



Project Summary

Evaluation of the Procedures for Identification of Hazardous Wastes: Part 1. Sampling, Extraction, and Inorganic Analytical Procedures

L. R. Williams, E. P. Meier, T. A. Hinnners, E. A. Yfantis, W. F. Beckert, and
T. E. Gran

A study was performed to evaluate the sampling, extraction, and analytical procedures (inorganic) proposed in the RCRA regulations for identifying wastes as hazardous by the toxicity characteristic. Twenty-seven different wastes were sampled and analyzed in accordance with the RCRA regulations. The high degree of heterogeneity found in many wastes underscores the need for a carefully designed sampling protocol to reproducibly obtain representative samples from each waste source. A protocol was developed and tested for obtaining composite samples from waste ponds or lagoons. Samplers tested, the pond sampler and the COLIWASA (composite liquid waste sampler), were found to be acceptable for sampling hazardous waste, when used in a well-designed sampling protocol. Reliability and reproducibility of the EP (extraction procedure) were evaluated (RSD <15%). The blade-type rotary extractor (as cited in the proposed regulations), a tumbling-type extractor, and a wrist-arm-type shaker were compared and found to yield similar EP extracts. The supporting analytical methods (atomic absorption spectrometry) were found to be highly reproducible for Cr and Pb, and

somewhat less for Ba (RSDs <3.1%; 4.6%; and 16.4%, respectively). Independent analyses of the same waste extracts by two laboratories were highly reproducible, i.e., the variance from analyses was negligible. However, differences in the EP extracts produced by the two laboratories show the need for a detailed and concise protocol for conducting the EP. Problems with sample contamination from the blade-type extractor (chromium) and the filtration apparatus (barium) were identified.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The rapid technological advances over the past several decades have significantly improved the American economy and lifestyle. However, improper disposal of hazardous wastes generated by industry as a result of these advances has created a hazard to both human health and the environ-

ment. The identification of those wastes and wastestreams which require special management because of their present or potential hazard is a high priority of regional, state, and federal interests.

Background of the study. This study was conducted in support of the EPA's Office of Solid Waste (OSW). The results are to be used by OSW to better define the reliability and reproducibility of sampling, extraction, and analytical procedures in regulations proposed (FR Dec. 18, 1978) and published (FR May 19, 1980) under Section 3001 of the Resource Conservation and Recovery Act (RCRA) of 1976 (and its amendments).

The problem. Previous studies (in some cases with wastes of unknown history) have demonstrated the utility and validity of the proposed methods. However, the EPA felt that additional studies (with wastes from known industrial sources) were warranted to confirm that valid and defensible data to support the regulatory requirements can be provided using these methods.

Purposes of the study. The purposes of the study were to 1) evaluate the reproducibility of the sampling and extraction procedures and the accuracy and precision of the analytical procedures described in the proposed regulations; 2) compare candidate extractor types for use with the proposed extraction procedure; and 3) evaluate the application of the proposed extraction procedure (and associated analytical procedures) to municipal sewage sludge samples. In addition, special studies were performed to identify sources of specific problems (i.e., barium and chromium contamination of extracts from extraction and filtration apparatus; high variability in flame atomic absorption analyses for barium; low mercury levels in extracts of samples known to be high in mercury; and low analytical recoveries for certain metals in some extract media). Interim findings from these studies were submitted to OSW and are reflected in the methods published in SW-846, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods" (1980).

Procedure

Theoretical assumptions underlying the study. The extraction procedure (EP) is intended to identify the potential for migration—from waste to the environment—of toxic constituents in an improperly managed waste. For purposes of regulation, a waste may be

considered hazardous, by the toxicity characteristic, if levels of specific toxic chemicals, in EP extracts of that waste, meet or exceed the stated limits. To test the procedures associated with the EP, test materials (waste samples) should be selected that are representative of the most difficult waste types to sample, extract and analyze. In this way, conservative estimates of the precision and accuracy of the procedures can be developed.

