



Project Summary

USEPA Method Study 35: SW-846 Method 3005: Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analyses by Flame Atomic Absorption Spectroscopy

Kenneth W. Edgell

An interlaboratory collaborative study was conducted to determine the precision and bias (recovery) of Solid Waste (SW-846) Method 3005 for total recoverable metals by flame atomic absorption on twenty-one elements in ground water. Method 3005 is entitled "Acid Digestion of Total Recoverable or Dissolved Metals For Analyses By Flame Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy" and includes instructions for quality control, sample preparation and analysis of samples by AA-Flame.

The study design was based upon Youden's non-replicate plan for collaborative tests of analytical methods. Each water type was spiked with six concentrations (as three Youden pairs) of the twenty-one test elements and was digested using a nitric/hydrochloric acid procedure and analyzed by flame atomic absorption spectroscopy. Test data from three spiked ground water sources were compared against reagent water as a control. The resulting data were analyzed using USEPA's computer programs entitled "Interlaboratory Method Validation Study" (IMVS). This study produced, for each element, measures of

precision and mean recovery for the acid digestion/flame atomic absorption spectroscopy and compared the performance of the method between each water type and reagent water.

This study was conducted by The Bionetics Corporation at the direction of the Environmental Protection Agency, Quality Assurance Research Division, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio under EPA Contract No. 68-03-3254. This report covers a period from September 10, 1986 to December 21, 1987. Analytical work was completed in September 1987.

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 ordering information following this document).

Introduction

The Hazardous Waste Management facility permit regulations were promulgated in July 1982 (40 CFR 265) and provide performance standards for the monitoring of ground waters at hazardous waste sites. To facilitate these standards, certain analytical methodology will be

required to assess the degree of ground water contamination at and around the area of the site. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), November 1986, Third Edition, is intended to provide 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 provided by the laboratories. Therefore, it is necessary to determine the bias (recovery) and precision of the methodology in interlaboratory method validation studies.

EMSL-Cincinnati of the USEPA develops/selects analytical methods and provides quality assurance (QA) support to the Office of Solid Waste (SW) as required by regulations. The QA program is designed to maximize the reliability and legal defensibility of water quality information collected by the Agency, the primary regulating authorities in the states, and by the private sector and commercial laboratories performing compliance analyses. The responsibility for providing QA support is assigned to the QA Branch of EMSL-Cincinnati. One QA activity is to conduct interlaboratory method validation studies to obtain precision and recovery statements for the Agency's operating program such as for the Office of Solid Waste.

This report describes an interlaboratory method validation study on Method 3005 entitled "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analyses by Flame Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy". In this study 21 trace metals were investigated using the total recoverable digestion procedure with flame atomic absorption spectroscopy. Nine commercial laboratories were selected by the Quality Assurance Branch of EMSL-Cincinnati to participate in this study based on technical criteria. The Bionetics Corporation, as primary contractor to the Quality Assurance Branch of EMSL-Cincinnati, was responsible for the collection and characterization of three ground waters for use as test waters in the study and the subsequent spiking with the analytes. Additional Bionetics activities included analyses of the samples to confirm the true concentrations, preparation of user instructions and report forms, preparation and distribution of the sample, screening of returned data for gross errors, and drafting of the final report. The raw data

were evaluated statistically by the Quality Assurance Research Division of EMSL-Cincinnati using a series of computer programs entitled "Interlaboratory Method Validation Studies" (IMVS).

Procedure

Method Summary

The method consists of acidifying a 100 mL sample with 2 mL of concentrated nitric acid and 5 mL of concentrated hydrochloric acid, which is then heated to about 90°C in a hood until the volume has been reduced to 15-20 mL. The sample is then filtered to remove insoluble materials. Sample volume is adjusted to 100 mL and analyzed for metals by AA-direct aspiration. The method is applicable to the following elements:

Aluminum	Magnesium
Antimony	Manganese
Arsenic	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

Arsenic and selenium were not tested in this study because these two elements are not recommended for analyses by flame atomic absorption spectroscopy. Either furnace technique atomic absorption or ICP analysis are recommended for arsenic and selenium analyses.

Selection of Participants

Twenty-four commercial laboratories responded to an abstract in the Commerce Business Daily for participants in the method validation study. Technical proposals were evaluated based upon laboratory experience and quality control within the laboratory and those laboratories whose proposals were acceptable were further evaluated based on their performance on preaward trace metal samples. The final participants selected for the formal study were the top nine laboratories of the preaward performance evaluation study.

