United States
Environmental Protection
Agency

Office of
Water Programs
Washington DC 20460

Norfolk Va.
January 17-18, 1980

Water

EPA

Seminar for Analytical Methods for Priority Pollutants

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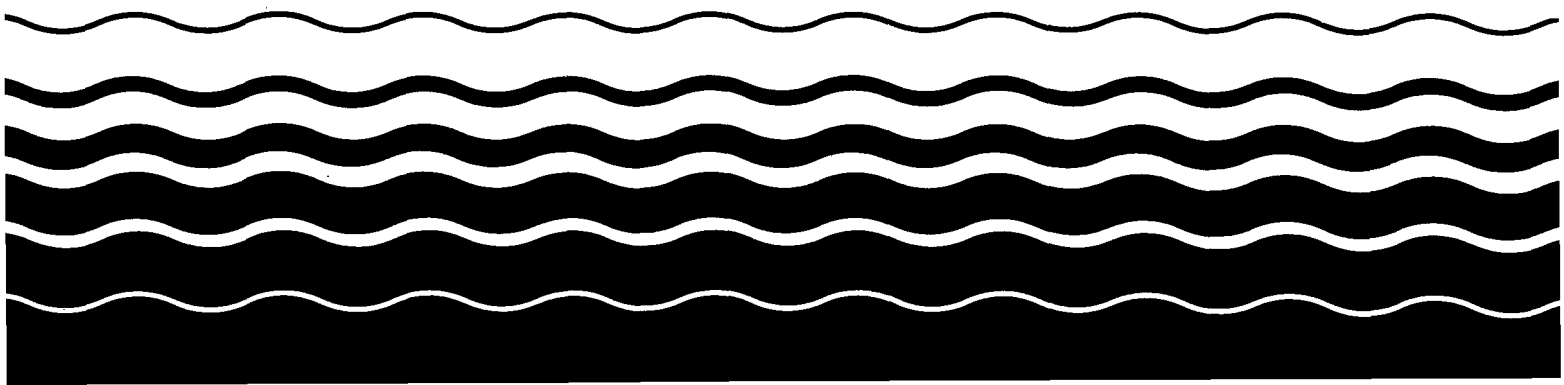

PREFACE

The Effluent Guidelines Division of EPA has been sponsoring a series of meetings to promote the free exchange of technical information among contractors, EPA personnel, and various industry groups concerned with analytical methods for the measurement of priority pollutants.

This paper summarizes the proceedings of a meeting held in Norfolk, Virginia, on the 17th and 18th days of January, 1980.

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INTRODUCTION

BY: WILLIAM TELLIARD
ROBERT SCHAFFER

MR. TELLIARD: GOOD MORNING. MY NAME IS BILL TELLIARD, AND I'M FROM EPA. AS SOME OF YOU MAY OR MAY NOT KNOW, WE'VE DONE THIS BEFORE, SO THIS MORNING, TO GET THINGS STARTED OFF, WE'D LIKE TO HAVE BOB SCHAFFER, THE DIVISION DIRECTOR FOR EGD, SAY A FEW THINGS, AND THEN WE HAVE A WHOLE LIST OF ANNOUNCEMENTS AND PROMISES TO MAKE YOU, AND THEN WE'LL GET TO THE FIRST SPEAKER.

MR. SCHAFFER: ONCE AGAIN, WELCOME TO NORFOLK AND OUR SEMINAR ON ANALYTICAL METHODS FOR PRIORITY POLLUTANTS. I WAS THINKING ON THE WAY DOWN, THE ONE REASON I GET TO COME IS BECAUSE I'M PAYING FOR IT. WE DON'T HAVE TO HAVE ANY KEYNOTE SPEAKERS OR ANY DIGNITARIES HERE TO GET A PRETTY GOOD CROWD, SO IT LOOKS AS IF YOU'RE ALL INTERESTED IN THE SUBJECT MATTER. I HOPE YOU'LL HAVE A GOOD SESSION.

I DON'T HAVE A GREAT DEAL TO SAY. WE'VE BEEN HERE BEFORE, AND SOME OF YOU WERE HERE YESTERDAY AT CHEMICAL MANUFACTURERS ASSOCIATION MEETING, WHO HAD A SIMILAR SESSION, AND YOU MAY GET SOME OF THE INPUT FROM THEIR DELIBERATIONS AS WELL TODAY.

SINCE OUR LAST MEETING, WE'VE MOVED INTO THE PHASE OF PROPOSING REGULATIONS BASED ON THE DATA THAT WE'RE GATHERING USING THE METHODS THAT YOU'VE BEEN DEVELOPING. I SAY THE METHODS THAT YOU'VE BEEN DEVELOPING BECAUSE THEY ARE STILL EVOLVING, AND WE'RE AWARE OF THAT. WE'VE COME A LONG WAY IN THAT WE KNOW A LOT MORE ABOUT WHAT WE'RE DOING AND WHAT OUR DATA MEANS AND WHAT TOXIC POLLUTANTS NEED TO BE CONTROLLED IN WHAT INDUSTRIES. WE'VE TRIED SOME NEW APPROACHES IN THE PROPOSED REGULATIONS, AND WE'LL TRY MORE IN THE FUTURE, AT LEAST UNTIL WE'RE ABLE TO USE THE SPECIFIC METHOD TO SET A LIMIT FOR A SPECIFIC TOXIC MATERIAL.

WE'RE NOT TOO CONCERNED ABOUT THE FACT THAT WE DON'T BECAUSE WE STILL FEEL WE'RE ABLE TO CONTROL THE TOXIC POLLUTANTS WITH THE APPROACHES THAT WE HAVE AVAILABLE TO US.

ANALYTICAL CHEMISTRY IS A FIELD THAT IS NOT FAMILIAR TO MANY FOLKS OUTSIDE THIS ROOM. I THINK THAT WHAT WE'RE DOING, IN A SENSE, IS DRAGGING THE AGENCY, ALBEIT KICKING AND SCREAMING, INTO THE FOREFRONT OF ANALYSIS OF ENVIRONMENTAL SAMPLES FOR SPECIFIC ORGANIC COMPOUNDS. I KNOW THAT MANY OF YOU HAVE SPENT HOURS, SOME VERY FRUSTRATING, IN MAKING WHAT PROGRESS WE HAVE TO DATE. I THINK THAT THE EFFORT WILL CONTINUE FOR A PERIOD OF TIME AND PROBABLY EXPAND. WE WERE TALKING

A LITTLE BIT YESTERDAY ABOUT MATRIX EFFECTS AND SO FORTH; WE'LL PROBABLY HAVE A FEW MORE WHEN WE GET INTO SOLID WASTE SAMPLES. WE'RE LOOKING TO MOVE INTO THIS AREA WITH THESE ANALYTICAL TECHNIQUES OR SIMILAR ANALYTICAL TECHNIQUES. AS MANY OF YOU KNOW, SOLID WASTE IS THE NEXT AREA THAT THE AGENCY IS MOVING INTO, THE REGULATION AND CONTROL OF THE DISPOSAL OF HAZARDOUS MATERIALS.

I WANT TO COMPLIMENT YOU ON YOUR PATIENCE AND DILIGENCE. WE'RE TRYING VERY HARD TO MAKE SURE THAT THE FEARS OF THE ONES THAT ARE BEING REGULATED BY OUR EFFORTS ARE ALLEVIATED TO A DEGREE. WE'RE TRYING TO MAINTAIN THE POSITION THAT WE REALLY AREN'T GOING TO DO SOMETHING CRAZY WITH THE DATA WE'RE GATHERING; NOBODY BELIEVES US YET, BUT WE'RE GOING TO PERSIST. WE DO NEED THE HELP, WE DO NEED SUGGESTIONS. BEING ON THE FOREFRONT, WE ARE DEVELOPING REGULATIONS AND METHODS AT THE SAME TIME. IT IS A LITTLE BIT UNIQUE; RATHER THAN HAVING TOOLS AVAILABLE TO US, WE HAVE TO DEVELOP THE TOOLS AS WE'RE GOING ALONG.

I HOPE YOU HAVE ANOTHER SUCCESSFUL MEETING AND THAT YOU GET SOMETHING OUT OF IT, AND IF WE HAVEN'T SOLVED ALL THE PROBLEMS BY THE END OF TOMORROW, WE MAY HAVE ANOTHER ONE NEXT YEAR. WE'RE SUSPICIOUS THAT WE'VE GOT ALL THE PROBLEMS SOLVED; THAT'S WHAT BILL

TOLD ME EARLIER, ANYWAY. NOW I'LL TURN THE PROGRAM BACK OVER TO BILL. I WILL BE AROUND FOR THE REST OF THE DAY. IF THERE ARE ANY PARTICULAR QUESTIONS THAT YOU HAVE ABOUT SOME OTHER ASPECTS OF THE PROGRAM, I'D BE HAPPY TO CHAT WITH YOU.

MR. TELLIARD: THANK YOU. WE HAVE A COUPLE OF QUICK ANNOUNCEMENTS. ONE IS, IF EVERYONE MAKES SURE THEY PLEASE REGISTER. WE WANT TO MAKE SURE YOU REGISTER BECAUSE THAT'S WHERE WE GET THE LIST TO SEND OUT THE INVITATIONS IF THERE IS ANOTHER ONE OF THESE SOME DAY. WE HAVE A COUPLE OF BREAKS SCHEDULED. WE ALSO HAVE AN OPEN SESSION TODAY, WHICH IS THE END PRODUCT OF PEOPLE SAYING WHAT ABOUT AND WHAT ABOUT AND WHAT ABOUT. SO THERE ARE A COUPLE OF FOLKS WHO ASKED TO HAVE NOT REALLY A BIG CHUNK OF TIME, SO WE JUST OPENED THE SESSION AND SAID FINE. IT STARTS AT 4, AND IT WILL RUN UNTIL THE BAND STARTS PLAYING, AND WE CAN DO THAT, AND IT'S KIND OF AS LONG AS YOU FOLKS WANT TO HAMMER ON SOME STUFF--EVERYTHING EXCEPT TUNING YOUR INSTRUMENT.

THE FIRST SPEAKERS TODAY ARE GOING TO TALK ABOUT A MICROEXTRACTION PROCEDURE THAT IS BEING UTILIZED BY THE ORGANIC CHEMICALS BRANCH FOR ANALYSIS OF, RIGHT NOW, A GREAT DEAL OF IN-PROCESS SAMPLES. THIS PARTICULAR METHODOLOGY IS UNIQUE TO THE ORGANIC CHEMICALS BRANCH

BECAUSE THEY'RE THE ONLY ONES DOING IT. SO WE THOUGHT WE WOULD LIKE TO HAVE THEM SAY SOMETHING ABOUT IT SO MAYBE SOME OF US CAN FALL BY THE WAYSIDE AND TRY IT, TOO.

WE'VE GOT THREE SPEAKERS, AND WE'D LIKE TO HAVE YOU HOLD YOUR QUESTIONS UNTIL EVERYBODY IS DONE. THE FIRST ONE IS JOHN RHOADES FROM SOUTHWEST RESEARCH INSTITUTE. THE SECOND PERSON WILL BE KATHY THRUN FROM ADL, A. D. LITTLE; THEN BILL COWEN FROM CATALYTIC. JOHN, DO YOU WANT TO START?

MICROEXTRACTION METHOD FOR SAMPLE PREPARATION

BY: JOHN RHOADES
KATHY THRUN
WILLIAM COWEN

MR. RHOADES: I KNOW THAT YOU'RE ALL WELL AWARE OF THE FACT THAT THE GAS CHROMATOGRAPHY WITH ITS SELECTIVE DETECTORS IS THE PRIMARY INSTRUMENTATION AND TECHNIQUE USED FOR THE DETERMINATIVE STEPS FOR MOST OF THE PRIORITY POLLUTANTS. UNFORTUNATELY, THERE IS A SAMPLE PREPARATION REQUIRED BEFORE ANY OF THIS GC ANALYSIS. NOW, THE PRESENT APPROACH, AND I'M SURE THAT YOU'RE WELL AWARE OF THIS AGAIN, IS TO TAKE A LITER OR A HALF A LITER OF WASTEWATER AND EXTRACT IT MULTIPLE TIMES WITH SEVERAL MILLILITERS OF SOLVENT. NOW, THERE'S SEVERAL DIFFERENT DETAILS ON THIS ONE, BUT I'M GOING TO LUMP THESE, AT THE MOMENT, INTO WHAT I'LL CALL THE EXHAUSTIVE EXTRACTION APPROACH TO DIFFERENTIATE WHAT I PROPOSE TO TALK ABOUT IN A MINUTE. NOW, WITH THAT APPROACH, THEN, THE COMBINED EXTRACT IS USUALLY CONCENTRATED IN A K-D AND USUALLY FOLLOWED BY SOME FORM OF COLUMN CHROMATOGRAPHY CLEANUP. I'M SURE YOU'RE ALL PRETTY WELL AWARE OF THIS.

NOW, IN THEORY, THIS IS A GOOD APPROACH. THERE'S ABSOLUTELY NOTHING WRONG WITH IT. YOU DO RUN INTO SOME PROBLEMS IN ACTUAL PRACTICE, IF YOU'VE BEEN OUT IN THE LAB AND DONE SOME OF THESE. NAMELY, YOU HAVE PROBLEMS TO SOME EXTENT WITH EMULSIONS; THERE IS ALSO A LOT OF GLASSWARE TO KEEP CLEAN. YOU HAVE TO BE QUITE METICULOUS; AND WHAT I BELIEVE IS BECOMING ONE OF THE PARTICULAR PROBLEMS WITH IT IS THAT YOU MAY BE EXCESSIVELY EXTRACTING INTERFERING MATERIALS. SO IT REALLY WORKS BEST WITH FAIRLY CLEAN SAMPLES.

NOW, WE HAVE BEEN USING AN ALTERNATE EXTRACTION APPROACH AT SOUTHWEST RESEARCH INSTITUTE. IT HAS CONSIDERABLE PROMISE AND HAS BEEN LABELED MICROEXTRACTION FOR THE LACK OF ANY BETTER NAME; BUT BASICALLY, MICROEXTRACTION IS VERY SIMPLE. IT'S A SINGLE EXTRACTION OF AN AQUEOUS SAMPLE WITH A VERY SMALL VOLUME OF SOLVENT. NOW, THERE'S NO FIXED RATIO OF SAMPLE TO SOLVENT, IT CAN BE AS HIGH AS 1,000 TO 1; GENERALLY WE PREFER TO WORK IN THE RANGE OF 100 TO 1 TO 10 TO 1, AND WE'RE ATTEMPTING TO STANDARDIZE ON SOME VOLUME IN THIS RANGE. NOW, BEFORE I GO INTO THE DETAILS AND THE MECHANICS OF THE ACTUAL EXTRACTION, I'D LIKE TO MAKE A COUPLE OF OTHER COMMENTS AND SHOW YOU SOME CURVES WHICH HOPEFULLY WILL GIVE YOU A LITTLE BIT BETTER FEEL FOR THE POSSIBILITIES OF THIS APPROACH.

NOW, FIRST OF ALL, I WOULD LIKE TO SAY THIS, THAT THE

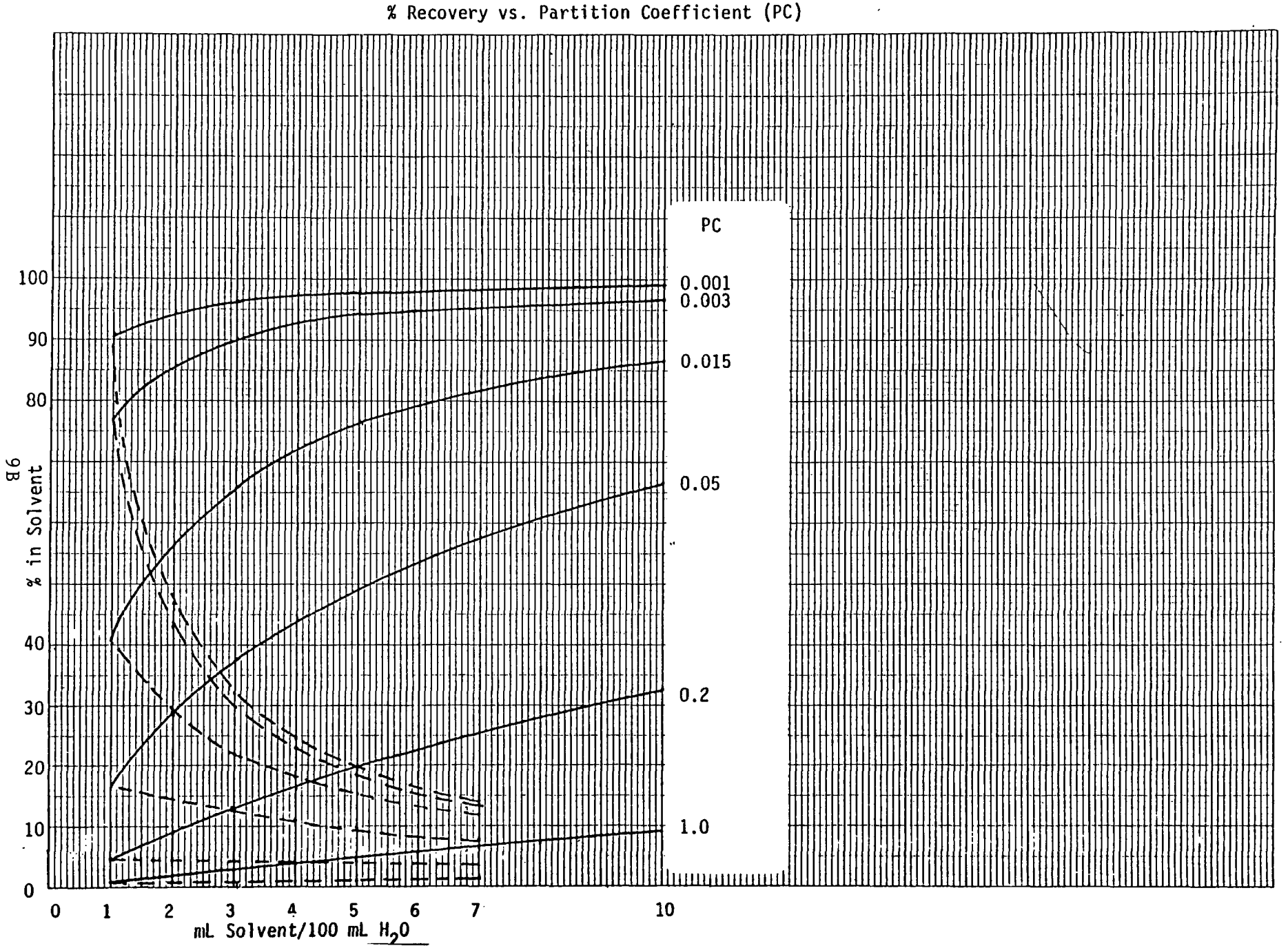
MICROEXTRACTION APPROACH DEPENDS ON BASICALLY TWO THINGS: THAT YOU DO, IN FACT, GET QUITE GOOD RECOVERY IN THE SOLVENT PHASE, AND TWO, THAT THE PARTITION COEFFICIENT IS REASONABLY CONSTANT OVER THE RANGE OF INTEREST. WELL, AS YOU CAN SEE, THERE'S NO HIGH-POWERED MATHEMATICS INVOLVED HERE. WHAT I WOULD MERELY LIKE TO SHOW HERE IS THAT IF WE LOOK AT EQUATION I, ALL IT REALLY SAYS HERE IS THAT IF YOU ADD UP THE AMOUNT WHICH IS IN THE SOLVENT AND THE AMOUNT WHICH IS IN THE WATER YOU, IN FACT, HAVE THE TOTAL AMOUNT THAT'S IN THE SAMPLE; THAT'S PRETTY STRAIGHTFORWARD.

THE NEXT EQUATION (II), WHICH IS THE ONE THAT WE HAVE SOME USE FOR, MERELY SAYS IF YOU DIVIDE THAT AMOUNT WHICH IS IN THE SOLVENT BY THE TOTAL AMOUNT, MULTIPLY IT BY 100, YOU HAVE THE PERCENT WHICH IS IN THE SOLVENT. SO IN OTHER WORDS, WE CAN CALCULATE THE PERCENT WHICH SHOULD BE IN THE SOLVENT IF WE KNOW THE VOLUME OF THE SOLVENT, THE VOLUME OF THE SAMPLE, AND THE PARTITIONING COEFFICIENT. NOW, USING THIS EQUATION, I'VE DRAWN UP A NUMBER OF CURVES HERE WHICH GIVE US SOME IDEA OF HOW EFFECTIVE, AT LEAST IN THEORY, THIS APPROACH TO EXTRACTION MIGHT BE FOR A NUMBER OF DIFFERENT PARTITIONING COEFFICIENTS. NOW, YOU CAN GO EITHER WAY ON THIS. AS I USE IT, THE PARTITIONING COEFFICIENT IS THE RATIO OF THE CONCENTRATION IN THE WATER TO THE CONCENTRATION

I. $AX + BZX = \text{TOTAL AMOUNT}$

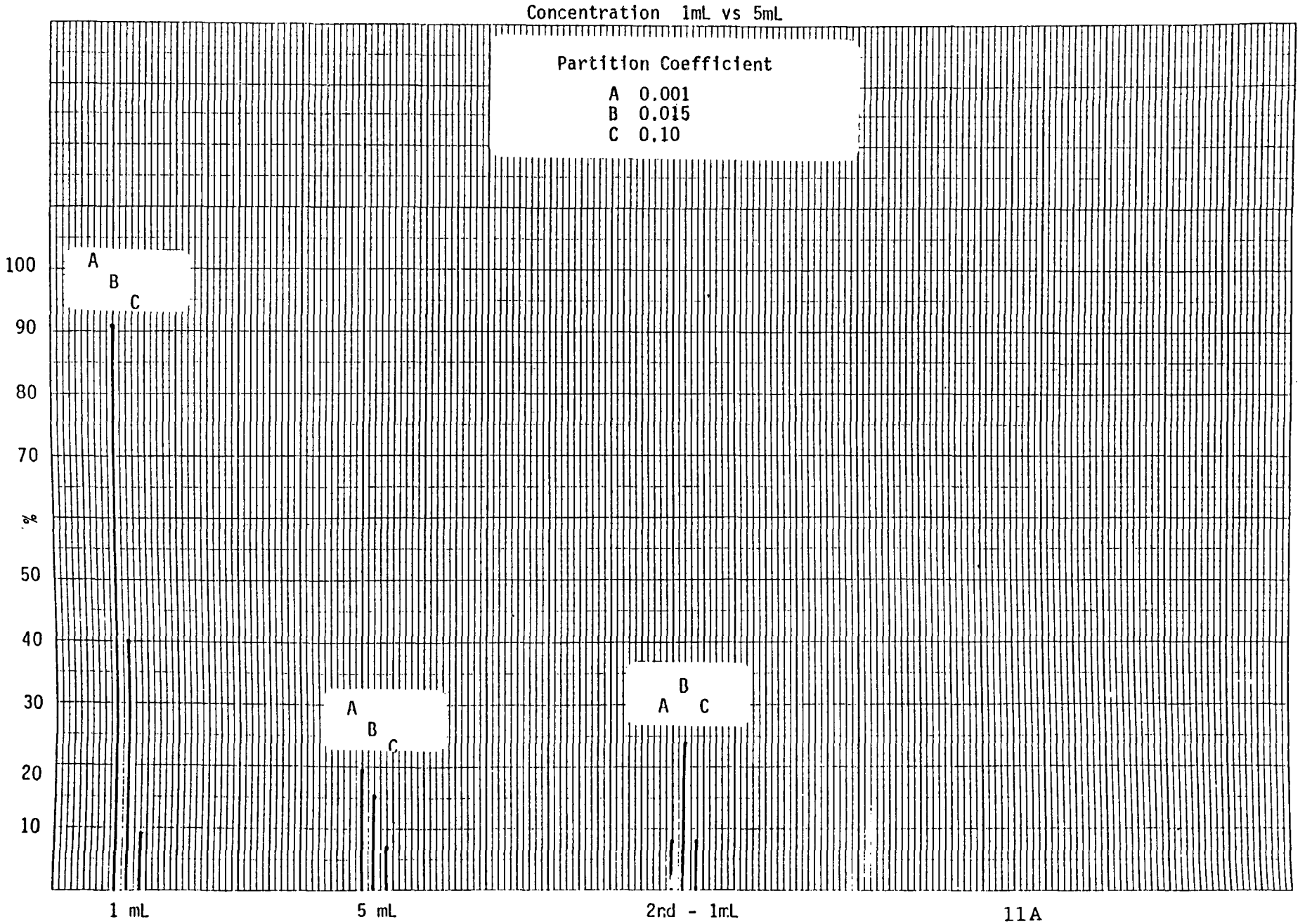
II. $\%\ \text{IN SOLVENT} = \frac{100A}{A + BZ}$

WHERE:
A = VOL. SOLVENT (ML)
B = VOL. WATER (ML)
Z = PART COEFF.
X = CONC. IN SOLVENT
ZX = CONC. IN WATER


% Recovery vs. Partition Coefficient (PC)
PC
0.001
0.003
0.015
0.05
0.2
1.0
% in Solvent
100
90
80
40
30
20
10
0
0
1
2
3
4
5
6
7
10
mL Solvent/100 mL H_2O

IN THE SOLVENT; IF YOU WANT TO FLIP IT AROUND THE OTHER WAY, WHY, YOU GET THE RECIPROCAL NUMBER. NOW, WE CAN SEE HERE THAT IF WE HAVE A MATERIAL THAT EXTRACTS QUITE WELL INTO THE SOLVENT, AS MOST OF THE PRIORITY POLLUTANTS APPEAR TO DO, WE CAN GET A RECOVERY ON MOST OF THEM OF 80 TO 100 PERCENT. IT MAY DO THIS NATURALLY, OR IT MAY BE FORCED BY SATURATING THE AQUEOUS SOLUTION WITH SALT. AT ANY RATE, ON A THEORETICAL BASIS YOU CAN SEE HERE IF YOU HAVE A PARTITIONING COEFFICIENT OF SOMEWHERE IN THE RATIO OF 1,000 TO 1, USING 100 MILLILITERS OF WATER, YOU CAN EXTRACT 90 PERCENT OF THE ANALYTE INTO THE 1 MILLILITER. THAT'S PRETTY GOOD RECOVERY. AS THE PARTITIONING COEFFICIENT DROPS DOWN, SO DOES THE AMOUNT THAT YOU RECOVER, BUT YOU CAN SEE, IF YOU HAVE GOOD RECOVERY, YOU GET 90 PERCENT IN THE FIRST MILLILITER; THAT ESSENTIALLY ALL YOU'RE DOING AS YOU CONTINUE TO EXTRACT IS DILUTE. NOW, THIS IS INDICATED BY THE DASHED LINES WHICH SHOW THE CONCENTRATION. SO YOU CAN SEE HERE, FOR INSTANCE, THAT IF YOU HAVE GOOD EXTRACTION WITH 1 MILLILITER, YOU GET ABOUT 90 PERCENT OF THE SAMPLE IN THE WATER. NO MATTER HOW MUCH MORE SOLVENT YOU USE, YOU CAN ONLY GET 10 PERCENT MORE; THAT'S IT. NOW, IF YOU EXTRACT MORE, BASICALLY WHAT HAPPENS IS YOU GET VERY LITTLE MORE OF THE ANALYTE YOU'RE AFTER, BUT IF YOU'RE LOADED WITH MATERIALS THAT

DO NOT EXTRACT VERY WELL, YOU WILL EXTRACT MORE OF THESE INTERFERENCES. THIS TENDS TO SHOW DOWN HERE, AND IT SHOWS A LITTLE BIT BETTER ON THIS NEXT GRAPH WHERE WE ARE SHOWING ONLY CONCENTRATIONS. NOW, HERE AGAIN, I'VE PICKED THREE DIFFERENT PARTITIONING COEFFICIENTS INDICATING THREE DIFFERENT MATERIALS. A IS QUITE SIMILAR TO MOST OF THE PRIORITY POLLUTANTS; B WOULD BE SOMETHING LOWER, MAYBE MORE LIKE PHENOL; AND C WOULD BE SOMETHING THAT'S VERY POORLY EXTRACTED. IF WE EXTRACT THIS INTO 1 MILLILITER, YOU CAN SEE THIS IS MORE OR LESS EQUIVALENT TO THE PEAK HEIGHT YOU WOULD GET IF YOU SHOT EQUIVALENT SHOTS IN A CHROMATOGRAPH; YOU WOULD GET A GOOD RESPONSE TO A, A SOMEWHAT REDUCED RESPONSE TO B, A VERY LOW RESPONSE TO C. IF WE EXTRACT THIS INTO 5 MILLILITERS, HERE IS THE RESPONSE WE WOULD GET (INDICATING). SO YOU CAN SEE WE REALLY HAVE LOST SOMETHING THAT WE'RE REALLY AFTER, AND THAT IS, THAT BY EXTRACTING WITH A SMALL VOLUME, WE HAVE, IN EFFECT, DONE SOME SELECTIVE EXTRACTION, AND THIS IS ONE OF THE THINGS WE ARE BASICALLY AFTER. WE GAIN NOTHING BY EXTRACTING A LOT MORE IN THE SENSE OF TOTAL RECOVERY. NOW, THEN, THIS EFFECT WE HAVE NOTICED QUITE FREQUENTLY. FOR INSTANCE, IN THE EXTRACTION OF PHENOLS, WHERE WE'RE USING THE MORE OR LESS CONVENTIONAL METHODS, WE HAVE HAD PRACTICALLY NO SUCCESS; WHEN USING THE MICROEXTRACTION


Concentration 1mL vs 5mL
Partition Coefficient
A 0.001
B 0.015
C 0.10
100
90
80
70
%
50
40
30
20
10
A
B
C
A
B
C
B
A
C
1 mL
5 mL
2nd - 1mL
11A

APPROACH, WE HAVE HAD QUITE GOOD SUCCESS, PRIMARILY BECAUSE WE HAVE A RELATIVELY CLEAN SAMPLE AS COMPARED TO EXHAUSTIVE EXTRACTION, WHICH EXTRACTS MORE OF THE INTERFERING COMPOUNDS. SO, IN A SENSE, WE CAN USE THE EXTRACTING PROCEDURE AS A PARTIAL CLEANUP, AND AS A MATTER OF FACT, THAT CAN BE THE CLEANUP. WE DID NOT USE ANY COLUMN CHROMATOGRAPHY TO CLEAN THE PLANT VERIFICATION SAMPLES.

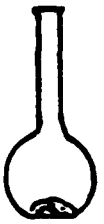
BEFORE I GET ONTO THE PRACTICAL ASPECTS OF MICRO-EXTRACTION, I WOULD LIKE TO MAKE ONE OTHER OBSERVATION WHICH I THINK MAY HAVE CONSIDERABLE IMPORTANCE DOWN THE ROAD, AND THAT IS, LOOKING AT THIS 1 AND 5 MILLILITER EXTRACTION AGAIN, YOU WILL NOTICE THAT IF WE EXTRACT WITH 1 MILLILITER, WE GET A PRETTY GOOD SIGNAL ON A; THERE'S QUITE A REDUCTION IN THE SIGNAL FROM A IN THE 1 MILLILITER AND A IN THE 5 MILLILITER. THERE IS LESS OF A REDUCTION IN SIGNAL AS THE PARTITIONING COEFFICIENT BECOMES LESS FAVORABLE. AS A MATTER OF FACT, YOU CAN CALCULATE THE PARTITIONING COEFFICIENT WITHOUT EVER KNOWING WHAT THE COMPOUND IS MERELY BY MEASURING THE PEAK HEIGHT OF THE 1 MILLILITER EXTRACT AND THE 5 MILLILITER EXTRACT. NOW, WE'VE DONE VERY LITTLE OF THIS, BUT IT DOES LOOK PROMISING DOWN THE ROAD. IT WOULD BE VERY ADVANTAGEOUS TO BE ABLE TO DETERMINE RECOVERY EFFICIENCIES AT THE LEVEL YOU'RE INTERESTED

WITH; ACTUALLY WHAT IS NATURALLY THERE AND NO SPIKING REQUIRED. THAT IS NOT THE WAY WE DETERMINED RECOVERY DATA FOR THE PLANT VERIFICATION DATA.

THE ACTUAL MICROEXTRACTION PROCESS IS REALLY VERY SIMPLE. BASICALLY, THE MECHANICS ARE, YOU TAKE A 100-MILLILITER VOLUMETRIC FLASK, PUT IN 100 MILLILITERS OF SAMPLE, PUT IN A MILLILITER OF SOLVENT, SHAKE IT UP FOR A COUPLE OF MINUTES, LET IT STAND UNTIL THE SOLVENT RISES INTO THE NECK, AND AS SOON AS THERE'S ENOUGH THERE TO GET INTO A MICROSYRINGE, YOU CAN SHOOT IT. THAT'S A LITTLE BIT OF A SIMPLIFICATION, BUT THAT'S THE MECHANICS OF IT, SO IN THIS REGARD, IT IS QUITE SIMPLE.

THE DATA THAT WILL BE PRESENTED BY THE OTHER SPEAKERS WAS OBTAINED FROM PLANT VERIFICATION STUDIES, AND AT THAT TIME, THE METHOD WAS MORE OR LESS BEING DEVELOPED, BUT BASICALLY, IT COMES DOWN TO THIS. IT'S VERY DIFFICULT TO MEASURE THE SOLVENT VOLUME AFTER YOU PUT THE 1 MILLILITER IN. DO YOU GET 1 MILLILITER BACK? WELL, AS A MATTER OF FACT, MOST OF THE TIME YOU GET IT BACK QUITE WELL, ESPECIALLY IN A SALTED SOLUTION, SO WE GENERALLY SALT, BUT THERE ARE TIMES WHEN IT MAY BE ADVANTAGEOUS NOT TO SALT. THE WAY WE DO IT RIGHT NOW IS TO RUN THE SAMPLE AS A DUPLICATE PAIR. WE TAKE TWO 100-MILLILITER VOLUMETRIC FLASKS; WE ADD ABOUT 30 GRAMS OF SALT

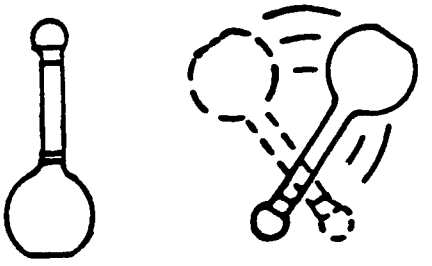
GENERAL MICRO-EXTRACTION PROCEDURE



1. ADD 30g NaCl TO A 100 ml VOL. FLASK.

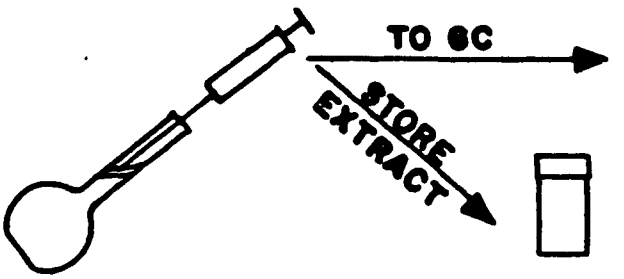
2. ADD 90 ml WATER SAMPLE, INTERNAL STD. AND SPIKE.

3. ADD 1 ml HEXANE.



4. STOPPER, SHAKE WELL APPROX. 2 MIN.

5. ALLOW PHASES TO SEPARATE.



6. SAMPLE WITH 10 µl SYRINGE FOR GC INJECTION.

or

7. SAMPLE WITH GLASS PIPET AND STORE HEXANE LAYER IN VIAL.

AND 90 MILLILITERS OF THE WASTEWATER TO EACH OF THE FLASKS. WE ADD TO EACH FLASK...I'M GOING TO CALL IT AN INTERNAL STANDARD, AND IT'S GOING TO THROW SOME OF YOU BECAUSE WE DON'T REALLY USE IT AS AN INTERNAL STANDARD. MAYBE I SHOULD SAY IT AS AN INTERNAL INDICATOR BECAUSE THE ONLY REASON WE ADD THIS INTERNAL INDICATOR IS SO THAT WE CAN NORMALIZE THE DATA.

IF THERE'S ANY DIFFERENCE IN RECOVERED VOLUMES OR DIFFERENCES IN SHOOTING, WE CAN COMPENSATE FOR THIS ON THE BASIS OF THE INTERNAL STANDARD. IT'S MERELY A TOOL TO GET AROUND VOLUMETRIC MEASUREMENT OF THESE VERY SMALL AMOUNTS OF SOLVENT. NOW, THEN, IN ONE OF THESE TWO SAMPLES, WE DO ADD A KNOWN AMOUNT OF THE COMPOUND OF INTEREST, OR COMPOUNDS OF INTEREST, SO AT THIS POINT IN TIME WE HAVE TWO SAMPLES. THEY ARE IDENTICAL IN EVERY RESPECT EXCEPT THAT ONE OF THEM HAS BEEN DOSED WITH A KNOWN AMOUNT OF MATERIAL. WE NOW SHAKE THESE FLASKS. I NOTICE HERE IT SAYS ABOUT TWO MINUTES; IT DOES NOT TAKE MUCH AGITATION. WE AT SOUTHWEST ACTUALLY HAVE A LITTLE ROTATING DEVICE WHERE WE ROTATE IT AT ABOUT 20 RPM, I THINK IT IS, AND LET IT GO FOR ABOUT TEN MINUTES. IT DOESN'T REALLY DO IT ANY MORE EFFECTIVELY, BUT EVERY SAMPLE IS HANDLED THE SAME, ESPECIALLY IN THE PAIR. THEN THIS PAIR IS ALLOWED TO STAND UNTIL SOLVENT RISES TO THE

TOP. YOU CAN, AT THIS POINT, EITHER SHOOT THE SAMPLE OUT OF EACH ONE OR YOU CAN TAKE SOME OF IT OUT, PUT IT IN A SMALL VIAL AND SAVE IT FOR ANALYSIS LATER. NOW, IF YOU GET A LITTLE SOLVENT LOSS, IT'S NOT REALLY A BIG DEAL BECAUSE YOU'VE GOT THE INTERNAL STANDARD IN THERE WHICH HELPS YOU IN YOUR CALCULATIONS.

NOW, WE HAVE THOSE TWO CHROMATOGRAMS, AND WE ALSO SHOOT A STANDARD SO THAT WE END UP WITH A STANDARD, A SO-CALLED UNSPIKED SAMPLE, AND A SPIKED SAMPLE. BY THE USE OF THESE EQUATIONS (ESTD, SPIKE-UNSPIKE), WE CAN NOW MAKE THE FOLLOWING CALCULATIONS. THE FIRST ONE, ON THE BASIS OF THE EXTERNAL STANDARD, WE CALCULATE THE MICROGRAMS PER LITER IN THE UNSPIKED SAMPLE. NOW, THIS IS JUST A STRAIGHTFORWARD ANALYSIS, AND IT GIVES US AN APPARENT CONCENTRATION IN MICROGRAM PER LITER. WHAT IS DOES, IT ASSUMES WE PUT IN 1 MILLILITER, THEREFORE WE GOT BACK 1 MILLILITER; IT ALSO ASSUMES 100 PERCENT EXTRACTION. IN MANY CASES, ACTUALLY THIS GIVES QUITE A GOOD FIGURE; IN SOME CASES IT DOESN'T BECAUSE YOU DO, IN FACT, GET A MATRIX EFFECT ON CERTAIN SAMPLES; ON OTHERS THERE IS HARDLY ANY MATRIX EFFECT. THIS IS WHERE THE SPIKED, UNSPIKED SAMPLE COMES IN. WE CAN NORMALIZE THE PEAK AREAS, PEAK HEIGHTS, WHAT-HAVE-YOU, ON THE UNSPIKED SAMPLE AND ON THE SPIKED SAMPLE, USING THE INTERNAL

CALCULATIONS

ESTD

$$\frac{R01 \times R03 \times R04}{R02 \times R05 \times R06} = \mu G/L$$

R01 = STANDARD NG INJECTED
R02 = AREA OF INJECTED STANDARD
R03 = AREA OF SAMPLE INJECTED
R04 = VOLUME OF EXTRACTING SOLVENT (µL)
R05 = VOLUME OF SAMPLE EXTRACT INJECTED IN µL
R06 = SAMPLE VOLUME EXTRACTED IN ML

SPIKE - UNSPIKE

$$R11 \times \frac{R14}{R12} = S16 = R16$$

$$\frac{R16 \times R15}{(R13 - R16)} = \mu G/L$$

R11 = AREA OF UNSPIKED SAMPLE
R12 = AREA OF IS IN UNSPIKED SAMPLE
R13 = AREA OF SPIKED SAMPLE
R14 = AREA OF IS IN SPIKED SAMPLE
R15 = µG/L ADDED
R16 = CORRECTED AREA OF UNSPIKED SAMPLE

STANDARD, SO THAT THEY ARE EXACTLY ON A COMPARABLE BASIS. WE NOW, THEN, CAN DETERMINE HOW MUCH IS IN THE UNSPIKED SAMPLE BY THE INCREASE IN THE PEAK HEIGHT OF THE DOSED SAMPLE. WE KNOW WHAT THAT IS, BUT IT'S ALL AUTOMATICALLY CORRECTED FOR EXTRACTION EFFICIENCY. SO WHEN YOU PROPORTIONATE THE PEAK HEIGHT OF THE UNSPIKED SAMPLE TO THE PEAK HEIGHT OF THE SPIKED SAMPLE LESS THE UNSPIKED SAMPLE, YOU END UP WITH THE ACTUAL MICROGRAMS PER LITER CORRECTED FOR VOLUME LOSSES, CORRECTED FOR EXTRACTED INEFFICIENCIES, AND EVEN CORRECTED FOR DIFFERENT SHOT SIZES. AS YOU CAN SEE, THERE ARE ABSOLUTELY NO VOLUME MEASUREMENTS IN THE CALCULATION (INDICATING).

NOW, THEN, WE WANT TO KNOW WHAT OUR RECOVERY IS. THE WAY WE DID THIS ON A CONSIDERABLE PORTION OF THE VERIFICATION PROGRAM WAS MERELY DIVIDE THE APPARENT CONCENTRATION THAT YOU FOUND BASED ON THE EXTERNAL STANDARD BY THE CONCENTRATION DETERMINED ON THE BASIS OF THE SPIKE-UNSPIKE CALCULATION.

ANOTHER WAY YOU CAN DO IT IS DETERMINE THE PEAK HEIGHT OR AREA FROM THE SPIKED SAMPLE AS COMPARED TO AN EXTERNAL SAMPLE. THERE ARE A NUMBER OF ADVANTAGES TO MICROEXTRACTION THAT I'VE TRIED TO POINT OUT DURING THIS TALK. IN ADDITION, THERE'S A MINIMUM OF GLASSWARE TO CLEAN, WHICH MINIMIZES CONTAMINATION.

NOW, THIS IS PARTICULARLY HELPFUL ON PHTHALATES. WE HAVE HAD MUCH MORE LUCK WITH PHTHALATES WITH MICROEXTRACTION THAN WITH THE MORE EXHAUSTIVE EXTRACTION APPROACH. WE HAVE HAD ESSENTIALLY NO EMULSION PROBLEM BECAUSE IT IS NOT NECESSARY TO QUANTITATIVELY RECOVER THE SOLVENT. TO BE ABLE TO GET ENOUGH SOLVENT TO SHOOT, IN MOST CASES, WE AGITATE SLOWLY SO WE DON'T SEEM TO GET MUCH IN THE WAY OF EMULSIONS AND SELDOM HAVE TO CONTEND WITH THEM. ANOTHER ADVANTAGE IS YOU CAN DO THE VOLATILES AS WELL AS THE SEMIVOLATILES. THE BIG ADVANTAGE, PERHAPS, IS THAT MICROEXTRACTION GIVES A CLEANER SAMPLE, AND THIS IS WHAT LETS YOU DO ANALYSES WHICH ARE OTHERWISE ALMOST IMPOSSIBLE. ONE OTHER ASPECT THAT WE LIKE ABOUT IT, BECAUSE WE ARE A RELATIVELY SMALL LAB, IS ONE PERSON DOES IT. WHOEVER OPERATES THE CHROMATOGRAPH IS JUST PREPARING SAMPLES AND WAITING TO SHOOT THEM, SO IT CAN BE A ONE-MAN OPERATION VERY EASILY. THE FACT THAT IT'S RAPID AND UNCOMPLICATED, I THINK, IS RATHER OBVIOUS.

ANOTHER HELP HERE THAT WAS POINTED OUT TO ME THE OTHER DAY, THERE ARE A FAIR NUMBER OF SAMPLES LOST FOR ONE REASON OR ANOTHER. IT ONLY TAKES A FEW MINUTES TO OBTAIN ANOTHER EXTRACT. NOW, THERE ARE SOME MINOR ADVANTAGES. THERE IS A LOT LESS

WASTEWATER TO SHIP AROUND THE COUNTRY, WHICH CAN GET TO BE QUITE A PROBLEM. IT CERTAINLY USES LESS SOLVENT, AND AS I WOULD SEE IT DOWN THE ROAD, THE MICROEXTRACTION MAY BE USED AS A POSSIBLE CLEANUP FOR THE MORE POLAR POLLUTANTS THAT PROBABLY WILL BE COMING UP. IN OTHER WORDS, YOU USE THE MICROEXTRACTION TO GET RID OF THAT WHICH IS EASILY EXTRACTABLE, AND THEN MACROEXTRACT FOR THOSE MATERIALS WHICH DO NOT EXTRACT VERY EASILY. TO ME, ALL THESE ADVANTAGES ADD UP TO THE FACT THAT YOU CAN JUST GET BETTER DATA WITH MICROEXTRACTION, AND I BELIEVE THIS WILL BE SUBSTANTIATED BY KATHY AND BILL IN THEIR TALK. THANK YOU.

MR. TELLIARD: KATHY, DO YOU WANT TO COME UP HERE, AND I'LL PUT THOSE ON FOR YOU, BEING SIX-FOOT EIGHT LIKE YOU ARE.

MS. THRUN: BILL COWEN AT CATALYTIC ASKED ARTHUR D. LITTLE, INCORPORATED, TO SYSTEMATICALLY EVALUATE THE EFFECTS ON EXTRACTION EFFICIENCY WHEN USING MICROEXTRACTION. ALL OF THIS WORK WAS DONE IN A CLEAN MATRIX. BILL WILL BE TALKING NEXT ABOUT THE RESULTS FROM A WASTEWATER MATRIX. THE MAJOR OBJECTIVE OF THE WORK I WILL DESCRIBE WAS TO DETERMINE IF CHANGES IN THE SAMPLE TO SOLVENT RATIO AFFECTED THE OBSERVED DISTRIBUTION COEFFICIENT. MAY I HAVE THE FIRST SLIDE?

EVALUATION OF MICROEXTRACTION METHOD

Analytes:	Benzene
	Toluene
	Ethyl Benzene
	O-Xylene
Solvent:	Pentane
Sample:	Solvent Ratios:
	100:1
	20:1
Effects Of:	Salt (Sodium Sulfate)
	Immiscible Organic (CCl_4)
	Miscible Organic (CH_3CN)

VARIOUS EFFECTS ON EXTRACTION EFFICIENCIES WHEN USING A MICROEXTRACTION TECHNIQUE TO EXTRACT BENZENE, TOLUENE, ETHYL BENZENE, AND ORTH-O-XYLENE FROM CLEAN WATER INTO PENTANE WERE STUDIED. WE EVALUATED TWO DIFFERENT SAMPLE SOLVENT RATIOS: 100 TO 1 AND 20 TO 1. FURTHER, WE STUDIED THE EFFECT OF SATURATING THE AQUEOUS ALIQUOT WITH SALT, AND IN AN ATTEMPT TO IMITATE POSSIBLE SAMPLE MATRICES, WE LOOKED AT THE EFFECTS OF ADDING AN IMMISCIBLE ORGANIC (CARBON TETRACHLORIDE) TO THE AQUEOUS ALIQUOT AND A MISCIBLE ORGANIC (ACETONITRILE) TO THE AQUEOUS ALIQUOT.

NEXT SLIDE. A MAJOR QUESTION TO BE ANSWERED BY THIS WORK WAS DO YOU REACH EQUILIBRIUM AT RELATIVELY HIGH SAMPLE SOLVENT RATIOS AND RELATIVELY SHORT EQUILIBRATION TIMES. TO ANSWER THAT QUESTION WE OBTAINED SOME LITERATURE VALUES FOR DISTRIBUTION COEFFICIENTS FOR BENZENE, TOLUENE, AND XYLENE. THAT WORK WAS DONE BY DELIGNY, ET AL., IN 1966 AND HE EXTRACTED WITH HEPTANE. FROM THOSE DISTRIBUTION COEFFICIENTS WE CALCULATED A PERCENT RECOVERY AT 100 TO 1 AND 20 TO 1 SAMPLE TO SOLVENT RATIOS, AND THEN COMPARED THOSE VALUES WITH OUR EXPERIMENTALLY DETERMINED VALUES. AS YOU CAN SEE, THERE'S REASONABLY GOOD AGREEMENT BETWEEN THE CALCULATED AND EXPERIMENTAL VALUES, EXCEPT PERHAPS FOR TOLUENE AND XYLENE AT 100 TO 1, AND THIS COULD BE BECAUSE DELIGNY USED HEPTANE, WHILE WE USED PENTANE.

SINGLE STAGE EXTRACTION EFFICIENCY

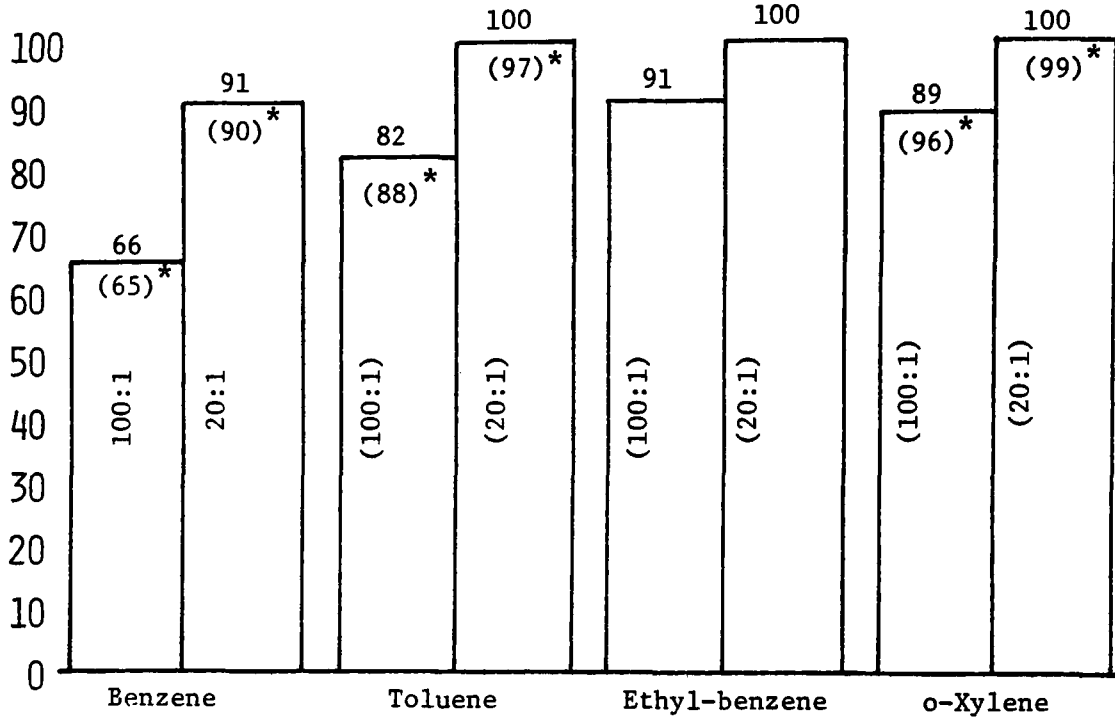
Substance	Distribution Coefficient	100:1		20:1	
		Calc.	Exptl.	Calc.	Exptl.
Benzene	182	65	66	90	91
Toluene	708	88	82	97	100
Xylene	2818	96	89	99	100

AN EXAMINATION OF THE AVERAGE RECOVERIES, PARTICULARLY THOSE FOR BENZENE AT 100 TO 1 SAMPLE TO SOLVENT RATIO INDICATES THAT SUCCESSIVE EXTRACTIONS WERE BEHAVING AS ONE WOULD PREDICT FROM THE THEORY OF MULTIPLE EXTRACTS AND THAT THE DISTRIBUTION COEFFICIENT WAS REMAINING ESSENTIALLY CONSTANT. BENZENE WAS EXTRACTED AT 66 PERCENT AT 100 TO 1 SAMPLE TO SOLVENT RATIO. IF THE SYSTEM IS AT EQUILIBRIUM, YOU WOULD EXPECT TO REMOVE 66 PERCENT OF THE REMAINING 34 PERCENT, OR 22 PERCENT, DURING THE SECOND EXTRACTION. EXPERIMENTALLY THAT NUMBER WAS 25 PERCENT. THEREFORE, THE EVIDENCE DOES SUPPORT THE HYPOTHESIS THAT EQUILIBRIUM IS REACHED WHEN USING MICROEXTRACTION. DIFFERENCES BETWEEN THE EXTRACTION EFFICIENCIES OBSERVED IN DUPLICATE EXPERIMENTS WERE QUITE SMALL. IN MOST CASES, THE RELATIVE RANGE FOR DUPLICATE FIRST EXTRACTIONS WAS LESS THAN 5 PERCENT.

NEXT SLIDE, PLEASE. THIS BAR GRAPH PRESENTS THE DATA, DEMONSTRATING THE EFFECT OF THE SAMPLE TO SOLVENT RATIO ON THE PERCENT RECOVERY OF BENZENE, TOLUENE, ETHYL BENZENE AND XYLENE FROM WATER. THERE WAS NO ADDED ORGANIC MATRIX AND NO SALT ADDED IN THESE SAMPLES. AS YOU WOULD EXPECT, YOU DO EXTRACT MORE AT 20 TO 1 THAN AT 100 TO 1 SAMPLE TO SOLVENT RATIOS. FOR EXAMPLE, TOLUENE WAS ABOUT 100 PERCENT EXTRACTED AT 20 TO 1, AND 82 PERCENT AT 100 TO 1. THE NUMBERS IN PARENTHESES ON THE BAR GRAPH ARE THE CALCULATED VALUES FOR THE PERCENT RECOVERIES (CALCULATED FROM DELIGNY'S DISTRIBUTION COEFFICIENT DATA).

FIGURE 1

EFFECT OF SAMPLE : SOLVENT RATIO ON PERCENT RECOVERY OF BTEX FROM WATER NO ADDED ORGANIC MATRIX



*Calculated equilibrium values

THE NEXT SLIDE. THIS BAR GRAPH PRESENTS THE DATA FOR EXTRACTING BENZENE AT A SAMPLE TO SOLVENT RATIO OF 20 TO 1, AND THE EFFECTS OF ADDING SALT TO THE SAMPLE, AS WELL AS THE EFFECTS OF ADDING 8 PARTS PER MILLION ACETONITRILE, 1,000 PARTS PER MILLION ACETONITRILE AND 1 PART PER MILLION CARBON TETRACHLORIDE TO THE AQUEOUS ALIQUOT. GENERALLY THE SALT DID INCREASE THE RECOVERY SOMEWHAT. FOR A SAMPLE TO SOLVENT RATIO OF 20 TO 1, ONLY THE BEHAVIOR OF BENZENE IS SHOWN BECAUSE RECOVERY OF THE OTHER THREE ANALYTES WAS ESSENTIALLY COMPLETE AFTER ONE EQUILIBRATION AT THE 20 TO 1 RATIO, REGARDLESS OF WHETHER ORGANICS OR SALT WERE PRESENT.

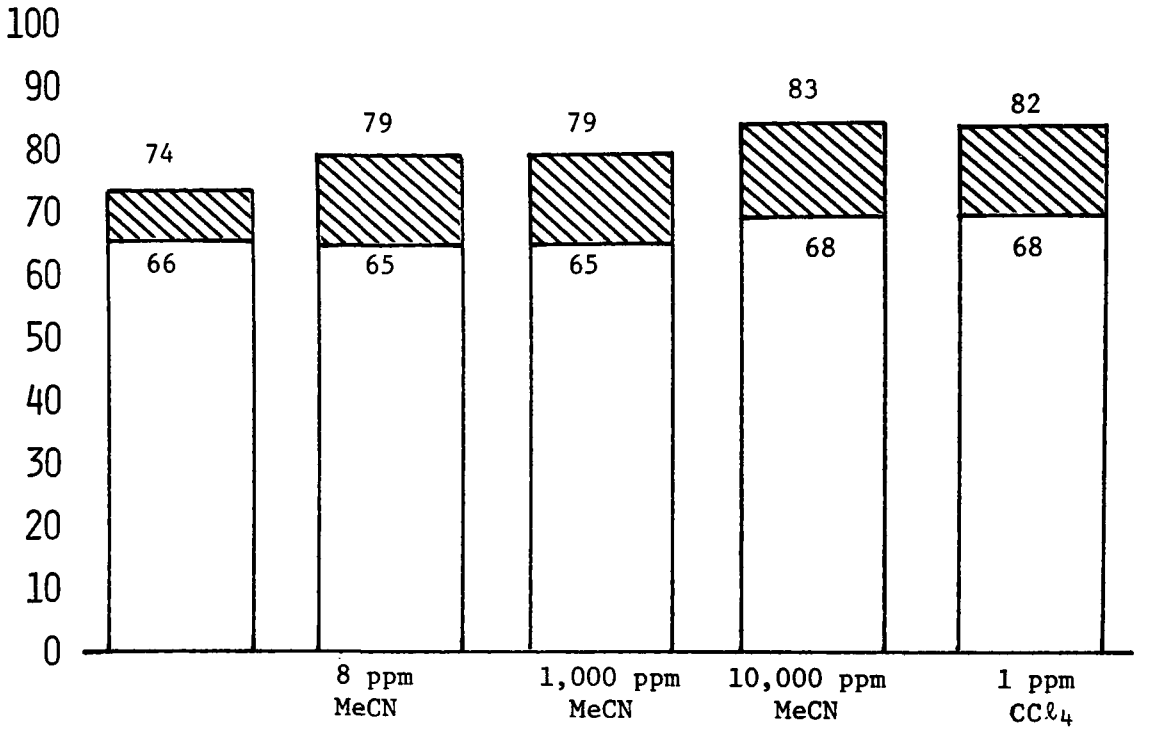
NEXT SLIDE, PLEASE. THIS BAR GRAPH PRESENTS THE DATA FOR RECOVERY OF BENZENE AT A SAMPLE TO SOLVENT RATIO OF 100 TO 1. ONCE AGAIN, THE SALT GENERALLY INCREASED THE RECOVERIES AND THERE DOES NOT SEEM TO BE ANY SIGNIFICANT EFFECT DUE TO ANY OF THE ORGANICS BEING ADDED, EITHER MISCIBLE OR IMMISCIBLE.

NEXT SLIDE, PLEASE. THIS IS THE RECOVERY DATA FOR TOLUENE AT 100 TO 1. THERE IS A SLIGHT INCREASE IN RECOVERY WHEN YOU ADD SALT. HERE, THOUGH, I'D LIKE TO DRAW YOUR ATTENTION TO THE BAR AT 10,000 PARTS PER MILLION ACETONITRILE. THE RECOVERY IS SOMEWHAT REDUCED WHEN THERE IS NO SALT PRESENT. TOLUENE WAS EXTRACTED AT 78 PERCENT, GIVING AN AVERAGE OF ABOUT 83 PERCENT FOR THE OTHER BARS. THAT EFFECT SEEMED TO BE OVERCOME WHEN SALT WAS ADDED, AND THE RECOVERY WAS INCREASED TO 93 PERCENT.

FIGURE 2

EFFECTS OF SALT AND ORGANICS
ON PERCENT RECOVERY OF BENZENE

SAMPLE : SOLVENT RATIO 100 : 1




Na_2SO_4 saturated


No Na_2SO_4

FIGURE 3

EFFECTS OF SALT AND ORGANICS BENZENE

SAMPLE : SOLVENT RATIO 20 : 1

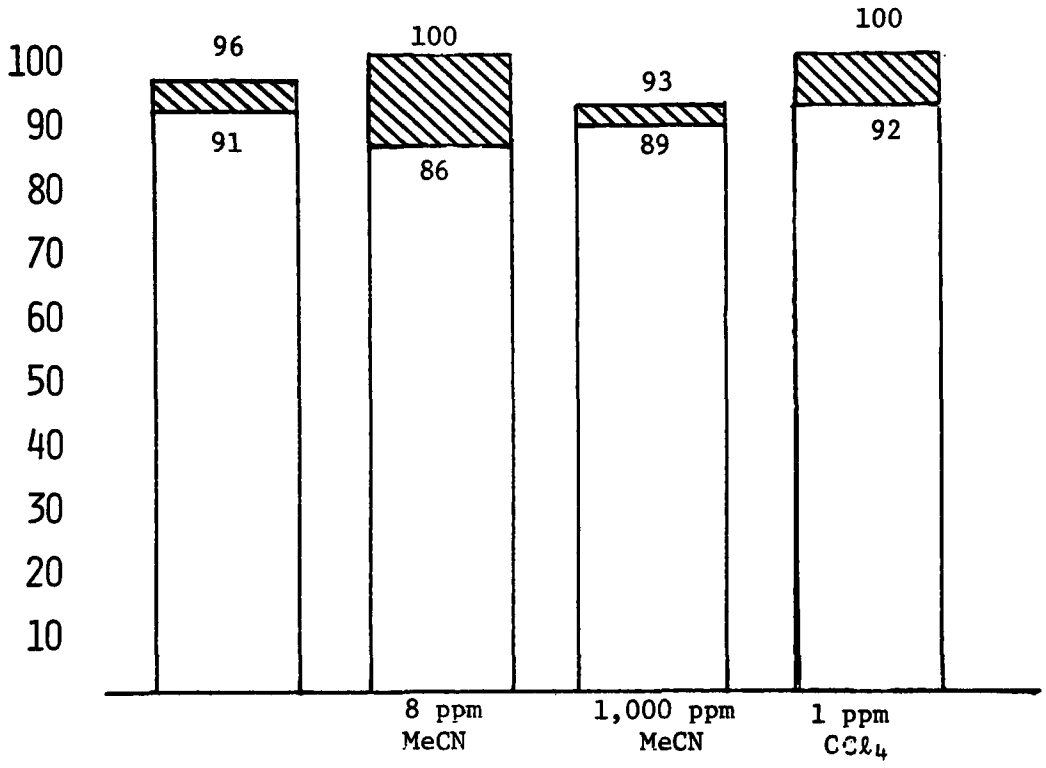
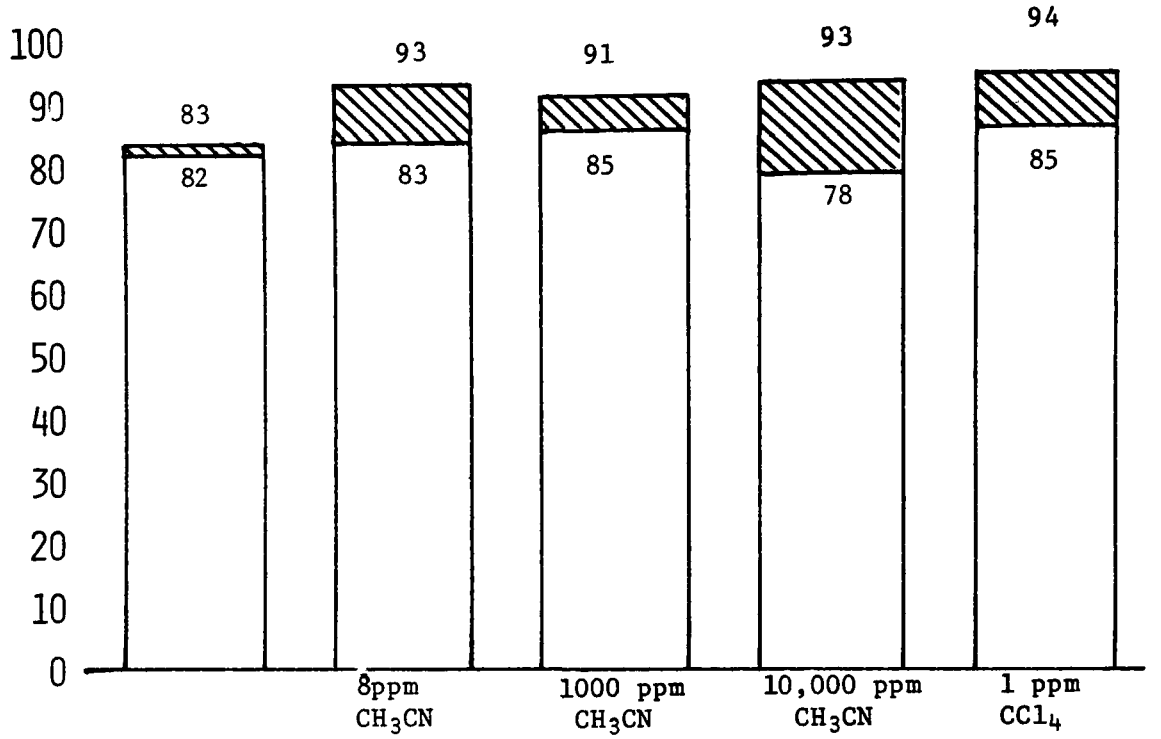


FIGURE 4

EFFECTS OF SALT AND ORGANICS TOLUENE

SAMPLE : SOLVENT RATIO 100 : 1



Na_2SO_4 Saturated

No Na_2SO_4

FOR ETHYL BENZENE AT 10,000 PARTS PER MILLION ACETONITRILE THAT EFFECT IS MORE STRIKING; THE RECOVERIES ARE SOMEWHAT LOWER WHEN THERE IS NO SALT ADDED, ELIMINATED WHEN YOU ADD SALT.

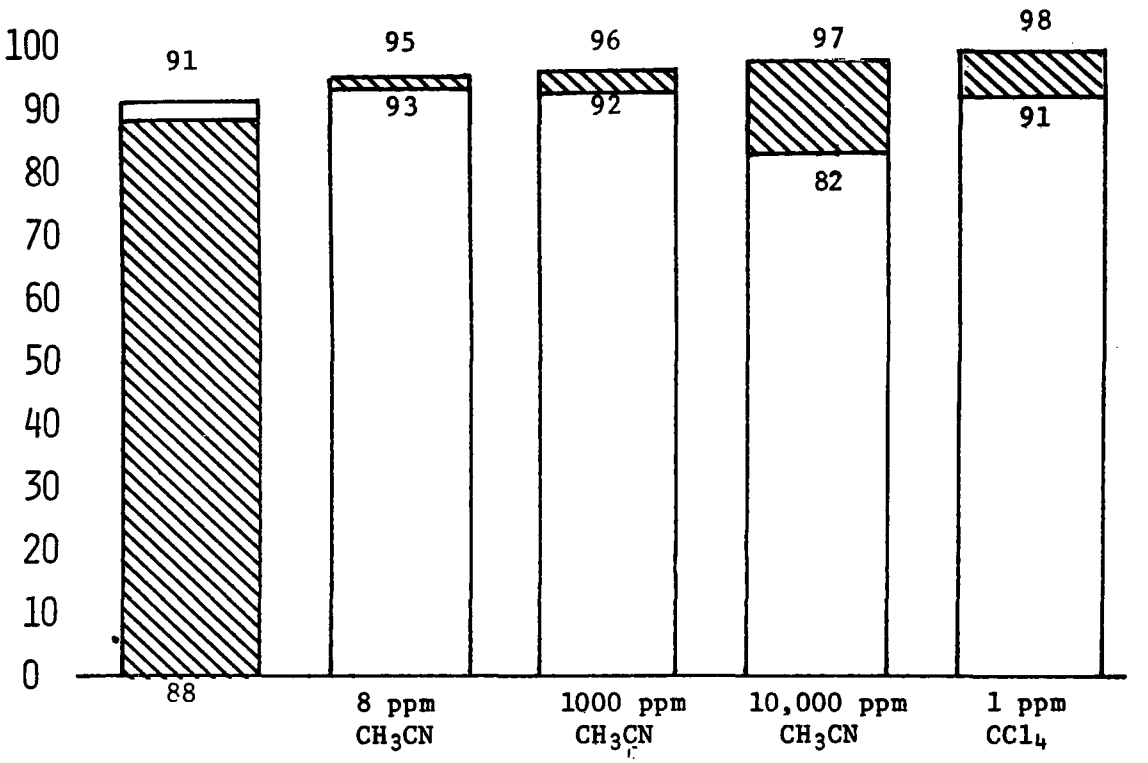
LAST BUT NOT LEAST, XYLENE, THAT EFFECT OF ACETONITRILE IS RATHER STRIKING; THE RECOVERY WAS 72 PERCENT WHEN 10,000 PARTS PER MILLION ACETONITRILE WAS PRESENT VERSUS THE APPROXIMATE AVERAGE OF 90 PERCENT RECOVERY WHEN LOWER CONCENTRATIONS OF OTHER ORGANICS WERE THERE. THAT RECOVERY WAS SUBSTANTIALLY INCREASED WHEN THE AQUEOUS ALIQUOT WAS SATURATED WITH SALT AND THE RECOVERY WAS INCREASED TO 100 PERCENT.

IN CONCLUSION, EVEN AT HIGH SAMPLE TO SOLVENT RATIOS, 100 TO 1, OR 20 TO 1, AND RELATIVELY SHORT EQUILIBRATION TIMES--WE USED TWO MINUTES' WORTH OF SHAKING FOR ALL OF THIS WORK--YOU DO REACH EQUILIBRIUM. THERE WAS NO INCREASE IN RECOVERY WHEN WE EXTRACTED FOR FIVE OR TEN MINUTES. SECONDLY, FOR SPECIES NOT STRONGLY EXTRACTED FROM THE AQUEOUS PHASE, SATURATION WITH SALT GENERALLY INCREASED RECOVERY. THERE IS SOME EVIDENCE THAT WHEN WATER SOLUBLE ORGANICS ARE PRESENT IN THE SAMPLE, THE RECOVERY WILL BE DECREASED, AS WE OBSERVED WHEN 10,000 PARTS PER MILLION ACETONITRILE WERE PRESENT; HOWEVER, SALT OVERCAME THAT EFFECT. MICROEXTRACTION, AS JOHN HAS POINTED OUT, GENERALLY EXTRACTS LOWER CONCENTRATIONS

FIGURE 5

EFFECTS OF SALT AND ORGANICS
ETHYL BENZENE

SAMPLE : SOLVENT RATIO 100 : 1



Na_2SO_4 Saturated

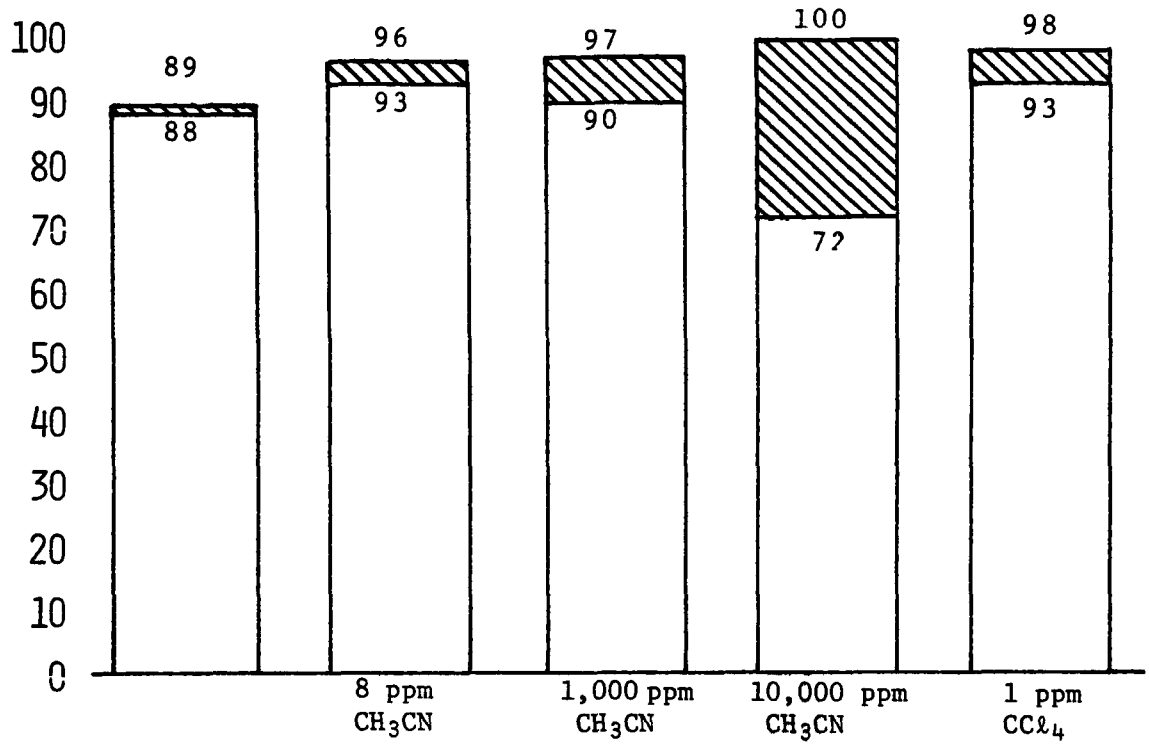
No Na_2SO_4

FIGURE 6

EFFECTS OF SALT AND ORGANICS

o-XYLENE

SAMPLE : SOLVENT RATIO 100 : 1



Na_2SO_4 saturated

No Na_2SO_4

OF NONVOLATILE, WATER SOLUBLE ORGANIC INTERFERNECES; THEREFORE, THERE IS LESS SAMPLE CLEANUP NECESSARY THAN YOU WOULD GENERALLY HAVE TO USE WITH AN EXHAUSTIVE EXTRACTION. BASED ON THIS WORK AND SOME OF THE DATA THAT BILL IS GOING TO SHOW US, I THINK THAT MICRO-EXTRACTION CAN INDEED BE A VERY REPRODUCIBLE CLEANUP AND CONCENTRATION STEP, AND WITH THAT, I'D LIKE TO TURN IT OVER TO BILL.

MR. COWEN: AT THIS POINT IN TIME, CATALYTIC HAS RECEIVED VERIFICATION DATA FROM ABOUT 32 ORGANIC CHEMICAL/PLASTICS PLANTS DURING BAT REVIEW OF THAT POINT SOURCE CATEGORY FOR EFFLUENT GUIDELINES DIVISION. AS JOHN HAS ALREADY POINTED OUT, THE SAMPLE PREPARATION METHODS AVAILABLE TO US AT THE BEGINNING OF THE BAT PROGRAM FOR NONPURGEABLE ORGANICS WERE EXHAUSTIVE, SEQUENTIAL LIQUID/LIQUID EXTRACTION, OR IN THE CASE OF PHENOLS, THE A 26 RESIN EXTRACTION METHOD, FOLLOWED BY SOLVENT EXTRACTION OF THE RESIN. THE EXTRACTIONS WERE THEN FOLLOWED BY AN EVAPORATIVE CONCENTRATION STEP AND SOME SORT OF A CLEANUP, GENERALLY COLUMN CLEANUP, STEP. THIS TYPE OF METHODOLOGY IS SIMILAR TO THE METHODOLOGY NOW BEING PROPOSED AS OF THE DECEMBER 3RD FEDERAL REGISTER.

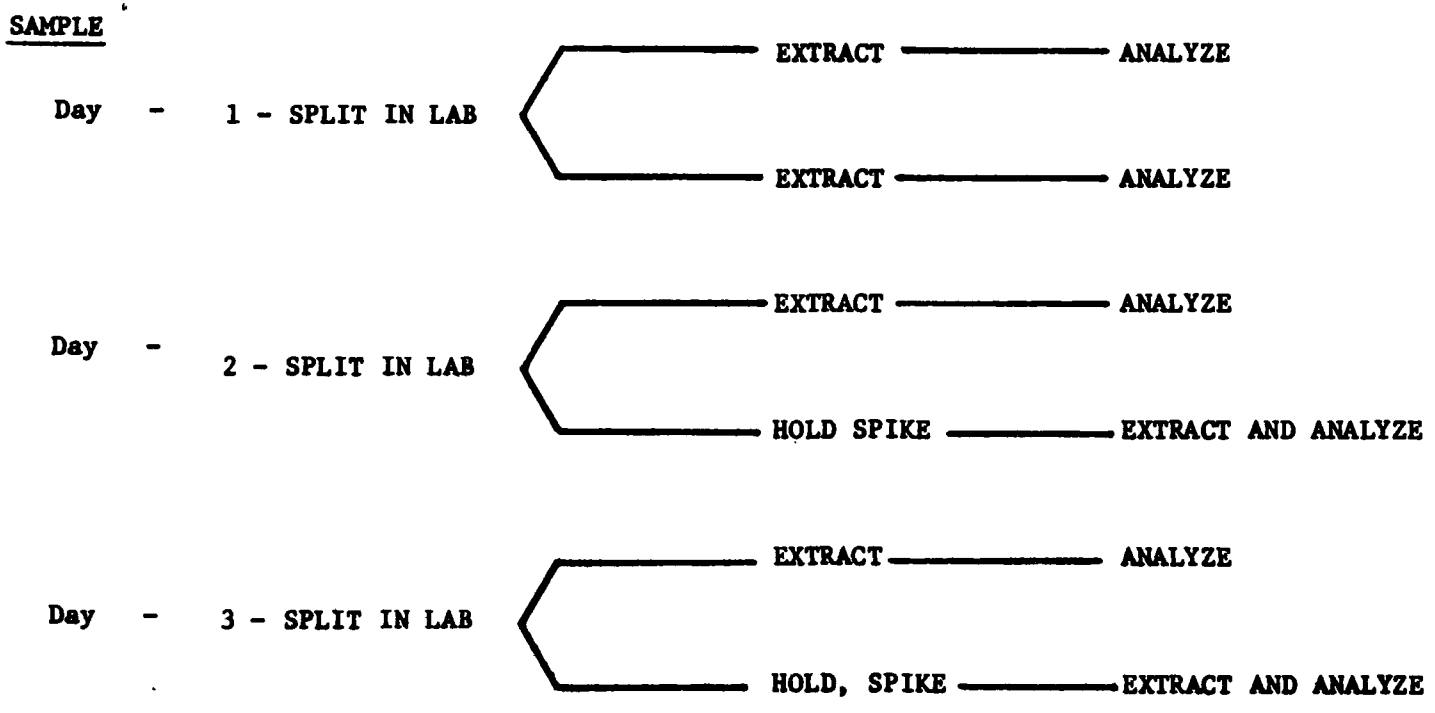
AS JOHN HAS TOLD YOU, SOUTHWEST CHOSE TO TRY THE SINGLE STEP MICROEXTRACTION PROCEDURE USING A SMALL

QUANTITY OF SOLVENT, RATHER THAN GOING WITH THE EXHAUSTIVE METHODS. WHAT I'D LIKE TO DO NOW IS SHOW YOU SOME OF THE PRECISION AND ACCURACY NUMBERS THAT HAVE COME IN FROM ALL OF THE CONTRACTORS AND FROM SOUTHWEST, TO COMPARE THE MICROEXTRACTION METHOD WITH SOME OF THE OTHER METHODS THAT WERE AVAILABLE IN OUR PROGRAM. THE QUALITY CONTROL DATA WERE COLLECTED BASICALLY UNDER THIS TYPE OF PROGRAM (SLIDE #1) WHERE WE HAD REPLICATE ANALYSES ON DAY ONE, AND ON DAY TWO AND DAY THREE WE REQUIRED THAT EACH SAMPLE BE SPIKED TO DETERMINE A SPIKE RECOVERY. JOHN HAS ALREADY GONE THROUGH THE METHODOLOGY FOR CALCULATING PERCENT RECOVERY FROM MICROEXTRACTION. FOR THE OTHER METHODS IT'S JUST THE COMMON METHOD OF TAKING THE SPIKED SAMPLE AND THE UNSPIKED SAMPLE AND REFERRING THEM BOTH TO AN EXTERNAL STANDARD CURVE AND COMPUTING THE PERCENT RECOVERY.

THE ACCURACY DATA, THEN, ON ALL OF THESE SLIDES WILL BE A PERCENT RECOVERY OF ADDED SPIKE. THE REPLICATION DATA WILL BE IN TERMS OF THE RELATIVE RANGE; THAT IS, THE RANGE OF THE TWO DUPLICATES THAT WERE RUN OVER THE MEAN VALUE OF THE TWO DUPLICATES MULTIPLIED BY 100, AND YOU SHOULD NOTE THAT IN THIS METHOD OF CALCULATION, 200 PERCENT FOR THIS REPLICATION NUMBER IS THE MAXIMUM YOU WILL GET. I SHOULD NOTE

SLIDE #1

ANALYSIS AND QA/QC PROGRAM



ALSO THAT THESE SAMPLES WERE COLLECTED FROM A WIDE VARIETY OF SAMPLE MATRIX TYPES, FROM CLEAN, WELL WATER FEEDS INTO THE PLANTS TO THE UNTREATED PROCESS WATERS. IN ALL CASES CONVENTIONAL DETECTORS, EITHER FID, EC, OR SOME OTHER DETECTOR, OTHER THAN MASS SPECTROMETRY WERE USED. IF WE START OUT WITH THE PHENOL METHOD THAT WAS USED AT THE BEGINNING OF THE PROGRAM, THIS IS THE A 26 RESIN, GCFID METHOD. YOU CAN SEE FROM THIS SLIDE (#2) THAT WE HAVE A WIDE RANGE OF SPIKE RECOVERIES OVER IN THE RANGE COLUMN AND WE HAVE A RELATIVELY HIGH STANDARD DEVIATION OF THE SPIKE RECOVERIES AS COMPARED TO THE AVERAGE, FOR ALL THE VARIOUS PHENOLS. IF WE COMPARE THIS DATA WITH THE MICROEXTRACTION PROCEDURE, WHICH WE HAVE ARBITRARILY NUMBERED UNDER OUR SYSTEM #7-5, I THINK YOU CAN SEE (SLIDE #3) THAT THERE'S A RELATIVELY LOW STANDARD DEVIATION AND NONE OF THE VALUES IN THE RANGE COLUMN EXCEED 200 PERCENT RECOVERY, SO THAT WE HAVE A RELATIVELY LOW VARIANCE OF OUR PERCENT RECOVERY OVER ALL THESE SAMPLE TYPES. OF COURSE, WE'VE GOT MOST OF THE DATA FOR PHENOL BECAUSE THAT'S THE ONE THAT HAS OCCURRED THE MOST COMMONLY IN THESE TYPES OF SAMPLES.

MR. TAYLOR: WHAT WAS THAT STANDARD DEVIATION PERCENT?

MR. COWEN: THIS STANDARD

SLIDE #2

SUMMARY OF SPIKE RECOVERIES (Revised 12/26/79)

(Percent Recovery)

Analytical Method # 5

Method Description: A-26 Resin/GC-FID Method

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Phenol	46	46	0-250	120
2,4-Dimethylphenol	61	42	0-208	42
2-Chlorophenol	54	52	0-236	22
2,4,6-Trichlorophenol	101	49	34-200	13
Pentachlorophenol	49	48	0-141	18
2,4-Dichlorophenol	126	58	63-215	8
2,4-Dinitrophenol	24	-	6-42	2
4-Nitrophenol	68	72	0-203	10
2-Nitrophenol	123	66	13-199	8

* All Values in Percent Recovery of Spikes

SLIDE #3

SUMMARY OF SPIKE RECOVERIES (Revised 12/26/79)

(Percent Recovery)

Analytical Method # 7-5

Method Description: Microextraction with FID Detector

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Phenol	52	14	13-79	53
4-Chloro-m-cresol	82	16	54-114	10
2-Nitro-phenol	53	13	27-71	13
4-Nitro-phenol	38	17	14-85	11
2,4-Dinitro-phenol	24	12	2-38	12
Pentachlorophenol	34	15	11-55	13

* All Values in Percent Recovery of Spikes

DEVIATION IS ABSOLUTE, IN PERCENT RECOVERY UNITS. YOU TAKE ALL OF THE PERCENT RECOVERY NUMBERS, THAT'S YOUR PARAMETER, AND THEN YOU CAN GET THE MEAN AND THE STANDARD DEVIATION OF THOSE PERCENT RECOVERIES, SO THE STANDARD DEVIATION REPORTED HERE IS NOT A PERCENT OF THE MEAN. SO THE RECOVERY FOR PHENOL WITH THIS METHOD WAS 52 PERCENT OVER ALL THE SAMPLES PLUS OR MINUS 14, IF YOU TALK ABOUT ONE STANDARD DEVIATION.

IF WE LOOK AT THE INDIVIDUAL SAMPLE RECOVERIES (SLIDE #4), WHERE WE ARE NOT LOOKING AT THE OVERALL DATA BASE FROM ALL THE DIFFERENT TYPES OF SAMPLES, BUT RATHER WE ARE TAKING ONE TYPE OF SAMPLE AND LOOKING AT IT, I WANTED TO SHOW HERE THE RECOVERIES ON DAY ONE, DAY TWO, AND DAY THREE. FOR SAMPLES WHERE WE HAD AT LEAST TWO AND IN SOME CASES THREE SPIKE RECOVERIES, ONE CAN SEE WHAT THE VARIATION WAS FOR A GIVEN SAMPLE ON THE THREE DAYS OF VERIFICATION, AND I THINK YOU CAN SEE THAT AT MOST WE HAVE A 30 PERCENT SPIKE RECOVERY DIFFERENCE BETWEEN ANY TWO DAYS. IF YOU JUST GLANCE AT SOME OF THE NUMBERS, YOU CAN SEE THAT IN SOME CASES THE AGREEMENT WAS QUITE GOOD. THIS IS THE SAME SAMPLING SITE SO THAT THE MATRIX IS SUPPOSED TO BE BASICALLY THE SAME, ALTHOUGH THE CONCENTRATIONS OF THE PRIORITY POLLUTANT MAY BE SHIFTING CONSIDERABLY.

SLIDE #4

Phenol Spike Recoveries for Individual Samples (Microextraction)

Sample No.	% Spike Recovery Day 1	Day 2	Day 3
1		60	58
2		53	79
3		44	67
4		46	75
5		42	64
6		56	62
7		40	67
8		66	61
9		43	70
10		56	64
11		37	59
12		60	68
13	54	66	58
14	42	61	65
15	39	51	69
16		38	54
17	37	62	59

IF WE LOOK AT THE REPLICATION OF THE MICROEXTRACTION METHOD, MOST OF OUR DATA ARE ON PHENOL (SLIDE #5). WE HAVE VERY LITTLE DATA ON THE OTHER PHENOLS AT THIS TIME. WE HAVE AN AVERAGE RELATIVE RANGE BETWEEN DUPLICATES OF 32 PERCENT, AND THAT IS FOR CONCENTRATIONS ABOVE TEN MICROGRAMS PER LITER; ALL OF THESE REPLICATION SLIDES ARE OF CONCENTRATIONS ABOVE TEN PARTS PER BILLION UNLESS NOTES. I HAVE LISTED HERE SOME REPLICATE DATA FROM CONCENTRATIONS LESS THAN TEN PARTS PER BILLION SO THAT YOU COULD GET AN IDEA OF THE AGREEMENT THAT WAS SEEN ON THESE SAMPLES, AND ALSO ONE SAMPLE THAT WAS RUN OF 4-CHLORO-M-CRESOL, SO YOU CAN SEE THAT THE REPLICATION IS QUITE GOOD, AND BY WAY OF REFERENCE, IF WE LOOK AT THE A 26 RESIN METHOD (SLIDE #6), THE AVERAGE IS ABOUT 84 PERCENT FOR PHENOL, WHERE MOST OF OUR DATA LIES. QUITE A FEW NUMBERS OF 200 PERCENT RELATIVE RANGE WERE SEEN.

