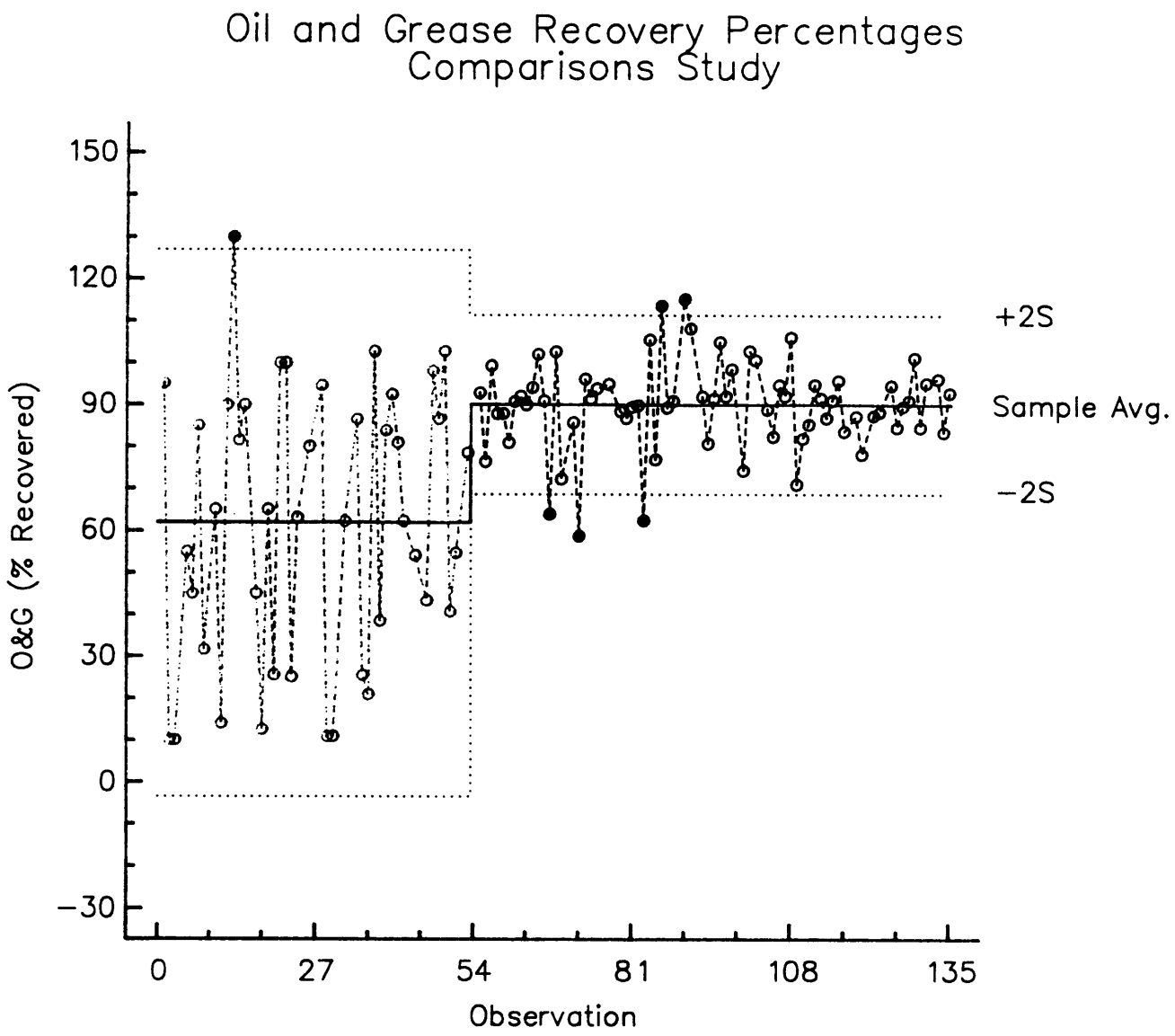
Blind1: Obs. 1–27
Blind2: Obs. 28–54
WP02: Obs. 55–81
WP03: Obs. 82–108
WP04: Obs. 109–135

FIGURE 10



Blind 1: Obs. 1–27
Blind2: Obs. 28–54
WP02: Obs. 55–81
WP03: Obs. 82–108
WP04: Obs. 109–135

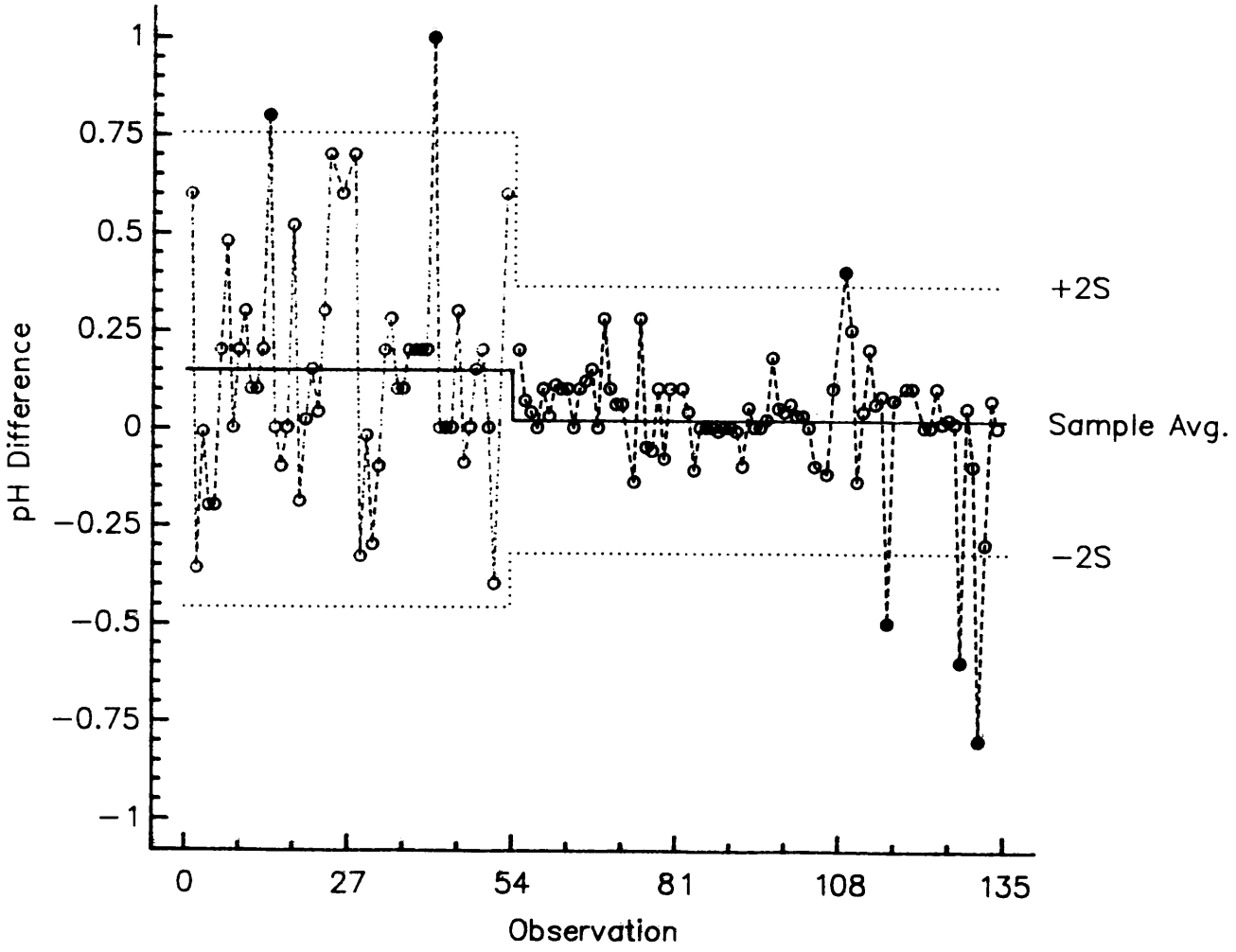
FIGURE 11



Blind1: Obs. 1–27
Blind2: Obs. 28–54
WP02: Obs. 55–81
WP03: Obs. 82–108
WP04: Obs. 109–135

FIGURE 12

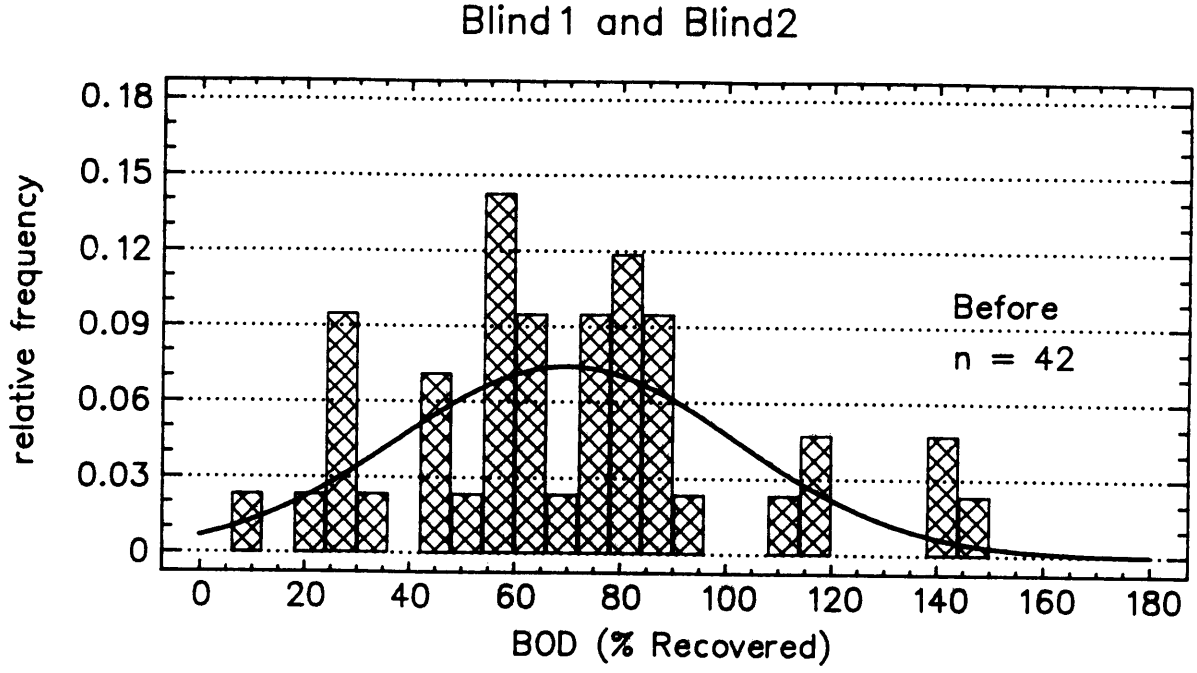
pH Differences Between Observed and Made–To Values Comparisons Study



Blind1: Obs. 1–27
Blind2: Obs. 28–54
WP02: Obs. 55–81
WP03: Obs. 82–108
WP04: Obs. 109–135

