5440

Evaluation of the Procedures for Identification of Hazardous Waste
Interim Report - August 1979

by

Eugene P. Meier, Llewellyn R. Williams, Robert G. Seals, Lawrence E. Holboke
and David C. Hemphill

SUMMARY

This is an interim report for the first four months of the hazardous waste studies being performed at the Environmental Monitoring Systems Laboratory-Las Vegas. The majority of this initial phase of the study was spent in collecting samples and establishing the laboratory analytical operation. Eleven manufacturing and waste disposal sites were visited and 26 different wastes were sampled. Although limited analytical data is available for this report, some tentative observations are presented and should be useful in preparing the guidelines and regulations for hazardous waste. The initial data indicate that the pond sampler gives reproducible results when used in accordance with the proposed regulations. Data obtained also indicate that the proposed extraction procedure is reproducible and should be acceptable for identification of hazardous waste. Some problems were encountered with the analytical procedures for barium and mercury. These problems are being investigated and will be discussed in more detail in the final report. The results and conclusions in this report are interim findings and are subject to change as more information and data are collected in this study.

INTRODUCTION

Background

The rapid technological advances in industry over the past several decades have significantly improved the American economy and lifestyle. However, the improper disposal of hazardous wastes generated by industry as a result of these advances has created a hazard to both human health and the environment. Congress recognized this problem, and in October 1976 enacted legislation - the Solid Waste Disposal Act as amended by the Resource Conservation and Recovery Act (RCRA) of 1976 (and its amendments) - to control the

U.S. Environmental Protection Agency

transportation and management of hazardous waste. Under the authority of this legislation the U.S. Environmental Protection Agency (EPA) issued proposed regulations for the identification, transportation, and treatment, storage and disposal of hazardous waste (Federal Register, Vol. 43, No. 243, Dec. 18, 1978, pp. 58946-59028).

The proposed Section 3001 regulations provide specific procedures for sampling, extraction, and analysis of wastes to identify those wastes which are hazardous due to the presence of leachable toxic components. Previous studies (in some cases with wastes of unknown history) have demonstrated the utility and validity of these methods. However, the EPA felt that additional studies with wastes from known industrial sources were warranted to better define the reliability and reproducibility of the proposed procedures. The EPA also recognized that a strong quality assurance program was required to assure, through standardization and quality control, that valid and defensible data are produced in response to the requirements in the regulations. This study was initiated in April 1979 to support these EPA requirements for the promulgation and enforcement of the hazardous waste regulations.

Objectives

The objectives of this study are to:

- Evaluate the sampling, extraction, and analytical procedures described in the proposed regulations and determine their reproducibility and, in the case of the analytical procedures, their accuracy when used for identification of hazardous waste.

- Initiate a quality assurance program to support the hazardous waste monitoring efforts that will result from promulgation of the hazardous waste regulations.

Scope of the Study

The program for FY 79 and FY 80 is being performed in four individual tasks.

- Task 1. Evaluation of the Proposed Sampling Procedures. This effort is evaluating the safety, reliability and reproducibility of the sampling procedures in the proposed Section 3001 regulations. The COLIWASA and pond sampler methodologies identified in the draft report, "Sampling Procedures for Hazardous Waste Streams" (EPA Grant No. R804692010), are being used to collect waste samples at typical waste sites. Any problems with the sampling procedures when used in the field are noted and will be reported. The waste samples are then delivered to the laboratory for analysis by physical and chemical methods to determine the reproducibility of the sampling procedures. The procedures to be evaluated and wastes to be sampled are determined jointly by the Office of Solid Waste (OSW) and the

Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV). If necessary, modifications to the sampling procedures may be developed and evaluated.

- Task 2. Evaluation of the Proposed Extraction Procedure (EP) and Analytical Methods. This effort is designed to evaluate the reliability and reproducibility of the extraction procedure (EP) described in the proposed Section 3001 regulations (Section 250.13(d)). It is also designed to evaluate the analytical methods that are proposed for use with the EP to determine their accuracy and precision when applied to the EP extracts from a variety of wastes. The number and priority of wastes to be used in the evaluations are determined jointly by the OSW and the EMSL-LV. If necessary, modifications to the EP and/or analytical methods will be recommended to the OSW and may be developed and evaluated.

- Task 3. Analysis of Specific Wastes from the Proposed Hazardous Waste List. The objective of this effort, to be performed in FY 80, is to characterize the wastes that have been placed on the hazardous waste list, in the proposed regulations. Samples of each waste will be collected, extracted, when necessary, and analyzed to determine the identity and concentrations of the hazardous components of these wastes.

- Task 4. Development of a Quality Assurance Program for Hazardous Waste Monitoring. The objective of this efort is to develop and coordinate a national quality assurance program for hazardous waste monitoring. Efforts in FY 79 and FY 80 will:

  1. Provide standard reference materials.
  2. Initiate a laboratory intercomparison program.
  3. Establish minimum laboratory standards and practices.
  4. Establish a laboratory evaluation program.
  5. Develop protocols for evaluation of equivalent methods.

APPROACH

Rationale for Waste and Waste Site Selection

The wastes and sites to be sampled were selected with the active assistance of industrial and government facilities that generate a variety of both hazardous and nonhazardous wastes. The criteria for selecting a waste to be sampled were initially determined by the ultimate use of the waste sample. For evaluating the sampling protocols it was determined that ideally the samples should have the following characteristics:

1. be nonhomogeneous,
2. be fluid (pourable at room temperature, 20°C),

3. be accessible to sampling using a liquid core sampler less than 10 feet long,
4. be available in sufficient quantity to allow at least 20 1-liter samples to be withdrawn without appreciably decreasing the amount of waste remaining (i.e., at least 800 liters), and
5. should contain one or more components which can be used as indicators of whether or not a series of aliquots of these samples are equivalent.

For evaluating the extraction procedure (EP), it was determined that the samples should have the following characteristics:

1. be able to be subdivided into subsamples of 100 gm size without introducing significant variability due to the subsampling procedure,
2. should contain one or more components which can be used as indicators to determine whether a series of repetitive extractions, each one performed on a new subsample of the test material, gives equivalent indicator concentrations in the extract,
3. should contain 25% w/w solids (i.e., separable by filtration and/or centrifugation), and
4. be available in a quantity sufficient to yield at least 5 kg solid.

For evaluating the analytical procedures it was determined that the samples should have the following characteristics:

1. must be from typical waste streams that are complex in nature,
2. should contain one or more of the materials in 250.13(d)(1) (43 FR 58956),
3. be able to be subdivided into samples of 100 gm size without introducing significant variability due to the subsampling procedures, and be available in quantities of at least 5 kg.

In many cases, it was difficult to use these criteria, because a priori information on the wastes was not available or no wastes with the desired characteristics were available from the facilities visited. Because of concerns about the proprietary nature of the industrial process that produced the wastes, many of the facility operators were hesitant to provide more than minimal information about the waste streams sampled. The wastes used in the study were selected to represent the most difficult materials for testing the sampling procedures, the EP, and the analytical procedures (i.e., they represented worst-case conditions for each procedure).

Sites Visited and Wastes Sampled

During the first phase of this study, eleven manufacturing and waste disposal sites were visited with 26 different wastes being sampled (Table 1). Brief descriptions of each site and waste follow:

Site A. This is a waste disposal facility that segregates its wastes by type of industry. The liquid wastes are placed in open ponds where waste volume is reduced by evaporation. In some cases there is movement of waste material from one pond to the next (in reality the ponds are not all segregated). Four ponds were sampled with the pond sampler at this site. Two of the ponds contained a liquid that the site operator identified as titanium dioxide process waste. The samples from these ponds were acidic (pH <1) and contained approximately 1% solids. The samples were brownish-green and could be separated into layers of an oily aqueous liquid and a dark-grey fine solid. The third pond was identified by the operator as an alkaline waste; however, the pH of the samples collected from different locations on the pond ranged from 2.3 to 7.7. These samples could be separated into layers of a greenish-yellow aqueous liquid and a light brown solid (approximately 6% solids). The fourth pond contained a waste identified by the operator as sulfonation tars. The samples collected could not be filtered by the proposed filtration procedure; however, they could be separated by the proposed centrifugation procedure into four layers (a thin dark-brown oil layer, a non-aqueous liquid layer, an aqueous layer and a very thin layer of solids).

TABLE 1. SITES SAMPLED DURING FY 79: IDENTIFICATION OF SITES, FACILITY FUNCTIONS, AND WASTE STREAMS SAMPLED

Site	Function of Facility	Waste Stream Sampled
A	Waste disposal	Ponds of TiO_2 process waste
		Pond of alkaline waste
		Pond of sulfonation tars
B	Paint manufacture	Drum of paint sludge
C	Chemical manufacture	Drum of laboratory wastewater
		Bags of pesticide waste
D	Chemical manufacture	Inlet, grit chamber, and pond of an API oil separator
		Dumpster of chromate oxidation paste
E	Steel manufacture	Waste dust pile from electric furnace baghouse

(continued)

TABLE 1. (Continued)

Site	Function of Facility	Waste Stream Sampled
		Filter cake waste from blast furnace scrubber
		Waste roll mill scale pile from water treatment plant
		Tank truck of lime sludge from ammonia still
F	Chemical manufacture	Alkyl chloride storage pit
		Epichlorohydrin waste sump
		Polymerized epichlorohydrin waste pits
G	Chemical manufacture	Filter cake from chlorine/mercury process stream
		Dumpster of asbestos waste, clean-up from chlorine process
H	Petrochemical manufacture	CPI* decant pit
		Activated biosludge
I	Chlorine manufacture	Waste chlorine sludge pile
J	Chemical manufacture	Industrial sewage filter cake from a truck
		Tank of chromate reduction clarifier underflow
		Drum of catalyst fines
K	Paint removal/ electroplating	Drums of plating waste identified as tin-lead solution
		Drums of alkali rust remover (red)
		Drums of oil/water organic solvent mixture

* CPI = Chemical Production Industries

Site B. Waste sludge from the solvent recovery operation was sampled at this paint production facility. A COLIWASA was used to obtain the samples from a 55 gallon drum. The samples were multicolored; had a high viscosity; had the odor of typical oil-based paint solvents; and, could not be filtered or centrifuged in accordance with the proposed procedures.

Site C. Two wastes were sampled at this chemical manufacturing facility. One was an acidic (pH $\simeq$ 1) laboratory waste from COD and other wastewater analyses performed in the facility's laboratory. The waste sample, collected from a 55 gallon drum with a COLIWASA, had a brown organic layer and a dark-orange-brown aqueous layer. The second waste was a solid material (composite of excess quality control samples contained in plastic bags) from the production of a urea herbicide.