IF WE SWITCH OVER NOW TO THE POLYAROMATIC HYDROCARBONS (SLIDE #7), THIS PROCEDURE IS BASICALLY EPA METHOD 610 EXCEPT THAT IN THIS PROGRAM THE CONTRACTOR DID NOT USE LIQUID CHROMATOGRAPHY AT THE END, HE USED CAPILLARY GC WITH FLAME IONIZATION DETECTION. THE RESULTS CAME OUT FAIRLY WELL EXCEPT IN THE CASE OF THE BENZO (B AND K) FLUORANTHENES; THE STANDARD DEVIATIONS

SUMMARY OF REPLICATE ANALYSES
(Percent Difference Between Replicates)

Analytical Method # 7-5

Method Description: Microextraction with FID Detector

Compound	Average*	Range*	No. of Replicate Pairs
Phenol	32	2-143	13
	Phenol Replicate Concentrations < 10 ug/l		
	Sample	Rep #1 (ug/l)	Rep #2 (ug/l)
	1	5.6	2.2
	2	7.9	7.6
	3	5.6	5.2
	4	4.9	3.2
	5	1.9	1.6
	6	0.8	1.1
	7	6.9	9.7
	8	2.2	2.6
	9	1.6	1.8
4-chloro-m-cresol	Replicate: pair	1.9 ug/l	1.7 ug/l

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value

SUMMARY OF REPLICATE ANALYSES

(Percent Difference Between Replicates)

Analytical Method # 5

Method Description: A-26 Resin/GC-FID Method

Compound	Average*	Range*	No. of Replicate Pairs
Phenol	84	17-200	21
2,4-Dimethyl phenol	83	31-153	5
2,4,6-Trichlorophenol	75	6-200	3
Pentachlorophenol	24	9-40	2

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value

Table 33

SUMMARY OF SPIKE RECOVERIES

(Percent Recovery)

Analytical Method # 17-4

Method Description: EPA Method 610, with Florisil Cleanup, FID Detection

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Fluoranthene	86	48	12-172	9
Pyrene	72	36	13-133	9
Phenanthrene	66	24	39-100	10
Anthracene	94	41	42-161	9
Naphthalene	36	17	12-71	12
Acenaphthylene	74	27	31-118	11
Fluorene	88	24	48-113	9

* All Values in Percent Recovery of Spikes

ARE RELATIVELY LOW COMPARED TO THE AVERAGES. NOW, THIS IS AN EXHAUSTIVE EXTRACTION METHOD SIMILAR TO THAT UNDER METHOD 610. MICROEXTRACTION FOR THESE KINDS OF COMPOUNDS SHOWED VERY LOW STANDARD DEVIATIONS (SLIDE #8), AND VERY GOOD AVERAGE PERCENT RECOVERIES IN THE 80 AND 90 PERCENT RANGE. YOU CAN SEE THE SMALL RANGE AND STANDARD DEVIATION FOR THESE KINDS OF COMPOUNDS. THERE WAS AN AWFUL LOT OF DATA ON THIS ONE. WE DID NOT, UNFORTUNATELY, HAVE AS MUCH DATA ON THE OTHER METHOD (610). WE HAD VERY LITTLE PRECISION DATA ON THE METHOD 610 (SLIDE #9).

GENERALLY THE REPLICATION WAS FAIRLY GOOD; 112 WAS THE HIGHEST RELATIVE RANGE VALUE WE HAD FOR THIS METHOD. TO COMPARE THAT WITH MICROEXTRACTION FOR THESE KINDS OF COMPOUNDS, AGAIN, THERE IS NOT A LOT OF DATA AT THIS TIME, BUT WE WERE GETTING VALUES OF AT MOST 24 PERCENT RELATIVE RANGE (SLIDE #10). FOR CONCENTRATIONS LESS THAN 10 PARTS PER BILLION, YOU CAN SEE THE EXCELLENT AGREEMENT BETWEEN THE TWO DUPLICATES WHEN THEY WERE RUN BY MICROEXTRACTION.

JOHN MENTIONED SOME OF THE PROBLEMS WITH PHTHALATES, AND I THINK THIS SLIDE (#11) WILL SHOW WHAT HE WAS TALKING ABOUT. THIS IS WHAT USED TO BE CALLED THE FEDERAL REGISTER METHOD, THE PESTICIDE EXTRACTION WITH 15 PERCENT METHYLENE CHLORIDE IN

SUMMARY OF SPIKE RECOVERIES
(Percent Recovery)

Analytical Method # 7-6

Method Description: Microextraction with FID Detector

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Fluoranthene	95	14	62-121	24
Pyrene	94	14	68-121	23
Phenanthrene	95	17	49-124	24
Anthracene	97	14	66-126	24
Benzo(a)anthracene	87	22	34-135	24
Naphthalene	90	18	48-134	24
Acenaphthylene	88	25	27-130	24
Fluorene	92	21	53-130	24

* All Values in Percent Recovery of Spikes

Table 34

SUMMARY OF REPLICATE ANALYSES

(Percent Difference Between Replicates)

Analytical Method # 17-4

Method Description: EPA Method 610, with Florisil Cleanup, FID Detection

Compound	Average*	Range*	No. of Replicate Pairs
Fluoranthene	24	22-26	2
Pyrene	27	6-51	3
Phenanthrene	42	11-110	4
Anthracene	16	7-25	3
Naphthalene	26	10-42	4
Acenaphthylene	29	6-73	4
Fluorene	38	4-112	4

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value

SUMMARY OF REPLICATE ANALYSES
(Percent Difference Between Replicates)

Analytical Method # 7-6

Method Description: Microextraction with FID Detector

Compound	Average*	Range*	No. of Replicate Pairs
Fluoranthene	14	-	1
Pyrene	19	-	1
Phenanthrene	12	4-21	2
Anthracene	12	-	1
Benzo(a)anthracene	28	-	1
Naphthalene	16	0.6-24	3
Acenaphthylene	10	2-18	2
Fluorene	12	0.3-23	2
	Replicate Pairs for Concentrations <		10 µg/l
Compound		Rep. #1 (µg/l)	Rep. #2 (µg/l)
Fluoranthene		5.4	4.3
Pyrene		9.1	6.9
Phenanthrene		2.4	N.D.
Anthracene		2.5	4.0
Benzo(a)anthracene		-	-
Naphthalene		2.0	2.0
Acenaphthylene		6.6	7.4
Fluorene		3.4	N.D.

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value
ND=Not Detected

SUMMARY OF SPIKE RECOVERIES (Revised 12/26/79)

(Percent Recovery)

Analytical Method # 3-3

Method Description: Federal Register Pesticide Extraction, Cleanup with EC Detector

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Bis(2-ethylhexyl) phthalate	56	56	0-333	92
Dimethyl phthalate	84	69	0-242	22
Diethyl phthalate	74	65	0-236	20
Di-n-butyl phthalate	66	66	0-310	55
Di-n-octyl phthalate	92	-	86-98	2

* All Values in Percent Recovery of Spikes

HEXANE WITH CLEANUP AND THEN GC/EC DETECTION, AND YOU CAN SEE THAT THE AVERAGE PERCENT RECOVERY AND THE STANDARD DEVIATION ARE SIMILAR OVER ALL OF THE SAMPLE TYPES; THERE WERE MANY SAMPLES WITH BIS (2-ETHYLHEXYL) PHTHALATE AND YOU CAN SEE SOME OF THE RANGES IN THE PERCENT RECOVERY THAT WERE EXPERIENCED DURING THE BAT PROGRAM WITH THIS METHOD. THE MICROEXTRACTION PROCEDURE (SLIDE #12) SHOWED AT MOST 29 PERCENT FOR THE STANDARD DEVIATION AND AVERAGE RECOVERIES FROM 61 TO 85 PERCENT. SO IF YOU COMPARE THE STANDARD DEVIATION AND THE AVERAGE AND THEN LOOK AT THE RANGES, WHICH HAVE A HIGHEST VALUE OF 112 PERCENT RECOVERY, YOU CAN SEE THAT QUITE GOOD RESULTS WERE OBTAINED WITH THIS METHOD OVER, AGAIN, A LARGE NUMBER OF SAMPLES FOR THE BEHP COMPOUND. THE PESTICIDE EXTRACTION, EXHAUSTIVE EXTRACTION PROCEDURE IN TERMS OF REPLICATION SHOWED SEVERAL 200 PERCENT VALUES (SLIDE #13), MEANING THAT IN A LOT OF THE DUPLICATE ANALYSES THERE WAS A NUMBER AND A "NOT DETECTED"; THAT WILL GIVE YOU 200 PERCENT WHEN YOU DO THIS KIND OF PERCENT RELATIVE RANGE CALCULATION. YOU CAN SEE AVERAGES OF 110 PERCENT AND 144 PERCENT FOR SOME OF THESE REPLICATION ANALYSES. SO THERE WERE PROBLEMS.

I HAVE TRIED TO BREAK DOWN THE SOUTHWEST RESEARCH MICROEXTRACTION DATA INTO GROUPS OF GREATER THAN 10 PARTS

SUMMARY OF SPIKE RECOVERIES (Revised 12/26/79)

(Percent Recovery)

Analytical Method # 7-4

Method Description: Microextraction with EC Detector

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Bis(2-ethylhexyl) Phthalate	85	25	14-118	50
Bis(n-butyl)phthalate	61	29	10-106	13
Bis(n-octyl)phthalate	82	21	36-112	13

* All Values in Percent Recovery of Spikes

SUMMARY OF REPLICATE ANALYSES (Revised 12/26/79)

(Percent Difference Between Replicates)

Analytical Method # 3-3

Method Description: Federal Register Pesticide Extraction, Cleanup with EC Detector

Compound	Average*	Range*	No. of Replicate Pairs
Bis(2-ethylhexyl) phthalate	110	5-200	31
Dimethyl phthalate	58	0-200	8
Diethyl phthalate	144	0-200	6
Di-n-butyl phthalate	86	4-200	14
Di-n-octyl phthalate	-	-	0

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value

PER BILLION AND LESS THAN 10 PARTS PER BILLION (SLIDE #14) SO THAT EACH COMPOUND'S DATA IS GROUPED TOGETHER AND THERE IS, ADMITTEDLY, VERY LITTLE DATA ON SOME OF THESE COMPOUNDS EXCEPT THE BEHP; BUT ONE INTERESTING THING IS THAT EVEN AT LESS THAN 10 PARTS PER BILLION, YOU ONLY HAVE AN AVERAGE VALUE OF 44 PERCENT FOR THE REPLICATION, AND IF YOU THINK ABOUT IT, WITH THIS METHOD OF CALCULATING THE RELATIVE RANGE, YOU CAN HAVE TWO DUPLICATE ANALYSES OF THE SAME SAMPLE IN WHICH ONE IS ONE PART PER BILLION AND THE OTHER ONE IS TWO PARTS PER BILLION AND THIS TYPE OF ANALYSIS WILL GIVE YOU A VALUE OF 67 PERCENT FOR THE RELATIVE RANGE. SO WE ARE NOT TALKING ABOUT VERY MANY MICROGRAMS PER LITER WHEN WE ARE DOWN AT THIS RANGE.

FINALLY, I WOULD LIKE TO SHOW SOME DATA THAT HAS SOMETHING TO DO WITH WHAT KATHY WAS TALKING ABOUT. THE OTHER MAJOR GROUP OF COMPOUNDS RUN WITH MICROEXTRACTION BY SOUTHWEST WAS THE NONCHLORINATED VOAS, THE BENZENE, TOLUENE, ETHYL BENZENE GROUP, AND THERE IS A LOT OF SAMPLES IN THIS GROUP AND YOU CAN SEE (SLIDE #15) THAT THE AVERAGE RECOVERIES ARE QUITE HIGH AND THE STANDARD DEVIATIONS ARE QUITE LOW RELATIVE TO THE AVERAGES. IF YOU REMEMBER KATHY'S SLIDE, WHEN YOU TAKE INTO CONSIDERATION THE STANDARD DEVIATION OF THE SPIKE RECOVERY, WE ARE TALKING ABOUT THE SAME RECOVERY RANGE

SLIDE #14

SUMMARY OF REPLICATE ANALYSES (Revised 12/26/79

(Percent Difference Between Replicates)

Analytical Method # 7-4

Method Description: Microextraction with EC Detector

Compound	Average*	Range*	No. of Replicate Pairs
Bis(2-ethylhexyl) phthalate (Conc. >10 µg/1)	26	0-74	5
Bis(2-ethylhexyl) phthalate (Conc. <10 µg/1)	44	0-148	20
Bis(n-butyl)phthalate (Conc. >10 µg/1)	21	9-28	3
Bis(n-butyl)phthalate (Conc. <10 µg/1)	36	0-67	8
Bis(n-octyl)phthalate (Conc. >10 µg/1)	29	-	1
Bis(n-octyl)phthalate (Conc. <10 µg/1)	20	0-35	7

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value

SUMMARY OF SPIKE RECOVERIES (Revised 12/26/79)

(Percent Recovery)

Analytical Method # 7-1, 7-3

Method Description: Microextraction with FID Detector

Compound	Average*	Std. Deviation*	Range*	No. of Samples Spiked
Benzene	101	19	50-160	62
Toluene	95	17	53-153	86
Ethylbenzene	93	17	32-130	49

* All Values in Percent Recovery of Spikes

THAT SHE FOUND WITH HER CLEAN WATER STUDIES; IN OTHER WORDS, ABOUT 85 TO 100 PERCENT SPIKE RECOVERIES. FINALLY, REPLICATION FOR THESE TYPES OF COMPOUNDS SHOWED THESE AVERAGES, 31 DOWN TO 7 PERCENT FOR THESE COMPOUNDS BY MICROEXTRACTION (SLIDE #16). AT THIS POINT, I WILL OPEN IT UP TO QUESTIONS TO EITHER MYSELF, JOHN OR KATHY. HOW MUCH TIME DO WE HAVE LEFT, BILL?

MR. TELLIARD: IF YOU HAVE ANY QUESTIONS, WOULD YOU GO TO ONE OF THE MIKES AND IDENTIFY YOURSELF SO WE CAN FOREVER BLAME YOU.

MR. SPRAGGINS: BOB SPRAGGINS, RADIAN CORPORATION. I HAVE SEVERAL QUESTIONS, BUT THEY ARE REAL SHORT. ONE, HOW DO YOU EXPLAIN THE FACT THAT CLASSICALLY IN CHEMISTRY WE ARE TOLD THAT ABOUT THREE EXTRACTIONS ARE NECESSARY; I KNOW THE EXTRACTION COEFFICIENT HAS SOMETHING TO DO WITH IT. HOW DO YOU EXPLAIN THAT YOU ARE GETTING SUCH GOOD RESULTS WITH ONE? HOW DO YOU EXPLAIN THIS BUSINESS ABOUT THE CALCULATION? I HAD A LITTLE TROUBLE GOING THROUGH THE CALCULATIONS. YOU WERE SAYING THE SPIKED MINUS THE UNSPIKED AND IT LOOKS LIKE THAT THERE IS A FRACTION OF THE SPIKE THAT IS NOT GOING TO BE RECOVERED. IT DOES NOT LOOK LIKE IT IS A REAL STRAIGHTFORWARD EQUATION, JUST LIKE ONE, A MINUS B, SO I WOULD LIKE TO HAVE SOME HELP THERE. THE THIRD

SLIDE #16

SUMMARY OF REPLICATE ANALYSES

(Percent Difference Between Replicates)

Analytical Method # 7-1,3

Method Description: Microextraction with FID Detector

Compound	Average*	Range*	No. of Replicate Pairs
Benzene	7	1-36	16
Toluene	12	0-92	28
Ethylbenzene	31	0-200	11

* All Values in Absolute Difference Between Replicates, Expressed as Percent of Mean Value

QUESTION WAS, HOW ARE YOU ADDING YOUR SPIKES IN? IF YOU'RE ADDING IT IN AN ORGANIC SOLVENT, IT SEEMS LIKE THIS ORGANIC SOLVENT COULD BE PLAYING SOME EFFECT AND YOU DIDN'T MENTION EXACTLY HOW THAT WAS BEING DONE.

MR. RHOADES: YES, I'LL TAKE THAT BACK. I'VE HIT THIS PRETTY FAST SO THERE ARE SOME LITTLE DETAILS THAT WE PROBABLY HAVE MISSED THAT REALLY SHOULD BE IN THE METHOD. YOUR FIRST QUESTION WAS WHY DO WE GET GOOD RECOVERY ON THE MICROEXTRACTION AS COMPARED TO THE EXHAUSTIVE EXTRACTION THAT HAS BEEN USED FOR YEARS. WELL, I'M PRETTY OLD, BUT THEY STARTED THE EXHAUSTIVE EXTRACTION BEFORE I REALLY GOT INTO THIS, SO I'M NOT SURE THAT I CAN ANSWER THAT, OTHER THAN TO SAY THIS: ONE OF THE BIGGEST ADVANTAGES OF THE MULTIPLE EXTRACTION AND THE EXHAUSTIVE EXTRACTION IS YOU CAN'T GET IT ALL OUT EACH TIME. IN OTHER WORDS, IF FOR INSTANCE, YOU EXTRACT, SAY, A LITER OF WATER WITH 60 MILLILITERS OF...I'LL PULL IT OUT OF A HAT, DCM, YOU WILL, IN FACT, GET A VERY GOOD RECOVERY. THE PROBLEM COMES IN, YOU DON'T USUALLY GET IT ALL OUT, SO YOU GET OUT, NOW YOU ADD AGAIN, NOW YOU'VE DILUTED, SO YOU APPROACH 100 PERCENT BY DILUTING AND EXTRACTING OUT. FOR ALL PRACTICAL PURPOSES, IT WAS ALL IN THE FIRST EXTRACTION; WHAT YOU LEFT BEHIND WAS THE VOLUME OF DCM THAT YOU LEFT BEHIND. NOW, THE ONLY REASON I

CAN SAY THAT IS, THERE'S NOTHING...THE CALCULATIONS HERE, THE INITIAL ONES, ARE QUITE STRAIGHTFORWARD AND INDICATE THAT IF YOU HAVE A MATERIAL THAT PARTITIONS, LET'S SAY, SOMETHING IN THE RANGE OF 1,000 TO 1 TO 10,000 TO 1, WHICH IS WHAT MANY OF THESE ARE, THE MATHEMATICS SHOW THAT YOU SHOULD GET GOOD EXTRACTION, THE RESULTS SHOW THAT YOU DO GET GOOD EXTRACTIONS. THAT'S ALL I CAN SAY.

MR. SPRAGGINS: YOU HAVE ME AT A SLIGHT DISADVANTAGE, BUT ON THE CALCULATIONS, IF YOU'RE GETTING CLOSE TO 100 PERCENT RECOVERY, I AGREE THAT IT'S A MINUS B, BUT IF YOU'RE NOT GETTING 100 PERCENT RECOVERY, WHICH IT MAY BE IN A REAL WORLD SAMPLE, IT LOOKS LIKE THE CALCULATIONS ARE A BIT MORE COMPLICATED, BUT I'LL HAVE TO GO BACK AND LOOK.

MR. RHOADES: IF YOU DEVELOP THE FORMULA, REALLY, THE FACT THAT YOU DON'T GET FULL EXTRACTION, IT WILL SHOW UP. IF YOU USE A LESS EFFICIENT OR THE PARTITIONING COEFFICIENT DOES NOT FAVOR AS GOOD EXTRACTION, MATHEMATICALLY YOU'RE STILL IN JUST AS GOOD A SHAPE. YOU KNOW THAT YOU HAVE NOT EXTRACTED ALL OF IT SO YOU CAN CORRECT IT; THAT'S ALL I...NOW, I THINK THAT ANSWERS THAT ONE.

NOW, I'M SURE THERE'S A LOT BETTER MATHEMATICIANS IN THIS ROOM THAN I AM, BUT IF YOU ACCEPT THE FIRST

EQUATION, WHICH I THINK IS DIFFICULT TO ARGUE WITH, THE TOTAL IS THE SUM OF THE PARTS IS WHAT THAT SAYS, THEN THE REST OF THAT IS JUST STRAIGHTFORWARD MATHEMATICS, AND THIS IS THE FORMULA THAT WE DEVELOPED THE CURVES FROM, AND ALL I CAN SAY HERE IS THAT THIS IS JUST A PURE MATHEMATICAL ANALYSIS BASED ON THAT FIRST SUPPOSITION, AND I DON'T ARGUE WITH ANYBODY FOR NOT BELIEVING THIS BECAUSE I FIND IT KIND OF DIFFICULT MYSELF, BUT I HAVE ACTUALLY DONE SOME OF THIS 1 AND 5, IT GOES JUST EXACTLY BY THE MATHEMATICS.

MS. THRUN: JUST TO HELP OUT THAT A LITTLE BIT. THE WORK THAT WE DID AT A.D.L., WE USED AN EXTERNAL STANDARD CURVE FOR ALL THOSE PERCENT RECOVERIES THAT DID AGREE WITH THE PARTITION COEFFICIENT LITERATURE VALUES. WE DIDN'T USE JOHN'S EQUATIONS WITH THE INTERNAL STANDARD; THAT'S WHY YOU SAW A FIGURE FOR XYLENE AS WELL AS THE OTHER THREE ANALYTES. DID EVERYBODY HEAR THAT?

MR. TELLIARD: No.

MS. THRUN: SORRY ABOUT THAT. THE WORK THAT WE DID AT A.D. LITTLE, WITH THE CLEAN MATRIX, WE DIDN'T USE JOHN'S EQUATION, WE USED A STRAIGHTFORWARD FOUR POINT CALIBRATION CURVE; THEREFORE, THOSE EQUATIONS WEREN'T USED. THE PARTITION COEFFICIENT, IN THE LITERATURE, WHEN YOU CALCULATED A

PERCENT RECOVERY, THAT AGREED VERY NICELY WITH THE EXPERIMENTAL VALUE; JUST AN ADDED POINT.

MR. RHOADES: I'LL THROW THIS IN. I THINK THAT WHAT'S HAPPENED IS THAT MANY OF THESE THINGS, THEY ARE EXTREMELY EASY TO EXTRACT AND THIS HAS NOT BEEN REALIZED BY MOST PEOPLE. THE MATRIX EFFECTS MAY OR MAY NOT BE OVEREMPHASIZED. THIS ONE DOES DEPEND LARGELY ON THE COMPOUND. FOR MANY OF THESE, I'LL SAY THE PURE HYDROCARBON TYPE, THEY APPARENTLY EXTRACT QUITE WELL WITHOUT SALTING IN MANY INSTANCES OR ANYTHING ELSE. AS YOU GET INTO THE MORE WATER SOLUBLES, FOR INSTANCE, PHENOLS, YOU START TO HAVE TROUBLES. NITROBENZENE, IF YOU DON'T SALT THAT, YOU DON'T GET MUCH BACK; IF YOU SALT IT, YOU DO. NOW, THERE ARE SOME STRANGE THINGS HERE AND I'LL THROW OUT SOME NUMBERS; UNFORTUNATELY, THEY'RE RECORDING THIS, BUT USING THE EXHAUSTIVE EXTRACTION APPROACH FOR PHENOLS FROM CLEAN WATER, IT IS MY UNDERSTANDING FROM THE WORK WE HAVE DONE AND I BELIEVE WORK OTHERS HAVE DONE THAT THE EXTRACTION EFFICIENCY RUNS AROUND 40 TO 45 PERCENT. NOW, THIS IS WITH THE REGULAR PROCEDURE OF AN ACID, OR A BASE CLEANUP AND THEN AN ACID EXTRACTION TYPE OF THING USING, WELL, I GUESS IT'S DCM IN THAT PROCEDURE. NOW, THEN, WE MOSTLY USE HEXANE; YOU'LL BE SURPRISED WHAT GOES INTO HEXANE.

EVERYBODY SAYS IT'S NOT POLAR ENOUGH. WELL, ALL I CAN SAY IS, TRY IT. IT DOES DO AMAZINGLY WELL, BUT IT DOESN'T DO EVERYTHING. WE USED DI(ISOPROPYL) ETHER TO EXTRACT THE PHENOL AND NOW YOU'RE NOT GOING TO BELIEVE ME. WE GET 70 PERCENT OF THE PHENOL INTO THE 1 MILLILITER OF WATER; THE EXHAUSTIVE EXTRACTION GETS 40 PERCENT. IT SHOWS THE DIFFERENCE OF THE SALTING.

MR. PATERSON: DI(ISOPROPYL) ETHER?

MR. RHOADES: DI(ISOPROPYL) ETHER, YES. THE REASON WE USE DI(ISOPROPYL) ETHER IS BECAUSE IT HAS LOW WATER SOLUBILITY AND IT HAPPENS TO BE...WELL TO EXTRACT. IT HAS PEROXIDES PROBLEM BUT HERE, AGAIN, REMEMBER, WE'RE USING 1 MILLILITER. WE BUY TREMENDOUS STOCKS OF THIS, WE BUY IT 500 MILLILITERS AT A TIME OR SOMETHING LIKE THAT.

MR. HENDERSON: I'M JIM HENDERSON WITH CARBORUNDUM. I'D JUST LIKE TO SUGGEST THAT SOMETIMES IN THE EXHAUSTIVE EXTRACTION PROCEDURES, YOU'RE NOW LOOKING AT TWO FACTORS; THAT IS, THE EXTRACTION RECOVERY AS WELL AS THE LOSSES FROM CONCENTRATION. I DON'T KNOW WHETHER YOU'RE MEASURING THE RECOVERY WITHOUT A CONCENTRATION STEP, BUT YOUR VALUES MAY BE CLOSER IN COMPARING YOUR MICRO-

EXTRACTION PROCEDURE WITH AN EXTRACTION WITH NO CONCENTRATION STEP, IF YOU'RE JUST INTERESTED IN THE PHENOMENON OF RECOVERY EFFICIENCY.

MR. RHOADES: WELL, THIS IS TRUE DEPENDING, REALLY, ON THE VOLATILITY OF THE COMPOUNDS. WE HAVE HAD, FOR INSTANCE, IN PESTICIDES AND PHTHALATES AND MANY OF THESE OTHERS, KUDERNA-DANISH IS EXTREMELY EFFICIENT. NOW, EVENTUALLY YOU GET DOWN TO THE POINT, FOR INSTANCE, YOU COULDN'T DO BENZENE BY EXHAUSTIVE EXTRACTION AND GO THROUGH A KUDERNA-DANISH, BUT IT WORKS VERY WELL. I HAVE NO COMPLAINTS ON THE EFFECTIVENESS OF KUDERNA-DANISH.

MR. HENDERSON: I NEED SOME CLARIFICATION ON SOME OF KATHY'S DATA. DID YOU INDICATE THAT THE ADDITION OF ONE PART PER MILLION OF CARBON TETRACHLORIDE TO THE WATER INCREASES THE RECOVERY EFFICIENCY?

MS. THRUN: A SIGNIFICANT EVENT FROM CARBON TETRACHLORIDE. THE ONLY EFFECT FROM ORGANICS THAT WE COULD SEE WAS WHEN YOU ADDED 10,000 PARTS PER MILLION OF ACETONITRILE; THEN YOU REDUCE THE RECOVERY.

MR. HENDERSON: THAT WAS A REDUCTION.

MS. THRUN: IT REDUCED IT,

AND THEN WHEN YOU ADDED SALT, YOU OVERCAME THAT EFFECT.

MR. HENDERSON: I STAND CORRECTED.

MR. RHOADES: I DID NOT ANSWER ONE OTHER QUESTION THE GENTLEMAN HAD OVER HERE, HOW DO WE SPIKE. GENERALLY, IN ACETONE WE MAKE UP SPIKING SOLUTIONS. WE GENERALLY SPIKE LESS THAN 100 MICROLITERS, IN 10 TO 100 MICROLITERS. FREQUENTLY, IF WE'RE GOING TO GO UP TO 100 MICROLITERS, WE THEN PUT 100 MICROLITERS OF ACETONE UNDER THE UNSPIKED SAMPLE, ALSO; BUT BASICALLY WE TRY TO GET EVERYTHING TO CANCEL OUT.

MS. THRUN: JUST TO TAKE THAT ONE STEP FURTHER. WHEN WE WERE SPIKING, WE SPIKED IT NEAT, IT WASN'T IN ANY SOLVENT; WITH MUCH DIFFICULTY, BUT WE SPIKED IT IN.

MR. BLOOM: SAUL BLOOM, EXXON RESEARCH. THE QUESTION I HAVE IS, OF THE DATA THAT WE'VE SEEN PRESENTED THIS MORNING, WERE THESE ON REAL WORLD SAMPLES OR JUST ON BLENDS IN WATER?

MS. THRUN: THE DATA THAT I PRESENTED WAS ALL ON CLEAN WATER, DIONIZED DISTILLED WATER. THE DATA THAT BILL PRESENTED WAS OUT OF SAMPLES COLLECTED FOR THE ORGANICS PLASTICS INDUSTRY AND THEY REPRESENTED VERY REAL SAMPLES.

MR. WALLIN: BRUCE WALLIN, E.C. JORDAN COMPANY. THIS IS A COMMENT, NOT A QUESTION. IN JUNE '79 AN ARTICLE WAS PUBLISHED IN THE JOURNAL OF AMERICAN WATERWORKS ASSOCIATION ON A...MAYBE WE CAN CALL IT A SEMI-MICROEXTRACTION PROCEDURE USING SINGLE STEP, 5 PERCENT, SOLVENT VOLUME, AND THEY FOUND, LOOKING AT TRIHALOMETHANES IN PARTICULAR, THAT THE PROCEDURE AGREED VERY WELL WITH THEORY. SINCE THEN WE'VE BEEN TRYING IT WITH SOME MORE REAL WORLD SAMPLES. OF COURSE, THEY USE A CLEAN MATRIX IN THEIR TEST, AND WE'RE ENCOURAGED WITH THE DATA THAT WE'RE GETTING, BUT IT'S MUCH TOO SOON TO SAY ANYTHING ABOUT THAT, EXCEPT THAT WE ARE ENCOURAGED.

MS. THRUN: YES, THERE WAS ALSO A RECENT PAPER IN THE JOURNAL OF CHROMATOGRAPHY BY MURRAY, WHO USED, I BELIEVE, 20,000 TO 1 SAMPLE TO SOLVENT RATIOS, AND HE WAS GETTING REASONABLE RECOVERIES FOR THE PESTICIDES, AND I THINK HE ALSO LOOKED AT PHTHALATES AND SOME HYDROCARBONS; SO THERE IS MORE AND MORE SUPPORT OF DATA OUT THERE.

MR. ENGELSKIRCHEN: I'M TODD ENGELSKIRCHEN FROM NALCO CHEMICAL COMPANY. WE HAVE USED THIS KIND OF PROCEDURE TO LOOK AT PRODUCT SAMPLES FOR TRACE MONOMERS, FOR EXAMPLE. WE DILUTE THE PRODUCT APPROXIMATELY 1 IN 5 AND THEN DO A MACROMICROEXTRACTION.

OUR SOLVENT TO DILUTION RATIOS ARE MUCH HIGHER AND WE HAVE MEASURED EXTRACTION EFFICIENCIES OVER 90 PERCENT BY SPIKING; WE USE SERUM VIALS BY SPIKING THROUGH THE SEPTUM WITH A CONCENTRATED SOLUTION. WE GET AROUND A LOT OF MECHANICAL PROBLEMS; WE CAN DETERMINE EXTRACTION EFFICIENCIES ON THE SAMPLES ONE AT A TIME. EVERY SAMPLE HAS ITS OWN EXTRACTION EFFICIENCY DONE ON THE SAME VIAL, AND WE CONSISTENTLY GET OVER 90 PERCENT FOR SOME THINGS THAT YOU WOULD NOT BE ABLE TO DO WITH THE STANDARD EXTRACTION PROCEDURE BECAUSE THE MATERIAL ITSELF IS TOO VOLATILE, I THINK; IN OUR HANDS, I HAVE NO DATA WITH ME, BUT IN OUR HANDS, IT'S WORKED WELL.

MR. OLLISON: WILL OLLISON, A.P.I. A BRIEF COMMENT TO THE FIRST SPEAKER. YOU MENTIONED ONE OF THE THINGS THE APPROACH WAS DEPENDENT UPON WAS THAT THE PARTITIONING COEFFICIENT MUST REMAIN CONSTANT OVER THE RANGE OF INTEREST; THAT'S THE RANGE OF VOLUME YOU'RE USING?

MR. RHOADES: NO. THE RANGE THAT I'M TALKING ABOUT IS THE CONCENTRATION RANGE OF THE MATERIAL OF INTEREST. IN OTHER WORDS, IF WE ARE WORKING AT SOMETHING LIKE 10 PARTS PER BILLION, WE DO NOT SPIKE, THEN, AT 10 PARTS PER MILLION. WE WILL SPIKE AT...AND I HAVE SOME DISAGREEMENT WITH MY COHORTS HERE. I DO NOT LIKE TO SPIKE AT, SAY, TWICE THE LEVEL;

EXPERIMENTAL ACCURACY IS NOT GOOD ENOUGH TO SUBTRACT A PEAK THAT BIG FROM ONE THAT BIG. So I ARBITRARILY HAVE PICKED A FACTOR OF 7. THIS GIVES YOU FAIRLY BIG IF YOU'VE GOT A GOOD RECOVERY, BUT IN THINGS LIKE PHENOL IT'S NOT THAT MUCH MORE; SO YOU DON'T HAVE AS MANY RERUNS, AND IN MY OPINION, THIS GIVES BETTER DATA, BUT IT EXPANDS...IT'S LESS THAN A FACTOR OF 10 IN CONCENTRATION.

MR. OLLISON: YOU MENTIONED ALSO THAT SALTING OUT OCCASIONALLY WAS A PROBLEM, ADDING SODIUM CHLORIDE WAS A PROBLEM, IN SOME SITUATIONS. WHEN IS THIS A PROBLEM?

MR. RHOADES: NO, I'M AFRAID I MISINFORMED YOU THERE. THERE ARE SOME INSTANCES WHERE YOU DO NOT NEED TO ADD SODIUM CHLORIDE. NOW, MOST OF THE PHTHALATE DATA THAT YOU SAW PRESENTED HERE BY BILL COWEN WAS NOT SALTED. THE REASON HERE IS, IN OUR HANDS, MAYBE WE'VE GOT A MESSY LAB, I DON'T KNOW; THE FEWER THINGS THAT COME IN CONTACT WITH A SAMPLE THAT YOU'RE DOING PHTHALATES, THE LESS PHTHALATES YOU FIND.

MR. OLLISON: A THIRD QUESTION WAS, IN ANY OF THE SAMPLES IN THESE STUDIES THAT HAVE BEEN REPORTED, WERE THERE APPRECIABLE LEVELS OF PARTICULATE MATTER AND DID THIS CONSTITUTE A PROBLEM IN THE TIME YOU EXTRACTED IT?

MR. RHOADES: Most of the samples were what I will call truly aqueous samples, and I will make no claims whatsoever when you get to a three-phase system.

MR. OLLISON: The final question would be, do you recommend this as a replacement for the sparging method for the volatiles?

MR. RHOADES: It's not my position to make recommendations. I do the work and I send the reports in.

MR. BRAIN: Devin Brain of the Procter and Gamble Company. I had a question on your graphs, John, on where you had the partition coefficients. Where the partition coefficient was quite small, I can understand how your technique works, but when you got down towards the bottom, you've got virtually a horizontal line, now where you...

MR. RHOADES: Yes, well, now, here, you see, I've gone down to a partitioning coefficient that says 1 to 1. In other words, it equally distributes. The point here is that if you extract with 1 milliliter, you now have 1 percent of it out. If you extract with 5 milliliters, you now have 5 percent of it out, but concentration-wise you've gained essentially nothing. So you're creeping up

ON THE TOTAL AMOUNT EXTRACTED; THE CONCENTRATION IS GOING DOWN VERY SLOWLY. THIS IS THE CLUE; IF YOU DO A TWO-VOLUME EXTRACTION LIKE THIS 1 AND 5 AND THE PEAK HEIGHT IS THE SAME IN BOTH CASES, YOU KNOW, YOU'RE GETTING VERY LITTLE OF IT. IF YOU'RE GETTING GOOD EXTRACTION, THE SECOND EXTRACTION WOULD BE MUCH LESS. FOR EXAMPLE, LET'S ASSUME YOU EXTRACT 100 PERCENT OF THE SAMPLE IN THE 1 MILLILITER; WHEN YOU EXTRACT WITH 5 MILLILITERS, YOU SHOULD HAVE 20 PERCENT OF THAT.

MR. BRAIN: THE CONCENTRATION WILL BE 20 PERCENT?

MR. RHOADES: THE CONCENTRATION WILL BE 20 PERCENT, YES, THANK YOU; THE TOTAL AMOUNTS, THE SAME.

MR. BRAIN: WHAT ARE YOU SUGGESTING IN THAT CASE WHERE YOU HAVE A FAIRLY HIGH PARTITION COEFFICIENT?

MR. RHOADES: USE A SMALL VOLUME IF THAT'S WHAT YOU'RE AFTER. IN MOST OF THE WORK THAT WE'VE DONE SO FAR ON THE PRIORITY POLLUTANTS, MOST OF THEM EXTRACT QUITE WELL. SO ON THAT BASIS THIS TENDS TO SHOW CONCENTRATION AS YOU EXTRACT. IT SAYS IF YOU EXTRACT...IF YOU HAVE A MATERIAL THAT EXTRACTS WELL, LIKE A HERE (INDICATING), IF YOU KEEP THE VOLUME LOW, YOU WILL GET PREFERENTIALLY A BETTER

RESPONSE FOR THAT COMPOUND THAN YOU WILL SOME OTHERS WHICH ARE NOT AS EFFECTIVELY EXTRACTED. AS A MATTER OF FACT, IF YOU GO UNTIL YOU GET EVERYTHING OUT IN ALL CASES, THEN EVERYTHING IS EXACTLY THE SAME. DOES THAT ANSWER YOUR QUESTION?

MR. BRAIN: THANK YOU.

MR. TELLIARD: BILL, I HAVE A QUESTION. ON THE EFFLUENTS AND THE DATA YOU SHOWED US ON THE PHTHALATES AND SO FORTH, WHAT WAS THE AVERAGE RANGE OF SOLIDS ON THOSE SAMPLES, 20 TO 30, 60-80? DO YOU HAVE ANY IDEA WHAT THE SUSPENDED SOLIDS WERE?

MR. COWEN: NO, WE DON'T HAVE ANY DATA ON THAT. NONE OF THOSE MEASUREMENTS WERE MADE DURING VERIFICATION. THERE WERE SOME SAMPLES, IN ANSWER TO THE OTHER QUESTION ON SOLIDS, THERE WERE SOME SAMPLES THAT ACTUALLY HAD SUSPENDED LATEX IN THEM. UNFORTUNATELY, WE DON'T HAVE A LOT OF DATA ON THAT RIGHT NOW AND THAT'S WHY JOHN IS SAYING THAT WE DON'T REALLY WANT TO SAY ANYTHING ABOUT ANY OF THOSE KINDS OF SAMPLES.

MR. WAY: JOHN WAY, DUPONT COMPANY. THE QUESTION I HAD, NOW, I CAN UNDERSTAND HOW THIS WORKS, BUT YOU'VE SAID NOTHING ABOUT WHAT YOU USE AS THE INTERNAL STANDARDS FOR

THESE VARIOUS CLASSES OF COMPOUNDS, AND IT SEEMS TO ME THAT THAT'S ONE OF THE CRITICAL THINGS THAT MAKES THE WHOLE THING WORK.

MR. RHOADES: YES, THAT WAS MY ASSUMPTION WHEN WE STARTED. SO IN GENERAL WE TRIED TO PICK COMPOUNDS THAT WERE SIMILAR. WE USED XYLENE IN SOME INSTANCES FOR THE BENZENE, TOLUENE, ETHYL BENZENE. NOW, YOU'LL NOTICE IN ONE OF THOSE, THE ETHYL BENZENE DATA WAS NOT VERY GOOD; WE HAD AN INTERFERENCE THERE WITH ONE OF THE XYLENES, THE COLUMN WE HAD. IT HAD NOTHING TO DO, REALLY, WITH THE EXTRACTION. IN THE PHTHALATES, SOMETIMES WHAT WE DO ON THESE...REMEMBER, YOU CAN RUN THESE FAIRLY FAST. WE WOULD TAKE A LOOK AT IT, FOR INSTANCE, ON THE DIETHYL. LET ME PREFACE THIS BY SAYING THIS, WE LOOKED FOR THOSE COMPOUNDS WE WERE TOLD TO LOOK FOR, NO MORE; SO FREQUENTLY WE WOULD JUST MAKE A QUICK EXTRACTION AND SHOOT IT. IF THERE WAS NO DIOCTYLPHTHALATE, WE'D PUT IT IN, THAT WAS IT.

NOW, THE OTHER THING THAT WE FOUND OUT IN A HURRY ON THIS, THOUGH, IS THAT REALLY THE ONLY THING THAT SHOULD END UP BEING DIFFERENT IS THAT WHICH YOU PUT IN THERE. SO ANYTHING, ALMOST, THAT'S THERE ACTS AS AN INTERNAL STANDARD OR REFERENCE MATERIAL. SO IN MY OPINION IT IS NOT AS CRITICAL AS I THOUGHT IT

WAS INITIALLY BECAUSE THE ONLY REASON FOR THIS IS NOT TO MAKE THE CALIBRATION CURVE OF THE COMPOUND OF INTEREST, MERELY TO NORMALIZE YOUR DATA.

MR. HENDERSON: JIM HENDERSON WITH CARBORUNDUM. JOHN, COULD WE LOOK AT THE BAR GRAPH AGAIN; I HAVE A QUESTION ABOUT THAT.

MR. RHOADES: THIS IS A THEORETICAL CALCULATION, YOU UNDERSTAND.

MR. HENDERSON: DO WE NOT HAVE TO MULTIPLY BY THE VOLUME TO GET THE TOTAL RECOVERY ON THESE? IN OTHER WORDS, THAT MIDDLE PLOT SHOULD BE MULTIPLIED BY FIVE, SHOULD IT NOT?

MR. RHOADES: YES, THIS SHOWS CONCENTRATION. WHAT I WAS TRYING TO SHOW HERE IS THE SELECTIVITY. IF YOU CONCENTRATED THIS 5 MILLILITERS TO 1 MILLILITER...

MR. HENDERSON: AND LOST NOTHING.

MR. RHOADES: ...EVERYTHING WOULD BE BACK UP HERE (INDICATING).

MR. HENDERSON: WELL, IT WOULD BE EXACTLY 100 PERCENT, THOUGH.

MR. RHOADES: YES, IF YOU KEEP GOING OUT. IF YOU GO ON OUT TO 50 MILLILITERS AND NOW, THEN, YOU MAY HAVE 100 PERCENT OF THIS ONE. THIS IS ONE OF THE POINTS

THAT I'M TRYING TO MAKE. IF THIS IS THE ONE YOU'RE INTERESTED IN, FINE. IF IT ISN'T, DON'T BE BURIED IN IT.

MR. HENDERSON: I WAS JUST TRYING TO RATIONALIZE THAT WITH YOUR PREVIOUS GRAPH. IT LOOKS LIKE, IF YOU LOOK AT THE TOP OF IT...

MR. RHOADES: IF YOU'LL NOTICE HERE, THE SOLID LINE IS THE TOTAL PERCENT RECOVERY. FOR INSTANCE, JUST TAKE THE TOP ONE. IT SAYS THAT YOU HAVE, IN THE 1 MILLILITER YOU WOULD HAVE 91 PERCENT AND, WELL, COME OUT HERE TO 7 MILLILITERS, THE BEST I CAN TELL YOU, YOU WOULD HAVE ABOUT 99 PERCENT OR SOMETHING LIKE THAT. THE CURVE LINE SHOWS THE CONCENTRATION; THIS I HAD THOUGHT MERELY SHOWED THAT A LITTLE BETTER.

MR. STANKO: GEORGE STANKO FROM SHELL DEVELOPMENT. I DON'T THINK THE ANSWER TO MY QUESTION IS GOING TO BE READILY AVAILABLE, BUT I'M GOING TO ASK IT ANYWAY. IT APPEARS THAT WE'VE BEEN SHOWN A METHOD WHERE THE CONCENTRATION FACTOR IS 20 TO 1. THE STANDARD DEVIATIONS THAT WE'VE BEEN SHOWN ARE SOMEWHERE, A THIRD TO 20 PERCENT LESS THAN WHAT WE'VE BEEN EXPERIENCING WITH THE PROTOCOL PROCEDURE, AND ALSO THE CONCENTRATION LEVELS THAT HAVE BEEN DISCUSSED ARE IN THE TEN PARTS PER BILLION

CONCENTRATION RANGE. IT'S A LITTLE DIFFICULT FOR ME TO UNDERSTAND; THE PROTOCOL PROCEDURE USES A CONCENTRATION FACTOR OF 1,000 TO 1; WHEN YOU'RE WORKING IN THE TEN PARTS PER BILLION RANGE, OUR STANDARD DEVIATIONS ARE THREE TO FOUR TIMES THAT OF THE METHOD I'VE SEEN HERE. SOMETHING JUST DOESN'T ADD UP.

MR. RHOADES: I'M NOT SURE WHETHER I COMPLETELY UNDERSTAND YOUR QUESTION. LET ME SAY THIS, THAT SOME OF THE STANDARD PROCEDURES YOU REALLY, YOU CONCENTRATE FROM...YOU EXTRACT FROM 1,000 MILLILITERS AND YOU END UP IN 10 MILLILITERS.

MR. STANKO: THAT'S 1,000 TO 1.

MR. RHOADES: WE EXTRACT FROM 100 AND END UP IN 1, WHICH IS 100 TO 1.

MR. STANKO: SOME OF THE DATA WERE SHOWN ON 20 TO 1 WHICH SEEMED TO BE THE OPTIMUM.

MR. RHOADES: NO. WELL, YOU DO NOT EXTRACT ALL COMPOUNDS WITH THE SAME EFFICIENCY AT ALL LEVELS. WHAT I THINK THAT WE'RE TRYING TO SAY HERE IS THAT THE RECOVERIES ARE GOOD EVEN DOWN TO 100 AND LESS; I WOULD THINK. I'VE DONE

SOME OF THIS WITH A GALLON WITH A MILLILITER, JUST TO SEE IF SOMETHING'S THERE AND YOU CAN DO THIS; YOUR QUANTITATION BEGINS TO FALL APART, HOWEVER.

MR. STANKO: WELL, THE BOTTOM LINE. IT APPEARS THAT YOU HAVE A TREMENDOUS INCREASE IN PRECISION OF ANY METHODS THAT WE'VE SEEN AND SOMEWHERE BETWEEN A 10 AND A 50-FOLD INCREASE IN SENSITIVITY, WHICH IS HARD TO EXPLAIN.

MR. RUSHNECK: GEORGE, LET ME ATTEMPT TO EXPLAIN THAT. DALE RUSHNECK, PJB LABS. IT'S REALLY DEPENDENT ON THE COMPOUND. A LOT OF THESE MICROEXTRACTION PROCEDURES USE THE ELECTRON CAPTURE DETECTOR FOR WHICH YOU DON'T NEED AS GREAT A CONCENTRATION FACTOR. THAT APPLIES TO THE PHTHALATES, GENERALLY TO THE CHLORINATED VOAS, TO THE PESTICIDES, AND SOME OF THE OTHER THINGS. YOU NEED THE CONCENTRATION FACTOR, FOR EXAMPLE, WHEN YOU'RE USING A FLAME IONIZATION DETECTOR BECAUSE THE SENSITIVITY ISN'T AS GREAT, AND THEREFORE, ALTHOUGH WE NORMALLY USE MICROEXTRACTION AT 100 TO 1, WHEN WE HAVE, LIKE, THE PHENOLS AND WE NEED TO DETECT THEM DOWN AROUND 10 MICROGRAMS PER LITER, WE HAVE TO GO TO THE BIG EXTRACTION, THE EXTENSIVE EXTRACTION, IN ORDER TO GET THAT DETECTION LEVEL.

MR. STANKO: WELL, I THOUGHT

THE DATA THAT WAS SHOWN HERE WAS ON PHENOLS AND I DON'T BELIEVE THAT APPLIES.

MR. RUSHNECK: YES, BUT I DON'T BELIEVE THOSE LEVELS WERE DOWN AROUND 10 MICROGRAMS PER LITER, WERE THEY?

MR. COWEN: WELL, THE LEVELS VARY; WE COULDN'T PUT ON EACH ONE, YOU KNOW, YOU'D HAVE TO PUT EACH NUMBER WITH ITS LEVEL. THEY ARE ALL ABOVE 10, BUT THAT IS ALL I CAN SAY, THEY ARE ALL OVER THE PLACE, THEY ARE ALL SORTS OF SAMPLE TYPES.

MR. STANKO: THE STANDARD DEVIATION FOR ANALYSES WILL BE MUCH DIFFERENT IF YOU'RE ANALYZING AT 1,000 PARTS PER BILLION VERSUS 100 PARTS PER BILLION OR 10 PARTS PER BILLION; YOUR DATA REALLY NEEDS TO BE QUALIFIED THERE.

MR. COWEN: WELL, WE SHOULD BREAK IT UP INTO CONCENTRATION RANGES, THAT'S TRUE. FOR NOW WE WERE TRYING TO SEE WHAT IT IS WITHOUT REGARD TO CONCENTRATION.

MR. STANKO: THANK YOU, SIR.

MR. TELLIARD: BEFORE ANYONE ELSE CAN GET TO A MICROPHONE, THANK YOU VERY MUCH KATHY, GEORGE, BILL. WE'RE GOING TO TAKE A BREAK NOW AND YOU'VE GOT TEN MINUTES TO GET YOUR COFFEE AND EAT YOUR PEAR AND GET BACK IN HERE.

MR. TELLIARD: LAST YEAR, THE LAST MEETING WE HAD, BRUCE COLBY FROM SYSTEMS, SCIENCE AND SOFTWARE GAVE A PRESENTATION ON, FOR LACK OF A BETTER TERM, ISOTOPE DILUTION OR THE STABLE LABEL APPROACH IN VOAS; SINCE THEN BRUCE HAS BEEN LOOKING AT THE APPLICATION TO A MUCH LARGER RANGE OF SAMPLES AND I THINK MOST OF THE BRANCH CHIEFS IN EGD WHO ARE PAYING ALL THIS MONEY FOR ANALYSIS ARE KIND OF HOPING THAT WE MIGHT FIND A METHOD HERE TO SAVE ME A FEW DOLLARS. NOW, I KNOW FOR ALL YOU CONTRACTORS THAT MAKES YOU FEEL WARM AND FUZZY INSIDE, THE THOUGHT OF ME SAVING A FEW DOLLARS, BUT ALSO I THINK IT MIGHT BE AN ALTERNATE SOLUTION TO THE 27 SPIKES, 15 ALIQUOTS, 37 RECOVERIES AND CUT DOWN A LITTLE BIT ON THE REPETITION THAT WE'RE PRESENTLY RUNNING; 33 RUNS TO GET 12 DATA POINTS IS SOMEWHAT EXPENSIVE, AND IN THE BACK OF OUR MINDS THESE ARE SOME OF THE SECRET THOUGHTS, WE'RE HOPING AGAIN THAT WE WILL MICROEXTRACT IT AND STABLE IT AND RUN IT AND I CAN GO HOME AND SIT AROUND THE HOUSE AND WATCH ALL THE DATA ROLL IN.

BRUCE HAS BEEN AT IT UNDER A CONTRACT THROUGH RTP AND LARRY JOHNSON'S FOLKS HAVE SPONSORED THE CONTRACT AND BRUCE IS HERE TODAY TO GIVE US KIND OF AN UPDATE ON HOW FAR HE IS WITH WHAT HE'S LOOKED AT.

Evaluation of Stable Labeled Compounds as Internal Standards for Quantitative GC/MS Analysis

By: Dr. Bruce E. Colby

I think first of all I'd like to say what we're doing, in looking at the use of stable label compounds as internal standards on a per compound basis, is nothing new; it's been going on for about the last 40 or so years, and it's a situation that has been applied almost exclusively in biological media where people were interested in a specific compound as opposed to being interested in a large range of compounds. As a consequence, the methodology has developed along fairly empirical lines. It's fairly straightforward to go in and try it this way, try it that way, make some decisions on what the best way to do it for this compound is, and then proceed on from there to apply the method. When we get into looking at some 40 or 50 compounds in a given run, it's not as easy to do it from an empirical standpoint; rather we have to have some sort of logical, reasonable, time-efficient way to go at picking the M/E's that should give us the best or at least very good results in terms of the analytical work. What we're really doing is to spike

EVERY GIVEN COMPOUND INTO EVERY SAMPLE, ONLY IN SPIKING IT INTO THE SAMPLE, WE PERTURB THE COMPOUND OR CHANGE THE COMPOUND BY LABELING IT, STABLE ISOTOPICALLY LABELING IT, AND IN THIS WAY THE MASS SPECTROMETER CAN TELL US THAT THIS ENTITY WAS WHAT WE SPIKED IN, THIS OTHER ENTITY, THE SAME COMPOUND, BUT DIFFERENT, NATURALLY ABUNDANT LABELING IS WHAT WAS THERE TO BEGIN WITH. SO IF WE WANT TO MEASURE PHENOL, WE'LL SPIKE A LABELED PHENOL AND DETERMINE RECOVERY FROM THE LABELED PHENOL IN THE SAME RUN EXACTLY AS WE'RE MAKING OUR MEASUREMENT. THIS WAY WE CANCEL OUT, AS WAS MENTIONED EARLIER, A LOT OF THE VARIABLES THAT CAN EXIST IN ANALYZING MULTIPLE SAMPLES. IT ALSO COSTS LESS MONEY BECAUSE WE ONLY HAVE TO DO IT ONE TIME. THERE IS ONE PREPARATION AND ONE ANALYSIS; THERE'S A LITTLE MORE DATA, BUT NOT ANY MORE DATA THAN ONE WOULD ENCOUNTER IN SPIKING A SAMPLE IN ADDITION TO THE ORIGINAL SAMPLE.

THE FIRST SLIDE, IF I CAN HAVE IT, WILL JUST GIVE US A QUICK LOOK AT WHAT WE'RE LOOKING FOR IN TERMS OF THE EVALUATION OR ACQUISITION OF RECOVERY INFORMATION. IDEALLY, WE'D LIKE TO GET RECOVERY INFORMATION ON EVERY COMPOUND THAT IS ON THE

RECOVERY INFORMATION

SITUATION	INFORMATION	METHOD
IDEAL	EVERY COMPOUND IN EVERY SAMPLE	SPLIT SAMPLE, SPIKE ONE PORTION, ANALYZE BOTH PORTIONS
ACCEPTABLE	MOST COMPOUNDS IN EVERY TENTH SAMPLE OF EACH MATRIX	SPLIT ONE OUT OF EVERY TEN SAMPLES FROM A GIVEN MATRIX, SPIKE ONE PORTION, ANALYZE BOTH PORTIONS
POTENTIAL ALTERNATIVE	MOST COMPOUNDS IN EVERY SAMPLE	SPIKE EACH SAMPLE WITH STABLE ISOTOPICALLY LABELED ANALOGS OF MOST COMPOUNDS

PRIORITY POLLUTANT LIST. THE WAY ONE WOULD DO THAT, OF COURSE, IS TO SPIKE EVERY SAMPLE AFTER IT HAS BEEN SPLIT AND TO ANALYZE BOTH PORTIONS. THE REASON I THINK SPIKING EVERY COMPOUND IS IMPORTANT IS THAT IF WE, IN FACT, DO NOT RECOVER ANY TCE, SAY, WE DON'T KNOW FOR SURE WHETHER THAT'S BECAUSE THERE IS NO TCE PRESENT, OR WHETHER IT'S REALLY PRESENT BUT WE'RE JUST NOT RECOVERING ANY OF IT. IF WE SPIKED TCE INTO THE SAMPLE AND COULDN'T RECOVER THAT, WE'D KNOW THAT THERE WAS SOMETHING TO BE CONCERNED ABOUT. IF WE SPIKE IT AND DO RECOVER IT, THEN WE KNOW AT LEAST THAT OUR ANALYTICAL METHOD IS FUNCTIONING.

THE AMOUNT OF EFFORT THAT WOULD GO INTO THAT KIND OF A SPIKING SITUATION GETS TO BE PRETTY LARGE AND IT CAN GET EXPENSIVE AND TIME-CONSUMING AND SO ON, SO THE IDEA HAS BEEN THAT WE'LL SPIKE LESS THAN ALL THE SAMPLES, SAY ABOUT 10 PERCENT OF THEM, ON AN OVERALL BASIS AND DO OUR RECOVERIES ON THOSE 10 PERCENT AND INFER ON THE OTHER 90 PERCENT THAT THAT'S VALID INFORMATION.

IN PRACTICE, IT SEEMS TO BE TURNING OUT THAT ABOUT 50 PERCENT OF THE SAMPLES ACTUALLY END UP BEING SPIKED WITH THE QA THAT'S BEING

APPLIED NOW ON A PER-EVENT BASIS. THE 10 PERCENT NUMBER IS MORE ASSOCIATED WITH, SAY, 1,000 SAMPLES FROM ONE PARTICULAR OUTFALL BEING LOOKED AT, AND THAT IS NOT THE WAY THESE THINGS ARE BEING DONE; THE 10 PERCENT WOULD BE BASED ON, SAY, FIVE YEARS FROM NOW SOMEBODY'S BEEN MONITORING THEIR EFFLUENT FOR THAT PERIOD OF TIME, IT PROBABLY WOULD DROP DOWN TO ABOUT 10 PERCENT. WHAT I AM SUGGESTING, THE POTENTIAL ALTERNATIVE WOULD BE TO SPIKE, AND I'M SAYING MOST OF THE COMPOUNDS, I THINK THAT THERE ARE SOME THAT THERE'S NOT TOO MUCH REASON TO SPIKE; THERE'S NO REASON, FOR EXAMPLE, TO PUT TCDD INTO THE WORLD IF WE DON'T NEED TO, AND TO LOOK AT THE SPIKED SAMPLE WHICH IS THE ONLY SAMPLE. WE NOW ARE BACK TO A VERY LOW LEVEL OF INCREASED ANALYTICAL WORK, WE HAVEN'T INCREASED THE NUMBER OF SAMPLES THAT WE NEED TO RUN AND WE STILL GET ALL OF THE INFORMATION THAT WE WOULD LIKE TO GET IN THE IDEAL SITUATION; THAT'S AT LEAST THE HYPOTHESIS.

THE PROBLEMS THAT MIGHT BE ASSOCIATED WITH DOING THIS, OR AT LEAST SOME OF THE MORE IMPORTANT ONES, ARE LISTED IN THE NEXT SLIDE. THE QUESTION OF COST AND AVAILABILITY OF ALL OF THESE COMPOUNDS, I GUESS I ALLUDED TO IT LAST YEAR AND IT SEEMED LIKE IT WOULD BE FAIRLY FAVORABLE, BUT NOT GREAT,

FEASIBILITY QUESTIONS OF STABLE ISOTOPE METHOD

1. COST/AVAILABILITY OF NECESSARY LABELED COMPOUNDS?
2. WILL LABELS EXCHANGE WITH SAMPLE MATRIX?
3. WHAT ARE THE EFFECTS OF ISOTOPIC PURITY?
4. HOW SHOULD THE DATA BE HANDLED?
5. WHAT ABOUT INSTRUMENT VARIABLES?

THAT SITUATION SEEMS TO BE CHANGING VERY RAPIDLY, AND I EXPECT THAT A VERY LARGE PERCENTAGE OF THESE COMPOUNDS WILL BECOME AVAILABLE IN THE NEXT YEAR. THE QUESTION OF EXCHANGE OF LABELS WITH THE SAMPLE MATRIX IS A CONCERN. WHAT HAPPENS IF WE PUT OUR LABELED COMPOUND IN AND THE LABEL COMES OFF OF THAT COMPOUND? WELL, CLEARLY THAT WOULD AFFECT THE RELIABILITY OF THE ANALYSIS, AND SO SOMETHING HAS TO BE DONE TO EVALUATE THAT SITUATION, AND I'LL EXPLAIN A LITTLE EXPERIMENT THAT WE DID TO AT LEAST GET A START ON THAT. WE DON'T KNOW ESSENTIALLY WHAT THE EFFECTS OF ISOTOPIC PURITY ARE, OR DO WE? WELL, WE'LL GET INTO SOME MATHEMATICS IN A MINUTE THAT WILL DEMONSTRATE THAT THIS SHOULDN'T BE A CONCERN FOR THE ANALYSIS. THE PAST DOES NOT EXPLAIN TO US PRECISELY HOW WE SHOULD HANDLE THE DATA, AND I BELIEVE WE NOW KNOW HOW TO DO THAT VERY RELIABLY, SO WE'LL TOUCH UPON THAT SOME.

INSTRUMENT VARIABLES; WE'VE LOOKED AT THAT. ALL I CAN SAY IS THAT I HAVEN'T BEEN ABLE TO TUNE AN INSTRUMENT (SORRY IF I'M NOT SUPPOSED TO TALK ABOUT TUNING), SUCH THAT WE CAN SERIOUSLY AFFECT AN ISOTOPE RATIO. THE TUNING OF THE INSTRUMENT AFFECTS ABUNDANCE

PATTERNS SEVERELY, BUT BECAUSE THE MEASUREMENTS THAT WE MAKE IN DOING THE ISOTOPE RATIOING ARE VERY CLOSE TOGETHER ON THE MASS SCALE, THERE IS VERY LITTLE DISTORTION OF THE ISOTOPE RATIO, AND IT'S SO VERY SMALL, AT LEAST AS FAR AS WE NEED TO CONTEND WITH IT, THAT IT'S IGNORABLE.

THE COST, IF I CAN GO BACK TO THAT, AND THE AVAILABILITY OF COMPOUNDS IS SHOWN IN THE NEXT SLIDE BY FRACTION. THERE ON THE TOP LINE ARE THE AVAILABLE COMPOUNDS IN TERMS OF WHAT IS CURRENTLY IN THE CATALOGS THAT THE LABELED COMPOUND MANUFACTURERS HAVE. PHENOL D6, WHICH IS VERY EASILY CHANGED TO D5, IS THE ONLY ACID COMPOUND THAT'S THERE; THERE WERE 13 BASE/NEUTRALS AND 15 OF THE VOLATILE COMPOUNDS. THE MANUFACTURERS HAVE AGREED THAT THEY INDEED CAN SYNTHESIZE ANYTHING YOU WANT, AND IN FACT, WE'VE GOT QUOTES NOW ON A VERY LARGE PERCENTAGE OF THESE COMPOUNDS, AND IT SEEMS THAT WE'LL BE PURSUING THAT, SO THE LIST WILL CHANGE VERY RAPIDLY NOW.

IF WE LOOK AT A COST ASSOCIATED WITH THE COMPOUNDS NOW, AND ASSUMING THAT WE'RE GOING TO SPIKE ALL PRIORITY POLLUTANTS, THE DOLLARS PER SAMPLE ARE GIVEN ON THE BOTTOM (INDICATING), AND THEY LOOK

COST/AVAILABILITY

	ACID COMPOUNDS	BASE/NEUTRAL COMPOUNDS	VOLATILE COMPOUNDS
CATALOG ITEMS (NUMBER)	1	13	15
CUSTOM SYNTHESIS (NUMBER)	10	34	16
COST ESTIMATE PER SAMPLE ($)	1.15	4.00	.003

ESTIMATED COST PER SAMPLE ANALYSIS = $5.15

LIKE VERY SMALL NUMBERS, AND INDEED THEY ARE, BECAUSE WE DON'T HAVE TO SPIKE THE SAMPLE WITH VERY MUCH OF THE COMPOUND. THE COSTS IN PURCHASING THE COMPOUND ARE BASED ON PURCHASING A GRAM, SO IF SOMEONE SOMEWHERE BUYS A GRAM, HE COULD THEN METER THIS OUT AS NEEDED TO PEOPLE DOING THE ANALYSES, AND ON A PER-ANALYSIS BASIS, THE COST BECOMES VERY LOW--A TOTAL OF ABOUT $5.15 FOR MATERIALS BASED ON QUOTATIONS FOR THESE COMPOUNDS. THE $5.15 BECOMES REALLY INSIGNIFICANT WHEN YOU THINK THAT SOMEONE'S GOT TO PACKAGE THESE THINGS UP AND DO ALL THE OTHER THINGS THAT HAVE TO BE DONE WITH STANDARDS, KEEP TRACK OF THEM AND PUT THEM IN LITTLE VIALS, SEND THEM HERE, SEND THEM THERE. THE $5 JUST DISAPPEARS INTO THE NOISE LEVEL OF THE COST DATA.

THE CUSTOM SYNTHESIS AND CATALOG ITEMS THAT WERE INCLUDED IN THIS ESTIMATE INCLUDED PRIMARILY DEUTERATED COMPOUNDS, BUT THERE ARE SOME DEUTERATED COMPOUNDS THAT DO SHOW EXCHANGE. ALSO, THERE ARE SOME COMPOUNDS THAT CANNOT BE DEUTERATED; PENTACHLOROPHENOL, HEXACHLOROETHANE, HEXACHLOROBENZENE, THINGS LIKE THAT, WE CAN'T DEUTERATE THOSE, SO THE COST IN THOSE

CASES WAS BASED ON C13 LABELED COMPOUNDS. THEY ARE MORE EXPENSIVE, BUT CLEARLY DON'T AFFECT THE OVERALL PRICE OF THINGS VERY MUCH. THE CONCERN FOR EXCHANGE WITH THE MATRIX IS ONE THAT WE'VE LOOKED AT AS BEST WE CAN, I THINK, AT THIS STAGE, AND THE WAY WE DID THAT IS ILLUSTRATED IN THE NEXT SLIDE.

WE FELT THAT WHAT WE'RE TRYING TO LOOK FOR IS, SAY, WITH CHLOROFORM HERE, THE EXCHANGE OF THE DEUTERIUM, IF WE WERE GOING TO USE DEUTERATED CHLOROFORM, WITH A PROTON FROM SOLUTION. I DON'T MEAN TO IMPLY THAT THIS EXCHANGE TAKES PLACE IN AN ACIDIC SOLUTION OR ANYTHING ELSE; JUST THAT THERE'S A PROTON OUT HERE SOMEWHERE AND IT CAN EXCHANGE, AND NOW WE HAVE CONVERTED OUR INTERNAL STANDARD TO THE PRIORITY POLLUTANT, AND THAT WOULD INCREASE THE APPARENT CONCENTRATION OF CHLOROFORM IN THE SAMPLE.

THE WAY TO STUDY THIS IS NOT NECESSARILY TO GO OUT AND BUY DEUTERATED CHLOROFORM, BECAUSE IF WE GOT INOT BUYING ALL OF THE DEUTERATED COMPOUNDS, IT WOULD GET VERY EXPENSIVE, AND WE WOULD UNNECESSARILY PURCHASE SOME THAT WOULDN'T WORK. SO WHAT WE DO IS LOOK AT THE NATURALLY ABUNDANT MATERIAL, REGULAR CHLOROFORM, BUT WE'LL

ISOTOPE EXCHANGE STUDY

EXCHANGE IN AN ANALYTICAL SITUATION:

$$CDCl_3 + H^+ \rightarrow CHCl_3 + D^+$$

EXCHANGE STUDY:

$$CHCl_3 + D^+ \rightarrow CDCl_3 + H^+$$

CONDITIONS STUDIED:

pD = 2, 7, 12

TIME (HR) = 0, 48, 96

TEMP (°C) = 0, 25

PREPARE IT IN A DEUTERATED ENVIRONMENT AND WE'LL STORE IT FOR A WHILE AND WE'LL ADJUST THE PD, THE EQUIVALENT OF PH, AND SEE WHAT HAPPENS, SEE IF WE CAN FIND SOME SITES ON SOME MOLECULES THAT DO EXCHANGE, AND THEN WE'LL KNOW THAT THOSE ARE ONES THAT WE SHOULDN'T TRY TO LABEL.

WELL, HERE ARE THE CONDITIONS ON THE BOTTOM (INDICATING). WE LOOKED AT PDS OF 2, 7, AND 12, AND WE LOOKED AT THESE OVER TIME PERIODS OF 0, WHICH IS CLOSE TO 0, 48 AND 96 HOURS, AND WE LOOKED AT TEMPERATURES OF CLOSE TO 0 AND ABOUT 25 DEGREES. SO WE'VE COVERED SITUATIONS THAT WOULD BE ON THE EXTREMES OF THE REQUIREMENTS FOR THE SAMPLE PREPARATION AS IT IS RIGHT NOW.

WHEN WE WENT THROUGH THIS EXPERIMENT WITH ALL OF THE COMPOUNDS THAT WE COULD GET IN SUFFICIENT QUANTITIES FOR STUDY, WE FOUND THAT THERE WEREN'T VERY MANY THAT DID SHOW EXCHANGE.

THE NEXT SLIDE SHOWS WHICH ONES THOSE ARE.

IN THE ACID FRACTION, ALL OF THE PHENOLIC PROTONS EXCHANGE; THERE ARE OTHER PROTONS ON THE RINGS THAT WE COULD LABEL, SO THE PHENOLIC PROTON PROTON IS NO REAL CONCERN THERE. IN

COMPOUNDS EXHIBITING EXCHANGE

ACID COMPOUNDS

ALL PHENOLIC PROTONS EXCHANGED

VOLATILE COMPOUNDS

CHLOROFORM

DICHLOROBROMOMETHANE

CHLORODIBROMOMETHANE

BROMOFORM

TRICHLOROETHYLENE

BASE NEUTRAL COMPOUNDS

FLUORENE

THE VOLATILE FRACTION, ALL THE TRIHALOMETHANES EXCHANGED; THEY EXCHANGE VERY EFFECTIVELY IN A BASIC MEDIUM. THESE WOULD HAVE TO BE LABELED EITHER WITH CHLORINE 35 OR 37 OR WITH THE CARBON 13. CARBON 13 CHLOROFORM IS ALREADY AVAILABLE, SO THAT'S NOT A PROBLEM. WE FOUND ONE BASE/ NEUTRAL COMPOUND, FLUORENE, WHICH EXCHANGED, AND WE BELIEVE THAT TO BE THE TWO PROTONS WHICH ARE ALIPHATIC IN CHARACTER COMPARED TO THE REMAINING PROTONS ON THAT COMPOUND.

WELL, THE COST DOESN'T LOOK BAD; SOME EXCHANGE DOES TAKE PLACE, BUT WE CAN WORK AROUND IT IN ALL OF THE CASES. THE NEXT THING BECOMES, HOW DO WE REALLY GO ABOUT SETTING UP AN ANALYSIS FOR MANY COMPOUNDS? AS I MENTIONED, GOING AT IT EMPIRICALLY WOULD BE JUST ONE HECK OF A TASK, AND FRANKLY, I WOULDN'T WANT TO UNDERTAKE IT. THE WAY TO GO AT IT, THEN, WOULD HAVE TO BE ON SOME SORT OF SYSTEMATIC BASIS, AND AS A RESULT, WE FELT THAT THE WAY TO DO THIS WAS TO GO BACK AND LOOK AT THE MODEL PER SE OF THE PRINCIPLE OF ISOTOPE DILUTION AND SEE WHERE THAT WOULD TAKE US IF WE LOOKED AT THE PARTICULAR PARAMETERS THAT WE HAVE TO DEAL WITH. WE HAVE TO SELECT M/E'S, MASSES THAT WE'RE GOING TO MAKE OUR MEASUREMENTS AT. WELL, THAT SOUNDS

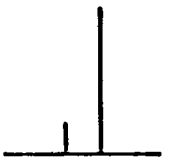
PRETTY EASY. IT REALLY IS, BUT WHEN YOU GET INTO 100 COMPOUNDS OR SOMETHING THAT GETS TO BE A LOT OF WORK IF YOU HAVE TO CHECK EACH ONE OUT SEPARATELY.

THE QUESTION OF, WELL, HOW MUCH DO WE SPIKE INTO THE SAMPLE IS ANOTHER CONCERN. AGAIN, THAT'S SOMETHING THAT'S NOT APPROPRIATE TO DO ON AN EMPIRICAL BASIS. HOW DO WE CALCULATE THE RESULTS? THERE ARE ANY NUMBER OF WAYS IN THE LITERATURE THAT ARE GIVEN FOR THAT SORT OF THING, AND IT HASN'T BEEN TOTALLY CLEAR WHICH ONE SHOULD BE USED AND WHEN. THE RELATIONSHIP BETWEEN THOSE DIFFERENT CALCULATING METHODS DOES NOW EXIST IN PRINT, AND AS A RESULT WE'RE ABLE TO TAKE THAT AND MAKE SOME GUESSES.

ANYWAY, LET'S LOOK AT THE MODEL A LITTLE BIT BECAUSE I'M GOING TO TALK ABOUT THE MODEL, AND THE NEXT SLIDE GIVES US A FAIRLY CLEAR IDEA, I THINK, OF WHAT'S GOING ON WHEN WE TALK ABOUT ISOTOPE DILUTION; IT DOESN'T MATTER WHAT KIND IT IS IN THIS SORT OF SLIDE, WHETHER IT'S INORGANIC OR ORGANIC OR ANYTHING ELSE. WHAT WE'RE DOING IS WE'RE TAKING THE PURE COMPOUND X, AND WE'LL CALL IT THE NATURALLY ABUNDANT MATERIAL THAT'S IN THE SAMPLE TO BEGIN WITH. IN THE EQUATIONS, WE'RE USING THE X AS AN

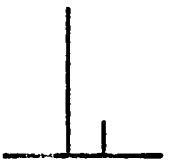
PRINCIPLE OF ISOTOPE DILUTION

PURE x



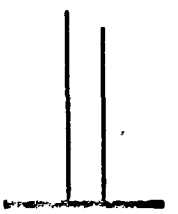
$$R_x = \frac{a_x}{b_x}$$

PURE y



$$R_y = \frac{a_y}{b_y}$$

MIXTURE



$$R_m = \frac{xa_x + ya_y}{xb_x + yb_y}$$

m/e a b

$$\frac{x}{y} = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$$

INDICATION OF THE NUMBER OF MOLES OF THAT COMPOUND PRESENT.

FOR PURE X, THERE ARE TWO M/E'S WHICH EXIST WHICH GIVE US AN ISOTOPE RATIO, R_X, WHICH IS GIVEN BY THE ABUNDANCE OF THE IONS AT M/E A OVER THE IONS AT M/E B. SO IT'S JUST THE AREA OF A OVER THE AREA OF B, AND THAT'S VERY EASILY DERIVED FROM THE DATA. THERE ALSO EXISTS FOR THE LABELED COMPOUND Y THAT WE'RE GOING TO ADD AN ISOTOPE RATIO, R_Y, WHICH HAS ABUNDANCES AT M/E'S A AND B WHICH, AGAIN, GIVES US AN ISOTOPE RATIO. THOSE SHOULD BE CONSTANT IN TIME. WE DON'T EXPECT THOSE EVER TO CHANGE UNLESS WE CHANGE, SAY, THE MANUFACTURE OF Y, AT WHICH POINT WE'D HAVE TO GO BACK AND REMEASURE THAT VALUE.

ANYWAY, IF WE TAKE AN UNKNOWN QUANTITY OF X AND MIX IT WITH A KNOWN QUANTITY OF Y, WE COME UP WITH A MIXTURE WHICH HAS PRODUCED AN ISOTOPE RATIO THAT BY DEFINITION HAS TO BE BETWEEN R_X AND R_Y, AND IT IS DEFINED OR GIVEN BY THE RELATIONSHIP THAT'S SHOWN. WHEN THIS IS SOLVED FOR X/Y, THE MOLE RATIO OF SAMPLE TO INTERNAL STANDARD CAN BE EXPRESSED SOLELY AS ISOTOPE RATIOS. THAT IS, BY KNOWING THE AMOUNT OF INTERNAL

STANDARD ADDED, WE CAN VERY EASILY CALCULATE THE QUANTITY OF UNLABELED COMPOUND ORIGINALLY PRESENT IN THE SAMPLE. THAT'S THE WHOLE PRINCIPLE OF ISOTOPE DILUTION.

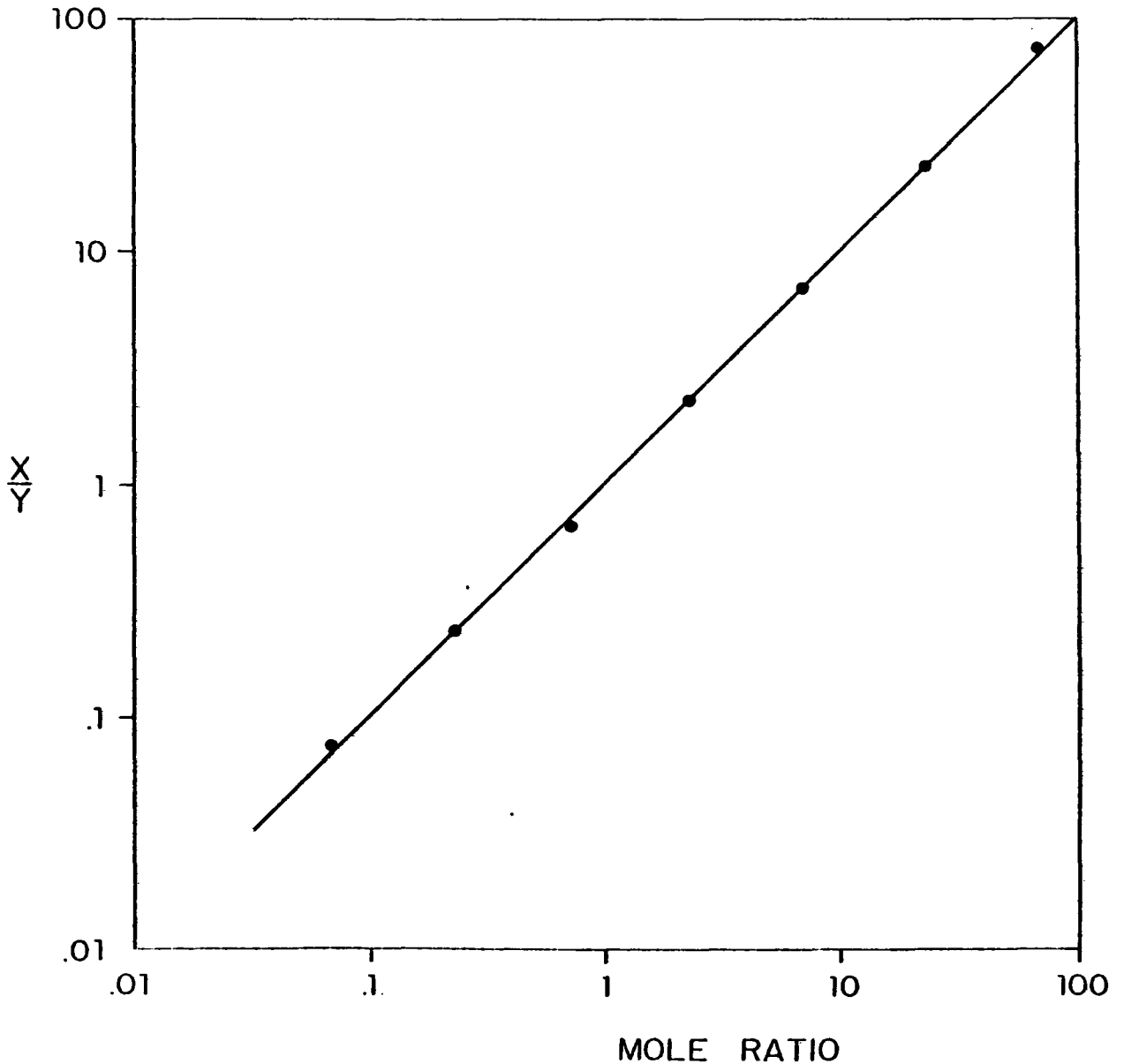
NOW, I'VE KIND OF SKIPPED OVER ONE LITTLE THING HERE; WE DON'T KNOW MANY ORGANIC COMPOUNDS THAT HAVE ONLY TWO ISOTOPE PEAKS IN THEIR MASS SPECTRUM. AS A RESULT, THERE'S ANOTHER TERM IN HERE WHICH I'VE LEFT OUT BECAUSE IT DOESN'T REALLY HAVE MUCH BEARING ON WHAT THE MODEL IS GOING TO TELL US. THE OTHER ISOTOPES AND FRAGMENT IONS AND EVERYTHING ELSE THAT THE SPECTRA HAVE IN THEM END UP AS TERMS OVER HERE ON THE RIGHT-HAND SIDE (INDICATING). THERE WOULD BE A TERM HERE WHICH WOULD CONSIST OF THE VALUE 1 MINUS THE ABUNDANCE OF THE OTHER ISOTOPES AND DIVIDED BY 1 MINUS THE NUMBER OR QUANTITY OF OTHER ISOTOPES IN EACH CASE. SO WHAT WE HAVE, THEN, IS ANOTHER TERM OUT HERE, THE INVISIBLE TERM, AND IF SOMEONE WANTS TO SEE WHAT IT REALLY IS AND WHAT IT LOOKS LIKE, I HAVE THAT IN MY NOTES AND I CAN SHOW IT TO YOU LATER, BUT IN ESSENCE, IT ALWAYS CANCELS OUT FOR ORGANIC MOLECULES. FOR THE PURPOSE OF USING THIS MODEL TO PREDICT, IT'S JUST MORE SIMPLE TO LEAVE IT OUT FOR NOW, THEN SEE IF, IN

FACT, THE PREDICTIONS AGREE WITH THE EXPERIMENTAL RESULTS. IF THEY DO, WELL, LET'S NOT WORRY ABOUT IT. IF THEY DON'T AGREE, LET'S TRY TO WORK THE MODEL IN THE MORE COMPLICATED FORM. IT TURNS OUT THAT THE MODEL IN THE SIMPLIFIED FORM WORKS ADMIRABLY, SO FOR NOW I'M GOING TO LEAVE IT OUT, BUT I WANT TO MENTION IT FOR THOSE PURISTS IN THE AUDIENCE WHO MAY GET VERY CONCERNED ABOUT THAT LATER.

THE QUALITY OF THIS TWO-ISOTOPE THEORY IS SHOWN IN THE NEXT SLIDE, WHICH LOOKS LIKE A CALIBRATION CURVE OR A REGRESSION LINE THROUGH A SERIES OF DATA POINTS, IS RATHER A SERIES OF DATA POINTS SHOWN IN THEIR RELATIONSHIP TO THE LINE THAT THE MODEL PREDICTS. AS YOU CAN SEE, THEY FALL VERY, VERY CLOSE TO THAT LINE. IN FACT, THEY'RE WITHIN EXPERIMENTAL ERROR IN ALL CASES. I SHOULD POINT OUT THAT THIS SET OF DATA WAS ACQUIRED FOR AN AMINO ACID DERIVATIVE, WHICH HAS VERY LITTLE BEARING ON US RIGHT NOW, BUT NEVERTHELESS HAD TO BE EXTRACTED; IT HAD TO BE DERIVATIZED AT BOTH ENDS OF THE MOLECULE.

ONE OF THOSE STEPS WAS A NONQUANTITATIVE ESTERIFICATION. EVEN SO, THE DATA FALLS VERY,

GABA DATA vs ISOTOPE DILUTION THEORY



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VERY NICELY ON THE LINE OR NEAR THE LINE THAT THE THEORY PREDICTS.

THE THEORY, THEN, LOOKS VERY PROMISING, AND THE QUESTION NOW BECOMES, WHAT ARE WE GOING TO DO WITH ALL OF THAT? WELL, LET'S SEE IF WE CAN DETERMINE WHICH WAY TO CALCULATE DATA THAT WE ACQUIRE ON REAL SAMPLES. WE COULD GO AHEAD AND USE THAT BIG EQUATION THAT WE HAD IN THE LAST SLIDE AND PROBABLY DO PRETTY WELL, BUT HOW WELL, AND DO WE REALLY NEED THAT? WELL, LET'S SEE WHAT THE SITUATION IS.

THE NEXT SLIDE SHOWS SOME OF THE EQUATIONS THAT ARE FAIRLY COMMONLY USED. THE MOST COMMON ONE IS THIS VERY SIMPLE EQUATION WHICH SIMPLY SAYS THAT THE MOLE RATIO OF SAMPLE TO INTERNAL STANDARD IS DIRECTLY RELATED TO THE ISOTOPE RATIO THAT ONE MEASURES FROM THE MIXTURE.

THAT'S VERY EASY TO LIVE WITH. IT MAKES TWO ASSUMPTIONS: ONE IS THAT THERE IS NO UNLABELED MATERIAL IN THE INTERNAL STANDARD TO BEGIN WITH; THE OTHER IS THAT THE UNLABELED MATERIAL HAS NO NATURAL ABUNDANCE AT THE HIGHER MASS M/Z. CLEARLY THE UNLABELED MATERIAL WILL NOT HAVE VERY MUCH OF THE LABELED MATERIAL IN IT. THERE IS A CERTAIN NATURAL ABUNDANCE OF

CALCULATION METHODS

EQUATION	ASSUMPTION	APPLICATION
$\frac{x}{y} = R_m$	$R_x \rightarrow \infty$; $R_y \rightarrow 0$	$10R_y < R_m < .1R_x$
$\frac{x}{y} = \frac{R_m(R_x + 1)}{R_x - R_m}$	$R_y \rightarrow 0$	$10R_y < R_m < .5R_x$
$\frac{x}{y} = \frac{R_m - R_y}{R_y + 1}$	$R_x \rightarrow \infty$	$2R_y < R_m < .1R_x$
$\frac{x}{y} = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$	NONE	$2R_y < R_m < .5R_x$

CARBON 1 AND CARBON 14 IN THE WORLD, AS WELL AS CARBON 12, AND THOSE ARE THINGS THAT THAT ASSUMPTION IS CONCERNED WITH, THOSE ABUNDANCES OF OTHER THINGS.

WELL, THIS GETS A LITTLE BIT AHEAD OF OURSELVES HERE (INDICATING), BUT THAT'S A RANGE THAT WE CAN DEFINE AS BEING APPLICABLE FOR THAT EQUATION, AND IT'S BASED ON THE WINDOW IN WHICH R_M FALLS IN RELATION TO: AT ONE END OF THE SCALE, THE ISOTOPE RATIO OF THE LABELED COMPOUND, AND AT THE OTHER END OF THE SCALE, THE ISOTOPE RATIO OF THE UNLABELED MATERIAL (INDICATING).