FIGURE 13

BOD Recovery Percentages Comparisons Study



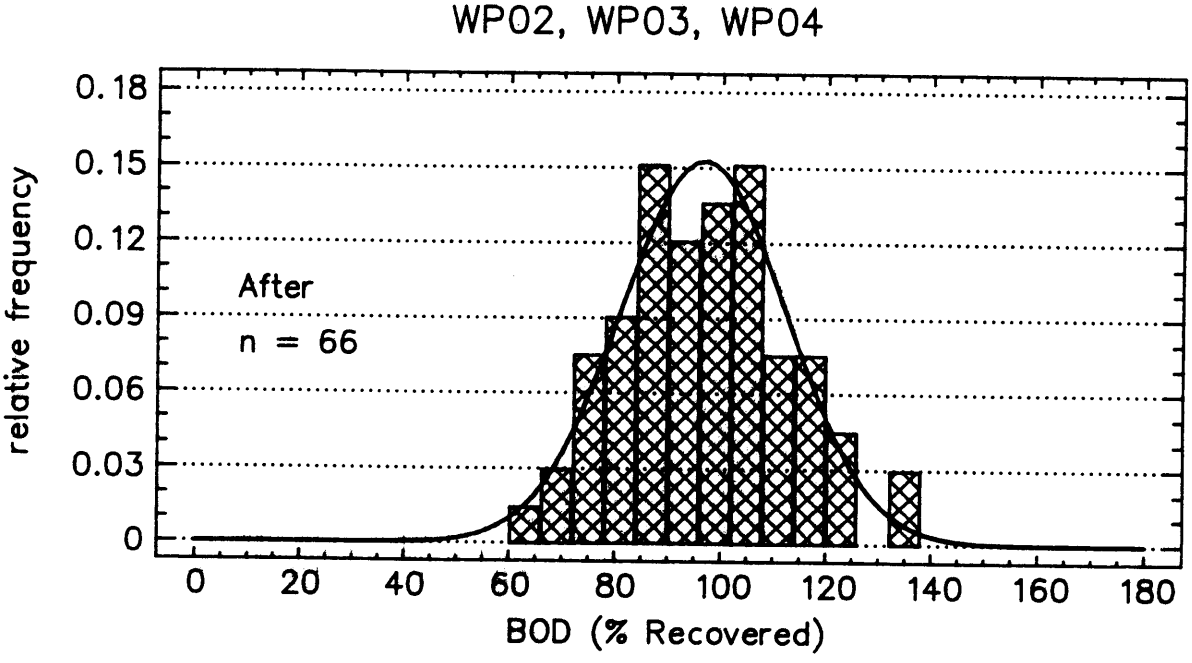
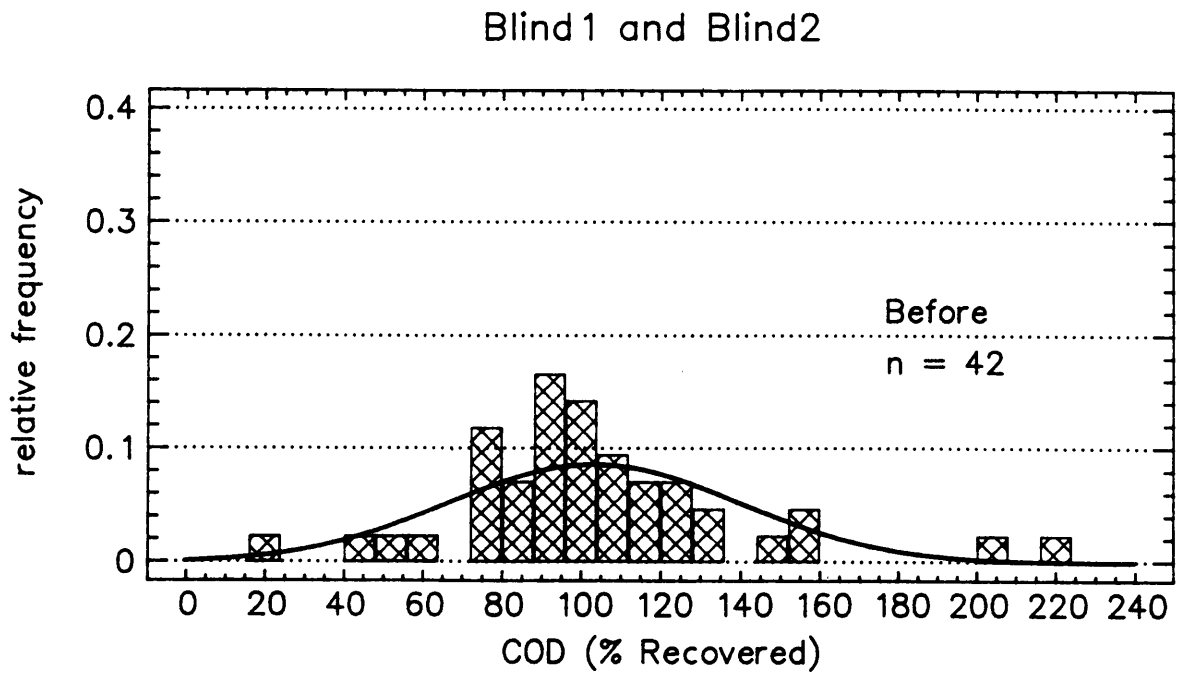


FIGURE 14

COD Recovery Percentages
Comparisons Study



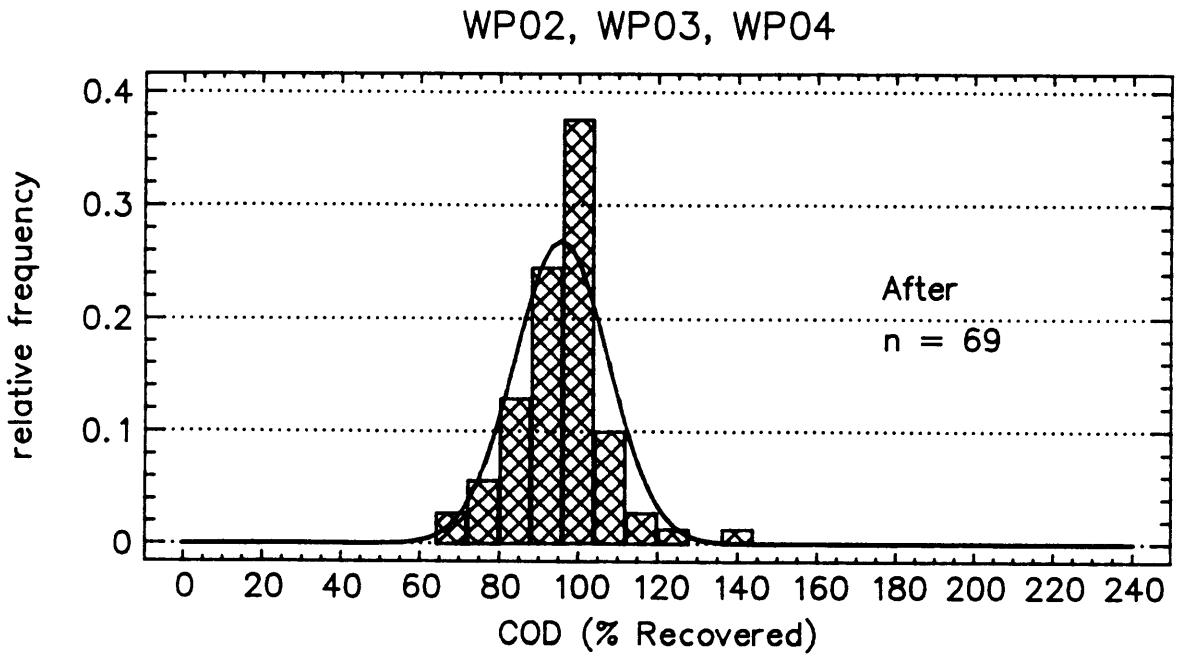
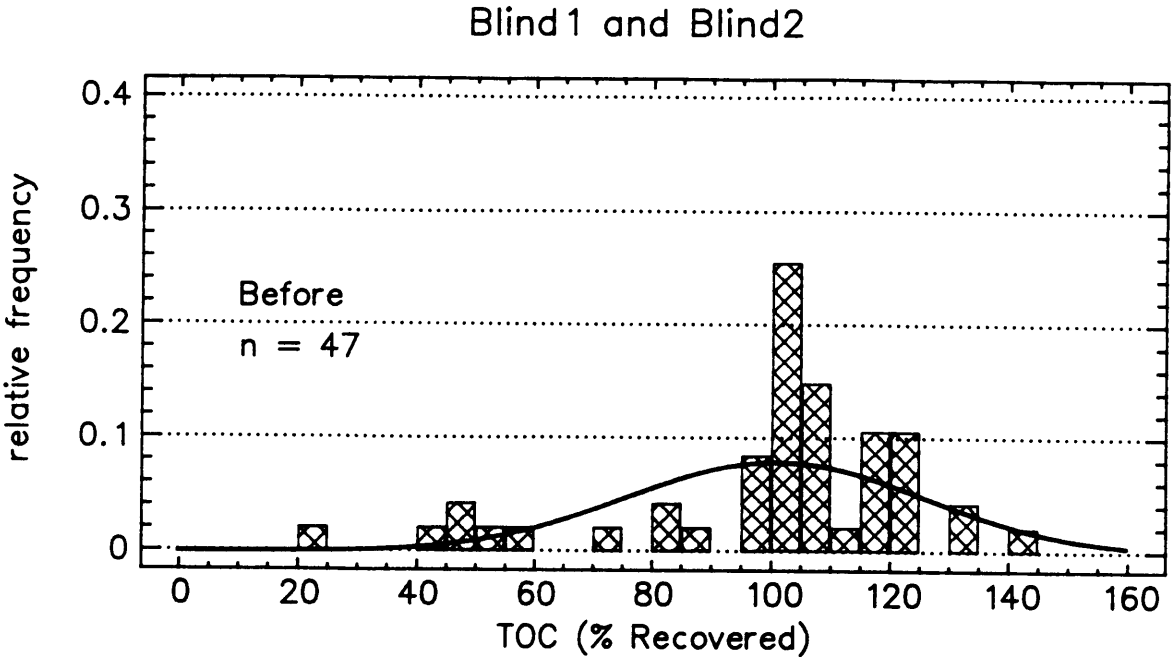


FIGURE 15

TOC Recovery Percentages
Comparisons Study



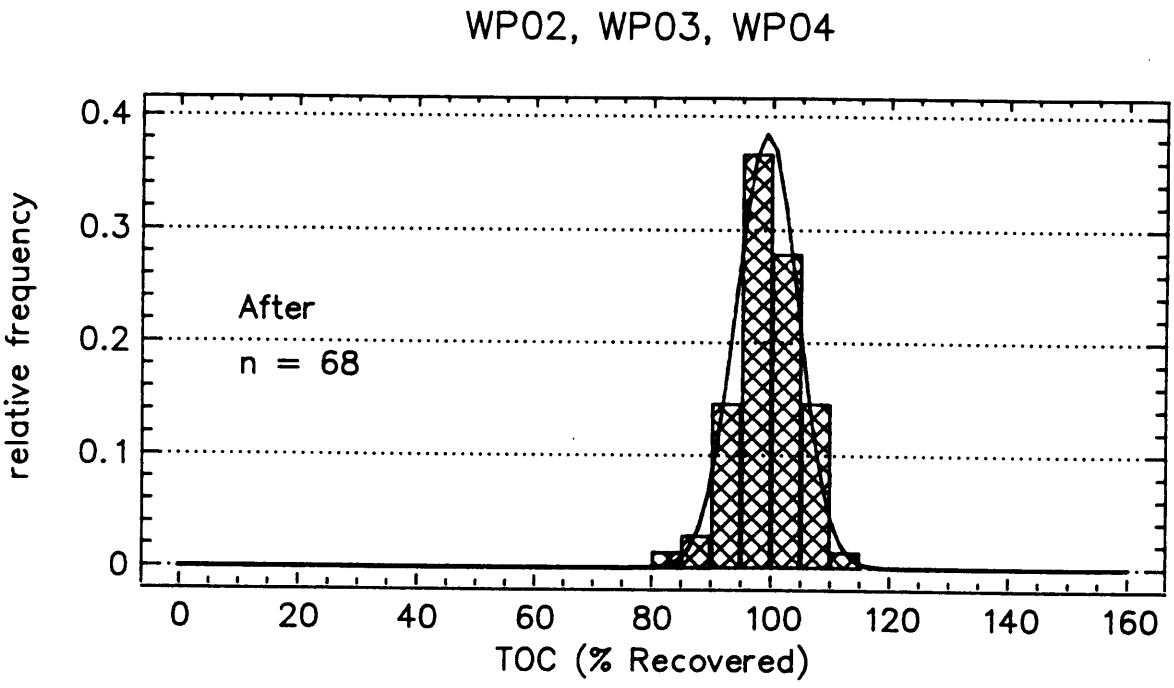
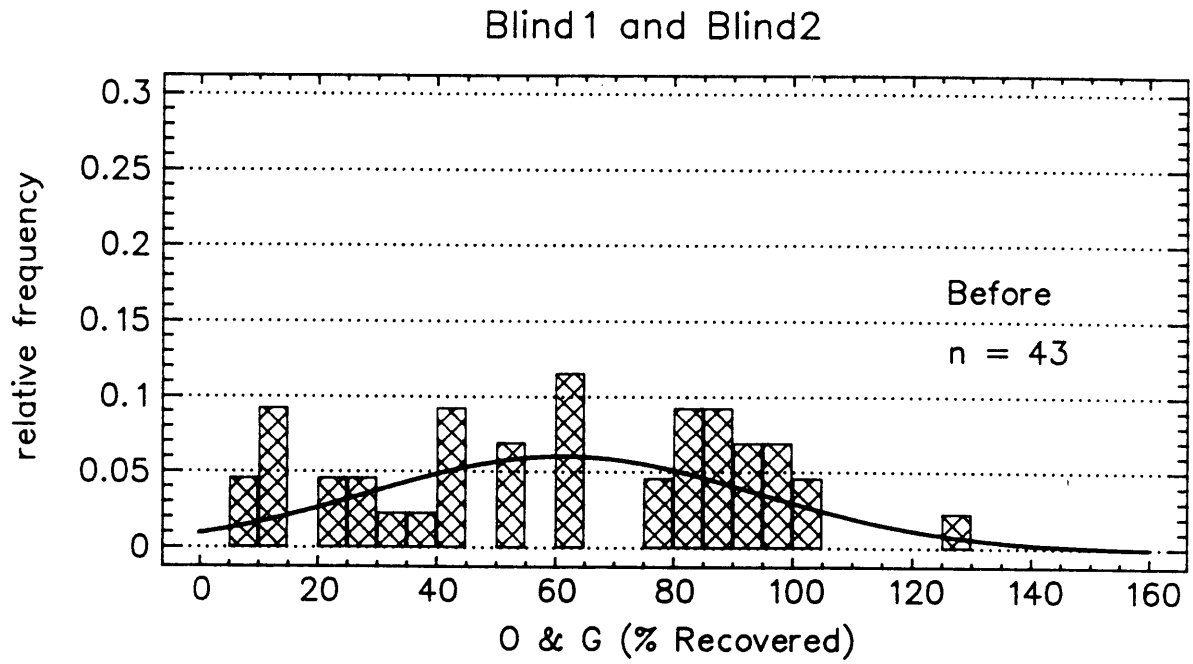


