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INDUCTIVELY COUPLED PLASMA-EMISSION SPECTROMETRY (ICP-ES) AT THE GEOCHEMICAL LABORATORY

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ABSTRACT

The Geochemical laboratory of the Geological Survey uses Inductively Coupled Plasma-Emission Spectrometry as its primary instrumentation for trace- and major-element analysis of rock, till, water, lake and stream sediment. Since the mid 1980s, methods have been developed for the measurement of all major elements and up to twenty trace elements in solid materials, and twenty-two elements in fresh waters. Methods developed over this period for solid materials incorporate lithium metaborate fusion for the dissolution of major elements and triple acid digestion for the dissolution of trace elements. Waters samples are filtered through a 0.45 μm filter and preserved with double-distilled nitric acid. Ultrasonic nebulization is used to improve the detection limits of 14 elements measured in water samples. A quality-control protocol based on the systematic measurement of blind duplicates and Standard Reference Materials throughout all sample batches is employed, the results of which are summarized in this paper.

INTRODUCTION

The Geochemical laboratory of the Department of Mines and Energy has been doing trace- and major-element analysis since the 1970s. Initially, all these determinations were made by Atomic Absorption Spectrometry (AAS), a single beam instrument for the analysis of trace elements and later a double-beam instrument for major elements. These instruments suited the analytical requirements of the laboratory but were not efficient for the analysis of large element suites because they measured only one element at a time, they were not automated, and the data obtained were manually recorded and calculated. With the advent of Mineral Development Agreements of the late 1970s and 1980s, the number of samples for geochemical analysis rose sharply. With this increase in volume also came the requirement to broaden the suite of elements analyzed. Soon it became clear that manual single-element determinations by AAS was neither an efficient nor cost-effective way to accommodate the increasing work load.

In the mid 1980s, Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) was adopted as an alternative to AAS for most of the laboratory's work. It is an attractive method for the routine analysis of trace and major elements because it is a true multi-element instrument, with excellent detection limits, wavelength coverage, linear dynamic range and can be readily automated.

INSTRUMENTATION

In 1985, the ICP-ES was put into service at the Department of Mines and Energy. This Applied Research Laboratories Model 3520 is a sequential instrument having wavelength coverage from 165 nm to 800 nm. A sequential design was chosen at the time to give the laboratory the most flexibility in the selection of analytical lines rather than a fixed line-set of a simultaneous instrument. With the new instrument operating, the AAS's for most elements became redundant. The benefits of the ICP-ES were apparent immediately. Soon, both the number of elements and the total number of determinations increased. Also turn-around time and analytical quality improved and more operator resources could be diverted to sample preparation.

This instrument, which is still in operation, eventually was used for the development of analytical methods for over thirty elements on such materials as rock, soil, lake sediment, stream sediment, water and vegetation samples at concentration levels from 100 ppt to 100 percent. Improved detection limits were obtained for the analysis of waters by the mating of an Ultrasonic Nebulizer with the ICP-ES.

With the sequential ICP-ES now performing the majority of the analysis, the cost effectiveness of this instrument became an issue. The main drawback with this design is that with more elements being measured per sample, operation

time increased proportionately, thus, increasing costs. Although the cost effectiveness of the instrument remained far greater than that of AAS, higher efficiency could be obtained with further automation and by use of a simultaneous ICP-ES.

The main advantage of simultaneous ICP-ES over a sequential design is its high speed measurement. This is because simultaneous instruments can measure all configured lines at the same time. The disadvantage of this design is that the configured lines are the only lines available for measurement. Initially, there were also physical limitations to the number of detectors that these instruments can be equipped with, so that line-sets had to be selected carefully to best address the routine requirements of the laboratory, a choice that involves compromise.

By 1993, a major advance in ICP-ES technology was introduced that takes advantage of fiber optics to transport light from the spectrometer to a bank of multiplexed photomultiplier tubes (PMT). This reduces the physical space limitation of configuring many PMT's and offers more choice of analytical lines. This is accomplished by feeding eight fiber optic channels to each PMT and placing a shutter in front of the PMT windows to allow the measurement of one line per PMT at a time. In a true sense, the design is purely simultaneous if one line per PMT is being measured. If in an analytical program a particular PMT has to measure more than one line, then it will measure the first line, and then the shutter will be moved to allow measurement of the second, up to a total of eight lines per PMT. With this configuration an instrument can measure up to 200 lines.

The instrument purchased was a Fisons Instruments Maxim III, which is fully automated with the capability to measure up to 200 lines in a multiplex fashion. The Maxim III ICP-ES has an axial torch design that provides for sightly better detection limits than traditional radial designs, but which reduces the linearity of the spectrometer such that the older radial instrument is still a better suited for the analysis of major elements. Even with the introduction of ICP-ES to the laboratory some elements such as Rb and some standardized methods still call for AAS as the first choice of measurement. In the past year, the only AAS that remains in use at the laboratory has also been automated by connection of a computer for control of an autosampler and for the digital collection of data.

METHODS

Analysis by ICP-ES includes major- and trace-element determinations on rock, soil, sediment and water. These can broken down into three separate procedures. Major-element analysis, usually performed on rocks, trace-element analysis of rock, soil and sediment and water analysis.

MAJOR ELEMENTS

Typically, 0.1 g of <180 micron material is weighed into a graphite crucible with 0.5 g of lithium metaborate. The sample and flux are mixed throughly and placed in a 1000°C furnace and fused. The samples are removed after one hour and tipped into a mixture of four percent hydrochloric acid and concentrated hydrofluoric acid contained in a polycarbonate digestion bottle. The caps are immediately sealed and the samples are placed in a water bath at 90°C. After 90 minutes, the samples are removed and 50 ml of 50 g/l boric acid solution is added, after which the samples are returned to the digestion bath. Following another 90 minutes of digestion the samples are removed, cooled, transferred to 100 ml volumetric flasks, made to volume and analyzed by ICP-ES (Licthe *et al.*, 1987).

All the elements analyzed are corrected for background and spectral interferences, where necessary. Table 1 lists each element analyzed along with its spectral line and method reporting limit. Included in this procedure are Ba, Cr and Zr, normally considered trace elements, which are carried out from this fusion method because of poor attack by mineral acids on certain mineral presentations of these elements, particularly barite, chromite and zircon.

Table 1. Reporting name, wavelength and method detection limits for major elements by ICP-ES

Reporting Name	Wavelength	Method Detection Limit
Al_2O_3	396.152	0.01%
Ba	455.403	1ppm
CaO	422.673	0.01%
Cr	205.550	50ppm
Fe_2O_3	233.280	0.01%
K_2O	766.490	0.01%
MgO	285.213	0.01%
MnO	294.942	0.01%
Na_2O	588.995	0.01%
P_2O_5	177.500	0.001%
SiO_2	288.150	0.01%
TiO_2	334.941	0.001%
Zr	343.023	1ppm

TRACE ELEMENTS

Trace-element analysis is performed on a large variety of sample media. Rock, soil and sediment are the materials most frequently analyzed. For the digestion of these materials, 1 g of sample is weighed into a 125 ml Teflon beaker. Potentially, highly organic samples such as soil, lake and stream sediment, are ashed at 500°C for four hours in porcelain crucibles to ensure that organic material is burnt off before digestion,

before they are transferred to the Teflon beakers. Five millilitres of concentrated hydrochloric acid, 15 ml of concentrated hydrofluoric acid and 5 ml of 1:1 perchloric acid is added to each sample. The samples are placed on a hotplate at 200°C and evaporated to dryness, after which the beakers are half filled with ten percent hydrochloric acid and returned to the hot plate at 100°C. When the residue is completely dissolved the samples are removed, cooled and transferred to 50 ml volumetric flasks. One ml of 50 g/l boric acid is added to each sample to complex any residual hydrofluoric acid. The samples are made to volume and analyzed by ICP-ES (Licthe *et al.*, 1987).

Table 2 lists all elements, spectral lines and detection limits for this method. Not all the twenty nine elements can be considered trace elements. The analysis of major and minor elements such as Al, Ca, Mg, Fe, K, Na, Mn, Ti, and P is useful for geochemical purposes, and also to correct for spectral interferences.

WATER ANALYSIS

The analysis of water samples does not require much sample preparation but does require great caution in the collection and stabilization of the sample to avoid sample contamination because of the low-level determinations that will be made. These precautions begin with the sample collection containers that should be of high-quality polyethylene or polypropylene void of any residual metals from the manufacturing process. The containers should be acid leached, washed with distilled and de-ionized water and dried before use. After the sample has been collected it should be filtered and stabilized as quickly as possible. A small field lab for these procedures is often the best approach for logistical reasons. If a field lab is not a viable option, the samples should be contained in a cooler with fridge packs and transported to an appropriate location for filtering and stabilization as soon as possible after collection.

