THE REGIONAL GEOCHEMICAL SURVEY:
EVALUATION OF AN ICP-ES PACKAGE*

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INTRODUCTION

In 1975, the Geological Survey of Canada (G.S.C.) established analytical methods for the British Columbia Regional Geochemical Survey (RGS) program (Garrett, 1974). These methods are consistent with those established for the National Reconnaissance program, facilitate national and provincial comparison by ensuring the data are of similar precision for a particular element and consistent with some relative baseline level in terms of accuracy. As a result, the G.S.C. and the British Columbia Geological Survey Branch have continued to use the same analytical system (that is, the same sample preparation and decomposition methods, with atomic absorption spectroscopy as the final determination step) to determine 13 elements in stream and lake sediments collected for the RGS program. In the early 1980s, simultaneous determination of 30 elements or more by inductively coupled plasma emission spectroscopy (ICP-ES) provided superior cost performance and has since replaced atomic absorption spectroscopy (AAS) as the popular method for determining concentrations of trace and major elements in sediments, soils and rocks. Inductively coupled plasma-emission spectroscopy also offers technical advantages over AAS (Fletcher, 1981; Thompson, 1986), namely:

● Virtually simultaneous multi-element analyses.

● Determination of trace and major elements in the same solutions, without dilution.

● Fewer molecular interferences and lack of interference due to formation of refractory compounds.

These cost and technical advantages suggested that a study was needed to determine if ICP-ES analyses might replace AAS determinations for many of the elements in the routine 13-element package. If findings were positive, future RGS surveys could benefit from the determination of many more elements with no increase in analytical costs. Accordingly, as part of the 1986 RGS program in the Whitesail Lake area (93E), one set of samples was analysed by standard RGS methods and a second set similarly prepared and digested but analysed by ICP-ES at the same commercial laboratory in order to test analytical quality. This preliminary report examines elemental responses from the ICP-ES determinations with respect to analytical sensitivities and reproducibility. Comparisons with standard RGS analytical methods are also discussed where appropriate. The results from this study enable preliminary recommendations to be made concerning the use of ICP-ES as the final determination step in future RGS programs.

PURPOSE OF STUDY

Fundamentally, we must determine if lower cost simultaneous determination of elements by ICP-ES is a suitable alternative to standard AAS determinations following the same type of digestion. In the case of the RGS, the provincial geochemical database must continue to conform to national standards, permitting exploration companies and governments to make informed policy decisions based on consistent data (Matysek, 1987; Gravel and Matysek, 1988). In this study the following questions are addressed:

● How do a pair of analyses obtained from the two approaches differ, and what biases are present?

● What are the precision characteristics of the two methods, at concentrations typical of stream and lake sediments?

● Which additional major and trace element concentrations reported as part of the ICP-ES package are adequately sensitive and precise?

● For which elements can regional trends be distinguished?

STUDY DATA: 1986 RGS-16 93E, WHITESAIL LAKE

A total of 1169 sediment samples were collected at a density of one sample per 13 square kilometres from streams (82 per cent) and lakes (18 per cent), of which 65 pairs of samples were field-site duplicates. All samples are field dried and sieved to –80-mesh for subsequent analysis. Included in the data set were 65 samples made from laboratory splits (analytical duplicates) of randomly selected sediment samples and 65 samples representing control standards. One field duplicate, one analytical duplicate and one control reference were randomly inserted into each batch of 20 samples. The locations of duplicates in the batches were unknown to the commercial laboratory contracted for the analytical work.

ANALYTICAL PACKAGES

CONVENTIONAL RGS — ATOMIC ABSORPTION SPECTROSCOPY

Most elements were determined following Lefort aqua regia digestion ($3HNO_3$:HCl). Three millilitres of concentrated nitric acid was added to 1 gram of each sample and heated in a boiling water bath for 30 minutes. The sample was then cooled to room temperature and 1 millilitre of concentrated hydrochloric acid added. Finally, following reheating

for 30 minutes in the water bath and cooling, the solution was made up to 25 millilitres with demineralized water and concentrations determined for zinc, copper, lead, nickel, cobalt, manganese, iron, silver and cadmium by flame AAS. Arsenic and antimony in solution were reduced to their hydrides and determined by flame AAS. Mercury was determined by flameless AAS following reduction to Hg^0 (vapour). Molybdenum was released from 0.5 gram of sample in a separate Lefort aqua regia digestion and barium was liberated from a 0.25 gram of sample with a hydrofluoric-perchloric-nitric acid (5:8:2) mixture. Both elements were determined by flame AAS.