FIGURE 16

Oil and Grease Recovery Percentages Comparisons Study



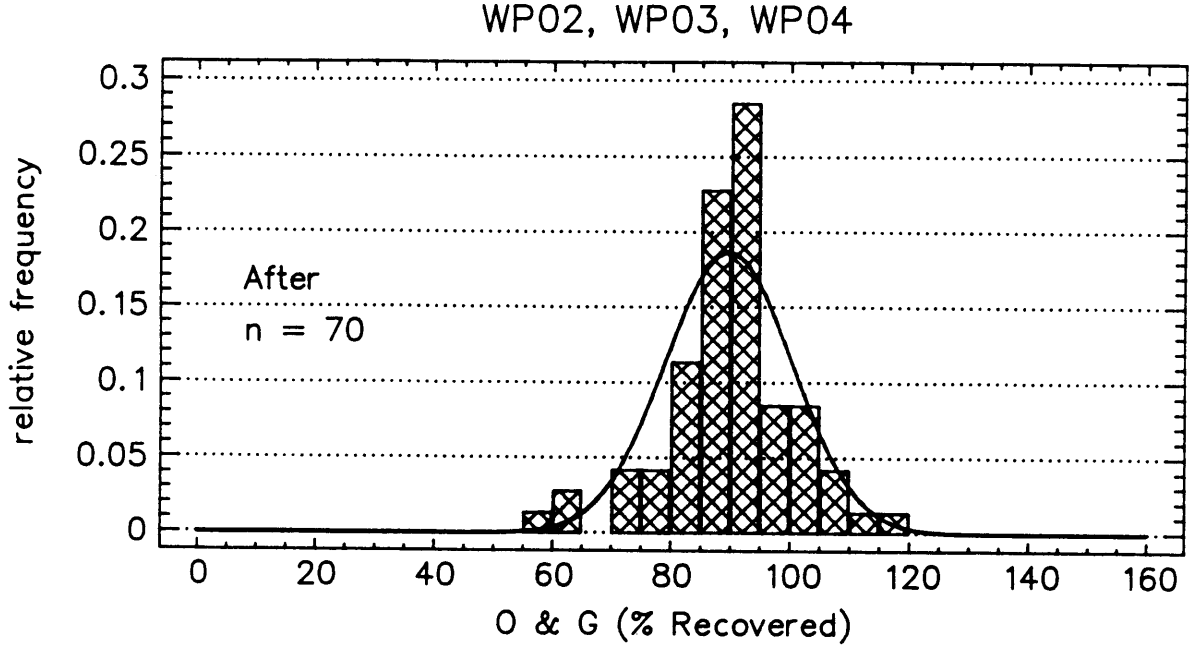
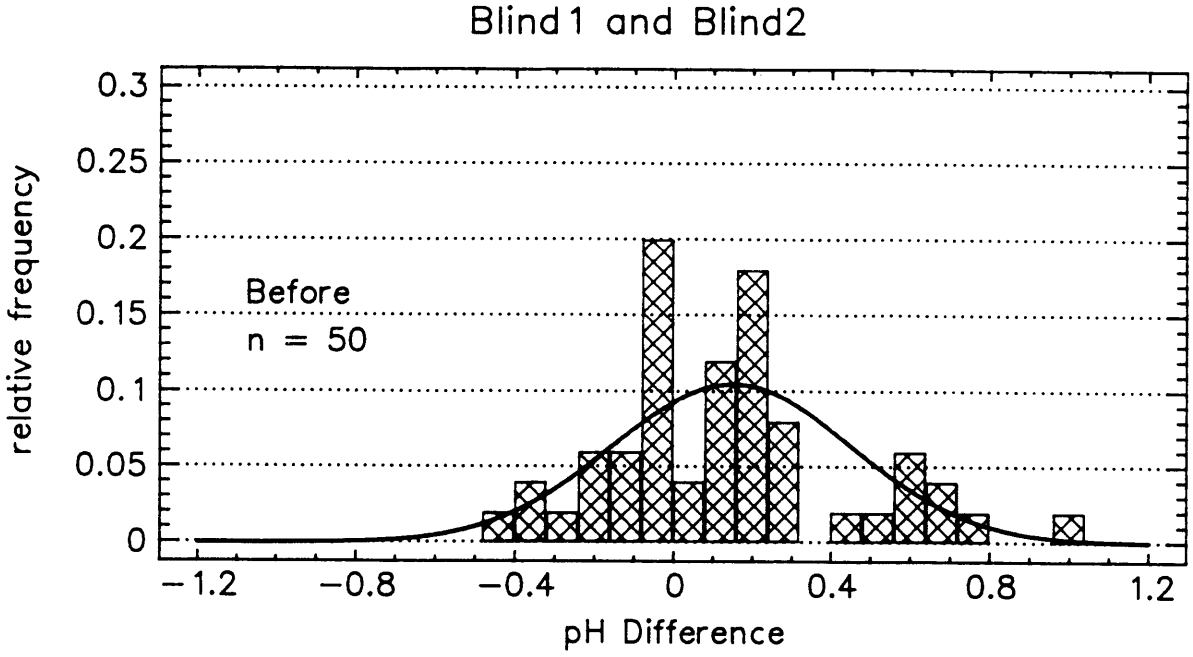
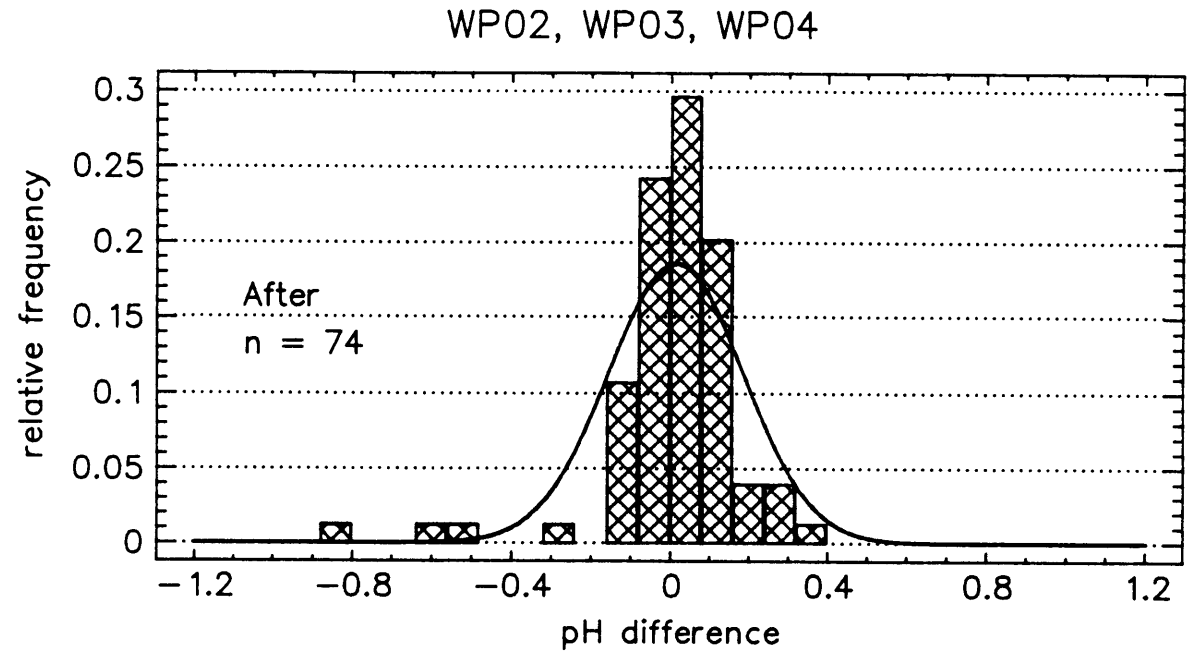


FIGURE 17

pH Differences Between Observed and Made–To Values Comparisons Study





[Blank Page]

MR. TELLIARD: We knew at this point in the program you would have been dulled into kind of a maze by numbers, facts, and science. So, now we are going to go into witchcraft and alchemy. We are going to talk about methods detection limits, levels of quantitation, and other artificial forms of reality that you can do.

Larry Keith is here, and he is from Radian Corporation, and what hat are you wearing today, ACS or Radian, or what uniform have you got on? A contractor for EPA? Which one?

MR. KEITH: Let's do Radian today.

MR. TELLIARD: Okay, he is a Radian today. Larry, you are on.

MR. STANKO: Excuse me. I would like to break in. There is a box that says Xerox on here that has 100 copies. Just leave your money on the side.

MR. TELLIARD: Okay.

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MR. KEITH: Bill and I first talked about the problems with MDLs about two years ago over in Germany when we were at the Dioxin '90 meeting. We discussed this science and the problems with MDLs, and we recognized that there are a lot of problems with them. Since that time, I have been working with the American Chemical Society to help resolve these problems.

The definition for MDL came about in 1983, and it came out of the Office of Drinking Water. The entire EPA essentially adopted the term.

However, the problem is that what was designed for drinking water perhaps doesn't always work well for other water matrices (for example sewage). Sewage, usually, does not closely resemble drinking water. Soils and other matrices are even farther away in terms of their resemblance to drinking water.

Thus, we are going to try to come up with a generic definition of method detection level, (which includes a name change) that, hopefully, everybody can agree upon. It will be a generic definition, one that doesn't tell you how to do it, so the protocol won't change, just the definition of the terms that everybody can agree upon.

What are the problems? [FIGURE 1] First of all, there is some unclear language in the definitions, and there are multiple definitions [FIGURE 2].

The ACS reliable detection level and the ASTM's limit of detection are the same concept. And the ACS term limit of detection and EPA's MDL are very closely related.

There is a general lack of sufficient guidance in using statistically based or related terms by statistically inexperienced users.

Our objective is to derive some revised consensus definitions that will provide: clearer definitions, fewer definitions, some accompanying recommendations, some accompanying usage guidance, and be clearly interrelated terms so that we keep things simple. [FIGURE 3]

We want these definitions to be widely encompassing, broad in their scope, so that all of the environmental situations are covered. And we want them to have broad support and acceptance within the entire scientific and technical community; those

who are the regulators and those who are the regulated.

First, let me review the difference between the level of detection (or the limit of detection) and the method detection limit. [FIGURE 4] Really, the only difference is the point of reference.

With the limit of detection (or level of detection), a blank that is the lowest concentration that can be determined to be statistically different from a blank at a specified level of confidence is used and the method detection limit, MDL is the lowest concentration that can be measured with 99 percent confidence if the analyte concentration is greater than zero.

Thus, there are two differences between the MDL and the LOD: (l) a confidence level is specified, and (2) zero is as the reference point with the MDL. The LOD does not specify a 99 percent confidence level (it recommends one) and it uses a blank as the reference point.

The recommended level in each case is 3 sigma, (3 standard deviations). These are basically levels where there is a binary yes/no decision that is made concerning whether or not an observed signal represents the presence or absence of an analyte.

Thus, the LOD takes into account any background interferences; the MDL doesn't.

There are three kinds of problems with the EPA definition of MDL. (1) It doesn't say what it means, (2) it is too specific and limiting and can paint EPA into a corner), and (3) it doesn't consider matrix effects when these are a problem. [FIGURE 5]

Let's discuss each of these problems. First, the use of "limit" is a misnomer. [FIGURE 6] When limit, is used it usually implies that you can't or shouldn't get below something, and that is not a true reflection of its use here.

Webster defines "limit" as "...impliessetting a point or a line beyond which you cannot or are not permitted to go" whereas "level" is "...themagnitude of a quantity considered in relation to an arbitrary reference value".

The values calculated by an MDL are arbitrary reference values. They are

not magic numbers. They are calculated, and they are also indirectly selected. They are selected based on the amount of confidence you want in elimnating false positives.

One person's confidence level of 99 percent might be a different person's confidence level of 95 percent. So, they are not magic numbers written in stone. They are selected and they are arbitrary.

Thus, "L"should stand for "level",because that is really what we mean, and I think we understand that when we are talking among ourselves. [FIGURE 7] However, although we may understand that we are really talking about "level",not everybody does.

The recommended 3 sigma above zero was arbitrarily chosen, because it provides greater than 99 percent confidence of eliminating false positives, However, for some cases less confidence is needed.

Therefore, we are going to try to change the name to "method detection level".

