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ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF GEOLOGICAL MATERIALS

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GEOLOGICAL SURVEY
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INTRODUCTION

The Geochemical Laboratory has been providing analyses to geoscientists of the Geological Survey of Newfoundland and Labrador (‘Geological Survey’) since the 1970s. Over that time, methods have evolved and instrumentation has changed. In the early years, reliance on Atomic Absorption Spectrometry and classical ‘wet chemistry’ methods was the norm. Today, the laboratory applies modern instrumentation to perform analyses by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), as well as other specialized analytical methods. Over the years, emphasis has been placed on expansion of the analytical capabilities of the Geochemical Laboratory through the acquisition of this modern instrumentation and using automated analysis, whilst maintaining acceptable standards of precision and accuracy through the application of quality control (QC) and quality assurance (QA) protocols. Today the lab performs analyses for over 60 elements and other parameters on a wide range of sample types, including rock, till, lake sediment, stream sediment, vegetation and water.

SAMPLE PREPARATION

GENERAL

All samples submitted by the geoscientists of the Geological Survey are subject to a chain-of-custody protocol. This involves the submission of digital data for each sample, comprising field number, location in UTM coordinates, sample description, required analyses and any special treatment required. The listing is cross-checked against the physical samples, and any errors or omissions are corrected upon consultation with the submitting geoscientist.

Each geoscientist has an assigned project number, which makes sample numbers unique. The digital descriptions are merged into the Laboratory Information Management System (LIMS) where a lab number is assigned, following the standard definitions listed in Table 1. Also at this stage, duplicate samples, samples of certified reference material, and blanks, are assigned numbers and inserted into the sample sequence, each at a frequency of one in every sequence of twenty samples. The analyses of the certified reference materials, unless obviously deviant (in which case the sequence of samples that includes the standard is re-analyzed; *see* below) are appended to a continually increasing dataset from which arithmetic mean and standard deviation are extracted on an ongoing basis (*see* appendices). The ratio of the mean value of analyses performed in the laboratory, to the ‘rec-

Table 1. Formulation of lab sample numbers

Lab Number Format	**XXXYZZZZ**
Project Number Code	XXX
Sample Type Code	Y
Sample Numbers	ZZZZ
Sample Type	**Code**
Vegetation	0
Stream Sediments	1
Lake Sediment	2
Soil / Till	3
Rock	4
Beach Sand	5
Lake Water	7
Stream Water	8
Overbank Sediment	9

ommended' value provided by the supplier, is termed the 'recovery' for that element. Recovery should ideally fall within five points of 100%, but this is not always achieved, for various reasons.

A block of analyses is rejected and repeated if the analysis of the standard within it falls outside the upper and lower control limits defined by the mean ± two standard deviations. The size of the block is defined by the last preceding and first following standard analyses that fall within these limits.

The recommended values, means, standard deviations, control limits, total analyses and recoveries, for all sample media currently analyzed in the laboratory, are listed in Appendices 1-20.

Duplicate analyses are checked by creating scatter plots and visually identifying pairs of analyses with uncharacteristically large spread. When such deviations are identified, the block of samples is subjected to the same process of rejection and repeat that is applied to deviant CRM analyses.

The above procedures provide the necessary quality-control parameters to assure and test the quality of the data before they are reported back to the submitting geoscientist.

ROCKS

Rock samples are submitted to the laboratory in clearly marked plastic bags. All pieces of rock are required to be no larger than fist size and to be fresh; that is to say, void of weathering and organic matter.

1. If the sample is wet, for example as a result of condensation in the sample bag, it is dried in a drying oven before further preparation.

2. The sample is passed through a Bico Braun Jaw crusher to produce fragments approximately 1 cm in diameter.

3. Approximately 75 ml of crushed material are pulverized for three to five minutes using a TM Engineering TM/S series mild steel ring-mill pulverizer to produce a sample powder of which at least 95% passes a 100 micron sieve.

4. A sample of the rock powder is stored in a pre-labelled 16 dram plastic vial and all remaining, partially crushed, material is retained and archived.

LAKE AND STREAM SEDIMENT, TILL AND SOIL

Samples are submitted to the laboratory in clearly labelled kraft sample bags.

1. If the samples are excessively wet, the sample bags are placed on an open plastic chain-link drying rack to air dry at ambient temperatures.