Site D. Samples were collected with a pond sampler from an API oil/water separator and a dumpster of chromate oxidation paste at this chemical manufacturing facility. The samples collected from the API separator contained oily dark-brown solids mixed with water (pH = 8). The chromate oxidation paste samples contained a clear liquid layer (pH $\simeq$ 7.5) and a layer of brown solids (approximately 10% solids).

Site E. Four wastes were sampled at this steel manufacturing facility. (1) A waste-dust pile from an electric furnace baghouse was sampled with a shovel. The sample was a dark-brown mixture of powdered and solid material that had a light fluffy texture. (2) Filter-cake waste from a blast furnace scrubber was sampled with a gloved hand. The sample was a black paste that appeared to contain a small amount of water. (3) A pile of waste roll-mill scale, from one of the facility's water treatment plants, was sampled with a plastic bottle. The sample was a mixture of crystalline solids (large and small pieces) that had a disagreeable odor. (4) A tank truck of lime sludge from an ammonia still was the final waste sampled at this site. The sample, taken with a shovel, was a light-brown mixture of solids in an alkaline liquid (pH = 11.6).

Site F. Three wastes were sampled with a pond sampler at this organic chemical manufacturing facility. (1) The first sample, collected from an alkyl chloride storage pit, was a rust-brown liquid (pH = 7) with suspended solids. (2) The second sample, collected from an epichlorohydrin waste sump, contained two layers, a liquid (pH = 9.7) and a gray solid. According to the plant operator, this waste was a mixture of caustic solids, phenols, and epichlorohydrin. (3) The remaining samples were taken from each of two pits of polymerized epichlorohydrin (epoxy resin). These samples contained sandy white solids in an alkaline aqueous liquid (pH $\simeq$ 12).

Site G. Two waste samples were collected with a small trowel from a chlorine-mercury process stream at this chemical manufacturing facility. The filter cake waste sample had two phases, water (pH = 5.6) and a light-brown solid. The second waste sample from this process contained asbestos solids and water (pH = 9.8).

Site H. An activated biosludge and a waste from a CPI (Chemical Production Industries) decant pit were sampled at this petrochemical facility. The biosludge sample (taken from a faucet in the pipeline from the settling tank) was a brown liquid (pH = 6.4) that contained a high concentration of suspended solids. The decant pit waste was from an adjacent oil refinery process stream. It was sampled with a pond sampler and yielded a black, oily liquid sample that had a disagreeable odor. The high organic concentration of this sample prevented measurement of its pH.

Site I. A waste pile of chlorine process sludge was sampled with a small trowel at this chlorine manufacturing facility. The waste sample was a dark-gray, paste-like solid.

Site J. Three wastes were sampled at this chemical manufacturing facility. (1) A sample of an industrial sewage filter cake was obtained from an open truck with a small trowel. (2) A sample (pH = 8.7) of liquid waste from a chromate reduction clarifier underflow was obtained from a faucet in the pipeline leading from the settling tank to a treatment plant. (3) The third waste sample was obtained (with a glass jar used as a scoop) from a drum of catalyst fines used in a proprietary chemical process.

Site K. Three wastes from a paint removal and electroplating operation were sampled at this facility. The wastes were stored in drums and were awaiting disposal by a commercial disposal company. The samples were obtained with the COLIWASA. (1) A plating waste identified as a tin-lead solution, yielded greenish-yellow acidic (pH <1) aqueous samples that had some suspended solids. (2) An alkali rust remover waste, identified as "red" because of its color, yielded dark red alkaline (pH ≃ 12) samples. (3) The samples obtained from an oil/water solvent waste had three phases, an oily surface layer, a tea-colored aqueous layer (pH ≃ 6.5) and a solid layer.

A major delay came about in commencing the experimental work due to problems in obtaining samples of wastes. Locating facilities having the required wastes and obtaining approval from the companies involved took considerable time and effort. In several cases the industrial operators were concerned about the proprietary nature of their process and required a confidentiality agreement from the EPA contractor who was making the visit and collecting the samples. Corporate approval of this agreement took up to four weeks to complete and resulted in some confusion and delays in the site visits and sampling efforts.

Shipment and Storage of Samples

The samples collected in the field were sealed in glass jars (caps had Teflon inserts). The jars, in turn, were sealed in individual plastic bags and packed in a properly labeled shipping container. Each shipping container was lined with a large plastic bag and filled with vermiculite packing material. The containers were locked and then shipped via Federal Air Express or truck to the laboratory in accordance with Department of Transportation regulations. Chain-of-custody is maintained for each sample. The samples were stored at room temperature (21 - 27°C) until use. No steps were taken to preserve the samples.

Sampling Procedure Evaluation

Rationale

In designing the sampling procedure evaluations, three general guidelines were followed:

1. The study is designed to evaluate only those methods that were specifically developed for this regulatory program (e.g., the pond sampler and COLIWASA).

2. The wastes to be sampled are to be selected from among those materials that would be most difficult to sample (i.e., a worst case situation such as a multiphase waste that contains immiscible liquids and solids of differing density and particle size).

3. The samples are to be obtained by personnel who are not knowledgeable in the variability or detailed physical or chemical characteristics of the specific wastes in order to simulate non-expert use of the sampling methodology.

The sampling methods in Appendix I of the proposed regulations include: (1) ASTM methods and (2) protocols from a draft EPA report, "Sampling Procedures for Hazardous Waste Streams," EPA Grant No. R804692010. The ASTM procedures are not being evaluated because the Agency assumes that they are standard procedures and have undergone sufficient evaluation through general use with materials of the type indicated in Appendix I of the proposed regulation. However, the protocols described in the draft report have not been evaluated for sampling wastes under field conditions. Since the pond sampler and COLIWASA had not been evaluated under field conditions and will have significant use in supporting the regulations, they were selected for evaluation in this study. The samplers are being used in accordance with the protocols in the draft report and are described in Appendix 1 of this report. The study is designed to determine the ability of these procedures to obtain a representative sample from a given waste source. The procedures are not being tested for use in sampling a waste over a period of time (i.e., to determine if the waste source changes with time).

Experimental Design

The experimental design for the sampler evaluations was developed with the recognition that it is very difficult to obtain representative samples from a heterogeneous waste source, especially in the case of large disposal ponds or pits. In the extreme case, it would be necessary to analyze an entire pond of waste to determine what combination of samples would be required to characterize the pond's composition. Of course, this is impractical; and, a statistical approach must be taken to obtain and analyze the minimum number of samples that are required to assure, with a stated degree of confidence, that the sample data is representative of the waste source. The initial experimental design was based on a one-sided parametric test that assumed a 4% significant deviation. This design required 39 samples from the source (i.e.,

39 samples/pond) to yield data with 95% confidence of avoiding Type I and Type II errors. (Type I errors, i.e., rejecting the hypothesis of no difference between means of sample populations when, in fact, no difference exists, are minimized by setting the critical probability level for chance differences very low, e.g., 5% or even 1%. Type II errors, i.e., accepting the hypothesis of no difference between means of sample populations when, in fact, a real difference exists are minimized by increasing the sample size and hence the discrimination of the test.) This approach was later modified to provide the appropriate number of samples required for a hierarchical (nested) analysis of variance (ANOVA) and to define the sources of variability present in the sequence of sampling and analysis.

Table 2 identifies the waste and regimen selected for evaluation of the pond sampler and the COLIWASA. The pond sampler was used to sample four different waste sources at two sites. The COLIWASA was used to sample five different waste sources at three sites. The overall strategy of this effort was to determine the ability of the sampling procedures to collect reproducible samples from a given waste source. There was no attempt to determine the changes that occur if a waste is sampled over a given period of time (i.e. all samples from any single source were collected on the same date).

TABLE 2. WASTES SAMPLED USING THE POND SAMPLER AND COLIWASA

Location	Waste	Sampling Regimen
	POND SAMPLER	
Site A	TiO_2 process waste	2 ponds, 10 samples/pond
	Alkaline waste	1 pond, 10 samples
	Sulfonation tars	1 pond, 10 samples
Site F	Polymerized epichlorohydrin waste	2 pits, 20 samples/pit
	COLIWASA	
Site C	Laboratory wastewater	4 drums, 3 samples/drum
Site B	API separator waste	15 drums, 3 samples/drum
Site E	Plating waste, tin/lead	3 drums, 3 samples/drum
	Alkali rust remover	3 drums, 3 samples/drum
	Oil/water/solvent waste	3 drums, 3 samples/drum

For the pond sampler, duplicate samples were taken at each of several locations in the pond or pit. The sampling locations were randomly selected; however, they were restricted to locations that could be safely accessed by the sampler operator. The number of samples obtained by the COLIWASA was restricted by the number of drums of waste available for sampling. In all cases triplicate samples were obtained from each drum. The samples were returned to the laboratory where duplicate or triplicate aliquots of the samples are being analyzed for chemical and physical parameters such as pH and percent solids (weight of filterable solids/weight of aliquot).

Percent solids and pH were initially selected for testing the reproducibility of the sampling procedures because these parameters were easy to determine and represented sample properties that effect the chemical data obtained by the EP. In most cases, waste samples are heterogeneous with respect to such properties as percent solids or aqueous:non-aqueous composition. While the elemental concentration in each phase may not change with location, the concentration observed with the EP will change if the relative quantity of each phase in the sample changes. When practical, the percent solids, immiscible phase composition, or some other easily obtained physical parameter will be used to evaluate the samplers.

The pH of the aqueous phase of each liquid sample is measured with a laboratory pH meter. The pH meter is calibrated with standard buffers at pH 4, 7, and 10 just prior to the measurements and rechecked after the measurements are completed. Percent solids were determined in accordance with the "Non-filterable Residue Method 160.2," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, OH 48268, March 1979. Duplicate or triplicate (when sufficient sample volume is available) aliquots of each sample are analyzed to determine the relative magnitude of variability that can be attributed to the laboratory analytical procedures.

Extraction Procedure (EP) Evaluation

Rationale

The proposed extraction procedure (EP) is a key step in the screening mechanism designed to identify those wastes that are hazardous and require special management because of their toxic characteristics. It should be noted that the EP is not intended to identify the total concentration of the toxic contaminant in the waste, but rather that leachable concentration that could occur in groundwater below the disposal site as a consequence of mismanagement. The approach taken to evaluate the EP was designed to:

1. determine the reproducibility of the EP described in the proposed regulations (43 FR 58956).
2. determine if the procedure, as written in the proposed regulations, is explicit enough for use by non-experienced personnel to obtain valid data.
3. determine the equivalency of the various extractors that could be used with the EP.

4. determine if the filtration and centrifugation methods are suitable alternatives for liquid-solid separation.
5. gain additional experience with the methods as background for preparation of guidelines manuals to assist those who will use the EP.

