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Project Summary

USEPA Method Study 7, Analyses for Trace Elements in Water by Atomic Absorption Spectroscopy (Direct Aspiration) and Colorimetry

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This report describes a study of USEPA Method 200.0, Atomic Absorption (AA) Spectroscopy (direct aspiration), and Colorimetry, for ten elements: aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, selenium and zinc, at trace levels in water.

The study design was based on Youden's original non-replicate plan (1) for collaborative evaluation of analytical methods.

Six sample concentrates, each containing the ten trace elements, were sealed in glass ampuls, verified as homogeneous and stable over time, and provided to the analysts with instructions for sample preparation and analyses. The analysts were instructed to add an aliquot of each concentrate to a volume of distilled water and to a volume of natural water (river, lake, estuary, tap, wastewater, etc.), and to perform AA or colorimetric analyses for the ten elements. Results from distilled water evaluated the proficiency of the method free of interferences while by-difference results from natural waters, analyzed with and without the increment, reveal interferences with the method from a particular sample matrix, if present. Samples were prepared in pairs, in which the concentrations of analytes were slightly different for each sample of a pair. Three pairs of samples were used: one contained the trace elements near minimum detectable levels, a second contained intermediate levels and the last contained higher levels, but all were to be within the linear response ranges of the calibration curves. The analysts performed single analyses on each sample for each analyte as in routine analyses. Analysts were cautioned that the lowest levels of analyte in the study might require concentration or extraction before measurement.

The data from a study which was conducted in 1972, were originally evaluated with the computerized collaborative study program (COLST) and used to produce precision and bias statements for the 1979 edition of USEPA's manual of water methods (2). These same data were re-evaluated for this report utilizing the current (FY86) EMSL-Cincinnati statistical program, Interlaboratory Method Validation Study (IMVS), to make the results comparable to similar studies involving the same metals by AA-Furnace and Inductively Coupled Plasma (ICP), also evaluated by IMVS. Mean recovery, overall standard deviation and single-analyst standard deviations were calculated for each element at each concentration and for the two water types. Regression equations for recovery and precision were generated, and practical effects of water type noted.

Introduction

The study was designed to evaluate the AA flame spectroscopy and colorimetry methods of analyses recommended for those metals most common in industrial discharges or most often cited in NPDES permits as contaminants: Aluminum (Al), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Selenium (Se), and Zinc (Zn). Since wastewater discharges to streams and lakes ultimately become public water supplies to other communities, most of these elements are of interest for analysis of drinking water supplies as well.

It is important that USEPA laboratories and water-oriented laboratories of other federal and state agencies and the private sector use methods of analyses which have been evaluated statistically for precision, bias, and general interferences under the controlled conditions of an interlaboratory study.

The participant laboratories should be representative of laboratories monitoring discharges, that is, permittees, consultant laboratories and the state and federal regulatory agencies. Consequently, regulatory needs established the elements, their concentrations, the methods of analyses and the laboratories who participated in this study.

Statistical parameters from the study were originally estimated using a computer program (COLST) developed in the mid-1970's. These statistics were published as the precision and bias statements in the current manual of USEPA methods (2). Several years ago, however, the statistical estimation procedure for method studies was modified to be compatible with the ASTM Standard D2777-77 (3). To make results of this study comparable to the recent studies conducted for the AA-furnace and ICP methods, it was necessary to re-evaluate the study data using the current computerized evaluation program, IMVS, to prepare this report. When the USEPA methods manual is updated, results from this re-evaluation will be used as the basis for relevant precision and bias statements.

Summary

The Quality Assurance Branch (QAB) of the Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) conducted an interlaboratory study on the USEPA methods of analysis for aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, selenium and zinc in water.

The methods evaluated in this study which are described in the 1971 edition of USEPA's methods (4) and included in Appendix A of the full report, are direct aspiration atomic absorption (AA) techniques, except for arsenic and selenium analyses which are silver diethyl-dithiocarbamate and diaminobenzidine colorimetric procedures, respectively.

