United States Department of the Interior

IN REPLY REFER TO:

NATIONAL WATER QUALITY LABORATORY
TECHNICAL MEMORANDUM 1994.08

March 4, 1994

To: Assistant Chief Hydrologist, PC&TS
        Regional Hydrologists
        Chief, Office of Water Quality
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        Regional Water-Quality Specialists
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        QA Manager, Yucca Mtn. Project
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        Employees, National Water Quality Laboratory

From: Peter F. Rogerson, Chief
        National Water Quality Laboratory
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Subject: Availability of ICP-MS and a comparison of its analytical capabilities with more established
         techniques

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SCOPE

Inductively coupled plasma-mass spectrometry (ICP-MS) methodology at the National Water Quality
Laboratory (NWQL) has been extensively evaluated. Results from short- and long-term studies obtained
over a 3-week evaluation period have verified that the technique is capable of providing a high level of
accuracy and acceptable precision for trace metals. Therefore, Schedule 1050 has been created for ICP-
MS analysis of filtered, acidified water samples. Schedule 1050 includes 15 trace elements.

DETAILS OF ICP-MS METHOD

Schedule 1050 currently includes aluminum, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, silver, uranium, and zinc. The sample matrix must have a specific conductance of less than 2,500 microsiemens per centimeter (µS/cm) at 25 degrees Celsius. Samples having a specific conductance greater than this limit will be diluted to less than 2,500 µS/cm prior to analysis. All the results produced by ICP-MS for environmental samples will be reported down to the minimum reporting level (MRL) of 1 µg/L for every analyte. All the analytes have an upper analytical limit of 100 µg/L, except for aluminum, barium, manganese, and zinc that have an upper limit of 1,000 µg/L. Results for samples that exceed the analytical limit will be diluted and reanalyzed or analyzed using an alternative technique.

A new ICP-MS schedule (Schedule 172) is also available to support the low-level inorganic sampling protocol. A complete description of the purpose and application of this schedule is described in the Office of Water Quality Technical Memorandum No. 94.06. In short, Schedule 172 will be used to analyze deionized water blanks arising from equipment and supplies used during field sampling and processing. Results corresponding to these analyses will be reported to the method detection limits (MDL) for each of the aforementioned 15 analytes, plus strontium and thallium. The MDL for an analyte is the concentration that can be reported at the 99 percent confidence level as determined by the procedure described in the U.S. Code of Federal Regulations, Title 40, part 136, Appendix B, p. 537-539. Only results pertaining to deionized water blanks will be reported to the MDL levels on a routine basis. Analytical work on environmental samples requiring results reported down to the MDL levels must be arranged on a custom basis and through a mutually agreed upon District/NWQL work proposal.

Attributes of ICP-MS that may be useful in determining if it is the method of choice for a particular study are listed in table 1. Information provided includes the analytes determined, concentration range, and the precision that can be expected at various concentration levels. Accuracy is ensured by appropriate internal quality control during the analysis. In addition, external control such as field blanks, replicate samples, split samples, and blind samples should be used by investigators to ensure quality and help in the interpretation of analytical results.

COMPARISON OF ICP-MS WITH OTHER ANALYTICAL METHODS FOR THE DETERMINATION OF TRACE ELEMENTS

Other analytical methods are available for determining most of the same analytes as determined by ICP-MS. The other methods are graphite furnace-atomic absorption spectrophotometry (GF-AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), direct current plasma-atomic emission spectrometry (DCP-AES), and flame-atomic absorption spectrophotometry (F-AAS). The analytical attributes of these other techniques are listed in tables 2 through 5. The analytical sensitivity and precision information listed in these tables can be used to rank the analytical methods as follows. In all cases, the accuracy of each technique is comparable when sample concentrations are within the technique's analytical working range.

Sensitivity	ICP-MS ~ GF-AAS > ICP-OES ~ DCP-AES > F-AAS
Precision	GF-AAS > ICP-MS ~ ICP-OES ~ DCP-AES > F-AAS
Cost per analyte	GF-AAS ~ F-AAS ~ DCP-AES > ICP-MS > ICP-OES

ICP-MS and GF-AAS have similar sensitivities for cadmium, cobalt, copper, lead, nickel, and silver, which are generally higher than for F-AAS, DCP-AES, and ICP-OES. When analyte concentrations are expected to be low, either ICP-MS or GF-AAS is best suited. However, GF-AAS at present is available only for cadmium, chromium, cobalt, copper, lead, nickel, and silver. If highly precise results are

required at low concentrations, the precision at the MRLs for GF-AAS is about a factor of 10 better than for ICP-MS. If high sensitivity is not required, then either ICP-OES or DCP-AES is the best choice. Samples with high levels of dissolved solids may be best analyzed by F-AAS, DCP-AES, or GF-AAS, depending on the required sensitivity. In addition, when results are needed for only a few analytes, F-AAS is most economical and for some analytes provides sensitivities that exceed or are equivalent to ICP-OES and DCP-AES.

