



Project Summary

USEPA Method Study 38 SW-846 Method 3010 Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Flame Atomic Absorption Spectroscopy

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An interlaboratory method validation study was conducted on SW-846 Method 3010, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Flame Atomic Absorption Spectroscopy," to determine the mean recovery and precision for analyses of 21 trace metals in surface and wastewaters. SW-846 Method 3010 includes instructions for quality control, sample preparation, and analysis of samples by flame atomic absorption spectroscopy (FLAA).

The study design was based upon Youden's non-replicate plan for collaborative tests of analytical methods. Four water matrices were spiked with 21 trace metals at six concentration levels, as three Youden pairs. Nine laboratories digested and refluxed the spiked water matrices with concentrated nitric acid, brought them to volume with dilute hydrochloric acid, and analyzed each for 21 trace metals by FLAA. The primary objective of the study was to analyze the results using USEPA computer programs entitled "Interlaboratory Method Validation Study" (IMVS) which produced measures of recovery and

precision for the 21 trace metals and compared the performance of the method between water types.

Two additional studies were also conducted on Method 3010. One study compared minimum detection limits (MDLs) reported in the SW-846 method manual to MDLs determined using Method 3010. Another study was conducted to verify that the lowest concentration levels of the optimum range given in the SW-846 method manual are valid. Comparison between the samples at the lowest concentration level specified in SW-846 and another sample at 50% that value were performed for mean recovery, overall precision, and single-analyst precision.

The studies were conducted by The Bionetics Corporation under the direction of the Quality Assurance Research Division, Environmental Monitoring Systems Laboratory, Cincinnati, OH under Contract No. 68-03-3254. Analytical work was completed as of November 30, 1987. The report covers a period from September 10, 1986 to February 28, 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 were promulgated in July, 1982 (40 CFR 265) and provide performance standards for the monitoring of ground waters, wastewaters and solid wastes at hazardous waste sites. To facilitate these standards, certain analytical methodology 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 provided by the laboratories. Therefore, it is important to evaluate the methodology through interlaboratory method validation studies.

The Environmental Monitoring Systems Laboratory, Cincinnati, OH (EMSL-Cincinnati) develops or selects analytical methods and provides quality assurance (QA) support for Agency programs involving water and wastewater regulations. In EMSL-Cincinnati the responsibility for providing support is assigned to the Quality Assurance Research Division (QARD). Its program is designed to provide the QA support needed to establish the reliability and legal defensibility of water and wastewater data collected by the Agency, the state regulating authorities, the private sector, and commercial laboratories performing compliance analyses. One of QARD's 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 an interlaboratory method validation study for SW-846 Method 3010, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Flame Atomic Absorption Spectroscopy." 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 using Method 3010.

The primary objective of the study was to characterize the behavior of Method 3010 in terms of recovery, overall and single-analyst precision, and the effect of water type on recovery and precision. The study was conducted with the cooperation of nine participating laboratories under the direction of the Quality Assurance Research Division, EMSL-Cincinnati. The Bionetics Corporation, as primary contractor to QARD, was responsible for the collection and characterization of the water matrices, preparation of analyte spiking solutions, preparation of user instructions and report forms, distribution of samples, and screening 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.

A second objective of the study was to compare the minimum detection limits (MDLs) reported in the SW-846 method manual to the MDLs determined for the 21 elements using Method 3010. The MDL for each element was obtained by measuring the noise level response for seven reagent water digestates with no detectable background. The mean and standard deviation of the noise level responses were then calculated. Then, each of the four water matrices was digested and used to prepare a 5 point calibration curve by the Method of Standard Additions. The MDLs were calculated using the following relationship:

$$MDL = 3(SD)/m$$

where,

- m = $(y-i)/x$ = slope of the calibration curve
- x = concentration (ug/mL)
- y = signal at concentration x
- i = intercept of the calibration curve
- SD = standard deviation of the noise level responses

A third study objective was to verify that the lowest concentration levels of the optimum range specified in the SW-846 method manual are valid. Comparison between the samples at the lowest concentration level and another sample at 50% that value was performed for mean recovery, overall precision and single-analyst precision.