2. When most of the water has evaporated, or if the samples are dry when submitted, the bags are placed in a drying oven at a temperature not exceeding 60°C, until dry.

3. The sample bags are removed from the oven and allowed to cool.

4. Each sample is disaggregated, by pounding the bag with a rubber mallet.

5. The disaggregated material is placed in a 200-mm diameter stainless-steel sieve and sieved until enough material to fill a 16 dram vial accumulates in the collection pan.

6. The sieved material is stored in a pre-labelled 16 dram plastic vial, and all remaining partially treated material is retained and archived.

VEGETATION

The procedure described below is sourced from Riddle (1993).

Vegetation samples submitted to the laboratory normally consist of conifer twigs (with needles) or bark. They are collected in clearly labelled paper bags; the use of polyethylene bags is discouraged.

1. The sample bags are placed on a plastic chain-link drying rack to allow the needles to dry.

2. When the twigs have dried sufficiently for most of the needles to break away from the branch, the remaining attached needles are removed by (gloved) hand.

3. Samples are placed in ceramic bowls and are ‘ashed’ in a muffle furnace, in which the temperature is slowly ramped to 550°C. If twigs or bark are to be analyzed, they are broken into small pieces first.

4. After four hours at 550°C, the samples are removed from the oven, cooled and weighed.

5. The bowls are returned to the oven and ashed for another hour at 550°C, removed and reweighed.

6. Stages 4 and 5 are repeated until constant weight is obtained, indicating that ashing is complete.

7. The ashed material is transferred to a pre-labeled 16 dram plastic vial.

WATER

Samples are collected in the field in pre-cleaned high-density polyethylene plastic bottles. They are kept under refrigeration until shipment to the laboratory.

1. On receipt, samples are filtered through a 0.45 micron filter disc, using an all-glass Millipore vacuum filtration apparatus.

2. The samples are acidified to 0.5% volume/volume double sub-boiled nitric acid (HNO_3). Samples can be stored for up to six months at room temperature (U.S. Environmental Protection Agency, 1983).

ANALYSIS OF MAJOR AND TRACE ELEMENTS BY ICP-OES AND ICP-MS AFTER BORATE FUSION

SAMPLE FUSION

The following method is derived from Cremer and Schlocker (1976).

1. Each rock-powder sample is brought into solution by fusion for 30 minutes at 1000°C, in a high-purity graphite crucible, using flux consisting of a combination of lithium metaborate ($LiBO_2$) and lithium tetraborate ($Li_2B_4O_7$) in a ratio of 0.06 grams sample to 1 grams of flux. The relative proportions of the two fluxes vary according to the type of material that is to be fused.

2. The molten bead is transferred from the crucible to a 100 ml digi-tube containing 10% double sub-boiled nitric acid.

3. The mixture is stirred on a magnetic stir plate until dissolved and then made up to a final volume of 100 ml.

MAJOR AND TRACE ELEMENTS BY ICP-OES

Analysis follows the methodology described by Lichte *et al.* (1987). The solution of fused sample is analyzed directly by ICP-OES for 18 elements. Table 2 lists the elements analyzed by this method, the way in which they are reported, the characteristic emission wavelengths, the units of measurement and the detection limits. These detection limits, and those listed in the tables that follow, are nominal.

Ferrous iron and loss-on-ignition (LOI), which are also reported in the major-element package, are determined by separate methods (*see* below).

Each instrument run, of variable length but typically of several hours, is initially calibrated with standards prepared from commercially available National Institute of Standards and Technology (NIST) traceable stock solutions. Interfering element concentration (IEC) solutions are measured to correct for interference by the spectra of one element with those of another. All spectral lines are corrected for background. Drift-correction and calibration-verification solutions are run at a frequency of one to every eight unknown samples to monitor signal drift and correct for it. All sample batches contain blanks, duplicates and certified reference materials (CRMs); analytical data for the latter (twelve in all) are listed in Appendix 1. Tables 3a and b list the analytical preferences and source settings for a typical run by this method.

