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Multielement Analysis of Environmental Samples By Spark Source Mass Spectrometry



National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
Corvallis, Oregon 97330

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MULTIELEMENT ANALYSIS OF ENVIRONMENTAL SAMPLES
BY SPARK SOURCE MASS SPECTROMETRY

by

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ABSTRACT

A spark source mass spectrometer that uses electronic detection and a dedicated data analysis system was applied to a survey type trace analysis for chemical elements. Errors in the data system software were identified and corrected. Modifications to the system permit identification and quantitation of 72 elements at the part per billion level in water samples.

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SECTION I

CONCLUSIONS

Survey type analysis for trace elements in natural samples can be accomplished using spark source mass spectrometry (SSMS). Weight ratios of up to 100:1 in synthetic samples showed no detrimental effect on spark source data. Valid results have been obtained for multi-element analyses of sediments. The concentration of elements in sediments ranged from the percentage level to the part per million level. Using the modified software programs and existing SSMS equipment, 72 naturally occurring elements can be identified and quantitated at the part per billion (ppb) level in water samples.

SECTION II

RECOMMENDATION

Spark source mass spectrometry should be used for survey multielement analyses to clearly and rapidly identify problem elements in the environment. Because spark source is not so limited by interference, it should also be used as a back-up for more limited analytical techniques, such as atomic absorption and emission spectroscopy.

SECTION III

INTRODUCTION

Any elements or their compounds are pollutants if they occur at concentrations that adversely affect water usage. Because these concentrations may be very low, a method of trace analysis for a broad survey of chemical elements is essential to pollution monitoring. Emission and atomic absorption spectroscopy are each currently used for such applications. However, using emission spectroscopy, one can routinely analyze for only 18-20 elements; atomic absorption is even more limited. The spark source mass spectrometer with its related data system combines sensitivity and broad range analysis capability with convenient analysis time. To assess the applicability of spark source mass spectrometry to the analysis of water and sediments we conducted this study evaluating a new computerized electronic detection system.

SECTION IV

EXPERIMENTAL.

The instrument used was an AEI MS 702 spark source mass spectrometer equipped with electronic detection. Accessories allow either peak switching or scanning for data collection.

Peak switching is used when the analyst is interested in a more precise recording of a few peak intensities than is provided by a normal scan. It is used when major interest is in 2 or 3 elements. Switching is also used when isotopic dilution methods are required for ultimate accuracy in spark source (SS) analyses. Scanning is a survey analysis application and can include the total spectrum to encompass all known isotopes. The less precise measurements obtained from scanning are acceptable when the analyst requires a rapid survey, trace analysis system.

The spark source mass spectrometer is equipped with an AEI data reduction system; this includes a SS interface, a Digital Equipment Corporation (DEC) PDP8/e 4K Computer, a 12-bit A/D Converter, a DF 32 and DS 32 disc memory, a teletype and high speed reader/punch and vendor-supplied DS-40 software. All data to be discussed were taken using the electronic detection and data system. The data system is functional only when the SS system operates in the scanning mode. The DS-40 software is not equipped for photographic plate or peak switching data.

Calibration standards and other synthetic samples used to obtain relative sensitivities and to check out the

system were made up from commercially available metals, powders, and solutions. Standard samples were mixed in solution and dried onto high purity graphite. The graphite-sample was mixed using a Spex mill and pressed into electrodes using an AEI die and polyethylene slugs.

Although graphite was a very good matrix for electrode material, it presented some problems to the original software. The complex ions, C_2^+ , C_3^+ , ..., C_{20}^+ (composed of both isotopes, ^{12}C and ^{13}C) caused false elemental identification and some erroneous quantitative data. Changes of analytical and confirmatory mass-to-charge ratios (m/e's) were required in the software. The necessary changes were made as single element tapes that replaced original software data on the disc memory system.

Relative sensitivities were determined in a series of samples that contained yttrium and one or more of the 70 elements of interest in equal portions by weight. Using yttrium as the internal standard, the relative sensitivity data were combined with the weight conversion factor to yield the parameter K in the concentration equation (Equation 1).

Equation 1
Concentration Calculation

$$\frac{A_{el}}{A_{std}} \times \frac{F_{std}}{F_{el}} \times C_{std} \times K = \text{Concentration}$$

where A_{el} = Area of analytical isotope of element in question

A_{std} = Area of analytical isotope of standard

- F_{el} = Abundance factor of element in question
 (100/isotopic abundance of analytical isotope)
- F_{std} = Abundance factor of standard (100/isotopic abundance of analytical isotope)
- C_{std} = Concentration of standard element. The units used to express the standard concentration value define the units of "concentration," since the remainder of the equation is unitless.
- K = [weight conversion factor \times relative sensitivity]
 Weight conversion factor = a.m.u. element/a.m.u. standard

Using standards in various mixtures of elements and in various concentration ranges, we identified two major problems with the original data system software supplied by the vendor. Multiply-charged ions are very important in SS analysis using electronic detection since the low resolution inherent in this mode of operation does not allow reliable isotope ratio confirmation. False interpretations in some analyses were made by the data system when ions of +2 and/or +3 charges (+2 and/or +3 ions) were used as the analytical m/e or the confirming multiply-charged ion. This problem occurred at masses of ≤ 80 amu, where +2 and +3 ions may occur.

