GEOCHEMICAL LABORATORY

by

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INTRODUCTION

The laboratory has been reorganized this year as a single unit which includes the assay laboratory and the routine analysis laboratory. Six permanent staff are employed, and the laboratory handles all data preparation, and about 80% of the chemical analyses for the Mineral Development Division. In addition the laboratory arranges for external analytical contracts where necessary.

The laboratory, which is located on Higgins Line in St. John's, is equipped with two atomic absorption spectrophotometers, one spectrophotometer, three infra-red analyzers, a fluorometer, and a digital specific ion meter. Sample preparation equipment includes a tungsten carbide shatter box, disc-mill with ceramic plates, two jaw crushers, an automatic sieve-shaker, and four drying ovens.

At present the lab is routinely performing the following analyses:

1) Major oxides on rocks: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, TiO_2, MnO, P_2O_5, LOI, S (total), CO_2 and H_2^+O;

2) Trace elements on rocks: Ba, Sr, Rb, Cu, Pb, Zn, Ni, Cr, Co, V, Cd, Ag, Mo, Li and Be;

3) Chemistry of lake sediments, stream sediments, soils and tills: Cu, Pb, Zn, Co, Ni, Ag, Mo, Mn, Fe, Cd and LOI;

4) Single element determinations on a variety of materials: F, W and Sn.

In addition there are currently two contracts with commercial laboratories, one for U determinations on a variety of materials by neutron activation/delayed neutron counting, and the second for determination of a variety of trace elements such as Zr, Y, Nb, Th, Ga, Ce and La on rocks by X.R.F., as these elements cannot be determined adequately using the equipment at present available in the lab.

Analytical quality of both internal and external analyses is monitored constantly by the inclusion of blind duplicate and control samples in every batch. The blind duplicate samples are introduced at the sample preparation stage, and the controls are inserted when the samples are weighed for digestion. Control samples consist of both international references materials where these are suitable and available, and internally prepared bulk samples to allow the monitoring of batch to batch variations. Quality criteria for precision and accuracy are established with reference to both the tolerance necessary to solve a particular geochemical problem, and what is practical for the analytical method being employed to allow reasonable productivity. Where data fail to meet the established criteria of precision or accuracy, the determinations are repeated.

DESCRIPTIONS OF ANALYTICAL PROCEDURES

1. The routine determination of major constituents of silicate rocks

A 0.1 g portion of sample is fused in a 9 mL graphite crucible with 0.5 g of lithium metaborate at 1000°C. The hot melt is poured into a 250 mL polycarbonate bottle containing 25 mL of 4 vol % HCl and 5 mL of concentrated HF, and digested at 90°C for 1.5 hours. After the contents are cooled to room temperature, 50 mL of 50 g/L boric acid

is added to complex the excess HF and the sample is digested again at 90°C for 1.5 hours. The solution is transferred into a 100 mL polyethylene volumetric flask, made to volume and mixed.

The oxides SiO_2, Al_2O_3, total iron as Fe_2O_3, MgO, CaO, Na_2O, TiO_2 and MnO are determined by atomic absorption spectroscopy, following the methods of Langymhyr and Paus (1968), Abbey (1968), and Buckley and Cranston (1971).

Phosphorus is determined spectrophotometrically on an aliquot of the solution from the fluoroboric acid digestion by reducing the yellow phospho-molybdate complex to the molybdenum blue complex with hydrazine sulphate (Riley, 1958; Hounslow and Moore, 1966).

Ferrous iron is determined on a separate portion of sample decomposed at room temperature in an HF solution containing a known amount of quinquivalent Vanadium, which oxidizes the ferrous iron as it passes into solution. After decomposition is complete the excess V^{+5} is reduced by a known quantity of ferrous ammonium sulphate, the excess ferrous iron being titrated with standard potassium dichromate using barium diphenylamine sulphonate as indicator. Boric acid is used to complex the HF, and H_3PO_4 the ferric iron (Wilson, 1955, 1960; Hounslow and Moore, 1966).

Loss on Ignition is determined at 1000°C by the method outlined by Hillebrand *et al.* (1953).