Selection and sampling of wastes. Waste and sites to be sampled were selected with the active assistance of industrial and government facilities that generate or dispose of a variety of hazardous and non-hazardous wastes. Eleven sites were visited and 27 different wastes were collected, by a variety of sampling methods, from pits, ponds, drums, tank trucks, waste piles, dumpsters, and process stream taps. Samples were shipped to the Laboratory under chain-of-custody and in conformance with Department of Transportation regulations.

Procedures for evaluating samplers. The pond sampler and COLIWASA (composite liquid waste sampler), used in accordance with published protocols (deVera et al., EPA-600/2-80-018, 1980), were the only sampling methods evaluated. The initial experimental design for testing the pond sampler (a one-sided parametric test) called for collection of 39 samples per pond. Subsequently, the design was modified to a hierarchical (nested) analysis of variance (ANOVA) to define the major sources of sampling and analytical variability. Samples were collected with the pond sampler from five different waste sources at two sites. Uniformity of samples with respect to pH and percent solids (Non-filterable Residue Method 160.2, "Methods for Chemical Analysis of Water and Wastes", EPA 1979) was used to estimate the reproducibility of the sampling procedure. Wet weights of sample solids—routinely measured in the EP to determine whether a minimum percent solids level is exceeded—were not considered precise enough to use in determining sample uniformity. A sampling plan was developed for collecting composites of random samples from accessible areas and was tested on Ponds 0 and 12.

The COLIWASA was used to sample five different drummed wastes at three sites. Uniformity of the samples with respect to percent solids and to the oil/

water ratio (for biphasic wastes) was used to estimate sampling reproducibility.

Procedure for evaluating the EP. The EP was used in essential agreement with the proposed regulations. Waste samples from three different ponds were used in initial tests of the EP with blade-type extractors. The resulting extracts were then analyzed by atomic absorption spectroscopy methods to determine how uniform the extracts were with respect to selected metals.

A hierarchical testing design was used to compare the blade-type extractor, a tumbling-type extractor, and a laboratory wrist-arm shaker. The test yielded 108 separate EP extracts from each of three waste sample types. Each extract was analyzed for barium, chromium, and lead. The data were subjected to analysis of variance to determine the sampling, extraction, and analytical variability with each waste type.

Procedure for evaluating analytical methods. The atomic absorption spectroscopy (AAS) methods evaluated are standard methods (EPA 1979) for analysis of water, wastewater, or industrial effluents. However, they had not previously undergone extensive testing with solid wastes or their extracts.

Extracts of the various types of samples collected were first screened using ICP (inductively coupled plasma emission spectroscopy) methods for a quick and "semi-quantitative" look at the metals of interest contained in each. Next, selected extracts—with and without "spikes" of metals in known concentration—were analyzed by AAS methods. Recovery (an indicator of accuracy) and reproducibility (precision) were determined from the data for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. Recovery of known concentrations of metals from acetate buffer and from selected waste extracts was compared with that from "standards" in nitric acid using linear regression analysis.

When the standard deviations for analyses of percent solids and for mean percent solids content by locations (based on these analyses) were compared, imprecision of the analyses was found to account for a large portion of the location-to-location differences noted. It is difficult to obtain uniform weights among waste samples dried under similar conditions, and small weight differences contributed heavily to the variability among low-solids samples.

Analysis of variance of Pond 0 solids data revealed significant differences (at the 5% level) between successive samples at the same location, while differences between locations were not significant. Pond 13 percent solids data also showed significant differences between successive samples, but significant differences were detected between locations (by analyses of both pH and percent solids data). The location-to-location differences noted indicate the highly heterogeneous nature of Pond 13.

When the mean values for each field sample were treated as single results, the average percent solids for Pond 0 and 13 were 1.45 ± 0.27 (n=8) and 4.47 ± 1.38 (n=10), respectively. The average pH for Pond 13 was 5.31 ± 1.85 (n=10). Even with very heterogeneous wastes, the pond samples were reproducible (within $\pm 35\%$) by either pH or percent solids analyses. The largest overall source of variability appears to be between locations on the ponds.