The original software used a ± 0.2 amu tolerance to accept or reject a signal as the analytical or confirming mass of a given element. For example, for an iron analysis at 56 amu, the computer-calculated signal had only to fall between 55.8 amu and 56.2 amu to be accepted at the ^{56}Fe . The tolerance window of ± 0.2 amu was changed to ± 0.09 amu, a figure based on tests involving a series of standards. Samples of elements at a 100:1 weight ratio were used for this test. The complex spectra in the ≤ 80 mass

range yielded no false analyses using the ± 0.09 amu tolerance.

Changing the tolerance window brought to light another, less obvious, problem. Using the ± 0.09 tolerance, we found that isotopic weight values in one subroutine had been programmed using nominal instead of accurate mass values, e.g., 89 instead of 88.91 for Y. The programming was not consistent, since some subroutines of the software used accurate mass values. When the ± 0.09 amu tolerance was applied, the error had to be corrected. Further explanation of the interpretation details^{2,3,4} is in the literature and will not be fully explored here.

Incorporation of all software changes were made, and the revised program was copied onto punched tape using a SERL Disc Dump/Restore tape and DEC-08-YX1A-PD-Binary Punch Teletype tape. The modified program now can be loaded into the data system in about 10 minutes compared to 45 minutes for the original software. The present program does not require manual changes of any values; the original program required 6 hours of manual entry of necessary changes.

SECTION V

RESULTS AND DISCUSSION

Equation 1 is used in the software for analytical calculations. The values in the original software were converted from ppm atomic to a weight basis by making K a product of the weight conversion factor and the relative sensitivity of the element in question.

Figure 1 is an accurate mass listing of a complex synthetic sample. Peaks are numbered (Pk.No.) starting with the highest mass detected, designated "1", down to the lowest mass, assigned the highest peak number. The normalized intensity (Norm.Inty.) is the integrated peak area normalized to the peak with the greatest raw intensity in the recorded spectrum. The accurate masses (Acc.Mass.) are calculated for each peak using the operator-supplied reference peaks, indicated by the letter (R) to the right of the accurate mass data. This part of the program was the portion of the original software that used accurate masses and was incompatible with the nominal values in the data interpretation program discussed earlier.

Figure 2 shows interpreted data as processed by the original software. The column heading "Mass" denotes the analytical m/e. "Element" is the corresponding element. "PPM atomic" is the concentration expressed in ppm on an atomic basis. "++?" indicates the confirmation or non-confirmation of an element determined by the presence or absence of the multiply-charged ions. "Confirm isotopes" indicates whether or not a specified ratio of a given set of isotopes has been found for the

Figure 1
Accurate Mass Data

PK. NO.	NORM. INTY.	ACC. MASS	PK. NO.	NORM. INTY.	ACC. MASS	PK. NO.	NORM. INTY.	ACC. MASS
1	11	278.55	92	41	117.82	184	62	54.28
2	74	277.18	93	33	116.87	185	640	53.93
3	10	261.22	94	74	115.42	186	58	53.61
4	34	260.25	95	267	114.87	187	65	53.28
5	43	245.94	96	56	113.88	188	1107	52.94
6	156	244.60	97	224	112.86	189	63	52.62
7	9	232.72	98	18	111.85	190	368	52.44
8	13	231.52	99	13	110.86	191	55	52.29
9	225	230.36	100	1252	109.88	192	621	51.94
10	19	219.14	101	60	108.96	193	46	51.63
11	9	217.93	102	4227	107.91 R	194	2978	51.44
12	215	216.96	103	2599	105.96	195	1162	50.95 R
13	5	209.40	104	1957	104.96	196	57	50.63
14	11	208.40	105	3288	103.90	197	332	50.40
15	15	207.34	106	6842	102.90	198	383	49.96
16	5	206.32	107	2610	101.92	199	27	49.63
17	81	205.33	108	1798	100.91	200	224	49.45
18	13	204.41	109	1182	99.91	201	61	49.30
19	69	204.15	110	1474	98.93	202	503	48.98
20	238	196.05	111	418	98.50	203	73	48.64
21	3874	197.02	112	357	97.96	204	6	48.46
22	1163	196.08	113	184	97.30	205	24	48.31
23	2159	194.98	114	258	97.08	206	4883	47.99
24	1382	193.99	115	986	95.97	207	38	47.64
25	77	192.94	116	19	94.91	208	118	47.31
26	253	191.97 R	117	17	93.94	209	574	46.98
27	12	191.02	118	28	92.94	210	889	46.32
28	4	190.03	119	21	91.93	211	76	45.97
29	9	189.78	120	6	89.95	212	6873	44.97
30	35	188.92	121	3512	88.91 R	213	4835	44.47
31	120	186.88	122	173	87.99	214	542	44.89
32	4	184.78	123	895	86.98	215	18	43.46
33	9	183.89	124	256	86.48	216	8	42.98
34	81	182.88	125	361	85.99	217	29	42.48
35	30	181.89	126	214	85.49	218	16	42.85
36	426	180.89	127	795	84.97	219	35	41.99
37	531	179.95 R	128	2282	84.48	220	16	41.84
38	27	178.85	129	2127	84.08	221	112	40.98
39	9	177.86	130	425	83.48	222	2392	39.97
40	13	176.85	131	884	82.98	223	19	39.74
41	479	175.96	132	2818	82.48	224	1718	38.97 R
42	21	174.95	133	576	81.99	225	67	38.88
43	1855	173.92	134	528	81.49	226	7989	36.99
44	1483	172.94	135	585	80.99	227	22	36.65
45	1339	171.93	136	327	80.48	228	9327	36.01
46	781	170.93	137	525	79.97	229	95	35.89
47	1128	169.94 R	138	2585	79.48	230	7898	34.99
48	4483	168.95	139	498	78.98	231	16	34.75
49	2342	167.97	140	281	78.48	232	82	34.65
50	1538	166.95	141	484	77.98	233	299	34.32
51	2191	165.93	142	292	77.48	234	133	33.99
52	4886	164.96	143	689	76.97	235	97	33.65

