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PROCEEDINGS:

SEMINAR ON ANALYTICAL METHODS

FOR PRIORITY POLLUTANTS

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Environmental Protection Agency
November 9 & 10, 1977
Denver, Colorado

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: 17 MAR 1978

SUBJECT: Proceedings-Seminar on Analytical Methods for Priority Pollutants

FROM: William A. Telliard, Chief
Energy & Mining Branch

TO: Robert B. Schaffer, Director
Effluent Guidelines Division

On November 9 & 10, 1977, a seminar was conducted, in Denver, Colorado, on the subject of Analytical Methods for Priority Pollutants. Nearly one hundred people attended this seminar, among them E.P.A. staff, industrial trade association representatives and technical contractors for this division. A complete list of attendees is included herein. From the seminar a record was prepared, which is presented with this memorandum.

The purpose of this package is to provide those concerned and working with Sampling and Analysis Procedures for the Screening of Industrial Effluents for Priority Pollutants (the protocol), an account of the issues discussed. These notes are organized following the same order as the agenda for the seminar. All topics of discussion have been restructured into a series of issues, with their associated discussion and resolutions. Furthermore, any comments or references submitted in writing are also included. In preparing this total package, it was considered advantageous to take the time to accept written comments for the record, as well as prepare a summary and table showing in which industries priority pollutants were found.

In addition to presenting a record of the seminar, an effort was made to recommend or suggest alternative ways of resolving any issues on the use of the protocol. It appears evident that those people attending this seminar found it to be useful. An opportunity was given to people using the protocol, to bring their questions and suggestions to a group of experienced chemists for consideration. In this regard, we have managed to straighten out and refine the analytical methods being used for BAT review studies. Moreover it seems evident that the protocol is a workable, reliable manual. Many laboratories are working with these procedures and have commented that they are effective in meeting the needs of the screening phase studies. The overall accomplishment of the seminar was one of fine-tuning the protocol.

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Seminar on Analytical Methods for Priority Pollutants

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VOA - Purge and Trap GC/MS

Introduction

The first day of the seminar was dedicated to the review of the procedures being employed for organic analysis. The morning session was dedicated to the review of the volatile organic analysis (VOA) and any issues or questions revolving about this particular aspect of the program. During the discussions such subjects as sampling, storage, compositing and the use of internal standards were addressed. In addition, questions regarding operating conditions and alternative procedures were also presented by the various participants. Since the close of the meeting, a number of written comments have been received in addition to the oral ones presented at the meeting and these comments will be noted throughout the proceedings.

Issue: Sample collection, Sample Site and Number of Samples

Discussion:

A number of questions were raised regarding the VOA samples with respect to collection, spiking, number of samples and container size.

Standard Oil: When should you spike a VOA sample in the field?

EPA: Spike a sample only before capping it. Do not pierce the septum with a needle.

Shell Comments: A number of questions were raised including:

1. what is the maximum storage time for VOA's at 4°C (without formation of bubbles)?
2. how many vials must be sampled?
3. can we composite VOA samples?
4. what is optimum volume for a sample vial?

Shell recommends a 45 ml vial; 125 ml is too large. See a more complete version of Shell comments in the comments section.

Resolution:

The protocol specifies a minimum of one sample per 24 hour period to be collected in duplicate. This is a minimum requirement and there is no reason why more samples could not be taken if sample crews were on

site. EPA, Cincinnati, recommends the use of teflon faced septum, sealed screw cap bottles. Glass vials with Bakelite screw caps with a hole in the center, as described in the protocol, have proven superior to crimp cap serum bottles.

Issue: Sampling and Preservation of Chlorinated Effluents or VOA Analysis

Discussion:

RETA has indicated in written comments (see the comment section) that the potassium iodide indicator paper specified in the protocol, was not adequately meeting the requirements of the field crews. Moreover they have gone to chlorometric procedures for determining residual chlorine.

A question was raised as to the affects of preserving with sodium thiosulfate. Reference was made to a paper prepared by C. Carol Morris of Havard which discussed such a problem.

Status:

At the present time, for chlorinated effluents, the field crews are to sample for two sets preserving one and not preserving the other. We would expect the contractor to run both the preserved and the unpreserved samples until such time as additional data can be gathered as to the total effect or lack there of, of the preservation of the free chlorine.

Issue: Suggested alternative, internal standards for use in VOA analysis.

Discussion:

MidWest Research replied to questions.

Q Do you have a problem with use of D-chloroform as a standard? Are there any cross contributions?

A. No problems.

Q. What level of concentration of D-chloroform was used?

A. 10 ppb.

Q. Did you find chloroform on the chromatogram while using D-chloroform as a standard?

A. Yes.

MidWest discussed problems with use of internal standards for volatiles. Protocol specifies use of bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane. They found interferences with these: Recommended use of D-chloroform and D8-toluene, found no interferences, generally good performers. D8 toluene was found to be cheap, available and not generally found in industrial effluents.

Midwest suggests use of multiple standards.

Monsanto Comments on Internal Standards

Monsanto has been measuring priority pollutants for the textile industry.

Problems included:

locating a source of 2-bromo-1-chloropropane;

use of 1,4-dichlorobutane; this compound elutes close to toluene; need an internal standard that elutes independently;

How pure is D-toluene?

Monsanto is concerned because toluene is seen in many effluents from this industry.

Recommended Status:

EPA still strongly recommends following the Protocol. If a laboratory finds that it is necessary to use an additional standard, this will be acceptable as long as it is adequately documented.

Issue: Internal GC/MS standards for the very volatile fraction

Discussion:

Radian: Noted that they have a problem storing very volatile standards, particularly vinyl chloride. Currently they are preparing

new standards in Teflon sealed hypovials under an argon atmosphere to prevent loss of the standard. However, they still have problems with volatile components.

EPA (Athens): Suggestion, make your own standards for very volatile compounds in the lab.

MRI: Stores sample tubes of vinyl chloride at 4°C and adds a plug of fresh adsorbent to minimize losses.

Resolution:

It is recommended that individual laboratories prepare their own standards for such things as vinyl chloride, methyl chloride, methylbromide, chloroethane and dichlorofluoromethane.

Issue: Storage of VOA samples prior to analysis

Discussion:

Q. (RETA) What is the validity of sample results after purged samples have been stored in traps?

A. (EPA Cincinnati) The olefins rearrange at 4°C to cis-trans isomeric forms. Compounds may also migrate on the trap, resulting in a change in peak geometry. In general, storing traps is not recommended. There are still too many unanswered questions.

NUS Comments: They do not recommend the storage of trap samples. They get unknowns which they cannot identify. Do not freeze trap samples. (See NUS findings in the reference section).

EPA (Kansas City): Reports they have stored VOA samples for up to 2 weeks. They place sealed vials into dessicators with activated carbon to prevent contamination with methylene chloride.

NUS Comments: They seal VOA trapped samples in metal cans and freeze them; or they store traps in glass tubes; seal ends of traps with Teflon and stainless steel. Then check seals after cooling to prevent loosening at Teflon caps.

RETA: They seal tubes with heat and store them under helium atmosphere and refrigeration. Storage results in wierd peaks; however, there were no losses. They accidentally analyzed a clean

trap that had been stored for 2 weeks and obtained the same wierd peaks. Could packing be the source?

Jacobs to EPA: Problems concerning the storage of samples must be resolved.

EPA (Cincinnati): Samples should be stored in vials, not on purge traps. Vials can be stored 2 weeks at 4°C with no noted loss of compounds.

Shell: Stored vials for a period of 2 weeks at 4°C with no problems; however, 21 day storage resulted in a reduction of compounds.

RETA: States that they stored some samples as long as two months.

Recommendation: The VOA samples should be preserved in teflon sealed containers at 4°C and in darkness. It is recommended, from the data and information available, that the samples be held no longer than two weeks prior to analysis and that the samples should not be transferred to traps for storage but rather left in their own containers.

Issue: Contamination of VOA samples with methylene chloride

Discussion:

A number of methods were recommended to protect the VOA samples prior to analysis from contamination. EPA Region VII laboratory suggested that the samples be stored in a desiccator containing activated carbon.

Monsanto: Comments that tubes trapped and sealed under a nitrogen atmosphere prevents contamination with methylene chloride. Monsanto further suggests that methanol used to spike the original sample may be a source of methylene chloride contamination.

Shell suggests prestoring of VOA samples in the field in a pint jar. This procedure prevents contamination with methylene chloride.

Resolution:

This suggestion from EPA Region VII would be useful if the problem is due to the laboratories layout or configuration. Then it is advisable to insure it against contamination by methylene chloride. The suggestion by Shell is also very useful.

Issue: Compositing VOA samples

Discussion:

Shell questioned whether, under the screening, it was permissable to composite the VOA samples. In addition, Shell has provided data (see their full comments) on the applicability of compositing the sample in the trap from a number of VOA samples.

Shell's comments on compositing included:

1. Their technique takes 3 individual grab samples during a 24-hour period and composites these samples in the Tekmar unit by injecting 2 ml from each grab sample.

2. One individual grab sample is too small to represent an entire waste stream.

UCC: Requested information on compositing VOA samples.

EPA (Cincinnati): Suggests pouring 2 ml from each of 3 samples into syringe. EPA prefers lab compositing, since field compositing tends to result in loss of low boilers.

NUS: Found that pouring VOA samples into a syringe resulted in a loss of methylene chloride.

Resolution:

Compositing of VOA's has been an acceptable practice and will continue to be so. The selection of syringe versus open pouring technique will be left to the analyst but must be documented.

Issue: Some considerations relating to the use of silica gel in the purge and trap technique.

Discussion:

Several comments were concerned with the collection and buildup of water in the tenax trap. They requested some alternatives or techniques to minimize the problem.

MidWest Research Institute (MRI) found problems with very volatile compounds, i.e., chloromethane, dichlorofluoromethane, vinyl chloride. These problems included water retention with use of silica gel and

bleed of column packing into GC/MS; water dumping on MS was also noted. Their solution: proceed without the use of silica gel; no problems encountered. Carborsive was suggested as an alternative to silica gel.

EPA Cincinnati commented: change silica gel often (1-2 times/week) to eliminate water retention.

Resolution:

EPA suggests that the operators simply increase the number of times per week that the silica gel is changed to insure no water buildup.

Issue: Mechanical and operating problems with the Tekmer Unit.

Discussion:

A number of commenters presented data related to operating problems as a result of certain mechanical or physical faults within the Tekmar unit. The following comments presented by Tom Bellar set forth the basic information. The second commenter, Shell presented a lengthy description of its reprogramming of its Tekmar. The new heap tracing diagram showing changes that Shell had made in its particular unit is presented in their full written comments.

Comments by EPA Cincinnati on Tekmar GCMS:

have tested units 1, 2 and 3 and have uncovered a variety of problems with these units

1. trap heater does not heat quickly enough; should be able to get 180°C in less than 1 min.; suggests use of heating tape to wrap trap in order to maintain temperature

2. trap may move inside oven - can be problem; make sure end of trap is heated sufficiently to give desorption.

3. check teflon plugs that hold desorbent in place; make sure it's secure.

4. temperature sensor may not monitor actual trap temperature; make sure trap is cooled to room temperature before next run.

Gave specifications of packing procedure

trap should be 24 cm long or longer
ID should be 0.105 in
wall thickness = 0.01 in
material should be 304 SS seamless

Packing:

5 mm glass wool plug
1 cm 3% OV-1 chromosorb 60/80 mesh
16 cm Tenax CG 60/80 mesh
8 cm silica gel - grade 15
5 mm glass wool plug

Recommended conditioning overnight with 20 ml/min purge gas, 200°C to ensure entire trap is heated; make sure all tubing is heated to remove water. Necessary to put purge gas filter in system; a1/4 lb 13x molecular sieve removes many interferences. Recommends frequent changing to reduce interference.

Shell's problems with Tekmar unit included:

1. Need to head trace every line including switching valve to eliminate water.
2. Teflon valves on ends of tubes need replacement
3. Samplers must be cleaned and stored at 105° to remove memory effects.
4. Need to replace brace fittings and o-rings with stainless steel fittings with Teflon barrels to eliminate memory effects. Shell operates sampler at 70°C to get better desorption and reduce memory effect. They also heat the transfer lines for the same reasons.

EPA (Cincinnati): Does not heat purging device because heating gives them increased chloroform values. In order to resolve early eluting compounds, the entire trap must be heated to 180°C in 30 seconds. Bellar's equipment takes 15 seconds.

Issue: Direct Aqueous Injection

Comments were received regarding acrolein and acrylonitrile in the direct aqueous method.

Discussion:

Region VII in their written comments have presented an argument that the present procedure is both costly in time and manpower and recommend that we look at an elevated temperature for the purging technique to encompass all of the volatile compounds.

FMC: Uses direct aqueous injection and injects 10-20 ul samples into a Tenax column.

MRI: Requested information about direct aqueous injection techniques.

EPA: Further investigations on this technique are proceeding.

Issue: Recovery data for the VOA analysis

Discussion:

Region VII S & A laboratory in their written comments have supplied some limited recovery data on analysis of VOA which they performed. This data is presented in the comment section.

DuPont has also submitted written comments to the Agency regarding the VOA procedure. Specific information contained under the comment section under DuPont would merit your review. Some comparative data is provided showing a comparison of the analysis performed by the steam electric industries contractor, NUS and the Agency's contractor, California Analytical Laboratories. The data presented shows a comparison between samples which were split between Mobil Chemical and the Agency and a comparison of both their GC/MS as well as their GC/UV are presented in these tables. Metals and classic parameter analysis are also compared.

Liquid-Liquid Extraction

EPA (Athens): In the course of screening analysis, three liquid-liquid extractions are performed (the acid, base/neutral, and pesticide fractions). The following questions refer to these extractions:

1. Are continuous extraction techniques being used?
2. Are contractors extracting two liters of sample?
3. What methods are being used to break emulsions?
4. Is 85 percent of the solvent used in the extraction being recovered?

Continuous Extractor

Midwest Research Institute (MRI): We have used continuous liquid-liquid extractors for the tanning industry. In general we have found extractions difficult due to emulsions. See diagram of apparatus in the reference section.

FMC: We have had problems with efficiency of base neutral extractions using a continuous extractor. In some cases we have had to spend as long as 24 hours in extraction using 50 milliliters of solvent.

California Analytical Laboratories (CAL): Use of less solvent to avoid dilution effects as well as an increased reflux rate can help your extraction problem.

EPA (Athens): We have been using a Hershberg-Wolfe continuous extractor available from Ace Glass, part number 6841-10. The advantage of this apparatus is reproducible droplet size. Only one liter of sample may be used, but this is no problem since the samples that form emulsions are generally too concentrated for the two liter sample to be used.

Analytical Research Laboratories, Inc. (ARLI): We have designed our own three stage extractor and gotten good recoveries. It has run as long as 3-4 days. It works well with marine waters but some problems with sediments are evident.

Hydroscience: We have used the Aldritch continuous extractor but plan to use shake-out due to the difficulty in cleaning the continuous extractor.

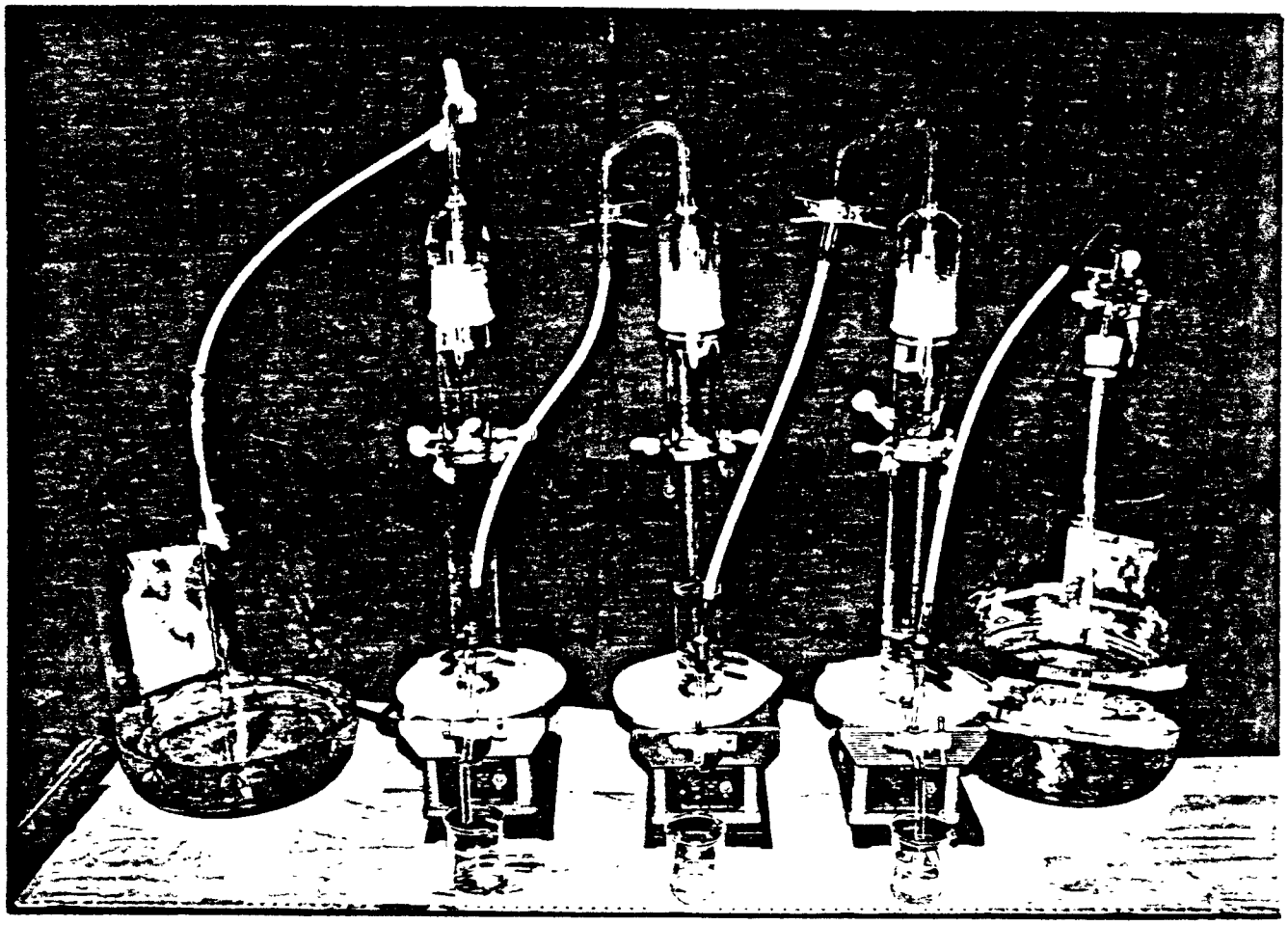
EPA (Athens): The muffle oven at 400°C may be used for cleaning. With the 4-liter extractor the solvent rinse and drying techniques must be used due to the size of the extractor.

National Council: We have not had success with continuous extraction on pulp mill samples.

Recommendation:

In the protocol, it is written that a continuous liquid-liquid extractor should be used when emulsions form. No specific type of apparatus is specified. A laboratory should document what they used.

Extraction Volume



Liquid - Liquid Extractor
Analytical Research Lab

CAL: We routinely use 1700 milliliters of sample for shake-out extractions with 250 milliliters of methylene chloride solvent. We continue to have problems with paint and ink process samples. These may be candidates for continuous extraction.

Emulsion Breaking and Solvent Recovery

DuPont: We use centrifugation for breaking emulsions.

EPA (Cincinnati): We have used centrifugation, also. 500 milliliter bottles are centrifuged at 1000 RPM for 5 minutes.

Monsanto (Dayton): We use centrifugation at 4,000 rpm for 4 minutes and are able to separate emulsions on textile samples. We recover 85 percent of the solvent.

Hydroscience: We generally do not achieve 85 percent recovery of solvent but find that recovery ranges from 50 percent to 90 percent depending on sample character. Some samples seem to pick up solvent.

CAL: More solvent may be used to increase solvent recovery.

EPA (Region VII): We normally achieve 85 percent solvent recovery. Our laboratory uses filtration through glass wool packs for breaking emulsions.

Standards

EPA (Athens): Some users of the Radian standards have complained that diphenylhydrazine is being converted to azobenzene. Studies at the Athens lab indicate that 1, 2-diphenylhydrazine decomposes to azobenzene in a number of solvents including methylene chloride and water. N-nitroso diphenylamine appears to decompose in the GC injection port at temperatures greater than 100°.

Monsanto (Dayton): We have experienced disappearance of d-10 anthracene in 10 percent of our samples and feel that anthracene may react in the procedure. We suggest spiking with 3 internal standards, D-anthracene and 2 others.

Acid Extract

Environmental Science and Engineering (ES&E): We have been analyzing phenols present in process waters from the wood preserving industry. It appears to us that the extraction procedure outlined in the EPA

protocol does not extract phenols efficiently. At present we are using the steam distillation method outlined in Analytical Chemistry, 1975, 47, 1325-29. We have data comparing the steam distillation to the shakeout method of extraction. (See E S & E written comments in the reference section).

EPA (Region VII): From our work we feel that the preservation methods may be masking phenols.

EPA (Athens): These samples are not preserved. Our work on similar samples to ES&E indicates that there are no problems with loss of phenols from degradation at high pH. In samples that form emulsions, however, it appears that the extraction efficiency of phenols drops significantly. Use of the continuous extractor in these cases improves extraction efficiency.

EPA (Region V): We have found that phenols can be preserved at pH > 11 if kept cold.

EPA (Region VII): Why is a grab sample for phenols taken as well as the acid fraction of the composite sample.

EPA: The grab sample is taken strictly for the classical 4AAP analysis for total phenols. The extraction followed by GC/MS is for the determination of 11 specific phenolic compounds.

EPA (Region IV): We have tried an experimental packing from Supelco for phenolics. It appears to work well but degrades quickly. We are evaluating this packing further.

EPA (Athens): Whereas Tenax GC has some faults, it nevertheless elutes all 11 of the phenolics.

EPA (Region V): Could not the phenols be derivatized? We realize that this could create more problems.

EPA (Athens): We have tried derivitization. It seems that while diazomethane derivitization works well, the extracts cannot be stored. Quenching of the reaction with acetic acid did not stop the degradation of components in the extract. Pentafluorobenzyl derivatives were also made but these were difficult to synthesize.

Mobil Research: We find interferences from isomers of dimethylphenol in our analysis.

MRI: Capillary columns may separate the isomers in question.

Conclusion:

Based on work done by this Agency and some of our contractors, we find that the assertion that phenols are destroyed at a high pH is not justified. Moreover, the use of steam distillation for a clean-up was discussed and accepted earlier. Under the present program derivatization is not an acceptable alternative.

Concentration and Extraction Handling

EPA (Athens): It has been pointed out that laboratories that are new to Kuderna-Danish evaporation of solvent may try to heat the solution slowly to avoid loss of components. In fact the reverse is true. Only by quick heating of the solvent can good recoveries of components be obtained.

EPA (Athens): The drying of extracts with sodium sulfate is a controversial subject. We feel that water is driven from the extract during K-D evaporation, as an azeotrope.

Shell Development: We believe that the drying step should be eliminated since it is a possible source of contamination. Also, 50 percent of the organics may be adsorbed by the sodium sulfate. We question the benefits of drying.

EPA (Cincinnati): We feel that drying the extract with sodium sulfate is a necessary step in processing the extract. Previous data documents this step and no data has been presented for effluent extracts without drying. The drying step also aids in separation of phases when emulsions are formed.

MRI: To avoid contamination of the extract by organics in the sodium sulfate we ash it at 650° in a muffle furnace and rinse with hexane.

Mobil Research: Where can sodium sulfate be obtained of a quality necessary for this procedure? How does one insure it is clean?

EPA (Cincinnati): We use Mallinkrodt granular. If an artifact persists, heat a shallow dish of the sodium sulfate at 400° for 2-3 hours.

DuPont; We use an additional blank of solvent through the drying tube.

Shell Development: We find that the drying takes 1-1.5 hours and costs too much in time to justify the supposed benefits.

EPA (Cincinnati): We do not take nearly this much time. How large is your drying tube?

Shell Development: 8 mm in diameter.

EPA (Cincinnati): Our tubes are 19-20 mm in diameter. Perhaps this is your problem.

MRI: Too much water in the drying tube can cause plugging. This could be checked, too.

EPA (Region IV): We have used a glass wool filter to prevent solids and water from plugging the drying tube.

Conclusion:

Extract drying using sodium sulfate remains the preferred procedure for residual water clean-up. Quality reagent and care in its use will prevent an introduction of contaminants through the drying step.

Polynuclear Aromatic Hydrocarbons

Mobil Research: We are seeing two problems in PAH identification. First, we cannot separate benz(a)anthracene and chrysene on our GC so we must report the peak as a combination of the two. Also, we find that in our effluent perylene interferes with benz(a)pyrene giving erroneously high results for benz(a)pyrene.

EPA (Athens): The retention times given for benz(a)anthracene and chrysene in the protocol are erroneous. These two cannot be separated on the recommended column. Our contractors are reporting these as the sum of the two. We were not aware of the perylene interferences with benz(a)pyrene. For the verification stage of analysis this must be taken into account. We are aware of your lab's work with GC-UV as a determining method.

Verification, Methods Validation and Quality Control

Manufacturing Chemist Association (MCA): We have a variety of concerns about the verification program. Before proceeding (from screening analysis to verification) three things should be established: (for these written comments, see the reference section).

(1) Define the analytical methods for the priority pollutants; what constitutes a limit of detection; in what manner is the data to be reported?

(2) The protocol needs definition: things such as the complex nature of industrial effluents; the VOA technique and the asbestos technique need clarification.

(3) Criteria should be specified for a given method so that alternate methods meeting those criteria could be used.

(4) Detection limits for the instrument have to be specified:

(a) the signal/noise ratio should be 2.5 to 1 or reported as not detected.

(b) sample should be rerun if the signal to noise ratio is low.

(5) Industry will challenge any and all data if the protocol is not specified more clearly.

EPA: The protocol was designed for screening analysis only. Verification methods have been under study for some time.

EPA (Cincinnati): Our policy for validation is as follows:

(1) The method must be an established method.
(2) Concentration levels should reflect those expected to be present. Thus, a variety of concentration ranges in distilled water and in the sample type should be studied
(3) Dosed distilled water samples for the ideal case should be analyzed in round robin fashion.
(4) Dosed field samples should be done in round robin.

Round robin parameters should be:

(a) 75 to 100 labs (ideally)
(b) minimum of 15 labs should return usable data
(c) minimum of 3 concentration levels should be used
(d) comparison of distilled water & sample data should be made
(e) outliers in data results should be rejected

EPA (EGD): We suggest 3 labs analyzing one sample. There is a need to agree upon criteria (i.e. method steps) for any analytical technique.

Mobil Research: Final validation should be done on actual (typical) waste water samples both a high and low concentration.

EPA: One possible validation scheme could be:

3 effluents
3 ranges
3 labs
3 replicates

American Cyanamid: Why are verification programs proceeding without an agreement between industry and the EPA on what constitutes a verification method/program?

EPA (EGD): The court dates (deadlines) remain whether or not we can agree on methods. Sampling for the verification must continue.

NUS: How will the verification program be altered after validation methods are established?

EPA: Changes (if any) will vary from project to project. It is possible that there will have to be revisits to the field for additional sampling.

NUS: Based on the deadline dates, validation for the methods will come after verification sampling has ended. In any event, the issue will probably wind up being solved in court.

EPA (EGD): What are your thoughts on the 3 lab, 3 sample, 3 concentration and 3 replicate validation?

EPA (Denver): We should look at more sample types and fewer concentration levels. Matrix interference is our outstanding problem.

EPA (Region V): A group of people will be gathered to discuss a validation scheme. The scheme should cover all compounds on protocol not just those found in the screening effort.

End of Day 1

Day 2 - <u>Methods Validation</u>

In a discussion the previous night a scheme for method validation was discussed and held to have merit by EPA and industrial chemists. The parameters were:

(a) 3 labs
(b) 7 determinations
(c) 7 spikes (3 concentrations)
(d) 7 samples
(e) validation done for only those compounds found in screening.

CAL: How can EPA arrive at a standard method which does not validate those compounds which are not found in the screening effort?

EPA (Region V): We also feel that all compounds should have validated methods.

EPA (EGD): There is not enough time or money to support a research program to validate methods for all compounds. Court dates have to be met.

Catalytic: What is the possibility of validating the screening analysis? We are concerned about the stability and storage of samples from field to lot.

EPA: There is no easy way to validate field screening procedures in the time left to do it.

Radian: Could the contractors spike some samples and analyze later?

EPA: This is a possibility as well as having a referee laboratory.

National Council: Many of the industrial effluents are heavy in solids and compound associated solids. Can one demonstrate by spiking the sample what is actually there? The sample, after all, is an extract from the real environment.

MRI: There are two consideration in view of the limited time available:

(a) Quality control on all steps of the procedure.
(b) Extensive validation on a few steps but many samples run.

Recommendation:

This issue is unresolved. EPA at Cincinnati is considering the problem in an attempt to find a practical solution.

Use of Blanks

There has been some confusion concerning the number of blanks necessary in the screening phase. Let's discuss the blanks for the volatile organic analysis (VOA). Each VOA sample should be collected in duplicate. This is not to say that each of these samples must be run separately. They simply provide, to the analyst, a backup sample if for some reason he should have difficulty with the first sample. Once a sample is opened, it has no further value, hence the need for duplicates. There should be a blank VOA sample which would be prebottled in the laboratory, taken to the facility, carried through the procedures and exposed to the various conditions at the facility during the sampling run. Therefore, for each plant there should be one VOA sample blank not a VOA sample blank for each point. The second issue is that of the use of field blanks for compositing samplers. The purpose of the field blank is to insure that contamination is not being picked up either from an inadequately cleaned sampler or a contaminated intake line. A number of options are provided for the use of field blanks. One, is of course, the use of manual compositing which would do away with the need for any field blank another option is instead of running the organic-free water through the sampler, the individual may utilize the water supply for that plant, i.e. city water, well water, river water, what ever, and that may be run through the sampler to purge it prior to use. At least in this particular case the need for one additional analysis is eliminated. The third option, which leaves much to be desired, would be the compositing of all the field blanks prior to analysis. This would lend very little creedance and require some additional sampling if you are looking for total background. The use of a sampler or field blank in sampling in process lines probably has limited application. That is to say, due to the high concentration and heavy loadings of these particular lines, the minor contamination that might be present probably wouldn't be noticed and probably wouldn't be looked for. Therefore as far as verification is concerned the application of influent field blanks probably lends little if any assistance to the program.

Data Reporting

Enclosed are two sets of data reporting formats. The first is the format to be utilized in reporting GC/MS screening analysis by our contractors and our regional offices. We would hope that both the

Environmental Research Laboratory
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Athens, Georgia 30605

DATE: December 28, 1977

SUBJECT: Format For Storage of Mass Spectrometry Data on 9-Track Magnetic Tape Proposed by Carborundum

FROM: W. M. Shackelford
Analytical Chemistry Branch

TO: William A. Telliard
Environmental Protection Agency
Effluent Guidelines Division
WH-552, 401 M Street, SW
Washington, DC 20460

The Carborundum Company has proposed a format for saving mass spectrometry data on 9-track magnetic tape. I have received a sample tape as well as documentation, and our computer center has read the tape and even written a simple program to plot out the data. I am sending along a copy of the documentation as well as a chromatogram reconstructed from the sample data.

Since this format was developed for Carborundum by Finnigan, we can expect all contractors who utilize the Finnigan-Incos GC-MS-computer system to be able to use this format.

I recommend that the proposed format be accepted. Bob Fluege of Carborundum is awaiting notification by the project officer.

Attachment

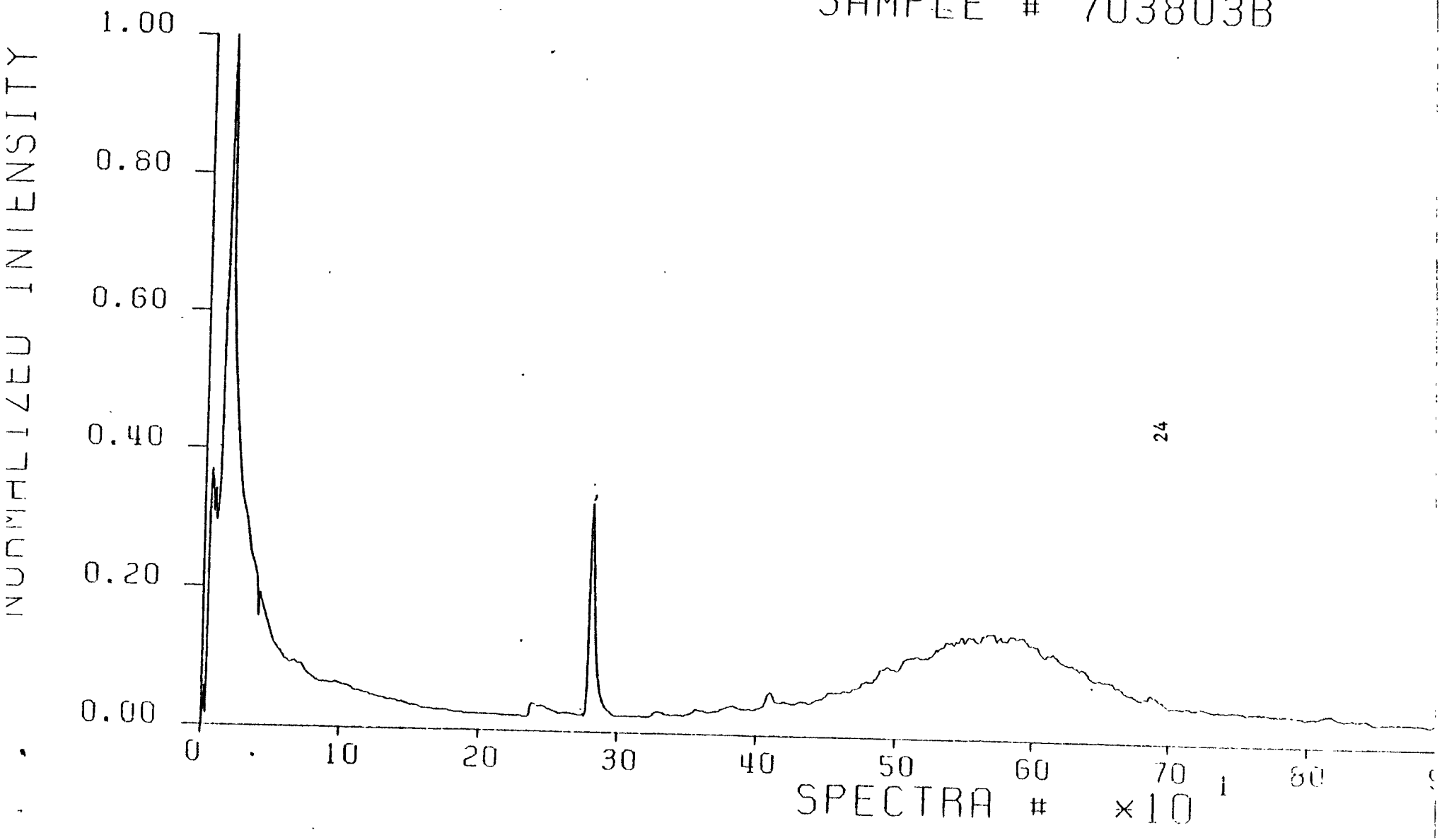
EPA FORM 1320-6 (REV. 3-76)

EXAMEPA.DS

```
C       THIS FILE DOCUMENTS THE FORMAT OF .EP FILES WRITTEN BY THE
C       MSDS COMMAND 'EPA'.

        WHAT FOLLOWS IS THE CONTENTS OF THE FILE BOS1.EP AFTER THE
        MSDS COMMAND 'EPA BOS1,,BOS1/D' IS EXECUTED.
                SEE 'EXFLEPA.DS' FOR A DISCUSSION OF THE ARGUMENTS.
                (THE /D MODIFIER WAS USED TO MAKE THIS OUTPUT PRETTY
                BY PUTTING A 'CR' AFTER EACH 80 CHARACTER LOGIAL RECORD.)
      THE SIX QUESTIONS ASKED BY 'EPA' WERE ANSWERED AS FOLLOWS:
        FIRST SCAN TO SAVE (1): 4
        LAST SCAN TO SCAN (200): 6
        LOWEST MASS TO SAVE (20): 'CR'
        HIGHEST MASS TO SAVE (250): 'CR'
        MINIMUM INTENSITY TO SAVE IN IONS (1): 'CR'
        MINIMUM INTENSITY TO SAVE AS % BASE (.1): 'CR'
                (THE ANSWER 'CR' MEANS USE THE PROMPT VALUE.
                THE PROMPT SCAN LIMITS ARE THE LIMITS OF THE DATA.
                THE PROMPT MASS LIMITS ARE THE SCANNED REGION.
                THE PROMPT MINIMUM INTENSITIES ARE THE SMALLEST ALLOWED.
                LARGER VALUES CAN RESULT IN SUBSTANTIAL REDUCTIONS IN
                THE DISK SPACE AND CPU TIME USED.)

BOS1        #     0  07/09/75 13:50
HC STANDARD                                                        INST: C
                                                                 SECS/SCAN:
ANAL: JEC       SUB: JEC       ACT: NONE      FOR: K                     M: 2
BOS1        #     4  07/09/75 13:50:00 +  0:24  BASE  69,     3668.  RIC
027034028003030018031004050022051090053002062007065004069999670012075003081
082000083004085005093025095007100048101012112004113020117002119224120005124
131182132008133010143016144001145003147003150008151021155009162019163013169
170003174002175005181170182007183006186005137005193023194002195002201006205
207001212007213007217007219048224003225006231084232005233000236010243031244
000000
BOS1        #     5  07/09/75 13:50:00 +  0:30  BASE  69,     3708.  RIC
027030030017031005036002044004045003050024051084062007065005069999070009081
082002083006085003087001093021095005103004410100911200811303011923212000613 4
131188132007133011135002137002143015145003150007151025155008162015163012169
170004175002181172182009183006186006193025194002200002201003205013212007213
217006219062225002229002231083232003233006236007243043244002245001248003000
BOS1        #     6  07/09/75 13:50:00 +  0:36  BASE  69,     1910.  RIC
027073030025031005044008050019051090062004065006069999075005081005082005083
085009086004093029095005100047101015112006113037119270131224132008133009143
145005150008151024155011162030167021169198170004175008181250182014183007186
193033195003200004201084205035212015213011217006219109220005225004231155232
236008237005243073000000


C       WHAT FOLLOWS DESCRIBES THE FORMAT OF THE PRECEEDING DATA.

C       THERE IS A 4 LINE (80 CHARACTERS/LINE) FILE HEADER.
C               THE FIRST LINES IN A VALID .EP FILE WILL BE A FILE
C               HEADER.  FILE HEADERS IN THE MIDDLE OF A .EP FILE RESULT
C               FROM THE USE OF THE EPA/A COMMAND.  THE FILE HEADER IS
C               IDENTIFIABLE BY A 0 IN THE SCAN NUMBER ENTRY IN THE FIRST
C               LINE.  THE FIRST FILE HEADER LINE CAN BE READ WITH THE SAME
C               FORMAT AS THE FIRST LINE OF A SCAN HEADER.

C       THE FIRST HEADER LINE CAN BE READ AS FOLLOWS:
        INTEGER NAME(6),IDATE(4)          ;(ASSUMING 2 CHARACTERS/WORD)
        READ(DSK,110) NAME,ISCAN,IDATE,IHOUR,IMIN
110     FORMAT(6A2,1X,I5,2A,4A2,I3,1A,I2)
```

```
      DATA READ:
C     NAME     ;12 CHARACTER NAME OF ORIGINAL DATA FILE
C     ISCAN    ;0 TO FLAG FILE HEADER FIRST LINE
C     IDATE    ;8 CHARACTER DATE AS 'MM/DD/YY'
C     IHOUR    ;HOUR AT START OF RUN
C     IMIN     ;MINUTE AT START OF RUN

C     THE SECOND HEADER LINE CAN BE READ AS FOLLOWS:
      INTEGER ISAMP(32),INST(3)
      READ(DSK,120) ISAMP,INST
120   FORMAT(32A2,10X,3A2)
C     DATA READ:
C     ISAMP    ;64 CHARACTER SAMPLE IDENTIFICATION
C     INST     ;6 CHARACTER INSTRUMENT NAME

C     THE THIRD HEADER LINE CAN BE READ AS FOLLOWS:
      INTEGER ICOND(32)
      READ(DSK,130) ICOND,SECPSCAN
130   FORMAT(32A2,10X,F6.2)
C     DATA READ:
C     ICOND            ;64 CHARACTER RUN CONDITIONS
C     SECPSCAN         ;SECONDS PER SCAN FOR DATA IN THIS FILE

C     THE FOURTH HEADER LINE CAN BE READ AS FOLLOWS:
      INTEGER ANALYST(4),SUBMITTED(4),ACCOUNT(4),FORMULA(10),LOWMASS,HIMA
      READ(DSK,140) ANALYST,SUBMITTED,ACCOUNT,FORMULA,LOWMASS,HIMASS
140   FORMAT(6X,4A2,6X,4A2,6X,4A2,5X,10A2,5X,I3,1X,I3)
C     DATA READ
C     ANALYST          ;8 CHARACTER 'ANALYST'
C     SUBMITTED        ;8 CHARACTER 'SUBMITTED BY'
C     ACCOUNT          ;8 CHARACTER 'ACCOUNT NO.'
C     FORMULA          ;20 CHARACTER 'FORMULA'
C     LOWMASS          ;LOWEST MASS POSSIBLY RECORDED
C     HIMASS           ;HIGHEST MASS POSSIBLY RECORDED

C     FOLLOWING A FILE HEADER WILL BE VARIABLE LENGTH BLOCKS REPRESENTING
C     ONE SCAN OF DATA (UNTIL THE END OF FILE OR ANOTHER FILE HEADER.)
C     EACH SCAN HAS THE FOLLOWING FORMAT:
C             HEADER LINE, 80 CHARACTERS
C             MASS/INTENSITY PAIRS IN 80 CHARACTER LINES
C             THE LAST LINE WILL HAVE A 0 MASS/INTENSITY AND SPACE FILL

C     THE SCAN HEADER LINE CAN BE READ AS FOLLOWS:
      INTEGER NAME(6),IDATE(4)
      READ(DSK,200) NAME,ISCAN,IDATE,IHOUR,IMIN,JMIN,JSEC,IBASE,BAREA,RIC
200   FORMAT(6A2,1X,I5,2X,4A2,I3,1X,I2,5X,I3,1X,I2,6X,I4,1X,F9.0,5X,F10.0)
C     DATA READ:
C     NAME     ;12 CHARACTER NAME OF ORIGINAL DATA FILE
C     ISCAN    ;SCAN NUMBER OF ORIGINAL DATA
C     IDATE    ;8 CHARACTER DATE AS 'MM/DD/YY'
C     IHOUR    ;HOUR AT START OF RUN
C     IMIN     ;MINUTE AT START OF RUN
C              ;RETENTION TIME AT END OF SCAN FROM START OF RUN
C     JMIN     ;MINUTES
C     JSEC     ;SECS
C     IBASE    ;NOMINAL MASS OF LARGEST PEAK
C     BAREA    ;INTENSITY OF LARGEST PEAK (BEFORE NORMALIZATION)
C     RIC      ;RECONSTRUCTED ION CURRENT = TOTAL INTENSITY RECORDED
C              ;IN THE SCAN (BEFORE NORMALIZATION)

C     THE  MASS/INTENSITY LIST CAN BE READ AS FOLLOWS:
      J12=J+12
      READ(DSK,300) (MASS(I),IAREA(I),I=J,J12),LINENUMBER
```

```
100     FORMAT(13(I3,I3),I2)
C       DATA READ:
C       MASS(I)             ;NOMINAL MASS (STRICTLY INCREASING)
C                           ;MASS(I) = 0 INDICATES THE END OF THE SCAN
C       IAREA(I)            ;INTENSITY AT MASS(I)
C                           ;SCALED TO INTENSITY OF BASE = 999
C                           ;WILL NEVER BE 0 IF MASS(I) NOT 0
C       LINENUMBER          ;VALID DATA HAS SEQUENTIAL LINENUMBERS
C                           ;STARTING WITH 1 FOR THE FIRST LINE OF MASSES.
C       (THERE WILL BE BLANK FILL AFTER A 0 MASS/INTENSITY.)
C       THERE IS A MAXIMUM OF 999 MASSES AND HENCE A MAXIMUM OF 77 LINES.
```


SAMPLE # 703803B
NORMALIZED INTENSITY
1.00
0.80
0.60
0.40
0.20
0.00
0
10
20
30
40
50
60
70
80
SPECTRA # ×10
24

SAMPLE I.D. _____

DATE INJECTED _____

STD. I.D. _____ CONTRACTOR _____

CONC. FACTOR _____ CATEGORY _____

Date Extracted _____

NO.[1]	COMPOUND	µg/l	NO.[1]	COMPOUND	µg/l
1B	acenaphthene		31A	2,4-dichlorophenol	
2V	acrolein		32V	1,2-dichloropropane	
3V	acrylonitrile		33V	1,2-dichloropropylene	
4V	benzene		34A	2,4-dimethylphenol	
5B	benzidine		35B	2,4-dinitrotoluene	
6V	carbon tetrachloride		36B	2,6-dinitrotoluene	
7V	chlorobenzene		37B	1,2-diphenylhydrazine	
8B	1,2,3,-trichlorobenzene		38V	ethylbenzene	
9B	hexachlorobenzene		39B	fluorathene	
10V	1,2-dichloroethane		40B	4-chlorophenyl phenyl ether	
11V	1,1,1-trichloroethane		41B	4-bromophenyl phenyl ether	
12B	hexachloroethane		42B	bis (2-chloroisopropyl) ether	
13V	1,1-dichloroethane		43B	bis (2-chloroethoxy) methane	
14V	1,1,2-trichloroethane		44V	methylene chloride	
15V	1,1,2,2-tetrachloroethane		45V	methyl chloride	
16V	chloroethane		46V	methyl bromide	
17B	bis (chloromethyl) ether		47V	bromoform	
18B	bis (2-chloroethyl) ether		48V	dichlorobromomethane	
19V	2-chloroethylvinyl ether		49V	trichlorofluoromethane	
20B	2-chloronaphthalene		50V	dichlorodifluoromethane	
21A	2,4,6-trichlorophenol		51V	chlorodibromomethane	
22A	parachlorometa cresol		52B	hexachlorobutadiene	
23V	chloroform		53B	hexachlorocyclopentadiene	
24A	2-chlorophenol		54B	isophorone	
25B	1,2-dichlorobenzene		55B	naphthalene	
26B	1,3-dichlorobenzene		56B	nitrobenzene	
27B	1,4-dichlorobenzene		57A	2-nitrophenol	
28B	3,3'-dichlorobenzidine		58A	4-nitrophenol	
29V	1,1-dichloroethylene		59A	2,4-dinitrophenol	
30V	1,2-trans-dichloroethylene		60A	4,6-dinitro-o-cresol	

SAMPLE I.D. _____

NO.[1]	COMPOUND	µg/l
61B	N-nitrosodimethylamine	
62B	N-nitrosodiphenylamine	
63B	N-nitrosodi-n-propylamine	
64A	pentachlorophenol	
65A	phenol	
66B	bis (2-ethylhexyl) phthalate	
67B	butyl benzyl phthalate	
68B	di-n-butyl phthalate	
69B	di-n-octyl phthalate	
70B	diethyl phthalate	
71B	dimethyl phthalate	
72B	benzo(a)anthracene	
73B	benzo(a)pyrene	
74B	3,4-benzofluorathene	
75B	benzo(k)fluoranthane	
76B	chrysene	
77B	acenaphthylene	
78B	anthracene	
79B	benzo(ghi)perylene	
80B	fluorene	
81B	phenanthrene	
82B	dibenzo(a,h)anthracene	
83B	ideno(1,2,3-cd)pyrene	
84B	pyrene	
85V	tetrachloroethylene	
86V	toluene	
87V	trichloroethylene	

NO.[1]	COMPOUND	µg/
88V	vinyl chloride	
89P	aldrin	
90P	dieldrin	
91P	chlordane	
92P	4,4'-DDT	
93P	4,4'-DDE	
94P	4,4'-DDD	
95P	a-endosulfan-Alpha	
96P	b-endosulfan-Beta	
97P	endosulfan sulfate	
98P	endrin	
99P	endrin aldehyde	
100P	heptachlor	
101P	heptachlor epoxide	
102P	a-BHC-Alpha	
103P	b-BHC-Beta	
104P	r-BHC-Gamma	
105P	g-BHC-Delta	
106P	PCB-1242	
107P	PCB-1254	
108P	PCB-1221	
109P	PCB-1232	
110P	PCB-1248	
111P	PCB-1260	
112P	PCB-1016	
113P	toxaphene	
129B	2,3,7,8-tetrachlorodibenzo-p-dioxin	

[1] As it appears in "Revised Recommended List of Priority Pollutants", Appendix A of EPA Contract No. , (1977)

♦Not detected. = ND

* = less than 10 ug/liter

contractors and the regions comply with this format. The second, is a description, provided by Athens, as to an acceptable format for the preserved and archived GC/MS data tapes. This system is applicable to a number of data units and is the one presently recommended by the Agency.

Screening of Blanks

The analytical protocol provides the analyst with the option of screening the blank samples on just GC prior to analysis. If he sees nothing of significance for any of the compounds of concern he may delete the requirement for looking at the total GC/MS run.

