

METHODS OF WATER ANALYSIS BY INDUCTIVELY COUPLED PLASMA-EMISSION SPECTROMETRY

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ABSTRACT

The development of rapid and reliable methods of analysis by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) has been undertaken for the determination of elemental concentrations in natural waters for applications in exploration and environmental geochemistry. This paper examines twenty-two elements (Li, Be, Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Y, Mo, Ba), which could supplement or, in some circumstances, replace data derived from the more traditional sample types.

The approach used to assess the methods developed for ICP-ES was to analyze subsamples by other independent methods and to use reference materials along with bulk-water samples to compare the results obtained. These methods included Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Atomic Absorption Spectrometry (AAS) and Ion Chromatography (IC).

INTRODUCTION

Exploration geochemists employ a variety of sample media in geochemical mapping. Traditionally, sampling of soil, sediments and rocks has been used for the preparation of geochemical maps. For environmental applications, trace-element levels in waters are commonly of much greater relevance than levels in sediment. In most cases, samples of solid materials require additional time and cost to obtain suitable sample solutions, which are appropriate for analysis by atomic spectroscopy methods.

Water samples have been used by geochemists in the past but their application has been limited due to a variety of problems ranging from sampling, sample preparation, reagent purity, and most importantly the sensitivity of available techniques. With modern instrumentation, purer reagents and proper sampling procedures, water analysis can at the least supplement and confirm the results obtained from analysis of more conventional sample media.

During the past year, methods have been developed and applied for the analysis of natural waters by ICP-ES. Twenty-two elements (Li, Be, Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Y, Mo, Ba) are routinely determined at the Newfoundland Department of Mines and Energy laboratories. Fluoride by ion-selective electrode, conductivity and pH are determined as well. These elements are currently being assessed in mineral exploration and environmental baseline studies in comparison to stream and lake sediment and vegetation.

A major problem in water analysis is the lack of available reference materials to evaluate the accuracy of derived methods. Methods can only be evaluated by comparison of

results with other independent methods, repeated analysis of bulk water samples and duplicate analysis.

METHODS

FIELD METHODS

All samples for this research were collected in the Baie Verte and Bay d'Espoir areas during the summer of 1991 (Finch *et al.*, 1992). Samples were collected from streams and lakes by immersing a polyethylene bottle into the water at sufficient depth to avoid sampling surfactant material or any bottom sediment. All samples were filtered using a 0.45 micron filter and acidified with glass-distilled nitric acid within twenty-four hours of collection. *In situ* conductivity and pH measurements were made at each site.

ANALYTICAL METHODS

The instrument used for all analyses was an ARL 3520 sequential Inductively Coupled Plasma-Emission Spectrometer (ICP-ES). For elements requiring more sensitivity, a Fisons Ultrasonic Nebulizer (USN) was used. The measurement of Na, Mg, Si, S, K, Ca, Fe and Mn was made by direct nebulization. The wavelengths of the analytical lines are listed in Table 1 and for most cases primary lines were used (Winge *et al.*, 1985). Before sample analysis, all analytical lines were investigated for interferences by scanning the region of the analytical line with elements whose spectra could potentially interfere. No significant interferences were discovered for these eight elements.

The scans of the analytical lines of the eight elements analyzed by direct nebulization also provided spectra to enable the determination of background correction measuring

Table 1. Wavelengths, background offsets, detection limits and method used for ICP-ES determinations

