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Project Summary

USEPA Method Study 37 SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils

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An interlaboratory collaborative study was conducted on SW-846 Method 3050, "Acid Digestion of Sediments, Sludges, and Soils," to determine the overall and single-analyst precision estimates for the analyses of 23 elements in sediments, sludges, and soils. SW-846 Method 3050 includes quality control, sample preparation, and analysis of samples by Flame Atomic Absorption (FLAA) and Graphite Furnace Atomic Absorption (GFAA).

The study design was based upon Youden's non-replicate plan for collaborative tests of analytical methods. Initially, 14 solid wastes were collected, dried, homogenized, and analyzed by Inductively Coupled Plasma (ICP) for the 23 metals of interest. Based upon these data, seven solid wastes were selected that contained naturally occurring elements over a relatively wide concentration range. Elements not occurring naturally were added (spiked) into each solid waste. In the formal study by eight laboratories, the solid wastes were digested with nitric acid and hydrogen peroxide, refluxed with nitric or hydrochloric acid, and analyzed for 21 elements by FLAA and for two elements, arsenic and selenium, by GFAA. The results were analyzed using USEPA computer programs entitled "Interlaboratory Method Validation Study (IMVS)." The computer programs produced measures of overall and single-analyst precision for the 21 elements analyzed by FLAA and for the two elements analyzed by GFAA.

The study was conducted by The Bionetics Corporation under the direction of the Quality Assurance Research Division, Environmental Monitoring Systems Laboratory, Cincinnati, OH (EMSL-Cincinnati) under Contract No. 68-03-3254. Analytical work was completed in August 1987. The study report covers a period from January 10, 1987, to February 5, 1988.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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

The Hazardous Waste Management facility permit regulations promulgated in July 1982 (40 CFR 265) provide performance standards for the monitoring of ground waters, wastewaters, and solid matrices at hazardous waste sites. To facilitate these standards, chemical and physical analyses are required to assess the degree of contamination at and around the area of the site. The manual: *Test Methods for Evaluating Solid Waste, Physical and Chemical Methods, (SW-846), November 1986, Third Edition,* provides a unified, up-to-date source of information on sampling and analyses related to compliance with Resource Conservation and Recovery Act (RCRA)

regulations. The success of these pollution control activities, particularly when legal action is involved, depends upon the reliability of the data generated by the laboratories; therefore, it is important to evaluate the methods through interlaboratory method validation studies.

The Environmental Monitoring Systems Laboratory, Cincinnati, OH, (EMSL-Cincinnati) develops/selects analytical methods and provides quality assurance (QA) support to agency programs involving water and waste regulations. In EMSL-Cincinnati, the responsibility for providing QA support is assigned to the Quality Assurance Research Division (QARD). Its QA program is designed to establish the reliability and legal defensibility of water and waste data collected by the Agency, the state regulating authorities, the private sector, and the commercial laboratories performing compliance analyses. One of its QA activities is to conduct interlaboratory method validation studies to evaluate analytical methods selected for the Agency's operating programs such as the Office of Solid Waste.

This report describes the interlaboratory method validation study for SW-846 Method 3050, "Acid Digestion of Sediments, Sludges, and Soils." The elements: aluminum, antimony, barium, beryllium, calcium, cadmium, chromium, cobalt, copper, iron, lead, magnesium,. manganese, molybdenum, nickel, potassium, silver, sodium, thallium, vanadium, and zinc were analyzed by flame atomic absorption spectroscopy (FLAA). Arsenic and selenium were analyzed by graphite furnace atomic absorption spectroscopy (GFAA). Originally, silver and antimony were included in Method 3050 and therefore included in this study. However, they were removed from the September 1986 revision of the method.

The primary objective of the study was to characterize the behavior of Method 3050 in terms of overall precision and single-analyst precision. The study was conducted with the cooperation of eight participating laboratories under the direction of the Quality Assurance Research Division, EMSL-Cincinnati. As primary contractor to QARD, The Bionetics Corporation was responsible for the collection and characterization of the solid matrices, preparation of user instructions and report forms, distribution of samples, and screening of the returned data for gross errors. The raw data were evaluated statistically by the QARD using a series of computer programs entitled "Interlaboratory Method Validation Studies" (IMVS). Upon review of the draft report by EMSL-Cincinnati, The Bionetics Corporation prepared the final report.

Description of Study

The study design was based upon Youden's original non-replicate design for collaborative evaluation of analytical methods. In this design, samples are prepared in pairs such that the analyte concentrations of the pairs vary between 5-20% from the mean of the pairs. Seven sample pairs, one for each solid matrix, were prepared to cover the optimum range of the method as specified in SW-846 or in the concentration range naturally occurring in the matrices.

Selection of Participating Laboratories

Twenty-four commercial laboratories responded to the abstract in the Commerce Business Daily, inviting participants for the method validation study. Their technical proposals were evaluated based upon laboratory experience and quality control practices. Laboratories whose proposals were acceptable were evaluated further in a preaward performance evaluation study. The participants selected for the formal study were the eight laboratories with acceptable proposals who performed best in the preaward study.