Table 2. Parameters for major and trace elements analyzed by ICP-OES

Element	Reported as	Wavelength (nm)	Unit	Detection Limit
Al	Al_20_3	394.401	%	0.01
Ba	Ba	455.403	ppm	1
Be	Be	313.042	ppm	0.1
Ca	CaO	315.887	%	0.01
Cr	Cr	205.560	ppm	1
Fe	Fe_2O_3	233.280	%	0.01
K	K_2O	766.490	%	0.01
Mg	MgO	383.230	%	0.01
Mn	MnO	294.920	%	0.001
Na	Na_2O	589.592	%	0.01
P	P_2O_5	177.495	%	0.001
Sc	Sc	361.384	ppm	0.1
Si	SiO_2	185.067	%	0.01
Sr	Sr	407.771	ppm	1
Ti	TiO_2	334.941	%	0.001
V	V	310.230	ppm	1
Y	Y	371.030	ppm	1
Zr	Zr	343.823	ppm	1

Note: The contents of Al, Ca, Fe, K, Mg, Mn, Na, P, Si and Ti are customarily reported as their respective oxides.

Table 3a. Analytical preferences for ICP-OES major- and trace-element analysis

Sample Options	# repeats	4
	Sample Flush Time (sec)	40
	Analysis Mode	Precision
Source	Sample Introduction	Nebulizer
Analysis Maximum Integration Times (sec)	Low Wavelength Range	15
	High Wavelength Range	5
Calibration Mode	Concentration	

Table 3b. Source settings for ICP-OES major- and trace-element analysis

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	50
	Pump Relaxation Time (sec)	30
	Pump Tubing Type	Tygon Orange/White
	RF Power (watts)	1350
	Nebulizer Flow (L/min)	0.55
	Auxiliary Gas (L/min)	1.5

FERROUS IRON AND LOSS-ON-IGNITION

Ferrous iron (Fe^{2+}) and LOI determinations are reported as a component of the major-element analytical package.

The ferrous-iron content of silicate rocks is determined by the Wilson Method (Wilson, 1960). The method is based on the use of the oxidizing agent ammonium vanadate (NH_4VO_3) in the presence of hydrofluoric (HF), sulphuric (H_2SO_4) and phosphoric (H_3PO_4) acids, and incorporates a volumetric / colorimetric finish.

1. Approximately 400 mg of sample are decomposed overnight in a mixture of 10 ml of concentrated HF and 5 ml of 10 grams per litre (g/l) NH_4VO_3 solution.

2. The next day, when decomposition is complete, 15 ml of 1 part concentrated phosphoric and 2 parts sulphuric acid are added to the digested sample and the solution is transferred to a 400 ml glass beaker containing 175 ml of saturated (50 g/l) boric acid (H_3BO_3). Ten ml of ferrous ammonium sulphate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] solution, at a concentration of 19 g/l, is added to the solution.

3. Final titration is made with potassium dichromate ($K_2Cr_2O_7$), using barium diphenylamine sulfonate ($Ba(C_6H_5 \cdot NH \cdot C_6H_4SO_3)_2$) as an indicator (Maxwell, 1968). The titration is performed, and endpoint determined, with a Mettler Toledeo T50 automatic titrator.

All data and results are processed with Mettler Toledeo LabX software. Data for two certified reference standards are listed in Appendix 2.

The gravimetric method of LOI analysis follows that described by Maxwell (1968):

1. 1 g of sample is weighed in a 25 ml porcelain crucible.

2. The crucible is placed in a muffle furnace at 1000°C for two hours.

3. The crucible is removed, placed in a desiccator and cooled to ambient temperature.

4. When cool, the sample is re-weighed and LOI is calculated by weight difference pre- and post-ignition.

Data for five certified reference standards for rock, till and lake sediment are listed in Appendices 3–5.

TRACE ELEMENTS BY ICP-MS

1. The fused and re-dissolved solution is diluted twenty times with 2% double sub-boiled nitric acid using a PrepFast SC-8 automated dilutor manufactured by Elemental Science Inc.

2. Samples are analyzed for 29 elements (Table 4) by a Thermo Instruments X-Series II ICP-MS, using collision-cell technology (CCT) with kinetic-energy discrimination (KED), as described in Thermo Scientific application note 40790 (Thermo Scientific, 2007a).

3. The run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions, and recalibrated every twenty samples. All sample batches contain blanks, duplicates and CRMs.

4. Scandium, indium and rhenium are added, via a mixing tee, as an internal standard to correct for drift and matrix effects.