ELEMENT nm	WAVELENGTH nm	BACKGROUND OFFSET nm	DETECTION PPB	METHOD
Si as SiO ₂	251.61	+0.0500	100	Direct
Mg	279.55	+0.0470	1	Direct
Ca	422.68	+0.0870	10	Direct
Na	589.59	+0.0810	10	Direct
K	766.49	±0.0670	100	Direct
Fe	259.94	-0.0500	5	Direct
Mn	257.61	+0.0520	2	Direct
S as SO ₄	180.73	-0.0395	100	Direct
Li	670.11	-0.0709	1	USN
Be	313.11	±0.0325	0.1	USN
Al	308.22	+0.0487	10	USN
P	178.89	±0.0235	5	USN
Sr	470.77	-0.0750	0.5	USN
Ba	455.40	-0.0709	1	USN
Ti	336.12	-0.0400	1	USN
Cr	267.72	-0.0440	1	USN
Co	228.62	-0.0320	1	USN
Ni	231.60	-0.0440	2	USN
Cu	324.75	-0.0460	1	USN
Zn	213.86	-0.0380	0.5	USN
Y	371.03	-0.0490	0.5	USN
Mo	202.03	±0.0245	1	USN

positions (Table 1). The position of these points must be greater than the half-peak-width from the base of the peak, but points farther from the peak are more desirable if they do not encounter signals from other matrix elements (ARL 1985). Three-sigma detection limits were determined for each analytical line by running blanks and standard solutions during each analytical run (Table 1). Operating parameters for the ICP are listed in Table 2.

For an analytical run, all standards were prepared fresh from existing stock solutions that were made with commercially available Spex-Industries-Inc. standards for plasma emission spectrometry. Blanks were prepared from deionized water and acidified with glass-distilled nitric acid to the concentration of the samples. The instrument was calibrated at the beginning of each run with the freshly prepared standards. Each element determination consisted of a thirty second pre-integration time, one off-peak background measurement and three on-peak measurements of five seconds. During the analytical run, instrument drift was monitored and regularly corrected.

Fourteen elements (Li, Be, Al, P, Ti, Cr, Co, Ni, Cu, Zn, Sr, Y, Mo, Ba) were determined by Ultrasonic Nebulization (USN). This approach was used for these elements because conventional direct nebulization does not provide adequate detection limits for their determination. This sample introduction technique provides better sensitivity for most elements by improving two important factors. First, nebulization efficiency is enhanced by presenting a finer, more uniform aerosol to the plasma, and second, in-line desolvation

Table 2. Operating parameter for ICP-ES

Gas Flow Rates	
Coolant	12 l/min
Plasma	0.8 l/min
Nebulizer	1 l/min
Solution Uptake Rate	
Direct	1.7 ml/min
USN	3.5 ml/min
RF Generator	
Incident Power	1200 watts
Reflected Power	< 10 watts
USN	
Transducer Incident Current	30 micro amps
Reflected Current	7 micro amps
Desolvation Tube	120°C
Cooling Water	1°C

of the sample solution provides a more concentrated aerosol to the plasma (ARL 1700796). These factors also reduce cooling of the plasma. Operating conditions for USN are given in Table 2.

All analytical lines are primary wavelengths (Table 1). Spectral interferences and background-measurement positions were determined in the same manner as elements determined

Table 3. Mean, percent relative standard deviation (RSD %) and number of determinations of RR-2 by ICP-ES and ICP-MS

ELEMENT	ICP-ES			ICP-MS		
	MEAN	RSD %	N	MEAN	RSD %	N
SiO ₂	1.37 ppm	11.2	21	1.54 ppm	5.6	21
Mg	1.54 ppm	1.2	21	1.45 ppm	2.8	21
Ca	7.46 ppm	1.5	21	6.75 ppm	1.5	21
Na	59.95 ppm	1.4	21			
K	0.93 ppm	4.9	21			
Fe	125 ppb	5.2	21	117 ppb	15.3	21
Mn	107 ppb	1.7	21	99 ppb	1.6	21
SO ₄	8.4 ppm	1.0	21			
Li	1.0 ppb	37.2	7	0.7 ppb	25.7	21
Be	0.07 ppb	58.5	7	0.01 ppb	600	21
Al	6.7 ppb	16.5	7	10.5 ppb	15.3	21
P	4.5 ppb	76.7	7			
Sr	33.2 ppb	5.1	7	35.5 ppb	1.3	21
Ba	20.1 ppb	7.1	7	20.9 ppb	2.1	21
Ti	1.9 ppb	45.4	7	0.9 ppb	33.3	21
Cr	0.5 ppb	40.0	14	0.1 ppb	320	21
Co	0.5 ppb	31.0	14	0.07 ppb	14.9	21
Ni	8.0 ppb	21.1	14	8.8 ppb	4.0	21
Cu	1.2 ppb	25.9	14	1.9 ppb	7.4	21
Zn	5.3 ppb	14.2	14	6.4 ppb	5.0	21
Y	0.1 ppb	66.6	14			
Mo	0.5 ppb	64.4	14	0.11 ppb	27.3	21