INDUCTIVELY COUPLED PLASMA — EMISSION SPECTROSCOPY

Half a gram of each sample was treated with Lefort aqua regia using the procedure described above. Concentrations of 28 elements were determined by ICP-ES (Table 5-4-1). The extent to which the Lefort aqua regia liberates many of these elements from resistant silicates and oxides is not well known though conventional aqua regia (HNO_3:3HCl) only weakly attacks these minerals.

LIMITATIONS OF THE COMPARISON

Only two multi-element packages from one laboratory are compared in this study, due to the following limitations:

● Splits of samples were used for each package, possibly resulting in subsampling errors.

● Different split weights were used for the AAS and ICP-ES determinations (1 and 0.5 gram, respectively) resulting in different sample to solution ratios.

● Although similar decomposition solutions (Lefort aqua regia) were used for most elements, other variables, such as the exact length of time the sample was digested, may result in significant differences.

COMPARISON OF THE AAS AND ICP-ES PACKAGES (Zn, Cu, Pb, Ni, Co, Mn, Fe, Ag, Mo, Cd, As, Sb)

REPORTED DETECTION LIMITS

The detection limits reported by the laboratory for both AAS and ICP-ES packages are considered in relation to average crustal abundances of the elements (Table 5-4-1). The number of samples reported as equal to or below detection limit shows important differences between analytical instruments and can be used to eliminate certain elements from further consideration. For example the considerable difference in detection limits for antimony (0.2 ppm for AAS, 5.0 ppm for ICP-ES) results in all samples being below the ICP-ES detection limit, versus 58 per cent for AAS. The proportion of determinations either below or equal to the ICP-ES detection limit is 91 per cent for cadmium, 89 per cent for silver, 82 per cent for molybdenum and 73 per cent for arsenic. Similarly, the proportion of determinations at or below the AAS detection limit is 70 per cent for cadmium, 84 per cent for silver, 61 per cent for molybdenum and 34 per cent arsenic. Both methods provide adequate sensitivity for the remainder of the elements. However, it is clear that neither analytical method provides adequate sensitivity for all elements that might reasonably be expected to be of

TABLE 5-4-1. SUMMARY STATISTICS FOR ALL ELEMENTS DETERMINED IN THIS STUDY

Element/ Unit	ELA	AAS				ICP-ES			
		IDL	≤DL (%)	Mean	CV (%)	IDL	≤DL (%)	Mean	CV (%)
A. Elements with ICP-ES and AAS determinations that are comparable									
Cu/ppm	12	1.0	0.0	25.2	23	1.0	0.4	28.6	21
Pb/ppm	18	1.0	16.5	5.5	61	2.0	17.2	8.6	36
Zn/ppm	51	1.0	0.0	78.5	12	2.0	0.3	71.0	13
Cd/ppm	0.1	0.1	70.3	0.2	38	0.5	91.4	0.6	92
Mo/ppm	1.3	1.0	61.1	1.5	155	1.0	81.7	2.2	114
Ni/ppm	4.5	1.0	0.9	12.4	35	1.0	1.0	12.3	35
Co/ppm	1	1.0	0.6	8.0	29	1.0	1.8	8.1	28
Fe/%	1.4	0.05	0.0	3.0	43	0.01	0.3	3.0	44
Mn/ppm	390	5.0	0.0	619.3	10	1.0	0.3	585.5	11
Ag/ppm	0.04	0.1	84.4	0.1	22	0.2	89.2	0.3	37
As/ppm	2.1	1.0	34.3	3.2	96	5.0	73.4	8.8	30
Sb/ppm	0.2	0.2	57.6	0.4	88	5.0	100.0	5.0	0
B. Elements with ICP-ES and AAS determinations that are not comparable									
Ba/ppm	840	10.0	0.0	608.5	8	10.0	0.3	104.2	13
C. Elements determined by ICP-ES or AAS only									
Hg/ppb	40	5.0	0.0	30.6	16				
*Al/%	—					0.01	0.5	1.5	104
*K/%	4.2					0.01	0.9	0.1	28
*Ca/%	—					0.01	0.3	0.6	94
*Mg/%	—					0.01	0.3	0.5	95
*Na/%	—					0.01	11.1	0.03	35
*Ti/%	—					0.01	4.0	0.1	30
P/ppm	600					10.0	0.3	735.0	5
*Sr/ppm	100					1.0	0.3	46.0	12
V/ppm	3.9					1.0	0.3	63.0	12
*Tl/ppm	—					10.0	100.0		
*Be/ppm	3					0.5	96.2	1.1	1090
Bi/ppm	0.3					2.0	99.9	2.1	24
*Cr/ppm	4.1					1.0	0.3	24.2	21
*La/ppm	—					10.0	56.9	14.3	17
*Ga/ppm	—					10.0	99.3	10.2	5