Analysis of Residual Chlorine

Concern was expressed at the meeting over the ability to measure free residual chlorine in all waters as specified by the Agency. A reference was sited which discusses the analytical problems revolving around the application of residual chlorine analysis. At present the Agency is looking into and attempting to evaluate the issue raised in this particular area. As resolution is reached, the information will be made available through the EPA Cincinnati office, the Environmental Monitoring and Support Lab.

Metals Analysis

Introduction

The opening presentation on metals analysis was made by Dr. Fairless of the EPA Region V S & A laboratory. Dr. Fairless presented a program describing the various data that has been generated during Phase I of the screening portion for a number of industrial categories. The presentation and a synopsis of his slides are presented in the next page.

Resolution of Phase II metals analysis is based on the suggestions provided by the attendees and subsequent conversations.

A memo has been prepared and distributed by EPA headquarters, which sets forward the procedures to be followed in the upcoming Phase of the metals screening program. A copy of this memo which includes the various industrial coding in contractor's codes is provided in the reference section of this document.

U S EPA
REGION V
CENTRAL REGIONAL LABORATORY
1819 WEST PERSHING ROAD
CHICAGO, ILLINOIS 60609
312-353-8370

PARAMETER----- MAGNESIUM METHOD NUMBER----- 537 DUPLICATE SAMPLES

LABORATORY----- CRL REGION 5 CHEMIST----- JIM KIRKPATRICK

METHOD DESCRIPTION-----ICAP ANALYSES OF PROCESS WATER

	FIRST VALUE	SECOND VALUE	AVERAGE	SUM	DIFFERENCE	RPD
SPL CONC	468 000	453 000	460 500	921 000	15 000	1 620
SPL CONC	180 000	237 000	208 500	417 000	- 57 000	13 660
SPL CONC.	11. 900	10 600	11 250	22 500	1 300	5. 770
SPL CONC	214 000	247 000	230 500	461. 000	- 33 000	7 150
SPL CONC.	233 000	237. 000	235 000	470 000	- 4 000	0. 850
SPL CONC	17 000	17 000	17 000	34 000	0 000	0 000
SPL CONC.	14 000	14 000	14 000	28 000	0 000	0 000
SPL CONC	14 000	13 000	13 500	27 000	1 000	3. 700
SPL CONC	13 000	13 000	13 000	26 000	0 000	0 000
SPL CONC	69 000	69 000	69 000	138 000	0 000	0 000
SPL CONC	28 000	19 500	23 750	47 500	8 500	17 890
SPL CONC	27 000	19 000	23 000	46 000	8 000	17. 390
SPL CONC	18 700	18 400	18 550	37 100	0 300	0 800
SPL CONC	17 000	19 000	18 000	36 000	- 2 000	5. 550
SPL CONC	6 000	19 000	12 500	25 000	- 13 000	52 000
SPL CONC	9 000	5 800	7. 400	14. 800	3 200	21 620
SPL. CONC	6 000	6 000	6 000	12 000	0. 000	0 000
SPL CONC	19 000	6 000	12 500	25 000	13 000	52. 000
SPL CONC	129 000	128 000	128 500	257 000	1 000	0 380
SPL CONC	150 000	140 000	145 000	290 000	10 000	3 440
SPL CONC	10 000	11 000	10 500	21 000	- 1 000	4 760
SPL CONC	284 000	192 000	238 000	476 000	92 000	19. 320
SPL CONC	340 000	193 000	266 500	533 000	147 000	27 570
SPL CONC	238 000	166 000	202 000	404 000	72 000	17. 820
SPL CONC	350 000	208 000	279 000	558 000	142 000	25 440
SPL CONC	191 000	195 000	193 000	386 000	- 4 000	1. 030
SPL CONC	4 000	5 000	4 500	9 000	- 1. 000	11 110
SPL CONC	14 000	14 000	14 000	28 000	0 000	0 000
SPL CONC	52 000	52 000	52 000	104 000	0 000	0 000
SPL CONC	22 000	22 000	22 000	44 000	0 000	0 000
SPL CONC	13 000	13 000	13 000	26 000	0 000	0 000
SPL CONC	9 000	14 000	11 500	23 000	- 5 000	21 730
SPL CONC	19 000	20 000	19 500	39 000	- 1 000	2 560
SPL CONC	19 000	19 000	19 000	38 000	0 000	0 000
NUMBER OF DATA PAIRS--			34			
SUM	3208 600	3815 300	3011 950	6023 900	635 300	335 160
AVERAGE	94 371	82 803	88 587	177 174	18 685	9 850
VARIANCE	15534 055	11413 415	13048 836	52195 343	1477 743	189 378
STD DEV	124 636	106 834	114 232	228 463	38 441	13 760
CONTROL LI	- 154 901	- 130 864	- 139 676	- 279 752	- 58 198	17 660
CONTROL LI	343 642	296 470	317 050	634 100	95 568	37 370

RANDOM VARIANCE SYSTEMATIC VARIANCE TOTAL VARIANCE

Acknowledgements -

H. Montgomery

T. Meszaros

T. Parks

A. Jirka

G. Kunselman

E. King

M. Carter

J. Kirkpatrick

C. Elly

E. Huff

D. May

General Observations

1. Samples are very variable in terms of relative concentrations both within and between different industries.

2. Frequently a sample has at least one parameter with a very high concentration relative to surface water and NPDES effluent discharge samples.

3. As a result of the above facts, the samples are difficult to analyze and the results show more scatter than is normal for other sample types.

Phase I - Quality Assurance

I General Operating Procedures

Samples were received unpreserved in different kinds of bottles. Upon arrival at the laboratory, sufficient acid was added to each sample to louder the pH to two. The sample was then allowed to stand for several days.

Aliquotes were taken for analyses by flameless AA and ICAP. Flameless AA analysis were made using standard addition techniques on each sample. The ICAP method uses a standard EPA digestion.

Potassium dichromate is added to the remaining sample and an aliquote taken for the mercury determination.

Quality Assurance

The CRL uses a semi-formal quality assurance program in which selected performance audits are conducted to provide an estimate of data quality. The following audits are run to monitor the ICAP method:

Audit	Frequency (%)
1. Reagent Blank	6
2. Laboratory Control Standard	4
3. Sample Spikes	4
4. Reference Standards	Monthly
5. Duplicate Samples	*
6. Duplicate Analyses	4

Laboratory Control Standards

(µg/l)

for 77 different runs over 8 months

Sept. 76 - April 77

	Mean	Std. dev.	Rel.Std.dev.(1%)
Ca*	20.6	1	5
Mg*	4.8	0.4	8
Na*	16.9	1	6
Ag	153	23	15
Al	922	68	7
B	452	37	8
Ba	952	43	5
Be	81.5	2.7	3
Cd	427	12	3
Co	442	16	4
Cr	300	14	5
Cu	492	21	4
Fe	2445	119	5
Mn	422	13	3
Mo	1102	42	4
Ni	513	16	3
Pb	5455	306	6
Sn	547	23	4
Ti	554	19	3

Laboratory Control Standards (cont'd)

	Mean	Std. dev.	Rel.Std.dev.(1%)
V	533	53	10
Zn	2695	121	4

* mg/l

2 Nov 1977

6a

Element #	Element	Detection Limit (ug/l)	Priority	AQC Spike Level
1	IS	0	0	0
2	TC	0	0	0
3	PM	0	0	0
4	B2	0	0	0
5	CA	7	1	10
6	CA2	5	1	10
7	MG	1	1	10
8	NA	15	1	10
9	AG	1	1	0
10	AL	50	1	1000
11	AL2	50	1	1000
12	B	50	1	400
13	BA	5	1	1000
14	BE	1	1	100
15	CD	2	1	400
16	CO	5	1	400
17	CR	5	1	400
18	CU	6	1	400
19	FE	170	1	1250
20	MN	5	1	400
21	MO	5	1	400
22	NI	5	1	400
23	PB	20	1	400
24	SN	5	1	400
25	TI	15	1	400

cont'd

Element #	Element	Detection Limit	Priority	AQC Spike Level
26	V	12	1	400
27	Y	16	1	400
28	ZN	60	1	400
29	XX	20	0	0
30	V2	1000	0	400

Separate samples were collected for mercury and the other metals at the beginning of the program. It is my understanding that the mercury sample was a grab and the ICAP sample was a composite in at least some of the cases. We tried to evaluate the data obtained from these "duplicate samples" as shown below.

8a

Metal Mg

Magnesium

Log Number	Result	Result	Log Number
17051	468	453	17056
52	180	237	55
53	11.9	10.6	57
54	214	247	59
58	233	237	60
17094	17	17	17099
5	14	14	100
6	14	13	101
7	13	13	102
8	69	69	103
17130	28	19.5	17133
1	27	19	32
4	18.7	18.4	35
6	K0.1	K0.1	37
17002	17	19	17007
08	6	19	09
01	9	5.8	03
00	6	6	06
04	19	6	05
17122	129	128	17126
3	150	140	7

Metal Mg

Magnesium (cont'd)

Log Number	Result	Result	Log Number
4	340	K300	8
5	10	11	9
17110	284	192	17116
1	340	193	7
2	238	166	8
3	350	208	9
4	191	195	20
5	4	5	21
17043	14	14	17045
44	52	52	46
47	22	22	48
49	13	13	50
17104	9	14	17107
5	19	20	8
6	19	19	9

Element	N	Ave RPD	Std. dev. RPD
Al	10	27	27
Sb	17	33	20
As	35	30	23
B	34	20	25
Ba	22	17	18
Be	5	15	16
Cd	4	14	19
Ca	35	15	22
Co	9	20	22
Cr	20	21	20
Cu	18	33*	29*
Fe	35	32	24
Pb	9	13	11
Mg	34	10	14
Mn	19	23	20
Hg	23	24	21
Mo	76	19	23
Ni	6	21	11
Se	33	33	24
Na	36	15	19
Sn	2	27	10
Ti	8	36	24
V	10	15	13
Zn	32	21	25

It is obvious from the data shown above that there is considerable scatter in the "duplicate" sample results. This scatter may result from -

Analytical method

Samples are not true duplicates

Normal Sampling & Analytical Precision

Labeling mistakes

From a comparison with our method performance audit results shown previously it would appear that scatter due to the analytical method is a minor part of the total data scatter.

Phase II

1. We believe increased efforts should be made to improve and define data quality for this project. As a minimum we recommend the following:

    a. All contractors should use the same sampling procedure and sample bottle type.
    b. All samples should be field preserved and reagent blanks taken for each survey.
    c. All samples should be identified with a single 6 digit number.
    d. Ten percent of all sites should be sampled in duplicate and one member of each duplicate pair should be analzyed in duplicate.

The steam electric metals data is available on request. These particular analysis were performed on split samples taken during the same relative time period and analyzed by both Carborundum, NUS and EPA. In addition, EPA, early on in the program made an error in its sample labeling procedure and forwarded two samples to the regional lab, one a grab and the other a composite. The data therefore for EPA will compare both a composite and a grab sample taken from the same source. This data is provided for your information and scrutiny.

The comparative data of EPA and Mobil is presented in the comment section. These samples were taken during the screening phase of the review of the petroleum refining industry.

Also available on request is a comparison of the metals analysis performed on samples collected from various coal mine discharges. These analysis were performed by EPA's Region V laboratory; Bituminous Coal Research in Monroeville, Pennsylvania, which used atomic absorption spectroscopy for its method and Versar, Incorporated of Springfield, Virginia, which also used atomic absorption. In addition, Peabody Coal Company analyzed similar sets of samples taken during the same time frame and this data may be provided. Moreover, a number of samples were supplied to Gulf South Research and they were analyzed both for organics by GC/MS and for metals by Spark Source Emissions Spectroscopy. All of these samples were taken during the same sampling period or are results of direct splits in the field. Therefore, tabulation of the coal data lends itself to the closer scrutiny of the metals analysis in general.

Issue: Digestion procedure for total metals.

A great deal of controversy has arisen over the application of "hard digestion" that is digestion in nitric acid to almost dryness and subsequent dilution in hydrochloric acid. A number of procedures described what would be called a soft digestion or a sulfuric leach discussions proceeded around this question and is included.

Resolution:

During Phase II of the screening and verification procedures all metal samples will undergo hard digestion by nitric and hydrochloric acid. They will not be taken to dryness as had been previously described due to the number of comments received on the possible loss by volatiliation or splattering of the sample in preparation.

Issue: Sampling Containers and Storage Bottles

Comments were received in regard to the increase in mercury level in a number of plastic containers.

Resolution:

Region V's S & A laboratory has carried out a number of studies relating to storage containers and as a result has recommended the following: Cap-while 43 400 MM, H-43 polypropylene smooth edge linerless cap-W. Braum Co., 300 North Canal St., Chicago, IL 60606, 312/FI6-6500, container -125 cc or 360 cc wide mouth, oblong polyethelyene (Monsanto) for use with 38-400 MM screw cap or 960 cc wide mouth for use with 43-400 MM Cincinnati Container Co., 2833 Spring Grove Ave., Cincinnati, OH 45225, 513/542-1515.

Issue: Preservation of metals samples

Resolution:

Based on the comments received, and in particular, a comment submitted by Calspan, which outlined their attempt at obtaining a variance from the DOT regulations, it has been decided that for Phase II as in Phase I metal samples will not be acidified (preserved) prior to shipment. Included is the letter submitted by Calspan to the Department of Transportation requesting a variance and stating their case. Furthermore there is included the subsequent denial by DOT to this request (see the comment section).

Asbestos Measurement

EPA (Athens) Presentation

EPA discussed their method for analyzing asbestos (chrysotile fibers). This interim method is available in the reference section. This method is scheduled for updating in August 1978. EPA has obtained precise results with this method. A complete study of sample preparation techniques by the Ontario Research Foundation will be available in 3 months. EPA (Cincinnati) is preparing standards for chrysotile fibers.

Calspan Presentation

Calspan has been performing chrysotile fiber counts and total fiber counts on samples from the ore mining and coal mining industries using the EPA analytical method. Calspan outlined a number of problems they have encountered in these analyses including:

Background fiber levels tend to vary in the diluent. They recommend using a non-aqueous diluent, i.e. methanol.

Fibers have been found to protrude through holes in the nucleopore filter.

A double carbon coating may be needed on the nucleopore filter.

With some fibers only partial SAED patterns or no patterns can be seen.

The amount of solids in some samples hindered analyses.

Q(Versar): What are background levels of asbestos in U.S. waterways?

A(Calspan): Little data exists; the available literature indicates these levels are between 10^5-10^7. Calspan recommends verification sampling for waste streams containing more than 1×10^8 chrysotile fibers.

A(McCrone): Reported 10^8-10^9 background levels in California.

Q(EPA Athens) Questioned the use of the exponential form for reporting data they had selected the unit "million fibers per liter (mfl)".

A(Calspan): Responded that they agree that this unit should be standardized.

Comments:

McCrone Compared the use of light microscopy with electron microscopy for asbestos analysis. Asbestos fibers larger than 0.25 in diameter can be seen, but smaller fibers (which are usually more numerous) are missed. Many more fibers can be seen with transmission electron microscopy. Using a TEM, fibers can be identified by electron diffraction, chemical information, as well as by morphology. McCrone commented that they had had problems with achieving a representative distribution of fibers on the particle/grid square (see the reference section).

EPA (Duluth) Presented slides and discussed the analytical method for asbestos. Commented that double carbon coating of nucleopore filter may distort the fiber and add to problems with the electron

TABLE 1. RESULTS OF SCREEN SAMPLE ANALYSIS OF TOTAL FIBER AND CHRYSOTILE ASBESTOS

FACILITY	ORE	WASTEWATER SOURCE	TOTAL FIBER (fibers/liter)	CHRYSOTILE (fibers/liter)
ALCOA	Al	TREATED MINE WATER	1.4×10^{9}	2.0×10^{8}
ASARCO-GALENA	Ag	TREATED MINE WATER	5.7×10^{7}	1.1×10^{6}
ASARCO-GALENA	Ag	TAILING POND EFFLUENT	2.1×10^{9}	1.8×10^{8}
KENNECOTT-SLC	Cu (02B)	TAILING POND EFFLUENT	4.3×10^{9}	6.7×10^{3}
KENNECOTT-SLC	Cu (04B)	TREATMENT PLANT EFFLUENT	1.5×10^{7}	7.8×10^{5}
KENNECOTT-SLC	Cu (06B)	TAILING POND EFFLUENT	3.7×10^{7}	8.2×10^{6}
KENNECOTT-SLC	Cu (08B)	TREATMENT PLANT EFFLUENT	4.9×10^{9}	7.7×10^{7}
WHITE PINE	Cu	TREATMENT SYSTEM EFFLUENT	8.2×10^{6}	5.5×10^{5}
ANACONDA-BUTTE	Cu	TAILING POND EFFLUENT	1.2×10^{9}	3.0×10^{8}
ANACONDA-BUTTE	Cu	TREATED MINE WATER	7.2×10^{7}	8.2×10^{6}
BUNKER HILL	Pb/Zn	TREATMENT SYSTEM EFFLUENT	4.1×10^{8}	4.1×10^{7}
HECLA-STAR	Pb/Zn	TAILING POND EFFLUENT	1.6×10^{9}	$< 3.3 \times 10^{5}$
ST. JOE-EDWARDS	Pb/Zn	TAILING POND EFFLUENT	3.4×10^{8}	2.4×10^{7}
HANNA-BUTLER	Fe	MINE WATER SETTLING POND	4.2×10^{7}	3.8×10^{6}
REPUBLIC	Fe	TAILING POND EFFLUENT	4.3×10^{7}	4.1×10^{6}
UCC-URAVAN	U	EFFLUENT FROM MILL SETTLING POND	1.2×10^{9}	1.5×10^{8}
LUCKY Mc MINING	U	TREATED MINE WATER	5.7×10^{8}	2.7×10^{7}
COTTER-SCHWARTZWALDER	U	TREATED MINE WATER	2.3×10^{9}	2.0×10^{8}
KERR-McGEE	U	TREATED MINE WATER	4.3×10^{8}	5.3×10^{7}
PLACER-AMEX	Hg	TAILING POND RECYCLE	7.7×10^{8}	5.7×10^{7}
McINTYRE DEVELOPMENT	Ti	MILL WATER TO RECYCLE	1.5×10^{8}	1.3×10^{6}
PINE CREEK-UCC	W	TREATED MINE WATER	3.3×10^{7}	8.2×10^{6}
MOLYCORP-QUESTA	Mo	TAILING POND EFFLUENT	3.3×10^{10}	2.0×10^{9}

TABLE 2. RESULTS OF SCREEN SAMPLE ANALAYSIS OF TOTAL FIBER AND CHRYSOTILE ASBESTOS
(U.S. STEEL–GENEVA MINE)

FACILITY	SAMPLE (W58-XI-COAL)	WASTEWATER SOURCE	TOTAL FIBER (fibers/liter)	CHRYSOTILE (fibers/liter)
GENEVA MINE (E. CARBON, UT.)	01B	WASTEWATER STORAGE TANK OVERFLOW	8.8×10^8	8.6×10^7
GENEVA MINE (E. CARBON, UT.)	02B	CARLSON PUMPS DISCHARGE (MINEWATER)	1.3×10^9	1.4×10^8
COAL PREPARATION PLANT (WELLINGTON, UT.)	05B	SETTLING POND DECANT	3.7×10^8	1.6×10^7

*CORRESPONDING BLANK – 2.2×10^5 fibers/liter
DETECTION LIMIT – 3.3×10^5 fibers/liter

TABLE 4. ORE FACILITIES EXHIBITING HIGHEST FIBER COUNTS

HIGHEST TOTAL FIBER COUNT (FIBERS/LITER)		HIGHEST CHRYSOTILE COUNT (FIBERS/LITER)	
$3.3 \cdot 10^{10}$	MOLY CORP - QUESTA - TAILING EFFLUENT	$2.0 \cdot 10^{9}$	MOLY CORP - QUESTA
$4.9 \cdot 10^{9}$	KENNECOTT-Cu-08B - TREATMENT EFFLUENT	$6.7 \cdot 10^{8}$	KENNECOTT-Cu-02B
$4.3 \cdot 10^{9}$	KENNECOTT-Cu-02B - TAILING EFFLUENT	$3.0 \cdot 10^{8}$	ANACONDA-BUTTE - TAILING EFFLUENT
$2.3 \cdot 10^{9}$	COTTER-SCHWARTZWALDER - TREATED MINE WATER	$2.0 \cdot 10^{8}$	COTTER-SCHWARTZWALDER
$2.1 \cdot 10^{9}$	ASARCO-GALENA - TAILING POND EFFLUENT	$2.0 \cdot 10^{8}$	ALCOA
$1.6 \cdot 10^{9}$	HECLA STAR	$1.8 \cdot 10^{8}$	ASARCO-GALENA - TAILING EFFLUENT
$1.4 \cdot 10^{9}$	ALCOA	$1.5 \cdot 10^{8}$	UCC-URAVAN
$1.2 \cdot 10^{9}$	ANACONDA-BUTTE - TAILING EFFLUENT	$7.7 \cdot 10^{7}$	KENNECOTT-Cu-08B
$1.2 \cdot 10^{9}$	UCC-URAVAN	$5.7 \cdot 10^{7}$	PLACER-AMEX
$5.7 \cdot 10^{8}$	LUCKY McMINING	$5.3 \cdot 10^{7}$	KERR McGEE

TABLE 6. CHRYSOTILE FIBER COUNTS EXPRESSED IN TERMS OF MASS FOR ORE MINING AND DRESSING FACILITIES

FACILITY	ORE	WASTEWATER SOURCE	APPROXIMATE CHRYSOTILE MASS (NANOGRAM/ l)*
ALCOA	Al	TREATED MINE WATER	70
ASARCO-GALENA	Ag	TREATED MINE WATER	0.39
ASARCO-GALENA	Ag	TAILING POND EFFLUENT	64
KENNECOTT-SLC	Cu (02B)	TAILING POND EFFLUENT	240
KENNECOTT-SLC	Cu (04B)	TREATMENT PLANT EFFLUENT	0.28
KENNECOTT-SLC	Cu (06B)	TAILING POND EFFLUENT	2.9
KENNECOTT-SLC	Cu (08B)	TREATMENT PLANT EFFLUENT	27
WHITE PINE	Cu	TREATMENT SYSTEM EFFLUENT	0.19
ANACONDA-BUTTE	Cu	TAILING POND EFFLUENT	110
ANACONDA-BUTTE	Cu	TREATED MINE WATER	2.9
BUNKER HILL	Pb/Zn	TREATMENT SYSTEM EFFLUENT	14
HECLA-STAR	Pb/Zn	TAILING POND EFFLUENT	< 0.12
ST. JOE-EDWARDS	Pb/Zn	TAILING POND EFFLUENT	8.5
HANNA-BUTLER	Fe	MINE WATER SETTLING POND	1.3
REPUBLIC	Fe	TAILING POND EFFLUENT	1.5
UCC-URAVAN	U	EFFLUENT FROM MILL SETTLING POND	53
LUCKY McMINING	U	TREATED MINE WATER	9.5
COTTER-SCHWARTZWALDER	U	TREATED MINE WATER	70
KERR-McGEE	U	TREATED MINE WATER	19
PLACER-AMEX	Hg	TAILING POND RECYCLE	20
McINTYRE DEVELOPMENT	Ti	MILL WATER TO RECYCLE	0.46
PINE CREEK-UCC	W	TREATED MINE WATER	2.9
MOLYCORP-QUESTA	Mo	TAILING POND EFFLUENT	700

*NANOGRAM/LITER = 10^{-9} GRAM/LITER

diffraction pattern. In addition, in many industrial effluents, organics may cloud or distort the electron diffraction pattern. Commented that small fibers are difficult to identify by diffraction pattern. Therefore they are often classified as ambiguous.

Discussing interlaboratory comparison of results, EPA commented that there has been considerable improvement in the last few years. Labs agree often on trends, but not on the magnitude on concentration.

Commented that long storage times hinder asbestos analysis. Fibers tend to settle out and clump together and they are difficult to redistribute.

Questions:

Q(Carborundum): What is the minimum number of fibers which should be counted?

A(McCrone): Depends upon the background levels of asbestos. Total suspended solids level also should be considered.

Q(RETA): What type of containers should be used for asbestos samples? How long can samples be stored?

A(EPA Duluth): Recommend 1 liter samples be collected in polyethylene containers. HgCl is recommended as an antibacterial agent. Samples should be immersed in an ultrasonic bath to prevent clumping. Samples should be filtered as soon as possible. They can be stored a long time but the container should be placed in an ultrasonic bath to disperse fibers. EPA does not recommend the use of a dispersal agent because it tends to break up fibers, resulting in a larger count.

Conclusion:

It is this Agency's position to recommend that the Transmission Election Microscopy method, as described by Dr. Charles Anderson, EPA (Athens) be utilized. In addition, a copy of the phamphlet Selected Silicate Minerals and their Asbestiform Varieties is provided with this package. This phamphlet is intended to serve as a basic source of information. We are thankful to William J. Campbell of the Bureau of Mines for supplying this publication.

Biological Monitoring

In an attempt to present some alternative or perhaps a surragate technology related to monitoring for organic or (possibly toxic) contaminants, a discussion was held on the use of biological organisms. A description was provided of the concept of the toxic lethal units as related to biological monitoring.

Mr. Rawlings of Monsanto Corporation presented a description of the present environmental assessment being carried out by Monsanto. This study relates to the reduction of toxic effluents from the textile industry. The Monsanto Program outlined the various stages of activities that are ongoing in the various biological and chemical test being employed to determine both the toxicity as well as the treatability of a number of effluents coming from various textile facilities. A brief description is provided along with the summation of the slides that were shown.

BIOASSAY TESTING OF INDUSTRIAL WASTEWATER

Presented to

EPA SEMINAR ON ANALYTICAL METHODS

November 9-10, 1977

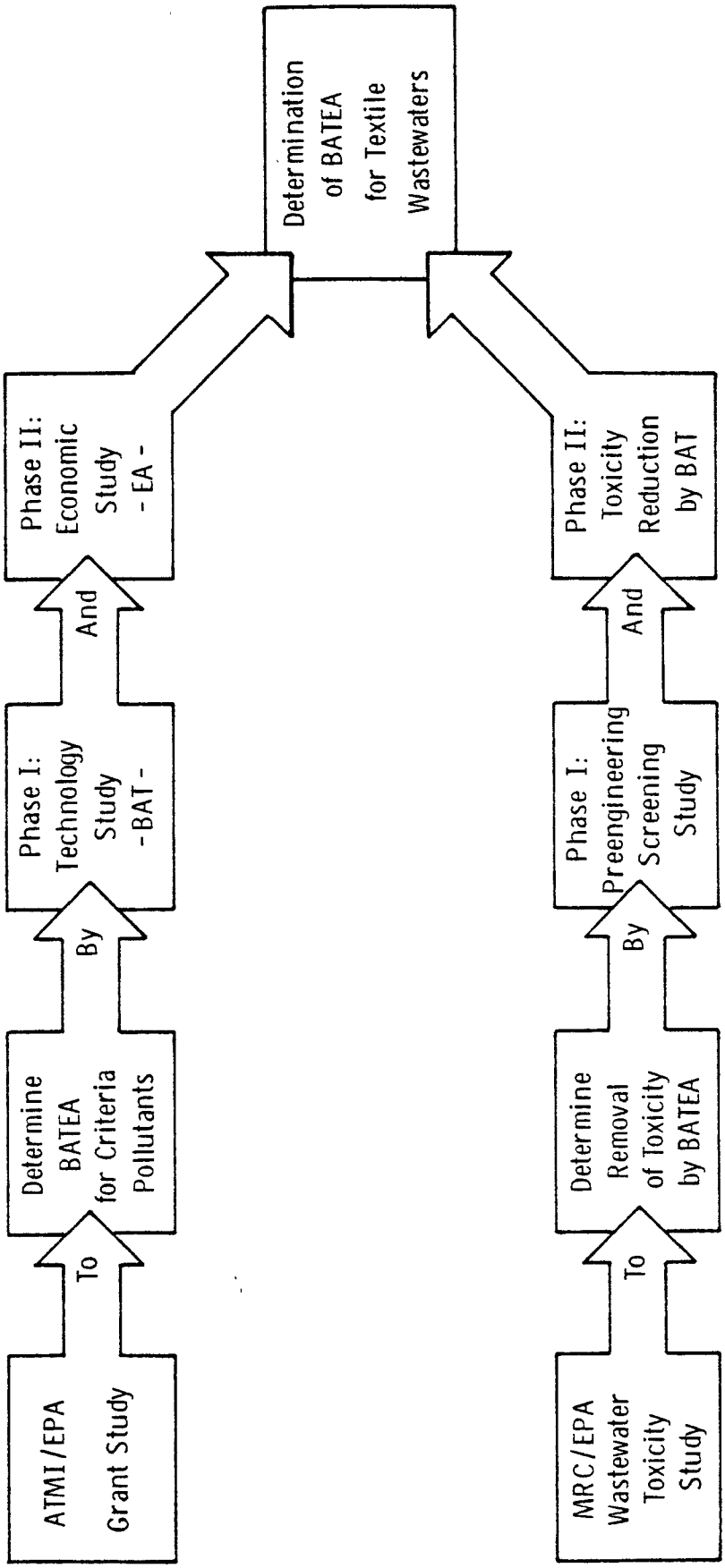
Denver, Colorado

by

Gary D. Rawlings
Senior Research Engineer

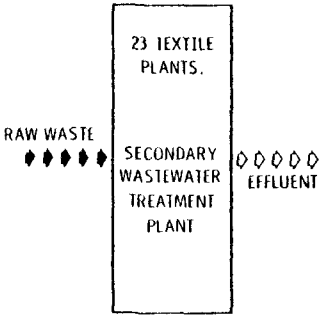
MONSANTO RESEARCH CORPORATION
1515 Nicholas Road
Dayton, Ohio 45407

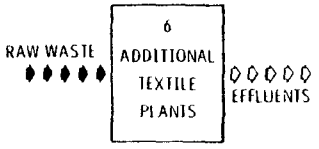
PROGRAM APPROACH



LEVEL OF EFFORT REQUESTED BY.

EPA - EFFLUENT GUIDELINES DIVISIONS (EGD) WASHINGTON, D C.	CHEMICAL PROCESSES BRANCH (CPB) IERL - INDUSTRIAL PROCESSES RESEARCH TRIANGLE PARK, NORTH CAROLINA	PROCESS MEASUREMENTS BRANCH (PHB) INDUSTRIAL PROCESSES DIVISION RESEARCH TRIANGLE PARK, NORTH CAROLINA
ANALYZE RAW WASTE FOR • 129 PRIORITY POLLUTANTS • CRITERIA POLLUTANTS ANALYZE EFFLUENT FOR • CRITERIA POLLUTANTS	ANALYZE EFFLUENT FOR • 129 PRIORITY POLLUTANTS • NUTRIENT SERIES • BIOASSAYS · MUTAGENICITY · CYTOTYXICITY · FRESHWATER SERIES · MARINE SERIES · 14 DAY RAT TEST · SOIL MICROCOSM	ANALYZE EFFLUENT FOR • LEVEL 1 CHEMICAL ANALYS'S

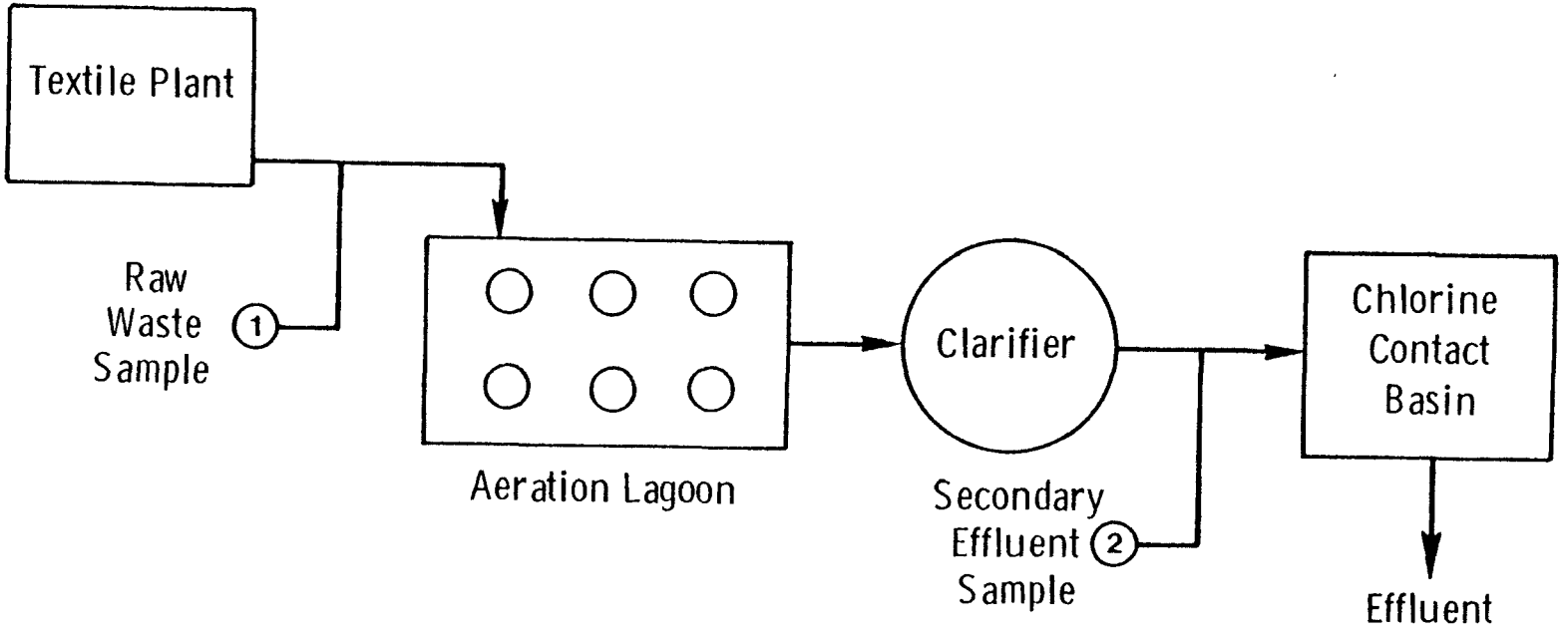


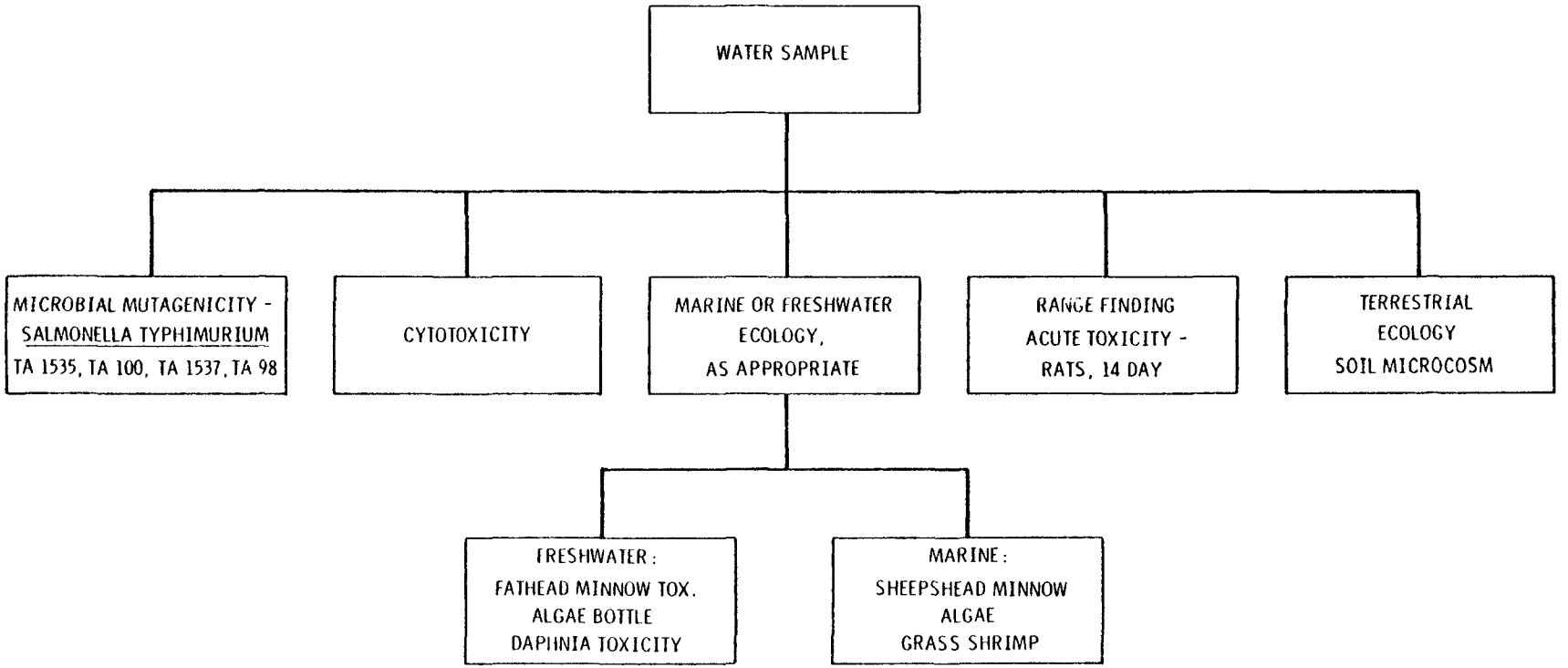


SAMPLE AND ANALYZE RAW WASTE AND EFFLUENT STREAMS FOR
- 129 PRIORITY POLLUTANTS
- CRITERIA POLLUTANTS

Nutrients	Criteria Pollutants
Ammonia	BOD_5
Nitrite	COD
Nitrate	Color (APHA)
Total Kjehldehl nitrogen	Sulfide
Orthophosphate	Phenol
Total phosphorus	Total suspended solids
Total organic carbon	pH

Phase I: SAMPLING

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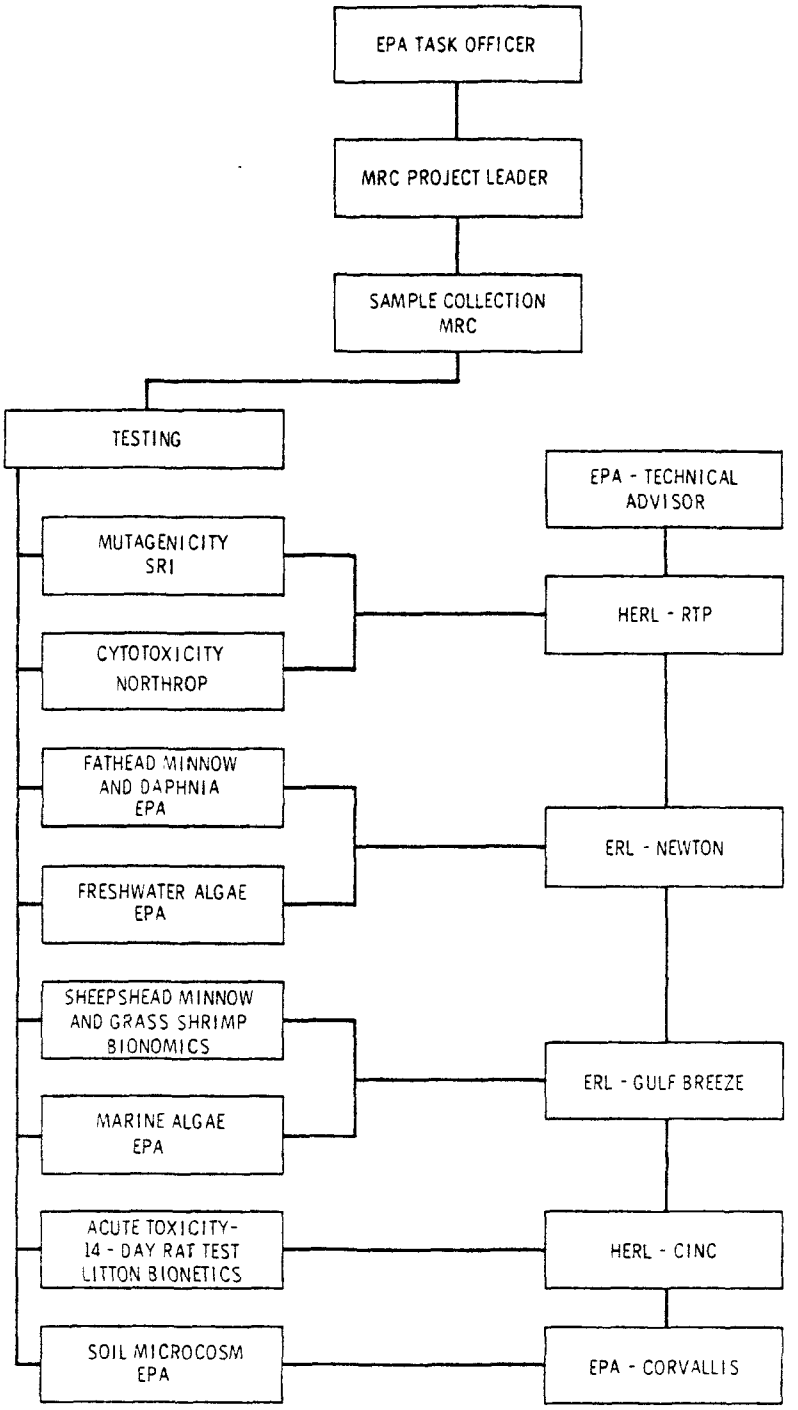
CYTOTOXICITY
MARINE OR FRESHWATER ECOLOGY, AS APPROPRIATE
RANGE FINDING ACUTE TOXICITY - RATS, 14 DAY
TERRESTRIAL ECOLOGY SOIL MICROCOSM
FRESHWATER: FATHEAD MINNOW TOX. ALGAE BOTTLE DAPHNIA TOXICITY
MARINE: SHEEPSHEAD MINNOW ALGAE GRASS SHRIMP

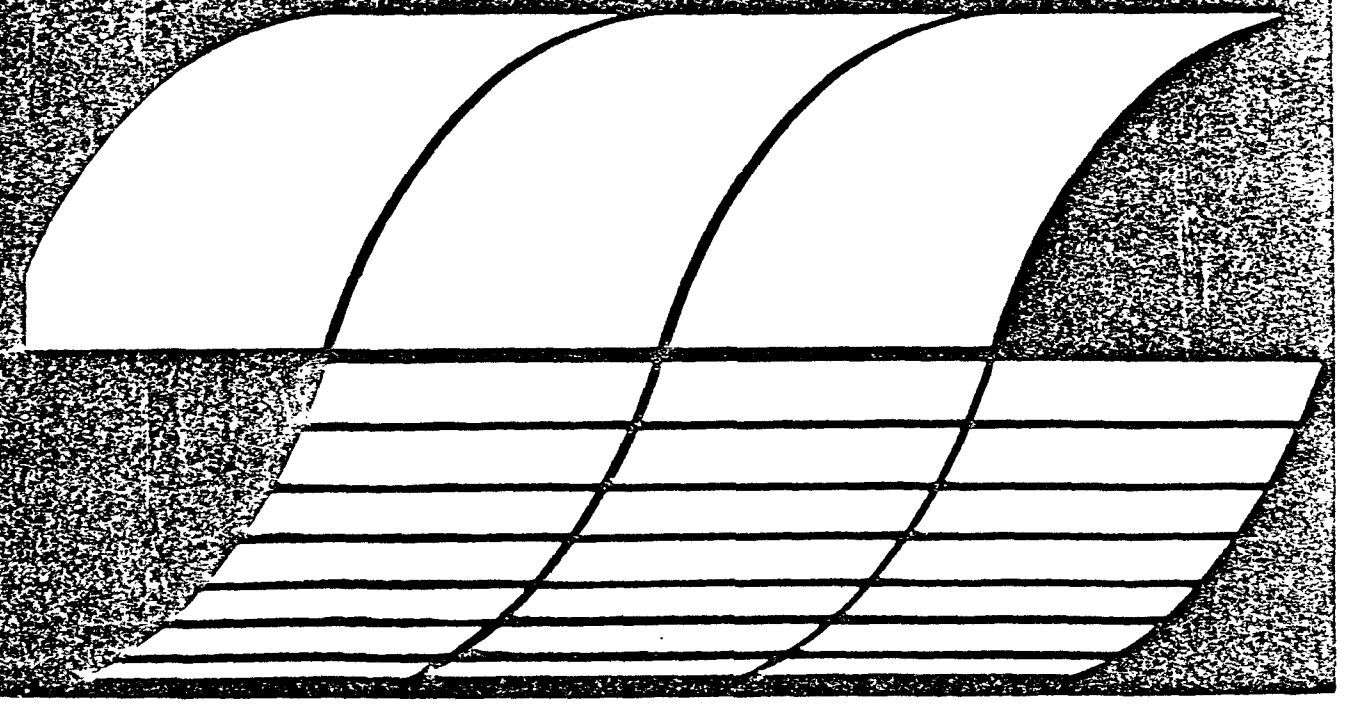

EPA TASK OFFICER
MRC PROJECT LEADER
SAMPLE COLLECTION MRC
TESTING
EPA - TECHNICAL ADVISOR
MUTAGENICITY SRI
CYTOTOXICITY NORTHROP
HERL - RTP
FATHEAD MINNOW AND DAPHNIA EPA
FRESHWATER ALGAE EPA
ERL - NEWTON
SHEEPSHEAD MINNOW AND GRASS SHRIMP BIONOMICS
MARINE ALGAE EPA
ERL - GULF BREEZE
ACUTE TOXICITY- 14 - DAY RAT TEST LITTON BIONETICS
HERL - CINC
SOIL MICROCOSM EPA
EPA - CORVALLIS

EPA

EPA-600/7-77-043
April 1977

IERL-RTP PROCEDURES MANUAL: LEVEL 1 ENVIRONMENTAL ASSESSMENT BIOLOGICAL TESTS FOR PILOT STUDIES

Interagency
Energy-Environment
Research and Development
Program Report



SAMPLING REQUIREMENTS

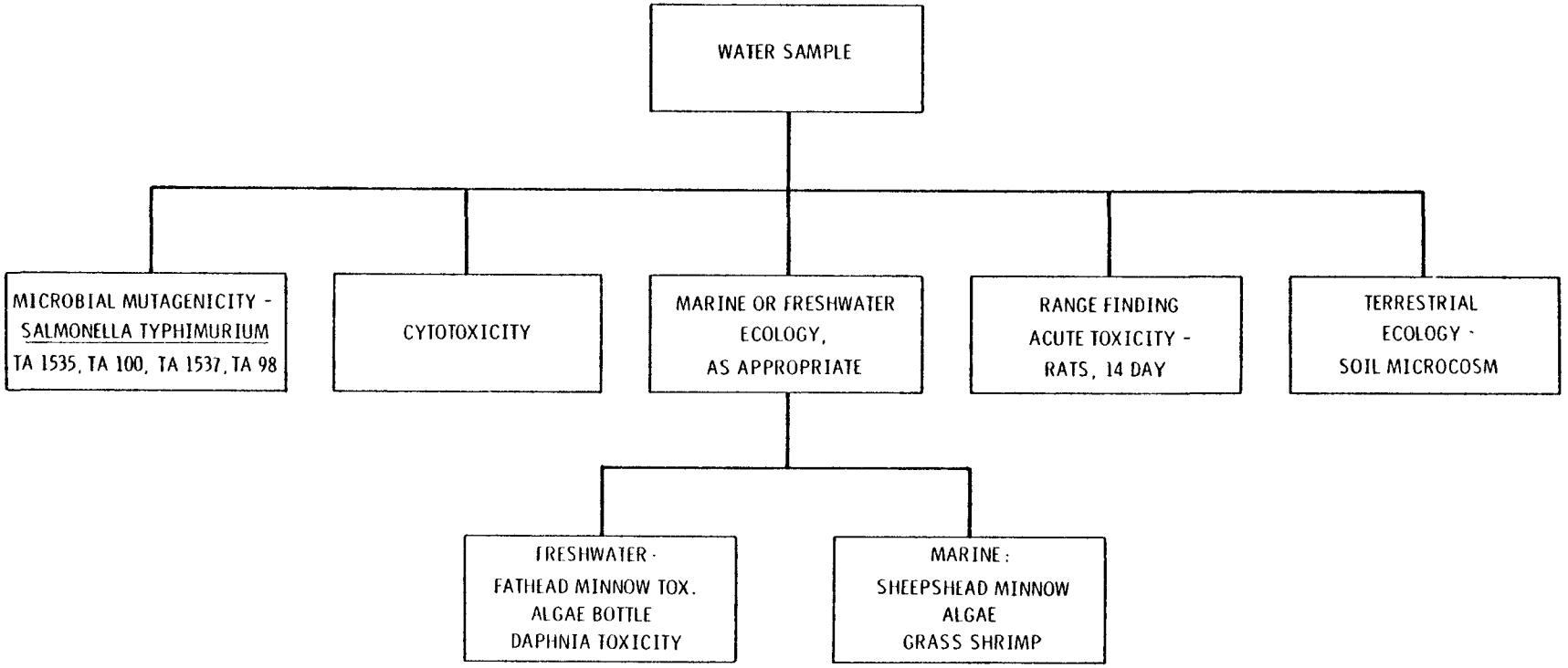
Biotest	Volume, liters
Ames test	0.25
Cytotoxicity	0.25
Fathead minnow and daphnia	60.0
Freshwater algae	9.6
Sheepshead minnow and grass shrimp	60.0
Marine algae	9.6
14-day rat test	1.0
Soil microcosm	0.1
TOTAL	146.8

MICROBIOLOGICAL MUTAGENICITY

Purpose:	To determine if a chemical mutagen is present in the wastewater.
Test species:	Salmonella typhimurium (Ames test) Saccharomyces cerevisiae D3 (yeast) Escherichia coli WP2 Bacillus subtilis
Method:	Subject each bacteria strain to the maximum dosage allowed by the test, if a positive response (mutagen present) occurs then proceed with a dose response test.

