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Project Summary

EPA Method Study 31: Trace Metals by Atomic Absorption (Furnace Techniques)

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An interlaboratory study in which 10 laboratories participated was conducted to provide precision and accuracy statements for the analysis of 18 metals by graphite furnace atomic absorption spectrometry. Samples were prepared and analyzed using procedures specified in "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79/ 020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, March 1979.

The study design was based on Youden's non-replicate design for collaborative tests of analytical methods. Three Youden pair samples of the test metals were spiked into six types of test waters and then analyzed. The test waters were three industrial effluents supplied by ERCO and three waters supplied by the subcontractor laboratories (laboratory pure water, finished drinking water, and surface water). The resulting data were statistically analyzed using the computer program entitled "Interlaboratory Method Validation Study" (IMVS).

The statistical analyses included rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precisions, and tests for the effects of water type on accuracy and precision.

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

The Safe Drinking Water Act (SDWA) and the National Pollutant Discharge Elimination System (NPDES) require that waters and waste be analyzed to determine their chemical content. The EPA was given a mandate to prepare methods which would be approved for the analysis of parameters of concern listed by these laws and resulting regulations.

The EPA staff of the Environmental Monitoring and Support Laboratory of Cincinnati, Ohio, provided the procedures for monitoring metal parameters in wastes and waters in the document entitled, "Methods for Chemical Analysis of Water and Wastes." The second edition of this manual, which was published in March 1979, added atomic absorption furnace methods to quantitate lower levels of metal parameters than those determinable by the flame atomic absorption methods specified in the first edition.

Energy Resources Co. Inc. (ERCO) was contracted by EPA to conduct a method study to define the accuracy and precision of the atomic absorption furnace procedure for the following 18 trace metals:

Aluminum	(Method 202.2)
Antimony	(Method 204.2)
Arsenic	(Method 206.2)
Barium	(Method 208.2)
Beryllium	(Method 210.2)
Cadmium	(Method 213.2)
Chromium	(Method 218.2)
Cobalt	(Method 219.2)
Copper	(Method 220.2)
Iron	(Method 236.2)
Lead	(Method 239.2)

Manganese	(Method 243.2)
Nickel	(Method 249.2)
Selenium	(Method 270.2)
Silver	(Method 272.2)
Thallium	(Method 279.2)
Vanadium	(Method 286.2)
Zinc	(Method 289.2)

Ten laboratories were selected by ERCO for participating in the method study following their successful analysis of performance evaluation samples. These laboratories then collected drinking, surface, and laboratory pure waters while ERCO supplied them with three different types of industrial effluents. These waters and effluents were analyzed to determine background levels of the elements of interest and subsequently specified volumes of unknown metal concentrates were added and the samples reanalyzed. The added level of each metal was determined by difference.

Youden's non-replicate collaborative test design was applied to 10 participating laboratories. Formal statistical techniques compatible with the Youden design were used to identify outliers, estimate the method's accuracy and precision, and test for the effect of water type. The formal statistical analyses were carried out using U.S. EPA's IMVS computer program.

Procedure

The study consisted of two distinct analysis phases. Phase I involved the selection of participating laboratories. An EPA-supplied list of laboratories and previous ERCO experience were used to solicit interested laboratories. Based on prior experience of the laboratories in graphite furnace analysis; assurance of adequate facilities, instrumentation, and personnel to complete the analyses in a timely manner; and cost estimates, 12 laboratories were selected to receive two pre-award performance evaluation samples. These samples contained acid solutions of eight of the 18 metals of interest in sealed glass ampules.

These solutions were spiked into laboratory pure water supplied by the individual participating laboratories and analyzed by the graphite furnace atomic absorption procedures to be employed in the interlaboratory study. The analytical results were submitted to ERCO for evaluation.

Based upon the individual laboratories' analytical results and the above criteria, 10 laboratories were selected for participation in the study.

Phase II consisted of the actual interlaboratory study. This study required the analysis of six different water matrices, spiked at six different concentrations (three Youden pairs) of all 18 analytes of interest. In addition, each participating laboratory performed an analysis of the six waters with no spiked compounds added. Each participating laboratory then issued a report of all results to ERCO.

The final step in the study was the statistical analysis of all data by Battelle Memorial Laboratories using EPA's INVS system.