Selection of Solid Waste Matrices

Initially, 14 solid waste matrices were screened for the 23 elements of interest by ICP analyses and seven solid wastes were selected that contained naturally occurring elements over a relatively wide concentration range. These were:

Solid Waste	Source
1	National Bureau of Standards River Sediment, SRM-1645
2	US EPA, Hazardous Soil QC Sample #1
3	Ethyl Corp., Electroplating Sludge
4	Marshall Space Flight Center (MSFC), Electroplating Sludge
5	US EPA, Shale I QC Sample WP 386
6	Varland Metal Service Inc., Electroplating Sludge
7	EPA Supplied Electroplating Sludge

Aluminum, calcium, iron, magnesium, manganese, potassium, and sodium were present in all seven samples and did not require fortification with spiking solutions. Cobalt, molybdenum, thallium, vanadium, beryllium, cadmium, arsenic, selenium, barium, silver, antimony, chromium, copper, lead, nickel, and zinc did not occur naturally or were at such low levels in the solid wastes that fortification was required.

Results and Discussion

The objective of this study was to characterize the performance of SW-846 Method 3050 in terms of overall precision and single-analyst precision for 23 trace metals in sludges, soils, and sediments. The IMVS computer programs were used to summarize the raw data and compile statistics for overall standard deviation, overall percent relative standard deviation, single-analyst standard deviation, single-analyst percent relative standard deviation, and mean recovery. Antimony and silver, which are listed in Table 1 are not included in the following discussions because they are no longer included in Method 3050.

The study was intended to answer two major questions about method performance:
(1) Does Method 3050 digestion procedure work equally well on all solid wastes studied?
(2) Do the matrix effects encountered from any of the seven solid wastes studied prevent establishment of a linear relationship between precision and mean recovery?

The following data treatment decisions were made on the statistics generated by the IMVS computer programs:
1) Both overall and single-analyst precision regression equations were recalculated after removal of atypical solid waste data.
(2) Weighted linear regression equations were not calculated with less than five sets of acceptable solid waste data. In these situations no regression equation was reported, and it was concluded that the data for the element had a strong matrix dependence. The reader is referred to Appendix C, Statistical Summaries, of the full report, for the individual solid waste precision statistics.
(3) For comparison purposes, a concentration value of five times (5x) the low concentration limit of the range studied was used as the mean recovery, in the regression equations, to calculate %RSDs. T'' value is believed to be representative of the reported data in this study.

Rejection of Outliers

For the entire study, the IMVS program rejected 75 data points (2.9%) of the 2576 data points submitted. The highest number of rejected points (10) occurred for barium while no thallium or beryllium data were rejected. Of the eight laboratories participating in the study, Laboratory 6 accounted for 25 of the 75 rejected data points.

Overall Precision

The IMVS computer programs calculated the overall precision for each of the seven Youden concentration pairs for this study. Utilizing another USEPA computer program, REGRESS, weighted linear regression equations were fitted to the submitted data. These regression equations, presented in Table 1, regressed overall precision (S) versus mean recovery (X) for all seven Youden concentration pairs (14 data points). Several regression equations were recalculated after deletion of solid waste data which did not show a clear relationship to the other solid waste data. The deleted solid waste data are identified with each regression equation.

The mean %RSD for all FLAA elements was 9.4%. Only two of these elements, aluminum (22.4%) and potassium (22.4%), had %RSDs greater than 15%, while fifteen elements had %RSDs less that 10%. The naturally occurring elements: aluminum, calcium, iron, magnesium, manganese, potassium and sodium, which did not require fortification, had a mean %RSD of 11.8%. Cobalt, molybdenum, thallium, and vanadium, which required spiking of all seven solid wastes, had a mean %RSD of 8.4%. Beryllium, cadmium, chromium, copper, lead, nickel, and zinc which were evaluated with a combination of spiked and unspiked solid wastes had a mean %RSD of 7.4%. Based on the mean %RSDs for these three groups, the overall precision obtained for all elements was very similar whether naturally present or spiked into the solid matrices.

The %RSD for the GFAA elements, arsenic and selenium, were 19.7% and 29.6%, respectively.

Barium regression equations are not presented in Table 1 because the precision data for each of the seven solid wastes were variable with no apparent relationship to mean recoveries. Precipitation reactions forming barium sulfate are suspected but have not been confirmed.

Single-Analyst Precision

The IMVS computer programs calculated the single-analyst precision (SR) for each of the seven Youden concentration pairs for this study. The seven results for each element were reduced to a single equation by weighted linear regression analysis. These regression equations, presented in Table 1, regressed single-analyst precision (SR) versus mean recovery (X) and can be used to estimate the percent relative single-analyst standard deviation (%RSD-SR) at any concentration level in the range studied.