Description of Study

Method Summary

In SW-846 Method 3010, 100 mL sample is digested with 3 mL concentrated nitric acid, evaporated about 5 mL on a hot plate, then combined with 3 mL concentrated nitric acid and refluxed. After cooling, 1:1 hydrochloric acid is added. The sample is then diluted to 100 mL with Type II water. The sample is then ready for analyses for aluminum, antimony, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, silver, sodium, thallium, vanadium, and zinc by flame atomic absorption spectroscopy (FLAA).

Study Design

The study design was based on Youden's non-replicate design for collaborative evaluation of an analytical method at several concentration levels over its linear range. According to Youden's design, two similar yet different samples are analyzed in pairs such that the concentration of the pairs varies between 5 and 20 percent of the mean of the pairs. For this study, six concentration levels, as three Youden pairs, were used (designated samples 1 - 6). The analyst was directed to do a single analysis for each sample and report one value for each element. Analyses in reagent water were evaluated to determine the proficiency of the method on a sample free of interference. Analyses in the other matrix waters were intended to reveal the effects of interferences on the method.

The primary contractor prepared the study samples by spiking measured amounts of standard solutions into the matrix waters being tested. Each spiked matrix water was then dispensed into replicate 120 mL bottles for distribution to participants. The analysts were instructed to quantitatively remove a 100 mL aliquot from each sample bottle for digestion and analysis. A matrix blank and a quality control sample, included in the study, were digested with six samples for each water type. Background concentration levels found in the matrix blanks were subtracted from the total concentration found in each sample. Acceptance limits were provided for the quality control samples to verify that the analytical system was in control. If not in control, the problem was to be corrected on fresh aliquots of the samples, associated

with that QC sample, had to be digested and reanalyzed.

Spiking solutions were provided for the MDL phase of the study. These concentrates were used to spike aliquots of the digested matrix waters by the Method of Standard Additions.

Finally, an additional Youden sample pair, designated 7-8, was included in this study. These samples were prepared at 50% of the concentration level of samples 5-6, which were at the lowest concentration level of the optimum working range specified in SW-846. Digestion and analyses of these samples were to proceed the same as for the regular six samples.

Verification Analyses

To assure that the spiking solutions were properly prepared, they were analyzed using freshly prepared standards before being spiked into the test waters. A set of spiked test waters was then digested and submitted to QARD analysts to verify sample integrity. These analyses confirmed the accuracy of the distributed samples.

Selection of Test Waters

The four test waters selected for this study were reagent water, as the control, Ohio River Water, an electroplating company effluent and a municipal sewage treatment plant secondary effluent.

Each test water was preserved, at the time of collection, by adjusting the pH to below 2.0. Prior to dispensing, each test water was thoroughly mixed to ensure homogeneity. Aliquots were removed from each, digested according to Method 3010, then sent to QARD analysts for Inductively Coupled Plasma Spectroscopy analyses to determine the background concentrations of the 21 elements covered in this study.

Selection of Participating Laboratories

The Quality Assurance Research Division of EMSL-Cincinnati selected the participating laboratories. As per the standard competitive bid process, an abstract of the scope of work was announced in the Commerce Business Daily. Interested laboratories were forwarded the complete request for proposal (RFP) which included the evaluation criteria upon which the offeror would be scored.

The submitted 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 nine laboratories with acceptable proposals who performed best in the preaward study.

Results and Discussion

The primary objective of this study was to characterize the performance of SW-846 Method 3010 in terms of recovery, overall precision, single-analyst precision and the effect of water type on recovery and precision. The statistical results for each of these performance characteristics will be discussed below.

Rejection of Outliers

In this study, the IMVS program rejected a total of 995 data points or 21.9% of the 4536 data points submitted. Reagent water had the lowest number of rejected data with 195. The number of rejected data was higher for the other test waters but did not vary significantly among the waters. The number of rejected data were 279 for Ohio River Water, 258 for municipal secondary effluent, and 263 for electroplating effluent. For a single element, across all water types, the number of rejected data ranged from a low of 25 for thallium to a high of 78 for beryllium. For purposes of this report, an element was considered to have excessive outliers if its total number of rejected data was equal to or greater than 54 (25% of the total submitted data). Using this criterion, the following eight elements fell into this category: aluminum (57), beryllium (78), chromium (56), cobalt (54), molybdenum (54), sodium (58), vanadium (61), and zinc (72). Laboratory 6 had the highest number of rejected data with 234 while Laboratory 7 had the lowest number of rejected data with 27.

