

Preliminary Review of the Effect of Analytical Method Variability on Regional Geochemical Survey Data, British Columbia

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INTRODUCTION

Regional geochemical drainage sediment data is commonly levelled before contouring to compensate for spatial and temporal variations that can be introduced by using different sample media and analytical methods. Linear 'edge effects' in the form of a visible 'step' along the common boundary between two adjacent survey maps are often revealed in large-scale contoured regional geochemical maps and can reflect merging of source data from separate surveys, each carried out at different times. The British Columbia regional geochemical survey (RGS) is an example of a large database populated by stream, lake-bottom and moss-mat sediment sample geochemistry data from over 50 individual surveys carried out since 1976, using several laboratories and analytical methods (Lett, 2005). As part of the Canada-wide National Geochemical Reconnaissance (NGR) program, the BC RGS has been carried out to conform to sample collection, quality control, sample preparation and sample analysis standards that were established by the Geological Survey of Canada (Garrett, 1974).

The protocol for analysis of the -80 mesh size (<0.177 mm) drainage sediment fraction to determine a range of geochemical pathfinder elements (e.g., As, Cu, Pb, Mo, Hg, Zn) is historically an aqua-regia (HCl-HNO₃) digestion followed by atomic absorption spectrophotometry (AAS) or, more recently, inductively coupled plasma-mass spectrometry (ICP-MS). Ideally, analyses produced by this protocol should be comparable from survey to survey allowing for variations due to routine sampling and analytical errors. In practice, however, subtle differences in the analytical method, especially the conditions of the digestion techniques used, introduce an additional variable into element determinations. Past studies have examined the geochemical effects of analyzing regional drainage sediment samples for elements with different methods. For example, Day et al. (1988) compared Ag, As, Cd, Co, Cu, Fe, Mo, Mn, Pb, Sb and Zn values of sediment samples determined using a Lefort aqua-regia (3HNO₃:HCl) digestion followed by AAS with values for the same elements determined by Lefort aqua-regia digestion followed by inductively cou-

pled plasma-emission spectrometry (ICP-ES). They found that there were statistically different concentrations for all of the elements, except Co, determined by the two methods.

This paper will illustrate three situations common to established regional geochemical survey programs that may introduce analytical variability. The first example compares element data from regional geochemical survey sample analyses. Initially, the samples were analyzed with aqua-regia digestion followed by AAS and later the archived sediment samples were reanalyzed with a HCl-HNO₃-H₂O digestion followed by ICP-MS. The second example briefly comments on a comparison of results for a control reference standard analyzed by aqua-regia digestion followed by ICP-MS at a single laboratory for two analytical projects completed in different years. The final example summarizes the results of analyzing Canada Centre for Mineral and Energy Technology (CANMET) reference materials by an aqua-regia digestion followed by ICP-MS at different laboratories for a range of elements commonly reported from regional drainage surveys. It is emphasized that for all three examples, the analytical results and discussions reported in this paper are very preliminary. They are intended to illustrate that these types of data complexity are inherent to the design and structure of RGS programs that have been conducted over many years.

METHODS COMPARISON: REANALYSIS OF RGS SAMPLES FROM NTS MAP AREA 093J

During 1985, stream sediment and water samples were collected from 1088 sites at an average density of one sample per 13 km² throughout the 14 770 km² of NTS map area 093J (McLeod Lake; Figure 1), central BC. The air-dried sediment samples were sieved through a -80 mesh (<0.177 mm) and ball milled. A total of 1152 sediment samples, duplicate samples and standard reference materials were analyzed at a commercial laboratory for Ag, As, Cd, Cu, Co, Hg, Fe, Mo, Mn, Ni, Pb, Sb, V, and Zn by an aqua-regia digestion followed by AAS. Original geochemical survey results were reported in Geological Survey of Canada Open File 1216 (Geological Survey of Canada, 1986). In 2005, archived stream sediment samples from the survey were reanalyzed at a second commercial laboratory for 37 elements, including those listed above, by leaching a 1 g sample with a HCl-HNO₃-H₂O (2:2:2, volume of solute per volume of solvent [v/v]) mixture at 95°C for one hour and then measuring the concentration of the 37 elements in the diluted solution by ICP-MS (Lett and Bluemel, 2006). The original As, Cd, Cu, Co, Hg, Fe, Mo, Mn, Ni, Pb, Sb, V and Zn values from 1986 can be compared statistically with archived sample determinations to establish if there are differences between the two datasets. A two-sample t-test is