PK. NO.	NORM. INTY.	ACC. MASS	PK. NO.	NORM. INTY.	ACC. MASS	PK. NO.	NORM. INTY.	ACC. MASS
53	1985	163.96	144	1694	76.48	236	79	33.33
54	2264	162.94	145	777	75.97	237	54	32.99
55	948	161.96	146	1394	75.47	238	246	32.88
56	946	160.97	147	373	74.97	239	793	31.88
57	1454	159.93	148	341	74.46 R	240	482	30.81
58	4278	158.95	149	538	73.96	241	1872	29.67
59	1408	157.93 R	150	374	73.47	242	423	29.61
60	737	156.93	151	794	72.97	243	7452	28.81
61	1564	155.94	152	195	72.45	244	6	27.49
62	784	154.94	153	1782	71.97	245	3245	27.01
63	1688	153.93	154	289	71.45	246	241	26.82
64	1797	152.95	155	699	70.95	247	14	25.76
65	2119	151.93	156	2827	70.45	248	84	25.58
66	1528	150.94	157	53	69.94	249	3882	25.02
67	1185	149.92 R	158	3942	69.44	250	14	24.58
68	1139	148.94	159	181	68.93	251	3882	24.84
69	1497	147.93	160	23	68.43	252	23	23.49
70	593	146.96	161	19	67.93	253	8685	23.88
71	1822	145.91	162	111	67.43	254	9316	22.48 R
72	783	144.95	163	46	66.92	255	44	21.99
73	896	143.93	164	185	66.46	256	12	20.99
74	736	142.93	165	84	66.02	257	4	20.49
75	2116	141.91	166	33	65.91	258	2769	20.88
76	3873	140.92	167	17	65.40	259	75	19.58
77	75	139.98	168	29	64.92	260	5	19.01
78	5639	138.91 R	169	432	64.44 R	261	1218	18.50
79	9	137.91	170	3910	59.93	262	517	18.62
80	72	136.88	171	12	58.99	263	4578	17.58
81	321	135.95	172	36	58.48	264	255	17.02
82	874	131.98	173	184	57.92	265	6482	16.81
83	46	129.92	174	43	57.48	266	173	15.49 R
84	43	127.98	175	81	57.08	267	554	14.99
85	28	125.88	176	51	56.92	268	10888	14.81
86	9	124.84	177	64	56.48	269	586	13.58
87	11	123.86	178	361	56.27	270	71	11.67
88	24	121.88	179	266	55.91	271	19	11.31
89	245	120.95	180	92	55.61	272	973	11.83
90	648	119.91 R	181	142	55.27	273	231	10.83
91	18	118.84	182	4452	54.87	274	46	9.33
			183	121	54.48	275	4579	9.02 R

