



Project Summary

USEPA Extraction Method Development Study for Trace Metals in Leachate

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A study was performed to determine the applicability of currently approved analytical methods for conducting the extraction procedure (EP) toxicity test required by the Hazardous Waste and Consolidated Permit Program. The first phase of the study was designed to determine the necessity for performing digestion of the EP leachates prior to trace element analysis and also to determine the effect, if any, of preservation on total metal concentrations. Four matrices were used for this phase of the study (river sediment, fly ash, low-pH sludge, and oil/water waste) and analyses were performed for 17 elements by both atomic absorption spectrophotometry (AAS) and by Inductively Coupled Argon Plasma Emission Spectrometry (ICP). Digestion of the leachates generally reduced interferences and improved the accuracy of the analyses. For one high sulfur waste, however, digestion introduced a chemical interference. Acid preservation of the wastes did not significantly affect the results.

The second phase of the study was designed to determine the effect of pH and time on metal concentrations in the leachate from low-pH sludge. Determinations were made for 17 elements in the EP extracts after adjustment of initial pH to levels of 2, 4, 6 and 8. Extractions were performed 0, 2, 8 and 16 hours following pH adjustment. All wastes exhibited a strong dependence on the initial pH of the wastes—the leachate concentrations were lowered at higher initial pH values. The time between pH adjustment and initiation of the extraction procedure did not alter the results.

The third phase of the study was designed to determine the efficiency of the EP toxicity procedure in extracting metal spikes from three standardized reference materials (river sediment, fly ash, and EPA Municipal Digested Sludge). The results of this phase confirmed the strong pH dependence of leachate concentrations found in Phase 2 and demonstrated that under normal EP extraction conditions extraction efficiencies for most metals are low.

A study was also performed to determine if metal concentrations were affected by various matrices encountered using the EP procedures (acetic acid [0.6%], nitric acid [0.5%], or acetic acid [0.6%]/nitric acid [0.5%]). Of all the 17 elements studied, only selenium exhibited a matrix effect from the dilute acids. The slopes of the selenium calibration curves generated by both ICP and AAS were enhanced in the presence of acetic acid.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, 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

This investigation was conducted in three separate phases with each phase focusing on specific questions related to the applicability of various aspects of approved methods for conducting the EP toxicity tests and subsequent analyses. Phase 1 of the study was designed to determine the necessity of performing

leachate digestion after the EP toxicity test and to determine the effect of preservation on metal concentrations. Four materials were tested—river sediment, fly ash, a low-pH sludge, and oil/water waste. For the oil/water waste, a separate extraction and analysis was performed on the oil phase. For all extractions, analyses were performed in triplicate using atomic absorption spectrophotometry (AAS) and inductively coupled argon plasma emission spectroscopy (ICP).

The second phase was designed to determine the effect of pH and time on leachate metal concentrations from the low-pH sludge. The waste was extracted at 0, 2, 8 and 16 hours after pH adjustment, with the pH adjustments being made at levels of 2, 4, 6 and 8 with 1.0 M sodium hydroxide. Analyses were performed in triplicate using both AAS and ICP.

The third phase of the study was designed to determine recovery of metal spikes from three standardized reference materials. The three standardized reference materials (river sediment, fly ash, and EPA Municipal Digested Sludge) were spiked in triplicate at three levels, extracted according to the EP toxicity test procedures, and analyzed using AAS and ICP.

Preliminary to all three phases, a calibration study was performed to determine the effect, if any, of the acid matrix (0.6% acetic, 0.5% nitric or 0.6% acetic and 0.5% nitric) on the slopes of the calibration curves.

Procedure

Calibration Study

Standards for the calibration study were prepared by dilution of 1000 ppm Fisher or Ventron certified reference standards with the appropriate matrix. Ultrex acetic and nitric acids were used for preparation of the standard matrices (0.6% acetic acid, 0.5% nitric acid, and 0.6% acetic acid/0.5% nitric acid). Mixed standards were used for all elements except As, Hg, Se and Ag which were prepared individually and were prepared daily to minimize losses.

Phase 1 Analyses

Phase 1 analyses were performed on samples of river sediment, fly ash, low-pH sludge, and oil/water waste. The Phase 1 procedures consisted of the following general analytical schemes:

Scheme 1—EP test with leachate digestion

Scheme 2—EP test without leachate digestion

Scheme 3—Digestion according to EPA procedures with sample stored at room temperature

Scheme 4—Digestion according to EPA procedures with sample preserved by addition of nitric acid (HNO₃) to pH <2

Analytical results from Schemes 1 and 2 were used to evaluate the requirement to digest leachates resulting from the EP test. Results for Schemes 3 and 4 were used to evaluate sample storage requirements.