The second problem is that EPA's definition of MDL is too limiting. It doesn't take into consideration situations where there are statistically significant background concentrations of an analyte, so you can't subtract background interferences. [FIGURE 8]

that really wasn't the intention when the 1983 definition was promolgated. But, that is what it has evolved to, and that is the way that people use it. One does not usually subtract background in making MDL calculations.

We believe we can derive a single definition that allows subtraction of background signals when they are significant and that will use the arbitrary zero concentration when they are not. And we propose not to have a 99 percent confidence level in a generic definition.

The third problem was one of not considering matrix effects. [FIGURE 9] The procedure for making MDL calculations is to take an analyte of interest and spike it into reagent water at 2 to 5 times above the instrument detection level (or estimated instrument detection level) and analyze it about seven or eight times. Then practical quantitation limits (PQLs) are estimated by multiplying the MDL times arbitrary values

that are dependent on how complex the matrix is.

EPA has come under criticism for generating PQLs in that rather arbitrary way.

Thus, EPA's desire is to replace PQLs with some revised definitions that have a stronger technical basis.

Thus, the objectives are: (1) to replace "limit" with "level"; (2) accommodate both zero and background-subtracted signals; (3) accommodate various confidence levels, (rather than only 99 percent); (4) use a representative matrix when making analytical measurements when it is appropriate (and don't when it is not appropriate or when you can't); and, (5) provide some guidance on the use and limitations to accompany the revised definition. [FIGURE 10]

The draft revised definition is: A method detection level is the lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank, that might be zero, with a specified confidence level for a given method and representative matrix. [FIGURE 11]

The MDL is based only on the risk of false positive detections (i.e., is the analyte correctly identified as present or not). There are also two other definitions that need to be considered: (1) a reliable detection level (RDL) which is based on the risk of false negative detections and (2) a reliable quantitation level (RQL). [FIGURE 12]

These definitions, the correctness of an analyte identity. That is a different question not addressed by MDLs.

When is an analyte present? [FIGURE 13] that is one of the most important decisions in low-level analyses. The first question that has to be answered is if an analyte is there or if it is not.

This is a binary decision, and there are two types: detected or not detected. [FIGURE 14] There are also only two true solutions: an analyte is either present or it is absent.

If an analyte is detected and it is present, then that is a correct decision. Likewise, if an analyte it is not detected and it is not present, that is also a correct decision.

The other two situations are where there is a false positive, (an incorrect decision that an analyte has been detected) or a false negative (an incorrect decision that an analyte is absent).

Consider a sample where an analyte of interest is absent. [FIGURE 15] Theoretically, if the instrument used for anaylsis can give negative values, an equal probability of positive and negative results will be obtained assuming a normal Gaussian bell-shaped distribution. [FIGURE 16]

The next example has a concentration of an analyte, equal to the recommended MDL of 3 standard deviations. The same situation will occur where there is a 50 percent probability of detect or non-detect above or below that concentration to provide a similar Gaussion distribution.

That means that there is a 50 percent probability of a signal falling below the MDL, in which case, it wouldn't be reported. Thus, there is a 50 percent probability of an incorrect decision, (a 50 percent probability of a false negative). [FIGURE 17]

Therefore, although the false positive probability is less than 1 percent, the false negative probability is 50 percent. [FIGURE 18] That is not a very reliable detection level!

What would be a reliable detection level? It is twice the method detection level. At that concentration, there would be a very low statistical probability of either a false positive or a false negative detection. [FIGURE 19]

Therefore, if reliable detection levels (RDLs) are desired, you have to establish them at a higher concentration than the MDL. It may not have to be twice the MDL, but the recommendation is going to be that an RDL be twice the MDL (in the absence of appropriate data) so that there will be a very low probability of a false negative decision [FIGURE 20].

If an RDL is set at twice the MDL and the recommended 3 standard deviations as an MDL is used, then the RDL would simply be 6 standard deviations. That is pretty simple and everyone can understand it.

In Figure 21, the true analyte concentration is to 6 standard deviations, and there is an approximately equal overlap in the small black areas which represent less

than 1 percent of the alpha and the beta type errors, (false positive and false negative errors).

The table in Figure 22 shows that there is nothing special about the values selected. The probabilities of false positives and false negatives are all statistically based. If 3 standard deviations is selected for an MDL, the risk of false positives is approximately 0.1 percent, but the risk of false negatives is 50 percent, as previously discussed.

If one wanted a 1 percent risk of false positives, 2.33 standard deviations could be selected. Then a corresponding RDL would be 4.66 standard deviations. If a 95 percent confidence level was sufficient, one could select with 1.64 standard deviations. Thus, you can select any appropriate confidence level -- it does not have to be based on 3 standard deviations for an MDL (although that is the recommended value).

Therefore, for a reliable detection level when using a given method and representative matrix, a single analysis should consistently detect analytes present in concentrations equal to or greater than the reliable detection level. [FIGURE 23]

When sufficient data are available, which will probably be infrequent, the RDL is the experimentally determined concentration at which false negatives and false positives are specified. Otherwise, (most of the time), the RDL is the concentration which is twice that of the method detection level.

The RDL is the recommended lowest level for qualitative decisions based on individual measurements, and it provides a much lower statistical probability of a false negative determination than the MDL.

To this point, we have only discussed qualitatively identifying an analyte of interest. The next consideration is how to reliably quantitate low concentration levels. [FIGURE 24]

In general, the higher the concentration of an analyte in a representative environmental matrix, the more reliably you are going to be able to calculate its concentration or to measure its concentration. Unlike the definitions of the MDL and the RDL, statisticians remind us that when a quantitation is based on an individual measurement, there is no direct statistical basis for its derivation. That is a significant

difference from the situation with the MDL (and the corresponding RDL).

In 1983, the American Chemical Society recommended 10 standard deviations for establishing a reliable quantitation level (RQL) at or above an average blank signal. [FIGURE 25]

The proposed revised definition is that the RQL be 2 times the RDL when based on individual measurements. This accommodates various RDLs that can be used. It also translates to a value of 4 times the MDL. It is an arbitrary factor, but at least it provides a consistent relationship between the proposed definitions of MDL, RDL, and RQL.

Thus, the draft definition for the RQL is: The RQL is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix.

The RQL is the concentration which is 2 times the reliable detection level, and it recognizes that the RDL estimates produced at different times by different operators for different representative matrices will not often exceed the RQL. [FIGURE 26]

The EPA plans to publish these proposed definitions along with some additional historical and background information and some questions in the Federal Register in August, 1992.

Notice that throughout the definitions of MDL, RDL and RQL, we have used the words "representative matrix." That was placed in the definitions because it is recognized that complex matrices may cause some significant analytical effects. When this occurs, a matrix related problem can be accommodated, if that is possible. Thus, reagent water will not have to be used to try to represent, for example, a petroleum refinery or a paper mill refinery or a sewage effluent. One can use a sewage effluent, or a petroleum refinery effluent to represent the appropriate matrix and that should be more accurate than using reagent water to represent those or other kinds of industrial effluents and other comoplex matrices (including soils and sediments).

The proposed definitions also will allow flexibility within EPA to vary the confidence levels to meet individual Agency needs. These proposed definitions are

sufficiently generic so that they shouldn't hamper various EPA offices or other government agencies from meeting their respective needs as long as everyone agrees on the them.

QUESTION AND ANSWER SESSION

MR. STANKO: George Stanko, Shell Development.

One of the problems has been this detection limit thing that has been going on for years, and we probably will never solve it here.

I would like to point out that, first, you cannot establish a distribution curve at zero. It is impossible. It has to be something measurable so that you can calculate standard deviation and then create a distribution curve. So, in theory, what was shown here is impossible to do in practice.

Another thing, there was an error in Figure 16. If you have one less molecule than the MDL, you have a 50.99 percent probability of a false positive and a 49.99 percent probability of a false negative. If the precise concentration in the sample is one molecule less than the listed MDL, you have a 50/50 probability of a false positive or a false negative, and not 50 percent false positives and 1 percent false negatives. That is a flaw.

Another problem I am having is that going from RDL to RQL does not include interlaboratory variability. It is done at a single lab, and it is multiplied by a factor of 2. It does not include interlaboratory variability.

Whenever you have a situation where you have exceeded your permit, somebody has caught you, there are always at least a two and/or three or four labs are doing samples, and it really throws you into the realm of this variability associated with interlaboratory measurements.

If you will take RDL and multiply it by 5, then I will accept your RQL.

DR. KEITH: Those are good comments to consider, George, and let me say that I understand that the curve in the Figure that I showed are only theoretical, but I was trying to show a simple concept.

So, even though, most instruments don't give, negative values (which I also pointed out), it was simply to try to pictorially show a concept.

MR. SNELLING: Ron Snelling from LSU.

I think this is a comment instead of a question. We had a project we were

working on where we were doing information theory to evaluate methods. I think it would have some real use in these, because information theory will help you relate your probabilities of false positives, false negatives.

There is a relationship between false positives and false negatives described by a curve, and you figure out your costs that are incurred with false positives and false negatives and try to find an optimum balance. With that, you can help determine how you set your detection limits and quantitation limits based on the effects of a false positive or a false negative.

DR. KEITH: Okay, thank you.

MR. DRIEDGER: Art Driedger from Wayne Analytical.

I was just curious if you were thinking of changing the way in which you would establish the spiking level?

DR. KEITH: No.

MR. DRIEDGER: Okay, and the other thing is earlier this afternoon, we had a talk where the spiking level was either done between 0.2 and 2 parts per billion, and I thought that would be difficult to compare on a given list and wondered if there is a way of using the relative standard deviation to more or less normalized some of the values out. In other words, you have, say, your MDL at 3 sigma, and then divide by the average value or, say, the average value recovered to account for the difference, you know, in absolute spiking value. Also even, for that matter, in recovery from the extraction procedure or what have you.

DR. KEITH: Doesn't that begin to get a little more into the protocol of how to do it which is what we are trying to stay away from? We don't want to say how to do it.

MR. DRIEDGER: Yes.

MR. YOCKLOVICH: Steve Yocklovich from Burlington Research.

I agree that determining the MDLs on reagent water samples has nothing to do with the matrices we work with, and you said this will allow us to look at the effects in different matrices, but working for a commercial lab, I wonder, does that mean we will be required to determine MDLs in every different matrix that we look at?

MR. TELLIARD: Yes.

MR. YOCKLOVICH: I mean in single samples.

DR. KEITH: If it is practical and EPA wants more realistic numbers, then, yes.

MR. YOCKLOVICH: Well, I am not concerned about the cost. It is not my money.

MR. TELLIARD: Eventually, it will be.

One point of clarification. Larry is talking about the Office of Water, and you should be aware that this is the Office of Drinking Water putting forth this proposal in a defense to do away with the PQL which, of course, is the "political quantitation level".

The dirty water people, us guys, haven't been involved, and we don't necessarily agree with all this, but we think it is really neat, you know. Again, your agency together.

DR. KEITH: Well, the other thing, though, is that there is a group within EPA called EMMCI which is kind of an overall Agency coordinator for harmonization of methods, etc. and it is also involved with these redefinitions to try to make sure that the various parts of EPA, like the dirty water folks and the Superfund folks, can have something that they can all buy into.

MR. TELLIARD: I think the point I am trying to make here is if you have a comment, it ain't over with yet. Get them in.

DR. KEITH: Right.

MR. LEVY: Nathan Levy, A&E Testing in Baton Rouge.

From an independent laboratory perspective, I would like to say thank you. We consider MDLs as making our day lousy. We are really tired of being pushed against the wall for these MDLs that were generated, usually, in DI water, and it has been a long time since we analyzed DI water for money.

As far as having to worry about establishing PQLs or RQLs or whatever you want to call it in each matrix, I think that is almost quite easy to do, because in order to establish whether or not you do have a positive hit, you have probably got to do

some dilutions or concentrations, etc.

And I appreciate George Stanko uncovering a farce in some of the laboratory community in which they do not adjust their MDLs by their dilution factors. That is another battle that some laboratories have to face when compared to laboratories who do practice the art of reporting MDLs in DI water against samples they have diluted by 10 and 100.

But I am really glad to see the Agency trying to work with us and trying to understand that we have a big problem with matrices and that MDLs and the old methods aren't appropriate.

DR. KEITH: Thanks for your comments. I have heard many, many people echo similar sentiments. I think there is a lot of discontent with the MDLs.

MR. STANKO: George Stanko. I would like to make one further comment.

Lloyd Curry told us that we should not report any value less than LOQ (limit of quantitation) in the ACS publication, and that the area between LOD and LOQ is totally unreliable. We, the regulated community, have to report a number on a permit, and most of us have been standing very tall and screaming that we will not report a value less than the current PQL.

If you change the rules from MDL to RDL and RQL, there needs to be some guidance, because, here again, we don't think it is realistic to report any value, a numerical value, less than RQL, and recognize the fact that the difference between RDL and RQL is an area where there is highly variable and uncertain data, and one should not be forced to report values that are totally unreliable.

And no value should be reported less than RDL, and, in fact, you have no physical evidence that has ever been detected.