Three sample concentrates were prepared as pairs with slightly different concentrations for each of the elements, with the intention of representing the full range of linear response. An aliquot of each concentrate was added to distilled water and natural water samples by the analysts. One measurement was made on the natural water as background and one measurement was made on each of the distilled water and natural water samples with the added increments. Recoveries from the natural water samples were calculated by difference. Statistical estimates such as mean recovery, standard deviation, and bias, were calculated from the results with each water sample and increment level. A review of revised detection limits in the current USEPA manual for the eight AA analytes by direct aspiration, shows that the lowest concentrations studied were too low for dependable results by AA, direct aspiration. Therefore, the regressions for AA methods, shown in Table 1, were developed from the estimates at the medium and high concentration levels. The regressions for colorimetric analyses of arsenic and selenium used all three concentration levels. The regression equations estimate the mean recovery $(\overline{X})$, overall standard deviation (S) and single-analyst standard deviation (S_r) which may be expected in routine work within the concentration (C) range indicated.

Results

The full report presents tables of all data received, data actually evaluated (see limitation below), and final basic statistics. Plots are also provided showing all statistics and the regressions given in Table 1.

Need to Limit Data Sets to 50 or Fewer Responses

The original AA study design utilized a very large number of laboratories (17 USEPA and 99 other federal, state, local agency, private and industrial laboratories). However, the present IMVS computer program limits to 50 the number of data sets it can treat statistically. Since the IMVS program is extremely complex and too difficult to modify in a limited time, it was necessary in these instances to randomly reduce data sets for a metal to 50 responses to accommodate use of the IMVS program.

Discussion and Conclusions

The statistical results of the study are fully detailed in Tables 52-69 and Figures 1-20 of the full report. However, a brief summary for each analyte follows:

Aluminum

At the 500-1200 μg/L levels, recoveries by direct aspiration were an excellent 96-103%, with overall relative standard deviation (RSDs) of 17-43% and single-analyst RSD of 12-19%. At the lowest level tested, 15-35 μg/L, mean recoveries averaged 236-1270% and overall RSD ranged from 69-119%, demonstrating the inadequacy of direct analysis at this concentration level. By comparison, concentration by evaporation for the low level samples showed improved but still high recoveries of 176-245% in distilled water and low level recoveries of 45-80% in natural waters. Overall RSDs from the concentration data were also improved but with somewhat higher RSD levels of 61-82% for distilled water than the 22-52% overall RSDs for natural waters.

Arsenic

Recoveries of arsenic by the silver diethyldithiocarbamate colorimetric method were similar (75-89%) over the entire range tested, 20-292 μg/L, for both distilled and natural waters. In contrast, the overall RSDs reduced with increased concentrations of arsenic for both distilled and natural waters; 42-51% at 20-29 μg/L levels, 28-33% at 67-80 μg/L levels and 20-27% at 266-290 μg/L levels of arsenic.

Cadmium

Recoveries of cadmium by direct aspiration were proportionately lower than with the concentration technique,

Table 1. Summary of Statistical Regressions USEPA Method Study 7, Trace Metals by AA/Colorimetry