Mean Recovery

The mean recoveries were calculated for the 21 elements in each water type by inserting the midpoint concentration of the range studied into the mean recovery equations given in Table 1. For reagent water the percent recoveries for the 21 trace metals were excellent, ranging from 91% to 108%, with silver (44%) being the only exception. For all waters, the recoveries ranged from 94% to 109% with barium (74%) and silver (28%) as the exceptions.

A look at the barium recovery estimates shows excellent results for

reagent water (97%) and Ohio River Water (98%) but extremely poor recoveries for the municipal secondary effluent (60%) and the electroplating effluent (42%). It was theorized that sulfur oxides were present in the later waters causing barium to precipitate as the sulfate.

Low silver recoveries, i.e., as low as 9%, were reported in all water types. The percent recoveries of silver in reagent water showed acceptable recovery for the low Youden pair samples, 98% and 96%, with a significant decrease in percent recovery with increasing concentrations. This indicates a solubility problem with silver at higher concentration levels.

Precision

The mean overall precision for all metals, expressed as %RSDs, across water types, ranged from 2.9% for thallium to 13.9% for calcium with two exceptions, barium (31.2%) and silver (65.7%). The poor silver precision was observed in all water types while the barium precision was acceptable for reagent water (13.9%) and Ohio River Water (12.0%) and poor for the municipal secondary effluent (31.6%) and the electroplating effluent (67.2%). The %RSDs in reagent water ranged from 2.6% (thallium) to 13.9% (barium) with the exception of silver (52.6%).

The single-analyst precision for all metals, expressed as %RSD-SRs, across water types, ranged from 1.6% (copper) to 7.6% (calcium) with two exceptions, barium (15.2%) and silver (37.4%). The poor single-analyst precision for silver was observed in all water types while the barium precision was acceptable for reagent water (6.5%) and Ohio River Water (8.4%) and poor for the municipal secondary effluent (16.9%) and the electroplating effluent (28.8%). The %RSD-SRs for all elements in reagent water ranged from 1.2% (nickel) to 8.0% (calcium) with silver 30.9% being the only exception.

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 type had on the results. Nine elements: calcium, cobalt, iron, manganese, molybdenum, sodium, antimony, zinc, and barium were found to have statistically significant matrix effects that were of practical significance when compared to reagent water. Lead was also found to have a statistically significant matrix effect but this was not considered to be of practical significance.

Practical significance was determined by a review of the retained data and judging whether the statistically significant matrix effects are influenced by the retention of errant data points or non-uniform recovery of one of the Youden sample pairs. If no anomalies are found, the effect was considered to be of practical significance. The effect of water type on analyses for silver was not evaluated because of the poor recovery and precision results obtained.

Method Detection Limits (MDLs)

Method detection limits (MDLs) were experimentally determined in the four test waters by nine participating laboratories. The MDL for each element in reagent water was compared with the MDLs found in the SW-846 method manual. This comparison showed for the elements: barium, molybdenum, cobalt, copper, nickel, and thallium, MDLs in this study were 1 to 1.5 times higher than the SW-846 MDLs. The MDLs for elements aluminum, beryllium, calcium, iron, magnesium, antimony, vanadium, silver, cadmium, chromium, manganese, lead, and zinc were 2 to 3 times higher than the SW-846 MDLs. The MDL for potassium was one fifth of the SW-846 MDL while the MDL for sodium was 7.5 times higher than the SW-846 MDL.

Evaluation of Lowest Concentration Levels

The final objective of this study was to verify that the lowest concentration levels specified in the SW-846 method manual are obtainable. Comparison between a sample at the lowest specified concentration level with another sample at 50% of that concentration level was performed for mean recovery, overall precision and single-analyst precision. The net changes in the mean recoveries were compared in reagent water for the 21 elements. The average percent recovery for the sample at 50% concentration level was only 3.0% lower than the average percent recoveries at the lowest concentration level specified by the SW-846 method manual. Twelve elements: aluminum, calcium, cobalt, chromium, copper, iron, magnesium, sodium, nickel, lead, vanadium, and barium had less than $\pm 5\%$ net change in percent recovery. Six elements: beryllium, cadmium, manganese, antimony, zinc, and potassium had a net change between $\pm (5\% - 10\%)$. For molybdenum and thallium, the percent recoveries for the 50% concentration

levels were 19.6% and 16.7% lower, respectively, than the percent recoveries for the lowest concentration specified in SW-846. Silver had a mean recovery 17.4% higher, for the 50% concentration level, when compared to the specified concentration.