MR. TELLIARD: There is a matter of faith, George.

Thanks, Larry, so much for coming in and doing this.

DR. KEITH: You're welcome.

Sources of Some Problems

Some of today's environmental analytical problems are caused by current definitions and others by conventions in reporting data from analyte concentrations at low levels.

Sometimes these problems are interrelated.

Problems With Current Definitions

Many of the problems with definitions currently in use evolve from:

- Unclear language used in definitions.
- Multiple definitions for the same term (i.e., ACS RDL and ASTM LOD are the same concept and ACS LOD and EPA MDL are closely related).
- Lack of sufficient guidance in applying statistically-based (or related) terms by statistically inexperienced users.

ACS Initiatives To Improve Current Definitions

ACS has engaged in conversation with EPA, ASTM and AWWA scientists to achieve revised consensus definitions that:

1. Provide clearer definitions
2. Provide fewer definitions
3. Provide definitions with accompanying recommendations
4. Provide definitions with accompanying usage guidance
5. Provide clearly interrelated terms.

- Revised definitions should be widely encompassing in their scope so that all environmental situations are covered.
- Revised definitions should have broad support and acceptance within the scientific and technical community.

The Difference Between MDL and LOD

Level of Detection (LOD)	Lowest concentration that can be determined to be statistically different from a blank at a specified level of confidence.
Method Detection Limit (MDL)	Lowest concentration that can be measured with 99% confidence that the analyte concentration is greater than zero.

- The recommended MDL is 3σ above "zero".
- The recommended LOD is 3σ above the blank signal.
- Both are levels where binary "yes/no" decisions are made concerning whether an observed signal represents presence of an analyte.
- The LOD takes into account background interferences in the blank from contamination but the MDL does not.

Problems With EPA's MDL

1. It doesn't say what it means.
2. It is too specific and limiting.
3. It does not consider matrix effects.

EPA's MDL Does Not Say What It Means

- Use of "Limit" is a misnomer.
  - Implies one cannot get below a "limiting value"

Webster's Collegiate Dictionary Definitions:

Limit: Limit implies setting a point or line ... beyond which something cannot or is not permitted to go.

Level: The magnitude of a quantity considered in relation to an arbitrary reference value.

- MDL pertains to the size of an observed signal -- not to "analyte concentrations."

"L" Should Stand For Level

MDL is a "level" selected on the basis of a statistical confidence level for eliminating false positive detections (Type I errors).

A recommended 3σ above zero is a value arbitrarily chosen because it provides >99% confidence that false positives will not be reported.

- For some cases an arbitrary confidence level of 95% or less may be acceptable.
- Zero is also an arbitrary point of reference; one could select the average concentration level of a blank (ACS LOD).

"Level" is what the MDL definition really means!

EPA's MDL Is Too Specific And Limiting

- It does not take into consideration situations where there are statistically significant background concentrations of an analyte.
- The above was never intended but it is common practice.
- A single definition could be made that allows subtraction of background signals when they are significant and keeps the arbitrary zero concentration as a reference point when they are not.
- A 99% confidence of excluding false positives in not always suitable.

EPA's MDL Does Not Consider Matrix Effects

Common Practice:

- Calculate an MDL by spiking analytes near the instrument detection level (IDL) into reagent water.
- Estimate Practical Quantitation Limits (PQL) by multiplying MDL times some arbitrary values which are dependent on matrix considerations.

In Reality:

MDLs are dependent on analyte, matrix, and method.

(Instrument and/or operator variability is part of the overall method variability)

Results:

An unrealistic use of EPA's MDLs that can cause significant analytical and regulatory problems.

Proposed Revisions To Method Detection Limit

- Replace "Limit" with "Level;"
- Accommodate both zero and background signals of an analyte as a reference point;
- Accommodate statistically variable confidence levels that may be used as a basis for estimating the probability of eliminating false positive detections;
- Use a representative matrix when making analytical measurements; and,
- Provide guidance on use and limitations to accompany revised definition.

Method Detection Level (MDL)

The lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and representative matrix. An *intralaboratory* MDL estimate represents the average detection capability of a single laboratory for a specific analyte, method and matrix at a given point in time. An *interlaboratory* MDL estimate represents the method detection capability for a specific analyte and specific matrix, determined in more than one laboratory.

Other Definitions

The MDL is based only on the risk of false positive detections (i.e., when is an analyte present?).

There are two other definitions that should be considered:

Reliable Detection Level (RDL) - based on the risk of false negative detections (i.e., when is an analyte absent?)

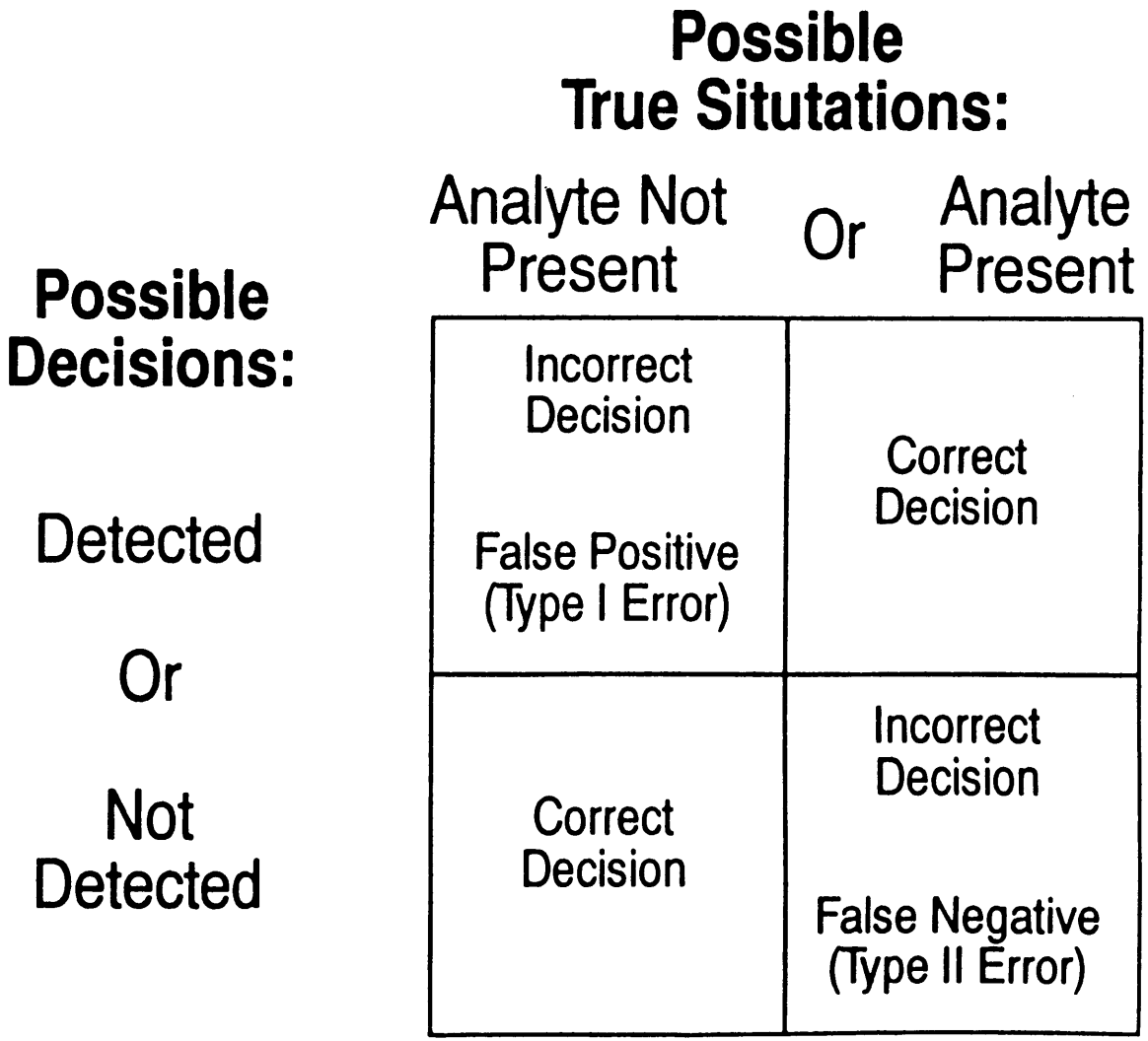
Reliable Quantitation Level (RQL) - a level at which quantitation of a detected analyte has good confidence, based on a single measurement result.

Note: Neither MDL, RDL, or RQL addresses the CORRECTNESS of an analyte identity -- only its detection and estimated concentration.

When Is An Analyte Present?

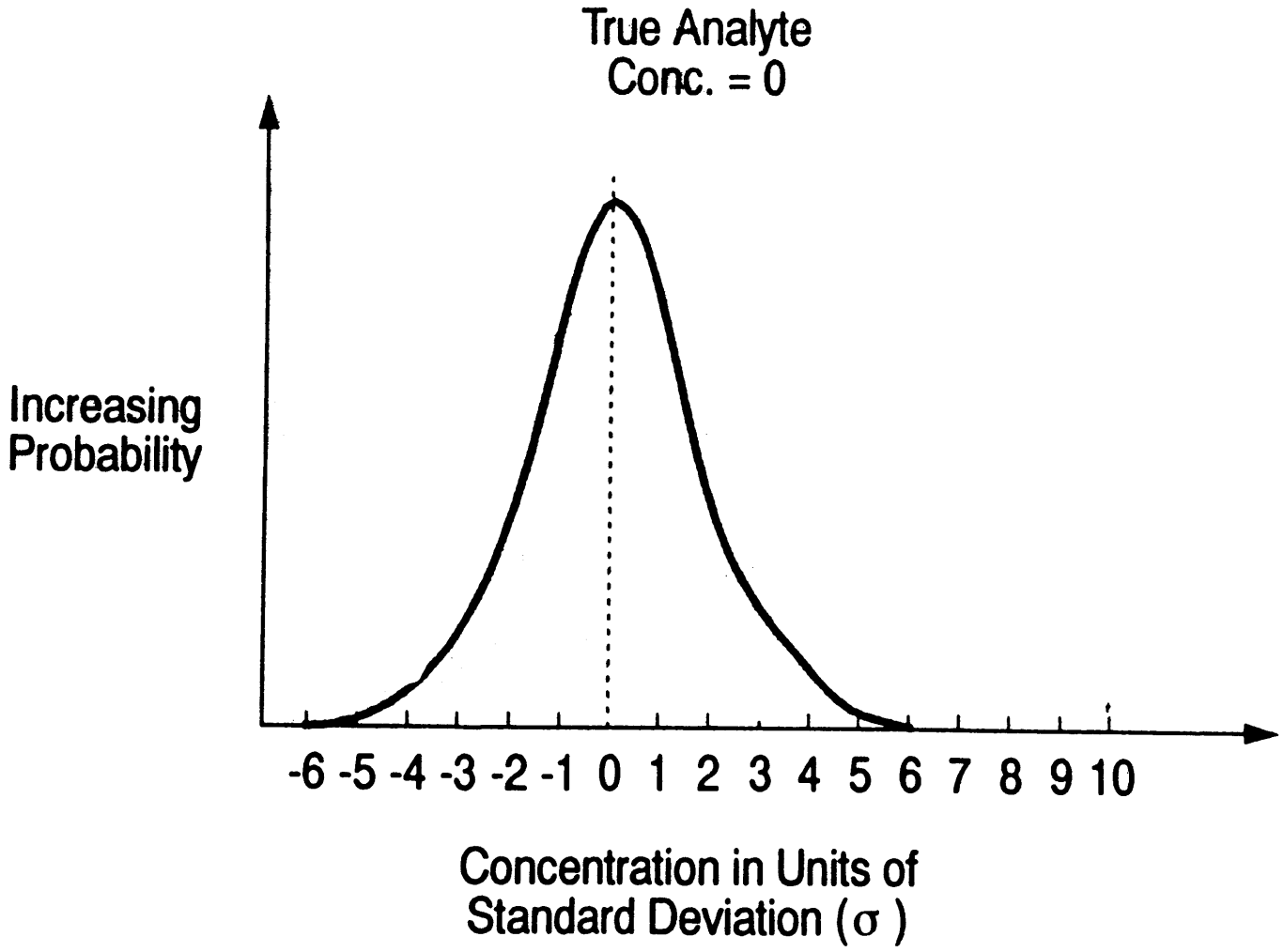
Detection of an identified analyte is the most important decision in low-level analysis. One of the first questions that must be answered is whether the analyte of interest is present in the sample.

A major problem with specifying an MDL is that it is a calculated concentration level that is indirectly selected. The concentration level of an MDL is calculated from the risks of false positives.


Possible True Situtations:
Analyte Not Present
Or
Analyte Present
Possible Decisions:
Detected
Or
Not Detected
Incorrect Decision
False Positive (Type I Error)
Correct Decision
Correct Decision
Incorrect Decision
False Negative (Type II Error)

Consider A Sample With No Analyte

In an example where the true concentration of an analyte is zero, there is, theoretically, an equal probability of positive and negative results, if a normal (Gaussion) error distribution is assumed.