Analyte	Concentration Range of Studied Data Used, μg/L	Recovery from Distilled Water By Direct Aspiration	Recovery from Natural Water of Choice By Direct Aspiration
Aluminum	500 to 1205	$\overline{X} = 0.979(\underline{C}) + 6.16$ $S = 0.066(\overline{X}) + 125$ $S_r = 0.086(\overline{X}) + 40.5$	$\overline{X} = 1.080(\underline{C}) - 57.6$ $S = 0.115(\overline{X}) + 108$ $S_r = 0.081(\overline{X}) + 57.0$
Arsenic*	20 to 292	$\overline{X} = 0850(\underline{C}) - 0.25$ $S = 0.198(\overline{X}) + 5.93$ $S_r = 0.122(\overline{X}) + 3.10$	$\overline{X} = 0.854(\underline{C}) + 2.03$ $S = 0.240(\overline{X}) + 3.54$ $S_r = 0.151(\overline{X}) + 0.97$
Cadmium	14 to 78	$\overline{X} = 0.919(\underline{C}) + 2.97$ $S = 0.108(\overline{X}) + 5.08$ $S_r = 0.120(\overline{X}) + 0.89$	$\overline{X} = 0.923(\underline{C}) + 3.15$ $S = 0.063(\overline{X}) + 5.10$ $S_r = 0.054(\overline{X}) + 1.63$
Chromium	74 to 407	$\overline{X} = 0.976(\underline{C}) + 3.94$ $S = 0.131(\overline{X}) + 4.26$ $S_r = 0.052(\overline{X}) + 3.01$	$\overline{X} = 0.977(\underline{C}) + 1.21$ $S = 0.116(\overline{X}) + 10.1$ $S_r = 0.036(\overline{X}) + 7.81$
Copper	60 to 332	$\overline{X} = 0.963(\underline{C}) + 3.49$ $S = 0.047(\overline{X}) + 12.3$ $S_r = 0.042(\overline{X}) + 4.60$	$\overline{X} = 0.936(\underline{C}) + 1.83$ $S = 0.086(\overline{X}) + 8.18$ $S_r = 0.022(\overline{X}) + 5.33$
Iron	350 to 840	$\overline{X} = 0.999(\underline{C}) - 2.21$ $S = 0.022(\overline{X}) + 41.0$ $S_r = 0.019(\overline{X}) + 21.2$	$\overline{X} = 0.956(C) + 42.1$ $S = -0.016(\overline{X}) + 93.8$ $S_r = -0.011(\overline{X}) + 64.2$
Lead	84 to 367	$\overline{X} = 0.961(\underline{C}) + 13.8$ $S = 0.028(\overline{X}) + 33.9$ $S_r = 0.011(\overline{X}) + 16.1$	$\overline{X} = 0.993(\underline{C}) + 12.2$ $S = 0.151(\overline{X}) + 17.3$ $S_r = 0.117(\overline{X}) + 5.92$
Manganese	84 to 469	$\overline{X} = 0.987(\underline{C}) - 1.27$ $S = 0.042(\overline{X}) + 8.95$ $S_r = 0.023(\overline{X}) + 4.90$	$\overline{X} = 0.982(\underline{C}) + 4.15$ $S = 0.051(\overline{X}) + 10.4$ $S_r = 0.026(\overline{X}) + 3.59$
Selenium*	4.7 to 49	$\overline{X} = 0.643(\underline{C}) + 1.23$ $S = 0.431(\overline{X}) - 0.69$ $S_r = 0.192(\overline{X}) - 0.18$	$\overline{X} = 0.584(\underline{C}) + 1.15$ $S = 0.613(\overline{X}) - 1.13$ $S_r = 0.330(\overline{X}) + 0.53$
Zinc	56 to 310	$\overline{X} = 0.999(\underline{C}) + 0.33$ $S = 0.078(\overline{X}) + 10.8$ $S_r = 0.049(\overline{X}) + 1.10$	$\overline{X} = 0.991(\underline{C}) + 1.51$ $S = 0.067(\overline{X}) + 12.3$ $S_r = 0.035(\overline{X}) + 4.76$

*Colorimetric analyses.

both in natural and distilled water. At cadmium levels of 14-18 μg/L, recoveries were 104-118% with overall RSDs of 33-43%, while at cadmium levels of 71-78 μg/L, recoveries were 94-99% with overall RSDs of 12-19%. At low cadmium levels of 1.4-2.8 μg/L, recoveries by direct aspiration were 125-312% with overall RSDs of 70-97%, suggesting direct analysis is inadequate at this level. By comparison, at cadmium levels of 1.4-2.8 μg/L, recoveries by extraction were 97-135% with overall RSDs of 43-67%. Similarly, recoveries by concentration were 97-187% with overall RSDs of 24-57%.