by direct nebulization. Detection limits for these elements (Table 1) were determined by measuring blanks and standards with each analytical run. The sample introduction system of the USN has a longer path length than direct nebulization so it is necessary to increase the pre-integration time to 45 seconds for this type of analysis. The number of on-peak signal measurements and off-peak background measurement is the same as that used for the direct nebulization. Integration times are also five seconds. Typically, instrument drift is more severe when using the USN but it can be monitored and corrected during analysis.

RESULTS

To examine the validity of the results achieved by ICP-ES, each element was also determined by a different, and generally more sensitive, method in another laboratory using the same sample or a field duplicate. From this interlaboratory comparison the suite of elements that can be measured satisfactorily by ICP-ES in surface waters in Newfoundland was determined and, as well, the elements for which another, more sensitive method is necessary were also identified. The samples were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the Centre for Earth Resources Research at Memorial University; determined by Atomic Absorption Spectrometry (AAS) and Ion Chromatography (IC) at the Geological Survey of Canada in Ottawa.

A bulk sample of Rennies River water was collected and prepared for analysis by the same procedures used for the

samples. This sample was analyzed by both ICP-ES and ICP-MS. Table 3 contains the means, precision expressed as percent relative standard deviation and the number of determinations made for each element.

In an effort to determine the accuracy and precision of these methods, a reference water sample, T-107 from the United States Geological Survey, was determined by ICP-ES and ICP-MS. Table 4 lists the most probable value, means, percent relative standard deviation and the number of determinations made by ICP-ES and ICP-MS respectively. The number of determinations for T-107 were limited due to the availability of this material.

The analysis of T-107 can give some insight into the accuracy and precision of the methods used for these analyses, but this sample is not similar in composition to Newfoundland waters. Analysis of the bulk Rennies River water sample is more representative of Newfoundland waters but its composition is not well characterized.

With the determination of elements from at least two independent methods, simple regressions and correlations were performed. This approach could aid in the determination of bias and confirmation of results obtained by ICP-ES. Table 5 shows correlation coefficients, slopes and the number of samples included in the regression. All regressions are significant at 99 percent confidence levels with the exception of Ti, which is significant at the 98 percent confidence level.

Table 4. Mean, percent relative standard deviation (RSD %) and number of determinations of T-107 by ICP-ES and ICP-MS

ELEMENT	MPV	ICP-ES			N	ICP-MS		
		MEAN	RSD %			MEAN	RSD %	N
SiO ₂	7.70 ppm	7.84 ppm	11.2	7		7.70 ppm	3.1	21
Mg	2.10 ppm	2.14 ppm	1.2	7		2.06 ppm	4.9	21
Ca	11.7 ppm	11.83 ppm	1.5	7		10.7 ppm	2.5	21
Na	20.7 ppm	21.37 ppm	1.4	7				
K	0.84 ppm	0.83 ppm	4.9	7				
Fe	52 ppb	53 ppb		1		50 ppb	64.0	21
Mn	45 ppb	49 ppb		1		44 ppb	1.4	21
SO ₄		19.8 ppm		1				
Li	193 ppb			1		203 ppb	5.5	21
Be	11.0 ppb	11.0 ppb		1		11.8 ppb	8.5	21
Al	220 ppb	231 ppb		1		216 ppb	5.1	21
P		1.0 ppb		1				
Sr	61 ppb	60.0 ppb		1		61 ppb	0.8	21
Ba	192 ppb					194 ppb	1.0	21
Ti						1.5 ppb	30.7	21
Cr	13.0 ppb					12.6 ppb	1.3	21
Co	11.0 ppb					10.8 ppb	0.9	21
Ni	28.1 ppb					26.1 ppb	1.8	21
Cu	30 ppb	27.0 ppb		1		29 ppb	2.4	21
Zn	75.8 ppb	78.0 ppb		1		85 ppb	3.3	21
Y		0.5 ppb		1				
Mo	15 ppb	15.0 ppb		1		15 ppb	0.8	21