Results and Discussion

The object of this study was to characterize the performance of graphite furnace atomic absorption procedures in terms of accuracy, overall precision, single-analyst precision, and the effect of water types on accuracy and precision. Through the statistical analysis of 8,640 analytical values, estimates of accuracy and precision were made and expressed as regression equations, which are presented in Table 1.

Of all 8,640 analytical values, 23% were rejected as outliers. The accuracy of the methods is obtained by comparing the mean recovery to the true values of concentration. The range of accuracy values (expressed as a percent relative error) was from 0.13% to 17,720%. This wide range was very dependent upon the individual analyte with the highest error being for zinc.

The overall standard deviation indicates the precision associated with the measurements generated by the 10 laboratories. The overall precision (expressed as a percent relative standard deviation) ranged from 0.55% to 171%. The highest relative standard deviation (worst precision) occurred for silver.

Statistical comparisons of the effect of water type were performed on all analytes. These indicated a practical effect of water matrix on the accuracy and/or precision of the methods in the following cases:

Arsenic in effluents 2 and 3
Beryllium in surface water
Nickel in effluents 2 and 3
Selenium in effluents 1 and 3
Silver in effluent 2
and Thallium in surface water and
effluent 2

Conclusions and Recommendations

Statistically significant matrix effects were found for several methods. Accuracy

and precision were, in general, poorest for the low concentration levels. Many laboratories could not achieve the recommended method detection limits. For several analytes accuracy and precision for the highest concentration levels were also poor, indicating that non-linearity might not have been detected by some analysts. Environmental contamination with Al, Fe, and Zn affected the accuracy and precision of these analyses. For four of the six waters, zinc had the highest percentage of data rejected. On average, 23% of the data were rejected. For individual laboratories, data rejection ranged from 12% to 36%. From all of the above it must be concluded that accurate and precise results may be obtained only by analysts thoroughly experienced in the use of graphite furnace methods.

It is recommended that instrumental parameters such as graphite type, background correction, sheath gas, and use of matrix modifiers be specified so that variability from these effects is minimized and separated from sample matrix effects. It is further recommended that more rigorous checks be made to determine if the method of standard additions is required for a particular analyte/matrix combination.

Table 1. EPA Method Study—Trace Metals by AA. Regression Equations for Accuracy and Precision for Compound 1

Water Type	Aluminum	Water Type	Aluminum
Applicable conc. range	(28.00-125.00) µg/L	Applicable conc. range	(26.80-120.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	SR = 0.23X + 6.45	Single-analyst precision	SR = 0.23X + 6.21
Overall precision	S = 0.42X + 5.83	Overall precision	S = 0.42X + 5.80
Accuracy	X = 0.70C + 32.36	Accuracy	X = 0.70C + 31.13
Drinking water		**Effluent 3**	
Single-analyst precision	SR = 0.12X + 21.97	Single-analyst precision	SR = 0.24X + 3.18
Overall precision	S = 0.25X + 14.45	Overall precision	S = 0.14X + 26.59
Accuracy	X = 1.10C + 39.21	Accuracy	X = 1.03C + 32.88
Surface Water			
Single-analyst precision	SR = 0.33X + 5.29		
Overall precision	S = 0.80X - 0.27		
Accuracy	X = -0.34C + 33.60		

Water Type	Aluminum	Water Type	Aluminum
Applicable conc. range	(11.00-58.30) mg/L	Applicable conc. range	(0.46-2.18) mg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	SR = 0.36X - 2.87	Single-analyst precision	SR = 0.39X - 0.14
Overall precision	S = 0.39X - 2.27	Overall precision	S = 0.39X - 0.09
Accuracy	X = 0.85C + 1.87	Accuracy	X = 0.85C + 0.08
Effluent 1		**Effluent 2**	
Single-analyst precision	SR = 0.16X + 0.88	Single-analyst precision	SR = -0.04X + 0.16
Overall precision	S = 0.26X + 2.24	Overall precision	S = 0.07X + 0.18
Accuracy	X = 1.12C - 2.89	Accuracy	X = 0.85C + 0.12