Tables 5a and b list the analytical preferences and source settings for a typical run. Data for twelve certified reference standards are listed in Appendix 6.

MAJOR AND TRACE ELEMENTS BY ICP-OES AFTER FOUR-ACID DIGESTION

This method, which is typically applied to lake and stream sediments, tills and rocks, is described in detail by Lichte *et al.* (1987).

1. If the sample contains organic material, it is pre-ashed in a 25 ml porcelain crucible, for four hours at 550°C in a muffle furnace.

2. 1 g of sample is weighed directly into a 125 ml Teflon beaker.

Table 4. Parameters for trace elements analyzed in rocks by ICP-MS

Element	Atomic Mass	Units	Detection Limit	Element	Atomic Mass	Units	Detection Limit
Ga	71	ppm	1	Gd	160	ppm	0.1
Ge	72	ppm	1	Dy	163	ppm	0.1
Sr	88	ppm	1	Ho	165	ppm	0.1
Y	89	ppm	1	Er	166	ppm	0.1
Nb	93	ppm	1	Tm	169	ppm	0.05
Mo	95	ppm	2	Yb	172	ppm	0.1
Sn	118	ppm	1	Lu	175	ppm	0.05
Cs	133	ppm	0.5	Hf	178	ppm	0.2
La	139	ppm	0.5	Ta	181	ppm	0.5
Ce	140	ppm	0.5	W	182	ppm	1
Pr	141	ppm	0.1	Tl	205	ppm	0.1
Nd	146	ppm	0.2	Bi	209	ppm	0.5
Sm	147	ppm	0.1	Th	232	ppm	0.1
Eu	153	ppm	0.05	U	238	ppm	0.1
Tb	159	ppm	0.1				

Table 5a. Analytical preferences for ICP-MS analysis in rocks

Sample Options	# repeats	3
	Sample Flush Time (sec)	Monitored
	Analysis Mode	Peak Jump
Source	Sample Introduction	PFA Nebulizer

Table 5b. Source settings for ICP-MS analysis in rocks

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	15
	Pump Relaxation Time (sec)	40
	RF Power (watts)	1400
	Nebulizer Flow (L/min)	0.9
	Auxiliary Gas (L/min)	0.7

3. 5 ml of concentrated hydrochloric acid (HCl), 5 ml of concentrated nitric acid (HNO_3), 2.5 ml of concentrated perchloric acid ($HClO_4$) and 15 ml of concentrated hydrofluoric acid (HF) are added to each beaker.

4. The samples are placed on a hotplate at 200°C and evaporated to dryness.

5. The beakers are half-filled with 10% hydrochloric acid and returned to the hot plate at 100°C.

6. When the residue is completely dissolved, the samples are removed, cooled and transferred to 50 ml storage tubes. One ml of boric acid (H_3BO_3; at a concentration of 50 grams per litre) is added to each sample, to complex any residual hydrofluoric acid, which can otherwise cause issues with degradation of the ICP glassware in the sample introduction system.

7. The samples are made up to a final volume of 50 ml with 10% HCL and analyzed by ICP-OES for 31 elements.

Each instrument run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions. Interfering element concentration (IEC) solutions are measured to correct for interference by the spectra of one element with those of another. All spectral lines are corrected for background. Drift-correction and calibration-verification solutions are run at a frequency of one to every 15 unknown samples, to monitor signal drift and correct for it. All sample batches contain blanks, duplicates and CRMs.

Table 6 lists elements, emission wavelengths and detection limits, and Tables 7a and b list the analytical preferences and source settings for a typical run. Analyses of certified reference standards for rocks, tills and lake sediments are listed in Appendices 7-9, respectively.

Table 6. Parameters for trace elements analyzed in rocks by ICP-MS

Element	Wavelength (nm)	Unit	Detection Limit	Element	Wavelength (nm)	Unit	Detection Limit
Al	257.510	%	0.01	Mn	294.920	ppm	1
As	189.042	ppm	2	Mo	202.030	ppm	1
Ba	455.403	ppm	1	Na	589.592	%	0.01
Be	313.042	ppm	0.1	Nb	316.340	ppm	1
Ca	211.276	%	0.01	Ni	231.604	ppm	1
Cd	228.802	ppm	0.1	P	178.284	ppm	1
Ce	404.076	ppm	1	Pb	220.353	ppm	1
Co	230.786	ppm	1	Rb	780.023	ppm	1
Cr	267.716	ppm	1	Sc	361.384	ppm	0.1
Cu	324.754	ppm	1	Sr	407.771	ppm	1
Dy	353.170	ppm	0.1	Ti	374.164	ppm	1
Fe	296.690	%	0.01	V	310.230	ppm	1
K	766.490	%	0.01	Y	371.030	ppm	1
La	333.749	ppm	1	Zn	231.856	ppm	1
Li	670.784	ppm	0.1	Zr	343.823	ppm	1
Mg	383.230	%	0.01				