MPV : Most Probable Value USGS

Figures 1 through 5 are XY plots for the elements Co, Cr, Cu, Mo and Ni. These plots are log transformed and depict the elements of intermediate degrees of detectability.

DISCUSSION

Twelve elements (Si, Mg, Ca, Na, K, Fe, Mn, S, Al, Sr, Ba, Zn), from a perspective of detection limits, are determined well by ICP-ES methods developed for this study. These elements are essentially 100 percent detectable for the 192 samples of Newfoundland lake and stream waters collected and analyzed in this dataset. Five of these elements (Si, Ca, Mg, Fe and S), actually have lower detection limits than those obtained by ICP-MS analysis where for example, Fe and Si are only 72 percent and 54 percent detectable respectively in this sample set by ICP-MS analysis.

The correlation coefficients (Table 5) of these twelve elements indicate generally very good linear association between the methods, regardless of whether the samples were analyzed by ICP-MS, AAS or IC. Although bias is evident between methods for some elements, as indicated by the slopes (Table 5), good agreement between methods is apparent from analysis of standard reference material T-107 (Table 4) and bulk water sample RR-2 (Table 3). However, some exceptions are notable. Calcium, by ICP-MS has a higher result than the most probable value (MPV) of T-107 (Table 4), whereas ICP-ES is much closer to this value.

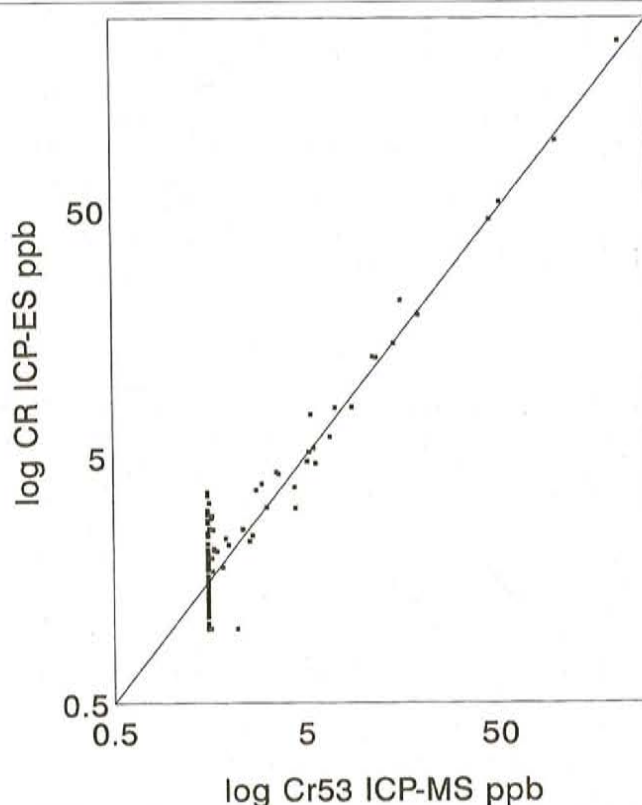


Figure 1. XY plot of log Cr by ICP-MS vs. log Cr by ICP-ES with slope of 1.09 and correlation coefficient of 1.00.