Selection and Collection of Water Samples

The types of water selected for the IMVS included reagent water as the control and three unfiltered ground waters from monitoring wells at different hazardous waste sites: a) Chem-Dyne, Hamilton, Ohio, b) Wayne Disposal,

Detroit, Michigan, and c) Coshocton Sanitary Landfill, Coshocton, Ohio. It should be noted that the unfiltered Wayne ground water contained significant amounts of calcium, chromium, nickel, and cobalt in the suspended solid fraction. Suspended solids concentrations in the unfiltered Chem-Dyne, Coshocton and Wayne waters were 142 mg/L, 69 mg/L, and 168 mg/L, respectively. Only the unfiltered waters were used in this study.

Description of Interlaboratory Method Validation Study

The design of the study is based upon Youden's original non-replicate design for collaborative evaluation of analytical methods. According to this design, two samples are prepared in pairs such that the analyte concentrations of the pairs vary between 5-20% of the mean of the pairs. Youden pairs are prepared at three different concentration levels, for each water, to cover the optimum range of the method specified in the SW-846 methods manual. A copy of the method and the instructions for sample preparation, with data report forms, were supplied to participants by USEPA. Each participant was required to analyze a quality control sample after every sixth sample and determine acceptable results within control limits. If out of control, the problem was to be corrected and the last six samples rerun. The primary objective of the study was to establish mathematical relationships which express the precision and mean recovery of the returned data as a function of mean recovery and true concentration, respectively. (See Table 1.)

Results and Discussion

The primary objective of this study was to characterize the performance of Method 3005 in terms of mean recovery, overall precision, and single-analyst precision on each of 21 trace metals in four different water matrices.

Rejection of Outliers

The analytical data, processed through the IMVS programs, underwent three outlier tests. First, the Youden's Laboratory Ranking Procedure was used to detect and reject data having a large systematic error associated with a particular laboratory. If the majority of a laboratory's data for a particular element-water combination was either biased high or biased low, compared to the other laboratories, the laboratory failed the lab ranking procedure, and all of their data were rejected

Table 1. Study 35, SW-846 Method 3005, Trace Metals, AA Flame Weighted Linear Regression Equations for Mean Recovery and Precision (in mg/L)