Experimental Design

The extraction procedure is being used in accordance with the proposed regulations, with minor clarifications of instructions necessary to facilitate sample extraction (see Appendix 2). A flow chart of the sample treatment required for the EP is shown in Figure 1. As shown, triplicate aliquots (minimum of 100 gm each) are obtained from a stirred waste sample and are separated into solid and liquid phases by either filtration or centrifugation. The liquid phase is stored under refrigeration until the solid phase has been extracted. The solid phase is then weighed and placed in a suitable extraction apparatus along with a volume of deionized water equal to 16 times the weight of the solid phase. For solutions of pH > 5, the pH of the solution is continuously adjusted to 5.0 ± 0.2 with 0.5 N acetic acid during agitation. However, the maximum amount of acid that is added during the extraction procedure is 4 ml per gram of solid phase, even if the pH of the solution does not reach 5.0 ± 0.2. Agitation is continued for 24 hours. The solution is then filtered and any solid material is discarded. The liquid extract is then adjusted with deionized water to a volume equal to 20 times that occupied by water at 4°C equal in weight to the solid phase added to the extractor. This solution is then added to the original liquid phase to produce the extraction procedure extract. The EP extract is split into two samples; one is acidified to preserve it for elemental analysis and the other is stored under refrigeration for organic analysis.

The EP is being evaluated with as many of the wastes collected (Table 1) as possible. Each sample is being extracted at least once for screening analysis by atomic emission spectroscopy to identify the major extractable toxic components that might be used for evaluation of the EP. Based on the screening data, the OSW and the EMSL-LV are determining the priority of the samples to be used for evaluation of the EP.

Triplicate aliquots of each sample are being treated as described in Figure 1. The extracts are analyzed by standard atomic absorption spectroscopy methods cited in Section 250.13(d) of the proposed regulations. The results are then averaged to determine a mean and the standard deviation for the triplicate analyses. The standard deviation identifies the reproducibility of the procedure.

If time permits, additional experiments will be performed to compare various extractors that might be used for performing the EP. Each extractor will be used to simultaneously extract a minimum of three aliquots from the same waste sample (i.e. comparison of two extractors requires a minimum of six aliquots, three per extractor). The waste sample for this comparison will be selected from those that have high concentrations of toxic elements. Each

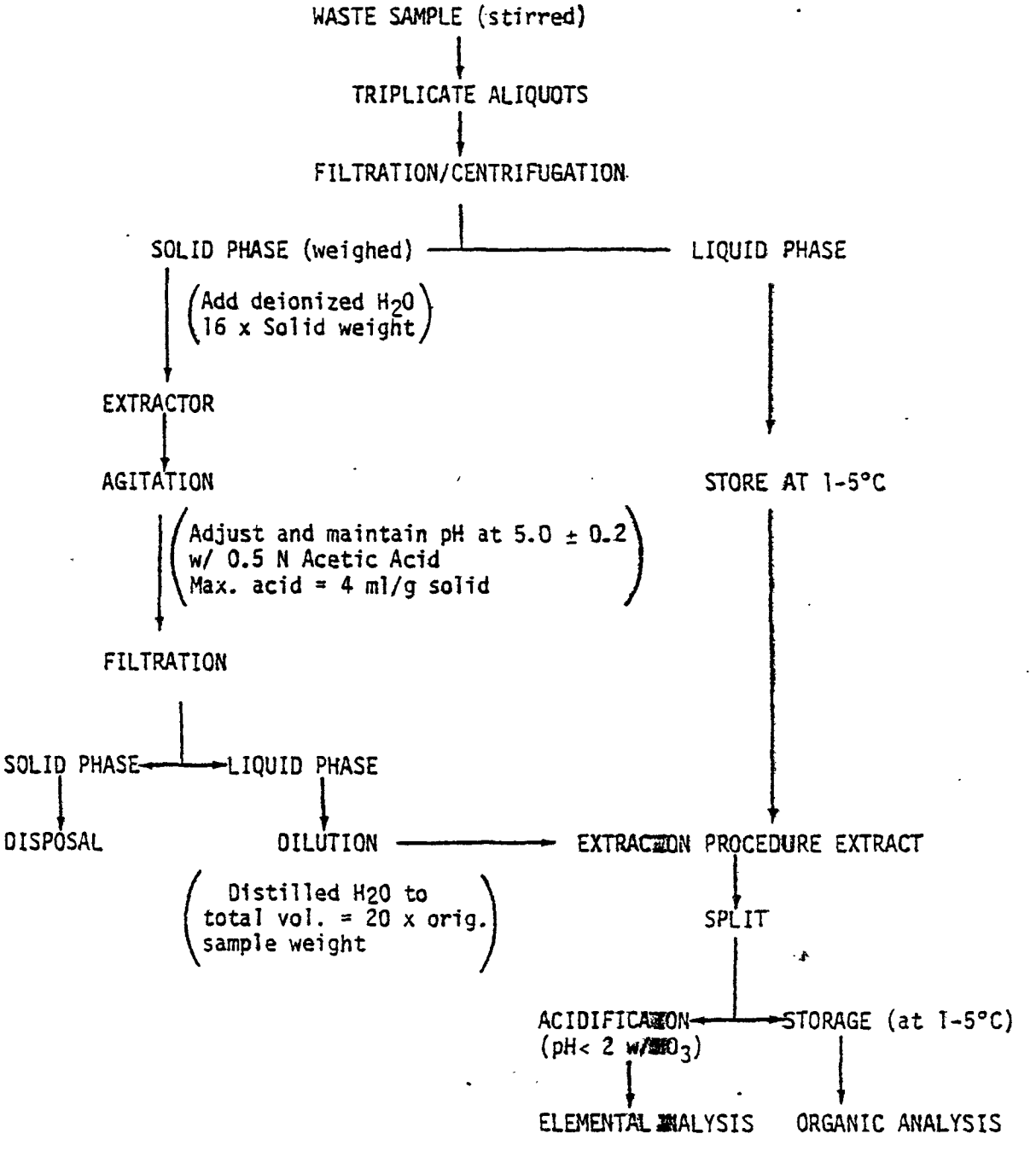

Figure 1. Flow Chart of the Extraction Procedure for Identification of a Hazardous Waste.

extract will be analyzed by the procedures cited in the proposed regulations. The means and standard deviations of the analytical results obtained by each extractor will be compared. An acceptable extractor should yield a mean that agrees with the mean obtained with the extractor in the proposed regulations, and should have an equivalent or lower standard deviation (i.e. equivalent or better reproducibility).

Additional experiments may be performed to examine other extraction procedures that have been suggested or used for the identification of hazardous waste. One waste sample has been extracted with deionized water in accordance with a procedure suggested by the ASTM. This procedure, while similar to the EP, uses distilled or deionized water instead of acetic acid buffer, does not subdivide solid samples into smaller units, has a higher solid to liquid ratio, and uses a less aggressive means of agitation. The OSW and the EMSL-LV will determine if additional experiments are to be performed to compare alternative identification procedures. The comparisons will use the EP and alternate identification procedures simultaneously to characterize the same waste sample(s). A minimum of three aliquots of the same waste sample(s) will be extracted in accordance with the instructions for each procedure (i.e. a minimum of three extractions per procedure). The extracts will be analyzed by the analytical methods cited in the proposed regulations. The means and standard deviations of the results obtained with the alternative procedures will be compared to that obtained with the EP.

Additional experiments are also being performed to identify any background interferences that may result from the equipment used for the EP. The filtration equipment and the extraction apparatus used in this study are made of stainless steel. Since the samples come in contact with the stainless steel surfaces, there is some concern that this will cause high background concentrations of metals, especially chromium in the EP extract. Two groups of blank samples, one consisting of deionized water and the other 0.13 N acetic acid (400 ml of 0.5 N acetic acid to 1600 ml of deionized water), are being tested (in accordance with the EP) to determine what background concentrations of metals will result from the equipment used to obtain the EP extract.

Analytical Procedures Evaluation

Rationale

The analytical procedures proposed for analysis of the EP extracts are standard methods for analysis of water, wastewater, or industrial effluents. They should be acceptable for analysis of liquid wastes and the EP extracts; however, they have not been extensively tested with samples of industrial "solid waste" or EP extracts of such waste. The approach taken in this phase of the study is therefore designed to obtain additional information on the accuracy and reproducibility of these analytical methods when they are applied to liquid wastes and the EP extract in accordance with the proposed regulations. Alternative methods that offer advantages in cost and accuracy may be identified and evaluated. If necessary, new methods will be developed and evaluated.

Experimental Design

The proposed regulations require the use of atomic absorption (AA) methods ("Methods for Chemical Analysis of Water and Wastewater," Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974) for the analysis of liquid wastes and the EP extract for arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver. The AA methods are being evaluated with EP extracts from various wastes known to contain one or more of the elements of interest.

Triplicate aliquots of the EP extracts are first analyzed in accordance with the proposed regulations. Aliquots are then spiked with known concentrations of the elements of interest and re-analyzed in accordance with the proposed regulations. The mean and standard deviation of the triplicate results obtained for each spiked sample matrix are used to evaluate the accuracy of the analytical method. Spike recovery is calculated by dividing the mean analytical result (less the concentration of that element in the unspiked sample) by the spike concentration, and multiplying by 100 to obtain percent recovery. The relative standard deviation is determined by dividing the standard deviation by the mean and multiplying by 100. The analytical methods should accurately and reproducibly indicate the increase in concentrations of the elements in the spiked samples. Spike recoveries will be determined for each analytical method in as many sample matrices as possible.

Additional experiments are being performed to determine the effect, if any, of the acetate buffer matrix of the EP extract on the analytical procedures. Solutions of known concentration are prepared in an acetate buffer matrix and in the standard matrix identified for each element in the "Methods for Chemical Analysis of Water and Wastewater." The standard curves (concentration vs. absorbance) for each element should be identical if no matrix problems exist.

A similar approach will be used to evaluate the analytical methods for endrin, lindane, methoxychlor, toxaphine, 2, 4-d and 2, 4, 5-TP Silvex. However, these studies will also determine if alternate improved methods are available for these organic compounds. Because of the low solubilities of these compounds in water, it is anticipated that these evaluations will be more difficult and time consuming.

Quality Assurance Program for Hazardous Waste Monitoring

Rationale

It is imperative that the data collected for management of hazardous waste be of known quality to ensure that both human health and the environment are adequately protected and that the regulations are enforceable. A quality assurance program is being developed to provide a standardized approach to monitoring hazardous waste operations and to allow continued evaluation of EPA, state and other laboratories who are responsible for conducting the measurement and monitoring that is required under the RCRA waste management system. This program is being coordinated by the EMSL-LV and will use quality assurance efforts already in place for the air and water programs.