Once in the lab, the samples should be passed through a 0.45 μm filter using a millipore type filtration apparatus. Care should be taken to avoid contamination form obvious sources such as jewelry or perspiration. Cross-contamination can be reduced by rinsing of the filtration apparatus between samples with distilled and de-ionized water and filtering a portion of the sample and discarding. Once the sample has been filtered it can be returned to the storage bottle that has been rinsed with distilled de-ionized water and a portion of the filtered sample. The samples are then preserved with the addition of nano-pure or double-distilled nitric acid to give a final acid concentration of 0.2 N (Finch *et al.*, 1992).

Elements for analysis in fresh waters by ICP-ES can be placed in two categories. First, there are those elements that

Table 2. Reporting name, wavelength and method detection limits for trace elements by ICP-ES

Reporting Name	Wavelength	Method Detection Limit
Al	396.152	0.01%
Ba	455.397	1ppm
Be	313.077	0.1ppm
Ca	422.673	0.01%
Ce	418.673	1ppm
Co	228.617	1ppm
Cr	205.561	1ppm
Cu	324.574	1ppm
Dy	353.170	0.1ppm
Fe	271.441	0.01%
Ga	294.364	1ppm
K	766.488	0.01%
La	408.670	1ppm
Li	670.784	0.1ppm
Mg	279.077	0.01%
Mn	403.447	1ppm
Mo	202.031	1ppm
Na	588.995	0.01%
Nb	319.497	1ppm
Ni	231.605	1ppm
P	213.617	1ppm
Pb	220.355	1ppm
Sc	361.383	0.1ppm
Sr	407.771	1ppm
Ti	307.864	1ppm
V	310.231	1ppm
Y	371.027	1ppm
Zn	213.857	1ppm
Zr	343.822	1ppm

are easily detectable by normal nebulization techniques and second, elements of low natural abundance in waters that require either pre-concentration or a specialized nebulization technique. For the more abundant, easily detectable elements, normal nebulization is sufficient to determine eight elements (Table 3). For the less abundant elements, a pre-concentration in the order of ten times is usually required. However, pre-concentration has its drawbacks. First, the samples must be taken through another preparation procedure. This could be another pathway to introduce contamination. A second drawback is the added expense of carrying out an extra preparation step. An alternative approach is ultrasonic nebulization. This nebulization technique pumps the sample over a high frequency peizo transducer producing a fine aerosol that can be more efficiently transported to the ICP torch. Also, incorporated in this nebulizer is a de-solvation tube. This provides some matrix stripping, which in turn, provides a degree of pre-concentration. The overall affect of this sample introduction technique is an improvement of three to ten times in detectable concentration without any further

Table 3. Reporting name, wavelength, nebulization and method detection limits for water analysis by ICP-ES

Reporting Name	Wavelength	Nebulization	Method Detection Limit
Ca	422.673	Concentric	10ppb
Fe	259.940	Concentric	5ppb
K	766.488	Concentric	100ppb
Mg	279.077	Concentric	1ppb
Mn	257.610	Concentric	2ppb
Na	589.590	Concentric	10ppb
SiO_2	251.610	Concentric	100ppb
SO_4	180.730	Concentric	100ppb
Al	308.220	Ultra-Sonic	10ppb
Ba	455.397	Ultra-Sonic	1ppb
Be	313.077	Ultra-Sonic	0.1ppb
Co	228.617	Ultra-Sonic	1ppb
Cr	267.720	Ultra-Sonic	1ppb
Cu	324.574	Ultra-Sonic	1ppb
Li	670.784	Ultra-Sonic	1ppb
Mo	202.031	Ultra-Sonic	1ppb
Ni	231.605	Ultra-Sonic	2ppb
P	178.890	Ultra-Sonic	5ppb
Sr	407.771	Ultra-Sonic	0.5ppb
Ti	336.120	Ultra-Sonic	1ppb
Y	371.027	Ultra-Sonic	0.5ppb
Zn	213.857	Ultra-Sonic	0.5ppb

sample preparation procedures (*Applied Research Laboratories). Table 3 lists the elements, analytical lines and method detection limits for this method.

PRECISION AND ACCURACY

At the laboratory, Standard Reference Materials (SRM) and blind duplicate pairs are included during digestion and preparation procedures in all sample batches for trace, major and water analysis at a frequency of one SRM and one duplicate pair in every twenty samples. Standard reference materials give a measure of analytical accuracy for particular elements that have been certified. The Certified Value (CV) or Recommended Value (RV) of an element is determined by statistical analysis of submitted results gathered through round robin studies from several laboratories. Duplicate samples are inserted in the sample batches at the time of sample preparation (crushing, pulverizing, sieving and filtering), where they remain blind to the technicians and analysts. These samples give an overall indication of the sample preparation and analytical precision.

Table 4 lists the RV's, average (AVG), standard deviation (STD), number of determinations (N) for SRM's used with major-element analysis. Averages for all the elements show good agreement with the recommended values with the exception of Cr, where agreement is poor at low levels (<100 ppm) due to the high detection limit of this element.

Tables 5a–d list the RV, average (AVG), standard deviation number (STD) analysis and percent relative standard deviation (RSD) for trace-element analysis. In general, most averages agree well with the RV's with the exception of Cr and Zr. Values are generally lower by mixed acid digestion techniques due to the incomplete attack on minerals such as chromite and zircon. The average values for Cr and Zr by fusion attack (major elements) gives much better agreement with the RV with the exception of Cr below 100 ppm.

Water analysis reference materials (RM) are listed in Table 6. The average values obtained for sample 1643D compare well with the RV's for this SRM. Reference material sample RR-3 is an in-house reference sample obtained in bulk from Rennie's River in St. John's. It was collected and preserved following the same procedure as water sample collection. It does not have any RV's associated with it, but is simply used as quality control sample and as reference material that better reflects the samples collected in the province. SRM 1643D is the only SRM that is available that has compositional values close to those of Newfoundland and Labrador natural waters, but even this sample is still not very representative of Newfoundland and Labrador natural waters, and to obtain reasonable working concentrations it was diluted five times. Finding commercially available SRM that are similar in composition to fresh water in Newfoundland and Labrador is a major problem with quality control in water analysis, and furthermore, most of these SRM's are prepared synthetically from salts. However, these SRM's are still useful, in that they are at least independently prepared and certified using robust statistcal analysis from round-robin inter-laboratory studies.

At the laboratory, SRM's used are the same media as the samples being analyzed. As a result of matching SRM's to the sample types analyzed, the overall accuracy and precision can be determined from the slopes and degree of fit (R^2) of plots for trace and major element of recommended value against the average value obtained for the SRMs (*see* Figure 1, for trace elements Zn, Co, and Figure 2 for major elements Fe and Mg). Over broad concentration ranges, no bias is apparent for any type and good agreement with RV's are exhibited by slopes that are close to one. The notable exceptions to these

* see Applied Research Laboratories, Ultrasonic Nebulization document #170796.

Table 4. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD % for ICP-ES major element analysis