Water Type	Aluminum, Al	Barium, Ba	Beryllium, Be	Calcium, Ca	Cadmium, Cd
Applicable Conc. Range	(5.00 - 50.00)	(1.05 - 20.90)	(0.04 - 2.00)	(90.00 - 300.00)	(0.04 - 1.86)
Reagent Water 1					
Single-Analyst Precision	SR = 0.056X - 0.18	SR = 0.050X + 0.02	SR = 0.038X + 0.00	SR = 0.022X + 1.96	SR = -0.003X + 0.02
Overall Precision	S = 0.082X - 0.13	S = 0.121X - 0.07	S = 0.066X + 0.00	S = 0.110X - 2.02	S = 0.027X + 0.01
Mean Recovery	X = 0.599C + 0.11	X = 0.967C - 0.02	X = 0.956C - 0.00	X = 0.905C + 12.12	X = 1.007C + 0.00
Ground Water 1					
Single-Analyst Precision	SR = 0.030X + 0.03	SR = 0.085X + 0.01	SR = 0.019X + 0.00	SR = 0.002X + 6.26	SR = 0.019X + 0.00
Overall Precision	S = 0.068X - 0.05	S = 0.171X - 0.00	S = 0.045X + 0.00	S = 0.172X - 5.47	S = 0.027X + 0.01
Mean Recovery	X = 0.918C + 0.18	X = 0.645C + 0.42	X = 0.961C + 0.00	X = 0.998C - 0.43	X = 0.986C + 0.00
Applicable Conc. Range	(5.00 - 50.00)	(1.05 - 21.00)	(0.04 - 2.00)	(24.00 - 75.00)	(0.04 - 1.86)
Reagent Water 2					
Single-Analyst Precision	SR = 0.030X + 0.00	SR = 0.071X - 0.02	SR = 0.013X + 0.00	SR = 0.186X - 3.89	SR = 0.013X + 0.01
Overall Precision	S = 0.073X - 0.05	S = 0.074X + 0.06	S = 0.026X + 0.01	S = 0.155X - 1.83	S = 0.015X + 0.01
Mean Recovery	X = 0.955C - 0.12	X = 0.926C - 0.06	X = 0.966C - 0.01	X = 0.951C + 0.28	X = 0.995C - 0.00
Ground Water 2					
Single-Analyst Precision	SR = 0.039X - 0.14	SR = 0.044X - 0.01	SR = 0.009X + 0.00	SR = 0.029X + 0.01	SR = 0.016X + 0.00
Overall Precision	S = 0.085X + 0.02	S = 0.062X + 0.02	S = 0.031X + 0.00	S = 0.045X + 1.86	S = 0.027X + 0.01
Mean Recovery	X = 0.941C - 0.16	X = 0.931C - 0.04	X = 0.961C + 0.00	X = 0.997C + 0.93	X = 1.007C - 0.00
Applicable Conc. Range	(5.00 - 50.00)	(1.05 - 21.00)	(0.04 - 2.00)	(6.00 - 27.00)	(0.04 - 1.86)
Reagent Water 3					
Single-Analyst Precision	SR = 0.046X + 0.03	SR = 0.034X + 0.09	SR = 0.012X + 0.00	SR = 0.143X - 0.88	SR = 0.014X + 0.00
Overall Precision	S = 0.090X + 0.04	S = 0.119X - 0.03	S = 0.032X + 0.01	S = 0.282X - 1.47	S = 0.038X + 0.00
Mean Recovery	X = 1.007C - 0.32	X = 1.078C - 0.12	X = 0.986C - 0.00	X = 0.878C + 0.43	X = 0.991C - 0.00
Ground Water 3					
Single-Analyst Precision	SR = 0.027X + 0.11	SR = 0.146X - 0.06	SR = 0.014X + 0.00	SR = 0.049X + 0.23	SR = 0.012X + 0.00
Overall Precision	S = 0.092X - 0.17	S = 0.214X + 0.06	S = 0.037X + 0.01	S = 0.368X - 0.04	S = 0.051X + 0.00
Mean Recovery	X = 0.998C - 0.25	X = 0.498C + 0.50	X = 0.984C - 0.00	X = 0.866C - 0.80	X = 0.978C - 0.00

X = Mean Recovery

C = True Value for the Concentration

for that element-water combination. Second, zero, negative, and non-detected data were rejected as unusable data. Finally, the Thompson Outlier Test was used to reject individual outliers.

For the entire project, the IMVS program rejected 1403 data points (20.6%) of the 6804 data points submitted. The percentage of rejected data did not vary significantly among water types. The lowest rejection was for reagent water 1, and the highest rejection was for ground water 3. Molybdenum had the lowest number of rejected data points (24) and copper had the highest (102). Of the nine laboratories participating in the study three accounted for 786 or 56% of all rejected data. The other six laboratories ranged from 74 to 130 rejected data points.

Mean Recovery

The mean recovery, X, of the retained data, was compared to the true values

supplied to the IMVS programs for each element at each spike concentration in each test water. These individual values are presented in Appendix C, in the main report, as 732 separate values. Subjecting these values for each water type to linear regression analysis yielded regression equations where mean recovery, X, was related to the true value, C, over the entire concentration range. The slope, m, of these regression equations can be used to estimate the percent recovery of each element as long as the intercept, b, is small (i.e., less than 5% of the value slope times true concentration, mC). Examination of the regression equations presented in Table 1 indicates that this criterion can be met for elements in all water types except calcium, sodium, magnesium, potassium, iron and chromium. For these elements, percent recovery estimates were calculated by inserting a midpoint concentration, from the range studied, for the value C. The X

value obtained divided by the midpoint concentration, C, times 100, will yield percent recovery. Only two elements had recoveries outside of the 90%-110% interval across water types: barium (85%) and silver (65%).

A closer look at the barium recovery estimates revealed large recovery differences for ground water 1 and ground water 3. These matrices appeared to have adversely affected barium recovery, possibly due to elevated sulfate levels. Reagent water recovery for barium was 98%.