The average overall %RSD for the sample at 50% the method concentration level was 4.9% higher than the average overall %RSD at the lowest concentration specified in the SW-846 method manual. Fourteen elements: aluminum, calcium, cobalt, chromium, copper, iron, magnesium, molybdenum, sodium, lead, vanadium, zinc, barium, and potassium had a net change in %RSD of less than $\pm 5\%$. Five elements: beryllium, cadmium, manganese, nickel, and antimony had a net change in %RSD between $\pm (5\% - 10\%)$. The overall %RSD for silver and thallium at the 50% concentration level was 14.0% and 26.9% respectively, higher than the %RSDs at the lowest specified SW-846 concentration.

The average single-analyst precision for samples at 50% the concentration level, was 0.9% higher than the samples at the lowest concentration level specified in SW-846. Twelve elements: aluminum, antimony, barium, beryllium, cadmium, cobalt, copper, magnesium, potassium, silver, sodium, and thallium had net changes less than $\pm 5\%$. Seven elements: calcium, chromium, lead, manganese, nickel, vanadium, and zinc had net changes between $\pm (5\% - 10\%)$. For iron and molybdenum, the single-analyst precision was 11.8% and 15.4% higher, respectively, for the 50% concentration level sample.

Conclusions

The primary objective of this study was to characterize the performance of Method 3010 in terms of recovery, overall precision, single-analyst precision, and the effect of water types on recovery and precision. Through the IMVS computer programs, statistical analyses of 4536 analytical values provided estimates of recovery and precision expressed as regression equations which are presented in Table 1. These equations may be used to predict the recovery and precision of the 21 elements over the range tested.

The IMVS programs rejected 995 data points (21.9%) of the 4536 data points submitted. The percentage of rejected data did not vary significantly among the water types, ranging from 20% for reagent water to 28% for Ohio River Water. Thallium had the fewest rejected

data with 15 while beryllium had the most with 78. The number of rejected data per laboratory ranged from 27 for Lab 7 to 234 for Lab 6. The rejected data were not evenly distributed among the laboratories. Labs 3, 4, 6 and 7 accounted for 624 of the 995 total rejected data (62.7%).

Recovery estimates for the 21 elements were calculated at the midpoint concentration of the range studied using the regression equations in Table 1. The average percent recovery of all elements across all water types were excellent ranging from 94% to 109% with two exceptions, silver (28%) and barium (74%).

Silver recoveries were concentration dependent. The silver concentration range used in this study was 0.10 to 4.0 ug/mL as recommended in the SW-846 method manual. In reagent water the percent recoveries of the low sample concentration pair, 0.10 and 0.15 ug/mL were 97.8% and 95.6% respectively. However, as the concentration level increased the percent recovery decreased dramatically to 20% at the 4.0 ug/mL concentration level. These findings support the conclusions of Hinners, EMSL-Las Vegas, as referenced in the main report.

Barium recoveries were good in reagent water (97%) and Ohio River Water (98%), but were poor in municipal secondary effluent (60%) and electroplating effluent (42%). It was theorized that the presence of sulfide oxides in the later two water matrices caused the barium to precipitate as barium sulfate.

For all metals, the overall standard deviations expressed as %RSD, were good. Across all water types the range was from 3% to 14% with the exception of silver (66%) and barium (31%). The high silver variability was observed in all four test waters while the barium %RSD was high in the municipal secondary effluent (32%) and the electroplating effluent (67%), and low in reagent water (14%) and Ohio River Water (12%).

The single-analyst standard deviations expressed as %RSD-SR, were good. Across all water types the range was from 2% to 8% with the exceptions of silver (34%) and barium (15%). The high silver variability was observed in all four test waters while the barium %RSD-SR was high in the municipal secondary effluent (17%) and electroplating effluent (29%) and low in reagent water (6%) and Ohio River Water (8%).