Chromium

Recoveries of chromium at the 74-407 μg/L levels by direct aspiration were similar in distilled and natural waters; 98-103% with overall RSDs of 14-27%.

At the lowest level tested (7.4-15 μg/L), recoveries by direct aspiration were 139-223% with overall RSDs of 38-87%, again similar for distilled and natural waters, and suggesting direct analysis is inadequate at this level. By contrast, recoveries by concentration and chelation extraction were improved; 90-117% with 13-24% overall RSD, and 89-124% with overall RSDs of 30-59%, respectively.

Copper

The recovery of copper by direct aspiration over the concentration range of 60-332 μg/L showed good recoveries of 93-104% with overall RSDs of 9-28%. Recovery by direct aspiration at the lower levels of 7.5-12 μg/L showed recoveries of 161-207% in natural and distilled waters, with overall RSDs of 67-88%, indicating its inadequacy at such a low level.

By comparison, chelation/extraction at the 7.5-12 μg/L levels of copper showed improved recoveries of 97-121% with overall RSDs of 45-55%, in natural and distilled waters.

Recoveries of 7.5-12 μg/L by the concentration procedure showed similar recoveries of 88-149% but with lower overall RSDs of 29-47% in natural and distilled waters.

Iron

There were excellent recoveries of iron with the direct aspiration method, (99-107%) with 7-23% average RSD at the 350-870 μg/L levels in distilled and natural waters. At the low iron concentraiton of 10-24 μg/L, recoveries by direct aspiration were very high (239-1241%) with 79-138% overall RSD, demonstrating the inappropriateness of direct analysis at such low levels.

In comparison, recoveries by the extraction procedure at the iron concentration 10-24 μg/L were 127-371% with a 43-80% overall RSD while recoveries by the concentration procedures were 95-226% with overall RSDs of 36-53% in distilled and natural waters.

Lead

Analyses for lead by direct aspiration showed good recovery of 105-119% and overall RSD of 28-37% at 84-101 μg/L level and excellent recovery of 99-104% and overall RSD of 12-22% at 334-367 μg/L level.

At the lower levels of 25-37 μg/L, recoveries and variability of direct analysis increased markedly with ranges of 142-204% recovery, and 70-90% RSD, as would be expected for results below the detection limit of direct analysis. Contrariwise, recoveries at the 25-40 μg/L level for extraction were an excellent 96-102%, but with a continued variability of 45-55% RSD. Recoveries by concentration were biased high at 110-125%, and with 25-62% RSD. Single laboratory % RSDs were about 1/2 of overall % RSD for all three procedures. An examination of the evaluated data in Table 41 through 43 shows that the high percent recoveries for all three procedures were due largely to a few extreme values which were not rejected by the outlier routines.

Manganese

At manganese levels of 84-469 µg/L, recoveries by direct aspiration were excellent in both distilled and natural waters, at 97-104%, with relatively small overall RSDs of 14-17% at 84-106 µg/L and 5.4-8.4% at 426-469 µg/L levels of manganese.

Recovery of manganese at levels of 11-17 µg/L by direct aspiration, however, were higher at 110-196% with overall RSDs of 41-96%, indicating how questionable direct analysis is at this level. By comparison, the extraction technique also showed rather poor recoveries of 91-227% with overall RSDs of 45-117%, while recoveries by concentration improved to 76-100% with overall RSDs of 10-32%.

Selenium

Contrary to arsenic, percent recoveries of selenium by the diaminobenzidine colorimetric method, were reduced with increased concentrations of selenium both in distilled and natural waters. At the 4.7-7.8 µg/L level of selenium recoveries were 75-93%, with overall RSDs of 18-38%. At the 12-19 µg/L levels, recoveries were 60-77% with 35-64% RSD. Similarly at the 43-49 µg/L levels, percent recoveries were 59-66% with overall RSDs of 40-56%.