INTERPRET ? !Y

Figure 2
Original Interpretation of Data

MASS	ELEMENT	PPM ATOMIC	±?? +++?	CONFIRM ISOTOPE	CHECK OVERLAP	COMPLEX IONS
197	GOLD	66.73	2+	-	-----NO MATRIX-----	
195	PLATINUM	111.56	2+	YES		
193	IRIDIUM	2.12	NO	NO		
189	OSMIUM	3.61	NO	NO		
182	TUNGSTEN	1.98	NO	NO		
181	TANTALUM	7.37	NO	-		
178	HAFNIUM	.60	NO	NO		
175	LUCEFIUM	.37	NO	NO		
174	YTTREFIUM	182.24	2+	YES		
169	THULIUM	77.28	2+	-		
166	ERBIUM	113.28	2+	NO		
165	HOLMIUM	69.37	2+	-		
163	DYSPROSIUM	155.98	2+	YES		
159	TERBIUM	73.68	2+	-		
158	GADOLINIUM	97.86	2+	YES		
153	EUROPIUM	58.82	2+	YES		
147	SAMARIUM	67.48	2+	NO		
146	NEODYMIUM	182.14	2+	YES		
141	PRASEODYME	66.71	2+	-		
140	CERIUM	1.42	NO	NO		
139	LANTHANUM	97.11	2+	-		
138	BARIUM	.24	NO	NO		
133	CESIUM	5.54	2+	-		
128	TELLURIUM	2.40	NO	YES		
121	ANTIMONY	7.60	NO	NO		
118	TIN	2.99	NO	YES		
115	INDIUM	3.56	2+	NO		
111	CADMIUM	1.85	2+	NO		
105	PALLADIUM	151.71	2+	NO		
103	RHODIUM	117.84	2+	-		
101	RUTHENIUM	182.76	2+	YES		
95	MOLYBDENUM	2.15	2+	YES	194(97)	
93	NIOBIUM	.49	2+	-		
98	ZIRCONIUM	.23	NO	NO	180(98)	
89	YTTRIUM	STANDARD				
88	STRONTIUM	3.58	NO	NO	176(88)	
					174(87)	
					172(86)	
85	RUBIDIUM	19.17	2+	NO	178(85)	
					174(87)	
79	BROMINE	16.88	NO	YES	156(79)	
					162(81)	
80	SELENIUM	18.89	NO	NO	168(80)	
					154(77)	
					156(78)	
75	ARSENIC	6.43	NO	-	158(75)	
72	GERMANIUM	113.56	2+	NO	148(72)	
					146(73)	
					144(74)	
69	GALLIUM	2.96	2+	NO	142(71)	
66	ZINC	1.21	2+	YES	132(66)	
					198(66)	
					128(64)	
					192(64)	
MASS	ELEMENT	PPM ATOMIC	±?? +++?	CONFIRM ISOTOPE	CHECK OVERLAP	COMPLEX IONS
63	COPPER	.46	NO	NO	126(63)	
					189(63)	
					138(65)	
68	NICKEL	255.98	NO	NO	195(65)	
					124(62)	
					116(54)	
59	COBALT	.21	2+	-	174(58)	
					118(59)	
56	IRON	5.85	3+	NO	177(59)	
					168(56)	
					186(54)	
					162(54)	
55	MANGANESE	76.68	2+	-		
52	CHROMIUM	16.96	NO	NO	184(58)	
					156(52)	
					186(53)	
51	VANADIUM	28.82	2+	-	159(53)	
					182(51)	
					153(51)	
48	TITANIUM	115.88	2+	YES	141(47)	
45	SCANDIUM	184.68	2+	-		
40	CALCIUM	41.28	NO	NO	86(43)	
39	POTASSIUM	32.48	2+	NO	82(41)	
35	CHLORINE	176.84	2+	NO		
34	SULPHUR	55.88	NO	NO	182(34)	
					66(33)	
					99(33)	
					96(32)	
31	PHOSPHORUS	13.66	2+	-		
28	SILICON	141.18	NO	NO	87(29)	
					68(38)	
27	ALUMINIUM	55.89	2+	-		
24	MAGNESIUM	67.22	NO	NO	48(24)	
					52(26)	
					78(26)	
23	SODIUM	149.56	2+	-		
19	FLUORINE	.89	2+	-	36(19)	
					57(19)	
16	OXYGEN	118.27	NO	-	34(17)	
					51(17)	
14	NITROGEN	172.22	NO	-	26(14)	
					38(15)	
					45(15)	
11	BORON	28.12	NO	YES	20(18)	
					38(18)	
9	BERYLLIUM	78.86	NO	-		

END OF RUN

element. This column should be of little interest because of interference from other isotopes and complex ions. "Check overlap" reminds the operator of possible multiply-charged ion interferences. "Complex ions" is a printout of matrix atoms that could possibly interfere at a given m/e. These ions, in general, in a graphite matrix-water analysis are constant and this portion of the analysis is bypassed to save computer time.

The choice of a reliable analytical mass is exemplified in Figures 2 and 3. Titanium has isotopes of 46, 47, 48, 49, and 50 amu, all of which are listed in Figure 1. Since polycarbon ion interference exists at 48 and 49 amu, the choices are reduced to 46, 47, and 50 amu. Possible interfering isotopes are ^{46}Ca and ^{50}V , leaving 47 as a probable analytical mass. Possible interference exists at mass 47 from a multiply-charged ion of mass 94, which, in this case, is listed as present in Figure 1. These interferences leave only two logical choices for the analytical mass. Since ^{47}Ti is a more abundant isotope than ^{49}Ti , the other available odd number mass, the multiply-charged ^{47}Ti isotope at 23.5 amu is used for identification and quantitation.

Errors present in the use of multiply-charged ions in the original program have been corrected. These errors occurred in analyses that had detectable +2 and/or +3 ions occurring within a nominal amu (Figure 1). This error was possible because of a wide tolerance (0.2 amu) in the original software.