Table 7a. Analytical preferences for ICP-OES analysis in tills, sediments and rocks

Sample Options	# repeats	4
	Sample Flush Time (sec)	40
	Analysis Mode	Precision
Source	Sample Introduction	Nebulizer
Analysis Maximum Integration Times (sec)	Low Wavelength Range	15
	High Wavelength Range	5
Calibration Mode	Concentration	

Table 7b. Source settings for ICP-OES analysis in tills, sediments and rocks

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	50
	Pump Relaxation Time (sec)	30
	Pump Tubing Type	Tygon Orange/White
	RF Power (watts)	1350
	Nebulizer Flow (L/min)	0.55
	Auxiliary Gas (L/min)	1.5

SILVER (Ag) ANALYSIS BY ICP-OES

1. 0.5 g of sample is weighed into a 10 ml digestion tube.
2. 2 ml of nitric acid are added, and the tubes are capped and left overnight.
3. The next day, the digestion tubes are heated in a digestion block at 90°C for two hours. The tubes are shaken every 30 minutes.
4. When digestion is complete, the samples are cooled and made up to a final volume of 10 ml with distilled deionized water and analyzed for silver by ICP-OES (Lichte *et al.*, 1987).

Each instrument run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions. Interfering element concentration (IEC) solutions are measured to correct for interference by the spectra of one element with those of another. All spectral lines are corrected for background. Drift-correction and calibration-verification solutions are run at a frequency of one to every 20 unknown samples, to monitor signal drift and correct for it. All sample batches contain blanks, duplicates and CRMs.

Table 8 lists the relevant emission wavelength, unit and detection limit, and Tables 9a and b list the analytical and source settings for a typical run. Analyses of certified reference standards for tills and lake-sediments are listed in Appendices 10 and 11, respectively.

Table 8. Parameters for Ag analyses by ICP-OES

Element	Wavelength (nm)	Unit	Detection Limit
Ag	328.068	ppm	0.1

Table 9a. Analytical preferences for Ag analyses by ICP-OES

Sample Options	# repeats	4
	Sample Flush Time (sec)	40
	Analysis Mode	Precision
Source	Sample Introduction	Nebulizer
Analysis Maximum Integration Times (sec)	Low Wavelength Range	15
	High Wavelength Range	5
Calibration Mode	Concentration	

Table 9b. Source settings for Ag analyses by ICP-OES

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	50
	Pump Relaxation Time (sec)	30
	Pump Tubing Type	Tygon Orange/White
	RF Power (watts)	1350
	Nebulizer Flow (L/min)	0.55
	Auxiliary Gas (L/min)	1.5

VEGETATION ANALYSIS BY ICP-MS AND ICP-OES

SAMPLE DIGESTION

1. 100 mg of previously ashed vegetation material are weighed into a 15 ml digestion tube. 3 ml of double sub-boiled hydrochloric acid and one ml of double sub-boiled nitric acid are added to the digestion tube.

2. The tubes are capped and agitated manually to mix the contents.

3. The digestion tubes are placed on a hot block at 90°C for two hours and their contents are mixed every 15 minutes.

4. The tubes are removed after two hours, cooled and their contents transferred to 50 ml digestion tubes.

5. The samples are made up to a volume of 50 ml with distilled deionized water and shaken manually to mix the contents.

6. Samples for ICP-MS analysis are diluted twenty times with 2% double sub-boiled nitric acid using a PrepFast SC-8 automated dilutor supplied by Elemental Science Inc.

7. Samples analyzed by ICP-OES are undiluted.

ICP-MS

Samples are analyzed for 34 elements by a Thermo Instruments X-Series II ICP-MS (Table 10), using collision-cell technology (CCT) with kinetic energy discrimination (KED).