Program

A repository for standard reference organic compounds is being developed jointly by the EMSL-LV and the Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-CIN). Additional reference materials will be developed for this program under an interagency agreement with the National Bureau of Standards (NBS). These reference materials will include soils, sludges, sediments and "waste-type" samples of known composition that can be used for methods evaluation, instrument calibration, and laboratory intercomparison studies.

Laboratory intercomparison studies will be initiated in FY80. These studies are designed to assure that the participating laboratories can obtain accurate data with the specific procedures and samples being tested. Samples of known composition will be distributed as "unknowns" to the participating laboratories for analysis by the appropriate procedures. These samples may require application of the EP or may simply require analysis for one or more components. Each participating laboratory will report its results to the EMSL-LV. All laboratory results will be combined into a single report (with laboratories identified by code numbers for confidentiality) which will be distributed to each laboratory. If an individual laboratory's results differ significantly from the true value or grand average of the reported results, that laboratory must identify the source of the discrepancy and take appropriate action to correct its analytical operations.

The quality assurance program will also include on-site laboratory evaluations. It is anticipated that on-site evaluations of EPA laboratories will be coordinated and performed by the EMSL-LV, whereas state and other laboratories will be evaluated by the appropriate EPA Regional office. These on-site evaluations are designed to determine if the laboratories that provide data for the hazardous waste programs have adequate facilities, equipment, and personnel and are using proper procedures for obtaining the data reported.

Quality assurance guidance will also be provided in the form of minimum laboratory standards and practices and other guideline documents and manuals. The EMSL-LV will develop protocols for evaluation of equivalent methods and will establish an equivalency program to evaluate new methods as they become available.

RESULTS AND DISCUSSION

Sampling Procedures Evaluation

Pond Sampler

Four ponds were sampled at site A. Two samples were taken at each of five locations on each pond. Samples from two of the ponds, Pond 0 and Pond 13, have been analyzed for pH and percent solids. Some difficulty has been encountered with filtration of the samples from the other two ponds; however, it is anticipated that the data for those samples will be provided in the final report. If sufficient sample material is available, the samples from

Site A will also be analyzed by the EP to determine the overall reproducibility of the procedure for identification of a hazardous waste when applied to waste in ponds.

Four factors contribute to the overall reproducibility observed in the analytical data obtained with the pond samples. These are:

1. the precision of the analytical procedure used to determine the parameter of interest in each sample.

2. the effect of the collection of the first sample on the second sample, when two samples are collected at the same location

3. the homogeneity of the waste in the pond being sampled.

4. the reproducibility of the sampling procedure.

The data obtained with the pond samples (Tables 3 and 6) can be analyzed to estimate the contribution of these four factors to the overall reproducibility of the pond sampler. The precision of the analytical procedure, Factor 1, can be estimated by comparing the results from replicate analysis of the same sample (Tables 4 and 7). The differences between two samples taken at the same location (Tables 5 and 8) reflect the reproducibility of the sampling procedure, Factor 4, and the effect (if any) of the collection of the first sample on the second sample, Factor 2. The homogeneity of the waste in the pond is reflected in the differences between samples from different locations on the pond (i.e. differences between the first sample taken at each location - Tables 4 and 7), Factor 3.

The data for the titanium dioxide process waste from Pond 0 are shown in Table 3. Because of the limited sample volumes, only duplicate aliquots were analyzed for each sample. The pH of the Pond 0 samples was very low (pH <1), thus the measurements with the pH meter were not reliable enough to identify differences between locations on the pond. However, the percent solids data can be used for this purpose. Differences between aliquots from the same sample (Table 3) reflect the reproducibility of the laboratory analytical procedure for determining pH or percent solids. The procedure for pH required insertion of a pH electrode into the aqueous phase, whereas the procedure for percent solids required collection of aliquots from the sample and analysis of those aliquots. The standard deviations reported in Table 4 provide a numerical indication of this reproducibility. If the standard deviations of the mean for each location (Table 5) are compared to the standard deviations for the analyses (Table 4), it appears that the laboratory analytical procedure for percent solids is largely responsible for the variation in the results. A hierarchical analysis of variance revealed that the differences between samples taken at the same location were significant at the 5% level ($F_{10,5} = 6.89$). However, the analysis of variance performed on the percent solids data for Pond 0 indicates no significant differences between locations ($F_{5,4} = 0.95$). If the mean value for each field sample (Table 4) is

TABLE 3. EVALUATION OF POND SAMPLER: RESULTS OF pH AND PERCENT SOLIDS ANALYSES OF DUPLICATE ALIQUOTS, FROM DUPLICATE SAMPLES OF WASTES TAKEN AT FIVE LOCATIONS ON POND 0, SITE A

Sample*	pH	Percent Solids	Sample	pH	Percent Solids
1A	0.23	1.24	3B	0.40	0.92
	0.23	1.26		0.46	1.83
1B	0.34	1.09	4A	0.51	1.54
	0.31	1.28		0.44	1.61
2A	--**	0.82	4B	0.37	--**
	--**	1.28		0.38	1.19
2B	0.22	2.09	5A	0.43	1.74
	0.17	1.28		0.43	1.84
3A	0.30	--**	5B	--**	1.55
	0.19	--**		--**	1.80

* Number = location on pond; A & B = 1st and 2nd sample [illegible] location.
** Data not reported - known discrepancies in analytical procedure.

TABLE 4. POND SAMPLER: MEANS AND STANDARD DEVIATIONS OF DUPLICATE ANALYSES FOR pH AND PERCENT SOLIDS IN WASTE SAMPLES FROM POND 0, SITE A

	pH				Percent Solids			
	First sample		Second sample		First Sample		Second Sample	
Location	$\bar{x}$	s(n = 2)	$\bar{x}$	s(n = 2)	$\bar{x}$	s(n = 2)	$\bar{x}$	s(n = 2)
1	0.23	0.00	0.33	0.02	1.25	0	1.19	0.13
2	--	--*	0.20	0.04	1.05	0.33	1.69	0.57
3	0.25	0.08	0.43	0.04	--	--*	1.38	0.64
4	0.48	0.05	0.38	0.01	1.58	0.06	--	--*
5	0.43	0.00	--	--*	1.79	0.07	1.68	0.18
Average	0.35		0.34		1.42		1.48	

* Data not reported - known discrepancies in analytical procedure.

TABLE 5. POND SAMPLER: MEANS AND STANDARD DEVIATIONS OF DATA THAT REFLECT DIFFERENCES BETWEEN TWO WASTE SAMPLES TAKEN AT EACH OF FIVE LOCATIONS ON POND 0, SITE A

	pH		Percent Solids	
Location	$\bar{x}$	s(n = 2)	$\bar{x}$	s(n = 2)
1	0.28	0.07	1.22	0.04
2	--	--*	1.37	0.45
3	0.34	0.13	--	--*
4	0.43	0.07	--	--*
5	--	--*	1.74	0.08
Average	0.35		1.44	

* Data not reported - known discrepancies in analytical procedure.

considered as a single result, the average percent solids for Pond 0 is 1.45 ± 0.27 (n = 8). Thus, the percent solids results for Pond 0 indicate that the pond sampler can reproduce samples with a relative standard deviation of ±19%, and that a large part of the variation in the results is due to the laboratory procedure for determining percent solids.

The data for the alkaline waste, Pond 13, are shown in Table 6. In this case, pH and percent solids measurements could be used to evaluate the reproducibility of the sampling procedure. Triplicate aliquots of each sample (two samples from each of five locations on the pond) were analyzed. The pH analyses were very reproducible for aliquots from the same sample (Table 7) with a relative standard deviation of less than ±4%. The standard deviation for percent solids analyses (Table 7) was similar to that observed for Pond 0; however, the results are more consistent because of the higher concentration of solids (relative standard deviation of less than ±8%). If the standard deviations of the mean for each location (Table 8) are compared to the standard deviations for the analyses (Table 7), it is evident that the variation due to analytical procedures is not significant when compared to variations between two samples taken at the same location. If the mean value for each field sample (Table 7) is considered as a single result, the average percent solids for Pond 13 is 4.47 ± 1.38 (n = 10) and the average pH is 5.41 ± 1.85 (n = 10). The data in Table 8 and the standard deviations for the average of all Pond 13 samples (relative standard deviations of 31% and 34% for percent solids and pH, respectively) indicate significant differences between locations on the pond. The differences in pH are especially

TABLE 6. EVALUATION OF POND SAMPLER: RESULTS OF pH AND PERCENT SOLIDS ANALYSES OF TRIPLICATE ALIQUOTS, FROM DUPLICATE SAMPLES OF WASTE TAKEN AT FIVE LOCATIONS ON POND 13, SITE A

Sample*	pH	Solids (%)	Sample	pH	Solids (%)
	6.96	4.06		5.22	5.07
1A	7.03	4.02	3B	5.20	4.82
	6.99	4.31		5.76	5.03
1B	7.55	5.80		6.95	3.50
	7.66	5.16	4A	7.05	3.67
	7.57	5.98		7.04	3.20
2A	2.43	3.13		6.70	3.48
	2.43	3.35	4B	6.75	3.99
	2.43	3.26		6.70	3.79
2B	2.33	5.66		5.33	6.13
	2.33	5.81	5A	5.03	5.60
	2.34	5.77		5.40	5.76
3A	4.89	5.91		4.70	1.93
	4.90	6.02	5B	4.74	2.08
	4.91	6.05		4.67	1.75

* Number - location on pond; A & B = 1st and 2nd sample at that location.

significant since they indicate extreme heterogeneity within the pond and also show that there is little mixing of the aqueous phase of the waste. Data for percent solids (Table 8) also indicate that for this measurement there were significant differences between samples taken at the same location. This might be expected with a liquid sample that has a significant solids concentration since the agitation created in taking the first sample could change the solids concentration observed in the second sample with little effect on the pH of the aqueous phase. Analysis of variance is being performed on this data and will be presented in the final report.