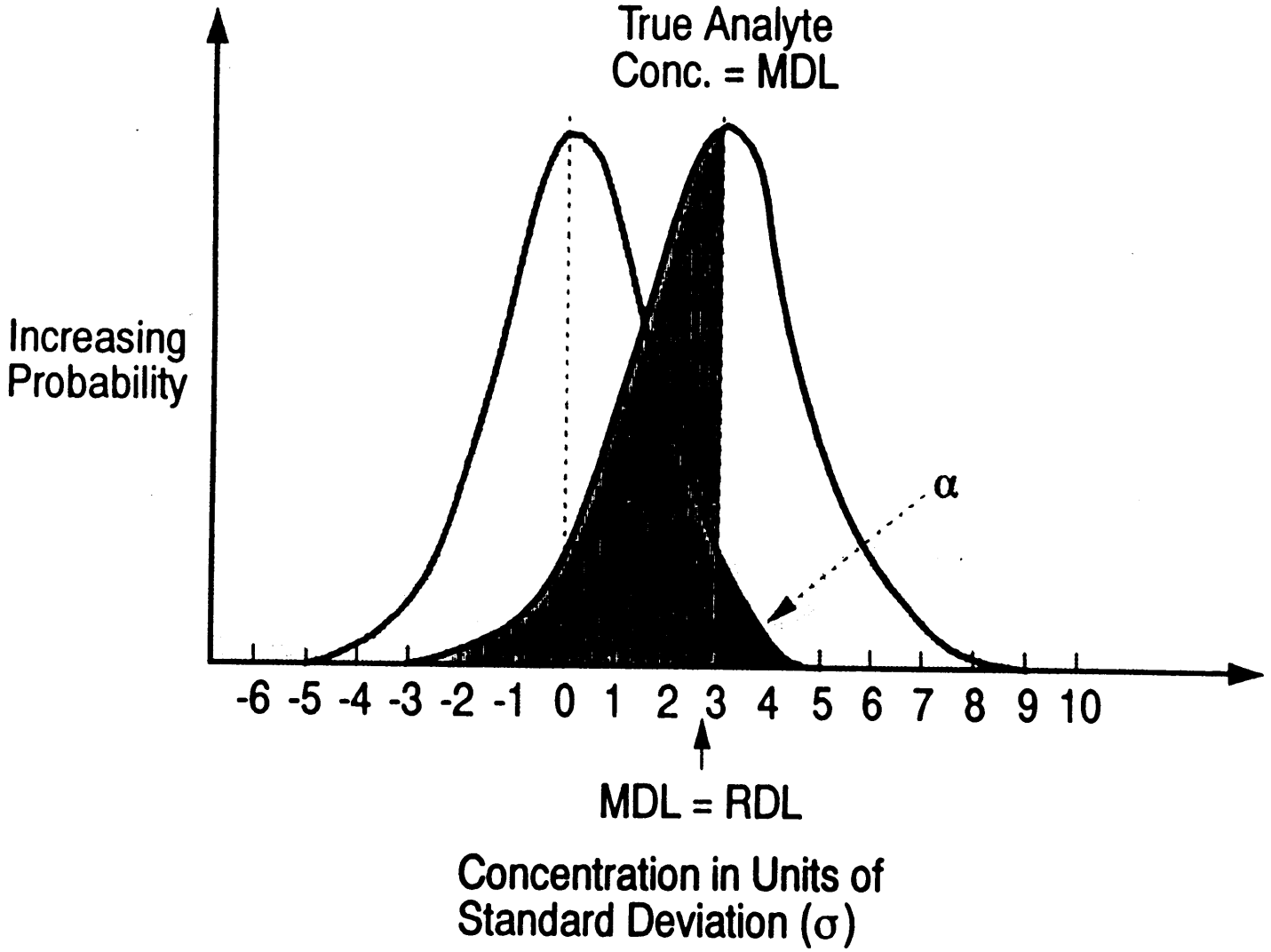

True Analyte
Conc. = 0
Increasing
Probability
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9 10
Concentration in Units of
Standard Deviation (σ)

False Positive Or Negative Risk Is Usually Not Equal

At a true concentration equal to the MDL, there is a 50% probability of an analyte signal falling above the MDL (i.e., 3σ above zero), resulting in a correct decision.

But there is also a 50% probability of the signal falling below the MDL resulting in an incorrect decision (false negative).

At the MDL risk of a false positive is <1% but the risk of a false negative is 50%.


True Analyte
Conc. = MDL
Increasing
Probability
α
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9 10
MDL = RDL
Concentration in Units of
Standard Deviation (σ)

When Is An Analyte Absent?

What About False Negative Detections?

The Method Detection Level addresses statistical confidence for avoiding false positive detections. However, near the recommended MDL of 3σ, while there is a <1% statistical probability of a false positive detection, there is still about a 50% statistically probability of a false negative (Type II error) detection.

A 50% probability of a false negative detection is not very reliable.

Question: What is a reliable level, where there is a very low statistical probability of either a false positive or false negative detection?

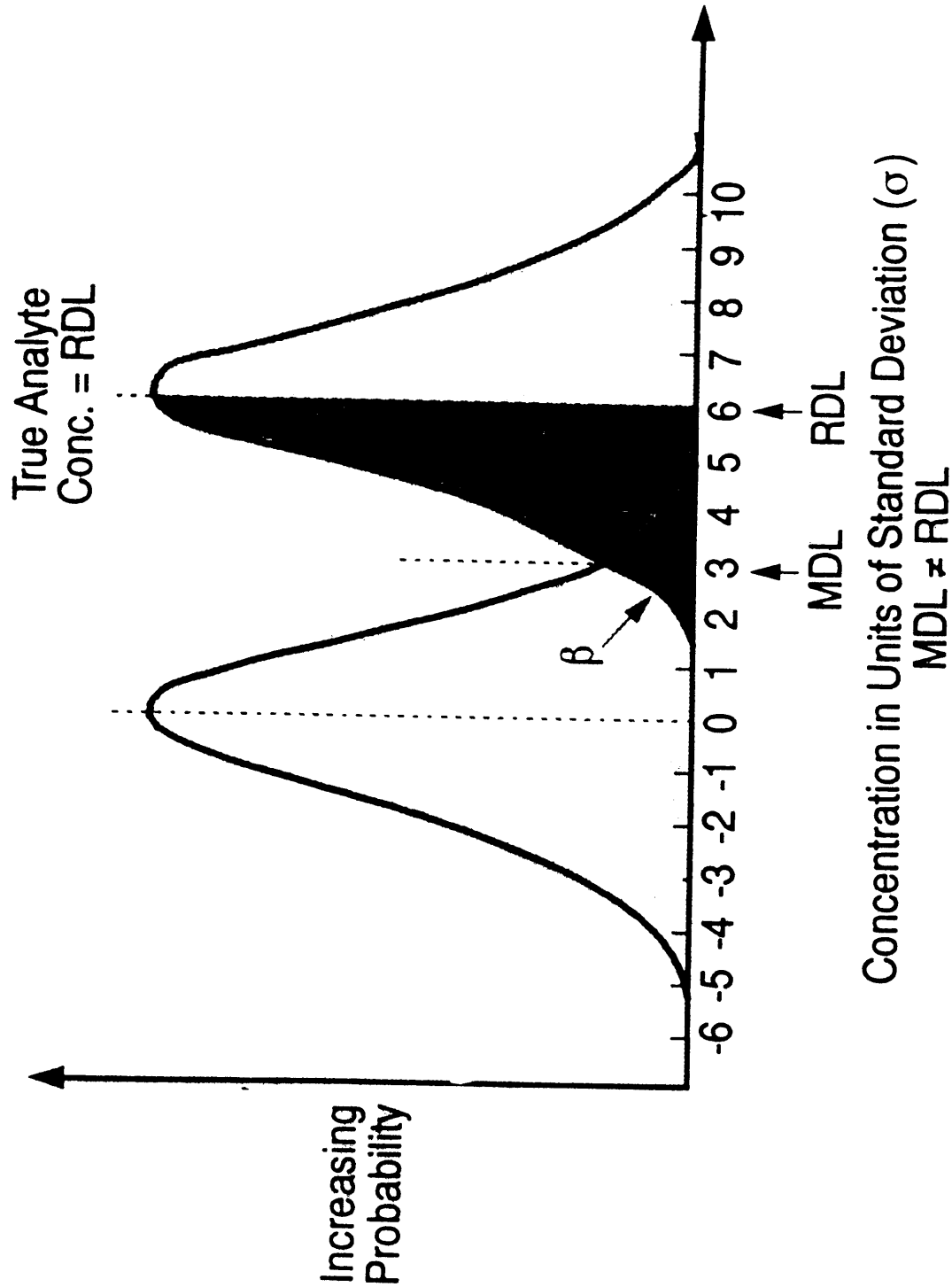
Answer: Twice the Method Detection Level.

Reliable Detection Level

An RDL must therefore be established at a higher concentration than the MDL so the risk of false negatives becomes acceptably low.

If the RDL is set at twice the MDL (i.e., 6σ) then the risk of false positives and false negatives is equal and <1% for each.

If MDL = 3σ, then RDL = 6σ.


True Analyte
Conc. = RDL
Increasing
Probability
β
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9 10
MDL
RDL
Concentration in Units of Standard Deviation (σ)
MDL ≠ RDL

Probability Of False Positive/Negative Determinations

MDL	False Positives [α][1]	RDL	False Negatives [β][2]
3σ	0.1%	3σ	50%
3σ	0.1%	4σ	16%
3σ	0.1%	5σ	2.3%
3σ	0.1%	6σ	0.1%
2.33σ	1%	2.33σ	50%
2.33σ	1%	4.66σ	1%
1.64σ	5%	3.29σ	5%

[1] True Conc. = 0
[2] True Conc. = RDL

Reliable Detection Level (RDL)

For a given MDL, method, and representative matrix, a single analysis should consistently detect analytes present at concentrations equal to or greater than the RDL. When sufficient data are available, the RDL is the experimentally determined concentration at which false negative and false positive rates are specified. Otherwise, the RDL is the concentration which is twice that of the Method Detection Level (RDL = 2 x MDL). The RDL is the recommended lowest level for qualitative decisions based on individual measurements, and it provides a much lower statistical probability of false negative determinations than the MDL.

Reliable Quantitation Level (RQL)

Both MDL and RDL only address the probability of correctly detecting (or not) an analyte which is truly present (or not).

What about a reliable level for quantitating analytes once they have been detected?

- In general, the higher the concentration of an analyte in a representative environmental matrix the more reliably its concentration will be able to be measured using a specific method.
- Unlike definitions of MDL and RDL, a RQL based on individual measurements has no direct statistical basis for its derivation.
- Given the above, any assigned level is arbitrary but it can at least be consistant!

Reliable Quantitation Level (Continued)

- Previous ACS recommendations for an RQL were at 10 σ above an average blank signal.
- The revised proposed level of an RQL is that it be at 2 times the RDL when based on individual measurements.
  - This accommodates various RDLs which may be used.
  - This also usually translates to a value 4x that of an MDL.
  - It provides an arbitrary but consistent relationship between proposed definitions of MDL, RDL, and RQL no matter what level of confidence is selected.
  - It slightly exceeds the original level of 10 σ recommended by ACS when the MDL that is selected is 3 σ. (4 x 3 σ = 12 σ)

Reliable Quantitation Level (RQL)

The RQL is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix. The RQL is the concentration which is two times the Reliable Detection Level (RQL = 2 x RDL). This recognizes that the RDL estimates produced at different times by different operators for different representative matrices will not often exceed the RQL.

Comments On Draft Definitions

- May be modified as a result of public comments
- Will place new emphasis on "representative matrix"
- Will allow flexibility within EPA to vary confidence levels to meet individual needs while using consistent "generic definitions"
- Recommended confidence levels will still be:
  MDL <1% False Positives (3s)
  RDL <1% False Negatives (6s)
  RQL (12s with individual measurements)

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MR. TELLIARD: We have saved the best to last. Dale is going to talk about the new non-conventional pesticides methods compendium that has recently been published.

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METHODS FOR NON-CONVENTIONAL PESTICIDES IN WASTEWATER

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ABSTRACT

On April 10, 1992, the U.S. Environmental Protection Agency (EPA) proposed a regulation to limit the discharge of 122 pesticide active ingredients (PAI's) into navigable waters and into publicly owned treatment works (POTW's) in the U.S. (57 FR 12560). This was a re-proposal of the regulation originally promulgated in 1985 (50 FR 40672) and voluntarily remanded in 1986 (51 FR 44911).

As a part of the proposed regulation, EPA proposed a compendium of analytical methods (Compendium) for the determination of 228 PAI's in wastewater. This Compendium includes the 600 and 1600 Series wastewater methods not promulgated to date and contains at least one method for each of the regulated PAI's. In addition to the methods in the Compendium, EPA also proposed to allow use of the 500 Series Drinking Water methods and the 200 Series metals methods for monitoring the regulated PAI's in discharges.