Using all Youden pairs, the regression equation for mean recovery of silver indicated an average recovery of 65% across all water types. The poor recovery data are attributed to the high level spikes (approximately 4 mg/L) which exceed the solubility of the acid mixture used in the method. The mean recovery of silver at the high concentration level was 53% across all water types. The

Table 1. (Continued)

Water Type	Cobalt, Co	Chromium, Cr	Copper, Cu	Iron, Fe	Potassium, K
Applicable Conc. Range	(0.96 - 6.00)	(0.44 - 10.50)	(0.15 - 5.00)	(2.70 - 11.30)	(7.00 - 34.50)
Reagent Water 1					
Single-Analyst Precision	SR = 0.003X + 0.04	SR = 0.029X + 0.02	SR = 0.004X + 0.01	SR = 0.028X + 0.04	SR = 0.049X - 0.16
Overall Precision	S = 0.021X + 0.02	S = 0.087X + 0.01	S = 0.028X + 0.00	S = 0.057X - 0.05	S = 0.103X - 0.24
Mean Recovery	X = 1.017C - 0.00	X = 1.064C + 0.01	X = 0.974C + 0.01	X = 0.958C - 0.03	X = 1.060C - 0.56
Ground Water 1					
Single-Analyst Precision	SR = 0.016X + 0.05	SR = 0.045X + 0.01	SR = 0.019X + 0.00	SR = 0.033X - 0.01	SR = 0.118X - 0.13
Overall Precision	S = 0.061X - 0.03	S = 0.095X + 0.00	S = 0.026X + 0.01	S = 0.083X - 0.15	S = 0.132X - 0.09
Mean Recovery	X = 1.084C - 0.06	X = 1.067C - 0.02	X = 0.970C + 0.01	X = 0.992C + 0.21	X = 1.091C - 0.79
Applicable Conc. Range	(0.36 - 6.00)	(0.44 - 10.50)	(0.15 - 5.00)	(6.75 - 22.50)	(0.33 - 14.20)
Reagent Water 2					
Single-Analyst Precision	SR = 0.023X + 0.01	SR = 0.010X + 0.00	SR = 0.010X + 0.00	SR = 0.17X + 0.11	SR = 0.060X + 0.01
Overall Precision	S = 0.053X - 0.01	S = 0.040X + 0.02	S = 0.016X + 0.00	S = 0.044X + 0.13	S = 0.069X + 0.06
Mean Recovery	X = 1.017C - 0.00	X = 1.065C - 0.01	X = 0.982C - 0.00	X = 0.949C + 0.65	X = 1.042C - 0.07
Ground Water 2					
Single-Analyst Precision	SR = 0.011X + 0.01	SR = 0.027X + 0.01	SR = 0.012X + 0.00	SR = 0.035X + 0.01	SR = 0.051X + 0.04
Overall Precision	S = 0.045X - 0.01	S = 0.136X + 0.03	S = 0.023X + 0.01	S = 0.110X - 0.28	S = 0.095X - 0.00
Mean Recovery	X = 0.988C + 0.01	X = 1.057C + 0.01	X = 0.969C - 0.00	X = 0.964C - 0.03	X = 0.987C - 0.01
Applicable Conc. Range	(12.00 - 60.00)	(13.10 - 43.80)	(0.15 - 5.00)	(2.70 - 11.30)	(0.33 - 14.20)
Reagent Water 3					
Single-Analyst Precision	SR = 0.025X + 0.19	SR = 0.018X + 0.30	SR = 0.004X + 0.01	SR = 0.013X + 0.08	SR = 0.040X + 0.03
Overall Precision	S = 0.056X + 0.11	S = 0.004X + 1.27	S = 0.023X + 0.00	S = 0.065X - 0.04	S = 0.073X + 0.08
Mean Recovery	X = 1.040C - 0.13	X = 1.038C + 1.31	X = 0.983C + 0.01	X = 0.935C + 0.03	X = 1.138C - 0.08
Ground Water 3					
Single-Analyst Precision	SR = 0.032X + 0.19	SR = 0.020X - 0.78	SR = 0.012X + 0.01	SR = 0.048X - 0.06	SR = 0.049X + 0.06
Overall Precision	S = 0.056X + 0.01	S = 0.013X + 2.66	S = 0.037X + 0.01	S = 0.043X + 0.19	S = 0.071X + 0.05
Mean Recovery	X = 1.062C - 1.06	X = 1.107C - 0.01	X = 0.992C + 0.00	X = 0.969C - 0.37	X = 1.189C - 0.05

X = Mean Recovery

C = True Value for the Concentration

mean silver recovery for the low and mid-range Youden pairs across all water types was 85%. It has been shown that silver is soluble at a concentration of 0.05 mg/L in a hydrochloric acid/nitric acid mixture but forms a significant precipitate at 0.5 mg/L. The optimum concentration range specified in SW-846 Method 3005, however, is 0.1 to 4.0 mg/L. Further investigation is needed concerning the acid mixture and optimum range of the method.