The run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions, and recalibrated every twenty samples. All sample batches contain blanks, duplicates and CRMs. Scandium, indium and rhenium are added, *via* a mixing tee, as an internal standard to correct for drift and matrix effects. Tables 11a and b list the analytical preferences and source settings for a typical run. Analyses for a certified pine-needle reference standard are listed in Appendix 12.

ICP-OES

Sample solutions are analyzed directly, for 11 elements, by a Thermo Instruments iCap 6500 ICP-OES (Table 12). The run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions and recalibrated every thirty samples. Yttrium is added, via a mixing tee, as an internal standard to correct for drift and matrix effects. All sample batches contain blanks, duplicates and CRMs. Tables 13a and b list the analytical preferences and source settings for a typical run. Analyses for a certified pine-needle reference standard are listed in Appendix 13.

Table 10. Parameters for elements analyzed by ICP-MS in vegetation samples

Element	Atomic Mass	Unit	Detection Limit	Element	Atomic Mass	Unit	Detection Limit
Ti	47	ppb	0.1	Ce	140	ppb	0.1
V	51	ppb	0.5	Pr	141	ppb	0.01
Cr	52	ppb	0.1	Nd	146	ppb	0.1
Ni	60	ppb	0.1	Sm	147	ppb	0.05
Ga	71	ppb	0.5	Eu	153	ppb	0.01
Ge	72	ppb	0.3	Tb	159	ppb	0.01
As	75	ppb	0.2	Gd	160	ppb	0.01
Se	78	ppb	0.1	Dy	163	ppb	0.1
Rb	85	ppb	0.1	Ho	165	ppb	0.01
Sr	88	ppb	0.1	Er	166	ppb	0.01
Y	89	ppb	0.10	Tm	169	ppb	0.01
Ag	107	ppb	0.10	Yb	172	ppb	0.01
Cd	111	ppb	0.1	Lu	175	ppb	0.01
Sn	118	ppb	0.1	Hf	178	ppb	0.01
Sb	121	ppb	0.1	Pb	208	ppb	0.1
Cs	133	ppb	0.1	Th	232	ppb	0.01
La	139	ppb	0.1	U	238	ppb	0.01

Table 11a. Analytical preferences for ICP-MS analysis of vegetation samples

Sample Options	# repeats	3
	Sample Flush Time (sec)	Monitored
	Analysis Mode	Peak Jump
Source	Sample Introduction	PFA Nebulizer

Table 11b. Source settings for ICP-MS analysis of vegetation samples

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	15
	Pump Relaxation Time (sec)	40
	RF Power (watts):	1400
	Nebulizer Flow (L/min)	0.9
	Auxiliary Gas (L/min)	0.7

Table 12. Parameters for elements analyzed by ICP-OES in vegetation samples

Element	Wavelength (nm)	Unit	Detection Limit	Element	Wavelength (nm)	Unit	Detection Limit
Al	169.079	ppm	10	Mg	383.230	%	0.01
Ba	455.403	ppm	1	Mn	257.610	%	0.01
Ca	315.887	%	0.01	Na	589.592	%	0.01
Cu	324.754	ppm	1	P	178.284	%	0.01
Fe	259.940	ppm	10	Zn	213.856	ppm	1
K	766.490	%	0.01				

Table 13a. Analytical preferences for ICP-OES analysis of vegetation samples

Sample Options	# repeats	3
	Sample Flush Time (sec)	Monitored
	Analysis Mode	Peak Jump
Source	Sample Introduction	PFA Nebulizer

Table 13b. Source settings for ICP-OES analysis of vegetation samples

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	15
	Pump Relaxation Time (sec)	40
	RF Power (watts):	1150
	Nebulizer Flow (L/min)	0.55
	Auxiliary Gas (L/min)	0.5

WATER ANALYSIS BY ICP-MS AND ICP-OES

ICP-MS

After filtration and preservation with 0.5% (volume/volume) double sub-boiled nitric acid, samples are analyzed for 50 elements by a Thermo Instruments X-Series II ICP-MS (Table 14), using collision-cell technology (CCT) with kinetic energy discrimination (KED) (Thermo Scientific, 2007b).