The results for the samples collected at site A indicate that even with a very heterogeneous waste the pond sampler has a reproducibility of better than

TABLE 7. EVALUATION OF POND SAMPLER: MEANS AND STANDARD DEVIATIONS OF TRIPLICATE ANALYSES FOR pH AND PERCENT SOLIDS IN WASTE SAMPLES TAKEN AT FIVE LOCATIONS ON POND 13, SITE A

	pH				Percent Solids			
	First sample		Second sample		First Sample		Second Sample	
Location	$\bar{x}$	s(n = 3)	$\bar{x}$	s(n = 3)	$\bar{x}$	s(n = 3)	$\bar{x}$	s(n = 3)
1	6.99	0.04	7.59	0.06	4.13	0.16	5.65	0.43
2	2.43	0.00	2.33	0.01	3.25	0.11	5.75	0.08
3	4.90	0.01	5.23	0.03	5.99	0.07	4.97	0.13
4	7.01	0.06	6.72	0.03	3.46	0.24	3.75	0.26
5	5.25	0.20	4.70	0.04	5.83	0.27	1.92	0.17
Average	5.32	0.06	5.31	0.03	4.53	0.17	4.41	0.21

TABLE 8. POND SAMPLER: MEANS AND STANDARD DEVIATIONS OF DATA THAT REFLECT DIFFERENCES BETWEEN TWO WASTE SAMPLES TAKEN AT EACH OF FIVE LOCATIONS ON POND 13, SITE A

	pH		Percent Solids	
Location	$\bar{x}$	s(n = 2)	$\bar{x}$	s(n = 2)
1	7.29	0.42	4.89	1.07
2	2.38	0.07	4.50	1.77
3	5.07	0.23	5.48	0.72
4	6.87	0.21	3.61	0.21
5	4.98	0.39	3.88	2.76
Average	5.32	0.26	4.47	1.31

±35%. The data generally indicate that the reproducibility of the laboratory procedures for obtaining and analyzing aliquots from field samples is better than ±8%. However, for samples with low solids (i.e. < 1%) the reproducibility of the laboratory procedure was not as good. The standard deviation does not change; however, the relative standard deviation (standard deviation ÷ sample mean x 100%) changes considerably because of the lower value for percent solids. As expected, the pH was very reproducible (better than ±2%) for the laboratory analytical procedure. Additionally, the data for percent solids indicate that there are differences between two consecutive samples taken at the same location on each pond. These differences, especially significant for Pond 13, indicate that for properties related to the solid/liquid phase composition, the composition of the second sample can be affected by the collection of the first sample at the same location. The largest overall source of variability appears to be between locations on the ponds. Surprisingly, the pH and percent solids data for Pond 13 showed similar differences between locations on the pond, even though they had different variabilities between samples taken at the same location. These results emphasize the fact that waste from sources such as disposal ponds may be very heterogeneous; and several samples from different locations on the pond are required for proper identification of hazardous waste.

If the two samples collected at each location are treated as independent samples, two duplicate sets of data can be identified for each pond (i.e. set of first samples vs. set of second samples). The average value for each set of data then provides a mathematical composite of the samples for that set. Comparison of the average (mathematical composite, Table 9) for each set of samples demonstrates a high degree of overall reproducibility for the pond sampler. These results indicate that a composite of five samples from different locations on a pond should provide a more reproducible indication of the pond's composition. Additional data obtained with composite samples is required to confirm this observation.

Future Efforts. Forty samples (20 samples/pit) have been collected with the pond sampler from two waste pits at site F. Five wastes (Table 2) were sampled from drums with the COLIWASA (total of 84 samples). These samples are being analyzed for pH, percent solids, total solids, and other chemical parameters (as time and sample volume permit) and the results will be included in the final report. A more detailed statistical analysis and discussion of the results of the sampler evaluations will be presented in the final report.

Extraction Procedure Evaluation

Progress

The extraction procedure (EP) is being evaluated to determine its reproducibility when used for the identification of hazardous waste. The EP extracts are first screened for arsenic, lead, cadmium, barium and chromium by inductively coupled plasma emission spectroscopy (ICP). The screening analyses are for qualitative identification and are restricted to those toxic elements (listed in the regulation) that can be analyzed by the ICP system at the EMSL-LV. The extracts are then analyzed for each element of interest by atomic absorption (AA) spectroscopy in accordance with the proposed regulations.

TABLE 9. REPRODUCIBILITY OF POND SAMPLER: MATHEMATICAL COMPOSITE OF FIRST AND SECOND SAMPLES FROM EACH LOCATION

Data	Pond 1 Sample 1 Composite	Pond 1 Sample 2 Composite	Pond 2 Sample 1 Composite	Pond 2 Sample 2 Composite
Mean pH	0.35	0.34	5.32	5.31
of mean	0.007		0.007	
RSD of mean	2.02		0.13	
Mean % solids	1.42	1.48	4.53	4.41
of mean	0.04		0.08	
RSD of mean	2.76		1.90	
Average RSD = 1.7				

Table 10 gives the ICP data collected in the initial phase of this study. These data indicate very high concentrations of the toxic elements in several of the extracts from samples from Site A. Samples from Pond O, Site A had to be diluted since the concentrations of As, Cr, and Pb exceeded the linear range of the analytical method. The extracts from samples from Pond IC, Site A; the pesticide waste from Site C; and the filter cake from Site G had low or insignificant concentrations of the metals that could be identified by the screening analysis.

Table 11 gives the AA data obtained in the initial phase of this study. The results confirm the ICP findings and provide quantitative values for the concentrations of barium, chromium and lead in the EP extracts. These three elements were selected for AA analysis in the initial phase because of their relatively high concentrations observed in the ICP screening analyses.

The samples from Pond O and Pond P (Site A) also contained relatively high concentrations of barium, chromium and/or lead. Triplicate aliquots from each of two samples from each pond were analyzed by the EP for two reasons; (1) to obtain better data on the reproducibility of the EP, and (2) to point out differences between two pond wastes that, according to the site operator, came from the same source. The standard deviations presented in Table 11 reflect the reproducibility of the analytical procedures performed on extracts from Ponds O and P.

TABLE 10. ICP SCREENING ANALYSIS OF EP EXTRACTS: APPROXIMATE ELEMENTAL COMPOSITION OF EXTRACTS FROM SELECTED WASTE SAMPLES

Sample (No. of Extracts Analyzed)	Approximate Concentration* (mg/l)				
	As	Ba	Cd	Cr	Pb
Site A, Pond 13, Location 1 (1)	1.3	0.2	0.5	1.8	0.5
Site A, Pond O, Location 2 (15)	168	10.8	4.2	1400	168
Site A, Pond P, Location 2 (7)	0.6	24.2	<0.2	124	1.2
Site A, Pond 10, Sulfonation Tars (2)	<0.4	1.08	<0.02	<0.02	<0.25
Site B, Paint Sludge, Sampled 4-19-79 (3)	0.8	1.13	0.06	7.1	1.2
(3)**	<0.4	1.57	0.05	0.09	<0.25
Site B, Paint Sludge, Sampled 6-13-79 (1)	0.6	18	0.02	4.1	0.25
Site C, Pesticide Waste (2)	<0.4	1.26	<0.02	<0.02	<0.25
Site D, Chromate Oxidation Paste	0.8	0.6	0.6	4.5	0.4
Site D, API Oil-Water Separator (3)	<0.4	<1.002	<0.02	3.6	<0.25
Site E, Electric Furnace Baghouse Dust (1)	1.6	0.8	<0.5	3.5	0.5
Site E, Blast Furnace Scrubber Filter Cake (1)	0.6	1.3	<0.02	0.4	7
Site E, Lime Sludge from Ammonia Still (1)	1.6	<1.002	<0.02	2.3	0.4
Site E, Mill Scale from Water Treatment Plant (1)	<0.4	<1.002	<0.02	3.1	<0.25
Site G, Filter Cake, Cl/Hg Process Stream (1)	<0.4	<1.002	<0.02	<0.02	<0.25
Site I, Chlorine Process Sludge (1)	1.8	1.07	--	0.3	0.9

* Chemical, physical and spectral interferences were not minimized. Results are corrected for dilution. Data for Ponds O and P, Site A represent averages from analyses of extracts from replicate samples; in some cases, extracts had to be diluted to bring values within the linear range of the instrument.

** By ASTM procedure with distilled water.

Data presented in Table 12 indicate significant differences in the elemental composition of the two wastes. However, since the variation of elemental composition within each pond is not known, additional EP data from the other samples from Ponds O and P are required to confirm this conclusion. The data in Tables 12 through 14 also give an indication of the reproducibility of the EP. For the worst case, barium analysis, the EP yielded a relative standard deviation of less than ±17%. The initial evaluation indicates that most of this variability is due to the analytical method (discussed in the section on analytical methods). This appears to be the case, since the results for lead and chromium yielded a relative standard deviation of less than ±5%.

TABLE 11. EVALUATION OF EXTRACTION PROCEDURE (EP): MEANS AND STANDARD DEVIATIONS FOR AA ANALYSES* OF EP EXTRACTS FOR BARIUM, CHROMIUM AND LEAD

	Barium (mg/l)		Chromium (mg/l)		Lead (mg/l)	
Waste Extracted	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Sulfonation Tars (Site A, Pond 10)	<0.9	--	<0.02	--	0.3	0.1
	<0.9	--	<0.02	--	0.3	0.1
Paint Sludge, Site B (Collected 4/19/79)	9.8	1.5	4.1	0.1	0.1	0.1
Paint Sludge, Site B (Collected 6/13/79)	5.15	0.32	1.02	0.13	0.08	0.1
	21.1	2.7	1.90	0.17	<0.08	--
Pesticide Waste, Site C	0.9	0.1	<0.02	--	<0.08	--
API Oil Separator Inlet, Site D	<0.9	--	9.1	0.1	0.1	0.1
	<0.9	--	1.2	0	0.1	0.1
	<0.9	--	1.0	0	0.1	0.2
Chromate Oxidation Paste, Site D	<0.9	--	7.9	0.2	<0.8	--
	<0.9	--	1.4	0.1	<0.8	--

(continued)

* Flame Atomic Absorption analyses performed in triplicate.

TABLE 11. (Continued)

Waste Extracted	Barium (mg/l) $\bar{x}$	Barium (mg/l) s	Chromium (mg/l) $\bar{x}$	Chromium (mg/l) s	Lead (mg/l) $\bar{x}$	Lead (mg/l) s
Electric Furnace Baghouse Dust, Site E	0.8	0.[illegible]	<0.32	--	0.13	0.04
	1.04	0.[illegible]	<0.32	--	0.13	0.03
	0.85	0.[illegible]	<0.32	--	0.13	0.04
Blast Furnace Scrubber Filter Cake, Site E	1.06	0.[illegible]	<0.32	--	15.3	0.7
	0.64	0.[illegible]	<0.32	--	14.4	0.7
	0.90	0.[illegible]	<0.32	--	11.6	0.7
Mill Scale, Water Treatment Plant, Site E	0.20	0.[illegible]	<0.32	--	<0.08	--
	0.19	0.[illegible]	<0.32	--	<0.08	--
	0.52	0.[illegible]	<0.32	--	<0.08	--
(1)	0.28	0.[illegible]	<0.32	--	<0.08	--
(1)	0.24	0.[illegible]	<0.32	--	<0.08	--
(1)	0.22	0.[illegible]	<0.32	--	<0.08	--
Lime Sludge, Ammonia Still, Site E (2)	2.7	1.6	<0.02	--	0.3	0.1
Filter Cake, Chlorine/Hg Process Stream, Site G	0.25	0.[illegible]	<0.32	--	0.10	0.06
	0.14	0.[illegible]	<0.32	--	<0.08	--
	0.15	0.[illegible]	<0.32	--	<0.08	--
(2)	0.9	--	<0.02	--	<0.08	--
Chlorine Process Sludge, Site I	0.48	0.[illegible]	<0.32	--	0.45	0.04
	0.40	0.[illegible]	<0.32	--	0.45	0.04
	0.98	0.[illegible]	<0.32	--	0.48	0.04
(2)	3.5	1.[illegible]	0.1	0	0.4	0.1

(1) Results obtained with wrist-arm shaker.