The mean %RSD-SR for the FLAA elements was 5.4% and ranged from cobalt (4.2%) to aluminum (8.6%). The ratio of the mean overall precision, %RSD, to the mean single-analyst precision, %RSD-SR, was 1.7:1. The naturally occurring elements: aluminum, calcium, iron, magnesium, manganese, potassium and sodium had a mean %RSD-SR of 5.8%. Cobalt, molybdenum, thallium and vanadium which required spiking of all seven solid wastes, had a mean %RSD-SR of 5.1%. Beryllium, cadmium, chromium, copper, lead, nickel, and zinc were analyzed from a combination of spiked and unspiked solid wastes and had a mean %RSD-SR of 5.2%. Based on the mean %RSD-SRs for these three groups, the within-laboratory precision obtained for all elements, whether naturally present or spiked into the solid matrices, was very similar.

The GFAA elements, arsenic and selenium, had %RSD-SRs of 11.4% and 23.0% respectively and were the only elements with %RSD-SRs above 10%.

Conclusions and Recommendations

SW-846 Method 3050 is recommended for the analyses of aluminum, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, sodium, thallium, vanadium, and zinc by flame atomic absorption (FLAA) and for the analyses of arsenic and selenium by graphite furnace atomic absorption (GFAA).

The linear regression equations obtained from this study and presented in Table 1 can be used to predict the overall and single-analyst precision of Method 3050 for these elements over the concentration range studied

The barium precision data obtained from this study were variable with no apparent relationship to mean recovery. Reactions, perhaps involving barium

sulfate as a precipitate, are theorized. Barium data from the Method 3050 digestion procedure should be evaluated relative to presence of sulfur or sulfur oxides in wastes tested.

Originally, silver and antimony were included in Method 3050 but were removed from the September 1986 revision of the method. They were, however, included in this study but are not recommended for analyses by Method 3050.

Table 1. Regression Equations for Overall (S) and Single-analyst (SR) Precision for SW-846 Method 3050

Element (Conc Range in µg/g)	Regression Equation[a]	Waste No. Deleted[b]	Data Set Corrected for Waste No.[c]
Aluminum (715-18700)	$S = 0.210X + 51.0$ $SR = 0.0742X + 41.2$		4A,4B
Antimony (63-1700)	$S = 0.145X + 10.58$ $SR = 0.0310X + 16.35$	1,7 1,7	
Beryllium (5.5-231)	$S = 0.0676X + 0.37$ $SR = 0.0411X + 0.26$		
Cadmium (5.6-154)	$S = 0.0437X + 0.78$ $SR = 0.0446X + 0.41$	6,7 6,7	1A, 1B, 2B
Calcium (11900-185000)	$S = 0.0893X - 66$ $SR = 0.0662X - 881$	7 7	5B
Chromium (67-97700)	$S = 0.0923X + 0.73$ $SR = 0.0564X + 0.66$	6 6	
Cobalt (91-624)	$S = 0.0525X + 7.22$ $SR = 0.0428X - 0.40$	6 6	
Copper (66-25800)	$S = 0.0636X + 0.0$ $SR = 0.0460X + 2.0$		7B
Iron (16900-123400)	$S = 0.0522X + 693$ $SR = 0.0364X + 162$		
Lead (715-20800)	$S = 0.0607X - 17.4$ $SR = 0.0292X + 4.3$	2,5 2,5	
Magnesium (2050-50700)	$S = 0.0572X + 106$ $SR = 0.0408X + 26$		
Manganese (287-1100)	$S = 0.0840X - 3.0$ $SR = 0.0618X - 6.2$		
Molybdenum (180-5600)	$S = 0.0739X - 3.5$ $SR = 0.0936X - 10.8$	1 1	All data sets corrected except 5A,5B
Nickel (22-75000)	$S = 0.0678X + 6.44$ $SR = 0.0437X + 5.64$		2A, 2B, 7B
Potassium (448-4100)	$S = 0.196X + 61.8$ $SR = 0.0739X + 16.1$		
Sodium (227-105700)	$S = 0.0646X + 26.4$ $SR = 0.0481X + 8.4$		
Thallium (129-2400)	$S = 0.0559X + 7.5$ $SR = 0.0213X + 4.3$		
Vanadium (334-7420)	$S = 0.133X - 4.2$ $SR = 0.0437X + 13.6$		6B
Zinc (93-188900)	$S = 0.0832X + 1.10$ $SR = 0.0639X + 1.33$	7	
Arsenic[d] (21-616)	$S = 0.188X + 0.98$ $SR = 0.0857X + 2.95$		5A, 6A, 7A, 7B
Selenium[d] (3.98-105)	$S = 0.192X + 2.06$ $SR = 0.187X + 0.85$		All data sets corrected
Barium[e] (123-11630)	No equation developed. See App. C in main report for individual statistics.		
Silver[e] (37-344)	No equation developed. See App. C in main report for individual statistics.		

[a] Weighted least squares technique.
[b] Indicates the waste deleted to arrive at the regression equation presented.
[c] Solid waste data set that was corrected for errant data points. See Section 5, Results and Discussion, for further details in main report.
[d] Analyzed by graphite furnace atomic absorption (GFAA). All other analyses by flame atomic absorption (FLAA).
[e] The individual data sets were too variable to fit a linear relationship; thus, no equations were developed.

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