The run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions and recalibrated every thirty samples. Scandium, indium and rhenium are added, via a mixing tee, as an internal standard to correct for drift and matrix effects. All sample batches contain blanks, duplicates and CRMs. Tables 15a and b list the analytical preferences and source settings for a typical run. Appendix 14 consists of ICP-MS analyses of two reference standards.

Table 14. Parameters for water analyses by ICP-MS

Element	Atomic Mass	Unit	Detection Limit	Element	Atomic Mass	Unit	Detection Limit
Mg	24	ppm	0.005	Cs	133	ppb	0.01
Al	27	ppb	2	Ba	137	ppb	0.1
K	39	ppm	0.01	La	139	ppb	0.01
Ti	47	ppb	0.5	Ce	140	ppb	0.01
V	51	ppb	0.05	Pr	141	ppb	0.005
Cr	52	ppb	0.05	Nd	146	ppb	0.01
Mn	55	ppb	0.1	Sm	147	ppb	0.005
Fe	56	ppb	1	Eu	153	ppb	0.005
Co	59	ppb	0.05	Tb	159	ppb	0.005
Ni	60	ppb	0.1	Gd	160	ppb	0.005
Zn	66	ppb	1	Dy	163	ppb	0.005
Ga	71	ppb	0.01	Ho	165	ppb	0.005
Ge	72	ppb	0.01	Er	166	ppb	0.005
As	75	ppb	0.05	Tm	169	ppb	0.005
Se	78	ppb	0.1	Yb	172	ppb	0.005
Rb	85	ppb	0.05	Lu	175	ppb	0.005
Sr	88	ppb	0.1	Hf	178	ppb	0.005
Y	89	ppb	0.01	Ta	181	ppb	0.02
Zr	90	ppb	0.01	W	182	ppb	0.02
Nb	93	ppb	0.05	Hg	202	ppb	0.05
Mo	95	ppb	0.1	Tl	205	ppb	0.5
Ag	107	ppb	0.01	Pb	208	ppb	0.05
Cd	111	ppb	0.01	Bi	209	ppb	0.01
Sn	118	ppb	0.1	Th	232	ppb	0.01
Sb	121	ppb	0.01	U	238	ppb	0.01

Table 15a. Analytical preferences for ICP-MS analysis of water samples

Sample Options	# repeats	3
	Sample Flush Time (sec)	Monitored
	Analysis Mode	Peak Jump
Source	Sample Introduction	PFA Nebulizer

Table 15b. Source settings for ICP-MS analysis of water samples

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	15
	Pump Relaxation Time (sec)	40
	RF Power (watts):	1400
	Nebulizer Flow (L/min)	0.9
	Auxiliary Gas (L/min)	0.7

ICP-OES

After filtration and preservation with nitric acid (*see* above), samples are analyzed for eight elements by a Thermo Instruments iCap 6500 ICP-OES (Table 16; Thermo Scientific, 2010). The run is initially calibrated with standards prepared from commercially available NIST traceable stock solutions and recalibrated when calibration verification fails. Yttrium is added *via* a mixing tee as an internal standard to correct for drift and matrix effects. All sample batches contain blanks, duplicates and CRMs. Tables 17a and b list the analytical preferences and source settings for a typical run. Appendix 15 consists of ICP-OES analyses of two reference standards.

FLUORIDE (F-) IN SOLID SAMPLES BY ALKALINE FUSION WITH ION-SELECTIVE ELECTRODE DETERMINATION

Fluoride is determined as described by Ficklin (1970).

Table 16. Parameters for water analyses by ICP-OES

Element	Wavelength (nm)	Unit	Detection Limit	Element	Wavelength (nm)	Unit	Detection Limit
Be	313.042	ppb	0.05	Na	589.592	ppm	0.01
Ca	315.887	ppm	0.01	P	178.284	ppb	3
Cu	324.754	ppb	3	S	180.731	ppm	0.01
Li	670.784	ppb	2	Si	251.611	ppm	0.01

Table 17a. Analytical preferences for ICP-OES analysis of water samples

Sample Options	# repeats	4
	Sample Flush Time (sec)	40
	Analysis Mode	Precision
Source	Sample Introduction	Nebulizer
Analysis Maximum Integration Times (sec)	Low Wavelength Range	15
	High Wavelength Range	5
Calibration Mode	Concentration	

Table 17b. Source settings for ICP-OES analysis of water samples

Nebulizer Pump	Flush Pump Rate (rpm)	100
	Analysis Pump Rate (rpm)	50
	Pump Relaxation Time (sec)	30
	Pump Tubing Type	Tygon Orange/White
	RF Power (watts)	1150
	Nebulizer Flow (L/min)	0.55
	Auxiliary Gas (L/min)	0.5

1. A 250 mg sample with 1 g of a flux consisting of two parts (by weight) of sodium carbonate (Na_2CO_3) and one part (by weight) of potassium nitrate (KNO_3) is fused in a nickel crucible in a muffle furnace at 800°C for ten minutes.