Modified procedures were utilized for the following elements: As and Se—EPA Methods 206.2 and 270.2, Hg—Method 245.1; and Sb—Method 204.2. Analyses were performed by AAS according to methods specified by EPA and Perkin-Elmer. Graphite furnace AAS was used for atomic absorption determination of As and Se and cold-vapor AAS was used for determination of Hg. All other elements were determined by flame methods. Analyses were also performed by ICP according to methods specified by EPA and Jarrell-Ash. Extractions and analyses were performed in triplicate.

The sequence of events occurring for each Scheme of Phase 1 of the project are summarized below:

Scheme 1—Divide sample aliquot into triplicates, perform EP extraction, digest the extract (separate digestions for Ag, Hg and Sb), analyze, spike, wait two weeks, analyze by AA.

Scheme 2—Divide sample aliquot into triplicates, perform EP extraction, analyze, spike, wait two weeks, analyze by AA.

Scheme 3—Divide sample aliquot into triplicates, digest the triplicates (separate digestions for Ag, Hg and Sb), analyze, spike, wait two weeks, analyze by AA.

Scheme 4—Exactly as in Scheme 3 only use the acid preserved sample aliquot.

Phase 2 Analyses

For the Phase 2 analyses of the low-pH sludge, 16 separate aliquots were removed, subsampled in triplicate, and adjusted to pH levels of 2, 4, 6 and 8 by addition of 1 M sodium hydroxide (NaOH). At times of 0, 2, 8 and 16 hours following pH adjustment, one triplicate subsample

from each pH level was extracted using the EP toxicity test procedure and analyzed for 17 trace metals. Details of extraction and analysis were identical to those described in the section entitled "Phase 1 Analyses," for Scheme 2.

Phase 3 Analyses

These standardized reference materials were prepared by drying, grinding, and homogenization of river sediment, fly ash, and EPA Municipal Digested Sludge (the latter material required only homogenization). After the determination of total metal concentrations, each sample was divided into 10 aliquots and prepared for extraction according to procedures specified for the EP toxicity test. After addition of distilled water, each material was spiked in triplicate at levels approximating 50, 100 and 150% of the total metal concentration using Fisher certified reference standards. An unspiked sample was subjected to the EP test as a control and to allow correction for the background metal concentration in the leachate. During addition of the standard spiking solutions, pH was either allowed to change or was maintained at its initial level by concurrent titration with 0.25 N sodium carbonate (Na₂CO₃). After spike addition, samples were extracted and analyzed using methods identical to those presented in Phase 1, Scheme 2.

Results and Discussion

Calibration Study

For each of 17 elements, the slope, intercept, and correlation coefficient for the calibration curve are presented. Actual calibration curves are also presented.

For all elements except Se, the slopes of the calibration curves for standards prepared in 0.6% acetic acid and 0.6% acetic acid/0.5% nitric acid were within ±5% of the slopes of the reference standards prepared in 0.5% nitric acid. In the case of Se, the slope of the calibration curve in the 0.6% acetic acid was 14% greater than the slope of the calibration curve in 0.5% nitric acid.

River Sediment

For nine elements (Al, Ba, Be, Cd, Fe, Pb, Mn, Ni and Zn) no statistically significant differences were observed between digested and undigested leachates.

Recoveries of spikes from the analyte solutions determined by AAS are presented. Recoveries were within the range

of 80-120% except for As, Hg, Ag and Zn, which had recoveries of 109-141%, 66-99%, 73-108% and 47-85%, respectively.

No significant differences were found between the digested and undigested EP leachates for any elements present above the detection limits for the river sediment sample. Significant differences between Schemes 3 and 4 (unpreserved and preserved sample aliquots, respectively) were found by AAS for As, Fe and Ag. However, none of these differences were statistically significant when analyzed by ICP. For all three elements, concentrations as determined by AAS were higher in the unpreserved sample.

Recoveries of spikes for all four schemes analyzed by AAS were between 80-120% except for As, Hg, Ag and Zn. Zinc recoveries were consistently low (47-85%), As recoveries consistently high (109-141%). Silver and Hg recoveries were low only for the nitric acid preserved (Scheme 4) samples. The Zn and As recoveries from the fly ash samples also followed these trends indicating a positive interference for As and a loss of Zn to the residual solids or to the glassware.

Recoveries of spikes of 11 elements (Al, Sb, Be, Cd, Cu, Fe, Mn, Hg, Ni, Ag and Tl) were in the range of 80-120%. Recoveries for the remaining six elements were as follows: As, 116-143%; Ba, 0-108%; Cr, 108-128%; Pb, 70-101%; Se, 30-95%; and Zn, 70-88%.