If the two samples collected at each location on Ponds 0 and 13 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 values (pH and percent solids) for each set of data then provide mathematical composites of the samples for that set. Comparison of these average values demonstrates the high degree of overall reproducibility for the pond sampler. Average relative standard deviations (RSDs) were 1.1% and 2.3% respectively, by pH and percent solids.

Analyses (for percent solids) of 216 aliquots [9 aliquots from each 12 one-gallon composite samples, from each of 2 ponds (Ponds 0 and 12)] indicate that sample-to-sample variability remains the greatest source of error in waste analysis. The cumulative RSD for Pond 12 composite samples (20.3%) is lower than previously noted with discreet pond sample comparisons. However, Pond 0 was found to be more heterogeneous (RSD of composite samples = 53.3%) than when it had been sampled five months previously.

Reproducibility of triplicate samples collected with the COLIWASA from each of 15 drums of API separator waste (as measured by average percent total solids) was very good (RSD = 1.1%). In a more rigorous test of the COLIWASA's ability to handle complex waste mixtures, an oil/water biphasic waste was sam-

Table 1. Average Means, Standard Deviations, and RSDs for AAS Analyses* of EP Extracts of Wastes from Ponds 0 and P

Sample Extracted	Barium (mg/l)			Chromium (mg/l)			Lead (mg/l)		
	\bar{x}	s	RSD (%)	\bar{x}	s	RSD (%)	\bar{x}	s	RSD (%)
Pond 0 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 spectrophotometric analyses performed in triplicate on each of three aliquots of sample extracts.

RSD = Relative Standard Deviation

Table 2. Relative Standard Deviations (RSD) of Extractions and Analyses for Selected Metals

Analysis (Sample source: Ponds 0 and P)	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

pled. The high reproducibility of triplicate samples from each of three drums (average RSD = 12.2%) allowed detection of significant drum-to-drum differences in oil/water ratio.

Extraction procedure (EP). Data in Tables 1 and 2 indicate the level of extraction reproducibility observed with waste samples from Ponds 0 and P. The high reproducibility of replicate extractions, with chromium and lead concentrations as indicators, closely approaches the analytical precision for these metals. Problems with barium contamination from prefilters and flame disturbances in the AAS analysis for barium—both of which were subsequently identified and largely resolved—resulted in lower precision of estimates based on this element.

Intralaboratory reproducibility of the EP with seven sewage sludges was rather good (RSD = 33% for average combined extraction and analytical reproducibility) considering the heterogeneous nature of such samples. Independent extraction of sludge samples

and analysis of extract splits by the Municipal Environmental Research Laboratory, Cincinnati, yielded excellent agreement on extract analyses but revealed procedural differences in the conduct of the EP.

A study was performed which compared the blade-type extractor with a tumbling-action extractor and a wrist-arm shaker using Pond 0, Pond 12, and biosolids samples. The average concentrations and standard deviations for each of three metals analyzed from the resulting EP extracts are shown in Table 3. The Student-Newman-Keuls multiple comparison test did not demonstrate one extraction technique to be "better" than another. The relative percent of total variance contributed by sample (63%), aliquots (20%), extraction techniques (10%) and analyses (7%) was estimated.

The similar performance of the three extractors is perhaps best summarized by comparing the RSDs for each extractor (overall RSD including the variability components associated with sampling, aliquoting and analysis):

Extractor	Overall RDS (as percent)		
	Pond 0	Pond 12	Biosolids
Blade-type (rotary)	10.8	226.4	12.8
NBS tumbling-type	10.0	129.7	10.8
Wrist-arm shaker	12.3	143.9	10.5

Some of the EP extracts, especially those with high concentrations of inorganic and organic materials, formed precipitates over a period of several days. Even acidification to pH <2 was not sufficient to totally prevent precipitation in the most concentrated samples. Prompt analysis is recommended to minimize this problem.