This paper gives an overview of the regulation and details of the Compendium.

INTRODUCTION

The Federal Water Pollution Control Act (FWPCA), also called the Clean Water Act, was passed by Congress in 1972 (PL 92-500).In 1976, several environmentally concerned plaintiffs brought suit against EPA for failure to enforce certain provisions of this Act.In a Consent Decree (reference 1), the Agency agreed to establish regulations for 23 major categories of industry (reference 2). The pesticides manufacturing industry is the last of the original 23 major industries to be regulated.

The regulation proposed on 10 April follows other EPA regulations to control the discharge of pollutants into surface waters (reference 3), in that the Agency studied the industry intensely to determine what pollutants are generated, which pollutants may be discharged, and the most effective treatment systems for reducing the concentration or amount of these pollutants in the discharge. The proposed regulation controls many of the "toxic pollutants" (the 126 "Priority Pollutants"), but most specifically non-conventional pollutants in the form of pesticide active ingredients (PAI's). Three conventional pollutants [biochemical oxygen demand (BOD), total suspended solids (TSS), and pH] were controlled by the original 1985 regulation.

The 10 April regulation is unique compared to other EPA wastewater regulations in that a given PAI may be manufactured at one or very few plants; the manufacturing process may be unique; the mix of pollutants generated may be unique; and an unusual treatment technology or group of technologies may be required to reduce or eliminate the pollutant in the discharge. The characteristics of the PAI, coupled with the uniqueness of the discharge, present an analytical challenge because routine methods used to measure the conventional or toxic pollutants cannot usually be used to measure PAI's in the discharge. As a result, EPA has adopted or developed methods for measurement of the PAI's.

THE PROPOSED REGULATION

EPA has proposed to establish effluent limitations guidelines based on, "best conventional pollutant control technology" (BCT), "best available technology" (BAT), "new source performance standards" (NSPS) based on "best demonstrated

technology"(BDT), and "pretreatment standards for new sources" (PSNS) and "pretreatment standards for existing sources" (PSES) for new and existing indirect dischargers. Indirect dischargers are those manufacturing plants that discharge to a POTW rather than discharge directly to a surface water. Effluent limitations guidelines are limits on the amount of pollutant allowed to be discharged and are either in the form of a concentration (mass per unit volume of water discharged) or of the maximum amount of the pollutant that can be discharged per amount of product manufactured (mass per unit mass of product manufactured). The discharger typically meets the limitations by using some form of treatment system for pollutant reduction. However, manufacturing process changes, re-use of process water, and improved housekeeping, among other actions, could reduce the cost of, or eliminate the need for, end-of-pipe treatment technologies.

The regulations are proposed for codification at 40 CFR Part 455, and are supported by a development document (reference 4) and an economic analysis (references 5 - 6). Legal authority for the regulation is under sections 301, 304, 306, 307, and 501 of the FWPCA, as amended by the Clean Water Act of 1977 (PL 95-217) and the Water Quality Act of 1987 (PL 100-4).

The preamble to the regulation gives technical data on the following major topics:

EPA's data gathering efforts
Subcategorization of the industry
Water use and wastewater characterization
Pollutant control technologiesEconomic considerations
Water quality analysesNon-water quality environmental impacts
Regulatory implementation

Tables at the end of the proposed regulation list the PAI's and give the proposed effluent limitations for those regulated.

APPROVED METHODS

Methods proposed to be approved for use in monitoring for PAI's are given in Table 1. Included are methods developed for determination of organic pollutants in wastewater and promulgated at 40 CFR Part 136 (49 FR 43234), methods for the determination of organic pollutants in drinking water (references 7 - 8), methods for determination of metals in water and other sample matrices (reference 9), and methods in the Compendium. Table 1 includes at least one EPA method for each analyte. For 24 PAI's, a single method is available; for 35 PAI's, two methods are available; for 26 PAI's, three methods are available; for 6 PAI's, four methods are available; and for 4 PAI's, five methods are available. EPA has allowed this flexibility in methods so that an analyst familiar with a given EPA water method will not be forced to use an alternative method and can overcome matrix interference problems.

EPA has allowed flexibility within methods previously proposed and promulgated. This flexibility is described in detail in the preamble to the 40 CFR Part 136 proposal and promulgation for the determination of organic pollutants in wastewater [49 FR 43234], and permits the analyst to "improve separations and lower the cost of measurements" provided all performance criteria in the method are met. Data documenting that all performance criteria have been met must be retained on file for inspection or later submission to EPA or the State, if requested. One of the objectives in allowing this flexibility is to encourage method improvement, particularly to overcome matrix interferences. EPA believes that promulgating multiple methods and allowing controlled flexibility within these methods will result in reliable and high quality data.

METHODS COMPENDIUM

The Compendium (reference 10) contains 41 methods covering 228 PAI's (analytes). Table 2 gives a list of the analytes, the Chemical Abstracts Service Registry Number for each analyte, and the methods in the Compendium for each analyte.

The purpose of producing the Compendium was to assemble all pesticide methods that EPA had developed and had not promulgated into a single volume so that analysts would have access to these methods. EPA recognizes that this set of methods

does not cover all PAI's ever manufactured. In developing the regulation, EPA studied more than 650 PAI's and found that although methods are available for determination of nearly all of these PAI's in product formulations, plant matter, food products, and other food related matrices, methods were not available for the determination of a majority of these 650 PAI's in environmental samples.

The Compendium includes methods developed by EPA's Environmental Monitoring Systems Laboratory at Cincinnati, Ohio (EMSL-Ci), methods developed by EPA's Engineering and Analysis Division (EAD) within EPA's Office of Science and Technology, and industry method IND-01 for organo-tin compounds. The EMSL-Ci developed methods have three digit numbers beginning with the number six (e.g., 622) and the EAD developed methods have four digit numbers beginning with 16 (e.g., 1656).

Many of the methods included in the Compendium were listed in Appendix E of EPA's original promulgation of the Part 455 rules (50 FR 40708). The methods were withdrawn in 1986 as a part of the remand of these rules (51 FR 44911). In the intervening years between the original promulgation/remand and the present, EPA has developed additional methods, has updated several methods to include more analytes, and has nearly eliminated dependency on industry and contractor developed methods.

DEVELOPMENT OF METHODS

Since the previous methods set was published, the trend of pesticides and herbicides produced and applied in the U.S. has shifted from chlorinated compounds toward phosphorus containing compounds and other substances found to be less persistent in the environment. This change has necessitated the development of analytical methods to measure these compounds in wastewater discharges and in other environmental samples. EPA has therefore developed additional methods as a part of its data gathering efforts for today's proposed rule.

Where possible, EPA avoids development of a new method by testing existing methods to determine if an active ingredient can be measured by these existing methods. If these tests are successful, EPA revises the method to incorporate the new analyte.In addition, EPA has attempted to consolidate multiple methods for the same

analyte by selecting a given method or writing a revised or new method and including as many analytes as possible in this method. For example, EPA has used wide-bore, fused silica capillary columns in recently developed gas chromatography (GC) methods for PAI's to increase resolving power so that more analytes can be measured simultaneously and so that these analytes can be measured at lower levels. Drinking water methods 507, 508, 515.1, and wastewater methods 1656, 1657, and 1658 represent GC methods that encompass large numbers of analytes.

On the other hand, it is frequently not possible to include an analyte or group of analytes in an existing method because the nature of the compound(s) does not lend itself to the techniques in the method. In these instances, an entirely separate method must be developed. In the methods proposed on 10 April, Method 1659 for Dazomet, Method 1660 for the Pyrethrins and Pyrethroids, and Method 1661 for Bromoxynil represent examples of methods that were developed specifically for an analyte or group of analytes.The method for Dazomet employs a base hydrolysis to convert Dazomet to methyl isothiocyanate (MITC) and gas chromatography with a fused silica capillary column and nitrogen/phosphorus detector for selective detection of MITC. The method for the Pyrethrins and Pyrethroids employs acetonitrile extraction of a salt saturated wastewater sample and high performance liquid chromatography (HPLC) for selective detection of these analytes.The method for Bromoxynil employs direct aqueous injection HPLC.

EPA solicited comments on the Compendium, and will attempt to use the comments to aid in further improvement of the methods.Informal, constructive comments on the methods may be submitted at any time to the EPA Sample Control Center (see reference 10).

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7. "Methods for the Determination of Organic Compounds in Drinking Water" EPA 600/4-89/039, Revised July 1991, National Technical Information Service, 5285 Port Royal Rd, Springfield VA 22162 (PB91-231480) (December 1988).

8. "Methods for the Determination of Organic Compounds in Drinking Water - Supplement I" EPA 600/4-90/020, National Technical Information Service, 5285 Port Royal Rd, Springfield VA 22162 (PB91-146027) (July 1990).

9. "Methods for the Determination of Metals in Environmental Samples" EPA 600/4-90/010, National Technical Information Service, 5285 Port Royal Rd, Springfield VA 22162 (PB91-231498) (June 1991).

10. "Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater", available from EPA Sample Control Center, 300 N Lee St, Alexandria VA 22314 (April 1992).

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Table 1

Methods Required for Nonconventional Pesticide Pollutants (1)

Name	CAS Registry Number (2)	PC Code (3)	Method(s)
Acephate	30560191	103301	1656
Acifluorfen	50594666	114401	1656/515.1
Alachlor	15972608	90501	1656/505/507/645
Aldicarb (Temik)	116063	98301	531.1
Ametryn	834128	80801	507/619
Atrazine	1912249	80803	1656/505/507/619
Azinphos methyl (Guthion)	86500	58001	1657/614/622
Benfluralin (Benefin)	1861401	84301	1656/627
Benomyl	17804352	99101	631
Biphenyl	92524	17002	1625/642
Bolstar (Sulprofos)	35400432	111501	622
Bromacil	314409	12301	1656/507/633
Bromacil, lithium salt	53404196	12302	1656/507/633
Bromoxynil	1689845	35301	1661/1625
Bromoxynil octanoate	1689992	35302	1656
Busan 40	51026289	102901	630/630.1
Busan 85	128030	34803	630/630.1
Butachlor	23184669	112301	1656/507/645
Captafol	2425061	81701	1656
Carbam-S	128041	34804	630/630.1
Carbaryl	63252	56801	531.1/632
Carbofuran	1563662	90601	531.1/632
Chloroneb	2675776	27301	508/608.1
Chlorothalonil	1897456	81901	1656/508/608.2
Chlorpyrifos	2921882	59101	1657/508/622
Cyanazine	21725462	100101	629
Dazomet	533744	35602	1659
2,4-D	94757	30001	1658/515.1/615
2,4-D Salts & Esters	94757		1658/515.1/615
2,4-DB Salts & Esters	94826	30801	1658/515.1/615
DCPA (Dacthal)	1861321	78701	1656/508/608.2
DEF	78488	74801	1657
Diazinon	333415	57801	1657/507/614/622
Dichlorprop Salts & Esters	120365		1658/515.1/615
Dichlorvos	62737	84001	1657/507/622
Dinoseb	88857	37505	1658/515.1/615
Dioxathion	78342	37801	614.1
Disulfoton	298044	32501	1657/507/614/622
Diuron	330541	35505	632
Endothall Salts & Esters	145733		548
Endrin*	72208	41601	1656/505/508/608/617
Ethalfluralin	55283686	113101	1656/627
Ethion	563122	58401	1657/614/614.1
Fenarimol (Rubigan)	60168889	206600	1656/507/633.1
Fensulfothion	115902	32701	1657/622
Fenthion	55389	53301	1657/622
Fenvalerate (Pydrin)	51630581	109301	1660
Glyphosate Salts & Esters	1071836	103601	547
Heptachlor*	76448	44801	1656/505/508/608/617
Isopropalin (Paarlan)	33820530	100201	1656/627
KN methyl	137417	39002	630/630.1
Linuron	330552	35506	632
MCPA Salts & Esters	94746	30501	1658/615
MCPP Salts & Esters	93652	31501	1658/615
Malathion	121755	57701	1657/614
Merphos (Tribufos)	150505	74901	1657/622/507
Methamidophos	10265926	101201	1657
Methomyl	16752775	90301	531.1/632
Methoxychlor	72435	34001	1656/505/508/608.2/617
Metribuzin	21087649	101101	1656/507/633
Mevinphos	7786347	15801	1657/507/622
Nabam	142596	14503	630/630.1
Nabonate	138932	63301	630.1
Naled	300765	34401	1657/622
Norfluorazon	27314132	105801	1656/507/645
Organotin (as Tin=7440315)	0-192		200.7/200.9/IND-01
Parathion ethyl	56382	57501	1657/614
Parathion methyl	298000	53501	1657/614/622
PCNB	82688	56502	1656/608.1/617
Pendimethalin (Prowl)	40487421	108501	1656
Permethrin	52645531	109701	1656/1660/608.2/508