Significant differences for fly ash EP leachates were found for Cu, Ni and Se by AAS and for Ba, Cd and Cr by ICP. Differences for Cu and Ni were not significant by ICP and Se was below the ICP detection limit. Cu and Ni by AA are affected by Fe and other transition metals. The difference in Ba concentrations between the digested and undigested leachates is over an order of magnitude (the undigested value higher).

As with the river sediment samples, Zn recoveries were consistently low, As recoveries consistently high. In addition, Cr recoveries were somewhat high particularly for the completely digested (Scheme 3) sample supporting the possibility of contamination during digestion.

Recoveries of Ba, Pb, Se and Ag were low for the digested EP leachate (Scheme 1). The fly ash sample was generated from fuel containing significant levels of sulfur and the possibility of sulfate formation during digestion with subsequent precipitation of insoluble sulfates (Ba, Pb, Ag) is highly likely. The low Se recovery cannot be explained by sulfate precipitation but may be due to the formation of nickel sulfides rather than nickel sele-

nides in the graphite furnace with subsequent loss of SeO₂.

Low pH Sludge

For the Scheme 1 and 2 data, concentrations of seven elements (Sb, Ba, Be, Hg, Se, Ag and Tl) were below the limit of detection of the analytical methods and no statistical comparisons could be performed. For six elements (Al, Cr, Cu, Fe, Pb and Mn), no significant differences were detected. For four elements (As, Cd, Ni and Zn), significant differences were detected using AAS results. For Cd, Ni and Zn, differences were not significant using ICP data. For the Scheme 3 and 4 data, which compared preserved and unpreserved sample aliquots, five elements (Sb, Be, Se, Ag and Tl) were below the limits of detection. By AAS, no significant differences were detected for Al, As, Ba, Cd, Cu, Pb, Mn and Zn. Significant differences were detected for Cd, Fe, Mn and Ni by AAS and for Cu, Fe, Pb, Mn and Ni by ICP.

Recoveries of spikes for 11 elements (Al, Sb, Be, Cd, Cr, Cu, Fe, Mn, Hg, Ni and Tl), were in the range of 80-120%. Recoveries for the remaining elements were as follows: As, 56-92%; Ba, 0%; Pb, 41-89%; Se, 78-98%; Ag, 7-24%; and Zn, 86-128%.

The AAS data for Schemes 1 and 2 indicate significant differences for As, Cd, Ni and Zn. Arsenic levels were below ICP detection limits while the ICP data for Cd, Ni and Zn showed no differences. The As values for the undigested leachate are higher than for the digested sample. Two possible causes are that As is lost during digestion or that there is a spectral interference in the undigested sample. Spike recoveries for the undigested sample averaged 56% and for the digested sample 84%, supporting the likelihood of an interference in the undigested sample.

The practical significance of the AAS Cd data is suspect. The high precision allows 0.23 and 0.24 mg/L to be statistically different.

The nickel data for the digested leachate are higher (by both AAS and ICP although not significant by ICP). Since the difference is small, contamination during digestion or slight nonhomogeneities in the sample aliquots are the likely causes. An enhancement of flame AAS analyses for Ni by large excesses of Fe is well known.

In the comparison of Schemes 3 and 4, the AAS data are significantly different for Cd but the ICP data are not. For Cu, the ICP data are significantly different while the AAS data are not. An examination of

the raw data again suggests that these results are the mathematical consequence of high precision rather than of a practical difference. The Pb data for ICP Scheme 3 (unpreserved) are higher than for the preserved sample while the AAS data show no difference. Both the Scheme 3 and Scheme 4 ICP values are higher than the AA results. The most likely explanation of this is that it is a consequence of a spectral interference from the extremely high levels of Fe, Mn or Ni present in this sample. If the difference were due to a true chemical change in the unpreserved sample or a sample nonhomogeneity, the AAS results should also reflect the increased concentration.

Recoveries of spikes from this waste were generally high with two exceptions: As and Se recoveries from the undigested EP leachate were low and elements forming insoluble sulfates had universally poor recoveries (Ba, Pb and Ag).

Oil/Water Waste

For data from Schemes 1 and 2, only two elements (Fe and Mn) were present at concentrations above the limit of detection and no significant differences were evident. For data from Schemes 3 and 4, all elements except Sb, As, Se, Ag and Tl were present at concentrations above the limit of detection and no significant differences were detected.