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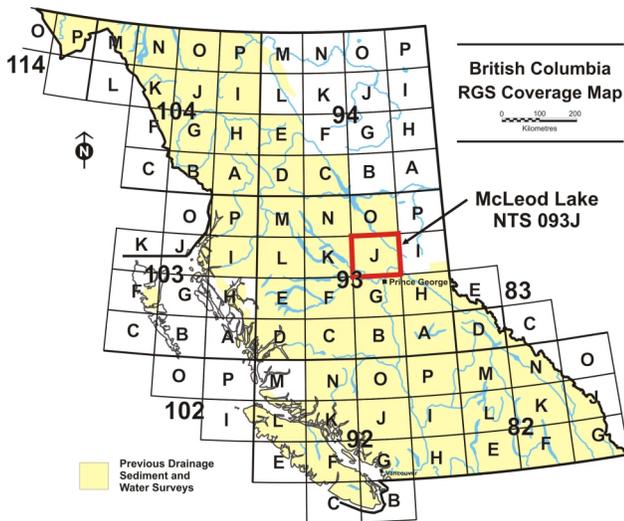


Figure 1. Location of the NTS 093J regional geochemical survey (RGS) area, British Columbia.

applied to determine if there is a difference at the 0.05% significance level between the population means for aqua-regia digestion and AAS compared to HCl-HNO₃-H₂O digestion and ICP-MS measured values. Silver was not included in the test because there is a large difference between the AAS and ICP-MS detection limits. An analysis of variance (F-test) is applied before the t-test to establish if the two populations have an equal or unequal variance. Once equality or inequality of variance is established, the appropriate t-test is applied to test the null hypothesis (*H₀*) that there is no significant difference between element population means (Davis, 1973). In Table 1, the t-test results for the 1986 aqua-regia digestion and AAS determined elements compared to the 2006 HCl-HNO₃-H₂O digestion and

Table 1. Summary of a t-test to determine if there is a difference at the 0.05% significance level between the population mean for elements (in 1152 stream sediment samples from NTS 093J, central British Columbia) determined by aqua-regia digestion followed by atomic absorption spectrophotometry (AAS) compared to means for the same samples reanalyzed by HCl-HNO₃-H₂O digestion followed by inductively coupled plasma-mass spectrometry (ICP-MS). A blue to red bar indicates a significant difference whereas a green bar indicates no difference. A red bar shows the higher of the two means. All values except Fe have been logarithmically transformed before statistical analysis.

Element	AAS	ICP-MS	AAS Mean	ICP-MS Mean
As (ppm)	Blue	Red	4.5	4.7
Cd (ppm)	Blue	Red	0.4	0.46
Co (ppm)	Blue	Red	10	11
Cu (ppm)	Green	Green	24	24.61
Fe (%)	Green	Green	2.14	2.22
Hg (ppb)	Red	Blue	141	132
Mn (ppm)	Green	Green	741	747
Mo (ppm)	Red	Blue	2	1.06
Ni (ppm)	Blue	Red	36	39.3
Pb (ppm)	Blue	Red	5	7.5
Sb (ppm)	Red	Blue	0.4	0.33
V (ppm)	Green	Green	37	40
Zn (ppm)	Blue	Red	72	74.5

ICP-MS values are summarized. A blue to red bar (low to high) indicates a significant difference between the means whereas a green bar indicates no difference. A comparison of the population means listed in Table 1 shows that they are generally very similar, allowing for differences in method detection limit. However, the t-test indicates that there is a statistical difference between the population means for 9 of the 13 elements and that only Cu, Fe, Mn and V results from 1986 appear to be comparable to the 2006 data.

YEAR TO YEAR COMPARISON: ANALYSIS OF REFERENCE MATERIAL FROM THE QUEST SURVEY AREAS

A similar pattern of statistical differences can also be observed when comparing control reference sample data that was reported by the same laboratory, but determined in different years. Data used in this study comprised a single standard that had been randomly inserted 77 times into the sample sequence of two separate Geoscience BC data-reanalysis projects in two years (Jackaman, 2008, 2009). Each analytical project included element determinations (by aqua-regia digestion followed by ICP-MS) for several thousand samples originating from a number of previous RGS programs. For most of the elements, t-test results indicated a difference in population means that was considered statistically significant with the exception of Au, Mn and Mo. In terms of their scientific significance with regards to exploration geochemistry, only the mean differences for Ag and Hg were found to be sufficiently large that they could have an adverse influence when interpreting merged data from several sources. These results suggest that combining data from different surveys into a single analytical package for large-scale reanalysis projects helps reduce the analytical variability commonly associated with complex geochemical datasets.