(2) Preliminary and test data.

TABLE 12. EVALUATION OF EXTRACTION PROCEDURE (EP): MEANS AND STANDARD DEVIATIONS FOR AA ANALYSES* OF EP EXTRACTS FROM WASTE IN PONDS O AND P, SITE A

	Barium (mg/l)		Chromium (mg/l)		Lead (mg/l)	
Sample Extracted	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
	1.85	0.02	1050	12	45.1	0.6
Pond O, 2A	1.55	0.14	1050	6	46.1	0.7
	1.57	0.34	1020	12	45.9	1.2
	1.30	0.28	950	12	43.0	0.8
Pond O, 2B	1.33	0.29	960	15	45.7	1.2
	1.39	0.09	920	25	41.8	0.9
	31.0	1.4	78.3	0.5	<0.8	--
Pond P, 2A	24.5	1.7	74.9	0.6	<0.8	--
	34.2	10.6	79.5	1.0	<0.8	--
	23.7	3.8	84.6	1.2	<0.8	--
Pond P, 2B	28.5	7.6	82.5	1.5	<0.8	--
	31.1	3.9	80.5	1.3	<0.8	--

* Flame Atomic Absorption analyses performed in triplicate on each of three aliquots of sample extracts. For s, n = 3.

TABLE 13. AVERAGE RELATIVE STANDARD DEVIATIONS (RSD'S) FOR VARIOUS LEVELS OF SAMPLING AND ANALYSIS

Sampling	RSD (%) pH			RSD (%) Percent Solids		
	Pond 0	Pond 13	Avg.	Pond 0	Pond 13	Avg.
Differences between aliquots of the same sample	10.1	0.9	5.5	17.6	4.7	11.2
Differences between duplicate samples taken at each location	26.5	4.8	15.4	13.6	30.3	22.0
Differences between locations on pond	21.5	36.5	29.0	19.9	16.9	18.4

Analysis (Sample source: Ponds 0 and P, Site A)	RSD (%) Barium	Chromium	Lead
Differences between replicate determinations on a given EP extract	14.9	1.3	2.0
Differences between replicate extractions on a given sample of waste	11.0	1.8	3.0

Stability of the Extract

A problem has been experienced with the stability of the EP extract. Some of the extracts, expecially those with high concentrations of other materials (such as inorganic salts and organics as observed by color and density of the extract), formed precipitates over a period of several days, even though they were preserved with acid (pH <2). This problem was observed early in the study and was addressed by adding a step to the extraction procedure. In this step the EP extract is split into two samples as it is prepared. One sample is stored in a refrigerator at 4°C until it can be analyzed for organics; the other sample is acidified to pH < 2 with nitric acid to preserve the sample for elemental analysis. Even with this step, some of the more concentrated samples produced a precipitate with a few days after preservation. This problem will be investigated in more detail in future studies.

Extractors

Data is also being collected to compare a wrist-arm type shaker to the extractor described in the proposed regulation. Preliminary data for barium in the mill-scale sample from Site E (Table 11) indicate good agreement between the two extraction devices, although the results obtained with the wrist-arm shaker appear to be less variable than those obtained with the proposed extractor. More data is required for a definitive statistical comparison of the two extractors.

Background Interferences

Blank samples (distilled water) identified in Table 15 were used during routine analyses as controls to check for contamination resulting from previous samples or from metallic components in the extraction or filtration systems. Seven extractors (coded 1-7) and three filter systems (coded 1-3) were used in the study; the results are shown in Table 15. In general, the data indicate that barium, chromium, and lead are not leached from the stainless steel components by distilled water. Blanks for extractors 1 and 5 indicated higher than anticipated contamination with Cr and/or Pb. While stainless steel components could contribute to Cr concentrations, it is unlikely that they would contribute Pb. Therefore, it is highly likely that the levels of Cr and Pb detected represent contamination from previous use of the extractors involved.

TABLE 14. EVALUATION OF EXTRACTION PROCEDURE (EP): AVERAGE MEANS AND STANDARD DEVIATIONS FOR AA ANALYSES* OF EP EXTRACTS OF WASTES FROM PONDS O AND P, SITE A

		Barium (mg/l)			Chromium (mg/l)			Lead (mg/l)		
Sample	Extracted	$\bar{x}$	s	RSD (%)	$\bar{x}$	s	RSD (%)	$\bar{x}$	s	RSD (%)
Pond O	2A	1.65	0.17	10.3	1040	17	1.6	45.7	0.5	1.1
	2B	1.34	0.05	3.7	943	21	2.2	43.5	2.0	4.6
Pond P	2A	29.9	4.9	16.4	77.6	2.4	3.1	--	--	--
	2B	27.8	3.7	13.3	82.5	2.0	2.4	--	--	--

* Flame Atomic Absorption analyses performed in triplicate on each of three aliquots of sample extracts.

(1) n = 3

(2) RSD = Relative Standard Deviation

TABLE 15. EVALUATION OF BACKGROUND CONCENTRATIONS OF ELEMENTS FROM EP EQUIPMENT: MEANS AND STANDARD DEVIATIONS OF TRIPLICATE AA ANALYSES OF DEIONIZED WATER BLANK SAMPLES FROM EXTRACTION AND FILTRATION APPARATUS

EP Equipment Tested	Ba (mg/l)		Cr (mg/l)		Pb (mg/l)	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Extractor 1*	<0.9	--	0.1	0	<0.08	--
" 2	<0.9	--	<0.02	--	<0.08	--
" 3	<0.9	--	<0.02	--	<0.08	--
" 4	<0.9	--	<0.02	--	<0.08	--
" 5	<0.9	--	0.1	0	0.1	--
" 6	0.12	0.02	<0.32	--	<0.08	--
" 7	0.10	0.03	<0.32	--	<0.08	--
Filtration apparatus 1	<0.9	--	<0.02	--	<0.08	--
" " 2	<0.9	--	<0.02	--	<0.08	--
" " 2	<0.06	--	<0.32	--	<0.08	--
" " 2	<0.06	--	<0.32	--	<0.08	--
" " 2	0.11	0.03	<0.32	--	<0.08	--
" " 2	0.09	0.01	<0.32	--	<0.08	--
" " 2	<0.06	--	<0.32	--	<0.08	--
" " 2	<0.06	--	<0.32	--	<0.08	--
" " 3	0.11	0.02	<0.32	--	<0.08	--
" " 3	0.16	0.03	<0.32	--	<0.08	--
" " 3	0.10	0.02	<0.32	--	<0.08	--
" " 3	0.12	0.03	<0.32	--	<0.08	--
Deionized H_2O**	<0.09	--	<0.02	--	<0.08	--

* Number assigned to, and maintained for specific pieces of apparatus.
** AA analysis of deionized water source from which blanks were drawn.

The regular analysis of blank samples is recommended to provide quality control and to identify problems with equipment contamination. Additional data with acidic blank samples (0.13 N acetic acid) that simulate the EP extract are being collected; the results will be presented in the final report.

Future Efforts

The extraction procedure will be evaluated with as many of the waste samples collected as possible. The EP will be used to characterize the samples from Site A to obtain additional information on the reproducibility of the total procedure for identification of hazardous waste (sampling through analysis).

Additional data will be collected to compare the different extractors that may be used for the extraction procedure. These include the extractor described in the proposed regulations, a wrist arm shaker available in our laboratory and a tumbling-action extractor developed especially for use with the EP by the National Bureau of Standards.

Analytical Procedures Evaluation

Progress

The proposed regulations require that atomic absorption methods be used for analysis of the EP extract for arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver. As described in the approach, these methods are being evaluated to determine their accuracy and reproducibility for analysis of the EP extract. Only limited data has been collected thus far.

The results from the analysis of the EP extracts for barium, chromium, lead and mercury are shown in Tables 11, 12, and 16 through 19. Problems were encountered in the analyses for barium. The data in Tables 11 and 12 show relatively high standard deviations for the analytical results for barium. This was probably due to a fluctuation in the AA detector response that was observed during the analyses. The cause of the fluctuation in detector response was not positively identified; however, several sources could account for this and the high standard deviations for the barium analyses:

1. The barium analysis requires a high temperature nitrous oxide flame. When analyzed, the extracts caused beads to form on the burner head. These beads cause fluctuation of the flame and can result in detector signal fluctuations. This problem was not observed with the standard solutions and appeared to be due to the extract matrix.

2. The barium lamp used as the source for these analyses may not have been functioning properly. However, it was a new lamp and provided stable signals with the barium standards.

3. Low spike recoveries and excessive variability were observed for the analyses (Table 16). When the method of standard additions was used

TABLE 16. QUALITY CONTROL DATA: COMPARISON OF BARIUM SPIKE RECOVERY FROM SELECTED SAMPLES (MATRICES)

Sample	Sample Conc. (mg/l)	Spike (mg/l)	Spiked Conc. (mg/l)	Spike Recovery (%)	RSD* (Analysis)
Site A, Pond P	3.10	2.00	4.96	93	11
Site B, Paint Sludge	1.96	2.00	3.98	101	33
Site D, Chromate Oxidation Paste	0.44	2.00	1.94	76	18
Site D, API Oil Separator	0.33	2.00	2.11	89	33
Site G, Filter Cake	0.15	2.00	1.84	84	7
Site I, Chlorine Process Sludge	0.39	2.00	2.28	94	23
Blank, Filtration Apparatus	0.10	2.00	2.10	100	1

* Relative Standard Deviation

TABLE 17. QUALITY CONTROL DATA: COMPARISON OF CHROMIUM SPIKE RECOVERY FROM SELECTED SAMPLES (MATRICES)

Sample	Sample Conc. (mg/l)	Spike (mg/l)	Spiked Conc. (mg/l)	Spike Recovery (%)	RSD* (Analysis)
Site A, Pond O	7.83	2.00	9.64	90	10
Site A, Pond O	10.5	2.20	12.6	95	8
Site B, Paint Sludge	1.02	2.00	2.15	108	6
Site D, Chromate Oxidation Paste	0.80	2.00	2.91	106	3
Site D, API Oils Separator	9.12	2.00	11.39	113	9
Site E, Blast Furnace Filter Cake	0	2.00	1.85	93	8
Site E, Mill Scale	0	2.00	2.03	102	8

* Relative Standard Deviation

TABLE 18. QUALITY CONTROL DATA: COMPARISON OF LEAD SPIKE RECOVERY FROM SELECTED SAMPLES (MATRICES)

Sample	Sample Conc. (mg/l)	Spike (mg/l)	Spiked Conc. (mg/l)	Spike Recovery (%)	RSD* (Analysis)
Site A, Pond O	4.5	2.00	6.69	110	6
Site A, Pond P	0.83	2.00	2.94	106	3
Site B, Paint Sludge	0.12	1.00	1.10	98	2
Site B, Paint Sludge	0	2.00	2.33	117	3
Site D, Chromate Oxidation Paste	0	1.00	1.14	114	2
Site D, API Oils Separator	0.14	1.00	1.28	114	5
Site E, Mill Scale	0	2.00	2.04	102	3

* Relative Standard Deviation

for barium analysis, higher results were obtained for those samples that had low spike recoveries. This indicates that the sample matrix has an interference that suppresses the barium signal, i.e. causes a low result. The method of standard additions corrects this problem; however, the precision of the data is reduced, i.e., the standard deviation for the analyses increases.