Oil phase analyses indicated measurable amounts of Al, Ba, Cu, Fe, Pb, Mn and Ni in the leachates. For purposes of comparison, concentrations were calculated on the same basis as the previous phase leachate. The fractions of the total metal contained in the oil phase were as follows: Al, 32-57%; Ba, 9-12%; Fe, 26-29%; Mn, 17-24%; and Ni, 44%.

For 15 elements (Sb, As, Ba, Be, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl and Zn), recoveries were in the range of 80-120%. Recoveries of the remaining elements were as follows: Al, 96-124%; and Hg, 15-104%.

Phase 2 Analyses

Aliquots of the sludge were adjusted to pH 2, 4, 6 and 8 with 1 M NaOH and then extracted at time intervals (post-pH adjustment) of 0, 2, 8 and 16 hours. Of the 17 elements in this study, 10 were present in the pH 2 samples at concentrations above the analytical detection limits (Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn).

None of the metals exhibited a strong leachate concentration dependence on the time interval between pH adjustment and extraction. However, 9 of the 10 elements present (As being the single

exception) exhibited strong concentration dependence on pH during the EP leachate generation. It should be noted that the aliquots of sludge which were adjusted to pH 6 or 8 were (at the appropriate time interval) adjusted to pH 5 as would be required by the EP test. The extracts were analyzed without digestion, that is, by procedures analogous to Phase 1, Scheme 2.

Phase 3 Analyses

The purpose of Phase 3 was to determine the efficiency of the EP in extracting metal spikes from standard reference materials. The materials chosen were fly ash, river sediment, and EPA Municipal Digested Sludge. The fly ash and river sediment were dried, ground, and homogenized prior to use. The samples of dried municipal sludge were composited to obtain a sufficient quantity of homogeneous material for the study.

Aliquots of all three materials were digested and analyzed in triplicate by AAS to provide the total bulk concentrations of the 17 metals in the reference materials. The results obtained by ERCO were confirmed by an outside laboratory.

Each sample was prepared for the EP extraction according to the EPA specified methods. After addition of distilled water to the dried ash, sediment and sludge, the samples were spiked (in triplicate) at three different concentration levels representing 150%, 100%, and 50% of the total metal content or 20, 10, and 5 times the detection limit for those elements which were not detected in the bulk analyses of the materials. Due to the acid content of the spiking solutions, the pH of the spiked sample/distilled water matrices ranged from 1.39 to 3.28. This pH range is low for EP extractions where the pH of neutral or basic sludges are typically adjusted to pH 5.0 ± 0.2 with acetic acid.

For a second series, the sample pH was maintained at its initial level during spike addition by concurrent titration with 0.25 N Na_2CO_3 . These samples were then adjusted to pH 5 and extracted according to the EP test procedure.

Blank spike recoveries at the 150%, 100%, and 50% levels for the pH 5 samples and at the 100% spike level for the low-pH samples are also included. Recoveries for most metals in the blank spikes were in the range 85% to 115% with the certain exceptions.

For the pH 5 adjusted river sediment samples, recoveries ranged from <1% to 169%; for the low-pH samples, the recoveries ranged from 1% to 323%. In

general, recoveries of the high (150%) spikes were higher than for the low (50%) spikes. The most obvious difference is that the recoveries for the low-pH samples are much higher and much closer to 100% than the pH 5 recoveries.

The recoveries of Se, Sb and As were poor for both low-pH and pH 5 extracts. These elements would most likely be present as oxyanions and would not precipitate as hydroxides. The most likely mechanisms of loss of those would be adsorption or co-precipitation.

Fly Ash

The fly ash samples were dried, ground, and homogenized prior to bulk analysis and Phase 3 extractions. Bulk concentrations of the elements of interest were determined by ERCO and verified by an outside laboratory.

Mean recoveries of 17 elements were calculated by averaging results for both AAS and ICP and correcting (where possible) for the concentration of each element determined from an unspiked EP for each material. The concentration of element recovered was then compared to the original concentration added to determine the percent recovery.

As with the river sediment samples, recoveries from the low-pH extracts were consistently better than from the pH 5 extracts and the recoveries of the anionic species (As, Sb, Se) were low at both pH values; Ni, again exhibited high recoveries (particularly by AAS) due to Fe interference. In addition, the fly ash samples exhibited low recoveries for those elements with insoluble sulfates (Ba, Pb) as did the fly ash samples utilized in Phase 1.

EPA Municipal Digested Sludge

Each sample was prepared for the EP extraction according to methods outlined by EPA and in the manner that was employed for the fly ash and river sediment samples. Mean recoveries were calculated by averaging results for both AAS and ICP and correcting (where possible) for the concentration of each element determined from the appropriate unspiked EP for each material. The concentration of element recovered was then compared to the original concentration added to determine the percent recovery.