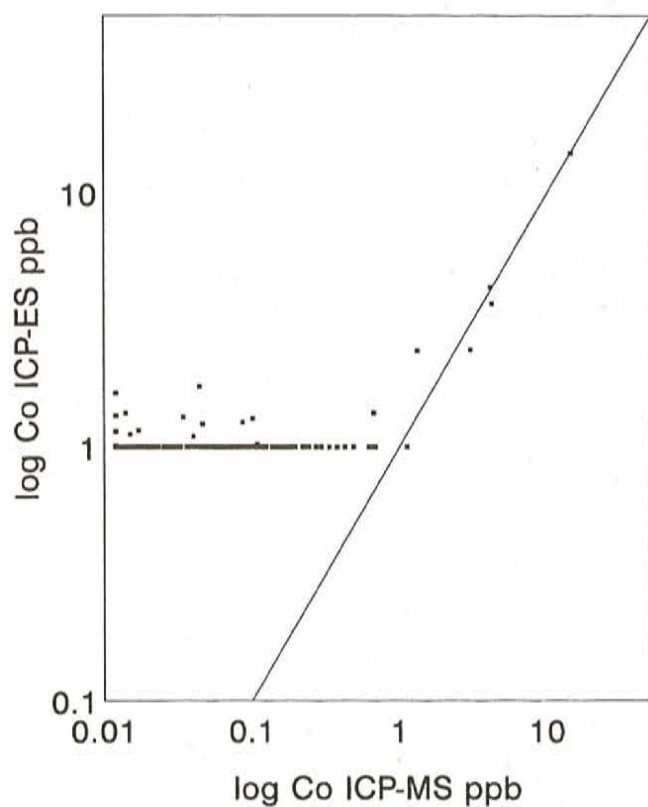


Figure 2. XY plot of log Co by ICP-MS vs. log Co by ICP-ES with slope of 0.87 and correlation coefficient of 1.00.

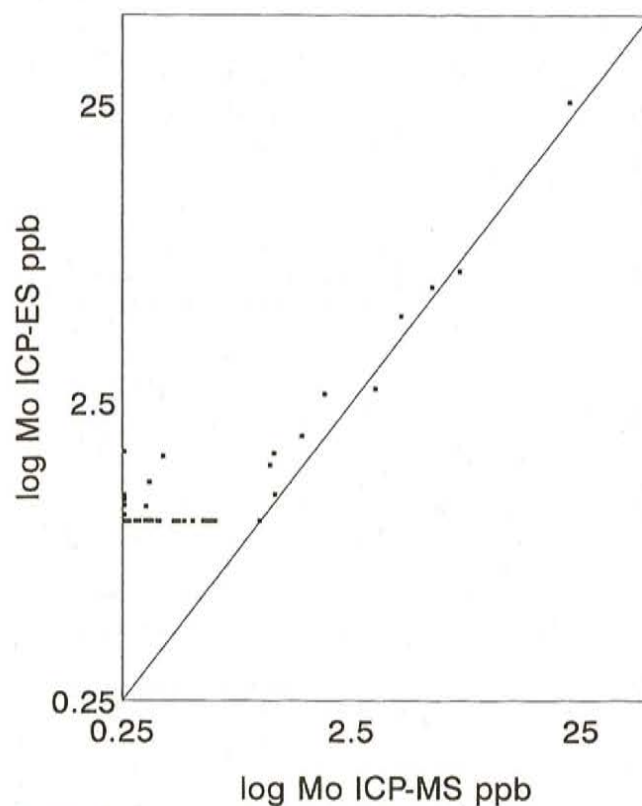


Figure 4. XY plot of log Mo by ICP-MS vs. log Mo by ICP-ES with slope of 1.08 and correlation coefficient of 0.99.