Water Type	Antimony	Water Type	Antimony
Applicable conc. range	(10.50-230.00) µg/L	Applicable conc. range	(11.00-240.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	SR = 0.14X + 1.09	Single-analyst precision	SR = 0.23X + 0.02
Overall precision	S = 0.40X + 0.88	Overall precision	S = 0.34X + 0.86
Accuracy	X = 0.65C + 0.56	Accuracy	X = 0.80C - 2.66
Effluent 1		**Drinking Water**	
Single-analyst precision	SR = 0.24X - 0.50	Single-analyst precision	SR = 0.21X - 0.14
Overall precision	S = 0.17X + 3.89	Overall precision	S = 0.18X + 0.73
Accuracy	X = 0.88C - 1.28	Accuracy	X = 0.87C - 2.14
Effluent 2		**Surface water**	
Single-analyst precision	SR = 0.12X + 4.23	Single-analyst precision	SR = 0.16X + 0.14
Overall precision	S = 0.09X + 9.56	Overall precision	S = 0.20X + 0.87
Accuracy	X = 0.73C + 5.80	Accuracy	X = 0.81C - 0.97
Effluent 3			
Single-analyst precision	SR = 0.22X + 0.37		
Overall precision	S = 0.33X + 0.87		
Accuracy	X = 0.61C + 0.31		

Water Type	Arsenic	Water Type	Arsenic
Applicable conc. range	(9.78-227.00) µg/L	Applicable conc. range	(10.20-237.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	SR = 0.08X + 2.82	Single-analyst precision	SR = 0.10X + 0.70
Overall precision	S = 0.17X + 1.98	Overall precision	S = 0.11X + 1.98
Accuracy	X = 1.02C + 3.30	Accuracy	X = 0.92C + 0.69
Effluent 1		**Drinking Water**	
Single-analyst precision	SR = 0.07X + 5.85	Single-analyst precision	SR = 0.06X + 1.96
Overall precision	S = 0.15X + 4.01	Overall precision	S = 0.12X + 1.49
Accuracy	X = 1.15C + 8.87	Accuracy	X = 0.93C + 0.62

Table 1. (Continued)

Water Type	Arsenic	Water Type	Arsenic
Applicable conc. range	(9.78-227.00) µg/L	Applicable conc. range	(10.20-237.00) µg/L

Effluent 2		**Surface Water**	
Single-analyst precision	$SR = 0.16X + 0.91$	Single-analyst precision	$SR = 0.09X + 0.80$
Overall precision	$S = 0.14X + 3.70$	Overall precision	$S = 0.13X + 2.75$
Accuracy	$X = 0.94C - 0.68$	Accuracy	$X = 0.91C - 1.29$
Effluent 3			
Single-analyst precision	$SR = 0.07X + 0.53$		
Overall precision	$S = 0.15X + 2.56$		
Accuracy	$X = 0.87C - 0.30$		

Water Type	Barium	Water Type	Barium
Applicable conc. range	(56.50-418.00) µg/L	Applicable conc. range	(59.10-437.00) µg/L

Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.12X + 4.80$	Single-analyst precision	$SR = 0.15X - 1.72$
Overall precision	$S = 0.36X - 8.62$	Overall precision	$S = 0.14X + 15.63$
Accuracy	$X = 0.84C + 83.71$	Accuracy	$X = 0.84C + 30.67$
Effluent 1		**Drinking Water**	
Single-analyst precision	$SR = 0.19X + 10.20$	Single-analyst precision	$SR = 0.11X + 2.22$
Overall precision	$S = 0.27X + 32.68$	Overall precision	$S = 0.37X - 10.56$
Accuracy	$X = 0.97C + 67.43$	Accuracy	$X = 0.92C + 36.50$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.29X - 13.14$	Single-analyst precision	$SR = 0.20X - 0.16$
Overall precision	$S = 0.58X - 27.91$	Overall precision	$S = 0.28X + 1.58$
Accuracy	$X = 0.84C + 42.52$	Accuracy	$X = 0.93C + 30.17$
Effluent 3			
Single-analyst precision	$SR = 0.69X - 39.17$		
Overall precision	$S = 0.34X + 9.88$		
Accuracy	$X = 0.24C + 65.63$		

Water Type	Beryllium	Water Type	Beryllium
Applicable conc. range	(0.45-10.90) µg/L	Applicable conc. range	(0.47-11.40) µg/L

Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.12X + 0.05$	Single-analyst precision	$SR = 0.10X + 0.08$
Overall precision	$S = 0.29X + 0.05$	Overall precision	$S = 0.11X + 0.18$
Accuracy	$X = 1.15C - 0.25$	Accuracy	$X = 0.98C - 0.05$
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.07X + 0.10$	Single-analyst precision	$SR = 0.03X + 0.11$
Overall precision	$S = 0.19X + 0.20$	Overall precision	$S = 0.14X + 0.07$
Accuracy	$X = 0.92C + 0.11$	Accuracy	$X = 1.01C - 0.07$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.12X - 0.05$	Single-analyst precision	$SR = 0.10X + 0.02$
Overall precision	$S = 0.07X + 0.19$	Overall precision	$S = 0.29X - 0.08$
Accuracy	$X = 1.08C + 0.01$	Accuracy	$X = 0.90C + 0.10$
Effluent 3			
Single-analyst precision	$SR = 0.13X - 0.00$		
Overall precision	$S = 0.20X + 0.08$		
Accuracy	$X = 0.92C - 0.03$		

Water Type	Cadmium	Water Type	Cadmium
Applicable conc. range	(0.43-12.00) µg/L	Applicable conc. range	(0.45-12.50) µg/L

Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.09X + 0.25$	Single-analyst precision	$SR = 0.10X + 0.05$
Overall precision	$S = 0.17X + 0.20$	Overall precision	$S = 0.27X - 0.05$
Accuracy	$X = 1.02C + 0.24$	Accuracy	$X = 0.95C + 0.09$

Table 1. *(Continued)*

Water Type	Cadmium	Water Type	Cadmium
Applicable conc. range	(0.43-12.00) µg/L	Applicable conc. range	(0.45-12.50) µg/L
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.14X + 0.42$	Single-analyst precision	$SR = 0.17X + 0.11$
Overall precision	$S = 0.32X + 0.15$	Overall precision	$S = 0.26X + 0.10$
Accuracy	$X = 0.75C + 0.39$	Accuracy	$X = 0.92C + 0.24$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.12X + 0.09$	Single-analyst precision	$SR = 0.22X - 0.13$
Overall precision	$S = 0.23X + 0.07$	Overall precision	$S = 0.38X + 0.10$
Accuracy	$X = 0.81C + 0.15$	Accuracy	$X = 1.04C + 0.15$
Effluent 3			
Single-analyst precision	$SR = 0.15X + 0.04$		
Overall precision	$S = 0.27X + 0.14$		
Accuracy	$X = 0.96C + 0.10$		

Water Type	Chromium	Water Type	Chromium
Applicable conc. range	(9.87-236.00) µg/L	Applicable conc. range	(10.30-246.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.18X + 0.73$	Single-analyst precision	$SR = 0.12X - 0.41$
Overall precision	$S = 0.20X + 1.14$	Overall precision	$S = 0.14X + 0.35$
Accuracy	$X = 0.89C + 0.11$	Accuracy	$X = 0.94C + 0.40$
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.14X + 0.88$	Single-analyst precision	$SR = 0.06X + 2.73$
Overall precision	$S = 0.21X + 3.87$	Overall precision	$S = 0.12X + 4.14$
Accuracy	$X = 0.87C + 1.09$	Accuracy	$X = 1.00C + 0.89$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.17X - 0.32$	Single-analyst precision	$SR = 0.12X - 0.12$
Overall precision	$S = 0.14X + 2.55$	Overall precision	$S = 0.26X - 0.04$
Accuracy	$X = 0.95C + 1.03$	Accuracy	$X = 0.91C + 0.47$
Effluent 3			
Single-analyst precision	$SR = 0.08X + 0.28$		
Overall precision	$S = 0.22X + 0.41$		
Accuracy	$X = 0.92C - 0.68$		

Water Type	Cobalt	Water Type	Cobalt
Applicable conc. range	(29.70-420.00) µg/L	Applicable conc. range	(24.80-407.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.09X + 0.50$	Single-analyst precision	$SR = 0.11X + 0.02$
Overall precision	$S = 0.25X - 2.99$	Overall precision	$S = 0.25X - 2.69$
Accuracy	$X = 0.88C + 1.36$	Accuracy	$X = 0.89C + 1.11$
Drinking water		**Effluent 1**	
Single-analyst precision	$SR = 0.12X + 1.60$	Single-analyst precision	$SR = 0.16X + 0.58$
Overall precision	$S = 0.23X + 1.24$	Overall precision	$S = 0.20X - 0.89$
Accuracy	$X = 0.92C + 0.44$	Accuracy	$X = 0.88C + 4.50$
Surface water			
Single-analyst precision	$SR = 0.14X - 1.00$		
Overall precision	$S = 0.18X - 0.14$		
Accuracy	$X = 0.92C + 2.01$		