CYTOTOXICITY TEST

Purpose:	To measure quantitatively cellular metabolic impairment and death resulting from exposure *in vitro* to toxicants.
Test species:	Rabbit alveolar macrophage
Method:	Dose response test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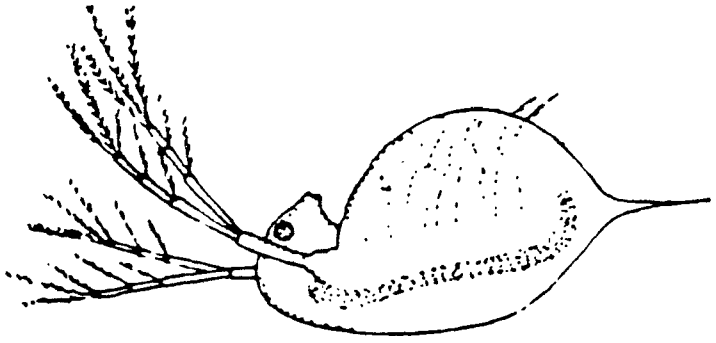

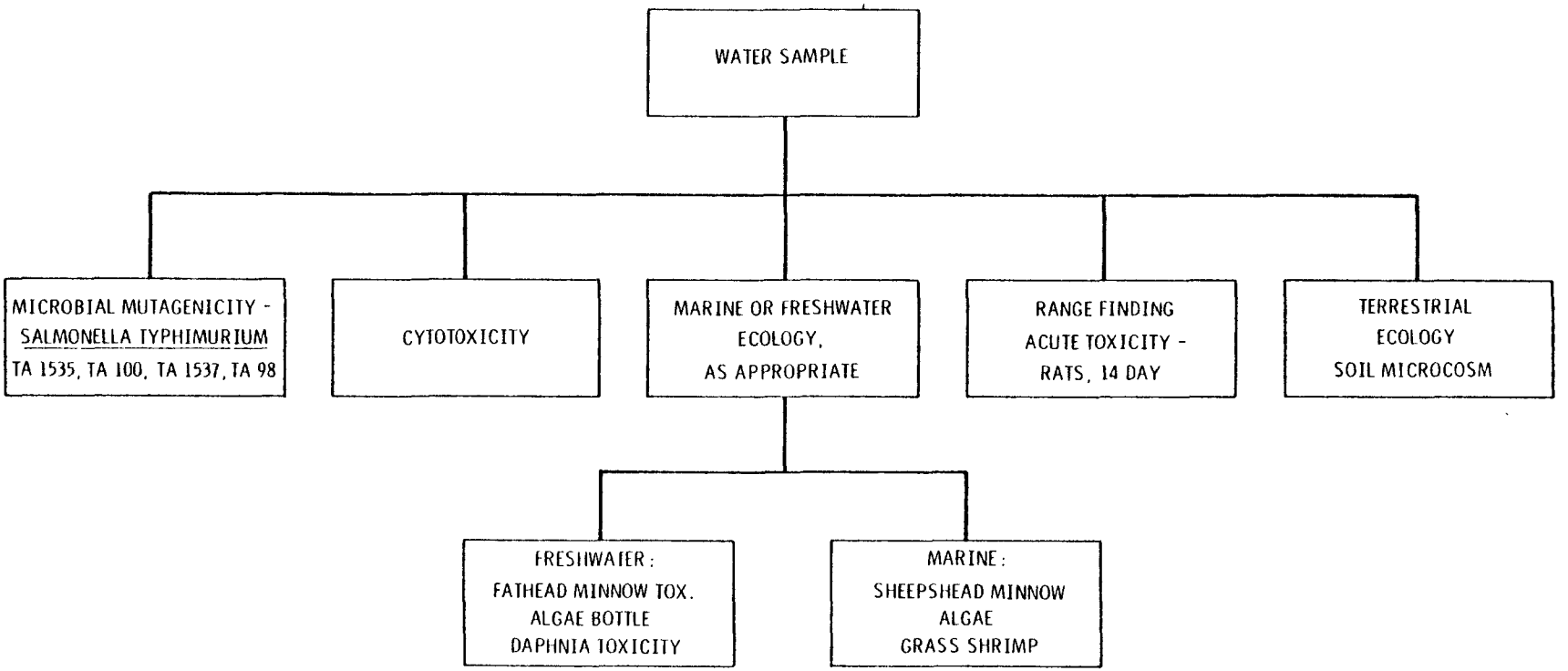
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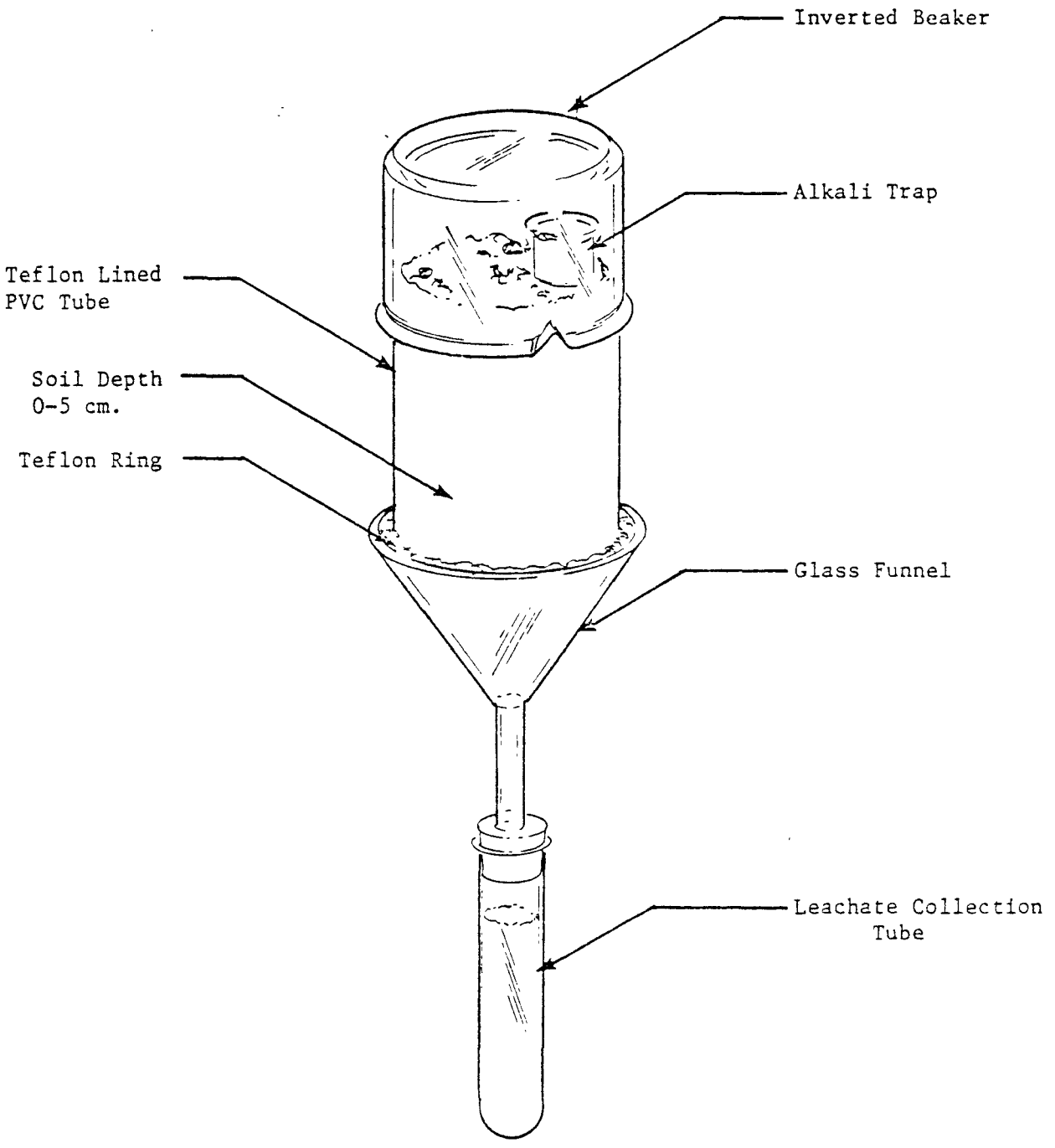

Inverted Beaker
Alkali Trap
Teflon Lined
PVC Tube
Soil Depth
0-5 cm.
Teflon Ring
Glass Funnel
Leachate Collection
Tube

UNITS OF MEASURE FOR ACUTE TOXICITY

EC_{50}: Effective concentration at which 50% of the test organisms reach the desired effect. The "effect", for example, can be growth inhibation or stimulation.

LC_{50}: Lethal concentration at which 50% of the test organisms die over a specified time period (usually 48 or 96 hours).

LD_{50}: Lethal dose at which 50% of the test organisms die over a specified time period (usually 14 - days).

Concentration: refers to the amount of sample (or toxicant) per unit volume of test solution. Used, for exapmle, with fish and shrimp tests.

Dose: refers to the measured amount of sample (or toxicant) that was fed to the test organism. Used for the 14-day rat test.

EXAMPLE

EC_{50} = 10.2% — This means that a 50% increase (or decrease) in the algal mass occurred when exposed to a solution containing only 10.2% of the secondary wastewater.

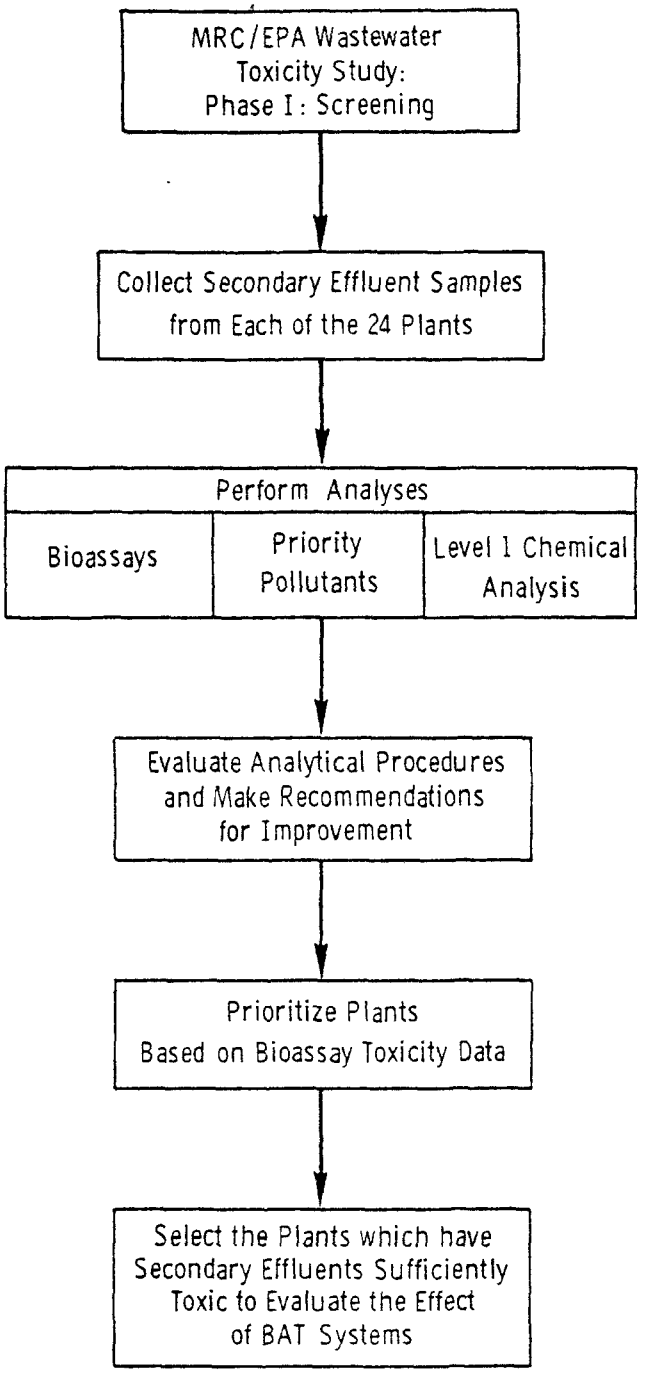
LC_{50} = 80.7% — This means that 50% of the fathead minnows died when placed in a tank containing 80.7 % secondary wastewater.

Note: These toxicity values are determined graphically from a series of dose reponse tests.

Plant code	ATMI code	Mutagenicity test	Cytotoxicity Tests: Viability % eff. conc.	Cytotoxicity Tests: ATP % eff. conc.	Freshwater Ecology Tests: Fathead minnow (LC_{50})	Freshwater Ecology Tests: Daphnia (LC_{50})	Freshwater Ecology Tests: Algae (LC_{50})	Marine Ecology Tests: Sheepshead minnow (LC_{50})	Marine Ecology Tests: Grass shrimp (LC_{50})	Marine Ecology Tests: Algae (EC_{50})	Treatment control range	Acute toxicity, 14-day rat test (LD_{50}) 10^{-3} m^3/kg
A	B	N.P.[a]	N.D.[b]	EC_{20} = 0.58	19.0	9.0	-[f]	62.0	21.2		-[f]	>10
B	EE	N.P.	N.D.	N.D.	N.A.T.[c]	N.A.T.	S G	>100	>100	-[3]	2 0	>10
C	V	N P.	EC_{50} = 9.17[e] EC_{20} = 1.68[e]	EC_{50} = 3.35[e] EC_{20} = 0.62[e]	46.5	41.0	H.G.	69.5	12.8	90	1.3	>10
D	DD	N.P	N.D.	N.D.	N.A T.	N A.T.	S.G	-[f]	-[f]	-[f]	-[f]	>10
E	CC	N.P	N.D.	N D.	N.A.T.	7.8	N.G.	>100	>100	10 to 50	-[f]	>10
F	L	N.P.	N D.	EC_{50} = 35.0 EC_{20} = 0.94	N.A.T.	81.7	H G.	>100	>100	85	2 3	>10
G	F	N P	N.D.	EC_{20} = 17.0	64.7	62.4	H.G.	>100	>100	59	1.3	>10
H	AA	N.P.	N.D.	N.D.	-[g]	40% dead at 100% conc	G/I	-[f]	-[f]	-[f]	-[f]	>10
J	Z	N.P	N.D.	EC_{20} = 1.11	N.A.T.	N.A.T.	S.G.	-[f]	-[f]	-[f]	-[f]	>10
K	P	N.P	N.D.	N.D.	N.A.T.	N.A.T.	S.G	>100	>100	77	1 8	>10
L	G	N.P	N.D.	EC_{50} = 3 52 EC_{20} = 0.40	23 5	28.0	G/I	>100	>100	1 -	1.1	10

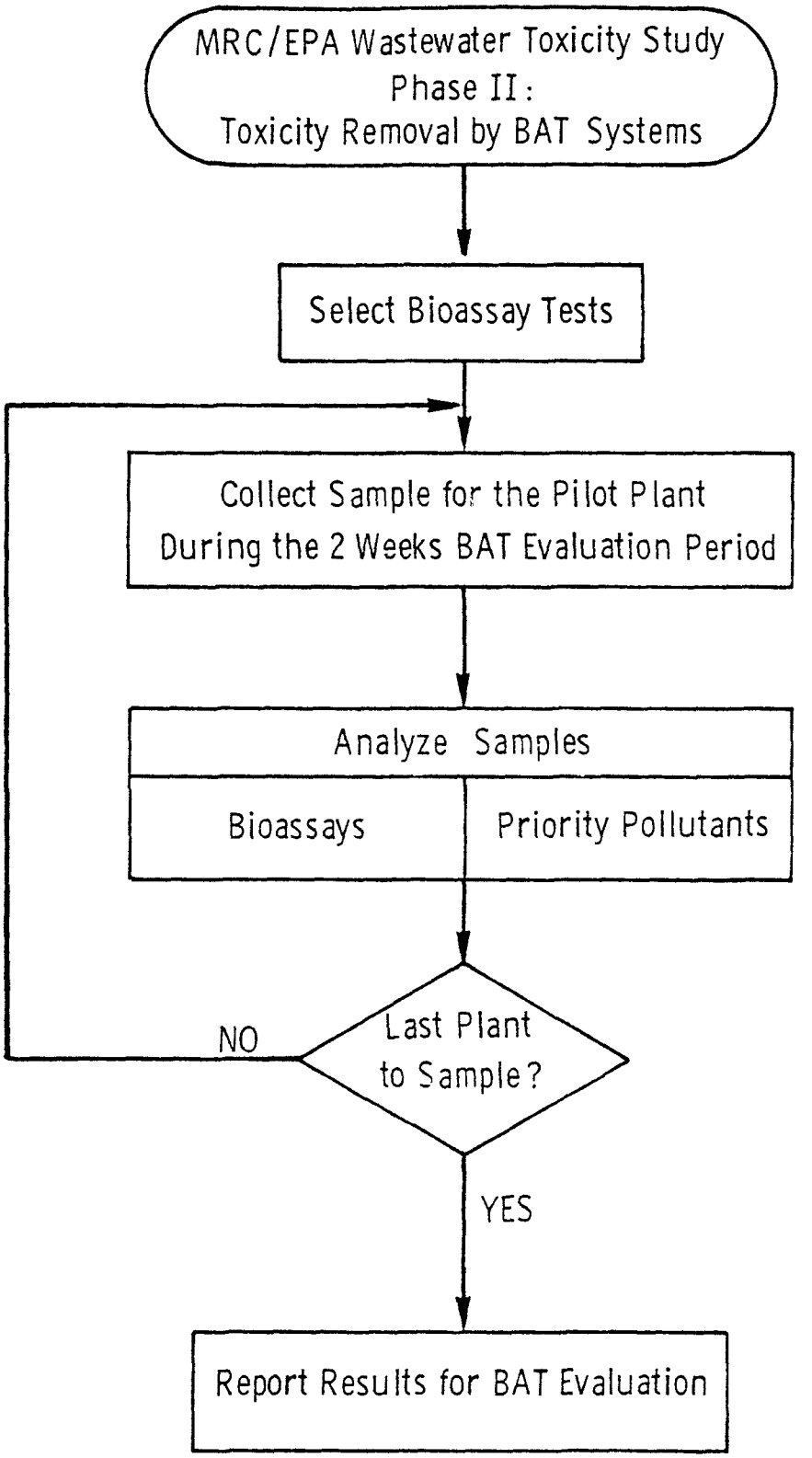
EXAMPLE OF BIOTEST RESULTS

Plant Code	Biotest, % secondary wastewater							
	1		2			3		
	A	B	C	D	E	F	G	H
A	0	1.5	19.0	9.0	---	62.0	21.2	59
B	0	0	0	0	0	>100	>100	90
C	0	7.4	55.2	6.3	94	37.5	14.0	50
D	39	1.3	48.8	100% Dead at all dilutions	95% in 2% solution	47.5	26.3	2.3
E	0	50.0	46.5	0	78.8% stimulation	68.0	34.5	70.0


MRC/EPA Wastewater
Toxicity Study:
Phase I: Screening
Collect Secondary Effluent Samples
from Each of the 24 Plants
Perform Analyses
Bioassays
Priority
Pollutants
Level 1 Chemical
Analysis
Evaluate Analytical Procedures
and Make Recommendations
for Improvement
Prioritize Plants
Based on Bioassay Toxicity Data
Select the Plants which have
Secondary Effluents Sufficiently
Toxic to Evaluate the Effect
of BAT Systems

PRIORITZATION OF TEXTILE PLANTS
BY
TOXICITY OF SECONDARY EFFLUENT

Toxicity Ranking	Plant
Most Toxic	Group 1: A, B
↓	Group 2: C, D, E
	Group 3: F, G, H
	Group 4: I, J
Least Toxic	Group 5: K, L, M, N, O, P, Q, R, S


MRC/EPA Wastewater Toxicity Study
Phase II:
Toxicity Removal by BAT Systems
Select Bioassay Tests
Collect Sample for the Pilot Plant
During the 2 Weeks BAT Evaluation Period
Analyze Samples
Bioassays
Priority Pollutants
Last Plant
to Sample?
NO
YES
Report Results for BAT Evaluation

BIOASSAYS USED FOR PHASE II

- Fathead Minnow
- Daphnia
- Freshwater Algae

SIX TERTIARY TREATMENT UNIT OPERATIONS

1. Reactor / Clarifier (using combinations of alum, lime, ferric chloride, and anionic and cationic polyelectrolytes)
2. Multimedia Filter
3. Granular Activated Carbon Columns
4. Powdered Activated Carbon (laboratory test)
5. Dissolved Air Floatation
6. Ozonation

SEVEN TERTIARY TREATMENT MODES FOR "BEST AVAILABLE TECHNOLOGY" EVALUATION

Mode A: Reactor/Clarifier → Multimedia Filter

Mode B: Multimedia Filter → Granular Activated Carbon Columns

Mode C: Multimedia Filter → Ozonator

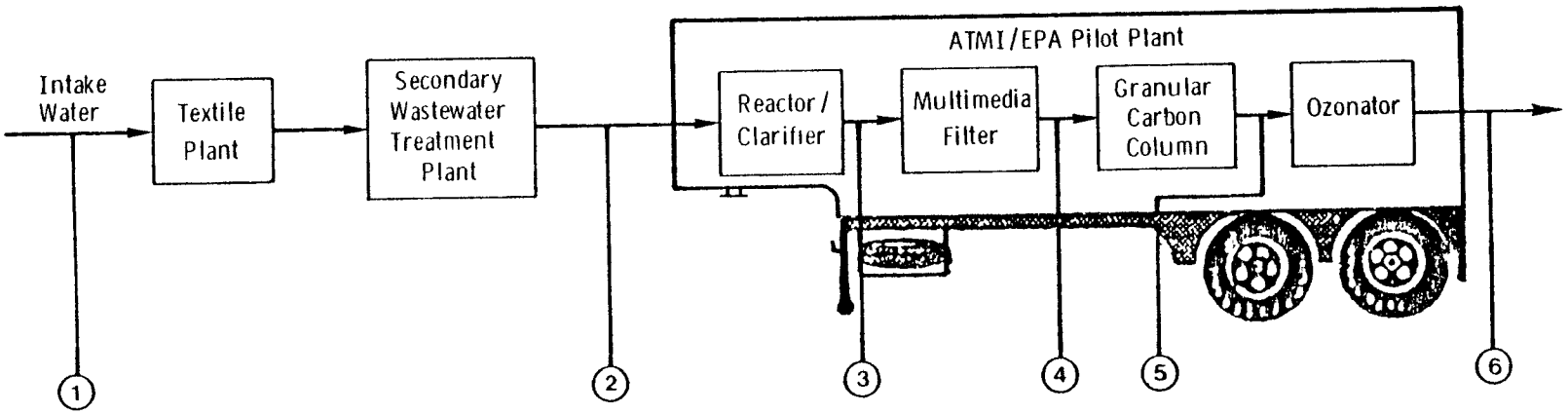
Mode D: Ozonator

Mode E: (Optional) Reactor/Clarifier → Multimedia Filter → Granular Activated Carbon → Ozonator

Mode F: Coagulation → Multimedia Filter

Mode G: Dissolved Air Floatation

SAMPLING LOCATIONS FOR PHASE II



INTERPRETATION OF BIOASSAY TEST RESULTS

Bioassay Results		Toxic Substance Interpretation
Inlet	Outlet	
+	+	Control Technology Is Not Effective
+	−	Control Technology Is Effective
−	+	Control Technology Is Deterimental
−	−	Control Technology Is Not Deterimental

Index of Comments

1. Bruce Long and Carol Hammer, Ryckman, Edgerley, Tomlinson and Associates, November 8, 1977, re: (1) Sampling and Shipment (2) Metals Digestion, (3) VOA storage.

2. John Way, E.I. DuPont De Memours & Company, November 15, 1977, re: Observations on the use of the E.P.A. sampling and analysis procedures for priority pollutants - VOA - Acid and Base/Neutrals.

3. C.W. Phillips, Mobil Oil Corporation, November 2, 1977, re: comparitives data on analytical results for samples taken concurrently.

4. F.P. Hochgesang, Mobil Research and Development Corporation, November 17, 1977, re: Acid Extractables - Phenolic compounds and Base/Neutral - polynuclear aromatics.

5. M.J. O'Neal, Shell Development Company, December 15, 1977, re: VOA apparatus, compositing and storage.

6. Dr. Robert Kleopfer, U.S. Environmental Protection Agency, Region VII, November 2, 1977. Comments concerning the experiences of the E.P.A. surveillance and Analysis Division, when using the protocol.

7. Memo, dated January 18, 1978, Subject: Action Concerning Region VII comments.

8. Letter: GC-MS internal standards, Radian Corporation, Dr. Larry Keith, November 21, 1977, corrected order of elution of the unchlorinated base/neutral compounds.

9. P. Micheal Terlecky, Calspan Corporation, December 19, 1977, subject: Shipment of nitric acid and DOT regulations.

10. A.W. Garrison, E.P.A., Athens, Georgia, December 22, 1977, Stability of two of the Consent Decree Pollutants.

RYCKMAN, EDGERLEY, TOMLINSON
AND ASSOCIATES
12161 Lackland Road
St. Louis, Missouri 63141
(314) 434-6960

a division of Envirodyne Engineers

November 8, 1977

Mr. William A. Telliard, Chief
Energy and Mining Branch
Effluent Guidelines Division
U. S. Environmental Protection Agency (WH-552)
Washington, DC 20460

Dear Mr. Telliard:

Ryckman/Edgerley/Tomlinson & Associates (RETA) appreciates the opportunity to attend EGD's seminar on sampling and analytical methods used for studies of priority pollutants in industrial wastewaters. We feel this seminar is timely and necessary.

RETA has been actively involved in the sampling and analytical portions of BAT Review studies for both screening and verification program in the Timber Processing, Petroleum Refining and, currently, Organic Chemicals and Plastic and Synthetic Materials Manufacturing point source categories. In the course of our involvement in these programs (since January, 1977) we have learned many things which we would like to pass on to your attention. Additionally, we have encountered certain aspects of the most recent (April, 1977) protocol that we feel require close attention with subsequent modification and have developed several questions, the answers to which are needed as soon as possible.

The points and questions we wish to pass on are the following:

I. Field Sampling, Sample Handling and Shipment

1) Can Teflon sample tubing be reused?

2) RETA is currently using Dow Corning selastic silicon rubber medical grade 3/8-inch I.D. pump tubing rather than tygon tubing.

3) The April, 1977 protocol requires a minimum aliquot volume of 100 ml. Shouldn't this minimal volume be 50 ml?

4) The composite metals sample is currently poured off from the NVO composite sample. It is our opinion that a separate metals composite sample should be collected by compositing grab samples in a glass bottle with re-distilled nitric acid already added.

5) Field experience has demonstrated that potassium-iodide starch paper is not sensitive to residual chlorine levels as low as 2 mg/l. RETA is therefore using the ortho Tolidine (OT) test in parallel to the KI-starch test. If the OT test is positive we are adding 0.6 gm of ascorbic acid to the cyanide sample and two drops of sodium thiosulfate to the VOA samples.

6) Current protocol calls for analysis of both the unpreserved and preserved VOA samples. RETA questions the value of analyzing the unpreserved sample especially when the cost of analysis is considered.

7) The April, 1977 screening protocol calls for preservation for phenols "...by addition of phosphoric acid or sulfuric acid to 4." RETA is adding 1.0 gram of $CuSO_4$ followed by the addition of phosphoric acid to lower the sample pH to 4.

8) Concerning sample blanks for VOA samples it is RETA's interpretation of the April, 1977 protocol that two VOA blanks are sent back per sampling site. These VOA blanks are sent back with the NVO composite.

9) Concerning VOA samples, our experinece has found vacuum bubbles formed in several VOA vials. We believe this to be due to the cooling of the sample with consequent volume reduction.

10) When several (more than one) sample sites require compositing to comprise one composite sample, the October, 1976 protocol permitted compositing of VOA samples at 4°C No mention is made of this procedure in the April, 1977 protocol.

11) RETA plans to perform GC/MS analysis on the influent to treatment and effluent from treatment only. GC analysis of the intake water will be performed for those priority pollutants found in the raw wastewater.

12) The April, 1977 protocol states, "When more than one laboratory is involved...the sample should if at all possible not be divided in the field but rather at the contractors laboratory." RETA is pouring off the metals fraction for those metals to be analyzed in RETA's lab and preserving in the field using re-distilled nitric acid. It is RETA's position that not preserving as soon as possible increases the time for metals adsorption on the NVO composite jug.

13) RETA requests greater detail on what constitutes "analytical method validation" as called for in your memorandum of June 23, 1977.

II. Analytical Considerations

1) The digestion procedures prescribed for metals. RETA is concerned a) that the level of nitric acid prescribed during digestion leads to low results for some of the metals, and b) that the addition of the nickel nitrate matrix must be done just prior to analysis for arsenic to avoid loss of the metal, thereby precluding addition and storage for analysis of both selenium and arsenic.

2) Direct aqueous injection for acrylonitrile and acrolein by GC/MS. Concern arises over the introduction of water into the mass spectrometer.

3) Holding times for analysis. Concern arises over the amount of time a volatile sample can be held prior to analysis and the recommended storage alternatives in light of apparent problems arising from storage of hermetically-sealed traps.

Thank you once again for the opportunity to attent this seminar and for your consideration of the points raised in this memorandum.

Bruce W. Long

Bruce W. Long, P.E.

Carol A. Hammer

Carol A. Hammer, Ph.D.

IC-6614-E REV. 4-74

DUPONT

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E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

WILMINGTON, DELAWARE 19898

INDUSTRIAL CHEMICALS DEPARTMENT
RESEARCH & DEVELOPMENT DIVISION
EXPERIMENTAL STATION

November 15, 1977

W. A. Telliard, Chief
Energy and Mining Branch, EGD
United States Environmental Protection Agency

ANALYSIS PROCEDURES FOR PRIORITY POLLUTANTS

In connection with our discussions at the Denver Seminar, you may find the attached useful. Comment B-5, in particular, refers to our experience with centrifugation as a method of breaking emulsions.

Please let me know if you need further information.

John W. Way
Research Supervisor

JWW/td
Attach.

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

TAD

cc: JBColeman, ICD, W
RCOtt, ICD, W
GDBarbaras

Industrial Chemicals Department
Research & Development Division
Experimental Station

October 5, 1977

TO: J. W. WAY

FROM: R. T. ITEN

OBSERVATIONS ON THE USE OF THE EPA SAMPLING AND ANALYSIS PROCEDURES FOR PRIORITY POLLUTANTS (PP's) IN INDUSTRIAL EFFLUENTS - EPA METHOD ISSUED 4/18/77

A. VOLATILE ORGANICS

1. Samples must be taken in specially cleaned glass bottles with Teflon® lined caps and analyzed within 14 days (refrigerate). No air bubbles are allowed in the bottle.

2. Pure water has to be prepared from distilled water passed over absorbent charcoal and stored in special clean glass bottles with Teflon® lined tops.

3. Tekmar Concentrator trap supplied in some cases cannot be used with the standard silica gel and Tenax GC - new columns must be made using Tenax GC only.

4. Tenax GC must be conditioned at least 16 hours at 350° C (Tekmar conditions it at 200°C).

5. Samples standards and work-up must be done in a lab separate from the analysis and pure water prep area.

6. Blank Water (and pure water from lab) sample must accompany sample and be treated the same.

7. Tekmar should be kept at 250° in trap bake mode overnight after running samples and also at least 15 minutes between samples (also before initial use).

8. Desorption tubes (sample tubes) should be cleaned with special water and baked 120°C between uses.

9. All gas supply lines should be cleaned and baked out before installation and only ultrapure Helium used.

10. Computer should have all PP's in search file.

11. All syringes should be cleaned only with the special high purity water, or non-PP high volatility solvents.

B. ACID AND BASE/NEUTRAL SAMPLES (see also all of part A)

1. Require 2 to 4 liters for each type of analysis.

2. Require 2 liters blank water as reference.

3. No stopcock or other lubricants can be used anywhere in the anlysis system. Only glass & Teflon® equipment may be used. (As in part A, all supply gases must be pure and delivered through clean gas lines.)

4. Sodium sulfate used for drying $MeCl_2$ extracts should be heated to 500°C for 2 hours and 1 lb. for each sample then washed with two 100 ml portions of $MeCl_2$ which is saved and analyzed as a composite. (Drying column is a one liter cylindrical separatory funnel with glass wool in bottom to hold 1 lb. of Na_2SO_4).

5. The $MeCl_2$ extraction step results (probably in most cases) in an emulsion which can only be broken by centrifugation in closed centrifuge tubes (Teflon® seals). IEC HN-S centrifuge 1800 RPM 50 ml cups 30 min.

6. Combined extracts should be followed through Na_2SO_4 drying column with two 100 ml portions of $MeCl_2$ which is added to total extract.

7. Note that all the precautions observed in A must also be observed here. Standards, especially, must be prepared under isolation and refrigerated as noted in procedures.

8. The use of a GC integrator is helpful in calculation of the quantitative data.

Mobil Oil Corporation

150 EAST 42ND STREET
NEW YORK, NEW YORK 10017

November 2, 1977

Robert B. Schaffer, Director
Effluent Guidelines Division (WH-552)
U.S. Environmental Protection Agency
401 M St., S.W.
Washington, D. C. 20460
Attn: Robert Dellinger

cc: Leon H. Myers
Arnold S. Vernick

TOXIC SUBSTANCES SURVEY
MOBIL REFINERY DATA
(AUGUSTA, KS.)

Dear Mr. Dellinger:

We have completed our review of both the priority pollutant data for "Refinery F" published in the September 30, 1977 Burns & Roe preliminary draft report and the "Refinery 6" section of the R. S. Kerr Environmental Research Laboratory screening survey report on the petroleum refining industry.

The purposes of this letter are to 1) draw comparisons between the Burns & Roe results and the Mobil data obtained on separate samples taken concurrently with the April 6-8, 1977 EPA sampling, 2) comment on certain observed deficiencies of the gas chromatography/mass spectrometer (GCMS) analytical protocol utilized by EPA, and 3) offer a few clarifying remarks for incorporation in the final R. S. Kerr Laboratory report.

The attached Tables 1, 3 and 4 present comparative data for any priority pollutant detected at Augusta by either EPA or Mobil. Table 2 provides an in-depth analysis (GCUV vs. GCMS) of the polynuclear aromatics (PNA) group of priority pollutants found in the base-neutral extractible semivolatiles.

Finally, our comparison and comments on analytical results for eight NPDES pollutant parameters (Burns & Roe page IV-31, Table IV-8) appears as the attached Appendix A.

Summary

- Table 1 presents comparative data for any volatile or semivolatile priority pollutant detected by either Mobil or EPA. In general, the data presented in Table 1 for those compounds that were detected by both Mobil and EPA agree to within a factor of 3 which is quite reasonable considering the low pollutant levels encountered.

- Overall, Mobil analytical methodology for the semivolatile pollutants enabled us to detect these pollutants at much lower levels than the protocol used by EPA. The two major factors contributing to this sensitivity advantage were (a) extracting a larger volume of water (15-20 liters vs. 2 liters), (b) evaporating more of the solvent to provide a more concentrated extract. Thus, whereas the EPA procedure detected only a total of five semivolatile pollutants in the Augusta water samples, twenty semivolatile pollutants were observed by the Mobil procedures. With the exception of two phenolic pollutants, all the priority pollutants observed by Mobil that were not detected by EPA, occur at concentrations less than 10 ug/l.

- Our major concern with the data reported by the EPA is the apparent failure to recognize certain deficiencies of the GCMS analytical protocol with regard to detection of several PNA priority pollutants. For example, the EPA data state, without any reservations, that chrysene and benzo(a)pyrene, BaP, are found in all three Augusta water samples. We maintain that the GCMS technique cannot unambiguously distinguish phenanthren from anthracene, chrysene from benzo(a)anthracene (BaA), or benzo(a)pyrene (BaP) from perylene. The EPA data for the base neutral priority pollutants should definitely be amended to reflect the facts that chrysene and BaA as well as BaP and perylene are indistinguishable. Mobil recognized the inadequacy of the GCMS protocol for the PNA class of priority pollutants and simultaneously carried out GCUV measurements on these compounds. Table 2 compares the GCUV results with both Mobil and EPA GCMS data. For both the cooling tower effluent (CTE) sample and the effluent from the oxidation pond (EOP) sample, the results obtained for benzo(a)pyrene by the more definitive GCUV technique are lower by close to a factor of 10 than the GCMS values.

Specific Comments

Comparisons between Mobil and EPA (Burns & Roe) results are treated below:

Methylene Chloride

EPA detected methylene chloride at levels of <10, 70, and <10 ug/l in the IPBS, CTE, and EOP samples respectively. However, the EPA blanks from these same three sites also contained methylene

chloride at the 50, ~10, and 50 ug/l level. The presence of methylene chloride in the EPA blanks at these levels suggests contamination of the samples in either the sampling or the analysis.

Mobil detected methylene chloride only in the IPBS sample at the 5 ug/l level.

Carbon Tetrachloride

Carbon Tetrachloride was detected by EPA at a concentration of greater than 50 ug/l in the IPBS sample. No carbon tetrachloride was detected by EPA in either the CTE or the EOP samples. The EPA blanks were likewise free of carbon tetrachloride. Mobil did not detect carbon tetrachloride in any of the Augusta samples including the duplicate EPA samples supplied to us by the EPA sampling team. It should be emphasized that the halogen selective gas chromatographic detector that was employed for the volatile organics analyses could detect carbon tetrachloride at the 1 ug/l. We feel that the detection of carbon tetrachloride by EPA is most likely a result of contamination within their analytical laboratory.

1,1,1-Trichloroethane

Agreement between Mobil and EPA for this priority pollutant is excellent. The compound was observed only in the IPBS sample - Mobil obtained 55 ug/l, EPA reported greater than 50 ug/l.

Benzene, Toluene and Ethylbenzene

The agreement for these three volatile organics between Mobil and EPA is quite reasonable. Neither Mobil nor EPA detected any of these aromatic hydrocarbons in the CTE or EOP samples. Mobil reported levels of 6, 14 and <0.5 ug/l for benzene, toluene, and ethylbenzene respectively in the IPBS sample, whereas EPA did not detect any of these hydrocarbons. The reason for the discrepancy on this site most likely is due to the fact that EPA utilized a GCMS technique for identification and quantitation as compared to the less specific flame ionization detector (FID) employed by Mobil. In this regard, the Mobil values should be considered strictly as upper limits.

Robert B. Schaffer
Director

November 2, 1977

Acid Extractable Semi Volatiles

EPA did not detect any priority pollutants in the acid extractable semivolatile category whereas Mobil observed three; namely, phenol, 2,4-dimethylphenol, and p-chloro-m-cresol. Phenol was observed in the Mobil EOP sample at a concentration of 59 ug/l. The EPA detection limits for the acid extractables vary from 10 to 100 ug/l depending on the nature of the other functional groups. For phenol and 2,4-dimethylphenol the detection limit is reported to be about 10 ug/l, and so EPA's inability to detect these components in the IPBS and the CTE samples is understandable. The fact that they did not see phenol in the EOP sample may be due to the manner in which EPA prepared their composite sample prior to extraction. Unlike the Mobil procedure, wherein all the water taken at a particular site over the three day sampling period was extracted, the EPA protocol called for withdrawing aliquots from each of the three 24-hour composite samples and then extracting this blended composite. In this procedure trace components could be easily lost to the glass walls of the original sample container, and we would expect that adsorption of trace organics would be most severe for highly functional compounds such as the phenols.

PNA's

In addition to our major concern noted in the summary regarding the ambiguities of the EPA GCMS protocol for accurate identification of certain PNA's, there are other cases where Mobil & EPA data differ by more than a factor of 3 that deserve comment. First, the Mobil and EPA GCMS data for the compound fluoranthane in the IPBS sample differ by close to a factor of 10. Mobil determined 3.4 ug/l whereas EPA observed 29 ug/l. However, the Mobil GCMS value of 3.4 ug/l is in excellent agreement with the Mobil GCUV value of 4.6 ug/l. In a similar fashion the EPA level of 10 ug/l for pyrene in the CTE sample is higher than the Mobil value of 2.9 ug/l. Here again the Mobil GCUV value of 2.6 ug/l is in excellent agreement with the Mobil GCMS result. These cases given added credibility to the accuracy of the Mobil data.

Pesticides

The EPA subcontractor, Rykman, Edgerly, Tomlinson & Associates (RETA), tentatively reported that δ -BHC, a chlorinated pesticide was "possibly" in the Augusta effluent. This tentative identification must be confirmed by GCMS and until confirmation is obtained this identification should be suspect. Our GCMS survey failed to detect any pesticides in the Augusta water samples.

Mobil

Robert B. Schaffer
Director

November 2, 1977

The following comments relate to the R. S. Kerr Laboratory draft report:

1. Refinery #6, page 2 - penultimate paragraph, last sentence: Replace "Sludge from .... soil farming" with "Oil recovered from the oil skimming pond is treated to remove recoverable oil. Sludge from the treating process is used for soil farming".

2. Figure 2, title should read "REFINERY WASTEWATER FACILITIES".

Please feel free to contact me if you have any questions.

C. W. Phillips /smj

C. W. Phillips

SMJackson/vah
Attachments

Table 1

Augusta Refinery Toxic Substances Survey
Comparison of Mobil and EPA Data for Priority Pollutants

Compound Name(s)	IPBS		CTE		EOP	
	Mobil µg/l	EPA[d] µg/l	Mobil µg/l	EPA[d] µg/l	Mobil µg/l	EPA[d] µg/l
Volatile Organics						
Benzene	6	ND	ND	ND	ND	ND
Toluene	14	ND	ND	ND	ND	ND
Ethylbenzene	< 0.5	ND	ND	ND	ND	ND
Carbon Tetrachloride	ND	> 50	ND	ND	ND	ND
Methylene Chloride	5	< 10	ND	70	ND	< 10
1,1,1-Trichloroethane	55	> 50	ND	ND	ND	ND
Acid Extractables						
Phenol	4	ND	6	ND	59	ND
2,4-dimethylphenol	5	ND	11	ND	8	ND
p-chloro-m-cresol	ND	ND	ND	ND	0.2	ND
Base Neutral Extractables						
bis(2-ethylhexyl)phthalate	5	ND	2.2	ND	10	ND
PNA's[a]						
Naphthalene	3.6	ND	ND	ND	0.1	ND
Acenaphthylene[c]	ND	ND	ND	ND	ND	ND
Acenaphthene	5	ND	ND	ND	ND	ND
Fluorene	9.6	ND	ND	ND	ND	ND
Phenanthrene + Anthracene	146	164	4.4	1.8	0.4	ND
Fluoranthene	3.4	29	ND	ND	0.2	ND
Pyrene	65	143	2.9	10	0.5	ND
Chrysene + Benzo(a)Anthracene	76	48	16	6.5	1.4	0.8
Benzo(b)Fluoranthene + Benzo(k)Fluoranthene	6.4	ND	1.8	ND	< 0.2	ND
Benzo(a)Pyrene + Perylene	54(b)	33	16	9.5	2.2	1.3
Indeno(1,2,3-cd)Pyrene	0.8	ND	1.0	ND	ND	ND
Dibenzo(a,h)Anthracene[c]	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)Perylene	5	ND	2.4	ND	ND	ND
Pesticides						
BHC	ND		ND		ND	trace[e]

(a) Mobil Data on PNA's is data determined by the GCMS technique.
(b) For this site only, BaP and perylene were individually determined by GCMS, BaP = 16 µg/l, perylene = 38 µg/l.
(c) This component was detected by GCUV.
(d) Data obtained by Burns & Roe.
(e) Preliminary EPA data that is based on GCEC.

Table 2

Augusta Refinery Toxic Substances Survey
Comparison of Mobil GCUV with Mobil and EPA GCMS for PNA's

	IPBS			CTE			EOP		
	Mobil GCUV	Mobil GCMS	EPA GCMS	Mobil GCUV	Mobil GCMS	EPA GCMS	Mobil GCUV	Mobil GCMS	EPA GCMS
Naphthalene	-	3.6	ND	-	ND	ND	-	0.1	ND
Acenaphthylene	1.5	< 0.1	ND	< 0.2	ND	ND	-	ND	ND
Acenaphthene	-	5	ND	-	ND	ND	-	ND	ND
Fluorene	3.2	9.6	ND	< 0.2	ND	ND	-	ND	ND
Pheranthrene	154	146	164	< 0.1	4.4	1.8	< 0.7	0.4	ND
Anthracene	13			1.5			< 1.2		
Fluoranthene	4.6	3.4	29	0.3	ND	ND	< 0.2	0.2	ND
Pyrene	69	65	143	2.6	2.9	10	0.4	0.5	ND
Chrysene	35	76	48	< 0.02	16	6.5	< 0.1	1.4	0.8
Benzo(a)Anthracene	30			8.6			0.3		
Benzo(b)Fluoranthene	1.5	6.4	ND	0.3	1.8	ND	< 0.4	< 0.2	ND
Benzo(k)Fluoranthene	< 0.1			< 0.1			< 0.6		
Benzo(a)Pyrene	-	16 (b)	33 (a)	1.9	16 (a)	9.5 (a)	< 0.1	2.2 (a)	1.3 (a)
Indeno(1,2,3-cd)Pyrene	<0.2	0.8	ND	< 0.1	1.0	ND	< 0.6	ND	ND
Dibenzo(a,h)Anthracene	0.5	ND	ND	0.1	ND	ND	< 0.6	ND	ND
Benzo(g,h,i)Perylene	3.8	5	ND	1.5	2.4	ND	< 0.7	ND	ND

(a) BaP and Perylene cannot be distinguished for these sites; this is a combined value.

(b) For the IPBS sampling site, Mobil was able to detect 38 ppb of perylene (molecular 252) as well.

TABLE 3

ANALYTICAL RESULTS FOR PRIORITY POLLUTANTS
CYANIDES, PHENOLICS, & MECURY
PAGE IV-41, TABLE IV-13, BURNS & ROE DRAFT REPORT

Cyanides mg/l

	Intake	CTB	Final Effluent
B&R	L0.03	0.52 to 0.83	0.06 to 0.08
Mob	0.00 average	0.02 average	0.02 average

Mobil results indicate much lower concentrations than Burns & Roe report. We believe this is significant and recommend that additional sampling and analysis should be carried out prior to statement of the cyanide content of water a Refinery F.

Phenolics mg/l

	Intake	CTB	Final Effluent
B&R	0.21	0.042 to 0.056	0.023 to 0.056
Mob	0.190 average	0.037 average	0.015 average

The interlaboratory agreement is acceptable.

Mercury mg/l

	Intake	CTB	Final Effluent
B&R	.0002 to .0009	.0004 to .0007	.0003 to .0004
Mob	0.000	0.000	0.000

Mercury content is shown to be less than one part per billion by all analyses of Refinery F water samples.

TABLE 4

ANALYTICAL RESULTS FOR PRIORITY POLLUTANTS
METALS
PAGE IV-46, TABLE IV-14, BURNS & ROE DRAFT REPORT

Silver ug/l

	Intake	CTB	Final Effluent
B&R	L5 to L250	L5 to L250	L5 to L25
Mob	ND	ND	ND

Silver was not detected in any analysis.

Beryllium ug/l

	Intake	CTB	Final Effluent
B&R	L2 to L26	L2 to L3	L2 to L3
Mob	ND	ND	ND

Beryllium was not detected in any analysis.

Cadmium ug/l

	Intake	CTB	Final Effluent
B&R	L1 to L200	L1 to L20	L1 to L20
Mob	ND	ND	ND

Cadmium was not detected in any analysis.

Chromium ug/l

	Intake	CTB	Final Effluent
B&R	60 to 72	44 to 79	7 to 73
Mob	59 average	38 average	15 average

Interlaboratory agreement is acceptable but range of Burns & Roe results for final effluent is rather high.

Copper ug/l

	Intake	CTB	Final Effluent
B&R	50 to 210	278 to 510	84 to 199
Mob	201 average	377 average	98 average

Interlaboratory agreement is acceptable.

TABLE 4 (cont'd)

Nickel ug/l

	Intake	CTB	Final Effluent
B&R	57 to 62	64 to 134	58 to 74
Mob	40 average	98 average	58 average

Interlaboratory agreement is acceptable.

Lead ug/l

	Intake	CTB	Final Effluent
B&R	L15 to L600	L15 to L60	L15 to L60
Mob	3 average	5 average	1 average

Interlaboratory agreement is acceptable.

Zinc ug/l

	Intake	CTB	Final Effluent
B&R	120 to 133	229 to 452	100 to 151
Mob	217 average	300 average	177 average

Mobil results may be somewhat high which suggests rechecking sampling and calibration.

Arsenic ug/l

	Intake	CTB	Final Effluent
B&R	27	41	31
Mob	15 averate	24 average	16 average

Interlaboratory agreement probably is acceptable although Burns & Roe results generally are higher than Mobil.

Antimony ug/l

	Intake	CTB	Final Effluent
B&R	L25	L25	L25
Mob	6 average	8 average	9 average

Interlaboratory agreement is acceptable.

Mobil Research and Development Corporation

RESEARCH DEPARTMENT
PAULSBORO, NEW JERSEY 08066

C. H. LECHTHALER
MANAGER
PROCESS RESEARCH AND
TECHNICAL SERVICE

November 17, 1977

Mr. William A. Telliard
Energy & Mining Branch/EGD (WH552)
U.S. Environmental Protection Agency
Room 907, East Tower
401 "M" Street, S.W.
Washington, D.C. 20460

Dear Mr. Telliard:

EPA SEMINAR ON ANALYTICAL METHODS
DENVER, COLORADO
NOVEMBER 9-10, 1977

As you requested, I have prepared the enclosed amplification of comments I made at the Denver seminar. Please feel free to contact me if you have any questions.