Low-level chromium and barium contamination was detected in 0.1N acetic acid blanks run through the EP apparatus (filters and blade-type extractor) following extraction of a waste sample and routine cleaning. Chromium levels in the blanks generally paralleled those in the preceding sample. A more rigorous post-extraction cleanup procedure was adopted and distilled water blanks were replaced by acidic blanks for routine monitoring of the EP apparatus.

To determine if abrasion/dissolution of stainless steel components was contributing to the chromium contamination of EP extracts, a rigorous extraction of abrasive material (fine sand) with aggressive (dilute nitric acid) and less aggressive (dilute acetic acid) extractants was carried out in blade-type extractors (with polyethylene tumbling-type extractors as controls). Chromium levels up to 0.18 mg/l were found in unfiltered nitric acid extracts from the blade-type extractors. No detectable chromium was leached from the sand or the tumbling-type extractor. One of the two unfiltered acetic acid extracts showed detectable (>0.01 mg/l) chromium

levels. The data suggest that the use of stainless steel extractors for testing strongly acidic, abrasive wastes may result in contamination of the extracts and should be avoided.

To investigate the source(s) of barium found in filtered acidic blanks, Nuclepore® and Millipore® glass-fiber prefilter pads and Nuclepore® polycarbonate filters were leached for 1-2 hours in dilute acid solutions. Barium (up to 4 mg/l) leached from the prefilter pads, but not from the filters.

Analytical procedures. Precision of the AAS analyses for barium, chromium, and lead in EP extracts are shown in Tables 1 and 2 (for Pond 0 and P samples) and Table 4 (for 11 other waste samples). For Pond 0 and P samples, the highest RSDs were 16.4% for barium, 3.1% for chromium, and 4.6% for lead. With other waste samples the average RSDs ranged from 11-66% for barium, <1-11% for chromium, and 5-140% for lead (average RSD <14% for extracts with ≥ 0.2 mg/l lead). Precision of AAS analyses of sludge digests averaged 11.1% (RSD) for barium, chromium, lead, arsenic, cadmium, and selenium.

Precision of the AAS analyses to determine spike recovery of eight elements of interest (As, Ba, Cd, Cr, Pb, Hg, Ag, and Se, in a variety of sample matrices) was quite high, with the exception of barium (Table 5).

When recovery of elements added (spiked) to sample extracts approaches 100%, it is an indication (but no guarantee) of accuracy. Table 5 shows average

recoveries near 100 percent from extracts of many waste samples. Low recovery (52%) of lead in an undiluted EP extract was corrected to 100% recovery with calibration by the method of standard additions and also by simple dilution of the extract. These techniques provide the necessary detection/correction for most suppression. Evidence for instrumental response enhancement was found (e.g., chromium, 144%, and selenium, 160%, Table 5).

Standards prepared in 0.2 M acetate buffer and EP extracts compared well with corresponding standards in nitric acid. Values for As, Ba, Cd, Cr, Hg, and Se were within 8% of the regression slope with the buffer and 10% with EP extracts. Lead was 13% low in the acetate buffer and mercury was 15% low in waste extracts (when the highest Hg value was deleted).

Discussion

Sampling results emphasize the fact that waste from sources such as disposal ponds may be very heterogeneous and that a number of samples from different locations on the pond are required to properly represent a waste for identification as hazardous or non-hazardous. Existing information on waste sources to be sampled, or better still, preliminary sampling data should be factored into any sampling design to assure that representative samples are obtained on a waste-by-waste basis. "Mathematical composites" of sample data indicate that a composite of five samples from different locations on a pond should provide a more reproducible indication of the pond's composition than is possible with a single, discreet sample.