After the tolerance was changed to ± 0.09 amu, all masses used in data interpretation had to be changed in the software, since the original software used nominal masses for data interpretation. The differences between

Figure 3
Modified Interpretation of +1 and +2 Ion Data

JULY SEVENTEEN	CONCEN TRATIONS	++? +++?	CONFIRM ISOTOPES	CHECK OVERLAP	COMPLEX IONS
197 GOLD	88.75	2+	-	-----NO MATRIX-----	
195 PLATINUM	258.88	2+	YES		
191 IRIIDIUM	2.88	NO	NO		
189 OSMIUM	8.15	NO	NO		
182 TUNGSTEN	7.29	NO	NO		
175 LUTECIUM	.52	NO	NO		
172 YTTERBIUM	146.22	2+	YES		
85 THULIUM	87.23	2+	-	169(85)	
167 ERBIUM	136.39	2+	YES		
165 HOLMIUM	102.67	2+	-		
163 DYSPROSIUM	230.85	2+	YES		
159 TERBIUM	126.73	2+	-		
158 GADOLINIUM	222.27	2+	YES		
153 EUROPIUM	104.12	2+	YES		
147 SAMARIUM	116.74	2+	NO		
143 NEODYMIUM	152.42	2+	NO		
141 PRASEODYME	96.06	2+	-		
140 CERIUM	2.04	NO	NO		
139 LANTHANUM	67.01	2+	-		
138 BARIUM	.31	NO	NO		
66 CESIUM	.49	2+	-		
128 TELLURIUM	2.81	NO	YES		
118 TIN	1.89	NO	NO		
115 INDIUM	2.32	NO	NO		
111 CADMIUM	3.80	NO	NO		
105 PALLADIUM	101.65	2+	NO		
51 RHODIUM	52.31	2+	-	103(51)	
50 RUTHENIUM	77.83	2+	NO	101(50)	
95 MOLYBDENUM	1.41	NO	-	190(95)	
89 YTTRIUM	STANDARD				
43 RUBIDIUM	.66	2+	-	85(43)	
				170(85)	
28 MANGANESE	.01	2+	-	55(28)	
				82(28)	
25 VANADIUM	.70	2+	-	51(25)	
				76(25)	
24 TITANIUM	1.47	2+	NO	47(24)	
				71(24)	
23 SCANDIUM	103.97	2+	-	45(23)	
20 CALCIUM	3.86	NO	NO	40(20)	
				60(20)	
20 POTASSIUM	.21	2+	YES	39(20)	
				82(41)	
18 CHLORINE	220.39	2+	-	35(18)	
16 PHOSPHORUS	.41	2+	-	31(16)	
14 ALUMINIUM	.58	2+	-	27(14)	
12 SODIUM	.63	2+	-	23(12)	
19 FLUORINE	.03	NO	-	38(19)	
				57(19)	
16 OXYGEN	19.84	NO	-	34(17)	
				51(17)	

JULY SEVENTEEN	CONCEN TRATIONS	++? +++?	CONFIRM ISOTOPES	CHECK OVERLAP	COMPLEX IONS
14 NITROGEN	27.55	NO	-	28(14)	
				30(15)	
				45(15)	
11 BORON	1.18	NO	NO	20(10)	
				30(10)	
9 BERYLLIUM	.94	NO	-		

END OF RUN

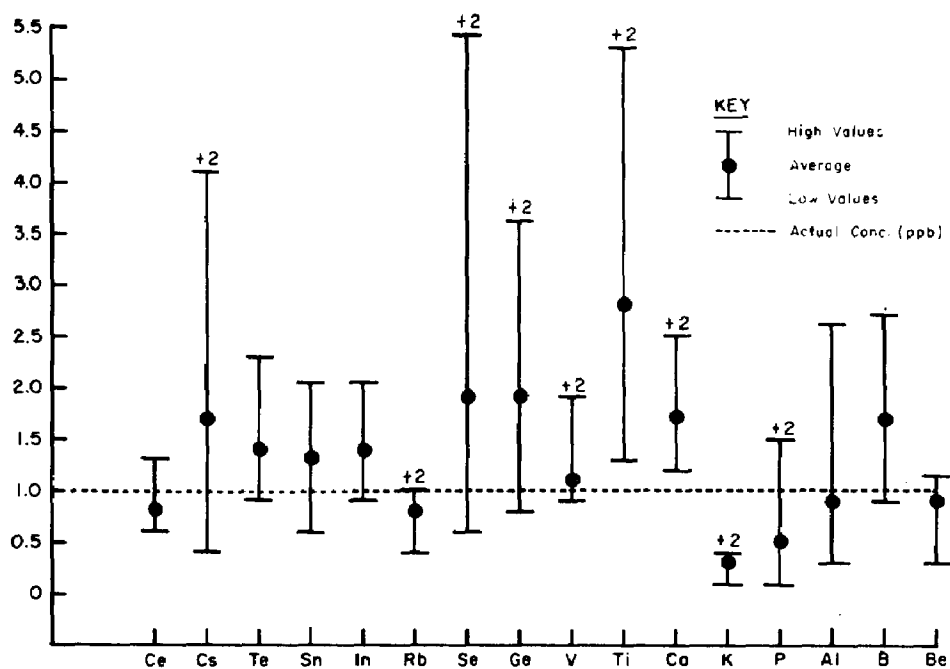
nominal mass and accurate mass calculated by the computer were in some cases greater than the new tolerance. In other cases, they allowed for very little instrumental and hardware error.