2. Sulphur, carbon dioxide and water of crystallization in silicate rocks

An infra-red method as developed by Bouvier and Abbey (1980) is used to determine simultaneously S, CO_2 and H_2^+O in rock samples. Briefly the procedure is as follows:

A 0.2 g portion of sample is weighed into a nickel boat and fused at 950°C with a 1.0 g mixture of equal parts Vanadium Pentoxide and Tungstic Anhydride. The evolved gases are carried in a dry nitrogen stream through a Beckman Model 865 infrared analyzer to determine the water present, and then on to two Beckman Model 864 infrared analyzers to determine the sulphur and carbon dioxide respectively. Each of the constituents of interest gives a millivolt reading on a three channel digital integrator, and this reading is converted to per cent concentration by comparison with known standards.

3. Trace elements in silicate rocks

To 1 g of sample in a 100 mL Teflon beaker are added 15 mL of concentrated HF, 5 mL of concentrated HCl and 5 mL of 50 vol % $HClO_4$. The sample is allowed to stand in the acid mixture overnight, and is then heated to dryness on a hot plate. The residue is taken up in 10 vol % HCl by gently heating on a hot plate. When cool the solution is made up to 50 mL with 10 vol % HCl. The elements Rb, Cu, Pb, Zn, Ni, Cr, Co, V, Mo, Li and Be are determined directly on this solution by atomic absorption spectroscopy. For Ba and Sr a 5 mL aliquot of the solution is transferred to a 25 mL volumetric flask to which 5 mL of a 5% La^{3+} solution and 6.5 mL of concentrated HCl are added. The solution is made up to 25 mL with deionized water, and Ba and Sr are determined by atomic absorption spectroscopy.

4. Lake sediment, stream sediment, soil and till

The Cu, Pb, Zn, Co, Ni, Cd, Mn, Fe, Mo and Ag content of drainage sediment, soil and till are determined by atomic absorption spectroscopy. Four different digestions are used depending on the sample type and element to be determined.

4.1 Cu, Pb, Zn, Co, Ni, Cd, Ag, Mn and Fe in lake sediment. To 1 g of sample in a glass test tube is added 6 mL of 4 M HNO_3 - 1 M HCl, and the mixture is allowed to stand overnight. The sample is then mixed, digested for 2 hours in a water bath at 90°C, mixed again and allowed to cool. The leach solution is made up to 20 mL with deionized water, mixed, and allowed to clear. The elements are determined by atomic absorption spectroscopy using an air-acetylene flame, and automatic simultaneous background correction using a deuterium lamp is employed for Pb, Co, Ni, Ag and Cd.

4.2 Cu, Pb, Zn, Co, Ni, Cd, Mn and Fe in stream sediment, soil and till. The procedure used is as described for lake sediments, except for a slightly different digestion method. Initially 3 mL of concentrated HNO_3 is added to 1 g of the sample in a test tube and allowed to stand overnight at room temperature. The tube is then placed in a water bath at 90°C for 30 minutes, following which 1 mL of concentrated HCl is added and the tube returned to the water bath for a further 90 minutes. When cool, the leach solution is made up to 20 mL with deionized water.

4.3 Silver in rock, stream sediment, soil and till. A separate digestion is used for Ag in these media as the concentration of HCl in the digestion described in 4.2 above causes Ag to precipitate as the chloride. A 2 mL aliquot of concentrated HNO_3 is added to 0.5 g of sample in a 10 mL test tube. The sample is allowed to digest overnight at room temperature, followed by a two hour digestion at 90°C in a water bath. When cool, the solution is made up to 10 mL with deionized water and mixed. The Ag content is determined by atomic absorption spectrophotometry, using an air-acetylene flame.

4.4 Molybdenum in lake and stream aediments, soil and till. A 0.5 g portion of sample is leached overnight in a test tube at room temperature with 1.5 mL of concentrated HNO_3, and then heated in a water bath at 90°C for 30 minutes. A 0.5 mL aliquot of concentrated HCl is added and the test tube returned to the water bath for a further 90 minutes. The tube is allowed to cool and the leach solution made up to 10 mL with 8 mL of a 1250 g/t Al^{3+} solution. The Mo content of the solution is determined by atomic absorption spectroscopy, using a nitrous oxide-acetylene flame.