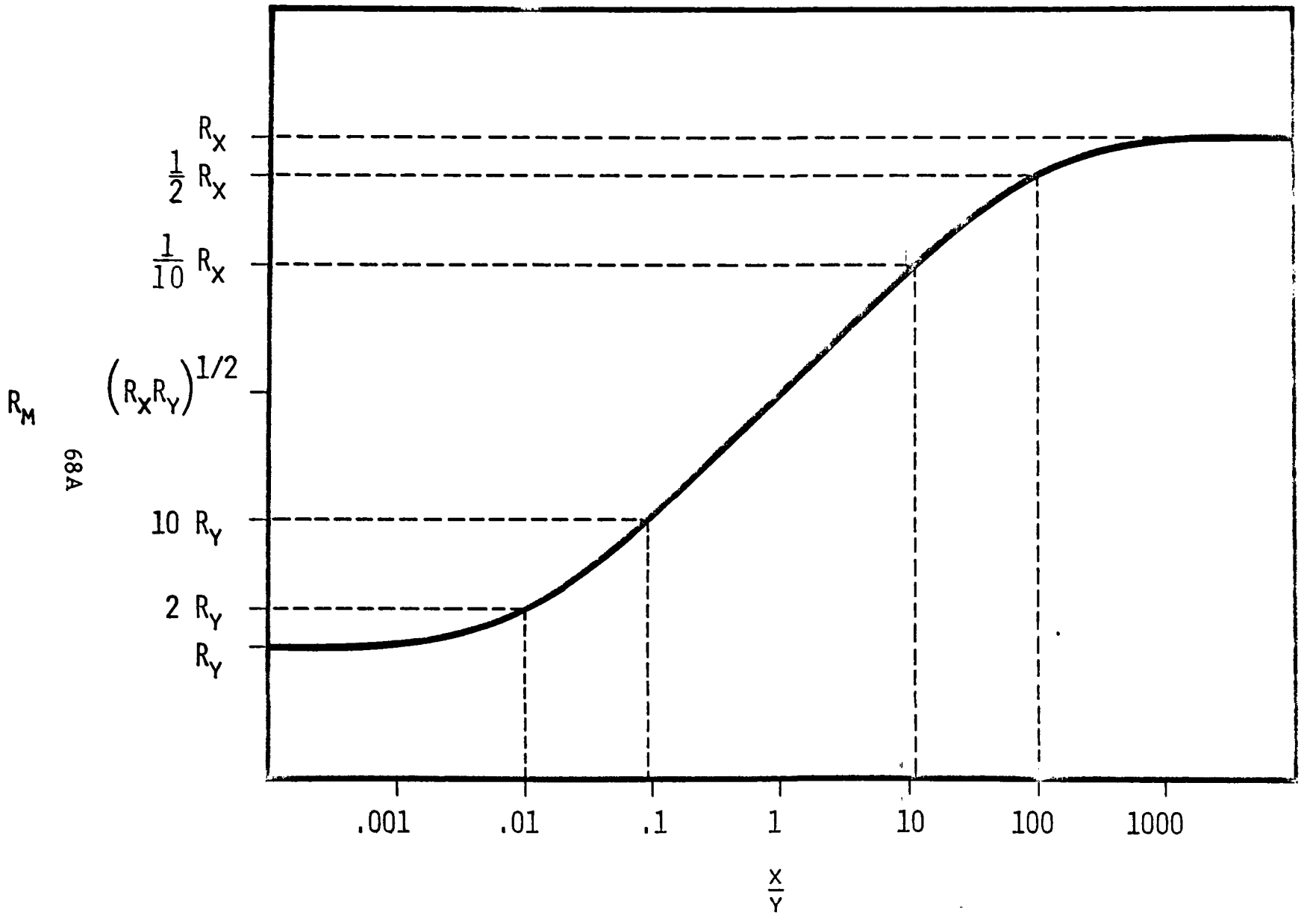
IF WE REACH A POINT WHERE THIS ASSUMPTION IS NO GOOD--IN OTHER WORDS, WE GET TOO CLOSE TO R_Y OR R_X--THEN WE HAVE TO MAKE A CORRECTION FOR THE AMOUNT OF MATERIAL THAT'S IN THERE.

THIS EQUATION MAKES THAT CORRECTION, AND YOU CAN SEE THAT THERE ARE TWO DIFFERENT PLACES IN THE EQUATIONS WHICH HAVE AN R_X VALUE IN THERE TO CARRY OUT THAT PROCESS. THERE IS AN EQUIVALENT SORT OF AN EQUATION WHEN THE MATERIAL THAT WE'VE PURCHASED SOMEWHERE AS A STANDARD HAS SOME ISOTOPIC IMPURITY IN IT, AND I JUST PUT THAT IN HERE ALSO BECAUSE WE MAY HAVE TO MAKE THAT CORRECTION. THIS CORRECTION IS ONE THAT IS OFTEN MADE; THIS

CORRECTION IS ONE THAT IS SELDOM MADE ON A FREQUENCY BASIS IN THE LITERATURE.

THE EQUATION HERE AT THE BOTTOM (INDICATING) MAKES BOTH CORRECTIONS AND IS THE MODEL. WE JUST ASSUME THAT THOSE CORRECTIONS WILL BE CORRECT, BUT AS YOU NOTICE OVER HERE, WE'RE NOT SAYING THAT WE CAN DEAL WITH ALL OF THE DATA THAT IT MIGHT BE POSSIBLE TO GENERATE, AND I'M GOING TO SKIP ON TO THE NEXT SLIDE, I PRESUME LEAVING MANY OF YOU IN A BIT OF A CONFUSED STATE RIGHT THERE, BUT I THINK HERE WE CAN SEE A LITTLE BIT MORE CLEARLY WHAT I'M SAYING.

IN TERMS OF R_X AND R_Y, WE HAVE OVER HERE THE RATIO OF THE MIXTURE (INDICATING) PLOTTED FOR A HYPOTHETICAL COMPOUND WHICH HAS ISOTOPE RATIOS OF 100 FOR R_X AND .01 FOR R_Y. THESE ARE FAIRLY COMMON SORTS OF NUMBERS TO ENCOUNTER WITH THIS METHOD, AND IT GIVES US A NICE PICTURE TO DEAL WITH. AT ANY RATE, WHEN WE USE THE SIMPLE EQUATION, X/Y IS EQUAL TO R_M, WE SAY WE CAN DEAL WITH THAT IN A WINDOW OF VALUES DEFINED BY 10 TIMES R_Y, AND GOING TO ONE-TENTH OF R_X, YOU CAN SEE THAT THAT IS A VERY STRAIGHT LINE HERE AND WE DON'T NEED TO


R_X
$\frac{1}{2}\ R_X$
$\frac{1}{10}\ R_X$
$(R_X R_Y)^{1/2}$
R_M
10 R_Y
2 R_Y
R_Y
.001
.01
.1
1
10
100
1000
$\frac{X}{Y}$

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MAKE ANY CORRECTIONS. THAT LINE IS SO CLOSE TO THEORETICALLY CORRECT THAT WE DON'T NEED TO WORRY ABOUT ANY ISOTOPIC INTERFERENCES THAT MIGHT BE TAKING PLACE. IN FACT, THE LINE THAT IS SHOWN STARTS TO CURVE OUT, AND YOU CAN SEE IT CURVING OUT VERY HEAVILY UP HERE (INDICATING), BUT IT STARTS TO CURVE IN AN S-SHAPE RIGHT HERE AT THE VERY CENTER POINT, OFF THIS WAY (INDICATING), AND FROM THE CENTER POINT OFF IN THAT WAY (INDICATING) RIGHT IN THE BEGINNING, BUT THE AMOUNT OF CURVATURE IN THAT REGION IS VERY LOW, SO WE DON'T NEED TO WORRY ABOUT THAT. THE ERRORS ARE GOING TO BE VERY, VERY SMALL. AS WE START TO MOVE OUT IN THE MOLE RATIO, NOW, TO A POINT WHERE WE HAVE MORE AND MORE X RELATIVE TO Y, WE START TO HAVE TO MAKE A CORRECTION FOR X, AND AS WE DO THAT, WE CAN SEE WE'VE GOT MORE AND MORE X IN THERE, WE'VE GOT TO MAKE SOME KIND OF CORRECTION FOR IT. SO WE NOW GET INTO A REGION WHERE WE'RE CORRECTING FOR THIS CURVATURE FOR R_X HERE AND R_Y DOWN HERE, DEPENDING UPON WHICH ONE OF THOSE EQUATIONS WE'RE DEALING WITH, AND AS WE DO THAT, WE CAN MAKE THE CORRECTION. BUT, AS CORRECTIONS HAVE A TENDENCY TO GO, THERE'S A LIMITING POINT AT WHICH

THE PROPAGATION OF ERRORS IN THAT CORRECTION STARTS TO OVERCOME THINGS AND WE REALLY OUGHT TO STOP. WE NEED TO MAKE SOME SORT OF PREDICTION AS TO WHAT THAT IS, AND I'LL SHOW YOU HOW THAT PREDICTION IS MADE. WHAT IT TURNS OUT IS THAT AT ABOUT ONE-HALF OF R_X AT THAT END AND 2 R_Y ON THAT END (INDICATING), AND BY GOING FROM THE MOST SIMPLE EQUATION, THEN, WHICH PUTS US ON THIS PART OF THE GRAPH (INDICATING), WE CHANGE FROM TWO ORDERS OF MAGNITUDE IN APPLICATION TO ABOUT FOUR ORDERS OF MAGNITUDE IN APPLICATION, AND WE'VE REALIZED IN THIS PARTICULAR SITUATION A DOUBLING OF THE CONCENTRATION RANGE THAT WE CAN DEAL WITH. FOUR ORDERS OF MAGNITUDE IS PROBABLY BETTER THAN ANYBODY'S GC/MS CAN DO ANYWAY, SO THAT OUGHT TO BE PLENTY. TWO ORDERS WOULD BE NICE; WE COULD DEAL IN HERE VERY EASILY. WHAT WE'LL FIND OUT IS THAT MANY OF THE R_X'S AND R_Y'S THAT WE ENCOUNTER IN PRACTICE ARE MUCH WIDER THAN THESE TWO THAT I'VE SELECTED HERE. THIS IS ALMOST ONE OF THE WORST CASES (INDICATING), BUT EVEN IN A WORSE CASE, A TYPICAL WORSE CASE, IT CAN WORK VERY NICELY.

THE FACT THAT IT CAN WORK IS SHOWN IN THE NEXT SLIDE, WHERE WE TOOK SOME DATA FOR SOME VOLATILE COMPOUNDS WHERE WE HAD THE ABILITY TO SELECT M/E'S

EFFECTS OF DATA REDUCTION METHOD ON QUANTITATION

COMPOUND	M/E's	M/E SELECTION FACTOR	DEVIATION FROM REGRESSION LINE (%) ASSUMPTION			
			$R_X \to \infty$ $R_Y \to 0$	$R_Y \to 0$	$R_X \to \infty$	-----
BENZENE	78/84	4.79	10	10	10	9
	50/56	3.91	10	10	28	23
	77/82	3.79	39	37	40	36
TOLUENE	92/100	8.29	7	10	10	10
	91/98	7.72	9	9	12	12
1,2-DICHLOROETHANE	62/67	8.94	9	10	10	9
	64/67	7.92	14	14	14	11
	98/104	6.19	28	28	28	18
	49/53	5.73	11	11	11	16
	98/102	2.73	54	69	69	36

FOR SEVERAL DIFFERENT MOLECULES AND THIS VALUE HERE (INDICATING), I HAVE SOMETHING CALLED M/E SELECTION FACTOR AND THAT IS VERY CLOSE TO THE DIFFERENCE BETWEEN R_X AND R_Y, AND AS R_X AND R_Y GET WIDER AND WIDER, FURTHER AND FURTHER APART, WE SHOULD BE ABLE TO WORK WITH WIDER AND WIDER CONCENTRATION RANGES.

ANYWAY, AS WE GO THROUGH THESE EQUATIONS WHERE WE HAVE THE SIMPLE EQUATION HERE (INDICATING) AND MOVING ACROSS TO THE MORE COMPLEX EQUATION, WHEN WE HAVE A NUMBER HERE THAT SAYS, THIS IS A FAIRLY LARGE NUMBER (INDICATING), THEN NO MATTER HOW WE CALCULATE THE DATA, WE'RE ON THAT SEGMENT OF THE R_M VERSUS X/Y CURVE THAT IS A STRAIGHT LINE. SO AS WE MAKE MORE AND MORE CORRECTIONS FOR THE CURVATURE, WE DON'T REALLY SEE ANYTHING BECAUSE THE STATISTICAL VARIATION IN THE MEASUREMENTS THEMSELVES REALLY DOESN'T GIVE US ANY NEW DATA.

AS WE MOVE DOWN THE LINE...WELL, LET'S MOVE RIGHT TO THE BOTTOM HERE (INDICATING). HERE WE HAVE A SITUATION WHERE FAILING TO MAKE CORRECTIONS RESULTS IN POOR DATA, BUT WHEN WE MAKE ALL OF THE CORRECTIONS, WE DO APPRECIATE AN IMPROVEMENT, AND YOU CAN SEE THAT THIS VALUE HERE (INDICATING) IS A SMALL VALUE COMPARED TO ALL

OF THE OTHERS.

I'M GOING TO TALK A LITTLE BIT MORE ABOUT WHAT THIS FACTOR IS LATER ON, BUT WHAT I WANT TO SAY IS THAT HERE ARE THREE COMPOUNDS; NO MATTER HOW WE CALCULATE IT, THE DATA COMES OUT REASONABLY WELL. IN EACH OF THESE CASES, THE VALUES THAT WE PREDICT WOULD WORK BEST WOULD BE 78 OVER 84, AND YOU CAN SEE THAT IN EACH ONE WE ALWAYS ARE PICKING OUT THE ONE THAT WORKS BEST AND SO IT SEEMS THAT WE AT LEAST HAVE FOUND OUT SOMETHING. WE'RE TALKING ABOUT PROPAGATED ERRORS, AND THOSE ARE REALLY WHAT WE'RE LOOKING AT IN THESE CALCULATIONS AND AS A RESULT I WANT TO JUST SHOW YOU A FEW LITTLE PIECES OF ARITHMETIC HERE THAT GIVE US AN IDEA THROUGH THE MODEL WHAT IS GOING TO HAPPEN.

THE NEXT SLIDE SHOWS US WHAT THE PROPAGATION OF ERRORS LOOKS LIKE ON A MATHEMATICAL BASIS. THIS IS YOUR BASIC PHYSICAL CHEMISTRY AT COLLEGE LEVEL AND THE MATHEMATICS GET A LITTLE INVOLVED AND THE EQUATIONS TEND TO RUN ACROSS SEVERAL PAGES, BUT IT ALL COMES DOWN TO SOMETHING THAT WE CAN AT

PROPAGATION OF ERRORS

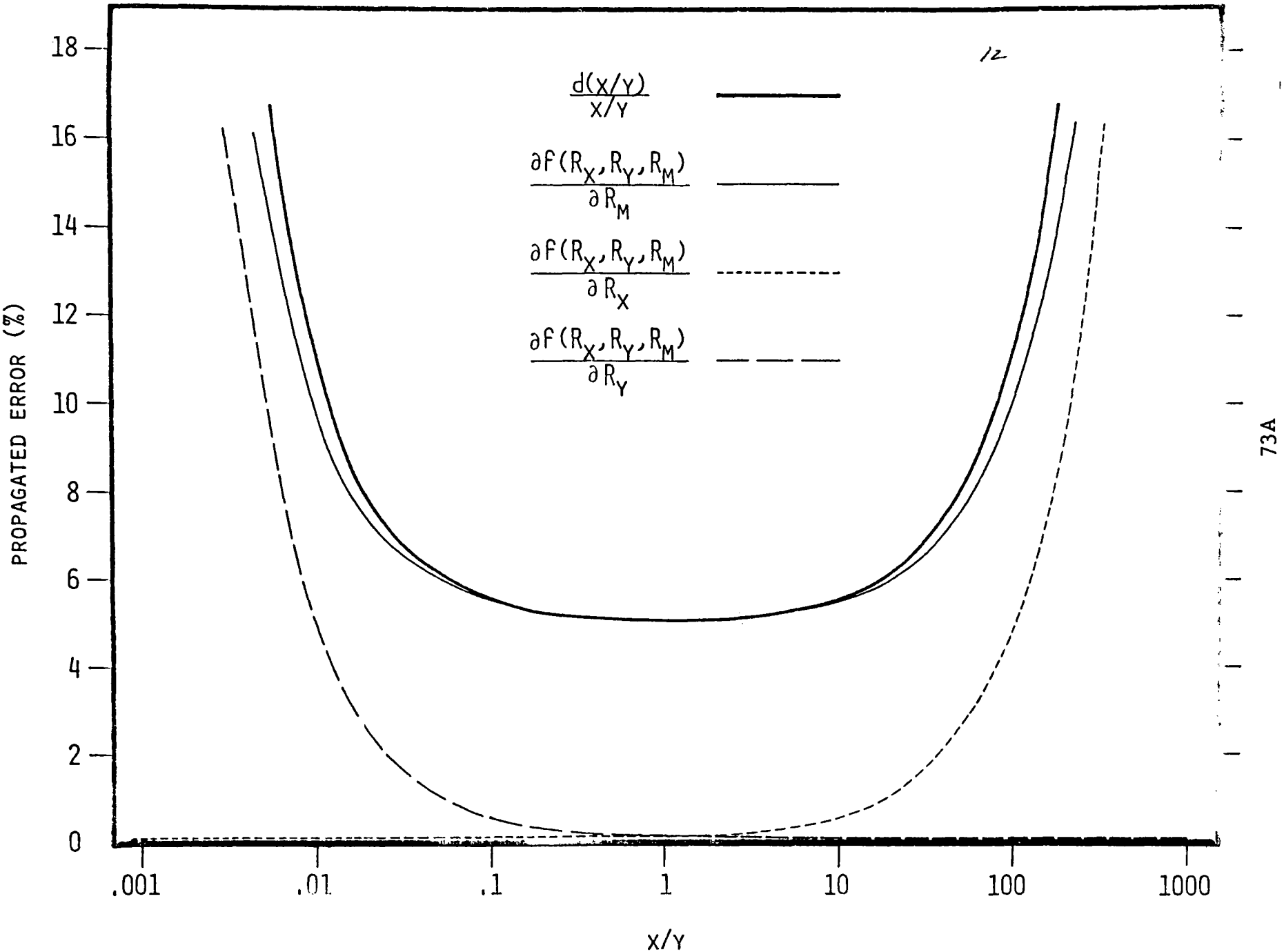
$$d(x/y) = \left[\left(\frac{\partial f(R_m)}{\partial R_x} \, dR_x \right)^2 + \left(\frac{\partial f(R_m)}{\partial R_y} \, dR_y \right)^2 + \left(\frac{\partial f(R_m)}{\partial R_m} \, dR_m \right)^2 \right]^{1/2}$$

WHERE

$$f(R_m) = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$$

$$\frac{d(x/y)}{(x/y)} = \left[\left(\frac{(R_m + 1)dR_x}{(R_x + 1)(R_m - R_x)} \right)^2 + \left(\frac{(R_m + 1)dR_y}{(R_y + 1)(R_y - R_m)} \right)^2 + \left(\frac{(R_x - R_y)dR_m}{(R_y - R_m)(R_m - R_x)} \right)^2 \right]^{1/2}$$

LEAST GET OUR TEETH INTO. IT'S JUST, I WANT TO SHOW YOU WHERE WE'RE GOING, HOW WE'RE GETTING THERE, AND WHAT WE END UP WITH. THE NEXT SLIDE SHOWS A PLOT OF PROPAGATED ERROR VERSUS THE MOLE RATIO OF X/Y. THE WAY THAT WE PLOTTED THIS UP WAS FOR EACH OF THE TERMS. THERE'LL BE A PROPAGATED ERROR ASSOCIATED WITH THE ISOTOPE RATIO OF THE MIXTURE, A PROPAGATED ERROR ASSOCIATED WITH THE ISOTOPE RATIO OF THE NATURALLY ABUNDANT MATERIAL, AND ANOTHER ONE FOR THE ENRICHED MATERIAL OR THE LABELED COMPOUND. ALL THREE COMBINE TO GIVE THE TOTAL PROPAGATED ERROR IN THE X/Y VALUE. IT, AS WE WOULD ASSUME, IS THE WORST LINE; IT'S ALWAYS THE HIGHEST LINE AND THAT MEANS IT HAS THE HIGHEST PERCENT ERROR. THE R_Y VALUE IS AFFECTING THE DATA MOST AT POINTS IN THE CURVE WHERE THERE IS RELATIVELY MORE Y THAN THERE IS X. IN OTHER WORDS, DOWN HERE WE START TO SEE THE PROPAGATED ERROR RISE, AND IT DOES RISE VERY QUICKLY AS WE GET OUT HERE TO SOME CERTAIN POINT (INDICATING). THE OTHER DIRECTION, WE COME DOWN ASYMPTOTICALLY; THERE'S VERY LITTLE Y WITH RESPECT TO X OUT HERE AT 1,000 (INDICATING), AND AS A RESULT, THE QUANTITY OF Y THAT'S PRESENT HAS VERY LITTLE BEARING ON THE AMOUNT OF ERROR THAT IT CREATES. THE R_X SITUATION IS JUST EXACTLY LIKE THIS ONE, BUT A MIRROR IMAGE OF


PROPAGATED ERROR (%)
18
16
14
12
10
8
6
4
2
0
.001
.01
.1
1
10
100
1000
X/Y
$\frac{d(X/Y)}{X/Y}$
$\frac{\partial f(R_X, R_Y, R_M)}{\partial R_M}$
$\frac{\partial f(R_X, R_Y, R_M)}{\partial R_X}$
$\frac{\partial f(R_X, R_Y, R_M)}{\partial R_Y}$

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IT AND FOR THE SAME REASON; AS WE GET MORE AND MORE X IN THERE, THE IMPACT THAT THAT HAS ON THE ERROR BECOMES GREATER AND GREATER AND AT SOME POINT OUT HERE (INDICATING) WE'VE GOT TO CALL A HALT TO WHAT WE'RE DOING BECAUSE THE PROPAGATED ERROR JUST SKYROCKETS.

AT ANY RATE, THE RM VALUE, IN OTHER WORDS, THE NUMBERS THAT WE'RE MEASURING IN THE MIXTURE OF THE TWO, THE SAMPLE THAT WE'RE ACTUALLY GOING TO GET OUR DATA FROM, SEEMS TO FAIRLY CLOSELY APPROXIMATE THE ULTIMATE ERRORS THAT WE SEE IN THE RATIO OF SAMPLE TO INTERNAL STANDARD AND YOU CAN SEE, WE'VE GOT A LIGHT CURVE HERE AND A DARKER CURVE HERE, AND AS A RESULT, IT SEEMS REASONABLE TO MAKE SOME GUESSES BASED ON THIS TERM IN THE PROPAGATED ERROR EQUATION TO SEE IF WE CAN SAY, WHERE SHOULD WE STOP WHEN WE MOVE OUT HERE? WE HAVE TO DRAW A LINE SOMEWHERE; WHERE ARE WE GOING TO DRAW THAT LINE AND NOT GO ANY FURTHER? AS A RESULT, WE WILL...WELL I'M GOING TO SHOW YOU SOME MORE ARITHMETIC IN THE NEXT SLIDE; WE CAN DO THAT KIND OF THING MATHEMATICALLY BY SUBSTITUTING IN FOR THE DX/Y OVER X/Y. IN OTHER WORDS, WE'RE GOING TO SAY THE PERCENT ERROR IS TWICE THE MEASUREMENT

M/E SELECTION

SAY THAT ACCEPTABLE RESULTS HAVE AN ERROR EQUAL TO TWICE THE ERROR IN THE R_M MEASUREMENT

$$\frac{d(x/y)}{(x/y)} = 2\frac{dR_m}{R_m} \cong \frac{(R_x - R_y)\,dR_m}{(R_y - R_m)(R_m - R_x)}$$

FOR $\left(\frac{x}{y}\right)_{max}$: $R_y \ll R_x$ and $R_y \ll R_m$ SO: $R_m \cong \frac{1}{2} R_x$

FOR $\left(\frac{x}{y}\right)_{min}$: $R_x \gg R_m$ and $R_x \gg R_y$ SO: $R_m \cong 2 R_y$

CONCENTRATION RANGE FOR SUCCESSFUL APPLICATION IS GIVEN BY:

$$\text{Log}\left(\frac{x}{y}\right)_{max} - \log\left(\frac{x}{y}\right)_{min} = \log\frac{(\frac{1}{2}R_x - R_y)(R_x + 1)}{(R_x - \frac{1}{2}R_x)(R_y + 1)} - \log\frac{(2R_y - R_y)(R_x + 1)}{(R_x - 2R_y)(R_y + 1)} = \log\frac{R_x}{R_y}$$

CONSEQUENTLY, TO MAXIMIZE CONCENTRATION RANGE, MAXIMIZE LOG $\frac{R_X}{R_Y}$

ERROR IN MEASURING THE ISOTOPE RATIO OF THE MIXTURE. THESE RUN AROUND 5 PERCENT OR SO. SO WE'RE GOING TO SAY, FOR NOW, 10 PERCENT ERROR WE'LL LIVE WITH; ANYTHING WORSE THAN THAT IS NO GOOD. WHERE IS PROPAGATED ERROR GOING TO GO FROM LESS THAN 10 PERCENT TO GREATER THAN 10 PERCENT? WELL, IT DOES THAT ON BOTH ENDS OF THE CURVE. IT DOES THAT ON THE X/Y MAX END AND ON THE X/Y MIN END. THESE SITUATIONS EXIST, AND WHEN THAT HAPPENS, YOU CAN GO THROUGH THIS EQUATION, AND WE COME OUT SAYING THAT IF R_M IS APPROXIMATELY EQUAL TO HALF OF R_X, THAT'S THE CROSSOVER POINT. SO AS LONG AS WE STAY WITH R_M'S THAT ARE LESS THAN HALF OF R_X, WE'LL BE IN BAD SHAPE.

AT THE OTHER END, AT THE MINIMUM END, THE SITUATION COMES OUT THAT R_M SHOULD BE GREATER THAN 2 R_Y. THIS IS THE CROSSOVER POINT, SO AS LONG AS WE STAY WITH R_M'S THAT ARE GREATER THAN 2 R_Y, THEN THE MODEL SHOULD HOLD AND WE SHOULD GET GOOD DATA. IF WE TAKE THE DIFFERENCE BETWEEN THE MAX AND THE MIN--AND REMEMBER WE DID THIS ON A LOG SCALE BECAUSE WE'RE LOOKING AT PERCENT THINGS--AND SUBSTITUTE INTO OUR FULL EQUATION THE VALUES ONE-HALF R_X AND 2 R_Y IN THE APPROPRIATE

PLACES, WE COME UP WITH THIS EXPRESSION, AND IT MERELY SAYS THAT FOR THE WIDEST CONCENTRATION RANGE OF APPLICATION, WE SHOULD SELECT M/E'S THAT GIVE US THE LARGEST NUMBER FOR THE LOG OF R_X/R_Y. THAT'S A PRETTY SIMPLE PLACE TO COME TO AFTER ALL OF THAT ARITHMETIC.

THE SELECTION OF M/E'S, THEN, CAN BE DONE FAIRLY SIMPLY BY JUST LOOKING AT THE RATIO OF THE ISOTOPE RATIOS. WHEN THAT NUMBER IS LARGE, THEN WE WILL HAVE A WIDE RANGE BETWEEN CONCENTRATIONS AT THE CUTOFF POINTS. THIS PART OF THE MODEL ONLY TAKES INTO ACCOUNT THE FACT THAT WE'RE GOING TO MAKE A MEASUREMENT AND THAT THE PRECISION OF THAT MEASUREMENT IS UNRELATED TO ANYTHING; THAT'S NOT TRUE.

THE PRECISION OF THE MEASUREMENTS IS RELATED TO THE ABSOLUTE AMOUNT OF SIGNAL WE CAN GET, BASED ON WHAT THE ABUNDANCE OF THE IONS OR THE M/E THAT WE'RE MEASURING IS. IF WE ARE LOOKING AT A PNA WHERE YOU'VE GOT MAYBE 80 PERCENT OF THE TOTAL IONIZATION IN THE PEAK THAT THE MEASUREMENT WILL LIKELY BE MADE AT, THAT WILL PROVIDE MORE PRECISE DATA THAN WILL THE

DATA THAT ONE WOULD ENCOUNTER FROM, SAY, DIMETHYL-NITROSAMINE, WHICH DOESN'T GIVE US TOO MUCH SIGNAL FROM A MASS SPEC STANDPOINT.

AS A RESULT, WE PLAYED AROUND A LITTLE BIT, AND I ADMIT THIS IS A LITTLE EMPIRICAL, BUT THE NEXT SLIDE GIVES US A LITTLE CORRECTION FACTOR, AN EMPIRICAL FACTOR, TO TAKE INTO ACCOUNT THE EFFECT THAT ABUNDANCE WILL HAVE ON THE SELECTION OF M/E'S. THE VALUE THAT WE CAME UP WITH A CORRECTION BASED ON THE LOG OF 2 OVER THE ABUNDANCE OF THE MORE ABUNDANT ISOTOPE IN THE UNLABELED COMPOUND PLUS THE ABUNDANCE OF THE MORE ABUNDANT ISOTOPE IN THE LABELED COMPOUND. THE LESS ABUNDANT OF THE TWO WE'RE NOT GOING TO WORRY ABOUT BECAUSE WE'VE ALREADY SAID WE'RE GOING TO BE IN A WINDOW, AND WHEN WE'RE IN THAT WINDOW THE AMOUNT OF SIGNAL THAT WE SEE IS GOING TO BE BASED ON THE TWO MORE ABUNDANT ISOTOPES AND NOT BE VERY MUCH AFFECTED BY THE TWO LESS ABUNDANT ISOTOPES. WHEN WE PUT ALL OF THAT TOGETHER, WE HAVE A TERM THAT WE'RE CALLING AN M/E SELECTION CRITERIA. IT IS AFFECTED VERY, VERY MUCH BY THE LOG OF R_X OVER R_Y. IT IS AFFECTED MUCH, MUCH LESS BY THIS OTHER TERM. THIS MAY CHANGE FROM 4 TO 12, SAY, WHEREAS THIS HARDLY EVER REACHES A NUMBER LARGER THAN TWO,

ION ABUNDANCE IN M/E SELECTION

$$\text{EMPERICAL FACTOR} = -\text{LOG}\left(\frac{2}{a_x + b_y}\right)$$

M/E SELECTION CRITERIA

$$\text{MAXIMIZE} \quad \text{LOG}\left(\frac{R_x}{R_y}\right) - \text{LOG}\left(\frac{2}{a_x + b_y}\right)$$

AND NORMALLY, IT'S CLOSER TO 1.2 OR SOMETHING LIKE THAT.

THE NEXT SLIDE SHOWS US, REALLY, THAT THIS M/E SELECTION CRITERIA DOES HAVE SOME REASONABLE EFFECT ON WHAT THE DATA LOOKS LIKE THAT WE END UP WITH FOR THE COMPLICATED EQUATION. WHAT WE DID WAS... THESE ARE THE SAME M/E'S THAT WE HAD BEFORE WHERE WE GOT OUR FACTOR UP HERE (INDICATING), SELECTION CRITERIA. THIS IS A CORRELATION COEFFICIENT OF THE DATA THAT WE OBTAINED FOR A SERIES OF SAMPLES RUN FROM ABOUT 1 TO 1,000 MICROGRAM PER LITER LEVEL AND WE HAD BETWEEN 5 AND 7 DATA POINTS PER CORRELATION COEFFICIENT. OVER HERE IS A MEAN DEVIATION (INDICATING) FROM THE REGRESSION LINE, WHICH IS ROUGHLY PERCENT ERROR, IF YOU WILL. WHAT WE'RE PREDICTING IS THAT, AS WE ORDER FROM LARGE TO SMALL, BEST TO WORST, WE WILL GET ON ANY GIVEN COMPOUND THE SAME ORDER IN PERCENT ERROR AND THAT'S WHAT WE SEE. WE SEE IT FOR BENZENE, WE SEE IT FOR TOLUENE, WE SEE IT FOR DICHLOROTHANE, AND HERE WE'RE GOING FROM A VERY LARGE NUMBER DOWN TO REALLY A VERY SMALL NUMBER (INDICATING). YOU CAN SEE THAT THAT FOLLOWS. THERE'S A LITTLE INVERSION HERE (INDICATING), BUT THERE'S NOT MUCH DIFFERENCE IN THESE FACTORS THAT WE'RE LOOKING AT OVER HERE, EITHER (INDICATING),

EFFECTIVENESS OF M/E SELECTION CRITERIA

COMPOUND	M/E's	$\log\left(\frac{R_x}{R_y}\right) - \log\left(\frac{2}{a_x + b_y}\right)$	CORRELATION COEFFICIENT	MEAN DEVIATION FROM REGRESSION LINE (%)
BENZENE	78/84	4.79	.998	9
	50/56	3.91	.994	23
	77/82	3.79	.981	36
TOLUENE	92/100	8.19	.999	10
	91/98	7.72	.998	12
1,2-DICHLOROETHANE	62/67	8.94	.998	9
	64/67	7.92	.997	11
	98/104	6.19	.993	18
	49/53	5.73	.997	16
	98/102	2.73	.975	36

SO I'M NOT REALLY TOO CONCERNED ABOUT THAT. ANYWAY, IT LOOKS LIKE WE'VE COME UP WITH A WAY TO PICK M/E'S ON A SYSTEMATIC BASIS.

IT SEEMS THAT WE'VE GOT SOME CRITERIA NOW FOR SELECTING THE CALCULATION METHOD, OR AT LEAST WHICH ONE WE CAN USE AND WHEN, AND THERE IS REALLY ONE OTHER THING THAT WE CAN COME UP WITH WITH THIS MODEL, AND COME UP WITH IT FAIRLY EASILY, AND THAT IS MAKING A PREDICTION OF HOW WE'RE GOING TO STANDARDIZE OUR SPIKING SOLUTION. IT'S ALSO RELATED TO HOW MUCH MATERIAL WE SHOULD THEN SUBSEQUENTLY SPIKE INTO OUR SAMPLES.

IF WE TAKE THE SECOND DERIVATIVE OF THE MODEL EQUATION WITH RESPECT TO...AND THE NEXT SLIDE HAS THAT IN IT...WITH RESPECT TO THE ERRORS THAT WE SEE IN R_M, THAT BEING THE PARAMETER THAT AFFECTS THE RESULTS MORE THAN ANYTHING ELSE, WE CAN CRUNCH THROUGH THIS HORRIBLE MOUNTAIN OF PAPERWORK AND COME UP WITH A VERY SIMPLE EXPRESSION THAT SAYS THAT THE BEST SITUATION IS GOING TO BE THE MEASUREMENT WHICH TAKES PLACE FOR AN R_M WHICH IS EQUAL TO THE SQUARE ROOT OF THE PRODUCT OF R_X TIMES R_Y. IN OTHER WORDS, WE CAN PREDICT THE BEST R_M; WE CAN THEN TAKE THIS R_M, STICK IT BACK IN THE EQUATION, AND CALCULATE THE BEST

QUANTITY OF LABELED MATERIAL TO ADD

$$\frac{d^2(x/y)/(x/y)}{(d\ R_m/R_m)^2} = 0$$

WHEN

$$R_m = (R_x R_y)^{1/2}$$

X/Y. THIS TURNS OUT TO BE RIGHT AT THE CENTER OF THE STRAIGHT SECTION OF THE CURVE, SO YOU CAN PRETTY MUCH SAY THATX/Y IS EQUAL TO R_M. WHATEVER R_M TURNS OUT TO BE, BASED ON THIS EQUATION, THAT'S WHAT WE SHOULD USE AS A RATIO FOR CALIBRATING OUR INTERNAL STANDARD. IF WE HAVE NO INFORMATION AHEAD OF TIME, SUCH AS WITH SAMPLES, WE CAN PREDICT A CONCENTRATION RANGE AND SHOOT FOR THE MIDDLE OF THAT RANGE. WE KNOW THAT RANGE BASED ON GUESSES, BUT WE CAN MAKE THOSE GUESSES AND HAVE A GO AT IT; THEN AT LEAST WE'LL BE DIRECTING OUR EFFORT IN SOME FORM.

THE NEXT SLIDE JUST SUMMARIZES THE THREE SIGNIFICANT THINGS THAT I'VE GONE THROUGH SO FAR. THE SELECTION OF M/E'S BASED ON THIS FACTOR, THE CALCULATION METHOD, AND I'VE ONLY INCLUDED TWO OF THEM BECAUSE IT JUST SEEMS TO ME THAT THERE'S LITTLE REASON TO USE THE OTHER TWO. MORE OFTEN THAN NOT, THIS ONE IS ADEQUATE; IT'S THE HEIGHT OF SIMPLICITY, AND IT'S EASY TO DETERMINE WHEN TO USE IT. WE CAN USE IT WHEN R_M IS BETWEEN THESE TWO VALUES OF R_X AND R_Y. WE ALWAYS WILL KNOW THESE AHEAD OF TIME. R_X

SUMMARY OF METHODOLOGY

BEST M/E's

$$\text{MAXIMUM} \quad \text{LOG}\left(\frac{R_x}{R_y}\right) - \text{LOG}\left(\frac{2}{a_x + b_y}\right)$$

CALCULATION METHOD

$$\frac{x}{y} = R_m \qquad \text{when} \quad 10R_y < R_m < .1R_x$$

$$\frac{x}{y} = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)} \qquad \text{when} \quad 2R_y < R_m < .5R_x$$

BEST MOLE RATIO FOR STANDARDIZATION

$$\frac{x}{y} \quad \text{where} \quad R_m = (R_x R_y)^{1/2}$$

NEVER CHANGES, AND R_Y'S VALUE WAS FOR THE MATERIAL THAT EITHER WE PURCHASED OR SOMEONE GAVE US (INDICATING).

IF R_M FALLS OUTSIDE OF THAT RANGE, WE USE THIS OTHER EQUATION, BUT AGAIN, THERE ARE LIMITATIONS, AND AS LONG AS WE DON'T FALL OUTSIDE OF THAT, WE CAN EXPECT THE RESULTS WILL BE FAIRLY GOOD. THE MOLE RATIO FOR STANDARDIZATION IS THE ONE WE JUST SAW A MINUTE AGO, AND I WON'T GO THROUGH THAT AGAIN.

THE PROOF, OF COURSE, IS IN THE APPLICATION, AND THE NEXT SLIDE SHOWS SOME RESULTS WE GOT FOR SOME PURGEABLES IN LABORATORY PURE WATER AND SOME SOAP SOLUTIONS. WE MADE THE SAMPLES AND WE KNOW HOW MUCH IS IN THEM, SO WE CAN COME UP WITH PERCENT ERRORS. WHEN WE USE STANDARD ADDITIONS, WHICH IS REALLY THAT CALCULATION THAT WE WERE LOOKING AT EARLIER THIS MORNING, THE RESULTS COME OUT LOOKING SOMETHING LIKE THIS FOR THOSE SAMPLES (INDICATING).

THE PURE WATER IS NOT TOO BAD; THE SOAP SOLUTIONS CAN GET PRETTY OUTRAGEOUS. PURGING SOAP SOLUTION IS NOT THE EASIEST THING IN THE

APPLICATION

SAMPLE	COMPOUND (DATA POINTS)	MEAN % ERROR STANDARD ADDITION	MEAN % ERROR ISOTOPE DILUTION
LABORATORY PURE WATER	BENZENE (5)	31	27
	TOLUENE (6)	21	23
	1,2-DICHLOROETHANE (4)	51	17
SOAP SOLUTION (HEAT)	BENZENE (5)	62	23
	TOLUENE (5)	87	17
	1,2-DICHLOROETHANE (4)	92	26
SOAP SOLUTION (SURFACTANT)	BENZENE (5)	59	24
	TOLUENE (4)	84	44
	1,2-DICHLOROETHANE (4)	108	58

WORLD; WE ASSUMED THAT WE WOULD HAVE PLENTY OF MATRIX EFFECTS.

AT THE SAME TIME, WE GOT SOME RESULTS. WHEN WE COMPARE THESE WITH THE ERRORS THAT WE SEE WITH ISOTOPE DILUTION, WE SEE THAT WHEN IT COMES OUT WELL OVER HERE, IT STILL COMES OUT WELL OVER HERE (INDICATING), BUT WHEN IT COMES OUT BAD OVER HERE, IT STILL COMES OUT WELL OVER HERE, AND THAT'S FAIRLY CONSISTENT UNTIL ALL OF A SUDDEN WE START TO HIT A SNAG DOWN HERE (INDICATING).

WELL, WE'RE BACK TO A PROBLEM THAT IS NOMINALLY INSURMOUNTABLE. WE'VE ADDED SOMETHING TO THE SOAP SOLUTION; WE ADDED A SURFACTANT WITH THIS SERIES OF SAMPLES, AND THAT SURFACTANT ENDED UP INTERFERING WITH THE ANALYSIS. IF WE'VE GOT INTERFERENCES, THE ONLY WAY WE CAN BEAT THEM IS TO GET RID OF THEM. THERE ARE NO TRICKS; IT'S A VERY SIMPLE CONCEPT. WE JUST DON'T ALWAYS KNOW HOW TO DO IT. SO I WANT TO POINT THIS OUT: ISOTOPE DILUTION METHOD WON'T OVERCOME INTERFERENCES. IF THERE IS AN INTER-FERENCE TO DEAL WITH, IT JUST HAS THE SAME PROBLEMS

AS ANY OTHER METHOD. WHEN THERE AREN'T INTERFERENCES, THE PRECISION IS HIGH AND THE ERROR IS LOW.

IF WE LOOK AT ANOTHER SET OF DATA, THIS TIME FOR SOME POTW SAMPLES, AND FOR A LARGER GROUP OF COMPOUNDS, WE FIND THAT THE ERROR FOR STANDARD ADDITIONS CAN GET VERY HIGH. FOR PHENOL, WE ENDED UP PREDICTING A NEGATIVE CONCENTRATION, AND RATHER THAN INCLUDE IT, I DECIDED TO IGNORE IT. AT THE SAME TIME, SOMETIMES WE HIT A VALUE SPOT ON , AND THEN THERE ARE OTHERS THAT ARE JUST TERRIBLE.

WITH ISOTOPE DILUTION, WE NEVER LOSE ANY DATA; WE NEVER GET ANY BAD ERROR SITUATIONS WHETHER WE'RE LOOKING AT LAB WATER, RAW SEWAGE OR TREATED SEWAGE. RAW SEWAGE IS NOT THE NICEST MATRIX THAT I'VE EVER DEALT WITH; THERE'S A LOT OF PARTICULATE MATERIAL IN IT, THERE'S A LOT OF STUFF IN IT. THE EFFLUENT IS A LOT CLEANER; THE PERCENT ERRORS ARE UNIFORMLY LOW, AROUND 15 PERCENT. WITH STANDARD ADDITION, THEY RUN AROUND 45 PERCENT (INDICATING).

NOW, A LITTLE BIT ABOUT HOW WE DID THIS, SINCE I'M TALKING PERCENT ERROR AND REAL SAMPLES.

APPLICATION

COMPOUND	PERCENT ERROR					
	STANDARD ADDITIONS*			ISOTOPE DILUTION**		
	LAB WATER	POTW INFLUENT	POTW EFFLUENT	LAB WATER	POTW INFLUENT	POTW EFFLUENT
BENZENE	11	11	11	14	4	9
TOLUENE	31	31	44	17	6	11
METHYLENE CHLORIDE	39	38	52	13	11	8
PHENOL	133	212	***	7	8	4
1,2-DICHLOROBENZENE	71	52	42	23	21	22
NAPHTHALENE	0	18	47	26	41	27
NITROBENZENE	2010	6	34	26	5	18
CHRYSENE	49	81	23	9	14	7
BENZO(a)PYRENE	42	72	11	14	24	7
MEAN	265(47)	56	33	17	15	13

* ONE DATA POINT PER ENTRY

** TWO DATA POINTS PER ENTRY

*** UNDEFINED; NEGATIVE CONCENTRATION

WE GOT THIS INFORMATION BASED ON THREE RUNS: ONE OF THE AS-ACQUIRED SAMPLE, ONE OF THE AS-ACQUIRED SAMPLE SPIKED WITH 100 MICROGRAMS PER LITER OF THESE COMPOUNDS, PLUS A THIRD RUN SPIKED WITH 1,000 MICROGRAMS PER LITER. FOR STANDARD ADDITIONS, WE TOOK THE DATA POINT FOR THE UNSPIKED SAMPLE AND SUBTRACTED IT AS A BACKGROUND LEVEL FROM VALUE THAT WE GOT FOR THE 100 MICROGRAM PER LITER SAMPLE. WE KNOW WE PUT 100 MICROGRAMS IN, SO WE SHOULD HAVE GOTTEN 100 MICROGRAMS BACK. PERCENT ERROR IS BASED ON HOW MUCH OF THE 100 MICROGRAMS PER LITER WE GOT BACK. SO WE REALLY DO KNOW THE PERCENT ERROR THERE.

WE NEEDED THE 1,000 MICROGRAM PER LITER SAMPLE WITH STANDARD ADDITIONS TO CARRY OUT THE STANDARD ADDITIONS CALCULATION BECAUSE TWO DATA POINTS ARE REQUIRED TO PRODUCE ONE CONCENTRATION VALUE. FOR THE ISOTOPE DILUTION, WE USED THE SAME PROCESS; THAT IS, WE SUBTRACTED THE BACKGROUND CONCENTRATION OF THE UNSPIKED SAMPLE FROM THE VALUE DETERMINED FOR THE SPIKED SAMPLE, AND CALCULATED OUR PERCENT ERROR BASED

ON THE RECOVERED CONCENTRATION OF OUR SPIKE. THE DATA OVER HERE (INDICATING) IS BASED ON THE PERCENT ERROR FOR BOTH THE 100 AND THE 1,000 MICROGRAM PER LITER VALUE. WE'VE GOT TWICE AS MUCH DATA INVOLVED IN THIS SERIES OF PERCENT ERRORS AS WE DO OVER HERE (INDICATING), BUT AT THE SAME TIME, THE ERROR VALUES ARE ALWAYS LOW. THEY AVERAGE ABOUT 15 PERCENT HERE, ABOUT 45 PERCENT HERE (INDICATING), ABOUT A FACTOR OF 3. WITH ISOTOPE DILUTION, WE GOT TWICE AS MUCH DATA FROM THE SAME SET OF RUNS.

IF WE EXTRAPOLATE THAT BACK TO COST PER SAMPLE, IT COSTS US HALF AS MUCH TO RUN AN ISOTOPE DILUTION SAMPLE AS IT DOES TO RUN A STANDARD ADDITION SAMPLE. IF WE ARE SPIKING AND CARRYING OUT STANDARD ADDITIONS-TYPE MEASUREMENTS TO A LARGE DEGREE, OR IF WE'RE DOING A LOT OF SPIKING AND RUNNING OF SPIKED PLUS UNSPIKED SAMPLES, WE COULD SAVE HALF OF THAT MONEY BY USING ISOTOPE DILUTION. THIS IS BECAUSE ALL OF THE SPIKING TAKES PLACE IN THE SAME SAMPLES THAT ARE BEING ANALYZED. SO WE'VE COVERED THE SAME INFORMATION BASE THAT

THE SPIKING COVERS, BUT WE'VE COVERED IT IN THE SAME SAMPLE MEDIA.

THESE APPLICATIONS SEEM TO PREDICT THAT WE'LL GET BETTER DATA AND WE'LL GET IT AT A LOWER COST BY USING ISOTOPE DILUTION RATHER THAN STANDARD ADDITION. THE DISADVANTAGES ARE MOSTLY ASSOCIATED WITH ROUTINE APPLICATION OF NEW TECHNOLOGY TO ENVIRONMENTAL-TYPE SAMPLES.

IN THE PAST, AS I MENTIONED EARLIER, IT'S TYPICALLY BEEN APPLIED TO DETERMINE ONE COMPOUND PER ANALYSIS, AND WHAT WE'RE TALKING ABOUT HERE IS POTENTIALLY 47 COMPOUNDS WITH THE BASE/NEUTRAL FRACTION. WELL, WE'RE TRYING TO DO 47 COMPOUNDS THERE, ANYWAY, AND WE GET MOST OF THEM, SO IT SEEMS PROMISING.

WE DON'T KNOW WHAT'S GOING TO HAPPEN IN ALL ENVIRONMENTAL SAMPLE SITUATIONS. WE DON'T KNOW WHAT ALL THE INTERFERENCES MIGHT BE, BUT WE DON'T KNOW THAT ANYWAY. WE DO KNOW THAT WE HAVE INTERFERENCES THE WAY WE ANALYZE NOW, AND I'M SURE THERE WILL BE NEW ONES AS WE LOOK

SUMMARY OF ISOTOPE DILUTION METHOD

ADVANTAGE

1. BETTER DATA
2. LOWER COST

DISADVANTAGE

1. NEW TECHNOLOGY FOR ROUTINE APPLICATIONS
2. NOT DEMONSTRATED FOR LARGE NUMBER OF ENVIRONMENTAL SAMPLE SITUATIONS

AT ADDITIONAL TYPES OF SAMPLES.

THE INTERESTING THING WITH ISOTOPE DILUTION IS THAT IF WE DON'T MAKE IT AT ONE SET OF M/E'S, WE MIGHT MOVE TO A SECONDARY SET OF M/E'S AND CHECK OUR CONCENTRATION CALCULATION. IF WE GET THE SAME NUMBER FROM TWO DIFFERENT M/E VALUES, THAT'S PRETTY CONVINCING THAT THERE'S NO INTERFERENCE AT EITHER OF THEM. IT'S NOT A GUARANTEE, BUT IT'S PRETTY CLOSE TO IT.

THE WAY WE PLAN TO GO IN THE FUTURE WITH THIS WORK IS TO BUY SOMETHING LIKE 40 ADDITIONAL LABELED COMPOUNDS. WE'LL USE THESE IN LOOKING AT MORE INDUSTRIAL SAMPLES. THERE WILL ALSO BE A COUPLE OF LABS OTHER THAN OURS GETTING INVOLVED. WE HOPE TO FIND THAT WHAT HAS WORKED IN THE PAST FOR THE BIOLOGIST WILL ALSO WORK FOR THE ENVIRONMENTAL CHEMIST. I HOPE WE'LL HAVE A LOT MORE GOOD INFORMATION FOR ANOTHER MEETING LIKE THIS, SHOULD WE EVER HAVE ONE.

IF THERE ARE ANY QUESTIONS, I WOULD BE PLEASED TO TRY TO ANSWER THEM.

Question and Answer Session

MR. OLLISON: Will Ollison, A.P.I. Two questions. One, you didn't say anything about when and where you spike your samples. I was wondering particularly about equilibrations of your isotopic spiked with three-phased samples.

DR. COLBY: We spiked the POTW samples, the extractables, about one-half hour prior to starting the extraction. They were spiked in the continuous liquid/liquid extractor and stirred before adding methylene chloride and adjusting the pH.

MR. OLLISON: Do you have any idea of the equilibration times into solid phases?

DR. COLBY: No, but if we blew it, if we waited longer, we'd do even better, wouldn't we?

MR. OLLISON: The second question would be, you mentioned only fluoranthenes as a polycyclic with exchange. I seem to recall last year there was some exchange with the D_{10} anthracene.

DR. COLBY: That's not

EXCHANGE PER SE. I BELIEVE THAT'S USUALLY CONSIDERED OXIDATION. I THINK THAT WHAT WAS TALKED ABOUT WAS D_{10} ANTHRACENE BEING OXIDIZED TO D_8 ANTHRAQUINONE.

MR. OLLISON: THAT MIGHT BE MY MISTAKE. IT WAS SOMETHING THAT WOULD DO WITH THE GLASS WOOL.

MR. CLAEYS: BOB CLAEYS, WITH THE NATIONAL COUNCIL, BRUCE. DID YOU BRING ALONG ANY OF YOUR EXCHANGE DATA FOR CHLOROFORM?

DR. COLBY: I THINK I MAY HAVE SOME OF IT.

MR. CLAEYS: CAN YOU GIVE US A ROUGH IDEA OF HOW FAST SOMETHING LIKE THAT WOULD EXCHANGE?

DR. COLBY: IF I DIG IN MY BRIEFCASE FOR A MINUTE. IN A BASIC SOLUTION?

MR. CLAEYS: NO, JUST A NEUTRAL SOLUTION.

DR. COLBY: IN A NEUTRAL SOLUTION. IF YOU DO IT VERY, VERY RAPIDLY, SPIKE IN YOUR SYRINGE, PUT THE VOA SAMPLE IN, AND PURGE IT, YOU'RE ONLY TALKING IN THE 10 PERCENT AREA. IT'S VERY REPRODUCIBLE. WE'VE DONE ISOTOPE DILUTION WITH DEUTERATED CHLOROFORM AND WE GET VERY REPRODUCIBLE AND ACCURATE RESULTS, BUT I WOULD HESITATE TO USE IT

ON A ROUTINE BASIS BASED ON THE FACT THAT I KNOW IT DOES EXCHANGE. IF THE SAMPLE IS BASIC, THE EXCHANGE IS 100 PERCENT AND IT'S FAST. IT'S VERY PH DEPENDENT.

MR. CLAEYS: RIGHT.

MR. PARR: JERRY PARR WITH RADIAN. CORRECT ME IF I'M WRONG, BUT I GET THE IMPRESSION ON YOUR COST FACTORS THAT YOU WERE GOING TO BE ABLE TO USE ALL OF THE DEUTERATED MATERIAL WHEN IN ACTUAL LAB PRACTICE, THE BASIS OF WASTAGE AND THE STABILITY OF THE STANDARDS AND HAVING TO REMAKE THEM, THAT COULD BE ONLY MAYBE 10 PERCENT OF WHAT YOU USE, WHICH WOULD MULTIPLE YOUR COSTS BY A FACTOR OF 10, WHICH BECOMES SIGNIFICANT, THEN, IN AN ANALYTICAL SITUATION.

DR. COLBY: I DON'T THINK I FOLLOWED THAT.

MR. PARR: YOUR COST PER YOUR STANDARD IN WHICH YOU CAME UP WITH $5.

DR. COLBY: COST PER SAMPLE, RIGHT.

MR. PARR: IF YOU BUY A GRAM OF THAT, HOW MUCH OF THAT GRAM ARE YOU GOING TO BE ABLE TO USE FOR SPIKING?

DR. COLBY: THAT MAKES THE

ASSUMPTION THAT WE'RE GOING TO USE THE WHOLE GRAM UP OVER SOME PERIOD OF TIME AND WE'RE NEVER GOING TO WASTE ANY OF IT.

MR. PARR: YES, AND I'M SAYING I THINK YOU'RE GOING TO WASTE 50 TO 80 PERCENT OF THAT GRAM IN TERMS OF HAVING TO REMAKE YOUR STANDARDS OR THE STABILITY OF YOUR STANDARDS OR THE FACT THAT YOU'VE GOT...

DR. COLBY: SO IT MAY COST...

MR. PARR: $50.

DR. COLBY: REALLY? NO, YOU'RE WASTING ALMOST 1,000 PERCENT. IF YOU WASTE 50 PERCENT FOR EVERY 100 MICROGRAMS NEEDED IN PRACTICE YOU ACTUALLY WASTE 100, SO YOU'D CONSUME 200; THAT WOULD MAKE IT $10.

MR. TELLIARD: YOU COULD WASTE $50 AT THE PRICE YOU GUYS ARE CHARGING US FOR SAMPLES. IT'S INSIGNIFICANT. I'M NOT SINGLING YOU OUT, I MEAN THESE GUYS.

MR. PARR: BUT IT GETS INTO EACH TIME YOU NEED TO MAKE...IT'S NOT ONLY THE COST OF THE MATERIAL, BUT THE COST OF THE LABOR AND PREPARING FRESH STANDARDS OVER THE PERIOD AND WHATEVER; I THINK IT CAN EVENTUALLY BECOME A FACTOR.

DR. COLBY: YOU'RE NOT ADDING TO THE SITUATION, YOU'RE JUST SAYING THAT IT'S THE SAME WITH THE ISOTOPICALLY LABELED COMPOUNDS. YOU HAVE TO MAKE UP ALL THOSE SOLUTIONS NOW JUST AS YOU WOULD WITH THE LABELED COMPOUNDS; THERE'S NO DIFFERENCE.

MR. PARR: YES, BUT SPIKING 1 IN 10 VERSUS SPIKING EVERY SAMPLE.

DR. COLBY: ALL RIGHT, YES, IF YOU WANT TO SPIKE 1 IN 10.

MR. PARR: YES. OKAY, THAT'S ALL.

MR. STANKO: GEORGE STANKO, SHELL DEVELOPMENT. I'D LIKE TO SUGGEST ONE FURTHER EXPERIMENT ON THIS SPIKING THAT I THINK IS IMPORTANT. I WOULD LIKE TO SEE YOU TAKE A LIQUID/LIQUID EXTRACTABLE SAMPLE AND FIELD SPIKE IT AT THE TIME THE SAMPLE WAS OBTAINED, TRANSPORT THE SAMPLE BACK TO THE LABORATORY, THEN ANALYZE THAT PARTICULAR SAMPLE. THEN, TAKE THE SPLIT OR EQUIVALENT SAMPLE THAT WAS OBTAINED IN THE FIELD, COLLECT IT AT THE LAB, PUT IT IN YOUR CONTINUOUS EXTRACTOR AND THEN SPIKE WITH YOUR STABLE LABEL. I THINK IF YOU CAN DEMONSTRATE THAT THERE IS NO DIFFERENCE, WHICH I THINK THERE WILL BE, I THINK THIS IS AN IMPORTANT THING TO CONSIDER.

DR. COLBY: RIGHT. WE'VE JUST

CONSIDERED WHAT HAPPENS AFTER THE SAMPLES ARRIVE IN OUR LABORATORY AND HAVE NOT CONSIDERED ANYTHING THAT MIGHT GO ON IN TRANSIT OR IN THE FIELD.

MR. STANKO: THAT'S AS IMPORTANT AS ANALYZING IT.

DR. COLBY: I AGREE.

MR. DAUN: BOB DAUN, RALTECH SCIENTIFIC. IN YOUR REVERSE EXCHANGE EXPERIMENTS, WHERE YOU EQUILIBRATED THE PRIORITY POLLUTANTS, I ASSUME YOU USED DEUTERATED WATER?

DR. COLBY: WE USED D_2O, AND USED DCL AND NAOD TO ADJUST THE PH.

MR. DAUN: WHAT RELATIVE CONCENTRATIONS OF PRIORITY POLLUTANT TO THE DEUTERATED WATER WERE USED? IN OTHER WORDS, DID YOU USE, SAY, YOU DIDN'T USE 100 PERCENT DEUTERATED WATER OR DEUTERATED...

DR. COLBY: 100 PERCENT.

MR. DAUN: IT WAS 100 PERCENT?

DR. COLBY: WELL, THAT'S WHAT THE MANUFACTURER TOLD ME.

MR. DAUN: YES. OKAY, I WAS WONDERING IF IT WAS, YOU KNOW, SOMETHING DOWN IN A VERY LOW RANGE OR IF IT WAS SOMETHING HIGH THAT WOULD REPRESENT A REAL SAMPLE-TYPE THING. THANK YOU.

MR. SPRAGGINS: BOB SPRAGGINS, RADIAN CORPORATION. YOUR PRICE PER SAMPLE, THAT'S BASED ON, LET'S SAY IF YOU'RE GOING TO DO BENZENE IN WATER, YOU'RE ADDING D_6 BENZENE, IS THAT CORRECT? IF YOU WERE GOING TO DO 10 COMPOUNDS IN WATER YOU WOULD ADD 10 INTERNAL STANDARDS SO THAT YOUR PRICE PER SAMPLE WOULD BE 10 TIMES THAT AMOUNT, CORRECT?

DR. COLBY: RIGHT AND THE PRICE PER SAMPLE THAT I HAD IN THE SLIDE WAS BASED ON...

MR. SPRAGGINS: ISN'T THE REAL PROBLEM IN...IS THAT IF YOU'RE DOING 10 OR 40 PRIORITY POLLUTANTS AND YOU ADD 10 TO 40 SPIKES, YOUR SPECTRUM GETS SO CLUTTERED THAT YOU HAVE A REAL POSSIBILITY OF INTERFERENCES; ISN'T THAT THE REAL PROBLEM?

DR. COLBY: I DON'T REALLY THINK THAT WE'RE TALKING ABOUT INTERFERENCES. WE LIKE THIS METHOD BECAUSE WE ARE MAKING THE MEASUREMENT FOR LABELED AND UNLABELED MATERIAL AT THE SAME INSTANT IN THE ION SOURCE IN MOST CASES. IF THERE ARE ANY FLUCTUATIONS IN INSTRUMENT PERFORMANCE, THOSE WOULD BE CANCELLED OUT. THE OBJECT IS TO CANCEL OUT AS MUCH AS WE CAN. YES, THERE WILL BE INTERFERENCES OCCASIONALLY.

MR. SPRAGGINS: MY ONLY POINT IS, IN A MASS SPECTRUM, THERE'S USUALLY MORE THAN TWO IONS. FOR EACH COMPOUND IT'S GOING TO GENERATE ITS OWN...

DR. COLBY: THAT'S RIGHT.

MR. SPRAGGINS: ...SO YOU'RE GOING TO HAVE A LOT MORE POSSIBILITY FOR INTERFERENCE THE MORE THINGS THAT YOU SHOVE IN THERE.

DR. COLBY: IF YOU CHECK BACK INTO MASS SPEC IN TERMS OF THE SPECTRA AND THE WAY THEY LOOK, USUALLY WE SEE LOSSES OF CERTAIN NUMBERS OF MASS UNITS BEFORE ANOTHER GROUP OF PEAKS, AND WHEN WE'RE LABELING COMPOUNDS, WE ARE NOT TALKING ABOUT LABELING THEM SUCH THAT WE WOULD HAVE A METHYL GROUP AND LABEL IT WITH 15 DEUTERIA; THAT WOULD GUARANTEE US OVERLAPS AND THINGS LIKE THAT.

MR. SPRAGGINS: AS I SAY, I AGREE THAT YOUR METHOD IS BETTER THAN WHAT WE'RE USING; I'M JUST SAYING THAT THERE ARE PRACTICAL LIMITATIONS TO IT.

DR. COLBY: RIGHT.

MR. TELLIARD: THANK YOU, BRUCE. IN PASSING, LET ME POINT OUT THAT BRUCE IS GOING TO CONTINUE ON THE WORK AND HE'S BEEN FUNDED BY LARRY JOHNSON FROM RTP TO PURCHASE THE COMPOUNDS, HAVE COMPOUNDS MADE. IN ADDITION TO THAT, THE FOLKS AT CINCINNATI HAVE AGREED TO LOOK AT ADDITIONAL COMPOUNDS BEING SYNTHESIZED OVER THE NEXT MONTHS OR WHATEVER AS THEY LOOK AT WHAT THEY FEEL MIGHT BE NEEDED. HOPEFULLY, IN A COUPLE OF MONTHS WE WILL HAVE A LOT MORE DATA ON REAL SAMPLES. THERE WILL BE TWO OTHER LABS PARTICIPATING IN IT, RUNNING REAL SAMPLES, SO TO SPEAK.

AFTERNOON SESSION

MR. TELLIARD: OUR NEXT SPEAKER IS BOB KLEOBFER FROM OUR REGION 7 S&A LABORATORY. BOB HAS APPEARED HERE BEFORE AND WE'LL KEEP MAKING HIM DO IT UNTIL HE GETS IT RIGHT. WE PASSED OUT COPIES OF A PAPER BOB HAS PUT TOGETHER ON A REVIEW OF THE QUALITY ASSURANCE FOR PRIORITY POLLUTANT ANALYSIS THAT HE HAS WRITTEN AND BOB IS GOING TO BASICALLY GO OVER THE PAPER TODAY AND KIND OF SUMMARIZE WHAT IT CONTAINED.

PRIORITY POLLUTANT METHODOLOGY
QUALITY ASSURANCE REVIEW, REGION VII

BY: ROBERT D. KLEOBFER

THIS IS THE FOURTH CONFERENCE THAT HAS BEEN HELD ON THE PRIORITY POLLUTANT METHODOLOGY, AND UNFORTUNATELY, OR MAYBE FORTUNATELY, DEPENDING ON YOUR POINT OF VIEW, I HAVE ATTENDED ALL FOUR. I HAVE COME UP WITH ONE OBSERVATION ABOUT ANALYTICAL CHEMISTS. I SUSPECT THAT IF YOU WERE TO CLONE AN ANALYTICAL CHEMIST, AND YOU WOULD HOLD A MEETING LIKE THIS WITH ALL OF HIS CLONES, I SUSPECT THERE WOULD STILL BE DISAGREEMENT ABOUT METHODOLOGY AMONG THE CLONES. IN SPITE OF THOSE PROBLEMS WITH ANALYTICAL CHEMISTS, I THINK THE BASIC SCREENING PROTOCOL THAT WAS PROPOSED TWO OR THREE YEARS AGO DID TURN OUT AND HAS BEEN DEMONSTRATED TO BE A SOUND ONE. OVER THE PAST FEW MONTHS I HAVE ATTEMPTED TO ACCUMULATE AS MUCH DATA AS I COULD FROM VARIOUS CONTRACTORS AND VARIOUS LABORATORIES ABOUT THE QUALITY OF THE DATA THAT HAS BEEN GENERATED USING THAT BASIC METHODOLOGY AS THE GUIDELINE. THIS PAPER THAT WE HAVE PASSED OUT IS BASED ON THE RESULTS FROM SEVEN DIFFERENT LABORATORIES AND IT INCLUDES OVER 10,000 DATA POINTS. SO THERE IS QUITE A BIT OF INFORMATION AVAILABLE NOW ON RECOVERY OF STANDARDS TO EITHER BLANK WATER OR TO REAL SAMPLES. THIS PAPER SIMPLY ATTEMPTS TO SUMMARIZE DATA

THAT WAS AVAILABLE TO ME. SEVEN LABORATORIES SUPPLIED THE DATA. I SUPPOSE I SHOULD START RIGHT OUT AND IMPLICATE, OR ACKNOWLEDGE, RATHER THAN IMPLICATE, THE LABORATORIES THAT SUPPLIED DATA. THE PRIMARY ONES WERE VERSAR, CARBORUNDUM, AND A.D. LITTLE AND THE REGION VII LAB.

I WILL START RIGHT OFF AND JUST GIVE THE BOTTOM LINE AS FAR AS THE ORGANICS GO, HOW WELL WE DID ON RECOVERING STANDARDS WHICH HAVE BEEN ADDED TO SAMPLES. WHAT I DID IS SIMPLY AVERAGE THE RECOVERIES FOR ALL OF THE ORGANICS. THIS IS SIMPLY LUMPING A LOT OF DATA TOGETHER AND THE RESULT WAS 73 PERCENT RECOVERY WITH A STANDARD DEVIATION BEING 26 PERCENT. I THINK THIS IS WHAT HAD SURPRISED MOST OF US FROM THE BEGINNING; WE DID NOT THINK THAT WE COULD DO THAT WELL, BUT THIS IS WHAT WE CAME UP WITH.

NOW, I HAVE BASICALLY ASSEMBLED THE DATA INTO EIGHT DIFFERENT TABLES AND RATHER THAN TRYING TO PUT IT ON A SLIDE PROJECTOR OR THE OVERHEAD PROJECTOR, IT WOULD BE MORE CONVENIENT TO SIMPLY REFER TO THE PAPER THAT I HANDED OUT.

LET'S BEGIN WITH TABLE NUMBER ONE, WHICH BEGINS AT THE END OF ALL OF THE DIALOGUE. TABLE NUMBER ONE, THAT SHOULD READ INTERLABORATORY COMPARISON, RATHER THAN INTRALABORATORY. IT GIVES COMPARISON

TABLE I. INTRALABORATORY COMPARISON[a]

Priority Pollutant Fraction[b]	LAB I	LAB II	LAB III	LAB IV	LAB V	LAB VII	Average[c]
Volatile (MS)	88±21	95±5	-	100±8	-	-	90±13
Volatile Sample Spike	82±24	101±9	93±13	107±9	-	-	92±15
Acid (MS)	90±18	89±5	-	67±14	82±16	-	84±13
Acid Sample Blank	92±34	72±10	62±12	60±15	84±17	-	76±19
B/N-(MS)	95±25	78±41	-	77±15	-	-	84±25
B/N Sample Spike	84±18	61±22	55±24	68±16	-	63±13	68±21
Pesticide (MS)	73±8	74±19	-	88±8	-	-	78±11
Pesticide Sample Spike	69±7	51±18	33±10	93±5	-	-	59±11
Metals (MS)	113±37	-	-	103±8	-	-	108±22
Metals Sample Spike	100±20	103±14		92±7	-	-	96±11
Cyanide (MS)	103±14	-	-	103±8	-	-	103±7
Cyanide Sample Spike	101±12	-	-	93±16	-	-	96±14
Phenolics (MS)	10±13	97±6	-	100±7	-	-	101±8
Phenolics Sample Spike	93±15	98±10	-	97±9	-	-	96±11

a) The values are in units of percent recovery (P) plus or minus (±) one standard deviations (Sp).
b) MS refers to the method standard or the standard addition to blank water. Sample spike refers to the standard addition to a sample.
c) P and Sp are weighted averages based on the number of data points contributed by each laboratory.

OF DATA SUPPLIED BY THE DIFFERENT LABORATORIES, BROKEN DOWN THIS TIME BY THE VARIOUS FRACTION TYPES, THE FIRST ENTRY BEING THE VOLATILES WITH THE STANDARD HAVING BEEN ADDED TO A BLANK SAMPLE; THE SECOND ENTRY BEING THE VOLATILE RESULTS WITH THE SPIKE BEING ADDED TO AN ACTUAL SAMPLE. YOU CAN SEE THAT THERE IS A REASONABLE AGREEMENT BETWEEN THE DIFFERENT LABORATORIES. THEN, IF YOU SCAN DOWN THE LAST COLUMN, WHICH SIMPLY AVERAGES EVERYTHING TOGETHER, YOU CAN SEE THAT IN ALL CASES EXCEPT FOR THE VOLATILE FRACTION, THE RECOVERY FROM THE SAMPLES, THE REAL SAMPLES, WERE LESS THAN THE RECOVERY WHEN STANDARDS WERE ADDED TO A BLANK WATER SAMPLE. FOR THE VOLATILES, WE SEEMED TO DO WELL WHETHER IT WAS A SAMPLE OR A BLANK WATER MATRIX.

NOW, ONE INTERESTING THING I WOULD LIKE TO POINT OUT HERE IS THAT WE STARTED OUT WITH METHODOLOGY THAT WAS SUBSTANTIALLY UNPROVEN EXCEPT FOR THE PESTICIDES. THE PESTICIDE METHODOLOGY WAS THE STANDARD GC ELECTRON CAPTURE METHOD, AND YOU CAN SEE THAT, OUT OF ALL THE FRACTIONS, THAT THE PESTICIDES GAVE US THE LOWEST RECOVERY. SO HERE WAS AN ESTABLISHED METHOD THAT GIVES US LOWER RECOVERY THAN THE OTHER METHODS.

NOW, IF WE GO ON TO TABLE TWO, WE BEGIN TO LOOK AT THE SPECIFIC COMPOUNDS IN THE VARIOUS GROUPS, AND AGAIN THE RESULTS FROM ALL OF THE LABORATORIES HAVE BEEN LUMPED TOGETHER, AND WE COME OUT WITH SORT OF AN AVERAGE STATEMENT ON THE PRECISION AND ACCURACY THAT WERE OBTAINED FROM THESE SEVEN DIFFERENT LABORATORIES. ON THE VOLATILE FRACTION WHICH IS COVERED IN TABLE TWO, WE DO NOT SEE ANY REAL SURPRISES. THERE DID SEEM TO BE SOME PROBLEM WITH DICHLOROMETHANE, AND I CANNOT IMAGINE WHY WE WOULD HAVE PROBLEMS WITH DICHLOROMETHANE. BUT, SERIOUSLY, IN OUR OWN LABORATORY THE BLANKS, ON OUR OWN PREPARED WATER, TYPICALLY CONTAINS 1 TO 2 PARTS PER BILLION OF METHYLENE CHLORIDE; IT IS A PROBLEM THAT IS HARD TO DEAL WITH, HARD TO SOLVE.

THE DATA, BY THE WAY, THAT IS LUMPED TOGETHER IN TABLE TWO GENERALLY IS IN THE RANGE OF 10 TO 1,000 PARTS PER BILLION WITH MOST OF THE DATA IN THE 20 TO 200 CATEGORY. WE CHOSE NOT, AT THIS POINT, TO TRY TO SEPARATE INTO LOW LEVEL SPIKES AND HIGH LEVEL SPIKES BECAUSE ON JUST SCANNING THE DATA WE DID NOT SEE ANY REAL SIGNIFICANT DIFFERENCE IN LOW LEVEL COMPARED TO HIGH LEVEL.

TABLE II. Purgeable Organics[a]

Compound	Method[b] Standard	Standard[c] Spike
Acrolein	77±30	32±30
Acrylonitrile	96±31	102±28
Benzene	89±12	93±24
Bromodichloromethane	97±11	103±31
Bromoform	94±14	88±12
Bromomethane	90±16	78±15
Carbon Tetrachloride	91±23	91±33
Chlorobenzene	94±23	103±24
Chlorodibromomethane	86±12	99±17
Chloroethane	67±22	60±23
Chloroform	90±18	91±26
Chloromethane	91±22	64±28
Dichlorodifluoromethane	108±11*	114±8*
1,1-Dichloroethane	83±10	87±21
1,2-Dichloroethane	102±12	103±27
1,1-Dichloroethylene	74±24	80±32
trans-1,2-Dichloroethylene	90±25	85±35
Dichloromethane	82±46	66±66
1,2-Dichloropropane	94±26	99±30
cis-1,3-Dichloropropene	95±15	98±20
trans -1-3-Dichloropropene	91±13	93±16
Ethylbenzene	109±19	106±28

Continuation of Table II

Compound	Method Standard	Sample Spike
1,1,2,2-Tetrachloroethane	81±31	78±31
Tetrachloroethylene	97±13	99±26
Toluene	96±22	97±25
1,1,1-Trichloroethane	92±21	94±36
1,1,2-Trichloroethane	102±14	103±19
Trichloroethylene	106±14	110±22
Trichlorofluoromethane	59±23	67±48
Vinyl Chloride	103±30	79±22

a) The values are in terms of P ± Sp. Data from 2-4 laboratories have been averaged except where noted with an (*) asterik. In general the concentration added ranged from 10 to 1000 parts per billion.
b) Standard addition to blank water.
c) Standard addition to sample.

*Data from only one lab were available.

NOW, I AM SURE THAT THE RECOVERIES AND THE STANDARD DEVIATION ARE GOING TO BE WORSE IF WE WERE TO LOOK AT LEVELS, SAY, BELOW 10 PARTS PER BILLION, WHERE WE ARE REALLY CHALLENGING THE ANALYTICAL METHOD.

TABLE THREE SUMMARIZES THE DATA FOR THE ACID FRACTION, THE PHENOLICS. THERE ARE NOT ANY REAL SURPRISES HERE, EXCEPT PERHAPS THERE WAS MENTION EARLIER THAT PHENOL IS GENERALLY RECOVERED AT 40 TO 50 PERCENT.

TABLE FOUR SUMMARIZES THE BASE NEUTRAL DATA AND HERE WE DO ENCOUNTER SOME PROBLEM COMPOUNDS. COMPOUNDS THAT WE CANNOT DO AS WELL AS OTHERS, AND ONE, FOR EXAMPLE, WOULD BE THE PHTHALATE ESTERS. GENERALLY THE RECOVERIES ARE QUITE LOW AND THE SCATTER IS A LOT WORSE.

OF COURSE, WE ALL KNOW THAT DICHLOROBENZIDINE IS SOMEWHAT DIFFICULT TO DO, AND THAT IS WHY YOU HAVE SUCH A LARGE STANDARD DEVIATION ON THAT ONE, I SUSPECT. THE HEXACHLOROCYCLOPENTADIENE RECOVERIES ARE NOT ANYTHING TO BRAG ABOUT, AND HERE WE SUSPECT THERMAL DEGRADATION AT THE INJECTOR IS COMING INTO PLAY HERE.

TABLE III. ACID FRACTION[a]

COMPOUND	METHOD[b] STANDARD	SAMPLE[c] SPIKE
2-Chlorophenol	80±22	71±23
4-Chloro-3-methylphenol	96±16	99±19
2,4-Dichlorophenol	86±24	84±23
2,4-Dimethylphenol	71±19	72±16
4,6-Dinitro-o-cresol	87±34	102±23
2,4-Dinitrophenol	89±22	92±40
2-Nitrophenol	95±22	87±22
4-Nitrophenol	65±33	59±46
Pentachlorphenol	87±24	84±22
Phenol	61±11	54±24
2,4,6-Trichlorphneol	91±22	80±24

a) The values are in terms of P ± Sp. Data from 2-5 laboratories have been averaged. In general the concentation added ranged from 20 to 2500 parts per billion.
b) Standard addition to blank water.
c) Standard addition to sample.

TABLE IV BASE/NEUTRAL FRACTION[A]

Compound	Method[b] Standard	Sample[c] Spike
Acenaphthene	90±22	78±24
Acenapthylene	83±22	79±27
Anthracene[d]	98±20	79±26
Benzidine	44±27	40±29
Benzo(a)anthracene[e]	105±33	51±24
Benzo(b)fluoranthene[f]	96±68*	41±21
Benzo(k)fluoranthene[f]	96±68	47±27
Benzo(a)pyrene	90±22	43±21
Benzyl Butyl Phthalate	49±39	49±22
Bis(2-chloroethyl) Ether	98±48	80±49
Bis(2-chloroisopropyl) Ether	154±136	96±88
Bis(2-ethylhexyl) Phthalate	70±33	66±50
4-Bromophenyl Phenyl Ether	80±25	63±25
2-Chloronaphthalene	88±20	79±21
Chrysene[e]	105±33	77±27
Dibenzo(a,h)anthracene	80±42	36±29
Di-n-butyl Phthalate	80±32	58±27
1,2-Dichlorobenzene	65±24	65±27
1,3-Dichlorobenzene	67±21	62±20
1,4-Dichlorobenzene	67±22	63±21
3,3'-Dichlorobenzidine	71±85	62±45

Compound	Method[b] Standard	Sample[c] Spike
Diethyl Phthalate	71±37	65±37
Dimethyl Phthalate	43±37	66±43
2,4-Dinitrotoluene	122±55	94±45
2,6-Dinitrotoluene	115±41	104±35
Di-n-octyl Phthalate	84±44	88±32
1,2-Diphenylhydrazine (and/or Azobenzene)	97±26	91±32
Fluoranthene	111±26	63±20
Fluorene	98±24	88±25
Hexachlorobenzene	98±31	76±31
Hexachlorobutadiene	76±26	77±45
Hexachlorocyclopentadiene	38±28	27±10
Hexachloroethane	63±22	58±23
Isophorone	66±36	67±22
Indeno(1,2,3-cd)pyrene	109±14	40±21
Naphthalene	83±24	89±51
Nitrobenzene	106±31	77±51
N-nitrosodipheylamine (and/or Diphenylamine)	72±22	66±25
N-Nitrosodi-n-propylamine	86±34	71±22
Phenanthrene	98±20	79±20
Pyrene	142±41	63±20
1,2,4-Trichlorobenzene	74±22	69±24

a) The values are in terms of P ± Sp. Data from 2-5 laboratories have been averaged except where noted with an (*) asterik. In general the concentration added ranged from 10 to 500 parts per billion.
b) Standard addition to blank water.
c) Standard addition to sample.
d,e,f) These isomers pairs are not separted by packed column GC. Also mass spectr data are not sufficiently unique to allow differentiation.
*Data from only one lab were available.

THEN, WE MOVE ON TO TABLE FIVE. WE HAVE GOT THE PESTICIDE DATA SUMMARIZED. THE ONE COMPOUND THAT STANDS OUT IS, ENDRIN ALDEHYDE, WITH A LARGE SCATTER ON THAT DATA. HERE WE SUSPECT THAT THE MATERIAL IS SIMPLY SENSITIVE TO OXIDATION. THE LEVELS OF SPIKING FOR THE PESTICIDES, BY THE WAY, ARE QUITE A BIT LOWER THAN FOR THE OTHER FRACTIONS. FOR THE PESTICIDES THE SPIKING CONCENTRATION RANGED IN GENERAL FROM A TENTH OF A PART PER BILLION UP TO 100 PARTS PER BILLION. SO THIS, IN PART, COULD EXPLAIN THE SOMEWHAT LOWER RECOVERIES FOR THE PESTICIDE FRACTION.

THEN IF WE MOVE ON TO TABLE SIX, WHICH COVERS THE METALS, CYANIDE, AND PHENOLICS BY THE COLORIMETRIC TEST, WE HAVE GOT A LOT OF DATA SUMMARIZED THERE. I DO NOT THINK THERE ARE ANY REAL SURPRISES THERE. OUR LABORATORY HAS JUST COMPLETED A COMPARABILITY STUDY WHERE WE ACTUALLY COMPARED ATOMIC ABSORPTION METHODOLOGY DIRECTLY WITH ICP METHODOLOGY, INDUCTIVELY COUPLED PLASMA, AND WE DO HAVE A PAPER AVAILABLE ON THAT RIGHT NOW AND IT SUMMARIZES OVER 5,000 DATA POINTS.

I DID NOT BRING 120 COPIES WITH ME BECAUSE IT IS A MUCH LARGER DOCUMENT, BUT IF YOU DO CARE

TABLE V. PESTICIDE FRACTION[a]

Compound	Method[b] Standard	Sample[c] Spike
Aldrin	72±13	55±12
alpha-BHC	78±13	55±12
beta-BHC	79±21	57±22
gamma-BHC	78±14	64±11
delta-BHC	82±16	61±16
Chlordane	81±17*	39±9*
4,4'-DDD	82±14	62±16
4,4'-DDE	76±14	57±18
4,4'-DDT	85±17	76±26
Dieldrin	71±14	62±16
Endosulfan I	65±14	61±13
Endosulfan II	67±19	66±14
Endosulfane Sulfate	74±39*	84±30*
Endrin	82±25	68±18
Endrin Aldehyde	64±76*	34±39*
Heptachlor	72±12	49±12
Heptachlor Epoxide	82±14	65±11
PCB	83±11*	42±13
Toxaphene	89±12*	-

a) The values are in terms of P ± Sp. Data from 2-4 laboratories have been averaged except where noted with an (*)asterik. In general the concentration added ranged from 0.1 to 100 parts per billion.
b) Standard addition to blank water.
c) Standard addition to sample.
*Data from only one lab were available.

TABLE VI. METALS, CYANDIE, AND PHENOLICS[a]

PARAMETER	METHOD[b] STANDARD	SAMPLE[c] SPIKE
Antimony	61±47*	103±24
Arsenic	120±20	97±25
Beryllium	89±16	94±20
Cadmium	91±18	98±23
Chromium	99±30	106±25
Copper	136±70	99±24
Lead	116±32	93±25
Mercury[d]	83±24	79±38
Nickel	84±62	101±26
Selenium	112±15	93±20
Silver	110±25	80±25
Thallium	99±33*	95±23
Zinc	122±44	106±37
Cyanide	103±7	96±14
Total Phenols	101±8	96±11

a) The values are in terms of P ± Sp. Data from 2-3 laboratories have been averaged exept where noted with an (*) asterik. In genral the concentration added ranged from 10 to 1000 parts per billion.
b) Standard addition to blank water.
c) Standard addition to sample.
d) Analyzed by the cold vapor technique.

*Data from only one lab were available.

TO SEE THAT DOCUMENT, JUST LEAVE ME YOUR NAME AND MAILING ADDRESS AND I WILL SEE THAT YOU GET ONE.

THE BOTTOM LINE ON THAT STUDY IS SIMPLY THAT THE TWO METHODS ARE INDEED COMPARABLE. THERE ARE SOME METALS THAT ARE BIASED HIGH ON ICP; OTHER METALS ARE BIASED SOMEWHAT HIGH ON AA, BUT IN GENERAL THE RESULTS ARE QUITE COMPARABLE.

IF WE MOVE ON NOW TO TABLE SEVEN, HERE WE HAVE SUMMARIZED THE DATA AT LEAST THAT I HAD AVAILABLE ON SURROGATE RECOVERIES, AND THESE ARE COMPOUNDS, OF COURSE, THAT ARE ADDED TO THE SAMPLE BEFORE THE EXTRACTION OR THE SPARGING IN THE CASE OF THE VOLATILES. THERE IS SOMEWHAT MORE LIMITED DATA AVAILABLE ON THE SURROGATES, BUT THE RESULTS ARE SUMMARIZED HERE AND I THINK YOU CAN READILY SEE THAT THERE ARE SOME COMPOUNDS WHICH ARE NOT GOOD CHOICES AS SURROGATES, ONE SUCH BEING THE DEUTERATED CHLOROFORM WHICH WAS DISCUSSED A WHILE AGO AS BEING A PROBLEM WITH THE DEUTERIUM EXCHANGE.

YOU CAN SEE THE DATA FOR THAT PARTICULAR COMPOUND HAS A GREAT DEAL OF SCATTER TO IT, AND IF YOU COMPARE THAT WITH WHAT WE GET ON THE SCATTER FROM THE NONDEUTERATED CHLOROFORM, IT SIMPLY IS NOT A GOOD SURROGATE. ON NONDEUTERATED CHLOROFORM THE

TABLE VII. PRIORITY POLLUTANT SURROGATES[A]

Compound	LAB III[b]	LAB IV[c]	LAB VIII[d]
(Purgeable Orgnaics)			
d_6-Benzene	-	93±22	-
Bromochloromethane	-	91±20	-
d-Chloroform	139±96	-	-
1,4-Dichlorobutane	-	85±24	-
d_4-1,2-Dichloroethane	119±29	-	-
d_2-Dichloromethane	146±55	-	-
d_{10}-Ethylbenzene	102±25	94±18	-
Fluorbenzene	96±20	-	-
d_8-Toluene	-	92±18	-
d_3-1,1,1-Trichloroethane	117±41	-	-
(Acids)			
2-Fluorphenol	76±36	-	-
Pentafluorphenol	84±30	50±22	101±39
d_5-Phenol	55±20	-	-
Trifluoro-m-cresol	72±42	-	-
(Base/Neutral)			
Decafluorobiphenyl	39±18	41±29	46±13
d_8-Nepthalene	76±22	-	-
2-fluornaphthelene	75±20	-	-
1-fluronaphthelene	69±18	-	-
d_{12}-benzo(a)anthracene	68±16	-	-
2-flurobiphenyl	63±5	-	-
d_5-aniline	57±36	-	-

Table VII (cont'd)

Compound	LAB III[b]	LAB IV[c]	LAB VIII[d]
2-fluroaniline	74±39	-	-
d_5-nitrobenzene	70±21	-	-

a) The values are in terms of P ± Sp. The concentration added ranged from 20 to 200 parts per billion.
b) The matrix for these surrogates included influent and effluent samples from 12 different industrial categories.
c) The matrix for these surrogates included POTW, detergent, and chemical disposal industries.
d) The matrix for these surrogates included POTW samples only.

SCATTER OR THE RESULT IS 91 PLUS OR MINUS 26; SO YOU CAN SEE FOR THAT REASON THAT DEUTERATED CHLOROFORM IS SIMPLY NOT A GOOD CHOICE FOR A SURROGATE.

IF I COULD POINT OUT ANOTHER ONE, ON THE ACID FRACTION, THE DEUTERATED PHENOL. NOW, THIS DOES APPEAR TO BE A GOOD CHOICE BECAUSE FOR THE SURROGATE, FOR THE DEUTERATED PHENOL, THE AVERAGE WAS 55 PLUS OR MINUS 20. FOR THE NONDEUTERATED COMPOUND THE OVERALL AVERAGE WAS 54 PLUS OR MINUS 24; SO IN THAT PARTICULAR INSTANCE YOU SEE GOOD COMPARISION BETWEEN A NONDEUTERATED AND THE DEUTERATED COMPOUND.