Water Type	Cobalt	Water Type	Cobalt
Applicable conc. range	(21.10-461.00) µg/L	Applicable conc. range	(29.30-435.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.09X + 0.03$	Single-analyst precision	$SR = 0.09X + 0.16$
Overall precision	$S = 0.25X - 1.99$	Overall precision	$S = 0.25X - 3.31$
Accuracy	$X = 0.89C + 0.29$	Accuracy	$X = 0.88C + 1.32$

Table 1. (Continued)

Water Type	Cobalt	Water Type	Cobalt
Applicable conc. range	(21.10-461.00) µg/L	Applicable conc. range	(29.30-435.00) µg/L

Effluent 2		Effluent 3	
Single-analyst precision	$SR = 0.09X + 3.21$	Single-analyst precision	$SR = 0.06X + 2.06$
Overall precision	$S = 0.13X + 1.76$	Overall precision	$S = 0.15X + 1.28$
Accuracy	$X = 0.95C + 0.43$	Accuracy	$X = 0.82C + 1.43$

Water Type	Copper	Water Type	Copper
Applicable conc. range	(10.10-234.00) µg/L	Applicable conc. range	(0.30-1.67) mg/L

Lab pure water		Lab pure water	
Single-analyst precision	$SR = 0.07X + 4.37$	Single-analyst precision	$SR = 0.13X - 0.02$
Overall precision	$S = 0.11X + 4.97$	Overall precision	$S = 0.13X - 0.00$
Accuracy	$X = 0.92C - 0.81$	Accuracy	$X = 0.93C + 0.01$

Effluent 1		Effluent 2	
Single-analyst precision	$SR = 0.22X - 0.44$	Single-analyst precision	$SR = 0.05X + 0.02$
Overall precision	$S = 0.21X + 1.21$	Overall precision	$S = 0.13X + 0.01$
Accuracy	$X = 0.96C - 0.10$	Accuracy	$X = 1.02C - 0.07$

Effluent 3	
Single-analyst precision	$SR = 0.13X + 1.95$
Overall precision	$S = 0.29X + 4.96$
Accuracy	$X = 0.81C + 0.42$

Water Type	Copper
Applicable conc. range	(10.60-245.00) µg/L

Lab pure water	
Single-analyst precision	$SR = 0.22X - 0.46$
Overall precision	$S = 0.21X + 1.29$
Accuracy	$X = 0.96C - 0.11$

Drinking water	
Single-analyst precision	$SR = 0.15X + 2.63$
Overall precision	$S = 0.34X + 3.39$
Accuracy	$X = 0.91C + 6.09$

Surface water	
Single-analyst precision	$SR = 0.06X + 1.18$
Overall precision	$S = 0.18X + 1.44$
Accuracy	$X = 1.00C - 0.26$

Water Type	Iron	Water Type	Iron
Applicable conc. range	(26.10-455.00) µg/L	Applicable conc. range	(25.00-435.00) µg/L

Lab pure water		Lab pure water	
Single-analyst precision	$SR = 0.30X + 26.13$	Single-analyst precision	$SR = 0.30X + 25.23$
Overall precision	$S = 0.35X + 13.23$	Overall precision	$S = 0.35X + 12.73$
Accuracy	$X = 1.40C + 11.73$	Accuracy	$X = 1.41C + 11.24$

Drinking water		Effluent 3	
Single-analyst precision	$SR = 0.30X + 1.06$	Single-analyst precision	$SR = 0.23X + 16.21$
Overall precision	$S = 0.36X + 9.15$	Overall precision	$S = 0.31X + 31.14$
Accuracy	$X = 1.20C + 10.35$	Accuracy	$X = 1.09C + 37.18$

Surface water	
Single-analyst precision	$SR = 0.35X - 3.95$
Overall precision	$S = 0.34X + 37.42$
Accuracy	$X = 1.10C + 96.38$