+ For both analytical packages, Lefort aqua regia was used to liberate the elements.

* Elements very poorly liberated by conventional aqua regia.

ELA—lithological abundance estimated from average for felsic rocks (Wedepohl, 1969). Data not available for all elements.

IDL—instrument detection limit.

≤DL—percentage of all samples (1299) less than or equal to the detection limit.

Mean—geometric mean of all samples above detection limit.

CV—coefficient of variation (standard deviation/mean) for all samples above the detection limit.

Blank—element not determined.

interest in these surveys. Although not necessarily required for exploration purposes, reliable estimation of background concentrations of these elements can be attained by preliminary preconcentration, or by using a more sensitive analytical method.

BIVARIATE SCATTER PLOTS

Scatter plots of ICP-ES versus AAS data (Figure 5-4-1) permit visual evaluation of differences by checking departures from the 45° $X_{ICP} = X_{AAS}$ line (X = concentration of element X). All data were log transformed so that departures from the line are shown with respect to the concentration of the element. For example, a 1 ppm departure at a concentration of 10 ppm appears the same as a 10 ppm departure at 100 ppm. In most cases, scatter is about the line (for example, X = Fe, Figure 5-4-1) though it is not clear what significance can be attached to a slight tendency for scatter
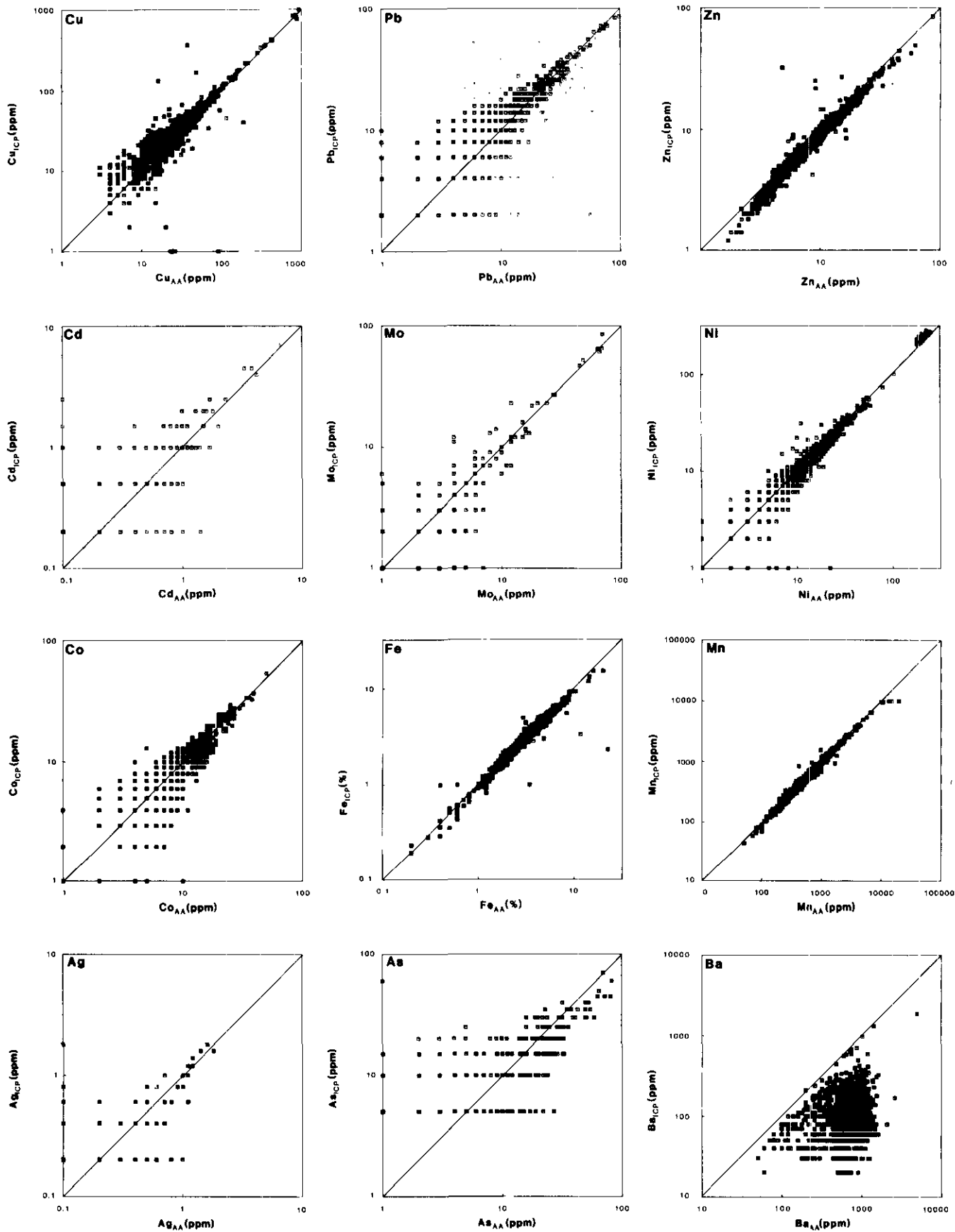
Figure 5-4-1. Scatter plots of concentrations determined by ICP-ES and AAS packages. Diagonal line shows $X_{ICP} = X_{AA}$. All 1299 samples are plotted on each diagram.