Very truly yours,

F. P. Hochgesang

mm
enclosure

cc: P. L. Gerard
C. W. Phillips

Supplementary Comments to Verbal Presentation by F. P. Hochgesang at EPA Seminar on Analytical Methods, November 9 & 10, 1977

Agenda Item IIA2

Acid Extractables - Phenolic Compounds

2,4-Dimethylphenol is only one of a group of 9 possible C-2 substituted phenolic compounds which may be found near the same GC/MS scan number. These phenolics are poorly resolved on packed GC columns. A SCOT column (70 meters x 0.5 mm ID glass; SE 30, silanized and deactivated) does resolve the unknown mixture to the extent that five peaks sometimes appear. The tentative identification of these five peaks in order of elution from the above SCOT column is:

1. 2,6-Dimethylphenol
2. 3,5 + 2,3-Dimethylphenol and 3 + 4-ethylphenol
3. 2,4 + 3,4-Dimethylphenol
4. C-2 alkylphenols
5. C-2 alkylphenols

Base/Neutral Extractables - Polynuclear Aromatics

Benzo(a)pyrene usually is found in the same GC/MS scan as perylene. GC/UV can distinguish each of the above PNA isomers and our experience indicates that perylene usually is present in higher concentration than benzo(a)pyrene. Other PNA's also appear as pairs when the EPA analytical protocol is used. Therefore we suggest that the component names applied to the EPA GC/MS protocol should be as follows:

Anthracene + Phenanthrene
Benz(a)anthracene + Chrysene
Benzo(a)pyrene + Perylene
Benzo(b)fluoranthene + Benzo(k)fluoranthene

Further, experience to date indicates that the concentrations of fluoranthene and pyrene as determined by the EPA subcontractor are higher than those values determined by Mobil. The Mobil data for these components when determined by both GC/UV and GCMS are in excellent agreement, but have been found to be 4 to 8 times lower than the EPA GC/MS values. We do not know the reason for these differences between the Mobil and EPA values for fluoranthene and pyrene at this time. We suggest that spiked samples be studied carefully in the validation and verification phases.

SHELL DEVELOPMENT COMPANY
A DIVISION OF SHELL OIL COMPANY
WESTHOLLOW RESEARCH CENTER
P. O. Box 1380
Houston, TX 77001

December 15, 1977

Mr. William A. Telliard
United States Environmental Protection Agency (WH552)
401 M St. S.W.
Washington, D. C. 20460

Dear Sir:

We are appreciative for the opportunity to have had P. A. Wadsworth and G. H. Stanko participate in the EPA Effluent Guidelines Division seminar on November 9 and 10 in Denver, Colorado.

At the seminar, some analytical work that had been done on compositing samples in the VOA apparatus and on the effect of storage time for VOA (vials) samples was disclosed. Also discussed, were a number of problems and modifications that have been made to the Tekmar LSC-1 unit. Enclosed, per your request are some of the data relating to the VOA analytical procedure and a schematic of some of the modifications made to the LSC-1 unit.

Attachment I and II indicate that one can composite VOA samples in the apparatus. The compositing technique reduces the number of individual analyses that are required to characterize a wastewater sample for a 24-hr period. However, Attachment II shows one of the disadvantages of the compositing technique. The individual VOA analyses revealed short term differences that probably would not have been detected by the compositing technique. Attachment II also indicates some of the potential problems of taking single grab samples in an attempt to define typical operations.

We have very limited data available on the storage of petroleum/chemical wastewater samples in VOA vials. Normally, our VOA samples are analyzed within three days from collection. Manpower limitations and backlog did not allow for a more thorough investigation. We collected a number of vials of a wastewater and ran VOA by GC/MS on days 0, 7, and 20. Examination of the mass spectra showed significant reductions in concentrations for many of the compounds for the sample run on the 20th day of the study. No significant differences were observed for the 7th day sample. The EPA Laboratory (EMSL) at Cincinnati indicated VOA vials can be safely stored at 4°C up to 14 days. The limited data that we have appears to be consistent with the Cincinnati recommended storage time.

Attachment III is the schematic which shows the modifications that have been made to the Teckmar LSC-1 unit. A number of additional changes were made that are not shown on the schematic. The brass/O-ring fittings on the sampler (glass) have been replaced with stainless steel fittings with Teflon ferrules. This change was necessary to eliminate a memory effect that was being observed. The samplers are cleaned off-line and then vacuum baked. Intractably dirty samplers are discarded. In order to eliminate still additional sources of memory effects, the stainless steel tubing and the six-port valve are all heated with electrical heating tapes. The temperature of the points indicated are monitored with thermocouples using a Doric 402A-J/C Trendicator.

We believe that our future participation in seminars such as was held in Denver to be of significant value to all concerned and we wish to again express our appreciation for the opportunity to have recently participated in such a seminar.

Very truly yours,

M. J. O'Neal

GHS/PAW/thc

M. J. O'Neal, Manager
Analytical - Chemical/Oil Department

cc: Judith G. Thatcher - API/DEA
Carl A. Gosline - MCA Staff
Ron O. Kagel - MCA/Dow

TEST OF COMPOSITING SAMPLE IN VOA APPARATUS

SAMPLE: REFINERY WASTEWATER

	CONCENTRATION, PPM. WT.	
SAMPLE	A	B
1430 3/15/77	4.50	2.83
2230 3/15/77	5.50	3.20
0630 3/16/77	6.36	5.79
AVERAGE	5.45	3.94
SAMPLE COMPOSITED IN VOA APPARATUS	5.83	3.02

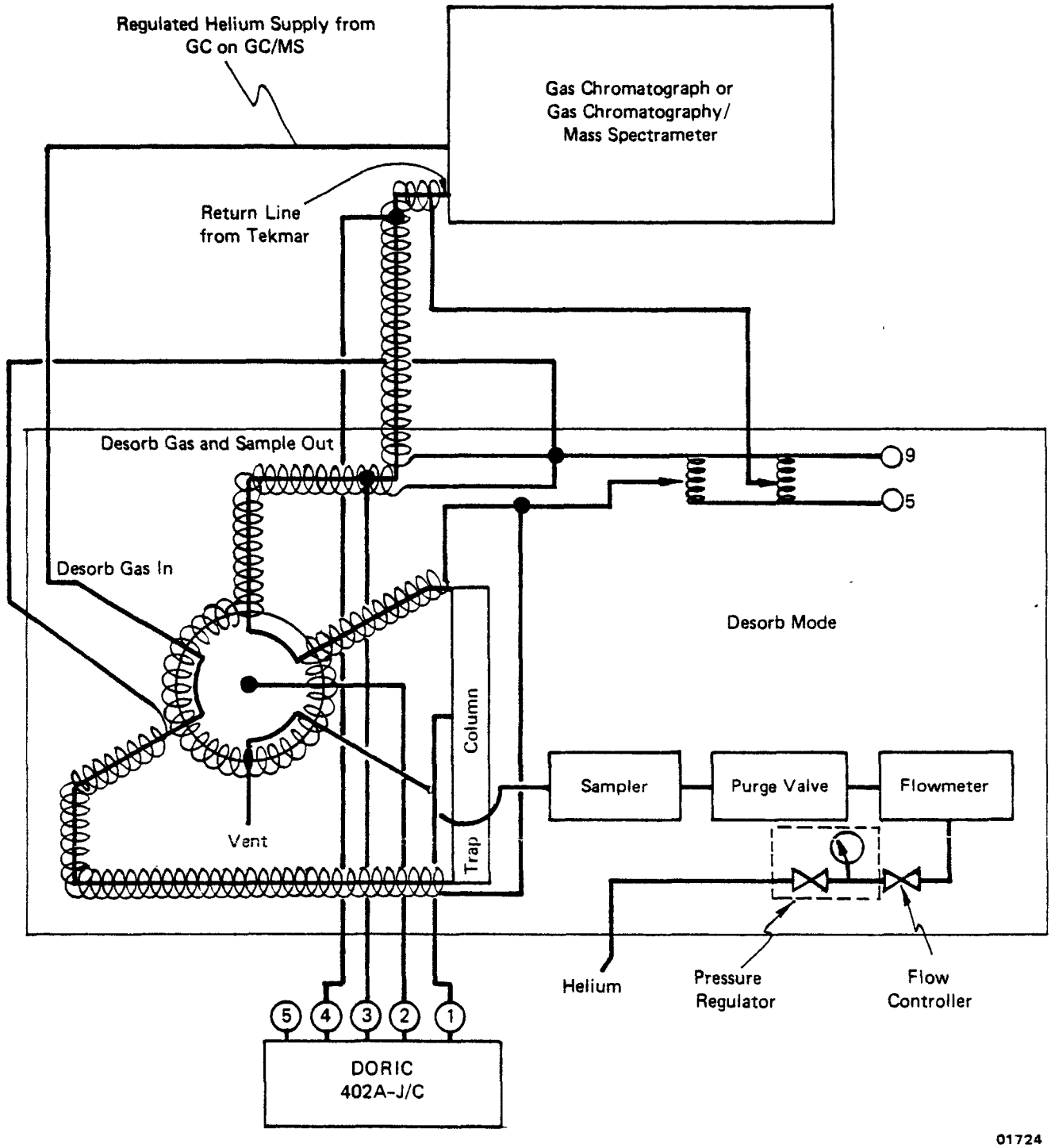
ATTACHMENT II

TEST OF COMPOSITING SAMPLE IN VOA APPARATUS

SAMPLE: PROJECT G

		COMPOUND CONCENTRATION, PPM. WT.		
		A	B	C
DAY 1	4/11	489.	0.081	0.063
DAY 2	4/12	370.	0.051	0.018
DAY 3	4/13	74.	0.011	0.010
AVERAGE		310	0.048	0.030
SAMPLE COMPOSITED IN VOA APPARATUS		354	------NOT CALCULATED------	

TEKMAR LSC-1 MODIFICATIONS



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: Comments on "Sampling and Analysis Procedure for Screening of Industrial Effluents for Priority Pollutants"

DATE: November 2, 1977

FROM: Robert D. Kleopfer, Ph.D., Chief, Organic Chemistry Section, SVAN-LABO CPH for
Charles P. Hensley, Acting Chief, General Analyses Section, SVAN-LABO CPH
William J. Keffer, P.E., Chief, Water Section, SVAN-TECH

TO: Files

Based on three months experience with sampling and analysis for the 129 priority pollutants, the Region VII Surveillance and Analysis Division has several comments to make concerning the guideline document which was provided by EMSL. Overall we feel that the recommended analytical protocol which was provided is a sound one. However, we did find some deficiencies and errors. Also, we have included some comments concerning the Radian consent decree standards which were provided by the Environmental Research Laboratory in Athens.

Organics by Purge and Trap

The recommended packing material as supplied by Supelco (Carbopack C/ 0.2%, Carbowax 1500 with a Chromosorb W/3% Carbowax 1500 precolumn) is not adequate for the analysis of chloromethane and dichlorodi-flurometnane which are the two most volatile compounds (boiling points of -24°C and -30°C, respectively) on the priority pollutant list. Discussions with Tom Bellar of EMSL indicate that the problem relates to variability in the quality of the packing material from batch to batch. Indications are that a batch which performs adequately has not yet been located.

Assuming an adequate analytical column were available, a modified purge method would be required for the analysis of dichlorodifluro-methane. In effect, this doubles the amount of time required to do all of the purgable compounds (from about 45 minutes to 90 minutes). We suggest that this compound be searched for only in selected samples. Bis(chloromethyl)ether cannot be analyzed by the purge and trap procedure. As noted in Table I of the procedure, the compound has a very short half-life in water and would not likely be found in a water sample anyway, considering that samples are at least 24-hours old before analysis begins.

In our laboratory, we have a difficulty with a methylene chloride background because of the large amounts of this solvent which are utilized in our extractions. In order to effectively deal with this problem, we store all of our volatile samples in sealed dessicators containing activated carbon. Nonetheless, we do routinely observe a methylene chloride background in most of the samples which we run. However, the background amounts to less than 20 PPB which is our reported detection limit.

Although in most instances for the purge and trap technique we can analyze successfully at concentrations much lower than 20 PPB, we are using that value as our lower detection limit. When compounds are detected at below that amount, it is considered a trace amount and indicated as such on the data sheet. Some of our recovery data for the purgable compounds are attached.

The mass spectrum for 1,1,1-trichloroethane does not have a base peak at mass 98 as indicated in Table II. The base peak is actually at mass 97.

Base/Neutral Compounds

An incorrect mass is given in Table IV for diethylphthalate. The correct mass for one of the characteristic EI ion should be 177 rather than 178. Mass 177 has a much greater relative abundance than mass 178.

According to published spectra, 2,4-dinitrotoluene does not have a significant mass 121 ion, which does occur for 2,6-dinitrotoluene. We suggest that the molecular ion (mass 182) be used for 2,4-dinitrotoluene.

The relative retention time, as reported in Table IV, is obviously incorrect for bis(2-chloroethyl)ether which would be expected to elute before bis(2-chloroisopropyl)ether. Also, the retention time for isoonorone is questionable. Retention times which we observed on an OV-17 column are attached.

All attempts to chromatograph 1,2-diphenylhydrazine in our laboratory resulted in a symmetrical peak giving spectra for azobenzene. In addition, the standard was analyzed using the solids probe for introduction into the mass spectrometer and spectra were obtained for both 1,2-diphenylhydrazine and azobenzene. The 1,2-diphenylhydrazine did not show significant peaks at masses 93 or 105 as indicated in Table IV. Azobenzene has significant ions at masses 77(100%), 105(40%), and 182(30%).

The mass spectrum for N-Nitroso-di-n-propylamine does not have a significant ion at mass 42. We suggest the use of mass 70 in its place.

The Region VII Laboratory has had much better performance utilizing a 3% OV-17 column compared with the recommended 1% SP-2250 column. A chromatogram demonstrating the separation attained on this column is attached along with a listing of the relative retention times.

Although we have been able to successfully chromatograph 40 nanograms of benzidine, our laboratory cannot consistently achieve this recommended performance level. We feel that this level is not practical for a high-volume laboratory.

The recommended analytical procedure is not adequate for the differentiation between certain isomeric pairs. These are anthracene and phenanthrene, chrysene and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene.

Extraction Recoveries

No provisions are made in the procedure for determination of the efficiency of the extraction process required for the base/neutral compounds, phenols, and pesticides. We feel that this is an important quality assurance technique which was overlooked. We have attached some recovery values which are based on a very limited number of runs. Note the zero recovery for hexachlorocyclopentadiene.

Phenols

Some of the relative retention times listed in Table V appear to be incorrect for the Tenax GC column.

The Tenax columns (glass) develop rather large gaps over a period of time and peak broadening occurs. The packing material hardens and the columns cannot be repacked.

Phenols analysis by the standard colorimetric method is a general analysis for a long list of phenol compounds. The list of priority pollutants has about eleven phenol compounds including phenol. Each of these compounds are analyzed for by gas chromatography. Since each compound is analyzed by GC, why analyze for a long list of phenol compound by a nonspecific method? By dropping this analysis, we would save about forty dollars per facility.

Data Storage

In order to minimize the amount of data storage on magnetic tape, we suggest that nothing be stored for those GC runs showing no discernable peaks. This would reduce the storage requirements by at least 25%.

Radian Consent Decree Standards

Ethylbenzene is not present in the purgable compounds standard as was indicated on the sheet supplied with the standard. Vinyl chloride, 2-chloroethylvinyl ether, and Bis(chloromethyl)ether are not present in the mix.

The data sheet does not indicate which isomer or isomers of 1,3-dichloropropylene are present in the mixture. The 2-chloroethylvinyl ether should be in the purgable standard rather than the base/neutral extractables. It is too volatile (B.P. = 109°) to analyze as an extractable compound.

The miscellaneous pesticides standard does not contain delta-BHC as indicated on the data sheet.

The Arochlor mixtures and the Toxaphene/Chlordane mixture have very little value in these analyses. The individual Arochlor formulations, Toxaphene, and Chlordane should be provided as separate standards.

The d_{10}-anthracene should be provided in a much more concentrated (x100) solution. Ten microliters per sample is required utilizing the 2000 PPM standard. The phenols mixture and the base/neutral extractables standard should be provided with 20 PPM of d_{10}-anthracene already included. This would facilitate determination of relative response ratios at one level.

We have been told that the concentrations for 4-Nitrophenol and 2,4-Dinitrophenol are incorrect as listed in the data sheet supplied by Radian. The correct values are 50 PPM and 1000 PPM, respectively.

Field Blank for Automatic Samplers

The only interferring contaminants which we have observed in the compositor blank samples have been trace amounts of di-n-butylphthalate and bis(2-ethylhexyl)phthalate. However, these have never been found at levels above our routine reported detection limit of 20 PPB. Therefore, we suggest that the number of compositor blank samples be reduced to one per sampling site (per plant). Of course, a blank should still be run ~~in the field~~ on every new batch of tubing which is used.

Sample Size

The recommended sample size for the extractable organics is two and one-half gallons. However, because of various field problems (batch discharges, etc.) it is not always practical to provide that much sample to the laboratory. Therefore, we are recommending that two liters be the minimum sample size which would be considered worthwhile to even ship back to the laboratory. This would allow analysis for the base/neutrals and the phenols.

Analytical Time Requirements

We estimate that the total time required to do the 114 organic compounds, 13 metals, and cyanide amounts to approximately four man-days per sample with the bulk of the effort (ca. 3.5 man-days) required for the organic compounds. This estimate does not include sample collection. The limiting factor for the rate of analysis (number of samples which can be analyzed per month) is GC/MS time. The Region VII Laboratory has been utilizing two work shifts in order to derive maximum benefit from our existing instrumentation. The GC/MS data output requirements with our present GC/MS configuration amounts to about five hours per sample. Thus, under ideal conditions (no instrumentation problems and no analytical problems) the maximum output amounts to three samples per day (16 hours). This number is further reduced to about two samples per day when one allows for quality assurance procedures (running of standards, etc.). The maximum rate for analysis of the priority pollutants is thus estimated to be 40 samples per month with one GC/MS/Data system being used 16 hours per day with zero down-time. This rate could be improved substantially for systems allowing data acquisition and data output to be performed simultaneously.

Metals

From our experience only copper and zinc should be first analyzed by flame atomic absorption. Other metals are usually present at very low concentrations and are analyzed for best by flameless atomic absorption.

"Green List" of Priority Pollutants

Compound #33 of the "Green List" is actually four different compounds - cis-1,2-dichloropropylene, trans-1,2-dichloropropylene, cis-1,3-dichloropropene, and trans-1,3-dichloropropene. The analytical procedure, however, does not refer to the 1,2-dichloropropylenes and it is not provided in the Radian standards. We assume that the 1,2-dichloropropylene on the "Green List" is a misprint.

Other Changes

1. Dilution Water - Due to the possibilities for contamination in the field, we will depart from the protocol requirement for a five liter blank flush of compositor lines for each setup. Blank flush water will be supplied by the laboratory in one-gallon containers. At the time of setup, a single one-gallon container will be opened minimizing exposure of the blank water to uncontrolled contamination. One and

one-half liters of blank water will be flushed through the tubing and disposed of and the ramaining two and one-half liters will be used as a blank for evaluation of contamination from tubing. It is suggested that the two and one-half liter portion be pumped from the one-gallon glass holding and blank water to a one-gallon glass jug emptied at the previous station. This procedure will eliminate the need for funnels and minimize opportunities for spillage and contamination.

2. Volatile Sample Containers - Handling of the volatile blanks and collection bottles is critical. It is recommended that these containers be refrigerated dry to the maximum extent possible including transport to and from sample sites and holding spaces.

3. Phenol Samples - All phenol samples will be collected, preserved, and handled according to routine Region VII procedures (one-liter cubi, $CuSO_4$ and H_3PO_4).

4. Cyanide Samples - All cyanide samples will be collected, preserved, and handled according to routine Region VII procedures (one-liter cubi, 10 pellets NaOH) with the following additions: (a) Litmus paper must be used to check for alkaline pH after preservation. (b) Where chlorination is practiced, the manipulation to zero residual prior to preservation will be done using the Hach DPD kits to be supplied by the laboratory and with ascorbic acid as the complexing agent according to the EGD protocol.

5. Three-Gallon Sample Bottle Tags - Field personnel will prepare and attach to the three-gallon containers, adequate tags for all analyses for priority pollutants and BATEA parameters to be determined from the composite. As a minimum, the following tags will be attached to the composite bottle:

Manila - BOD_5, COD, pH, cond
Manila - NFS, (Cl, SO_4, if needed)
Yellow - NH_3-N, TKN, NO_2-NO_3-N, Total P
White - Do not list metals to be analyzed for, if it is covered by the priority pollutant list.
Blue - Organics

6. Dissolved Parameters - In those few cases where dissolved parameters analyses are required, field personnel will be required to use an aliquot from the three-gallon sample and provide field filtration and preservation in separate containers.

7. Teflon Tubing - Teflon tubing is used for sample intake line to the automatic compositor. The Teflon tubing is shipped back to

Region VII Laboratory, cleaned, and capped with aluminum foil before being used at a different sample site. This has worked very well for field operating procedures.

8. Data Handling - See attached memorandum dated October 6, 1977.

9. Instead of shipping blank volatile organic water samples to and from the sampling site, our laboratory will perform a weekly blank check on glassware and distilled water.

Attachment

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: October 6, 1977

SUBJECT: Data Handling and Reporting Procedures for Effluent Guidelines Division

FROM: Robert L. Markey
Director, Surveillance and Analysis Division, Region VII

TO: Mr. Robert B. Schaffer
Director, Effluent Guidelines Division, WH-552

The Region VII SVAN Division, in conjunction with the Data Processing Branch, has developed a complete data transfer, storage, and retrieval system including quality control checks which now handles up to 100,000 data points per year and maximizes the utilization of computer storage, collating, and retrieval of the data. This system was developed in response to needs of the NPDES program chain of custody requirement and complies with the national program as outlined in the NPDES Compliance Sampling Manual (Exhibit 1). Complete details for normal application of this procedure are contained in the Water Section Data-Handling System memorandum (Exhibit 2). Much of the potential for data turnaround is due to the development of the local data system, Laboratory Management System (LAMS).

The LAMS data system is a Region VII system to accumulate and edit data before it is released to the user or to the Storet system. The Laboratory Management System is operational on the COMNET IBM-370/168 system. COMNET, in Washington, D.C., is the vendor for our data system. The LAMS programs are stored on the vendor's USER and WORK disks and on Regionally dedicated 3330-II disks. The Data Processing Branch is responsible for the keypunching of all input data. The Data Processing Branch inputs data with a Data 100 terminal in the Regional Office. To input data to the system we need three records: (1) a station location sheet that describes the location of the sample site in space, (2) a field sheet that assigns a laboratory number to information such as flow, sampling personnel codes, sampling equipment codes, field measurement, and analyses requested, and (3) a laboratory bench card that gives the analytical results for each sample.

After the analyses are completed, a LAMS Report printout is given to the laboratory for editing. After all corrections are made, the laboratory releases the data to the user.

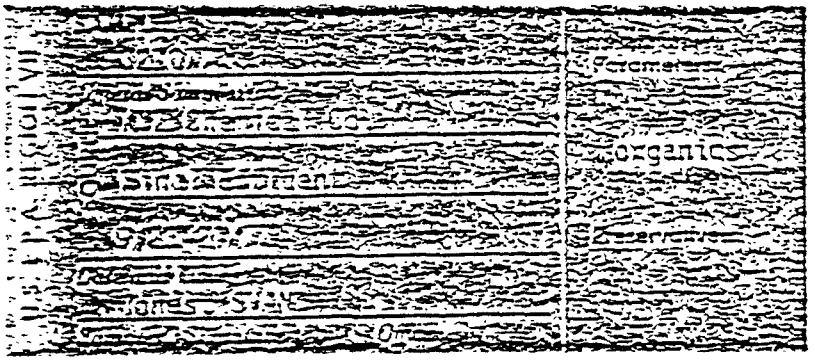
With the advent of the sample collection efforts for EGD, we have encountered for the first time the need to accomodate confidentiality of the data for certain samples. The addition of contractor laboratories participating in portions of the analytical effort also adds a new aspect to our system. It is our intent to identify key potential problem areas and recommended solutions for your review in this

EPA Form 1320 6 (Rev. 3-76)

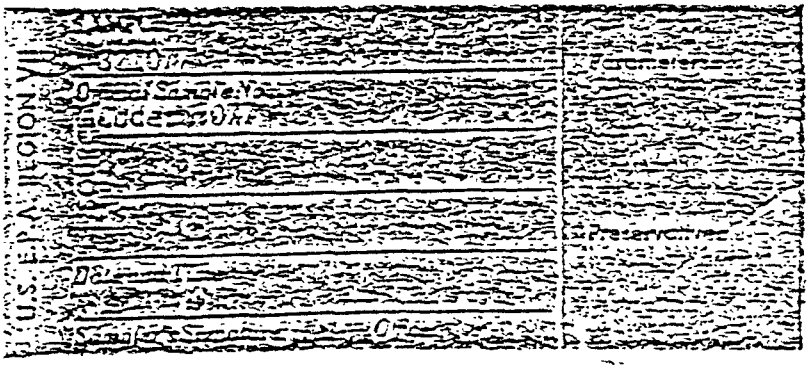
submittal. In accordance with verbal directions received from John Newbrough on October 3, 1977, we will cease sampling activities at specific process line effluents where confidentiality requests from the discharger are expected until your staff has had an opportunity to prepare a completely satisfactory program based on this package we are submitting.

1. The field collection, handling, and shipment procedure under normal chain of custody is considered adequate and no procedural modifications need be made prior to receipt of samples at the regional laboratory.

2. Samples collected by the EPA field crews identify the individual facility sampled as well as specific sites at the facility in order to provide assistance to laboratory personnel in establishing desirable levels for specific analyses and for comparing multiple samples from a given site. An example of these tags is given below:



All samples going to the contract laboratories are tagged and checked through our organics laboratory unit. These samples are retagged by laboratory personnel with only the laboratory number and an industrial code number. As shown below, the contract laboratory will only know that they received a sample from Region VII from the petroleum industry with the lab number 321077.



Samples for contractor analyses are stored in a specific area away from other samples and work in progress to prevent any access to in-house samples by contractor personnel.

3. The regional laboratory facility is reasonably secure. Environmental Protection Agency, SVAN personnel are the sole tenants; and a four-digit combination lock entry system is provided to restrict entry. Facility security could be improved significantly by more frequent changes of the combination and more restricted distribution of the access number outside of SVAN. Ideally, access to the building should be controlled by a contract guard/ID system on a 24-hour per day basis. Such a system would provide a major improvement over the alternative choice which would require a multiple system of safes and for secure file cabinets in at least six areas of the lab to cover such items as field sheets, draft reports, custody sheets, bench cards, samples and data printouts, and a consequent major loss of efficiency and increase in space commitment which could be used for better purposes.

4. As indicated earlier, the LAMS system is an in-house system requiring several access codes to reach the data and is a major element in our overall data handling system. It is essential that we maintain the LAMS system in order to handle the volumes of data in an effective manner. The potential confidentiality by utilization of a password access requirement by minor modifications in the station locator cards and by a more rigid control system on transfer and release of the data output and elimination of the data from the storage system. These changes are being implemented and will result in rigid documentation of the data management by the SVAN Data Coordinator and verified erasing of all results from LAMS on a timely basis after the final copy is approved.

5. For the organic parameters, the first numerical data are produced when the organic chemist interprets the gas chromatogram and mass spectral data. All of these numerical data are recorded on one set of summary sheets. The data coordinator will keep these sheets secure until they are transmitted to EGD by a chain-of-custody sheet.

All mass spectrograph data are stored on magnetic disks. These disks will be transmitted to Athens, Georgia, by chain-of-custody. The Athens Laboratory will transfer these data to 9-track tapes and erase the disks. The erased disks will then be returned to Region VII.

6. It is our suggestion that individual sample data from the contractor analyzed samples be returned to the Region VII laboratory for quality control review and compilation with all other samples from a given facility in order to develop an easily understood

single data package for each facility with an explanation of the technical aspects of the field effort.

7. All field records, notes, facility descriptions, and other information utilized by the field personnel for sample collection efforts are held in a separate file within the SVAN facility prior to being notified by EGD of the desired disposition of these items.

8. At the completion of the Region VII portion of the monitoring effort, it is our intent to deliver to EGD as confidential material in a separate envelope with return receipt requested. For each facility we will produce and deliver only a single copy of the complete facility field data and the laboratory data package marked confidential with all subsequent distribution to be handled by EGD. This includes supplying NPDES permit data to the appropriate EPA Regional Office.

2 Attachments

EXHIBIT - 1

NPDES COMPLIANCE SAMPLING MANUAL

U.S. ENVIRONMENTAL PROTECTION AGENCY

ENFORCEMENT DIVISION

OFFICE OF WATER ENFORCEMENT

COMPLIANCE BRANCH

F O R E W O R D

The NPDES compliance inspection program represents a significant commitment of resources by the States and EPA to the verification of permit effluent limitations and assurance that permit requirements for monitoring, reporting and compliance schedules are being met and enforced on a nationally consistent basis. While compliance inspections make up only one segment of the overall national water enforcement program, they are highly visible and may be the only direct contact that the permittee has with regulatory personnel. Thus, compliance inspections must be performed in a thorough, professional manner, with nationally consistent coverage of key compliance elements. Reporting of inspection data must also cover the key compliance elements so that the data derived from this program can be aggregated nationally, regionally and by States for purposes such as program assessment, budget development and reporting to Congress.

The previously distributed NPDES Compliance Evaluation Inspection Manual (CEI) described the objectives and procedures for performing non-sampling inspections. The NPDES Compliance Sampling Inspection Manual (CSI) describes technically sound procedures, derived from the first hand experience of EPA and State personnel directly involved in compliance inspections, for the collection of representative samples, flow measurement, sample handling and field quality assurance.

The CEI and CSI Manuals and the revised Compliance Inspection Report Form, in conjunction with the annual program guidance and other memoranda dealing with inspection policy, form the framework for the compliance inspection program. Following the procedures and policies outlined in these documents will improve the quality of NPDES compliance inspections, enhance the value of data derived from these inspections, and better serve the needs of the overall NPDES enforcement program.

The manual is made-up in a loose-leaf format so that revisions or additions can be easily accomodated. Any comments or additions you may wish to make should be directed to the Compliance Inspection Manual Review Committee, Compliance Branch (EN-338), Enforcement Division, Office of Water Enforcement, U.S. Environmental Protection Agency, 401 M Street, S.W., Washington, D.C. 20460.

June 1977

Assistant Administrator
for Enforcement

SECTION VIII - CHAIN OF CUSTODY PROCEDURES

A. Introduction

As in any other activity that may be used to support litigation, regulatory agencies must be able to provide the chain of possession and custody of any samples which are offered for evidence or which form the basis of analytical test results introduced into evidence in any water pollution case. It is imperative that written procedures be available and followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed. The primary objective of these procedures is to create an accurate written record which can be used to trace the possession and handling of the sample from the moment of its collection through analysis and its introduction as evidence.

A sample is in someone's "custody" if:

1. It is in one's actual physical possession; or
2. It is in one's view, after being in one's physical possession, or
3. It is in one's physical possession and then locked up so that no one can tamper with it; or
4. It is kept in a secured area, restricted to authorized personnel only.

B. Survey Planning and Preparation

The evidence gathering portion of a survey should be characterized by the conditions stipulated in the permit or the minimum number of samples required to give a fair representation of the wastewater quality. The number of samples and sampling locations, determined prior to the survey, must satisfy the requirements for NPDES monitoring or for establishing a civil or criminal violation.

A copy of the study plan should be distributed to all survey participants in advance of the survey date. A pre-survey briefing is helpful to reappraise survey participants of the objectives, sampling locations and chain of custody procedures that will be used.

C. Sampling Collection, Handling and Identification

1. It is important that a minimum number of persons be involved in sample collection and handling. Guidelines established in this manual for sample collection, preservation and handling should be used. Field records should be completed at the time the sample is collected and should be signed or initialed, including the date and time, by the sample collector(s). Field records should contain the following information:

(a) unique sample or log number;

(b) date and time;

(c) source of sample (including name, location & sample type);

(d) preservative used;

(e) analyses required;

(f) name of collector(s);

(g) pertinent field data (pH, DO, Cl residual, etc.);

(h) serial numbers on seals and transportation cases.

2. Each sample is identified by affixing a pressure sensitive gummed label or standardized tag on the container(s). This label should contain the sample identification number, date and time of sample collection, source of sample, preservative used and the collector(s') initial(s'). Analysis required should be identified. Where a label is not available, the same information should be affixed to the sample container with an indelible, water proof, marking pen. Examples of sample identification tags are illustrated in Figure VIII-1.

3. The sample container should then be placed in a transportation case along with the chain of custody record form, pertinent field records and analysis request form as needed. The transportation case should then be sealed or labeled. All records should be filled out legibly in pen.

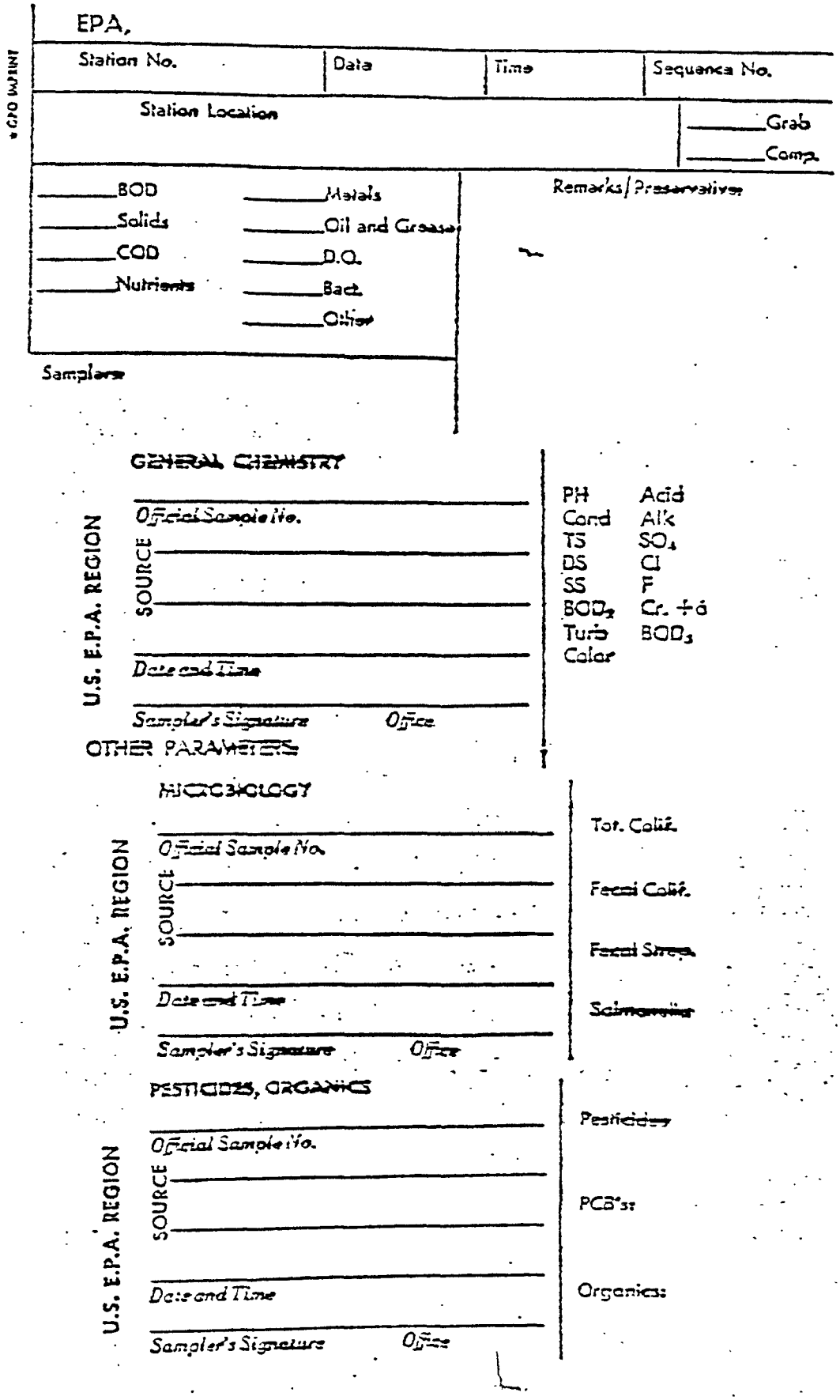


FIGURE VIII-1

SAMPLE IDENTIFICATION TAG EXAMPLES

The use of the locked and sealed chests will eliminate the need for close control of individual sample containers. However, there will undoubtedly be occasions when the use of a chest is inconvenient. On those occasions, the sampler should place a seal around the cap of the individual sample container which would indicate tampering if removed.

4. When samples are composited over a time period, unsealed samples can be transferred from one crew to the next crew. A list of samples will be made by the transferring crew and signed for by a member of the receiving crew. They will either transfer the samples to another crew or deliver them to laboratory personnel who will then acknowledge receipt in a similar manner.

5. Color slides or photographs taken of the sample outfall location and of any visible pollution are recommended to facilitate identification and later recollection by the inspector. A photograph log should be made at the time the photo is taken so that this information can be written later on the back of the photo or the margin of the slide. This should include the signature of the photographer, time, date, site location and brief description of the subject of the photo. Photographs and written records, which may be used as evidence, should be handled in such a way that chain of custody can be established.

D. Transfer of Custody and Shipment

1. When transferring the possession of the samples, the transferee must sign and record the date and time on the chain of custody record. Custody transfers, if made to a sample custodian in the field, should account for each individual sample, although samples may be transferred as a group. Every person who takes custody must fill in the appropriate section of the Chain of Custody Record. To prevent undue proliferation of custody records, the number of custodians in the chain of possession should be as few as possible.

2. The field custodian or field inspector, if a custodian has not been assigned, is responsible for properly packaging and dispatching samples to the appropriate laboratory for analysis. This responsibility includes filling out, dating, and signing the appropriate portion of the Chain of Custody Record. A Chain of Custody Record format containing the necessary procedural element is illustrated in Figure VIII-2.

3. All packages sent to the laboratory should be accompanied by the Chain of Custody Record and other pertinent forms. A copy of these forms should be retained by the originating office (either carbon or photo copy).

4. Mailed packages can be registered with return receipt requested. If packages are sent by common carrier, receipts

FIGURE VIII-2

CHAIN OF CUSTODY RECORD

SURVEY				SAMPLERS: (Signature)					
STATION NUMBER	STATION LOCATION	DATE	TIME	SAMPLE TYPE: Water: Comp.	Water: Grab	Air	SEQ. NO.	NO. OF CONTAINERS	ANALYSIS REQUIRED

Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by Mobile Laboratory for field analysis: (Signature)	Date/Time

Dispatched by: (Signature)	Date/Time	Received for Laboratory by:	Date/Time
Method of Shipment:			

Distribution: Orig.—Accompany Shipment
1 Copy—Survey Coordinator Field Files

EPA 831-44

should be retained as part of the permanent chain-of custody documentation.

5. Samples to be shipped must be so packed as not to break and the package so sealed or locked that any evidence of tampering may be readily detected.

E. Laboratory Custody Procedures

Chain of Custody procedures are also necessary in the laboratory from the time of sample receipt to the time the sample is discarded. The following procedures are recommended for the laboratory:

1. A specific person shall be designated custodian and an alternate designated to act as custodian in the custodian's absence. All incoming samples shall be received by the custodian, who shall indicate receipt by signing the accompanying custody forms and who shall retain the signed forms as permanent records.

2. The sample custodian shall maintain a permanent log book to record, for each sample, the person delivering the sample, the person receiving the sample, date and time received, source of sample, sample identification or log number, how transmitted to the laboratory and condition received (sealed,

unsealed, broken container, or other pertinent remarks). A standardized format should be established for log book entries.

3. A clean, dry, isolated room, building, and/or refrigerated space that can be securely locked from the outside shall be designated as a "sample storage security area."

4. The custodian shall ensure that heat-sensitive, light-sensitive samples, radioactive, or other sample materials having unusual physical characteristics, or requiring special handling, are properly stored and maintained prior to analysis.

5. Distribution of samples to the section chiefs who are responsible for the laboratory performing the analyses shall be made only by the custodian.

6. The laboratory area shall be maintained as a secured area, restricted to authorized personnel only.

7. Laboratory personnel are responsible for the care and custody of the sample once it is received by them and shall be prepared to testify that the sample was in their possession and view or secured in the laboratory at all times from the moment it was received from the custodian until the time that the analyses are completed.

8. Once the sample analyses are completed, the unused portion of the sample, together with all identifying labels, must be returned to the custodian. The returned tagged sample should be retained in the custody room until permission to destroy the sample is received by the custodian.

9. Samples shall be destroyed only upon the order of the Laboratory Director, in consultation with previously designated Enforcement officials, or when it is certain that the information is no longer required or the samples have deteriorated. The same procedure is true for tags and laboratory records.

F. Evidentiary Considerations

Reducing chain of custody procedures as well as the various promulgated laboratory analytical procedures to writing will facilitate the admission of evidence under rule 803(6) of the Federal Rules of Evidence (PL. 93-575). Under this statute, written records of regularly conducted business activities may be introduced into evidence as an exception to the "Hearsay Rule" without the testimony of the person(s) who made the record. Although preferable, it is not always possible to have the individuals who collected, kept, and analyzed samples testify in court. In addition, if the opposing party does not intend to contest the integrity of the sample or testing evidence, admission under the Rule 803(6) can save a great deal of trial time. For these reasons, it is important that the procedures

followed in the collection and analysis of evidentiary samples be standardized and described in an instruction manual which, if need be, can be offered as evidence of the "regularly conducted business activity" followed by the lab or office in generating any given record.

In criminal cases however, records and reports of matters observed by police officers and other law enforcement personnel are not included under the business record exceptions to the "Hearsay Rule" previously cited (see Rule 803(8), P.L. 93-595). It is arguable that those portions of the compliance inspection report dealing with matters other than sampling and analysis results come within this exception. For this reason, in criminal actions records and reports of matter observed by field investigators may not be admissible and the evidence may still have to be presented in the form of oral testimony by the person(s) who made the record or report, even though the materials come within the definition of business records. In a criminal proceeding, the opposing counsel may be able to obtain copies of reports prepared by witnesses, even if the witness does not refer to the records while testifying, and if obtained, the records may be used for cross-examination purposes.

Admission of records is not automatic under either of these sections. The business records section authorizes admission "unless the source of information or the method or circumstances

of preparation indicate lack of trustworthiness," and the caveat under the public records exception reads "unless the sources of information or other circumstances indicate lack of trustworthiness."

Thus, whether or not the inspector anticipates that his or her compliance inspection report will be introduced as evidence, he or she should make certain that the report is as accurate and objective as possible.

TENAX GC

Green List Number / Compound Name	STORET Number	Sample Number: Spectrum Number Using 3 min Delay	RRT Relative to 2-Nitrobenzene	Ions Used	% Recovery for 25-500 BBB Spike			
24 2-Chlorophenol	34586	38	0.61	128 64 130	55			
65 Phenol	32730	27	0.53	94 65 66	30			
31 2,4-Dichlorophenol	34601	98	1.09	162 164 98	56			
57 2-Nitrophenol	34591	87	1.00	139 65 109	55			
22 P-chloro-M-cresol	34452	130	1.34	142 107 144	61			
21 2,4,6-Trichlorophenol	34621	146	1.46	196 198 200	58			
34 2,4-Dimethylphenol	34606	88	1.01	122 107 121	46			
59 2,4-Dinitrophenol	34616	191	1.82	184 63 154	43			
60 4,6-Dinitro-O-cresol	34657	208	1.95	198 182 77	58			
58 4-Nitrophenol	34646	198	1.87	65 139 109	52			
64 Pentachlorophenol	39032	243	2.23	266 264 268	56			
DEUTERATED ANTHRACENE	—	260	2.36	188 94 80	—			
—			130					

3% OV-17 on 100/120 mesh Gas-Chrom Q

Green List Number / Compound Name	STORET Number	Sample Number: Spectrum Number using 3 min delay	QAT Relative to HCB	Ions Used	% Recovery for IC-5008 Spike			
26 1,3-Dichlorobenzene	34566	11	0.41	146 148 113	99			
27 1,4-Dichlorobenzene	34571	15	0.42	146 148 113	99			
12 Hexachloroethane	34396	23	0.46	117 199 201	88			
25 1,2-Dichlorobenzene	34536	22	0.46	146 148 113	99			
42 Bis (2-chloro isopropyl) ether	34283	30	0.48	45 77 79	115			
52 Hexachloro butadiene	34391	59	0.59	225 223 227	70			
8 1,2,4-Trichlorobenzene	34551	61	0.60	74 109 145	110			
55 Napthalene	39250	68	0.62	128 127 129	107			
18 Bis (2-chloroethyl ether)	34273	22	0.46	93 63 95	90			
53 Hexachlorocyclo-pentadiene	34386	88	0.70	237 235 272	0			
56 Nitrobenzene	34447	55	0.57	77 123 65	78			
43 Bis (2-chloroethoxy) methane	34278	68	0.63	93 95 123	90			
20 2-Chloronapthalene	34200	111	0.78	162 164 127	90			
1 Acenaphthene	34205	135	0.87 131	154 153 152	90			

PRIORITY POLLUTANTS: Base/Neutral Extractables

Green List Number / Compound Name	STORET Number	Sample Number: SA No.	RRT	IONS	% recovery			
54 Isophorone	34408	~~54~~	~~0.56~~	82 95 138	101			
80 Fluorene	34381	154	0.93	166 165 167	90			
36 2,6-Dinitrotoluene	34626	144	0.90	165 63 121	87			
37 (AZO BENZENE) 1,2-Diphenyl-hydrazine	34346	(161)	(0.95)	(77 105 182)	94			
35 2,4-Dinitrotoluene	34611	155	0.94	165 63 182	87			
62 N-Nitrosodiphenylamine	34433	166	0.97	169 168 167	99			
9 Hexachlorobenzene	39700	172	1.00	284 142 249	100			
41 4-Bromophenyl phenyl ether	34636	173	1.00	248 250 141	106			
81 Phenanthrene	34461	193	1.07	178 179 176	97			
78 Anthracene	34220	193	1.07	178 179 176	97			
71 Dimethylphthalate	34341	139	0.88	163 164 194	66			
70 Diethylphthalate	34336	161	0.96	149 177 150	97			
39 Fluoranthene	34376	236	1.24	202 101 100	120			
64 Pyrene	34469	246	1.27	202 101 100	120			

PRIORITY POLLUTANTS: Base/Neutral Extractables

Green List Number / Compound Name	STORET Number	Sample Number: Sc. No.	RRT	IONS	% Recovery			
68 Di-n-butyl-phthalate	39110	214	1.15	149 150 104	105			
5 Benzidine	39120	258	1.32	184 92 185	—			
67 Butyl-benzyl-phthalate	34292	277	1.38	149 91	99			
76 Chrysene	34320	297	1.44	228 229 226	83			
66 Bis(2-ethylhexyl) phthalate	39100	288	1.41	149 167 279	63			
72 Benzo(a)Anthracene	34526	297	1.45	228 229 226	83			
74 Benzo(b)Fluoranthene	34230	367	1.70	252 253 125	107			
75 Benzo(k)Fluoranthene	34242	367	1.70	252 253 125	107			
73 Benzo(a)Pyrene	34247	402	1.83	252 253 125	107			
83 Indeno(1,2,3-cd)-pyrene	34403	577	2.46	276 138 277	121			
82 Dibenzo(a,h)-Anthracene	34556	590	2.51	278 139 279	131			
79 Benzo(g,h,i) perylene	34521	635	2.68	276 138 277	121			
61 N-Nitrosodimethylamine	34438	—	—	42 74 44	—			
63 N-Nitrosodi-n-Propylamine	34428	42	0.54	130 101 70	101			

PRIORITY POLLUTANTS: Base/Neutral Extractables

Green List Number / Compound Name	STORET Number	Sample Number						
		SD. NO.	RRT	IONS	% RECOVERY			
40 4-Chloro-phenyl pheryl ether	34641	154	0.93	204 206 141	84			
28 3,3'-Dichlorobenzidine	34631	308	1.49	252 254 126	67			
69 Di-n-octyl phtalate	34596	326	1.53	149 167 279	63			
77 Acenaphthylene	34200	130	0.85	152 153 151	94			
DEUTERATED ANTHRACENE		193	1.07	188 94 80	–			

PRIORITY POLLUTANTS: Volatile Organics

CARBOPACK C/0.2% CARBOWAX 1500 with BP Column of Chromosorb G/3%

Green List Number / Compound Name	STORET Number	Sample Number: Spectrum Number	QAT Relative to Benzene	Purging Efficiency	Ions Used			
2 Acrolein	34210	—	—	—	—			
3 Acrylonitrile	34215	—	—	—	—			
45 Chloromethane	34418	—	—	—	50 52			
50 Dichlorodifluoromethane	32105	—	—	—	85 87 101			
46 Bromomethane	34413	7	0.04	-	94 96	—		
88 Vinyl Chloride	39175	15	0.08	-	62 64			
16 Chloroethane	34311	12	0.07	-	64 66			
44 Methylene Chloride	34423	25	~~0.14~~ 0.14	-	49 51 84			
49 Trichlorofluoromethane	34488	30	0.16	-	101 103			
29 1,1-Dichloroethylene	34501	33	0.18	83%	61 96 98			
30 Trans-1,2-Dichloro-ethylene	34546	53	0.29	93%	61 96 98			
23 Chloroform	32106	74	0.40	-	83 85			
10 1,2-Dichloroethane	34531	83	0.45	-	62 64 98			
11 1,1,1-Trichloroethane	34506	95	0.52	93%	97 99 117			

PRIORITY POLLUTANTS: Volatile Organics

Green List Number / Compound Name	STORET Number	Sample Number						
		Sa. No.	RRT					
6 Carbon tetrachloride	32102	98	0.54	89%	117 119 121			
48 Bromodichloromethane	32101	117	0.64	84%	83 85 127			
17 Bis-chloromethyl ether	34268	—	—	—	—			
32 1,2-Dichloropropane	34541	126	0.69	93%	63 65 112			
33 A Trans-1,3-Dichloro-propene	34561	133	0.73	90%	75 77	—		
51 Dibromochloromethane	34306	152	0.83	73%	129 127 208			
33 B Cis-1,3-Dichloropropene	34561	148	0.81	90%	75 77			
14 1,1,2-Trichloroethane	34511	150	0.82	84%	83 85 97			
4 Benzene	34030	136	0.71	105%	78			
19 2-Chloroethylvinyl ether	34576	157	0.86	—	63 65 106			
47 Bromoform	32104	183	1.00	64%	171 173 175			
15 1,1,2,2-Tetrachloroethane	34475	208	1.14	55%	83 85 131			
85 1,1,2,2-Tetrachloroethene	34516	199	1.09	82%	129 131 164			
13 1,1-Dichloroethane	34496	51	0.28	—	63 65 83			

PRIORITY POLLUTANTS: Volatile Organics

Green List Number / Compound Name	STORET Number	Sample Number						
		Spec. No.	QRT					
87 Trichloroethylene	39180	134	0.73	-	95 97 130			
86 Toluene	34010	205	1.12	78%	91 92			
7 Chlorobenzene	34301	223	1.22	82%	112 114			
38 Ethyl benzene	34371	241	1.32	-	91 106			
Bromochloro Methane		53	0.29	-	49 130 128			
1,4-Dichlorobutane		207	1.13	-	55 90 92			

PRIORITY POLLUTANTS: Pesticides

Green List Number / Compound Name	STORET Number	Sample Number					
		49.3E-30 + 62.CY-21G QQT RELATIVE TO ALDRIN	1.5% OV-7 1.95% QF-1 QQT RELATIVE TO ALDRIN				
96 β-endosulfan	34356	2.51	3.48				
102 α-BHC	39337	0.48	0.53				
104 γ-BHC	34264	0.57	0.68				
103 β-BHC	39338	0.51	0.78				
89 Aldrin	39330	1.00	1.00				
100 Heptachlor	39410	0.82	0.82				
101 Heptachlor epoxide	39420	1.37	1.54				
95 α-endosulfan	34361	1.71	1.94				
98 Dieldrin	39380	2.01	2.34				
93 4,4'-DDE	39320	1.78	2.21				
94 4,4'-DDD	39310	2.45	3.39				
92 4,4'-DDT	39300	3.02	4.08				
98 Endrin	39390	2.30	2.90				
97 Endosulfan sulfate	34351						

Environmental Research Laboratory
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Athens, Georgia 30605

DATE: January 18, 1978

SUBJECT: Action Concerning Region VII Comments on "Sampling and Analysis Procedure for Screening of Industrial Effluents for Priority Pollutants"

FROM: W. M. Shackelford
Analytical Chemistry Branch

TO: William A. Telliard
Environmental Protection Agency
Effluent Guidelines Division
WH-552, 401 M Street, SW
Washington, DC 20460

In a memo dated 2 November chemists at the Region VII Surveillance and Analysis Laboratory commented on strengths and weaknesses of the analysis protocol for the consent decree analysis program. Several of the "deficiencies and errors" mentioned in the Region VII memo refer to typographical errors, while others are the result of differences in judgment. This memo will deal with each comment from the consecutive sections "Base/Neutral Compounds"--"Radian Consent Decree Standards" in the Region VII memo.