Table 1. *(Continued)*

Water Type	Iron	Water Type	Iron
Applicable conc. range	(1.03-5.59) mg/L	Applicable conc. range	(0.37-2.61) mg/L
Lab pure water		Lab pure water	
Single-analyst precision	$SR = 0.04X + 0.13$	Single-analyst precision	$SR = 0.06X + 0.03$
Overall precision	$S = 0.05X + 0.27$	Overall precision	$S = 0.07X + 0.08$
Accuracy	$X = 1.01C + 0.07$	Accuracy	$X = 1.42C - 0.17$
Effluent 1		Effluent 2	
Single-analyst precision	$SR = 0.28X + 0.04$	Single-analyst precision	$SR = 0.18X - 0.03$
Overall precision	$S = 0.41X - 0.13$	Overall precision	$S = 0.22X - 0.01$
Accuracy	$X = 1.16C - 0.25$	Accuracy	$X = 1.00C + 0.04$

Water Type	Lead	Water Type	Lead
Applicable conc. range	(10.40-243.00) µg/L	Applicable conc. range	(10.90-254.00) µg/L
Lab pure water		Lab pure water	
Single-analyst precision	$SR = 0.17X - 0.88$	Single-analyst precision	$SR = 0.20X + 0.42$
Overall precision	$S = 0.17X + 1.36$	Overall precision	$S = 0.28X - 0.66$
Accuracy	$X = 1.06C - 2.26$	Accuracy	$X = 0.83C + 1.35$
Effluent 1		Drinking water	
Single-analyst precision	$SR = 0.22X - 0.14$	Single-analyst precision	$SR = 0.07X + 1.39$
Overall precision	$S = 0.23X - 0.06$	Overall precision	$S = 0.21X + 2.56$
Accuracy	$X = 0.81C + 2.05$	Accuracy	$X = 0.85C + 0.50$
Effluent 2		Surface water	
Single-analyst precision	$SR = 0.14X + 1.00$	Single-analyst precision	$SR = 0.19X + 0.11$
Overall precision	$S = 0.22X + 1.40$	Overall precision	$S = 0.18X + 1.73$
Accuracy	$X = 0.86C - 2.12$	Accuracy	$X = 0.92C - 0.96$
Effluent 3			
Single-analyst precision	$SR = 0.22X + 1.48$		
Overall precision	$S = 0.34X + 1.86$		
Accuracy	$X = 0.70C + 1.63$		

Water Type	Manganese	Water Type	Manganese
Applicable conc. range	(0.44-14.80) µg/L	Applicable conc. range	(91.00-484.00) µg/L
Lab pure water		Lab pure water	
Single-analyst precision	$SR = 0.27X + 0.31$	Single-analyst precision	$SR = 0.03X + 11.34$
Overall precision	$S = 0.44X + 0.48$	Overall precision	$S = 0.05X + 11.20$
Accuracy	$X = 1.00C + 1.46$	Accuracy	$X = 0.55C + 12.98$
Drinking water		Effluent 1	
Single-analyst precision	$SR = 0.16X + 0.51$	Single-analyst precision	$SR = 0.04X + 40.27$
Overall precision	$S = 0.38X + 0.52$	Overall precision	$S = 0.11X + 32.01$
Accuracy	$X = 0.90C + 1.38$	Accuracy	$X = 0.97C - 6.66$
Surface water			
Single-analyst precision			
Overall precision			
Accuracy			

Water Type	Manganese	Water Type	Manganese
Applicable conc. range	(111.00-666.00) µg/L	Applicable conc. range	(0.42-14.20) µg/L
Lab pure water		Lab pure water	
Single-analyst precision	$SR = 0.05X + 8.13$	Single-analyst precision	$SR = 0.27X + 0.31$
Overall precision	$S = 0.07X + 9.19$	Overall precision	$S = 0.43X + 0.47$
Accuracy	$X = 0.93C + 9.38$	Accuracy	$X = 1.00C + 1.40$
Effluent 2		Effluent 3	
Single-analyst precision	$SR = 0.26X + 3.47$	Single-analyst precision	$SR = 0.23X + 0.52$
Overall precision	$S = 0.32X - 6.30$	Overall precision	$S = 0.48X - 0.28$
Accuracy	$X = 0.78C - 8.22$	Accuracy	$X = 0.46C + 2.56$

Table 1. (Continued)