INTERLABORATORY COMPARISON: ANALYSIS OF REFERENCE STANDARD BY AQUA-REGIA DIGESTION FOLLOWED BY ICP-MS

Partial dissolution of minerals in stream sediment and soil samples by aqua-regia digestion followed by ICP-MS analysis is now commonly available commercially for routine determination of up to 50 ore-indicator and pathfinder elements, including Ag, As, Cd, Co, Cu, Fe, Hg, Mo, Mn, Ni, Pb, Sb, V and Zn. Acid digestion methods and ICP-MS analysis have been previously reviewed by Chao and Sanzalone (1992) and Hall (1992). While aqua-regia digestion is sufficiently aggressive to completely dissolve native Au and most mineral sulphides, it will only partially release metals from mineral oxides and rock-forming aluminosilicate minerals. The amount of metal liberated by the acid mixture from oxide, silicate and refractory minerals can vary depending on the reaction conditions such as digestion temperature, digestion time and operating conditions of the instruments used to measure element concentrations in the solution. Consequently, identical samples, when analyzed by different laboratories using an aqua-regia digestion followed by a combination of ICP-ES and ICP-MS, may return slightly different element concentrations from each laboratory. The disparity between element values detected by different laboratories in the same sample may be small

and have negligible effect on the ability to distinguish element anomalies within data generated from detailed, property-scale surveys. However, the small differences become more critical when attempting to merge and level large-scale survey analytical data from several independent sources. Consequently, it was decided to have several laboratories analyze geochemical standard reference materials for Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn using aqua-regia digestion followed by ICP-MS and then compare the results reported.

Sample Batch Preparation and Geochemical Analysis

A batch of samples, consisting of CANMET stream sediment standards STSD-1, STSD-3 and STSD-4, was assembled for analysis. A single bottle of each CANMET standard was homogenized for two hours in a roller mixer, the contents of the bottle decanted on a clean paper sheet and 4–5 g aliquots measured into three groups of pre-numbered Ziploc® bags. The standards were then assembled in random order and assigned a unique, blind identification number to create three identical sample batches. Each batch was submitted to a commercial laboratory for routine aqua-regia digestion followed by ICP-MS. The analytical method requested at each laboratory was that routinely used to generate regional geochemical survey data for the BC Geological Survey (BCGS) and Geoscience BC (Jackaman, 2009).

Results of the Geochemical Analysis

Statistical analysis of the reported geochemical data for the standards is in progress and final results will be reported in a future publication. For this reason, only preliminary results will be presented and discussed in this paper. Mean and percent relative standard deviation (%RSD) have been calculated from eight, repeat, random determinations of each of the CANMET drainage sediment standards (STSD-1, STSD-3, STSD-4). The samples were analyzed for elements including those noted above. Table 2 lists the mean and %RSD values for the elements in standard STSD-1 determined by each laboratory, along with the corresponding CANMET recommended mean value reported by Lynch (1990), for a concentrated HCl-HNO₃ digestion followed by ICP-MS. Most of the mean values for elements reported by the laboratories are within 15% of the CANMET recommended mean value. However, the mean value reported by individual laboratories may be higher or lower depending on the element determined in STSD-1. Among likely reasons for the variations observed between laboratory reported and recommended means for elements in STSD-1 are differences in the detection limit reported by a laboratory for some of the elements and the conditions of the analytical method used, including the digestion procedure. Analytical precision, based on the %RSD values, is

commonly better than 5% for most of the elements in STSD-1. Larger %RSD values, greater than 5%, for Ag, Mo and Hg can be explained by a higher detection limit for these elements reported by some of the laboratories and the influence of a wider range of high or low outlier values on calculated precision.

CONCLUSIONS

Comparison of geochemical data from identical regional stream sediment samples analyzed first by an aqua-regia digestion followed by AAS and then later by HCl-HNO₃-H₂O digestion followed by ICP-MS reveals small, but statistically significant differences between the population mean values for 9 of the 13 elements determined. There are also statistically significant differences between the population mean values for the majority of elements measured from year to year in sediment reference standards by aqua-regia digestion followed by ICP-MS at one laboratory.