	P_2O_5 %	Fe_2O_3 %	Cr ppm	TiO_2 %	MnO %	MgO %	Al_2O_3 %	Zr ppm	Ba ppm	CaO %	K_2O %	Na_2O %	SiO_2 %
AGV-1 (Andesite)													
RV	0.49	6.77	20	1.05	0.09	1.53	17.15	227	1226	4.94	2.92	4.26	58.84
AVG	0.50	6.82	14	1.05	0.10	1.54	17.24	220	1260	4.95	2.90	4.17	59.22
STD	0.01	0.09	15	0.02	0.00	0.02	0.14	3	18	0.07	0.05	0.19	0.38
N	4	4	4	4	4	4	4	4	4	4	4	4	4
RSD %	2.3	1.3	102.9	1.5	2.6	1.5	0.8	1.5	1.4	1.5	1.7	4.7	0.6
BCR-1 (Basalt)													
RV	0.36	13.41	16	2.24	0.18	3.48	13.64	190	681	6.95	1.69	3.27	54.11
AVG	0.34	13.46	4	2.22	0.19	3.48	13.39	178	691	6.90	1.68	3.29	54.40
STD	0.00	0.29	6	0.02	0.00	0.02	0.10	2	11	0.04	0.01	0.00	0.15
N	2	2	2	2	2	2	2	2	2	2	2	2	2
RSD %	1.3	2.2	156.6	0.8	1.1	0.7	0.8	1.3	1.5	0.5	0.3	0.1	0.3
BHVO-1 (Basalt)													
RV	0.27	12.23	289	2.71	0.17	7.23	13.80	179	139	11.40	0.52	2.26	49.94
AVG	0.27	12.36	280	2.75	0.17	7.28	13.68	161	135	11.38	0.52	2.29	49.88
STD	0.01	0.15	34	0.03	0.00	0.14	0.18	2	3	0.22	0.01	0.04	0.65
N	7	7	7	7	7	7	7	7	7	7	7	7	7
RSD %	4.1	1.2	12.3	1.2	2.5	1.9	1.3	1.1	2.1	1.9	1.3	1.6	1.3
G-2 (Granite)													
RV	0.14	2.66	9	0.48	0.03	0.75	15.38	309	1882	1.96	4.48	4.08	69.08
AVG	0.14	2.66	2	0.49	0.03	0.78	15.37	314	1947	1.92	4.44	4.06	68.63
STD	0.01	0.03	6	0.01	0.00	0.03	0.10	14	13	0.03	0.05	0.02	0.27
N	5	5	5	5	5	5	5	5	5	5	5	5	3
RSD %	8.6	1.3	329.1	1.4	4.4	3.7	0.7	4.5	0.7	1.4	1.1	0.5	0.4
MAG-1 (Marine Mud)													
RV	0.16	6.80	97	0.75	0.10	3.00	16.37	126	479	1.37	3.55	3.83	50.36
AVG	0.17	7.06	103	0.73	0.10	3.07	16.39	123	504	1.39	3.45	3.86	51.11
STD	0.01	0.07	39	0.01	0.00	0.03	0.15	3	6	0.02	0.08	0.04	0.39
N	8	8	8	8	8	8	8	8	8	8	8	8	8
RSD %	6.6	1.0	37.3	1.6	3.5	1.1	0.9	2.2	1.2	1.7	2.3	1.0	0.8
QLO-1 (Quartz Latite)													
RV	0.25	4.35	3	0.62	0.10	1.00	16.18	185	1370	3.17	3.60	4.20	65.55
AVG	0.25	4.31	14	0.61	0.09	1.02	16.30	176	1443	3.18	3.58	4.20	65.26
STD	0.01	0.05	42	0.01	0.00	0.01	0.12	1	13	0.01	0.05	0.05	0.70
N	5	5	5	5	5	5	5	5	5	5	5	5	4
RSD %	2.4	1.1	290.9	1.9	2.0	1.1	0.7	0.8	0.9	0.5	1.3	1.3	1.1
RGM-1 (Rhyolite)													
RV	0.05	1.86	4	0.27	0.04	0.28	13.72	219	807	1.15	4.30	4.07	73.45
AVG	0.04	1.82	43	0.26	0.04	0.27	13.75	216	852	1.18	4.30	4.06	73.06
STD	0.00	0.02	23	0.00	0.00	0.01	0.17	4	9	0.03	0.06	0.05	0.32
N	3	5	4	5	4	5	4	5	5	5	5	5	4
RSD %	9.3	1.1	54.2	1.4	5.4	2.6	1.2	2.0	1.1	2.3	1.4	1.2	0.4
SCO-1 (Shale)													
RV	0.21	5.14	68	0.63	0.05	2.72	13.67	160	570	2.62	2.77	0.90	62.78
AVG	0.20	5.23	81	0.59	0.05	2.75	13.80	162	599	2.58	2.70	0.92	63.00
STD	0.01	0.07	33	0.01	0.00	0.04	0.08	7	8	0.05	0.03	0.01	0.20
N	5	5	4	5	5	5	5	5	5	5	5	5	4
RSD %	4.0	1.3	41.0	1.6	2.9	1.5	0.5	4.5	1.4	1.9	1.0	1.4	0.3
SDC-1 (Mica Schist)													
RV	0.16	6.90	64	1.01	0.11	1.69	15.75	290	630	1.40	3.28	2.05	65.85
AVG	0.15	6.98	57	0.99	0.12	1.73	15.80	317	660	1.41	3.24	2.07	65.86
STD	0.02	0.06	42	0.02	0.00	0.01	0.09	17	5	0.01	0.06	0.02	0.24
N	5	5	5	5	5	5	5	5	5	5	5	5	4
RSD %	12.1	0.8	74.0	2.2	0.8	0.4	0.6	5.5	0.8	0.5	1.8	0.8	0.4
STM-1 (Syenite)													
RV	0.16	5.22	4	0.14	0.22	0.10	18.39	1210	560	1.09	4.28	8.94	59.64
AVG	0.15	5.23	4	0.13	0.23	0.11	18.36	1251	600	1.13	4.20	8.98	58.91
STD	0.01	0.10	40	0.00	0.00	0.02	0.22	25	21	0.02	0.05	0.12	0.83
N	12	12	12	12	12	12	12	12	12	12	12	12	9
RSD %	8.6	1.8	1088.3	2.7	2.2	22.4	1.2	2.0	3.5	2.0	1.2	1.3	1.4
VS-N (Glass)													
RV	0.00	4.14	700	1.08	0.10	4.51	13.44	700	1000	4.53	8.12	5.95	55.57
AVG	0.03	3.98	642	1.05	0.10	4.35	13.16	701	974	4.30	7.85	6.20	55.62
STD	0.02	0.04	63	0.01	0.00	0.01	0.05	11	22	0.07	0.12	0.03	0.45
N	4	4	4	4	4	4	4	4	4	4	4	4	2
RSD %	45.9	0.9	9.7	0.6	1.4	0.2	0.4	1.6	2.2	1.7	1.5	0.4	0.8

Table 5a. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD%) of lake sediment SRM's for ICP-ES trace elements analysis

SRM		Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga	Ti ppm
LKSD-1	RV	10	31	698	331	82	11	16	2.8	1.04		3010
	AVG	9	26	678	321	81	11	14	2.8	0.98	10	3002
	STD	0.5	7.8	23.5	8.4	2.8	0.4	4.0	0.1	0.0	3.1	92.4
	RSD %	4.9	29.5	3.5	2.6	3.5	3.7	28.5	2.4	3.8	31.7	3.1
	N	77	77	77	77	77	77	77	77	77	77	77
LKSD-2	RV	-5	57	1222	209	44	17	26	4.3	1.01		3460
	AVG	1	50	1286	208	42	20	24	4.4	1	17	3419
	STD	0.3	8.2	50.0	6.4	2.1	0.8	4.5	0.1	0.0	3.3	108.0
	RSD %	27.7	16.5	3.9	3.1	5.0	4.1	18.3	2.9	4.2	19.5	3.2
	N	68	68	68	68	68	68	68	68	68	68	68
LKSD-3	RV	-5	87	1091	152	29	30	47	4.0	1.2		3330
	AVG	1	73	1050	145	30	34	46	4.1	1.1	18	3229
	STD	0.2	4.1	40.2	4.4	2.2	1.3	2.9	0.1	0.0	3.0	106.8
	RSD %	22.6	5.7	3.8	3.0	7.2	4.0	6.3	2.9	4.0	16.9	3.3
	N	78	78	78	78	78	78	78	78	78	78	78
LKSD-4	RV	-5	33	1440	194	91	11	31	2.8	0.56		2270
	AVG	2	30	1468	191	91	12	31	3.0	1	10	1980
	STD	0.3	3.6	66.1	6.0	3.5	0.7	2.9	0.1	0.0	3.0	73.3
	RSD %	15.2	12.0	4.5	3.1	3.9	5.3	9.5	3.1	5.1	33.1	3.7
	N	62	62	62	62	62	62	62	62	62	62	62

Table 5b. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD%) of stream sediment SRM's for ICP-ES trace elements analysis

STSD-1	RV	-5	67	1658	178	35	17	24	4.53	1.33		4496
	AVG	1	47	1653	177	36	19	21	4.6	1.25	10	3599
	STD	0.2	4.5	25.5	4.7	2.0	0.9	1.1	0.1	0.0	1.6	95.4
	RSD %	29.5	9.5	1.5	2.6	5.5	4.8	5.2	1.7	1.9	16.2	2.7
	N	8	8	8	8	8	8	8	8	8	8	8
STSD-2	RV	13	116	1397	246	66	19	53	5.25	1.88		4736
	AVG	12	85	1369	244	69	21	49	5.3	1.78	22	4777
	STD	0.2	3.9	34.9	1.5	1.4	0.6	2.9	0.1	0.1	1.1	190.3
	RSD %	1.6	4.6	2.5	0.6	2.0	3.1	5.9	1.2	4.2	5.0	4.0
	N	5	5	5	5	5	5	5	5	5	5	5
STSD-3	RV	6	80	1571	204	40	16	30	4.32	1.33		4316
	AVG	6	61	1618	206	43	18	28	4.4	1.24	14	3629
	STD	0.3	3.7	60.9	4.3	2.7	0.5	1.3	0.1	0.0	2.2	150.1
	RSD %	5.5	6.1	3.8	2.1	6.2	2.9	4.5	1.6	1.7	15.6	4.1
	N	7	7	7	7	7	7	7	7	7	7	7
STSD-4	RV	-5	93	960	107	18	13	30	3.99	1.28		4556
	AVG	1	68	947	99	18	15	26	4.0	1.21	15	4252
	STD	0.1	2.9	20.6	3.0	2.8	0.5	0.7	0.1	0.0	1.3	101.9
	RSD %	7.5	4.2	2.2	3.1	15.5	3.4	2.5	3.5	1.5	8.8	2.4
	N	5	5	5	5	5	5	5	5	5	5	5

Table 5c. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD%) of till SRM's for ICP-ES trace elements analysis