Statistical comparisons were performed on all elements to determine if there were

effects due to water type. The statistically significant matrix effects for calcium, cobalt, iron, manganese, molybdenum, sodium, zinc, silver and barium were found to be of practical significance. The statistically significant matrix effects were not considered to be of practical significance for lead and antimony. The silver statistics were too variable to draw any conclusions.

Method detection limits (MDLs) were determined experimentally by nine laboratories on 21 elements in the four test waters. In reagent water, the experimental MDLs for barium, molybdenum, cobalt, copper, nickel, and gallium were equivalent to the SW-846 method manual MDLs (1 to 1.5 times the SW-846 MDLs). Aluminum, beryllium, calcium, iron, magnesium, antimony, vanadium, silver, cadmium, chromium, manganese, lead, and zinc had MDLs 2 to 3 times higher than those reported in the SW-846 manual. Potassium was one fifth lower and sodium was 7.5 times higher than the SW-846 MDLs. Except for potassium and sodium, the experimentally determined MDLs in this study approximated the MDLs reported in SW-846.

The analyses of the additional Youden sample pair indicated that Method 3010 can be used to analyze elements at a concentration level 50% lower than recommended in SW-846 with a decrease in recovery on the average of 3.0% and a decrease in overall and single-analyst precision on the average of 0.9% and 0.9%, respectively.

Recommendations

SW-846 Method 3010 is recommended for the analysis of aluminum, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, sodium, nickel, lead, antimony, thallium, vanadium, zinc, and potassium in wastewaters. The linear regression equations obtained from this study, and presented in Table 1, can be used to predict the mean recovery, overall precision and single-analyst precision of these elements at concentrations in the ranges investigated in this study.

Statistical review of barium data revealed low recovery and poor precision (high variability) in municipal secondary effluent and electroplating effluent but good recovery and precision from reagent water and Ohio River Water. Precipitation reactions involving barium sulfate have been hypothesized for these matrix effects. Analysts are cautioned to

interpret barium data carefully from any water matrix.

The mean recovery of silver was found to decrease significantly with increasing concentration in the range studied (0.1 -

4.0 ug/mL). These findings, as well as those of Hinners, suggest that further investigation into the optimum working range for silver analyses is recommended

Table 1. Study 38, SW 846 Method 3010. Trace Metals, AA Flame Weighted Linear Regression Equations for Mean Recovery and Precision (in µg/ml).

Water Type	Aluminum, Al	Beryllium, Be	Calcium, Ca
Applicable Conc. Range	(5.00 - 50.00)	(0.04 - 2.00)	(18.00 - 120.00)
Reagent Water			
Single-Analyst Precision	SR = 0.054X + 0.17	SR = 0.019X + 0.01	SR = 0.097X - 0.87
Overall Precision	S = 0.086X - 0.02	S = 0.118X + 0.00	S = 0.117X - 0.02
Mean Recovery	X = 1.026C - 0.29	X = 0.913C + 0.00	X = 1.001C + 2.12
Water 1			
Single-Analyst Precision	SR = 0.02X + 0.09	SR = 0.020X + 0.00	SR = 0.105X - 0.71
Overall Precision	S = 0.071X - 0.07	S = 0.054X - 0.00	S = 0.200X - 2.41
Mean Recovery	X = 0.947C - 0.25	X = 0.951C + 0.00	X = 0.938C - 1.36
Water 2			
Single-Analyst Precision	SR = 0.021X + 0.08	SR = 0.032X + 0.00	SR = 0.018X + 2.46
Overall Precision	S = 0.026X + 0.37	S = 0.048X + 0.00	S = 0.122X + 1.29
Mean Recovery	X = 0.993C - 0.32	X = 0.966C + 0.00	X = 1.051C + 0.97
Water 3			
Single-Analyst Precision	SR = 0.024X - 0.02	SR = 0.020X + 0.00	SR = 0.016X + 2.67
Overall Precision	S = 0.036X + 0.06	S = 0.038X + 0.00	S = 0.167X - 0.95
Mean Recovery	X = 1.019C - 0.21	X = 0.967C + 0.00	X = 0.894C + 2.28