DECAFLUOROBIPHENYL IS PROBABLY NOT A GOOD CHOICE FOR A SURROGATE, EITHER, BECAUSE THE RECOVERIES ARE SOMEWHAT LOW. WE EXPLAINED THIS AS BEING DUE TO THE VOLATILITY. WE SUSPECT THAT THE LOSSES HERE ARE PROBABLY TAKING PLACE DURING THE KUDERNA-DANISH CONCENTRATION, BUT IT MIGHT BE A GOOD CHOICE FROM THE STANDPOINT OF JUST CONTROLLING KUDERNA-DANISH EXTRACTION OR CONCENTRATION PROCESSES. I SUSPECT THAT IF YOU WERE TO LET YOUR EXTRACT GO TO DRYNESS, THAT YOUR RECOVERY WOULD PROBABLY BE CLOSE TO ZERO FOR DECAFLUOROBIPHENYL.

IF WE MOVE ON TO TABLE EIGHT, WE HAVE HERE DIVIDED THE PRIORITY POLLUTANTS, OR AT LEAST THE BASE NEUTRAL PRIORITY POLLUTANTS, INTO TWO GROUPS. ONE GROUP WE CALL THE NONREACTIVE BASE NEUTRAL COMPOUNDS; THE OTHER GROUP WE TERM THE REACTIVE BASE NEUTRAL COMPOUNDS, AND THAT WOULD INCLUDE THINGS SUCH AS BENZIDINE, THE BIS (2-CHLOROETHYL) ETHER, THE PHTHALATES, DIPHENYLHYDRAZINE, HEXACHLOROBUTADINE, HEXACHLOROETHANE AND ISOPHORONE. THESE ARE COMPOUNDS THAT WE KNOW ARE REACTIVE JUST BASED ON THEIR STRUCTURE, AND IF WE GROUP THESE TOGETHER, YOU DO SEE THAT THE RECOVERIES ARE LOWER AND THE SCATTER IS HIGHER IN MOST CASES.

FINALLY, IF WE MOVE ON TO TABLE NINE, I HAVE ATTEMPTED HERE SIMPLY TO SUMMARIZE SOME OF THE PROBLEM COMPOUNDS AS FAR AS THE ANALYSES OF THE PRIORITY POLLUTANTS GO. FOR EXAMPLE, ANYBODY WHO USES A LARGE AMOUNT OF DICHLOROMETHANE IN THEIR EXTRACTION ROOM IS PROBABLY GOING TO HAVE BACKGROUND PROBLEMS IN THEIR ANALYSES BY THE PURGE AND TRAP METHOD. I THINK MOST OF THESE OTHERS WE HAVE PROBABLY DISCUSSED BEFORE AT SOME OF OUR MEETINGS, SO NOTHING REALLY EARTHSHAKING THERE.

TABLE VIII. REACTIVITY GROUPS OF THE B/N PRIORITY POLLUTANTS

	Method Standard Analysis		Matrix Spiked Analysis	
	Nonreactive Group	Reactive Group	Nonreactive Group	Reactive Grou
Laboratory	P+Sp	P+Sp	P+Sp	P+Sp
I	102±26	86±21	87±18	78±17
II	93±31	52±46	60±21	64±25
III	-	-	58±26	48±12
IV	82±10	67±18	71±12	63±18
VII	-	-	65±11	57±17

Nonreactive B/N Compounds: Acenapthene, Acenapthylene, Anthracene, Benzo(a)anthracene Benzo(g,h,i)perylene, benzo(a)pyrene, 2-Chloronaphthalene, 1,2-,1,3-. and 1,4-Dichloro benzene, 2,6-Dinitrotoluene, Fluoranthene, Fluorene, Hexachlorobenze, Napthalene, Nitrobenzene, Pyrene, and 1,2,4-Trichlorobenzene.

Reactive B/N Compounds: Benzidine, Bis(2-chloroethyl) Ether, Bis(2-ethylhexyl), Diethyl, and Dimethyl Phthalates, 1,2-Diphenylhydrazine, Hexachlorobutadiene, Hexachloroethane, and Isophorone.

TABLE IX PROBLEM PRIORITY POLLUTANTS

COMPOUND	PROBLEM
Dichloromethane	Frequently found in blanks and samples because of in lab contamination.
bis(chloromethyl)ether	Readily hydrolyzed in water.
N-nitrosodimethylamine	Poor chromatographic properties.
Di-n-butylphthalate	Frequently found in blanks.
Bis-(2-ethylhexyl)phthalate	Frequently found in blanks.
1,2-diphenylhydrazine	Thermally decomposes to diphenyl amine and tetraphenylhydrazine.
Benzidine	Poor chromatographic properties.
Hexachlorocyclopentadiene	Subject to thermal decomposition.
Endrin Aldehyde	Is readily oxidized.
Anthracene and Phenanthrene	Coelute on packed columns.
Chrysene and benzo(a)-Anthracene	Coelute on packed columns.
benzo(b)fluoranthrene and benzo(k)fluoranthrene	Coelute on packed columns.

IN SUMMARY, WE HAVE LOOKED AT THE RESULTS THAT CAN BE OBTAINED FROM DIFFERENT LABORATORIES AND WE FIND THAT THERE IS PRETTY GOOD AGREEMENT FROM LABORATORY TO LABORATORY ON THE RECOVERIES OF STANDARDS ACTUALLY ADDED TO THE SAMPLE OR TO THE CLEAN MATRIX, AND I THINK IT SHOWS THAT THE METHOD THAT WAS SELECTED SEVERAL YEARS AGO WAS, INDEED, A SOUND ONE. THANK YOU.

I WOULD BE HAPPY TO ATTEMPT TO ANSWER ANY QUESTIONS THAT YOU MIGHT HAVE.

MR. SPRAGGINS: SPRAGGINS, RADIAN CORPORATION. WE HAVE SOME LIMITED DATA ON TWO SAMPLES THAT WERE MADE UP AS SURROGATES AND THEN THEY WERE ANALYZED AT A LATER DATE, AFTER INITIALLY BEING USED, BUT THIS WAS A MUCH LATER DATE, AND WE SEEM TO FIND A PROBLEM WITH THE 2-FLUOROPHENOL AND I WAS JUST WONDERING IF YOU HAD NOTICED THAT. IT SEEMED LIKE THE CONCENTRATION HAD DROPPED RELATIVE TO THE OTHER COMPOUNDS WITH TIME. HAVE YOU NOTICED THIS SAME EFFECT?

MR. KLEOBFER: WHICH COMPOUND?

MR. SPRAGGINS: IT WAS THE 2-FLUOROPHENOL, AND I MUST SAY OUR DATA IS LIMITED AT THIS POINT, BUT IT DID SEEM LIKE THERE WAS A PROBLEM THERE.

MR. KLEOBFER: WELL, THAT PARTICULAR SURROGATE WAS USED BY A DIFFERENT LABORATORY. OUR OWN LABORATORY, BY THE WAY, IF YOU'RE INTERESTED, IS LABORATORY FOUR; LABORATORY FOUR IN THIS WRITE-UP IS ACTUALLY REGION VII. I AM NOT GOING TO REVEAL THE NAMES OF THE OTHER LABORATORIES. I SIMPLY DO NOT HAVE ANY EXPERIENCE WITH THAT PARTICULAR SURROGATE, SO I COULDN'T COMMENT ON THAT.

MR. BLOOM: SAUL BLOOM, EXXON RESEARCH. I'VE GOT A COUPLE OF QUESTIONS PERTAINING TO

TABLE ONE. AS I UNDERSTAND IT FROM THE FOOTNOTES, THAT THE LAST COLUMN, THE AVERAGE WOULD BE ESSENTIALLY AN ARITHMETIC AVERAGE OF RECOVERY, WEIGHTED ACCORDING TO HOW MANY DATA POINTS EACH LABORATORY...

MR. KLEOBFER: IT'S WEIGHTED ACCORDING TO THE NUMBER OF DATA POINTS AVAILABLE FROM THE VARIOUS LABS, RIGHT.

MR. BLOOM: IS THAT WHAT YOU DID WITH THE STANDARD DEVIATIONS AS WELL, BECAUSE THAT'S WHAT IT APPEARS TO BE, AND IF YOU DID, I SUGGEST TO YOU THAT THAT IS NOT THE PROPER WAY.

MR. KLEOBFER: THE STANDARD DEVIATION IN THAT CASE WAS COMPUTED BY TAKING AS A DATA POINT THE RECOVERY FOR EACH INDIVIDUAL COMPOUND BY A PARTICULAR LABORATORY AND SIMPLY COMPUTING THE STANDARD DEVIATION BASED UPON THAT INFORMATION.

MR. BLOOM: YES, BUT THE POINT IS THAT THE STANDARD DEVIATION, WHEN YOU HAVE MORE THAN ONE LABORATORY, IS THE SQUARE ROOT OF THE SUM OF THE SQUARES, WHICH MAKES THE NUMBER PROGRESSIVELY WORSE, NOT BETTER AS YOU'VE REPRESENTED IT.

MR. KLEOBFER: WELL, YOU HAVE TO REALIZE THAT WE DID MAKE SOME ASSUMPTIONS WHEN WE ATTEMPTED TO TAKE RESULTS FROM VARIOUS LABORATORIES. FOR EXAMPLE, THE SPIKING LEVELS RANGE FROM...WELL, IN

THE CASE OF THE VOLATILES, GENERALLY RANGE FROM 10 TO MAYBE 500 PARTS PER BILLION, SO WE WERE TAKING DATA FROM DIFFERENT LABORATORIES AND DIFFERENT SPIKING LEVELS AND ATTEMPTING TO LUMP IT TOGETHER. IT IS JUST AN ATTEMPT TO SUMMARIZE THE RESULTS.

MR. BLOOM: YES, BUT WHAT YOU HAVE IN TABLE ONE, THE AVERAGE COLUMN, IS AN ARITHMETIC COMPUTATION FROM THE ONES TO THE LEFT OF IT, WEIGHTED BY THE NUMBER OF DATA POINTS, IS THAT NOT CORRECT?

MR. KLEOBFER: No.

MR. BLOOM: THAT IS WHAT YOU HAVE DONE WITH THE STANDARD DEVIATIONS AS WELL, OR THAT IS WHAT IT APPEARS TO BE.

MR. KLEOBFER: AGAIN, LET ME TRY TO POINT OUT AGAIN. THE STANDARD DEVIATION COMPUTED HERE FOR THE AVERAGE TOOK INTO ACCOUNT THE RESULT FOR EVERY COMPOUND FROM EVERY LABORATORY. IF YOU ARE INTERESTED IN SPECIFIC LABORATORIES BY SPECIFIC COMPOUNDS, I CAN SUPPLY THAT DATA TO YOU, BUT IN ORDER TO KEEP THINGS ABBREVIATED, I HAVE ATTEMPTED TO SUMMARIZE IT THIS WAY.

MR. BLOOM: WELL, IF I MAY,

LET ME TRY A SIMPLIFIED CASE. LET'S SAY THAT I WAS LABORATORY A AND YOU WERE B AND I GOT 100 PLUS OR MINUS 5 AND YOU GOT 100 PLUS OR MINUS 15; THAT DOESN'T MAKE THE AVERAGE OF BOTH OF US 100 PLUS OR MINUS 10, AND THAT'S WHAT TABLE ONE SEEMS TO REPRESENT.

MR. KLEOBFER: WELL, WHAT YOU GOT, THOUGH, WAS 100 PLUS OR MINUS 5 OVERALL, BUT IF YOU LOOK AT THE INDIVIDUAL COMPOUNDS YOU MAY HAVE A 90 PLUS OR MINUS 10, A 70 PLUS OR MINUS 6, AND SO FORTH AND ALL OF THAT WAS INCLUDED IN THIS COMPUTED STANDARD DEVIATION.

MR. MARRS: DAVE MARRS, STANDARD OIL. A QUESTION, BOB. IS THIS DATA ON REPLICATE SAMPLES OR WERE EACH OF THESE SAMPLES SPIKED AND PREPARED IN THE INDIVIDUAL LABORATORIES? IN OTHER WORDS, WAS THE SAMPLE PREPARED AT ONE PLACE AND SENT TO SEVEN LABS AND THAT'S WHERE YOU GET THIS NUMBER FROM?

MR. KLEOBFER: NO, THESE ARE ALL DIFFERENT SAMPLES, THEY REPRESENTED POTW SAMPLES, THEY REPRESENTED SAMPLES FROM THE DETERGENT INDUSTRY, THE TANNING INDUSTRY, ALL TYPES OF SAMPLE MATRICES WERE INCLUDED HERE. WE DID NOT ATTEMPT TO COME UP WITH SOME SORT OF UNIFORM MATRIX. THE

ONLY THING THAT WOULD BE UNIFORM, WELL, WHICH SHOULD BE UNIFORM, WOULD BE THE METHOD STANDARD, THE STANDARD ADDED TO THE BLANK WATER; EVERYTHING ELSE IS JUST WHATEVER WAS AVAILABLE.

MR. MARRS: BUT WAS EVEN THE METHOD STANDARD PREPARED IN THE SAME PLACE AND SENT OUT, OR WAS IT PREPARED IN EACH LABORATORY AND THEN THEY WENT AHEAD AND ANALYZED IT?

MR. KLEOBFER: FOR THE FOUR PRIMARY LABORATORIES THAT SUBMITTED DATA, TWO OF THE LABORATORIES USED THE SAME SPIKING SOLUTIONS. THE OTHER TWO LABORATORIES MADE UP THEIR OWN SPIKING SOLUTIONS.

MR. MARRS: I GUESS WHAT I'M GETTING AT, AND THEN COMES THE STATEMENT PART, IS ONE OF THE REAL CONCERNS, AND YOU MENTIONED A CORRECTION HERE AT THE HEAD OF TABLE ONE, CHANGING IT FROM INTRALABORATORY TO INTERLABORATORY COMPARISON. MY UNDERSTANDING OF THIS DATA IS THAT IT IS REALLY THE PERCENT RECOVERIES, IT IS INTRALABORATORY PERCENT RECOVERY, IT IS NOT TRUE INTERLABORATORY COMPARISON BECAUSE THEY WEREN'T...

MR. KLEOBFER: FROM THE STANDPOINT THAT THE LABORATORY PREPARED ITS OWN STANDARDS, ITS OWN SPIKING SOLUTIONS.

MR. MARRS: I ASSUME THAT'S QUALIFIED IN THE TEXT?

MR. KLEOBFER: YES, IT IS.

MR. MARRS: THE OTHER COMMENT I HAVE IS ON YOUR PRESENTATION OF STANDARD DEVIATION, SHOULDN'T YOU...AT LEAST MY UNDERSTANDING OF STATISTICS IS THAT TWO STANDARD DEVIATIONS, ASSUMING THE DATA ARE NORMALLY DISTRIBUTED, ENCOMPASSES 95 PERCENT OF THE VARIABILITY, WHICH IS A PRETTY MUCH ACCEPTED STANDARD, AND IF YOU BEGIN TO DOUBLE THESE STANDARD DEVIATIONS, YOU'RE PRETTY MUCH AT YOUR PERCENT RECOVERIES IN A LOT OF THE CASES.

MR. KLEOBFER: THAT IS TRUE. IN FACT, IF YOU GO TO THE THREE STANDARD DEVIATIONS THAT EPA RECOMMENDS FOR SOME OF THEIR OTHER PARAMETERS, THAT GIVES YOU A RANGE IN SOME CASES 0 TO 100 PERCENT.

MR. MARRS: OR GREATER.

MR. KLEOBFER: OR GREATER, WHICH GIVES YOU A LOT OF ROOM FOR ERROR.

MR. STANKO: GEORGE STANKO, SHELL DEVELOPMENT. BOB, I'D LIKE TO QUOTE ONE OF YOUR CONCLUSIONS FROM YOUR REPORT. 'WE CAN BE CONFIDENT THAT FALSE POSITIVE ANALYSES ARE CONSIDERABLY LESS LIKELY THAN FALSE NEGATIVE ANALYSES SO THAT WHEN A PRIORITY POLLUTANT IS DETECTED IN THE ENVIRONMENT WE KNOW THAT

THE MEASURED QUANTITY IS PROBABLY SMALLER THAN THE TRUE VALUE.' THERE WAS A MEETING HERE OF CMA YESTERDAY, THERE WAS SOME SLIDES PRESENTED FROM A REPORT, CHEMICAL MANUFACTURERS ASSOCIATION. I'D LIKE TO PROJECT ONE OF THE SLIDES.

THIS SUMMARIZES THE DATA THAT'S INCLUDED IN CHEMICAL MANUFACTURERS REPORT CONCERNING THE BEST METHODOLOGY, ACCORDING TO YOUR REPORT, THE VOLATILE ORGANICS, WHICH WE CONCUR WITH YOU. THIS SLIDE, THE WAY IT'S PRESENTED, SHOWS THE TIMES THAT WE HAVE QUALITATIVE AGREEMENT OR DISAGREEMENT BETWEEN EPA LABS VERSUS COMPANY LABS. THE NUMBER 656 REPRESENTS THOSE TIMES WHEN THE EPA LAB AND THE COMPANY LAB AGREED THAT A COMPOUND WAS NOT PRESENT IN A PARTICULAR ENVIRONMENTAL SAMPLE. THE BOTTOM RIGHT-HAND CORNER, THE 132, IS THE NUMBER OF TIMES THAT THE EPA LAB AND THE COMPANY LAB BOTH AGREED THAT THE COMPOUND WAS IN THE ENVIRONMENTAL SAMPLE. THE DIAGONAL, THE 656 AND THE 132, INDICATE THE TIMES WE AGREE QUALITATIVELY. THE UPPER RIGHT-HAND CORNER, THE EPA DETECTED COMPOUNDS IN THEIR SAMPLES 132 TIMES THAT THE COMPANY LABORATORIES DID NOT. CONVERSELY, THE COMPANY LABORATORIES FOUND COMPOUNDS 55 TIMES THAT WERE NOT REPORTED BY THE EPA LABORATORIES; THAT PARTICULAR DIAGONAL REPRESENTS THE AMOUNT OF DISAGREEMENT ON WHETHER A COMPOUND IS

QUALITATIVELY PRESENT OR NOT PRESENT. THE CMA HAS NOT TRIED TO IDENTIFY THESE AS FALSE POSITIVES OR FALSE NEGATIVES. OUR OWN WORK AT SHELL, WE HAVE INDICATED THAT THERE IS CONSIDERABLE DISAGREEMENT QUALITATIVELY ON WHETHER A COMPOUND IS PRESENT OR NOT. TO QUOTE SOME DATA THAT HAS BEEN RELEASED TO THE AGENCY, THREE COMPETENT LABORATORIES ANALYZED THE SAME SPLIT SAMPLE; OF THE 38 COMPOUNDS THAT WERE REPORTED BY ONE OF THE THREE LABORATORIES, THERE WERE ONLY FOUR COMPOUNDS THAT ALL THREE LABORATORIES AGREED WERE THERE.

I HAVE NOT TRIED TO IDENTIFY THESE AS FALSE POSITIVES OR FALSE NEGATIVES; I DON'T KNOW WHAT THEY ARE. I HAVE NOT SEEN ANYTHING IN YOUR REPORT THAT CLEARS UP THIS PARTICULAR PROBLEM, YET SOMEHOW YOU ARE ABLE TO MAKE A STATEMENT THAT THE POSSIBILITY OF A FALSE POSITIVE IS RATHER REMOTE. COULD YOU EXPLAIN HOW YOU CAME TO THAT CONCLUSION?

MR. KLEOBFER: WELL, GEORGE, I THINK IF YOU WERE TO QUALIFY YOUR DATA AND JUST LIMIT YOURSELF TO THOSE COMPOUNDS THAT ARE PRESENT IN A REASONABLE QUANTITY, AND LET'S SAY, IN THE CASE OF THE VOLATILES, AT 20 PARTS PER BILLION OR ABOVE, I THINK YOUR TABLE WOULD HAVE LOOKED QUITE DIFFERENT THAN WHAT IT DID. IN OTHER WORDS, HOW MANY OF THESE

DATA POINTS ARE DUE TO LOW LEVELS OF VOLATILES WHERE THERE'S MORE LIKELY TO BE A MISTAKE?

MR. STANKO: MOST OF THE DATA POINTS WERE 10 PARTS PER BILLION OR LESS, WHICH IS SORT OF THE ASSUMED LIMIT OF DETECTION, IF YOU WANT TO CALL IT THAT. THE HIGHER PERCENTAGE OF THESE VALUES INCLUDED ON THESE TABLES ARE IN THE HIGHER RANGE AT 20 PLUS. WE CONCUR WITH WHAT YOU HAVE REPORTED HERE ON THE USE OF THE FLUORINATED SURROGATES; WE HAVE EXPERIENCED THE SAME PROBLEMS THAT YOU HAVE. WE ALSO CONCUR, IF YOU TAKE DISTILLED WATER AND ADD THE COMPOUNDS IN, THAT THE RECOVERIES ARE VERY SIMILAR, BUT WE DO NOT CONCUR IF YOU TAKE OUR PARTICULAR MATRIX-TYPE SAMPLES THAT YOU WILL GET AS HIGH A RECOVERY AS YOU DO IN DISTILLED WATER.

MR. KLEOBFER: OKAY, BUT YOU'D DISAGREE WITH THE ONE STATEMENT.

MR. STANKO: I WOULD DISAGREE WITH THE ONE STATEMENT BECAUSE I SEE NOTHING IN THIS PARTICULAR REPORT THAT ALLOWS YOU TO COME TO THAT PARTICULAR CONCLUSION. I AM STILL ON BLOCK NUMBER ONE, WHICH TELLS ME THAT THERE IS DISAGREEMENT, BUT I CANNOT DISTINGUISH BETWEEN FALSE POSITIVES OR FALSE NEGATIVES, AND I DON'T SEE HOW YOU CAN, EITHER, AND MAKE THIS PARTICULAR STATEMENT.

MR. KLEOBFER: WELL, I STAND BY MY STATEMENT; WE DISAGREE.

MR. TELLIARD: OUR NEXT SPEAKER IS WALT SHACKELFORD FROM ATHENS. AS YOU KNOW, WHEN WE STARTED THIS PROGRAM, ONE OF OUR ATTEMPTS WAS TO, SINCE WE'RE SPENDING THIS TRIG-A-BUCK PER SAMPLE ANALYSIS, WAS NOT TO THROW THE DATA AWAY LOOKING FOR 1, 2-DIPHENYL BAD STUFF; SINCE WE WERE GOING TO GET OUR HANDS ON A SAMPLE, WE'D LIKE TO GET AS MUCH UTILITY OUT OF IT AS POSSIBLE, AND THEREFORE, IT WAS DECIDED EARLY ON THAT THE TAPES WOULD BE STORED AND SENT OFF TO ATHENS FOR LATER EXAMINATION, AS WELL AS THE EXTRACTABLE CONCENTRATES.

OVER THE LAST YEAR, NOW, WALTER HAS BEEN WORKING ON PUTTING A PROGRAM TOGETHER AND GETTING TRIAL RUNS AT IT AND BASICALLY WHAT HE'S GOING TO TALK ABOUT TODAY IS THE STATUS AND UPDATE ON THE MASS SPECTRAL DATA PROGRAM.

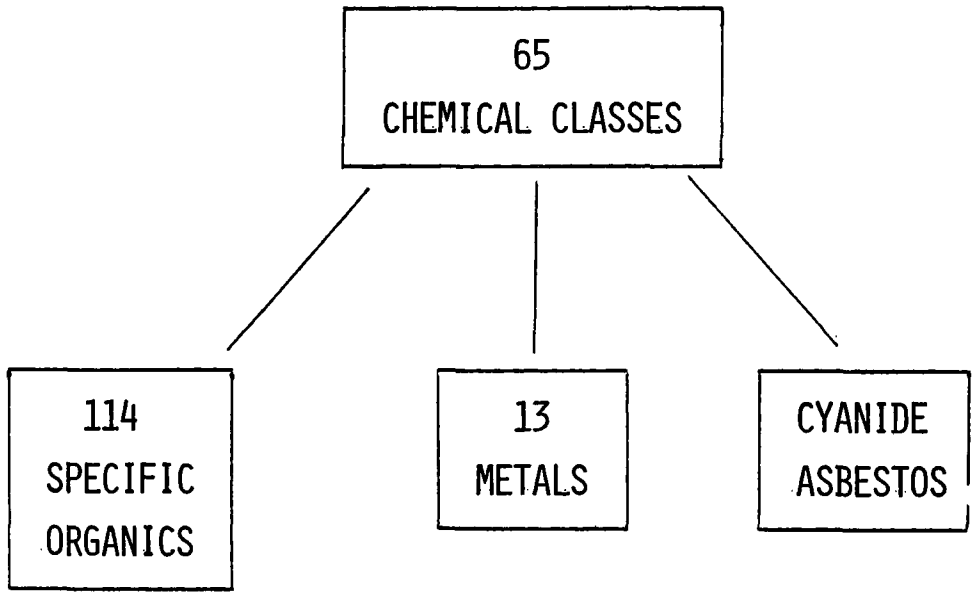
EXAMINATION OF MASS SPECTRAL DATA TAPES FOR CHARACTERIZATION OF SAMPLE COMPOSITION

BY: WALTER SHACKELFORD

AS BILL MENTIONED, WE HAVE HAD A PROJECT FOR ABOUT A YEAR AT ATHENS TO BEGIN TO SURVEY THE RAW DATA THAT'S BEEN SAVED ON MAGNETIC TAPE FROM THE SCREENING PHASE OF THE PRIORITY POLLUTANT PROGRAM. IF I COULD HAVE THE FIRST SLIDE, I'D LIKE TO GO THROUGH SOME MATERIAL THAT MIGHT BE A LITTLE REDUNDANT, BUT IT WILL GIVE THE RATIONALE FOR THE PROGRAM AS WE HAVE IT. FOR THOSE OF YOU THAT ARE NOT AWARE OF IT, THE CONSENT DECREE, AS IT WAS SIGNED IN JUNE OF '76, LISTED 65 COMPOUNDS AND COMPOUND CLASSES. PRETTY EARLY IN THE GAME IT WAS RECOGNIZED THAT TO LOOK FOR EVERY COMPOUND IN EACH CLASS WOULD BE A TASK THAT WAS BEYOND THE SCOPE OF THE RESOURCES THAT WERE AVAILABLE. THROUGH A PROCESS OF SELECTION THAT INVOLVED LOOKING AT WHAT COMPOUNDS WERE MANUFACTURED IN QUANTITY OR WHAT HAD BEEN FOUND BEFORE, THE LIST WAS RESOLVED INTO THE COMPOUND LIST THAT WE RECOGNIZE NOW AS THE PRIORITY POLLUTANTS. THE SPECIFICS ON THAT RESOLUTION WERE PUBLISHED IN PROCEEDINGS OF A PETROLEUM REFINERY WASTEWATER MEETING IN 1977 AND THEN AGAIN IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY LAST YEAR.

SLIDE 2 PLEASE. THE ANALYSIS PROGRAM HAD TO BE

CONSENT DECREE



ANALYSIS PROGRAM

A. ORGANIC ANALYSIS ACCOMPLISHED BY GC/MS -- RAW DATA SAVED ON MAGNETIC TAPE

B. AFTER INITIAL ANALYSIS FOR 114 ORGANICS, MAGNETIC TAPE IS SURVEYED FOR OTHER ORGANICS

C. EXTRACTS OF EACH SAMPLE SAVED FOR LATER STUDY

DESIGNED TO TAKE INTO ACCOUNT THE FACT THAT WE ARE NOT LOOKING FOR EVERY COMPOUND IN EVERY GROUP. WE ARE LOOKING FOR A FEW SPECIFIC ONES. SINCE IT HAD BEEN DECIDED THAT GS/MS WAS TO BE USED, WE WOULD SAVE ALL THE RAW DATA IN COMPUTER READABLE FORM. THUS, IF SOME OTHER COMPOUNDS BECAME OF INTEREST LATER, WE COULD GO BACK AND SEARCH THIS DATA.

ALSO, TO PROVIDE CONFIRMATION, EACH EXTRACT FROM EACH SAMPLE WOULD BE SAVED FOR LATER REANALYSIS. WE HAVE A PROGRAM FOR CONFIRMATION THAT HAS JUST GOTTEN UNDER WAY. IT SOON BECAME APPARENT THAT THE MAGNITUDE OF DATA THAT WAS GOING TO BE SAVED ON MAGNETIC TAPE MADE IT PRACTICALLY IMPOSSIBLE TO GO THROUGH THE DATA MORE THAN ONE TIME IN THE COMPUTER SURVEY. SO THE IDEA BECAME TO SURVEY THE TAPES FOR EVERY COMPOUND THAT WE CAN FIND USING STATE OF THE ART COMPUTERIZED DATA REDUCTION. THE FINALIZED PROGRAM BECAME A STUDY TO LOOK FOR EVERY COMPOUND THAT CAN BE FOUND BY COMPUTERIZED SPECTRUM MATCHING TECHNIQUES. THEN GET THE MATCHER CONFIRMED, IF POSSIBLE, BY REANALYZING THE EXTRACT, AND LIST THOSE COMPOUNDS FOR FUTURE GUIDELINES OR REGULATIONS.

SLIDE 3 PLEASE. OUR PROJECT OBJECTIVES WERE TO BUILD AND REFINE THE GC/MS DATA SYSTEM THAT WAS

Project Objectives

A. Build and refine GC/MS data survey system

B. Provide efficient identification of organic compounds in GC/MS data

C. Gather statistics of selected identified and unidentified organic compounds by industrial category

D. Build historical library

E. Meet milestone schedule

NECESSARY TO SURVEY THIS DATA; TO PROVIDE SOME EFFICIENT MEANS OF IDENTIFICATION OF THESE ORGANIC COMPOUNDS WITHOUT HAVING A CHEMIST SIT DOWN AND LOOK AT EVERY SPECTRUM; THEN COLLECT STATISTICS ON BOTH THOSE SPECTRA WHICH HAVE BEEN TENTATIVELY IDENTIFIED AND ALSO KEEP STATISTICS ON THOSE SPECTRA THAT ARE NOT MATCHED IN THE LIBRARY BY MATCHING THEM AGAINST EACH OTHER TO FIND THOSE REOCCURRING SPECTRA THAT WE DO NOT HAVE ANY REFERENCES FOR.

WE WANTED TO BUILD A HISTORICAL LIBRARY THAT WOULD INCLUDE ALL OF THE COMPOUNDS THAT WE ARE FINDING, THEIR GC RETENTION TIMES AND THEIR SPECTRA. THUS, IN FUTURE USE, THE MATCHING PROCESS BECOMES MORE DEFINITIVE BECAUSE ONE KNOWS A RETENTION TIME FOR THESE COMPOUNDS. FINALLY, WE WANTED TO BE ABLE TO MEET OUR MILESTONE SCHEDULE (SLIDE 4).

THIS SCHEDULE WAS PUT FORTH WELL BEFORE WE HAD ANY FUNDS, PEOPLE, OR ANY KNOWLEDGE THAT ANYONE WOULD LET US DO THE PROJECT. WE MADE THE FIRST MILESTONE AND THE SECOND MILESTONE. OUR THIRD MILESTONE IS ONE YEAR'S WORK AT FULL SPEED IN WHICH WE ARE TO ANALYZE 10,000 GC/MS RUNS BY OUR COMPUTER METHODS.

THE 6TH SLIDE SHOWS HOW WE'RE FARING RIGHT NOW. AT THE PRESENT TIME WE'VE GONE THROUGH 3,200 GC/MS RUNS AND HAVE LOOKED AT SAMPLES FROM ALL 21

MILESTONES

100	GC/MS Runs Analyzed	April 1, 1979
1000	GC/MS Runs Analyzed	Sept. 1, 1979
10,000	GC/MS Runs Analyzed	Sept. 1, 1980
20,000	GC/MS Runs Analyzed	Sept. 1, 1981

PROJECT STATUS

> 3200	DATA FILES PROCESSED AS OF JANUARY 4, 1980
21	INDUSTRIAL CATEGORIES INCLUDED
~ 20%	IDENTIFICATION EFFICIENCY (AVERAGE 4 MONTHS)

INDUSTRIAL CATEGORIES. OUR IDENTIFICATION EFFICIENCY, THAT IS WHAT FRACTION OF THE SPECTRA CHOSEN FOR MATCHING ARE MATCHED, IS ABOUT 20 PERCENT. AS WE MOVE ALONG I'LL SHOW YOU HOW THAT FIGURE SHOULD IMPROVE. IN TALKING WITH DR. STEPHEN HELLER, WHO SPONSORED THE BUILDING OF THE EPA-NIH DATA BASE, IN CROSS-CHECKING COMPOUNDS I WAS INFORMED THAT ONLY ABOUT 12 PERCENT OF THOSE COMPOUNDS KNOWN TO BE MANUFACTURED IN INDUSTRY ARE FOUND IN THE LIBRARY OF SPECTRA.

SLIDE 7 PLEASE. THIS IS A PROFILE OF THE DATA WE HAVE LOOKED AT IN TERMS OF INDUSTRIES. THE CATEGORY N/A TAKES INTO ACCOUNT STANDARD RUNS AND THOSE SAMPLES FOR WHICH THE CONTRACTOR WHO ANALYZED THEM DID NOT KNOW THE INDUSTRIAL CATEGORY. THE DIFFERENCES IN PERCENTAGES HERE ARE REALLY ONLY FORTUITOUS; THEY JUST HAPPEN TO BE THE RUNS THAT WE LOGGED IN FIRST. NOW, THE COMPUTER PROGRAM IS BUILT AROUND ABOUT FIVE MAJOR PORTIONS. THE FIRST PORTION, WHICH IS TURNED ABOUT TO BE THE MOST TIME-CONSUMING, IS THE INVENTORY PROCESS. WE ARE PRESENTLY USING THE INFORM DATA BASE MANAGEMENT SYSTEM TO TAKE CARE OF OUR INVENTORY.

SECOND, WE HAVE THE DATA ANALYSIS PART OF THE SYSTEM, WHICH INVOLVES THREE MAJOR COMPUTER PROGRAMS. THE CLEANUP PROGRAM, WHICH WAS DEVELOPED BY TOM RINDFLEISCH AND HIS CO-WORKERS AT STANFORD UNIVERSITY,

PROFILE OF SAMPLES ANALYZED
BY INDUSTRIAL CODE
(1/10/80)

	Industry
15.81%	Public Owned Treat Works
11.17%	Pulp & Paper
7.52%	Foundries
7.15%	Paint & Ink
6.94%	Organic Chemicals
6.89%	Auto & Other Laundries
6.11%	Inorganic Chemicals
5.64%	Coal Mining
3.91%	Electronics
3.08%	Mechanical Products
2.24%	Pesticides Mfg.
2.19%	N/A
2.09%	Pharmaceuticals
2.04%	Printing & Publishing
1.83%	Transportation Equipment
1.77%	Nonferrous Metals
1.62%	Plastics & Synthetics
1.57%	Textile Mills
1.57%	Rum Industry
1.46%	Rubber Processing
1.41%	Photographic Industries
1.20%	Porcelain/Enameling
1.04%	Leather Tanning
.78%	Industry Unknown
.73%	Organics & Plastics
.73%	Amusements & Athletic Goods
.68%	Plastics Mfg.
.57%	Ore Mining
.16%	Steam Electric
.05%	Timber Products
.05%	Petroleum Refining

LOOKS AT GC/MS DATA AND EXTRACTS MASS SPECTRA WHERE IT SEES PEAKING OF A CERTAIN NUMBER OF IONS WITHIN A TWO SCAN WINDOW, EXTRACTS THAT SPECTRUM AND PASSES IT ON TO THE THIRD LARGE PART OF THE PROGRAM, THE PROBABILITY BASED MATCHING SYSTEM. THIS MATCHING SYSTEM WAS DEVELOPED BY FRED MCLAFFERTY AT CORNELL. MUCH OF THE DEVELOPMENT WORK WAS DONE UNDER A GRANT SPONSORED BY THE ATHENS LABORATORY. THE FOURTH PART IS THE HISTORICAL LIBRARY. MANY IDEAS IN PART CAME FROM, AGAIN, WORK AT STANFORD UNIVERSITY FROM DENNIS SMITH, TOM RINDFLEISCH, AND BILL FITCH. THIS PART OF THE PROGRAM TAKES OUR ANSWERS (THOSE SPECTRA THAT ARE MATCHED WITHIN OUR SPECIFICATIONS), PUTS THEM INTO A DATA BASE MANAGEMENT SYSTEM ALONG WITH THE GC RETENTION TIME, THE INDUSTRY FROM WHICH THE SAMPLE CAME, AND THE ANALYTICAL CONTRACTOR THAT COLLECTED THE DATA ORIGINALLY.

A FINAL PART IS UNKNOWN, OR MISS LIBRARY. THIS LIBRARY ALSO KEEPS SIMILAR STATISTICS TO THOSE IN THE HISTORICAL LIBRARY, BUT CONCERNS ITSELF ONLY WITH THOSE SPECTRA THAT HAVE NOT BEEN IDENTIFIED BY SPECTRUM MATCHING. IN THAT WAY WE'RE ABLE TO FIND REOCCURRING UNMATCHED SPECTRA AND PRIORITIZE THEM FOR SOME SORT OF ANALYSIS IN WHICH WE WOULD USE MORE EXTENSIVE ANALYTICAL TECHNIQUES ON THE SAVED EXTRACT

SUCH AS HIGH RESOLUTION MASS SPEC OR GC/FTIR.

SLIDE 8 PLEASE. I'D LIKE TO GO THROUGH THE CLEANUP PROGRAM BRIEFLY. IF YOU'RE INTERESTED IN READING ABOUT IT, THERE WAS A PAPER BY RINDFLEISCH IN JULY OF '77 IN ANALYTICAL CHEMISTRY. CLEANUP DETECTS COMPONENTS THAT ELUTE AT LEAST TWO SCANS FROM EACH OTHER AND SUBTRACTS LOCAL BACKGROUND THAT IT CALCULATES FOR EACH MASS. IT THEN APPLIES A SYMMETRY OR PEAK BROADNESS SCREEN ON PEAKS SUCH THAT COLUMN BLEED, WHICH NORMALLY IS GOING TO EXHIBIT A BROAD PEAK, WOULD BE ELIMINATED. UNFORTUNATELY, IF A COMPONENT OF INTEREST HAS A BROAD PEAK, THEN IT GETS ELIMINATED ALSO. CLEANUP WAS WRITTEN ORIGINALLY TO BE AN INTERACTIVE PROGRAM WHERE ONE VARIES THE PROGRAM PARAMETERS TO GET THE MOST ACCURATE FIT OF THE DATA. OF COURSE, WE DON'T HAVE THAT LUXURY; WE DO NOT OPERATE IT INTERACTIVELY, AND WE'RE PRESENTLY TRYING TO CHANGE THE SYSTEM SUCH THAT WE COULD DYNAMICALLY VARY SOME OF THESE PARAMETERS DURING COMPUTER ANALYSIS.

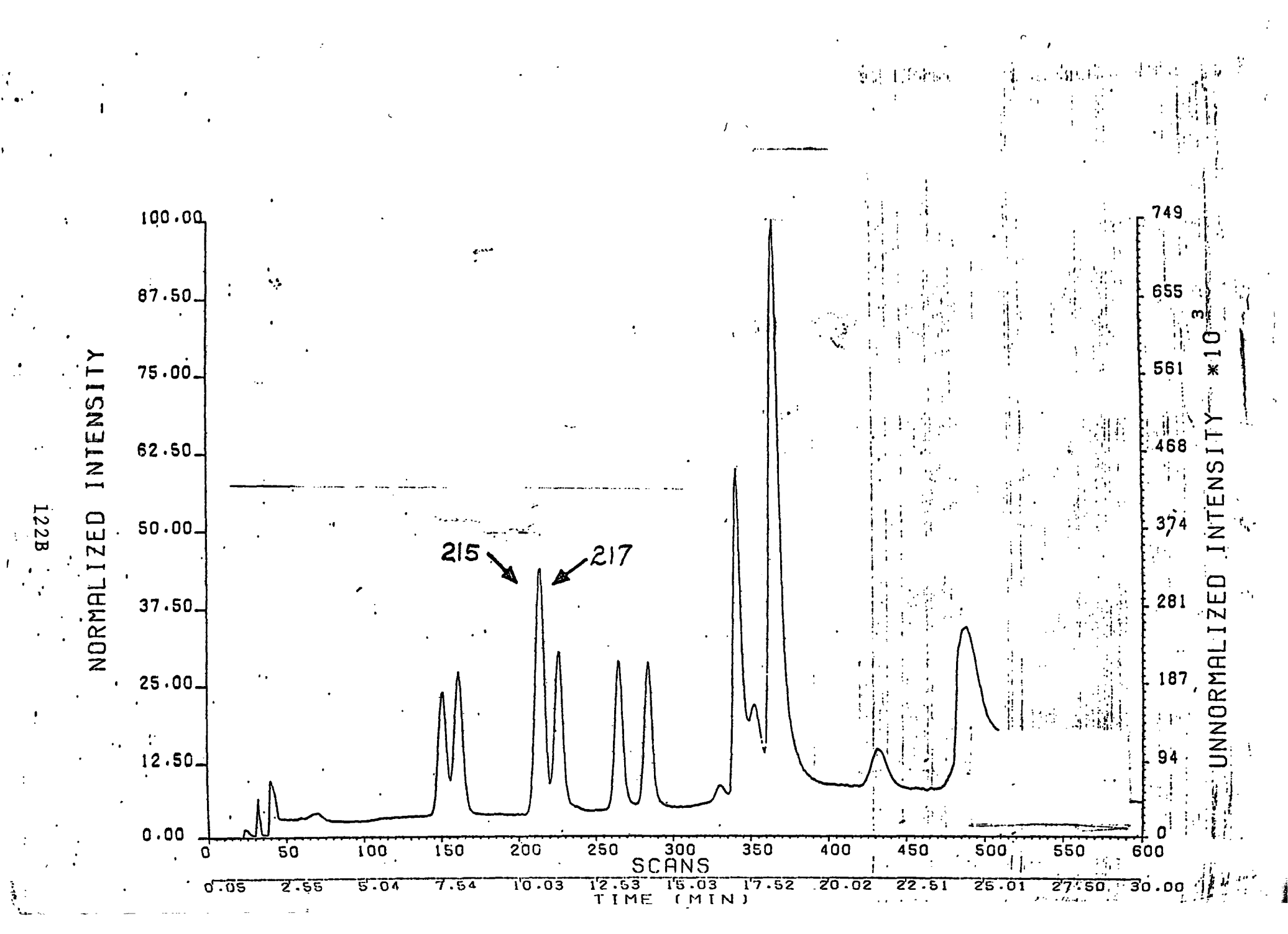
SLIDE 9 PLEASE. THIS IS AN EXAMPLE OF RESULTS IN THE EASIEST CASES. I'M NO DIFFERENT FROM ANYBODY ELSE; THESE ARE THE ONLY ONES I SHOW WHEN I GIVE A TALK. HERE WE HAVE A PICTURE OF THE 11-PHENOL MIXTURE THAT MOST OF THE PEOPLE IN THE ROOM HAVE

CLEANUP

A. DETECTS COMPONENTS ELUTING 2 OR MORE SCANS APART

B. SUBTRACTS BACKGROUND FOR EACH MASS

C. ELIMINATES COLUMN BLEED


NORMALIZED INTENSITY
100.00
87.50
75.00
62.50
50.00
37.50
25.00
12.50
0.00
UNNORMALIZED INTENSITY *10^3
749
655
561
468
374
281
187
94
0
215
217
0
50
100
150
200
250
300
350
400
450
500
550
600
SCANS
0.05
2.55
5.04
7.54
10.03
12.53
15.03
17.52
20.02
22.51
25.01
27.50
30.00
TIME (MIN)

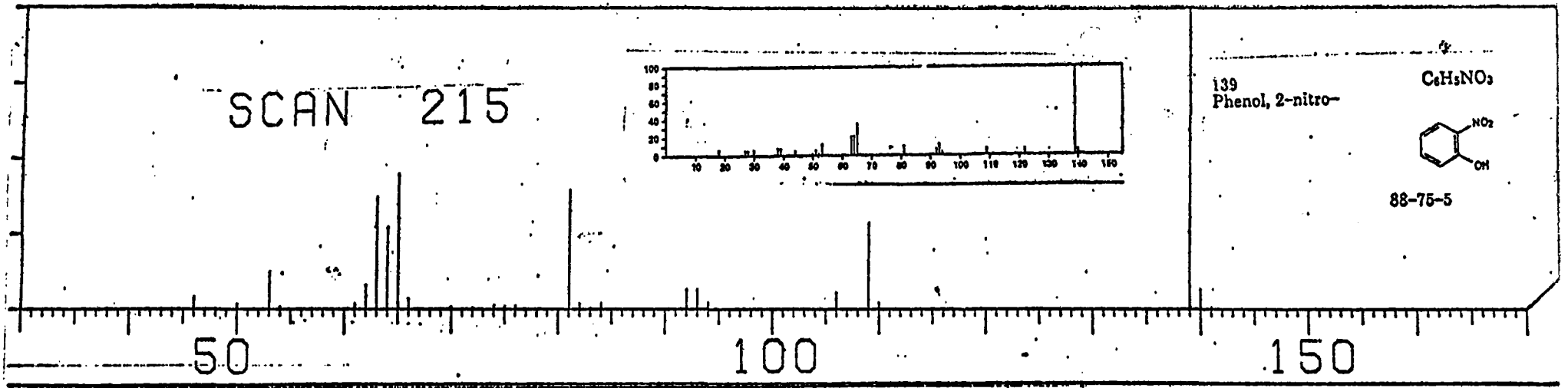
122B

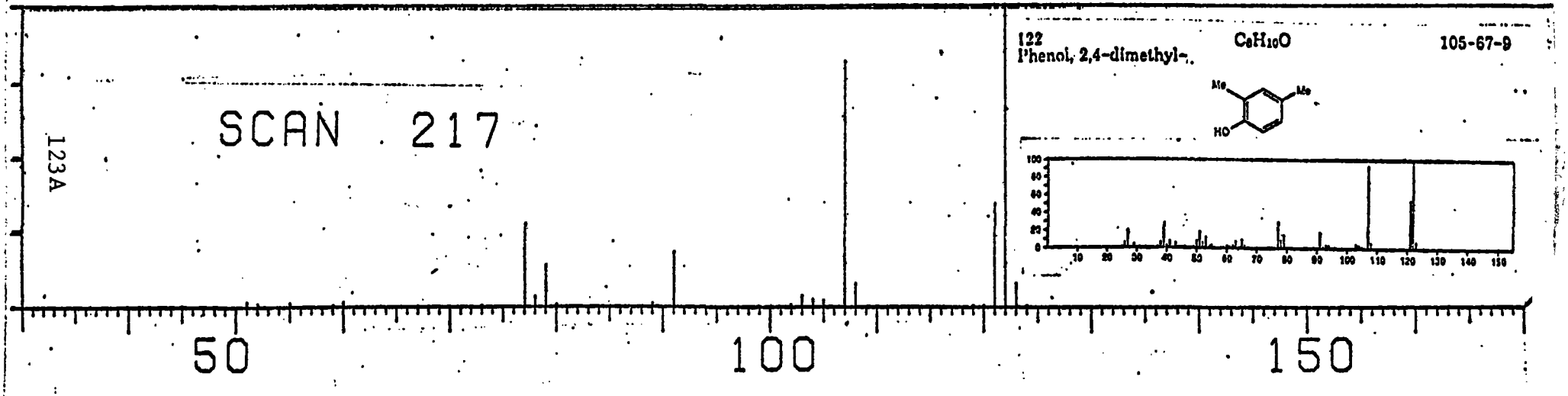
RUN ON TENAX. NOTICE THE PEAK THAT HAS SCANS 215 AND 217 MARKED. LOOKS LIKE A NICE SYMMETRICAL PEAK WITH ONLY ONE COMPONENT.

SLIDE 10. AFTER RUNNING THROUGH THE CLEANUP PROGRAM WE FIND THERE ARE ACTUALLY TWO COMPONENTS, ONE WHICH IS O-NITROPHENOL, THE OTHER ONE DIMETHYL-PHENOL. THE REFERENCE SPECTRA ARE PRINTED UP IN THE CORNER OF THE SLIDE. THIS IS, OF COURSE, AN IDEAL CASE.

SLIDE 11. STATISTICS CONCERNING HOW CLEANUP COMPARED TO A HUMAN SITTING AT A TERMINAL DOING MANUAL PEAK FINDING AND BACKGROUND SUBTRACTION WERE COLLECTED. OUR OBJECTIVE FOR THE COMPUTER PROGRAMS IS TO DUPLICATE THE ROUTINE OPERATOR OPERATING MANUALLY AT A TERMINAL. IN MANUAL PEAK FINDING, THE OPERATOR IN THESE CASES SAW THE NUMBER OF PEAKS SHOWN IN THE LEFT-HAND COLUMN. OF THOSE NUMBERS OF PEAKS HE WAS ABLE TO FIND AFTER SUBTRACTING BACKGROUND AND SEARCHING WITH HIS COMPUTER TO MATCH SPECTRA, HE WAS ABLE TO IDENTIFY THE NUMBER OF COMPOUNDS SHOWN IN THE NEXT COLUMN. IN RUNNING CLEANUP, WE FOUND THE NUMBER OF COMPONENTS SHOWN IN THE THIRD COLUMN. THE NUMBER OF IDENTIFICATIONS IS SHOWN IN THE FINAL COLUMN. FOR INSTANCE, IN SAMPLE NUMBER ONE, CLEANUP-PBM IDENTIFIED 18 COMPONENTS THAT WERE THE

Example of CLEANUP Program Output for near co-eluting compounds (SCAN 215, 2-nitrophenol and SCAN 217, 2,4-dimethylphenol). Spectra acquired under GC/MS conditions of protocol.
SCANTIME = 3.0 sec.





RUN NAME - 1795

VERSION 01-1

PEAK FINDING

MANUAL		CLEANUP-PBM	
PEAKS	ID'S	PEAKS	ID'S
30	18	46	18(6)
18	7	44	7(4)
31	11	41	11(2)
26	10	43	10(2)

SAME AS WERE FOUND MANUALLY. THEN CLEANUP-PBM IDENTIFIED 6 ADDITIONAL COMPONENTS. AS YOU LOOK DOWN THE LIST, YOU'LL SEE THAT WE WERE ABLE TO DUPLICATE THE IDENTIFICATIONS THAT THAT MANUAL MODE WAS MAKING. WE ALSO WERE ABLE TO FIND A FEW MORE. HOWEVER, AS YOU CAN TELL BY LOOKING AT THE SLIDE, OUR PERCENTAGE OF IDENTIFICATIONS DROPPED CONSIDERABLY. THE DATA DISPLAYED ON THE SLIDE IS BETTER THAN OUR AVERAGE, SINCE THIS DATA WAS ACQUIRED USING CAPILLARY COLUMNS. THUS, WE HAD BETTER RESOLVED PEAKS TO WORK WITH.

SLIDE 12, PLEASE. THE PROBABILITY BASED MATCHING SYSTEM WAS CHOSEN FIRST OF ALL BECAUSE IT'S A REVERSE SEARCH. WE KNEW THAT WE WERE GOING TO GET A LOT OF MIXED SPECTRA, AND REVERSE SEARCHING ALLOWS ONE TO LOOK FOR THE KNOWN SPECTRUM IN THE UNKNOWN SPECTRUM. THE ADVANTAGE COMES IN WHERE ONE HAS A SPECTRUM THAT'S ACTUALLY THE SUM OF TWO DIFFERENT SPECTRA. ONE IS ABLE TO GET A GOOD FIT FOR THE KNOWN DESPITE THE PRESENCE OF OTHER MASSES DUE TO IMPURITIES. IN MANY CASES ONE CAN GET TWO GOOD MATCHES FOR TWO DIFFERENT COMPONENTS IN THE SAME SPECTRUM. THOSE OF YOU THAT USE THE FINNIGAN-INCOS SYSTEM KNOW THAT THERE IS A REVERSE SEARCH CAPABILITY THERE THAT WILL ALLOW YOU TO DO THE SAME THING. I BELIEVE THE HEWLETT-

PBM

A. REVERSE SEARCH--LOOKS FOR REFERENCE IN UNKNOWN

B. SEVERAL MATCH PARAMETERS FOR EVALUATION OR FIT

PACKARD SYSTEM SUPPLIES PBM WITH IT.

ONE THING WE LIKED ABOUT PBM IS THAT THERE ARE A NUMBER OF PARAMETERS THAT LET ONE EVALUATE THE FIT. THERE'S A GENERAL OVERALL QUALITY OF THE MATCH; THE DIFFERENCE FROM A PERFECT MATCH SCORE; WHETHER OR NOT THE MOLECULAR ION WAS FOUND; HOW MANY PEAKS OF THE KNOWN WERE NOT OBSERVED IN THE UNKNOWN. THESE PARAMETERS ALL HELP IN DECIDING WHETHER OR NOT ONE HAS A GOOD MATCH. ANOTHER REASON FOR USING PBM WAS THAT IT HAD BEEN EVALUATED IN THE LITERATURE AND WAS SHOWN TO BE EQUAL TO OTHER MATCHING SYSTEMS IN TERMS OF FORWARD SEARCHING, THAT IS, IN TERMS OF ONE COMPONENT MATCHING, AND CERTAINLY SUPERIOR IN TERMS OF MIXTURES.

SLIDE 13, PLEASE. NOW, HERE WAS AN INTERESTING POINT WE RAN INTO. WE FOR SOME TIME HAD BEEN USING DIFFERENT DATA BASES IN OUR LABORATORY FOR MATCHING. ONE IS A COLLECTION OF SPECTRA THAT WERE MORE OR LESS HAPHAZARDLY PUT TOGETHER AND CONTAINED, ONCE THE DEUTERATED COMPOUND SPECTRA AND THOSE COMPOUNDS WITH MOLECULAR WEIGHT OVER 450 WERE TAKEN OUT, ABOUT 37,000 SPECTRA. ANOTHER LIBRARY WE HAD AVAILABLE TO US WAS A DATA BASE WITH ABOUT 32,000 DIFFERENT SPECTRA. OUR DATA BASE OF 37,000 ACTUALLY DOES HAVE 32,000 DIFFERENT SPECTRA, BUT IT ALSO HAS MANY

DATA BASE RECALL

DATA BASE I	DATA BASE II	MANUAL ID
TOLUENE (75+)	TOLUENE (75+)	TOLUENE
7-OXABICYCLO 2.2.1 HEPTANE (49+)	2-CYCLOHEXENE-1-OL (76+)	2-CYCLOHEXENE-1-OL
PHTHALIDE (56,-2)	METHYL BENZOATE (69+)	METHYL BENZOATE
HEXACOSANOIC ACID (102,-3)	OCTADECANOIC ACID (105+)	OCTADECANOIC ACID

DUPLICATE SPECTRA. IT HAS BEEN OUR OPINION AND THAT OF SOME OTHER PEOPLE THAT DUPLICATE SPECTRA WILL AID IN MATCHING, SINCE THEY MANY TIMES CAN TAKE INTO ACCOUNT THE DIFFERENCES IN INSTRUMENTATION. DATA BASE I WAS OUR SPECTRUM LIBRARY OF SOME 32,000 SPECTRA WITH NO DUPLICATE SPECTRA. THESE ARE THE BEST MATCHES DELIVERED BY PBM. DATA BASE II IS THE LIBRARY THAT HAS MANY DUPLICATE SPECTRA. USING DATA BASE II, WE FIND DIFFERENT COMPOUNDS AS THE BEST MATCH FROM THOSE FOUND USING DATA BASE I. THE MANUAL IDENTIFICATION AGREED WITH DATA BASE II AND IN A COUPLE OF CASES DID NOT AGREE WITH DATA BASE I. WHY DID THIS HAPPEN? WELL, DATA BASE I DID NOT GIVE YOU A CHOICE, FOR INSTANCE, OF METHYLBENZOATE SPECTRA SINCE IT ONLY HAD ONE. TO BE SURE, IN DATA BASE II WE HAD THE SAME SPECTRUM OF METHYLBENZOATE THAT WAS IN DATA BASE I. HOWEVER, AS YOU MIGHT WELL IMAGINE, THE SPECTRUM THAT WAS IN BOTH DATA BASE I AND IN DATA BASE II GAVE A POOR MATCH. IN DATA BASE II WE HAD SEVERAL METHYLBENZOATE SPECTRA AND WE GOT A MUCH BETTER MATCH USING THEM.

SLIDE 14. THE NEXT THING WE WANTED TO LOOK AT WAS RELATIVE RETENTION TIMES. AS YOU KNOW, A MAJORITY OF THE ANALYSIS DONE IN THIS SCREENING PHASE WAS DONE USING VERY SIMILAR CONDITIONS. IN FACT, WE HAD

USE OF RETENTION TIMES

COMPOUND	RANGE OF RRT	RANGE OF K
DIOCTYLPHTHALATE	0.03	45 - 100
PHTHALIDE	0.01	57 - 77
TOLUIC ACID	0.03	48 - 85

ACTUALLY ASKED THAT THEY ALL BE RUN UNDER THE SAME CONDITIONS. IN TAKING A LOOK, WE FELT THAT IF WE GOT A SPECTRUM MATCH OF SUFFICIENT QUALITY (DEFINED EMPIRICALLY) PLUS A RELATIVE RETENTION TIME MATCH WITHIN A VERY CLOSE WINDOW (ALSO DETERMINED EMPIRICALLY), WE COULD SEND THAT DATA TO THE HISTORICAL LIBRARY WITHOUT THE INTERFERENCE OR THE HELP OF A CHEMIST. OF COURSE, IF EITHER THE RETENTION TIME OR THE SPECTRUM MATCH WAS NOT GOOD, THEN WE WOULD HAVE TO HAVE A CHEMIST TO EVALUATE THE DATA. IF YOU TAKE A LOOK AT WHAT WE FOUND IN THIS PARTICULAR SLIDE, YOU SEE THAT THE RANGE OF RELATIVE RETENTION TIMES FOR EACH OF THESE THREE COMPOUNDS ARE VERY, VERY NEAR TO EACH OTHER. WE ONLY HAD A RANGE OF 0.03 OF A RETENTION TIME UNIT FOR THE DIOCTYL PHTHALATE, WHEREAS IN MATCHING THE SPECTRUM FOR THAT SAME COMPOUND (RUN IN DIFFERENT LABORATORIES) THE RANGE OF K, THAT IS THE OVERALL QUALITY OF THE MATCH, WAS A FACTOR OF TWO. THE SAME GOES FOR THE OTHER TWO COMPOUNDS SHOWN. ONE CAN SEE THERE'S A MUCH GREATER RANGE IN THE MATCH PARAMETER THAN THERE IS IN THE RELATIVE RETENTION TIME. WE WERE MILDLY EXCITED ABOUT THIS. WE DIDN'T KNOW HOW WELL THE CORRELATION FROM LAB TO LAB WOULD BE, BUT THIS GAVE US A LITTLE BIT OF ENCOURAGEMENT.

SLIDE 15, PLEASE. WE DETERMINED EMPIRICALLY SOME RELATIVE RETENTION TIME WINDOWS AND COLLECTED SOME STATISTICS. THE RELATIVE RETENTION TIME MATCHES FROM LAB TO LAB HAVE BEEN UNBELIEVABLY GOOD. THE REASON FOR THIS IS THAT SO MANY PEOPLE ARE USING AUTOMATED GC/MS SYSTEMS THAT REQUIRE THEM TO HAVE GOOD PRECISION IN RELATIVE RETENTION TIMES TO EFFICIENTLY ANALYZE THESE PRIORITY POLLUTANTS. HERE IS AN EXAMPLE OF TWO LABORATORIES WHOSE DATA WAS OUTSIDE THE PRECISION WINDOW FOR RELATIVE RETENTION TIME, YET FELL VERY CLOSE TO EACH OTHER. WE WERE ABLE TO APPLY A LINEAR CORRECTION FACTOR THAT BROUGHT THESE INTO LINE WITH EVERYONE ELSE. OUR WINDOW FOR THE SP-2250 COLUMN IS ±.06 RELATIVE RETENTION TIME UNITS. AS YOU CAN TELL, AFTER APPLYING THE CORRECTION, THEY WERE BROUGHT WELL WITHIN THOSE LIMITS.

SLIDE 16, PLEASE. HERE ARE THE SAME TWO LABORATORIES ON THE SP-1240-DA COLUMN. AGAIN, WE WERE ABLE TO APPLY A LINEAR CORRECTION THAT BRINGS THEM INTO THE SAME RANGE AS ALL THE OTHER LABORATORIES.

SLIDE 17. AT THE OUTSET IT WAS OBVIOUS THAT THERE WERE GOING TO BE PROBLEMS ASSOCIATED WITH COMPOUNDS THAT HAD VERY SIMILAR SPECTRA. WE DECIDED TO PROCURE A NUMBER OF HOMOLOGOUS SERIES STANDARDS AND GET THEM

Table I. Mean RRT's for two labs before and after correction, compared with mean RRT's for other labs for 1% SP-2250.

Compound	$\overline{RRT}$ for two labs before correction	after correction[1]	RRT for all other labs
Xylenes	.041	.137	.133
2-N-Butoxyethanol	.090	.180	.166
C_3 Benzenes	.111	.200	.208
Naphthalene	.375[2]	.438	.457
Methyl Naphthalenes	.491	.542	.553
C_2 Naphthalenes	.612	.651	.663
Fluorene	.796[2]	.816	.838

[1] corrected using following formula:

$$RRT_{corrected} = RRT_{orig} + 0.1\ (1 - RRT_{orig}) \quad (\text{for } RRT_{orig} < 1)$$

[2] one observation only

Table II. Mean RRT's for two labs before and after correction compared with mean RRT's for other labs for 1% Sp-1240-DA.

Compound	$\overline{RRT}$ for two labs before correction	$\overline{RRT}$ for two labs after correction[1]	RRT for all other labs
Naphthalene	.180	.344	.343
Methyl Naphthalene	.280	.424	.453
Benzothiazole	.293[3]	.434	.475[3]
Phenol	.322	.458	.467[2]
Cresols	.371	.497	.489
C_2 Naphthalenes	.383	.506	.542
Xylenols	.466	.573	.589
C_3 Naphthalenes	.524	.619	.661
Dibenzofuran	.612	.690	.719

[1]Corrected using following formula:

$$RRT_{corrected} = RRT_{orig} + 0.2\ (1 - RRT_{orig}) \quad (\text{for } RRT_{orig} < 1)$$

[2]RRT from Protocol

[3]one observation only

HOMOLOGOUS SERIES STANDARDS

C_6 - C_{19} N-ALKANES

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

C_6 - C_{10} ALKENES

C_8 - C_{22} ALKENES

C_4 - C_{22} N-ALCOHOLS

C_3 - C_{16} ALDEHYDES

C_4 - C_{14} PRIMARY AMINES

C_4 - C_{18} SECONDARY AND TERTIARY AMINES

BENZENOID HYDROCARBONS

DICARBOXYLIC ACIDS

DIMETHYL ESTERS OF DICARBOXYLIC ACIDS

C_3 - C_{18} FATTY ACIDS

C_3 - C_{12} GLYCOLS

C_3 - C_{10} GLYCOL ETHERS

LOW BOILING ESTERS

C_3 - C_{19} METHYL KETONES

PHENOLS

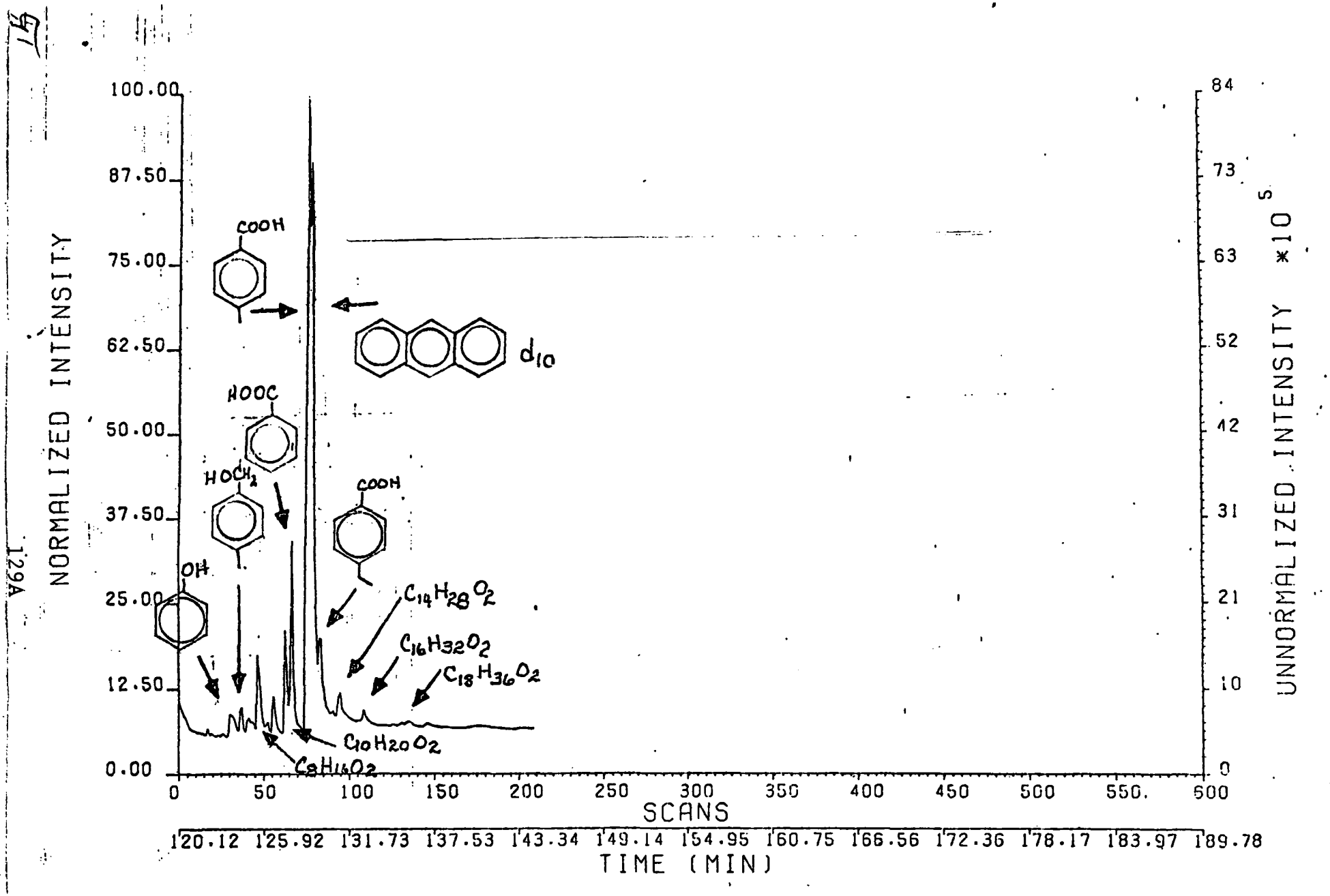
PHTHALATE ESTERS

RUN ON THE GC/MS BY TWO LABORATORIES. SINCE WE KNEW THAT WE WERE GETTING GOOD CONSISTENT RELATIVE RETENTION TIMES, THESE WERE PUT IN OUR LIBRARY. THE MAIN SELECTION CRITERIA WERE THAT THEY WERE AVAILABLE AND CONSTITUTED A PROBLEM AREA.

SLIDE 18. THIS IS AN EXAMPLE OF THE WAY THINGS CAN WORK (IN THE BEST CASE, OF COURSE). AS YOU SEE HERE, WE HAVE MANAGED TO IDENTIFY A LARGE NUMBER OF COMPOUNDS IN AN ACID FRACTION.

SLIDE 19, PLEASE. HERE ARE SOME SELECTED RESULTS FROM OUR HISTORICAL LIBRARY. REMEMBER, OF COURSE, THAT ALL OF THESE COMPOUNDS ARE TENTATIVE AND HAVE NOT BEEN CONFIRMED CHEMICALLY. ALL THAT THIS SLIDE DEMONSTRATES IS THAT SOME CHEMICALS SHOW UP IN SOME INDUSTRIES SELECTIVELY.

SLIDE 20. AS I SAID BEFORE, WE'RE TAKING SPECTRA THAT DO NOT MATCH WITH THE REFERENCE LIBRARY, MATCHING THESE AGAINST EACH OTHER TO SELECTIVELY PRIORITIZE THOSE THAT REOCCUR. NEXT, THE EXTRACT, CORRESPONDING TO A SAMPLE IN WHICH THIS COMPOUND WAS FOUND IN HIGH CONCENTRATION, IS ANALYZED TO IDENTIFY THIS COMPONENT BY USING MORE EXTENSIVE METHODS OF ANALYSIS. THIS PROJECT IS UNDERWAY NOW VIA A CONTRACT BETWEEN THE ATHENS LABORATORY AND RESEARCH TRIANGLE INSTITUTE. AT THE PRESENT TIME, RTI IS ANALYZING EXTRACTS THAT


NORMALIZED INTENSITY
UNNORMALIZED INTENSITY *10^5
100.00
87.50
75.00
62.50
50.00
37.50
25.00
12.50
0.00
84
73
63
52
42
31
21
10
0
COOH
HOOC
HOCH2
OH
COOH
d10
C14H28O2
C16H32O2
C18H36O2
C10H20O2
C8H16O2
0
50
100
150
200
250
300
350
400
450
500
550.
600
SCANS
120.12 125.92 131.73 137.53 143.34 149.14 154.95 160.75 166.56 172.36 178.17 183.97 189.78
TIME (MIN)

SELECTED HISLIB RESULTS

COMPOUND	TOTAL HISLIB ENTRIES	% OF ENTRIES FOUND IN INDICATED INDUSTRY	INDUSTRY
BENZALDEHYDE	7	71%	PULP & PAPER
DIMETHYLSULFONE	8	100%	PULP & PAPER
α-PINENE	9	66%	PULP & PAPER
β-PINENE	9	89%	PULP & PAPER
TRIBUTYLPHOSPHATE	10	50%	PULP & PAPER
		40%	PAINT & INK
BORNEOL	10	70%	PULP & PAPER
		30%	PAINT & INK
2,4-DIHYDROXYACETOPHENONE	7	86%	PULP & PAPER
DIPHENYLETHER	5	80%	ORGANICS & PLASTICS
BENZOTHIAZOLE	4	75%	RUBBER PROCESSING
TETRAHYDROFURAN	5	100%	TEXTILE MILLS
2-ETHYL-1-HEXANOL	25	68%	PAINT & INK
2-METHYLANTHRACENE	13	54%	COAL MINING
1&3&9 METHYLPHENANTHRENE	14	92%	COAL MINING
DIBENZOFURAN	3	75%	COAL MINING
PYRENE	6	67%	COAL MINING

PROGRAM FOR IDENTIFICATION OF UNKNOWNS

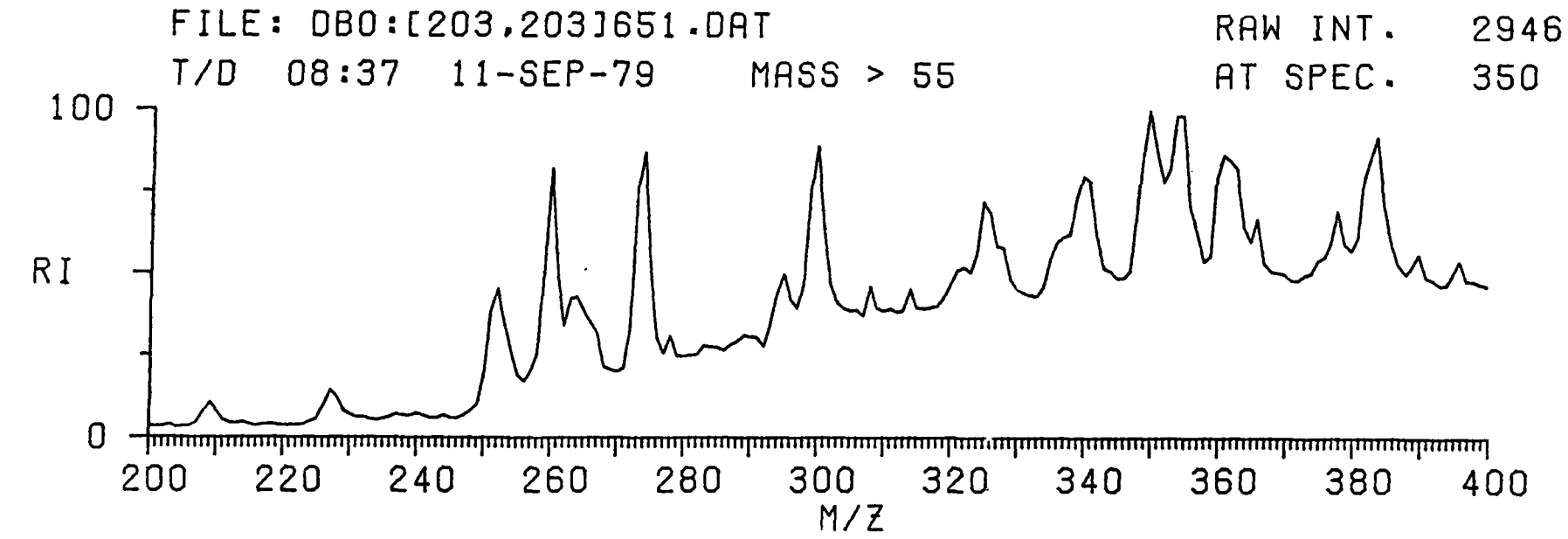
A. UNKNOWNS WITHIN A GIVEN RETENTION TIME WINDOW ARE MATCHED AGAINST EACH OTHER TO DETERMINE FREQUENCY OF OCCURRENCE.

B. THOSE UNKNOWNS WITH THE HIGHEST FREQUENCIES OF OCCURRENCE AND RELATIVE CONCENTRATIONS ARE DESIGNATED FOR FURTHER STUDY UNDER TASK 160.

CONTAIN SOME OF OUR TENTATIVELY IDENTIFIED COMPOUNDS TO BE CONFIRMED BY COINJECTION WITH A STANDARD.

SLIDE 21. ONE OF THE BIG PROBLEMS WE HAVE HAD IS TRYING TO DETERMINE THE INTERNAL STANDARD IN MANY OF THESE RUNS. MANY TIMES IT'S BY FAR THE SMALLEST COMPONENT OF THE RUN AND BURIED IN THE BACKGROUND. WE WANTED TO DO SOMETHING TO HELP US FIND THIS COMPONENT BY LOOKING AT THE SPECIFIC ION PLOTS FOR CHARACTERISTIC IONS OF THE INTERNAL STANDARD. THIS IS AN EXAMPLE OF HOW THE BACKGROUND SUBTRACT MODULE LOOKS.

AT THE TOP OF THE SLIDE YOU'LL SEE MASS 55 AS IT'S SEEN IN THE RAW DATA. ON THE BOTTOM, IT IS MASS 55 AFTER THE BACKGROUND SUBTRACT IS DONE. THE PROGRAM ACTUALLY HELPS THE PEAK FINDING ALGORITHM BY MAKING THE PEAKS THAT ARE ACTUALLY THERE STAND OUT. AFTER WE HAD DONE THIS, WE FOUND WE COULD PUT IT TO SOME OTHER USES SUCH AS REVERSE SEARCHING AS IS DONE IN PRIORITY POLLUTANT ANALYSIS. WE WERE ASKED TO LOOK AT SOME PAINT AND INK EFFLUENT SAMPLES TO SEE IF WE COULD FIND SOME CHLORINATED BIPHENYLS. OUR PROGRAM PEAK, THE INTERNAL STANDARD FINDER, WAS ADAPTED TO USE MASSES CHARACTERISTIC OF SEVERAL PCBs INSTEAD OF THE MASSES OF THE INTERNAL STANDARD. WE DID NOT FIND ANY PCBs, BUT WE DID FIND SOME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100
RI
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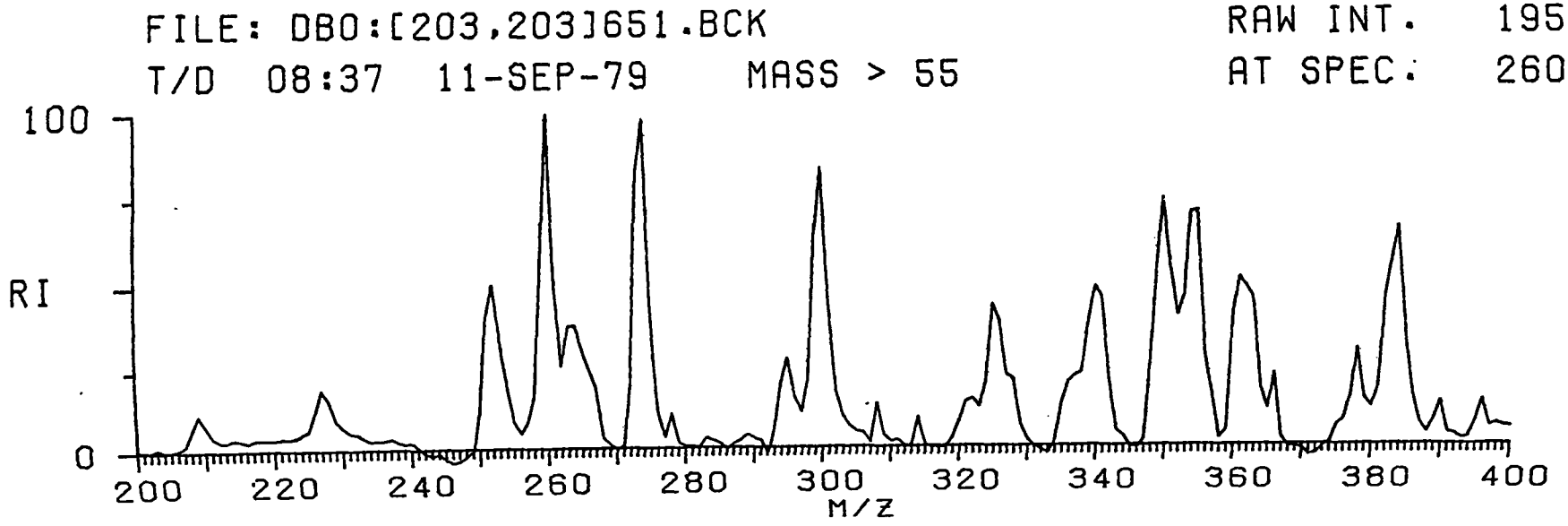
M/Z

130A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AT SPEC. 260
100
RI
0
200 220 240 260 280 300 320 340 360 380 400
M/Z

CHLORINATED AROMATICS THAT MATCHED ONE OR MORE OF THE PCB MASSES WE WERE LOOKING FOR.

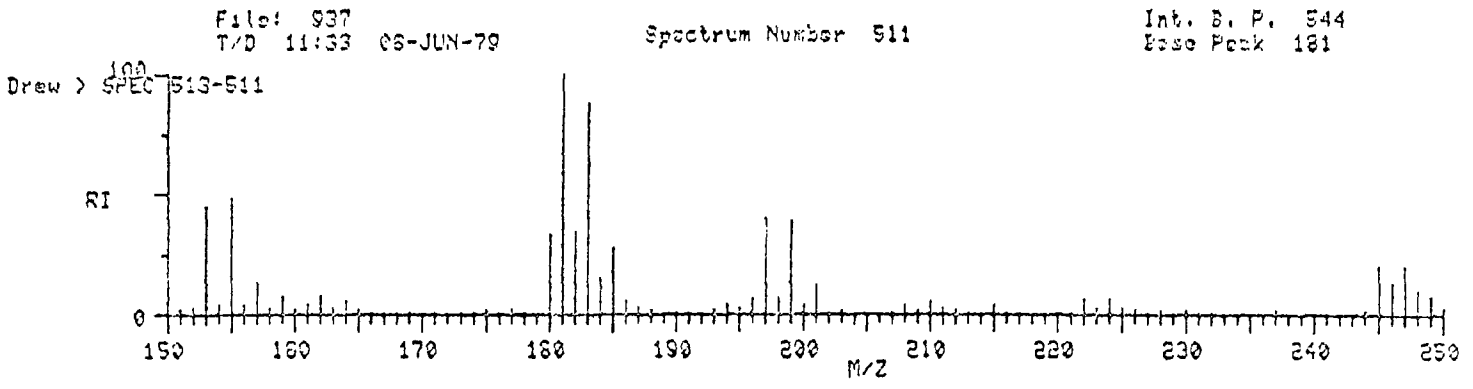
THE IMPORTANT PART HERE IS THE FACT THAT WE HAD SOME 20,000 SPECTRA TO GO THROUGH TO FIND THESE PCBs, AND THIS ALGORITHM ALLOWED US TO REDUCE THE DATA DOWN TO ONLY 34 SPECTRA OF INTEREST.

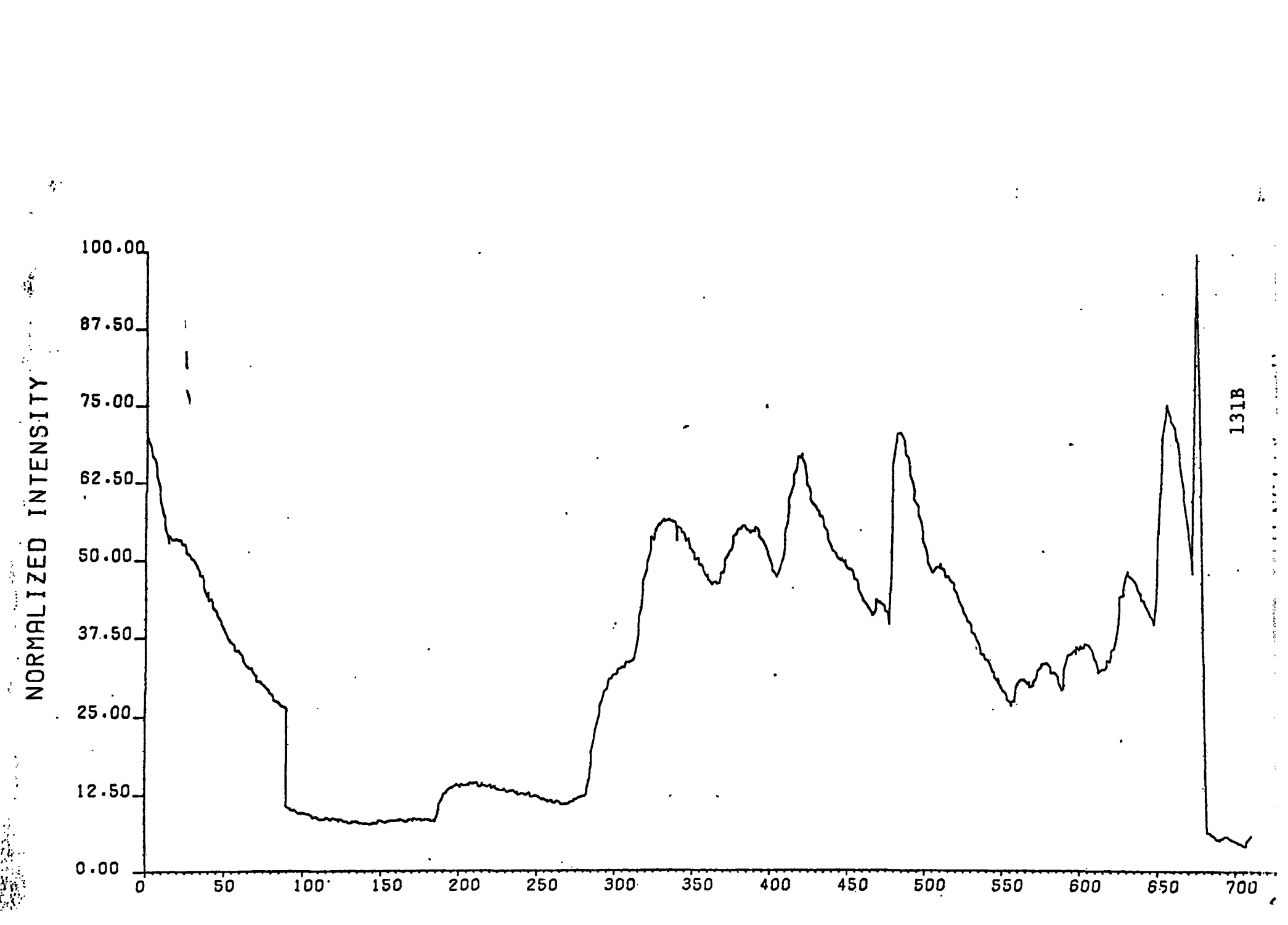
SLIDE 22 IS AN EXAMPLE OF ONE OF THE SPECTRA THAT WE FOUND IN THAT PARTICULAR RUN AND YOU CAN SEE THE CHLORINE PATTERN EASILY.

AS I HAVE SAID, I HAVE SHOWN YOU THE BEST OF OUR DATA. AS YOU CAN IMAGINE, THE TYPE OF DATA IN SLIDE 23 DOESN'T WORK TOO WELL SOMETIMES, AND THIS IS REALLY NOT THE WORST OF IT. AS YOU WHO HAVE RUN SOME OF THESE SAMPLES KNOW, WE GET HUMPOGRAMS MANY TIMES. THE COMPUTER PROGRAM JUST CAN'T HANDLE THIS, SO WE'RE ENDEAVORING TO IMPROVE THE SYSTEM. I CAN ENTERTAIN QUESTIONS AT THIS TIME IF THERE ARE ANY.

CHLORINATED ORGANIC FOUND WHEN REVERSE SEARCH EMPLOYED

SPEC 513/150,250

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87.50
75.00
62.50
50.00
37.50
25.00
12.50
0.00
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
131B

Question and Answer Session

MR. SPRAGGINS: Walt, this is real interesting data. I'm very interested in this sort of program. Have you got any data yet, or how long will it be before you have data on concentration?

MR. SHACKELFORD: Well, as you can imagine our concentrations are really meaningless, for we know none of the response factors. I hate the fact that the computer prints out numbers, I wish it would only print big and little, but that's really about all we're willing to say on concentration. In other words, we assume that D_{10} anthracene and all of the compounds we looked at have the same response factor (of course, that's foolishness), but that's really the only way we can get some indication.

MR. SPRAGGINS: Are you trying to plot the data out that gives you an idea of what the compound identifications look like versus concentration for a given industry over a series of industries, the number of times you actually find a compound within an industry? Have you got any plots like this?

MR. SHACKELFORD: We have

NOT DONE ANY PLOTS AT THE PRESENT TIME. THAT SLIDE I SHOWED, SLIDE 19, SHOWS SOME OF THE COMPOUNDS THAT WERE SHOWING UP IN SOME INDUSTRIES. WE PREFER TO WAIT UNTIL WE GET SOME OF OUR DATA BACK FROM THE CONFIRMATION STUDY BEFORE WE ATTEMPT TO CHARACTERIZE AN INDUSTRY. FOR INSTANCE, DREW SAUTER WHO IS WORKING WITH THE LAS VEGAS LAB NOW, IS ONE OF THE PEOPLE WHO DESERVES PRINCIPAL CREDIT FOR THIS WORK. HE HAS PUT FORTH SEVERAL VERY GOOD IDEAS THAT WE ARE GOING TO PURSUE TOWARD A PATTERN RECOGNITION TYPE OF STUDY ON THE COMPOUNDS FOUND IN VARIOUS INDUSTRIES.