Precision

To compare the overall and single-analyst precision and the percent relative standard deviations (%RSD), the mean recovery was calculated by using as the true concentration (C) a mid-point value in the concentration range studied. This calculated mean recovery was inserted

into the overall and single-analyst standard deviation regression equations given in Table 1. The overall %RSD for a single water type ranged from 2.0% for copper to 40.3% for silver. The average overall %RSD for all water types ranged from 2.7% for copper to 33.0% for silver. The average %RSD for all elements/water type was 8.5%.

The single-analyst (SA) %RSD for a single water type ranged from 0.1% to 36.0% for barium and silver, respectively. For all water types and elements, the average SA %RSD ranged from 2.9% to 5.1%. The average SA %RSD or all elements/water types was 4.3%, which is almost one-half of the overall %RSD.

Effects of Water Type

The recovery and precision estimates across water types were subjected to an

analysis of variance test to determine the effect water types had on the results. Establishment of a statistically significant effect due to matrix type does not necessarily mean that the effect was of practical importance. Practical importance was determined by reviewing the retained data and judging whether the statistically significant matrix effects were influenced by the retention of several errant data points or the non-uniform recovery of one Youden concentration pair. If no anomalies were observed, the statistically significant matrix effect was considered to be of practical importance.

Fifteen elements had 18 occurrences that implied a statistically significant effect by one of the matrix waters. Thirteen of the eighteen occurrences show small differences in the percent recovery and %RSD values compared to their reagent water counterparts. Only four elements (barium, cobalt, iron, and lead) showed practical differences in the percent recovery and %RSD values compared to

Table 1. (Continued)

Water Type	Magnesium, Mg	Manganese, Mn	Molybdenum, Md	Sodium, Na	Nickel, Ni
Applicable Conc. Range	(30.00 - 125.00)	(0.05 - 3.35)	(0.75 - 37.50)	(27.50 - 110.00)	(0.25 - 5.50)
Reagent Water 1					
Single-Analyst Precision	SR = 0.000X + 1.51	SR = 0.008X + 0.01	SR = 0.055X + 0.04	SR = 0.070X - 2.03	SR = 0.022X + 0.01
Overall Precision	S = 0.052X + 1.03	S = 0.052X + 0.02	S = 0.223X + 0.05	S = 0.042X - 0.10	S = 0.025X - 0.01
Mean Recovery	X = 0.960C + 1.61	X = 0.983C + 0.00	X = 0.951C - 0.02	X = 0.960C - 0.85	X = 1.002C - 0.00
Ground Water 1					
Single-Analyst Precision	SR = 0.018X + 0.62	SR = 0.030X + 0.00	SR = 0.053X + 0.06	SR = 0.015X + 0.90	SR = 0.026X + 0.00
Overall Precision	S = 0.147X - 1.45	S = 0.054X + 0.00	S = 0.192X + 0.03	S = 0.025X - 1.45	S = 0.024X + 0.05
Mean Recovery	X = 0.902C + 1.22	X = 1.002C + 0.00	X = 0.967C + 0.04	X = 0.955C - 0.63	X = 0.993C - 0.01
Applicable Conc. Range	(4.50 - 30.00)	(1.12 - 3.90)	(0.75 - 37.50)	(11.00 - 41.30)	(0.25 - 5.50)
Reagent Water 2					
Single-Analyst Precision	SR = 0.019X + 0.04	SR = 0.087X - 0.08	SR = 0.032X + 0.01	SR = 0.001X + 0.34	SR = 0.013X + 0.03
Overall Precision	S = 0.030X - 0.12	S = 0.083X - 0.05	S = 0.138X - 0.02	S = 0.045X - 0.16	S = 0.050X + 0.03
Mean Recovery	X = 0.855C + 2.29	X = 1.018C - 0.01	X = 1.009C - 0.03	X = 1.007C - 0.82	X = 1.011C - 0.02
Ground Water 2					
Single-Analyst Precision	SR = 0.017X + 0.11	SR = 0.071X - 0.03	SR = 0.036X + 0.02	SR = 0.019X - 0.01	SR = 0.012X + 0.04
Overall Precision	S = 0.050X - 0.04	S = 0.064X - 0.00	S = 0.160X - 0.05	S = 0.045X + 0.06	S = 0.036X + 0.06
Mean Recovery	X = 0.859C + 1.87	X = 0.992C - 0.01	X = 1.004C + 0.06	X = 0.941C + 0.41	X = 1.008C - 0.04
Applicable Conc. Range	(5.00 - 30.00)	(0.08 - 3.35)	(0.75 - 37.50)	(550.00 - 2750.00)	(4.5 - 27.50)
Reagent Water 3					
Single-Analyst Precision	SR = 0.022X + 0.01	SR = 0.006X + 0.02	SR = 0.030X + 0.04	SR = 0.055X - 8.96	SR = 0.017X + 0.11
Overall Precision	S = 0.070X - 0.22	S = 0.060X + 0.02	S = 0.104X + 0.03	S = 0.042X + 0.61	S = 0.043X + 0.00
Mean Recovery	X = 0.957C + 0.29	X = 1.010C + 0.01	X = 1.146C - 0.08	X = 0.982C + 17.94	X = 0.992C + 0.01
Ground Water 3					
Single-Analyst Precision	SR = 0.053X + 0.24	SR = 0.015X + 0.01	SR = 0.026X + 0.03	SR = 0.020X + 09.76	SR = 0.034X - 0.03
Overall Precision	S = 0.103X - 0.04	S = 0.051X + 0.01	S = 0.118X - 0.03	S = 0.125X - 0.47	S = 0.107X + 0.34
Mean Recovery	X = 0.923C + 0.23	X = 1.010C - 0.01	X = 1.130C + 0.00	X = 1.057C - 13.96	X = 0.975C + 0.66