5. Miscellaneous single element determinations on rocks, drainage sediments, soils and tills

5.1 Tin. A 0.5 g portion of sample is fused with 2.5 g of lithium metaborate in a 9 mL graphite crucible at 1000°C for 1 hour. The hot melt is poured into a Teflon beaker containing 50 mL of 10 vol % HCl. The melt is digested on a hot plate at 40°C overnight. The temperature is increased to 100°C and the digestion continued for 2 hours.

The contents are transferred into a 100 mL volumetric flask, diluted to volume with 10 vol % HCl and mixed. The Sn is determined by hydride generation on an atomic absorption spectrophotometer.

5.2 Tungsten. This colorimetric method is used for determining W in rock, soil, till, stream sediment and lake sediment. The procedure, which is based on those described by Aruscavage and Campbell (1978) and Terashima (1980), is as follows.

To 0.5 g of sample in 100 mL Teflon beaker are added 2 mL of 2% Fe solution, 2 mL of concentrated $HClO_4$ and 10 mL concentrated HF, and the sample is allowed to stand overnight. The sample is taken to dryness on a hot plate at 200°C. When cool, 1 mL of water is added to loosen the residue which is then dissolved in a 30% $SnCl_2$ solution at 100°C on the hot plate and transferred to a stoppered test tube. The test tube

is placed in a 90°C water bath for 15 minutes, following which 2 mL of 1% Zn dithiol solution is added, the sample mixed and returned to the bath for a further 30 minutes. The resulting complex is extracted with 5 mL of petroleum ether and the absorbance read at 630 nm on a spectrophotometer. The absorbance is compared with those of chemical standards which are prepared in the same manner as the samples.

5.3 Fluorine in rocks, drainage sediments, soil and till. A 0.25 g portion of sample is mixed with 1 g of a 2:1::Na_2CO_3:KNO_3 flux and fused for 10 minutes in a nickel crucible over a Fisher burner. The residue is dissolved in deionized water and transferred to 100 mL polyethylene beakers. A 10 mL aliquot of 10% citric acid solution and 1 mL of 10 g/t fluoride solution is added, and the solution made up to 100 mL with deionized water. The fluoride concentration is measured using fluoride-ion specific electrodes and a digital ionanalyser, and the fluorine concentration estimated by comparison with standards.

CONCLUSION

The number and types of analyses performed in the laboratory in the 12 month period between September 1, 1981 and August 31, 1982 are given in Table 1. In summary, about 3500 drainage sediment samples were analysed for 11 elements and loss on ignition, 2200 rocks were analysed for 11 major oxides, loss on ignition and an average of 10 trace elements, and, for about 1350 rocks, S, CO_2 and H_2^+O were determined. Single element analyses on a variety of sample types included 1432 for W, 550 for Sn and nearly 10,000 for F. Altogether, over 100,000 determinations were carried out last year.

To meet future demand, which is for a greater variety of elements on a slightly smaller volume of samples, it will be necessary to purchase additional equipment. An inductively coupled plasma spectrometer is being considered to meet the changing work load, and if acquired, the proportion of analyses being sent to outside laboratories would be further reduced.

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TABLE 1. Output from the geochemical laboratory of the Mineral Development Division from September 1, 1981 to August 31, 1982

	Samples Digested	Number of Determinations
DRAINAGE SEDIMENTS, SOIL, TILL		
Cu, Pb, Zn, Co, Ni, Mn, Fe, Ag, Cd	3,760	33,727
Mo	3,213	3,213
Loss on Ignition	3,701	3,701
SILICATE ROCK ANALYSIS		
Trace elements		
Cu, Pb, Zn, Co, Ni, Ba, Sr, Rb, Cr, V, Ag, Be, Li, Mo, Cd	2,119	22,205
Major oxides		
SiO_2, Al_2O_3, Total Iron as Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, MnO	2,217	19,953
P_2O_5	2,217	2,217
FeO	1,139	1,139
Loss on Ignition	1,626	1,626
H_2^+O, S and CO_2	1,344	4,032
MISCELLANCEOUS SAMPLE TYPES		
Fluorine	9,786	9,786
Tungsten	1,432	1,432
Tin	550	550
TOTAL		103,581