MR. TELLIARD: THE NEXT SPEAKERS ARE GOING TO TALK ABOUT THE PRECISION AND ACCURACY STUDIES THAT WE HAD INITIATED LAST MEETING. WE'VE DONE SOMETHING LIKE 14 INDUSTRIES. BASICALLY, WHAT HAS HAPPENED IS WE WERE GOING TO BLIND YOU WITH DATA AND ALL THAT GOOD STUFF; HOWEVER, MY CONTRACTOR WAS BUSY HAMMERING OLD CHEMICAL DATA FROM THE MANUFACTURING CHEMISTS' GROUP, AGAIN, FOR TWO YEARS, SO GEORGE CAN MAKE YOU SLIDE, SO THEY NEVER GOT TO MY DATA. WE'RE GOING TO GIVE YOU A GENERAL OVERVIEW FROM MIKE CARTER AND ALSO BOB BEIMER FROM TRW, WHO IS WORKING ON A LITTLE DIFFERENT PART OF THE STUDY, WHICH IS WHAT WE'RE CALLING A SOLIDS STUDY OR SUSPENDED SOLIDS STUDY.

PRECISION AND ACCURACY STUDIES

BY: MIKE CARTER

AS BILL MENTIONED, THERE IS A PRECISION AND ACCURACY STUDY GOING ON DESIGNED TO LOOK AT APPROXIMATELY 28 INDUSTRIAL SAMPLES THAT WILL PRETTY MUCH COVER THE RANGE OF INDUSTRIAL CATEGORIES. SOME OF THEM, APPARENTLY, WE NEED TO LOOK AT MORE THAN ONCE. IN AT LEAST ONE CASE, WE'VE REPEATED AN INDUSTRY BECAUSE THE DATA JUST WAS NOT TOO GOOD. WE GOT A LOT BETTER RESULTS THE SECOND TIME AROUND. SINCE WE'RE ONLY ABOUT HALFWAY THROUGH, WE HAVEN'T GOTTEN ALL THE DATA PLUGGED INTO A DATA BASE YET. UNTIL THEN, NO STATISTICAL WORK CAN BE DONE ON IT, SO WE'RE JUST NOT GOING TO BE IN A POSITION TO GIVE ANY NUMBERS SUCH AS BOB KLEOBFER DID.

IN GENERAL, IT'S MY IMPRESSION THAT THE RECOVERIES AND STANDARD DEVIATIONS ARE COMPARABLE TO WHAT BOB HAS SHOWED YOU. THE STUDY DOES LOOK AT BOTH INFLUENT TO TREATMENT AND EFFLUENT FROM TREATMENT. THERE ARE DUPLICATES RUN AT FIVE DIFFERENT CONCENTRATIONS IN EACH TYPE OF SAMPLE. ONE OF THE CONCENTRATIONS IS A NONSPIKED LEVEL. THE SPIKE LEVELS ARE NOT BASED ON THE CONTENT OF THE SAMPLE; IT'S MORE BASED ON THE INDICATED CONCENTRATIONS

FROM SCREENING THAT OCCURRED IN THAT INDUSTRY. SO WE ATTEMPT TO MAKE FOUR SPIKES THAT WILL FAIRLY WELL BRACKET THE CONCENTRATIONS THAT WERE INDICATED BY THE OUTPUT FROM THE SCREENING QUANTITATION. ONE BIT OF INFORMATION THAT IS COMING OUT A LOT IS THAT THE EFFLUENT FROM TREATMENT IS A LOT EASIER MATRIX TO WORK WITH THAN THE INFLUENT TO TREATMENT, AND THAT'S NOT REALLY SURPRISING.

OF THE STUDIES THAT WE HAVE TO DATE, THE TIMBER INDUSTRY GIVES A STRIKING CONTRAST BETWEEN THE TWO MATRICES. I AM TALKING ABOUT STANDARD DEVIATIONS IN GENERAL; IN THE BASE/NEUTRAL, AS HIGH AS 200 PERCENT RECOVERY, WHEREAS IN THE EFFLUENT, THE STANDARD DEVIATION DROPS DOWN TO THE RANGE OF 15 TO 20. IT'S A VERY DRAMATIC DEMONSTRATION OF THE EFFECT OF MATRIX.

ONE ASPECT THAT IS BEING LOOKED AT IN THE PRECISION AND ACCURACY STUDY IS WHAT WE ARE REFERRING TO AS CROSSOVER. BY THAT, WE MEAN THAT AFTER A FRACTIONATION IS PERFORMED, ACCORDING TO THE PROTOCOL, THE ACID FRACTION IS ANALYZED BY GC/MASS SPEC FOR THE PRESENCE OF BASE/NEUTRALS AND VICE VERSA. BOB KLEOBFER MENTIONED THAT THE PHTHALATES TEND TO BE VERY TROUBLESOME. PART OF THIS PROBLEM, I THINK, IS DUE TO THE FACT THAT A LOT OF THE PHTHALATES DO NOT COME

OUT WHOLLY IN THE BASE/NEUTRAL FRACTION. A SIGNIFICANT CONCENTRATION OF SOME OF THEM END UP IN THE ACID FRACTION. SO THE FACT THAT YOU'RE NOT LOOKING AT ALL THE PHTHALATE IN ONE ANALYSIS COULD VERY WELL EXPLAIN A LOT OF THE SCATTER. THIS CROSSOVER APPEARS TO BE MATRIX DEPENDENT BECAUSE IT IS NOT CONSISTENT FROM INDUSTRY TO INDUSTRY. THE PHTHALATES AND THE PHENOLICS ARE THE MOST TROUBLESOME OF THE PRIORITY POLLUTANTS IN THE CROSSOVER STUDY.

THE STUDY THAT BOB BEIMER IS GOING TO TALK ABOUT ADDRESSES THE EFFECT OF TOTAL SUSPENDED SOLIDS. TO DATE WE HAVE HAD FOUR SAMPLING EPISODES OR STUDIES THAT WERE DONE BY BOTH TRW AND CARBORUNDUM. WE HAVE NOT DONE ANY COMPARISON BETWEEN THE TWO LABORATORIES YET. THAT, OF COURSE, WILL BE A VERY REASONABLE THING TO DO. WE SHOULD BE ABLE TO PRESENT STATISTICAL DATA SHOWING AVERAGE RECOVERIES AND STANDARD DEVIATIONS ON THESE STUDIES AT A LATER DATE.

I'LL ENTERTAIN ANY QUESTIONS BEFORE BOB STEPS UP HERE; IF I CAN ANSWER A QUESTION, I'LL BE GLAD TO.

QUESTION AND ANSWER
SESSION

MR. CATES: LARRY CATES WITH RADIAN. HOW SIGNIFICANT, YOU KNOW, ROUGHLY, JUST A BALLPARK, WHAT RANGES DO YOU FIND THE CROSSOVER IN TERMS OF PERCENT FROM, LIKE, THE PHENOLS AND THE PHTHALATES, OR ARE WE TALKING ABOUT MAYBE A TEN PERCENT OF A GIVEN PHENOL BEING IN THE BASE NEUTRAL FRACTION OR WHAT KIND OF RANGE?

MR. CARTER: IN AN EXTREME CASE, AND I'M TALKING ABOUT AN INFLUENT TO TREATMENT THAT'S A VERY BAD MATRIX, THE INDICATED RECOVERY CAN BE OVER 100 PERCENT OF PHTHALATE SHOWING UP IN THE ACID FRACTION. THIS IS NOT A GENERALIZED STATEMENT; THIS IS REALLY AN OUTLIER-TYPE EVENT, BUT IT WOULD BE SOMETHING THAT COULD HAPPEN ON AN INDIVIDUAL DETERMINATION.

MR. CATES: THEN FOLLOWING FROM THAT, THEN, SINCE IT IS MATRIX DEPENDENT, THE CROSSOVER EFFECT, WOULD YOU GUESS THAT YOU OBSERVE CROSSOVER OF PHTHALATES AND PHENOLS IN, MAYBE, WHAT PERCENTAGE OF THE EXTRACTS? MAYBE 5, 10 PERCENT, 50 PERCENT? I'M TRYING TO GET SOME FEEL FOR THE SIGNIFICANCE OF THE PROBLEM.

MR. CARTER: I REALLY CAN'T GIVE YOU A GOOD ESTIMATE OF THAT NUMBER. WE'RE ONLY HALFWAY THROUGH THE STUDY. MOST OF THE TIME YOU DON'T

GET A CROSSOVER OF MORE THAN--AND I'M JUST TRYING TO RECALL THE NUMBERS--MORE THAN MAYBE 30, 40 PERCENT IN MOST CASES.

MR. KEEN: GARY KEEN, CONTINENTAL OIL. I HAVE OBSERVED CROSSOVER WITH PHTHALATES BECAUSE OF HALF-ESTERS THAT WILL BE EXTRACTED BECAUSE THEY ARE REALLY AN ACID; THEY THEN DISPROPORTIONATE IN THE INJECTOR TO GIVE PHTHALIC ANHYDRIDE AND THE DIESTER.

MR. CARTER: THANK YOU.

MR. MARRS: DAVE MARRS, STANDARD OIL. ONE QUESTION REGARDING THE SPIKING. WHAT SPIKING LEVELS DID YOU CHOOSE? YOU MENTIONED FIVE LEVELS; DID YOU HAVE ANY BALLPARK KIND OF FIGURES?

MR. CARTER: WELL, AS I MENTIONED, ONE SPIKE LEVEL IS NOT REALLY A SPIKE LEVEL, IT IS JUST THE AMBIENT SAMPLE SO WE'LL HAVE SOMETHING TO BASE THE SPIKE RECOVERY ON. THE OTHER SPIKE LEVELS WERE BASED ON THE REPORTED CONCENTRATIONS FROM THAT INDUSTRY. IN GENERAL, IT WAS, FOR THE INFLUENT TO TREATMENT, SOMETHING LIKE 50, 200, 500, 750. IN THE EFFLUENT FROM TREATMENT, IT WOULD BE 20 TO 50, 100, 250, 500. AS I SAID, WE

TRIED TO BRACKET WHAT HAD ACTUALLY BEEN REPORTED.

MR. MARRS: IN CHOOSING YOUR LEVELS FOR SOME OF THE PARTICULARLY INSOLUBLE SOLUBLE COMPOUNDS, DID YOU GIVE SOME THOUGHT TO THE SOLUBILITY LIMIT, SAY, OF A PAH OR SOMETHING LIKE THAT AND MAKE THAT YOUR UPPER LIMIT IN CHOOSING YOUR SPIKING LEVEL?

MR. CARTER: IN GENERAL, YES, WE TRIED TO DO THAT, AT THE SAME TIME, TRYING TO ADDRESS ANY REPORTED VERY HIGH FIGURES.

MR. MARRS: WHAT SOLVENT DID YOU USE FOR YOUR SPIKING?

MR. CARTER: METHYLENE CHLORIDE FOR EXTRACTABLES AND METHANOL FOR PURGEABLES.

DR. COLBY: BRUCE COLBY, SYSTEMS, SCIENCE AND SOFTWARE. WHEN THE EXTRACTIONS ARE BEING DONE, IS THERE A PRECAUTION TAKEN TO ASSURE THAT THE pH IS NOT CHANGING AS A FUNCTION OF TIME? I MEAN, IF WE SET UP AN EXTRACTION AND EITHER SHAKE IT OR WAIT FOR IT TO GO THROUGH A CONTINUOUS EXTRACTION, OCCASIONALLY THE pH WILL ACTUALLY CHANGE DURING THE PROCESS. IS THAT BEING CHECKED FOR?

MR. TELLIARD: YES, WE MEASURE pH, WE MEASURED pH AFTER EACH EXTRACTION BEFORE DISCARDING AND AFTER EACH EXTRACTION.

MR. HENDERSON: JIM HENDERSON WITH CARBORUNDUM. JUST TO FOLLOW UP ON YOUR QUESTION A LITTLE BIT, BRUCE, I DO KNOW THAT IN ONE SET OF SAMPLES, FOR SURE, THEY WERE MADE BASIC AT THE BEGINNING OF THE RUN AND THEY WERE NOT BASIC AFTER THE 24-HOUR PERIOD, AND AFTER THAT PHENOMENON OCCURRED, WE BEGAN TO MEASURE PHS BEFORE THE EXTRACTION STARTED, AFTER THE BASIC EXTRACTION, AFTER THE ACID EXTRACTION.

MR. CARTER: ONE OTHER THING THAT IS BEING DONE IN THE PRECISION AND ACCURACY STUDY IS THAT SURROGATE SPIKES SUCH AS BOB KLEOBFER SPOKE OF ARE ALSO BEING SPIKED AND THE PRECISION AND ACCURACY OF THOSE ALSO ADDRESSED.

MR. MARRS: DAVE MARRS, SOHIO. GETTING BACK TO THE USE OF METHYLENE CHLORIDE AS A SPIKING SOLVENT, HAVE YOU DONE ANY WORK OR DO YOU HAVE ANY DATA TO SHOW THAT THE STUFF ACTUALLY GETS INTO THE WATER PHASE WHEN YOU USE METHYLENE CHLORIDE AS YOUR SPIKING SOLUTION?

MR. CARTER: THE SPIKING SOLUTIONS ARE DESIGNED SO THAT YOU'RE ADDING SUCH A SMALL AMOUNT OF METHYLENE CHLORIDE THAT THE SOLUBILITY OF METHYLENE CHLORIDE AS STATED, FOR INSTANCE, IN THE

CHEMICAL-RUBBER HANDBOOK WOULD NOT BE EXCEEDED. THERE HAVE BEEN NO REAL STUDIES DESIGNED TO ASSESS THAT SOLUBILITY, BUT WE DID REFER TO THE LITERATURE FOR THE SOLUBILITY OF METHYLENE CHLORIDE.

MR. RHOADES: JOHN RHOADES WITH SOUTHWEST RESEARCH INSTITUTE. WE FOUND THAT IF YOU GET REAL BASIC, IF YOU GET DOWN TO PH12 OR SO, YOU'LL GET PRACTICALLY NO DIMETHYL BACK; YOU'VE GOT TO STAY UP AROUND 10 OR SO. TO SOME EXTENT THE SAME THING AS WITH THE DIETHYL.

PRECISION AND ACCURACY STUDIES

By: Robert G. Beimer

I want to start off by saying that I prepared the slide material that I'm going to present here, but I expected Bill Telliard to present this. If I had known I was going to present it, I'd have done a better job of putting the slides together.

I want to talk briefly, and I do mean briefly, about some of the work we're doing on the precision and accuracy study. I'm not going to go into any of the actual analyses that we performed and the recovery of the priority pollutants because that data really hasn't all been put together to a point where it can make a lot of sense. I want to address initially the crossover problem and show some data we have generated which illustrates the crossover problem. The last statement that was made here about not going to a high pH for the base/neutral fraction really leads into this. The majority of what I've got here...well, excuse me, all of what I've got here is related to surrogate species rather than priority pollutant species. Now, the reason that I'm showing surrogate compounds is because these materials were all spiked at the same

LEVEL IN ALL OF THE SAMPLES. MIKE CARTER SAID THAT THERE WERE FIVE SPIKING LEVELS FOR THE PRIORITY POLLUTANTS, AND THAT'S TRUE, BUT IN EACH ONE OF THOSE SAMPLES WE SPIKED THE SURROGATES AT 100 MICROGRAMS PER LITER, CONSTANT, THROUGHOUT. SO ALTHOUGH THERE WAS A SLIGHTLY DIFFERENT MATRIX BECAUSE OF THE VARYING SPIKING LEVELS OF THE PRIORITY POLLUTANTS, THE SURROGATE MATERIALS THEMSELVES WERE CONSTANT.

NOW, I'M GOING TO TELL YOU WHAT'S ON HERE BECAUSE I DOUBT THAT YOU CAN SEE THIS VERY WELL.

THE FOUR INDUSTRIAL CATEGORIES THAT ARE PRESENTED ON THIS SLIDE ARE NONFERROUS METALS, INORGANIC CHEMICALS, PUBLICLY OWNED TREATMENT WORKS, AND THE TEXTILE INDUSTRIES. ALL OF THESE SAMPLES WERE EXTRACTED USING METHYLENE CHLORIDE IN 24-HOUR CONTINUOUS LIQUID/LIQUID EXTRACTORS. THE FIRST THREE INDUSTRIES WERE EXTRACTED AT AN INITIAL pH OF 11, MEASURED WITH A pH METER BEFORE AND AFTER EXTRACTION, AND THE FINAL CATEGORY, THE TEXTILE INDUSTRY, WAS EXTRACTED INITIALLY AT A pH OF 12.

NOW, IF YOU LOOK AT THE RECOVERIES, WHAT IS PRESENTED HERE IS THE PERCENTAGE OF THE VARIOUS SURROGATE MATERIALS FOUND IN EACH FRACTION. NOW, IF YOU LOOK AT

THE FIRST ONE, 2-FLUOROPHENOL. IN THE ACID FRACTION FOR THE NONFERROUS METALS CATEGORY, FOR INSTANCE, 70 PERCENT WAS FOUND IN THE ACID FRACTION AND 30 PERCENT IN THE BASE/NEUTRAL FRACTION. GOING ACROSS TO D_5 PHENOL, WHICH IS LESS OF AN ACID THAN 2-FLUOROPHENOL, ONLY 11 PERCENT OF THE D_5 PHENOL WAS FOUND IN THE ACID FRACTION, WITH 89 PERCENT FOUND IN THE BASE/NEUTRAL FRACTION. NOW, D_5 PHENOL IS A LOT LIKE PHENOL, SO IF YOU'RE DOING YOUR EXTRACTION AT A PH OF 10 OR 11, MOST OF YOUR PHENOL IS IN THE BASE/NEUTRAL SIDE, AND IF YOU'RE NOT ANALYZING THE BASE/NEUTRAL FRACTION FOR THE PHENOLS, YOU'RE MISSING THEM.

IF YOU GO DOWN TO THE BOTTOM LINE, NOW, THE TEXTILE INDUSTRY EXTRACTED AT A PH OF 12. VIRTUALLY ALL OF THE MATERIAL WAS FOUND IN THE FRACTION WHERE IT BELONGED; ROUGHLY 100 PERCENT--IT'S 98 PERCENT IN SOME CASES--WAS FOUND IN THE ACID FRACTION. SO THIS CROSSOVER, IF YOU WANT TO REFER TO IT THAT WAY, VARIES SLIGHTLY WITH THE INDUSTRIAL CATEGORY, WHICH SAYS THAT IT'S PROBABLY VARYING SOMEWHAT IN TERMS OF THE MATRIX, BUT MORE SPECIFICALLY, IT FOLLOWS THE OF THE MOLECULES THAT WE'RE LOOKING AT ON THAT CHART. IN SHORT, THE BETTER THE ACID, THE MORE IT'S FOUND IN THE ACID FRACTION, AND THE POORER THE ACID, THE LOWER THE PK IT'S FOUND IN THE

BASE/NEUTRAL FRACTION. SO YOU'VE GOT TO FORCE THE SITUATION, ESPECIALLY USING CONTINUOUS EXTRACTORS. YOU'VE GOT TO FORCE THE SITUATION SO THAT YOU DON'T ALLOW A SIGNIFICANT AMOUNT OF THE PHENOL TO BE EXTRACTED IN THE BASE NEUTRAL FRACTION WHEN YOU'RE NOT ANALYZING THAT FRACTION FOR THE PHENOLIC COMPOUNDS. OBSERVATION NUMBER ONE.

NOW, WE CAN COME BACK TO THAT IF ANYBODY HAS ANY QUESTIONS ON IT, BUT I WANT TO TALK NOW ABOUT THE SECOND PART OF THE STUDY THAT WE ARE DOING, AND THAT IS THE EFFECT OF TOTAL SUSPENDED SOLIDS ON PRIORITY POLLUTANT RECOVERY. NOW, AGAIN, WHEN WE STARTED PUTTING THIS MATERIAL TOGETHER, WE LOOKED AT ALL THE PRIORITY POLLUTANTS AND THEN WE THOUGHT, YOU KNOW, WE'RE TRYING TO AVERAGE TOGETHER APPLES AND ORANGES WHEN WE'RE TAKING AVERAGES OF SPIKING LEVELS AT 20, AND SPIKING LEVELS AT 2,000 AND TRYING TO MEASURE THE EFFECT OF THE TOTAL SUSPENDED SOLIDS ON THOSE PRIORITY POLLUTANTS. THEREFORE, AGAIN, WE WENT BACK TO THE SURROGATE MATERIALS THAT WE WERE SPIKING, ALL SPIKED AT THE SAME CONCENTRATION, AND USED THOSE TO TRY TO ESTABLISH THE EFFECT OF SOLIDS ON PRIORITY POLLUTANT RECOVERY. SO WHAT I'LL SHOW YOU IS THE EFFECT OF SOLIDS ON SURROGATE MATERIAL RECOVERY AND YOU CAN TRANSLATE THAT TO PRIORITY POLLUTANT RECOVERY IF YOU WISH; I HOPE THAT BEFORE TOO

LONG, AS WE GET MORE INDUSTRIAL CATEGORIES DEVELOPED, WE CAN HAVE ENOUGH DATA THAT WE CAN TALK ABOUT THIS KIND OF INFORMATION ON PRIORITY POLLUTANTS DIRECTLY, BUT AT THIS POINT, ALL WE CAN TALK ABOUT ARE THE SURROGATES.

THE MOST CONFUSING THING ABOUT THIS WHOLE THING IS EXPLAINING WHAT WE DID. IN THIS STUDY, WE WERE DOING THE STANDARD PRIORITY POLLUTANT ANALYSIS FOR ORGANIC COMPOUNDS BY TAKING A REPRESENTATIVE AMOUNT OF THE SOLIDS AND THE LIQUID AND EXTRACTING IT IN A CONTINUOUS EXTRACTOR; ANALYSIS NUMBER ONE, THE NORMAL ANALYSIS. ANALYSIS NUMBER TWO, WE SPIKED THE MATERIAL INTO THE WATER, ALLOWED IT TO INCUBATE FOR EIGHT HOURS, AND THEN FILTERED THE SOLUTION AND PROCEEDED TO PERFORM PRIORITY POLLUTANT ANALYSIS. IN THE THIRD CASE, WE FILTERED THE WATER AND THEN SPIKED IT WITH THE PRIORITY POLLUTANTS AND WENT AHEAD WITH THE ANALYSIS.

NOW, WHAT THIS CHART REPRESENTS FOR THE NONFERROUS METALS INDUSTRIAL CATEGORY IN THE FIRST COLUMN, COLUMN A, IS THE RATIO OF THE RECOVERY SPIKED BEFORE FILTERING DIVIDED BY THE RECOVERY SPIKED AFTER FILTERING. WHAT THIS MEANS IS, AS THE NUMBERS APPROACH ONE, THERE IS NO SOLIDS EFFECT ON THE

RECOVERY. THE SMALLER THE NUMBER, THE GREATER THE EFFECT OF SOLIDS ON RECOVERY. THE FIRST SIX COMPOUNDS UP THERE ARE BASE/NEUTRAL SURROGATE MATERIALS. THE LAST FOUR ARE ACID SURROGATE MATERIALS, AND AS YOU CAN SEE, YOU CAN ALMOST DRAW A LINE ACROSS THAT SAYS THERE IS AN EFFECT OF THE SOLIDS IN THE WATER ON THE RECOVERY OF THE BASE/NEUTRALS, BUT THERE IS VIRTUALLY NO EFFECT ON THE RECOVERY OF THE ACIDS. WELL, THAT'S NOT TERRIBLY SURPRISING; I MEAN, THE ACID MATERIALS CERTAINLY LIKE THE WATER REASONABLY WELL. THE SOLIDS CONTENT IN THIS PARTICULAR PLANT WAS 2.6 MILLIGRAMS PER LITER, AND THAT'S AWFULLY LOW, BUT NEVERTHELESS, THERE IS AN OBSERVED EFFECT.

THE SECOND COLUMN, COLUMN B, IS THE RATIO OF THE RECOVERY SPIKED WITH NO FILTERING DIVIDED BY THE RECOVERY SPIKED AFTER FILTERING. NOW, THE SOLIDS ARE STILL THERE IN THE FIRST CASE, SO THAT WHAT YOU'RE ACTUALLY MEASURING HERE IS HOW WELL DO YOU RECOVER THE PRIORITY POLLUTANTS FROM THE SOLIDS? YOU'RE NOT TAKING THE SOLIDS AND PRESUMABLY REMOVING THE PRIORITY POLLUTANTS WITH THEM, BUT REALLY MEASURING THE EFFECTIVENESS OF YOUR EXTRACTION ON THE SOLID MATERIAL WHILE IT'S STILL PRESENT. SO THE SMALLER THE VALUE, THE GREATER THE EFFECT OF THE SOLIDS ON RECOVERY, AND THE

CLOSER TO IT ONE GETS, THE LESS THE EFFECT, AND IF YOU WANT TO DRAW ANY CONCLUSIONS FROM THAT, YOU CAN. I DON'T SEE THAT THERE IS A DIFFERENCE. IT LOOKS TO ME LIKE YOU'RE GETTING EVERYTHING, OR VERY NEARLY EVERYTHING, BACK AS LONG AS THE SOLIDS ARE STILL PRESENT. IN OTHER WORDS, IN THE FIRST CASE, THERE WAS A RECOVERY PROBLEM WHERE THE MATERIAL WAS 'ADSORBED' ON THE SOLIDS, AND THEN WHEN YOU FILTERED THE SOLIDS, YOU TOOK SOME OF THE PRIORITY POLLUTANT WITH THEM.

THE SECOND PLANT IS AN INORGANIC CHEMICALS PLANT. MOST OF THE SOLIDS IN THIS PARTICULAR INDUSTRIAL CATEGORY WERE BORATES BECAUSE OF THE NATURE OF THE PLANT; 36.3 MILLIGRAMS PER LITER FOR THE SUSPENDED SOLIDS, AND AS YOU CAN SEE FROM THE FIRST COLUMN, THERE'S VIRTUALLY NO EFFECT OF THE SOLIDS ON ANY OF THE PRIORITY POLLUTANTS. SO WHAT DOES THAT SAY? IT DOESN'T SAY THAT IT IS THE SOLIDS THAT CAUSED THE PROBLEM, IT'S WHAT THEY ARE, AND THAT'S BASICALLY THE CONCLUSION WE HAVE COME TO; THE SOLIDS CONTENT HERE IS ALMOST AN ORDER OF MAGNITUDE HIGHER THAN IN THE FIRST PLANT WHERE THERE WAS AN EFFECT, AND IN THIS CASE, THERE IS NO EFFECT. SO THAT'S NOT TERRIBLY SURPRISING; THE NATURE OF THE SOLID MATERIAL IN THE SAMPLE AND THE ADSORPTIVE CHARACTERISTICS OF THAT SOLID MATERIAL AFFECT THE RECOVERY. AGAIN, VERY LITTLE EFFECT ON THE OTHER SIDE IN THE SECOND COLUMN AS WELL.

THE THIRD COLUMN IS A PUBLICLY OWNED TREATMENT WORKS (POTW) SAMPLE. IN THIS CASE, THERE MAY BE SOME EFFECT OF THE SOLIDS IN THE FIRST COLUMN, AS YOU CAN SEE. AGAIN, LITTLE OR NO EFFECT WHEN THE EXTRACTION IS CONDUCTED WITH THE SOLIDS IN PLACE.

THAT'S BASICALLY WHERE WE ARE, AND LIKE I SAY, WE ONLY REALLY HAVE DATA HERE ON THREE PLANTS. WE HAVE A FOURTH ONE THAT'S NOW FINISHED; BY THE TIME THIS IS DONE, WE'LL PROBABLY HAVE TEN OR TWELVE, AND AT THAT POINT WE CAN PROBABLY PRESENT MORE INFORMATION AND BEGIN TO GET, PERHAPS, A LITTLE MORE STATISTICAL SIGNIFICANCE FROM THE DATA THAT WE'RE GENERATING. THANK YOU.

QUESTION AND ANSWER SESSION

VOICE FROM THE AUDIENCE: THE PHENOMENON OF CROSSOVER HAS ALWAYS KIND OF BOTHERED ME. I CAN UNDERSTAND THE PHTHALATE SITUATION, SOME ALKALINE, SAPONIFICATION OF ESTERS; ONE CAN CLASSICALLY EXPLAIN THAT AWAY. PHENOL CROSSOVER AT PH10, PK IS AROUND 9, 9 SOMETHING, 10, YOU CAN EXPLAIN IT THAT WAY, BUT I'VE ALWAYS HAD SOME PROBLEMS WITH THE PHENOMENON OF APPARENT CROSSOVER OF SOMETHING LIKE OLEIC ACID; I'VE DONE MORE WORK WITH THE ADDITIONAL COMPOUND THAN THE ACTUAL PRIORITY CONSENT DEGREE OF ORGANIC, AND I REALLY WONDER IF THERE IS A SOLUBILITY PHENOMENON OCCURRING WHERE, SAY, THE ANION OF A FAIRLY STRONG ACID OR MODERATELY STRONG ACID, LIKE OLEIC, IS SOLUBLE IN THE ORGANIC PHASE TO SOME EXTENT, OR IS IT A PHYSICAL PROBLEM IN THE EXTRACTION ITSELF. WE ALKALINIZE THE SOLUTION, TREAT IT WITH ORGANIC SOLVENT, MIX IT, LET IT SEPARATE, BRING IT DOWN THROUGH THE SEPARATORY FUNNEL. I CAN FORESEE THE ANIONIC HYDROPHOBIC MOLECULE ORIENTING ITSELF AT THE SOLVENT WATER INTERFACE AND COMING DOWN AND POSSIBLY BREAKING THROUGH AT THAT LAST MOMENT WHEN WE'RE TRYING TO GET ALL OF OUR SOLVENT OR HAVE A MATRIX PROBLEM WHERE IT'S KIND OF DIFFICULT TO GET A GOOD SEPARATION, COLLECT THE ORGANIC MATERIAL, ADD SODIUM SULFATE TO DRY IT. I CAN SEE A PHYSICAL CARRY-OVER OF THIS SCHIZOPHRENIC MOLECULE INTO THE DRYING MATERIAL

MATERIAL AND THEN BEING RELEASED. I GUESS WHAT I'M GETTING AT IS, IS THAT POSSIBLE, AND IF SO, IS THERE ANYTHING THAT WE CAN DO TO TEST THAT HYPOTHESIS USING, FOR EXAMPLE, WHAT WE'VE TALKED ABOUT EARLIER THIS MICROEXTRACTION TECHNIQUE WHERE WE DON'T SEPARATE THE SOLVENT PHYSICALLY, WE JUST TAKE AN ALIQUOT OF THE SOLVENT AND ANALYZE IT DIRECTLY. IT JUST DOESN'T MAKE SENSE TO ME THAT THESE MOLECULES SHOULD GET IN THE ORGANIC PHASE UNLESS THEY'RE BEING PHYSICALLY CARRIED THROUGH OR THEY'RE CHELATING WITH SOMETHING THAT IS NEUTRALIZING THE CHARGE AND MAKING A MORE ORGANIC SOLUBLE. ONE EXAMPLE OF THAT WOULD BE THE METHYLENE BLUE CHELATE WITH ORGANIC SULFATES AND SULFONATES WOULD BE AN ANALOGY THAT I CAN DRAW.

MR. BEIMER: No.

MR. SPRAGGINS: BOB SPRAGGINS, RADIAN CORPORATION. I GUESS MOST OF US HERE HAVE SEEN EVEN A MORE DRASTIC CROSSOVER WITH SOMETHING LIKE NAPHTHALENE WHEN IT'S OCCURRED IN MORE THAN ONE FRACTION AND IT'S HARD TO EXPLAIN WHY IT WOULD BE. BOB, ARE YOU GOING TO LOOK AT THESE SOLIDS ELEMENTALLY TO SEE WHAT'S THERE, WHAT METALS MIGHT BE THERE TO CHELATE, FOR INSTANCE; BECAUSE I'LL BET YOU IF YOU LOOK IN COTTON & WILKINS, YOU COULD FIND A METAL THAT COULD BE IN THOSE SOLIDS THAT WOULD CHELATE VERY WELL WITH PHENOXIDE AND

AND ALL ITS SUBSTITUTED DERIVATIVES. YOU HAD SAID THAT PHENOLS LIKE WATER, BUT I THINK IT'S ALSO A PRETTY NUCLEOPHILE, TOO, SO YOU COULD PROBABLY FIND SOME INSTANCES WHERE PHENOL WOULD BE BAD ITSELF.

MR. BEIMER: I THINK DEPENDING ON THE INDUSTRIAL CATEGORY THAT YOU'RE LOOKING AT, YOU'VE GOT A PRETTY GOOD IDEA OF THE TYPE OF MATERIALS THAT ARE IN THAT WASTEWATER. AS I SAY, THE ONE THAT WE WERE MOST FAMILIAR WITH WAS ONE THAT WE SAMPLED OURSELVES, AND SO WE KNEW THAT THE SOLID MATERIALS IN THE WATER WERE BORATES, BUT, FOR INSTANCE, WITH THE INORGANIC CHEMICALS PLANT, I HAVE NO HISTORY ON THAT PLANT, SO I REALLY DON'T KNOW WHAT WAS IN THE WATER AND IT IS NOT PART OF THE STUFF THAT WE'RE DOING TO DETERMINE WHAT IS THE MAKEUP OF THE SOLIDS. I'VE GOT A PRETTY GOOD IDEA WHAT THEY WERE IN THE POTW.

MR. TELLIARD: THE ANSWER TO YOUR QUESTION IS NO. HE DOES NOT DO METALS. HE DOES NOT DO WINDOWS NOR DOES HE DO METALS.

MR. SAUTER: DREW SAUTER, EPA. I'D JUST LIKE TO OFFER AN OBSERVATION ABOUT THE CROSS-OVER EFFECT. YOU KNOW, IT HAS TO HAPPEN. THE PKA OF PHENOL IS 10; THAT MEANS THAT HALF THE MOLECULES ARE PROTONATED. IF YOU TAKE PHENOL AND YOU PUT IT IT WILL DISSOLVE IN SOLVENT, SO IF IT DOESN'T HAPPEN, THERE'S

SOMETHING WRONG. AS YOU INDICATED, IT MAKES SENSE THAT THE MORE ACIDIC PHENOLS ARE IONIZED; THEREFORE ARE SOLUBLE IN THE ORGANIC PHASE. ANY COMPOUND LESS ACIDIC THAN PHENOL, ALKYOL PHENOLS, DIMETHYL PHENOL, THINGS OF THAT NATURE WILL DO THE SAME THING. SO IT'S REALLY TO BE EXPECTED. HOPEFULLY, THE EXTRACTION IS DONE IN SUCH A WAY THAT MOST OF IT WOULD GO TO THE ACID PHASE, I WOULD THINK, SO THAT NONE OF THAT STUFF IS SURPRISING, I GUESS.

MR. BEIMER: I WAS TRYING TO POINT OUT...

MR. SAUTER: JUST ADDRESSING THE CROSSOVER.

MR. BEIMER: WHAT I WAS TRYING TO POINT OUT IS THE PROCEDURES CALL FOR pH 11 OR GREATER MEASURED WITH HYDRONIUM PAPER. THE DIFFERENCE BETWEEN 11 AND 12 IS REMARKABLE; IT'S THE DIFFERENCE BETWEEN KEEPING MOST OF THE ACID SPECIES, AT LEAST ON THE BASIS OF THESE SURROGATES, KEEPING MOST OF THE ACID SPECIES IN THE ACID FRACTION AND LOSING UP TO 90 PERCENT OF THEM IN THE BASE/NEUTRAL FRACTION FOR THE LESS ACIDIC PHENOLS. YOU'RE NOT GOING TO HAVE A PROBLEM WITH PENTACHLOROPHENOL OBVIOUSLY, IT'S ALL GOING TO STAY IN THE ACID FRACTION, BUT PHENOL ITSELF, YOU RUN THE RISK OF RECOVERING 20, 30 PERCENT OF IT, DEPENDING UPON THE pH AT WHICH YOU DO

YOUR BASE/NEUTRAL EXTRACTION.

MR. HENDERSON: JIM HENDERSON WITH CARBORUNDUM. BOB, LET ME ASK YOU TO CONFIRM THAT YOU GET MORE CROSSOVER OF ALL COMPOUNDS WITH LIQUID-LIQUID EXTRACTION THAN YOU DO WITH MANUAL EXTRACTION.

MR. BEIMER: YES, THERE'S NO DOUBT ABOUT THAT. THE EXTRACTION EFFICIENCY IS SIGNIFICANTLY IMPROVED, WITH THE EXCEPTION OF THE PAINT PLANT SAMPLES WE'RE RUNNING NOW, WHICH PLUG THE LIQUID-LIQUID EXTRACTOR.

MR. HENDERSON: IN SOME CASES THERE ARE ALSO CONCENTRATION DEPENDENT FACTORS, PARTICULARLY WITH POLYNUCLEARS, AS I RECALL, AND IN SOME CASES COMPOUNDS LIKE PHTHALATES RUN VERY WELL AND IN SOME CASES YOU GET WILD VARIATIONS.

MR. BEIMER: I STILL QUESTION WHETHER OR NOT THE PROBLEM WITH PHTHALATES IS ONE OF CROSSOVER OR ONE OF CONTAMINATION; I'M STILL A LITTLE IFFY ON THAT SUBJECT.

MR. TELLIARD: THE NEXT PART OF THE PROGRAM IS GOING TO TAKE A LOOK AT THE VERIFICATION DATA, OR SOME OF IT, THAT WE HAVE BEEN GENERATING OVER THE LAST COUPLE OF MONTHS. NOW, THIS DATA ISN'T AS EXCITING AS THE DATA SUPPLIED BY CHEMICAL MANUFACTURERS GROUP BECAUSE IT'S NEW, BUT WE'LL SHOW IT ANYHOW. DEAN NEPTUNE, WHO MOST OF YOU KNOW, IS GOING TO MAKE THE PRESENTATION ON THE VERIFICATION DATA.

Verification Procedures - Results to Date
By: Dean Neptune

I have a couple of things I want to share with you that are not exactly on this topic. Many of you have seen in the past a memo dealing with the priority pollutants we have observed to date in the screening activities across all the industrial categories. To give everybody an idea of how things are changing or not changing, since last year, we have put together an update of the priority pollutant frequency listing, tabulations, and descriptions.

This listing includes most of the screening samples taken to date.

In case you are interested, I have about 150 copies at the door on your way out, and if you're not interested, please leave it, maybe somebody else that is would like to have the copy.

As you know, there have been several different strategies that we have defined at this point as being acceptable for developing verification data. One of these recently appeared in the December 3rd Federal Register, methods 624 and 625, which is utilizing the GC/MS approach. The second approach was that also outlined and put together by Cincinnati on methods 601 through 613 which are ostensibly GC methods with the exceptions being one HPLC and one GC/MS

IN THE METHODS 601 THROUGH 613. IN ADDITION TO EMSL-CINCINNATI GC METHODS ARE THE ORGANIC CHEMICALS BRANCH WHICH ARE ALSO OSTENSIBLY GC METHODS.

AS YOU CAN SEE, WE HAVE A NUMBER OF DIFFERENT APPROACHES FROM AN ANALYTICAL STANDPOINT THAT CAN BE USED TO DEVELOP ANALYTICAL DATA. WHICH ONE IS BEST? WHICH ONE IS WORST? IT DEPENDS. WHAT IS THE REGULATORY STRATEGY THAT THE PROJECT OFFICER FOR THE INDUSTRIAL CATEGORY IS PLANNING ON USING CAN BE VERY IMPORTANT IN WHICH ANALYTICAL STRATEGY IS BEST SUITED. THE NATURE OF THE SAMPLE MATERIAL CAN DRIVE THE PROJECT OFFICER IN ONE DIRECTION OR ANOTHER. WITH THE ALL GC METHODOLOGIES, THERE IS ALWAYS SELECTED CONFIRMATION OF A MINIMUM OF 10 PERCENT OF THE SAMPLES BY GC/MS. SO IT ISN'T JUST A NONSPECIFIC DETECTOR THAT WE ARE BASING OUR DATA ON FOR AN IDENTIFICATION, BUT IT IS THE CHARACTERIZATION THAT WILL BE PROVIDED BY THE GC MEASUREMENT PLUS A MINIMUM OF 10 PERCENT, GC/MS CONFIRMATION OF THE IDENTIFICATION OF MATERIALS.

AS PART OF THE GC EFFORT FOR METHODS 601 THROUGH 613, PLUS THE ORGANIC CHEMICALS BRANCH, THERE ARE A NUMBER OF DIFFERENT ACCEPTABLE COLUMN PACKING MATERIALS FOR EACH METHOD. WE HAVE A SUPPLY FOR EPA USE THAT WE HAVE GOTTEN FROM SUPELCO, ALTHOUGH THERE ARE A NUMBER OF OTHER MANUFACTURERS THAT EITHER DO OFFER FOR SALE OR CAN OFFER FOR SALE VERY SIMILAR PRODUCTS;

THESE JUST HAPPEN TO BE PROVIDED FOR US UNDER CONTRACT BY SUPELCO. ALSO, SUPELCO HAS DONE SOME ADDITIONAL QUALITY ASSURANCE WORK TO DEMONSTRATE THE UTILITY OF THE COLUMN PACKING MATERIAL BEFORE WE ACCEPTED IT. AT THE DOOR ON YOUR WAY OUT, THERE WILL BE A LISTING OF ALL THE COLUMN PACKING MATERIALS, BY METHOD. THIS WILL BE PARTICULARLY INTERESTING IF YOU ARE TRYING TO DO SOME GC WORK. IF IT'S NOT OF REAL INTEREST TO YOU, PLEASE LEAVE THE COPY FOR SOMEBODY ELSE.

WHAT WE WANT TO START TO TALK ABOUT HERE TODAY IS SOME SELECTED RESULTS OF THE VERIFICATION STUDIES TO DATE. WE'RE GOING TO BE TALKING ABOUT ONE INDUSTRIAL CATEGORY; THIS IS OUR FIRST LOOK, SO WE DON'T HAVE ANALYSES LIKE THESE TO SHOW YOU ACROSS A LARGE NUMBER OF INDUSTRIAL CATEGORIES. WE ARE STARTING TO GET ENOUGH DATA SO THAT THIS COULD BE POSSIBLE.

AS I MENTIONED, THESE RESULTS ARE ON THE VERIFICATION STUDIES TO DATE. FOR THOSE OF YOU WHO PERHAPS AREN'T AS FAMILIAR WITH THE TERMINOLOGY AS IT IS BEING USED, LET ME GO BACK AND REFRESH YOUR MEMORY OR GIVE YOU A LITTLE BIT OF INFORMATION THAT WILL HELP YOU WHEN YOU GO BACK AND DO A LITTLE BIT MORE READING.

IN SCREENING STUDIES WE WERE TRYING TO MAKE A

DETERMINATION OF PRESENCE OR ABSENCE AND AN ESTIMATE OF CONCENTRATION. BY THE VERY NATURE OF WHAT WE WERE DOING IN SCREENING, WE WERE ACCEPTING FALSE POSITIVE IDENTIFICATIONS SO THAT WE DID NOT ELIMINATE ANY COMPOUNDS. THE REASON FOR THAT IS WE WERE GOING TO USE THE SCREENING DATA TO FOCUS OUR EFFORTS IN VERIFICATION. WHAT THAT ALL BOILS DOWN TO IS IF WE DIDN'T SEE IT IN SCREENING, THE CHANCES OF US MAKING A CONCERTED EFFORT TO LOOK FOR IT IN VERIFICATION WERE VERY SMALL. ONLY IF WE HAD SOME OTHER INFORMATION SUGGESTING THAT WE SHOULD HAVE BEEN SEEING IT FOR ONE REASON OR ANOTHER DID WE THEN GO BACK AND INCLUDE PRIORITY POLLUTANT COMPOUNDS THAT WERE NOT OBSERVED IN SCREENING. SO THE SCREENING DATA WAS VERY IMPORTANT TO US. IN VERIFICATION, ACTIVITIES WERE FOCUSED BY SCREENING. THE OBJECTIVES HERE WERE TO PROVIDE A CONFIRMATION OF THE IDENTIFICATIONS OF PRIORITY POLLUTANTS THAT WERE OBSERVED DURING SCREENING.

WE WERE ALSO TO DEVELOP QUANTITATIVE NUMBERS IN WHICH WE COULD STATE SOME CONFIDENCE FOR THE AMOUNT OF THOSE PRIORITY POLLUTANTS THAT WERE PRESENT. A THIRD OBJECTIVE WE ALSO HAD IN VERIFICATION WAS TO USE THIS DATA TO DETERMINE THE OVERALL TREATMENT CAPABILITIES OF DIFFERENT POLLUTION ABATEMENT SYSTEMS

FOR REMOVING PRIORITY POLLUTANT COMPOUNDS. THESE WERE THE STATED OBJECTIVES TWO YEARS AGO; THEY HAVEN'T WAVERED OR CHANGED ONE BIT.

I HAVE A COUPLE OF THINGS THAT I WANT TO POINT OUT TO YOU. I AM PROVIDING YOU WITH ACTUAL PLANT SAMPLING DATA. NOT CLEAN WATER SPIKES, NOT A BEST INDUSTRY, NOT A WORST INDUSTRY, BUT ONE OF THE INDUSTRIES IN WHICH WE HAVE DONE QUITE A BIT OF VERIFICATION STUDIES TO DATE, AND WHAT WE ARE GOING TO BE TALKING ABOUT IS POTENTIAL MANIPULATIONS THAT MAY BE DONE TO MEASURE LABORATORY PERFORMANCE OR A PROJECT OFFICER FOR A GIVEN INDUSTRIAL CATEGORY MAY DO TO DEVELOP EFFLUENT DISCHARGE STANDARDS FOR SPECIFIC PRIORITY POLLUTANTS.

IF YOU REMEMBER, I STARTED TALKING ABOUT 624 AND 625 AND 601 THROUGH 613, AND THE ORGANIC CHEMICALS BRANCH METHODS. THIS DATA IS BASED ON JUST THE GC/MS METHODS. THE 624, 625 WITH THE VERIFICATION QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS. WHAT WE HAVE DONE IS TO DETERMINE FROM THE DATA COLLECTED THE RECOVERIES FOR EACH OF THE PRIORITY POLLUTANTS IN THIS INDUSTRIAL CATEGORY THAT WERE SPIKED. THE FORMULA THAT YOU SEE UP HERE IS SIMPLY THAT USED IN DETERMINING THE PERCENT RECOVERY OF THE SPIKE FROM THIS; IF YOU'LL NOTICE, IT WAS BASED

UPON FIVE FACILITIES, FIVE SAMPLING EPISODES, AS WE CALL THEM. AN EPISODE BEING A VISIT TO ONE PLANT FOR A SAMPLING.

THERE WERE FOUR OF THESE PLANTS THAT WERE DONE BY ONE LABORATORY; THE FIFTH PLANT WAS DONE BY A SECOND LABORATORY. ALL THE DATA IS INCLUDED. THE OUTLIERS, THOSE DATA THAT WERE DETERMINED TO BE UNACCEPTABLE, WERE DETERMINED BY APPLYING A PLUS OR MINUS TWO STANDARD DEVIATIONS. SINCE THIS IS CONSIDERED TO BE A QUANTITATIVE QUESTION AND NOT A QUALITATIVE QUESTION, THOSE DETERMINATIONS IN WHICH THERE WAS 0 PERCENT RECOVERY, I.E., THE SPIKE OF THE PRIORITY POLLUTANT COULD NOT BE RECOVERED, WERE DELETED FROM THE CALCULATIONS AND NOT CONSIDERED. THERE WAS NO QUESTION OR DOUBT WHETHER THE MATERIAL WAS PRESENT OR NOT. THE SPECTRUM FOR THE MATERIAL, FOR INSTANCE, PHENOL WAS THERE, THE MATERIAL WAS THERE; THEREFORE, IT COULD NOT BE 0 OR ANY NUMBER LESS THAN 0. SO ALL THE VALUES WILL BE SOME NUMBER GREATER THAN 0 FOR THE RECOVERIES.

IN ADDITION TO THAT, FOR DETERMINING WHETHER THE PARTICULAR RUN WAS ACCEPTABLE OR NOT, AS COMPARED TO THE INITIAL LIMITS OF ACCEPTABILITY, DETERMINED ON THE INITIAL PHASE, THE LIMITS OF CONTROL WERE DETERMINED ONCE AGAIN BY USING THE FORMULA YOU SEE

UP HERE FOR THE R-C VALUE. WHERE DOES THIS FORMULA COME FROM? IF YOU LOOK IN METHOD 624 AND 625 IN THE QUALITY ASSURANCE/QUALITY CONTROL DIRECTIONS THAT WERE INCLUDED IN THE FEDERAL REGISTER DECEMBER THE 3RD OR IN THE NUMEROUS COPIES THAT WE'VE BEEN SENDING OUT AND DISTRIBUTING OVER THE PAST SIX MONTHS, YOU'LL FIND ALL OF THIS INFORMATION IN THE FORMULA IN THERE, PLUS EXAMPLES OF HOW THEY SHOULD BE UTILIZED.

FOR THIS INDUSTRIAL CATEGORY, IN THE ACID FRACTION, THE PERCENT RECOVERIES ARE PLUS OR MINUS TWO STANDARD DEVIATIONS. THAT WOULD BE CIRCA 95 PERCENT CONFIDENCE THAT ALL OF THE RECOVERY DATA FOR EACH OF THESE COMPOUNDS WOULD FALL WITHIN THAT RANGE. FOR INSTANCE, PHENOL. SOME NUMBER GREATER THAN 0, BUT LESS THAN 77.8 PERCENT, AS AN EXAMPLE. THE INDENTED COMPOUNDS THAT YOU SEE THERE ARE THE SURROGATE COMPOUNDS.

THE NEXT COLUMN PROVIDES THE TOTAL NUMBER OF VALUES IN THE CALCULATION, THE NUMBER OF OUTLIERS, IN OTHER WORDS, THE NUMBER OF VALUES THAT FOR ONE OF THE REASONS I GAVE ABOVE WAS THROWN OUT, AND THE NUMBER OF TIMES 0; IN OTHER WORDS, NO RECOVERY OF THE PRIORITY POLLUTANT SPIKE OCCURRED. ONE OF THE THINGS THAT WE ARE FINDING IS THAT BETWEEN 30 AND 40 DATA POINTS APPEARS TO BE AN ADEQUATE NUMBER OF DATA POINTS FROM WHICH TO

START TO DEVELOP PERCENT RECOVERIES AND POTENTIALLY LABORATORY CONTROL NUMBERS OR DISCHARGE STANDARDS FOR GIVEN PRIORITY POLLUTANT DISCHARGES. THE REASON WHY I'M POINTING THAT OUT IS THAT, IF YOU WILL REMEMBER, UNLIKE THE PRIORITY POLLUTANTS, THE SURROGATES, FOR INSTANCE, THE 2-FLUOROPHENOL, THE PENTAFLUROPHENOL, ALPHA/ALPHA-TRIFLUROMETACRESOL AND THE D_5 PHENOL, YOU'LL NOTICE THAT THE NUMBER OF VALUES ASSOCIATED WITH THOSE COMPOUNDS IS HIGHER THAN WITH THE OTHERS. THE REASON WHY THEY ARE ALL SPIKED AT 100 PARTS PER BILLION IN EACH SAMPLE. THEREFORE, THERE IS A LOT MORE DATA BECAUSE EACH AND EVERY SAMPLE WILL LEND US A DATA POINT.

YOU'LL NOTICE THERE IS QUITE A BIT OF VARIABILITY HERE, BUT ALL THE VALUES THAT ARE OCCURRING IN HERE ARE PROVIDING US WITH REASONABLE COVERAGE. IF YOU WOULD PLEASE KEEP IN MIND SOME OF THE THINGS YOU'RE SEEING FOR 2-NITROPHENOL AND 2-CHLOROPHENOL, THE MINIMUM RECOVERY OF ABOUT 20 PERCENT IN ONE CASE AND ABOUT 28 PERCENT IN THE OTHER.

IN THE BASE/NEUTRALS WE ARE SEEING APPROXIMATELY THE SAME OVERALL RECOVERY RANGE. ONE OF THE THINGS THAT ALLOWED US TO POOL MORE DATA IS A T TEST OF THE 2X, THE 10X AND THE 100X SPIKING LEVELS AND THE RECOVERIES ASSOCIATED WITH EACH OF THOSE SPIKING

LEVELS. THERE WAS NO DIFFERENCE IN THE PERCENT RECOVERY BETWEEN ANY OF THOSE LEVELS FOR ALMOST EVERY SINGLE PRIORITY POLLUTANT.

WE ONLY HAD ONE OR TWO IN WHICH THERE WAS A DIFFERENCE BETWEEN ANY OF THE LEVELS OF SPIKING, AS FAR AS THE PERCENT RECOVERY IS CONCERNED. SO ALMOST ACROSS THE BOARD NO DIFFERENCE IN RECOVERY, NO MATTER WHAT THE LEVEL OF SPIKING, NO STATISTICAL DIFFERENCE.

IF YOU WOULD, THE FIRST COMPOUND UP THERE, THE 1, 2, 4-TRICHLOROBENZENE WITH THE RECOVERY OF BETWEEN 28 AND 92 PERCENT, KEEP THAT IN MIND. HERE'S A VOLATILE FRACTION AND SOME OF THE THINGS THAT WE'RE FINDING IN THERE. YOU'LL NOTICE THAT, UNLIKE THE VALUES THAT WE WERE LOOKING AT IN THE ACID AND THE BASE NEUTRAL FRACTION, THAT A LARGE NUMBER OF THESE COMPOUNDS ARE PROVIDING US WITH RECOVERIES 150 - 200 PERCENT. OBVIOUSLY, SOMETHING IS OCCURRING WITH OUR INTERNAL STANDARD THAT WE'RE USING FOR QUANTITATION. UNLIKE IN THE ACID AND THE BASE NEUTRAL FRACTION WHERE THE INTERNAL STANDARD FOR QUANTIFICATION, THE D_{10} ANTHRACENE, IS ADDED IMMEDIATELY BEFORE ANALYSIS, IN THE VOLATILE FRACTION, THE INTERNAL STANDARDS THAT ARE USED IN THERE ARE ACTUALLY ADDED TO THE SAMPLE, PURGED FROM THE SAMPLE,

TRAPPED, DESORBED AND THEN SHUNTED INTO THE INSTRUMENT. OBVIOUSLY SOMETHING IS OCCURRING WITH THE INTERNAL STANDARDS AND THEY ARE NOT BEING PURGED, TRAPPED, OR DESORBED WITH EQUAL EFFICIENCIES. THIS MAY VERY WELL LEAD TO SOME SLIGHT ALTERATIONS ON THE PROTOCOL AS TO WHERE THE INTERNAL STANDARDS PERHAPS SHOULD BE ADDED TO PROVIDE US WITH SOME BETTER DATA.

IN THIS PARTICULAR GROUP, THE MAIN THING TO KEEP IN MIND THERE IS THE 1, 2-TRANS-DICHLOROETHYLENE, THE FOURTH FROM THE BOTTOM HERE, AND THE 1, 1, 1-TRICHLORETHANE, WHICH IS THE THIRD FROM THE TOP. THE REASON WHY THESE PARTICULAR COMPOUNDS HAVE BEEN SELECTED IS THAT RATHER THAN TRYING TO PROVIDE A GREAT DEAL OF DATA ACROSS THE BOARD FOR EVERYTHING, AND SELECTED NEITHER THE BEST NOR THE WORST OF ALL THE VALUES THAT WE HAD, TO THEN TAKE ONE MORE STEP BASED UPON THE ACCEPTABILITY OF THE RC VALUES WHICH YOU'LL SEE FOR EACH OF THE COMPOUNDS. THIS IS BASED UPON PAIRED OR DUPLICATE ANALYSES WHICH THE RC WAS CALCULATED. HOW A PROJECT OFFICER MAY DECIDE AND SELECT WOULD NOT BE THE ARBITRARY MANNER IN WHICH I HAVE MADE THAT SELECTION, BUT JUST, AS I POINTED OUT EARLIER, JUST FOR EXAMPLE, I COLLECTED A NUMBER OF DIFFERENT PRIORITY POLLUTANTS, NEITHER THE BEST NOR THE WORST, TO SEE WHAT MINIMUM LEVELS WE COULD, WITH

A STATED CONFIDENCE, MEASURE AND PERHAPS ESTABLISH LAB CONTROL LIMITS AND EFFLUENT DISCHARGE STANDARDS. SO IN MAKING THEIR CHOICES THERE WOULD BE A NUMBER OF POTENTIALLY DIFFERENT REASONS WHY THEY WOULD SELECT ONE PARTICULAR MATERIAL TO TRY AND REGULATE VERSUS ANOTHER OR REJECT ONE.

YOU'LL NOTICE THAT FOR ALL OF THEM HERE THE VALUES ARE CLOSE. THIS IS FOR THE 2X OR 20 MICROGRAMS PER LITER LEVEL AT WHICH THESE VALUES WERE TAKEN. SO WE'VE GOT, LIKE, FIVE DATA PAIRS PLUS ON THE CONTINUING PLUS THE INITIAL. BASED UPON THESE BEING ACCEPTABLE DATA POINTS WITHIN CONTROL AS COMPARED TO THE INITIAL AND THE CONTINUING VALUES, ONE CAN START, DEPENDING UPON YOUR STRATEGY, TO REGULATE A SPECIFIC PRIORITY POLLUTANT. FOR THE 2-NITROPHENOL, A LEVEL THAT WE CAN MEASURE ON A CONTINUING BASIS ACROSS THIS INDUSTRIAL CATEGORY WITH A 95 PERCENT CONFIDENCE THAT THE DATA MEASUREMENT WILL BE CORRECT, WILL BE 70 MICROGRAMS PER LITER; THAT COULD BE AN EFFLUENT DISCHARGE LIMIT AT THAT LEVEL. FOR THE 2-CHLOROPHENOL, 100 MICROGRAMS PER LITER. FOR THE 1,2,4-TRICHLOROBENZENE, 70 MICROGRAMS PER LITER. FOR THE 1,2-TRANS-DICHLORO-ETHYLENE, 30 MICROGRAMS PER LITER, AND FOR THE 1, 1, 1-TRICHLOROETHANE, 30 MICROGRAMS PER LITER.

OF COURSE EVERYONE, I'M SURE, REMEMBERS THAT THE

DISCHARGE REGULATIONS ARE GOING TO BE BASED UPON TREATMENT TECHNOLOGY RATHER THAN ON SOME ECOLOGICAL IMPACT OR HUMAN HEALTH IMPACT. THEREFORE, THE NUMBERS THAT WE'RE MOST INTERESTED IN MEASURING ARE THOSE THAT WOULD BE ASSOCIATED WITH THE POTENTIAL TREATABILITY FOR THESE COMPOUNDS. DR. STRYER, USING THE MOLECULAR ENGINEERING APPROACH, AND HE HAS PUBLISHED SEVERAL DIFFERENT VOLUMES ON THIS PARTICULAR APPROACH, HAS PROVIDED SOME THEORETICAL AND EMPIRICAL CONFIRMATIONS OF VALUES FOR VARIOUS PRIORITY POLLUTANTS AND THEIR TREATABILITY. THE LEVELS THAT HE HAS PROVIDED FOR THE PRIORITY POLLUTANTS ARE WELL WITHIN THE RANGE THAT WE'RE TALKING ABOUT. THEY ARE BETWEEN 10 AND 100 MICROGRAMS PER LITER. SO WE'RE WORKING IN THE SAME BALLPARK IN WHICH HIS MOLECULAR ENGINEERING APPROACH SHOWS THAT TREATMENT OR TREATABILITY HAS A POTENTIAL OF OCCURRING. DOES ANYBODY HAVE ANY QUESTIONS THEY'D LIKE TO ASK?

Question and Answer Session

MR. BEIMER: Bob Beimer, TRW. I would like to offer an alternative to your VOA recovery where you said that the problem was probably based on difficulties with the internal standard. I'd like to say that the way the recoveries are measured on the VOA portion of the analysis is that you do your spike sample, you run it, you turn around and spike superclean water at a similar level and do the analysis and you calculate recovery. It turns out that at least one of those internal standards is in a very clean region for most of the samples that we've ever dealt with, and I don't think the problem is with that, but the problem is with the fact that if you spike a real world sample you can probably purge it better than you can deionized or superclean water. The alternative, of course, is that when you standardize for the base neutral or acid fraction samples, you're standardizing with a concentration of material in a solvent and you're injecting that directly into the chromatograph. The corollary would be to take your standard and extract from deionized water and then analyze it and call that your standard, if you were going to relate it to the VOA portion of the analysis. What I am

SUGGESTING IS THAT, INDEED, YOU CAN PURGE MANY MATRIX WATERS BETTER THAN YOU CAN PURGE DEIONIZED WATER. WHEN YOU MAKE UP YOUR STANDARDS BY PURGING DEIONIZED WATER, THAT'S WHERE YOUR ERRORS ARE COMING IN OR YOUR HIGH NUMBERS FOR RECOVERY.

DR. NEPTUNE: I THINK YOU HAVE A CORRECT STATEMENT IN THAT THERE ARE MORE THAN ONE DIFFERENT POTENTIAL SUGGESTION AS TO WHAT THE PROBLEM MAY BE, AND THERE MAY BE SEVERAL THINGS INTERACTING. I WAS JUST MENTIONING THAT WAS ONE POTENTIAL POSSIBILITY OF WHAT THE PROBLEM WAS. ONE OF THE THINGS THAT WAS POINTED OUT THIS MORNING BY SOUTHWEST RESEARCH INSTITUTE WAS THAT THEY ROUTINELY ADDED SALT TO THEIR MICROEXTRACTION TECHNIQUE TO INCREASE THE YIELD IN THEIR EXTRACTION, AND THE DIRTIER THE SAMPLE OR THE HIGHER CONCENTRATION OF CONTAMINANTS, ONE WOULD EXPECT A YIELD INCREASE.

MR. BEIMER: WHAT IS BEING SAID HERE IS THE FACT THAT EVEN WHEN YOU USE DEIONIZED WATER TO PURGE FROM, YOU HAVE A MATRIX EFFECT. WHEREAS IF YOU STANDARDIZE SIMPLY BY MAKING UP A KNOWN CONCENTRATION IN A SOLVENT AND INJECTING IT INTO A GAS CHROMATOGRAPH YOU DON'T HAVE ANY OF THOSE MATRIX EFFECTS. SO YOU WOULD EXPECT IT IN EVERYTHING ELSE YOU DO THAT YOU'RE GOING TO HAVE LESS THAN 100 PERCENT

RECOVERY WHEN YOU'RE DOING THE GC/MS TYPE ANALYSIS. THE RIGHT WAY WOULD BE TO MAKE UP YOUR STANDARD AND INJECT IT DIRECTLY ON THE COLUMN, DON'T PURGE IT FROM DEIONIZED WATER, AND YOU'D FIND ALL YOUR RECOVERIES GO DOWN WELL BELOW 100 PERCENT BECAUSE WE'VE TRIED IT.

DR. NEPTUNE: THAT IS ONE OF THE OPTIONS THAT WE WERE LOOKING AT, WHERE DOES ONE ENTER INTO THE ANALYTICAL SCHEME, THE STANDARD FOR QUANTIFICATION, AND THAT ONE WOULD BE AT THE SAME TIME YOU'RE SWEEPING, DESORBING FROM YOUR TRAP YOUR PRIORITY POLLUTANTS, AND SWEEPING IT ON TO THE COLUMN WHICH IS WHAT YOU'RE SUGGESTING. RIGHT?

MR. BEIMER: YES.

MR. MILLER: I'M MIKE MILLER FROM MOBIL RESEARCH AND DEVELOPMENT AND I HAVE TWO QUESTIONS FOR YOU. THE FIRST RELATES TO THE SAME PROBLEM, THE VOAS. WHAT INTERNAL STANDARD WERE YOU USING FOR THAT; THE FEDERAL REGISTER DOES NOT SPECIFY A COMPOUND TO BE USED AS AN INTERNAL STANDARD IN METHOD 624.

DR. NEPTUNE: THERE WAS A TOTAL OF THREE: CHLOROBROMOBUTANE; THE PROPANE WHICH IS SUGGESTED IN THERE, BUT HAS NOT BEEN AVAILABLE, AND 1,4-DICHLOROBUTANE.

MR. MILLER: THOSE ARE SUGGESTED AS SURROGATE STANDARDS RATHER THAN INTERNAL STANDARDS.

DR. NEPTUNE: NO, THOSE WERE THE INTERNAL STANDARDS.

MR. MILLER: YOU USED THEM AS INTERNAL STANDARDS; I SEE.

DR. NEPTUNE: YES, FOR QUANTIFICATION.

MR. MILLER: THE SECOND QUESTION IS, ON MOST OF THE DATA THAT YOU SHOWED UP THERE, YOU REJECTED A CERTAIN NUMBER OF OUTLYING DATA POINTS. WHAT WAS THE CRITERIA FOR THEIR REJECTION?

DR. NEPTUNE: THAT WAS WHAT I WAS TRYING TO DISCUSS TO START WITH. REJECTED DATA WERE EITHER ZERO VALUES, IN OTHER WORDS, 0 PERCENT RECOVERY. THE RATIONALE THAT I GAVE YOU FOR NOT ACCEPTING 0S WAS THAT THIS WAS A QUANTITATIVE PROBLEM AND NOT A QUALITATIVE PROBLEM. IT WAS NOT A QUESTION OF WHETHER THE MATERIAL WAS PRESENT OR ABSENT.

MR. MILLER: YOU HAD TWO COLUMNS UP THERE, ONE WAS THE 0S; HOW ABOUT THE OUTLYING ONES?

DR. NEPTUNE: IN THE SECOND

ONE WAS THE OUTLIERS; AS I MENTIONED, ANYTHING THAT DID NOT FALL WITHIN THE LIMITS OF ACCEPTABILITY WHICH WAS PLUS OR MINUS TWO STANDARD DEVIATIONS.

MR. MILLER: WAS THE STANDARD DEVIATION SIGMA DETERMINED WITH THOSE DATA POINTS INCLUDED OR WITHOUT THEM?

DR. NEPTUNE: WITH THEM.

MR. MILLER: IN THE FIRST SLIDE THAT YOU HAD UP THERE, THERE WAS A SET OF DATA, I THINK IT WAS THE SECOND LINE DOWN, I DON'T REMEMBER THE COMPOUND OFFHAND, WHERE YOU HAD 37 DATA POINTS INCLUDED, 11 DATA POINTS EXCLUDED AS OUTLIERS.

DR. NEPTUNE: CORRECT.

MR. MILLER: THAT MEANS THAT OUT OF 48 DATA POINTS, YOU EXCLUDED 11 OF THEM ON THE BASIS OF THE FACT THEY FELL OUTSIDE TWO SIGMA; THAT'S NEARLY ONE-QUARTER OF YOUR DATA POINTS, WHEREAS TWO SIGMA SHOULD HAVE ONLY FIVE PERCENT FALLING OUTSIDE THAT. HOW IS THAT MATHEMATICALLY EVEN POSSIBLE?

DR. NEPTUNE: I CAN EXPLAIN THAT FOR YOU. INITIALLY, IT WAS DETERMINED USING ALL THE DATA POINTS. IN OTHER WORDS, IN THIS CASE IT WOULD HAVE BEEN SOME 48 DATA POINTS, AND THE DETERMINATION WAS MADE HOW MANY DATA POINTS OF

THOSE FELL OUTSIDE, AND THOSE OUTLIERS WERE DELETED. AT THAT POINT, WHEN THE INITIAL DATA POINTS WERE DELETED, THE STANDARD DEVIATION WAS THEN BASED UPON THE DATA BASE WITH THOSE OUTLIERS DELETED. THE QUESTION YOU ASKED ME AT FIRST WAS WERE THEY INCLUDED IN THE INITIAL DETERMINATION OF STANDARD DEVIATION. THE ANSWER IS YES. WERE THEY IN THE FINAL? THE ANSWER IS NO.

MR. MILLER: SO DO I UNDERSTAND YOU CORRECTLY, THEN, THAT YOU INCLUDED ALL THE DATA POINTS INITIALLY?

DR. NEPTUNE: CORRECT.

MR. MILLER: THEN YOU CALCULATED TWO SIGMA; THREW OUT THOSE THAT WERE OUTSIDE THAT LIMIT.

DR. NEPTUNE: CORRECT.

MR. MILLER: RECALCULATED A STANDARD DEVIATION.

DR. NEPTUNE: CORRECT.

MR. MILLER: DID YOU AGAIN THROW OUT THOSE WHICH WERE NOW OUTSIDE THE RECALCULATED TWO SIGMA?

DR. NEPTUNE: IF THERE WERE ANY THAT FELL INTO THAT CATEGORY, YES.

MR. MILLER: SO YOU HAD A

SMALLER VALUE AND YOU RECALCULATED THE STANDARD DEVIATION, AGAIN THROWING OUT ANYTHING THAT WAS OVER TWO SIGMA.

DR. NEPTUNE: CORRECT.

MR. MILLER: WHEN YOU FINISH, THEN, YOU SAY THAT 95 PERCENT OF ALL RESULTS SHOULD FALL WITHIN THAT FINAL CATEGORY?

DR. NEPTUNE: OF THAT DATA BASE, THAT SELECTED DATA BASE.

MR. MILLER: IS THAT STATISTICALLY SOUND?

DR. NEPTUNE: THE SELECTION OF DETERMINING OUTLIERS, WE'VE ASKED THAT SAME QUESTION AND THE ANSWER THAT WE HAVE BEEN GIVEN IS YES.

SOME OF THE THINGS THAT WERE ACTUALLY OCCURRING WITHIN THE SAMPLES THAT WERE GIVING SOME OF THESE RATHER LARGE RECOVERIES, IN SOME SAMPLE MATRICES, THE D_{10} ANTHRACENE WHICH WAS USED AS THE INTERNAL STANDARD WAS FOR ONE REASON OR ANOTHER BEING OXIDIZED. ONE OF THE THINGS WE KNOW IT WAS BEING OXIDIZED TO WAS THE ANTHROQUINONE, AND HENCE YOUR INTERNAL STANDARD, AS IT WAS ADDED, WAS DISAPPEARING, AND AS IT WOULD DISAPPEAR, SOMETIMES AS MUCH AS TWO-THIRDS OF IT WOULD DISAPPEAR WITHIN A VERY FEW SECONDS. CONSEQUENTLY ONE WOULD GET A MUCH LARGER NUMBER OR

PERCENT RECOVERY BASED UPON THE INTERNAL STANDARD THERE. THAT SITUATION WAS OCCURRING IN THOSE SELECTED SAMPLES. ARE THERE OTHER QUESTIONS?

MR. RONAN: RESTATE THE QUESTION.

DR. NEPTUNE: WHY DON'T I JUST LET THE GENTLEMAN WHO RAISED THE QUESTION RESTATE IT.

MR. MILLER: I WAS QUESTIONING THE STATISTICAL VALIDITY OF CALCULATING A STANDARD DEVIATION BASED ON A SET OF DATA AND THEN THROWING OUT THE DATA POINTS WHICH FELL OUTSIDE TWO SIGMA, CONTRACTING THAT STANDARD DEVIATION, AGAIN THROWING OUT DATA THAT WERE MORE THAN TWO STANDARD DEVIATIONS OF THE CONTRACTED VERSION, GETTING A YET SMALLER CONTRACTED VERSION AND AGAIN THROWING OUT DATA, AND FINALLY ARRIVING AT SOME VALUE WHERE YOU NO LONGER HAD ANYTHING FALLING OUTSIDE OF PLUS OR MINUS TWO SIGMA AND THEN STATING THAT IN A TYPICAL SET OF ANALYSES, 95 PERCENT OF THE RESULTS SHOULD FALL WITHIN THAT VERY NARROW STANDARD DEVIATION, OR PLUS OR MINUS TWO SIGMA. MY ORIGINAL QUESTION WAS QUESTIONING THE STATISTICAL VALIDITY OF REPEATEDLY THROWING OUT DATA AND RECALCULATING THE STANDARD DEVIATIONS.

DR. NEPTUNE: SEVERAL EXPLANATIONS WERE GIVEN FOR THE NUMBERS THAT WERE BEING DELETED. THE OBSERVATIONS THAT WERE BEING DELETED WERE THOSE THAT ONE HAD AN EXCUSE FOR OTHER REASONS TO ALSO DELETE. I GAVE YOU ONE EXAMPLE, THE D_{10} ANTHRACENE DISAPPEARING.

MR. MILLER: IF THAT IS THE REASON THAT OUTLIERS ARE EXCLUDED, THEN ANY DATA FOR WHICH YOU HAVE REASON TO BELIEVE THEY ARE NOT VALID SHOULD BE EXCLUDED BEFORE ANY STANDARD DEVIATION IS CALCULATED. ALL DATA SHOULD BE EXCLUDED.

DR. NEPTUNE: IT ESSENTIALLY RESULTED IN THAT VERY SAME ACTIVITY OCCURRING.

MS. HOLTZCLAW: WE DID THIS RATHER THAN JUST ARBITRARILY SAYING WE KNOW THERE WAS A PROBLEM. ONE OF THE PROBLEMS THAT WE DEAL WITH IS WE DON'T SEE ALL DATA IN THE LABORATORY. WITH THE TWO SIGMA DEVIATION WE WERE ABLE TO DELETE, IN MANY CASES, SEVERAL ANOMALOUS DATA POINTS. WE WENT BACK IN SOME CASES SEVERAL TIMES THROUGH THE DATA NARROWING OUR LIMITS.

THE REASON WE'RE DOING THIS IS NOT NECESSARILY TO BE SETTING LIMITS DIRECTLY ON THIS POINT, BUT TO GIVE US A CUT TO BE ABLE TO GO BACK TO THE LABORATORIES AND SAY, THESE ARE THE NUMBERS THAT WE FEEL

ARE FALLING OUT OF RANGE, LOOK AT YOUR DATA, RECALCULATE YOUR DATA, RECHECK YOUR INITIAL REPORTING. IF NECESSARY, GO BACK AND RESHOOT THAT SAMPLE; THAT'S WHAT THIS FIRST CUT IS GIVING US. IT'S GIVING US A STARTING POINT TO TRY TO HANDLE THE MASSES OF DATA THAT ARE COMING IN.

DR. NEPTUNE: AS I MENTIONED TO YOU, PERHAPS THE MOST IMPORTANT PART, THE OBSERVATIONS THAT ARE DISAPPEARING ARE ALSO THE ONES IN WHICH THE LABORATORY THEMSELVES RAISED A QUESTION AS TO THEIR VALIDITY.

MS. HOLTZCLAW: IN THE MAJORITY OF CASES, THERE IS A LEGITIMATE REASON FOR THROWING THEM OUT. IN THE LONG RUN, WE ARE WORKING WITH STATISTICIANS, WE ARE TRYING TO FIND THE BEST WAY, BUT WHEN YOU PICK ANY STATISTICAL METHOD OF WORKING THE DATA, YOU'RE NOT GOING TO HAVE EVERYBODY HAPPY WITH IT. WE MAY ULTIMATELY HAVE TO SAY WE HAVE TO INCLUDE THAT NUMBER, BECAUSE IT'S JUST A MATRIX PROBLEM THAT'S GOING TO OCCUR.

MR. MILLER: HAVE YOU TRIED TAKING ACTUALLY RANDOMLY GENERATED DATA, GENERATED ANY WAY THAT YOU WANT TO, AND APPLYING THAT SAME PROCEDURE TO IT AND SEEING HOW MANY DATA YOU CAN THROW OUT THAT WAY?

MS. HOLTZCLAW: No, we have not.

MR. MILLER: I suspect you'll throw out over half.

MS. HOLTZCLAW: Let me give you an example of going through this. We had one set in which we had about 30 numbers. Out of these 30, the majority of them fell within the range of 40 to 70 percent recovery, and when I say the majority, I mean about 20 of them. The others, we had about four that we could link directly from information we had gotten at the laboratory, that hit about 250 or 500; the rest of them varied up and down. There were some negative recoveries, there were some 0 percent recoveries, they varied on up to one that was at 1,200. We could have set our range to fit that 1,200, but when you look at the data, there is something wrong with that 1,200. It gives us a manageability with the data; that's how we're using it.

MR. MYERS: I might say that that's exactly how you identify outliers in ASTM27-77 procedure.

MS. HOLTZCLAW: If you have a better suggestion, we're open. We've been

WORKING WITH ALL OF THE STATISTICIANS WE CAN GET TOGETHER AND NOT A ONE CAN GIVE US WHAT EVERYBODY AGREES IS A GOOD WAY OF THROWING OUT OUTLIERS.

MR. PATTERSON: A. R. PATTERSON, ALLIED CHEMICAL. THE IDEA OF THE EXERCISE WAS TO EVALUATE THE METHOD AND FIND OUT WHAT THE RECOVERY IS, AND REALLY WHAT YOU FOUND OUT IS THAT IN ABOUT TWO-THIRDS OF THE SAMPLE, YOU'RE WITHIN 95 PERCENT CONFIDENCE; IN ONE-THIRD OF THE SAMPLES, YOU'RE ALL OVER THE BALLPARK.

MS. HOLTZCLAW: BUT WE DON'T KNOW WHY YET.

MR. PATTERSON: I KNOW, BUT IT'S STILL THE SAME PEOPLE USING THE SAME METHOD.

MS. HOLTZCLAW: THAT'S AGREED, BUT YOU'VE GOT TO REALIZE THAT WE'RE WORKING IN SEVEN DIFFERENT LABORATORIES. WE'RE WORKING, IN MANY CASES, ROUND-THE-CLOCK SHIFTS; WE'RE WORKING WITH VARYING LEVELS OF TECHNICIANS DOING THE WORK.

MR. PATTERSON: WELL, THAT'S NOT GOING TO BE ANY DIFFERENT FROM THE WAY IT WILL BE USED.

MS. HOLTZCLAW: BUT I'M SAYING WE HAVE TO HAVE SOME WAY TO GO BACK AND DOUBLE-CHECK SOME OF THOSE NUMBERS.

DR. NEPTUNE: ONE OF THE THINGS THAT MAKES IT LOOK LIKE WE'RE JUST THROWING OUT A NUMBER HERE OUT OF A SERIES AND A NUMBER THERE. THAT IS NOT THE CASE. THESE ARE USUALLY WHOLE SAMPLING EPISODES THAT ARE DISAPPEARING. IN OTHER WORDS, A WHOLE DAY'S WORTH OF DATA, NOT ONE DATA POINT OUT OF A RUN FOR THAT DAY ARE WE THROWING OUT.

MR. PATTERSON: DR. ROGERS WAS HERE YESTERDAY, AND I SHARE HIS OPINION ON THE THING, IF I RUN A SERIES OF MEASUREMENTS AND THEN I CALCULATE 95 PERCENT CONFIDENCE FOR THOSE MEASUREMENTS, I CAN'T, IF I THROW OUT A WHOLE BUNCH OF THEM. THEN, OBVIOUSLY, THERE'S ONLY TWO-THIRDS OF THE DATA BEING CONSIDERED AND THAT'S WHAT MOST OF YOUR MEASUREMENTS INDICATED.

DR. NEPTUNE: IT MAKES SENSE FROM THE STANDPOINT THAT SOMETHING WAS WRONG WITH THE ANALYSES ON THOSE DAYS AND THIS, ALSO, CONFIRMS THE FACT THAT THOSE SAME NUMBERS SHOULD NOT BE A PART OF THE DATA BASE.

MS. HOLTZCLAW: WHEN WE GO BACK, WE MAY FIND THAT ANOTHER THIRD OF THOSE FALL BACK IN. THIS IS A FIRST CUT OF THE DAY.

MR. PATTERSON: I MEAN, THE SAME THING IS LIKELY TO HAPPEN WHEN SOMEONE ELSE DOES

IT LATER ON.

DR. NEPTUNE: THE SAME THING IS LIKELY TO HAPPEN...I DON'T UNDERSTAND THE QUESTION.

MR. PATTERSON: THAT ONE SET OF THEM ARE GOING TO BE BAD NUMBERS, BUT IT STILL LOOKS TO ME LIKE TWO-THIRDS CHANCE OF GETTING...AS HIGH AS 95 PERCENT, IF I RAN THE SAME NUMBERS HERE.

DR. NEPTUNE: OF THE DATA BASE, IT'S A 95 PERCENT CHANCE.

MR. PATTERSON: NOT ON THE ENTIRE DATA BASE.

DR. NEPTUNE: I MENTIONED IT WAS A SELECTED DATA BASE AND THERE WAS A RATIONALE FOR SELECTING IT. SO ON THE SELECTED DATA BASE, IT'S TRUE.

MR. DAVIS: ABE DAVIS, HOOKER CHEMICAL. YOU REALLY HAVE TWO THINGS YOU'RE CONSIDERING, AND I DON'T THINK IT'S FAIR TO THROW OUT 0 OR 1,200 PERCENT OR ANY NUMBER UNTIL YOU CONSIDER BOTH THE FACT THAT YOU MUST DETERMINE AN INTERNAL STANDARD WHICH IS ALLOWED TO VARY AND THE COMPONENT OF INTEREST THAT YOU'RE MEASURING WHICH IS ALLOWED TO VARY, AND THEREFORE 0 IS JUST AS REAL, EVEN THOUGH YOU'VE ADDED MATERIAL TO IT, AS 110 OR 223 BECAUSE THAT IS A TRUE NUMBER. I THINK THAT, THE LITTLE

I KNOW ABOUT STATISTICS, THIS WHOLE PROBLEM IS FRAUGHT WITH NOTHING BUT PROBLEMS, TO BE BLUNT. YOU'RE TRYING TO COME OUT WITH SOME MEASURE AND I THINK WHAT YOU HAVE TO SAY ON SOMETHING THAT YOU THROW OUT THIS NUMBER OF SAMPLES, THAT YOU'VE GOT TO GO BACK AND CORRECT THE METHOD AND REALLY NOTHING SHOULD BE ACCEPTED.

MS. HOLTZCLAW: WE NEED TO GO BACK AND FIRST CORRECT THE NUMBERS IF THEY NEED CORRECTION. WHAT YOU'RE SEEING HERE IS A FIRST CUT FROM THAT DATA BASE. WE HAVE NO WAY OF KNOWING WHEN WE GET NUMBERS FROM OUR LABORATORIES IF THEY WERE PROPERLY CALCULATED.

MR. MILLER: AS I UNDERSTAND WHAT YOU'RE SAYING, THEN, WHAT YOU'RE SAYING IS THAT THE DATA BASE ON WHICH YOU DID THESE CALCULATIONS IS UNRELIABLE.

DR. NEPTUNE: NO, INCORRECT.

MS. HOLTZCLAW: NO, THAT'S NOT WHAT I'M SAYING.

MR. HENDERSON: WELL, THE THING PEOPLE CAN'T UNDERSTAND AND I AGREE WITH IT, YOU'RE DETERMINING A PRECISION LEVEL WHICH OUGHT TO INCLUDE 19 OUT OF 20 POINTS AND, IN FACT, IT ONLY

INCLUDES 12 OUT OF 20 OR SOME SUCH THING.

MS. HOLTZCLAW: ON A FIRST CUT.

DR. NEPTUNE: IS THAT A STATEMENT OR A QUESTION, JIM?

MR. HENDERSON: THAT'S A SUMMARY OF THE OBJECTION TO THE METHOD OF CALCULATION.

MR. TELLIARD: WAIT. THE POOR PEOPLE OVER HERE ARE TRYING TO TAKE IT DOWN AND WE HAVE STRANGE VOICES APPEARING AND SO FORTH. IF YOU'RE GOING TO TALK, GO TO THE MICROPHONE AND IDENTIFY YOURSELF BECAUSE THEY'RE GOING TO BEAT ME UP IF YOU DON'T DO THAT.

MR. HENDERSON: I'M HOLDING ONTO THIS MICROPHONE AND I'M JIM HENDERSON WITH CARBORUNDUM. I THINK PEOPLE MIGHT BE A LITTLE MORE SATISFIED IF, WHEN YOU CHECK THE NUMBER AND THE ANALYSIS AND THE CALCULATIONS APPEAR TO HAVE BEEN DONE CORRECTLY, YOU PUT THAT NUMBER BACK INTO THE DATA BASE.

DR. NEPTUNE: RIGHT.

MS. HOLTZCLAW: YES.

DR. NEPTUNE: IN OTHER WORDS, THERE WAS A REASON FOR EXCLUDING THE NUMBER. IN OTHER WORDS, IF THERE WAS A RATIONALE OR REASON

FOR EXCLUDING THE NUMBER, IT WAS THERE. IN OTHER WORDS, IN THE LABORATORY, INDEPENDENTLY OF OURSELVES, WAS PROVIDING THE INFORMATION WHEN THERE WERE PROBLEMS WITH NUMBERS OR WITH A GIVEN RUN.

MR. MYERS: THERE IS NO PROBLEM. YOU CAN GO BACK AND PUT THAT DATA POINT BACK INTO THE DATA BASE AND RECALCULATE AGAIN.

MS. HOLTZCLAW: THAT'S CORRECT. LET ME PUT IT ANOTHER WAY. WHAT WE'RE TRYING TO DO AT THIS POINT IS TO SET SOME TYPE OF QUALITY CONTROL LIMITS ON THE DATA THAT WE'RE WORKING WITH, THE REASON BEING THAT WE ARE WORKING WITH DATA FROM A NUMBER OF LABORATORIES; IN SOME CASES WE ARE DEALING WITH DATA THAT IS GENERATED BY INDUSTRY, AND WE'VE GOT TO HAVE A COMMON POINT AT WHICH TO START. A YEAR FROM NOW WE'D LIKE TO BE ABLE TO TAKE THAT SUBCATEGORY AND TELL PEOPLE THAT WHEN THEY DID SAMPLES IN THAT THAT THEY SHOULD FALL WITHIN THIS RANGE OF PERCENT RECOVERIES AND THE DIFFERENCE BETWEEN DUPLICATE SAMPLES. WHAT WE ARE TRYING TO DO AT THIS POINT IS BEGIN TO SET SOME QUALITY CONTROL LIMITS FOR THAT DATA AND BY DOING THAT, A QUALITY CONTROL LIMIT OF MINUS 170 PERCENT TO PLUS 350 PERCENT DOES US NO GOOD WHATSOEVER. SO WE'VE GOT TO TAKE IT DOWN AND WE'VE GOT TO BEGIN SAYING

WHICH NUMBERS ARE OBVIOUSLY PROBLEMS. NOW, THEY MAY BE MATRIX PROBLEMS. THEY MAY BE CALCULATION PROBLEMS, BUT AT THIS POINT THEY ARE PROBLEM NUMBERS. THEN, WE'VE GOT TO GO BACK AND FIND OUT WHY THOSE NUMBERS ARE PROBLEMS. WE HAD ONE WHOLE EPISODE THAT DROPPED OUT WHEN WE DID THIS. THERE MAY WELL BE A PROBLEM WITH THAT PARTICULAR PLANT. IF THAT'S THE CASE, THOSE NUMBERS NEED TO BE BACK IN THERE.