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toward either the $X_{ICP} > X_{AAS}$ or the $X_{ICP} < X_{AAS}$ regions (for example, X = Cu and X = Zn). Regression analysis was used to quantify differences between results.

REDUCED MAJOR-AXIS REGRESSION

The extent and sign of the difference between the ICP-ES and AAS packages are determined by calculating regression equations from the duplicate data. Ideally the regression equations would have slopes (B_1) of 1 and y-axis intercepts (B_0) of zero:

$$X_{ICP} = B_1 X_{AAS} + B_0.$$

The reduced major axis regression method is used to give a regression fit close to that indicated by visual evaluation of the data, as well as 95 per cent confidence limits about the slope and intercept, to test departure from the ideal case. Nine categories of results are recognized (Table 5-4-2) involving deviations of slope (rotational or proportional bias, Figure 5-4-2) and intercepts (translational or fixed bias, Figure 5-4-3) from the model. Cobalt is the only element where $X_{ICP} = X_{AAS}$ ($B_1 = 1$, $B_0 = 0$, with 95 per cent confidence, Figure 5-4-4). The five chalcophile elements arsenic, silver, lead, copper and cadium are in a group where $B_1 > 1$ and $B_0 > 0$ whereas molybdenum, nickel and manganese are in the opposite group. Zinc and iron are transitional cases.

TABLE 5-4-2. SUMMARY OF BIASES
DETERMINED BY REGRESSION
(All results are at 95% confidence level.)