Table 1 *(continued)*

Name	CAS Registry Number (2)	PC Code (3)	Method(s)
Pentachlorophenol*	87865	63001	525/604/625/1625
Phorate	298022	57201	1657/622
Phosmet	732116	59201	1657/622.1
Prometon (Promitol)	1610180	80804	507/619
Prometryn	7287196	80805	507/619
Pronamide (Kerb)	23950585	101701	507/633.1
Propachlor	1918167	19101	508/608.1
Propanil	709988	28201	632.1
Propazine	139402	80808	507/619
Pyrethrin I	121211	69008	1660
Pyrethrin II	121299	69006	1660
Simazine	122349	80807	505/507/619
Stirofos (Tetrachlorvinphos)	22248799	83701	1657/507/622
TCMTB	21564170	35603	637
Tebuthiuron (Spike)	34014181	105501	507
Terbacil	5902512	12701	507/633
Terbufos (Counter)	13071799	105001	1657/507/614.1
Terbuthylazine (Gardoprim)	5915413	80814	619
Terbutryn	886500	80813	507/619
Toxaphene*	8001352	80501	1656/505/508/608/617
Triadimefon (Bayleton)	43121433	109901	507/633
Trifluralin	1582098	36101	508/617/627
Vapam (Metam)	137428	39003	630/630.1
Ziram	137304	34805	630/630.1

(1) Method numbers have been updated since publication of the proposed regulation [57 FR 12560]
(2) A number assigned by the Chemical Abstracts Service Registry
(3) Pesticide Code, formerly the Shaughnessy code—a code issued by EPA's Office of Pesticide Programs
* Priority Pollutant

Table 2

Pesticides with Methods in the Compendium

Pesticide	CAS Registry Number	Applicable Method(s)
Acephate	30560-19-1	1656,1657
Acifluorfen	50594-66-6	1656
Alachlor	15972-60-8	645
Aldrin	309-00-2	617,1656
Allethrin (Pynamin)	584-79-2	1660
Ametryn	834-12-8	619
Aminocarb	2032-59-9	632
Amobam	3566-10-7	630,630.1
AOP	—	630
Aspon	3244-90-4	622.1
Atraton	1610-17-9	619
Atrazine	1912-24-9	619,1656
Azinphos ethyl	2642-71-9	1657
Azinphos methyl	86-50-0	614,622,1657
Barban	101-27-9	632
Basalin (Fluchloralin)	33245-39-5	646
Bendiocarb	22781-23-3	639
Benfluralin	1861-40-1	627,1656
Benomyl	17804-35-2	631
Bensulide	741-58-2	636
Bentazon (Basagran)	25057-89-0	643
alpha-BHC	319-84-6	617,1656
beta-BHC	319-85-7	617,1656
gamma-BHC	58-89-9	617,1656
delta-BHC	319-86-8	617,1656
Biphenyl	92-52-4	642
Bromacil	314-40-9	633,1656
Bromoxynil octanoate	1689-99-2	1656
Bromoxynil	1689-84-5	1661
Busan 40	51026-28-9	630,630.1
Busan 85	128-03-0	630,630.1
Butachlor	23184-66-9	645,1656

Table 2 *(continued)*

Pesticide	CAS Registry Number	Applicable Method(s)
Butylate	2008-41-5	634
Captafol	2425-06-1	1656
Captan	133-06-2	617,1656
Carbam-S	128-04-1	630,630.1
Carbaryl	63-25-2	632
Carbendazim	10605-21-7	631
Carbofuran	1563-66-2	632
Carbophenothion	786-19-6	617,1656
CDN	97-00-7	646
Chlordane	5103-74-2	617,1656
Chlorfevinphos	470-90-6	1657
Chlorobenzilate	510-15-6	608.1,1656
Chloroneb	2675-77-6	608.1,1656
Chloropicrin	76-06-2	618
Chloropropylate	5836-10-2	608.1,1656
Chlorothalonil	1897-45-6	608.2,1656
Chlorpropham	101-21-3	632
Chlorpyrifos methyl	5598-13-0	622,1657
Chlorpyrifos	2921-88-2	622,1657
Coumaphos	56-72-4	622,1657
Crotoxyphos	7700-17-6	1657
Cyanazine	21725-46-2	629
Cycloate	1134-23-2	634
Cycloprate	54460-46-7	616
Cyfluthrin (Baythroid)	68359-37-5	1660
Dalapon	75-99-0	615,1658
Dazomet	533-74-4	1659
2,4-D	94-75-7	615,1658
2,4-DB	94-82-6	615,1658
DBCP	96-12-8	1656
DCPA	1861-32-1	608.2
4,4'-DDD	72-54-8	617,1656
4,4'-DDE	72-55-9	617,1656
4,4'-DDT	50-29-3	617,1656
Deet	134-62-3	633
DEF	78-48-8	1657
Demeton	8065-48-3	614,622,1657
Diallate	2303-16-4	1656
Diazinon	333-41-5	614,622,1657
Dibromochloropropane	96-12-8	608.1
Dicamba	1918-00-9	615,1658
Dichlofenthion	97-17-6	622.1,1657
Dichlone	117-80-6	1656
Dichloran	99-30-9	608.2,617
Dichlorophene	97-23-4	604.1
Dichlorprop	120-36-5	615,1658
Dichlorvos	62-73-7	622,1657
Dicofol	115-32-2	617,1656
Dicrotophos	141-66-2	1657
Dieldrin	60-57-1	617,1656
Dimethoate	60-51-5	1657
Dinocap	39300-45-3	646
Dinoseb	88-85-7	615,1658
Dioxathion	78-34-2	614.1,1657
Diphenamid	957-51-7	645
Diphenylamine	122-39-4	620
Disulfoton	298-04-4	614,622,1657
Diuron	330-54-1	632
Endosulfan I	959-98-8	617,1656
Endosulfan II	33213-65-9	617,1656
Endosulfan sulfate	1031-07-8	617,1656
Endrin aldehyde	7421-93-4	617,1656
Endrin	72-20-8	617,1656
Endrin ketone	53494-70-5	1656
EPN	2104-64-5	614.1,1657
EPTC	759-94-4	634
Ethalfluralin	55283-68-6	627,1656
Ethion	563-12-2	614,614.1,1657
Ethoprop	13194-48-4	622,1657
Ethylene dibromide	106-93-4	618

Table 2 *(continued)*

Pesticide	CAS Registry Number	Applicable Method(s)
Etridiazole	2593-15-9	608.1,1656
EXD	502-55-6	630.1
Famphur	52-85-7	622.1,1657
Fenarimol (Rubigan)	60168-88-9	633.1,1656
Fenitrothion	122-14-5	622.1
Fensulfothion	115-90-2	622,1657
Fenthion	55-38-9	622,1657
Fenuron	101-42-8	632
Fenuron-TCA	4482-55-7	632
Fenvalerate	51630-58-1	1660
Ferbam	14484-64-1	630,630.1
Fluometuron	2164-17-2	632
Fluridone	59756-60-4	645
Fonophos	944-22-9	622.1
Heptachlor epoxide	1024-57-3	617,1656
Heptachlor	76-44-8	617,1656
Hexachlorophene	70-30-4	604.1
Hexamethyl-phosphoramide	680-31-9	1657
Hexazinone	51235-04-2	633
Isodrin	465-73-6	617,1656
Isopropalin	33820-53-0	627,1656
Kepone	143-50-0	1656
Kinoprene	42588-37-4	616
KN Methyl	137-41-7	630,630.1
Leptophos	21609-90-5	1657
Lethane	112-56-1	645
Linuron	330-55-2	632
Malathion	121-75-5	614,1657
Mancozeb	8018-01-7	630
Maneb	12427-38-2	630
MBTS	120-78-5	637
MCPA	94-74-6	615,1658
MCPP	7085-19-0	615,1658
Mercaptobenzothiazole	149-30-4	640
Merphos	150-50-5	622,1657
Metham	137-42-8	630,630.1
Methamidophos	10265-92-6	1657
Methiocarb	2032-65-7	632
Methomyl	16752-77-5	632
Methoprene	40596-69-8	616
Methoxychlor	72-43-5	608.2,617,1656
Metribuzin	21087-64-9	633,1656
Mevinphos	7786-34-7	622,1657
Mexacarbate	315-18-4	632
MGK 264-A	113-48-4	633.1
MGK 264-B	113-48-4	633.1
MGK 326	136-45-8	633.1
Mirex	2385-85-5	617,1656
Molinate	2212-67-1	634
Monocrotophos	6923-22-4	1657
Monuron	150-68-5	632
Monuron-TCA	140-41-0	632
Nabam	142-59-6	630,630.1
Nabonate	138-93-2	630.1
Naled	300-76-5	622,1657
Napropamide	15299-99-7	632.1
Neburon	555-37-3	632
Niacide	8011-66-3	630
Nitrofen (TOK)	1836-75-5	1656
Norflurazon	27314-13-2	645,1656
Organo-tin	—	IND-01
Oryzalin	19044-88-3	638
Oxamyl	23135-22-0	632
Parathion ethyl	56-38-2	614,1657
Parathion methyl	298-00-0	614,622,1657
PCB-1016	12674-11-2	617,1656
PCB-1221	11104-28-2	617,1656
PCB-1232	11141-16-5	617,1656
PCB-1242	53469-21-9	617,1656

Table 2 *(continued)*

Pesticide	CAS Registry Number	Applicable Method(s)
PCB-1248	12672-29-6	617,1656
PCB-1254	11097-69-1	617,1656
PCB-1260	11096-82-5	617,1656
PCNB	82-68-8	608.1,617,1656
Pebulate	1114-71-2	634
Pendimethalin	40487-42-1	1656
Permethrin	52645-53-1	608.2,1656,1660
Perthane	72-56-0	617,1656
o-Phenylphenol	132-27-4	642
Phorate	298-02-2	622,1657
Phosmet	732-11-6	622.1,1657
Phosphamidon	13171-21-6	1657
Picloram	1918-02-1	644
Polyram	9006-42-2	630
Profluralin	26399-36-0	627
Prometon	1610-18-0	619
Prometryn	7287-19-6	619
Pronamide	23950-58-5	633.1
Propachlor	1918-16-7	608.1,1656
Propanil	709-98-8	632.1
Propazine	139-40-2	619,1656
Propham	122-42-9	632
Propoxur	114-26-1	632
Pyrethrin I	121-21-1	1660
Pyrethrin II	121-29-9	1660
Resmethrin	10453-86-8	616,1660
Ronnel	299-84-3	622,1657
Rotenone	83-79-4	635
Secbumeton	26259-45-0	619
Siduron	1982-49-6	632
Simazine	122-34-9	619,1656
Simetryn	1014-70-6	619
Sodium dimethyldi-thiocarbamate	128-04-1	630,630.1
Stirofos (Tetrachlorvinphos)	961-11-5	622,1657
Strobane	8001-50-1	617,1656
Sulfotepp	3689-24-5	1657
Sulprofos (Bolstar)	35400-43-2	622
Sumithrin (Phenothrin)	26002-80-2	1660
Swep	1918-18-9	632
2,4,5-T	93-76-5	615,1658
TCMTB	21564-17-0	637
TEPP	107-49-3	1657
Terbacil	5902-51-2	633,1656
Terbufos	13071-79-9	614.1,1657
Terbuthylazine	5915-41-3	619,1656
Terbutryn	886-50-0	619
Tetramethrin	7696-12-0	1660
Thiabendazole	148-79-8	641
Thionazin	297-97-2	622.1
Thiram	137-26-8	630,630.1
Tokuthion	34643-46-4	622,1657
Toxaphene	8001-35-2	617,1656
2,4,5-TP	93-72-1	615,1658
Triadimefon	43121-43-3	633,1656
Trichlorofon	52-68-6	1657
Trichloronate	327-98-0	622,1657
Tricresylphosphate	78-30-8	1657
Tricyclazole	41814-78-2	633
Trifluralin	1582-09-8	617,627,1656
Trimethylphosphate	512-56-1	1657
Trithion methyl	953-17-3	1657
Vacor	53558-25-1	632.1
Vernolate	1929-77-7	634
ZAC	—	630
Zineb	12122-67-7	630,630.1
Ziram	137-30-4	630,630.1

CLOSING REMARKS

MR. TELLIARD: I would like to thank you all for coming. We have been doing this for 15 years, and we are going to try to get it right one time. We will be back next year.

I would like to thank Harry McCarty for putting together the technical program, and I would like to thank Jan Sears arrangement for the aquarium and the steak house activity and I would like to ask you for a round of applause for their people.

Next year's agenda is open for discussion. If you have any ideas of sessions you would like to have or think would be advantageous, informative, and so forth, please give me a buzz and drop me a line, and we will see if we can accommodate you. If you have suggestions on papers or if you would like to present at this assembly, please give me a call. You only have 12 months and 28 days left to get it in, because we are always about a year late.

So, thanks so much for coming, thank you for your attention, and thank you, speakers.

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15th ANNUAL EPA CONFERENCE ON ANALYSIS OF POLLUTANTS IN THE ENVIRONMENT

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