TILL-1	RV	2	65	930	98	22	18	24	4.81	1.30		5990
	AVG	0.3	54	924	93	21	18	21	4.9	1.19	19	5584
	STD	0.4	1.2	19.3	1.9	3.7	0.6	1.0	0.1	0.0	2.4	180.4
	RSD %	108.6	2.1	2.1	2.1	17.1	3.5	4.9	1.8	2.4	13.1	3.2
	N	30	30	30	30	30	30	30	30	30	30	30
TILL-2	RV	14	74	750	130	31	15	32	3.84	1.30		5300
	AVG	12	59	714	123	30	15	30	3.9	1.03	21	5200
	STD	0.7	2.3	19.8	3.8	3.9	0.5	1.5	0.1	0.0	2.7	216.7
	RSD %	5.5	3.9	2.8	3.1	12.8	3.4	5.0	2.8	2.7	12.6	4.2
	N	29	29	29	29	29	29	29	29	29	29	29
TILL-3	RV	2	123	490	56	26	15	39	2.78	1.03		2910
	AVG	0.3	95	484	52	24	15	38	2.8	0.95	14	2930
	STD	0.4	4.0	23.2	2.4	3.5	0.7	2.4	0.1	0.0	3.2	137.5
	RSD %	121.6	4.2	4.8	4.7	14.7	4.9	6.4	4.5	5.0	22.2	4.7
	N	26	26	26	26	26	26	26	26	26	26	26
TILL-4	RV	16	53	880	70	50	8	17	3.97	0.76		4840
	AVG	14	38	879	67	49	8	14	4.1	0.69	20	4867
	STD	0.7	1.2	28.6	1.6	3.0	0.6	0.7	0.1	0.0	3.0	196.1
	RSD %	4.8	3.3	3.3	2.3	6.1	7.4	5.0	1.9	3.1	15.1	4.0
	N	22	22	22	22	22	22	22	22	22	22	22

Table 5a. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD %) of lake sediment SRM's for ICP-ES trace elements analysis

SRM	V ppm	Be ppm	Sc ppm	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba ppm	Li ppm	K %
LKSD-1	50	1.1	9	19	4.1	700	250	16	27	430	7	0.95
	52	0.7	8	21	3.97	728	267	18	27	397	7	0.96
	1.5	0.0	0.2	0.6	0.1	20.4	6.8	1.6	4.1	47.5	0.6	0.0
	2.9	2.6	2.9	2.7	2.3	2.8	2.5	8.4	15.0	12.0	8.7	3.1
	77	77	77	77	77	77	77	77	77	77	77	77
LKSD-2	77	2.5	13	44	6.51	2020	220	68	108	780	20	2.19
	79	2	12.2	40	6.20	2179	239	68	120	777	22.8	2.23
	3.0	0.0	0.4	1.3	0.1	81.5	7.3	2.3	5.3	21.9	0.8	0.1
	3.8	2.6	3.5	3.4	2.2	3.7	3.0	3.4	4.4	2.8	3.7	3.2
	68	68	68	68	68	68	68	68	68	68	68	68
LKSD-3	82	1.9	13	30	6.60	1440	240	52	90	680	25.0	1.84
	83	1.5	12	27	6.29	1548	252	51	96	684	28.8	1.90
	2.6	0.0	0.4	0.8	0.1	55.1	6.7	1.9	4.4	19.2	0.9	0.1
	3.2	2.4	3.2	3.2	2.1	3.6	2.7	3.8	4.6	2.8	3.3	3.0
	78	78	78	78	78	78	78	78	78	78	78	78
LKSD-4	49	1.0	7	23	3.10	500	110	26	48	330	12	0.68
	50	0.8	7	22	2.94	576	128	27	51	339	13.4	0.65
	2.6	0.0	0.3	0.8	0.1	35.8	5.0	1.9	3.7	13.2	0.7	0.0
	5.2	3.4	4.8	3.8	2.0	6.2	3.9	7.1	7.3	3.9	5.5	5.3
	62	62	62	62	62	62	62	62	62	62	62	62

Table 5b. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD %) of stream sediment SRM's for ICP-ES trace elements analysis

STSD-1	98	1.6	14	42	4.76	3872	170	30	51	630	11	1.04
	93	1.1	13	35	5.24	4378	192	29	48	650	15.1	1.06
	2.3	0.0	0.2	0.6	0.1	212.5	5.6	1.3	4.0	14.5	1.5	0.0
	2.5	1.7	1.2	1.7	2.0	4.9	2.9	4.3	8.4	2.2	9.6	1.7
	8	8	8	8	8	8	8	8	8	8	8	8
STSD-2	101	5.2	16	37	8.52	1084	400	59	93	540	65	1.76
	100	4.3	14	32	9.77	1147	426	54	90	542	78.5	1.78
	3.3	0.0	0.4	0.7	0.1	51.1	5.3	1.2	1.6	13.1	5.6	0.1
	3.3	0.7	3.0	2.1	1.3	4.5	1.2	2.2	1.8	2.4	7.1	3.9
	5	5	5	5	5	5	5	5	5	5	5	5
STSD-3	134	2.6	13	36	5.77	2633	230	39	63	1490	28	1.49
	133	2.2	12	31	6.57	3037	255	37	63	1451	36.9	1.51
	4.7	0.1	0.2	0.6	0.1	129.8	5.1	1.9	3.6	33.7	3.2	0.0
	3.6	2.3	1.9	2.0	1.9	4.3	2.0	5.1	5.8	2.3	8.6	2.7
	7	7	7	7	7	7	7	7	7	7	7	7
STSD-4	106	1.7	14	24	6.40	1471	350	24	44	2000	14	1.33
	109	1.2	12	21	7.26	1666	371	24	43	1803	17.1	1.35
	1.3	0.0	0.1	0.5	0.1	37.1	6.1	1.5	4.2	135.5	0.3	0.0
	1.2	2.4	1.2	2.3	1.3	2.2	1.6	6.3	9.8	7.5	1.7	2.0
	5	5	5	5	5	5	5	5	5	5	5	5

Table 5c. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD %) of till SRM's for ICP-ES trace elements analysis

TILL-1	99	2.4	13	38	7.30	1420	291	28	71	702	15	1.84
	107	1.5	13	27	8.21	1557	295	29	74	713	17.3	1.77
	2.4	0.0	0.4	0.6	0.3	63.3	6.2	1.1	4.4	17.2	1.1	0.0
	2.3	1.7	3.0	2.1	3.7	4.1	2.1	3.8	5.9	2.4	6.1	2.1
	30	30	30	30	30	30	30	30	30	30	30	30
TILL-2	77	4.0	12	40	8.50	780	144	44	98	540	47	2.55
	82	3.3	12	19	9.84	826	144	43	100	534	53.2	2.43
	3.3	0.1	0.4	0.4	0.4	34.1	3.4	1.4	5.5	15.5	3.5	0.1
	4.0	4.4	3.4	2.4	3.9	4.1	2.4	3.3	5.4	2.9	6.6	3.7
	29	29	29	29	29	29	29	29	29	29	29	29
TILL-3	62	2.0	10	17	6.50	520	300	21	42	489	21	2.00
	67	1.2	10	13	7.28	545	306	21	45	496	25.0	2.01
	2.7	0.1	0.5	0.6	0.3	22.2	12.9	1.6	3.9	22.2	1.6	0.1
	4.1	9.0	5.0	4.3	4.7	4.1	4.2	7.9	8.7	4.5	6.4	4.1
	26	26	26	26	26	26	26	26	26	26	26	26
TILL-4	67	3.7	10	33	7.60	490	109	41	78	395	30	2.70
	72	3.0	10	17	8.83	520	114	42	83	390	33.8	2.57
	2.0	0.1	0.4	0.5	0.4	18.1	2.7	1.5	5.1	7.0	2.0	0.1
	2.8	1.9	3.8	2.8	4.0	3.5	2.4	3.6	6.2	1.8	5.8	3.9
	22	22	22	22	22	22	22	22	22	22	22	22

Table 5d. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD%) of rock SRM's for ICP-ES trace elements analysis