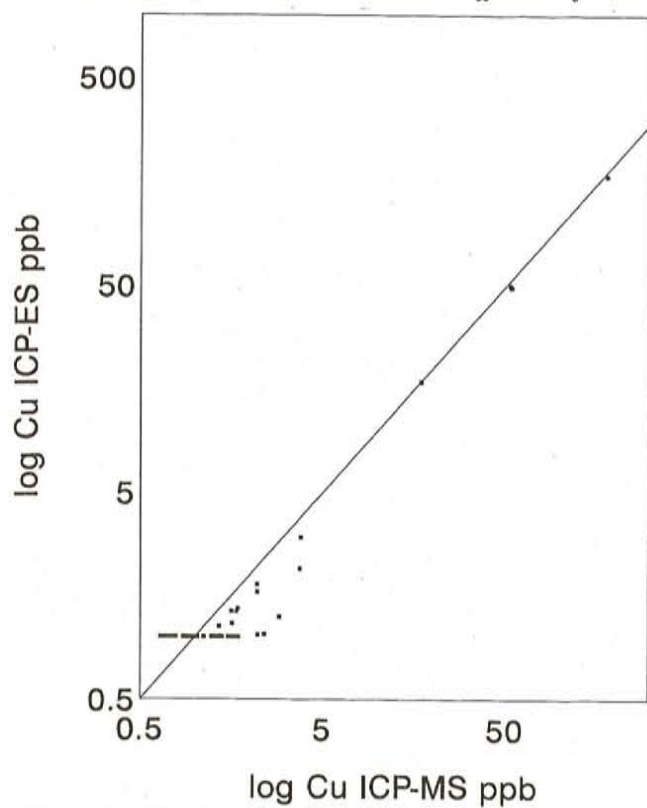


Figure 3. XY plot of log Cu by ICP-MS vs. log Cu by ICP-ES with slope of 0.95 and correlation coefficient of 1.00.

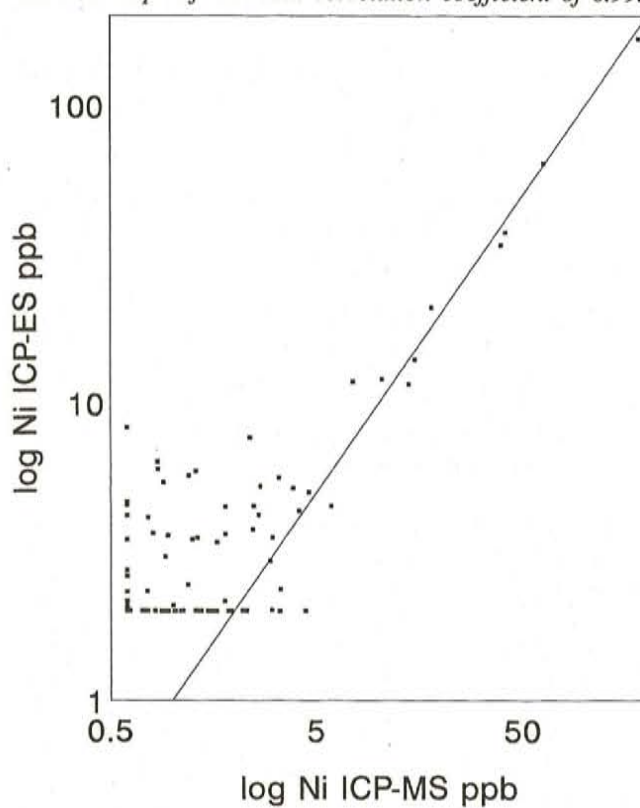


Figure 5. XY plot of log Ni by ICP-MS vs. log Ni by ICP-ES with slope of 0.91 and correlation coefficient of 1.00.

Table 5. Correlation coefficients (R), slopes and number of samples (N) above detection limits for ICP-MS, AAS and IC versus ICP-ES

ELEMENT	ICP-MS			AAS			IC		
	R	SLOPE	N	R	SLOPE	N	R	SLOPE	N
SiO ₂	0.96	1.08	89						
Mg	1.00	1.01	192	1.00	1.02	192			
Ca	0.99	1.08	192	0.99	0.96	192			
Na				1.00	1.00	192			
K				0.93	1.00	168			
Fe	0.99	1.08	138	0.84	1.01	150			
Mn	1.00	1.09	192	1.00	1.14	61			
SO ₄							0.98	1.00	192
Li									
Be									
Al	0.95	0.87	192						
P									
Sr	1.00	0.89	192						
Ba	1.00	0.95	192						
Ti	0.79	0.68	11						
Cr	1.00	1.09	43						
Co	0.99	0.87	20						
Ni	1.00	0.91	54						
Cu	1.00	0.95	16						
Zn	1.00	0.88	192	0.97	0.96	89			
Y									
Mo	0.99	1.08	19						

Silicon and Al are higher by ICP-ES than the ICP-MS result and ICP-MS determinations for these elements is in better agreement with the MPV of T-107 (Table 4).