X = Mean Recovery

C = True Value for the Concentration

their reagent water and were considered to be of practical importance.

Minimum Detection Limits (MDLs)

The average MDL for each water type/element, in almost all cases, agreed closely, indicating virtually no effect of water type on the magnitude of the MDLs. A comparison of these MDLs with the MDLs listed in SW-846 for ground waters showed close agreement for barium, beryllium, magnesium, vanadium, cadmium, chromium, manganese, nickel, molybdenum, and zinc. Elements with higher MDLs than listed SW-846 MDLs were aluminum, calcium, iron, sodium, antimony, and thallium. Elements with lower MDLs than the SW-846 MDLs were potassium, cobalt, copper and lead. These lower detection limits determined from this IMVS study include zero responses reported by the participating laboratories.

Therefore, the average standard deviation was lower, which subsequently reduced the MDLs as calculated in the IMDL equation.

Evaluation of Laboratory Performance with Low Concentration Samples

The final objective of the study was to evaluate the performance of the participating laboratories' performance with samples containing trace metal at concentrations slightly above the MDLs reported in SW-846 methods. Therefore, the three ground waters and reagent water were spiked with Youden pair concentration levels approximating 5x MDL. These were compared with the lowest Youden pair concentrations near the lowest part of the optimum range reported in the SW-846 methods; this was approximately 10x MDL.

The overall %RSD and single-analyst %RSD were used to evaluate per-

formance. Analytes that could not be evaluated due to high background concentration levels in the natural matrices included calcium, iron, potassium, magnesium, manganese, and sodium. Ground water 3 data was also excluded for nickel, copper, cobalt, chromium, and zinc for the same reason.

The overall and single-analyst %RSDs were computed by the IMVS program for each water type. The overall %RSD was averaged between each of the Youden pairs and reported for each water type, with the single-analyst %RSDs for each analyte. To facilitate a general conclusion for all water types at a 5x MDL concentration level versus the lower concentration level of the optimum range, the overall %RSDs were combined, and an average was calculated. The single-analyst %RSDs were similarly treated.