Base/Neutral Compounds

A) The protocol should be corrected such that 177 is one of the characteristic masses for diethylphthalate instead of 178.

B) After reflecting on the ions for 2,6-dinitrotoluene and 2,4-dinitrotoluene, it appears that corrections should be made such that:

2,4-dinitrotoluene--165(100), 63(31), 182(11)

Apparently, the ions for 2,6-dinitrotoluene were put in the space for 2,4-dinitrotoluene by mistake.

C) It is true that bis(2-chloroethyl ether) elutes before bis(2-chloroisopropyl ether) on 3% OV-17 but this order is reversed on 1% SP-2250. We observed this in our lab as well.

D) Published values for the 42 ion for N-nitroso-di-n-propylamine all indicate a significant intensity. Mass 42 is also characteristic of all alkyl nitrosamines.

E) The diphenylhydrazine problems have been commented upon in a memo to you from Wayne Garrison and Fred Haeberer.

F) 3% OV-17 was tried in this lab and found to give bleed problems. The 1% SP-2250 is equivalent to 1% OV-17. Our work showed essentially equivalent chromatography with the two packings (3% OV-17 and 1% SP-2250) except for some changes in retention times.

G) Chromatography of benzidine is a necessary evil, but the amount used could be increased to 100 ng.

H) We are aware of several PAH isomers that cannot be separated on the recommended column. They cannot be separated easily on capillary columns either. We will have to live with reporting them as the sum of the two isomers.

Extraction Recoveries

A) A provision for the determination of extraction recovery efficiencies should definitely be made for the verification stage. Other labs have not experienced troubles extracting hexachlorocyclopentadiene. This probably needs study.

Phenols

A) Relative retention times for phenols in the protocol should be corrected as listed below:

	RRT
Phenol	0.79
2-chlorophenol	0.84
2-nitrophenol	1.00
2,4-dimethylphenol	1.02
2,4-dichlorophenol	1.06
p-chloro-m-cresol	1.27
2,4,6-trichlorophenol	1.34
2,4-dinitrophenol	1.68
4-nitrophenol	1.73
4,6-dinitro-o-cresol	1.82
pentachlorophenol	2.01

These agree reasonably well with other data. The original data was taken before Tenax GC had been fully evaluated in this lab.

B) One help for the gaps in Tenax is to condition a new column at $\leq 225^{\circ}C$, pack together when spaces develop, then use normally. This can minimize the gap formation.

C) You have commented previously on the use of the 4AAP method for phenols.

Data Storage

A) It has been stressed that each VOA, B/N, and Acid extract must be run in the GC/MS and the data saved. In following up this point with Dr. Kleopfer, he assured me that he is running all the samples on the GC/MS and not just screening with GC to avoid GC/MS samples with no flame detected peaks.

Radian Consent Decree Standards

A) Radian inadvertantly left ethylbenzene out of the VOA mix. Vinyl chloride and bis(chloromethyl ether) are present in the mix. Dr. Tom Bellar has commented that the vials must be opened at 20°C to keep from losing these two. The 2-chloroethyl vinyl ether was put in the B/N vial. New standards have been promised by Dr. Larry Keith of Radian. He has been made aware of the shortcomings of the first set. The new sets will have more divisions for more ease of identification of individual components. Concentrated samples of the d_{10}-anthracene have been on order for several months. Dr. Keith said that contractual problems in HQ were the hold up.

B) Corrections to the standards identification sheets have been made to reflect the proper concentrations.

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UNCHLORINATED BASE/NEUTRAL PRIORITY POLLUTANTS

ORDER OF ELUTION

Protocol (EPA)		Identification by Gas Chromatography (Radian)	
Compound	RRT	Compound	RRT
naphthalene	0.57	isophorone	0.46
acenaphthylene	0.83	naphthalene	0.51
acenaphthene	0.86	acenaphthalene	0.81
isophorone	0.87	acenaphthene	0.83
fluorene	0.91	dimethyl phthalate	0.88
phenanthrene	1.09	fluorene	0.92
anthracene	1.09	diethyl phthalate	0.98
dimethyl phthalate	1.10	phenanthrene	1.10
diethyl phthalate	1.15	anthracene	1.10
fluoranthene	1.23	dibutyl phthalate	1.23
pyrene	1.30	fluoranthene	1.30
di-n-butyl phthalate	1.31	pyrene	1.34
butyl benzyl phthalate	1.46	butyl benzyl phthalate	1.51
chrysene	1.46	benzo(a)anthracene	1.57
bis(2-ethylhexyl) phthalate	1.50	bis(2-ethylhexyl) phthalate	1.57
benzo(a)anthracene	1.54	chrysene	1.57
benzo(b)fluoranthene	1.66	benzo(b)fluoranthene	1.74
benzo(k)fluoranthene	1.66	benzo(k)fluoranthene	1.77
benzo(a)pyrene	1.73	benzo(a)pyrene	1.80
indeno(1,2,3-c,d)pyrene	2.07	indeno(1,2,3-c,d)pyrene	2.07
dibenzo(a,h)anthracene	2.12	dibenzo(a,h)anthracene	2.13
benzo(ghi)perylene	2.12	benzo(ghi)perylene	2.13

Calspan Corporation
P.O. Box 235
Buffalo, New York 14221
Tel. 716 632-7500

Calspan

19 December 1977
PMT:hf-67

Mr. William Telliard
Chief, Energy and Mining Branch
Effluent Guidelines Division (WH-552)
USEPA
Washington, DC 20460

Dear Mr. Telliard:

This letter is for the purpose of updating you on the situation regarding the transport of hazardous materials which was mentioned at the Denver analytical seminar. As you are probably aware, the Department of Transportation has a regulation (49CFR172-101 Hazardous Materials Table) forbidding the transport of nitric acid aboard passenger aircraft. In keeping with the requirements of the regulation and in view of the fact that the EPA Standard Method for metal analyses calls for acid stabilization of samples to pH <2, Calspan filed for an exemption to this regulation so that field sampling for LOE Task 11 would proceed uninterrupted.

On December 15, 1977, Calspan received a reply from the DOT denying our request to transport nitric acid (~100 ml) in a specially prepared field sampling kit. (Enclosed is a copy of Calspan's request for exemption describing the conditions under which the acid shipment would take place and also a copy of the denial.)

Since the most recent revision of the sampling protocol specifies field stabilization of metal samples (verbally given by you at the Denver seminar) and in view of the recent ruling by DOT on our request, we feel that this situation should be brought to the attention of all contractors involved in the field sampling phase of the Effluent Guidelines Program. This regulation by the DOT may seriously jeopardize the ability of contractors to provide accurate metal analyses on unstabilized wastewater samples. We would appreciate any assistance on your behalf to resolve this situation with DOT and kindly request you inform us of any change which may be affected by your action. Thank you.

Sincerely,

P. Michael Terlecky, Jr.

P. Michael Terlecky, Jr. Ph.D.
Head, Environmental Sciences Section
Environmental & Energy Systems Dept.

Enclosures

Calspan Corporation
P.O. Box 235
Buffalo, New York 14221
Tel. (716) 632-7500

Calspan

28 September 1977
PMT:pL-37

Office of Hazardous Material Operations
U.S. Department of Transportation
Washington, D.C. 20590
Attn: Exemptions Branch

Gentlemen:

Item 1.

In accordance with subpart B, Section 107.103, Calspan Corporation seeks exemption of the requirements of 49CFR 172.101 Hazardous Material Table (HNO_3 forbidden aboard passenger aircraft) and seeks to determine what may be carried in "Chemical reagent kits" as described in Section 173.286. According to Section 107.103,b(1), three copies of this request are submitted herein for your review and approval.

Item 2.

Specifically, we seek to carry aboard passenger aircraft chemical reagent test kits during sampling expeditions in support of requirements of the U.S. Environmental Protection Agency (USEPA Contract 68-01-3281) to set national effluent standards for various point source categories pursuant to P.L. 92-500 (Federal Water Pollution Control Act Amendments - 1972) and various state, local, and regional agencies and industrial customers. The chemical reagent test kits are necessary in order to properly preserve wastewater samples for subsequent analysis in our laboratories in Buffalo, New York. Without certain stabilizing agents, these samples degrade resulting in a loss of value of the sample for analytical and regulatory purposes.

Item 3.

The applicant for this exemption is:

Calspan Corporation
Attn: Environmental and Energy Systems Department
P.O. Box 235
Buffalo, New York 14221
716-632-7500

Item 4.

In accordance with DOT 15(A) spec. 173.268(a); d(1) and i(1), the proposed method of shipping is as follows: a small plastic container (bottle) with a threaded acid-resistant cap cushioned by absorbent packing material is enclosed in a glass bottle with threaded acid-resistant plastic cap. This glass container is then enclosed in an individual, tightly sealed metal can and surrounded by vermiculite (mineral matter) packing inside. The metal cans are then placed in wooden boxes, surrounded by cushioning material (vermiculite). The wooden boxes are then secured with lids, screwed into place and properly labeled as to the items contained therein.

The wooden boxes mentioned above are constructed of white pine stock with 3/4" walls and have reinforced ends with a total thickness of 1 1/2". The lid is also constructed of 3/4" stock and when secured in place with 1 1/4" screws affords an effective seal capable of withstanding transportation handling. Photographs of this proposed method of shipping are attached. Construction blueprints were not utilized in the assembly of this item and hence are not included in this report.

Drop tests have been performed on the proposed transport containers (wooden boxes) in accordance with DOT 15(A) spec. 178.168-6: Gluing Efficiency Wood Drop Test. The specification states that for containers with a gross weight less than one hundred and fifty (150) pounds, the container, when filled to capacity with sand and/or sawdust, shall be capable of withstanding eight (8) drops from 1 foot (12 inches) onto solid concrete, 1 on each corner, without exposure of contents. Such performance has been attained (and exceeded) on the proposed containers and it is expected that these containers will withstand the type of handling normally associated with transportation of materials on commercial carriers.

Item 5.

See attached table.

Item 6.

We believe that the level of safety achieved will meet or exceed that required by the regulations and will ensure that no additional risks to life or property will occur as a result of the granting of this exemption. Our record of shipment of explosives and other materials over the past 30 years is exemplary with four full time personnel at Calspan devoted to packaging, shipping and receiving activities alone. Because of our experience, and because the small amounts of reagents needed present no additional risk, we respectfully request approval of our exemption at the earliest possible time.

Item 7.

The proposed mode of transportation for the chemical kits is by commercial aircraft. Separate shipment of chemical reagent kits by other carriers or by cargo aircraft will seriously affect our ability to support EPA requirements in rural areas of the U.S. and would adversely affect our acquisition of some $1 million worth of environmental sampling and analytical business annually. Receipt by our engineers and technicians of these kits simultaneously with receipt of sampling equipment and containers (shipped as baggage) is essential to the timely and economical conduct of our work for which the Federal government is the main supporter.

Due to the small amounts of material being shipped (3 containers of 100 ml (3 oz.) each) and considering the extraordinary care under which these kits are prepared and packaged, it is felt that there will be no increased risks associated with the shipment of these materials.

Item 8.

As previously mentioned in Item 2, these kits are required for the proper execution of the water sampling phase of a variety of EPA-sponsored programs directed toward the establishment of national effluent guideline regulations for numerous point source categories. This work as described by P.L. 92-500 is a continuous effort and is due to be continued for an indefinite period of time. Each sampling trip arranged for data collection in conjunction with the above-mentioned programs lasts an average of 4 days. During this time the chemical kits are transported to the sampling site, used as required and when empty, returned to Calspan.

Item 9.

The small amounts of materials due to be transported do not constitute any increased safety hazard when packaged and shipped as proposed above. It is strongly felt that the time and effort invested in the execution of precautionary measures for shipment of these hazardous substances is consistent with the public interest and will adequately protect against the risks of life and property which are generally associated with the transportation of hazardous materials.

Item 10.

It is not necessary to process this application on a priority basis. We do respectfully request, however, that the handling of this resubmitted application be given all due consideration with regard to expeditious review. This is necessary in order that our company may not experience any interruption in the acquisition of the aforementioned government contracts which represent a significant financial investment.

If there are any technical questions related to the materials to be carried or the kits themselves, contact our Dr. P. Michael Terlecky at (716) 632-7500, x538.

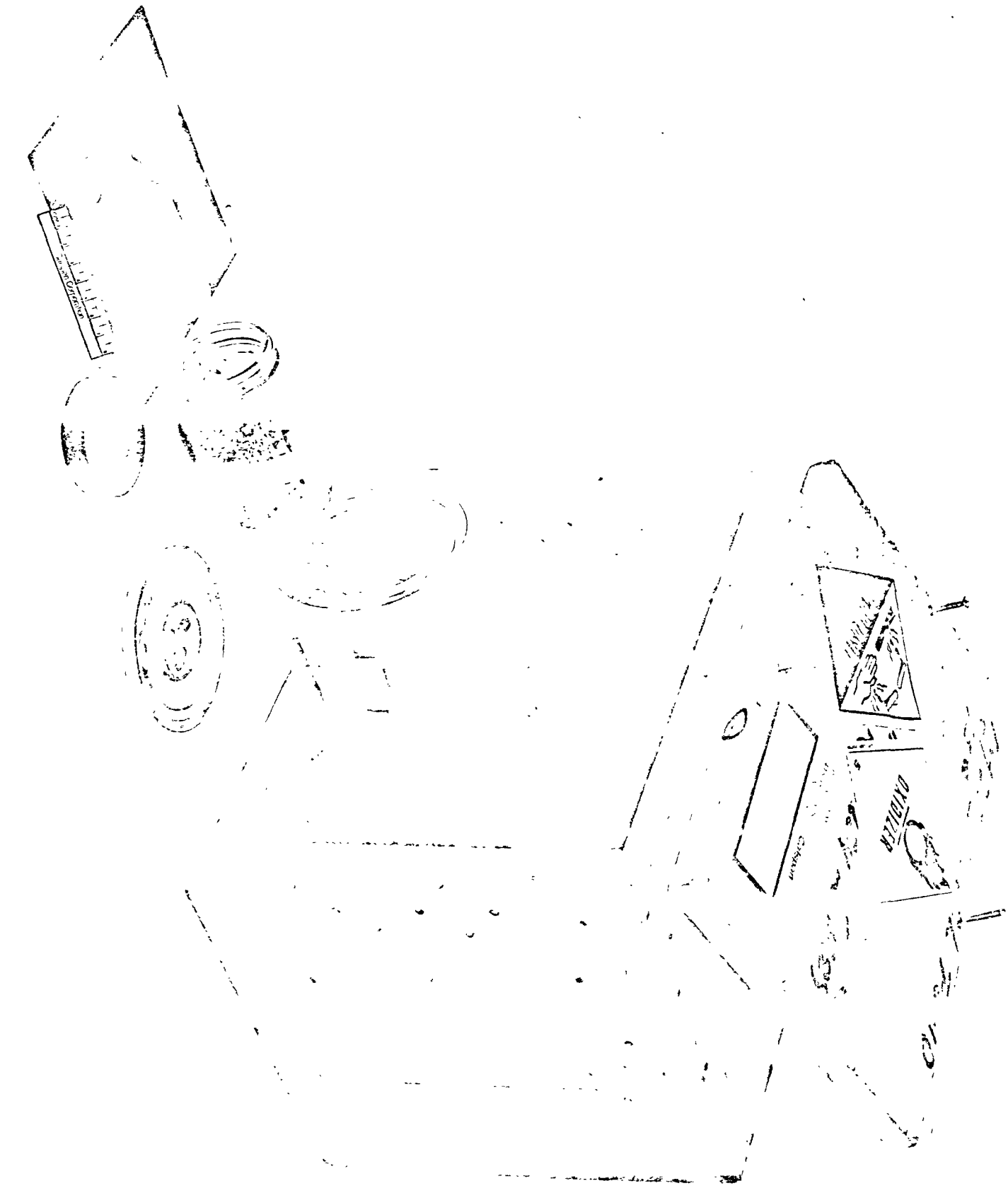
Sincerely,

Roland J. Pilie, Head
Environmental & Energy Systems Department

ITEM 5. CHEMICAL REAGENT KIT CONSTITUENTS

Chemical Name	Common Name (Chemical Formula)	Hazard Classification	Form	Quantity	Properties	Material Characteristics
Nitric Acid (Concentrated-70%)	Engraver's Acid Azotic Acid (HNO_3)	Oxidizer Corrosive	Liquid	100 ml (3 oz.)	Transparent colorless or yellowish fuming, suffocating, caustic, and corrosive liquid	b.p 86°C m.p. -41.6°C sp.gr. 1.504 vap.pr. 62mm ref.in. 1.3960 visc. 0.761cp
Sulfuric Acid (Concentrated-95%)	Oil of Vitriol Battery Acid (H_2SO_4)	Corrosive	Liquid	100 ml (3 oz.)	Dense, oily liquid, colorless to dark brown, miscible with water, very reactive, dissolves most metals, causes charring	b.p. range 315-338°C m.p. 10.4°C sp.gr. 1.84
Phosphoric Acid (Concentrated-85%)	Orthophosphoric Acid (H_3PO_4)	Corrosive	Liquid	100 ml (3 oz.)	Clear, colorless, odorless, sparkling liquid or transparent crystalline depending on concentration and temperature	m.p. 42.35°C sp.gr. 1.834
Sodium Hydroxide	Caustic Soda Lye White Caustic (NaOH)	Corrosive	Dry Pellets	100 gm. (3 oz.)	White, deliquescent flakes, lumps or sticks, crystalline fracture, soluble in water, alcohol and glycerol	b.p. 1390°C m.p. 318°C sp.gr. 2.13

Ref: The Condensed Chemical Dictionary, Eighth Edition, Van Nostrand Reinhold Company, 1971



DEPARTMENT OF TRANSPORTATION
MATERIALS TRANSPORTATION BUREAU
WASHINGTON, D.C. 20590

DEC 9 1977

Mr. Roland J. Pilie
Environmental and Energy
Systems Department
Calspan Corporation
P.O. Box 235
Buffalo, New York 14221

Dear Mr. Pilie:

This is in response to your application dated September 28, 1977 (7844-N), filed in accordance with Section 107.103 of Title 49, Code of Federal Regulations, (49 CFR), for permission to ship chemical kits containing 70 percent nitric acid, sulfuric acid, phosphoric acid and solid sodium hydroxide pellets by passenger carrying aircraft.

In accordance with the Code of Federal Regulations, Title 49, Section 107.109(c), the request is denied.

The reason for denial is failure of the application to satisfy the requirements of Section 107.103 as follows:

1. In accordance with 49 CFR 107.103(b)(9)(i) you have made general statements as to why you believe that your proposal to include 70% nitric acid in the chemical kit will achieve a level of safety at least equivalent to that specified in the regulation from which the exemption is sought. However, it is obvious that no practical packaging for any hazardous material will result in the same level of safety as will be achieved by precluding that material from transport.

2. Also 49 CFR 173.286(b) and (b)(1) limits the contents of chemical kits to corrosive liquids for which exceptions are provided in 49 CFR 172.101. Therefore, nitric acid of concentration of 40% or less is not authorized to be included in a chemical kit. It would, therefore, be more hazardous to permit nitric acid of concentration exceeding 40% to be included in a chemical kit thereby further reducing the specified level of safety.

In addition, as noted below, some of your requests are unnecessary in that the regulations already authorize shipment by passenger carrying aircraft.

1. Section 173.286(b) provides for shipment of sulfuric acid and phosphoric acid in chemical kits under conditions that make your request for exemption for these commodities unnecessary.

2. Section 173.244 provides for shipment of sodium hydroxide solid as a limited quantity such that no exemption is necessary for the package you described in your application.

Sincerely,

Alan I. Roberts
Director
Office of Hazardous Materials
Operations

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
~~SOUTHEAST~~ ENVIRONMENTAL RESEARCH LABORATORY
ATHENS, GEORGIA 30601

December 22, 1977

Mr. J. B. Anderson, Editor
Analytical Quality Control Newsletter
EMSL
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Dear Mr. Anderson:

Enclosed is an article describing preliminary results of investigations by Dr. Fred Haeberer of the Analytical Chemistry Branch into the stability of two of the Consent Decree Pollutants. This should be of interest to the many of your readers who are involved in analysis of these pollutants, and we request that you publish it in your Newsletter. We are also planning to publish these results in the Athens ERL quarterly report, which will probably be published in 2 or 3 months.

Sincerely yours,

Arthur W. Garrison

Arthur W. Garrison
Analytical Chemistry Branch

cc: Dr. Jim Lichtenberg, EMSL, Cincinnati
Dr. William Telliard, Effluent Guidelines Division, EPA
Dr. Walter Shackelford, ACB
Dr. Ron Webb, ACB

Analysis of Consent Decree Pollutants

Various researchers and contractors involved in the analysis of the base-neutral extractable priority pollutants have noted that both the GC retention time and the mass spectral fragmentation pattern of N-nitrosodiphenylamine (one of the priority pollutants) and diphenylamine are apparently identical. Our studies on this problem have shown that as N-nitrosodiphenylamine (mp 67°C) is heated it begins to decompose as soon as it is in the liquid state. Above 145°C the decomposition proceeds very quickly yielding diphenylamine and tetraphenylhydrazine. The identities of these two compounds were established by infrared and mass spectral data.

When N-nitrosodiphenylamine is subjected to gas chromatography under the conditions imposed by the Consent Decree Protocol, i.e., inlet temperature 275°C, decomposition occurs in the inlet, resulting in a single sharp symetrical peak that has been identified as diphenylamine (elution temperature 161°C, RRT 0.97). This compound is formed in 40 to 80% yield. Formation of tetraphenylhydrazine in the GC inlet may also occur, but has not been established since this compound does not elute under the protocol conditions. No GC peak that could be identified as N-nitrosodiphenylamine has to date been observed.

Identification of this nitrosamine via the regimen of the protocol is inconclusive and it is therefore suggested that the apparent presence of this compound be currently reported as "N-nitrosodiphenylamine and/or diphenylamine" until a valid analytical method can be developed. We are investigating liquid chromatography as a separation tool for nitrosamines, including N-nitrosodiphenylamine.

Preliminary work with 1,2-diphenylhydrazine (hydrazobenzene--another priority pollutant) indicates that it also degrades, perhaps not in the GC inlet, but definitely in solution, forming azobenzene as the major product, along with aniline and an unknown of mw 184. Current data have eliminated benzidine as the unknown's identity and indicate that it might be a N-phenylphenylenediamine. This decomposition occurs in methanol and methylene chloride (the solvent for the protocol standards), as well as in water. Additional work is needed on this problem before any concrete recommendations can be made. (Alfred F. Haeberer, 404-546-3187, FTS-250-3187).

Index of References

1. letter: Examples of trap packing deterioration. NUS, Miss C. Ellen Gonter, November 15, 1977.

2. A Brief Evaluation of Phenol Extraction Procedures. Environmental Science and Engineering, Inc., November 9, 1977.

3. Analytical Problems in Effluent Analysis, Dow Chemical Company, R.O. Kagel.

4. Draft - Priority Pollutant Validation Protocol, Dow Chemical Co. R.O. Kagel and R. H. Stehl.

5. Memo, dated November 23, 1977, Subject: Metals Analysis-Chicago Regional Laboratory.

6. Preliminary Interim Procedures for Fibrous Asbestos, Charles H. Anderson and J. MacArthur Long, U.S. E.P.A., Environmental Research Laboratory, Athens, Georgia.

7. Analytical Methodology for the Determination of Asbestos by Transmission Election Microscopy. Walter C. McCrone Assoc., Inc.

8. Preservation of Phenolic Compounds in Wastewaters, M.J. Carter and M.T. Huston, E.P.A., Central Regional Laboratory.

9. Diagram of Liquid-Liquid extractor, MIDWEST Research Institute, C.L. Haile.

NUS CORPORATION
CYRUS WM. RICE DIVISION

ANALYTICAL SERVICES LABORATORY
15 NOBLE AVENUE • PITTSBURGH, PA. 15205
412-343-9200

November 15, 1977

Mr. William A. Telliard
Chief, Electric Utilities &
Mining Branch
Effluent Guidelines Division
U.S. Environmental Protection Agency
Waterside Mall
401 M Street, S.W.
Washington, D.C. 20460

Dear Bill:

Enclosed are examples of what is believed to be trap packing deterioration.

1. February 2, 1977, 5.0 ml of sample was purged according to the Bellar-Lichtenberg procedure (EPA-670/4-74-009). The trap was sealed with stainless steel caps and frozen. July 14, 1977, the trap was allowed to warm to room temperature and run on GC/MS. The trap was sealed with Teflon caps, and stored in a drawer at ambient temperature. July 21, 1977, the trap was desorbed onto the GC column, and the resultant curve 1 obtained.

2. July 21, 1977, 5.0 ml of the retain sample was purged, trapped, desorbed, etc. according to the Bellar-Lichtenberg procedure, (March 1977 trap packing) and the resultant curve 2 obtained.

This was not an isolated case.

The peaks at 5.3 and 13.5 have appeared in most of the traps that were frozen. The peak at 15.5 "grows" larger with time in an eight-hour period, even though the trap is heated at 180°C with nitrogen at 40 ml/min flowing through it for 20 to 30 minutes between runs..

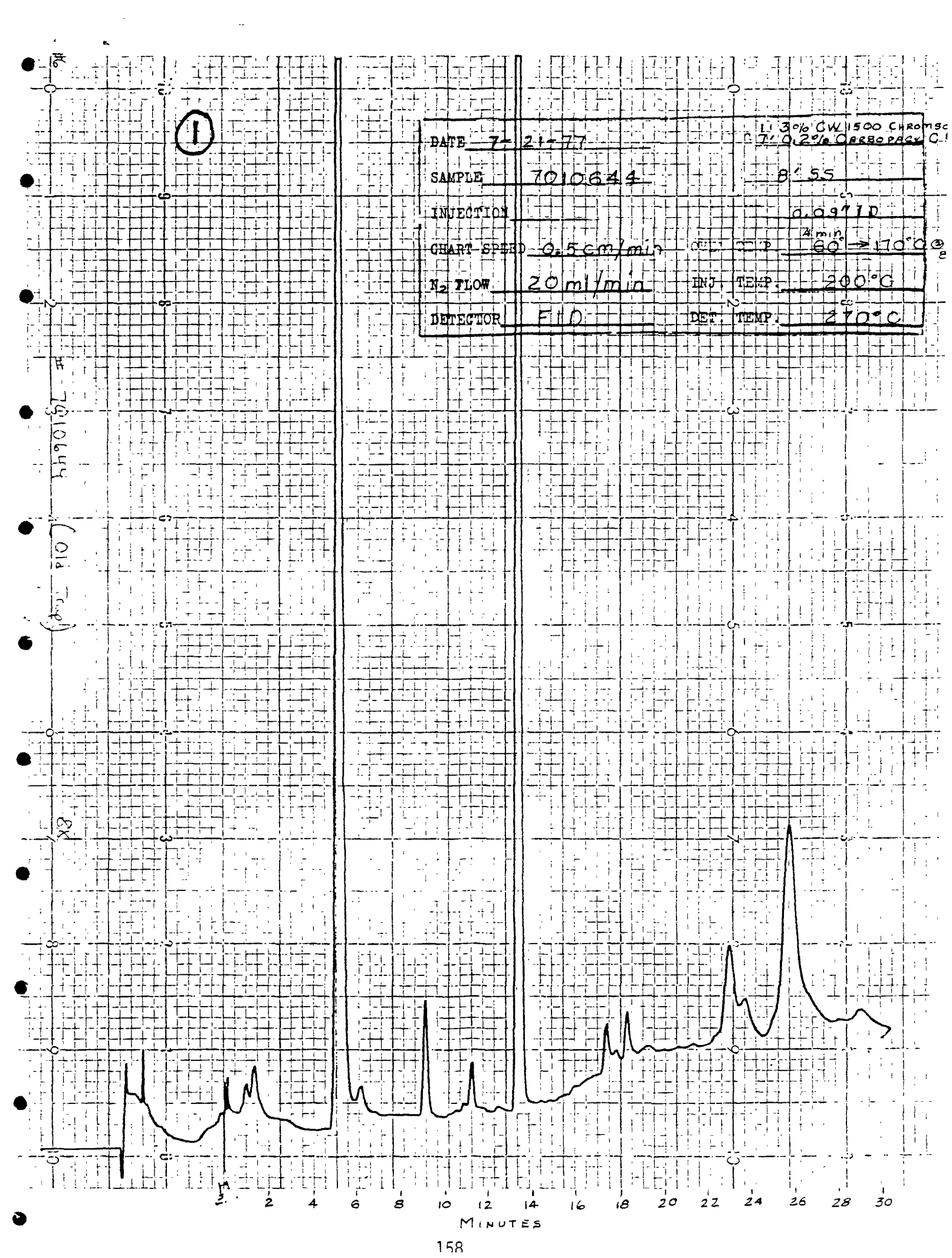
At present we are using one trap per day, following the procedure as written (some samples are diluted before purging), and not using the freezing technique.

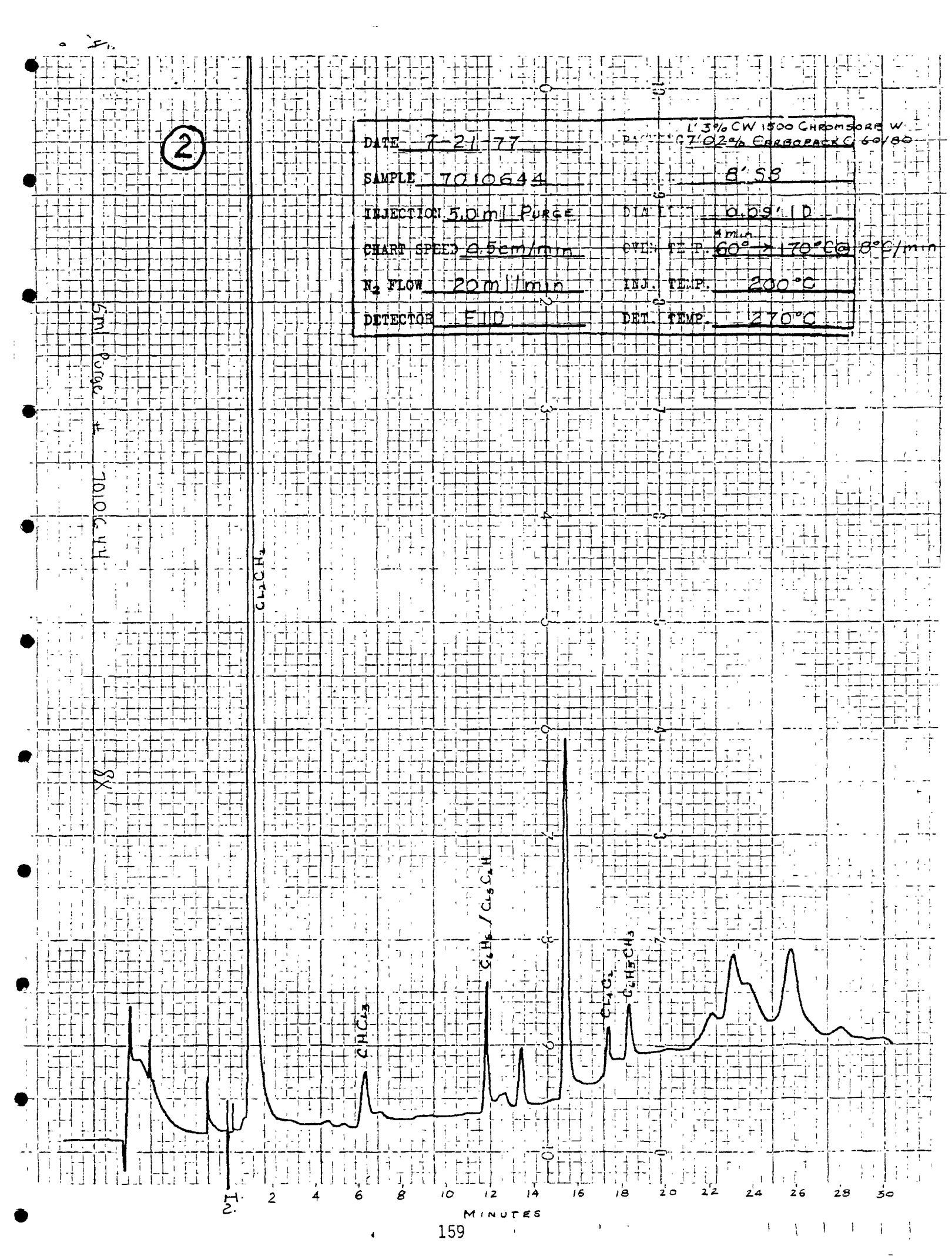
Sincerely,

Ellen

(Miss) C. Ellen Gonter, Manager
Water Laboratories Department

Enclosure


1
DATE 7-21-77
SAMPLE 7010644
INJECTION
CHART SPEED 0.5 cm/min
N2 FLOW 20 ml/min
DETECTOR FID
B 55
0.09" ID
60° → 170°C @ 4°/min
INJ. TEMP. 200°C
DET. TEMP. 270°C
MINUTES


2
DATE 7-21-77
SAMPLE 7010644
INJECTION 5.0ml Purge
CHART SPEED 0.5cm/min
N_2 FLOW 20ml/min
DETECTOR FID
L' 3% CW 1500 CHROMSORB W
7'02% CARBOPACK C 60/80
8' SS
0.09" ID
4 ml/m
OVEN TEMP. 60° → 170°C @ 8°C/min
INJ. TEMP. 200°C
DET. TEMP. 270°C
5ml purge #7010644
8X
CH_2Cl_2
$CHCl_3$
C_6H_6 / $C_{15}C_2H$
CCl_4C_2
$C_6H_5CH_3$
MINUTES
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30

environmental science and engineering, inc.
P. O. BOX 13454 • GAINESVILLE, FLORIDA 32604 • 904 / 372-3318

75-054-104

A BRIEF EVALUATION OF PHENOL EXTRACTION PROCEDURES

Prepared by:

ENVIRONMENTAL SCIENCE AND ENGINEERING, INC.
P. O. BOX 13454, UNIVERSITY STATION
GAINESVILLE, FLORIDA 32604

NOVEMBER 9, 1977

For:

EFFLUENT GUIDELINES DIVISION
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Introduction

This report is the end result of a very brief study on the effectiveness of the current protocol method for extraction and analysis of the acidic (phenolic) fraction of the semi-volatile extractables. Alternative methods were also investigated and the results are discussed here.

It should be noted that this study, which was designed and executed in about 150 man hours, is in no way conclusive. The presentation of the data in this report is for discussion purposes and to help in the solution of a very complex problem.

Procedures for Phenol Analysis

I Base/Neutral and Acidic Extraction (Similar to EPA Protocol)

1) The sample should be preserved with $CuSO_4$ and phosphoric acid to pH=4 as in Standard Methods, 14th Edition, p. 576.
2) Measure 100 ml of the sample into a 250 ml separatory funnel.
3) Adjust the pH of the sample to pH=12 with 6N NaOH solution.
4) Extract the sample with 50 ml of methylene chloride. Shake for 2 min. and let emulsion break. Repeat the extraction with 25 ml and 25 ml of methylene chloride. Save the methylene chloride layers for base-neutral analysis.
5) Adjust the pH of the sample to pH=2 with concentrated HCl solution.
6) Extract with 50 ml, 25 ml, 25 ml of methylene chloride. Transfer the methylene chloride layers through a 75 mm diameter glass funnel containing a glass wool plug and a 2 cm layer of anhydrous sodium sulfate to a 500 ml Kuderna-Danish apparatus with a 10 ml receiver.
7) Evaporate the extract down to 1.0 ml.
8) Add 10 ul of a 2 ug/ul d_{10}-anthracene internal standard solution to the 1.0 ml of the extract.
9) Inject 2 ul of the extract on the gas chromatograph/mass spectrometer using the GC conditions given in part II.
10) Calculate the amount of phenols in the sample using relative response factors with respect to the d_{10}-anthracene internal standard obtained from standard solutions.

II Steam Distillation and Extraction Method

1) The sample should be preserved with $CuSO_4$ and phosphoric acid to pH=4 as in Standard Methods, 14th Edition, p. 576.

2) Measure 500 ml of the sample into the 1 liter boiling flask of the distillation apparatus. Add several glass boiling beads.

3) Distill 450 ml of the sample, stop the distillation and when boiling ceases add 50 ml phenol-free distilled water to the distilling flask. Continue distillation until a total of 500 ml has been collected.

4) Transfer the distillate to a 1 liter separatory funnel washing the distillate container with several rinses of distilled water. Combine the washings into the separatory funnel.

5) Adjust the pH of the distillate to pH=12 with 6N NaOH solution. Check the pH with pH paper. Extract with 250 ml, 100 ml, 100 ml of methylene chloride. Each time the separatory funnel should be shaken for 2 minutes. Let the layers separate and draw off and discard the methylene chloride layer.

6) Adjust the pH of the remaining aqueous distillate in the separatory funnel to pH=2 with concentrated HCl. Check pH with pH paper.

7) Extract with 200 ml, 100 ml, 100 ml of methylene chloride. The funnel should be shaken for at least 2 minutes each time.

8) Draw off the methylene chloride layers and pass through a glass funnel containing a small amount of anhydrous sodium sulfate into a 500 ml Kuderna-Danish apparatus with a 10 ml receiver.

9) Add a glass boiling bead and concentrate the combined methylene chloride extracts to 1.0 ml on a boiling water bath.

10) Add 10 ul of a 20 ug/ul solution of d_{10}-anthracene to the 1.0 ml extract.

II Continued

11) Inject 2 ul of the sample onto a gas chromatographic column using the conditions given below.

MS/GC conditions:

Column: 6 ft x 2 mm i.d. glass

Packing: Tenax GC, 60/80 mesh

Flow: 30 ml/min, Helium

Column Temperature: 180°C to 300°C at 8°C/min

Injector Temp.: 250°C

Jet Temp: 290°C

Transfer Line: 290°C

12) Calculate the amount of phenols in the sample using mass spectrometer detection based upon relative response factors with respect to d_{10}-anthracene obtained from standard solutions.

TABLE I

Distilled Water Spiking Experiments

Compound	I Acidic Extraction Only		II 1) Base Neutral Extraction 2) Acidic Extraction		III 1) Steam Distillation 2) Acidic Extraction	
	% Recovery					
		%RSD		%RSD		%RSD
Phenol	---	---	---	---	---	---
0-Chlorophenol	92.5	11.4	88.9	8.0	75.7	5.4
0-Nitrophenol	89.1	5.6	90.4	6.1	73.5	6.7
2,4-Dichlorophenol	88.2	5.1	91.2	7.0	78.2	6.2
4-Chloro-m-cresol	88.4	0.8	87.9	4.4	85.9	4.9
2,4,6-Trichlorophenol	89.6	1.5	94.9	5.7	78.1	8.4
2,4-Dinitrophenol	---	---	---	---	---	---
p-Nitrophenol	57.7	0.6	56.5	5.1	3.1	0
4,6-Dinitro-o-cresol	97.5	3.7	95.4	8.4	67.8	16.8
Pentachlorophenol	87.5	1.7	89.5	5.7	80.7	5.7

I and II} 1 liter of water spiked with 100 ug of each phenol
III } 500 ml of water spiked with 100 ug of each phenol
Phenol and 2,4-Dinitrophenol were not included in standard solution

Creosote Waste Spiking Experiments

	IV 1) Base-Neutral Extraction 2) Acidic Extraction		V 1) Steam Distillation 2) Base-Neutral	3) Acidic Extract
	% Recovery			
		%RSD		
Phenol	90.7	9.2	93.0	6.3
0-Chlorophenol	88	17.	100.6	1.1
0-Nitrophenol	85	4.2	78	5.6
2,4-Dichlorophenol	77	4.7	42	8.5
4-Chloro-m-cresol	88	22.	100	3.5
2,4,6-Trichlorophenol	76	11.7	72	7.6
2,4-Dinitrophenol	47	16.5	39	24
p-Nitrophenol	76	10.7	7.5	33
4,6-Dinitro-o-cresol	67	3.	43	34
Pentachlorophenol	93	12.	37	27

IV } 1 liter of water spiked with 1 mg of each phenol
V } 500 ml of water spiked with 1 mg of each phenol

PROPOSED ALTERNATE METHODS

III Liquid-Liquid Extraction Using Labeled Internal Standard

1) The sample should be preserved with $CuSO_4$ and phosphoric acid to pH=4 as in Standard Methods, 14th Edition, p. 576.
2) Measure 500 ml of the sample into a 1 liter separatory funnel.
3) Prepare a stock solution in acetone of the labeled internal standard (e.g. phenol-d_6) containing 100 ug/ml of the labeled compound.
4) Spike the sample with an aliquot of the labeled internal standard solution. (e.g. 10 ml x 100 ug/ml=1000ug)
5) Adjust the pH of the sample to pH=12 with 6N NaOH solution. Add 250 ml of methylene chloride to the sample and shake very gently for about 5 minutes. A gentle rolling action is used to prevent emulsion formation. Draw off the methylene chloride layer and repeat the extraction with 100 ml and 100 ml of methylene chloride. Discard the methylene chloride layers.
6) To the remaining aqueous sample in the separatory funnel, add concentrated hydrochloric acid to bring the pH to 2.
7) Extract the sample with 200 ml of methylene chloride using a gentle rolling motion as before. Repeat the extraction with 100 ml and 100 ml more of methylene chloride. Transfer the extracts through a glass funnel containing a small amount of Na_2SO_4 (anhydrous) into a 500 ml Kuderna-Danish apparatus which includes a 10 ml receiver.
8) Concentrate the methylene chloride extracts down to 1.0 ml on a boiling water bath.

III Continued

9) Inject 2 ul of the concentrate onto a gas chromatograph/mass spectrometer using the conditions given in Procedure II.

10) Calculate the extraction efficiency of the labeled internal standard based upon response factors determined from standard runs. Correct the response for the other phenols assuming the same extraction efficiency as the internal standard.

11)a) From Standard Solution,

_____ $R_{F_{IS}} = \frac{Area_{IS}}{W_{IS}}$

$R_{F_{IS}}$ = response factor for internal standard

$Area_{IS}$ = observed MS response for internal standard

W_{IS} = amount of internal standard injected (ng).

_____ $R_{F(A,B,...)} = \frac{W_{(A,B,...)}}{Area_{(A,B,...)}} \times R_{F_{IS}}$

$R_{F(A,B,...)}$ = response factor for phenolic component A,B,...

$W_{(A,B,...)}$ = amount of component A,B,... injected (ng)

b) From Sample Extract Injection,

_____ Extraction Efficiency for internal standard (EEf_{IS}) = $\frac{Area_{IS}}{R_{F_{IS}}} \cdot W_{IS}$

$Area_{IS}$ = observed MS Area for internal standard in sample injection

(b) Continued

W_{IS} = Amount of internal standard expected in sample injection (ng)

$$\text{(ug/ml) } ppm_{(A,B,...)} = \frac{Area_{(A,B,...)}}{Area_{IS}} \times \frac{W_{IS}}{VI} \times 500 \times R_{F_{(A,B,...)}}$$

WHERE,

$ppm_{(A,B,...)}$ = concentration of phenolic component in sample in (ug/ml)

$Area_{(A,B,...)}$ = MS area of phenolic component in sample injection

$Area_{(IS)}$ = MS area of internal standard in sample injection

W_{IS} = amount of internal standard expected in sample injection (ng)

VI = volume of injection (ul)

500 = dilution factor

ANALYTICAL PROBLEMS IN EFFLUENT ANALYSIS

R. O. KAGEL

ENVIRONMENTAL SERVICES

DOW CHEMICAL COMPANY

628 BUILDING

MIDLAND, MICHIGAN

ANALYTICAL PROBLEMS IN EFFLUENT ANALYSIS

The most frustrating aspect of analyzing a complex effluent stream for specific organic compounds is the almost total lack of validated analytical method for those compounds, in that media, at low concentrations. Specifically, these analyses usually involve the effluent stream at the point where it interfaces with public waters. Here, the concentration of any specific organic compound is most certainly well below the part per million level. A few comparative definitions of parts per million (ppm), parts per billion (ppb), and parts per trillion (ppt) are given in Figure 1 in order to put the magnitude of the analytical problem into proper perspective.

At these levels it is extremely difficult, very tedious and usually costly - but not impossible - to obtain statistically meaningful analytical data. A statistically meaningful result can be obtained only by using validated analytical methods. Analytical procedures as such are not validated. Validation involves the statistical treatment of the data to determine the accuracy, precision, sensitivity and reproducibility of an analytical procedure from laboratory to laboratory or even from analyst to analyst within a laboratory. In other words, validation provides a common denominator for agreement on what an analytical result really means.

During the last five years, many industrial and government laboratories have been busy developing analytical procedures for determining trace levels of specific organic compounds in aqueous media. The increased activity in this direction is the result of two things. First (Figure 2), is the stagnation of analytical technology associated with those methods that represent the shot gun approach to effluent analysis - the BOD's, TOD's, TOC's etc. These methods provide gross parameters that characterize the quality of the effluent and are used as control parameters in most waste treatment plants. The state of the art of

this methodology has not changed appreciably over the past 10-15 years and for all practical purposes, this area of analytical technology has become stagnant.

During the same time frame, significant state of the art developments did occur in separations and detection technology. Gas chromatography-mass spectrometry (GC-MS) is rapidly becoming a common place tool in most analytical laboratories. Applied to effluent analyses, the GC-MS represents the high powered rifle with a telescopic sight for it allows the analytical chemist to zero-in on some specific compounds.