Water Type	Cadmium, Cd	Cobalt, Co
Applicable Conc. Range	(0.04 - 2.00)	(2.50 - 15.00)
Reagent Water		
Single-Analyst Precision	SR = 0.017X + 0.00	SR = 0.032X - 0.05
Overall Precision	S = 0.029X + 0.00	S = 0.066X - 0.07
Mean Recovery	X = 0.993C + 0.00	X = 0.985C + 0.01
Water 1		
Single-Analyst Precision	SR = 0.016X + 0.00	SR = 0.015X + 0.06
Overall Precision	S = 0.034X + 0.00	S = 0.086X + 0.00
Mean Recovery	X = 0.989C - 0.00	X = 0.992C - 0.09
Water 2		
Single-Analyst Precision	SR = 0.022X + 0.00	SR = 0.014X + 0.21
Overall Precision	S = 0.042X + 0.01	S = 0.056X + 0.20
Mean Recovery	X = 0.988C + 0.00	X = 0.961C + 0.39
Water 3		
Single-Analyst Precision	SR = 0.019X + 0.00	SR = 0.031X - 0.04
Overall Precision	S = 0.029X + 0.01	S = 0.044X + 0.08
Mean Recovery	X = 1.001C + 0.00	X = 0.990C - 0.05

X = Mean Recovery

C = True Value for the Concentration

Water 1 = Ohio River Water

Water 2 = Municipal Secondary Effluent

Water 3 = Electroplating Effluent

Table 1. (Continued)

<i>Water Type</i>	<i>Chromium, Cr</i>	<i>Copper, Cu</i>	<i>Iron, Fe</i>	<i>Magnesium, Mg</i>
<i>Applicable Conc. Range</i>	<i>(0.50 - 10.00)</i>	<i>(0.20 - 5.00)</i>	<i>(0.30 - 5.00)</i>	<i>(5.00 - 40.00)</i>
<i>Reagent Water</i>				
<i>Single-Analyst Precision</i>	$SR = 0.019X + 0.06$	$SR = 0.012X + 0.01$	$SR = 0.010X + 0.05$	$SR = 0.022X - 0.03$
<i>Overall Precision</i>	$S = 0.090X + 0.01$	$S = 0.030X + 0.01$	$S = 0.051X + 0.03$	$S = 0.058X - 0.24$
<i>Mean Recovery</i>	$X = 1.082C - 0.03$	$X = 0.997C + 0.00$	$X = 0.955C + 0.01$	$X = 1.027C - 0.02$
<i>Water 1</i>				
<i>Single-Analyst Precision</i>	$SR = 0.030X - 0.00$	$SR = 0.024X - 0.00$	$SR = 0.031X + 0.06$	$SR = 0.009X + 0.22$
<i>Overall Precision</i>	$S = 0.079X + 0.03$	$S = 0.026X + 0.01$	$S = 0.058X + 0.10$	$S = 0.020X + 0.35$
<i>Mean Recovery</i>	$X = 1.093C + 0.02$	$X = 0.988C + 0.00$	$X = 0.962C - 0.12$	$X = 1.018C - 0.10$
<i>Water 2</i>				
<i>Single-Analyst Precision</i>	$SR = 0.027X + 0.03$	$SR = 0.010X + 0.00$	$SR = 0.002X + 0.08$	$SR = 0.072X - 0.10$
<i>Overall Precision</i>	$S = 0.071X + 0.03$	$S = 0.022X + 0.01$	$S = 0.027X + 0.10$	$S = 0.059X + 0.07$
<i>Mean Recovery</i>	$X = 1.116C - 0.06$	$X = 0.993C + 0.01$	$X = 0.985C - 0.05$	$X = 1.021C - 0.20$
<i>Water 3</i>				
<i>Single-Analyst Precision</i>	$SR = 0.034X + 0.00$	$SR = 0.016X - 0.00$	$SR = 0.026X + 0.04$	$SR = 0.014X + 0.08$
<i>Overall Precision</i>	$S = 0.088X + 0.07$	$S = 0.036X + 0.01$	$S = 0.075X + 0.06$	$S = 0.034X - 0.00$
<i>Mean Recovery</i>	$X = 1.077C - 0.02$	$X = 0.997C + 0.00$	$X = 1.065C - 0.15$	$X = 1.011C - 0.03$