The ratio of the %RSDs (i.e., %RSD for 5x MDL divided by the %RSD for the lower concentration level) provided a

Table 1. (Continued)

Water Type	Lead, Pb	Antimony, Sb	Vanadium, V	Zinc, Zn
Applicable Conc. Range	(0.75 - 18.80)	(0.75 - 37.50)	(1.88 - 93.80)	(0.05 - 1.13)
Reagent Water 1				
Single-Analyst Precision	SR = 0.040X + 0.01	SR = 0.012X + 0.04	SR = 0.047X + 0.04	SR = 0.023X + 0.00
Overall Precision	S = 0.046X + 0.05	S = 0.042X + 0.19	S = 0.121X - 0.09	S = 0.018X + 0.01
Mean Recovery	X = 1.037C + 0.00	X = 1.039C + 0.16	X = 1.051C - 0.16	X = 0.979C + 0.00
Ground Water 1				
Single-Analyst Precision	SR = 0.030X + 0.01	SR = 0.032X + 0.03	SR = 0.024X + 0.08	SR = 0.020X + 0.00
Overall Precision	S = 0.054X - 0.01	S = 0.045X + 0.14	S = 0.123X + 0.17	S = 0.042X + 0.01
Mean Recovery	X = 0.949C + 0.12	X = 1.058C + 0.09	X = 1.092C - 0.08	X = 0.975C + 0.00
Applicable Conc. Range	(0.75 - 18.80)	(0.75 - 37.50)	(1.88 - 93.80)	(0.05 - 1.13)
Reagent Water 2				
Single-Analyst Precision	SR = 0.025X + 0.04	SR = 0.031X + 0.03	SR = 0.035X + 0.06	SR = 0.002X + 0.01
Overall Precision	S = 0.043X + 0.02	S = 0.046X + 0.06	S = 0.062X + 0.11	S = 0.013X + 0.01
Mean Recovery	X = 1.024C + 0.02	X = 1.049C + 0.05	X = 1.045C - 0.04	X = 0.985C - 0.00
Ground Water 2				
Single-Analyst Precision	SR = 0.027X - 0.01	SR = 0.005X + 0.11	SR = 0.040X + 0.02	SR = 0.039X + 0.00
Overall Precision	S = 0.038X + 0.05	S = 0.049X + 0.15	S = 0.107X - 0.03	S = 0.053X + 0.01
Mean Recovery	X = 1.010C + 0.04	X = 1.022C - 0.03	X = 1.050C - 0.12	X = 0.950C + 0.01
Applicable Conc. Range	(0.75 - 18.80)	(0.75 - 37.50)	(1.88 - 93.80)	(0.22 - 1.13)
Reagent Water 3				
Single-Analyst Precision	SR = 0.013X + 0.07	SR = 0.022X + 0.08	SR = 0.063X - 0.07	SR = 0.004X + 0.01
Overall Precision	S = 0.022X + 0.13	S = 0.038X + 0.06	S = 0.104X - 0.17	S = 0.013X + 0.01
Mean Recovery	X = 1.034C + 0.01	X = 1.050C + 0.02	X = 1.091C - 0.08	X = 0.962C + 0.01
Ground Water 3				
Single-Analyst Precision	SR = 0.045X + 0.03	SR = 0.008X + 0.14	SR = 0.020X + 0.12	SR = 0.005X + 0.01
Overall Precision	S = 0.072X - 0.01	S = 0.031X + 0.13	S = 0.115X - 0.04	S = 0.007X + 0.01
Mean Recovery	X = 0.811C + 0.11	X = 1.031C - 0.02	X = 1.091C + 0.10	X = 0.966C + 0.01

X = Mean Recovery

C = True Value for the Concentration

measure of the magnitude of the increase in the %RSD when operating on a routine basis at 5x MDL. For most trace metals, the overall %RSD increased, anywhere from 3.8 times to 1.1; antimony showed no increase, and slight decreases in the overall %RSD were observed for lead and cadmium. The largest overall %RSD at the 5x MDL level occurred for aluminum; this can be explained in part by the fact that the concentration was only one-tenth of the lower limit of the optimum range, and significant quantities of indigenous aluminum were present in each of the three natural matrices.

The smallest overall %RSD at the 5x MDL level occurred for copper. The average overall %RSD for all analytes in the lower concentration level was 15.3% whereas the 5x MDL was 22.1%.

The ratio of the single-analyst %RSD varied from 0.7 for lead to 3.8 for aluminum. Generally, the single-analyst %RSD increased with decreasing concentration, but lead, silver and cadmium

showed slight decreases with decreasing concentration. On the average, for all analytes, the lower concentration had 8.8% RSD, and the 5x MDL samples had 10.8% RSD.