No problems were encountered in the analyses of EP extracts for chromium and lead (Tables 11, 12, 17 and 18). Although limited data is available, the standard deviations and percent recoveries are those that would be expected for analyses of water and wastewater. The high relative standard deviations noted for lead analyses that yield values approaching the lower detection limit is not unexpected.

Only two extracts have been analyzed for mercury (Table 19). Although these samples were expected to contain high mercury concentrations, the EP extracts had less than 4 µg/l. Aliquots of the waste samples were digested (aqua regia) and the digested samples were analyzed for mercury. The results (Table 19) show that the waste samples contained high concentrations of

TABLE 19. EVALUATION OF EXTRACTION PROCEDURE (EP): COMPARISON OF MERCURY CONCENTRATIONS (COLD VAPOR AA) IN WASTE SAMPLE DIGESTS WITH THOSE ESTIMATED FROM EP EXTRACT CONCENTRATIONS

	EP Extract (µg/l)		Reconstructed* Sample (µg/g)		Digested** Sample (µg/g)	
Waste Sample	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Filter Cake, Site G	<0.2	--	<0.0004	--	1970	110
Chlorine Process Sludge, Site I	3.7	0.2	0.074	0.004	840	130

* Calculated from extract concentration and dry weight of solids in the waste sample extracted.

mercury (approximately 1 mg Hg/gm waste); however, the proposed procedure identified only a very small fraction of the mercury present. The mercury may be in the form of organo-mercury compounds or may be irreversibly bound to the solids in the matrix. If so, the results simply suggest that the mercury would not leach out from the waste under acidic (pH = 5.0) conditions. However, if the sample does contain high concentrations of elemental or ionic mercury, the results may indicate that the extraction procedure or analytical method is inadequate for identifying mercury hazards. More work is required to identify the form of mercury present in these samples and to clarify the questions concerning the use of the extraction procedure for identification of leachable mercury in waste samples.

CONCLUSIONS AND RECOMMENDATIONS

It must be emphasized that the discussion, conclusions, and recommendations presented in this report are based on only the first four months of study. The additional data being collected should provide confident conclusions concerning the sampling procedures (Pond Sampler and the COLIWASA), the EP, and the analytical methods. However, several tentative conclusions can be made from these limited data.

(1) Future studies should provide better coordination between the sampling team and the industry being sampled. If a contractor is collecting the samples, many of the industrial operators require a confidentiality agreement from the contractor. Corporate approval of this agreement can take up to four weeks to complete. Future efforts should also attempt to collect more information about the process stream(s) producing the waste. This will facilitate characterization of the waste; will allow more specific conclusions about the hazard of the waste stream itself; and may aid in identification of modifications to the industrial process to reduce or eliminate the hazard.

(2) The procedures for identification of hazardous waste should require composite as well as individual samples from the waste source. The number of samples in the composite would be proportional to the size of the source and/or *a priori* knowledge of the waste homogeneity. For disposal pits or ponds, the samples should be taken from evenly spaced locations (if accessible) around the pit or pond. Further studies are recommended.

(3) The limited data collected for the pond sampler were obtained from a heterogeneous waste and indicate that even under such "worst-case" conditions the sampler yielded a reproducibility of ±4% or better. Indeed, analysis of "mathematically composited" data suggests that use of composite samples can yield a reproducibility as good as ±4 percent. Data from liquid/solid composition of consecutive samples from the same location suggest that much of the variability between these samples can be avoided by strict adherence to the protocols for use of the pond sampler, i.e. consecutive samples be sufficiently separated by time and/or space that removal of the first sample does not influence the composition of the second.

(4) The extraction procedure in the proposed regulations yielded data with a relative standard deviation of less than ±15% for a heterogeneous waste sample (i.e., under worst-case conditions).

(5) There is a problem with the stability of the EP extract even with acidification to pH<1 as a preservation step. Stability appears to be a problem only with highly concentrated extracts; however, this problem should be investigated in more detail.

(6) Very limited data indicate that a wrist-arm shaker and the extractor described in the proposed regulations produce equivalent results. Additional data is required for a definitive comparison of the two extractors.

(7) The analytical methods for chromium and lead (at levels >0.3 mg/l) were found to be highly reproducible (RSD= 1.3% and 2.0%, respectively).

(8) The high relative standard deviations for barium analyses (RSD = 14.9%) suggest problems with the analytical method for barium. This potential problem should be investigated in more detail.

(9) The extraction procedure and/or the analytical method for mercury may not identify the presence of mercury in waste. Additional work is required to determine the cause of the low mercury results found with the two waste samples studied.

APPENDIX 1.

USE OF THE POND SAMPLER AND COLIWASA

POND SAMPLER

The pond sampler is simply a 1000 ml glass beaker affixed with a clamp to the end of an 8-15 ft adjustable aluminum handle (Figure A-1). It is used to collect liquids and semisolids from ponds, pits, and lagoons. Two persons are required for sampling; both personnel must be wearing all the proper personal safety equipment. Samples can be taken at or below the surface. The stepwise procedure for use of the pond sampler is presented below.

- The operator must make sure the sampler is clean and put together properly.
- Sample at the desired depth and distance from the edge. To collect a sample, the beaker is lowered into the pond in an inverted position. At the required depth, turn the handle to upright the beaker. Withdraw the sampler.
- Pour the sample into the sample container slowly.
- Clean the sampler after each sample. When taking multiple samples from the same pond, take care to move far enough from the previous grab sample location to get an undisturbed sample.
- Close the container, record all information in the logbook and on appropriate forms after each sample, and attach the proper labels and seals to the sample container.
- Clean sampler thoroughly and pack away.

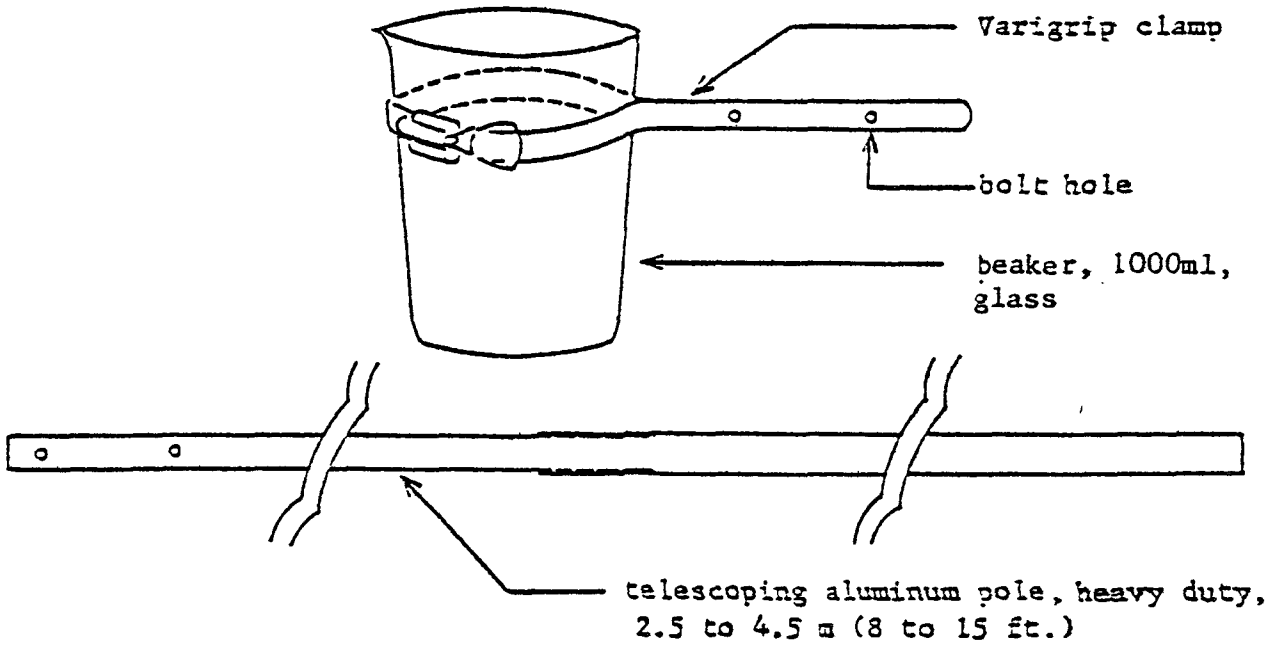

Figure A-1. Pond Sampler

Modified from draft report by de Vera et al, California Department of Health Services, for the Municipal Environmental Research Laboratory, Cincinnati, Ohio. (Grant No. R804692010)

COLIWASA

The COLIWASA (COmposite LIquid WAste SAmpler) is a tube-type sampler, 5 feet long and between 1-3/8 and 1-5/8 inches in diameter (ID) (Figure A-2). It can be fabricated from various materials to sample almost any kind of liquid waste from drums, barrels, or vacuum trucks. A stepwise procedure for use of the COLIWASA is presented below.

- The operator must make sure the COLIWASA is clean and is functioning properly so the stopper fits tightly. Adjust the stopper rod length if necessary.

- Two persons are required for sampling; both personnel must be wearing all the proper personal safety equipment. Company personnel must have already opened the waste storage vessel.

- Open the T-handle and push it down so it lies on the locking block forming a T between the handle and sample tube.

- Lower the sampler carefully into the waste storage vessel, maintaining the sampler in a vertical attitude and making sure visually that the waste inside the tube is even with the waste outside the tube (this is not possible with an opaque PVC or a stainless steel COLIWASA). This is to maintain a representative sample.