Water Type	Nickel	Water Type	Nickel
Applicable conc. range	(26.20-461.00) µg/L	Applicable conc. range	(27.40-482.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.17X + 0.34$	Single-analyst precision	$SR = 0.21X - 2.45$
Overall precision	$S = 0.26X + 1.89$	Overall precision	$S = 0.23X + 1.98$
Accuracy	$X = 0.84C + 6.46$	Accuracy	$X = 0.93C - 2.02$
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.10X + 3.46$	Single-analyst precision	$SR = 0.12X + 4.43$
Overall precision	$S = 0.16X + 4.72$	Overall precision	$S = 0.27X + 2.20$
Accuracy	$X = 0.67C + 10.56$	Accuracy	$X = 0.81C + 0.75$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.13X + 2.39$	Single-analyst precision	$SR = 0.10X + 4.38$
Overall precision	$S = 0.24X + 5.60$	Overall precision	$S = 0.16X + 9.37$
Accuracy	$X = 0.85C - 4.74$	Accuracy	$X = 0.81C + 2.47$
Effluent 3			
Single-analyst precision	$SR = 0.04X + 1.88$		
Overall precision	$S = 0.18X + 9.11$		
Accuracy	$X = 0.84C - 9.99$		

Water Type	Selenium	Water Type	Selenium
Applicable conc. range	(10.00-235.00) µg/L	Applicable conc. range	(10.50-246.00) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.06X + 0.65$	Single-analyst precision	$SR = 0.10X + 0.50$
Overall precision	$S = 0.17X + 0.14$	Overall precision	$S = 0.14X + 2.18$
Accuracy	$X = 0.93C - 0.20$	Accuracy	$X = 0.98C + 1.28$
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.05X + 3.19$	Single-analyst precision	$SR = 0.05X + 2.23$
Overall precision	$S = 0.19X + 1.76$	Overall precision	$S = 0.16X + 3.16$
Accuracy	$X = 0.88C - 2.45$	Accuracy	$X = 1.07C + 0.19$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.11X + 3.14$	Single-analyst precision	$SR = 0.15X + 0.25$
Overall precision	$S = 0.19X + 2.78$	Overall precision	$S = 0.17X + 1.64$
Accuracy	$X = 1.11C - 2.78$	Accuracy	$X = 1.00C - 0.66$
Effluent 3			
Single-analyst precision	$SR = 0.17X + 0.20$		
Overall precision	$S = 0.40X + 2.55$		
Accuracy	$X = 0.84C - 2.14$		

Water Type	Silver	Water Type	Silver
Applicable conc. range	(8.48-56.50) µg/L	Applicable conc. range	(0.45-13.60) µg/L
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.19X - 0.95$	Single-analyst precision	$SR = 0.15X + 0.03$
Overall precision	$S = 0.17X + 0.35$	Overall precision	$S = 0.18X + 0.15$
Accuracy	$X = 0.79C + 2.78$	Accuracy	$X = 0.96C + 0.17$
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.06X + 0.78$	Single-analyst precision	$SR = -0.02X + 0.77$
Overall precision	$S = 0.28X - 1.05$	Overall precision	$S = 0.20X + 0.17$
Accuracy	$X = 0.90C + 0.96$	Accuracy	$X = 0.82C + 0.81$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.28X + 1.11$	Single-analyst precision	$SR = 0.10X - 0.07$
Overall precision	$S = 0.65X + 0.26$	Overall precision	$S = 0.56X + 0.06$
Accuracy	$X = 0.49C + 0.03$	Accuracy	$X = 0.87C + 2.46$
Effluent 3			
Single-analyst precision	$SR = 0.34X - 2.10$		
Overall precision	$S = 0.38X - 1.06$		
Accuracy	$X = 0.70C + 4.27$		

Table 1.   *(Continued)*

Water Type	Thallium	Water Type	Thallium
Applicable conc. range	*(10.00-241.00) µg/L*	Applicable conc. range	*(10.50-252.00) µg/L*
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.15X + 0.03$	Single-analyst precision	$SR = 0.06X + 0.41$
Overall precision	$S = 0.12X + 0.96$	Overall precision	$S = 0.11X + 0.13$
Accuracy	$X = 0.87C - 1.24$	Accuracy	$X = 0.88C - 0.10$
Effluent 1		**Drinking water**	
Single-analyst precision	$SR = 0.09X + 0.41$	Single-analyst precision	$SR = 0.09X - 0.29$
Overall precision	$S = 0.30X - 0.04$	Overall precision	$S = 0.26X - 1.14$
Accuracy	$X = 0.76C - 1.12$	Accuracy	$X = 0.89C - 0.89$
Effluent 2		**Surface water**	
Single-analyst precision	$SR = 0.16X - 0.20$	Single-analyst precision	$SR = 0.10X + 0.02$
Overall precision	$S = 0.14X + 1.58$	Overall precision	$S = 0.25X - 0.14$
Accuracy	$X = 0.62C - 1.06$	Accuracy	$X = 0.84C - 1.15$
Effluent 3			
Single-analyst precision	$SR = 0.06X + 0.00$		
Overall precision	$S = 0.19X + 0.33$		
Accuracy	$X = 0.81C - 1.70$		