IF, HOWEVER, THE PROGRAM THAT THE PERSON WAS CALCULATING THEM WITH WAS INCORRECT, THEN THOSE NUMBERS MAY BE NEEDED TO BE THROWN OUT, RECALCULATED. WE ARE NOT SAYING THAT WE'RE GOING TO TAKE A NUMBER OF 50 PARTS PER BILLION AND MULTIPLY IT BY A PERCENT RECOVERY OF 50 PERCENT AND COME UP WITH OUR NUMBER; BUT WE ARE SAYING THAT WE'RE TRYING TO BEGIN TO DO SOMETHING WORKABLE WITH OUR DATA. WE'RE TRYING TO BEGIN TO GET IT INTO A RANGE THAT WE HAVE SOME CONFIDENCE IN, AND WHAT WE'RE DOING FOR NOW IS THEN GOING BACK, LOOKING AT THE DATA, REWORKING THAT RANGE. HOPEFULLY, WHEN WE HAVE ENOUGH DATA, AND WE'RE TALKING IN MOST CASES ABOUT 40 TO 50 DATA POINTS, WHICH IS A NUMBER OF PLANTS TO HAVE TO ANALYZE IN A SUBCATEGORY, THAT WE WILL BE ABLE TO SAY, THIS IS THE CONFIDENCE THAT WE HAVE IN THIS DATA. AS FAR AS THE POINT ABOUT DROPPING 0S, WE ARE CONSIDERING THOSE TO BE NONDATA

POINTS AT THIS TIME BECAUSE THEY DON'T TELL US ANYTHING ABOUT THE SAMPLE. IN OTHER WORDS, WHEN WE HAVE A 0 PERCENT RECOVERY, THEY ARE NOT, AT THIS TIME, TELLING US ANYTHING ABOUT THAT SAMPLE. NOT WHEN WE'RE TRYING TO ACHIEVE THE CONTROL LIMITS.

DR. NEPTUNE: WE'VE GOT ONE LAST QUESTION HERE.

MR. MYERS: I DON'T HAVE A QUESTION. MY NAME IS HARRY MYERS, I'M WITH NUS CORPORATION. IN TREATING ANY BODY OF DATA, IF YOU ESTABLISH A STANDARD DEVIATION FOR THAT BODY OF DATA AND APPLY YOUR T VALUES, IF YOU WANT TO GO TWO STANDARD DEVIATIONS, YOU WILL IDENTIFY A CERTAIN NUMBER OF OUTLIERS. YOU MUST REITERATE YOUR EVALUATION AND RE-ESTABLISH A NEW STANDARD DEVIATION EXCLUDING THOSE OUTLIERS.

DR. NEPTUNE: THAT'S EXACTLY WHAT WAS DONE.

MR. MYERS: AND THAT'S EXACTLY WHAT YOU'RE DOING. IT EXACTLY FOLLOWS THE PROCEDURES FOR IDENTIFICATION OF OUTLIERS IN ASTM27-77, THERE'S NO PROBLEM WITH THAT.

MR. TAYLOR: MY NAME IS PAUL TAYLOR, I'M WITH CALIFORNIA ANALYTICAL LABS. I HAVE TWO COMMENTS. FIRST OF ALL, DEAN MADE A MISTAKE IN

PUTTING THIS SLIDE TOGETHER AND PRESENTING IT AS, OR MANY OF US TAKING IT AS, A FINAL PRODUCT. IT'S ACTUALLY A WORKING DOCUMENT THAT'S BEING USED TO SET PERFORMANCE CRITERIA FOR ANALYTICAL LABORATORIES AND THAT'S EXACTLY WHAT HE'S DOING. WHETHER THEY THROW OUT DATA FOR THE FIRST 25 PERCENT OF THE FIRST 40 DATA POINTS IS PERHAPS UPSETTING TO SOME OF YOU, BUT IF YOU'RE DOING IT YOURSELF IN YOUR OWN LABORATORY, AND USING IT AS A PERFORMANCE, DEVELOPING A PERFORMANCE CRITERIA, YOU WOULD PROBABLY DO THE SAME THING AT THE START. THE PROBLEM IS, IF DEAN WERE DOING THIS WITH 5,000 DATA POINTS WITH AN ESTABLISHED DATA BASE AND STILL THROWING THE THINGS OUT, WELL, THAT, YOU KNOW, ARBITRARILY, AS MANY OF YOU SEEM TO BE TAKING IT, THEN YOU PROBABLY SHOULD GET A ROPE AND STRING HIM UP.

DR. NEPTUNE: THANKS, PAUL.

MR. TAYLOR: I WAS ONLY TRYING TO HELP, DEAN.

DR. NEPTUNE: IF YOU WOULD, PLEASE DON'T FORGET THERE WILL BE TWO HANDOUTS ON THE WAY OUT, ONE ON THE PRIORITY POLLUTANT FREQUENCY LISTING AND ONE ON THE GC COLUMN PACKING MATERIAL.

MR. TELLIARD: ON THE WAY OUT THERE WILL ALSO BE A SET OF COPIES OF THE

304H PROPOSED METHODOLOGY. THERE'S ONLY 120 OF THEM; IF YOU HAVE A COPY, PLEASE DON'T TAKE THEM.

TOMORROW WE START AT 8. IT'S ONLY 4:30, SO IF ANYBODY HAS ANYTHING THEY WANT TO VOICE, VENT, OR WHATEVER, WE'LL HAVE SOME TIME IN THE MORNING.

JANUARY 18, 1980

INTRODUCTION

BY: WILLIAM TELLIARD

MR. TELLIARD: FOR THOSE OF YOU WHO WERE FORTUNATE ENOUGH TO HAVE AN AGENDA OF THIS MEETING, A VERY RARE ITEM, I UNDERSTAND, YESTERDAY WE CUT SHORT AND DID NOT HAVE AN OPPORTUNITY FOR THE OPEN SESSION, WHICH WAS SOMETHING SCHEDULED DUE TO THE FACT THAT A NUMBER OF PEOPLE HAD SOME COMMENTS THAT THEY WANTED TO TAKE AN OPPORTUNITY TO GIVE YOU THEIR THOUGHTS ON A COUPLE OF MATTERS. SO FOR THE NEXT 30 MINUTES WE WILL BE GLAD TO TALK TO YOU ABOUT ANYTHING YOU WANT.

MR. RICE: I AM JAMES RICE. I AM A CONSULTING ENGINEER. I AM HERE TODAY IN MY CAPACITY AS A CONSULTANT TO THE UTILITY WATER ACT GROUP, WHICH IS AN AD HOC ORGANIZATION REPRESENTING THE STEAM ELECTRIC POWER GENERATING INDUSTRY IN THE RULE-MAKING THAT EPA IS CONDUCTING. ONE OF THE ITEMS THAT WE ARE VERY MUCH CONCERNED WITH DEALS WITH METHOD DETECTION LIMITS. I GATHER SOME MENTION WAS MADE OF THIS ON WEDNESDAY; I WAS NOT ABLE TO BE HERE FOR THAT MEETING. WE ARE VERY MUCH CONCERNED WITH DETECTION LIMIT DEFINITIONS, PARTICULARLY AS THEY HAVE APPEARED IN THE PROPOSED CONSOLIDATED DRAFT PERMIT ON THE DEFINITIONS

GIVEN THEREIN FOR THEM AND THE USE MADE OF THEM. THAT PLACES THEM SQUARELY IN THE EFFLUENT LIMITATION BUSINESS INASMUCH AS THE APPLICATION BASE LIMITS ARE A MULTIPLE OF THE DETECTION LIMIT FOR METHODS, SO THAT HOW THAT IS DEFINED IS EXTREMELY IMPORTANT, WE FEEL.

I MIGHT ALSO ADD, OF COURSE, THAT OUR INDUSTRY IS NOT CONCERNED WITH ORGANIC MATTER AS MOST OF YOU ARE, BUT WE ARE VERY MUCH CONCERNED WITH THE PRIORITY POLLUTANT ELEMENTS SINCE THEY APPEAR IN SOME OF OUR DISCHARGES IN VARYING AMOUNTS, AND WE ARE CONCERNED THUS IN THE CURRENT 304-H PROPOSALS OF DECEMBER 3RD WITH THE ICAP METHODS AND THEIR EQUIVALENCY TO THE PRESENT 304-H ASPIRATED AA AS WELL AS THE 1979 MCAW CONTAINING THE GRAPHITE FURNACE AA METHOD.

AS A RESULT OF THAT CONCERN, AND BOTH OF THESE THINGS RUN TOGETHER, UWAG CONDUCTED IN 1979 AN EXTENSIVE ROUND ROBIN. THERE WERE INITIALLY SOME 31 COOPERATING LABORATORIES. I DON'T THINK IN ANY CASE THERE WERE LESS THAN ROUGHLY, AFTER ELIMINATION OF ALL OUTLIERS AND RANKING OF LABS, AND I MIGHT ADD I AM REALLY VERY MUCH CONCERNED THAT EPA DID NOT APPARENTLY FOLLOW, AND I SUGGEST THEY DO, D-2777, METHOD FOR THE DETERMINATION OF PRECISION AND BIAS OF COMMITTEE D-19 METHODS. THAT IS AN EXCEPTIONALLY WELL LAID OUT PROGRAM FOR ESTABLISHING PRECISION AND BIAS

OF METHODS. IT GIVES ALL OF THE DETAILS OF THE STATS NECESSARY AND THE PROCEDURES TO BE FOLLOWED TO MAKE DEFINITIVE STATEMENTS ABOUT THE PRECISION AND BIAS OF METHODS, AND I SUGGEST THAT IT BE USED.

BUT ANYWAY, THAT ROUND ROBIN SERVED THE PURPOSE OF GETTING BOTH INTERLABORATORY AND SINGLE LABORATORY PRECISION DATA FOR ARSENIC, CHROMIUM, COPPER, NICKEL AND ZINC. WE DID IT IN ONLY TWO MATRICES. WE WERE NOT IN THE BUSINESS OF METHODS DEVELOPMENT. WE WERE IN THE BUSINESS OF ESTABLISHING AND VALIDATING EXISTING METHODS IN A WAY THAT WE FEEL, WE HOPE, WILL BE A GUIDE FOR EPA IN THEIR VALIDATION OF METHODS. SO THAT THE CONDUCT OF THAT WAS IN ONLY TWO MATRICES, THE OHIO RIVER AT A POINT SOMEWHERE DOWNSTREAM OF PITTSBURGH, AND ALSO IN THE EFFLUENT FROM A FLY-ASH BASIN ON A LARGE STEAM GENERATING PLANT, AND IT WAS SETTLED EFFLUENT. SO THAT IN TOTAL THESE WERE IN THE BALLPARK AS BEING THE KINDS OF MATRICES THAT WE FEEL THAT WE WOULD SEE AND WOULD AT LEAST DEMONSTRATE THE METHOD IN SOME WAY IN A RATHER NORMAL SITUATION, WE DID THAT. THAT INFORMATION HAS BEEN PUBLISHED BY UWAG, IT IS AT THE PRINTERS, WILL BE DISTRIBUTED AND AVAILABLE TO EPA. IN FACT, EMSL CINCINNATI WAS ONE OF THE PARTICIPATING LABORATORIES IN THAT PROGRAM. WE CONDUCTED IT VERY, VERY STRICTLY IN ACCORDANCE WITH D-2777.

OUR CONTRACTOR WAS NUS CORPORATION IN PITTSBURGH. THEIR RESPONSIBILITY WAS TO ORGANIZE, RIGHT TO PROTOCOL THAT WAS TO BE FOLLOWED AND A VERY TIGHT PROTOCOL. WE LEFT NOTHING TO INDIVIDUAL CHOICE IN ORDER BECAUSE WE FEEL THAT ANY METHOD IS NO BETTER THAN THE WAY THAT IT IS WRITTEN, AND THE DATA THAT YOU GATHER IS NO BETTER THAN THE WRITTEN METHOD. YOU MUST ALWAYS KEEP THAT IN MIND. IF YOU LEAVE A LOT OF LOOPHOLES, YOU ARE GOING TO GET A LOT OF SCATTER IN THE DATA. SO THAT WE TRIED TO DO THIS THE BEST WE COULD, AND I THINK WE WERE QUITE SUCCESSFUL. I MIGHT, FOR YOUR INFORMATION, POINT OUT THAT SUCH A ROUND ROBIN PROGRAM CONDUCTED ON THE TWO MATRICES FOR FIVE ELEMENTS AT BASE LEVEL PLUS FOUR SPIKES COST APPROXIMATELY $150,000. IT IS NOT INEXPENSIVE TO CONDUCT ROUND ROBINS, BUT THE INUDSTRY FELT THAT THIS WAS ITS CONTRIBUTION. WE ARE NOT JUST HERE TO CRITICIZE WHAT OTHERS ARE DOING, BUT WE FELT THAT IT WAS ABSOLUTELY NECESSARY TO PUT OUR MONEY WHERE OUR MOUTH WAS, SO WE PUT THIS PROGRAM TOGETHER.

BUT OUT OF THAT, THEN, COMES A NUMBER OF THINGS. FIRST, BY BEING A WELL CONDUCTED PROGRAM WE COULD MAKE VERY ACCURATE STATEMENTS ABOUT OUR RESULTS. WE COULD USE THOSE ACCURATE STATEMENTS THEN FURTHER AS A BASIS FOR DERIVING OR UTILIZING IN DERIVATIONS OF

DEFINITIONS FOR LIMIT OF DETECTION AND THE LIKE, SO THAT WE COULD SHOW THE IMPACT OF THESE DEFINITIONS IN A REAL SENSE ON REAL WORLD SAMPLES.

ONE OF THE KEY FEATURES OF THIS INTERLABORATORY EFFORT THAT WE PUT ON WAS TO WRITE A PROTOCOL THAT INCLUDED THE SAMPLE BOTTLE AND ITS MANIPULATION IN TRANSMISSION. WE FEEL THIS IS VITAL IN ANY PROGRAM DEALING WITH SUBSTANCES IN THE MICROGRAM PER LITER LEVEL, THAT THERE IS NO WAY, UNTIL YOU HAVE RUN EXTENSIVELY OVER A LONG PERIOD OF TIME AND A LOT OF MATRICES, OF RULING OUT THE RANDOM ERRORS THAT COME INTO, IN AN INTERLABORATORY SITUATION, THAT PORTION OF THE OVERALL PROCEDURE THAT IS INVOLVED FROM THE POINT AT WHICH A SAMPLE IS SPLIT UNTIL THE DATA IS REPORTED. WE THINK THIS IS VITAL TO UNDERSTAND THIS DIFFERENCE BETWEEN ANY DEFINITIONS THAT I WILL GIVE YOU THAT WE HAVE DEVELOPED FOR LIMIT OF DETECTION AND SO ON, AND THOSE THAT HAVE BEEN COMMONLY EMPLOYED, AND AS I UNDERSTAND FROM THE FIRST DRAFT, ARE TO BE PROPOSED BY EPA AS MDL, METHOD DETECTION LIMIT.

THE REAL WORLD SITUATION BEGINS IN COMPLIANCE MONITORING WITH WHEN THE TWO PARTIES, THE REGULATED AND THE REGULATOR, GATHER AT AN NPDS DISCHARGE POINT, COLLECT A SAMPLE, SPLIT IT, AND SEND IT TO THEIR RESPECTIVE LABORATORIES, EACH ONE OF WHICH IS QUALIFIED,

EACH ONE OF WHICH FOLLOWS VALIDATED AND WELL WRITTEN PROCEDURES, AND EACH ONE OF WHICH REPORTS THE RESULTS. THOSE RESULTS WILL BE DIFFERENT, WE KNOW THAT. THE QUESTION IS, IS THE DIFFERENCE SIGNIFICANT.

ALSO, THE RESULTS THAT ONE GAINS, HOW DOES ONE COMPARE THEM WITH AN EFFLUENT LIMITATION THAT HAS BEEN ESTABLISHED, BE IT AT THE DISCHARGE PIPE OR A WATER QUALITY STANDARD IN THE STREAM. IN BOTH OF THOSE SITUATIONS YOU ARE DEALING WITH TWO PEOPLE, TWO LABS. YOU CANNOT JUST LOOK AT WHAT A SINGLE LAB MIGHT DO BECAUSE ANY ONE LAB, AS YOU WELL KNOW, OPERATING BY ITSELF IN ISOLATION, CAN GET GREAT REPRODUCIBILITY ON A METHOD. IT CAN REFINE ITSELF IN ITS TECHNIQUES AND USE GOOD QC AND IT WILL HAVE A VERY PRECISE METHOD, BUT THAT DOES NOT MEAN THAT ITS NUMBER CAN BE REPRODUCED BY SOME OTHER LABORATORY DOING PRECISELY THE SAME THING WITH JUST AS QUALIFIED PEOPLE AND WITH EXACTLY THE SAME KIND OF INSTRUMENTATION AND PROCEDURE.

INTERLABORATORY PRECISION IS A TERM DEVELOPED TO COVER THAT SITUATION. IT IS ABSOLUTELY THE ONLY WAY THAT YOU CAN RECONCILE, OR AT LEAST UNDERSTAND AND ASSESS DIFFERENCES BETWEEN TWO LABORATORIES, AND THE COMPLIANCE MONITORING SITUATION IS THE DIFFERENCE BETWEEN TWO LABORATORIES AT THE MINIMUM. NOW, INTERNALLY, THE SAME DEFINITIONS THAT I WILL GIVE YOU CAN BE USED

SUBSTITUTING ONLY ONE PARAMETER FOR INTERNAL QUALITY CONTROL. THE BASIS OF OUR DEFINITION, AND REALLY THAT OF EPA'S, IS NOISE; METHOD NOISE, WE LIKE TO SAY, NOT INSTRUMENTAL NOISE, METHOD NOISE, AND THE METHOD IS THE SUM OF THE WHOLE; IT BEGINS WITH THAT SPLIT OF THE SAMPLE, THE SORPTION OR DESORPTION ON THE BOTTLE SURFACE, THE GUY'S THUMBPRINT THAT GOT IN THE CAP THAT YOU DIDN'T KNOW ABOUT, AND ALL THOSE SORTS OF THINGS THAT OCCUR AS RANDOM COMMON AND UNCOMMON ERRORS THAT CREEP INTO A PROCEDURE. ONE MUST TAKE THAT INTO ACCOUNT.

IN THAT OUTER AREA, THAT INTERLABORATORY PRECISION CAN BE THE BASIS OF A NOISE DEFINITION, AND THAT IS EXACTLY WHAT WE DID. WE COVERED A SUFFICIENT RANGE OF CONCENTRATIONS IN OUR TEST AND THEN BY DIVIDING OR CURB FITTING IN A WAY, IN OUR CASE IT WAS SERVED BY USING TWO DIFFERENT REGRESSION ANALYSES, ONE OVER THE WHOLE RANGE OF THE DATA TO EXPRESS THE WHOLE RANGE OF OUR ANSWERS, AND THE OTHER WAS TO EXPRESS OVERALL PRECISION AS A FUNCTION OF THE MEAN CONCENTRATION OF ALL THE PARTICIPATING LABS IN ONLY THE VERY LOWEST END OF THAT RANGE, AND FOR OUR PURPOSES ZERO TO 100 MICROGRAMS PER LITER WAS THE LOW END OF THAT RANGE. THEN ONE CAN DETERMINE THE Y INTERCEPT, THE ZERO CONCENTRATION VALUE, AND THE ACCURACY OF ONE'S ESTIMATE

OF THAT Y INTERCEPT IS STATISTICALLY ANALYZABLE ALSO, SO THAT YOU CAN ARRIVE AT THE VALUE THAT CONSTITUTES THE TRUE METHOD NOISE.

IF YOU USE THAT DEFINITION FOR NOISE, YOU CAN THEN CREATE A WHOLE SERIES OF VERY LOGICAL DEFINITIONS TO UTILIZE IN COMPARING ANY SET OF RESULTS THAT YOU WISH, AS LONG AS EVERYONE UNDERSTANDS THE GROUND RULES. IN DEVELOPING THESE DEFINITIONS, WE FOLLOWED ALMOST EXACTLY THOSE THAT WERE PROPOSED IN 1968 IN ANALYTICAL CHEM BY LLOYD CURRIE AT THE NATIONAL BUREAU OF STANDARDS, QUITE A RECOGNIZED EXPERT IN THE STATISTICS OF ANALYTICAL CHEMISTRY. HIS FIRST LIMIT, AND ONE THAT CORRESPONDS TO THE CURRENT EPA-PROPOSED MDL, REALLY, IN THE FINAL FACT OF IT, SKIP THE TERMINOLOGY, IS CRITICAL LIMIT, AND THAT IS THAT NUMBER THAT YOU MUST EXCEED TO MAKE THE DECISION AT A GIVEN RISK THAT WHAT YOU GOT, THAT ONE VALUE WAS NOT TRULY ZERO. THAT IS LLOYD CURRIE'S CRITICAL LIMIT, THAT HAPPENS TO BE THE ESSENCE OF THE PROPOSED MDL. IT IS A CONFIDENCE LEVEL, A T-VALUE, SINGLE-SIDED FOR RISK TIMES THE STANDARD DEVIATION OF THE BACKGROUND, OR BASELINE, NOISE AS WE HAVE DEFINED IT, THE Y INTERCEPT OF OVERALL PRECISION VERSUS CONCENTRATION.

WHEN YOU START AT THAT POINT, YOU CAN DEVELOP THEN A LOGICAL SERIES OF SITUATIONS, THE FIRST BEING

THE CRITICAL LIMIT WHICH IS THAT POINT AGAIN THAT YOU MAKE THAT DECISION, WAS IT PRESENT, AND YOU HAVE A DEFINITE ASSIGNED RISK. WE USED A HALF A PERCENT THAT CORRESPONDS TO THE 99 PERCENT CONFIDENCE LEVEL, AND THAT SEEMS TO BE THE ACCEPTABLE ONE IN COMPLIANCE MONITORING. YOU COULD USE ANOTHER ONE AS LONG AS EVERYBODY AGREES TO WHAT RISK YOU ARE REALLY TALKING ABOUT. HAVING DONE THAT, YOU CAN THEN CREATE THE NEXT VALUE THAT CURRIE DOES, AND HE CALLS THAT HIS LIMIT OF DETECTION. THE LIMIT OF DETECTION IS REALLY THE LOWEST VALUE AT, AGAIN, A STATED CONFIDENCE LEVEL THAT EXCEEDS THE CRITICAL LIMIT. SO THAT IN EFFECT IT IS THE LOWEST VALUE THAT YOU ARE SURE WILL NOT BE REPORTED BY SOMEONE AT THAT 99 PERCENT CONFIDENCE LEVEL AS ZERO. THAT IS THE NEXT LOGICAL PROGRESSION.

NOW THERE IS STILL ANOTHER MEASURE OF THE PERFORMANCE OF A METHOD, AND THAT IS THE LIMIT OF QUANTIFICATION, OR WE CALLED IT LIMIT OF DETERMINATION, AGAIN FOLLOWING CURRIE. THE LIMIT OF DETERMINATION INTRODUCES ANOTHER CONCEPT, WHAT SORT OF ERROR ARE YOU WILLING TO TOLERATE NORMALLY IN A RESULT, QUANTIFIED RESULT. CURRIE, IN HIS DISCUSSION, USES A STANDARD DEVIATION OF 10 PERCENT OF THE AMOUNT PRESENT AS AN ACCEPTABLE ANALYTICAL ERROR, AND THAT IS FAIRLY COMMON. WE CHOSE IN OUR PROPOSED DEFINITIONS TO USE 20 PERCENT,

AND THAT JUST SIMPLY FACES THE REALITY THAT IN THE MICROGRAM PER LITER CONCENTRATION RANGE FOR THE METALS THAT WE WERE TESTING, THERE ARE SOME THAT WOULD NOT QUALIFY AT ALL, ZINC HAPPENED TO ONE OF THEM, IF YOU USE 10 PERCENT, BECAUSE THE STANDARD DEVIATION OF THE METHOD, IT NEVER GETS DOWN TO 10 PERCENT, FOR ZINC IT HAPPENS TO BE 20 PERCENT OR GREATER AT ALL CONCENTRATION LEVELS, SO WE CHOSE 20 PERCENT. HAVING DONE THAT, THEN YOU CAN ESTABLISH THE LIMIT OF QUANTIFICATION, OR LIMIT OF DETERMINATION, AS THAT VALUE WHERE THE LOWEST VALUE WHEREIN THE PRECISION OF THE METHOD IS EQUAL TO 20 PERCENT OF THE LEVEL AT WHICH YOU ESTABLISH.

SO THAT SET OF THREE DEFINITIONS NOW GIVES YOU A REAL GOOD WORKING BASE TO COMPARE WITH ANY OTHER LABORATORY; IF YOU SUBSTITUTE SINGLE LABORATORY PRECISION, WHICH YOU GET IN YOUR OWN OR THAT WHICH HAS BEEN DEVELOPED AS THE AVERAGE AS A POOLED SINGLE LABORATORY PRECISION AMONG MANY LABS, THEN YOU ARE ABLE TO FOLLOW THESE SAME DEFINITIONS, HAVE YOUR OWN CRITICAL LIMIT, UNDERSTANDING THAT IS WITHIN YOUR LAB, IT IS WHAT YOU AS AN ANALYST CAN SAY STATISTICALLY ABOUT YOUR RESULT, YOU CAN APPLY IT TO YOUR LIMIT OF DETERMINATION AS WELL, BUT ALWAYS WITHIN YOUR OWN FACILITY. IT CAN BE FOR PROCESS CONTROL PURPOSES, IT CAN BE FOR ANY OTHER THAT YOU NEED.

BUT WHEN YOU GO OUTSIDE, AND YOU ARE IN COMPLIANCE MONITORING, YOU ARE COMPARING TWO LABS, AND WHEN YOU DO THAT YOU MUST USE INTERLABORATORY PRECISION.

AS I MENTIONED EARLIER, ONE OF THE KEY FEATURES WAS INCLUSION OF THE PREPARATION OF THE SAMPLE BOTTLE IN THE OVERALL METHOD FOR WHICH INTERLABORATORY PRECISION WAS OBTAINED. WE CHOSE, AND WE FEEL THIS IS VERY IMPORTANT BECAUSE ABSORPTION, DESORPTION POTENTIAL IN MICROGRAM PER LITER LEVELS IN THE CONTAINERS, TO HAVE THE SAMPLE BOTTLES PREPARED BY THE PARTICIPATING LABORATORY. THEY WERE PURCHASED IN BULK; THEY WERE DISTRIBUTED TO EACH OF THE PARTICIPANTS; EACH OF THE PARTICIPANTS THEN PREPARED THAT SAMPLE BOTTLE IN ACCORDANCE WITH THE PROTOCOL; HE WASHED IT, ACID RINSED IT, WASHED IT, DID ALL THE THINGS THAT WERE NECESSARY; PUT THAT BOTTLE BACK IN A BAG WITH ALL THE ONES THAT HE HAD FINISHED AND SENT THEM BACK TO THE COLLECTION POINT AGAIN, AND OUT IN THE FIELD WHERE THESE BULK SAMPLES WERE OBTAINED AND SPLIT, THEN EACH LABORATORY HAD HIS SAMPLE BOTTLES FILLED BY OUR CONTRACTOR, NUS, AND RETURNED TO HIM.

NOW JUST TO SHOW YOU WHAT THAT DOES, AND WE THINK IS A MAJOR FACTOR IN THE DIFFERENCE BETWEEN THE SINGLE LABORATORY PRECISION STATEMENTS THAT WE WERE ABLE TO DEVELOP AND THOSE THAT EPA HAS PUBLISHED IN THE

MCAW 79, 600/4/79020. IN THAT THERE ARE ONLY TWO PRECISION STATEMENTS, PERIOD, FOR THE GRAPHITE FURNACE METHODS AND THEY ARE FOR ARSENIC AND CHROMIUM, AT LEAST AMONG OUR FIVE. NOW I CAN'T SAY THAT THERE MAY NOT BE SOME FOR OTHER THAT THOSE FIVE.

FOR ARSENIC AND CHROMIUM, EPA'S SINGLE LABORATORY PRECISION AT THE 50 MICROGRAM PER LITER LEVEL IS 1.1 MICROGRAMS PER LITER FOR ARSENIC AND 0.2 MICROGRAMS PER LITER FOR CHROMIUM, THAT'S TOTAL, NOW ALL OF THESE ARE TOTAL ON THE SAMPLE. UWAG'S POOLED SINGLE LABORATORY PRECISION FROM THIS ROUND ROBIN WAS 5.5 MICROGRAMS PER LITER FOR ARSENIC, AND 5.1 MICROGRAMS PER LITER FOR CHROMIUM. A FACTOR OF FIVE FOR ARSENIC AND A FACTOR OF 25 FOR CHROMIUM, NUMERICAL VALUE FOR PRECISION THAT MUCH LARGER. WE ATTRIBUTE THAT LARGE DIFFERENCE TO THIS EXTENDED PROTOCOL. I WOULD URGE, AND WE ARE URGING EPA, AND I WOULD URGE ALL OF YOU IN ANY INDUSTRY, ROUND ROBINS OR OTHERWISE, TO TAKE THAT FACT INTO ACCOUNT, AND IF AT ALL POSSIBLE TO HAVE THE SAMPLE BOTTLE PREPARATION BY THE PARTICIPATING LABORATORY BE MADE PART OF THE PROTOCOL FOR WHICH YOU DEVELOP THE PRECISION DATA.

THANK YOU.

MR. TELLIARD: THANKS, JIM. ANYONE ELSE WHO WOULD LIKE TO...GEORGE.

MR. STANKO: GEORGE STANKO, SHELL DEVELOPMENT. WHEN THE BELL RANG ON ROUND 15 YESTERDAY AFTERNOON, I HAD A COUPLE OF QUESTIONS NOT PERTAINING TO STATISTICS. MAYBE SOMEONE THAT IS HERE COULD ANSWER THESE.

I THOUGHT I HEARD SOMEONE SAY, PARTICULARLY DEAN, THAT THE ORGANIC CHEMICAL BRANCH, GC METHODS THAT WERE USED FOR VERIFICATION, THE PAUL FERINTHALL METHODS, ARE CONSIDERED EQUIVALENT TO THE PROPOSED 601 THROUGH 613, DECEMBER 3RD PROPOSAL OF THE FEDERAL REGISTER; AM I CORRECT IN ASSUMING THIS?

MR. TELLIARD: YES.

MR. STANKO: THE SECOND PART, DEAN, I LOOKED AT THE HANDOUT THAT WAS GIVEN YESTERDAY WHEN WE LEFT THE ROOM, AND AS FAR AS I COULD TELL, THERE WAS NOTHING IN THAT HANDOUT THAT WOULD INDICATE HOW YOU WENT FROM THE DATA TO THE RC VALUE, AND THEN YOU SORT OF GIVE AN EXAMPLE OF HOW THESE MIGHT BE RELATED TO NUMERICAL VALUE. IS THERE ANYTHING ON THE PARTICULAR EXAMPLE OR ANYTHING LIKE THAT, COULD IT BE MADE AVAILABLE TO INDUSTRY SO WE CAN FOLLOW YOU?

MR. NEPTUNE: DEAN NEPTUNE, EPA. GEORGE, THE DECEMBER 3RD FEDERAL REGISTER HAS EVERY SINGLE FORMULA AND MANIPULATION THAT WAS DONE IN THERE IN THE EXAMPLED QUALITY ASSURANCE, QUALITY CONTROL.

I STATED THAT YESTERDAY WHEN WE STARTED; I WILL REMIND EVERYBODY AGAIN. EVERY FORMULA IS IN THE DECEMBER 3RD FEDERAL REGISTER NOTICE THAT WAS PROPOSED FOR PUBLIC COMMENT. IT IS ALL PRINTED IN THERE; IT IS ALL THERE FOR YOU, GEORGE.

MR. STANKO: DEAN, I FOLLOWED EVERYTHING DOWN TO THE RC VALUE, BUT HOW DID YOU GET FROM THE RC VALUE TO THE PROPOSAL OF, SAY, 30 PARTS PER BILLION FOR DICHLOROBENZENE?

MR. NEPTUNE: AS I ALSO MENTIONED, GEORGE, THOSE WERE THE RC VALUES FOR THE 2X LEVEL. IN OTHER WORDS, IN THIS CASE IT WAS 20 MICROGRAMS PER LITER, AS I MENTIONED. FROM THAT WE TOOK THE RANGE, THE WORST CASE NUMBER IN THE RANGE, WHICH WAS ALWAYS THE LOWEST RECOVERY, AND CORRECTED FROM THERE TO WHAT WE SAID WAS A POTENTIAL OR ONE MEANS BY WHICH ONE MAY ESTABLISH A VALUE. IN OTHER WORDS, WE TOOK THE WORST POSSIBLE CASE, THE MOST CONSERVATIVE, GEORGE, THE ABSOLUTE, AND GAVE IT THE HIGHEST NUMBER THAT WE COULD COME UP WITH, NOT THE BEST NUMBER, THE WORST NUMBER, GEORGE.

MR. STANKO: I WASN'T TOO CLEAR ON THAT AND I DIDN'T PICK THAT OUT OF THE HANDOUT.

MR. NEPTUNE: THAT WASN'T IN

ANY OF THE HANDOUTS. THE TWO HANDOUTS YESTERDAY SIMPLY RELATED TO THE COLUMN PACKING MATERIALS FOR METHODS 601 THROUGH 613, PLUS THE ORGANIC CHEMICALS BRANCH. THE OTHER HANDOUT SIMPLY RELATED TO, AS I MENTIONED, SCREENING AND THE DATA THAT WE HAD COLLECTED TO DATE ON PRIORITY POLLUTANT FREQUENCY AND VARIOUS DIFFERENT CUTS BY THE INDUSTRIAL CATEGORIES AND CUTS ON THAT VERY SAME DATA.

MR. STANKO: I THINK THAT CLEARS IT UP. THANK YOU, DEAN.

MR. KAGEL: RON KAGEL, DOW. I WOULD JUST LIKE TO COMMENT ON JIM RICE'S PRESENTATION; I CERTAINLY SUPPORT HIM. THERE IS ANOTHER STUDY GOING ON QUITE INDEPENDENT OF WHAT JIM DID. IT IS BEING CONDUCTED BY THE ACS, ENVIRONMENTAL COMMITTEE. THEY HAVE A DRAFT DOCUMENT ON GUIDELINES FOR ENVIRONMENTAL MEASUREMENTS, AND WE HAVE HAD THE OPPORTUNITY TO REVIEW THAT DOCUMENT IN ADDITION TO JIM RICE'S WORK AND WE SEE THAT THE BOTTOM LINE, THE TWO REACH THE SAME CONCLUSIONS; JIM GETS THERE BY SLIGHTLY DIFFERENT MEANS. I HAVE MADE THAT AVAILABLE TO SOME OF THE PEOPLE IN THE AGENCY.

ON WEDNESDAY WHEN PROFESSOR ROGERS TALKED, ONE OF HIS THREE MAJOR POINTS WAS THAT THE NEED FOR AN INTERMEDIATE, AND HE WAS PUSHING NBS TO KIND OF MEDIATE

BETWEEN THE INDUSTRIAL HALF AND THE GOVERNMENT HALF WHEN WE GET INTO THESE REGULATION SITUATIONS. I THINK PERHAPS IN THIS CASE THE ACS MIGHT SERVE AS A GOOD NEUTRAL, DISINTERESTED THIRD PARTY TO TRY TO WORK OUT SOME OF THE DIFFERENCES WE HAVE ON THIS, SO I URGE YOU TO TAKE ADVANTAGE OF THAT.

MR. TELLIARD: WE ARE NOW BACK ON THE SCHEDULE AGAIN AND THE NEXT SPEAKER IS GOING TO TALK TO YOU A LITTLE BIT ABOUT SURROGATES. IT IS JIM LONGBOTTOM FROM ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY IN CINCINNATI.

EVALUATION OF CANDIDATE COMPOUNDS AS SURROGATE SPIKES

BY: JIM LONGBOTTOM

THE DISCUSSIONS THAT WE HAVE HAD SO FAR IN THE MEETING HAVE CONCENTRATED IN TWO AREAS THAT ARE OF CONCERN: PROBLEMS WITH THE METHOD, AND QUALITY CONTROL PROCEDURES THAT ARE IN USE OR PROPOSED. THE PROBLEMS OF THE METHODS THAT WE WERE TALKING ABOUT CAN BE DIVIDED INTO REACTIONS BETWEEN THE PRIORITY POLLUTANTS AND REACTANT MATRICES, CARRY-OVER OF THE PHENOLS AND BASE/NEUTRALS INTO OTHER FRACTIONS, AND THE PROBLEM WITH SOLIDS AND THEIR EFFECT ON RECOVERIES.

THE QUALITY ASSURANCE PROCEDURES ARE THE ONE THAT DEAN NEPTUNE DISCUSSED IN DEPTH YESTERDAY THAT HAS BEEN OFFERED AS AN EXAMPLE IN THE DECEMBER 3RD FEDERAL REGISTER USING RC VALUES FOR DETERMINING PERFORMANCE CRITERIA, AND THE ISOTOPIC DILUTION APPROACH THAT IS BEING WORKED ON OUT AT SYSTEMS, SCIENCE AND SOFTWARE BY BRUCE COLBY.

WE HAVE BEEN LOOKING AT ANOTHER POSSIBLE APPROACH TO TRY TO TAKE ADVANTAGE OF THE EMSL REPOSITORY, WHICH IS CURRENTLY GATHERING UP A COLLECTION OF ALL THE PRIORITY POLLUTANTS FOR

DISTRIBUTION TO ANYONE WHO WILL WANT THEM IN THE FUTURE. WE ARE LOOKING AT INTERNAL STANDARD COMPOUNDS, SPIKING SOLUTIONS AND SURROGATE SPIKES TO OFFER THROUGH OUR REPOSITORY. SO WE HAVE BEEN TRYING TO EVALUATE THE MOST EFFECTIVE USE OF SURROGATES. IT APPEARS FROM A PRACTICAL STANDPOINT THE SURROGATES, HOWEVER THEY ARE USED, WHETHER IT IS BY ISOTOPIC DILUTION OR IN SOME OTHER WAY SUCH AS WHAT IS BEING USED BY DEAN'S PROGRAM, OFFER THE BEST HOPE FOR A CONTROL MONITORING PROCEDURE FOR THE PRIORITY POLLUTANT ANALYSIS AT A REASONABLE COST.

WE ARE EVALUATING DATA TO FIGURE OUT THE BEST WAY TO USE SURROGATE SPIKES, AND I WOULD LIKE TO JUST OFFER UP ONE POTENTIAL APPROACH TO IT. AS I MENTIONED, ONE OF THE THINGS THAT WE HAVE BEEN DISCUSSING IS THE PROBLEMS IN THE METHOD. IF WE START THERE AND RECOGNIZE THE WEAKNESS OF THE METHODS AND IDENTIFY THE PROBLEM COMPOUNDS ON THE PRIORITY POLLUTANT LIST, WE CAN CONCENTRATE ON THOSE COMPOUNDS AS WE ATTEMPT TO DEVELOP PERFORMANCE CRITERIA.

THE SECOND STEP WOULD BE TO USE THE PROBLEM AREAS OF THE METHOD TO SELECT OUR SURROGATE SPIKES. THIRD, WE COULD ESTABLISH RECOVERY

CRITERIA FOR THESE MATERIALS AND USE THE CRITERIA TO IDENTIFY PROBLEM SAMPLES AND PROBLEM ANALYSES. THEN, FOR THAT FRACTION OF THE COMPOUNDS, OR FRACTION OF THE SAMPLES THAT FAIL TO MEET THE PERFORMANCE CRITERIA, WE IDENTIFY THAT THERE IS A PROBLEM, WHETHER IT IS A MATRIX EFFECT OR SOLIDS OR WHATEVER. THEN WE ESTABLISH A PROTOCOL FOR FOLLOW-UP ACTION, DEVELOPING ADDITIONAL STEPS TO DEFINE WHAT IS DONE IF YOU DO NOT GET ACCEPTABLE RECOVERY. THEN WE CAN CONCENTRATE OUR QA AND QC EFFORTS ON THE PROBLEM SAMPLES, RATHER THAN ARBITRARILY RUNNING EVERY TENTH SAMPLE OR SPIKING 100 PERCENT OF THE SAMPLES WITH ALL OF THE PRIORITY POLLUTANTS, OR ANY OF THE OTHER APPROACHES THAT HAVE BEEN DISCUSSED HERE.

IN SUMMARY, THE APPROACH I AM SUGGESTING WILL ESTABLISH CRITERIA TO SORT OUT THE GOOD SAMPLES FROM THE BAD SAMPLES AND THEN REQUIRE ADDITIONAL EFFORT TO DEFINE THE APPLICABILITY OF THE METHOD TO THE BAD SAMPLES.

THE PRINCIPAL ADVANTAGE OF THIS APPROACH WOULD BE IF WE HAD PERFORMANCE CRITERIA FOR THESE PARTICULAR SURROGATES, WE COULD ELIMINATE THE NEED FOR THE FRONT-END DEVELOPMENT OF RC VALUES AND CRITICAL LIMITS AND EVERYTHING ELSE. WE WOULD

SIMPLY ANALYZE THE SAMPLE, AND IF WE MET ALL PERFORMANCE CRITERIA FOR OUR SAMPLE, THEN THAT IS IT. IF WE HAVE CHECKED OUR PROBLEM AREAS, THEN IT IS NOT A PROBLEM SAMPLE, AND THE RESULTS WOULD BE ACCEPTABLE.

TO TRY TO EVALUATE SOME OF THESE PROBLEM AREAS, I HAVE BEEN LOOKING AT THE CARBORUNDUM ACCURACY AND PRECISION REPORTS THAT ARE BEING DEVELOPED FOR EFFLUENT GUIDELINES. IF WE LOOK AT THE PURGEABLES, CARBORUNDUM, LIKE MANY OF THE CONTRACTORS, USES THE BROMOCHLOROMETHANE AND 1,4-DICHLOROBUTANE AS INTERNAL STANDARDS IN THE METHOD AND CALCULATES CONCENTRATIONS FROM THEM. IN THEIR STUDY THEY LOOKED AT PERHAPS HALF A DOZEN OTHER SURROGATE SPIKES THAT WERE BEING USED IN THE EFFLUENT GUIDELINES DIVISION TO DEFINE, HOPEFULLY, RELATIONSHIPS BETWEEN PRIORITY POLLUTANT RECOVERIES AND SURROGATE SPIKES.

IN THE PURGEABLES, I THINK IT IS MOST IMPORTANT THAT IF WE ARE GOING TO USE THE INTERNAL STANDARD PROCEDURE, THAT WE COME UP WITH AN INTERNAL STANDARD THAT IS OUR BEST SURROGATE. IF YOU WANT TO SELECT A SURROGATE IN TERMS OF ITS RECOVERY BEING IDENTICAL TO THE OTHER COMPOUNDS

BEING MEASURED, IN THE CASE OF THE VOLATILE PROCEDURE WE ARE TALKING ABOUT, THAT SHOULD BE OUR INTERNAL STANDARD. THAT IS THE ONE THAT SHOULD BE USED TO CALCULATE ALL OF OUR RESULTS, NOT TO MONITOR OUR QUALITY CONTROL. SO IN LOOKING AT THE VOLATILE DATA, WE CONCENTRATED ON WHICH OF THE COMPOUNDS COULD SERVE AS THE BEST INTERNAL STANDARD OF THE ONES THAT WERE BEING USED. WE EVALUATED D_2 METHYLENE CHLORIDE, D_3 DICHLOROETHANE AND D_4 TRICHLOROETHANE AS INTERNAL STANDARDS, FOR EXAMPLE.

IF WE SWITCHED OUR DATA BASE USING THESE COMPOUNDS, ARBITRARILY CALLING THEM THE INTERNAL STANDARD, AND RECALCULATED OUR DATA BASE, COULD WE IMPROVE THE DATA BASE? ARE THESE DEUTERATED COMPOUNDS BETTER INTERNAL STANDARDS THAN THE ONE ACTUALLY USED? AFTER STEPPING THROUGH SOME OF THE CALCULATIONS, WE FOUND THAT, NO, THE DATA DID NOT IMPROVE BY USING ANY OF OUR SURROGATE SPIKES AS THE INTERNAL STANDARD. WE INVESTIGATED A LITTLE DEEPER AND REALIZED THAT WE WERE GETTING ISOTOPIC INTERFERENCES FOR THOSE COMPOUNDS SUCH AS DEUTERATED METHYLENE CHLORIDE. THE SURROGATE SPIKE RECOVERIES CORRELATED VERY NICELY WITH THE SPIKED CONCENTRATION LEVELS OF METHYLENE CHLORIDE, FOR EXAMPLE. BRUCE

COLBY TELLS ME THAT I NEED TO APPLY HIS ISOTOPIC DILUTION MATHEMATICS TO RESOLVE THE DATA.

WE GOT TO WONDERING WHAT YOU WOULD DO WITH A SURROGATE SPIKE IF YOU WERE LOOKING AT THE WEAKNESS OF THE METHOD, IN THIS CASE, PURGE AND TRAP. IF YOU WANT TO MONITOR, FOR EXAMPLE, TRAP BREAKTHROUGH, YOU MIGHT COME UP WITH A FREON AND CHECK FOR BREAKTHROUGH OF THE FREON. YOU MIGHT ALSO ADD A COMPOUND THAT DOESN'T PURGE VERY EFFECTIVELY TO MONITOR FOR MATRIX EFFECTS. HOWEVER, SINCE THE MAJORITY OF THE PURGEABLES ARE HALOGENATED, IT IS VERY DIFFICULT, WITHOUT GETTING INTO ISOTOPIC DILUTION CALCULATIONS, TO COME UP WITH A COMPOUND, A DEUTERATED COMPOUND, AT ANY RATE, WITH ION FRAGMENTS THAT COULD BE CLEANLY RESOLVED FROM THE NONDEUTERATED FORM OF WHAT YOU ARE MEASURING. SO WE HAVE BEEN KIND OF GOING IN CIRCLES.

LET'S LOOK AT THE PROBLEM AS (1) WHAT ARE YOU TRYING TO MEASURE; (2) WHAT ARE THE MECHANICAL PROBLEMS OF THE METHOD; AND (3) WHAT ARE THE LIKELY MATRIX EFFECTS. THEN LET'S SET UP OUR CONTROLS FOR A SYSTEM TO SEPARATE GOOD DATA FROM DATA THAT NEEDED FURTHER DEFINITION OR INVESTIGATION.

TO MONITOR THE MECHANICAL PROBLEMS, WE MIGHT KEY IN ON THE ACTUAL AREA COUNTS THAT ARE BEING GENERATED

BY EACH OF OUR INTERNAL STANDARDS. THE ANALYST COULD PERFORM AN INTERNAL OR EXTERNAL STANDARD CALIBRATION WITH THE FIRST RUN, THEN CALCULATE ALL OF HIS SAMPLES BASED ON THE INTERNAL STANDARD, BUT ALSO CHECK THE ACTUAL AREAS GENERATED BY INTERNAL STANDARDS IN EACH RUN AGAINST WHAT THEY SHOULD BE, BASED ON THE PURE WATER MATRIX. WE COULD DEVELOP AN ACTION BASED ON THE AREAS. IF YOUR INTERNAL STANDARD AREA COUNT FALLS BELOW OR ABOVE A CERTAIN LEVEL, THEN YOU SHOULD REPEAT THE ANALYSIS. IT SEEMS LIKE ONE OF THE THINGS THAT HAPPENS IS THAT INSUFFICIENT INTERNAL STANDARD IS ADDED, OR TOO MUCH INTERNAL STANDARD, AND ALL THE NUMBERS CALCULATE OUT VERY HIGH OR VERY LOW. THAT IS AN EXAMPLE OF WHAT PRISCILLA HOLTZCLAW WAS MENTIONING YESTERDAY; WHEN YOU LOOK AT DATA AND SEE A PATTERN LIKE THAT, YOU KNOW THERE IS A PROBLEM.

IF WE USE THE INTERNAL STANDARD APPROACH, ANOTHER PROBLEM THAT KEEPS COMING UP WITH THE PURGEABLES IS BACKGROUND CONTAMINATION. I DON'T FEEL THAT A FIXED PROGRAM TO CALCULATE CONCENTRATIONS FROM ONLY ONE INTERNAL STANDARD IS ADEQUATE. AS YOU SET UP YOUR CONTROLS, YOU SHOULD USE TWO OR THREE INTERNAL STANDARDS. YOU CHECK AREAS IN YOUR MATRIX AGAINST THE RESPONSE IN YOUR STANDARD, THEN SELECT

THE INTERNAL STANDARD BASED UPON BEST AGREEMENT WITH YOUR FIRST STANDARD RUN OF THE DAY.

AS AN EXAMPLE, IN THIS PARTICULAR DATA BASE THAT WE WERE LOOKING AT, BECAUSE OF CONTAMINATION FROM THE UNDEUTERATED FORMS OF THE SURROGATE SPIKES, BROMOCHLOROMETHANE TURNED OUT TO BE THE BEST INTERNAL STANDARD TO USE FOR THE EARLY ELUTERS. HOWEVER, THIS COMPOUND IS FOUND REGULARLY IN DRINKING WATERS AND RIVERS, SO WE MAY WANT TO GO TO A LABELED FORM OF THAT COMPOUND TO EVEN FURTHER ENHANCE OUR ABILITY TO GET USEFUL DATA USING IT AS AN INTERNAL STANDARD.

IF WE LOOK AT THE ACID FRACTION, WHERE WE ARE ENCOUNTERING CARRY-OVER OF PHENOLS INTO THE BASE/NEUTRAL FRACTION, WE COULD AGAIN CONSIDER THE WEAKNESSES OF THE METHODS. THE CARBORUNDUM DATA GENERALLY CORRELATES PKAS WITH CARRY-OVER. WE SHOULD CONCENTRATE ON A PERFORMANCE CRITERIA FOR THE RECOVERY OF A DEUTERATED WEAK ACID, FOR EXAMPLE, DIMETHYLPHENOL, THE WEAKEST ACID IN THE GROUP. IN THAT CASE, WHERE WE DIDN'T ACHIEVE A RECOVERY THAT MET THE CRITERIA, WE SHOULD ANALYZE THE BASE/NEUTRAL FRACTION FOR THE PHENOLS AND ADD UP THE TOTAL. SO IN THOSE CASES WHERE WE DO HAVE CARRY-OVERS AND DO NOT ACHIEVE AN ACCEPTABLE RECOVERY OF OUR WEAKEST ACID, WE WOULD AUTOMATICALLY RUN THE BASE/NEUTRALS

TO PICK UP THE CARRY-OVER TO ADD UP THE TOTAL. THESE ARE THE TYPES OF THINGS THAT WE COULD CONSIDER.

FOR THE STRONGER ACIDS, WE WOULD NEED A SURROGATE TO MAKE SURE THAT OUR PH WAS LOW ENOUGH. WE MIGHT WANT TO MONITOR THIS USING A LABELED NITROPHENOL. I THINK WE NEED, AGAIN, TO HAVE MORE THAN ONE INTERNAL STANDARD WORKED INTO THESE METHODS BECAUSE OF THE POSSIBILITY OF CHEMICAL REACTION FOR THE INTERNAL STANDARDS AND THE POSSIBILITY OF INTERFERENCES.

FOR THE BASE/NEUTRALS, I THINK WE COULD LOOK FOR ADDITIONAL CONTROLS. WE WOULDN'T HAVE TO DEMONSTRATE THAT OUR INITIAL PH WAS HIGH ENOUGH TO EXTRACT THE BASES, SINCE WE CAN MONITOR PH WITH A WEAK ACID, BUT WE SHOULD BE INTERESTED IN DEVELOPING SURROGATES FOR THOSE COMPOUNDS THAT ARE SENSITIVE TO CHEMICAL REACTION AND THOSE MATERIALS SUCH AS THE LARGER PAHS THAT ARE DIFFICULT TO EXTRACT IN THE PRESENCE OF SOLIDS TO MONITOR FOR THAT MATRIX EFFECT.

WHERE THE SURROGATE RECOVERY IDENTIFIES WHAT IS CLEARLY A MATRIX EFFECT, SUCH AS IN THE CASE OF SOLIDS, LOW RECOVERY FOR OUR PAH INDICATOR, OUR QC PROTOCOL COULD REQUIRE THAT WE HAVE THAT SAMPLE

SPIKED WITH PRIORITY POLLUTANTS AND DEVELOP A RECOVERY STATEMENT FOR THAT SAMPLE TO DEFINE WHAT ACTUALLY IS GOING ON IN THAT MATRIX.

THAT IS THE APPROACH THAT WE ARE CURRENTLY EXAMINING. WE ARE INTERESTED IN MINIMIZING AS MUCH AS POSSIBLE THE OVERHEAD COST OF RUNNING 15 SAMPLES UP FRONT TO DEFINE THE OPERATOR'S INDIVIDUAL PERFORMANCE LIMIT. WE FEEL THAT WE CAN APPLY THE RESOURCES OF THE REPOSITORY THAT WE OPERATE AT EMSL-CINCINNATI AND PROVIDE SURROGATE STANDARDS AND A QC SYSTEM THAT COULD BE STANDARDIZED AND USED TO PRODUCE QUALITY DATA. THE QC OVERHEAD IS LIMITED TO PROBLEM SAMPLES, WHETHER IT IS 15 PERCENT OF THE SAMPLES, OR 30 PERCENT, OR WHATEVER FIGURE IS DEEMED APPROPRIATE. ACTIONS ARE TAKEN IF SURROGATE SPIKE RECOVERIES ARE NOT MET, AND THE DATA FOR SAMPLES THAT THE METHOD WORKS FOR FROM OUR SURROGATE POINT OF VIEW COULD BE ACCEPTED AS IS.

QUESTION AND ANSWER SESSION

MR. DAVIS: ABE DAVIS, HOOKER CHEMICAL. I WOULD JUST LIKE A SIMPLE EXPLANATION SO I KNOW I AM ON THE SAME WAVELENGTH AS YOU ARE.

WOULD YOU DEFINE THE DIFFERENCE IN YOUR TERMINOLOGY BETWEEN SPIKE, SURROGATE SPIKE AND INTERNAL STANDARD? DURING YOUR TALK I SEEMED TO JUMP BACK AND FORTH AND I'M NOT SURE I KNOW THE DIFFERENCE.

MR. LONGBOTTOM: WE HAD THAT PROBLEM IN OUR LABORATORY WITH THE DEVELOPMENT OF THE USE OF THE SURROGATE SPIKE. IN FACT, WHEN WE PUT OUT THE ORIGINAL PURGE AND TRAP, IT WAS OUR INTENTION TO USE BROMOCHLOROMETHANE, 2-BROMO-1-CHLOROPROPANE AND 1,4-DICHLOROBUTANE AS SURROGATE SPIKES, BUT WE DIDN'T USE THAT TERM AT THAT TIME, SO WE CALLED THEM INTERNAL STANDARDS AND THEY HAVE BEEN ADOPTED AS INTERNAL STANDARDS.

AN INTERNAL STANDARD FROM THE PURGE AND TRAP PERSPECTIVE WOULD BE THE TRADITIONAL INTERNAL STANDARD THAT IS USED FOR A FULL METHOD, THAT IS, WHERE YOU CORRECT YOUR RESULTS ON YOUR RECOVERY. AN INTERNAL STANDARD FOR THE METHOD 625 WOULD BE ONE THAT IS

ADDED RIGHT BEFORE GC/MS ANALYSIS TO BE USED AS AN INSTRUMENT CALIBRATION DEVICE. A SURROGATE SPIKE CURRENTLY DOESN'T SERVE ANY PURPOSE IN THE PURGE AND TRAP BECAUSE THEY ARE ADDED AT THE SAME TIME AS INTERNAL STANDARDS IN COMMON PRACTICE. IF YOU ARE GOING TO SPIKE SOMETHING, YOU MIGHT AS WELL SPIKE AN INTERNAL STANDARD. IN METHOD 625, THE SURROGATE SPIKE WOULD BE A COMPOUND THAT IS ADDED BEFORE EXTRACTION TO CHECK ON THE APPLICABILITY OF THE METHOD TO THE MATRIX AND THE PERFORMANCE OF THE OPERATOR.

WAS THERE ANOTHER TERM?

MR. DAVIS: JUST STRAIGHT SPIKES.

MR. LONGBOTTOM: AS WE ARE USING IT AS THE ADDITION OF ANY OF THOSE INTERNAL STANDARDS, SURROGATE SPIKES, PRIORITY POLLUTANTS IN A MINIMUM VOLUME OF SOLVENT, TYPICALLY 20 MICROLITERS, BEFORE GC/MS OR BEFORE ANALYSIS; THAT IS, COMPOUNDS THAT ARE ARTIFICIALLY ADDED.

MR. DAVIS: YOU ARE NOT DEFINING SPIKE AS SIMPLY A COMPOUND THAT YOU ARE LOOKING FOR. IN A PRIORITY POLLUTANT, THAT COULD ALSO BE AN ADDITION OF THE SURROGATE SPIKE, THEN?

MR. LONGBOTTOM: YES, IT WOULD

BE A SURROGATE SPIKE, AN INTERNAL STANDARD SPIKE.

MR. DAVIS: So spike would then include also the universal spike and universal surrogate spikes, the other is not...

MR. LONGBOTTOM: Yes.

MR. SPRAGGINS: Bob Spraggins, Radian. I would like to share with you a few of my observations. For over a year I personally ran the purge and trap device at Radian, and there were certain things that we found out about the methodology. Since that time we have tried to incorporate in our own work some internal quality assurance programs. One of the criteria we like to use is that the first internal standard contain at least 4,000 area counts so that we get a reasonable area count for the second internal standard. This area ratio, if you will, between the two, we have observed, depending on purging efficiency of the sample, can range anywhere from about 2.7 up to about 4, and generally it is around 2 and a half, 2.7, whatever.

In the beginning we worried if we weren't real close to that purging efficiency, but by running standards we found out that it really didn't matter too much if we were at 4, or maybe a little over 4; we still, by running standards, could calibrate very

NICELY. THE PROBLEM COMES IN WHEN YOU STICK THE SURROGATES IN THE SAMPLE AT 100 PPB. IF YOU HAVE ANY KIND OF CONTAMINATION IN THE SAMPLE AT ALL, AND THAT IS, AFTER ALL, WHAT WE ARE TRYING TO DO, WE ARE TRYING TO MEASURE SAMPLE CONTAMINATES, NOT SURROGATES, YOU END UP WITH ABOUT FOUR COMPOUNDS THAT ELUTE IN THE MIDDLE OF THE CHROMATOGRAM, BENZENE, TRICHLOROETHYLENE, D6 BENZENE, AND DIFLUOROTETRACHLOROETHANE, AND IF THEY ARE ALL IN THERE AT AROUND 100PPB, THEN YOU ARE GOING TO HAVE A SATURATED SYSTEM ON A HEWLETT-PACKARD MACHINE, AND YOU ARE GOING TO HAVE PROBLEMS ANALYZING THAT SAMPLE.

SO WHAT MY OPERATORS HAVE HAD TO DO IS LOWER THEIR GAIN TO AROUND TWO 2,500 AREA COUNTS TO COMPLY WITH THE ADDING OF THE SURROGATES TO KEEP THE THINGS ON SCALE. WHAT THIS DOES IS LOWER THE DETECTION CAPABILITY FOR SOME OF THE PRIORITY POLLUTANTS. SOME OF THEM ARE 50 TO 100 TIMES POORER THAN THE BEST RESPONDERS. I AGREE WITH YOU WHOLEHEARTEDLY THAT AN AREA COUNT, YOU SHOULD KEEP TRACK OF YOUR AREA COUNTS ON YOUR INTERNAL STANDARDS, AND WE TRY TO DO THAT. IF THERE IS SOMETHING FISHY FROM ONE RUN TO THE NEXT, WE WANT TO KNOW ABOUT IT SO WE KEEP A HANDLE ON IT, AND THIS IS PROBABLY A GOOD CRITERIA TO USE. I THINK WE DO HAVE A LITTLE BIT OF A PROBLEM

WITH SURROGATES IN THE VOAs AT 100 PPB.

MR. LONGBOTTOM: YOU WOULD SUGGEST A LOWER CONCENTRATION.

MR. SPRAGGINS: I THINK SO, YES.

MR. STANKO: GEORGE STANKO WITH SHELL DEVELOPMENT. THIS IS NOT REALLY A QUESTION OR A CRITICISM. I THINK MANY OF US FEEL THAT THERE ARE SOME PROBLEMS IN THE WAY PEOPLE ARE USING THE KUDERNA-DANISH EVAPORATOR. WE HAVE NOTICED IN EVALUATING OUR DATA CERTAIN WAYS TO SORT OF GIVE US A WARM FEELING, I AM NOT SAYING THIS IS AN ABSOLUTE WAY OF EVALUATING WHETHER THE EVAPORATION STUFF WAS DONE PROPERLY, BUT IT SORT OF GIVES YOU A WARM FEELING THAT WHEN YOU FIND TOLUENE IN YOUR VOA ANALYSES OF AN ENVIRONMENTAL SAMPLE, AND THEN WHEN YOU GO THROUGH YOUR BASE/NEUTRAL EXTRACTION AND ARE ABLE TO DETECT TOLUENE IN THE BASE/NEUTRAL EXTRACT, WE FEEL THAT THE CHANCES OF OVERHEATING OR OVERSTRIPPING OF THE ENVIRONMENTAL POLLUTANTS, IT PROBABLY DID NOT HAPPEN. IN OTHER WORDS, WE THINK THIS MAY BE ONE PROCEDURE THAT OUGHT TO BE CONSIDERED AS AN INDICATION OF WHETHER YOU ARE TAKING YOUR EXTRACT DOWN TOO FAR, OVERHEATING IT, OR THE POSSIBILITY OF LOSING PRIORITY POLLUTANTS.

THIS IS JUST AS A SUGGESTION THAT MIGHT BE TRIED.

MR. LONGBOTTOM: WE WERE LOOKING AT THE DEUTERATED DICHLOROBENZENE, WHICH IS AVAILABLE AND IS BEING USED BY SOME OF THE LABORATORIES NOW, BEING THE EARLIEST ELUTER, MOST VOLATILE OF THE PRIORITY POLLUTANTS, AND I THINK TOLUENE WOULD BE VERY APPROPRIATE ALSO.

MR. KLEOBFER: BOB KLEOBFER, EPA. JIM, I AM SORT OF UNEASY ABOUT YOUR APPROACH OF SELECTING THE COMPOUNDS THAT ARE MOST DIFFICULT TO DO AND COMING UP WITH YOUR PERFORMANCE CRITERIA, BECAUSE IF YOU JUST LOOK AT SOME OF THE DATA THAT I HAVE GATHERED OUT OF THE BASE/NEUTRAL FRACTION JUST AS AN EXAMPLE. IF YOU TAKE THE WORST CASE, WHICH IS DECAFLUOROBIPHENYL, WHICH IS 39 PLUS OR MINUS 18 FOR ONE STANDARD DEVIATION, AND IF YOU APPLY THE USUAL CRITERIA, WHICH IS THREE SIGMA, TO THAT WORST CASE SITUATION, THAT ALLOWS YOU A RECOVERY BETWEEN MINUS 15 PERCENT UP TO 93 PERCENT AS BEING ACCEPTABLE, AND OF COURSE THAT IS A WIDE ENOUGH RANGE, YOU CAN DRIVE A TRUCK THROUGH.

ON THE OTHER HAND, IF YOU SELECT A COMPOUND THAT IS EASIER TO DO SUCH AS THE 2-FLUOROBIPHENYL, YOUR RANGE IS MUCH LESS; IN THAT CASE IT IS 48 TO 78, BASED ON THREE SIGMA. IT JUST SEEMS TO ME THAT YOU REALLY HAVE TIGHTER CONTROL OVER THE SITUATION IF YOU SELECT

COMPOUNDS WHICH ARE EASIER TO DO.

MR. LONGBOTTOM: I PROPOSED THAT THE PERCENTAGE OF OUTLIERS BE YOUR QUALITY CONTROL AND SUGGESTED THAT WE COULD ARBITRARILY SELECT WHAT WE WANTED, WE COULD THROW OUT 15 PERCENT. IF WE CONCENTRATE ON 1 PERCENT OUTLIERS, WE WOULDN'T FIND VERY MANY; THE RANGE FOR ACCEPTANCE WOULD BE TOO WIDE. HOWEVER, IF WE BACKED THAT OFF TO CRITERIA THAT ALLOWED FOR MORE WORK, 15 PERCENT, 20 PERCENT, AND CONCENTRATED ON THOSE, I THINK OUR CRITERIA WOULD BE MUCH TIGHTER.

MR. KLEOBFER: SO YOU ARE SUGGESTING THAT WE USE SOMETHING LESS THAN THREE SIGMA FOR THE CRITERIA, THEN.

MR. LONGBOTTOM: THIS IS WHAT DEAN AND PRISCILLA HAVE BEEN STRUGGLING WITH--FINDING ACCEPTANCE LIMITS THAT MAKE SENSE TO THEM, AND THEY WANT TO INTUITIVELY THROW OUT THESE OUTLIERS AND PUT THE GOOD DATA INTO A SEPARATE CASE. I'M NOT SURE THAT I AM EXPLAINING IT ANY BETTER THAN IT WAS EXPLAINED YESTERDAY, BUT NO, I AM NOT HAPPY WITH THE THREE SIGMA, I AM NOT HAPPY WITH THE DATA WE GENERATE WITH THE THREE SIGMA, THE PERFORMANCE CRITERIA, AND WHAT I'D LIKE TO DO IS BACK OFF WITH A HIGHER PERCENTAGE, TIGHTER REINS, AND FIND OUT WHAT IN THE WORLD IS GOING ON WITH THOSE OUTLIERS, IMMEDIATELY, AS PART OF THE

METHOD.

MR. SPRAGGINS: BOB SPRAGGINS, RADIAN. JIM, YOU SAID EARLIER THAT IF YOU TRIED TO RECALCULATE SAMPLES BASED UPON SURROGATES RATHER THAN THE INTERNAL STANDARDS, IT DID NOT HELP MATTERS.

MR. LONGBOTTOM: IT WOULD HAVE HELPED MATTERS HAD THE SAME MATHEMATICS BEEN APPLIED THAT BRUCE COLBY APPLIES.

MR. SPRAGGINS: OKAY, BECAUSE IT SEEMED LIKE IF YOU PUT TWO DIFFERENT COMPOUNDS IN AND SAY YOU PUT 100 PPB OF D_6 BENZENE, AND YOU MEASURED 100 PPB OF D_6 BENZENE AND THEN YOU MEASURED FIVE TIMES AS MUCH TRICHLOROETHYLENE AS YOU SAID YOU PUT IN OR WHATEVER, THAT MAYBE THAT FIVE TIMES AS MUCH WOULD NOT BE AN OUTLIER THEN BECAUSE YOU HAD A GOOD FIX ON YOUR SURROGATE, BUT IF INDEED YOU MEASURED FIVE TIMES AS MUCH OF THE SURROGATE ALSO, AND YOU RATIOED THIS BACK TO 100 OR WHATEVER, THEN YOU SHOULD COME UP WITH A REASONABLE NUMBER FOR YOUR PRIORITY POLLUTANT SPIKE, IS THIS NOT CORRECT?

MR. LONGBOTTOM: YES, I DID THIS WITH A HAND CALCULATOR AND I COULD NOT FACTOR IN ALL THOSE FORMULAS THAT BRUCE USED TO RESOLVE OUT AND COME UP WITH THE TYPE OF CORRELATIONS THAT BRUCE HAS BEEN DEMONSTRATING.

MR. SPRAGGINS: WE HAVE DONE SEVERAL THINGS WITH OUR PURGE AND TRAP DEVICE, ONE OF THEM IS AMBIENT AIR MONITORING. WE TAKE THE LITTLE TUBE OUT TO THE FIELD AND PULL OR PUCH AN AIR SAMPLE THROUGH IT AND MEASURE BENZENE LEVELS OR WHATEVER, AND WE HAVE DONE WHAT I THINK ARE SOME FAIRLY INTERESTING STUDIES WHERE WE PUT AN INTERNAL STANDARD ON IN THE FIELD, AND BRING IT BACK IN, AND PUT ANOTHER ONE ON RIGHT AS IT GOES INTO THE INSTRUMENT. WE HAVE ALSO DONE SOME OF THIS IN WATER STUDIES, AND I AM SURPRISED AT GENERALLY THE GOOD EFFICIENCY OF GETTING THE MATERIAL BOTH ON THE COLUMN OF THE TRAP AND OFF, BUT THIS IS A LIMITED STUDY AND I DO NOT WANT TO BACK IT UP WITH ANY NUMBERS.

MR. TELLIARD: THANKS, JIM. OUR NEXT SPEAKER IS MIKE CARTER. MIKE IS GOING TO TALK TO YOU ABOUT SOMETHING COMPLETELY DIFFERENT CALLED METALS; THESE ARE THE HARD CHUNKS.

PROTON INDUCED X-RAY EMISSION ELEMENTAL ANALYSIS

By: Mike Carter
George Grant

MR. CARTER: The instrumental technique that is on the agenda, which I understand few people have a copy of, is proton induced X-ray emission. Our interest in this analytical measurement is based on the fact that a lot of our samples for elemental analysis have an insoluble residue, even after the standard methods for sample digestion, and we are interested in knowing something about what is in that solid residue. Pixe has the capability to look at solid samples, and as a little extra benefit, it also has good performance on some of the metals that are problem metals for AA and ICP methods. It is a method that gives us good sensitivity. It is a survey technique; it looks at a lot of metals at one shot, so the cost per determination is quite reasonable.

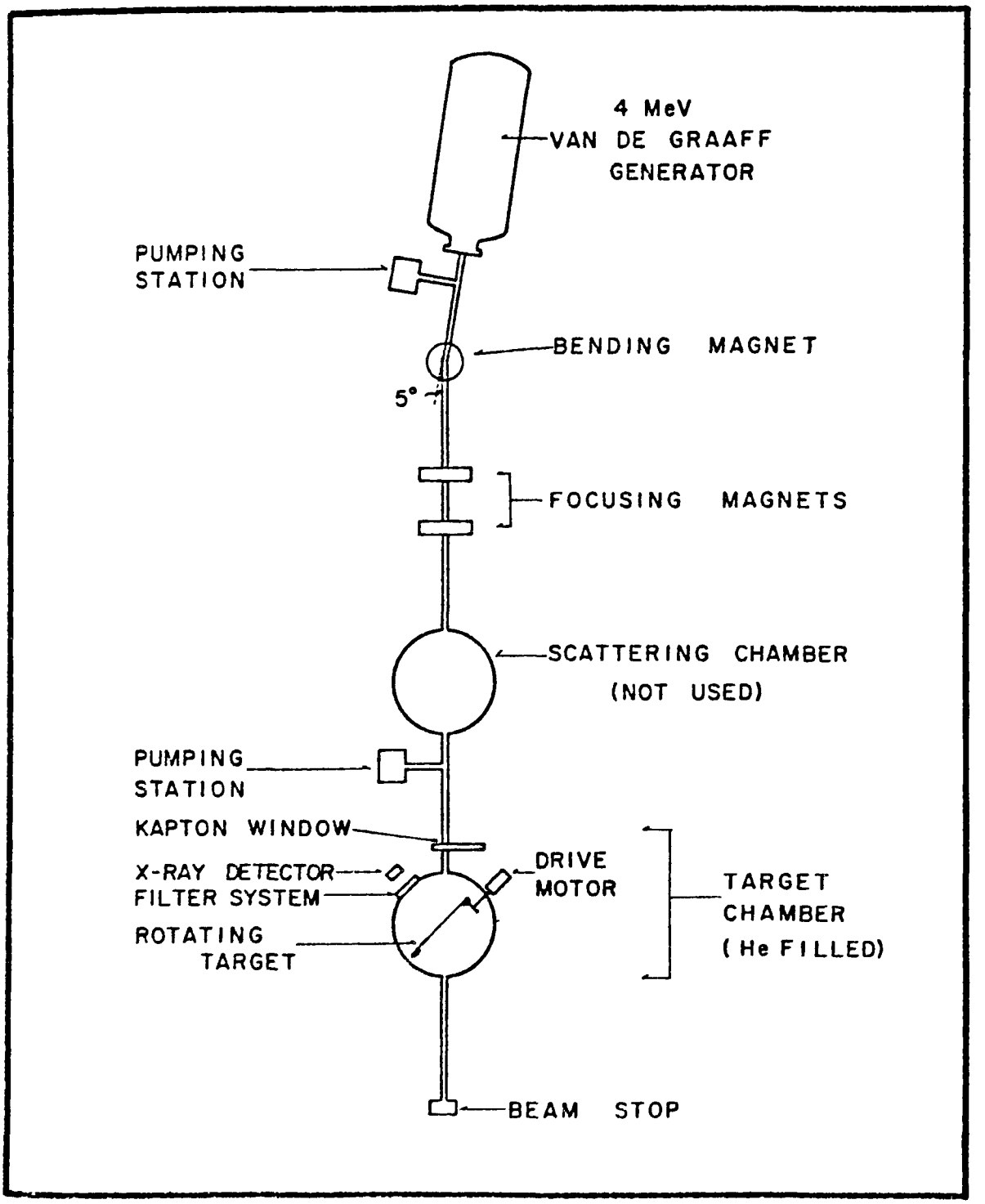
The laboratory doing this work for us follows the standard Cincinnati-type sample prep techniques; they analyze the digestate and any residue that remains, and we get an idea of how some of these elements are being distributed between the digestate

AND ANY RESIDUE.

SO WITH THAT BACKGROUND I AM GOING TO TURN THE REST OF THE PRESENTATION OVER TO DR. GEORGE GRANT, WHO IS WITH THE VIRGINIA ASSOCIATED RESEARCH CAMPUS UP THE ROAD IN NEWPORT NEWS, VIRGINIA.

DR. GRANT: THANK YOU, MIKE. OUR LABORATORY'S MAIN STRENGTH IS IN TRACE ELEMENT ANALYSES. WE HAVE THREE TECHNIQUES, WE HAVE PIXE (PROTON INDUCED X-RAY EMISSION), WE HAVE GRAPHITE FURNACE AA CAPABILITY AND SELECTIVE ION ELECTRODES. ALL OF YOU DOING METALS WORK, I AM SURE, ARE FAMILIAR WITH AA, SO I WON'T SAY MUCH ABOUT THAT THIS MORNING. HOWEVER, I WOULD LIKE TO DO TWO THINGS; I WOULD LIKE TO DESCRIBE HOW THE TECHNIQUE IS PERFORMED, GIVE YOU SOME IDEA OF THE KIND OF CAPABILITY WE HAVE AND POINT OUT A COUPLE OF AREAS WHERE WE DO, I THINK, HAVE THE CAPABILITY OF PROVIDING INFORMATION COMPLEMENTARY TO THE ANALYSES NOW BEING PERFORMED BY AA OR ICAP ON THESE SAMPLES.

IF I COULD HAVE SLIDE ONE, PLEASE. THE BASIC HEART OF THE TECHNIQUE IS THE VAN DE GRAAF ACCELERATOR WHICH ACCELERATES PARTICLES. WE USE A PROTON BEAM AT AN ENERGY OF ABOUT 3.8 MEV. THE PROTON BEAM COMES DOWN THE CHAMBER HERE, IT IS A VACUUM SYSTEM; IT GOES THROUGH A WINDOW WHICH PROVIDES ISOLATION

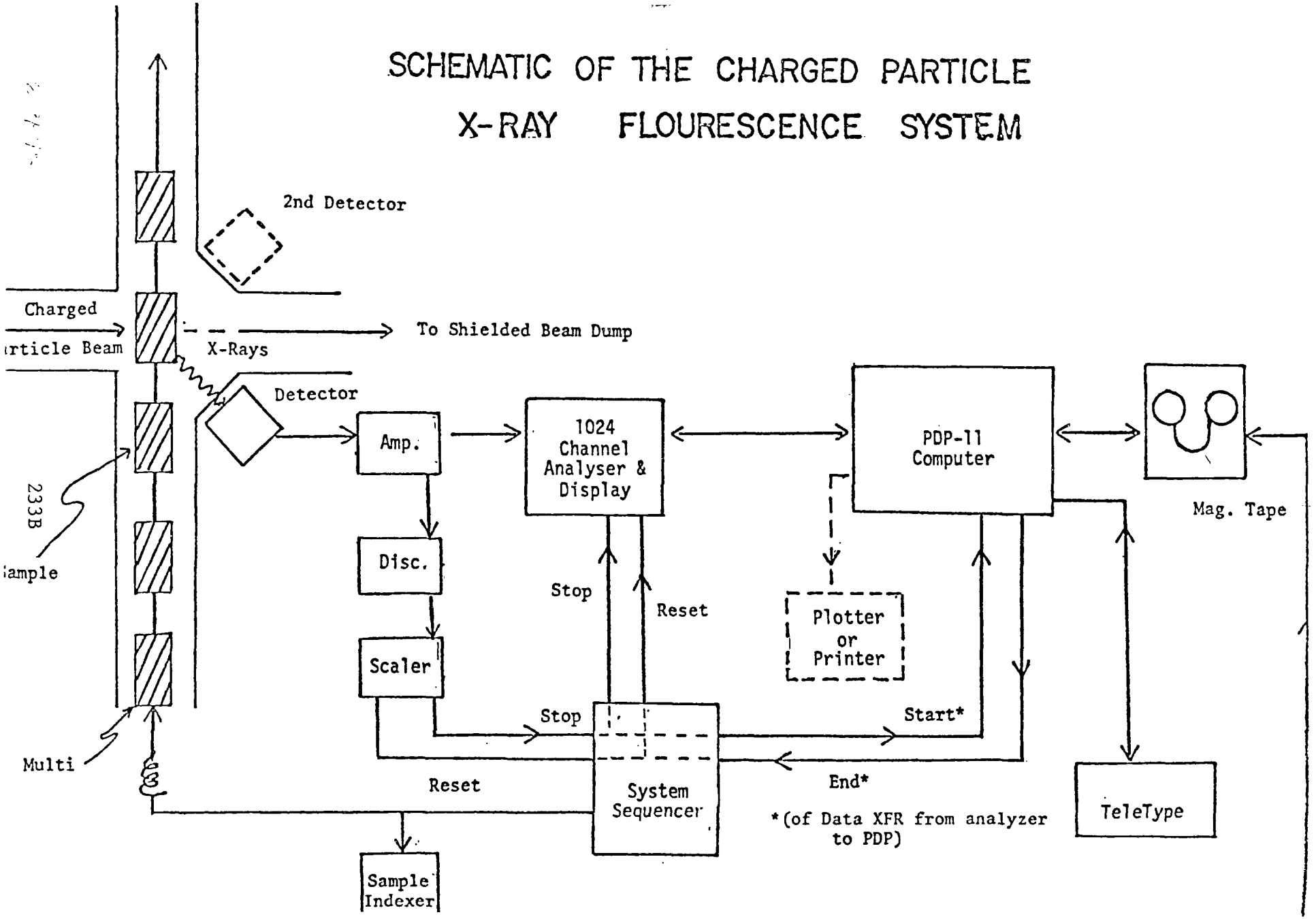

4 MeV
VAN DE GRAAFF
GENERATOR
PUMPING
STATION
BENDING MAGNET
5°
FOCUSING MAGNETS
SCATTERING CHAMBER
(NOT USED)
PUMPING
STATION
KAPTON WINDOW
X-RAY DETECTOR
FILTER SYSTEM
DRIVE
MOTOR
ROTATING
TARGET
TARGET
CHAMBER
(He FILLED)
BEAM STOP

BETWEEN THE VACUUM SYSTEM INTO THE SAMPLE COMPARTMENT. THIS IS A TOP VIEW OF THE SYSTEM, X-RAYS EMITTED OR GO THROUGH A FILTER SYSTEM HERE INTO A LITHIUM-DRIFTED SILICON DETECTOR. THE FILTER SYSTEM VARIES FROM INSTALLATION TO INSTALLATION. WE HAVE DELIBERATELY CONSTRUCTED A FILTER WHICH ATTENUATES THE LIGHTER X-RAYS FROM MORE ABUNDANT ELEMENTS SUCH AS MAGNESIUM, ALUMINUM AND SO FORTH, IN ORDER TO ENHANCE OUR CAPABILITY FOR TRANSITION ELEMENTS AT A MID-RANGE AND HEAVIER ELEMENTS. IN OTHER WORDS, WE HAVE OPTIMIZED OUR SYSTEM FOR FIRST-ROW TRANSITION ELEMENTS AND HEAVIER.

SLIDE 2, PLEASE. THIS IS A PICTURE OF THE SYSTEM. OBVIOUSLY IT IS NOT A BENCH-TOP MODEL. THE ACCELERATOR HERE IS FILLED WITH SULFUR HEXAFLUORIDE AS A DIELECTRIC GAS. THE SAMPLE COMPARTMENT IS RIGHT UP IN HERE.

SLIDE 3, PLEASE. THIS IS A SCHEMATIC OF THE SYSTEM. ON THE LEFT-HAND SIDE WE SEE THE TYPE OF SAMPLE ARRANGEMENT WE HAVE. THIS CONSISTS OF A TRAY THAT IS APPROXIMATELY THREE FEET LONG, CONTAINING 11 COMPARTMENTS UPON WHICH WE INSTALL THE SAMPLES THAT ARE PREPARED IN THE ANALYTICAL LAB. I THINK, IF YOU CAN REMEMBER IN THAT PREVIOUS SLIDE, THAT THAT IS

SCHEMATIC OF THE CHARGED PARTICLE X-RAY FLOURESCENCE SYSTEM



HARDLY A VERY CLEAN ENVIRONMENT FOR TRACE ELEMENT ANALYSES. ALL OF THESE SAMPLES ARE PREPARED IN THE ANALYTICAL LAB, AND THE TARGETS WERE MADE FOR PIXE ANALYSIS IN A CLEAN ROOM. THEY ARE INSTALLED IN THIS 11-COMPARTMENT TRAY THAT IS PUT IN A SEALED PLEXIGLAS CONTAINER AND THEY ARE TRANSPORTED FROM AN ANALYTICAL LAB TO THE ACCELERATOR THROUGH THAT. THEY ARE ONLY OPEN FOR A BRIEF INSTANT WHILE THE TRAY IS BEING INSERTED IN THE SAMPLE COMPARTMENT.

INSTEAD OF RUNNING SAMPLES UNDER HIGH VACUUM, WE RUN THEM IN APPROXIMATELY 100 MILLIMETERS OF HELIUM AND WE ROTATE THE SAMPLES, WHICH IS A LITTLE DIFFERENT FROM WHAT MOST PEOPLE DO WITH PIXE.

THE ADVANTAGES OF THIS TECHNIQUE ARE THAT THE HELIUM PROVIDES COOLING. THE ROTATION OF THE TARGET ALSO PROVIDES COOLING, ALLOWING US TO USE HIGHER BEAM CURRENTS AND INCREASE OUR SENSITIVITY. SO WE HAVE, I THINK, EXCELLENT SENSITIVITY FOR ALL THE ELEMENTS ACROSS THE SPECTRUM. WHILE THE PARTICLE BEAM COMES IN HERE, THE X-RAY IS EMITTED, THE DATA IS ACQUIRED BY 1,000 CHANNEL, MULTI-CHANNEL ANALYZER. AT THE PRESENT TIME THE DATA ARE DUMPED THROUGH A TELETYPE AND ANALYZED BY A COMPUTER OFF-LINE. WE DO HAVE THIS PDP-11 COMPUTER NOW AND THE SOFTWARE IS BEING WRITTEN AND DEBUGGED AND I HOPE IN A MATTER OF WEEKS THAT WE

WILL BE ON-LINE, ELIMINATING THIS VERY TROUBLESOME TELETYPE.

IF I MIGHT HAVE SLIDE 4, PLEASE. THIS IS AN EXAMPLE OF THE DATA AND WHAT WE DO WITH IT. THOSE OF YOU WHO WERE OVER AT LOCKHART'S LAST NIGHT, I WILL POINT OUT THAT ALONG WITH YOUR FAVORITE GOLDEN BEVERAGE, YOU GET A LOT OF TRACE ELEMENTS IN YOUR CLAMS; THAT IS WHAT THE SAMPLE WAS IN THIS CASE. THE SPECTRUM CONSISTS OF A SET OF MULTIPLET PEAKS. IN THIS CASE WE USE INDIUM, TYPICALLY, AS AN INTERNAL STANDARD. THIS PEAK, AND THAT ONE AND THAT ONE ARE ALL FROM INDIUM THAT WE ADD IN KNOWN AMOUNTS TO THE SAMPLE AFTER DIGESTION. WE HAVE CALIBRATED INTO THE COMPUTER ON DISC THE EXPERIMENTAL LINE SHAPES FOR EACH ELEMENT FROM ALUMINUM THROUGH URANIUM, AND THE COMPUTER PROGRAM DECONVOLUTES THE SPECTRUM AND ESTIMATES THE PEAK AREAS FOR EACH OF THE MULTIPLETS FOR EACH ELEMENT PRESENT IN THE SAMPLE, BEGINNING WITH THE MAJOR PEAKS AND SEQUENTIALLY SCANNING THROUGH AND PICKING UP THE MINOR PEAKS AS WE GO.