Sampling precision, as indicated by RSDs of percent solids data, is influenced

Table 3. Extractor Comparison—Mean and Standard Deviation of Concentrations of Metals Extracted with the Three Extractor Types

	Ba			Cr			Pb		
	W	N	R	W	N	R	W	N	R
Pond 0	$\bar{x}=6.21$ $s=1.25$	$\bar{x}=5.40$ $s=0.72$	$\bar{x}=3.72$ $s=0.84$	$\bar{x}=917$ $s=113$	$\bar{x}=948$ $s=94.6$	$\bar{x}=907$ $s=94.6$	$\bar{x}=36.70$ $s=3.96$	$\bar{x}=36.95$ $s=4.37$	$\bar{x}=36.50$ $s=4.56$
Pond 12	NO ANALYSES PERFORMED			$\bar{x}=0.66$ $s=0.95$	$\bar{x}=0.37$ $s=0.48$	$\bar{x}=0.53$ $s=1.20$	$\bar{x}=0.58$ $s=0.51$	$\bar{x}=0.48$ $s=0.34$	$\bar{x}=0.67$ $s=0.84$
Biosolids	$\bar{x}=1.56$ $s=0.48$	$\bar{x}=1.38$ $s=0.41$	$\bar{x}=1.22$ $s=0.50$	$\bar{x}=0.31$ $s=0.13$	$\bar{x}=0.23$ $s=0.06$	$\bar{x}=0.17$ $s=0.06$	$\bar{x}=0.38$ $s=0.04$	$\bar{x}=0.37$ $s=0.04$	$\bar{x}=0.39$ $s=0.05$

W = Wrist-Arm Shaker

N = NBS Tumbling-Type Extractor

R = Blade-Type Extractor

greatly by small differences in mean percent solids (the denominator in calculating the RSD), especially in samples with low solids. In general, RSDs based on percent solids are lower (better precision) with samples higher in solids (e.g., >5%). At the same time, for a given sample type, the lower the solids content, the less influence small changes are likely to have on the composition of the resulting extracts.

Specifications and design advantages for the DAT (drum and tank) sampler developed at this Laboratory can be found in the report from which this summary was written.

The blade-type extractor tended to yield lower extract concentrations of the metals measured than the other two types tested, especially for samples with low solids (Pond O). Of the three extractor types, the blade-type agitates the samples least and appears most dependent upon a minimum solids content in the sample for effective extraction.

Clogging of the nitrous oxide-acetylene burner, by extracts high in dissolved solids, was found to be a major reason for poor precision in the analyses of EP extracts for barium. Sample dilution or use of furnace AAS techniques should be used to avoid this problem.

Table 4. Atomic Absorption Analyses* of EP Extracts for Barium, Chromium, and Lead: Mean Values (mg/l) and Relative Standard Deviations

	Barium		Chromium		Lead	
	\bar{x}	RSD (%)	\bar{x}	RSD (%)	\bar{x}	RSD (%)
Sulfonation Tars	n.d.	—	n.d.	—	0.3(2)	33
Paint Sludge (collected 4-19-79)	9.8	15	4.1	2	0.1	100
(collected 6-13-79)	13.1(2)	10	1.5(2)	11	0.08	125
Pesticide Waste	0.9	11	n.d.	—	n.d.	—
API Oil Separator Inlet	n.d.	—	3.8(3)	<1	0.1(3)	140
Chromate Oxidation Paste	n.d.	—	4.7(2)	5	n.d.	—
Electric Furnace Baghouse Dust	0.9(3)	14	n.d.	—	0.13(3)	28
Blast Furnace Scrubber Filter Cake	0.87(3)	11	n.d.	—	13.8(3)	5
Mill Scale, Water Treatment Plant	0.3(6)	11	n.d.	—	n.d.	—
Filter Cake, Chlorine/ Hg Process Stream	0.18(3)	32	n.d.	—	0.1	60
Chlorine Process Sludge	0.62(3)	66	n.d.	—	0.46(3)	9

*Flame atomic absorption analyses performed in triplicate

n.d. Not detected

() Average means (and corresponding average RSDs) based upon number of extracts indicated in parentheses.