Water type	Vanadium	Water type	Vanadium
Applicable conc. range	*(151.00-982.00) µg/L*	Applicable conc. range	*(144.00-939.00) µg/L*
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.12X + 2.14$	Single-analyst precision	$SR = 0.12X + 1.96$
Overall precision	$S = 0.53X - 44.69$	Overall precision	$S = 0.53X - 42.61$
Accuracy	$X = 0.75C + 26.06$	Accuracy	$X = 0.75C + 25.26$
Drinking water		**Effluent 1**	
Single-analyst precision	$SR = 0.04X + 21.95$	Single-analyst precision	$SR = 0.04X + 19.60$
Overall precision	$S = 0.18X + 14.92$	Overall precision	$S = 0.24X + 4.39$
Accuracy	$X = 1.00C - 14.73$	Accuracy	$X = 1.05C - 7.45$
Surface water		**Effluent 2**	
Single-analyst precision	$SR = 0.15X - 5.47$	Single-analyst precision	$SR = 0.13X + 14.33$
Overall precision	$S = 0.15X + 0.56$	Overall precision	$S = 0.11X + 19.77$
Accuracy	$X = 0.96C - 11.91$	Accuracy	$X = 0.94C - 17.68$

Water type	Vanadium
Applicable conc. range	*(1.36-6.03) mg/L*
Lab pure water	
Single-analyst precision	$SR = 0.05X + 0.01$
Overall precision	$S = 0.11X - 0.01$
Accuracy	$X = 0.96C + 0.04$
Effluent 3	
Single-analyst precision	$SR = 0.12X - 0.04$
Overall precision	$S = 0.21X - 0.13$
Accuracy	$X = 0.99C - 0.18$

Water type	Zinc	Water type	Zinc
Applicable conc. range	*(0.54-17.40) µg/L*	Applicable conc. range	*(1.31-6.41) mg/L*
Lab pure water		**Lab pure water**	
Single-analyst precision	$SR = 0.56X - 1.19$	Single-analyst precision	$SR = 0.24X + 0.04$
Overall precision	$S = 1.03X - 1.03$	Overall precision	$S = 0.30X + 0.11$
Accuracy	$X = 2.93C + 1.02$	Accuracy	$X = 1.18C - 0.31$

Table 1. *(Continued)*

Water type	Zinc	Water type	Zinc
Applicable conc. range	(0.54-17.40) µg/L	Applicable conc. range	(1.31-6.41) mg/L
Drinking water		Effluent 1	
Single-analyst precision	SR = 0.31X + 6.80	Single-analyst precision	SR = 0.35X + 0.19
Overall precision	S = 0.99X + 0.69	Overall precision	S = 0.69X + 0.10
Accuracy	X = 1.29C + 14.50	Accuracy	X = 0.42C + 0.84
Surface water			
Single-analyst precision	SR = 0.59X – 5.51		
Overall precision	S = 1.06X – 0.04		
Accuracy	X = 2.43C + 7.16		

Water type	Zinc	Water type	Zinc
Applicable conc. range	(24.60-189.00) µg/L	Applicable conc. range	(0.51-16.70) µg/L
Lab pure water		Lab pure water	
Single-analyst precision	SR = 0.24X + 1.21	Single-analyst precision	SR = 0.56X – 1.04
Overall precision	S = 0.31X + 1.45	Overall precision	S = 1.00X – 0.63
Accuracy	X = 1.11C – 2.76	Accuracy	X = 2.93C + 0.86
Effluent 2		Effluent 3	
Single-analyst precision	SR = 0.86X – 19.95	Single-analyst precision	
Overall precision	S = 0.77X – 3.46	Overall precision	S = 1.27X – 11.00
Accuracy	X = 1.04C + 9.58	Accuracy	X = 8.83C + 54.05

X = Mean recovery.
C = True value for the concentration.

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