THE ANALYSIS I HAVE SHOWN HERE YOU WILL NOTE ON THE LEFT-HAND SIDE THAT THE Y-AXIS IS LOG OF THE COUNTS PER CHANNEL; IN OTHER WORDS, IT IS A SEMILOGARITHMIC DISPLAY HERE. FIRST IS THE X-RAY ENERGY IN KEV FROM ZERO TO 40. THE TRACES I HAVE SHOWN HERE

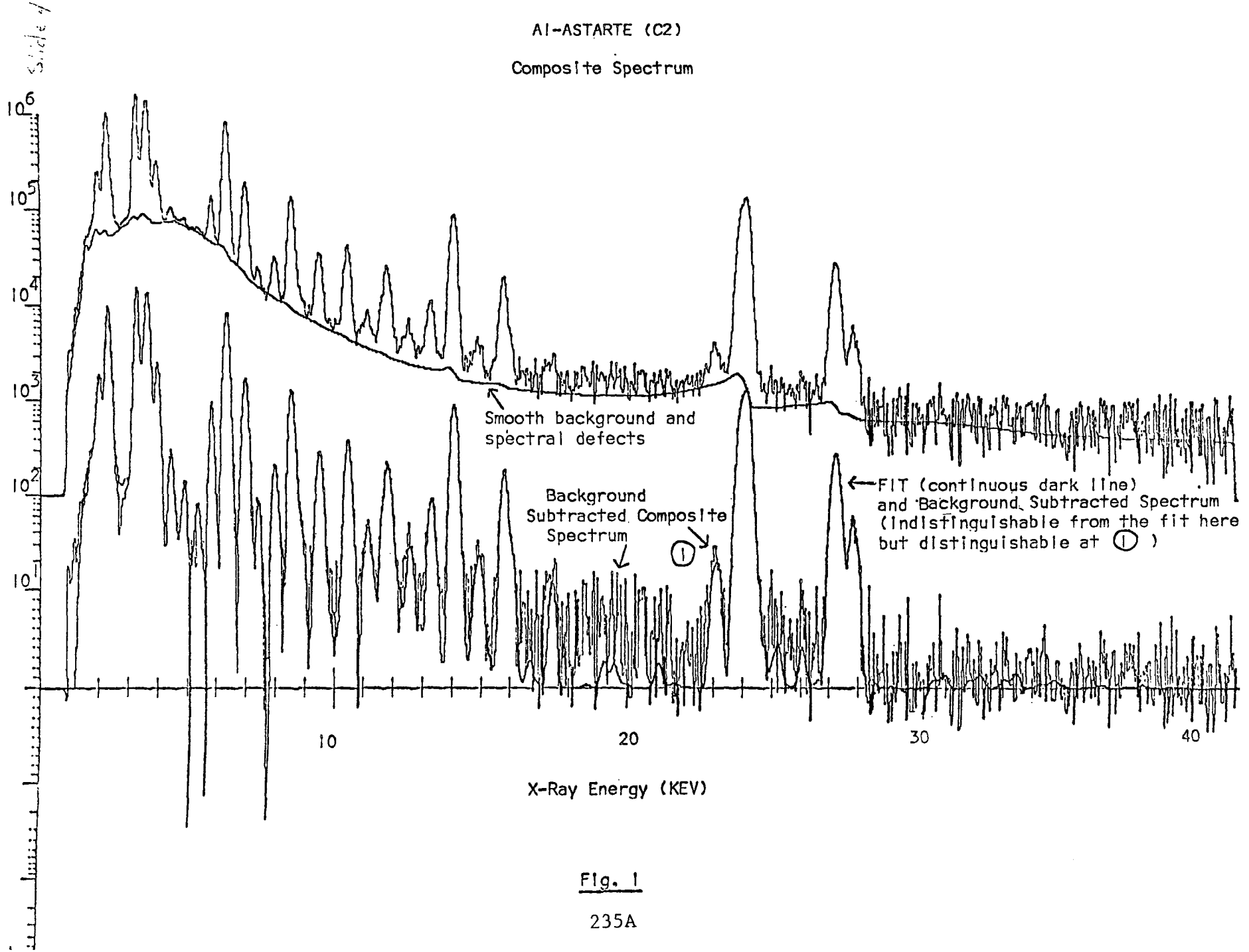

Al-ASTARTE (C2)
Composite Spectrum
10^6
10^5
10^4
10^3
10^2
10^1
Smooth background and spectral defects
Background Subtracted Composite Spectrum
1
FIT (continuous dark line) and Background Subtracted Spectrum (Indistinguishable from the fit here but distinguishable at 1)
10
20
30
40
X-Ray Energy (KEV)

Fig. 1

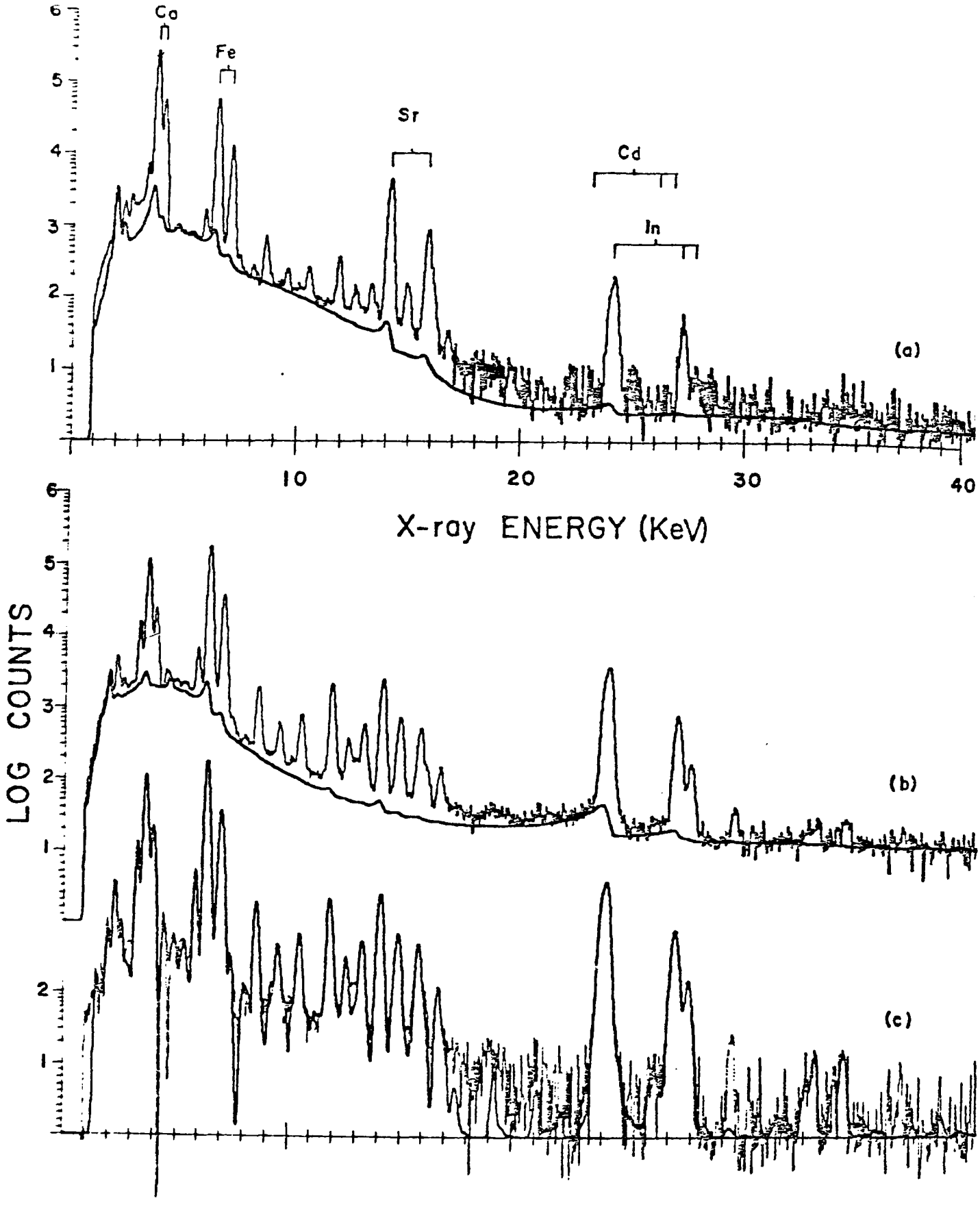
CONSIST OF FOUR. THE TOP TRACE CONSISTS OF THE RAW DATA WITH A LINE DRAWN THROUGH THE THOUSAND POINTS. THE NEXT TRACE UNDERNEATH IT, RIGHT HERE, CONSISTS OF THE COMPUTER-CALCULATED BACKGROUND; THIS IS COMPLETELY DONE BY THE COMPUTER. THE BOTTOM TWO TRACES ARE THE RAW DATA MINUS COMPUTED BACKGROUND AND ALSO THE SUMS OF THE COMPUTED CURVES FROM THE DECONVOLUTED DATA. I THINK YOU CAN SEE, IN MOST CASES YOU CANNOT DISTINGUISH ONE LINE FROM THE OTHER; THEY ARE SUPERIMPOSABLE, WHICH IS AN INDICATION OF THE QUALITY OF OUR FIT THROUGH THE DATA.

I THINK YOU CAN SEE HERE, THIS PARTICULAR PEAK IS THE CADMIUM YOU ATE, WHICH IS FAIRLY ABUNDANT IN CLAMS. YOU CAN SEE THAT THERE IS A LITTLE BIT OF A DISCREPANCY HERE BETWEEN A FEW OF THE DATA POINTS FOR THE RAW DATA MINUS BACKGROUND IN THE FITTED PEAK. THE FINAL STEP, AFTER THE DECONVOLUTION IS FITTED, IS TO COMPUTE THE CONCENTRATION OF EACH COMPONENT IN THE SAMPLE, AND THE COMPUTER PROGRAM COMPARES THE COMPUTED CONCENTRATION TO THE STATISTICAL PARAMETERS. WE COUPLE IN THE UNCERTAINTY IN THE BACKGROUND SUBTRACTION, COMPUTATION, THE STATISTICAL NOISE WHICH VARIES THROUGHOUT THE SPECTRUM, AND SO EACH ELEMENTAL CONCENTRATION ALSO HAS A STANDARD DEVIATION COMPUTED FOR THAT CONCENTRATION, AND

OF COURSE WE USE A TWO STANDARD DEVIATION CRITERION SO THAT ANY COMPUTED CONCENTRATION LESS THAN TWO STANDARD DEVIATIONS IS REPORTED AS A DETECTION LIMIT NUMBER.

THAT IS HOW THE SYSTEM IS SET UP. I WON'T TALK ABOUT PRIORITY POLLUTANT MEASUREMENTS TODAY BECAUSE, FOR ONE REASON, WE HAVE ONLY RECENTLY BEGUN MAKING MEASUREMENTS, BUT I WILL TELL YOU INSTEAD ABOUT A FAIRLY COMPLETE STUDY WE HAVE PERFORMED IN THE PAST WHICH WAS PERFORMED ON SEDIMENTS. THESE ARE OCEAN SEDIMENTS AND WE WERE ATTEMPTING TO DETERMINE THE METALS THAT ARE LEACHABLE FROM THE SEDIMENTS. THE EXPERIMENTAL PROCEDURE WAS A FIVE NORMAL NITRIC ACID LEACH FOR TWO HOURS AT ROOM TEMPERATURE, AND THEN WE PERFORMED A VARIETY OF PIXE AND ATOMIC ABSORPTION MEASUREMENTS ON THESE LEACHATES.

ON SLIDE 5 IS SHOWN SOME OF THE TYPE OF DATA WE HAD. THESE REPRESENT THE EXTREMES OF BEHAVIOR THAT WE OBSERVED. ON THE TOP TRACE IS THE PIXE SPECTRUM FOR WHAT I AM CALLING A HIGH CALCIUM SAMPLE. THIS IS A SAMPLE IN WHICH THERE WAS A LOT OF BIOLOGICAL MATERIAL AND THEREFORE SKELETAL FRAGMENTS CONTAINING HIGH CALCIUM. THESE ALSO TENDED TO HAVE LARGE CONCENTRATIONS OF IRON AND STRONTIUM, AS YOU CAN SEE FROM THE SPECTRUM.


Ca
Fe
Sr
Cd
In
(a)
(b)
(c)
LOG COUNTS
X-ray ENERGY (KeV)
10
20
30
40

ON THE BOTTOM TRACE IS A SPECTRUM REPRESENTATIVE OF WHAT I CALL A LOW CALCIUM SAMPLE WHICH CONSISTED MAINLY OF SILICA AND INORGANIC COMPONENTS, VERY LITTLE BIOLOGICAL ACTIVITY, AND THEREFORE WAS MUCH LOWER IN CALCIUM. NOW, THE APPARENT PEAKS ARE COMPARABLE, YOU WILL SEE HERE IN THIS CASE, BECAUSE WE ARE ABLE TO RUN THE SAMPLE, WHICH WAS LOW IN ABUNDANT ELEMENTS, NAMELY, CALCIUM, FOR A LONGER TIME PERIOD, THUS GETTING BETTER STATISTICS ON THE TRANSITION ELEMENTS IN THIS RANGE HERE. SO WE ARE LIMITED, AS ANYBODY IS IN A SYSTEM FOR THE DYNAMIC RANGE, THE PROBLEM THAT WAS ADDRESSED JUST A MINUTE AGO, WITH TOO MUCH SURROGATE SPIKE. WE CAN COUNT UP TO 10^6 COUNTS AND THEN WE HAVE TO STOP, SO IN OUR TECHNIQUE THE PRESENCE OF AN ABUNDANT ELEMENT GIVING US A LARGE PEAK WILL REDUCE THE DETECTION LIMITS FOR ANY OF THE OTHER ELEMENTS PRESENT IN THE SAMPLE.

ON SLIDE 6 I HAVE A SET OF TYPICAL ELEMENTS THAT WE FOUND IN THESE SEDIMENT LEACHES. AS I MENTIONED, THE TECHNIQUE GIVES US A VALUE FOR EVERY ELEMENT BETWEEN ALUMINUM AND URANIUM INCLUSIVE.

MANY OF THE ELEMENTS ARE TYPICALLY FOUND AS DETECTION LIMIT NUMBERS, SO I HAVE NOT INCLUDED THEM IN THIS SLIDE. I WOULD ALSO POINT OUT THAT FOR SOME OF THE

Typical Marine Sediment Components (ppm, dry wt.) After 5N HNO_3 Leach

Atomic Symbol	High Calcium Station (A2SB) Concentration	Absolute Std. Dev.	Low Calcium Station (C1B1) Concentration (ppm)	Absolute Std. Dev.
Al	516.	84.	47.8	5.0
Si	Less Than 2SD	55.40	65.6	3.3
P	Less Than	19.94	19.4	3.6
S	84.	26.	189.7	1.7
Cl	492.	19.	17.63	0.80
K	739.	18.	80.88	0.61
Ca	3.086%	0.058	580.6	2.3
Sc	50.7	4.5	1.07	0.22
Ti	Less Than 2SD	0.91	2.786	0.089
• V	6.40	0.92	1.411	0.088
Cr	1.56	0.70	0.404	0.063
Mn	48.8	1.4	24.49	0.16
Fe	2241.	42.	324.2	1.3
Co	5.61	0.92	0.561	0.078
Ni	1.88	0.37	0.165	0.020
Cu	2.46	0.24	0.234	0.014
Zn	11.61	0.34	2.250	0.020
• As	1.14	0.19	0.510	0.017
Br	2.67	0.15	3.049	0.023
• Rb	1.09	0.10	0.028	0.010
Sr	111.8	2.2	3.413	0.025
Cd	Less Than 2SD	0.24	0.096	0.034
*In	66.8	1.3	66.70	0.25
Sn	Less Than 2SD	0.26	0.206	0.037
Ba	Less Than 2SD	1.31	Less Than 2SD	0.28
Ce	11.8	2.6	0.83	0.27
Hg	Less Than 2SD	0.44	Less Than 2SD	0.01
Pb	6.10	0.38	1.284	0.031

ELEMENTS, THE SENSITIVITY IS RELATIVELY POOR. FOR EXAMPLE, ALUMINUM IS ON THE RAGGED EDGE; OUR DETECTION LIMITS ARE NOT GOOD FOR THAT, SO GENERALLY SPEAKING WE WILL DETERMINE ALUMINUM BY ATOMIC ABSORPTION IF THAT NUMBER IS DESIRED.

BUT YOU CAN SEE, ON THE LEFT-HAND SIDE I HAVE THE TYPICAL CONCENTRATIONS DETERMINABLE IN A HIGH CALCIUM STATION, THAT IS, ONE REPRESENTING A LOT OF BIOLOGICAL ACTIVITY, A LOT OF SKELETAL FRAGMENTS, ET CETERA, AND OVER HERE A LOW CALCIUM STATION. YOU WILL NOTICE, I HAVE NOT, OF COURSE, ATTEMPTED TO RESTRICT MY ELEMENTS TO THE PRIORITY POLLUTANT LIST AND IN ADDITION TO THE 13 ELEMENTS OF INTEREST, WE CAN EASILY SEE A NUMBER OF OTHER TRANSITION ELEMENTS, INCLUDING SOME HEAVIER ELEMENTS THAT ARE COMMONLY FOUND IN ENVIRONMENTAL SAMPLES.

IN OUR STANDARD DEVIATIONS OVER HERE, YOU CAN MAKE A ROUGH ESTIMATE OF WHAT OUR DETECTION LIMIT WOULD BE IN THIS TYPE OF SAMPLE BY JUST DOUBLING THIS NUMBER. I ALSO POINT OUT THAT THESE NUMBERS ARE IN PARTS PER MILLION DRY WEIGHT. THEY ARE NOT SOLUTION CONCENTRATIONS, AND ALMOST ALL THE NUMBERS I AM SHOWING YOU TODAY ARE COMPUTED IN PARTS PER MILLION DRY WEIGHT. AS YOU ARE ALL AWARE IN DOING ICAP AND AA MEASUREMENTS, THE USUAL DISCUSSION

TABLE-10 (contd.)

(Master Mix Solution Analyses-PIXE and AA)

Solution #2

Element	Known CONC (ug/ml)	PIXE Analysis		
		(6166-3)*	(6166-4)*	(6325-3)*
Cr	2.00	1.97 .03	1.90 .02	2.06 .02
Ni	5.00	4.89 .03	4.92 .02	5.21 .03
Cu	5.00	4.84 .03	4.83 .02	5.10 .03
Rb	1.009	0.98 .01	0.99 .01	1.01 .01
In	25.00	25.0	25.0	25.0
Cs	10.28	10.3 .2	10.1 .1	10.3 .1
Pb	5.00	4.82 .03	4.81 .02	4.99 .03

OF THE DETECTION LIMITS IS BASED UPON SOLUTION CONCENTRATIONS, AND OF COURSE IN TERMS OF AN INDUSTRIAL EFFLUENT, WHICH IS LIQUID, THAT IS PROBABLY THE MOST RELEVANT VARIABLE. BUT IN TERMS OF A SOLID SAMPLE, PARTICULATES OR SAMPLE SLUDGES, PARTS PER MILLION DRY WEIGHT IS PROBABLY THE MORE RELEVANT COMPARISON TO MAKE.

WE USE A VARIETY OF TECHNIQUES FOR CALIBRATION OF PIXE AND FOR CHECKING OUR QUALITY CONTROL, ONE OF WHICH IS ILLUSTRATED IN SLIDE 7.

THESE ARE MASTER MIXES, AND THEY ARE COMPLETELY ANALOGOUS TO THE EPA CHECK SAMPLES. I DO NOT HAVE A SLIDE OF THE CHECK SAMPLES, BUT WE HAVE ANALYZED SOME AND GET EXCELLENT DETECTION LIMITS AND REPRODUCIBILITY FOR THEM.

THIS PARTICULAR STUDY WAS DONE OVER A SIX-MONTH PERIOD ON THE SAME SOLUTION. WE WERE TESTING, REALLY, TWO VARIABLES HERE: THE STABILITY OF THE SOLUTION THAT WE WERE ABLE TO MAKE UP FROM REAGENT GRADE CHEMICALS, AND FURTHERMORE, THE STABILITY OF THE PIXE SYSTEM. THERE WAS NO RECALIBRATION OF PIXE DURING THIS TIME, THOUGH THESE TWO WERE RUN ON THE SAME DAY, IN THE SAME TRAY, AND THIS LAST ONE WAS RUN SIX MONTHS LATER ON THE SAME SOLUTION, SO ANY DIFFERENCES REFLECT BOTH SOLUTION CHANGES AND PIXE

CHANGES. AS YOU CAN SEE, THE DIFFERENCES ARE VERY MINOR.

ON SLIDE 8 WE ARE VERY CONCERNED ABOUT THE ANALYTES' STABILITY. AS ANYBODY DOING TRACE ELEMENT ANALYSIS IS AWARE, IF YOU ARE USING A SINGLE-ELEMENT-AT-A-TIME ANALYTICAL METHOD SUCH AS ATOMIC ABSORPTION, AND YOU ARE ANALYZING A LARGE NUMBER OF SAMPLES, A RUN FOR ONE ELEMENT MAY TAKE YOU FOUR HOURS. SO UNLESS YOU HAVE A LOT OF INSTRUMENTS AVAILABLE TO YOU, THE ANALYSIS FOR A MULTIELEMENT ANALYSIS OF A SAMPLE MAY TAKE SEVERAL DAYS. WE WERE CONCERNED ABOUT WHETHER THE SAMPLES, ONCE PREPARED IN THE FORM OF AN ANALYTE, WOULD BE STABLE FOR A MUCH LONGER TIME PERIOD THAN WE MIGHT ENCOUNTER IN THE LAB DURING THAT ANALYSIS.

THIS STUDY WAS DONE OVER A THREE-WEEK PERIOD, WHICH FAR EXCEEDED THE TIME THAT WE WOULD BE DOING THE ANALYSIS, WHICH WAS TYPICALLY A COUPLE OF DAYS. THE FOUR REPLICATIONS, THEN, ARE FOUR TARGETS MADE FROM THE SAME SOLUTION FOR THIS PARTICULAR STATION WHICH WAS A LOW CALCIUM STATION WITH LOW BIOLOGICAL ACTIVITY. EACH PIXE TARGET WAS SPOTTED AND ANALYZED COMPLETELY INDEPENDENTLY OVER A PERIOD OF THREE WEEKS. IF YOU LOOK AT THE DATA, YOU WILL SEE THAT THERE ARE PRACTICALLY NO CHANGES WHATEVER THAT SHOW A TREND, WITH

Sediment Leach

Analyte Stability Study (3 week period)

Sample C4-3 (Cruise 1)

Element	R1	R2	R3	R4	Mean ± S.D
CA	14819 200	15175 210	14933 280	15879 310	15202 ± 356
TI	45.3 1.1	49.6 1.2	44.5 1.5	48.7 1.6	47.0 ± 1.88
V	14.45 .90	12.24 .90	14.2 1.2	15.9 1.3	14.2 ± 1.15
CR	6.41 .65	4.96 .65	6.98 .84	8.61 .84	6.7 ± 1.12
MN	85.6 1.6	82.3 1.6	85.1 2.1	87.6 2.2	85.1 ± 1.64
FE	3932. 53	3925. 55	4057. 75	4169. 82	4021. ± 86.92
CO	9.44 .92	8.85 .91	7.2 1.2	6.4 1.2	7.9 ± 1.05
NI	2.70 .29	3.14 .24	2.92 .39	2.81 .40	2.89 ± 0.14
CU	7.10 .27	6.60 .16	7.13 .37	6.84 .38	6.92 ± 0.18
ZN	23.82 .40	25.56 .41	23.47 .54	23.60 .57	24.11 ± 0.73
AS	4.18 .20	4.14 .20	4.24 .26	4.13 .27	4.175 ± 0.03
SR	78.7 1.1	78.5 1.1	79.5 1.5	79.5 1.6	78.97 ± 0.31

THE POSSIBLE EXCEPTION OF IRON AND COBALT DOWN HERE WHICH DID SHOW A SLIGHT TREND. HOWEVER, IF YOU ANALYZE THIS TREND AS A FUNCTION OF TIME, INCLUDING THE STATISTICAL UNCERTAINTIES IN EACH OF THOSE NUMBERS, YOU FIND THAT THE TREND IS NOT SIGNIFICANT, SO A VERY SLIGHT TREND WAS THERE BUT AT A VERY LOW LEVEL OF SIGNIFICANCE.

HAVING SATISFIED OURSELVES THAT THE ANALYTES, WITH REAL SAMPLES, WERE STABLE OVER A TIME PERIOD MUCH LONGER THAN THAT WHICH WE WOULD HAVE IN THE LAB, WE FELT COMFORTABLE IN OUR AA DATA. OF COURSE THE PIXE TARGETS, WHEN WE DO THOSE MEASUREMENTS, ARE MADE UP IMMEDIATELY AFTER PREPARATION OF THE ANALYTE. I MIGHT DESCRIBE JUST BRIEFLY THE PREPARATION OF THE TARGETS, THERE ARE TWO TYPES. IF WE HAVE A SAMPLE THAT IS SOLUBILIZABLE, SUCH AS AFTER AN ACID DIGESTION, THEN WE SPOT THAT SAMPLE, AFTER DOPING WITH INDIUM OR ANOTHER SUITABLE INTERNAL STANDARD, ONTO A THIN POLYMER FILM THAT WE MAKE IN OUR OWN LAB. WE HAVE BEEN UNABLE TO PURCHASE COMMERCIALLY FILMS THAT ARE THIN ENOUGH AND CLEAN ENOUGH SIMULTANEOUSLY IN ORDER TO USE FOR OUR ANALYSIS. I MIGHT ADD, AS A BALLPARK FIGURE, OUR TYPICAL PIXE SENSITIVITIES FOR THE ELEMENTS ACROSS THE PERIODIC TABLE FALL IN THE RANGE OF .1 TO 10 NANOGRAMS PER SQUARE CENTIMETER ON THE TARGET.

NOW, THESE CAN BE INCREASED BY RUNNING FOR A LONGER TIME PERIOD AND GETTING BETTER STATISTICAL PRECISION, BUT THAT IS A REASONABLE WORKING NUMBER.

THE FIRST TYPE OF TARGET WE MAKE IS FROM A SOLUBLE SAMPLE. WE DOPE THAT INTERNALLY, SPOT IT ON A TARGET AND IT IS DRIED IN AN INFRARED OVEN IN THE CLEAN ROOM. ONCE THE SAMPLE IS DRIED, WHICH TAKES A MATTER OF A FEW HOURS, THESE TARGETS, IF THEY ARE NOT RUN IMMEDIATELY ON THE ACCELERATOR, ARE STORED IN SEALED PLASTIC TRAYS; THEY ARE STABLE INDEFINITELY IN THAT WAY.

THE OTHER TYPE OF TARGET THAT WE CAN DO, AND I THINK IT MAY REPRESENT A LITTLE BIT DIFFERENT CAPABILITY THAN YOU HAVE WITH ICAP OR AA, IS A POWDER TARGET. WE ARE ABLE TO ANALYZE SOLID SAMPLES. WE HAVE USED, FOR EXAMPLE, POWDERED BOVINE LIVER, ORCHARD LEAVES, NBS PINE NEEDLES AND SO FORTH AS CALIBRATION CHECKS; IN FACT, WE HAVE EVEN DONE A STUDY OF TRACE ELEMENT UPTAKE IN PINE TREES BASED ON ANALYSIS OF THE POWDERED PINE NEEDLE SAMPLE. WE CAN ANALYZE THESE WITHOUT DOING A DIGESTION. THE RESTRICTION IS THAT THE THICKNESS OF THE POWDERED SAMPLE OR SOLID SAMPLE ON THE TARGET MUST BE THIN ENOUGH THAT X-RAY ATTENUATIONS ARE INSIGNIFICANT. WE ALSO DO HAVE A METHOD FOR CORRECTING FOR X-RAY

ATTENUATION, BUT WE PREFER, IF AT ALL POSSIBLE, TO MAKE THE LAYER THIN ENOUGH THAT WE DO NOT HAVE TO DO THAT CORRECTION. THOSE ARE THE TWO GENERAL TYPES OF TARGETS THAT WE DO.

IF I COULD HAVE SLIDE 9, PLEASE. I KNOW THIS IS NOT A GOOD SLIDE BECAUSE THERE IS TOO MUCH INFORMATION ON IT. I DID WANT TO SHOW YOU THE STATISTICAL APPROACH. THIS STUDY WAS DONE IN ORDER TO TEST THE COMPARABILITY OF THE MEASUREMENTS FOR THESE PARTICULAR ELEMENTS THAT WE WERE LOOKING AT BY ATOMIC ABSORPTION AND BY PIXE. IN OTHER WORDS, WE WANTED TO SHOW EXACTLY HOW COMPARABLE THE DATA WOULD BE IF WE LOOKED AT IT BY ONLY ONE OF THE ANALYTICAL METHODS, SO WE WANTED TO DO A STATISTICAL ANALYSIS. WE PERFORMED PIXE AND ATOMIC ABSORPTION ANALYSES FOR SEVEN ELEMENTS ON APPROXIMATELY 144 SEDIMENT LEACHATES OF VARIOUS TYPES, AND WE EVALUATED THE DATA IN THIS WAY. THIS IS ONLY PART OF THE DATA.

I MIGHT ADD THAT ONE OTHER THING WE WERE INVESTIGATING AT THIS POINT WAS SAMPLING VARIABILITY. NUMBERS ONE THROUGH SIX HERE REFLECT SIX GRAB SAMPLES TAKEN AT THE SAME SITE, AT THE SAME TIME, AND FOLDED INTO THE DIFFERENCES BETWEEN THESE NUMBERS, THEN, IS SAMPLING VARIABILITY AS WELL AS ANALYTICAL VARIABILITY. B-1 AND B-2 WERE

TABLE V - PIXE/AA Ratio for 5N HNO_3 Sediment Leachates

Sample[a]	Cr	Fe	Ni	Cu	Zn
1	2.2 ± .5 / 2.63 ± .03 =0.84 ± .21	930 ± 21 / 924 ± 60 =1.01 ± .07	1.0 ± .2 / 1.3 ± .3 =0.77 ± .26	0.77 ± .15 / 0.71 ± .02 =1.08 ± .21	6.6 ± .2 / 6.3 ± .1 =1.05± .04
2	3.6 ± .5 / 2.71 ± .07 =1.33 ± .18	896 ± 23 / 904 ± 59 =0.99 ± .07	0.7 ± .2 / 1.2 ± .3 =0.58 ± .24	0.48 ± .14 / 0.60 ± .02 =0.81 ± .24	6.0 ± .2 / 5.8 ± .3 =1.04± .04
3	3.5 ± .4 / 2.59 ± .07 =1.35 ± .19	897 ± 20 / 900 ± 59 =1.00 ± .07	0.9 ± .2 / 1.2 ± .3 =0.75 ± .24	0.50 ± .11 / 0.57 ± .04 =0.88 ± .22	5.7 ± .2 / 5.5 ± .1 =1.04± .04
4	2.7 ± .4 / 2.47 ± .05 =1.09 ± .17	800 ± 15 / 826 ± 58 =0.97 ± .07	1.0 ± .2 / 1.0 ± .4 =1.00 ± .45	0.41 ± .10 / 0.51 ± .05 =0.81 ± .21	5.4 ± .1 / 5.1 ± .1 =1.06± .03
5	b / 2.67 ± .12	962 ± 17 / 941 ± 57 =1.02 ± .06	0.8 ± .2 / 1.2 ± .3 =0.67 ± .26	0.66 ± .1 / 0.61 ± .05 =1.08 ± .19	6.6 ± .2 / 5.7 ± .2 =1.17± .06
6	2.8 ± .4 / 2.36 ± .03 =1.19 ± .19	728 ± 16 / 796 ± 57 =0.92 ± .08	1.1 ± .2 / 1.0 ± .3 =1.10 ± .39	0.67 ± .12 / 0.59 ± .02 =1.14 ± .22	5.2 ± .2 / 5.1 ± .2 =1.02± .06
B1	2.9 ± .4 / 2.54 ± .03 =1.14 ± .17	815 ± 18 / 847 ± 58 =0.96 ± .07	1.1 ± .2 / 1.1 ± .3 =1.00 ± .36	0.81 ± .11 / 0.62 ± .01 =1.32 ± .18	6.1 ± .2 / 5.9 ± .1 =1.04± .04
B2	2.5 ± .4 / 2.50 ± .06 =1.00 ± .17	766 ± 16 / 849 ± 58 =0.90 ± .06	1.0 ± .2 / 1.2 ± .2 =0.83 ± .26	0.58 ± .13 / 0.57 ± .02 =1.02 ± .23	5.6 ± .2 / 5.2 ± .1 =1.08± .04
SB	2.1 ± .4 / 2.2 ± .1 =0.95 ± .20	870 ± 10 / 781 ± 39 =1.11 ± .06	1.0 ± .2 / 0.9 ± .3 =1.11 ± .43	0.85 ± .12 / 0.58 ± .02 =1.46 ± .22	6.1 ± .1 / 7.1 ± .4 =0.85± .07
Mean Ratio ± S.D.	1.11 ± .18	0.99 ± .06	0.87 ± .19	1.07 ± .22	1.04 ± .08

[a] High calcium station: B1 = Blend of 1,2 & 3; B2 = Blend of 4,5 & 6; SB = Super Bler

[b] PIXE target contamination, solution exhausted.

BLENDS OF THREE OF THE SIX SAMPLES, AND B-3, WE ARE CALLING IT SB HERE, WAS A SUPER BLEND OF ALL SIX, SO THAT REPRESENTS COMPOSITE BEHAVIOR WHEREAS THE INDIVIDUAL SAMPLES REFLECT SAMPLING VARIABILITY.

FOR EACH OF THOSE, WE MEASURED A VALUE BY ATOMIC ABSORPTION WHICH IS IN THE DENOMINATOR. WE MEASURED A VALUE BY PIXE, EACH WITH A STANDARD DEVIATION. WE COMPUTED THE RATIO OF THOSE TWO NUMBERS WITH ITS STANDARD DEVIATION WITH A ROOT MEAN SQUARE COMBINATION OF ERRORS AND WE COMPUTED A MEAN VALUE FOR THE ENTIRE SET OF DATA AT THIS PARTICULAR SAMPLING LOCATION WITH ITS STANDARD DEVIATION.

FINALLY, THE 144 SAMPLES WE DID WE COMPUTED A GRAND MEAN. NOW IF EVERYTHING IS EXACTLY RIGHT, THE GRAND MEAN SHOULD BE EQUAL TO 1.0 AND ALSO, ANOTHER WAY OF EVALUATING THE DATA IS THAT 95 PERCENT OF THE SAMPLES SHOULD BE WITHIN TWO STANDARD DEVIATIONS OF ONE. THIS IS THE WAY WE ARE EVALUATING THE DATA.

ON SLIDE 10, I HOPE YOU CAN SEE THIS, ALTHOUGH IT IS A LITTLE DARK. FOR CHROMIUM, OUR WORKING CONCENTRATION RANGE (AGAIN DRY WEIGHT CONCENTRATIONS) WAS .3 TO 4 PARTS PER MILLION; THE MEAN RATIO CLEARLY IS WITHIN ONE STANDARD DEVIATION OF UNITY, AND SO FORTH.

Present Work

5N HNO_3 Sediment Leachats

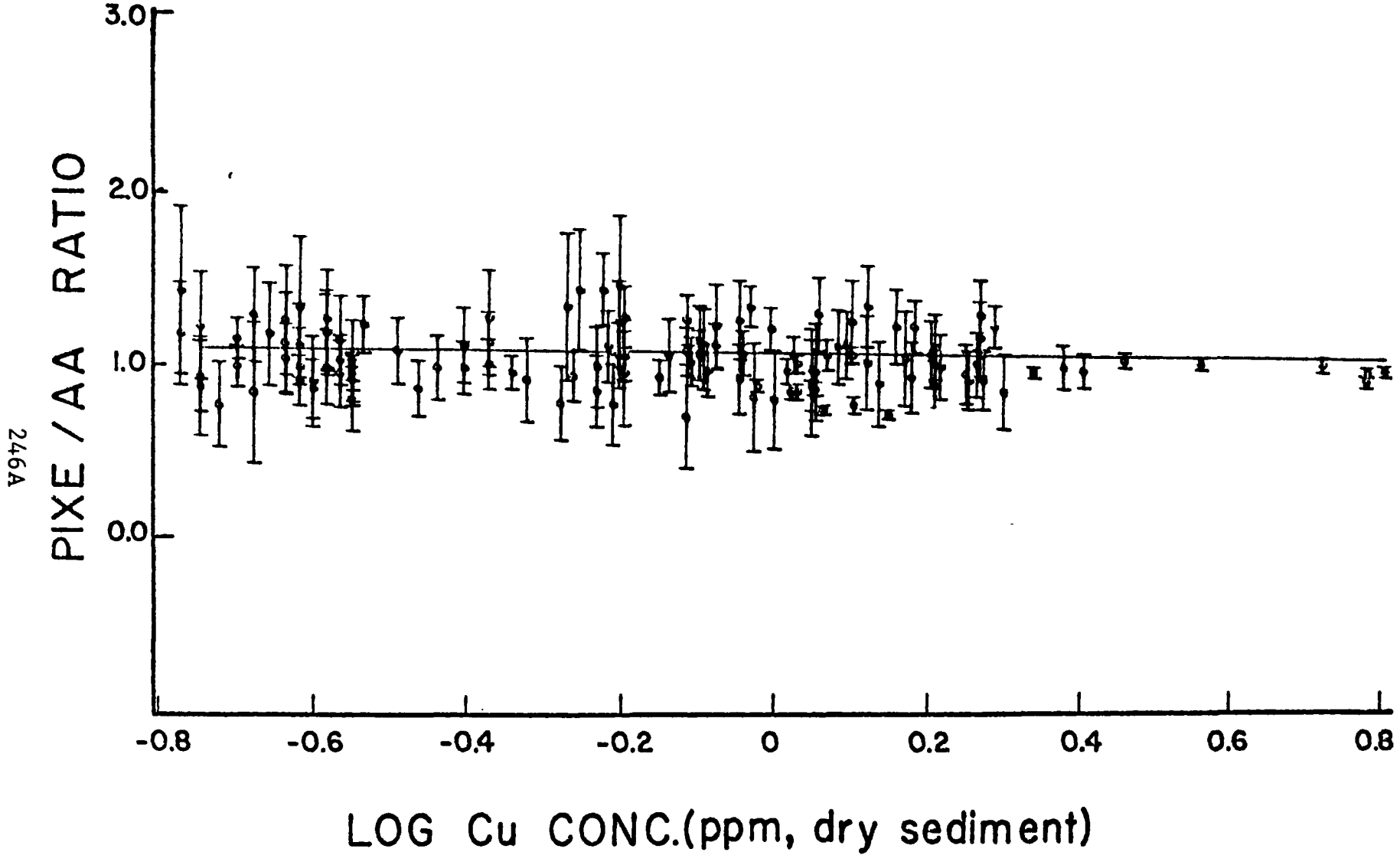
Element	Dominant Conc.Range (Dry wt)	PIXE / AA Mean Ratio±S.D.
Cr	0.3-4ppm	1.06 ± .21
Fe	300-2500ppm	0.99 ± .05
Ni*	0.1-3ppm	0.97 ± .31
Cu*	0.2-2ppm	1.07 ± .16
Zn	2 -12ppm	1.05 ± .10
In	25-70ppm	1.02 ± .04
Pb	1 -6ppm	0.95 ± .09

* Practically 50% or more of the concentrations measured in these metals were in the fraction of a ppm range.

THE STANDARD DEVIATIONS WERE GENERALLY FAIRLY SMALL WITH THE EXCEPTION OF NICKEL, AND THE REASON IT WAS SO SMALL IS THAT MANY OF THE NICKEL NUMBERS WERE VERY CLOSE TO DETECTION LIMITS, AND SO THE 30 PERCENT RELATIVE STANDARD DEVIATION THERE REPRESENTS A LOT OF NUMBERS THAT ARE NEAR DETECTION LIMITS FOR ONE TECHNIQUE OR THE OTHER.

SLIDE 11, PLEASE. WE ALSO ATTEMPTED TO EVALUATE CONCENTRATION BIAS BECAUSE A GROUP MEAN OBSCURES THE FACT THAT YOU MIGHT BE SYSTEMATICALLY HIGH AT LOW CONCENTRATIONS, AND LOW AT HIGH ONES OR VICE VERSA. SO THIS IS A PLOT OF THE PIXE/AA RATIO VERSUS THE LOG OF CONCENTRATION OVER APPROXIMATELY A FACTOR OF 50, VARIATION IN CONCENTRATION, AS MEASURED BY ATOMIC ABSORPTION, AND THIS IS PIXE/AA RATIO. THE VERTICAL BARS REPRESENT PLUS OR MINUS ONE STANDARD DEVIATION IN THE RATIO. I THINK YOU CAN SEE THAT THE LINE WE HAVE DRAWN REPRESENTS THE DATA WELL, AND FURTHER THAT THERE DOES NOT APPEAR TO BE ANY DETECTABLE CONCENTRATION BIAS AS A FUNCTION OF CONCENTRATION.

THIS IS FOR COPPER CONCENTRATION, WHICH REPRESENTS ONE OF THE ELEMENTS WHERE A LOT OF THE CONCENTRATIONS WERE NEAR DETECTION LIMITS. AT LOW COPPER CONCENTRATIONS, YOU CAN SEE BY THE VERTICAL BARS, THE

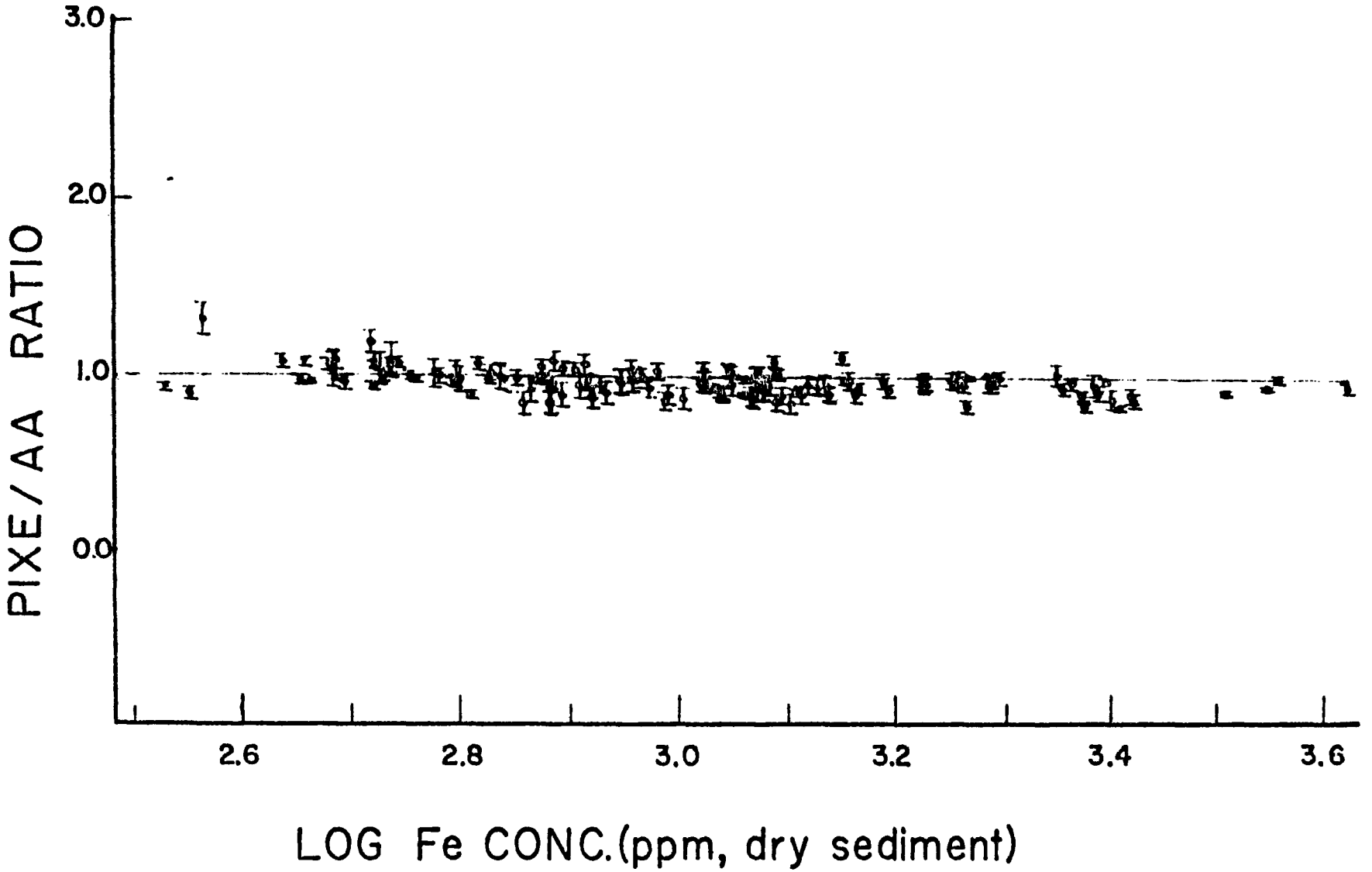

3.0
2.0
1.0
0.0
PIXE / AA RATIO
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
LOG Cu CONC.(ppm, dry sediment)

2496A

STANDARD DEVIATIONS WERE QUITE LARGE. EVEN SO THERE DOES NOT APPEAR TO BE ANY BIAS NEAR THE DETECTION LIMIT. OF COURSE AT HIGHER CONCENTRATIONS THE MEASUREMENTS GOT MORE AND MORE PRECISE, SO THE NUMBERS ARE MUCH CLOSER TO THE MEAN VALUE. THIS IS THE TYPE OF PLOT THAT WE OBSERVED WITH AN ELEMENT WHERE THE CONCENTRATIONS WERE REASONABLY CLOSE TO DETECTION LIMITS.

SLIDE 12 SHOWS A PLOT WHICH WAS FOR IRON, WHICH IS GENERALLY ABUNDANT IN THESE SAMPLES, AND WHERE ALMOST ALL THE MEASUREMENTS WERE QUITE PRECISE. AGAIN I THINK YOU CAN SEE THAT THERE IS NO DETECTABLE BIAS AS A FUNCTION OF CONCENTRATION.

WE DID ONE OTHER SERIES OF TESTS ON THESE SAMPLES. WE ALSO DID A TOTAL DIGESTION. INSTEAD OF DOING THE DIGESTION THAT I HAVE DESCRIBED HERE, WITH FIVE NORMAL NITRIC ACID, WE ALSO DID A TOTAL DIGESTION USING HYDROFLUORIC ACID TO DISSOLVE THE SILICATE MATRIX AND IT WAS OF INTEREST TO EXAMINE THE COMPARABILITY OF THE PIXE/AA DETERMINATIONS ON THAT TYPE OF MATRIX. I MIGHT ADD THAT FLUORIDE CREATES A LOT OF PROBLEMS FOR US BECAUSE WHEN FLUORIDE IS IRRADIATED WITH PROTON BEAMS, YOU GET SOME VERY HIGH ENERGY PHOTONS GIVEN OFF WHICH CAUSE PROBLEMS WITH THE DETECTOR, SO THAT REPRESENTS A DIFFICULT MATRIX


3.0
2.0
1.0
0.0
PIXE/AA RATIO
2.6
2.8
3.0
3.2
3.4
3.6
LOG Fe CONC.(ppm, dry sediment)

FOR US, FOR PIXE MEASUREMENTS.

WE WERE INTERESTED IN SEEING HOW COMPARABLE WE WERE IN THAT PARTICULAR MATRIX, WHICH GENERALLY HAD MUCH HIGHER CONCENTRATIONS OF THE METALS, AND ALSO IN DETERMINING WHAT FRACTION OF THE TOTAL METALS WERE AVAILABLE IN A RELATIVELY MILD TREATMENT WITH FIVE NORMAL NITRIC ACID.

SLIDE 13 SHOWS A SUMMARY ONLY OF WHAT WE FOUND IN THIS CASE. YOU CAN SEE, IN GENERAL, THE CONCENTRATION RANGES ARE MUCH HIGHER FOR THE TOTAL DIGEST. THE RATIOS STILL ARE WITHIN ONE STANDARD DEVIATION OF ONE, BUT YOU WILL NOTICE THAT THE UNCERTAINTIES IN THOSE MEAN RATIOS ARE MUCH LARGER, AND NICKEL AND COPPER VALUES ARE NOT PARTICULARLY GOOD. THE LARGE UNCERTAINTY IN NICKEL VALUE IS ALMOST A DIRECT CONSEQUENCE OF THE AMOUNT OF IRON PRESENT IN THE SAMPLE WHICH AT VERY HIGH LEVELS AS CONSTITUTES AN INTERFERENCE. YOU WILL ALSO NOTICE THAT THERE ARE VERY SMALL NUMBERS OF SAMPLES FOR WHICH A RATIO COULD BE COMPUTED, THAT IS, WE EXCLUDED, IN COMPUTING THE RATIO, THOSE NUMBERS WHICH WERE WITHIN A FACTOR, I AM NOT SURE OF THE EXACT ONE, BUT I BELIEVE IT WAS A FACTOR OF TWO OR THREE, OF THE DETECTION LIMIT BECAUSE OF THE VERY POOR PRECISION THAT THOSE WOULD HAVE.

ON SLIDE 14, I HAVE A COMPARISON OF THE PERCENT

Table 8-A-5. PIXE/AA comparison summary for sediment total digests.

Element	Dominant Conc. Range	PIXE/AA Mean Ratio + S.D.	No. of Ratios Computed
Cr	10-30 ppm	1.11 ± .39	48[a]
Fe	.3 to 3%	0.94 ± .05	94
Ni	0-20-ppm	1.48 ± .50	18[a,b]
Cu	0-5 ppm	1.49 ± .50	28[a,c]
Zn	10-50 ppm	1.05 ± .23	94
Pb	6-16 ppm	1.04 ± .23	94

a. Unusually high background due to high fluorine content caused a severe deterioration in both the precision and the detection sensitivity as compared to sediment leachates (Table 8-A-1) causing several concentrations to be below or near detection limit in these metals.

b. Ni was complicated in PIXE by severe spectral distortions caused by high concentration of fluorine. Apparently some low level spectral distortion is still present in the analysis accepted here for average PIXE/AA ratio computation.

c. Total digest solutions received were very dilute (30X) as compared to sediment leachates. Since only a few drops of these solutions are placed on the PIXE film to dry, even very low level Cu contamination makes a significant contribution to the near detection limit Cu levels present in these solutions.

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Cr	10-30 ppm	1.11 ± .39	48[a]
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Cu	0-5 ppm	1.49 ± .50	28[a,c]
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c. Total digest solutions received were very dilute (30X) as compared to sediment leachates. Since only a few drops of these solutions are placed on the PIXE film to dry, even very low level Cu contamination makes a significant contribution to the near detection limit Cu levels present in these solutions.

Table 8-22. Percent leachable of total metal concentration (dry weight) for cluster stations (A-F).

Metal	Range of leachable/total x 100	Median %
Ba	<4	<2
Cd	*	*
Cr	5-20	8
Cu	6-50	25
Fe	8-24	10
Ni	2-40	16
Pb	20-60	35
V	6-40	15
Zn	4-50	27

*Concentration too low.

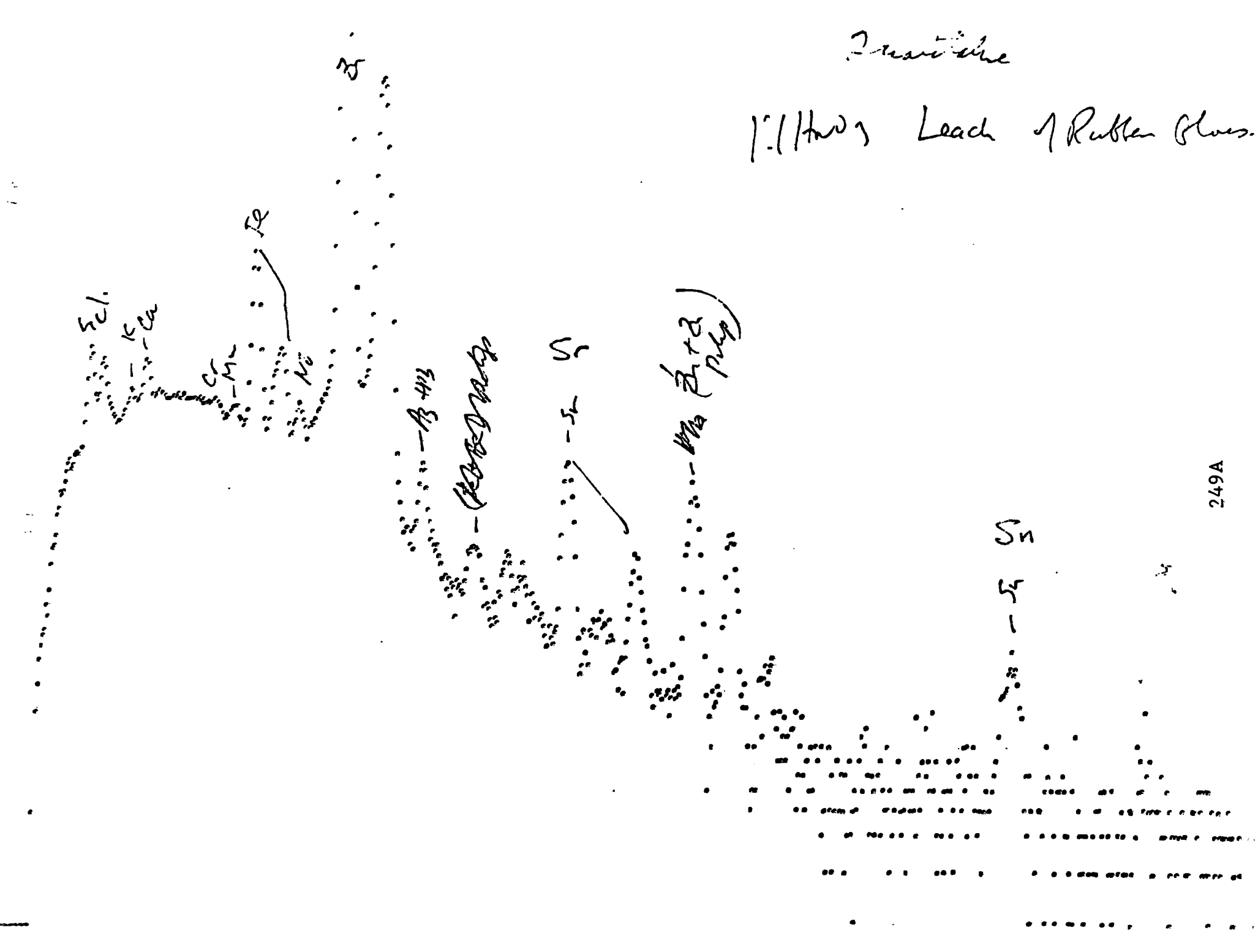
OF THE METALS THAT WERE AVAILABLE IN THE FIVE NORMAL NITRIC ACID LEACH COMPARED TO THE TOTAL METALS AS DETERMINED BY THE SECOND DIGESTION PROCEDURE. YOU CAN SEE IN GENERAL THEY ARE AROUND 15 PERCENT. LEAD WAS CONSIDERABLY HIGHER AT 35, COPPER 25 PERCENT, AND ZINC WAS 27 PERCENT AVAILABLE. NOW THIS IS REPRESENTATIVE OF ALL OF THE 144 VALUES THAT WE HAD IN THIS SET OF SAMPLES.

THAT REPRESENTS A FAIRLY COMPLETE STUDY. I THINK YOU CAN SEE FROM THIS THE KINDS OF THINGS THAT WE CAN DO. I WILL JUST SHOW YOU A VERY BRIEF SET OF OTHER KINDS OF SAMPLES THAT WE ARE DOING.

IF I MAY HAVE SLIDE 15 PLEASE. THIS IS REAL RAW DATA. WE HAVE AN X, Y PLOTTER IMMEDIATELY AFTER IRRADIATING THE SAMPLE WE CAN PLOT THIS DATA. YOU CANNOT SEE IT ON THE SLIDE, BUT WE HAVE THE YIELD CURVE ON THE CHART PAPER, WHICH BASICALLY IS THE RELATIVE NUMBER OF X-RAY PHOTONS PER ATOM, ALL THE WAY ACROSS THE PERIODIC TABLE. WITH THAT YEILD CURVE AND KNOWLEDGE OF ONE ELEMENT PRESENT, WE CAN DO A SEMIQUANTITATIVE ANALYSIS WITH A PAIR OF DIVIDERS OFF THIS PLOT. HOWEVER, THAT IS NOT WHY I PRESENTED THIS. I DID THIS EXPERIMENT IN THE LAB TO CONVINCE ONE OF OUR NEW LAB PEOPLE THAT THEY SHOULD NOT DIP THEIR HANDS, EVEN IF THEY WERE

Preparation

Filtering Leach of Rubber Gloves



COVERED WITH RUBBER GLOVES, IN THE ACID SOLUTION THEY WERE USING TO WASH LABWARE. THIS REPRESENTS A PAIR OF RUBBER GLOVES THAT WAS DIPPED IN NITRIC ACID, ONE-TO-ONE, FOR A RELATIVELY SHORT PERIOD OF TIME. EVERYBODY KNOWS THERE IS A LOT OF ZINC IN ANY KIND OF RUBBER MATERIAL, BUT I THINK YOU CAN SEE FROM THE APPEARANCE OF THE SPECTRUM, THERE ARE ALSO CONSIDERABLE AMOUNTS OF TIN, ARSENIC, LEAD, STRONTIUM AND VARIOUS OTHER THINGS. SO THIS IS A CAPABILITY THAT WE HAVE OF DOING A VERY QUICK SCAN ON A SAMPLE. WE ALSO EVALUATE MATERIALS OCCASIONALLY, GLOVE POWDER, FOR EXAMPLE; ALL LABORATORY GLOVES COME WITH POWDER IN THEM. WE CAN ALMOST IDENTIFY THE MANUFACTURER FROM THE FINGERPRINT CAUSED BY THE TRACE ELEMENTS PRESENT AS A POTENTIAL CONTAMINANT IN THE LAB. WE HAVE ALSO EVALUATED PAINTS AND THAT SORT OF THING THAT WE ARE GOING TO USE IN CONSTRUCTING LAB APPARATUS.

THE ABILITY TO DO A QUICK QUALITATIVE MEASUREMENT IS VERY HELPFUL TO US. I MIGHT ADD ONE OTHER THING, MIKE MENTIONED IT A WHILE AGO. PIXE IS A BLIND TECHNIQUE; THAT IS, WE DO NOT HAVE TO HAVE PRIOR KNOWLEDGE OF THE SAMPLE. IF IT CONTAINS ANY ELEMENT HIGHER THAN ALUMINUM, IN SIGNIFICANT QUANTITIES WE ARE GOING TO SEE IT, AND WE DO NOT HAVE TO KNOW THAT WE ARE LOOKING FOR COPPER IN THE SAMPLE OR WHATEVER,

SO IT IS A VERY GOOD SCREENING TOOL; IT NOT ONLY GIVES US THE NUMBER OF ELEMENTS PRESENT, BUT ALSO CAN GIVE US THE QUANTITATIVE MEASUREMENT.

MAY I HAVE SLIDE 16 PLEASE. THESE ARE SOME MEASUREMENTS WE MADE ON BIOTA, CLAMS, SCALLOPS, STARFISH, FISH AND VARIOUS BIOLOGICALS, AND AGAIN WE MADE DUPLICATE MEASUREMENTS. WE MEASURED THESE CONCENTRATIONS BY PIXE AND ALSO BY ATOMIC ABSORPTION, COMPUTED THE RATIO IN EXACTLY THE SAME WAY THAT I HAVE DESCRIBED PREVIOUSLY FOR THE SEDIMENTS, AND THESE ARE THE KINDS OF RATIOS THAT WE COME UP WITH. AGAIN YOU WILL NOTICE THAT THE STANDARD DEVIATION IN THE MEAN RATIO IS RELATIVELY HIGH FOR SOMETHING LIKE CHROMIUM BECAUSE OF THE DIFFICULTY IN DOING CHROMIUM IN A BIOLOGICAL SAMPLE, BY ATOMIC ABSORPTION. THESE WERE DONE WITH STANDARD ADDITION, I MIGHT ADD, THE CHROMIUM VALUES.

NICKEL REPRESENTS A SIMILAR PROBLEM; THE CONCENTRATION OF NICKEL IN BIOLOGICALS IS VERY LOW, AND A LOT OF THE NUMBERS ARE QUITE CLOSE TO DETECTION LIMITS.

IF I MIGHT HAVE SLIDE 17 PLEASE. THIS DEMONSTRATES ANOTHER CAPABILITY OF THE TECHNIQUE, I BELIEVE. WE CAN DO MULTIELEMENT ANALYSES ON VERY SMALL SAMPLE SIZES. THIS HAPPENS TO BE BLOOD PLASMA,

PIXE-AA Comparison Summary - Biota Total Digests

Element	Dominant Conc. Range	PIXE/AA Mean Ratio ± S. D.	No. of Ratios Computed
Cr	0-5 ppm	1.09 ± .46	16
Fe	100-3000 ppm	1.01 ± .22	157
Ni	0-5 ppm	1.03 ± .56	80
Cu	10-100 ppm	1.09 ± .16	175
Zn	50-1000 ppm	0.96 ± .11	177
Cd	0-10 ppm	1.02 ± .17	62
Pb	0.5-13 ppm	1.22 ± .35	86†

†Standard addition analyses were performed for all samples for Cr, Fe and Pb. Severe suppression (20-50% recovery in standard addition analyses) of flameless AA absorbance readings for Pb was observed in a large number of samples. Because of the severity of matrix suppression of AA readings, it is suspected that standard addition corrections did not completely compensate for the suppression, thus causing the average PIXE/AA ratio to be somewhat greater than 1.0 for Pb. Some of the samples also had a very small mass (50-100 mg dry weight digested to yield 25 ml final volume) which combined with their very low Pb concentration in the dry sample made the final solutions extremely dilute in Pb and, therefore, more sensitive to even low level Pb contamination. (Pb is a common contaminant).

CONC. ARE IN UG/G UNLESS NOTED ABOVE VALUE — HUMAN BLOOD PLASMA

K	CA	S	CL	CR	MN	FE	NI	CU	ZN	BR	AS	SE	RB	SR
1020	90.	1280	4220	ND	ND	2.7	ND	.86	1.34	3.59	ND	.10	1.13	.06
10	2.	20	60	.2	.1	.1	.10	.08	.05	.07	.03	.02	.04	.01
930	84.	1140	3950	ND	ND	1.98	ND	.81	1.21	3.47	ND	.09	1.09	.05
10	2.	20	50	.2	.2	.10	.08	.07	.04	.06	.02	.02	.03	.01
1010	89.	1220	4140	ND	ND	1.4	ND	.89	1.28	3.54	ND	.11	1.19	.06
10	2.	20	60	.2	.1	.1	.10	.07	.05	.07	.02	.02	.04	.01
1010	97.	1310	4200	ND	.3	1.3	ND	.86	1.32	3.67	ND	.14	1.19	.08
10	2.	20	60	.2	.1	.1	.10	.08	.05	.07	.02	.02	.04	.01
950	95.	1230	4110			1.4		.87	1.36	3.54		.13	1.16	.06
10	2.	20	50			.1		.07	.05	.06		.02	.03	.01
1080	90.	1200	4240	ND	ND	1.8	ND	.85	1.25	3.46	ND	.12	1.16	.04
10	2.	20	50	.2	.1	.1	.09	.05	.04	.06	.02	.02	.03	.01
1060	90.	1160	4100	ND	ND	1.6	ND	.80	1.20	3.55	ND	.09	1.18	.04
10	2.	20	50	.2	.1	.1	.08	.06	.04	.06	.02	.02	.03	.01
1070	88.	1210	4070	ND	ND	1.82	ND	.84	1.22	3.53	ND	.10	1.23	.058
10	1.	20	50	.2	.2	.08	.07	.06	.04	.06	.02	.02	.03	.010

AND WE CAN EASILY DETECT, WITH A FAIRLY ROUTINE MEASUREMENT, ABOUT 10 OR 12 ELEMENTS IN THIS PLASMA INCLUDING SELENIUM, RUBIDIUM, STRONTIUM WHICH ARE LESS COMMONLY DETERMINED IN BLOOD PLASMA, BUT NEVERTHELESS RESULT FROM THE SINGLE MEASUREMENT. I MIGHT ADD, THIS SET OF DATA IS DONE ON 100 MICROLITERS OF BLOOD PLASMA, SO WE DO NOT NEED A LARGE VOLUME. WE CAN PUSH THAT FURTHER; I AM QUITE SURE WE COULD DO A REASONABLE ANALYSIS ON AS LITTLE AS 10 OR 20 MICROLITERS. WE PREFER TO USE LARGER AMOUNTS BECAUSE IT IS MORE REPRESENTATIVE AND MAKES US LESS PRONE TO PARTICULATE CONTAMINATION, WHICH IS ONE OF THE PROBLEMS WITH A TECHNIQUE LIKE PIXE.

THE BOTTOM THREE REPRESENT THREE SEPARATE 100-MICROLITER PORTIONS OF THE SAME PLASMA SAMPLE, EACH RUN INDEPENDENTLY THROUGH THE PIXE ANALYSIS, EACH DOPED IN THE LAB INDEPENDENTLY AND RUN THROUGH THE ANALYSIS. I THINK YOU CAN SEE FROM THE REPRODUCIBILITY HERE THAT WE CAN, IN FACT, IN A RATHER DIFFICULT MATRIX GET EXCELLENT RESULTS. BY THE WAY, THERE WAS NO DIGESTION PERFORMED ON THESE SAMPLES EITHER, SO ALL THE PROTEINS AND LIPIDS AND EVERYTHING ELSE WERE STILL IN THE BLOOD PLASMA SAMPLE.

TWO FINAL SLIDES. THESE ARE SOME SAMPLES WE ARE DOING FOR AN AGENCY THAT IS INTERESTED IN ANIMAL

EXPERIMENTS, AND ONE OF THE VERY IMPORTANT THINGS IN A NUTRITIONAL SENSE IS TO KNOW COMPLETELY THE TRACE ELEMENTS THAT ARE IN THE DIET. THERE IS A NEED TO MONITOR THINGS WHICH ARE ADDED TO THE FEED SUCH AS SELENIUM, MOLYBDENUM AND SO FORTH; THOSE ARE NOT TOXIC ELEMENTS BUT ADDED AS A NECESSARY DIETARY INGREDIENT. ALSO, OF COURSE, IT IS OF INTEREST TO GET SOME INFORMATION ON ELEMENTS THAT MAY NOT BE ADDED BUT MAY BE FORTUITOUSLY PRESENT AND REPRESENT A POSSIBLE INTERFERENCE WITH THE MEASUREMENTS THEY ARE TRYING TO MAKE.

I HAVE OMITTED FROM SLIDE 18 ALL THE ELEMENTS WHICH WERE NOT DETECTED IN THESE PARTICULAR SAMPLES. THESE TWO ARE TWO COMPLETELY INDEPENDENT DETERMINATIONS ON AN ACID DIGESTED RAT DIET. THE BOTTOM SET OF DATA IS TWO ADDITIONAL MEASUREMENTS ON A DIFFERENT RAT DIET AND THE BOTTOM LINE IS THE MEAN AND STANDARD DEVIATION OF THOSE TWO SEPARATE DETERMINATIONS.

ON SLIDE 19 I HAVE SOME ADDITIONAL ELEMENTS. I THINK YOU CAN SEE HERE, I POINT OUT, FOR EXAMPLE, THE SELENIUM VALUES. THESE ARE ALSO PARTS PER MILLION DRY WEIGHT IN SOMETHING THAT CONTAINS A LOT OF ORGANIC MATERIAL BEFORE THE DIGESTION. YOU CAN SEE THAT THE TWO REPLICATE PIXE TARGETS ARE IN VERY

PIXE Analyses of Purified Rat Diets

Average Tables - Concentrations are in UG/G Unless Noted

	P	S	K	CA	TI	V	CR	MN	FE	CO	NI	CU	ZN
RD	440	500	1290	920	ND	.8	.7	32.	14.0	.4	ND	1.6	11.7
1892	30	20	50	40	.7	.2	.3	1.	.7	.1	.06	.1	.3
	530	610	1570	1150	.8	.9	1.2	38.	17.2	.7	ND	1.72	13.5
	90	30	50	40	.3	.3	.5	1.	.7	.1	.05	.10	.4
Mean	480	550	1400	1000	.4	.9	1.0	35.	16.	.5	.05	1.66	13.
(s.d.)	70	70	200	200	.6	.2	.3	4.	2.	.2	.04	.08	1.

	P	S	K	CA	TI	V	CR	MN	FE	CO	NI	CU	ZN
RD	530	590	1580	1030	ND	.9	ND	36.	11.5	ND	ND	1.6	21.2
1894	90	30	50	30	.6	.4	.4	1.	.6	.1	.06	.1	.6
	520	580	1490	1010	ND	ND	1.2	34.4	10.9	ND	ND	1.6	20.9
	90	30	40	30	.4	.3	.4	1.0	.5	.07	.05	.1	.5
Mean	530	590	1530	1020	.0	.7	.7	35.0	11.2	.00	.03	1.60	21.0
(s.d.)	70	20	60	20	.4	.3	.6	.8	.5	.07	.04	.08	.4

PIXE Analyses of Purified Rat Diets

Average Tables - Concentrations are in UG/G Unless Noted

	AS	SE	RB	SR	ZR	MO	CD	TE	PT	PB
RD	.07	.80	ND	.93	.11	.85	ND	1.1	ND	ND
1892	.01	.03	.01	.04	.03	.05	.07	.4	.07	.03
	ND	.85	.08	1.01	.18	.96	.17	.8	ND	.13
	.02	.03	.02	.04	.03	.05	.08	.4	.08	.03
Mean	.05	.82	.05	.97	.15	.91	.1	.9	.02	.09
(s.d.)	.03	.03	.04	.06	.05	.08	.1	.3	.05	.05

	AS	SE	RB	SR	ZR	MO	CD	TE	PT	PB
RD	ND	.64	.06	.92	.17	1.46	.21	.9	ND	.25
1894	.02	.03	.02	.04	.02	.07	.10	.4	.07	.04
	ND	.69	.07	.99	.15	1.49	.22	1.3	ND	.29
	.01	.03	.02	.04	.02	.06	.08	.3	.05	.03
Mean	.00	.66	.07	.96	.16	1.47	.22	1.1	.03	.27
(s.d.)	.01	.04	.01	.05	.02	.05	.06	.2	.05	.03

GOOD AGREEMENT AND THAT WE CAN EASILY DISTINGUISH DIFFERENT DIETARY LEVELS OF THE SELENIUM FROM THE SAMPLE; OTHER THINGS THAT ARE FORTUITOUSLY PRESENT, RUBIDIUM, ZIRCONIUM, QUITE A BIT, AND SOMETHING OF CONSIDERABLE INTEREST TO ME IS TELLURIUM. WE HAVE BEEN CALIBRATED FOR TELLURIUM FOR A LONG PERIOD OF TIME, BUT I HAD NOT SEEN IT IN NATURAL SAMPLES UNTIL RECENTLY. SO YOU CAN SEE THAT IT IS PRESENT IN DIETS, WE HAVE SEEN IT IN TISSUE SAMPLES. THAT ELEMENT IS NOT ON THE CURRENT PRIORITY POLLUTANT LIST AND IT IS NOT MY POSITION TO MAKE RECOMMENDATIONS, BUT WE CAN MEASURE THE ELEMENT IN A VARIETY OF SAMPLES. WE HAVE ALSO SEEN IT IN SOME INORGANICS AND SO FORTH.

THAT IS THE LAST OF THE SLIDES. LET ME JUST CLOSE BY POINTING OUT TO YOU A FEW AREAS WHERE I THINK THE CAPABILITIES OF PIXE REPRESENT SOME COMPLEMENTARY MEASUREMENTS THAT WILL ADD TO THE DATA AVAILABLE BY A TECHNIQUE WHICH REQUIRES A SOLUBLE SAMPLE AS A PRACTICAL MATTER. WE HAVE THE CAPABILITY OF ANALYZING THINGS LIKE SUSPENDED PARTICULATE MATTER. I THINK AN INTERESTING QUESTION CAME UP YESTERDAY WHEN WE WERE TALKING ABOUT THE RECOVERY OF THE ORGANIC PRIORITY POLLUTANTS FROM A SAMPLE WHICH CONTAINS PARTICULATES, AND THE QUESTION WAS RAISED AS TO WHETHER THERE MIGHT BE METALS ON THOSE PARTICULATES WHICH WOULD

COMPLEX THE ORGANICS AND CAUSE A TRANSFER. WE HAVE DONE PARTICULATES ISOLATED FROM BOTH WATER AND AIR SAMPLES. WE ARE SET UP TO ANALYZE SAMPLES ON NUCLEOPORE, MILLIPORE, BOTH 47 MILLIMETERS AND 37 MILLIMETER SAMPLES. ALL THAT IS NECESSARY FOR US TO CONDUCT THIS ANALYSIS IS TO MOUNT THE DRIED FILTER, OBTAIN A SAMPLE, OF COURSE, TO MOUNT THE DRY FILTER IN A PLASTIC HOLDER THAT WE HAVE DESIGNED FOR THE PURPOSE, ASSEMBLE IT INTO THE TRAY AS WE DO IT. IN OTHER WORDS, NO DIGESTION IS REQUIRED IN ORDER TO DO THAT ANALYSIS.

NOW, IF ANY OF YOU HAVE DONE SUSPENDED PARTICULATE MATTER BY MORE CONVENTIONAL PROCEDURES, THAT IS, DIGESTING A ONE-MILLIGRAM SAMPLE, OR SOMETHING OF THAT ORDER, AND MAKING IT UP TO ENOUGH VOLUME TO DO A MULTIELEMENTAL ATOMIC ABSORPTION ANALYSIS, YOU RECOGNIZE ALL OF THE PROBLEMS YOU HAVE WITH CONTAMINATION AND DETECTION LIMITS. SO WE ARE ABLE TO DO AIR PARTICULATES AND PARTICULATES IN WATER OR SOME SORT OF A SOLUTION ENVIRONMENT. WE CAN ANALYZE TISSUE SLICES. IT IS NOT NECESSARY TO DO A DIGESTION. IF YOU HAVE A THIN SAMPLE, WHICH COULD BE A BIOPSY OR A THIN FILM, POLYMER FILMS. OF COURSE THAT IS ONE OF OUR REAL PROBLEMS IS TO KEEP OUR POLYMER FILMS CLEAN ENOUGH SO THAT WE DO NOT HAVE ANY SIGNIFICANT

CONTAMINATION, BUT WE ARE SET UP TO ROUTINELY MEASURE THOSE. SLAGS, WE ARE ABLE TO DO POWDERED SLAG SAMPLES AND WE HAVE ALSO DONE COMPARISONS WITH THE DIGESTED SLAG SAMPLE.

ONE FINAL THING THAT MIKE MENTIONED BEFORE THAT I WOULD LIKE TO REITERATE. IT IS QUITE OBVIOUS THAT SOME SAMPLES, AND I CANNOT CLAIM TO HAVE SEEN A REPRESENTATIVE SET, DO LEAVE A SUBSTANTIAL RESIDUE AFTER THE CONVENTIONAL EPA PROCEDURE. IN THE PAST, I THINK IN MOST CASES THIS RESIDUE HAS BEEN FILTERED OUT AND DISCARDED, BUT WE ARE LOSING AN AWFUL LOT OF INFORMATION AND I DO NOT WANT TO POINT OUT ANY SPECIFICS, BUT THERE ARE A LOT OF ELEMENTS IN OUR EXPERIENCE WITH A VARIETY OF DIGESTIONS THAT TYPICALLY COME UP IN THIS PRECIPITATE SUCH AS TITANIUM, NIOBIUM, STRONTIUM, POTASSIUM, RUBIDIUM, AND THERE CAN EASILY BE SOME CARRY-OVER OF SOME OF THE PRIORITY POLLUTANTS AS WELL.

SO WE ARE ABLE, IN THE COURSE OF THE DIGESTION, IF A PRECIPITATE IS FORMED, AS LONG AS THE PARTICLE SIZE IS SUFFICIENTLY SMALL, WE CAN GET A QUANTITATIVE MEASURE OF THE ELEMENTAL CONSTITUTENTS IN THAT PRECIPITATE; IN THE EVENT THAT THE PARTICLE SIZE IS TOO LARGE, WE CAN AT LEAST IDENTIFY ELEMENTS PRESENT EASILY WITHOUT WORRYING ABOUT THE ACCURACY OF AN X-RAY

ATTENUATION CORRECTION.

THANK YOU VERY MUCH.

MR. CARTER: IF ANYONE WOULD LIKE TO ASK ANY QUESTIONS AT THIS POINT, WE WOULD ATTEMPT TO ANSWER THEM.

QUESTION AND ANSWER SESSION

MR. DAVIS: I HAVE SEVERAL; ABE DAVIS, HOOKER CHEMICAL. WOULD YOU COMMENT ON THE MATRIX AND SENSITIVITY, MATRIX EFFECTS, ABSORPTION ENHANCEMENT AND SENSITIVITY OF THIS METHOD AS OPPOSED, SAY, TO X-RAY FLUORESCENCE, BOTH ENERGY AND WAVELENGTH DISPERSIVE; IS IT COMPLEMENTARY OR DOES IT COVER A WIDER RANGE?

DR. GRANT: I WOULD SAY THAT THE INTERFERENCES IN OUR TECHNIQUE, LET ME PREFACE MY REMARKS BY SAYING I DO NOT DO X-RAY FLUORESCENCE SO I AM NOT INTIMATELY AWARE OF THE SPECIFIC PROBLEMS THERE, BUT I WOULD VENTURE TO SAY THAT THE MAJOR INTERFERENCES WITH THE TECHNIQUE CONSIST OF SPECTRAL OVERLAPS. AS I SAID, EACH ELEMENT IS CHARACTERIZED BY A MULTIPLET OF LINES, AND IN GENERAL, IN THE FIRST ROW TRANSITION ELEMENTS, THE K-ALPHA LINE OF THE NEXT ELEMENT IN THE PERIODIC TABLE OVERLAPS THE K-BETA LINE OF THE PRECEDING ONE, SO THAT IS THE SOURCE OF THE INTERFERENCE THAT I MENTIONED, THAT LARGE AMOUNTS OF IRON INTERFERE WITH NICKEL BECAUSE IT IS AN ADJACENT ELEMENT. SO WE HAVE MUCH THE SAME INTERFERENCES IN THAT CASE THAT X-RAY FLUORESCENCE HAS.

THE CHIEF DIFFERENCE BETWEEN, I THINK, THE CONVENTIONAL X-RAY FLUORESCENCE AND THE PIXE PROCEDURE IS IN THE EFFICIENCY WITH WHICH THE X-RAYS ARE GENERATED, AND IN THE BACKGROUND RADIATION AT HIGHER ENERGY LEVELS, AND THIS ENABLES US TO GET A BETTER SIGNAL-TO-NOISE RATIO FOR THE HEAVY ELEMENTS LIKE INDIUM AND CADMIUM, TIN, IN THAT RANGE OF THE SPECTRUM, SAY FROM THE MIDPOINT OUT, SO WE DO GET IMPROVED SENSITIVITIES BECAUSE OF THAT. OUR COMPUTER PROGRAM, WE HAVE A VERY SLOW COMPUTER AT THE MOMENT, BUT IT TAKES BETWEEN AN HOUR AND TWO HOURS TO COMPUTE THE RESULTS OF THIS SPECTRUM, SO WE ARE DOING A LOT OF THINGS, WE DO CORRECT AUTOMATICALLY FOUR INTERFERENCES, THAT IS, OVERLAPPING PEAKS, AND THAT, UNCERTAINLY, I NEGLECTED TO MENTION IT WHEN I MENTIONED HOW WE GET A STANDARD DEVIATION, IS ALSO FOLDED INTO THE STANDARD DEVIATION.

I GUESS THE BEST MEASURE I WOULD SAY WITH HOW WELL WE ARE ABLE TO DECONVULUTE SPECTRUM IS...SEVERAL OF THOSE TABLES I SHOWED YOU INCLUDED DUPLICATE TARGETS, TWO TARGETS MADE FROM THE SAME SOLUTION. THERE IS NO QUESTION ABOUT HOW WELL YOU PREPARED YOUR SAMPLES OR ANY OF THAT; IT IS SIMPLY MEASURING THE REPLICATION IN THE PIXE MEASUREMENT ITSELF, AND I THINK YOU WILL NOTICE, I HOPE YOU WILL RECALL, THAT IN GENERAL THE

REPLICATION BETWEEN TWO TARGETS WAS AS GOOD AS THE ESTIMATED STATISTICAL UNCERTAINTY ON ANY INDIVIDUAL TARGET, WHICH MEANS THAT OUR ERROR ESTIMATES ARE QUITE REASONABLE.

MR. DAVIS: WHAT I WAS CONCERNED WITH IS, OF COURSE YOU HAVE THE SPECTRAL OVERLAP, K-ALPHA, K-BETA TYPE OF THING; THAT HAS GOT TO BE WITH THE EMISSION SPECTRA THAT YOU ARE LOOKING AT, BUT WHAT I AM CONCERNED ABOUT, YOU BROUGHT UP THE IRON-NICKEL. DOES A PRESENCE OF A LARGE AMOUNT OF IRON REDUCE THE NICKEL BECAUSE THE IRON ABSORBS, OR DOES YOUR THIN FILM TECHNIQUE REDUCE THAT MATRIX EFFECT, ABSORPTION IN THIS CASE, OR ENHANCEMENT IN OTHER CASES, THE FACT THAT IRONS ENHANCE, DO YOU HAVE TO RESORT TO SOMETHING LIKE COLBY'S MAGIC PROGRAM, THAT IS WHAT I AM CONCERNED ABOUT.

DR. GRANT: I CANNOT COMMENT ON THE DETAILS BECAUSE I DID NOT WRITE THE PROGRAM THAT COMPUTES THE CORRECTION AND THAT PERSON IS NOT HERE. HOWEVER, I COULD RESPOND TO THAT IN MORE DETAIL IF YOU ARE INTERESTED. AS FAR AS THE QUESTION OF WHETHER A PRESENCE OF A LARGE AMOUNT OF IRON WOULD INTERFERE WITH A LIGHTER ELEMENT BY X-RAY ATTENUATION, YES, THAT IS A PROBLEM IF THE THICKNESS OF THE SAMPLE ON THE TARGET, WHETHER IT ARISES FROM A POWDERED SAMPLE

OR A SPOTTED SOLUBLE SAMPLE, IF THE THICKNESS IS SUFFICIENTLY LARGE, THERE WILL CERTAINLY BE X-RAY ATTENUATION. WE HAVE THE PROGRAM, WE DO A TWO-PASS CALCULATION. THE FIRST PASS DOES NOT ASSUME ANY ABSORPTION. THEN THE THICKNESS OF ANY ELEMENT ON THAT TARGET IS COMPUTED FROM THE FIRST PASS CALCULATION. SO FOR EXAMPLE, IF THERE IS A LOT OF IRON ON THE TARGET WE COMPUTE THE NUMBER OF NANOGRAMS PER SQUARE CENTIMETER OF IRON ON OUR TARGET, AND FROM THAT THE CORRECTION IS ESTIMATED AND A SECOND PASS IS DONE WHICH DOES THE CALCULATION FOR ATTENTUATION FOR ALL OF THE LIGHTER ELEMENTS, AND ALSO SELF-ATTENTUATION FOR IRON.

WE HAVE A HARD COPY PRINTOUT OF BOTH OF THOSE SO THAT WE CAN GO BACK AND LOOK AT THEM AND SEE WHETHER THERE WAS A SIGNIFICANT CORRECTION COMPUTED, AND I MIGHT ADD THAT EVEN THOUGH ALL OF OUR DECONVOLUTION IS UNDER COMPUTER CONTROL, THE FINAL STEP IN EVERY ONE OF OUR PROCEDURES IS TO EXAMINE MANUALLY THE FIT, THE AGREEMENT AND FIT BETWEEN THE COMPUTED CURVE AND THE DATA MINUS BACKGROUND CURVE AND IF THEY DON'T OVERLAP SATISFACTORILY, A NEW CALCULATION IS DONE. THERE ARE SOME ADJUSTMENTS THAT CAN BE MADE IN THE CALCULATION. SO YES, WE DO HAVE A THICKNESS CORRECTION, BUT OUR GENERAL APPROACH TO

THAT IS IF WE HAD A SAMPLE WITH A LARGE AMOUNT OF IRON IN IT AND WE RAN A TARGET AND FOUND THAT SIGNIFICANT CORRECTIONS WERE TO BE MADE, WE WOULD IN GENERAL TRY TO GO BACK AND DILUTE THE SAMPLE SO THAT THE AVERAGE CONCENTRATION OF IRON IN THE SAMPLE WERE LOWER AND REDO THE ENTIRE CALCULATION.

MR. DAVIS: ONE LAST QUESTION. HAVE YOU TRIED USING THE MILLEPORE FILTERS AS A PLACE TO YOUR SPECIAL PLASTIC, AND WOULD YOU COMMENT ON THE SAMPLE PREP BECAUSE I THINK YOUR PROBLEMS ARE VERY SIMILAR TO THOSE THAT X-RAY FLUORSCENCE MUST EXPERIENCE.

DR. GRANT: I AM NOT SURE WHAT YOU MEAN BY THE SAMPLE PREP RATHER THAN THE MILLEPORE...

MR. DAVIS: SAMPLE PREP, HOW DO YOU GET IT ONTO THE FILM, HOW DO YOU KEEP THE THICKNESS UNIFORM, ET CETERA. I REALIZE YOU SPIN AND THIS WILL AVERAGE OUT THESE, SHALL WE SAY NONUNIFORMITY OF THE THICKNESS.

DR. GRANT: YES.

MR. DAVIS: I THINK THE SAMPLE PREP IS QUITE CRITICAL, AND CAN YOU GET AWAY WITH THE COMMERCIAL FILTER SUCH AS MILLEPORE?

DR. GRANT: IN MOST OF THE

PIXE DETERMINATIONS ACROSS 137 MILLIMETER FILTER TO GET THE DISTRIBUTION ACROSS THE DIAMETER, AND FROM THAT YOU CAN INTEGRATE THE AREA UNDER THE CURVE AND OBTAIN A QUANTITATIVE MEASURE ON THE ENTIRE SAMPLE. THAT OF COURSE REQUIRES SEVEN PIXE MEASUREMENTS INSTEAD OF ONE, BUT EVEN IN A NONUNIFORM DISTRIBUTION WE CAN STILL GET A QUANTITATIVE ANSWER ON THE THING.

I WOULD SAY, NOT HAVING A TREMENDOUS AMOUNT OF EXPERIENCE WITH THE SAMPLING FILTERS, I WOULD SAY THERE ARE SOME REAL PROBLEMS WITH GETTING UNIFORM FILTERS ON THAT TECHNIQUE. OF COURSE, IF YOU DO A DIGESTION OF THAT FILTER, THAT KIND OF ELIMINATES THE PROBLEM, BUT IT ADDS IN ALL OF THE COMPLICATIONS WITH BLANK CONTAMINATION, LOSS OF SAMPLES, THE COMPLETENESS OF THE DIGESTION AND THAT SORT OF THING.

MR. BLUM: SAUL BLUM, EXXON RESEARCH. I DON'T HAVE A QUESTION, I HAVE A COMMENT. ONE OF THE SLIDES, I BELIEVE IT WAS ON LEACH EGG, SHOWED QUADRUPLICATE RESULTS FROM WHICH AVERAGE AND STANDARD DEVIATIONS WERE COMPUTED. I RAN THROUGH THE CALCULATION BECAUSE IT LOOKED A LITTLE OPTIMISTIC. IT LOOKED AS IF A POPULATION STANDARD DEVIATION WAS COMPUTED. YOU MIGHT WANT TO GO BACK AND RECHECK THOSE; YOU SHOULD BE USING A SAMPLE STANDARD DEVIATION WHICH WOULD MAKE THE NUMBERS SOMEWHAT HIGHER.

DR. GRANT: THANK YOU, I WILL HAVE TO GO BACK AND CHECK THAT.

MR. CAPTER: IF THERE ARE NO MORE QUESTIONS, THERE IS SOME COFFEE OUTSIDE, SO YOU CAN TAKE A BREAK.

THE NEXT PRESENTATION WAS SCHEDULED FOR 10 AND IT IS ABOUT FIVE UNTIL 10 RIGHT NOW. MAYBE WE CAN SHOOT FOR ABOUT A 10:20 RECONVOCATION HERE.

(WHEREUPON, A BREAK WAS TAKEN.)

MR. TELLIARD: WE HAVE UP HERE WITH US TODAY BOB MEDZ FROM THE OFFICE OF RESEARCH. BOB IS CHAIRMAN OF THE 304-H COMMITTEE, WHICH IS CHARGED WITH PUTTING OUT 'METHODS' FOR THE MEASUREMENT OF 'POLLUTANTS.' YOU HAVE SEEN THE FIRST PART OF TWO, WHICH WERE RECENTLY PROPOSED, BASICALLY COVERING THE ORGANICS, ICAP PROCEDURE. THERE IS A SECOND PACKAGE WHICH WILL CONTAIN BIOMONITORING, SOME OF THE METHODOLOGY USED IN THE ORGANIC CHEMICALS GROUP, THE MICROEXTRACTION TECHNIQUE, THE METHODS FOR ASBESTOS, AND A DEFINITION FOR DETECTION LIMIT, AND AN UPDATE OF ALL THE TABLE REFERENCES FOR METALS AND RESIDUAL CHLORINE AND WHATEVER ELSE.

WE CAN BE HAPPY TO ANSWER ANY OF YOUR QUESTIONS, AND THE ONLY THING WE CANNOT DO IS GRANT YOU AN EXTENSION ON THE COMMENT PERIOD.