The information provided here should help you make a decision on the most appropriate method to use for a particular study. If you need additional information or have questions related to ICP-MS or trace metal determinations in general, please call or EDOC John Garbarino (303-467-8098, JRGARB) or Ed Zayhowski (303-467-8150, ZAYHOWSK).

Attachments (Tables 1-5)

Table 1 -- ICP-MS attributes and analytical precision

[ICP-MS, inductively coupled plasma-mass spectrometry; µg/L, micrograms per liter, µS/cm, microsiemens per centimeter, conc., concentration; RSD, relative standard deviation]

ATTRIBUTES

· ICP-MS is a multielement technique.
· The analytical range is 1 to 100 µg/L for antimony, beryleum, cadmium, chromium, cobalt, copper, lead, molybdenum, nickel, silver, and uranium; 1 to 1,000 µg/L for aluminum, barium, manganese, and zinc.
· Minimum reporting level (MRL) is 1 µg/L for all analytes.
· Samples having specific conductance greater than 2,500 µS/cm will be diluted prior to analysis.

ANALYTICAL

Expected precision at the stated concentrations is based on analyses of 24 samples over a period of 3 weeks, n=24.

Aluminum		Antimony		Barium	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
1	140	1	20	1	40
5	30	5	8	5	8
10	15	8	6	8	8
20	6			45	3

Beryllium		Cadmium		Chromium	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
1	30	1	40	1	30
5	8	5	10	5	7
10	6	7	8	10	4
16	5			15	3

	Cobalt		Copper		Lead	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
1	30	1	40	1	30
5	7	5	10	5	8
11	3	10	6	10	4
		17	4		

	Manganese		Molybdenum		Nickel	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
1	20	1	30	1	30
5	5	5	8	5	10
13	3	12	4	11	6
28	3	20	4		

	Silver		Uranium		Zinc	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
1	40	1	20	1	30
5	9	5	5	5	10
14	3	75	4	18	4

Table 2 -- GF-AAS attributes and analytical precision

[GF-AAS, graphite fumace-atomic absorption spectrophotometry; µg/l-, micrograms per liter; µS/cm, microsiemens per centimeter, conc., concentration; RSD, relative standard deviation]

ATTRIBUTES

· GF-AAS is a single-element technique.
· The analytical range, lab code, and method number vary with analyte and are tabulated below.
· Minimum reporting levels (MRL) are 1 µg/L for every analyte except chromium, which is 0.5 µg/L.
· Samples having specific conductance greater than 10,000 µS/cm will be diluted prior to analysis.

Analyte	Lab code, method	Analytical range (µ/L)	
Cadmium	1554, I-1238	1-5.0	
Chromium	1936, I-1233	0.5-25.0	
Cobalt	1556, I-2243	1-25.0	
Copper	1558, I-2274	1-25.0	
Lead	1560, I-2403	1-25.0	
Nickel	1562, I-2503	1-25.0	
Silver	1552, I-2724	1-10.0	I

ANALYTICAL PRECISION

Expected precision at the stated concentrations is based on short- and long-term operation, n=7 to 35.

Cadmium		Chromium		Cobalt	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
1	4	0.7	57	2	33
5	4	1.8	22	5	11
20	11	10	4	25	9
		25	8		

Copper		Lead		Nickel	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
2	6	2	2	2	8
5	4	12	7	4	18
20	5	24	4	11	7

Silver	
Conc. (µg/L)	Percent RSD
2	32
7	13
10	12

Table 3 -- ICP-OES attributes and analytical precision

[ICP-OES, inductively coupled plasma-optical emission spectrometry; µg/L, microgams per liter, mg/L; milligram per liter; µS/cm, microsiemens per centimeter; conc., concentration; RSD, relative standard deviation]

ATTRIBUTES

· ICP-OES is a multielement technique.
· The analytical range is from the MRL to 10 mg/L for barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, silver, strontium, vanadium, and zinc. The following analytes have different upper limits as indicated: Calcium, 400 mg/L; magnesium, 100 mg/L; sodium, 400 mg/L; and silica, 100 mg/L.
· Minimum reporting levels (MRL) vary with analyte and are tabulated below.

Analyte	MRLµg/L, except where noted, <2,000 µS/cm	MRL µg/L, except where noted, >2,000 but <6,000 µS/cm
Barium	2	6
Beryllium	0.5	1.5
Cadmium	1	3
Calcium	0.02 mg/L	0.06 mg/L
Chromium	5	15
Cobalt	3	9
Copper	10	30
Iron	3	9
Lead	10	30
Lithium	4	12
Magnesium	0.01 mg/L	0.03 mg/L
Manganese	1	3

Molybdenum	10	30
Nickel	10	30
Silica (SiO2)	0.01 mg/L	0.03 mg/L
Silver	1	3
Sodium	0.2 mg/L	
Strontium	0.5	1.5
Vanadium	6	18
Zinc	3	9

ANALYTICAL PRECISION

Expected precision at the stated concentrations is based on long-term operation, n=8 to 16.