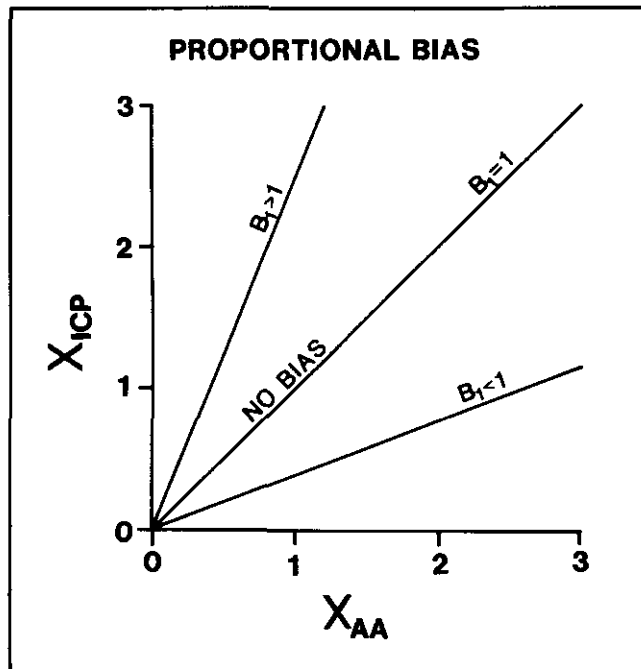| Rotational Cases	Translational cases		
	$b_0 < 0$	$b_0 = 0$	$b_0 > 0$
$b_1 < 1$	Mo, Ni, Mn		
$b_1 = 1$	Fe	Co	
$b_1 > 1$	Zn		Cu, Pb, Cd, Ag, As

Figure 5-4-2. Examples of proportional (or rotational) bias. X_{AA} and X_{ICP} are concentrations of element X determined by AAS and ICP-ES, respectively. Units are arbitrary.
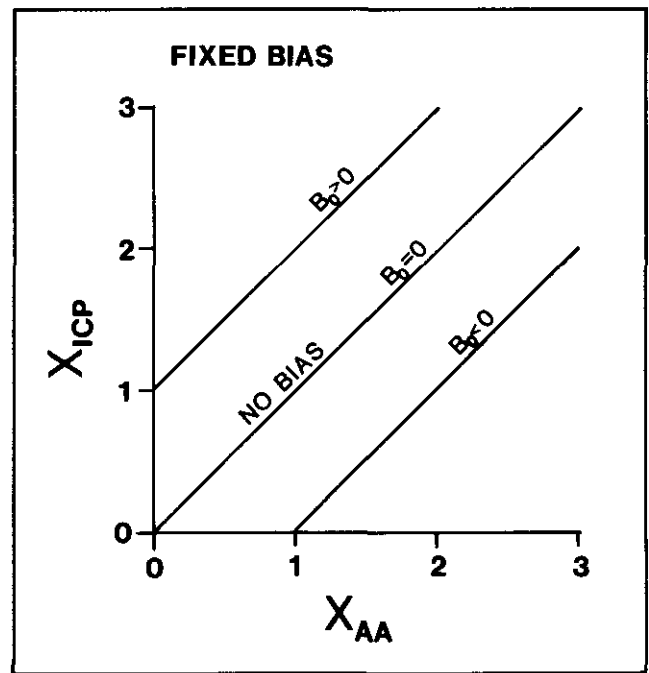

Figure 5-4-3. Examples of fixed (or translational) bias. X_{AA} and X_{ICP} are concentrations of element X determined by AAS and ICP-ES, respectively. Units are arbitrary.
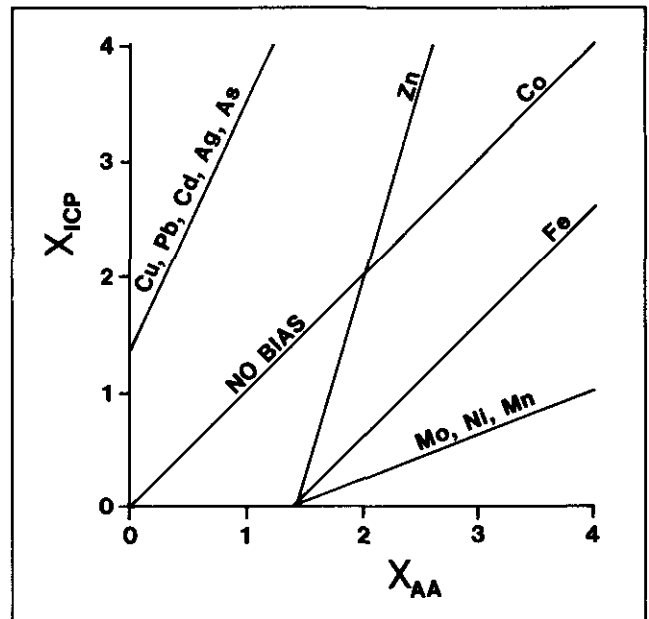

Figure 5-4-4. Diagrammatic summary of results presented in Table 5-4-2 showing types of bias. X_{AA} and X_{ICP} are concentrations of element X determined by AAS and ICP-ES, respectively. The relative position of lines and axis units are arbitrary.