Five elements (Co, Cr, Cu, Mo, Ni) fall into an intermediate range of detectability for ICP-ES methods studied. Chromium has the highest level of detection at 50 percent and Cu the lowest at 8 percent. The ICP-MS data for Co has a much lower detection limit with 72 percent of the samples being detectable versus 10 percent of the data for ICP-ES. Chromium by ICP-ES is approximately twice as detectable as ICP-MS at 50 percent and 27 percent respectively. The other elements of this group (Mo, Ni) have essentially the same levels of detectability.

Table 5 indicates strong correlations between the comparative methods used for these five elements. Caution should be taken due to the low number of detectable samples in this group and high regression weighting given to some samples that have very high concentrations (Figures 1 to 5). Examination of the slopes obtained from linear regressions for this set of elements indicates that method bias is not too extreme. Analyses of T-107 by ICP-MS show good agreement with the most probable value (Table 4) and single determinations by ICP-ES for Cu and Mo also agree well with the most probable value.

The final five elements (P, Be, Li, Y, Ti) are the group with the lowest number of detectable samples. Phosphorus

by ICP-MS or IC is not detectable for any of the samples. The detection limit for ICP-ES is 5 ppb but only a few percent of the samples have measurable concentrations. The Ti analyzed by ICP-MS has a relatively high degree of detection at 46 percent for this sample set, but there is a poor correlation between this method and ICP-ES determinations due in part to fairly high RSD values for both methods. However, the correlation is significant at the 98 percent confidence level. The Ti regression of ICP-ES versus ICP-MS produces a slope of 0.68 indicating a substantial bias. It is apparent that determinations made by ICP-ES are substantially lower than the ICP-MS data.

Li and Be have lower detection limits by ICP-ES than ICP-MS but even by ICP-MS these elements are detectable in only a few samples. The analyses of Be by both methods shows good agreement with the MPV for T-107 but this value is well above detection limits for both methods. Yttrium was analyzed by only one method, ICP-ES, and no comparisons could be made. The detection limit by ICP-ES was 0.5 ppb, yet only a few samples were detectable out of 192.

CONCLUSION

Inductively Coupled Plasma-Emission Spectrometry methods presented in this paper show promise for the direct determination of seventeen of twenty two elements that were determined in this study. Twelve elements (Si, Mg, Ca, Na, K, Fe, Mn, S, Al, Sr, Ba, Zn) are essentially detectable in all samples analyzed for this study and show good agreement

to other comparative methods. These elements should provide useful data for the exploration geochemist.

Five elements (Co, Cr, Cu, Mo, Ni), although not detectable in every sample collected, still may provide some useful insight or at least supplement other data.

The final group of elements (P, Be, Li, Y, Ti) have the fewest number of detectable samples. Background, and even in some cases what must be anomalous values, are well below detection limits of these ICP-ES methods. Analysis by ICP-MS from 250 lake-water samples of the eastern United States was only able to detect 39 elements out of 49 (Henshaw *et al.*, 1989). In general, in comparison with ICP-ES, ICP-MS is more sensitive for the analysis of most elements with exception of the lighter elements.

For these elements and others that may be analyzed by ICP-ES, further work will have to be carried out to achieve acceptable levels of detections for water samples. This may include chelation pre-concentration methods such as those developed by G.E.M. Hall at the Geological Survey of Canada for the analysis of rare-earth elements and base metals (Finch *et al.*, 1992). Other options may include simple pre-concentration of the samples.

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