The value of these changes can be seen by comparing the accurate mass, the original interpretation, and the modified system (Figures 1, 2, and 3). In the original interpretation (Figure 2) niobium is incorrectly reported and confirmed using the +2 ion. Confirmation of +2 for niobium was supposedly made at 93/2 amu or 46.5 amu. In checking the accurate mass listing (Figure 1) the only ion occurring between 46 and 47 amu is 46.32 amu, which is a +3 ion of ^{139}La . This error is due to the ± 0.2 amu as the 46.5 amu confirmation. It can be seen in the output of the corrected system (Figure 3) that niobium is neither reported nor confirmed. This error occurred also for gallium, zinc, cobalt, and iron in the original data (figure 2).

Using the modified software system, a series of samples having highly varying concentration ratios and atomic weight differences has been analyzed. Results are shown in Figures 4 and 5. Coefficients of variation for each element are given in Tables 1 and 2. These values are based on 9 separate runs using a fresh set of electrodes for each analysis. The statistical data shown agree with those reported earlier by this laboratory.²

Results of the analyses of natural samples show comparable precision to the data shown in Tables 1 and 2. Tables 3 and 4 represent the analysis of an effluent sample sent to our laboratory. The sample was prepared by centrifugation. The liquid was then decanted carefully to preserve the integrity of the pellet. Two one-

FIGURE 4
SAMPLE *1
GROUP I



SAMPLE *1
GROUP II

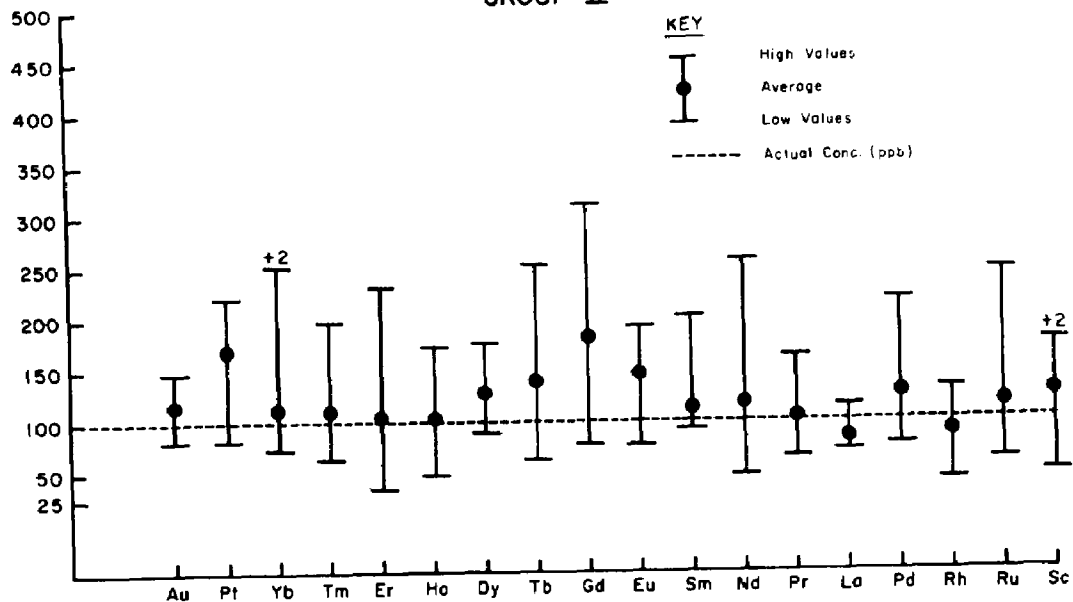
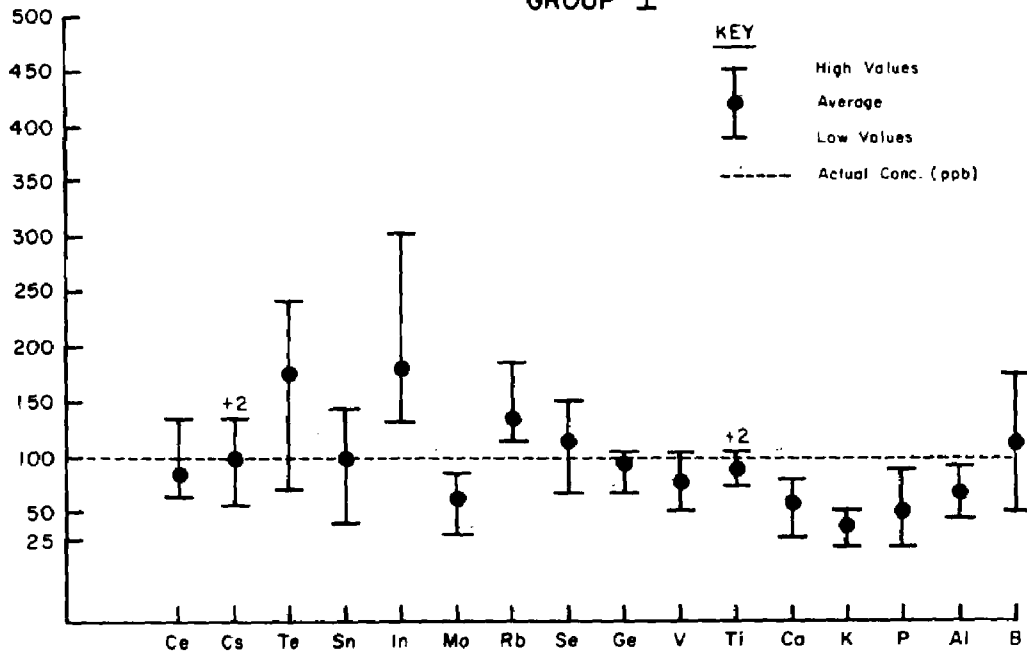