The combined use of separations technology, extraction of organic components from a waste water using an organic solvent such as hexane or ether, followed by preconcentration and then detection by GC-MS appears to be the universal approach to trace component analysis. Figure 3 shows a typical example of this type of approach. Three liters of a synthetic mixture of several compounds were extracted with diethyl ether, preconcentrated by a factor of 3000 and analyzed by GC-MS. All of these components are present at the ppb level. Once the identity of each peak in the chromatogram has been established by GC-MS, then subsequent analysis (Figure 4) are performed - in this case - by election capture gas chromatography. This is simply to avoid tying up a GC-MS which can range in price from $40K to $350K with routine analysis which could easily be done on a $5K to $6K gas chromatograph. The latter are readily available in most laboratories, can easily be set up to do the analysis, and can be readily interfaced with a computer to massage the data. These analytical procedures for identifying and quantitating most of the components in an effluent stream tend to be exceedingly tedious, time consuming and hence quite costly. A good chromotographer working in concert with a good mass spectroscopist, given enough time, the proper instrumentation, a wide choice of column packings, will eventually develop an analytical procedure for analyzing just about any system.

A good example of the kind of data generated by this approach is the Environmental Protection Agency (EPA) study of the New Orleans area water supply.[1] Some 66 organic compounds, 10 of which are shown in Figure 5, were reported to be present many at concentrations at or less than 1 ppb. This study was one of the sources used, by EPA, to develop the list of 65. The EPA research people who did this study were very careful to emphasize that the values reported represent highest concentration values rather than absolute values. This is because when a component was determined by different methods, the reported concentrations differed to some extent. Also, efficiency values (recovery) for each stage of the analytical procedure were not determined, i.e., the efficiency of carbon absorption of the compound from water, losses incurred in drying the carbon, the efficency of desorption, and losses incurred in concentrating the solvent to low volumes. Without knowledge of these factors, one is hard pressed to judge how good the results are because each step in the analytical procedure introduces some error into the determination. The results are probably good to ±50% at best and perhaps as much as ±100%, or even more. The difference between 1 ppb and 2 ppb is probably not significant in terms of the over all goals of the New Orleans study. The New Orleans study was an exceptionally fine piece of work but unfortunately it was not carried to completion - the procedures were not validated. Hence it would be difficult for any two analysts to produce numbers that would satisfactorily agree. It is obvious that for the purpose of establishing effluent guidelines and monitoring effluents one needs to establish better control and better technical criteria on the analytical data. In general, analytical chemist whether in industry or government are as genuinely concerned about the accuracy, precision, sensitivity, and reproducibility of their numbers as they are about developing the analytical procedures which generate the numbers.

For a number of years, the residue analytical chemists were faced with a similar analytical problem that involved the generation of meaningful analytical data for pesticide residues in animal tissue, plants, soil and water. Working together with USDA and FDA, they developed a mutually

acceptable technical protocol for validating their analytical methods. This protocol, the 10-10-10 principle, could easily be extended to the case of effluent analysis, which in the broadest sense is a form of residue analysis.

The mechanics of the 10-10-10 principle are shown in Figure 6. Ten determinations are made on a control sample to determine interferences. In residue studies the control is an untreated crop, soil, animal, etc. A suitable control for effluent analysis is a synthetic sample of plant effluent spiked with all compounds known to be present except the one being analyzed. In this way the level of interference is determined.

The fortified samples are used to determine recoveries. Samples of control are usually spiked with the compound of interest at various concentration and then spike is run through the entire analytical procedure. This will show losses due to absorption on glassware, charcoal absorption and desorption efficiencies, extraction efficiencies, and the like. Generally, recoveries better than 85% are acceptable. Realistically recoveries may range from 50% to 85%. The lower values are acceptable if consistent results are obtained with replicate samples.

Finally, 10 determinations are run on different aliquots of the same samples to determine the precision of the procedure. The statistics of the analytical procedure are usually verified by two independent laboratories.

The 10-10-10 principle first surfaced in the 1950's. It was later advocated by Harris and Cummings[2], USDA, (in 1964) as the absolute minimum data requirement necessary to support the registration of a pesticide use. In recent years the 10-10-10 principle has become accepted protocol for validating analytical procedures in most pesticide studies. It would be ironic if any data less than this would be deemed adequate for drawing conclusions about effluent studies.

An example of the application of the 10-10-10 principle to a residual herbicide metabolite in soil is shown in Figure 7. The chromatograms represent a 5 ppb standard of the material, a soil control and the control samples spiked at 5, 10, 100 and 500 ppb. The control is a soil sample which has not been exposed to the herbicide.

Figure 8 shows the results of 10 determinations on 3 different control soils. An interference is noted at the 0.4 ppb level. The percent error at 2σ (2 standard deviations) or the 95% confidence level is ±50%. The blank is normally subtracted from recovery and precision data. In this case, the blank is negligible.

The recovery data from spiked controls is shown in Figure 9. The spike normally extends to 1/10 of the value of interest. The average recovery shown here is 90% with an error of ±3% at the 2σ level. The small error is due to the large number of determinations, 25. The error would have been larger if only 10 determinations had been run.

As shown in Figure 10, the precision of the analytical procedure based on 10 determinations of different aliquots of a sample each containing about 500 ppb, is ±13%.

These statistics apply to any subsequent single operator determination as long as there is no deviation from the method. For example, as shown in Figure 11, a value of 484 ppb corrected for recovery and blank translates into 537± 63 ppb.

This is of course an idealized example. Normally blanks are not negligible, the recoveries are not 90% and the error may easily range up to ±50%. However, once the procedure has been validated any competent analytical chemist should be able to generate numbers which are within the range of the stated errors.

This type of validation scheme was recently used by Symons, et al[3], EPA Cincinnatti Labs, to determine single operator precision and accuracy for the determination of organohalides in chlorinated drinking waters. The single operator precision for two replicate determinations, shown in Figure 12, varies between 5 and 20% at the 1σ level. The accuracy determined by two different laboratories on solutions of known concentration, Figure 13, shows recoveries ranging, for example, between 64 and 94% for a given compound. At the present, no known data of this nature appears in the open literature for specific organic compound in an effluent stream. There is a rather significant difference between analyzing drinking water and an effluent stream. The latter is a more complicated system and the procedure and method that apply to drinking water are probably not transferable to effluent analysis. The EPA is aware of this and is presently developing appropriate analytical protocol for effluent analysis. Industry will be a contributing party to the development of this protocol.

In conclusion, by applying validated analytical methods, statistically meaningful values for the concentration of an organic compound in our effluent can be obtained and, at least these numbers, mutually agreed upon. Once the precision, accuracy, sensitivity, and reliability of the methods has been established, it is then possible to establish effluent guidelines, to monitor, B.A.T., and to affect protection of the environment with a reasonable cost/benefit ratio.

References

1. Environmental News, Nov. 8, 1974; Draft Analytical Report; New Orleans area water supply study. EPA, Lower Mississippi River Facility, Region VI, S&A.
2. T. H. Harris & J. G. Cummings, Residue Rev. 6, 104 (1964).
3. J. M. Symons et al, J. Am. Water Works Assoc. 67, 634 (1975).

FIGURE 1

TRACE CONCENTRATION UNITS

UNIT	10^{-6} 1 ppm	10^{-9} 1 ppb	10^{-12} 1 ppt
LENGTH	1 inch/16 miles	1 inch/16,000 miles	1 inch/16,000,000 miles (A six inch leap on a journey to the sun)
TIME	1 minute/2 years	1 second/32 years	1 second/320 centuries
MONEY	1¢/$10,000	1¢/$10,000,000	1¢/$10,000,000,000
WEIGHT	1 ounce/31 tons potato chips	1 pinch salt/10 tons potato chips	1 pinch salt/10,000 tons potato chips
VOLUME	1 drop vermouth/ 80 "fifths" gin	1 drop vermouth/ 500 barrels gin	1 drop vermouth/ 250,000 hogsheads gin or 1 drop vermouth in a pool of gin covering the area of a football field-43' deep or 1 drop vermouth in 520 30,000 gal tank cars of gin
AREA	1 sq. ft/23 acres	1 sq. ft/36 sq. miles	1 sq. in/250 sq miles
ACTION	1 bogey/3,500 golf tournaments	1 bogey/3,500,000 golf tournaments	1 bogey/3,500,000,000 golf tournaments
	1 lob/1,200 tennis matches	1 lob/1,200,000 tennis matches	1 lob/1,200,000,000 tennis matches
QUALITY	1 bad apple/2,000 barrels	1 bad apple/2,000,000 barrels	1 bad apple/2,000,000,000 barrels
RATE	1 dented fender/10 car lifetimes	1 dented fender/10,000 car lifetimes	1 dented fender/10,000,000 car lifetimes

FIGURE 2

ANALYSIS OF WASTE STREAMS
-STATE OF THE ART-

- GROSS PARAMETERS
  - BIOCHEMICAL OXYGEN DEMAND (BOD)
  - TOTAL OXYGEN DEMAND (TOD)
  - TOTAL ORGANIC CARBON (TOC)
  - TOTAL DISSOLVED SOLIDS (TDS)

- INDIVIDUAL COMPONENTS
  - SEPARATION TECHNOLOGY
  - LIQUID CHROMATOGRAPH (LC)
  - GAS CHROMATOGRAPH (GC)
  - GAS CHROMATOGRAPH-MASS SPECTROMETRY (GC-MS)

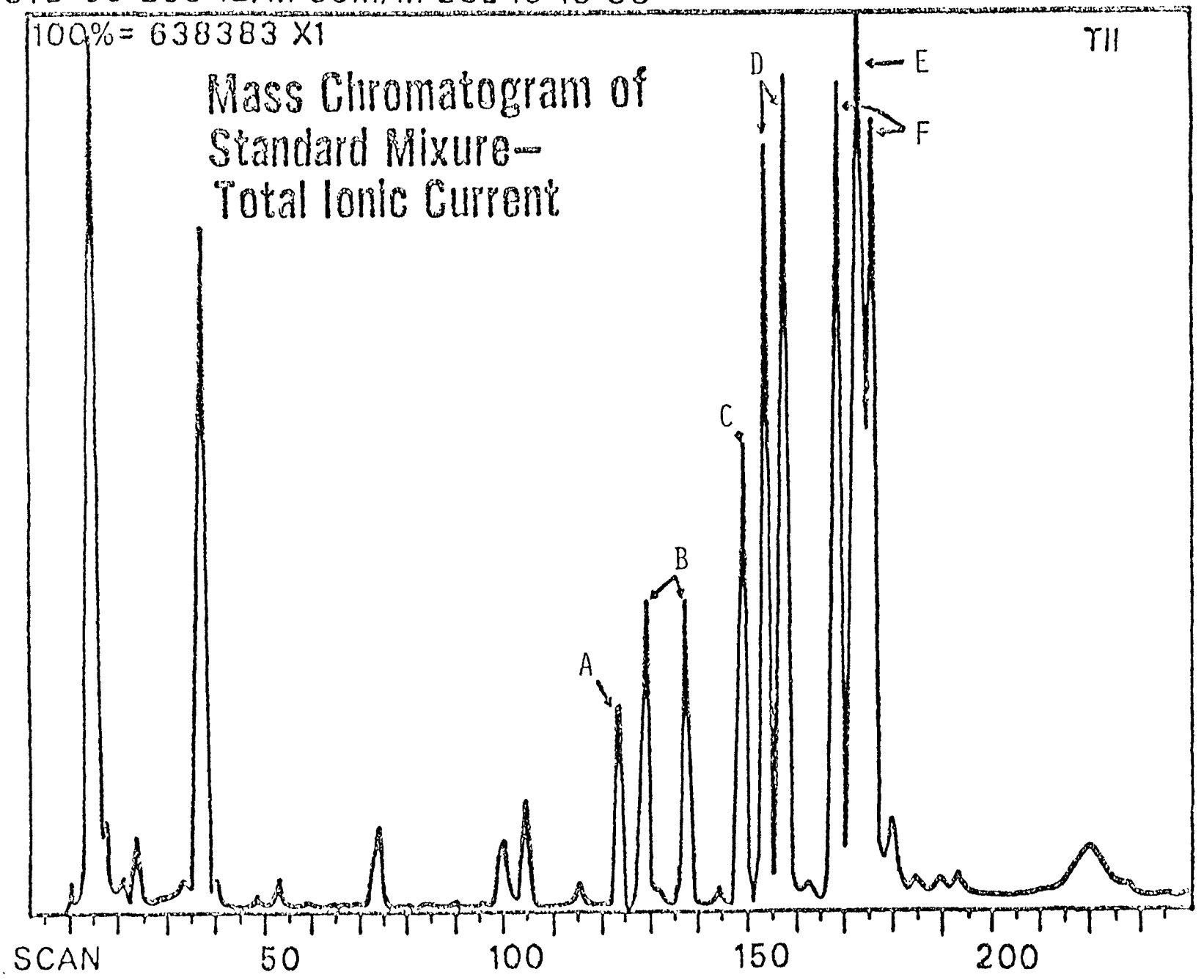
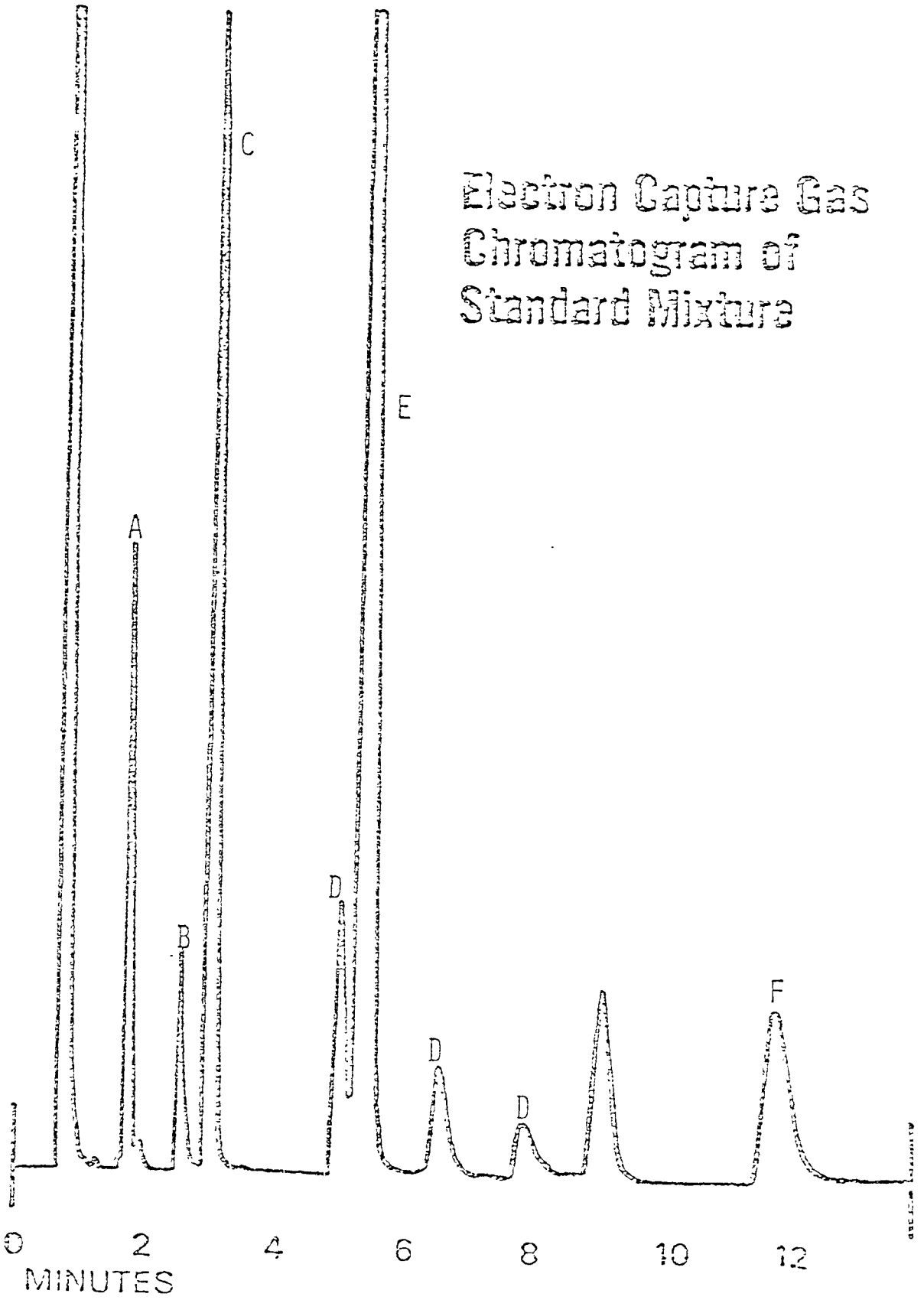

NHM1
STD 90-250 12/M 35M/M 2UL 10-10 UC
100%= 638383 X1
TII
Mass Chromatogram of
Standard Mixure-
Total Ionic Current
A
B
C
D
E
F
SCAN
50
100
150
200

FIGURE 4



Electron Capture Gas Chromatogram of Standard Mixture

FIGURE 5

ORGANIC COMPOUND IDENTIFICATION

NEW ORLEANS AREA WATER SUPPLY STUDY[1]

	COMPOUND	HIGHEST MEASURED CONCENTRATION µg/l (ppb) CARROLLTON WATER PLANT	JEFFERSON #1 WATER PLANT	JEFFERSON #2 WATER PLANT
1	Acetaldehyde	D-VOA	NE	NE
2	Acetone	D-VOA	NE	NE
3	Alkylbenzene-C_2 isomer	0.05	ND	ND
4	Alkylbenzene-C_2 isomer	0.33	ND	ND
5	Alkylbenzene-C_2 isomer	0.11	0.03	ND
6	Alkylbenzene-C_3 isomer	0.01	ND	ND
7	Alkylbenzene-C_3 isomer	0.04	0.05	0.02
8	Alkylbenzene-C_3 isomer	0.02	ND	ND
9	Atrazine * (2-chloro-4-ethylamino-6-isopropylamino-s-triazine)	5.0	4.7	5.1
10	Deethylatrazine (2-chloro-4-amino-6-isopropylamino-s-triazine)	0.51	0.27	0.27

FIGURE 6

METHODS VALIDATION

THE "10-10-10" PRINCIPLE

10 DETERMINATIONS OF A CONTROL TO DETERMINE INTERFERENCES

10 DETERMINATIONS OF A FORTIFIED SAMPLE TO DETERMINE RECOVERY VALUES

10 DETERMINATIONS OF ACTUAL SAMPLE TO DETERMINE PRECISION OF THE METHOD

FIGURE 7

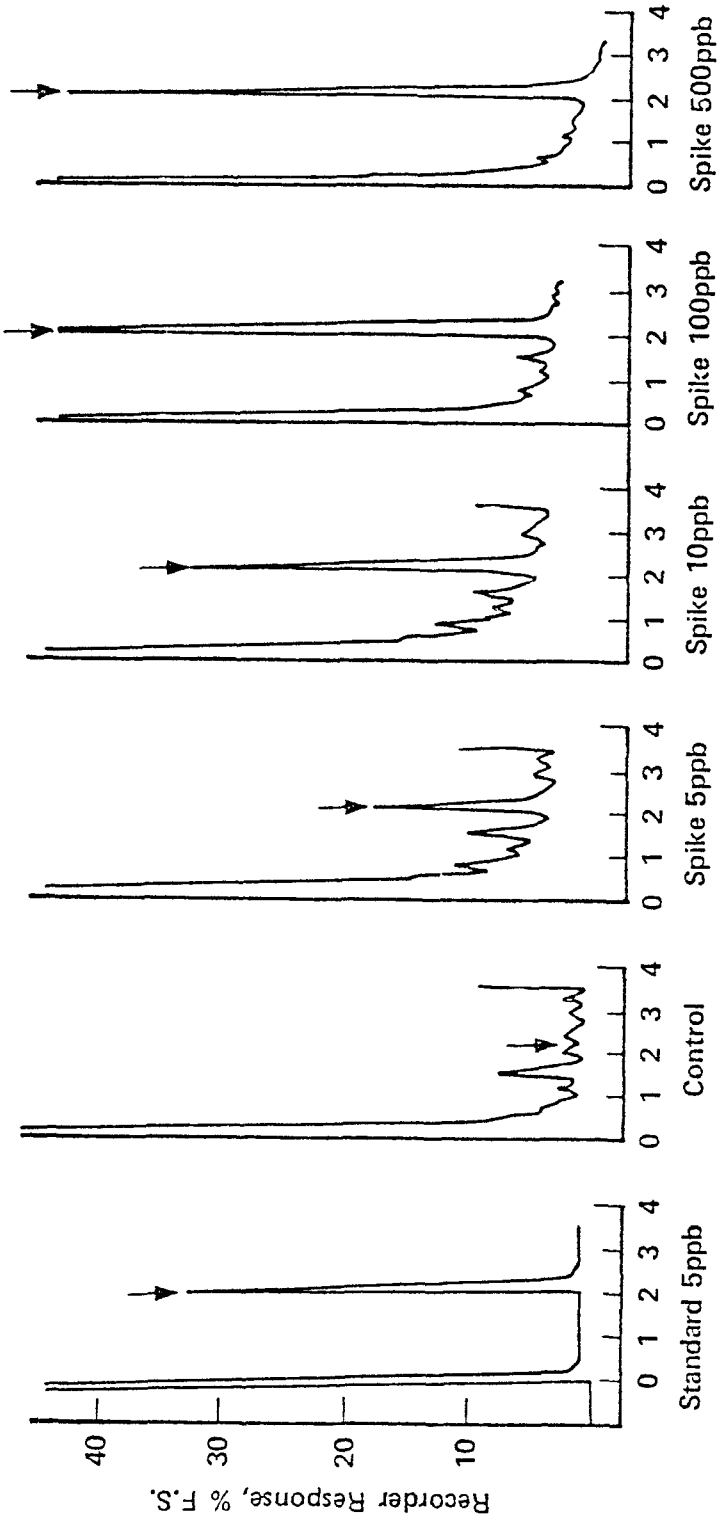

Recorder Response, % F.S.
40
30
20
10
0 1 2 3 4
Standard 5ppb
Control
Spike 5ppb
Spike 10ppb
Spike 100ppb
Spike 500ppb

FIGURE 8

PRECISION OF BLANK

n	Concentration ppb X_i
1	0.5
2	0.3
3	0.4
4	0.2
5	0.3
6	0.4
7	0.4
8	0.3
9	0.4
10	0.5

$\bar{X} = .4$

$\Sigma(X_i - \bar{X})^2 = .1$

$$\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n - 1}} = .1$$

Relative standard deviation at 95% confidence level

$$\frac{2\sigma}{\bar{X}} \ 100\% = 50\%$$

$$X\left(1 \pm \frac{2\sigma}{\bar{X}} \ 100\%\right) = .4 \pm .2\text{ppb}$$

FIGURE 9

AGR Number	Location	ppb Added	ppb Found	% Recovery
113549	Corvallis	5	4.8	96
121954	Davis		4.3	86
122195	Davis		4.5	90
118092	Fargo		3.9	78
127406	Fargo		4.8	96
114598	Bozeman		4.3	86
121955	Davis	10	9.2	92
112239	Pendleton		8.3	83
117038	Pendleton		9.6	96
119526	Corvallis		9.7	97
114597	Bozeman		8.6	86
121954	Davis	50	43.6	87
122194	Davis		45.1	90
113424	Fargo		44.3	89
132581	Bozeman		43.7	87
114596	Bozeman		44.7	89
113548	Corvallis		49.7	99
121921	Davis	100	86.7	87
130768	Bozeman		99.5	100
128288	Pendleton		99.8	100
130510	Fargo	500	405	81
112240	Pendleton		410	82
122982	Bozeman		484	97
130767	Bozeman	1000	888	89
128286	Pendleton		973	97
				90±3*

*95% confidence limits for the mean.

AVERAGE PERCENTAGE RECOVERY

$$\bar{R}_n = \frac{\Sigma R_n}{n} = 90\% = .90$$

Relative standard deviation at 95% confidence level of $\bar{R}_n$.

$$\frac{2\sigma R_n}{\bar{R}_n \sqrt{n}} \quad 100\% = 3\%$$

$$\bar{R}_n = 90 \pm 3\%$$

FIGURE 10

PRECISION OF AN ANALYSIS

n	Concentration ppb X_i
1	436
2	451
3	410
4	484
5	447
6	451
7	443
8	437
9	433
10	492
$\bar{X}$ =	448

$$\Sigma(X_i - \bar{X})^2 = 5210$$

$$\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n - 1}} = 24$$

Relative standard deviation at 95% confidence level

$$\frac{2\sigma}{\bar{X}} \ 100\% = 11\%$$

$$X\left(1 \pm \frac{X2\sigma}{\bar{X}} \ 100\%\right) = 484 \pm 53 \text{ppb}$$

FIGURE 11

A C T U A L C O N C E N T R A T E

$$C = \frac{484(1 \pm 11\%)}{.90(1 \pm 3\%)} = 537(1 \pm 11\%) = 537 \pm 63\text{PPB}$$

CONC FOUND PPB	BLANK PPB	% RECOVERY DETERMINED	CONCENTRATE AFTER CORRECTION
484 ± 53	0.4±2.	90 ± 3%	537 ± 63PPB

FIGURE 12

DETERMINATION OF PRECISION[3]

Compound	LOW CONCENTRATION Spiked Conc. µg/ℓ	LOW CONCENTRATION Relative σ percent	HIGH CONCENTRATION Spiked Conc. µg/ℓ	HIGH CONCENTRATION Relative σ percent
Chloroform	2	6	18	7
1,2-dichloroethane	1	5	*	*
Carbon tetrachloride	2	14	*	*
Bromo-dichloromethane	2	5	20	7
Dibromo-chloro methane	2	10	30	13
Bromoform	4	20	30	12

*Not determined at high concentration

FIGURE 13

DETERMINATION OF ACCURACY[3]

(CONCENTRATION - µg/ℓ)

	Chloroform		1,2-Dichloro-ethane		Carbon Tetrachloride	
Calculated	75	60 (±6-7%)	10	5 (±5%)	10	6 (±14%)
Lab A	63 (84)	46 (77)	9 (90)	6 (120)	9 (90)	5 (83)
	65 (87)	46 (77)	10 (100)	5 (100)	8 (80)	6 (100)
Lab B	61 (81)	54 (90)	10 (100)	5 (100)	8 (80)	6 (100
	76 (101)	69 (98)	10 (100)	4 (80)	6 (60)	4 (67)

	Bromo-dichloro methane		Dibromo-chloro-methane		Bromoform	
Calculated	40	24 (±5-7%)	24	19 (±10-13%)	40	23 (±12-20%)
Lab A	39 (98)	22 (92)	23 (96)	14 (74)	40 (100)	18 (78)
	40 (100)	23 (96)	23 (96)	18 (94)	38 (95)	24 (108)
Lab B	35 (88)	21 (88)	17 (71)	13 (68)	48 (120)	24 (104)
	38 (95)	19 (75)	15 (63)	12 (63)	45 (13)	29 (126)

DRAFT

PRIORITY POLLUTANT VALIDATION PROTOCOL

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The Dow Chemical Company
Midland, Michigan 48640

1. ANALYTICAL METHODOLOGY

The methods for the priority pollutants are those listed in "Analytical Methods for the Verification Phase of the Bat Review" issued by Effluent Guidelines Division, Office of Water and Hazardous Materials, U.S. Environmental Protection Agency. Alternate Analytical methods will be considered if they are properly substantiated in accordance with the following validation Protocol. Methods must be described in sufficient detail in a step-wise fashion that a competent analyst, unfamiliar with the specific procedure can apply the method. Modifications of published methods must be described fully. One method may suffice for simultaneous analysis of several components.

2. VALIDATION PROTOCOL

The validation protocol is a modification of the EPA-EMSL Analytical Quality Control Program[1] and the Winter[2] (EPA-EMSL) interlaboratory validation study program. Each analytical procedure must be validated by an adequate number of control values and recovery values to establish the precision and accuracy. Validation is necessary for an analytical procedure to become an analytical method. The validation should be repeated by at least three independent laboratories. Participating laboratories must conform to the requirements specified by Winter. In accordance with EPA-EMSL analytical quality control programs, seven determinations for control and recovery values are a minimal data requirement.

A. Best Achievable Limit of Detection (LOD)

The best achievable LOD is obtained from the analyses of seven samples of organic free water carried through the entire analytical procedure. The observed peak-to-peak noise, O^B, and the average peak-to-peak noise, $\bar{O}^B$, are determined. The best achievable limit of detection, LOD_B is defined as:

$$LOD_B = 2.5\ \bar{O}^B$$

B. Control Values

Control values are those obtained in the analyses of seven samples of plant influent carried through the entire analytical procedure. The observed control values, O^I, the average value, $\bar{O}^I$, and the standard deviation, $\sigma_{\bar{O}^I} = \left[\Sigma \frac{(O^I - \bar{O}^I)^2}{n-1}\right]^{1/2}$ are determined. The practical limits of detection of the procedure (LOD_I) are defined as:

a. If $\bar{O}^I > 2.5\ \bar{O}^B$, then $LOD_I = 2.5\ \sigma_{\bar{O}^I}$

b. If $\bar{O}^I \leq 2.5\ \bar{O}^B$, then $LOD_I = 2.5\ \bar{O}^I$

C. Recovery Values

A single sample of plant effluent is analyzed to obtain the observed sample concentration, O^S. The amount found, C_f,

$$C_f = O^S - \bar{O}^I$$

Recovery values are obtained in analyses of fortified samples carried through the entire analytical procedure. The level of fortification is a function of C_f and LOD_I as follows:

a. If $C_f \geq 10\ LOD_I$, then fortify with C_f (so the total concentration is $\sim 2C_f$) and run seven determinations through the entire analytical procedure. Calculate the average percent recovery, $\bar{R}^S_f$ and the standard deviation (at 95% confidence level).

$$2\sigma_{\bar{R}^S_f} = \frac{2}{\sqrt{n}} \left[\frac{\Sigma (R^S_f - \bar{R}^S_f)^2}{n-1}\right]^{1/2}$$

b. If $C_f < 10 LOD_I$ then fortify with 1x, 3x, and 10x LOD_I and run 3,2,2 determinations, respectively, through the entire analytical procedure. Calculate the average percent recovery, $\bar{R}^S_f$, and the standard deviation, $\sigma_{\bar{R}^S_f}$, as shown above.

D. Precision Values

The precision of a single determination, O^S, at the 95% confidence level is calculated from the recovery data as:

$$2\sigma_O^S = \frac{2}{\bar{R}_f^S}\left[\frac{\Sigma\,(R_f^S - \bar{R}_f^S)^2}{n-1}\right]^{\frac{1}{2}}$$

E. Calculation of Data

The actual concentration, Ca, and the standard deviation, σ_{Ca} is:

$$Ca \pm 2\sigma_{Ca} = \frac{O^S\left(1 \pm 2\,\frac{\sigma_{R_f^S}}{\bar{R}_f^S}\cdot 100\%\right) - \bar{O}^I\left(1 \pm 2\,\frac{\sigma_{O^I}}{\bar{O}^I}\cdot 100\%\right)}{\bar{R}_f^S\left(1 \pm 2\,\frac{\sigma_{R_f^S}}{\bar{R}_f^S\sqrt{n}}\cdot 100\%\right)}$$

F. Reporting of Data

a. Any result where $O^S < LOD_I$ is reported as "N.D. (LOD_I)" meaning, not detected, with the detection limit given in parenthesis.

b. If $LOD_I \leq O^S < 4\ LOD_I$ the result is reported as a qualitative result. A second determination must be run. The two separate results and an average will be reported as quantitative results.

c. For $O^S \geq 4\ LOD_I$ a single determination is reported as a quantitative result.

REFERENCES

1. Handbook for Analytical Quality Control in Water and Wastewat Laboratories EPA-EMSL 1976.

2. J. A. Winter, "Validation of Environmental Measurement Methodology" Int. Conf. On Environmental Sensing and Assessment, September 14-19, 1975.

NOV 23 1911

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE:

SUBJECT: Metals Analysis - Chicago Regional Laboratory

FROM: William A. Telliard, Chief
Energy and Mining Branch

TO: Branch Chiefs, EGD
Project Officer, EGD

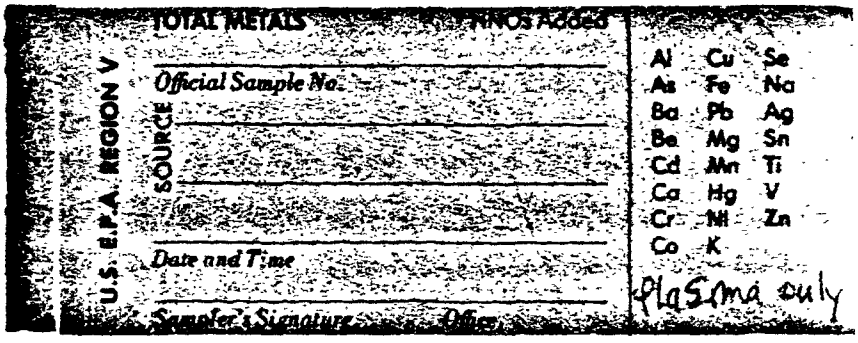
The following memo addresses a recent meeting that was held between representatives of this office and several staff members from the Region V Laboratory, with regards to the negotiation for additional analytical support. Arrangements have been made for an additional 1,000 samples to be analyzed by the Chicago Regional Laboratory.

The following information pertains to the labeling, sampling and type of containers to be utilized in the forth coming program for metal analysis.

During the previous period of time, a number of points have been raised regarding the use of uniformity in both the container and sample size. The following notes should be made available to contract personnel as well as the Surveillance and Analysis Divisions:

1. Labeling Codes - Attachment A of this memo contains a list of codes numbers to be used on labels which will be supplied to you for those samples to be analyzed for metal parameters. A code number shall be a six digit code, the first two digits indicate the industrial category, the second two digits refer to the contractor or sampling group and the third set is the sample number. These codes and the labeling information are contained in Appendix A. The regional lab will utilize this coding system for their computer which handles the data output.

Example:



11 22 57
Sample No.

This code number means that this particular sample contains coal mining water (11) taken by Versar (22) and that this is the 57th bottle or sample taken.

2. Samples shall not be preserved with acid as it is written in the Screening Protocol. This procedure in the only way to comply with the Department of Transportation regulations against shipping corrosive materials. Samples shall be prepared for analysis of total metals by a hard digestion at the Chicago Regional Labs. This means that a combination of nitric acid and hydrochloric acid shall be added for samples analyzed by the plasma unit.

3. Data Turnaround Time - Twenty-two elements can presently be determined with the plasma unit. A number of parameters must still be done by either flameless AA or flame AA for the purpose of identification. To enable a better utilization of time, it is recommended that the primary contractor (most of which have atomic absorption capabilities) run the following parameters; selenium, arsenic, antimony thallium and silver. Twenty-two additional parameters can be supplied by the Central Regional Lab with the plasma unit. This will cut down on the time delays due to the limited instrumentation available in the laboratory.

4. Sample Type - As has previous been the case, samples from the screening portion of the program shall be taken from the composite sample (either influent or effluent or both) well mixed and then put into a properly labeled container.

Additional sample capabilities will hopefully be made available, some time after the first of the year. Until then, we will be

limited to the 1,000 samples that have been negotiated. The need for metals analysis for screening samples by all project officers should be made known to myself or Gail Goldberg, as soon as possible, so that scheduling can be afforded.

5. Quality Control - The Central Regional Laboratory will continue to maintain a quality control file for all samples run for EGD. This quality control file will be periodically supplied to the Division and as needed can be incorporated into any court record. The quality control file is probably the most complete effort that the Division has been able to obtain. It specifies the recoveries, performance of the instrument, and the individual sample variability on a day-by-day basis. This information will be made available through the Energy and Mining Branch to the project officers and their contractors, as the need arises. The quality control program at Central Regional Lab is far superior to any program that has previously existed in the Division. It can insure you that the metals analysis data are properly framed and within the confines in definition of the performance standards specified under 304(g). As each project comes to a conclusion this data will be made available to the individual project officers and Branches for inclusion in their record. A period of a two weeks notice will be greatly appreciated, this notification again, should be made in writing to Gail S. Goldberg so that we may solicit the computer output for the quality control data for those samples.

6. Samples, are collected as before meaning that there exists only one sample for metal analysis per sampling site. The possibility of collecting duplicates was considered. This idea had to be rejected in view of time limits and financial constraints.

7. The use of old labels for metals analysis, like the one shown in the screening protocol should be discontinued. New labels as shown in point 1. of this memo shall be distributed to you. Only these new labels are compatible with the Chicago Lab computer.

Sampling Contractor Code Number

01. EPA Region I
02. EPA Region II
03. EPA Region III
04. EPA Region IV
05. EPA Region V
06. EPA Region VI
07. EPA Region VII
08. EPA Region VIII
09. EPA Region IX
10. EPA Region X
11. National Enforcement Investigations Center
12.
13. Hamilton Standard
14. Colin A. Houston & Associates
15. Environmental Science & Engineering , Inc.
16. Ryckman, Edgerley, Tomlinson and Associates, Inc.
17. E.H. Richardson Associates
18. Mid-West Research Instutute
19. NUS - Cyrus Rice Division
20. Burns & Roe, Inc.
21. Calspan Corporation
22. Versar Incorporated
23. Jacobs Engineering Company
24. E.C. Jordan Co., Inc.
25. Sverdrup & Parcel and Associates, Inc.

26. Carborundum Corporation

27. TRW

28. Industrial Environmental Research Lab, Cincinnati

Industrial Code Numbers

01 - Timber Products
02 - Steam Electric
03 - Leather Tanning
04 - Iron & Steel mfg.
05 - Petroleum Refining
06 - Nonferrous Metals
07 - Paving & Roofing
08 - Paint & Ink
09 - Printing & Publishing
10 - Ore Mining
11 - Coal Mining
12 - Organic Chemicals
13 - Inorganic Chemicals
14 - Textile Mills
15 - Plastics & Synthetics
16 - Pulp & Paper
17 - Rubber Processing
18 - Soaps & Detergents
19 - Auto & other Laundries
20 - Pesticides mfg.
21 - Photographic Industries
22 - Gum & Wood Industries
23 - Pharmaceuticals
24 - Explosives
25 - Adhesive & Sealants
26 - Battery mfg.
27 - Plastics mfg.
28 - Foundries
29 - Coil Coating
30 - Porcelain/Enameling
31 - Aluminum
32 - Copper
33 - Electronics
34 - Shipbuilding
35 - Electroplating
36 - Oil and Gas Extraction

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: NOV 2 0 1977

SUBJECT: Sample Codes

FROM: William Telliard, Chief
Energy and Mining Branch

TO: All EGD Project Officers

You will inform your sampling contractor to use the same digit coding system for metals and organic samples. This six digit code system is explained in the attached memo. Keeping the same code number for all portions of samples greatly reduces the amount of data processing and any changes for error in correlating samples.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: NOV 23 1977

SUBJECT: Chicago Lab - New address

FROM: William Telliard, Chief
Energy and Mining Branch

TO: All EGD Project Officers

The Chicago Lab has moved. The new address is:

U.S. Environmental Protection Agency
Region V, Central Regional Laboratory
536 South Clark
Chicago, Illinois 60605

Please send screening samples for metals analysis only, to the above address.

PRELIMINARY INTERIM PROCEDURE

FOR

FIBROUS ASBESTOS

by

Charles H. Anderson and J. MacArthur Long

Analytical Chemistry Branch
U.S. Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30601

FIBROUS ASBESTOS

(Preliminary Interim Procedure)

(Transmission Electron Microscopy Method)

1. Scope and Application

1.1 This method is applicable to drinking water and water supplies.

1.2 The method determines the number of asbestos fibers/liter, their size (length and width), the size distribution, and total mass. The method distinguishes chrysotile from amphibole asbestos. The detection limits are variable and depend upon the amount of total extraneous particulate matter in the sample as well as the contamination level in the laboratory environment. Under favorable circumstances 0.1 MFL (million fibers per liter) can be detected. The detection limit for total mass of asbestos fibers is also variable and depends upon the fiber size and size distribution in addition to the factors affecting the total fiber count. The detection limit under favorable conditions is in the order of 0.1 ng/l.

1.3 The method is not intended to furnish a complete characterization of all the fibers in water.

1.4 It is beyond the scope of this method to furnish detailed instruction in electron microscopy, electron diffraction or crystallography. It is assumed that those using this method will be sufficiently knowledgeable in these fields to understand the methodology involved.

1.5 The method outlined below is based upon what is considered to be state-of-the art practice but it is emphasized that at present no single analytical procedure for asbestos is universally accepted. As a result no inter-laboratory comparisons are presented and the procedure should <u>not</u> be considered as a standard method.

2. Summary of Method

2.1 A variable, known volume of water sample is filtered through a membrane filter of sufficiently small pore size to trap asbestos fibers. A small portion of the filter with deposited fibers is placed on an electron microscope grid and the filter material removed by gentle solution in organic solvent. The material remaining on the electron microscope grid is examined

in a transmission microscope at high magnification. The asbestos fibers are identified by their morphology and electron diffraction pattern and their length and width are measured. The total area examined in the electron microscope is determined and the number of asbestos fibers in this area is counted. The concentration in MFL (millions of fibers/liter) is calculated from the number of fibers counted, the amount of water filtered, and the ratio of the total filtered area/sampled filter area. The mass/liter is calculated from the assumed density and the volume of the fibers.

3. Definitions

Asbestos - A generic term applied to a variety of commercially useful silicate minerals that may have a fibrous structure.

Fiber - Any particle that has parallel sides and a length/width ratio greater than or equal to 3:1.

Aspect Ratio - The ratio of length to width.

Chrysotile - A nearly pure hydrated magnesium silicate, the fibrous form of the mineral serpentine, possessing a unique layered structure in which the layers are wrapped in a helical cylindrical manner about the fiber axis.

Amphibole - A silicate mineral whose basic structural unit is a double silica chain (Si_4O_{11}), but with a variable composition and a layered structure that is easily cleaved to form a fiber.

Detection Limit - The calculated concentration in MFL, equivalent to one fiber above the background or blank count.

Statistically Significant - Any concentration based upon a total fiber count of five or more in 20 grid squares.

4. Sample Handling and Preservation

4.A Sampling

It is beyond the scope of this procedure to furnish detailed instructions for field sampling; the general principles of sampling waters are applicable. There are some considerations that apply to asbestos fibers, a special type of particulate matter. These fibers are small, and in water range in length from .1 μm to 20 μm or more. Because of the range of size there may be a vertical distribution of particle sizes. This distribution will vary with depth

depending upon the vertical distribution of temperature as well as the local meteorological conditions. Sampling should take place according to the objective of the analysis. If a representative sample of a water supply is required a carefully designed set of samples should be taken representing the vertical as well as the horizontal distribution and these samples composited for analysis.

4.1 Containment Vessel

The sampling container shall be a clean polyethylene, screw-capped bottle capable of holding at least one liter. The bottle should be rinsed at least two times with the water that is being sampled prior to sampling.

NOTE: Glass vessels are not suitable as sampling containers.

4.2 Quantity of Sample

A minimum of approximately one liter of water is required and the sampling container should not be filled. It is desirable to obtain two samples from one location.

4.3 Sample Preservation

No preservatives should be added during sampling and the addition of acids should be particularly avoided. If the sample cannot be filtered in the laboratory within 48 hours of its arrival, sufficient amounts (1 ml/l of sample) of a 2.71% solution of mercuric chloride to give a final concentration of 20 ppm of Hg may be added to prevent bacterial growth.

5. Interferences

5.1 Misidentification

The guidelines set forth in this method for counting fibrous asbestos require a positive identification by both morphology and crystal structure as shown by an electron diffraction pattern. Chrysotile asbestos has a unique tubular structure, usually showing the presence of a central canal, and exhibits a unique characteristic electron diffraction pattern. Although halloysite fibers may show a similar streaking to chrysotile they do not exhibit its characteristic triple set of double spots or 5.3A layer line. It is highly improbable that a non-asbestiform fiber would exhibit the distinguishing chrysotile features. Although amphibole fibers exhibit characteristic morphology and electron diffraction patterns, they do

not have the unique properties exhibited by chrysotile. It is therefore possible though not probable for misidentification to take place. Hornblende is an amphibole and, in a fibrous form, will be mistakenly identified as amphibole asbestos.

It is important to recognize that a significant variable fraction of both chrysotile and amphibole asbestos fibers do not exhibit the required confirmatory electron diffraction pattern. This absence of diffraction is attributable to unfavorable fiber orientation and fiber sizes. The results reported will therefore be low as compared to the absolute number of asbestos fibers that are present.

5.2 Obscuration

If there are large amounts of organic or amorphous inorganic materials present, some small asbestos fibers may not be observed because of physical overlapping or complete obscuration. This will result in low values for the reported asbestos content.

5.3 Contamination

Although contamination is not strictly considered an interference, it is an important source of erroneous results, particularly for chrysotile. The possibility of contamination should therefore always be a consideration.

5.4 Freezing

The effect of freezing on asbestos fibers is not known but there is reason to suspect that fiber break down could occur and result in a higher fiber content than was present in the original sample. Therefore the sample should be transported to the laboratory under conditions that would avoid freezing.

6. Equipment and Apparatus

6.1 Specimen Preparation Laboratory

The ubiquitous nature of asbestos, especially chrysotile, demands that all sample preparation steps be carried out to prevent the contamination of the sample by air-borne or other source of asbestos. The prime requirement of the sample preparation laboratory is that it be sufficiently free from asbestos contamination that a specimen blank determination using 200 ml of asbestos-free water yields no more than 2 fibers in twenty grid squares of a conventional 200 mesh electron microscope grid.

In order to achieve this low level of contamination, the sample preparation area should be a separate conventional clean room facility. The room should be operated under positive pressure and have incorporated electrostatic precipitators in the air supply to the room, or alternatively absolute (HEPA) filters. There should be no asbestos floor or ceiling tiles, transite heat-resistant boards, nor asbestos insulation. Work surfaces should be stainless steel or Formica or equivalent. A laminar flow hood should be provided for sample manipulation. Disposable plastic lab coats and disposable overshoes are recommended. Alternatively new shoes for all operators should be provided and retained for clean room use only. A mat (Tacky Mat, Liberty Industries, 589 Deming Rd., Berlin, Connecticut 06037, or equivalent) should be placed inside the entrance to the room to trap any gross contamination inadvertently brought into the room from contaminated shoes. Normal electrical and water services, including a distilled water supply should be provided. In addition a source of ultra-pure water from a still or filtration-ion exchange system is desirable.

6.2 Instrumentation

6.2.1 Transmission Electron Microscope. A transmission electron microscope that operates at a minimum of 80 KV, has a resolution of 1.0 nm and a magnification range of 300 to 100,000. If the upper limit is not attainable directly it may be attained through the use of auxiliary optical viewing. It is mandatory that the instrument be capable of carrying out selected area electron diffraction (SAED) on an area of 300 nm. The viewing screen shall have either a millimeter scale, concentric circles of known radii, or other devices to measure the length and width of the fiber. Most modern transmission microscopes meet the requirements for magnification and resolution.

An energy-dispersive X-ray spectrometer is useful for the identification of suspected asbestiform minerals; this accessory to the microscope, however, is not mandatory.

6.2.2 Data Processor. The large number of repetitive calculations make it convenient to use computer facilities together with relatively simple computer programs.

6.2.3 Vacuum Evaporator. For depositing a layer of carbon on the Nuclepore filter, and for preparing carbon coated grids.

6.2.4 Low Temperature Plasma Asher. To be used for the removal of organic material (including the filter) from samples containing so much organic matter that asbestos fibers are obscured. The sample chamber should be at least 10-cm diameter.

6.3 Apparatus, Supplies and Reagents

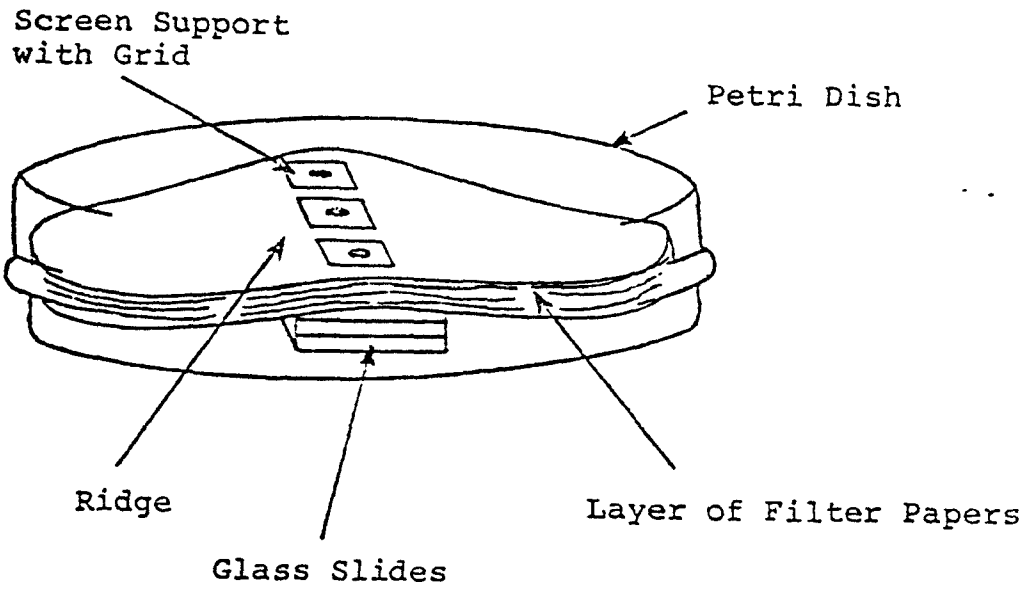
6.3.1 Jaffe Wick Washer. For dissolving Nuclepore filter (if Nuclepore is used in sample preparation). Assemble as in 8.2A.1. It is illustrated in Figure 1.