Conclusions and Recommendations

Method 3005 is recommended for the analysis of all specified elements except silver in ground water matrices. The linear regression equations obtained from this study can be used to predict the precision and mean recovery of the covered elements at any concentration in the ranges investigated in this study.

Except for silver and barium, the mean recovery across the three water types studied ranged from 91% to 108% with two exceptions. Barium showed extremely low mean recoveries from ground water 1 (67%) and ground water 3 (50%).

Barium recovery from reagent water was 98%.

For silver, the mean recovery of each of the three Youden pairs decreased significantly with increased concentration in the range studied (0.1-4.0 mg/L). The digestion procedure in SW-846 Method 3005 employs hydrochloric acid, and precipitation occurred at the high concentration levels. Further studies should be conducted to determine the optimum silver concentration range for this method or the appropriate acid mixture to be used in the digestion procedure.

The overall standard deviation expressed as %RSD, averaged across the waters studied, ranged from 2% to 19%. The only exception was silver with a %RSD of 34%.

The single-analyst standard deviation expressed as the previously defined SA %RSD, averaged across all water types, ranged from 1% to 7%. Silver was again the only exception at 22% with %RSD ranging from 14% to 36%.

Table 1. (Continued)

Water Type	Silver, Ag	Thallium, Tl
Applicable Conc. Range	(0.09 - 4.13)	(0.94 - 20.70)
<i>Reagent Water 4</i>		
Single-Analyst Precision	$SR = 0.213X - 0.00$	$SR = 0.038X + 0.01$
Overall Precision	$S = 0.418X - 0.02$	$S = 0.054X + 0.08$
Mean Recovery	$X = 0.578C + 0.04$	$X = 0.945C + 0.04$
<i>Ground Water 1</i>		
Single-Analyst Precision	$SR = 0.360X - 0.00$	$SR = 0.020X + 0.07$
Overall Precision	$S = 0.415X - 0.00$	$S = 0.063X + 0.01$
Mean Recovery	$X = 0.534C + 0.03$	$X = 0.987C + 0.07$
<i>Ground Water 2</i>		
Single-Analyst Precision	$SR = 0.167X - 0.01$	$SR = 0.031X + 0.07$
Overall Precision	$S = 0.247X - 0.01$	$S = 0.087X - 0.01$
Mean Recovery	$X = 0.696C + 0.02$	$X = 0.960C + 0.09$
<i>Ground Water 3</i>		
Single-Analyst Precision	$SR = 0.143X - 0.00$	$SR = 0.009X + 0.12$
Overall Precision	$S = 0.279X - 0.01$	$S = 0.041X + 0.07$
Mean Recovery	$X = 0.729C + 0.02$	$X = 1.000C + 0.07$
$X = \text{Mean Recovery}$ $C = \text{True Value for the Concentration}$		

statistical comparisons were performed on all analytes to determine effects of water type. Statistically significant effects were found for barium, beryllium, cobalt, chromium, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel, lead, antimony, thallium, and zinc. The effect was not, however, considered of practical importance for any analytes except barium, cobalt, iron, and lead (See Treatment of Data section in the main report for details.)

Interlaboratory MDLs were determined for 21 trace elements. Comparison with MDLs specified in SW-846 showed close agreement for barium, beryllium, magnesium, vanadium, cadmium, chromium, manganese, nickel, molybdenum, silver, and zinc. Elements exhibiting greater MDLs than those in SW-846 methods were aluminum, calcium, iron, sodium, antimony and thallium. Elements exhibiting MDLs less than those in SW-846 methods were potassium, cobalt, copper, and lead.

The SW-846 methods specify optimum concentration ranges for trace metal analyses which usually begin at 10x MDLs. A pair of spiked samples were included in this study to obtain overall and e-analyst precision data at approximately 5x MDL. The percent overall

%RSD of the 10x MDL samples averaged 16.0% for all elements; this agreed well with 22.7% for the 5x MDL level. The single-analyst %RSD for the 10x MDL samples averaged 9.1% for all elements; this agreed well with 11.2% for the 5x MDL level.

Kenneth W. Edgell is with The Bionetics Corporation, Cincinnati, OH 45246

Edward L. Berg is the EPA Project Officer (see below).

The complete report, entitled "USEPA Method Study 35: SW-846 Method 3005: Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analyses by Flame Atomic Absorption Spectroscopy," (Order No. PB 89-190 573/AS; Cost: \$28.95, 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

Cincinnati, OH 45268

United States
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