PRECISION

Variation of precision may indicate that element determinations by the ICP-ES package are more or less precise than the conventional package at the levels encountered in stream sediments. Precision (P_C), given by:

$$P_C = \frac{2s_c}{C} \cdot 100$$

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where s_c is the estimated standard deviation at concentration C, can be determined by repeated re-analysis of a few samples. Four control reference standards were analysed 12 to 18 times. At concentrations greater than 10 times the detection limit P_C is 15 per cent or less for both ICP-ES and AAS determinations of copper, zinc, nickel, cobalt, iron and manganese, a level generally considered satisfactory (Table 5-4-3).

TABLE 5-4-3. PRECISION CHARACTERISTICS FOR SELECTED ELEMENTS

Control Std./ Method	N	Cu Mean (ppm)	P_C (%)	Zn Mean (ppm)	P_C (%)	Ni Mean (ppm)	P_C (%)	Mn Mean (ppm)	P_C (%)	Fe Mean (ppm)	P_C (%)
1/AAS	12	81	7	150	8	49	13	490	9	5.2	9
ICP	12	89	9	130	5	46	7	430	6	4.7	6
2/AAS	17	49	16	120	11	230	11	670	13	3.5	10
ICP	17	51	11	110	5	270	5	640	6	3.5	7
3/AAS	18	35	13	94	8	200	8	580	9	3.1	6
ICP	18	35	15	87	7	230	7	560	8	3.2	8
4/AAS	17	80	12	110	8	190	9	1100	10	3.4	7
ICP	17	87	7	110	8	210	8	1100	8	3.4	8

OTHER ELEMENTS

BARIUM

Barium concentrations determined by AAS are significantly greater than those determined by ICP-ES (Figure 5-4-1) due to the difference in strength of digestions used. Barite is not vigorously attacked by Lefort aqua regia (ICP-ES) but was completely decomposed by the stronger digestion used for the AAS determination.

ELEMENTS DETERMINED BY ICP-ES OR AAS ONLY (TABLE 5-4-1)

Of the 10 trace and minor elements determined only by ICP-ES, titanium, vanadium, phosphorus, strontium, lanthanum and chromium have high percentages of samples above the detection limit. Conversely, the sensitivity levels for gallium, thallium, beryllium and bismuth determined by the ICP-ES package are so poor that less than 0.5 per cent of samples had concentrations greater than the detection limit. Five major elements were also determined as part of the ICP-ES suite (aluminum, potassium, calcium, sodium, magnesium) and, with the exception of sodium, almost all samples were reported as above the detection limits (Table 5-4-1). Mercury was determined uniquely by AAS, and all samples reported above the detection limit (5 ppb) with an average of 31 ppb.

DETERMINATION OF REGIONAL TRENDS

It is essential to test if data determined by different analytical methods can be used to recognize similar regional trends. Ideally, this would involve a detailed analysis of the published RGS maps to determine if the same mineral exploration decisions would be made with data from either package. The problem can be tackled directly by asking the question: Is the variability introduced during sample collec-

tion, preparation, digestion and analysis insignificant when compared to the regional variability of interest to the mining industry and governments? The question can be answered to a limited extent by using analysis of variance (ANOVA) for blind and field duplicates.

ANALYSIS OF VARIANCE

For this study, field and analytical duplicates were separated into stream (53 pairs) and lake (12 pairs) data sets. Elements exhibiting the majority (greater than 75 per cent) of their values near the detection limit such as silver, molybdenum and cadmium were eliminated from the data sets. The summary of AAS results determined at the 95 per cent confidence level, presented in Table 5-4-4, shows that regional variability for cobalt, iron, nickel, manganese, copper, lead, zinc, barium and arsenic is not obscured by within-site or laboratory variability. Conversely, regional zinc and lead values in lake sediments determined by AAS are difficult to interpret because within-lake sampling variability is significant.