6.3.2 Condensation Washer. For use in dissolving the Millipore filter when using the Millipore sample preparation method. A system with controlled heating, controlled refluxing, and a cold finger for holding the electron microscope (EM) sample grids. At least two systems are commercially available. Figure 2 is an illustration of one design that has proven satisfactory.

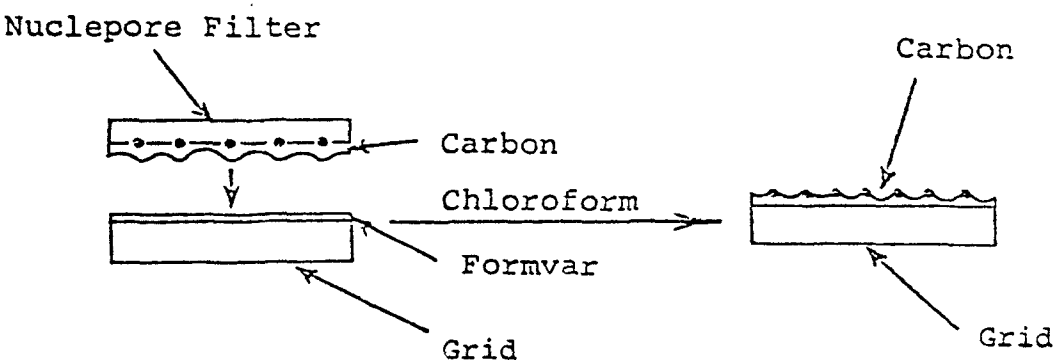
6.3.3 Filtering Apparatus. 47-mm funnel (Cat. No. XX1504700, Millipore Corporation, Order Service Dept., Bedford, MA 01730). Used to filter water samples. 25-mm funnel (Millipore Cat. No. XX1002500). Used to filter dispersed ash samples.

6.3.4 Vacuum Pump. For use in sample filtration. Should provide vacuum up to 20 inches of mercury.

6.3.5 EM Grids. 200-mesh copper or nickel grids, covered with carbon-coated collodion for use with the Millipore-condensation washing technique. Formvar-backed grids, without a carbon coating are used in the Nuclepore-Jaffe sample preparation method. These grids may be purchased from manufacturers of electron microscopic supplies or prepared by standard electron microscopic grid preparation procedures. Finder grids may be substituted and are useful if the re-examination of a specific grid opening is desired.



A.



B.

Figure 1. Modified Jaffe Wick Method
A. Washing Apparatus
B. Washing Process

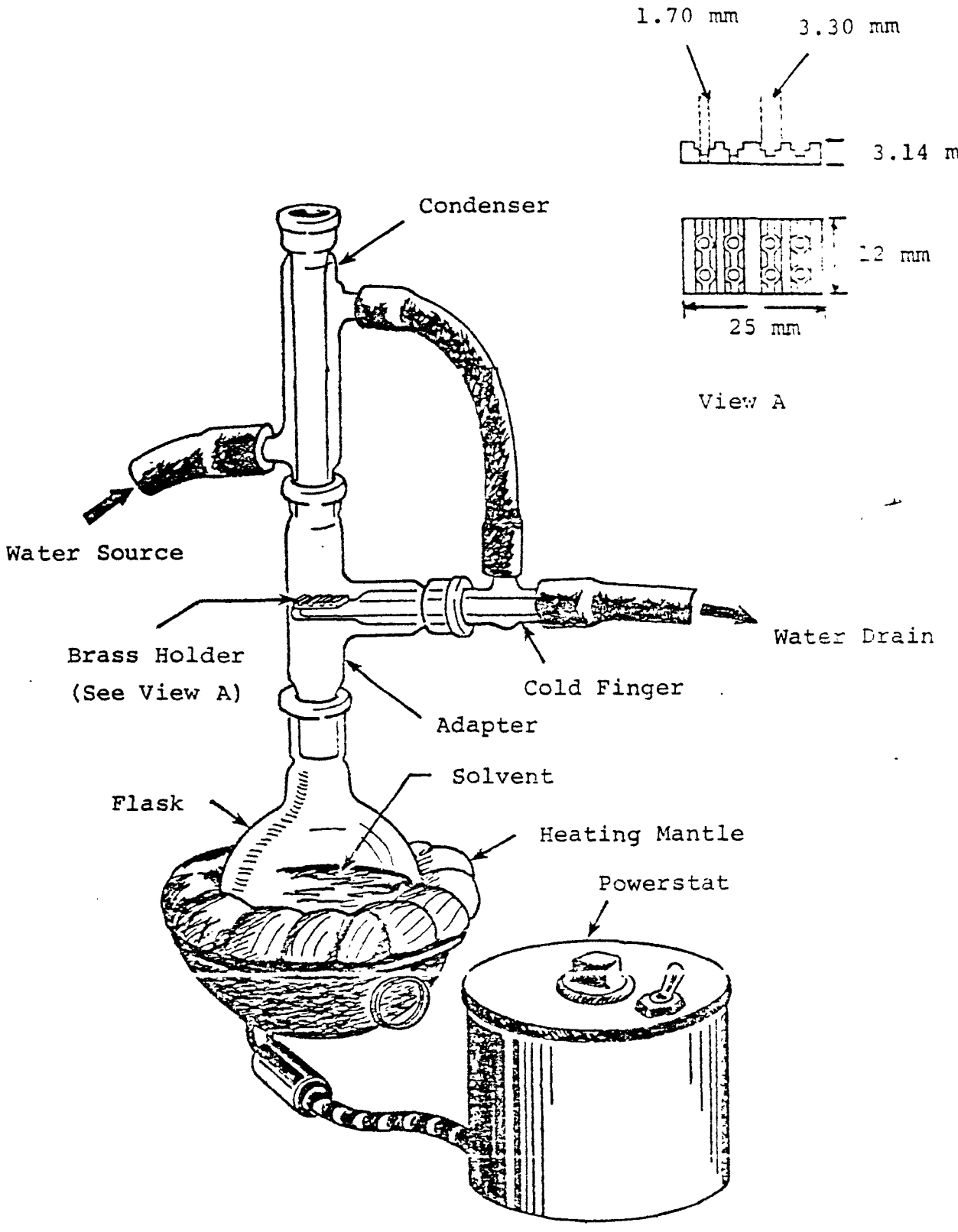


Figure 2. Condensation Washer

6.3.6 Membrane Filters.

47-mm diameter Millipore membrane filter, type HA; 0.45 µm pore size. For filtration of water sample.

47-mm diameter Nuclepore membrane filter; 0.1 µm pore size. (Nuclepore Corp, 7035 Commerce Circle, Pleasanton, CA 94566) For filtration of water sample.

47-mm diameter Millipore membrane filter type BS; 2 µm pore size. Used as a Nuclepore filter support on top of the glass frit.

25-mm diameter Millipore membrane filter, type HA; 0.45 µm pore size. To filter dispersed ashed Millipore filter.

25-mm diameter Nuclepore membrane filter; 0.1 µm pore size. To filter dispersed ashed Millipore filter.

25-mm diameter Millipore membrane filter, type BS; 2.0 µm pore size. To be used as a Nuclepore filter support on top of the glass frit.

6.3.7 Glass Vials. 30-mm diameter x 80-mm long. For holding filter during ashing.

6.3.8 Glass Slides. 5.1-cm x 7.5-cm. For support of Nuclepore filter during carbon evaporation.

6.3.9 Scalpels. With disposable blades and scissors.

6.3.10 Tweezers. Several pairs for the many handling operations.

6.3.11 "Scotch" Doublestick tape. To hold filter section flat on glass slide while carbon coating.

6.3.12 Disposable Petri dishes, 50-mm diameter, for storing membrane filters.

6.3.13 Static Eliminator, 500 microcuries Po-210. (Nuclepore Cat. No. V090POL00101) or equivalent. To eliminate static charges from membrane filters.

6.3.14 Carbon rods, spectrochemically pure, 1/8" dia., 3.6 mm x 1.0 mm neck. For carbon coating.

6.3.15 Carbon rod sharpener. (Cat. No. 1204, Ernest F. Fullam, Inc., P. O. Box 444, Schenectady, NY 12301) For sharpening carbon rods to a neck of specified length and diameter.

6.3.16 Ultrasonic Bath. (50 watts, 55 KHz). For dispersing ashed sample and for general cleaning.

6.3.17 Graduated Cylinder, 500 ml.

6.3.18 Spot plate.

6.3.19 10 µl Microsyringe. For administering drop of solvent to filter section during sample preparation.

6.3.20 Carbon grating replica, 2160 lines/mm. For calibration of EM magnification.

6.3.21 Cork borer (1/8 inch diameter). For sampling prepared Millipore filters.

6.3.22 Filter paper. S & S #589 Black Ribbon or equivalent (9-cm circles). For preparing Jaffe Wick Washer.

6.3.23 Screen supports (copper or stainless steel) 12 mm x 12 mm, 200 mesh. To support specimen grid in Jaffe Wick Washer.

6.3.24 Brass holder. For holding specimen in condensation washer. See Figure 2, View A.

6.3.25 Chloroform, spectro grade, doubly distilled. For dissolving Nuclepore filters.

6.3.26 Acetone, reagent grade or better. For dissolving Millipore filters.

6.3.27 Asbestos. Chrysotile (Canadian), Crocidolite, Amosite. UICC (Union Internationale Contre le Cancer) Standards. Available from Duke Standards Company, 445 Sherman Avenue, Palo Alto, CA 94306.

6.3.28 Petri dish, glass (100 mm diameter x 15 mm high). For modified Jaffe Wick Washer.

6.3.29 Alconox. (Alconox, Inc., New York, NY 10003) For cleaning glassware. Add 7.5 g Alconox to a liter of distilled water.

6.3.30 Aerosol OT, 0.1% solution (Cat. No. So-A-292, Fisher Scientific Company, 711 Forbes Avenue, Pittsburgh, PA 15219) Used as dispersion medium for ashed Millipore filter. Prepare a 0.1% solution by diluting 1 ml of the 10% solution to 100 ml with distilled water. Filter through 0.1-µm Nuclepore filter paper before using.

6.3.31 Parafilm. (American Can Company, Neenah, WI) Used as protective covering for clean glassware.

6.3.32 Pipets, disposable, 5 ml and 50 ml.

6.3.33 Distilled or deionized water. Filter through 0.1-µm Nuclepore filter for making up all reagents and for final rinsing of glassware, and for preparing blanks.

6.3.34 Mercuric chloride, 2.71% solution w/v. Used as sample preservative. See 4.3. Add 5.42 g of reagent grade mercuric chloride ($HgCl_2$) to 100 ml distilled water and dissolve by shaking. Dilute to 200 ml with additional water. Filter through 0.1-µm Nuclepore filter paper before using.

7. Preparation of Standards

Reference standard samples of asbestos that can be used for quality control for a quantitative analytical method are not available. It is, however, necessary for each laboratory to prepare at least two suspensions; one of chrysotile and another of a representative amphibole. These suspensions can then be used for intra-laboratory control and furnish standard morphology photographs and diffraction patterns.

7.1 Chrysotile Stock Solution.

Grind about 0.1 g of UICC chrysotile in an agate mortar for several minutes, or until it appears to be a powder. Weigh out 10 mg and transfer to a clean 1 liter volumetric flask, add several hundred ml of millipore filtered distilled water containing 0.1 percent Aerosol OT and one ml of a 20,000 ppm solution of mercury and then make up to 1 liter with the 0.1 percent Aerosol filtered distilled water. To prepare a working solution, transfer 10 ml of the above suspension to another 1-liter flask, add 1 ml of a 20,000 ppm solution of mercury and make up to 1 liter with the same 0.1 percent aerosol OT solution. This suspension contains 100 µg per liter. Finally transfer 1 ml of this suspension to a 1-liter flask,

add 1 ml of a 20,000 ppm solution of mercury and make up to volume with the 0.1 percent aerosol OT solution. The final suspension will contain 5-10 MFL and is suitable for laboratory testing.

7.2 Amphibole Stock Dispersion.

Prepare amphibole suspensions from UICC amphibole samples as in Section 7.1.

7.3 Identification Standards

Prepare electron microscopic grids containing the UICC asbestos fibers according to 8, Procedure, and obtain representative photographs of each fiber type and its diffraction pattern for future reference.

8. Procedure

8.1 Filtration.

The separation of the insoluble material, including asbestiform minerals, through filtration and subsequent deposition on a membrane filter is a very critical step in the procedure. The objective of the filtration is not only to separate, but also to distribute uniformly the particulate matter such that discreet particles are deposited with a minimum of overlap.

The volume filtered will range from 50-500 ml. In an unknown sample the volume can not be specified in advance because of the presence of variable amounts of particulate matter. In general sufficient sample is filtered such that a very faint stain can be observed on the filter medium. The maximum loading that can be tolerated is 20 $\mu g/cm^2$, or about 200 µg on a 47-mm diameter filter; 5 $\mu g/cm^2$ is near optimum. If the total solids content is known, an estimate of the maximum volume tolerable can be obtained. In a sample of high solids content, where less than 50 ml is required, the sample should be diluted with filtered distilled water so that a minimum total of 50 ml of water is filtered. This step is necessary to allow the insoluble material to deposit uniformly on the filter. The filtration funnel assembly must be scrupulously clean and cleaned before each filtration. The filtration should be carried out in a laminar flow hood.

NOTE 1: The following cleaning procedure has been found to be satisfactory:

Wash each piece of glassware three times with distilled water. Following manufacturer's recommendations use the ultrasonic bath with an Alconox-water solution to clean all glassware. After the ultrasonic cleaning rinse each piece of glassware three times with distilled water. Then rinse each piece three times with deionized water which has been filtered through 0.1-µm Nuclepore filter. Dry in an asbestos-free oven. After the glassware is dry, seal openings with parafilm.

8.1.1 Filtration

a. Assemble the vacuum filtration apparatus incorporating either the .1-µm Nuclepore backed with 2-µm Millipore, or the .45-µm Millipore filter. See 8.2A.2 or 8.2B.2.

b. Vigorously agitate the water sample in its container.

c. If the required filtration volume can be estimated, either from turbidity estimates of suspended solids or previous experience, immediately withdraw the proper volume from the container and add the entire volume to the 47-mm diameter funnel. Apply vacuum sufficient for filtration but gentle enough to avoid the formation of a vortex. If a completely unknown sample is being analyzed, a slightly modified procedure must be followed. Pour 500 ml of a well-mixed sample into a 500 ml graduated cylinder and immediately transfer the entire contents to the prepared vacuum filtration apparatus. Apply vacuum gently and continue suction until all of the water has passed through the filter. If the resulting filter appears obviously coated or discolored, it is recommended that another filter be prepared in the same manner, but this time using only 200 or 100 ml of sample.

NOTE 1: Do not add more water after filtration has started and do not rinse the sides of the funnel.

d. Disassemble the funnel, remove the filter and dry in a covered petri dish.

8.2 Preparation of Electron Microscope Grids.

The preparation of the grid for examination in the microscope is a critical step in the analytical procedure. The objective is to remove the organic

filter material from the asbestos fibers with a minimum loss and movement and with a minimum breakage of the grid support film. Two alternative procedures are acceptable:

A. Nuclepore Filter, Modified Jaffe Wick

B. Millipore Filter, Condensation Washer

If the sample contains organic matter in such amounts that interfere with fiber counting and identification a preliminary ashing step is required. See 8.5.

NOTE 1: Two alternatives for grid preparation are suggested because the superiority of one technique over the other has not been substantiated by sufficient experimental evidence. The differences between the two techniques of sample preparation lie in the filtering medium (Nuclepore vs. Millipore), whether the filter is carbon coated, and in the method of dissolving the filter material. There is evidence that the condensation washing procedure can lose amphibole fibers and that amphiboles are more susceptible to loss than chrysotile.

8.2A Nuclepore Filter, Modified Jaffe Wick Technique.

8.2A.1 Preparation of Modified Jaffe Washer

Place three glass microscope slides (75 mm x 25 mm) one on top of the other in a petri dish (100 mm x 15 mm) along a diameter. Place 14 S & S #589 Black Ribbon filter papers (9-cm circles) in the petri dish over the stack of microscope slides. Place three mesh copper screen supports (12 mm x 12 mm) along the ridge formed by the stack of slides underneath the layer of filter papers. Place an EM specimen grid on each of the screen supports. See Fig. 1.

8.2A.2 Vacuum Filtration Unit

Assemble the vacuum filtration unit. Place a 2-µm Millipore filter type BS on the glass frit and then position a 0.1-µm Nuclepore filter, shiny side up, on top of the Millipore filter. Apply suction to center the filters flat on the frit. Attach the filter funnel and shut off the suction.

8.2A.3 Sample Filtration

See 8.1.1.

8.2A.4 Sample Drying

Remove the filter funnel and place the Nuclepore filter in a loosely covered petri dish to dry. The petri dish containing the filter may be placed in an asbestos-free oven at 45° C for 30 minutes to shorten the drying time.

8.2A.5 Selection of section for carbon coating

Using a small pair of scissors or sharp scalpel cut out a retangular section of the Nuclepore filter. The minimum approximate dimensions should be 15 mm long and 3 mm wide. Avoid selection near the perimeter of the filtration area.

8.2A.6 Carbon Coating the Filter

Tape the two ends of the selected filter section to a glass slide using "Scotch" tape. Take care not to stretch the filter section. Identify the filter section using a china marker on the slide. Place the glass slide with the filter section into the vacuum evaporator. Insert the necked carbon rod and, following manufacturer's instructions, obtain high vacuum. Evaporate the neck, with the filter section rotating, at a distance of approximately 7.5 cm from the filter section to obtain a 30-50 nm layer of carbon on the filter paper. Evaporate the carbon in several short bursts rather than continuously to prevent overheating the surface of the Nuclepore filter.

NOTE 1: Overheating the surface tends to crosslink the plastic, rendering the filter dissolution in chloroform difficult.

NOTE 2: The thickness of the carbon film can be monitored by placing a drop of oil on a porcelain chip that is placed at the same distance from the carbon electrodes as the specimen. Carbon is not visible in the region of the oil drop thereby enabling a visual estimate of the deposit thickness by the contrast differential.

8.2A.7 Grid Transfer

Remove the filter from the vacuum evaporator and cut out three sections somewhat less than

3 mm x 3 mm and such that the square of Nuclepore fits within the circumference of the grid. Pass each of the filter sections over a static eliminator and then place each of the three sections carbon-side down on separate specimen grids previously placed in the modified Jaffe Washer. Using a microsyringe, place a 10-µl drop of chloroform on each filter section resting on a grid and then saturate the filter pad until pooling of the solvent occurs below the ridge formed by the glass slides inserted under the layer of filter papers. Place the cover on the petri dish and allow the grids to remain in the washer for approximately 24 hours. Do not allow the chloroform to completely evaporate before the grids are removed. To remove the grids from the washer lift the screen support with the grid resting upon it and set this in a spot plate depression to allow evaporation of any solvent adhering to the grid. The grid is now ready for analysis or storage.

8.2B Millipore - Condensation Washer Technique

8.2B.1 Operation of Condensation Washer

Fill the extractor flask to 40% capacity with acetone. Filter the acetone through 0.1-µm Nuclepore filter paper before using. Adjust the tap water flow rate to 10 ml/sec by allowing the water exiting from the cold finger to run into a graduated cylinder for 30 seconds. Set the variable transformer, regulating the heater power-input, to approximately 45 volts. Sufficient heat should be applied to generate acetone vapors at the required condensation or reflux level without boiling or simmering. The reflux level should be even with the top of the cold finger and just below the stainless steel grid. (Important: See Note 1). After the system has been running for twenty minutes, check the reflux level of the acetone. Place a heavily lined index card behind the adaptor so that when viewed from the front of the adaptor the cold finger is parallel to the heavy lines on this card. Locate the reflux level by noting the illusionary wavy motion of the heavy lines on the index card. If the reflux level is too high, increase, or if too low, decrease the tap water flow rate. Do not allow pooling of the solvent to occur on the grids. At very low flow rates keep a careful

check to ensure that the water valve does not shut itself off. To account for changes in the tap water temperature, establish the correct flow rate daily.

NOTE 1: The relative position of the acetone condensation level to the grid level is critical to the successful operation of the condensation washer. If the condensation level is too low, the Millipore filter will not be sufficiently removed within a reasonable period of time and the asbestos fibers cannot be successfully counted; if the level is too high, excessive washing occurs with a resulting loss of fibers and rupture of the carbon film. As each extractor has different characteristics, several test runs should be made on blank Millipore-loaded grids to determine the optimum operating conditions.

NOTE 2: It has been suggested that the rate of acetone condensation, observed as drops from the end of the cold finger, should be 10 drops per 30-45 seconds.

NOTE 3: A constant pressure regulator may be required in the water line if a constant flow cannot be otherwise attained.

8.2B.2 Vacuum Filtration Unit

Assemble the vacuum filtration unit. Place a 0.45-μm Millipore filter on the glass frit. Turn on the suction and center the filter on the frit. Attach the filter funnel and turn off suction.

8.2B.3 Sample Filtration

See 8.1.1.

8.2B.4 Sample Drying

Remove the filter funnel and place the Millipore filter in a petri dish in an asbestos-free oven at 45° C for at least two hours to dry.

8.2B.5 Sampling of Filter

Using a well sharpened (1/8 inch diameter) cork borer, cut three circular sections from the filter. Keep one-half of the filter undisturbed for future reference or if an

ashing step is required (See 8.5). Avoid sampling near the perimeter of the filtration area.

8.2B.6 Grid Transfer

Pass each filter section over a static eliminator and then place each section particulate side down on carbon coated specimen grids previously placed in the brass holder. Add a 10-µl drop of acetone to each of the grids using a micro syringe. Place the brass holder on the cold finger of the condensation washer which has been charged with acetone. After the correct reflux level has been established (8.2B.1) insert the brass block holding the grids and check a few minutes later to make certain that the acetone reflux is near but below grid level. Allow the acetone to reflux for 7-8 hours to dissolve away the filter and leave the residue deposited on the carbon substrate of the grid. Turn off the heating mantle. Remove the brass block holding the grids when no drops of acetone can be seen falling from the cold finger. The grids are now ready for analysis or storage.

NOTE 1: The addition of 10 µl of acetone directly to the filter, while recommended, may, in the opinion of some investigators, increase the risk of removing particulates from the filter. There are no data available to show it has a deleterious effect.

8.4 Electron Microscopic Examination

8.4.1 Microscope Alignment and Magnification Calibration

Following the manufacturer's recommendations carry out the necessary alignment procedures for optimum specimen examination in the electron microscope. Calibrate the routinely used magnifications using a carbon grating replica.

NOTE 1: Screen magnification is not necessarily equivalent to plate magnification.

8.4.2 Grid Preparation Acceptability

After inserting the specimen into the microscope adjust the magnification low enough

(300X - 1000X) to permit viewing complete grid squares. Inspect at least 10 grid squares for fiber loading and distribution, debris contamination, and carbon film continuity.

Reject the grid for counting if:

1) The grid is too heavily loaded with fibers to perform accurate counting and diffraction operations. A new sample preparation either from a smaller volume of water or from a dilution with filtered distilled water must then be prepared.

2) The fiber distribution is noticeably uneven. A new sample preparation is required.

3) The debris contamination is too severe to perform accurate counting and diffraction operations. If the debris is largely organic the filter must be ashed and redispersed (see 8.5). If inorganic the sample must be diluted and again prepared.

4) The majority of grid squares examined have broken carbon films. A different grid preparation from the same initial filtration must be substituted.

8.4.3 Procedure for Fiber Counting

There are two methods commonly used for fiber counting. In one method (A) 100 fibers, contained in randomly selected fields of view, are counted. The number of fields plus the area of a field of view must be known when using this method. In the other method (B), all fibers (at least 100) in several grid squares or 20 grid squares are counted. The number of grid squares counted and the average area of one grid square must be known when using this method.

NOTE 1: The method to use is dependent upon the fiber loading on the grid and it is left to the judgement of the analyst to select the optimum method. The following guidelines can be used: If it is estimated that a grid square (80 μm x 80 μm) contains 50-100 fibers at a screen magnification of 20000X it is convenient to use the field-of-view counting method. If the estimate is less than 50, the grid square method of counting should be chosen. On the other hand, if the fiber count

is estimated to be over 300 fibers per grid square, a new grid containing less fibers must be prepared (through dilution or filtration of a smaller volume of water).

8.4.3A Field-of-View Method

After determining that a fiber count can be obtained using this method adjust the screen magnification to 10-20000X. Select a number of grid squares which would be as representative as possible of the entire analyzable grid surface. From each of these squares select a sufficient number of fields of view for fiber counting. The number of fields of view per grid square is dependent upon the fiber loading. If more than one field of view per grid square is selected, scan the grid opening orthogonally in an arbitrary pattern which prevents overlapping of fields of view. Carry out the analysis by counting, measuring and identifying (see 8.4.4) approximately 50 fibers on each of two grids.

The following rules should be followed when using the field of view method of fiber counting. Although these rules were derived for a circular field of view they can be modified to apply to square or rectangular designs.

1) Count all fibers contained within the counting area and not touching the circumference of the circle.

2) Designate the upper right-hand quadrant as I and number in clockwise order. Count all fibers touching or intersecting the arc of quadrants I or IV. Do not count fibers touching or intersecting the arc of quadrants II or III.

3) If a fiber intersects the arc of both quadrants III and IV or I and II count it only if the greater length was outside the arc of quadrants IV and I, respectively.

4) Count fibers intersecting the arc of both quadrants I and III but not those intersecting the arc of both II and IV.

These rules are illustrated in Fig. 3.

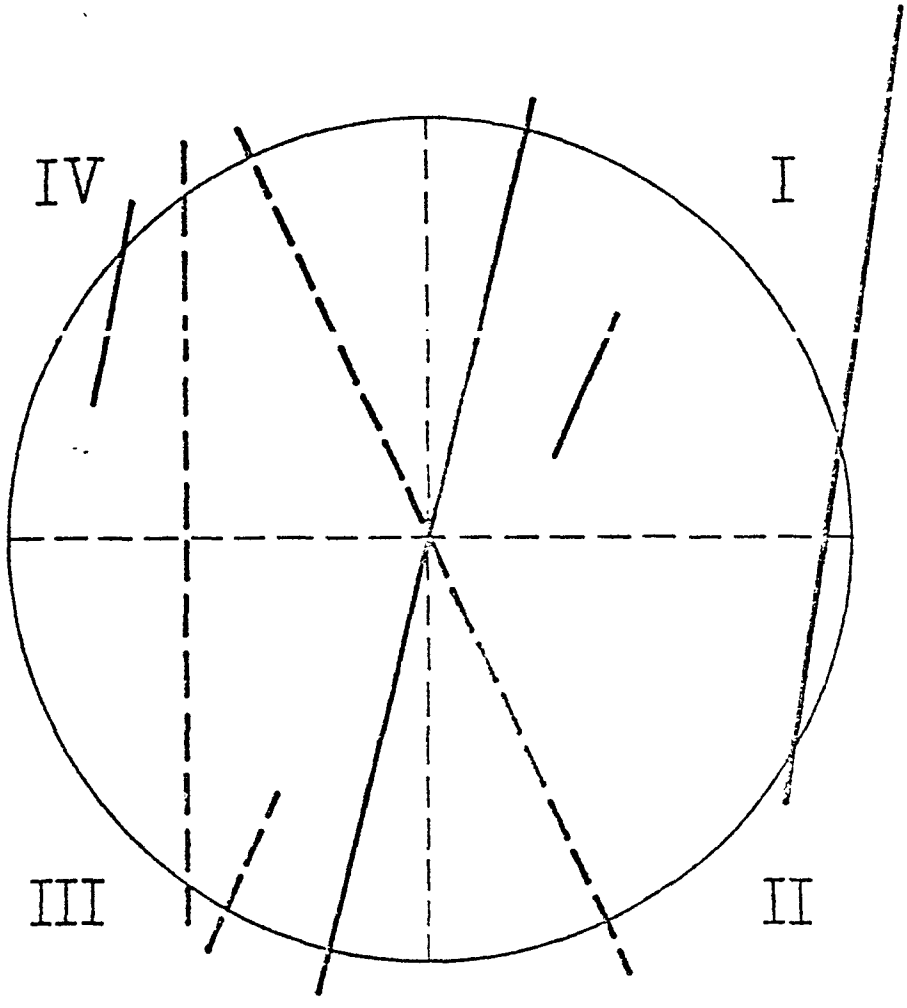


Figure 3. Illustration of Counting Rules for Field-of-View Method

8.4.3B Grid Square Method

After determining that a fiber count can be obtained using this method adjust the screen magnification to 10-20000X. Position the grid square so that scanning can be started at the left upper corner of the grid square. While carefully examining the grid, scan left to right, parallel to the upper grid bar. When the perimeter of the grid square is reached adjust the field of view up one field width and scan in the opposite direction. The tilting section of the fluorescent screen may be used conveniently as the field of view. Examine the square until all the area has been covered. The analysis should be carried out by counting, measuring and identifying (see 8.4.4) approximately 50 fibers on each of two grids or until 10 grid squares on each of two grids have been counted. Do not count fibers intersecting a grid bar.

8.4.4 Measurement and Identification

Measure and record the length and width of each fiber having an aspect ratio greater than or equal to three. Disregard obvious biological, bacteriological fibers and diatom fragments. Examine the morphology of each fiber using optical viewing if necessary. Tentatively identify, by reference to the UICC standards, chrysotile or possible amphibole asbestos. Attempt to obtain a diffraction pattern of each fiber. Move the suspected fiber image to the center of the screen and insert a suitable selected area aperture into the electron beam so that the fiber image, or a portion of it, is in the illuminated area. The size of the aperture and the portion of the fiber should be such that particles other than the one to be examined are excluded from the selected area. If an incomplete diffraction pattern is obtained move the particle image around in the selected area to get a clearer diffraction pattern or to eliminate possible interferences from neighboring particles.

Determine whether or not the fiber is chrysotile or an amphibole by comparing the diffraction pattern obtained to the diffraction patterns of known standard asbestos fibers. Confirm the tentative identification of chrysotile and amphibole

asbestos from their electron diffraction patterns. Classify each fiber as chrysotile, amphibole, non-asbestos, no diffraction and ambiguous.

NOTE 1: It is convenient to use a tape recorder during the examination of the fibers to record all pertinent data. This information can then be summarized on data sheets or punched cards for subsequent automatic data processing.

NOTE 2: Chrysotile fibers occur as single fibrils, or in bundles. The fibrils generally show a tubular structure with a hollow canal, although the absence of the canal does not rule out its identification. Amphibole asbestos fibers usually exhibit a lath-like structure with irregular ends, but occasionally will resemble chrysotile in appearance.

NOTE 3: The positive identification of asbestos by electron diffraction requires some judgement on the part of the analyst because some fibers give only partial patterns. Chrysotile shows unique prominent streaks on the layer lines nearest the central one and a triple set of double spots on the second layer line. The streaks and the set of double spots are the distinguishing characteristics of chrysotile required for identification. Amphibole asbestos requires a more complete diffraction pattern to be positively identified. As a qualititative guideline, layer lines for amphibole, without the unique streaks (some streaking may be present), of chrysotile, should be present and the arrangement of diffraction spots along the layer lines should be consistent with the amphibole pattern. The pattern should be distinct enough to establish these criteria.

NOTE 4: Chrysotile and thin amphibole fibers may undergo degradation in an electron beam; this is particularly noticeable in small fibers. It may exhibit a pattern for a 1-2 seconds and disappear and the analyst must be alert to note the characteristic features.

NOTE 5: An ambiguous fiber is a fiber that gives a partial electron diffraction pattern resembling asbestos, but insufficient to provide positive identification.

8.4.5 Determination of Grid Square Area

Measure the dimensions of several representative grid squares from each batch of grids with an optical microscope. Calculate the average area of a grid square. This should be done to compensate for variability in grid square dimensions.

8.5 Ashing

Some samples contain sufficiently high levels of organic material that an ashing step is required before fiber identification and counting can be carried out. If a Nuclepore filter was used for the original preparation and if the preliminary examination of the initial preparation shows that this condition exists, carry out the filtration step on a new water sample using a .45-μm Millipore filter. If a Millipore filter was used initially the unused half from 8.2B.5 can be ashed.

NOTE 1: A Millipore filter is specified because it is more readily oxidized under the specified ashing conditions.

Place the dried Millipore filter paper containing the collected sediment into a glass vial (28 mm diameter x 80 mm high). Position the filter such that the filtration side touches the glass wall. Place the vial in an upright position in the low temperature asher. Operate the asher at 50 watts (13.56 MHz) power and 2 psi oxygen pressure. Ash the filter until a thin film of white ash remains. The time required is generally 6 to 8 hours. Allow the ashing chamber to slowly reach atmospheric pressure and remove the vial. Add 10 ml of filtered distilled water containing 0.1 percent filtered Aerosol OT to the vial. Place the vial in an ultrasonic bath for 1/2 hour to disperse the ash. Dilute the sample if required.

Assemble the 25 mm diameter filtering apparatus. (See Note 1) Center a 25 mm diameter 0.45-μm Millipore or .1-μm Nuclepore filter (with the 2-μm Millipore backing) on the glass frit. Apply suction and recenter the filter if necessary. Attach the filter funnel and turn off the suction. Add the water containing the dispersed ash from the vial to the filter funnel. Apply suction and filter the sample. After drying this filter it is ready to be used in preparing sample grids as in 8.2A or 8.2B.

NOTE 2: In specifying a 25-mm diameter filter it is assumed that the ashing step is necessary mainly because of the presence of organic material and that the smaller filtering area is desirable from the point of view of concentrating the fibers. If the sample contains mostly inorganic debris such that the smaller filtering area will result in over-loading the filter, the 47-mm diameter filter should be used.

NOTE 3: It will be noted that a 10-ml volume is filtered in this case instead of the minimum 50-ml volume specified in 8.1.1. These volumes are consistent when it is considered that there is approximately a 5-fold difference in effective filtration area between the 25-mm diameter and 47-mm diameter filters.

8.6 Determination of Blank Level

Carry out a blank determination with each batch of samples prepared, but a minimum of one per week. Filter a fresh supply (500 ml) of distilled, deionized water through a clean .1-μm membrane filter. Using the selected filter type, filter 200 ml of this water, prepare the electron microscope grid, and count exactly as in the procedures 8.1 - 8.4. Examine 20 grid squares and record this number of fibers. A maximum of two fibers in 20 grid squares is acceptable for the blank sample.

NOTE 1: The monitoring of the background level of asbestos is an integral part of the procedure. Upon initiating asbestos analytical work, blank samples must be run to establish the initial suitability of the laboratory environment, cleaning procedures, and reagents for carrying out asbestos analyses. Analytical determinations of asbestos can be carried out only after an acceptably low level of contamination has been established.

9. Calculations

9.1 Fiber Concentrations

Grid Square Counting Method - If the Grid Square Method of counting is employed, use the following formula to calculate the total asbestos fiber concentration in MFL.

$$C = (F \times A_f) / (G \times A_g \times V_o \times 1000)$$

If ashing is involved use the same formula but substituting the effective filtration area of the 25-mm diameter filter for A_f instead of that for the 47-

mm diameter filter. If one-half the filter is ashed, multiple C by two.

C = Fiber concentration (MFL)

F = number of fibers identified in "G" grid squares

A_f = effective filtration area of filter paper (mm^2) used in grid preparation used for fiber counting

A_g = Average area of one grid square (mm^2)

G = number of grid squares analyzed

V_o = original volume of sample filtered (ml)

Field-of-View Counting Method - If the Field-of-View Method of counting is employed use the following formula to calculate the total asbestos fiber concentrations (MFL)

$$C = (F \times A_f \times 1000) / (A_v \times Z \times V_o)$$

If ashing is involved use the same formula but substituting the effective filtration area of the 25-mm diameter filter for A_f instead of that for the 47-mm diameter filter.

C = fiber concentration (MFL)

F = number of fibers identified in area examined (A_v x Z)

A_f = effective filtration area of filter paper (mm^2) used in grid preparation for fiber counting

A_v = area of one field of view (μm^2)

Z = number of fields of view examined

V_o = original volume of sample filtered (ml)

9.2 Estimated Mass Concentration

Calculate the mass (μg) of each fiber counted using the following formula:

$$M = L \times W^2 \times D \times 10^{-6}$$

If the fiber content is predominantly chrysotile, the following formula may be used:

$$M = \frac{\pi}{4} \times L \times W^2 \times D \times 10^{-6}$$

where M = mass (µg)

L = length (µm)

W = width (µm)

D = density of fibers (g/cm³)

Then calculate the mass concentration (µg/l) employing the following formula.

$$M_c = C \times \bar{M}_f \times 10^6$$

where M_c = mass concentration (µg/l)

C = fiber concentration (MFL)

$\bar{M}_f$ = mean mass per fiber (µg)

To calculate $\bar{M}_f$ use the following formula:

$$\bar{M}_f = \sum_{i=1}^{n} M_i / n$$

where M = mass of each fiber, respectively

n = number of fibers counted

NOTE 1: Because many of the amphibole fibers are lath shaped rather than square in cross section the computed mass will tend to be high since laths will in general tend to lie flat rather than on edge.

NOTE 2: Assume the following densities: Chrysotile 2.5, Amphibole 3.25

9.3 Aspect Ratio

The aspect ratio for each fiber is calculated by dividing the length by the width.

10. Reporting

10.1 Report the following concentration as MFL

a. Total fibers

b. Chrysotile

c. Amphibole

10.2 Use two significant figures for concentrations greater than 1 MFL, and one significant figure for concentrations less than 1 MFL.

10.3 Tabulate the size distribution, length and width.

10.4 Tabulate the aspect ratio distribution.

10.5 Report the calculated mass as µg/l.

10.6 Indicate the detection limit in MFL.

10.7 Indicate if less than five fibers were counted.

10.8 Include remarks concerning pertinent observations, (clumping, amount of organic matter, debris) amount of suspected though not identifiable as asbestos (ambiguous).

11. Precision

11.1 Intra Laboratory

The precision that is obtained within an individual laboratory is dependent upon the number of fibers counted. If 100 fibers are counted and the loading is at least 3.5 fibers/grid square, computer modeling of the counting procedure shows a relative standard deviation of about 10% can be expected.

In actual practice some degradation from this precision will be observed but should not exceed ± 15% if several grids are prepared from the same filtered sample. The relative standard deviation of analyses of the same water sample in the same laboratory will increase due to sample preparation errors and a relative standard deviation of about ± 25 - 30% will occur. As the number of fibers counted decreases, the precision will also decrease approximately proportional to $\sqrt{N}$ where N is the number of fibers counted.

11.2 Inter Laboratory

While there have been numerous inter laboratory testing programs, there have been few carried out using the same procedure. Those that have been done indicate that agreement within a factor of two is achieved if 100 fibers can be counted.

12. Accuracy

12.1 Fiber concentrations

As no standard reference materials are available, only approximate estimates of the accuracy of the procedure can be made. At 1 MFL, it is estimated that the results should be within a factor of 10 of the actual asbestos fiber content.

This method requires the positive identification of a fiber to be asbestos as a means for its quantitative determination. As the state-of-the art precludes the positive identification of all of the asbestos fibers present, the results by this method, as expressed as MFL, will be biased on the low side and assuming no fiber loss represent .2 - .6 of the total asbestos fibers present.

12.2 Mass concentrations

As in the case of the fiber concentrations, no standard samples of the size distribution found in water are available. The accuracy of the mass determination should be somewhat better than the fiber determination because a larger fraction of the large fibers, which contribute the major portion of the mass, are identifiable. This will reduce the bias of low results due to difficulties in identification. At the same time, the assumption that the thickness of the fiber equals the width will result in a positive error in determining the volume of the fiber and thus give high results for the mass.

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Analytical Methodology for the Determination of Asbestos by Transmission Electron Microscopy

The analytical procedure used by Walter C. McCrone Associates, Inc., for the determination of asbestos in environmental samples is substantially similar to that given in the U.S. EPA "Preliminary Interim Procedure for Determining Fibrous Asbestos".* Although this procedure was written for water samples, the techniques for preparation of the filter for examination and the criteria for the identification of the asbestiform minerals are equally applicable to air samples. Details of the procedure follow.

Working in a laminar flow clean bench (see attached laboratory description), discs approximately 3 mm in diameter are punched out of the filter. These discs are then placed face-down on previously carbon-coated electron microscope support grids either of copper, if only chrysotile is expected, or nylon. Nylon is used for samples in which there is a reasonable likelihood of amphibole fibers in order that chemical analyses may be performed on the fibers, by either the X-ray energy or wavelength dispersive system fitted to the microscope. The use of nylon minimizes extraneous X-ray signals from the support grid which would otherwise saturate the detector system. Such an analysis is essential in order to classify the amphibole type present. The grids are then transferred to a cold finger in a Soxhlet extraction apparatus in which the membrane filter is dissolved using acetone for Millipore Type MF and for Gelman GN-6 Metricel filters or chloroform for Nuclepore filters. A "wicking" method may also be used for Nuclepore filters but is unsuitable for the Millipore or Gelman types. Previous work has shown us that there is very little risk of contamination in transferring the filter on the electron microscope grid to the Soxhlet extractor. Further-

*Available from U.S. EPA Environmental Research Laboratory, Athens, GA 30601.

more, by dissolving the filter in situ on the grid ("direct transfer"), the risk of losing portions of the sample is minimal. Techniques involving transfer of a liquid suspension directly to the electron microscope grid are more subject to error since there is frequently a size separation as the meniscus of the drying drop recedes. Procedures involving "rub-out" techniques, though of some value in obtaining mass concentration data are not applicable to fiber number or size distribution determinations as they intentionally degrade the fibers to unit fibrils thus altering their size and simultaneously increasing their numbers.

The sample grids are examined on the electron microscope (JEM 200 *[1] or EMMA 4*[2]) using a magnification such that the intermediate lens aperture is in focus in the specimen plane. It is thus possible, by inserting the aperture and switching to the diffraction position, to obtain a selected area electron diffraction (SAED) pattern of the fiber with no other adjustments to the microscope. In this way it is possible to spot check the diffraction pattern of individual fibers very rapidly. The JEM 200 is used on those samples in which only chrysotile is of interest. EMMA 4, with the capability for X-ray fluorescence analysis of individual fibers, is used where the identification of amphibole types present is required. Both instruments have a selected area electron diffraction capability.

Prior to commencing measurement the electron microscope grid is scanned at a low magnification, approximately 2000-4000X to ensure uniformity of dispersion on the filter. In the case of non-uniform deposition, which may occur for example with cemented or aggregated fibers, several grids may be examined from the same filter. This prior examination indicates to the analyst which areas should be examined to obtain a truly representative analysis of the sample. Magnifications in excess of 10,000 X are required for

*1 JEM 200. 200 Kv transmission electron microscope manufactured by Japan Electron Optics Laboratories (JEOL)

*2 EMMA 4. Combined 100 Kv transmission Electron Microscope-Microprobe Analyzer manufactured by Associated Electrical Industries (AEI)

the observation of the smallest chrysotile fibrils present.

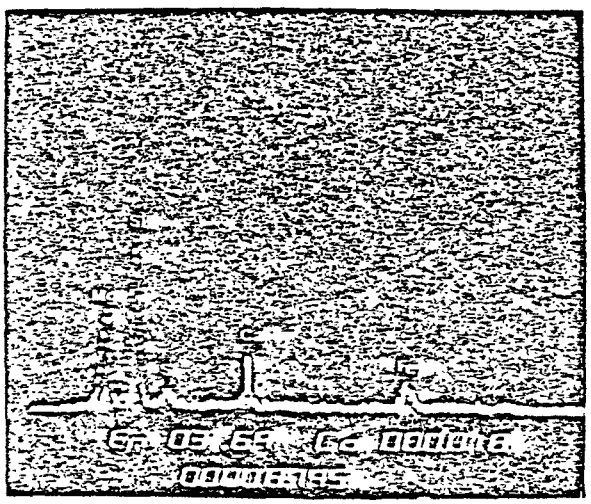
The magnification of examination used in the JEM 200 is 14,600 on the viewing screen; that used in EMMA 4 is 24,800. As stated above, these magnifications are based on user convenience in switching from viewing to diffraction.

The length and width of each asbestos fiber is recorded. Only fibers which are positively identified as asbestos are measured. Interpolation from intervals scribed on the viewing screen allows an accuracy of measurement on the screen of approximately 0.05 cm. This corresponds to an accuracy in size measurement of about 0.02-0.04 μm. Measurements of the individual fibers are computer processed to give listings of the length and width of the fibers, together with a computed mass of each fiber computed on the basis of density, D, and dimensions, L and W ($D \times L \times W^2$). A value of 3.3 is taken as the mean density of amphibole fibers: a density of 2.3 is used for chrysotile. Because many of the amphiboles are lath-shaped rather than square in cross section, this figure may well be slightly high, since the laths will, in general, tend to lie flat rather than on edge. There is, however, a finite possibility that some laths will be on edge and, due to the very small size of many of the fibers of interest, the approximation to a square fiber will not give more than a slightly high bias to the mass readings. The program automatically assigns the longest dimension to the fiber length and excludes all particles with an aspect ratio below three.

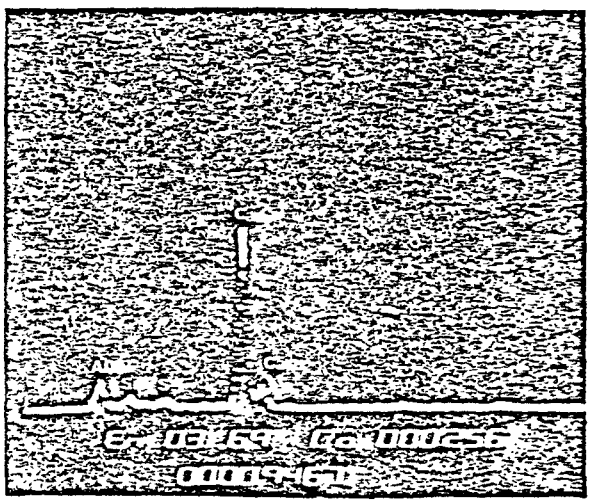
Also presented in the computer printout are the calculated number of fibers per unit volume, the calculated mass of fiber per unit volume, the size distribution of the fibers based on length and width, and the distribution of fibers by aspect ratio together with the relevant statistical information on these parameters. A physical description of the sample accompanies the measurements and is considered an integral and essential part of the analysis. A sample of a complete analysis, description and computer printout is attached.

Sample

Much chunky and chiplike material ranging to quite large sizes and showing a wide range of composition — Mg, Si and some Fe, mainly Si, mainly Ca or Fe-Si types — although the Mg-Si type predominates. Additionally, fine agglomerate material, organic matter, some spherical inorganic particles and chrysotile are found,in this sample. The spheroidal particles are found normally, to be Al-Si-Fe composition but wide ranging variation does occur. Antigorite laths (e.g. fibers) noted. Occasional "massive" fibers are present or fibers which are lathlike. These are found to contain Mg-Si-Ca-Fe and some S, consistently.