FIGURE 5
SAMPLE #2
GROUP I



SAMPLE #2
GROUP II

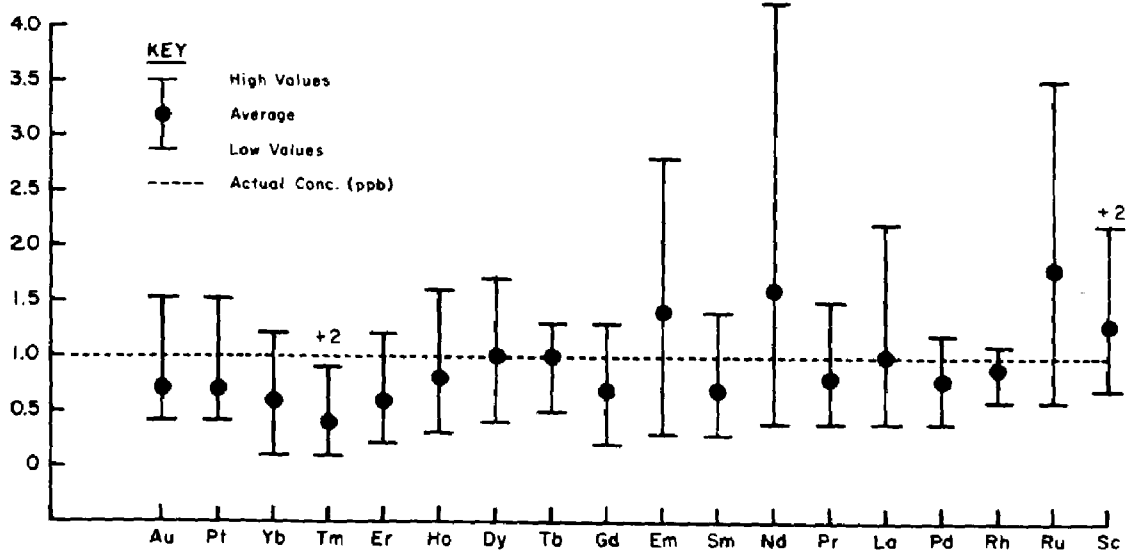


Table 1. GROUP I COEFFICIENTS OF VARIATION EXPRESSED
IN PERCENT

Element	Sample #1	Sample #2
Ce	3×10^1	38
Cs	2×10^1	53
Te	2×10^1	73
Sn	3×10^1	60
In	2×10^1	70
Rb	3×10^1	38
Se	3×10^1	33
Ge	2×10^1	16
V	3×10^1	16
Ti	2×10^1	21
Ca	1×10^1	19
K	5×10^1	45
P	6×10^1	33
Al	3×10^1	31
B	2×10^1	33
Be	2×10^1	53

Table 2. GROUP II COEFFICIENTS OF VARIATION EXPRESSED
IN PERCENT

Element	Sample #1	Sample #2
Au	17	4×10^1
Pt	27	5×10^1
Yb	54	4×10^1
Tm	38	2×10^1
Er	59	4×10^1
Ho	43	4×10^1
Dy	22	4×10^1
Tb	45	3×10^1
Gd	41	3×10^1
Eu	25	8×10^1
Sm	31	4×10^1
Nd	58	10×10^1
Pr	32	3×10^1
La	16	6×10^1
Pd	36	2×10^1
Rh	32	4×10^1
Ru	50	10×10^1
Sc	32	4×10^1

Table 3. ANALYSES OF EFFLUENT SAMPLE

Part I - SS Analysis of Water (Results Expressed in Parts Per Million by Weight)							
Element	Avg	#1	#2	Element	Avg	#1	#2
Mg	20	27	14	Pb	0.6	0.8	0.4
P	15	15	15	Cu	0.6	0.5	0.7
Ca	10	12	8	Zn	0.5	0.6	0.4
K	9	14	6	Mn	0.3	0.4	0.2
Fe	7	7	6	Sr	0.2	0.2	0.2
Al	7	11	5	Co	0.1	0.09	0.08