Zinc

Direct aspiration analyses for zinc showed good recovery (99-102%) at the 56-310 µg/L levels, with 10-29% overall RSD. However, at the lowest levels (7-11 µg/L), recoveries ballooned to 182-252%, with overall RSDs of 81-102%, demonstrating the questionable value of direct analyses at such a low concentration level. The low-level statistics were due largely to the extreme values which were not rejected in outlier tests.

Comparison of analytical results for the low-level zinc samples (7-11 µg/L) by direct aspiration, extraction, and concentration showed similar recoveries of 182-252% for direct aspiration, 98-283% for extraction, and 120-205% for concentrations with overall RSDs of 44-109%. One must conclude that the lowest levels tested were marginal for a number of laboratories.

Percentage of Data Considered Outliers

A question that commonly arises regarding statistical analysis of method study data is what percentage of the responses were considered outliers and omitted in estimating the statistical

characteristics of the method when properly performed. Overall, 6291 responses were evaluated in this study for the analytical conditions being considered, i.e., direct measurement at all three concentration levels, and, where applicable, extraction and concentration at the low-concentration level, with up to 50 laboratories reporting. Of this total, 16.8% of the values were rejected as less than values, zeros or statistical outliers. The rejection percentages for recovery from distilled and natural water were similar, 17.0% and 16.7%, respectively. Overall rejection percentages differed somewhat among the analytes studied, from a high of 23.9% for selenium to a low of 12.4% for manganese. Where the rejection percentage was highest it was usually caused by problems quantifying results for the low-concentration samples, i.e., frequent zeros and less thans, particularly from direct aspiration. The exception is the selenium method, which produced the highest percentage of rejected data by a slight margin over cadmium (23.0%) and aluminum (21.7%), primarily because of a consistent high bias in the selenium data from several laboratories. These results support the previous conclusion that the lowest concentrations studied were too low for proper quantitation by direct aspiration, but do not otherwise suggest general problems.

Natural Water Used in the Study

Another interesting sidelight is the diversity of the "natural water" each participant chose to use. Of the 119 laboratories reporting recoveries from what has been called throughout this report a "natural water," 97 described the source as a river, stream, creek, pond, lake, reservoir, spring or well, 15 described it as a tap water, 4 a salt water, and 3 described some type of effluent.

Interpreting Results from the Comparison Between Waters

Finally, to understand the results from the comparison between waters (Table 71 of the full report), it was necessary to develop two more summary tables. Overall precision was summarized in Table 2 for the study analytes, while percent recovery was summarized in Table 3, as shown on the following pages. Entries in the first, second, fourth, fifth, seventh, and eighth

columns of both Tables were averaged (or pooled) from the appropriate pair of entries in Tables 52 through 69 of the full report.

The next to last column of Table 2 shows that manganese has the smallest pooled RSD of all the study analytes and iron is next to the smallest. Since all comparisons between distilled and natural water results, RSD and percent recovery, are measured relative to pooled RSD, tests for manganese and iron are going to be the most sensitive to differences.

The last column of Table 2 shows that, relative to their pooled RSD, iron and selenium have the largest average differences between overall RSD estimates for the two waters at the concentrations used to fit the regressions in Table 1, with values of 0.40 and 0.28, respectively. Similarly, Table 3 shows that, relative to the pooled RSD, percent recoveries for the two waters differed most for iron and manganese, with values of 0.30 and 0.25, respectively. Thus it would seem, the statistically significant differences between waters primarily stem from differences in precision of the selenium data, differences in recovery for manganese, and a combination of the two for iron.

Review of the relevant tables and figures in the full report suggest that there is no *practical* difference in the recovery of iron and manganese between the two waters and hence no matrix effect. However, the differences in precision for iron and selenium between the distilled and natural waters do appear of practical importance, suggesting that recoveries of iron and selenium from some natural waters are adversely effected and sample effects are significant.