Probe of large chunky material



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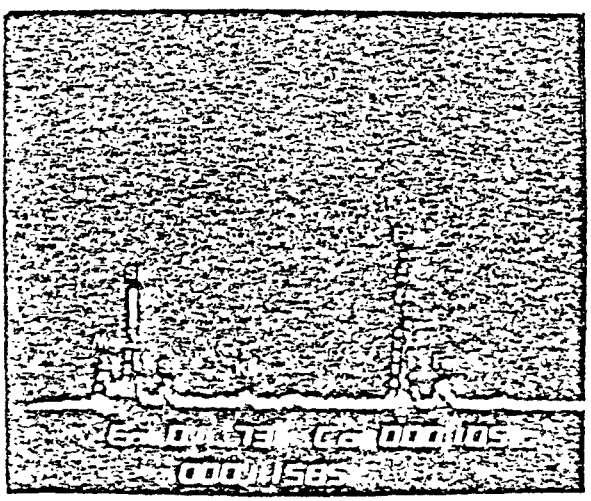

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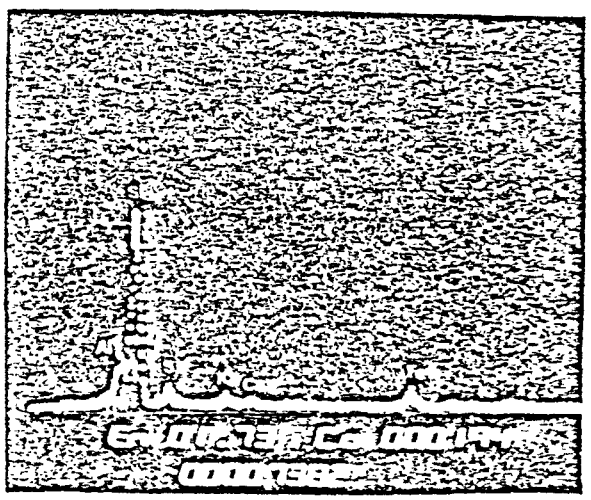
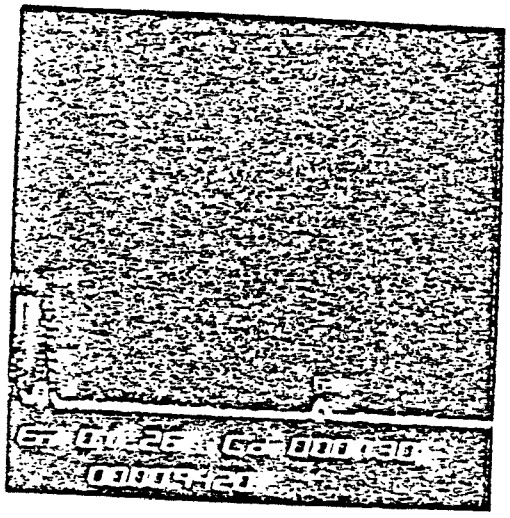
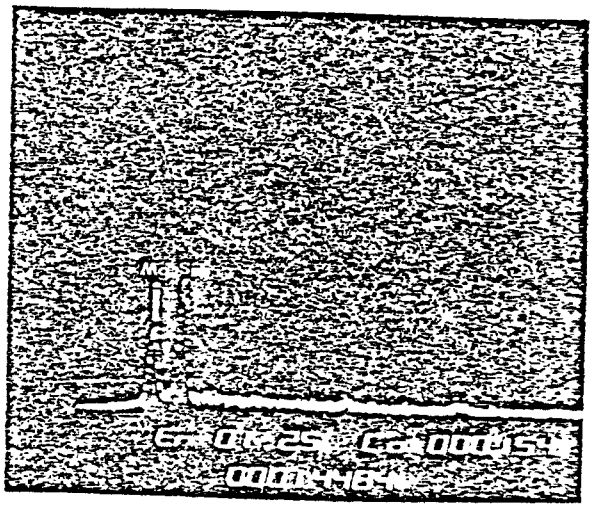


Probe of large chiplike material

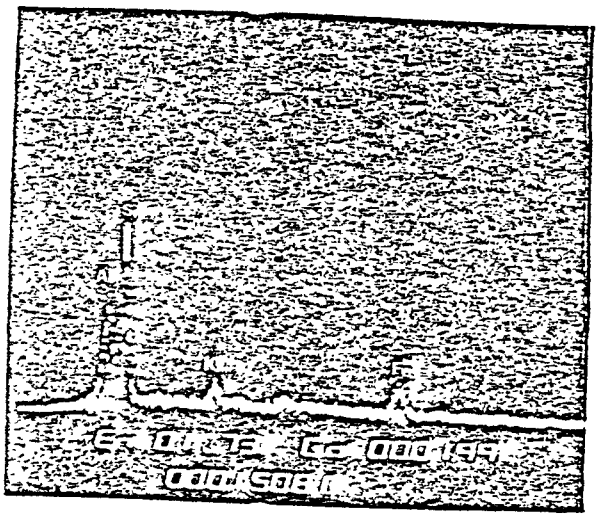
Sample



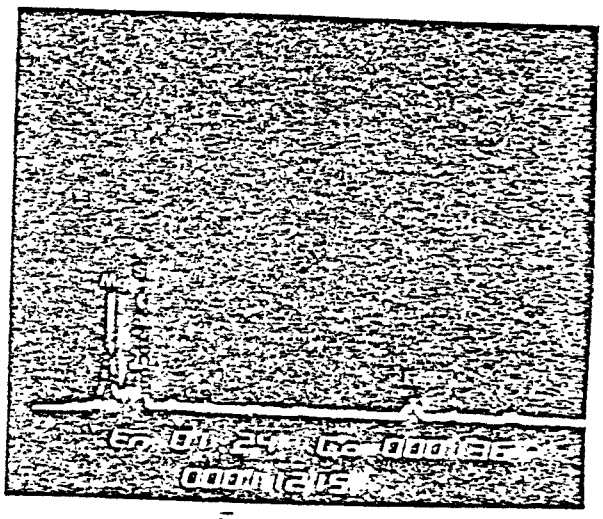
Probe of chrysotile



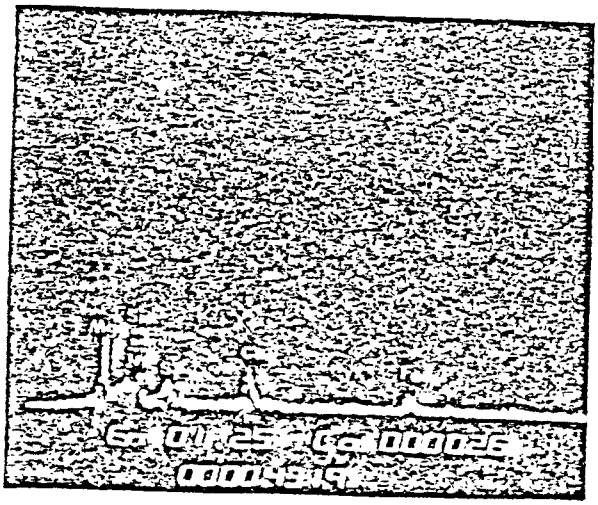
Probe of chrysotile bundle



Probe of typical spherical particle



Probe of antigorite lath



Probe of small lathlike fiber

SAMPLE : (CHRYSOTILE)

FIBER CONCENTRATION BY NUMBER/PER LITER : 0.42E+05
FIBER CONCENTRATION BY MASS/PER LITER : 0.001 GRAMS*10**-6
VOLUME FILTERED : 1000.0 ML
GRID SQUARES COUNTED : 40
TOTAL SUSPENDED SOLIDS: 0.000 MG PER LITER
PH = 0.0

DESCRIPTIVE STATISTICS

NO. OBS. = 32

	VARIABLE	MEAN	VARIANCE	STANDARD DEVIATION	STANDARD ERROR
1	LENGTH	0.10805E+01	0.85446E+00	0.92437E+00	0.16341E+00
2	WIDTH	0.38941E-01	0.11709E-02	0.34218E-01	0.60469E-02
3	ASPECT RATIO	0.31521E-02	0.49823E+03	0.22331E-02	0.39479E-01
4	MASS	0.16647E-01	0.43676E-02	0.66088E-01	0.11683E-01

	SKEWNESS	KURTOSIS	MAX	MIN	RANGE
1	0.22302E+01	0.62031E+01	0.48414E+01	0.34219E+00	0.45993E+01
2	0.73565E+01	0.89736E+01	0.18160E+00	0.20200E-01	0.16140E+00
3	0.12941E+01	0.11660E+01	0.10147E+03	0.73333E+01	0.94099E+02
4	0.47003E+01	0.21751E+02	0.36700E+00	0.20000E-03	0.36680E+00

SAMPLE : (CHRYSOTILE)

	LENGTH	WIDTH	ASPECT RATIO	MASS
1	2.0930	0.1412	14.8571	0.0953
2	0.8473	0.0403	21.0000	0.0073
3	0.4433	0.0282	15.7143	0.0006
4	0.2824	0.0282	10.0000	0.0005
5	1.8155	0.0282	64.2857	0.0077
6	1.2507	0.0403	31.0000	0.0047
7	0.9683	0.0282	34.2857	0.0018
8	0.3228	0.0282	11.4286	0.0006
9	0.4035	0.0202	20.0000	0.0004
10	1.3717	0.0202	68.0000	0.0013
11	0.6859	0.0282	24.2857	0.0013
12	1.3314	0.0403	33.0000	0.0050
13	1.2507	0.0605	20.6667	0.0105
14	0.4841	0.0282	17.1429	0.0009
15	1.3717	0.0282	48.5714	0.0033
16	0.2421	0.0202	12.0000	0.0002
17	0.6052	0.0282	21.4286	0.0011
18	1.2507	0.0282	44.2857	0.0023
19	0.3631	0.0202	18.0000	0.0003
20	0.3228	0.0202	16.0000	0.0003
21	0.9683	0.0202	48.0000	0.0009
22	0.4438	0.0605	7.3333	0.0037
23	0.6859	0.0282	24.2857	0.0013
24	1.1700	0.0202	58.0000	0.0011
25	0.3631	0.0403	9.0000	0.0014
26	4.8414	0.1816	26.6667	0.3479
27	2.8643	0.0282	101.4286	0.0053
28	0.5245	0.0202	26.0000	0.0005
29	1.7752	0.0403	44.0000	0.0066
30	0.4035	0.0403	10.0000	0.0015
31	1.2911	0.0403	32.0000	0.0043
32	1.5331	0.0202	76.0000	0.0014

SAMPLE :

DISTRIBUTION BY LENGTH

LENGTH		NUMBER	PERCENT	CUMULATIVE PERCENT
0.0	0.5	11	34.37	34.37
0.5	1.0	7	21.87	56.25
1.0	1.5	8	25.00	81.25
1.5	2.0	3	9.37	90.62
2.0	2.5	1	3.13	93.75
2.5	3.0	1	3.13	96.87
3.0	3.5	0	0.00	96.87
3.5	4.0	0	0.00	96.87
4.0	4.5	0	0.00	96.87
4.5	5.0	1	3.13	100.00

DISTRIBUTION BY WIDTH

WIDTH		NUMBER	PERCENT	CUMULATIVE PERCENT
0.0	0.1	30	93.75	93.75
0.1	0.2	2	6.25	100.00

DISTRIBUTION BY ASPECT RATIO

ASPECT RATIO		NUMBER	PERCENT	CUMULATIVE PERCENT
3	10	4	12.50	12.50
10	20	8	25.00	37.50
20	30	7	21.87	59.37
30	40	4	12.50	71.87
40	50	4	12.50	84.37
50	60	1	3.13	87.50
60	70	2	6.25	93.75
70	80	1	3.13	96.87
80	90	0	0.00	96.87
90	100	0	0.00	96.87
100	110	1	3.13	100.00
110	120	0	0.00	100.00
120	130	0	0.00	100.00
130	140	0	0.00	100.00
140	150	0	0.00	100.00
150	160	0	0.00	100.00
160	170	0	0.00	100.00
170	180	0	0.00	100.00
180	190	0	0.00	100.00
190	200	0	0.00	100.00
* OVER 200		0	0.00	100.00

Phenolic File

PRESERVATION OF PHENOLIC COMPOUNDS IN WASTEWATERS

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DRAFT

BRIEF

The combination of strong acid or base with sample storage at 4°C stabilized phenolic compounds in wastewaters for at least 3-4 weeks. There is a positive relationship between microbiological activity and chemical stability of the samples studied.

ABSTRACT

Copper sulfate and phosphoric acid with sample storage at 4°C is a common preservative technique used for phenolic compounds in wastewaters. However, there are no data showing its effectiveness. A study was conducted to compare the preservation method with the addition of strong base or acid and sample storage at 25° and 4°C. The addition of 1 ml conc H_2SO_4/l with sample storage at 4°C was most consistently effective in preserving stability for 3-4 weeks. However, the other chemical preservatives were found to be effective for at least 8 days. Substantial loss of phenolic compounds rapidly occured in all samples unless the chemical preservative was added immediately after sample collection. A positive correlation was found between loss of phenolic compounds and microbiological activity suggesting the latter was the dominant factor in determining sample stability.

INTRODUCTION

The 1972 Amendments to the Clean Water Act have resulted in limitations on the concentration and loading of pollutants that can be discharged by industries and municipalities (1). The need to monitor these discharges has substantially increased the number of environmental samples requiring analysis, especially for toxic substances such as phenolic compounds.

Kelly has reviewed the literature for methods of analyses of phenolic compounds in wastewaters (2). The most common methods are the 4-aminoantipyrine (4-AAP) (3-6) and 3-methyl-2-benzothiazolinone hydrazone (MBTH) (7,8) colorimetric procedures and the ultraviolet bathochromic shift method (9). The difficulty and equipment requirements for these methods often results in samples being shipped

Chemical Analysis of Samples. The first analysis of each sample was completed within two hours of sample collection. All samples, standards and blanks were distilled from acidic solution, to separate phenolic compounds from potential interferences (13). The distillates were analyzed by an automated version of the 4-aminoantipyrine method shown in figure 1.

The buffered potassium ferricyanide reagent was prepared by adding 2.0 g potassium ferricyanide, 2.1 g boric acid, 3.75 g potassium chloride, 44 ml of 1 N sodium hydroxide and 0.5 ml Brij-35 (Technicon Corp. No. T21-0110) to a volumetric flask and diluting to 1 l. The 4-aminoantipyrine reagent was prepared by diluting 0.65 g of the chemical to 1 l. Both reagents were filtered through a 0.45 µm membrane filter before use.

Two control standards were prepared and preserved with copper sulfate and phosphoric acid by an independent analyst at the beginning of each study to check on the consistency of the day-to-day standard preparation and instrument calibration.

Standard Plate Count. Plate count agar was prepared fresh just before use, added to petri dishes and 1, 0.1 and 0.01 ml of each sample was plated in triplicate (13). All samples were incubated at 35°C for 24 hrs. Only those plates having 30-300 colonies were considered valid and the values reported in Table I are an average of the three replicate dilutions.

RESULTS AND DISCUSSION

The stability of phenolic compounds in non-wastewaters aqueous solutions has been studied by several investigators. Phenolic compounds are good preservatives at high concentrations (>0.5%) but are readily biodegraded at lower concentrations (14-17). Chambers and Kabler found no detectable nonbiological degredation (15). Extremes in pH (18-22), temperature (23-26) and the use of toxic chemicals (27-29) have been used to reduce microbiological activity in aqueous solution. Strong base (4,30,31), acid (4) and copper sulfate-phosphoric acid (11,12) in combination with temperature control have been used to stabilize phenolic compounds in surface waters.

to a large centralized laboratory for analysis. The shipping process can lead to substantial delays between sample collection and analysis. As a result, the effectiveness of the sample preservation technique will substantially affect the accuracy of the data. It is also necessary to consider sample stability during the collection process, especially if the 24-hour composite method is used (10).

Very little data exist in the literature to give guidance about the best method to stabilize phenolic compounds in wastewaters. The current recommended technique (11) is a modification of work performed over thirty years ago (12). Ettinger, et al., found that copper sulfate effectively preserved river water and river water seeded with sewage for two to four days when the samples were stored at 25°C. Subsequent to the work of Ettinger, phosphoric acid was added to the copper sulfate preservative to keep the metal ions in solution when added to alkaline samples (11). In addition, it was recommended that all samples be stored at 4°C until analysis.

No data was presented until 1974 about the effectiveness of the combined phosphoric acid, copper sulfate, 4°C storage technique for preserving phenolic compounds in water samples. Afghan, et al., showed that either strong acid or base has more effective in retarding bacterial activity and stabilizing phenol in Great Lakes' waters than the combined copper sulfate preservative (4).

The observation of Afghan raises doubt that the copper sulfate - phosphoric acid preservation method is best for stabilizing phenolic compounds in wastewaters. Therefore, a study was undertaken to determine the most effective and practical preservation method and maximum allowable holding time for phenolic compounds in wastewaters.

METHODS

Preparation of Samples. Fresh samples were collected in 5 gal high density polyethylene jugs and immediately brought to the laboratory. The water samples were homogonized with a Tekmar Super Dispax system, preserved and split into 250 ml high density polyethylene bottles. Some samples were spiked with phenol to raise the starting concentration to a level that could be accurately measured. The samples were preserved and stored as described in figures 2-5.

Chemical Analysis of Samples. The first analysis of each sample was completed within two hours of sample collection. All samples, standards and blanks were distilled from acidic solution, to separate phenolic compounds from potential interferences (13). The distillates were analyzed by an automated version of the 4-aminoantipyrine method shown in figure 1.

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The stability of phenolics in three different wastewaters preserved with copper sulfate - phosphoric acid and stored at 4°C was studied first. The results are shown in Figure 2. The raw sewage was fairly weak with a biochemical oxygen demand (BOD) of only 95 mg/l and the treated sewage sample was collected after secondary biological treatment but before chlorination. The industrial wastewater was collected from the Grand Calumet River which is essentially a composite from the South Chicago, industrial area.

Since the samples chosen for study often had low background concentrations of phenolics, each was spiked with phenol as needed so that changes in phenolic concentration would be easier to determine. Phenol was chosen for the spike because Kaplin, et al., found phenol to be the least stable of all the phenolic compounds in natural waters (32-35).

The most important result of study 1 was the rapid loss of phenolics from the samples at 4°C with no addition of any chemical preservative. The percentage loss of phenolics within 24 hrs. for the industrial waste, raw and treated sewage samples was 85, 80 and 40%, respectively. Ettinger, et al., reported that an unpreserved river water sample stored at 2°C lost only 15% of the original phenolic content after 4 days (12). However, the same sample stored at 25°C lost all of its phenolic compounds within 2 days. The results from these two studies show that the loss of phenolics from unpreserved samples is variable depending upon sample type but significant in all cases. The expected precision of sample analysis was determined from daily analysis of the control A and B samples to be ± 12 µg/l (2σ). There was no statistically significant change in phenolic concentration over the 22 day study for the samples preserved with copper sulfate-phosphoric acid and stored at 4°C. However, there were large day-to-day changes in the concentration of phenolics measured. This poor precision was determined to be caused by the problem in taking a representative sample for analysis due to the presence of particulate matter. The problem was solved in later studies by homogenizing all samples before analysis.

In the second study (figure 3), the effectiveness of the combined copper sulfate-phosphoric acid preservative was sutdied vs. sample type. Activated sludge was added to raw sewage to create a sample that was organically rich and biologically active. This sample was stable for 12 days, but degraded to 85% of the original

phenol concentration after 33 days. The other samples were stable for the duration of the study. The dip in all values on day 1 of the study was attributed to improper calibration.

Baylis reported the use of 1.2 ml 1 N NaOH/l of sample to preserve phenolic compounds in potable water samples(30). However, Ettinger, et al., found Baylis' procedure to be ineffective for sewage seeded stream samples (12). Kaplin and Frenko found that a hundred-fold increase in base concentration was effective for preserving stream waters (31). Afghan, et al., verified the effectiveness of the higher concentration of base for preserving lake waters (4). Afghan also showed that 0.1 M HCl was an effective preservative.

The effectiveness of strong base or acid in preserving phenolic compounds was compared with copper sulfate in the third study (figure 4). The concentration of phenolic compounds was stable in the raw sewage sample studied when stored at 4°C regardless of the preservative used. However, the sulfuric acid and copper sulfate preserved samples deteriorated rapidly after eight and two days, respective when stored at 25°C.

Doetsch and Cook reported that a common feature of acidophilic bacteria was a resistance to copper ions (28). Growth of acidophilic bacteria occurs at pH 2-5 which is the pH range for the copper sulfate preservative. These facts makes the use of copper sulfate at pH 4 suspect as a good preservative, especially if the samples are not stored at 4°C. The same sample with 2 ml conc H_2SO_4/l - which produces a pH of about 1.5 - at 25°C was stable for eight days. Kushner has reported far fewer microorganisms can tolerate pH 1.5 than 4 (22). It is interesting to note that even at pH 1.5 but at 25°C that the phenolic concentration decreased substantially. This observation indicates that, while neither acidification or cold storage stabilizes phenolic compounds in a wastewater, the combination does.

In order to evaluate the biological induced degredation of phenolic compounds, microbiological activity was measured on a raw and secondary treated sewage. Samples were preserved as indicated in Table I and total plate counts taken after 1 hr. (day 0), 8 and 20 days. The only secondary sewage aliquot that showed any significant activity was the chemically unpreserved sample stored at 4°C. The

microbiological activity noted corresponds very closely with the chemical stability of phenolics in treated sewage found in studies 1 and 2.

The unpreserved raw sewage sample stored at 4°C showed very great microbiological activity which corresponds to the phenolic instability noted in Study 1. The addition of 2 ml conc H_2SO_4/l initially reduced the microbiological activity significantly. However, by day eight, the activity increased five-fold and then decreased slightly again by day twenty. This trend corresponds closely with the rapid loss of phenolics in Study 3, after day eight and then a moderate but continued loss thereafter. The same sample stored at 4°C with 2 ml conc H_2SO_4/l showed at least a ten-fold lower microbiological activity and a corresponding increase in chemical stability shown in Study 3.

The raw sewage sample with copper sulfate-phosphoric acid and stored at 4°C exhibited greater microbiological activity than the aliquot with sulfuric acid. This observation corresponds to the moderate effectiveness of this preservative - stability in studies 1 and 3 and instability of the raw sewage in Study 2. Addition of strong caustic also lowered the microbiological activity of the raw sewage sample. However, the higher concentration of caustic, 10 ml 10 N NaOH/l, was required for a quick initial kill. The high initial microbiological activity of the 2 ml 10 N NaOH/l aliquot did not affect the chemical stability found in Study 3.

Increasing the concentration of H_2SO_4 two-fold with storage at 25°C, reduced the microbiological activity to the same level as the aliquot stored at 4°C with 2 ml conc H_2SO_4/l. A fourth study was conducted to determine if a greater acid concentration could preserve phenolic stability without cold storage. The results in Figure 5, show good stability for the aliquots preserved with 2 ml H_2SO_4/l at 4°C and 4 ml H_2SO_4/l at 25°C. The aliquot with 2 ml H_2SO_4/l at 25°C showed a substantial loss of phenolic compounds after the eighth day.

The enhanced stability of the samples preserved with the higher acid concentration is excellent evidence that the greatest cause of sample instability is caused by microbiological and not chemical acitivity. Gordon claimed that phenolic compounds in many refinery effluent waters can be oxidized in acid solution (35). However,

he did not state the temperature conditions for storage or provide any data to support the claim. Emerson noted that phenol was less reactive under oxidizing acidic than basic conditions (37). Stewart (38) and Waters (39) also noted that phenolic compounds were more reactive in basic solution. However, in practice basic preservation does not cause instability of phenolic compounds especially if stored at 4°C (4,30,31,36).

CONCLUSIONS AND RECOMMENDATIONS

All samples quickly lost phenolic compounds in the absence of a chemical preservative, even if stored at 4°C. Therefore, all samples must be chemically preserved at the time of collection. The chemical preservative must be added to the first aliquot of a composite sample.

The desired time period for holding samples determines the choice of chemical preservatives. All preservatives studied, NaOH, H_2SO_4 and $CuSO_4$ - H_3PO_4, were effective - no more than 5% phenolic compound loss - for at least 12 days when the samples were stored at 4°C. Strong base or acid were effective for 26 and 28 days, respectively, when the samples were stored at 4°C.

The use of acid or base preservation has the advantage of eliminating the use of one separately preserved bottle specifically for phenolics analysis (11,13). The choice of acid or base preservation will depend on whether cyanide (base preserved) or nutrient (acid preserved) analyses will be performed. The advantage of acid preservation is that sulfides, a common interference in the colorimetric methods, will be driven out of the sample (35). The basic preservation will be advantageous if any organic extraction is required in the analysis method to remove organic interferences (13).

Use of 2 ml conc H_2SO_4/l with sample storage at 4°C is recommended over the use of 4 ml conc H_2SO_4/l at 25°C. The former conditions combine the preservative qualities of low temperature and pH and are milder conditions chemically which should reduce the possibility of undesirable chemical reactions.

ACKNOWLEDGEMENT

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Mention of trade names or commercial products does not imply endorsement by the Environmental Protection Agency or the Central Regional Laboratory.

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Table I. Effectiveness of Preservatives in Sterilizing Sewage as Indicated by Total Plate Counts

Preservation Method [a]	Total Plate County, Colonies/ml		
Raw Sewage	Day 0[c]	Day 8	Day 20
4°C	>>>30,000	>>>30,000	>>>30,000
2 ml conc H_2SO_4, 25°C	730	3,500	2,200
2 ml conc H_2SO_4, 4°C	---	70	200
4 ml conc H_2SO_4, 25°C	560	40	b
$CuSO_4$, H_3PO_4, 4°C	6,300	800	600
2 ml 10N NaOH, 4°C	28,000	110	270
10 ml 10N NaOH, 4°C	230	90	100
Secondary Treated Sewage Before Chlorination			
4°C	23,000	20,000	5,400
2 ml conc H_2SO_4, 25°C	<30	<30	<30
2 ml conc H_2SO_4, 4°C	---	<30	<30
4 ml conc H_2SO_4, 25°C	<30	<30	<30
$CuSO_4$, H_3PO_4, 4°C	<30	<30	<30
2 ml 10N NaOH, 4°C	40	<30	<30
10 ml 10N NaOH, 4°C	<30	<30	<30

[a] Volume of acid or base added per liter of sample. Copper sulfate, phosphoric acid preservative prepared as described in ref. 13. Temperatures refer to storage conditions.

[b] Confluent colonies

[c] Plated within 1 hr. of preservation

Figure 1. Automated phenol manifold diagram. Numbers in parentheses correspond to the flow rate of the pumptubes in ml/min. Numbers adjacent to glass coils and fittings are Technicon Corp. part numbers

Figure 2. Plot of stability of phenolic compounds in several wastewaters with time; Study 1. All samples with points plotted as "B" were preserved with 1.0g $CuSO_4 \cdot 5\ H_2O$/l, the pH brought to 4.0 with phosphoric acid and then stored at 4°C. Samples plotted as "A" were stored at 4°C with no chemical preservatives. Both industrial waste, raw and treated sewage samples were spiked with phenol to bring their initial concentrations to 50, 100 and 60 µg/l, respectively.

Figure 3. Plot of stability of phenolic compounds in several wastewaters with time; Study 2. All samples were stored at 4°C. The industrial waste, raw and treated sewage samples were spiked with phenol to bring their initial concentrations to 110, 165 and 110 µg/l, respecti

Figure 4. Plot of stability of phenolic compounds in a raw sewage sample preser with several chemicals; Study 3. Aliquots 1 and 2 were preserved wit copper sulfate and phosphoric acid and stored at 25 and 4°C, respecti Aliquots 3 and 4 were preserved with 2ml conc H_2SO_4/l and stored at 25 and 4°C, respectively. Aliquot 5 was preserved with 2 ml 10 N NaOH/l and stored at 4°C. Aliquots 1-4 were spiked with phenol to bring their initial concentrations to 125 µg/l. Aliquot 5 was spiked with phenol to bring its initial concentration to 130 µg/l.

Figure 5. Plot of stability of phenolic compounds in a raw sewage sample preserved with several concentrations of sulfuric acid. Aliquots 3 and 5 were preserved with 2 ml conc H_2SO_4/l and stored at 25 and 4°C, respectively. Aliquot 4 was preserved with 4 ml conc H_2SO_4/l and stored at 25°C. All samples were spiked with phenol to bring their initial concentration to 130 µg/l.

Figure 1

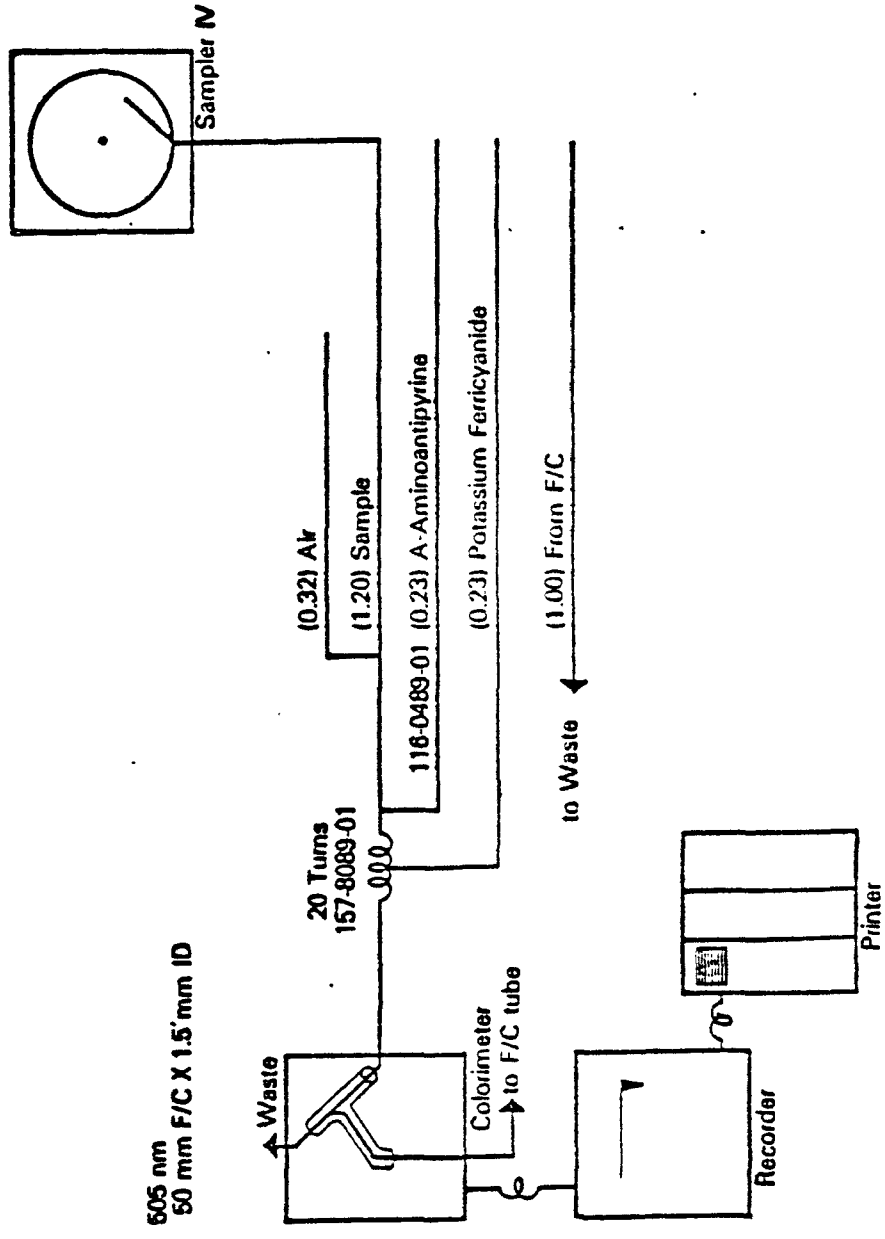

Sampler IV
(0.32) Air
(1.20) Sample
116-0489-01 (0.23) A-Aminoantipyrine
(0.23) Potassium Ferricyanide
(1.00) From F/C
to Waste
20 Turns
157-8089-01
505 nm
50 mm F/C X 1.5 mm ID
Waste
Colorimeter
to F/C tube
Recorder
Printer

Figure 2.

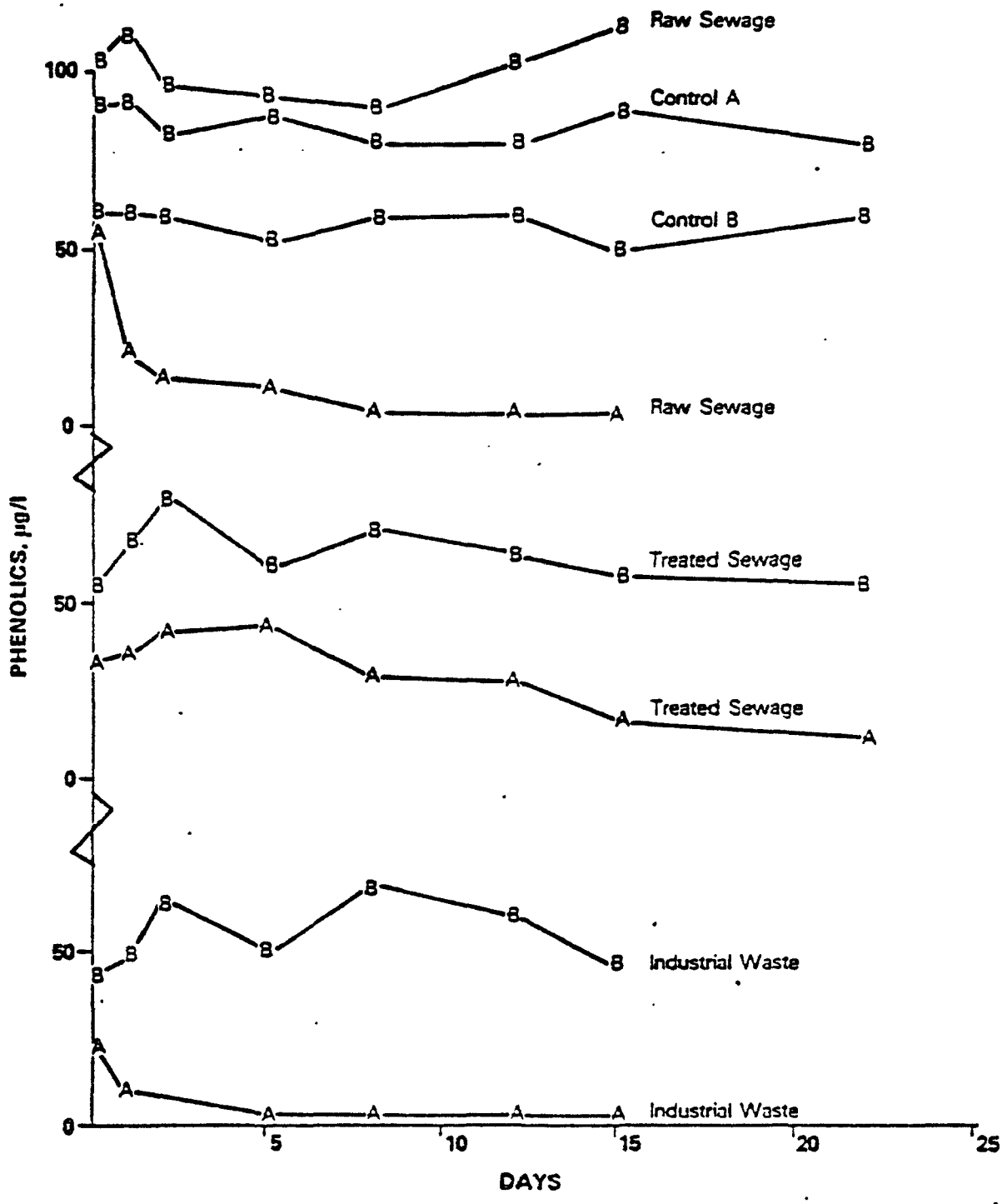

Raw Sewage
Control A
Control B
Raw Sewage
Treated Sewage
Treated Sewage
Industrial Waste
Industrial Waste
PHENOLICS, µg/l
100
50
0
50
0
50
0
5
10
15
20
25
DAYS

Figure 3.

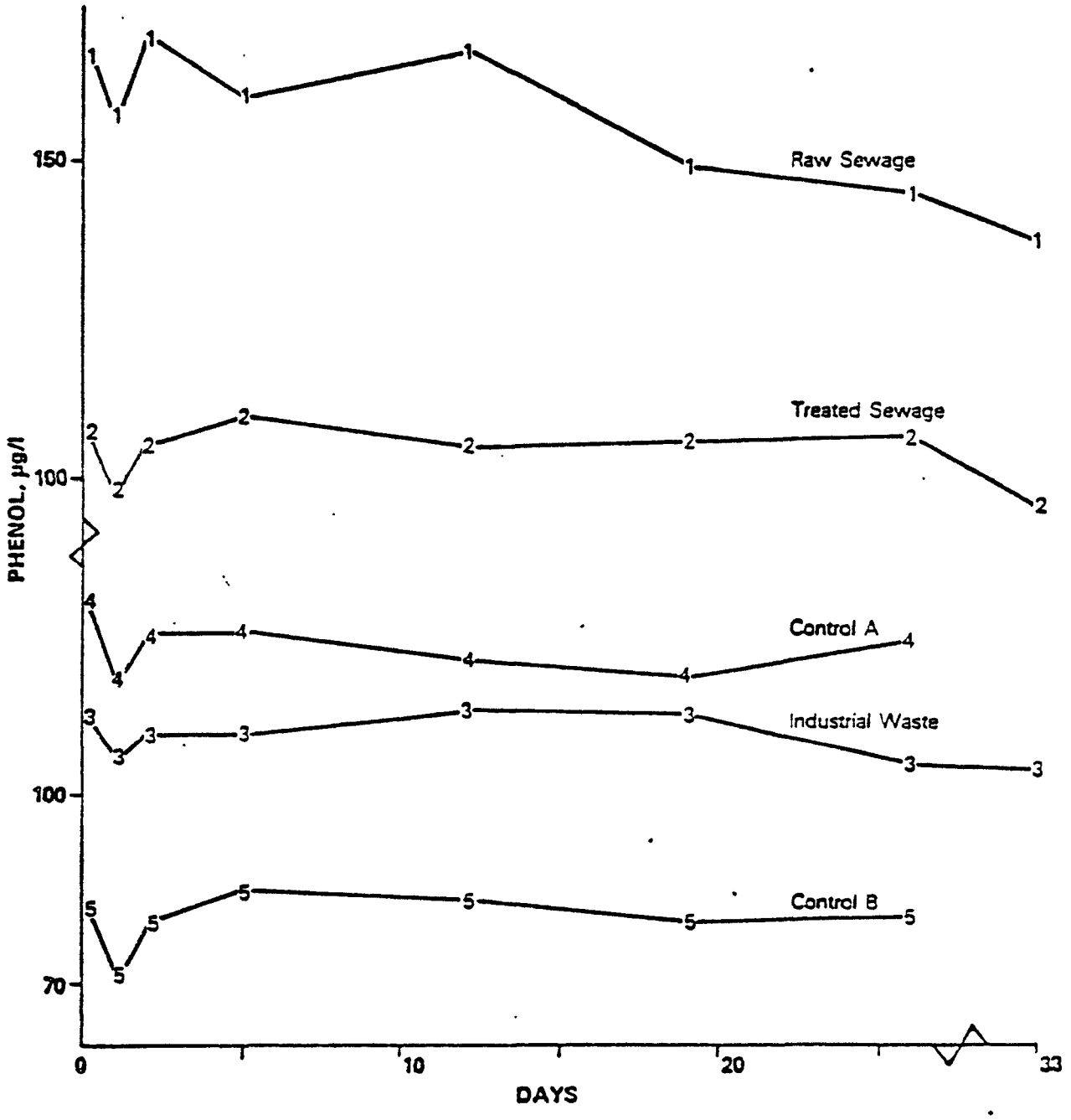

150
100
100
70
PHENOL, µg/l
Raw Sewage
Treated Sewage
Control A
Industrial Waste
Control B
0
10
20
33
DAYS

Figure 4.

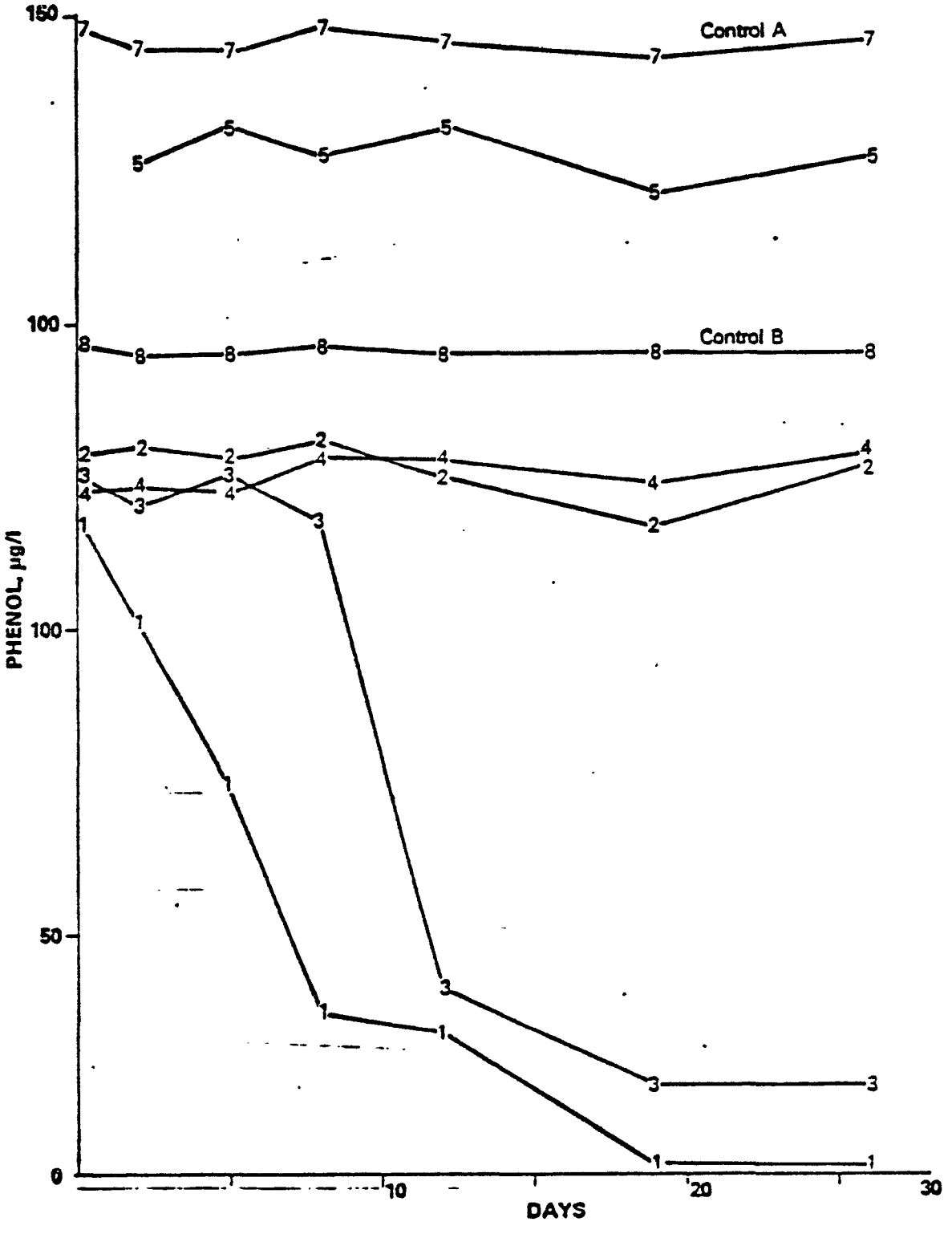
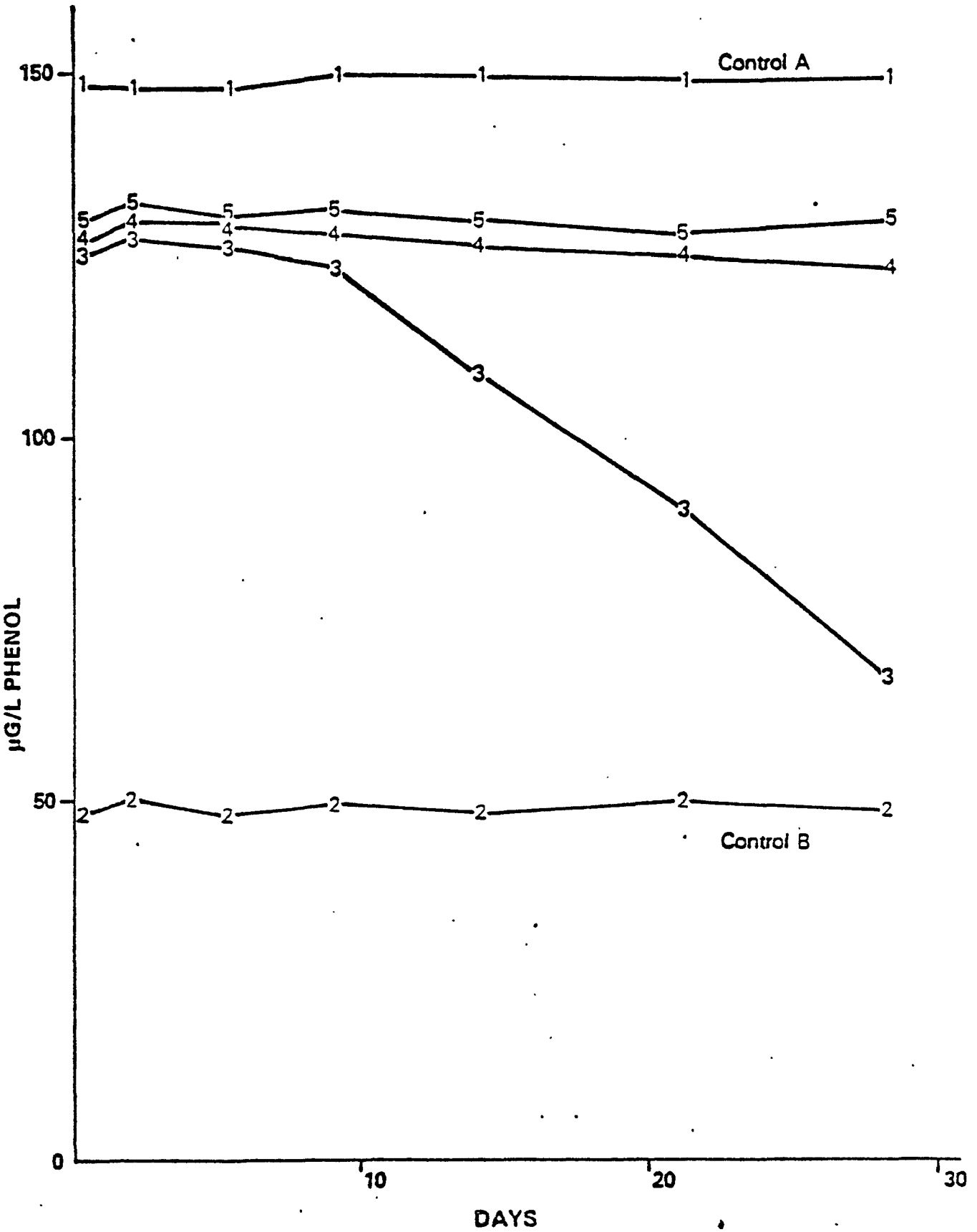


Figure 5



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February 1, 1978

Dr. W. A. Telyard, Chief
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Dear Bill:

Enclosed is a drawing of the liquid-liquid extractor we used for extracting tannery wastewaters for base/neutral and acidic priority pollutants. The design was patterned after the Hershberg-Wolf extractor sold by Ace Glass. The precision bore leveling device was eliminated to facilitate getting them easily fabricated locally.

This simplified model is not totally automated. The stopcock requires periodic adjustment to maintain the appropriate solvent level in the sample chamber. As I told Gail, we have designed a simple modification of the solvent return to eliminate periodic readjustments but have not had time to check it out to our satisfaction. We'll pass along this modification as soon as we can.

Please let me know if we can help further.

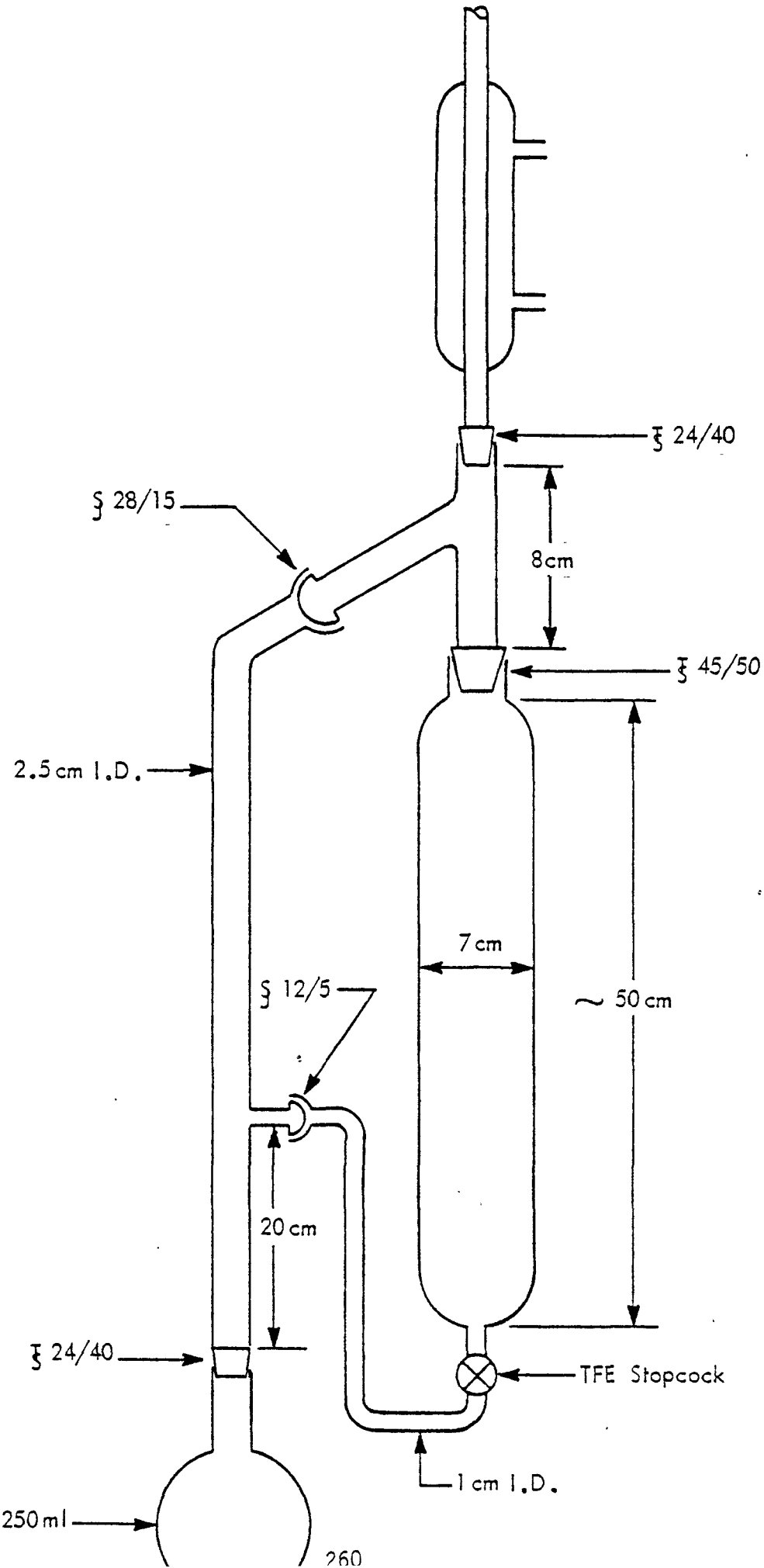
Best regards,

Clarence

Clarence L. Haile
Senior Chemist
Program Manager,
Mass Spec Center

Enclosure

CLH:lm


§ 24/40
§ 28/15
8cm
§ 45/50
2.5 cm I.D.
7 cm
§ 12/5
~ 50 cm
20 cm
§ 24/40
TFE Stopcock
1 cm I.D.
250 ml
260

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Environmental Protection Agency
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