Part II - SS Analysis of Major Concentration Elements in Sediment Analysis (Results in Weight Percent)

Element	Avg	#1	#2	Element	Avg	#1	#2
Fe	10	10.1	9.8	K	0.3	0.22	0.40
Mg	4	6	3	Al	0.3	0.27	0.35
Ca	2	2.9	1.8	P	0.2	0.24	0.12
Mn	0.8	1.0	0.6				

Part III - SS Analysis for the Lower Concentration Elements in Sediment (Results Expressed in Parts Per Million by Weight)

Element	Avg	#1	#2	Element	Avg	#1	#2
Sr	45	35	55	Sc	3	3.0	3.4
Ba	40	33	47	La	2	1.6	3.1
Ti	14	18	11	Sm	2	2.0	2.7
Zn	11	14	8	Cu	2	3.2	1.1
Zr	8	10	6	V	2	1.4	2.5
Ce	6	8	5	Pb	1	0.9	1.4
Y	5	6	4	Nb	1	1.4	0.4
Co	5	8	3	Rb	1	0.96	0.60
Er	3	3	3	As	1	0.5	1.5
Nd	3	3	--	Be	1	0.8	1.5
				Cs	0.5	0.5	0.47

Table 4. RELATIVE SENSITIVITY STUDY IN SEDIMENT USING INDIUM AND YTTRIUM CROSS CHECK (Established Relative Sensitivities Have Been Applied to All Results)

Part I -- Sediment Plus Standards

Calculated Weight Percent		
Major Element	Yttrium Standard	Indium Standard
Fe	10	9
Mn	0.8	1.0
Ca	2.3	2.5
K	0.3	0.2
P	0.2	0.1
Al	0.3	0.2
Mg	4.0	4.4

Part II-- Dilution of Above Sample with More Unspiked Sample

Calculated Concentration in ppm by Weight		
Minor Element	Yttrium Standard	Indium Standard
Ce	6	10
Ti	14	11
La	4	2
Ba	40	58
Nb	1	1
Zr	8	10
Sr	45	38

Part III--Sediment with Added Elements

Weighed amounts of these elements were added to the sediment for analysis using yttrium as the internal standard and applying relative sensitivities

Weight Percent

	Added	Found
Ba	6.8	7.2
Zr	4.7	4.2
Sr	3.8	3.4

milliliter water samples were spiked with yttrium as the internal standard. These were dried on graphite and compacted into electrodes for analysis. The sediment samples were dried at 110°C for two hours, weighed and spiked dry using yttrium and indium as the internal standards.

The validity of using relative sensitivity coefficients, which were obtained from very dilute solutions, in analyzing sediments was tested by two experiments. In the first of these, the sediment samples mentioned above were spiked with both yttrium and indium and analyzed using first yttrium and then indium as the internal standard. Table 4 (Parts I and II) shows a negligible difference between the values, establishing the validity of a single reference standard.

In the second experiment, relatively gross amounts of barium, strontium, and zirconium salts were added to the sediment; the sample was analyzed using the dilute-solution-derived sensitivity coefficients relative to yttrium. Results (Table 4, Part III) are in excellent agreement with the known concentrations. The relative sensitivities calculated from solutions with concentrations at the ppm levels, were therefore suitable for this analysis with concentrations in the percent range. Taken together, these two experiments indicate that, for these elements, there is no significant shift in relative sensitivity coefficients between very dilute solutions and complex sediments.

Background data from a reservoir study (Table 5) show another application of SS analysis of natural samples. The reservoir has been the site of a number of recurring fish kills. The SS data will be compared later to data

Table 5. SS ANALYSES OF RESERVOIR WATER

Element	SS	AA
Pb	2 ppb	≤ 50 ppb*
Ba	160 ppb	
Ce	2 ppb	
Te	1 ppb	
Sn	10 ppb	
Cu	5 ppb	12 ppb
Ni	8 ppb	≤ 50 ppb*
Co	5 ppb	
Cr	20 ppb	≤ 50 ppb*
V	3 ppb	
Zn	60 ppb	40 ppb
Ti	20 ppb	
Fe	2 ppm	3.5 ppm
Mn	60 ppb	
P	30 ppb	
Sr	2 ppm	

*AA detection limit for method used

to be taken at the time of future fish kills. Comparison results with atomic absorption (AA) were available for some elements and are noted. Coefficients of variation for these SS data range from 19 to 50% and average 33% on the analysis.

SECTION VI

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4. Title

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6.

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EPA-660/2-74-001, January 1974**

16. Abstract

A spark source mass spectrometer that uses electronic detection and a dedicated data analysis system was applied to a survey type trace analysis for chemical elements. Errors in the data system software were identified and corrected. Modifications to the system permit identification and quantitation of 72 elements at the part per billion level in water samples.

17a. Descriptors ***Mass Spectrometry, *Trace Analysis, *Survey Analysis,
*Analytical Techniques, *Water Pollution, *Sediment Analysis**

17b. Identifiers ***Spark Source Mass Spectrometry, Computerized Data System,
Electrical Detection**

17c. COWRR Field & Group **05A**

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