SRM		Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga	Ti ppm
SY-2	RV	1.8	9.5	1900	248	85	8.6	9.9	4.41	1.62	29	899
	AVG	0.2	7	1814	246	85	9	5	4.4	1.47	29	890
	STD	0.3	2.0	39.2	5.5	2.3	0.3	1.3	0.1	0.0	4.1	19.6
	RSD %	117.1	30.0	2.2	2.2	2.7	3.8	23.1	2.2	2.4	14.1	2.2
	N	49	49	49	49	49	49	49	49	49	49	49
SY-4	RV		12	527	93	10	2.8	9	4.2	0.33	35	1720
	AVG		10	518	96	10	3	6	4.4	0.27	38	1830
	STD	0.5	9.9	11.9	2.6	5.3	0.5	5.1	0.1	0.0	3.5	73.4
	RSD %	1037.7	98.7	2.3	2.7	55.0	20.0	81.3	2.6	2.7	9.2	4.0
	N	49	49	49	49	49	49	49	49	49	49	49
MRG-1	RV	1	430	343	191	10	87	193	12.55	8.17	17	22600
	AVG	1	287	236	193	4	86	156	12.5	7.71	21	25947
	STD	0.4	11.7	7.8	7.5	0.7	2.6	5.4	0.4	0.2	4.7	863.5
	RSD %	48.2	4.1	3.3	3.9	20.1	3.1	3.5	3.3	2.8	22.5	3.3
	N	40	40	40	40	40	40	40	40	40	40	40
WGB-1	RV		291	430	31.5		29.8	76	4.69	5.67		5040
	AVG		269	347	35		29	64	4.4	4.85	12	5593
	STD	0.3	5.6	6.8	1.3	0.5	0.4	2.6	0.1	0.2	2.4	107.5
	RSD %	165.1	2.1	1.9	3.7	10.3	1.4	4.0	1.8	4.9	19.5	1.9
	N	10	10	10	10	10	10	10	10	10	10	10

Table 6. Average (AVG), recommended values (RV), standard deviation (STD) and number of determination (N) for ICP-ES water analysis

	Fe ppb	SO_4 ppm	Mn ppb	Si ppm	Mg ppm	Ca ppm	K ppm	Na ppm	Mo ppb	P ppb	Ni ppb
RR-3											
AVG	61	10.7	205	1.7	1.33	6.58	1.5	77.05	0	5	1
STD	7.3	0.5	7.2	0.2	0.1	0.2	0.1	1.9	1.5	1.7	2.1
N	121	126	126	126	126	126	126	126	95	94	97
RSD %	12.0	4.5	3.5	12.6	8.7	2.6	5.1	2.5	642.6	34.4	156.3
1643D											
AVG	22	0.2	7	0.1	1.91	7.15	0.47	2.32	20	3	12
RV	21		7				0.46		21		12
STD	7.9	0.2	2.1	0.1	0.1	0.2	0.1	0.10	2.4	1.5	2.8
N	45	45	45	45	45	45	45	45	38	38	40
RSD %	35.6	93.8	29.1	162.8	3.3	2.2	26.1	4.3	11.8	45.4	24.0

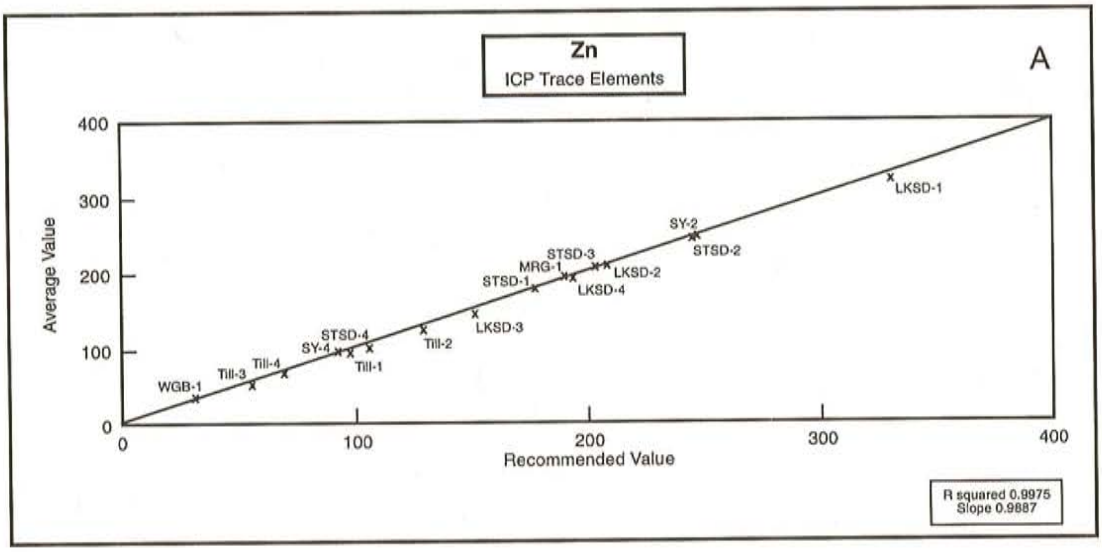


Figure 1a. *Average value versus recommended value for the trace element Zn.*

Table 5d. Recommended value (RV), average (AVG), standard deviation (STD), number of determinations (N) and percent relative standard deviation (RSD %) of rock SRM's for ICP-ES trace elements analysis

SRM	V ppm	Be ppm	Sc ppm	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba ppm	Li ppm	K %
SY-2	50	22.0	7	128	6.37	2500	271	75	175	460	95	3.69
	51	21.9	7	127	6.81	2479	269	75	174	458	92.3	3.40
	1.2	0.4	0.2	2.6	0.2	35.7	4.3	1.6	4.8	6.8	1.3	0.1
	2.4	1.9	3.0	2.1	2.7	1.4	1.6	2.1	2.8	1.5	1.4	1.6
	49	49	49	49	49	49	49	49	49	49	49	49
SY-4	8	2.6	1.1	119	10.69	819	1191	58	122	340	37	1.38
	7	2.8	1	119	12.02	831	1124	63	128	348	38.1	1.43
	0.6	0.1	0.1	3.6	0.3	13.5	79.3	1.8	4.4	7.1	0.8	0.0
	8.5	2.1	7.5	3.0	2.2	1.6	7.1	2.9	3.4	2.0	2.1	2.8
	49	49	49	49	49	49	49	49	49	49	49	49
MRG-1	526	0.6	55	14	4.48	1300	266	9.8	26	61	4.2	0.15
	520	0.4	53	14	4.32	1315	262	14	27	49	3.7	0.15
	17.8	0.0	2.7	0.5	0.1	22.9	6.9	1.1	3.2	1.2	0.2	0.0
	3.4	3.0	5.2	3.3	2.8	1.7	2.6	8.3	11.8	2.4	4.1	3.8
	40	40	40	40	40	40	40	40	40	40	40	40
WGB-1	222		44	14.6	5.90	1100	118	8.7		851		0.78
	212		35	15	5.56	1056	100	11		820		0.78
	6.4	0.0	1.6	0.3	0.3	21.3	2.8	1.3	3.2	12.6	1.0	0.0
	3.0	1.4	4.6	2.0	5.4	2.0	2.8	11.5	20.5	1.5	2.4	2.9
	10	10	10	10	10	10	10	10	10	10	10	10

Table 6. Average (AVG), recommended values (RV), standard deviation (STD) and number of determinations (N) for ICP-ES water analysis

	Co ppb	Zn ppb	Al ppb	Cr ppb	Ti ppb	Y ppb	Be ppb	Cu ppb	Ba ppb	Sr ppb	Li ppb
RR-3											
AVG	0	42	20	1	-0	0	0.0	5	23	26.6	1
STD	0.7	2.3	6.9	0.6	0.5	0.1	0.1	1.5	1.4	2.0	0.2
N	97	97	97	97	95	95	95	95	95	95	95
RSD %	347.4	5.4	35.2	47.2	-404.5	40.2	614.1	33.7	6.4	7.7	44.8
1643D											
AVG	5	15	31	4	1	0	4.8	6	10	49.5	3
RV	5	15	23	4			4.6	4	10	52.7	3
STD	0.9	3.0	4.0	0.7	0.2	0.2	0.4	1.9	0.5	2.6	0.2
N	39	39	39	39	38	38	38	38	38	38	38
RSD %	18.9	19.8	12.8	18.3	18.1	193.4	8.0	33.5	5.1	5.2	7.0