TABLE 5-4-4. SUMMARY OF BALANCED TWO FACTOR ANALYSIS OF VARIANCE

Analytical Method	Regional trends not significant with respect to field site variability		Regional trends not significant with respect to laboratory sub-sampling variability	
	Streams (n = 53)	Lakes (n = 12)	Streams (n = 53)	Lakes (n = 12)
AAS	—	Zn, Pb	—	—
ICP-EX	—	Pb	Pb	—

n = The maximum number of duplicate pairs available for each sampling media Pairs containing detection limit values were omitted.

Elements evaluated:
AAS: Zn, Cu, Pb, Ni, Co, Mn, As, Fe, Ba.
ICP-ES: Zn, Cu, Pb, Ni, Co, Mn, As, Fe, Ba, Al, Ca, Cr, Mg, P, K, Na, Sr, Ti, V.

A comparison of ICP-ES ANOVA results for the same suite of elements, shows that only lead determinations in stream sediments are characterized by significant laboratory subsampling variability, perhaps partly due to poor precision near the detection limit. All the major elements (potassium, calcium, magnesium, aluminum, sodium) as well as the trace and minor elements (phosphorus, titanium, lanthanum, strontium, vanadium and chromium) determined only by ICP-ES have insignificant within-site and laboratory subsampling errors compared to regional variability.

SUMMARY

Despite the stated limitations of this study, the following results are applicable to future British Columbia Regional Geochemical Surveys:

● Determinations of copper, zinc, cobalt, nickel, manganese and iron by Lefort aqua regia digestion followed by ICP-ES appear to satisfy the standards of the RGS, that is, results are sufficiently sensitive and precise and are well correlated with AAS determinations. In addition, within-stream sample site and laboratory variabilities are relatively small and insignificant for the majority of these

elements determined by ICP-ES. Concentration differences between sample sites account for most of the survey variability.

- The ICP-ES package evaluated in this study should not be used to determine antimony, cadmium, silver, molybdenum or arsenic in the RGS stream and lake sediment surveys due to their high detection limits. Antimony and arsenic can be analysed by ICP-ES if they are first reduced to their hydrides as in the conventional RGS package (Thompson, 1986).

- Although AAS provided better sensitivity characteristics than ICP-ES for silver, cadmium, molybdenum, antimony, arsenic and lead, they are only marginally adequate for silver, cadmium and molybdenum. Research should be initiated to lower detection limits for these elements.

- Statistically different concentrations for all comparable elements (except cobalt) are obtained with the two analytical packages. In a future study, elemental maps will be asssessed to evaluate whether concentration differences between methods are geochemically significant.

- The ICP-ES package provides adequate sensitivity and precision across concentration ranges normally encountered for major elements (sodium, potassium, aluminum, calcium, magnesium) as well as several trace and minor elements (barium, vanadium, strontium, titanium, chromium). However, the usefulness of data for elements contained in resistant minerals not attacked by LeFort aqua regia (barium, titanium, chromium, sodium, potassium, aluminum, calcium, magnesium) should be determined.

- Certain additional trace elements routinely determined as part of the ICP-ES package (gallium, lanthanum, bismuth, beryllium, thallium) do not completely satisfy the standards of the RGS since their detection limits are much greater than concentrations normally encountered in stream sediments.

- The cost of determining seven elements (zinc, copper, lead, cobalt, nickel, manganese, iron) of the standard RGS 12-element suite by ICP-ES is 18 per cent less than the same group determined by AAS. In addition, 12 other elements (barium, aluminum, potassium, calcium, magnesium, sodium, strontium, titanium, phosphorus, vanadium, chromium, lanthanum) are reported as part of the ICP-ES package and are of satisfactory quality. The geochemical significance of these additional elements will be investigated in future studies.

CONCLUSION

Despite some inherent limitations to the study, it is clear that the use of ICP-ES as the final determination step for routine RGS determinations of copper, lead, zinc, nickel, manganese and iron is significantly cheaper and as precise and sensitive as RGS methods currently employed, and provides information on additional elements.

ACKNOWLEDGMENTS

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