Barium		Beryllium		Cadmium	
Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD
47	5	10	4	4	12
58	4	15	3	9	8
200	1	23	2	14	4
248	2	52	2		

Calcium		Chromium		Cobalt	
Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD
5	2	12	10	10	8
12	2	18	7	15	5
35	2	35	4	23	2
74	1				

Copper		Iron		Lead	
Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD
17	11	52	5	13	19
30	7	106	3	18	21
50	4	191	2	26	15
		273	3	35	9

Lithium		Magnesium		Manganese	
Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD
16	5	0.8	12	34	5
45	1	2	4	50	3
68	2	9.3	2	65	3
		53	1	455	2

Molybdenum		Nickel		Silica	
Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD	Conc. (μg/L)	Percent RSD
15	11	17	23	6.9	1
34	7	28	17	9.9	1
50	3	57	9		
104	5				

Silver		Sodium		Strontium	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
2	58	12	3	32	3
5	45	21	2	61	4
12	29	97	2	250	2

Vanadium		Zinc	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
10	11	56	4
17	2	66	4
30	3	76	3

Table 4 -- DCP-AES attributes and analytical precision

[DCP-AES, direct current plasma-atomic emission spectrometry; µg/L, microgams per liter, µS/cm, microsiemens per centimeter, conc., concentration; RSD, relative standard deviation]

ATTRIBUTES

· DCP-AES is a single-element technique.
· The analytical range is 10 to 10,000 µg/L for aluminum and boron.
· Samples having specific conductance geater than 10,000 µS/cm will be diluted prior to analysis.
· MRLs and analytical method are tabulated below.

Analyte	Lab code	MRL (µg/L)	Method
Aluminum	1284	10	I-1054-86
Boron	1183	10	I-1114-86

ANALYTICAL PRECISION

Expected precision for DCP-AES at the stated concentrations are based on long-term operation with variable populations of n = 10 to 18.

Aluminum		Boron	
Conc. (µg/L)	Percent RSD	Conc. (µg/L)	Percent RSD
13	15	30	6
30	10	40	4
73	12	215	2
132	8		

Table 5 -- F-AAS attributes and analytical precision

[F-AAS, Flame-atomic absorption spectrophotometry; µg/L, microgams per liter, µS/cm, microsiemens per centimeter; conc., concentration, RSD, relative standard deviation]

ATTRIBUTES

· F-AAS is a single-element technique.
· The analytical range and MRLS vary with analyte and are tabulated below.

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                                MRL            Upper limit
   Analyte       Lab code      (µg/L)           (µg/L)        Method
   ==================================================================
   Antimony      77, hydride     1                 15         I-1055-85
   Barium        7             100              5,000         I-1084-85
   Beryllium     170            10                200         I-1095-85
   Cadmium       126            10                250         I-1135-85
   Calcium       12              0.01 mg/L        60 mg/L     I-1152-85
   Chromium      16,chelation   10                400         I-1236-85
   Cobalt        148            50              1,000         I-1239-85
   Copper        151            10              1,000         I-1270-85
   Iron          172            10              1,000         I-1381-85
   Lithium       39             10              1,000         I-1425-85
   Lead          191           100              4,000         I-1399-85
   Magnesium     40              0.01   mg/L      50 mg/L     I-1447-85
   Manganese     42             10              1,000         I-1454-85
   Molybdenum    110,chelation   1                 50         I-1490-85
   Nickel        197           100              1,000         I-1499-85
   Sodium        59              0.01 mg/L        80          I-1735-85
   Strontium     62             10              5,000         I-1800-85
   Zinc          67             10                500         I-1900-85
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ANALYTICAL PRECISION

Expected precision for F-AAS at the stated concentrations are based on short- and long-term operation or interlaboratory results with variable populations.

Antimony			Barium			Beryllium	
Conc.	Percent		Conc.	Percent		Conc.	Percent
(µg/L)	RSD		(µg/L)	RSD		(µg/L)	RSD
2	2		162	38		27	19
20	3		800	16		38	12

Cadmium			Calcium			Chromium	
Conc.	Percent		Conc.	Percent		Conc.	Percent
(µg/L)	RSD		(µg/L)	RSD		(µg/L)	RSD
12	49		0.84	24		22	27
14	31		11	6		31	23
			50	8			
			110	8			

Cobalt			Copper			Iron	
Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD
6	57		79	15		100	31
16	27		600	9			
19	11						

Lead			Lithium			Magnesium	
Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD
7	7		54	9		0.1	50
13	51		484	5		2.0	9
						55	7
						120	7

Manganese			Molybdenum			Nickel	
Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD
70	20		2	36		10	80
256	9		30	11		20	46

Sodium			Strontium			Zinc	
Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD		Conc. (µg/L)	Percent RSD
0.20	35		82	34		41	35
2.8	13		1,400	9		253	14
56	5					437	7
97	5						

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Supersedes: None

Key Words: Inductively coupled plasma-mass spectrometry (ICP-MS), Trace metals, water analysis