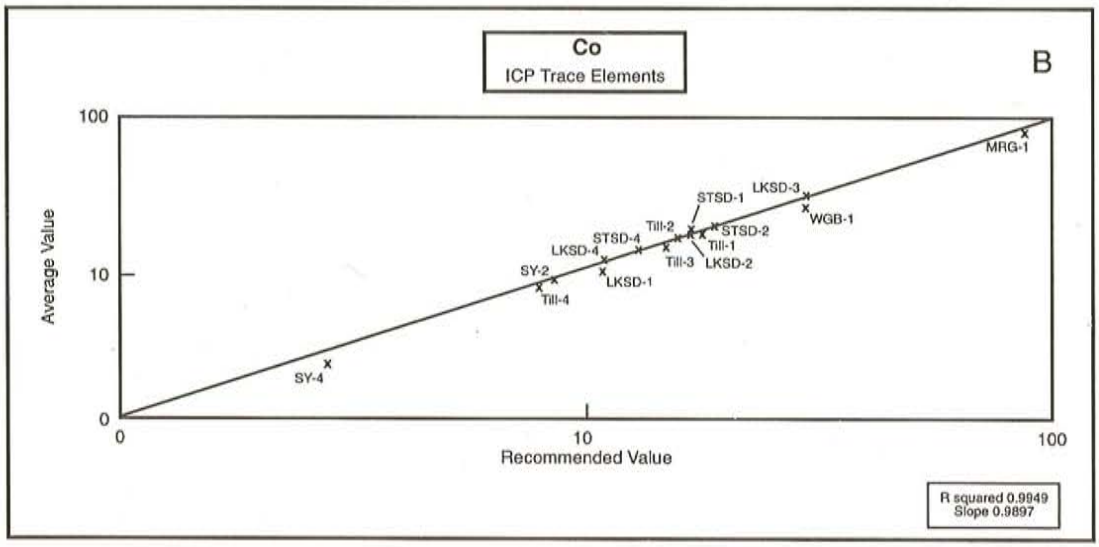
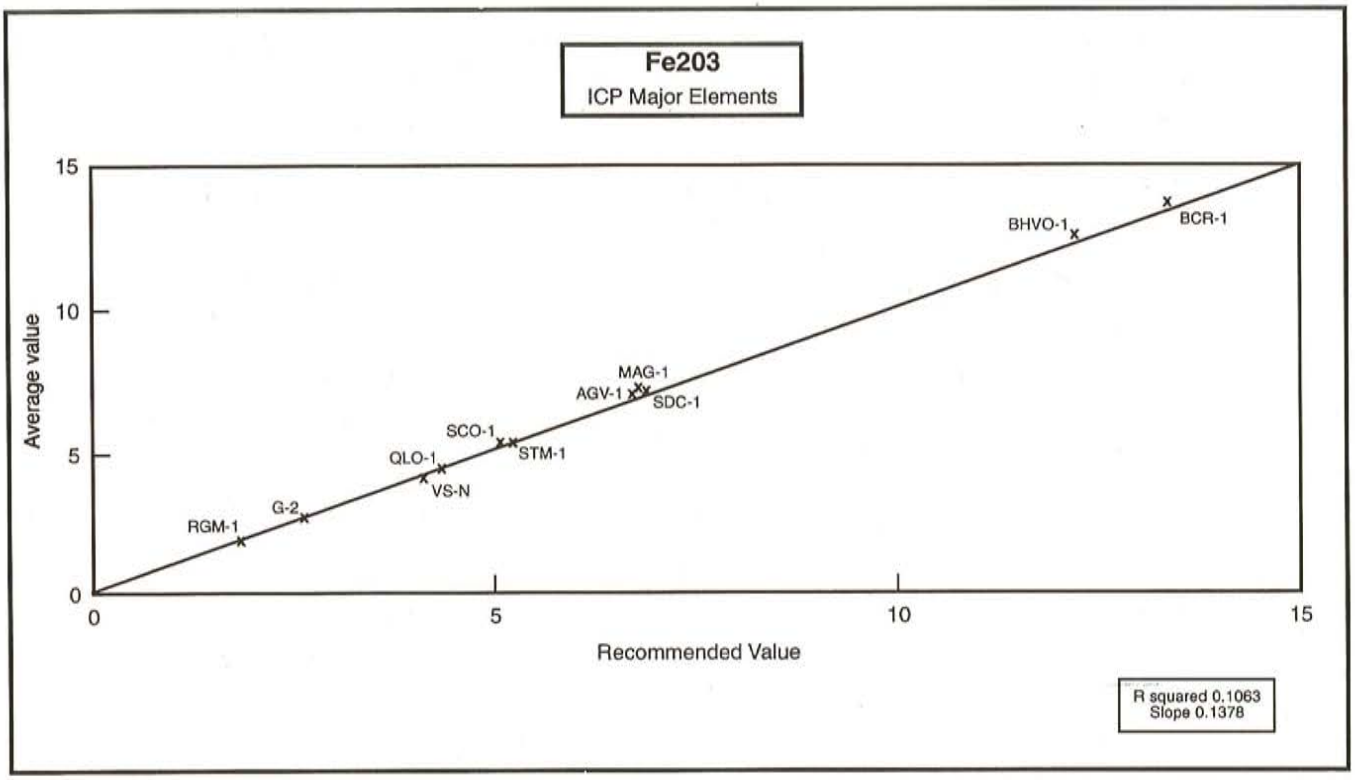


Figure 1b. *Average value versus recommended value for the trace element Co.*



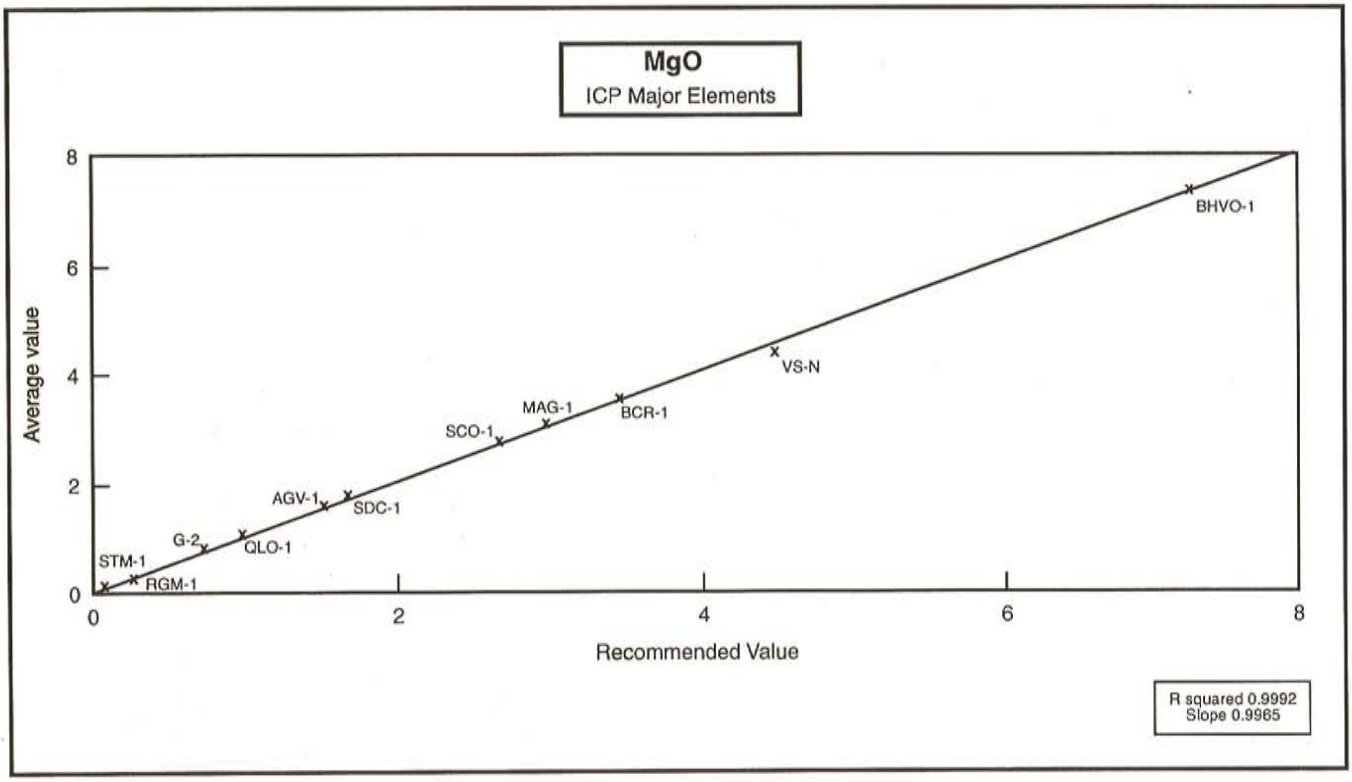


Figure 2. *Average value versus recommended value for major elements (Fe and Mg).*