Table 5. Spike Recoveries of Selected Elements from Various Sample Matrices

Element	No. of Samples	Spike Recovery (%)		Analyses
		Average	Range	Average RSD (%)
Lead	18	107.1	64-120	2.8
Mercury	3	87.0	78-97	0.3
Silver	7	96.0	94-98	0.0
Arsenic	7	109.6	102-122	3.0
Cadmium	7	99.1	95-104	1.1
Selenium	7	105.1	38-160	4.9
Barium	19	95.3	33-120	10.1
Chromium	18	105.5	89-144	3.9

Low mercury responses in waste extracts appear to have resulted from instrumental suppression by some waste component since good agreement was observed between Hg standards prepared in acetate buffer and nitric acid. Calibration by the standard additions method should compensate for such suppression. Inadequate oxidation of EP extracts in the digestion step could explain low mercury recoveries and should be investigated.

"Memory effect", false high readings resulting from inadequate cleanout of the AAS nebulizer and burner system between solutions, was largely eliminated by appropriately scheduled rinses and prolonging the solution uptake prior to measurement.

Conclusions and Recommendations

The following conclusions and recommendations are based upon data presented and observations made during the study period:

- The method developed and standardized for sampling ponded wastes provided representative composite samples of the ponded wastes tested. It is recommended that background information, including preliminary sampling data, be obtained and factored into the sampling design on a waste-by-waste basis to assure that samples obtained are representative of the waste site sampled.

- The Composite Liquid Waste Sampler (COLIWASA) provided reproducible samples from drums of the liquid wastes tested. Present design of the COLIWASA prevents adequate sampling of the bottom-most layer in drums or tanks. The alternative sampler design proposed (DAT Sampler) should be evaluated with liquid wastes in drums, tanks, or vacuum trucks.
- In intralaboratory studies, the proposed Extraction Procedure was found to be reproducible ($RSD < \pm 15\%$ for the waste types sampled). However, interlaboratory studies indicate that adherence to clear, detailed, step-by-step protocols is needed to eliminate misinterpretation or substitution of non-equivalent procedural elements. The EP should be evaluated to determine its applicability to oily or solvent-containing waste samples.
- A problem with contamination of acidified extracts by barium leached from glass-fiber prefilters was identified. Until prefilters are identified which do not contribute barium to the filtrate, it is recommended that a 100-ml portion of 0.1N acetic acid precede each waste sample through the prefilter and be stored for possible future use in determining blank correction for the sample. It is anticipated that such blank correction would only be used in the event that the barium levels in the samples exceed the criteria level for hazardous waste identification by the toxicity characteristic.
- Intra- and interlaboratory studies indicate that atomic absorption spectroscopy is an accurate and highly reproducible method for analysis of most inorganic components of waste extracts.
- Some problems in the analyses of barium and mercury remain to be resolved. The method of additions is recommended to provide interference correction. Extracts very high in dissolved solids concentrations may cause build-ups of material which alter the flame characteristics of the atomic absorption spectrometer. Such samples should be diluted prior to analysis or analyzed by furnace procedures.
- The three extractor types compared (i.e., the blade-type, NBS tumbler-type, and the wrist-arm shaker) provide comparable waste extracts when used in the proposed EP.

- When possible, EP extracts should be analyzed immediately, as some waste extracts are not stable over a period of hours or days.
- Applicability of the EP toxicity criterion for mercury should be re-evaluated, as low EP recoveries may be misleading with respect to the toxicity hazard presented by wastes containing high levels of Hg in temporarily insoluble forms. Inadequate oxidation of mercury-containing EP extracts should be investigated to explain low mercury recoveries.

The EPA authors L. R. Williams, E. P. Meier, T. A. Hinnners, E. A. Yfantis, and W. F. Beckert are with the Environmental Monitoring Systems Laboratory, Las Vegas, NV; and T. E. Gran is with Northrop Services, Inc., Las Vegas, NV. L. R. Williams is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of the Procedures for Identification of Hazardous Wastes: Part 1. Sampling, Extraction, and Inorganic Analytical Procedures," (Order No. PB 81-203 804; Cost: \$9.50, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
P.O. Box 15027
Las Vegas, NV 89114*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335



Official Business
Penalty for Private Use \$300

PS 0000329
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604