<i>Water Type</i>	<i>Manganese, Mn</i>	<i>Molybdenum, Md</i>	<i>Sodium, Na</i>	<i>Nickel, Ni</i>
<i>Applicable Conc. Range</i>	<i>(0.10 - 3.00)</i>	<i>(1.00 - 40.00)</i>	<i>(96.00 - 600.00)</i>	<i>(0.30- 5.00)</i>
<i>Reagent Water</i>				
<i>Single-Analyst Precision</i>	$SR = 0.020X + 0.01$	$SR = 0.064X + 0.25$	$SR = 0.038X - 1.82$	$SR = 0.004X + 0.02$
<i>Overall Precision</i>	$S = 0.030X + 0.01$	$S = 0.107X + 0.22$	$S = 0.068X - 0.42$	$S = 0.029X + 0.03$
<i>Mean Recovery</i>	$X = 1.019C + 0.01$	$X = 1.031C - 0.012$	$X = 1.025C - 0.17$	$X = 0.991C - 0.01$
<i>Water 1</i>				
<i>Single-Analyst Precision</i>	$SR = 0.011X + 0.00$	$SR = 0.058X - 0.01$	$SR = 0.025X - 0.80$	$SR = 0.015X + 0.01$
<i>Overall Precision</i>	$S = 0.020X + 0.02$	$S = 0.111X - 0.05$	$S = 0.038X + 0.37$	$S = 0.051X - 0.00$
<i>Mean Recovery</i>	$X = 1.008C - 0.01$	$X = 1.011C + 0.019$	$X = 0.986C + 2.44$	$X = 0.997C - 0.01$
<i>Water 2</i>				
<i>Single-Analyst Precision</i>	$SR = 0.006X + 0.01$	$SR = 0.049X + 0.02$	$SR = 0.066X - 2.56$	$SR = 0.026X + 0.03$
<i>Overall Precision</i>	$S = 0.027X + 0.01$	$S = 0.143X - 0.07$	$S = 0.066X + 2.03$	$S = 0.032X + 0.05$
<i>Mean Recovery</i>	$X = 0.987C - 0.00$	$X = 1.051C + 0.107$	$X = 0.991C - 1.80$	$X = 1.020C - 0.02$
<i>Water 3</i>				
<i>Single-Analyst Precision</i>	$SR = 0.020X + 0.00$	$SR = 0.043X + 0.08$	$SR = 0.050X + 0.14$	$SR = 0.008X + 0.04$
<i>Overall Precision</i>	$S = 0.048X + 0.00$	$S = 0.123X - 0.02$	$S = 0.033X + 11.92$	$S = 0.034X + 0.02$
<i>Mean Recovery</i>	$X = 1.024C + 0.00$	$X = 1.002C + 0.043$	$X = 0.988C - 8.91$	$X = 1.011C - 0.01$

X = Mean Recovery

C = True Value for the Concentration

Water 1 = Ohio River Water

Water 2 = Municipal Secondary Effluent

Water 3 = Electroplating Effluent

Table 1. (Continued)