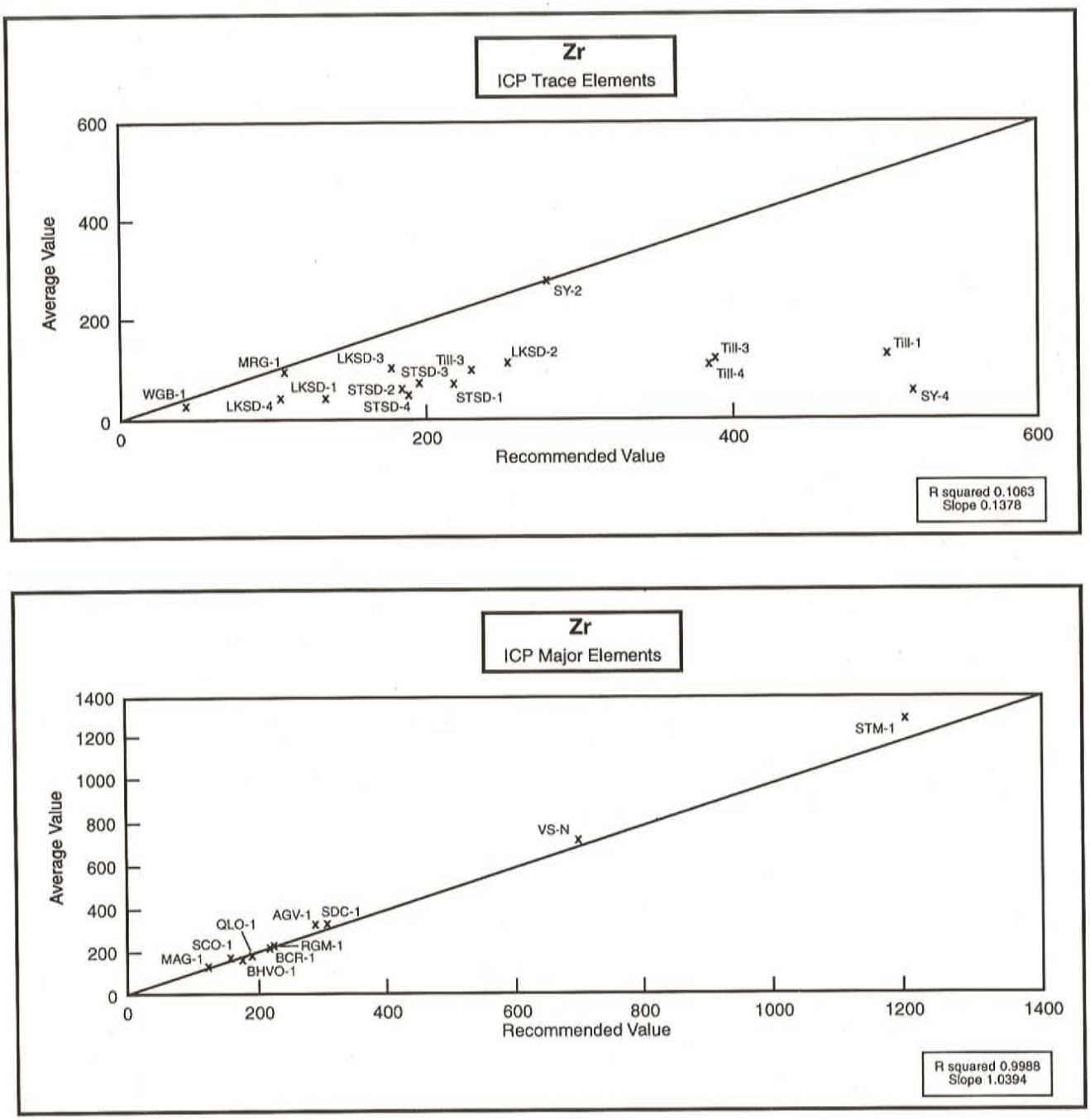


Figure 3a. *Average value versus recommended value for Zr by ICP-ES.*

observations are Zr and, to a lesser degree, Cr digested and determined for ICP trace elements (Figures 3a and b). Zirconium yields a poor correlation and slope. This is due mainly to incomplete attack by mineral acids on zircon and chromite. However, when fused with lithium metaborate in the major-element procedure, the slopes and correlations for Zr an Cr are much better, indicating that this would be the preferred method for their determination. The slopes and degree of fit (R^2) for all major and trace elements from similar plots are listed in Table 7.

As stated previously, duplicate data will give an overall indication of precision for a method. In general, analytical precision for all elements analyzed by each method is very good when determinations are made above the levels of detection. The usual error is within three to five percent as expressed as the percent difference of the means divided by the average. For many elements, the precision is better than three percent. Figures 4 and 5 show scatter plots of duplicate pairs for Ca and Ba as determined by the major-, trace- and water-analysis methods. These plots show the excellent pre-

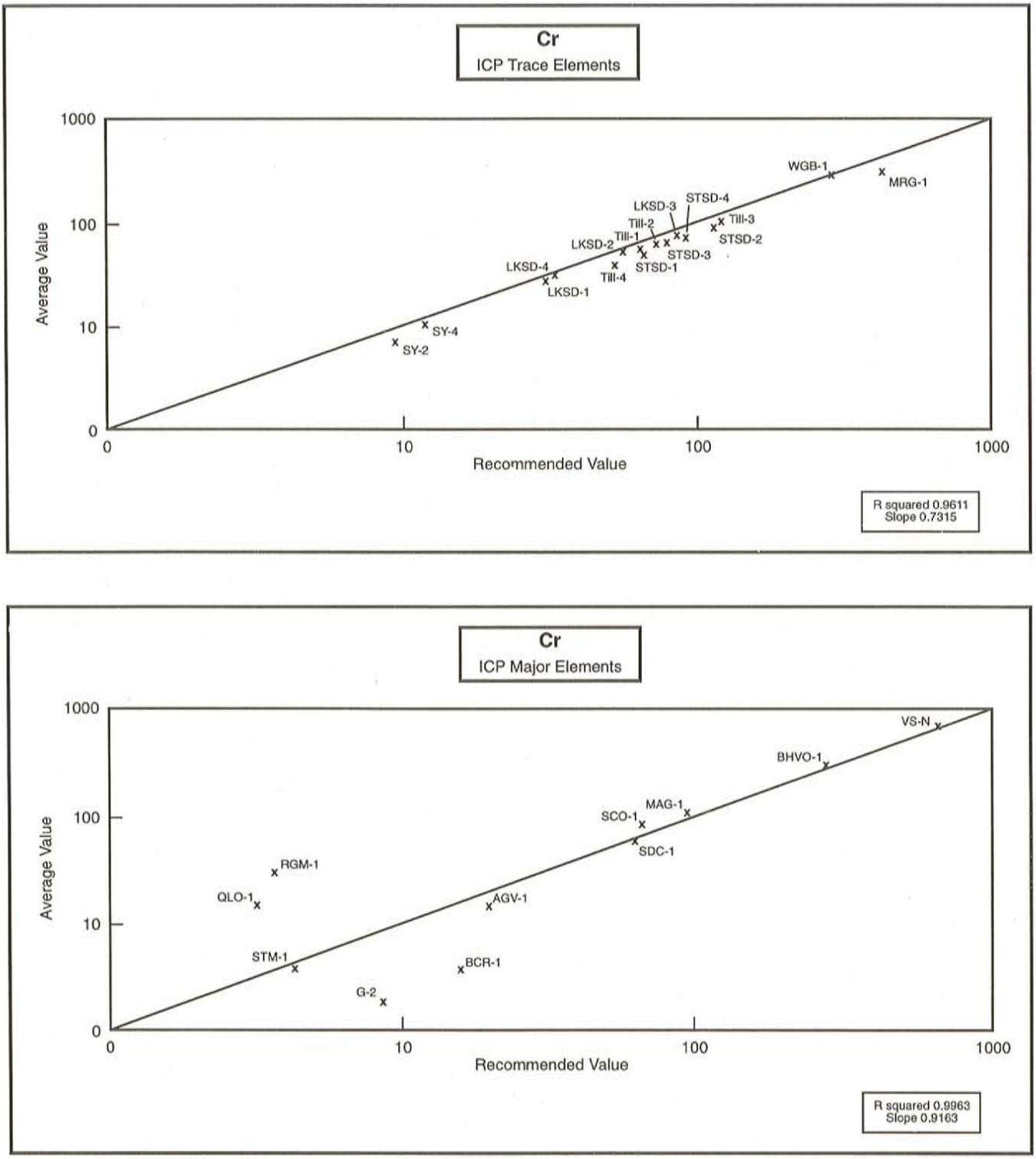
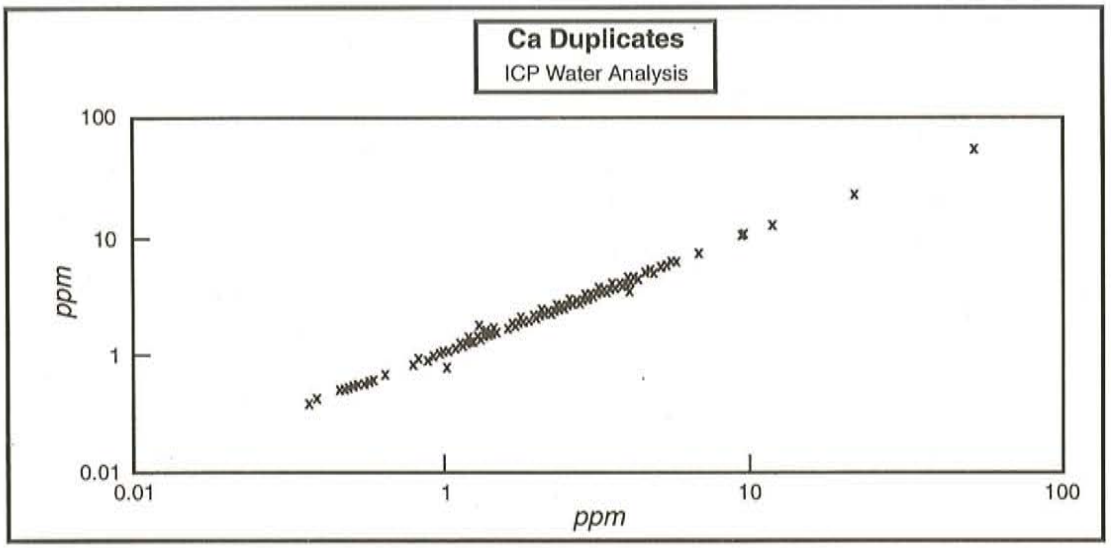