2. The fused residue is leached with distilled deionized water.

3. The alkaline extract is neutralized with 10 ml 10% (weight/volume) citric acid and the resulting solution is diluted to 100 ml with distilled deionized water. The pH of the resulting solution should be between 5.5 and 6.5.

4. The fluoride content of the test solution is measured using a fluoride ion-selective electrode with a Mettler Toledo T50 Ion Meter. Standards contain flux solution and citric acid, in the same ratio as the sample solution. All sample batches contain blanks, duplicates and CRMs. Fluoride is reported in micrograms per millilitre (equivalent to ppm).

Fluoride analyses of certified reference standards for rocks, tills and lake sediments are listed in Appendices 16-18, respectively.

FLUORIDE IN WATER SAMPLES WITH ION-SELECTIVE ELECTRODE DETERMINATION

1. 47.5 mL of filtered but un-acidified sample are poured into a 50 mL disposable beaker.

2. 50 uL of 100 ppm F solution are added to each beaker (100 ppb spike).

3. 2.5 mL of total ionic strength adjustment buffer (TISAB III) are added to each beaker.

4. Calibration standards are made to match the matrix of the samples using the same ratio of standard solution and TISAB III.

5. The fluoride content of the test solution is measured using a fluoride ion-selective electrode with a Mettler Toledo T50 Ion Meter. Fluoride is reported in micrograms per litre (equivalent to ppb).

Certified reference material is not available for fluoride in water.

NEUTRON ACTIVATION ANALYSIS

Instrumental Neutron Activation Analysis (INAA) is a sensitive and accurate analytical method that identifies and quantifies elements in a sample, through analysis of characteristic gamma rays emitted during radioactive decay after being irradiated in a research nuclear reactor. These distinct energy signatures provide positive identification of the targeted elements present, while their intensity is proportional to the concentration of the element in the sample.

Samples of sediment, till or rock are weighed in-house and encapsulated in plastic 40 ml vials supplied by the analytical laboratory. The weight is recorded and the sample is shipped to a contracted laboratory for analysis.

The following procedure is currently in operation at Maxxam Analytics (R. Allen, *pers. comm.*); if future analyses are conducted at a different facility, it is recommended that these parameters be verified.

1. Samples are irradiated with flux wires and an internal standard (1 for 11 samples) at a thermal neutron flux of $7 \times 10^{11} n/cm^2 s$.

2. After 7 days (to allow Na_{24} to decay), samples are counted on a high-purity Ge detector with a resolution better than 1.7 KeV.

3. Using the flux wires, the decay-corrected activities are compared to a calibration developed from multiple certified international reference materials.

The internal standard is only a check on the accuracy of the analysis, and is not used for calibration purposes. Ten to 30% of the samples are checked by re-measurement.

Required routine detection limits are listed in Table 18. Analyses of four certified reference till standards, and three lake standards, can be found in Appendices 19 and 20, respectively.

Table 18. Required routine INAA detection limits

Element	Detection Limit	Unit	Element	Detection Limit	Unit
Au	1	ppb	Lu	0.05	ppm
Sb	0.1	ppm	Rb	5	ppm
As	0.5	ppm	Sm	0.1	ppm
Ba	50	ppm	Sc	0.1	ppm
Br	1	ppm	Se	1	ppm
Ce	3	ppm	Na	0.05	%
Co	2	ppm	Ta	0.2	ppm
Cs	0.5	ppm	Tb	0.5	ppm
Cr	10	ppm	Th	0.1	ppm
Eu	0.5	ppm	U	0.1	ppm
Fe	0.10	%	W	1	ppm
Hf	1	ppm	Yb	0.5	ppm
La	1	ppm	Zr	100	ppm

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