CANMET standard reference materials have been analyzed repeatedly by aqua-regia digestion followed by ICP-MS at several commercial laboratories. Precision (%RSD) for most of the elements reported from the aqua-regia digestion followed by ICP-MS analysis are within limits ($\pm 15\%$) that are generally accepted as satisfactory for routine geochemical exploration purposes. However, differences between mean values reported by each laboratory for a reference standard suggest that the raw data from different laboratories, while of good quality, should be used with caution when merged and processed to display large regional geochemical patterns.

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Table 2. Mean and relative standard deviation (%RSD) for elements in Canada Centre for Mineral and Energy Technology (CANMET) sediment standard STSD-1, determined by laboratories A, B and C by an aqua-regia digestion followed by inductively coupled plasma-mass spectrometry. The CANMET recommended means for STSD-1 are from Lynch (1990).

Element	Lab A Mean	Lab B Mean	Lab C Mean	CANMET Mean	Lab A %RSD	Lab B %RSD	Lab C %RSD
Ag (ppb)	308	268	328	300	6.9	4.9	3.4
As (ppm)	18.9	20.6	20.9	17	2.2	2.3	2.7
Cd (ppm)	0.93	1.08	0.86	0.8	4.2	4.7	3.4
Co (ppm)	13.4	13.9	13.6	14.00	1.6	2.9	2.7
Cr (ppm)	24.4	28.6	26.1	28.00	2.6	2.5	2.4
Cu (ppm)	31.63	37.94	34.40	36.00	2.2	2.3	2.5
Fe (%)	3.53	3.39	3.28	3.50	1.7	1.8	2.6
Hg (ppb)	112	101	109	110.00	3.3	5.0	6.0
Mn (ppm)	3810	3729	3499	3740	1.3	2.5	2.7
Mo (ppm)	0.97	0.99	1.02	2	5.9	2.0	2.7
Ni (ppm)	16.9	21.1	19.6	18	2.9	3.1	2.4
Pb (ppm)	33.86	38.11	32.48	34	4.5	3.3	3.9
Sb (ppm)	2.27	2.46	2.31	2	2.4	3.9	3.6
V (ppm)	44	46	45	47	3.4	2.3	2.8
Zn (ppm)	157.08	166.68	158.88	165	2.4	2.8	2.6

REFERENCES

- Chao, T.T. and Sanzolone, R.F. (1992): Decomposition techniques; *Journal of Geochemical Exploration*, Volume 44, pages 65–106.
- Davis, J.C. (1973): Statistics and data analysis in geology; *John Wiley and Sons*, New York, 550 pages.
- Day, S.J., Matysek, P.F. and Johnson, W.M. (1988): The regional geochemical survey: evaluation of an ICP-ES package; in *Geological Fieldwork 1987, BC Ministry of Energy, Mines and Petroleum Resources*, Paper 1988-1, pages 503–508.
- Garrett, R.G. (1974): Field data acquisition methods for applied geochemical surveys at the Geological Survey of Canada; *Geological Survey of Canada*, Paper 74-62, 36 pages.
- Geological Survey of Canada (1986): National Geochemical Reconnaissance - British Columbia regional geochemical survey - McLeod Lake (NTS 93J); *Geological Survey of Canada*, Open File 1216 and *BC Ministry of Energy, Mines and Petroleum Resources*, Regional Geochemical Survey 15.
- Hall, G.E.M. (1992): Inductively coupled mass spectrometry in geoanalysis; *Journal of Geochemical Exploration*, Volume 44, pages 201–250.
- Jackaman, W. (2008): QUEST Project sample reanalysis; *Geoscience BC*, Report 2008-3.
- Jackaman, W. (2009): QUEST-West Project sample reanalysis (NTS 93E, 93F, 93L, 93M); *Geoscience BC*, Report 2009-5.
- Lett, R.E.W. (2005): Regional geochemical survey database on CD; *BC Ministry of Energy, Mines and Petroleum Resources*, GeoFile 2005-17, CD-ROM.
- Lett, R.E.W. and Bluemel, B. (2006): A reanalysis of regional geochemical stream sediment samples from the McLeod Lake area (NTS map sheet 93J); *BC Ministry of Energy, Mines and Petroleum Resources*, GeoFile 2006-9.
- Lynch, J. (1990): Provisional element values for eight new geochemical lake sediment and stream sediment reference materials. LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3, STSD-4; *Geostandards Newsletter*, Volume 14, pages 153–167.