References

1. Youden, W. J. and E. H. Steiner, 1975. Statistical Manual of the Association of Official Analytical Chemists, AOAC, 1111 North 19th Street, Suite 210, Arlington, VA 22209.
2. Methods for Chemical Analysis of Water and Wastes, 1979. U.S. Environmental Protection Agency, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.
3. Annual Book of ASTM Standards, Section 11, Water and Environmental Technology, *11.01,* Water (1) Current year. American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

Table 2. Summary of Pooled Overall Relative Standard Deviation (RSD)

Analyte	Low Pair			Medium Pair			High Pair			Avg. Diff.	Pooled RSD	Avg. Diff. / Pooled RSD
	D*	N*	Diff.	D	N	Diff.	D	N	Diff.			
Al		NA**		29.35	35.00	5.65	18.35	18.77	0.41	3.03	26.34	0.12
As	49.82	44.67	−5.15	30.08	30.88	0.80	21.59	23.73	2.14	−0.74	35.04	−0.02
Cd		NA		40.47	35.23	−5.24	17.45	13.41	−4.04	−4.64	29.00	−0.16
Cr		NA		18.11	23.90	5.78	14.37	14.51	0.13	2.96	18.14	0.16
Cu		NA		23.18	21.35	−1.82	9.18	11.52	2.34	0.26	17.39	0.01
Fe		NA		12.80	21.18	8.38	7.77	10.52	2.75	5.56	14.00	0.40
Pb		NA		36.12	31.91	−4.21	12.40	20.05	7.65	1.72	26.83	0.06
Mn		NA		14.27	15.88	1.61	6.01	7.47	1.46	1.54	11.70	0.13
Se	25.06	35.34	10.28	43.14	55.40	12.26	40.10	54.22	14.12	12.22	43.50	0.28
Zn		NA		25.09	26.65	1.56	11.80	10.54	−1.26	0.15	19.94	0.01

*Distilled and Natural water samples.
**"NA" means statistics from the low concentration sample pair were not used to fit the regressions in Table 1.

Table 3. Summary of Percent Recovery

Analyte	Low Pair			Medium Pair			High Pair			Avg. Diff.	Pooled RSD
	D*	N*	Diff.	D	N	Diff.	D	N	Diff.		
Al		NA**		98.85	97.17	−1.69	98.67	103.19	4.52	1.42	0.05
As	83.73	77.27	−6.46	83.49	81.95	−1.55	86.77	84.97	−1.80	−3.27	−0.09
Cd		NA		110.16	111.80	1.64	96.52	97.10	0.58	1.11	0.04
Cr		NA		102.35	98.95	−3.40	98.74	98.13	−0.61	−2.00	−0.11
Cu		NA		101.14	96.13	−5.01	96.56	94.33	−2.23	−3.62	−0.21
Fe		NA		99.34	106.68	7.34	99.66	100.79	1.14	4.24	0.30
Pb		NA		110.89	111.85	0.96	100.43	103.53	3.11	2.03	0.08
Mn		NA		97.27	102.43	5.16	98.50	99.27	0.77	2.96	0.25
Se	88.06	77.68	−10.38	71.45	67.08	−4.38	65.43	60.43	−5.01	−6.59	−0.15
Zn		NA		100.59	101.55	0.96	99.95	99.66	−0.29	0.33	0.02

*Distilled and Natural water samples.
**"NA" means statistics from the low concentration sample pair were not used to fit the regressions in Table 1.

4. Methods for Chemical Analysis of Water and Wastes, 1971. U.S. Environmental Protection Agency, 16020...07/71, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

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The complete report, entitled "USEPA Method Study 7, Analyses for Trace
Elements in Water by Atomic Absorption Spectroscopy (Direct Aspiration) and
Colorimetry," (Order No. PB 86-208 709/AS; Cost: $22.95, subject to change)
will be available only from:
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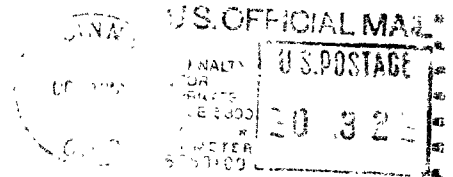> Springfield, VA 22161
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