VOICE FROM THE AUDIENCE: WHEN IS THE SECOND PACKAGE GOING TO BE AVAILABLE?

MR. MEDZ: THE COMMITTEE WILL BE MEETING IN THE MIDDLE OF FEBRUARY TO CONSIDER THE SECOND PACKAGE AND GIVE ITS FINAL APPROVAL AS TO WHAT WILL BE IN THE SECOND PACKAGE. YOU HAVE HAD AN APPROXIMATION OF WHAT IT WILL CONTAIN, BUT THE COMMITTEE WILL DETERMINE ITS FINAL NATURE. WE WOULD BE CONVENING IN MID-FEBRUARY ON THAT, WHICH MEANS IT WILL PROBABLY BE PREPARED SOMETIME IN MARCH.

MR. TELLIARD: ANY QUESTIONS?

MR. HAMLIN: PHIL HAMLIN, ITT RAYONIER. I HAD SOME OTHER QUESTIONS, OTHER THAN ON THE 304 METHODS, BUT I WOULD LIKE TO ASK SOME QUESTIONS ON THOSE, TOO.

WHAT IS GOING TO BE THE PURPOSE OF THE CARBONACEOUS BOD METHOD?

MR. MEDZ: THE CARBONACEOUS BOD METHOD IS A COMPLETELY NEW PARAMETER. SOME OF THE STATES WANT TO INCLUDE CARBONACEOUS BOD IN SOME OF THE THINGS THEY ARE DOING. THEY WANT AN IMPROVED METHOD BY WHICH THEY COULD MAKE MEASUREMENTS OF CARBONACEOUS BOD. THE QUESTION HAS COME UP, IS CARBONACEOUS BOD GOING TO BE AN APPROVED OPTION TO THE CONVENTIONAL FIVE-DAY BOD. NO, THAT IS NOT THE

INTENTION OF THE PROPOSAL. IT IS A COMPLETELY NEW PARAMETER. AS OF THIS TIME, NO LIMITATIONS HAVE BEEN WRITTEN ON CARBONACEOUS BOD. SOME OF THE PERMITS PEOPLE USING THE BEST ENGINEERING JUDGMENT MIGHT CHOOSE TO WANT TO USE IT ALSO AS A MEASURE OF SOME OF THE PERMITTING CONDITIONS, BUT UP UNTIL NOW, CARBONACEOUS BOD HAS NOT BEEN USED.

MR. HAMLIN: DO YOU ANTICIPATE A SCREENING OR VERIFICATION PHASE AS TO REASONABLE LEVELS OF CONTROL FOR CARBONACEOUS BOD IF IT IS PROPOSED TO PUT THAT OUT AS A PERMIT LIMITATION?

MR. MEDZ: AS FAR AS THE SCREENING LEVEL TO BE PROPOSED ASSOCIATED WITH THE CARBONACEOUS BOD, THAT HAS NOT BEEN DETERMINED; I CANNOT ANSWER THAT.

MR. HAMLIN: DO YOU ANTICIPATE DOING THAT, BILL?

MR. TELLIARD: NO.

MR. MEDZ: NO.

MR. HAMLIN: AS I LOOKED OVER THE 600 METHODS, IT SEEMS TO ME THAT THOSE METHODS ARE NOT REASONABLY...I SHOULD SAY, THE EXPECTATIONS OF BEING ABLE TO INTRODUCE THOSE METHODS INTO A PLANT FOR ROUTINE MONITORING AND COMPLIANCE PURPOSES IS NOT REALISTIC. I WOULD SUBMIT THAT THOSE

METHODS WOULD BE SUBJECT TO SERIOUS INTERFERENCES IN A LOT OF PLANT APPLICATIONS.

SECONDLY, IT SEEMS TO ME THAT THE WAY THEY ARE CURRENTLY PROPOSED, THE GC/MASS SPEC SYSTEM BECOMES ESSENTIALLY THE REFERENCE METHOD FOR ALL THE OTHER 600 PROCEDURES, IS THAT CORRECT?

MR. MEDZ: NO, SIR, THEY ARE BEING PROPOSED AS OPTIONS OF THE PERSON WHO WANTS TO MAKE THE MEASUREMENT.

MR. HAMLIN: STAND-ALONE PROCEDURE?

MR. MEDZ: THEY ARE STAND-ALONE PROCEDURES.

MR. HAMLIN: BUT IN ALL INSTANCES, I BELIEVE, YOU MAKE A STATEMENT SOMETHING TO THE EFFECT THAT IF THERE IS A QUESTION AS TO THE VALIDITY OF THE DATA BEING REPORTED, IT HAS TO BE CONFIRMED BY GC/MASS SPEC, IS THAT NOT CORRECT?

MR. MEDZ: ONLY IDENTITY, IF THERE SEEMS TO BE ANY UNCERTAINTY AS TO WHAT THE IDENTITY OF THE COMPOUND IS FROM THE GC RUN ITSELF, THE...

MR. TELLIARD: THAT IS THE SAME THING WE DID OVER THE PESTICIDE WHERE YOU HAVE SEEN IT AND WE CAN CONFIRM IT WHEN THERE IS A MASS PROBLEM.

MR. MEDZ: THE CONFIRMATORY TEST CAN BE A SECOND COLUMN, IT CAN BE GC/MS, BUT IT HAS TO BE CONFIRMED BY SOME MEANS, IF THERE IS ANY DOUBT THAT THE PEAK COMING OFF THE GC IS NOT ONE OF THE CONSENT OF EPA AGENTS.

MR. HAMLIN: THEN THIS LEADS BACK INTO THE QUESTION ABOUT WHAT IS GOING TO BE THE ROLE OF THE INDICATOR OF A SURROGATE COMPOUND, INTERNAL STANDARD OR AN INDICATOR PARAMETER. YESTERDAY WHEN DEAN NEPTUNE WAS MAKING HIS DISCUSSION ABOUT THE PROBLEM WITH THE PURGE AND TRAP AND WHETHER TO INTRODUCE INTERNAL STANDARD, I THINK THERE WAS SOME COMMENT ABOUT INJECTING IT STRAIGHT ON THE INSTRUMENT. THAT SEEMS TO ME THAT ONLY PROVES THE PERFORMANCE OF THE INSTRUMENT, IT DOES NOT PROVE THE METHOD. SO THE QUESTION NOW IS, IS IN THE 600 METHODS, DO YOU INTEND THAT THE SURROGATE OR INTERNAL STANDARDS BE INJECTED IN THE FIELD, INJECTED AT THE TIME OF SAMPLING OR INJECTED IN THE LABORATORY OR INJECTED INTO THE INSTRUMENT?

MR. MEDZ: THAT IS ALL A QUESTION OF THE QUALITY ASSURANCE THAT IS GOING TO BE REQUIRED ALONG WITH THE METHODS, AND WE HAVE NOT REALLY PROPOSED ANY QUALITY ASSURANCE YET. THE QUALITY ASSURANCE PROTOCOL THAT WAS INCLUDED IN THE PROPOSED

PACKAGE IS STRICTLY PROVIDING SOME OF OUR THINKING IN THIS AREA, BUT IT IS NOT MADE PART OF THE REGULATORY LANGUAGE YET.

MR. HAMLIN: IS THERE NOT A QUALITY ASSURANCE AND QC IN THE PROPOSED REGULATIONS?

MR. MEDZ: THERE IS A QC SECTION IN EACH OF THE METHODS, BUT THAT IS A VERY, VERY LIMITED, VERY MINIMAL QC THAT IS WRITTEN INTO THE METHODS THEMSELVES.

MR. HAMLIN: SO YOU ARE ANTICIPATING A FUTURE PUBLICATION OF THE QA, QC TO SUPPLEMENT THE CURRENTLY PUBLISHED AND PROPOSED 600 METHODS.

MR. MEDZ: THAT WILL DEPEND ON YOUR COMMENTS, SIR. WE ARE ASKING THE COMMUNITY, THE PERSONS THAT ARE USING THESE METHODS, FOR THEIR IDEAS IN THIS AREA.

MR. HAMLIN: I WILL SUBMIT THAT IN THE TIME SINCE PUBLICATION OF THE PROPOSED METHODS AND THE DEADLINE FOR COMMENTS, THERE IS NOT ADEQUATE TIME TO EVALUATE IT.

MR. MEDZ: TO THAT I CANNOT MAKE A COMMENT BECAUSE THE AGENCY HAS TO MAKE THAT DETERMINATION.

MR. HAMLIN: ALL RIGHT, ANOTHER

QUESTION I WILL ASK YOU. I DID NOT SEE ANY EVIDENCE IN THE PUBLICATION THAT SHOWED A COMPARISON OF DATA BETWEEN THE PROTOCOL GC/MASS SPEC SYSTEM AND ANY OF THE OTHER 600 METHODS.

MR. MEDZ: TO DATE, THAT KIND OF INFORMATION IS JUST BEING GENERATED.

MR. HAMLIN: I WOULD ALSO SUBMIT, THEN, I WOULD LIKE TO SEE THAT TYPE OF INFORMATION BEFORE YOU CLOSE THE COMMENT PERIOD.

MR. TELLIARD: WE AGREED THAT THE ONLY REPORT DATA THAT IS PRESENTLY AVAILABLE IS THE DATA THAT HAS COME IN FROM CINCINNATI STUDIES ON THEIR METHODS AND WHAT DATA YOU HAVE ALREADY SEEN FROM US ON THE GC/MS METHODS. AS A DIRECT EQUIVALENCY, QUOTE, EXAMINATION, NO, IT HAS NOT BEEN DONE.

MR. HAMLIN: LET ME ASK YOU THIS. IN ESTABLISHING LIMITS OF PRECISION IN THE SURROGATE METHODS, ARE YOU PROPOSING TO USE SAMPLES IN PURE WATER, OR SAMPLE SPIKES IN ACTUAL AFFLUENT SAMPLES TO ESTABLISH LIMITS OF DETECTABILITY?

MR. MEDZ: YOU DO NOT MEAN SURROGATE METHODS, DO YOU, SIR, YOU MEAN THE ALTERNATE METHODS?

MR. HAMLIN: WELL, OKAY, THE

ALTERNATE, THEN.

MR. MEDZ: IN THE ALTERNATE METHODS, THE ESTABLISHMENT OF THE PRECISION AND ACCURACY OF THESE METHODS IS A SUBJECT OF FOLLOW-ON STUDIES BY THE AGENCY RIGHT NOW, AND THESE STUDIES WON'T BE COMPLETED UNTIL THE END OF THIS FISCAL YEAR.

MR. HAMLIN: WOULD THOSE NOT IMPACT THE VALIDITY OF THESE METHODS?

MR. MEDZ: THESE METHODS RIGHT NOW REFLECT WHAT THE AGENCY FEELS IS THE BEST REPRESENTATION OF THE STATE OF THE ART IN MAKING THESE LOW LEVEL RESIDUE ANALYSES FOR THE CONSENT DECREE POLLUTANTS. WHAT WE WANT TO DO RIGHT NOW IS TO ESTABLISH THAT WITHIN THE ENTIRE COMMUNITY, RESEARCH COMMUNITY, THE REGULATED COMMUNITY, THAT WE HAVE GOT A GOOD FIRST APPROXIMATION OF THE STATE OF THE ART.

MR. HAMLIN: I DO NOT THINK YOU HAVE DEMONSTRATED THAT UNLESS YOU CAN SHOW THE COMPARISON BETWEEN THE RESULTS USING THESE METHODS AND THE METHOD USED IN THE VERIFICATION PROCEDURE.

MR. MEDZ: THE COMPARISON THAT WE WILL HAVE INITIALLY IS WE WILL HAVE PRECISION AND ACCURACY STATEMENTS ON THE TWO METHODS APPLICABLE TO SPECIFIC DISCHARGES. THAT WILL NOT BE THE KIND OF

INFORMATION WE GENERATE FROM INTERLABORATORY, COLLABORATIVE TESTING, BUT IT WILL BE A FIRST APPROXIMATION AS TO THE COMPARABILITY OF THE TWO METHODS.

MR. HAMLIN: I WON'T BELABOR THE POINT; YOU HAVE NOT CONVINCED ME TOTALLY ABOUT THAT.

IN THE PROPOSED CONSOLIDATED PERMIT REGULATIONS WHICH THIS KIND OF RELATES TO, YOU HAVE STATED SOMETHING TO THE EFFECT THAT, IF THERE WAS NO KNOWLEDGE AS TO REAL DISCHARGE LEVELS OF POLLUTANTS, THAT A PERMIT CONDITION OF FIVE TIMES THE DETECTION LIMIT COULD BE IMPOSED ON THE PERMIT. THE QUESTION I AM ASKING NOW IS, WHAT IS BEING USED TO ESTABLISH DETECTION LIMITS?

MR. MEDZ: AT THE PRESENT TIME, THE ONLY APPROXIMATION WE HAVE OF DETECTION LIMITS OF THESE METHODS ARE THOSE DETECTION LIMITS THAT WERE DETERMINED BY THE CONTRACTORS USING THESE PROCEDURES IN REAL WORLD SAMPLES, RECOVERIES FROM RELATIVELY CLEAN DISCHARGE WATERS, BUT THEY ARE TREATED EFFLUENTS. NOW AS FAR AS THAT CONSIDERATION THAT YOU HAVE JUST DISCUSSED ON THE COMBINED PERMITS FORM REGULATION, I DO NOT KNOW WHAT THE FINAL FORM OF THAT IS GOING TO BE; I DO NOT KNOW IF THAT REQUIREMENT WILL

CARRY OVER INTO THE FINAL REGULATION OR NOT. SOME FORM OF IT PROBABLY WILL, BUT I DON'T KNOW EXACTLY WHAT THE FORM OF THAT WILL BE IN THE FINAL REGULATION.

DETECTION LIMIT, I THINK, STILL BECOMES AN EXTREMELY CRITICAL QUESTION ANY TIME WE'RE USING ANY OF THESE ANALYTICAL METHODS, AND I THINK IT IS TIME, I THINK THE STATE OF THE ART WILL ALLOW US TO START PROVIDING LANGUAGE BY WHICH THE DETECTION LIMIT CAN BE DETERMINED, DEFINED AND DETERMINED EXPERIMENTALLY. IN ORDER TO INTERACT WITH THE PERSONS THAT HAVE TO USE THIS METHOD, TO FIRM UP WHAT THE DETECTION LIMITS OF THIS METHOD ACTUALLY ARE, IN THE NEXT PACKAGE WE INTEND TO PROPOSE A DEFINITION AND EXPERIMENTAL PROCEDURES BY WHICH DETECTION LIMIT MIGHT BE DETERMINED. AS I SAY, THIS IS PROPOSED. JUST LIKE THE DECEMBER 3RD PACKAGE IS PROPOSED, IT'S NOT A FINAL REGULATION YET. IT WON'T BE FINAL UNTIL WE GET ALL YOUR COMMENTS AND EVALUATE THE COMMENTS AND MAKE CERTAIN THAT OUR DATA BASE ADEQUATELY DEFINES THE STATE OF THE ART AND THESE METHODOLOGIES.

MR. HAMLIN: WELL, WHAT I'M CONCERNED ABOUT IS, I NOTICE IN THE STATEMENT AS TO THE PRECISION FOR THE BOD METHOD, THAT STATEMENT IS BASED UPON THE STANDARD OF GLUCOSE AND GLUTAMIC

STANDARD. I WOULD SUBMIT THAT THE UNCERTAINTY OF REAL SAMPLES IS MUCH, MUCH GREATER THAN THAT OF THE STANDARD, AND TO ALLUDE THAT THE PRECISION OF THE METHOD IS EQUAL TO THE STANDARD, I THINK, IS INACCURATE. I THINK THAT ANY METHOD SHOULD BE AND CERTAINLY THE METHOD SHOULD BE BASED UPON THE PERFORMANCE BASED ON REAL SAMPLES AND NOT IDEAL STANDARDS OR SAMPLES INJECTED IN JUST PLAIN WATER.

IF YOU DON'T MIND, I'D JUST LIKE TO GO OFF, VERY BRIEFLY, ON THE 600 METHODS AND MAKE A GENERAL COMMENT ABOUT SOME OF THE THINGS WE TALKED ABOUT YESTERDAY EVENING. AS NEAR AS I CAN TELL, I HAVEN'T SEEN ANY EVIDENCE OF THE AGENCIES ATTEMPTING TO SEPARATE SAMPLING ARTIFACTS DATA FROM COMPOUND OCCURRENCE IN EFFLUENT SAMPLES. ONE OF OUR EXPERIENCES HAS BEEN THAT WE WERE SAMPLED LAST SUMMER AND SPLIT SAMPLES WITH THE CONTRACTOR. THEY REPORTED TOLUENE AS PRESENT IN OUR EFFLUENT. WE HAVE SUBSEQUENTLY RESAMPLED AND WE ALSO DETECTED TOLUENE IN ONE OF OUR SAMPLES WHERE WE TRACED IT TO THE FACT THAT THE PERSON TAKING THE SAMPLE WORE A PAIR OF RUBBER GLOVES. WHAT I'M SUGGESTING HERE IS THAT YOU HAVE A LOT OF DATA THAT HAS ARTIFACT INFORMATION BASED UPON THE SAMPLING TECHNIQUES THAT WERE USED IN SECURING THE SAMPLES,

AND I SUGGEST THAT THE AGENCY CONSIDER SENDING BACK A QUESTIONNAIRE TO THE COMPANIES THAT WERE TESTED AND SAMPLED DURING THE VERIFICATION PROCEDURES TO ASK SIMPLY, ARE THE COMPOUNDS LISTED REASONABLY GENERATED BY YOUR PROCESS, TO SEPARATE OUT THOSE COMPOUNDS THAT ARE A RESULT OF THE MANUFACTURING PROCESS AND POSSIBLE CONTAMINATION THROUGH SAMPLING, WHATEVER IT IS. I THINK THAT WOULD BE A REASONABLE RESPONSE.

ALSO, I'D LIKE TO REITERATE THAT ANY STANDARD BE A TEST OF THE METHOD AND NOT THE PERFORMANCE OF THE INSTRUMENT AND I THINK THAT'S REALLY IMPORTANT. THANK YOU.

MR. MEDZ: THANK YOU.

MR. MARRS: DAVE MARRS, STANDARD OIL. DR. MEDZ, BILL TELLIARD INDICATED THAT WE COULD ASK FOR ANYTHING BUT AN EXTENSION; THAT'S BEEN ASKED FOR, I THINK; BUT COULD YOU ENLIGHTEN US A LITTLE BIT OF WHETHER...WHAT TIME-TABLE THE AGENCY IS LOOKING AT TO PROMULGATE THESE METHODS?

MR. MEDZ: THE TIME-TABLE OF THE AGENCY, THE PERMITS APPARATUS WANTS TO RENEW THE PERMITS STARTING IN THE APRIL TIME FRAME. THIS REGULATION IS EXTEMELY IMPORTANT TO

THAT ACTIVITY AND THE AGENCY WOULD LIKE VERY MUCH TO HAVE THESE REGULATIONS IN PLACE BY THEN. I'M COMMITTED TO THAT.

MR. MARRS: NOT BEING A LAWYER, I DON'T UNDERSTAND THE INS AND OUTS OF THE CLEAN WATER ACT REAL WELL, BUT COULD YOU EXPLAIN A LITTLE BIT ABOUT, OR MAYBE SOMEONE ELSE IN THE AGENCY, ABOUT THE USES THAT ONCE THESE METHODS ARE PROMULGATED THEY WILL HAVE IN TERMS OF COMPLIANCE MONITORING AND ENFORCEMENT?

MR. MEDZ: IF THESE METHODS ARE APPROVED IN A FORM SIMILAR TO WHAT THEY ARE RIGHT NOW, THEN THAT WILL DEPEND UPON YOUR COMMENTS.

I CAN'T ASSURE YOU THAT THEY'LL STAY THE WAY THEY ARE BECAUSE I HAVEN'T SEEN ALL OF YOUR COMMENTS YET; BUT ASSUMING YOUR COMMENTS DO NOT DRASTICALLY CAUSE THE AGENCY TO CHANGE THOSE METHODOLOGIES, THOSE METHODOLOGIES WILL BE THE LEGAL METHODS BY WHICH A DISCHARGER HAS HIS OPTION OF MAKING HIS MEASUREMENTS TO SHOW COMPLIANCE, AND THE METHOD, THEN, THAT WILL HAVE TO BE SHOWN BY THE ENFORCEMENT PEOPLE WHO NEED TO BE THE ONE THAT THE DISCHARGER HAS SELECTED TO USE. WE RECOGNIZE WHEN YOU'RE TALKING ABOUT PARTS PER BILLION, THERE ARE NO TWO METHODS THAT WILL GIVE YOU IDENTICALLY THE SAME RESULTS; WE RECOGNIZE THIS,

BUT WE HAVE TO GET AS GOOD AN APPROXIMATION OF THE STATE OF THE ART RIGHT NOW THAT WILL ALLOW THE DISCHARGER AND THE ENFORCER TO USE THE SAME YARDSTICK TO MEASURE THE DISCHARGE, AND WE THINK WE'VE COME UP WITH A PRETTY GOOD APPROXIMATION OF THE STATE OF THE ART TO BE ABLE TO DO THIS. YOUR COMMENTS MIGHT CHANGE OUR MINDS, I DON'T KNOW.

MR. MARRS: I WOULD HOPE SO.

MR. BLOOM: SAUL BLOOM, EXXON RESEARCH. YESTERDAY WE HEARD THE INVESTIGATORS DESCRIBING MICROEXTRACTION, AND IN THE COURSE OF QUESTION AND ANSWER PERIOD, THE INVESTIGATORS ACKNOWLEDGED THE FACT THAT THE WORK WAS STILL IN THE RESEARCH AND DEVELOPMENT PHASE. THIS MORNING WE HEAR THE AGENCY INTENDS TO PROPOSE THIS IN THE SECOND PACKAGE AS A METHOD, AND MY QUESTION IS, IS IT THE POSITION OF THE 304H COMMITTEE TO RECOMMEND TO THE AGENCY TO PROMULGATE METHODS THAT ARE STILL IN THE R AND D PHASE?

MR. MEDZ: ONE OF THE THINGS WITH WHICH WE ARE EXTREMELY CONCERNED IS COST OF ANALYSIS TO THE REGULATED COMMUNITY. IF THERE APPEAR TO BE ADVANTAGES, COST ADVANTAGES TO THE DISCHARGER, IN USING SUCH A PROCEDURE AS A MICROEXTRACTION

TECHNIQUE, AND IF WE FEEL THAT THE PRECISION AND ACCURACY OF THE DATA THAT'S GENERATED FROM THAT PROCEDURE WILL BE SUFFICIENT IN ACCURACY AND PRECISION TO MAKE CERTAIN THAT THE AGENCY INTERESTS ARE PROTECTED, THEN WE WOULD PROPOSE SUCH A PROCEDURE FOR CONSIDERATION, STRICTLY BECAUSE IT WILL GIVE A COST BENEFIT TO THE DISCHARGER.

AGAIN, THE METHOD WILL BE PROPOSED AND IT WILL NOT BE MADE A FINAL APPROVED METHOD WITHOUT BEING DEVELOPED TO THE EXTENT WHERE TECHNICALLY IT CAN GIVE A PRECISION AND ACCURACY WHICH THE ENFORCEMENT AND PROGRAMATIC INTERESTS OF THE AGENCY REQUIRE. I DON'T KNOW, DOES THAT ANSWER YOUR QUESTION?

MR. BLOOM: WELL, I GATHER THAT WHAT YOU'RE SAYING IS THAT IF IT LOOKS PROMISING AND IT LOOKS COST-EFFECTIVE, THEN IT WILL BE PROPOSED, EVEN THOUGH IT'S INCOMPLETE.

MR. MEDZ: THAT'S RIGHT.

MR. BLOOM: THANK YOU.

MR. CLAEYS: BOB CLAEYS FROM THE NATIONAL COUNCIL. WE'RE A LITTLE BIT CONFUSED THAT THESE ARE PROPOSED METHODS, YOU'RE GOING TO ASK FOR COMMENTS, AND THEN IT SOUNDS LIKE THEY'LL BECOME FINAL METHODS. DO WE GET THE COMMENT AGAIN ON THE FINAL METHOD, BECAUSE I SUBMIT RIGHT NOW THESE

PROPOSED METHODS ARE AT BEST, AS WRITTEN IN THE DECEMBER 3RD REGISTER, THEY'RE SO POORLY WRITTEN THAT THERE'S A LOT OF DISTANCE BETWEEN THESE PROPOSED METHODS AND WHAT MAYBE COME OUT AS FINAL METHODS. SO WILL WE HAVE A CHANCE TO COMMENT ON THE, QUOTE, FINAL METHOD?

MR. MEDZ: NO. YOU CAN COMMENT ON IT, BUT WE WILL PROBABLY...WE WON'T REPROPOSE, IF THAT'S WHAT YOUR QUESTION IS.

MR. LICHTENBERG: JIM LICHTENBERG, EPA. I JUST WANT TO MAKE A COUPLE OF COMMENTS WITH REGARD TO SOME OF THE QUESTIONS THAT HAVE BEEN RAISED. ONE, YOU KNOW, THE MICROEXTRACTION PROCEDURE WHICH WAS PRESENTED YESTERDAY. THAT IS NOT GOING TO BE PROPOSED AS AN ACROSS-THE-BOARD APPLICATION. IT'S BEING PROPOSED ON A VERY LIMITED BASIS FOR THOSE APPLICATIONS WHERE IT HAS BEEN USED AND SHOWN TO WORK IN A PARTICULAR INSTANCE. IT'S NOT PROPOSED ACROSS-THE-BOARD. THAT SAME GOES FOR THE REST OF THE METHODS INVOLVED THAT ARE NOT THE 600 SERIES METHODS. THEY ARE BEING OR WILL BE, I UNDERSTAND, PROPOSED AS METHODS TO BE USED OR THAT MAY BE USED IN THOSE SPECIFIC AREAS WHERE THEY HAVE BEEN USED IN THE PRELIMINARY WORK AND HAVE DATA TO SUPPORT THEM IN THE PROGRAMS THAT HAVE BEEN USING THEM. IN TERMS OF THE INTERLABORATORY STUDIES THAT

ARE GOING ON, WE ARE LOOKING AT A WHOLE CROSS SECTION OF SAMPLE TYPES FROM THE CLEANEST WATER TO REPRESENTATIVE WASTE EFFLUENTS IN THE INTERLABORATORY STUDIES GOING ON. THERE ARE 20 LABORATORIES, MINIMUM, PARTICIPATING IN THESE STUDIES AND THEY ARE A CROSS SECTION OF LABORATORIES UNDER CONTRACT, SO WE ARE LOOKING AT PROPER SAMPLE TYPES WITHIN EACH INDIVIDUAL METHOD. WE DO HAVE ONGOING, IN OUR SHOP, ANALYTICAL INVESTIGATIONS IN TERMS OF ACCURACY AND PRECISION WITH THE 624 AND 625 METHODS AND AN INTERLABORATORY STUDY IS PLANNED FOR THOSE AS WELL.

OTHER AREAS, THE METALS ANALYSIS AREAS, THERE IS ALSO WORK GOING ON IN OUR SHOP IN THOSE AREAS. I JUST WANTED TO TRY TO MAKE A FEW POINTS OF CLARIFICATION.

MR. HOCHGESANG: MY NAME IS FRANK HOCHGESANG, I'M WITH MOBIL OIL COMPANY. I HAPPEN TO ALSO BE CHAIRMAN OF AN ANALYTICAL TASK FORCE WITHIN THE AMERICAN PETROLEUM INSTITUTE. I'M TRYING TO CONTINUE, JUST A LITTLE, THE DISCUSSION THAT'S BEEN GOING ON, BUT I'D LIKE TO RESTRICT MY COMMENTS TO METHODS 624 AND 625. THOSE GC/MS METHODS ARE THOSE THAT HAVE BEEN USED IN THE REFINERY SURVEY COLLECTING OF DATA BASE AND THEY HAVE BEEN THE STATE OF THE ART, THE BEST THAT COULD BE DONE, AND BOTH INDUSTRY AND EPA HAVE WORKED TOGETHER TO TRY TO GET THE MOST VALID NUMBERS

POSSIBLE. WHAT CONCERNS ME IS THAT WE HAVE, OVER THE PAST YEAR OR SO, DEVELOPED SOME INFORMATION THAT GENERALLY SEEMS TO BE TECHNICALLY VALID WHICH INDICATES CONSIDERABLE ANALYTICAL UNCERTAINTY BETWEEN LABORATORIES, EXPERIENCED LABORATORIES, WHEN THESE METHODS ARE APPLIED AND IN MY CASE, THE PETROLEUM WASTEWATERS. THAT UNCERTAINTY IS IN THE RANGE OF 10 TO 50 MICROGRAMS PER LITER. SO MY CONCERN IS WE'RE ADVANCING FROM COLLECTING THE DATA BASE, IN MY OPINION, TO A COMPLIANCE MONITORING AND POTENTIAL ENFORCEMENT PROBLEMS AND WITHOUT HAVING ESTABLISHED WHAT THE INTERLABORATORY REPRODUCIBILITY OF THESE THINGS IS, IT JUST SEEMS TO BE, HOW SHALL I SAY IT, OPENING UP A WHOLE SITUATION OF TURMOIL. I WONDERED IF YOU HAD ANY COMMENT ABOUT THE HOW, THE RESULTS OF THESE TESTS THAT WILL BE APPLIED NOW IN THE NEAR FUTURE, LIKE IN NPDS PERMIT APPLICATIONS AND PERMIT WRITERS' SETTING, THEN THE CONTROL LIMITS, ANY COMMENT YOU MIGHT MAKE ABOUT THE ANALYTICAL REPRODUCIBILITY, ESPECIALLY OF THOSE METHODS WHICH HAVE BEEN MOST WIDELY USED.

MR. TELLIARD: FRANK, WE HAVE ON THE STREET PROPOSED REGULATIONS FOR THE PETROLEUM INDUSTRY. WHAT ARE THE PARAMETERS FOR REGULATING, FRANK. PHENOL, CHROME; ALL RIGHT. WE'VE GOT METHODS FOR PHENOL AND CHROME, FRANK. WE DIDN'T

GIVE YOU 1, 2-DIPHENYL BAD STUFF, WE DIDN'T PUT THAT ANYWHERE IN THE REGULATION. SAMARIUM WAS NOT IN THERE, WE DO NOT INTEND TO REGULATE THAT. ANYTHING WE PUT IN THAT REGULATION WE HAD DATA ON AND WE HAD A PROVEN METHOD FOR. NOW YOU CAN ACCUSE ME, I'M SURE YOU'RE GOING TO SEND IN YOUR COMMENTS DURING THIS COMMENT PERIOD, THAT YOU WANT ME TO ADD PHENOL, YOU WANT ME TO ADD XYLENE, TETRAETHYL LEAD AND A FEW OTHER PARAMETERS, YOU'D FEEL BETTER, RIGHT, YOU'RE GOING TO DO THAT. THE INDUSTRY IS GOING TO TELL ME, GIVE US MORE PARAMETERS.

MR. HOCHGESANG: BILL, YOU HAVE A WAY OF COMING BACK WITH A VERY PERTINENT COMMENT.

MR. TELLIARD: I THINK THAT WAS A TRANSLITERAL TRANSIT OF A STICK IT IN YOUR EAR, BUT GO AHEAD.

MR. HOCHGESANG: WELL, TO TRY TO RESPOND, WE HAVE WORKEDCOLLECTIVELY AND FOUND THAT THERE'S NO NEED TO PUT ADDITIONAL PARAMETERS OF SPECIFIC TOXICS AND PETROLEUM. HOWEVER, I'M STILL CONCERNED THAT THESE METHODS AREN'T GOING TO BE USED TO FURTHER COLLECT THE DATA BASE AND THAT WAS IN THE NATURE OF THE QUESTION THAT I HAD PUT OUT TO SEE IF ANYONE CAN COMMENT AT THE MOMENT. I THINK IT'S A DIFFICULT SITUATION, BUT WE'RE ALL IN IT.

MR. TELLIARD: WELL, I THINK THAT, YOU KNOW, WE HAVE CONTINUALLY SAID THAT IF WE'RE GOING TO PUT A NUMBER IN A REGULATION, WHETHER IT BE SAMARIUM OR BOD, WE'LL HAVE THE DATA FOR IT. NOW, WE HAVE ALSO IN THE PREAMBLE, PETROLEUM POINTED OUT THE FACT THAT, YES, WE'RE GOING TO PICK OUT A COUPLE OF REFINERIES, WE'RE GOING TO GO OUT THERE AND WE'RE GOING TO SAMPLE LONG TERM WITH THESE METHODS AND GENERATE SOME DATA THAT MAY OR MAY NOT BE USABLE. WE RECOGNIZE THAT THERE'S CERTAIN LIMITATIONS WITHIN ALL OF THIS STUFF. WE'VE BEEN FIGHTING OVER THIS NOW FOR TWO YEARS, WORKING TOGETHER, PULLING IT TOGETHER AND, YOU KNOW, WE STARTED FROM 0. SO YES, WE'RE GOING TO GO LOOK AT PETROLEUM REFINING WITH METHODOLOGY, AND IF THE METHODS AREN'T ANY GOOD AND THE DATA ISN'T ANY GOOD, WE'RE NOT GOING TO USE IT, SIMPLE ENOUGH.

MR. HOCHGESANG: FAIR ENOUGH.

MR. MARRS: BILL, JUST TO FOLLOW UP AND THIS IS DAVE MARRS, STANDARD OIL. JUST TO FOLLOW UP ON THAT. THE CONCERN FOR THESE METHODS GOES BEYOND THE EFFLUENT GUIDELINES. FIRST OF ALL, IN THE EFFLUENT GUIDELINES YOU DID MENTION THAT YOU ARE ALSO LOOKING AT ETHYL BENZENE, BENZENE TOLUENE, AND A COUPLE OF OTHERS, BUT IN ADDITION THESE METHODS, ONCE THEY BECOME PROMULGATED, WILL BECOME APPLICABLE FOR USE

BY THE STATES AND WITH ALL DUE RESPECT TO THE STATE EPA'S THAT I HAVE DEALT WITH, THESE PEOPLE ARE LIGHT-YEARS BEHIND THE PEOPLE IN THIS ROOM IN TERMS OF ORGANIC ANALYSIS, AND I THINK THAT, YOU KNOW, IN TERMS OF WHAT YOU'RE DOING, OKAY, MAYBE YOU CAN GET BY WITH IT; BUT BY PROMULGATING THESE METHODS AND GIVING THEM THE FORCE OF LAW, YOU ARE ESSENTIALLY OPENING THEM UP TO PEOPLE WHO MAY OR MAY NOT BE ABLE TO USE THEM AND THINGS MAY GET OUT OF CONTROL.

MR. TELLIARD: THIS GOES BACK TO THE SYNDROME OF, YOU KNOW, GUNS DON'T KILL PEOPLE, PEOPLE KILL PEOPLE, AND THAT'S WHY WE HAVE POLICEMEN; I CAN'T ANSWER THAT. TRUE, THE AGENCY IS TAKING ITS BEST SHOT AT A RATHER HARD QUESTION IN ANALYTICAL CHEMISTRY, BUT YOU CAN RUN BOD'S, PH'S AND NEVER GROW IN KNOWLEDGE, AND I DON'T THINK WE WANT TO DO THAT, EITHER. SOMEONE SAYS MAYBE THE RATE OF GROWTH IS A LITTLE BIT EXTRAPOLATED AND PERHAPS IT IS. WE DON'T DENY THAT; BOB IS UP TO HIS BEHIND WITH ALLIGATORS AND WE'VE GOT SOME HARD QUESTIONS AND WE'RE TRYING TO GIVE IT OUR BEST SHOT. I THINK BEING REALISTIC, THE COMMENTS WE RECEIVE FROM YOU GIVE US A LEATHER TOY TO GO WITH OUR MANAGEMENT WITH AND SAY WELL, MAYBE WE OUGHT TO EXTEND IT; MAYBE WE OUGHT TO DO SOMETHING HERE. I THINK THE COMMENTS ARE IMPORTANT

FROM THIS COMMUNITY BECAUSE YOU'RE THE MOST KNOWLEDGEABLE AT IT. WHEN I SAID COMMENTS, TELLING US WE'RE DUMB, I MEAN I DON'T MIND YOU OPENING THAT WAY; BUT IF YOU'D PUT SOME MEAT INTO IT LIKE A NUMBER OR TWO, OR SOME DATA, JUST SENDING US A LETTER SAYING WE'RE DUMB REALLY DOESN'T HELP US TOO MUCH. I MEAN, THAT'S WHERE YOU GET THE ONE-LINER BACK, THANK YOU.

MR. MEDZ: THANK YOU, BILL.

MR. TELLIARD: THANK YOU, BOB.

(APPLAUSE.)

MS. WARNER: MY NAME IS BEV WARNER FROM MONSANTO RESEARCH IN DAYTON. YOU'VE HEARD THEM TALK ABOUT THE 600 METHODS 601 THROUGH 613, AND YOU'VE HEARD MR. LICHTENBERG MENTION THE VALIDATION STUDIES, THE INTERLABORATORY VALIDATION STUDIES. I HAPPEN TO BE PRINCIPAL INVESTIGATOR FOR INTERLABORATORY VALIDATION STUDY; WE'RE GOING TO BE STARTING ON SOME OF THESE METHODS. THAT'S 601, 602, 603, AND 613 AND WITHIN THE NEXT TWO WEEKS OR SO, I'LL BE SENDING OUT BID PACKAGES. SO IF ANY OF YOU ARE INTERESTED, YOU CAN CALL ME AT MONSANTO AND I'LL SEND YOU OUT AND YOU CAN GET A CHANCE TO BID ON PARTICIPATING IN THIS AND YOU CAN GET YOUR COMMENTS BACK TO THE EPA THROUGH ACTUALLY DOING THE SAMPLES, AND IF YOU'RE NOT REALLY FAMILIAR WITH THE PROGRAM, IT STARTS OUT WITH TWO TEST SAMPLES

TO TRY OUT THE METHODS, JUST TO BECOME FAMILIAR WITH THE METHODS AND WITH THE INSTRUMENTATION, AND ONE THAT WE'RE GOING TO BE SENDING OUT WILL BE...WE'LL BE SENDING OUT AMPULES THAT YOU'D SPIKE WATER WITH.

ONE WILL BE SPIKED IN DISTILLED WATER AND ONE WILL BE AN EFFLUENT WATER THAT MOST LIKELY HAS THE PROPOSED COMPOUNDS IN IT. YOU TRY OUT THE METHOD WITH THAT, WORK AROUND WITH IT, AND THEN EPA IN CINCINNATI WILL HOLD A MEETING WITH EVERYBODY THAT PARTICIPATES IN IT. YOU GET TO AIR YOUR GRIPES, AIR THE PARTS OF THE METHOD THAT YOU DON'T THINK WORKS, WE'LL WORK ON IT, TRY TO WORK IT OUT AND THEN WE'LL SEND OUT THE ACTUAL METHOD SAMPLES. THESE WILL BE DISTILLED WATER FROM YOUR LAB, ONE SURFACE WATER, ONE DRINKING WATER, AND THREE EFFLUENT WATERS FOR EACH CATEGORY. SO IF YOU'RE INTERESTED AND YOU REALLY WANT TO AIR...YOU WANT TO GET PAID FOR PLAYING AROUND WITH THESE METHODS TO SEE WHAT THEY'RE LIKE, WRITE ME AT MONSANTO OR CALL ME AT MONSANTO AND I'LL BE GLAD TO SEND YOU OUT THE PACKAGES.

MR. TELLIARD: THANK YOU. SINCE WE'VE RESOLVED ALL OUR ANALYTICAL PROBLEMS IN ANALYZING WATER SAMPLES, WE THOUGHT WE WOULD MOVE ON TO ANALYZING SLUDGES; SOME SORT OF A CHALLENGE SINCE THIS STUFF IS ALL DONE NOW AND JOAN FISK, WHO PRESENTLY

WORKS FOR VYER, IS GOING TO TALK TO YOU ABOUT A PROPOSED PROTOCOL FOR THE MEASUREMENT OF OUR PRIORITY POLLUTANTS IN SLUDGES. THE METHOD THAT IS BEING PROPOSED HERE, WE WILL HAVE COPIES OF IT AND WE'LL LEAVE IT OUT ON THE TABLE AGAIN AS YOU LEAVE IF YOU WANT TO PICK UP A COPY.

PRELIMINARY METHODS FOR ORGANIC AND ELEMENTAL ANALYSIS OF SLUDGES

By: Joan Fisk

I'm not sure there's an appropriate time of day to talk about sludge because I don't think anybody likes to think about it, especially before lunchtime.

It's an obvious concern in the establishment and implementation of effluent guidelines to gather information on the nature of the conservatism of pollutants. We must discover what pollutants are destroyed by treatment systems and which are transferred from one media to another; that is, from the wastewater discharge to residual waste, which we shall describe by the all-encompassing term, 'sludge.' The sludges from both industrial and POTW sources are ultimately disposed of either in storage drums or landfills--their impact on the environment, unknown, without knowledge of their polluting or hazardous natures. Any methodology developed for analysis of sludges and information obtained by these methods will also be instrumental in aiding the programs of the Office of Solid Waste, which go hand in hand with our own missions. Analyses will be required for the constituents

OF THE SOLID WASTES BEFORE MOBILITY AND SOIL ATTENUATION STUDIES CAN OCCUR.

I WILL ATTEMPT TO DESCRIBE THE PROTOCOL DEVELOPED BY MIDWEST RESEARCH INSTITUTE IN KANSAS CITY. IT'S PROBABLY GOING TO SOUND A LITTLE LIKE ED HERLIHY AND HIS RECIPES FROM THE KRAFT KITCHEN AND YOU'LL HAVE TO PARDON THAT. THIS PROTOCOL, FOR EXPEDIENCY'S SAKE, WAS DESIGNED AROUND THE EXISTING SAMPLING AND ANALYSIS METHODS FOR WASTEWATER, WITH APPROPRIATE MODIFICATIONS WHEN NECESSARY, OF WHICH THERE WERE MANY. SINCE YOU SHOULD ALL BE FAMILIAR WITH THE 304H METHODS, I'LL EMPHASIZE THE CHANGES AND ADDITIONS THAT ARE ESSENTIAL DUE TO THE DIFFICULT MATRIX THAT SLUDGE IMPARTS. I MIGHT MENTION ALSO, AT THIS POINT THAT THE METHOD HAS BEEN ADAPTED FOR POTW SLUDGES ONLY, AND ALL THE RECOVERY DATA THAT WE POSSESS IS FOR THESE SAMPLES. WE DO NOT PRESENTLY HAVE INFORMATION AS TO THE APPLICABILITY OF THE METHODS TO INDUSTRIAL SLUDGES, THOUGH WE CAN PREDICT THAT SOME INDUSTRIES WILL PRESENT PROBLEMS. HOPEFULLY, THEY WILL BE TAKEN CARE OF BY MORE INTENSIVE AND/OR A DIFFERENT TYPE OF SAMPLE CLEANUP. MRI DOES HAVE ON ITS PHASE II AGENDA TO INVESTIGATE TWO OTHER INDUSTRIES UNDER THEIR CONTRACT, WHICH IS SUPERVISED BY PROJECT OFFICER STEVE BILLETS OF EMSL

IN CINCINNATI. ALSO, I MUST MENTION THAT THE PROTOCOL WHICH YOU ARE GOING TO SECURE AT THE FRONT OF THE ROOM, IF YOU PROMISE ME YOU'LL ONLY TAKE ONE, DOES HAVE CHANGES AND REVISIONS IN IT, AND THE COVER PAGE REALLY IS NOT ACCURATE. A LOT OF THIS REVISION WORK AND THE METALS METHODS WHICH ARE ATTACHED AND THE CAPILLARY METHODS WHICH ARE ATTACHED WERE DONE UNDER DR. EARL HANSEN, EVEN THOUGH CLARENCE HAILE WAS THE PERSON WHO WAS INVOLVED IN THE ORIGINAL RESEARCH.

NOW, I WILL TRY TO PROCEED WITH THE PROTOCOL. FOR THE PURGEABLE ORGANICS, THE METHOD OF BELLAR AND LICHTENBERG IS BASICALLY UTILIZED WITH SOME REVISIONS. THE SAMPLE OF SLUDGE IS DILUTED TO .5 PERCENT TOTAL SOLIDS FOR CONFORMITY'S SAKE. IT'S NECESSARY TO RUN PERCENT SOLIDS DETERMINATIONS ON EACH SAMPLE. THIS INFORMATION WILL ALSO BE NECESSARY IF ANYONE DOES WANT THE RESULTS ON A DRY WEIGHT BASIS. AS A SIDELINE, THE POTW VOA SAMPLE IS COMPOSITE OF SIX 4-HOUR SAMPLES MIXED AT THE LABORATORY. WE DO NOT KNOW, AT THIS TIME, WHETHER OR NOT THE INDUSTRIAL SAMPLES WILL HAVE TO BE COMPOSITED. THE TEKMAR LIQUID SAMPLE CONCENTRATOR, LSC-1 OR ITS EQUIVALENT IS USED WITH SUITABLE MODIFICATIONS, SUCH AS, THE TRAP IS PACKED IN THE FOLLOWING ORDER: GLASS WOOL IN THE

INLET END, FOLLOWED BY OV-1, TENAX, SILICA GEL, CHARCOAL AND THEN AGAIN GLASS WOOL, WHICH DOES DIFFER FROM THE WASTEWATER REQUIREMENTS OF ONLY TENAX AND SILICA GEL. THE TRAP MUST BE INSTALLED SO THAT THE PURGED EFFLUENT ENTERS THE TENAX END OF THE TRAP OR IT DOESN'T WORK RIGHT. AFTER CONDITIONING THE TRAP, YOU TRANSFER THE PROPER AMOUNT OF SLUDGE TO CONTAIN 50 MILLIGRAMS OF DRY SOLIDS WITH A PIPETTE WITH THE TIP CUT OFF, THEN YOU BRING YOUR LEVEL UP TO 10 MILLILITERS WITH YOUR ORGANIC-FREE WATER AND ADD YOUR METHOD RECOVERY SPIKES. THEN YOU PROCEED WITH YOUR PURGE AND TRAP IN THE USUAL WAY, BACKFLUSHING INTO THE GC WITH THE PROPER PROGRAMMING, WHICH IS ALL IN THE PROTOCOL AND WHICH I'M SURE YOU ALL PROBABLY KNOW ALREADY INSIDE OUT. YOU HOLD THIS PROGRAMMING UNTIL COMPLETE COMPOUND ELUTION HAS OCCURRED AND THEN THE PURGING DEVICE MUST BE CLEANED OR CHANGED BETWEEN SAMPLES BECAUSE SLUDGES, NEEDLESS TO SAY, ARE GOING TO PROVIDE MUCH DIRTIER AND MANY MORE PROBLEMS WITH DIRT THAN YOUR WASTEWATER SAMPLES OR ANY KIND OF A CLEAN WATER SAMPLE. THE SAMPLE IS ANALYZED BY GC/MS USING A COLUMN PACKED WITH .2 PERCENT CARBOWAX, 1500 ON 80/100 MESH CARBOPACK C. THE MASS SPEC SHOULD BE

REPETITIVELY SCANNED OVER THE RANGE, M/E, 20 TO 275 AT 3 TO 5 SECONDS PER SCAN. YOUR STANDARDS, BLANKS, SAMPLE PRESERVATIONS AND QA/QC REQUIREMENTS ARE DESCRIBED IN THE PROTOCOL. NOW, WE COME TO THE HARD PART, THE EXTRACTION OF THE SEMIVOLATILE ORGANICS.

FOUR SAMPLES MAY BE PREPARED AT A TIME, IF ADEQUATE EQUIPMENT IS AVAILABLE IN YOUR LABORATORY FOR HOMOGENIZATION, CENTRIFUGATION, EXTRACTION, AND YOUR KD CONCENTRATION. YOU THOROUGHLY MIX THE SLUDGE SAMPLES BY HOMOGENIZING IN THE SAMPLE BOTTLE USING A HIGH-CAPACITY TISSUEMIZER OR THE EQUIVALENT. YOU QUICKLY REMOVE AN 80 MILLILITER ALIQUOT INTO A 100-MILLILITER GRADUATE, TRANSFER THE ALIQUOT INTO A 250-MILLILITER CENTRIFUGE TUBE.

YOU BASIFY EACH ALIQUOT EQUAL TO OR GREATER THAN PH 11 WITH SODIUM HYDROXIDE AND MIX BRIEFLY WITH THE HOMOGENIZER TO HAVE A UNIFORM PH, OR AS CLOSE TO A UNIFORM PH AS ONE CAN GET WITH SLUDGE. YOU ADD 80 MILLILITERS OF METHYLENE CHLORIDE TO EACH SAMPLE AND HOMOGENIZE AGAIN BRIEFLY SO YOU DON'T HAVE ANY HEAT FROM FRICTION, AND YOU CENTRIFUGE AT 3,000 RPM'S FOR 30 MINUTES. YOU WITHDRAW YOUR EXTRACT FROM THE CENTRIFUGE TUBE BY INSERTING A 100-MILLILITER PIPETTE INTO THE

SOLIDS CAKE AT THE WATER-METHYLENE CHLORIDE INTERFACE AND THEN YOU DISCHARGE THE EXTRACT INTO A 500-MILLILITER SEPARATORY FUNNEL. YOU REPEAT THE EXTRACTION TWICE MORE, YOU DRY IT, AND K-D THE COMBINED EXTRACTS AFTER WASHING THE DRYING COLUMN AND FOLLOWING YOUR USUAL PROCEDURES AND YOU THEN TRANSFER YOUR EXTRACT TO A VOLUMETRIC AND YOU STORE AT 4 DEGREES FOR GPC CLEANUP.

THE GPC CLEANUP IS PROBABLY ONE OF THE MOST SIGNIFICANT ADDITIONS TO THE METHOD, VARYING FROM YOUR PROTOCOL FOR YOUR OTHER 304H METHODS. FOR THE GEL PERMEATION CHROMATOGRAPHY CLEANUP, A GPC AUTO PREP 1002, MADE BY ANALYTICAL BIOCHEMISTRY LABS, INCORPORATED, OR ITS EQUIVALENT, WHICH WOULD BE A BANK OF COLUMNS SET UP FOR GPC WITH BIO BEADS SX-3, AND THIS HAS TO BE PROPERLY CALIBRATED AS DESCRIBED IN THE PROTOCOL. THE SAMPLE EXTRACTS ARE PROCESSED USING THE DUMP; COLLECT AND WASH PARAMETERS WHICH YOU ESTABLISHED IN YOUR CALIBRATION, AND THE CALIBRATION, OBVIOUSLY, HAS TO BE RIGHT OR YOU'RE GOING TO LOSE SOME OF YOUR IMPORTANT ANALYTES IN THESE FRACTIONS. THE CLEANED EXTRACTS ARE ALSO CONCENTRATED AND STORED FOR YOUR GC/MS ANALYSES.

THE BASE/NEUTRAL / PESTICIDE EXTRACT IS ANALYZED BY GC/MS USING THE 3 PERCENT SP-2250 ON 100/120 MESH SUPELCOPORT UNDER THE APPROPRIATE

CONDITIONS. THE MS SHOULD BE REPETITIVELY SCANNED OVER THE RANGE M/E 40 TO 475 AT THREE SECONDS PER SCAN AND THE EXTRACT SHOULD BE SPIKED WITH 50 MICROLITERS OF THE D_{10} ANTHRACENE, INTERNAL STANDARD. THE DATA HANDLING STANDARD AND BLANK INFORMATION AND QA/QC REQUIREMENTS, AGAIN, ARE IN THE PROTOCOL.

ANOTHER SIGNIFICANT CHANGE IS THAT WE ARE CONSIDERING THE ADDITION OF CAPILLARY METHODS. WE HAVE PURSUED THE POSSIBILITY OF USING CAPILLARY COLUMN GC/MS FOR GETTING BETTER INFORMATION ABOUT THE BASE/NEUTRAL AND PESTICIDE FRACTION. SEVERAL BASE/NEUTRAL EXTRACTS WERE SHOT PRIOR TO AND AFTER FLOROCIL CLEANUP. THE AVAILABLE INFORMATION DOES NOT INDICATE THAT THERE WILL BE MUCH BETTER RESOLUTION IN PACKED COLUMNS. I THINK THIS SHOWS US THAT MRI DOES REALLY GOOD WORK WITH PACKED COLUMNS. HOWEVER, IN INSTANCES OF VERY DIFFICULT SAMPLES, SUCH AS ZIMPRO SLUDGES, THE CAP METHOD MAY BE USEFUL. IT WILL BE USING AN SE-54 CAPILLARY COLUMN, EVALUATED BY PROPER TESTING SUCH AS THE GROB STANDARDIZED QUALITY TESTS FOR CAPILLARY COLUMNS PUBLISHED IN THE JOURNAL OF CHROMOTOGRAPHY, NUMBER 156.

THE GROB TEST OFFERS INFORMATION ABOUT THE ABSORPTION OF THE HYDROXYL FUNCTION AND THE ALDEHYDE FUNCTION, SEPARATION EFFICIENCY, ACID BASE BEHAVIOR, FILM THICKNESS, AND IT DOES THIS USING A SINGLE MIXTURE. HOWEVER, I BELIEVE MORE STRINGENT TESTS ARE GOING TO BE NECESSARY THAN THE GROB TESTS. WE ARE GETTING INFORMATION THAT MANY, MANY CAPILLARY COLUMNS ARE PASSING THE GROB TEST AND STILL WE ARE LOSING SOME VERY IMPORTANT BAD ACTORS IN THE BASE/NEUTRAL FRACTION, AND I AM IN THE PROCESS OF GETTING SOME INFORMATION ON NEW MIXTURES THAT ARE BEING MADE UP TO MAKE MUCH MORE APPROPRIATE TESTS, AND WHEN THIS IS ALL PUT TOGETHER, ANYBODY WHO WANTS THE INFORMATION WILL BE ABLE TO HAVE IT.

THE FLOROCIL CLEANUP WAS EXAMINED FOR THE EXTRACTS TESTED, BUT IT DID SHOW A SIGNIFICANT LOSS OF ANALYTE IN MOST CASES, THOUGH A CLEANER BACKGROUND DID EXIST.

SHORTCOMINGS: THESE ORGANIC PRIORITY POLLUTANT ANALYSES IN SLUDGE SUFFER BASICALLY THE SAME AS THOSE OF THE WASTEWATER SAMPLES, SUCH AS THE DETECTION OF BENZIDENE AND SOME OF YOUR OTHER TROUBLEMAKERS. HOWEVER, I DO NOT BELIEVE THESE ARE A PROBLEM WITH THE METHODOLOGY BUT IN THE POOR CHROMATOGRAPHY OF THESE

TYPES OF CONSTITUENTS.

NOW, I'M GOING TO COME TO OUR METALS ANALYSES. I'LL POINT OUT THAT THE PROTOCOL FOR THE METALS THAT IS ATTACHED IS NOT REALLY WRITTEN UP AS A PROTOCOL. IT'S SORT OF A SKETCHY DESCRIPTION OF WHAT IS BEING DONE, AND EVENTUALLY IT WILL BE WRITTEN UP AS A PROTOCOL, OR SOMETHING WILL. MRI HAS BEEN UTILIZING FOUR DIGESTIONS FOR THE ANALYSIS OF THE 13 PRIORITY POLLUTANTS. FOR BERYLLIUM, CADMIUM, CHROMIUM, COPPER, NICKEL, SILVER, THALLIUM, AND ZINC, THEY'RE USING AN ALIQUOT OF SLUDGE UNDERGOING A PRELIMINARY OXIDATION BY REFLUXING WITH NITRIC AND SULFURIC ACID UNTIL YOUR OXIDES OF NITROGEN FUMES ARE GONE, THE SOLUTION CLARIFIES AND THE SOLIDS LIGHTEN IN COLOR. THE SAMPLE IS COOLED AND NITRIC AND PERCHLORIC ACID, WHICH IS EVERYBODY'S FAVORITE, ARE ADDED AND THE SAMPLE IS HEATED TO THE OXIDIZING STAGE OF THE PERCHLORIC ACID. AFTER THE REMAINING ORGANIC MATERIAL IS DESTROYED, THE SAMPLE IS TRANSFERRED WITH DI WATER TO A SMALL BEAKER, THE REMAINING PERCHLORIC ACID FUMED OFF AND THE SULFURIC ACID REMAINS. THE SAMPLE IS DILUTED AND ANALYZED BY FLAME ATOMIC ABSORPTION. ANY SAMPLE THAT IS DETECTED AT

LESS THAN 20 MICROGRAMS PER KILOGRAM, WE ARE GOING TO REQUEST TO BE REANALYZED BY FLAMELESS AA. WE EXPECT THE MOST LIKELY CANDIDATES WILL BE BERYLLIUM AND THALLIUM.

THE SECOND DIGESTION FOR ARSENIC, ANTIMONY AND SELENIUM: AN ALIQUOT IS REFLUXED FOR APPROXIMATELY 8 HOURS--IT SOUNDS LIKE A LONG TIME--WITH NITRIC ACID AND SULFURIC; IT IS COOLED AND ALIQUOTS OF 30 PERCENT HYDROGEN PEROXIDE ARE ADDED. THE SAMPLE IS EVAPORATED, REFLUXED FOR ABOUT TWO HOURS WITH A MIXTURE OF NITRIC AND HYDROCHLORIC AND DILUTED. GASEOUS HYDRIDE GENERATION WILL BE USED FOR ANALYSIS.

THE THIRD DIGESTION IS FOR LEAD, AND THE MAIN REASON BEING WE CANNOT PULL IT OUT OF THE FIRST DIGESTION BECAUSE OF THE SULFURIC ACID. AN ALIQUOT IS DRYED AND ASHED FOR 8 HOURS. THE SAMPLE IS REFLUXED FOR 2 HOURS WITH NITRIC ACID AND COOLED. MORE NITRIC IS ADDED AND EVAPORATED. THE SAMPLE IS CENTRIFUGED AND RINSED. THE RINSES ARE EVAPORATED AND DILUTED WITH 10 MILLILITERS OF NITRIC ACID. FLAME AA WILL BE USED FOR ANALYSIS, AND FLAMELESS IF ABSOLUTELY NECESSARY, WHICH WILL BE HIGHLY UNLIKELY.

OUR LAST METAL, BUT CERTAINLY NOT LEAST,

IS MERCURY. AN ALIQUOT OF SAMPLE IS CENTRIFUGED AND THE SUPERNATANT DECANTED AND TREATED AS A SEPARATE SAMPLE. THE SUPERNATANT IS REFLUXED FOR 16 HOURS WITH NITRIC ACID AND SULFURIC ACID IN AN OIL BATH MAINTAINED AT 60 DEGREES. IT IS THEN REACTED FOR ABOUT 4 HOURS WITH 6 PERCENT POTASSIUM PERMANGANATE.

THE EXCESS PERMANGANATE IS REMOVED BY DROPWISE ADDITION OF SALT/HYDROXLAMINE HYDROCHLORIDE SOLUTION. THE CENTRIFUGE SOLID IS TRANSFERRED TO A BEAKER BY RINSING WITH NITRIC ACID. THE RINSE SAMPLE IS REFLUXED FOR 30, BELIEVE IT OR NOT, HOURS OR UNTIL THE SAMPLE IS DECOLORIZED. WE'RE HOPING IT WON'T REALLY TAKE 30 HOURS, BUT THEY EVIDENTLY DO SOMETIMES. IT IS REFLUXED WITH SULFURIC ACID AND COOLED AND AGAIN REACTED WITH PERMANGANATE, WHICH THE EXCESS IS REMOVED WITH THE HYDROXLAMINE HYDROCHLORIDE. THE SOLID AND LIQUID FACTIONS ARE ANALYZED SEPARATELY FOR MERCURY BY THE COLD VAPOR TECHNIQUE.

I MIGHT NOTE HERE THAT ALL THE DATA SO FAR SHOWS THAT THE MERCURY HAS ADSORBED COMPLETELY INTO THE SOLID PHASE. THIS HAS BEEN FOUND TO BE TRUE EVEN WITH THE SPIKES. HOWEVER, THE AQUEOUS PHASE MUST ALSO BE ANALYZED, AS WE CAN'T REALLY BE

POSITIVE THAT THIS WILL ALWAYS BE TRUE. POOR RECOVERY DATA WAS OBTAINED WHEN THOSE PHASES WERE NOT SEPARATED. AS YOU CAN GUESS, THE MAIN PROBLEMS ASSOCIATED WITH THESE METHODS ARE THE ENORMOUS TIMES UTILIZED FOR DIGESTIONS AND THE NUMBER OF DIGESTIONS, AND I THINK YOU'RE GOING TO HAVE TO USE AN AWFUL LOT OF GLASSWARE.

WE'RE PRESENTLY DISCUSSING, ONLY DISCUSSING, POSSIBILITIES FOR REDUCING THE NUMBER OF DIGESTIONS SUCH AS PULLING ARSENIC, SELENIUM, AND ANTIMONY OUT OF THE FIRST DIGESTION BY REMOVING THE OXIDES OF NITROGEN, WHICH WOULD BE A HINDRANCE TO HYDRIDE GENERATION. WE COULD ALSO POSSIBLY GET LEAD OUT OF THE FIRST DIGESTION BY DISSOLVING THE LEAD IN AMMONIUM ACETATE LIKE YOU WOULD DO IN YOUR DITHIZONE METHOD FOR COLORIMETRIC ANALYSIS.

SOMEBODY ELSE DID SUGGEST A POSSIBILITY TO ME OF USING THE MERCURY DIGESTION FOR ARSENIC, SELENIUM AND ANTIMONY AS LONG AS THE EXCESS PERMANGANATE IS ADEQUATELY REMOVED. THIS WOULD BE VERY IMPORTANT SINCE YOU'RE DOING A REDUCTION WITH STANNOUS CHLORIDE AND YOU MIGHT HAVE A LITTLE PROBLEM WITH THE PERMANGANATE AND THE STANNOUS CHLORIDE HAVING A BATTLE.

ANOTHER PROBLEM WITH THE METHOD IS THE USE OF

PERCHLORIC ACID. SOME PEOPLE ARE AFRAID OF IT. IT IS CONSIDERED UNDESIRABLE BECAUSE OF THE DANGER OF EXPLOSION WHEN IN CONTACT WITH ORGANIC MATTER. A SPECIAL PERCHLORIC ACID HOOD IS DEFINITELY AN ASSET. THE USE OF SULFURIC ACID IN THE DIGESTION IS A SAFETY FACTOR, BUT SOMETIMES PEOPLE ARE STILL AFRAID OF IT. WE'VE ALSO CONSIDERED THE USE OF A METHOD DEVELOPED BY EMSL, CINCINNATI, ENTITLED INTERIM METHOD FOR THE ANALYSIS OF ELEMENTAL PRIORITY POLLUTANTS IN SLUDGE, DATED DECEMBER 1978, AND I KEEP HOPING THAT THIS 'INTERIM' METHOD WILL BECOME SOMETHING BEYOND THE 'INTERIM' METHOD AND BECOME A 'FINAL' METHOD. THE PROTOCOL DEMANDS THE SEDIMENT METHOD FOR COLD VAPOR ANALYSIS OF MERCURY, WHICH IS RIGHT IN YOUR EPA METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTE.

THE OTHER PRIORITY POLLUTANT METALS ARE ANALYZED FROM A SINGLE DIGESTION, AND THE SAMPLE IS DRIED, PULVERIZED AND MIXED; NITRIC ACID IS ADDED, AND THE SAMPLE IS REFLUXED TO NEAR DRYNESS. THE SAMPLE IS COOLED; NITRIC ACID IS ADDED AGAIN AND REFLUXED AGAIN ALMOST TO DRYNESS; COOLED AGAIN AND MORE NITRIC IS ADDED, AND THEN 3 PERCENT HYDROGEN PEROXIDE. YOU RETURN THE BEAKER TO A HOT PLATE AND YOU WARM TO START THE PEROXIDE REACTION, THEN

YOU HEAT UNTIL THE CESSATION OF EFFERVESCENCE. DEPENDING ON THE METHOD OF ANALYSIS OR PARAMETER TO BE DETERMINED, FURTHER REFLUX AND FILTRATION WILL BE NECESSARY AND ALSO THE ADDITION OF MATRIX MODIFIERS IN SOME CASES.

UNFORTUNATELY WE HAVE LITTLE OR NO DATA ON THIS ALL-ENCOMPASSING DIGESTION. IT SOUNDS VERY IDEAL, BUT UNTIL WE GET SOME KIND OF DATA TELLING US HOW IDEAL IT IS, WE REALLY CAN'T DO TOO MUCH WITH IT.

NOW, FOR THE PIECE DE RESISTANCE, FOR OUR VISITING CAPITALISTS, THE PEOPLE WHO ARE INTERESTED IN HOW THEY CAN MAKE SOME MONEY AROUND HERE. AN IFB IS PRESENTLY IN THE CONTRACTS OFFICE AND WILL HOPEFULLY BE ON THE STREET BY MARCH OR APRIL FOR THE ANALYSIS OF POTW AND INDUSTRIAL SLUDGES UTILIZING THESE METHODS. IN ADDITION, THE TRADITIONAL PARAMETERS OF TOC, COD, AND TOTAL SUSPENDED SOLIDS WILL BE REQUIRED. SOME PEOPLE MAY WANT TO KNOW WHY WE CHOSE TOC, AND THE MAIN REASON IS IT'S THE LESSER OF TWO EVILS BETWEEN TOCs AND BODs; THAT'S REALLY ABOUT THE BEST REASON I CAN GIVE. THE IFB WILL CONSIST OF 1,000 SAMPLES, 5 BID LOTS OF 200 SAMPLES EACH. THE LAB MUST BE CAPABLE OF PROCESSING 20 SAMPLES

PER MONTH. YOU MUST KEEP IN MIND THAT THE METALS WILL INVOLVE ABOUT 3,000 ANALYSES, WHICH, IF YOU FIGURE IT OUT, IS 200 SAMPLES TIMES 13 METALS, PLUS SOME BEING DONE BY FLAMELESS, THAT'S ABOUT THE BEST NUMBER WE COULD COME UP WITH. WE DECIDED ON COMBINING THE INORGANIC ANALYSES IN THIS IFB PARTLY BECAUSE I THINK IT MIGHT BE VERY HELPFUL IN BALANCING THE WORKLOAD OF A LABORATORY, AND WE CHOSE AA FOR THIS BECAUSE WE ARE SOMEWHAT LIMITED WITH ICAP BECAUSE EVERYBODY DOESN'T HAVE ONE. I THINK ALMOST EVERYBODY HAS AN AA.

I WOULD LIKE TO INVITE TO THE PODIUM AT THIS TIME EARL HANSEN FROM MIDWEST RESEARCH INSTITUTE. EARL IS GOING TO HELP ME FIELD ANY QUESTIONS REF. THE PROTOCOL, AND WE MAY CALL UPON JIM LONGBOTTOM, ALSO, SINCE HE WAS INVOLVED IN THE ORIGINAL CONTRACT. HE MAY HAVE TO ANSWER SOME OF OUR QUESTIONS, IF HE WOULD LIKE TO COME UP. SO IF YOU HAVE ANY QUESTIONS ON PROTOCOL, THEY SHOULD BE DIRECTED PROBABLY TO EARL AND IF IT'S ANYTHING ABOUT THE IFB, THEY SHOULD BE DIRECTED TO ME.

DR. HANSEN: I'D LIKE TO MAKE ONE COMMENT WITH REGARD TO THE METALS ANALYSIS. I'M SURE THAT SOME PEOPLE WHO ARE FAMILIAR WITH THAT PORTION OF THE ANALYTICAL LOAD MIGHT BE A LITTLE SHELLSHOCKED AT THE AMOUNT OF TIME IT APPEARS IT TAKES TO GET THOSE ANALYSES DONE.

TO QUOTE A PHRASE OF BILL'S, WE'VE BEEN EXAMINING WHY WE'RE IN THE SWAMP SINCE ABOUT SEPTEMBER ON A SUPPORT OF A SURVEY PROGRAM FOR EPA, POTW SLUDGE ANALYSIS. SO MUCH OF THE METHODS DEVELOPMENT WHICH WAS DONE FOR THE METALS ANALYSIS WAS DONE PREVIOUS TO OUR BEGINNING THIS PROJECT AND SO WE REALLY HAVEN'T HAD MUCH TIME TO OPTIMIZE THE METALS ANALYSIS METHODS AND I'D SUGGEST THAT THERE IS PROBABLY A SUBSTANTIAL AMOUNT OF METHODS OPTIMIZATION WHICH CAN BE DONE WITH REGARD TO THE METALS.

MR. MOBERG: BUD MOBERG, ARLI. THERE WERE SOME DIFFERENCES BETWEEN THIS METHOD SO FAR AS THE GLASS COLUMN, EIGHTH-INCH COLUMN, AND THE PROTOCOL. FOR EXAMPLE, IT WAS SUGGESTED THE 2250DB HAD BEEN USED AND HERE YOU OMITTED THE DB TREATMENT; AT LEAST IT DOESN'T SHOW IT IN THE WRITING.

DR. HANSEN: WE'RE NOT USING DB.

MR. MOBERG: YOU'RE NOT USING THE DB. CAN YOU GIVE ANY REASON FOR THAT?

DR. HANSEN: YOU'VE GOT TO GET THE HISTORICAL APPLICATION ON THAT DEVELOPMENT PROGRAM WHICH IS OUTLINED, OR AT LEAST YOUR HISTORY. DO YOU HAVE A COMMENT ON THAT, JIM?

MR. LONGBOTTOM: WHAT'S THE QUESTION, I'M SORRY.

MR. MOBERG: THIS METHOD DOES NOT SHOW 2250DB, BUT JUST THE 2250 PACKING MATERIAL.

MR. LONGBOTTOM: YES.

MR. MOBERG: THERE IS AN IMPROVEMENT OF THE DB MATERIAL OVER THE 2250 STRAIGHT. IS THERE ANY REASON FOR BACKTRACKING?

MR. LONGBOTTOM: I DON'T THINK ON THE WHOLE THE DB REALLY WORKED OUT THAT WELL. THERE WERE PEOPLE THAT WEREN'T HAPPY WITH THE SEPARATIONS, FOR ONE THING, AND JUST BY CONSENSUS WE'VE JUST MIGRATED BACK TO THE 2250 AND ELIMINATED THE BASE DEACTIVATION.

MR. MOBERG: I SEE.

DR. NEPTUNE: DEAN NEPTUNE, EPA. I THINK I CAN SPEAK TO THAT A LITTLE BIT MORE CLEARLY. YES, WE DID GET SOME 2250DB MATERIAL WHICH WAS VERY ADEQUATE AND IN MANY CASES SUPERIOR TO THE

2250 FOR PROVIDING SEPARATIONS. THE PRIMARY REASON WHY WE HAVE NOT CONTINUED TO USE THE DB WAS BECAUSE OF THE RELATIVELY SHORT COLUMN LIFE THAT ONE HAS WITH USING THE DB. IF YOU'LL REMEMBER, MOST OF THE MATERIALS THAT WE WERE FINDING YOU'D GET LIKE 25 RUNS AND THAT MIGHT BE A GOOD COLUMN, ASSUMING THAT YOUR SAMPLES WERE NOT EXTREMELY CRUDDY AND IT WAS THE CONSENSUS OF EVERYBODY THAT THE ADVANTAGE GAINED FROM THE DB WAS NOT LARGE ENOUGH TO MAKE UP FOR THE DISADVANTAGE OF THE VERY SHORT COLUMN LIFE.

MR. MOBERG: I WAS CONCERNED WITH THE BENZIDINE PRINCIPALLY BECAUSE IT WAS SO MUCH BETTER WITH THE DB.

DR. NEPTUNE: THAT'S EXACTLY RIGHT.

MR. MOBERG: BUT WE STILL HAD THE SAME LIMITATIONS ON BENZIDINE WITHOUT THE DB. I GUESS THAT'S THE IMPLICATION.

DR. NEPTUNE: YES, THAT'S CORRECT, AND AS I WAS POINTING OUT, THERE WERE, IN SOME CASES, AN ADDED ADVANTAGE AND THAT'S ONE VERY GOOD EXAMPLE OF WHAT YOU'RE TALKING ABOUT, OF USING THE DB; BUT THE OTHER DISADVANTAGES OF THE EXTREMELY SHORT COLUMN LIFE FAR OUTWEIGHED THE ADVANTAGES FROM

TRYING TO USE IT.

MR. MOBERG: I SEE. ANOTHER QUESTION OR TWO. YOU HAVE SUGGESTED A SCAN TIME OF 3 SECONDS RATHER THAN 3 TO 5, AND IF YOU JUST SAY 3, I THINK THAT YOU CAN LOAD UP YOUR DISKS A LOT FASTER AND WE HAVE A SLIGHT PROBLEM THERE OF CHANGING ALL OF OUR PROGRAMS AND THEN MAKING COMPARISONS BETWEEN THIS PROGRAM AND THE SCREENING PROGRAM AS WELL. NO COMMENT?

DR. HANSEN: ARE YOU TALKING ABOUT METHODS 624 AND 625?

MR. MOBERG: IN HERE, THE SCAN TIME AND THE TEMPERATURE PROGRAMMING THAT WAS INCREASED 10 DEGREES A MINUTE SO THAT NOW YOU'RE GOING TO CHANGE ALL OF YOUR RELATIVE RETENTION, I MEAN YOUR RETENTION TIMES RATHER DRAMATICALLY AT LEAST IN THE EARLY PART OF THE CHROMATOGRAM.

DR. HANSEN: I BELIEVE THAT QUESTION SHOULD BE DIRECTED...

MR. MOBERG: WELL, IT'S TO MRI OR TO EPA OR WHOEVER WANTS TO HANDLE IT.

DR. HANSEN: WE'VE BEEN UTILIZING THIS PROTOCOL AS WRITTEN ON THE SURVEY PROGRAM, AND WE'VE COMPLETED PROBABLY SEVEN PLANTS' WORTH OF POTW SLUDGES. SO I CAN'T RESPOND TO THE HISTORICAL PART OF

YOUR QUESTION WITH REGARD TO HOW BOTH CONDITIONS WERE ARRIVED AT, BUT WE HAVE BEEN USING THOSE CONDITIONS.

MR. MOBERG: MANY OF THE SCREENING LABORATORIES HAVE BEEN USING SLIGHTLY SLOWER RATES.

DR. HANSEN: THAT'S NOT RELATED TO THE DATA BASE AT THIS TIME, WE'RE JUST DOING THE ANALYSIS.

MR. MOBERG: EXCEPT THAT THIS IS THE WAY AN IFB WILL COME OUT AND IF YOU'RE GOING TO RESPOND AND YOU HAVE WORK FROM BOTH CASES NOW, YOU HAVE PARAMETERS THAT ARE DIFFERENT AND IT DOES MAKE IT A LITTLE HEAVY TO KEEP CHANGING PARAMETERS.

MS. FISK: THAT'S A GOOD POINT.

DR. HANSEN: THAT'S A HEAVY, REALLY.

MS. FISK: YOU CAN'T EXPECT US TO PICK UP ALL THE PROBLEMS ALL AT ONE TIME.

MR. TELLIARD: THE NEXT QUESTION.

MR. FISHER: JOAN, BOB FISHER WITH THE NATIONAL COUNCIL OF THE PAPER INDUSTRY. AS YOU KNOW, THERE IS ALSO CONSIDERABLE EFFORT ONGOING

AMONG EPA AND ITS CONTRACTORS DESIGNED TOWARD DEVELOPING METHODS FOR THE GENERATION OF AND THE ANALYSIS OF AN ARTIFICIAL LEACHATE FROM SLUDGES. DOES YOUR WORK INTERFACE WITH THAT WORK AT ALL? IN OTHER WORDS, YOU'RE LOOKING AT, IF I UNDERSTAND CORRECTLY, ESSENTIALLY TOTAL PRIORITY POLLUTANTS IN A SLUDGE.

MR. TELLIARD: YES, WE ARE LOOKING AT THAT.

MR. FISHER: IN THIS PROGRAM?

MR. TELLIARD: YOU MEAN DOES THIS METHOD APPLY TO A LEACHABILITY TEST, IS THAT THE QUESTION?

MR. FISHER: IS YOUR ACTIVITY ADDRESSING LEACHATE ANALYSES AT ALL? I MEAN, A GENERATION OF AN ARTIFICIAL LEACHATE AND THE ANALYSIS OF THAT LEACHATE?

MS. FISK: WE ARE NOT ADDRESSING THE PROBLEM OF LEACHATE TESTING AT THIS POINT IF YOU'RE REFERRING TO SOIL ATTENUATION OR MOBILITY STUDIES; WE'RE HOPING THAT SOME OF THE METHODS THAT WE'RE DEVELOPING WILL BE USEFUL IN FINDING OUT WHAT IS IN THESE SOLID WASTES. SO THAT WHEN THEY'RE CONCERNED WITH THEM LEACHING,

WE CAN HAVE SOME INFORMATION AS TO WHAT STARTED OUT IN THERE.

DR. NEPTUNE: BOB, IN REGARDS TO YOUR QUESTION...

MS. FISK: YES, I WAS JUST GOING TO SAY PERHAPS DEAN NEPTUNE MIGHT...

DR. NEPTUNE: ...TOTAL CONTENT.

MR. TELLIARD: TOTAL CONTENT.

MS. FISK: NOT LEACHING.

MR. FISHER: DO YOU INTEND TO LEAVE YOUR WORK THERE, AT TOTAL?

MR. TELLIARD: RIGHT NOW. I MEAN, WE DO, US; BUT THAT DOESN'T MEAN THAT OTHER OFFICES HAVEN'T GOT OTHER NEEDS.

MR. LICHTENBERG: JIM LICHTENBERG, EPA. JUST A POINT OF CLARIFICATION ON ARE YOU GOING TO LEAVE THE WORK THERE; NO, WE ARE APPROACHING THAT PROBLEM IN-HOUSE IN OUR RESEARCH WORK IN CINCINNATI OF THE LEACHATE PROBLEM AND A SEDIMENT PROBLEM IN GENERAL.

MR. TELLIARD: OUR NEXT SPEAKER IS GOING TO DISCUSS AN OVERVIEW AND AN UPDATE ON A PROGRAM WE STARTED ABOUT THIS TIME LAST YEAR, IT WAS NOT QUITE THIS TIME, IT WAS A LITTLE LATER, ON THE SELF-MONITORING PROGRAM FOR ASBESTOS ANALYSIS. PRISCILLA HOLTZCLAW FROM EGD IS GOING TO KIND OF BRING YOU UP TO DATE.

UPDATE ON ASBESTOS ANALYSIS PROGRAM
SELF MONITORING

BY: PRISCILLA HOLTZCLAW

AS BILL MENTIONED, WE BEGAN THIS PROGRAM APPROXIMATELY A YEAR AGO. OUR INTENTION IS TO SCREEN THE INDUSTRIES THAT WE ARE CURRENTLY INVOLVED WITH IN EGD. FOR SAMPLING AND ANALYSIS PURPOSES, ASBESTOS HAS BEEN SINGLED OUT AS A UNIQUE PRIORITY POLLUTANT BECAUSE OF THE DIFFERENCES IN THE ANALYSIS TECHNIQUES. TO GIVE THOSE OF YOU WHO ARE NOT FAMILIAR WITH IT JUST A QUICK BACKGROUND; THE WAY WE ARE APPROACHING IT IS THAT WE ARE USING ONE PROGRAM TO OVERVIEW ALL THE DIFFERENT INDUSTRIES. WE ARE USING A SELF-SAMPLING TECHNIQUE IN WHICH WE CONTACT THE PLANT WITH THE 308 LETTER, WE SEND THEM A PREPARED SAMPLING KIT AND A DESCRIPTION OF THE POINTS AT WHICH WE WANT WATERS TO BE TAKEN FOR ANALYSIS, AND WE SEND THEM THE NAME OF THE LABORATORY TO FORWARD IT TO.

WE ARE ANALYZING ONE PLANT PER ACTIVE SUB-CATEGORY IN EGD AND WE HAVE DECIDED TO LOOK AT THIS TIME FOR CHRYSOTILE FIBERS ONLY. AS OF RIGHT NOW, WE HAVE BEEN WORKING WITH 22 DIFFERENT INDUSTRIAL CATEGORIES AND HAVE TAKEN SAMPLES IN 99 ACTIVE SUBCATEGORIES. THE DATA IS BACK IN-

HOUSE AT THIS POINT AND IT IS BEING DISSEMINATED TO THE VARIOUS PROJECT OFFICERS AND TO THOSE PARTICULAR FACILITIES THAT HAVE REQUESTED TO RECEIVE THE INFORMATION. WE HAVE TAKEN APPROXIMATELY 450 SAMPLES; OUT OF THESE, 300 HAVE BEEN ANALYZED. THE REMAINING SAMPLES CONSIST OF RAW WATER SAMPLES; IN OTHER WORDS THE INFLUENT TO THE PLANT. THESE WERE PREPARED, THE GRIDS WERE PREPARED FOR ANALYSIS, BUT WERE NOT ANALYZED UNTIL WE DETERMINED WHETHER THERE WAS ASBESTOS IN THE EFFLUENT FROM THE PLANT. WE'VE BEEN ANALYZING THAT DATA; WE ARE NOW GOING BACK AND REVIEWING, DETERMINING WHICH RAW WATERS NEED TO BE DONE AND THAT DATA, AGAIN, WILL BE FORWARDED TO THE PLANTS.

WE ARE EVALUATING THE DATA FROM AN ANALYTICAL POINT OF VIEW ONLY. IN OTHER WORDS, WE ARE SAYING THAT THE DATA IS ANALYTICALLY SIGNIFICANT IF THE LEVEL OF CHRYSOTILE IS FIVE TIMES THE DETECTION LIMIT.

IN ASBESTOS ANALYSIS, WHICH IS AN ELECTRON MICROSCOPE TECHNIQUE, THE DETECTION LIMIT IS DETERMINED AS THAT LEVEL (CONCENTRATION) THAT WOULD BE IN A LITER OF WATER IF YOU SAW ONE FIBER DURING YOUR ANALYSIS.

LET ME STRESS, THIS IS AN ANALYTICAL SIGNIFICANCE, WE ARE NOT AT THIS TIME ATTEMPTING TO MAKE ANY DETERMINATION ON THE BASIS OF HEALTH OR TREATABILITY STANDPOINTS. BECAUSE IT IS SCREENING, WE ARE ONLY SAYING, YES, THERE IS A POSITIVE INDICATION OF CHRYSOTILE OR NO, THERE IS NOT A POSITIVE INDICATION OF CHRYSOTILE. OF THE RAW WASTE IN THE FINAL EFFLUENT SAMPLES THAT WE HAVE EVALUATED TO DATE, ABOUT 60 PERCENT ARE SHOWING POSITIVE INDICATIONS OF CHRYSOTILE.

WE ARE EXPECTING A NUMBER OF THESE TO FALL OUT WHEN WE GO BACK AND REVIEW THE RAW WATERS TO SEE WHETHER THE MATERIAL IS SIMPLY BEING PASSED THROUGH THE PLANT. IN SOME CASES, WE KNOW THAT THE CHRYSOTILE IS BEING PRODUCED AS A PRODUCT OF THEIR MANUFACTURING PROCEDURE. IN OTHER CASES, IT APPEARS THAT IT IS MORE AN ARTIFACT OF THE PLANT, I.E., IT IS COMING FROM FILTERS OR FROM ASBESTOS PIPE THAT IS BEING DISINTEGRATED.

WHILE WE ARE DOING THIS INITIAL EVALUATION OF THE DATA TO HELP THE PROJECT OFFICERS, WE ARE ALSO USING WHAT WE'RE GETTING BACK TO EVALUATE THE METHOD ITSELF. THE ONE THAT WE ARE USING WAS DEVELOPED FOR DRINKING WATER AND WE HAVE RUN INTO SOME PROBLEMS TRYING TO ADAPT THIS TO THE WASTEWATERS, NAMELY, THE HIGH LEVELS OF SOLIDS THAT ARE INTERFERING.

FOR THIS EVALUATION PURPOSE, WE ARE SPLITTING SAMPLES BETWEEN LABORATORIES. WE ARE RECOUNTING PREPARED GRIDS BY THE SAME LABORATORY, WE ARE SWITCHING GRIDS BETWEEN LABORATORIES TO HAVE THEM COUNTED BY ANOTHER LABORATORY. WE ARE USING STANDARD SAMPLES TO ATTEMPT TO DETERMINE SOME MEASURE OF PRECISION BETWEEN LABORATORIES, AND WE ARE ENCOURAGING THE DEVELOPMENT OF METHODS BY OTHER PEOPLE TO HELP US WITH THIS PROBLEM. WE ARE ALSO LOOKING FOR SOME WAY TO DETERMINE THE ACCURACY OF ASBESTOS COUNTING BECAUSE THIS IS ONE THING THAT WE HAVE NO INFORMATION ON AT THIS TIME.

THAT'S JUST ABOUT THE UPDATE. IN OTHER WORDS, WE'RE IN THE MIDDLE OF THE PROJECT; WE'RE SAYING, YES, WE ARE FINDING CHRYSOTILE IN THE WASTEWATERS; NO, WE CANNOT SAY AT THIS TIME WHETHER FROM A REGULATION STANDPOINT IT IS SIGNIFICANT. THIS IS A SCREENING EFFORT. WE ARE NOT TAKING THE NUMBERS AND PUTTING A SIGNIFICANCE ON THE NUMBERS, WE ARE SIMPLY PUTTING A SIGNIFICANCE ON THE PRESENCE OR ABSENCE OF THE CHRYSOTILE. WE ARE PREPARING TO GO BACK,

WORKING WITH THE PROJECT OFFICERS, TO RESAMPLE SOME OF THE SUBCATEGORIES, TO ENLARGE OUR DATA BASE, AND TO TRY TO MAXIMIZE THESE METHODS IN THE DETERMINATION OF ASBESTOS IN THE WASTEWATERS THAT WE ARE INTERESTED IN.

ARE THERE ANY QUESTIONS?

MR. DAVIS: ABE DAVIS, HOOKER CHEMICAL. ONE VERY TRIVIAL QUESTION; HOW ARE YOU DIFFERENTIATING CHRYSOTILE FROM ANY OTHER TYPES OF ASBESTOS?

MS. HOLTZCLAW: WE'RE USING SELECTED AREA ELECTRON DIFRACTION.

MR. TELLIARD: THAT BRINGS TO AN EXCITING CONCLUSION ANOTHER ONE OF THESE. I'D LIKE TO THANK YOU ALL FOR COMING. I'D LIKE TO THANK THE INDUSTRY PEOPLE FOR PARTICIPATING. I'D LIKE TO THANK OUR OWN PEOPLE FROM BOTH THE REGIONAL LABS AND FROM THE R&D LABORATORIES FOR TAKING THE TIME TO COME UP AND ALSO FOR THE HELP THEY'VE BEEN GIVING US OVER THE LAST YEAR. THIS IS THE THIRD IN A SERIES. WE DID HAVE A COMMITTEE MEETING LAST NIGHT; WE DID JUST MAKE SOME VERY LARGE DECISIONS. WE DECIDED THAT THIS TIME THE PROCEEDINGS COVERED WILL BE READ, AND WE HOPE TO HAVE THEM OUT A LITTLE BIT FASTER THAN WE DID LAST TIME. THANK YOU AGAIN FOR YOUR ATTENTION AND THANKS FOR COMING.