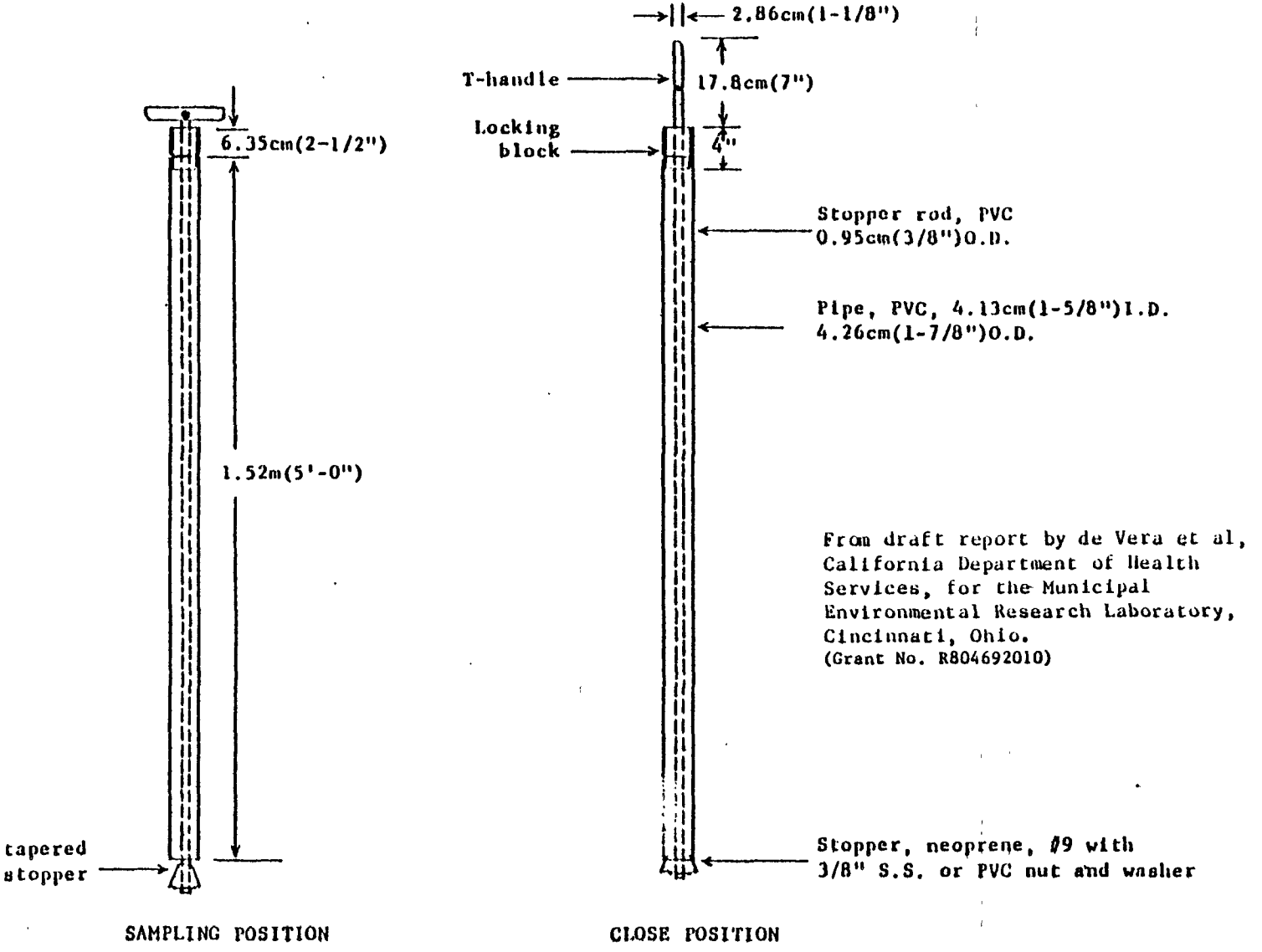

Figure A-2. COMPOSITE LIQUID WASTE SAMPLER (COLIWASA)

- When the sampler hits the bottom of the waste storage vessel, or until only 6 inches of the sampler is not immersed, pull upward on the handle until the handle can be turned so that one end rests firmly on the locking block.

- Withdraw the sampler with one hand and carefully wipe the outside of the tube with a reinforced fiber paper towel in the other hand; the second person may have to do this.

- Place the sampler directly above the sample container and slowly open the T-handle to release the sample through the bottom and into the sample container.

- Close the container, record all information in the logbook and on appropriate forms, and attach the proper labels and seals to the sample container.

- Immediately clean the sampler.

APPENDIX 2

PROTOCOL: EVALUATION OF THE EXTRACTION PROCEDURE FOR IDENTIFICATION OF HAZARDOUS WASTE

This is a summary of the protocol followed in the evaluation of the extraction procedure for identification of hazardous waste. A flow chart for this protocol is given in Figure 1 in the text.

Safety Note

Laboratory personnel are required to wear safety glasses, rubber or vinyl gloves, a lab coat or coveralls and safety shoes or rubber boots when handling hazardous waste samples. Respirators are to be worn when there is a possible hazard due to toxic gases or vapors from the sample. All contaminated dry waste materials (excess samples of dry waste, paper towels, disposable beakers, etc.) are to be sealed in plastic bags and placed in cardboard boxes for proper disposal. Used solvents and other contaminated liquid wastes are to be sealed in metal, glass, or plastic containers, as appropriate, and stored in a closed hood or sealed drum (in a restricted area) until disposal. All waste containers are to be labeled, "Hazardous Waste," and must include the type of waste, the date, and the worker's initials on the label. All hazardous wastes are to be disposed of by a commercial contractor at a disposal facility approved for such wastes.

Treatment Prior to Extraction

Triplicate aliquots (100 grams each) of each waste sample are separated into solid and liquid phases by filtration. If the sample is a liquid but cannot be filtered through a 0.45 micron filter, it is centrifuged to obtain phase separation. If neither filtration nor centrifugation will separate the material into solid and liquid phases, the sample is treated as a solid.

Weight Determinations

The filters to be used for the filtration step are not removed from their packaging until they are weighed to determine their tare. They are then stored on clean watch glasses or in petri dishes until they are used for filtration of the sample. The analytical balances used to weigh the filters are calibrated monthly with standard weights and are checked with a standard 100 mg weight just before each weighing. The date and results of the calibration are recorded in the balance log book. An annual calibration with standard weights traceable to the National Bureau of Standards is performed

when the balances are cleaned and serviced. The EPA property number of the balance is recorded in the laboratory notebook with the data obtained with that balance.

Filtration Method

All filtrations are performed in a fume hood to protect the operator from any toxic vapors that emanate from the sample. A Nuclepore filter holder (Nuclepore Corp., Pleasanton, CA 94566) equipped with a 1.5 liter reservoir is used for the filtration in the following steps:

1. Place a weighed glass fiber pre-filter (124 mm diameter, Millipore AP 25124, Nuclepore P040, or equivalent) and a weighed 0.45 micron filter membrane (Millipore type HAWP 142, Nuclepore type 112007, or equivalent) in the filter holder with the pre-filter on top (upstream).

2. Add the sample (known weight) to the reservoir. Seal the reservoir and pressurize it with argon to a maximum of 75 psi. Continue the filtration until less than 5 ml. of liquid is released during a 30 minute period. The sample may not require the maximum pressure for filtration; however, for some dense samples the reservoir must be held at 75 psi before the sample is identified as non-filterable.

3. After liquid flow stops, depressurize and open the top of the reservoir. Remove the filters and solid sample and place in a petri dish or other suitable container. Repeat steps 2 and 3 if the sample size exceeds the capacity of the reservoir.

4. Store the liquid fraction at 1-5°C for use in the extraction procedure.

5. Weigh the filtered solid sample (filters included) to determine the weight of the solid material collected (i.e. subtract tare weights of filters from total sample weight). Extract the filtered sample (solid material and filters) by the extraction procedure.

6. If the sample does not filter, use the centrifugation method to separate the solid and liquid phases.

Centrifugation Method

An International Centrifuge, size 2, model K (International Equipment Company, Boston, Mass.) is used for the centrifugation in the following steps:

1. Centrifuge the sample for 30 minutes at 2300 rpm under controlled temperature (20 - 40°C).

2. Measure the size of the liquid and solid layers to the nearest mm (0.40 inch) and calculate the liquid to solid ratio.

3. Repeat steps 1 and 2 until the liquid to solid ratios for two consecutive 30 minute centrifugations agree within 3%.

4. Decant or siphon off the liquid layers and extract the solid by the extraction procedure. Store the liquid fraction at 1-5°C for use in the extraction procedure.

Extraction Procedure (EP)

The solid material, obtained by the filtration or centrifugation method from liquid samples or as an aliquot from solid samples, must be able to pass through a 9.5 mm (3/8") standard sieve. It is anticipated that the particle size of the samples obtained for this study will meet this requirement. If the sample will not pass through a 9.5 mm sieve it must be ground to size or must be subjected to the structural integrity procedure (Federal Register, Vol. 43, No. 243, Dec. 18, 1978).

The extraction procedure is performed in the following steps:

1. Weigh the solid material obtained from the waste sample and place it in an extractor as identified in the proposed regulation. A suitable extractor will not only prevent stratification of the extraction solution but will also ensure that all sample surfaces are continuously brought into contact with well mixed extraction solution. With the exception of special studies, the extractor referenced in the proposed regulation will be used for this program.

2. Add to the extractor a weight of deionized water equal to 16 times the weight of solid material added to the extractor.

3. Agitate the sample at 40 rpm and adjust the pH of the solution to 5.0 ± 0.2 with 0.5N acetic acid. Maintain the pH at 5.0 ± 0.2 and continue agitation for 24 hours. Do not add more than 4 ml. of acid for each gram of solid. If the solution pH is less than 5, do not add any acid during the extraction. Maintain the temperature of the solution at 20-40°C during the extraction. Follow the procedure for manual pH adjustment in the proposed regulations.

4. Measure and record the pH at the end of the 24 hour extraction period.

5. At the end of the 24-hour extraction period separate the liquid and solid fractions of the extraction material by the filtration method described above. Adjust the volume of the resulting liquid phase with deionized water so that its volume is 20 times that occupied by a quantity of water at 4°C equal in weight to the initial quantity of solid material placed in the extractor.

6. Combine this solution with the original liquid phase obtained in the filtration or centrifugation step. Mix thoroughly and split the combined solution into two equal samples. Store one sample under refrigeration at 1-5°C for organic analysis. Preserve the second sample for elemental analysis by addition of Ultrex® nitric acid to reduce the sample pH to less than 2.

Analysis

The samples obtained by the extraction procedure are analyzed in accordance with the methods given in the proposed regulations. All samples should be analyzed as soon as possible after they are collected.