Recoveries of the metals in the blank spikes were all between 90% and 110% with the exception of Ag which is unstable in the mixed standards and Hg which was spiked at low levels.

Recoveries of the metals in the extracts were extremely poor. For the pH 5 ex-

tracts, no element exhibited recoveries in the 80% to 120% range. For the low-pH extracts only four of the 51 recoveries were in the 80% to 120% range. Recoveries in the pH 5 extracts were all extremely low (except Hg) while the low-pH recoveries were highly erratic. For the low-pH extracts, Sb, Pb, Ba, Se and Ag exhibited low recoveries. The Ag was expected to be low since the spike solution contains chloride and precipitates the Ag. The digested sludge apparently contains sulfate which would selectively precipitate Pb and Ba. The Sb and Se recoveries, as with the fly ash and river sediment, were low for both the low-pH and pH 5 extracts.

Comparison of AAS and ICP Recoveries

While the intent of Phase 3 was to determine the ability of the EP test to leach spikes from standard reference materials, the data are also useful in observing the comparative performance of AA and ICP. Both techniques were used to analyze the same undigested EP leachates with the same spike levels and consequently comparison of their performance was straightforward.

Conclusions and Recommendations

The EP toxicity test was designed to indicate the concentrations of eight metals (As, Ag, Ba, Cd, Cr, Hg, Pb and Se) present in a waste in forms which would allow them to become mobile (solubilized) in a mildly acidic (pH 5 acetic acid) medium. Analyses of the generated leachates are performed by atomic absorption spectrophotometry (AAS).

The conclusions which may be drawn from this study and recommendations based upon the conclusions are summarized below.

Calibration Study

- For 16 of the 17 metals studied, the dilute nitric acid or dilute acetic acid matrices used for the EP toxicity test had no effect on the slopes of the calibration curves. The acetic acid matrix enhanced the Se signal by both AAS and ICP. Since enhancements of almost 10% were found for both AAS and ICP, it is recommended that the method of standard additions be used for Se analyses or at least that a test be performed to ensure that standard additions are not needed for every EP leachate.

Phase 1 (Acid Preservation and Digestion Study)

- Digestion of the EP leachates removes several interferences and is generally recommended prior to analysis by either AAS or ICP. However, digestion may cause losses from certain samples such as the high sulfur containing fly ash studied here. Digestion caused formation of sulfate and subsequent precipitation of Ba, Ag and Pb.
- Acid preservation of the samples used in this study caused little difference in analytical results.
- The ICP analyses of undigested leachates were less subject to interference than were AAS analyses.
- Even though the leachate digestion of the fly ash resulted in losses of Ba, Ag and Pb for this sample, it is recommended that the digestion be performed. Several matrix interferences in all the wastes were eliminated by the digestion procedure which otherwise would have required time-consuming techniques such as standard additions.

Phase 2 (pH and Storage Time Study)

- The time that a sample is stored (0 to 16 hours) prior to the initiation of the EP leachate generation had no effect on the metal concentrations in the leachate.
- The pH of the sample prior to the initiation of the EP leachate generation is extremely important. This may be true only for selected wastes such as the ones used in this study, i.e., one with a high Fe content which may precipitate at pH 5 or one with a high sulfate concentration which may also cause precipitation. It would be useful to perform Phase 2 on wastes where hydroxide or sulfate precipitation were less likely.

The fact that the leachate concentrations are pH dependent was further confirmed by the Phase 3 data. Due to this variability in recovery (extraction efficiency) it is recommended that the intent of the EP toxicity test be emphasized, i.e., that it is an indicator of the concentration of mobile metal species not a total extraction procedure.

Phase 3 (Extraction Efficiency Study)

- The pH 5 dilute acetic acid matrix used for the leachate generation in the EP toxicity test is not capable of leaching many metals from a solid waste and is incapable of preventing precipitation or adsorption of metal ions spiked into the solution. In fact, a river sediment containing 5,700 $\mu\text{g/g}$ Al and 9,200 $\mu\text{g/g}$ Fe was leached with an acetic acid pH 5 solution containing 42.5 mg/L Al (and 68.5 mg/L Fe) with recoveries of the metals in solution being less than 3%.
- As in Phase 1, the ICP analysis of undigested leachates was less subject to interference (as measured by % recoveries) than was AAS.

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John D. Pfaff is the EPA Project Officer (see below).

The complete report, entitled "US EPA Extraction Method Development Study for Trace Metals in Leachate," (Order No. PB 86-118 981/AS; Cost: \$16.95, subject to change) will be available only from:

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