<i>Water Type</i>	<i>Lead, Pb</i>	<i>Antimony, Sb</i>	<i>Thallium, Tl</i>	<i>Vanadium, V</i>
<i>Applicable Conc. Range</i>	(0.80 - 20.00)	(1.20 - 40.00)	(1.00 - 20.00)	(2.25 - 99.00)
<i>Reagent Water</i>				
<i>Single-Analyst Precision</i>	SR = 0.018X + 0.03	SR = 0.023X + 0.19	SR = 0.009X + 0.07	SR = 0.064X + 0.15
<i>Overall Precision</i>	S = 0.019X + 0.09	S = 0.044X + 0.20	S = 0.021X + 0.05	S = 0.109X - 0.02
<i>Mean Recovery</i>	X = 1.031C - 0.02	X = 1.057C - 0.25	X = 1.039C - 0.03	X = 1.047C + 0.003
<i>Water 1</i>				
<i>Single-Analyst Precision</i>	SR = 0.028X + 0.05	SR = 0.031X + 0.10	SR = 0.019X + 0.05	SR = 0.045X - 0.06
<i>Overall Precision</i>	S = 0.047X + 0.01	S = 0.066X + 0.12	S = 0.033X + 0.05	S = 0.099X - 0.12
<i>Mean Recovery</i>	X = 1.023C + 0.04	X = 1.055C - 0.22	X = 1.028C - 0.04	X = 1.052C + 0.06
<i>Water 2</i>				
<i>Single-Analyst Precision</i>	SR = 0.030X + 0.01	SR = 0.017X + 0.14	SR = 0.016X + 0.01	SR = 0.027X + 0.01
<i>Overall Precision</i>	S = 0.046X + 0.05	S = 0.039X + 0.19	S = 0.017X + 0.06	S = 0.128X - 0.14
<i>Mean Recovery</i>	X = 1.046C - 0.08	X = 1.049C - 0.11	X = 1.028C - 0.03	X = 1.056C - 0.08
<i>Water 3</i>				
<i>Single-Analyst Precision</i>	SR = 0.047X - 0.02	SR = 0.003X + 0.07	SR = 0.013X + 0.05	SR = 0.011X + 0.03
<i>Overall Precision</i>	S = 0.082X - 0.04	S = 0.006X + 0.19	S = 0.024X + 0.05	S = 0.079X - 0.04
<i>Mean Recovery</i>	X = 0.976C + 0.03	X = 1.050C + 0.01	X = 1.032C - 0.01	X = 1.055C + 0.03

<i>Water Type</i>	<i>Zinc, Zn</i>	<i>Silver, Ag</i>	<i>Barium, Ba</i>	<i>Potassium, K</i>
<i>Applicable Conc. Range</i>	(0.10 - 1.00)	(0.10- 4.00)	(1.00 - 20.00)	(4.80 - 30.00)
<i>Reagent Water</i>				
<i>Single-Analyst Precision</i>	SR = -0.009X + 0.01	SR = 0.343X - 0.03	SR = 0.067X - 0.02	SR = 0.012X + 0.38
<i>Overall Precision</i>	S = 0.035X + 0.01	S = 0.583X - 0.05	S = 0.142X - 0.03	S = 0.080X + 0.02
<i>Mean Recovery</i>	X = 0.984C + 0.01	X = 0.402C + 0.07	X = 0.961C + 0.05	X = 0.923C + 0.15
<i>Water 1</i>				
<i>Single-Analyst Precision</i>	SR = 0.039X + 0.02	SR = 0.221X - 0.00	SR = 0.089X - 0.05	SR = 0.069X + 0.00
<i>Overall Precision</i>	S = 0.067X + 0.02	S = 0.765X - 0.04	S = 0.127X - 0.07	S = 0.113X - 0.10
<i>Mean Recovery</i>	X = 0.983C - 0.06	X = 0.172C + 0.07	X = 0.970C + 0.07	X = 0.916C + 0.01
<i>Water 2</i>				
<i>Single-Analyst Precision</i>	SR = -0.022X + 0.05	SR = 0.368X - 0.03	SR = 0.197X - 0.17	SR = 0.055X + 0.18
<i>Overall Precision</i>	S = -0.007X + 0.06	S = 0.601X - 0.05	S = 0.361X - 0.27	S = 0.107X + 0.01
<i>Mean Recovery</i>	X = 0.959C + 0.02	X = 0.345C + 0.06	X = 0.536C + 0.64	X = 0.921C + 0.37
<i>Water 3</i>				
<i>Single-Analyst Precision</i>	SR = 0.021X + 0.02	SR = 0.979X - 0.06	SR = 0.389X - 0.42	SR = 0.032X + 0.36
<i>Overall Precision</i>	S = 0.026X + 0.02	S = 0.956X - 0.01	S = 0.874X - 0.84	S = 0.052X + 0.45
<i>Mean Recovery</i>	X = 0.953C + 0.00	X = 0.058C + 0.06	X = 0.329C + 0.86	X = 0.961C - 0.06

X = Mean Recovery

C = True Value for the Concentration

Water 1 = Ohio River Water

Water 2 = Municipal Secondary Effluent

Water 3 = Electroplating Effluent

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The complete report, entitled "USEPA Method Study 38 SW-846 Method 3010 Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Flame Atomic Absorption Spectroscopy," (Order No. PB 89-181 945/AS; Cost: \$21.95, subject to change) will be available only from:

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