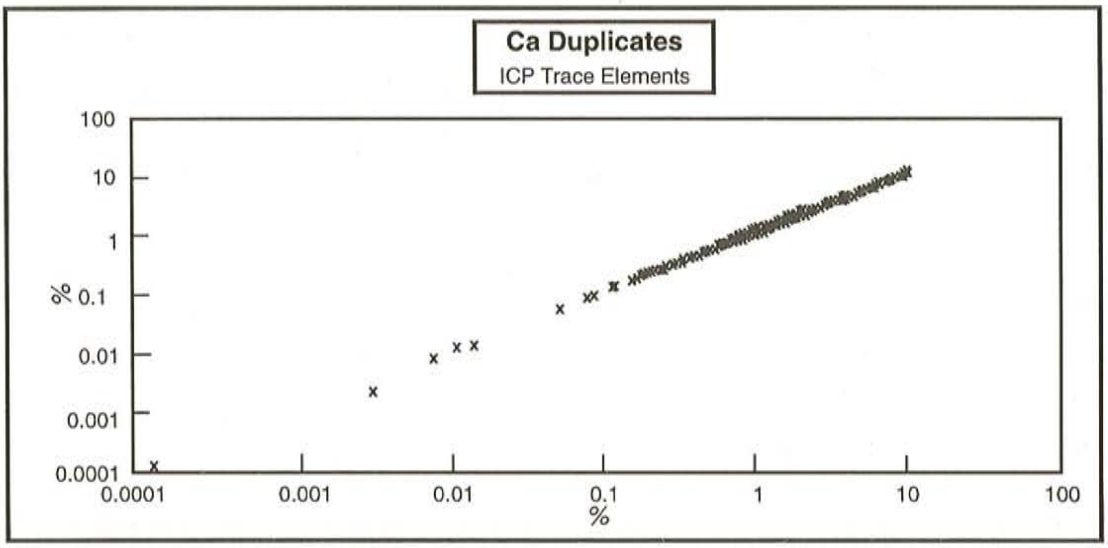
Figure 3b. *Average value versus recommended value for Cr by ICP-ES.*

precision of these determinations over very large dynamic ranges of concentration. These precision plots are typical of those obtained for most elements analyzed at the laboratory.

CONCLUSION

With the introduction of ICP-ES, the capability of the laboratory has grown to provide a broad range of analytical services to the Geological Survey of Newfoundland and Labrador. These services include multi-element suites for the determination of major-element, trace-element and water analysis. All methods have quality control protocols that measure and document the precision and accuracy of all





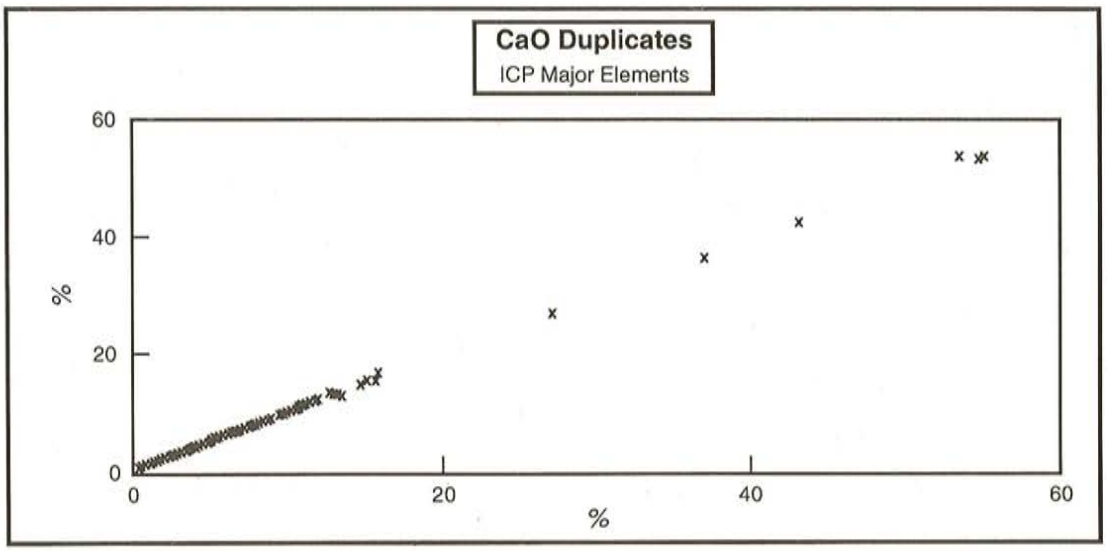
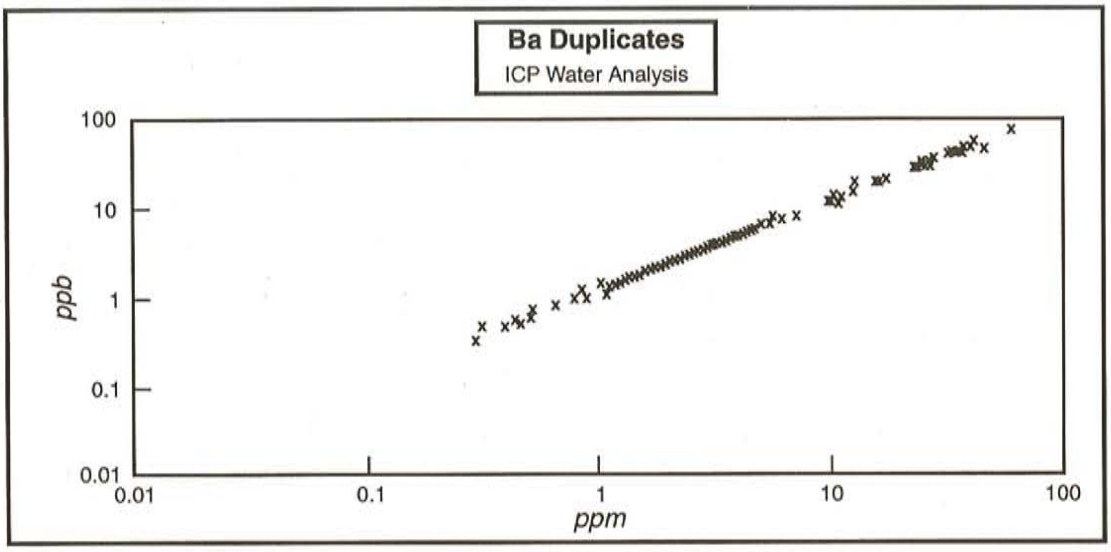
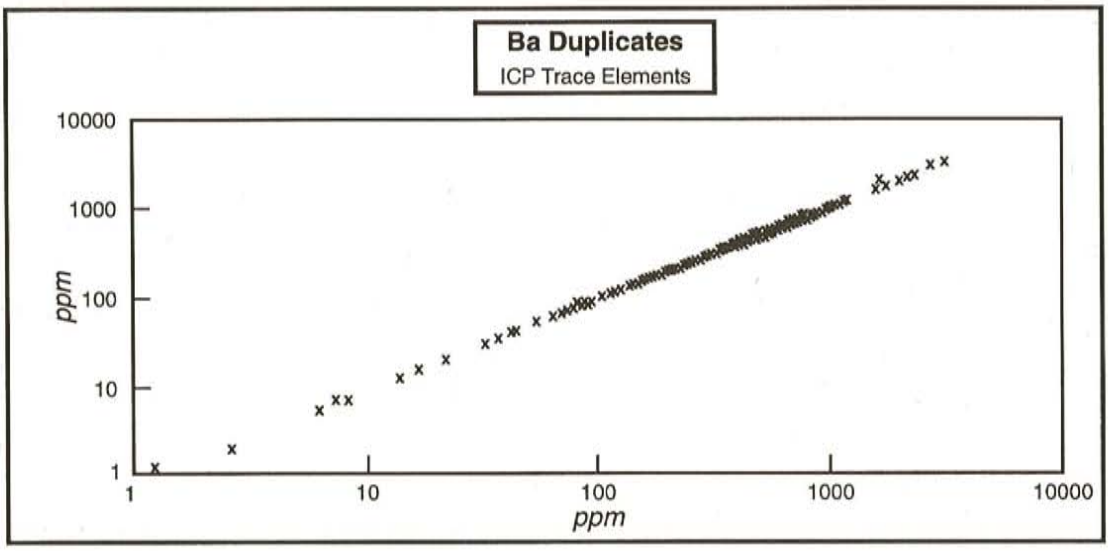


Figure 4. *Scatter plots of duplicate pairs for Ca by ICP-ES.*





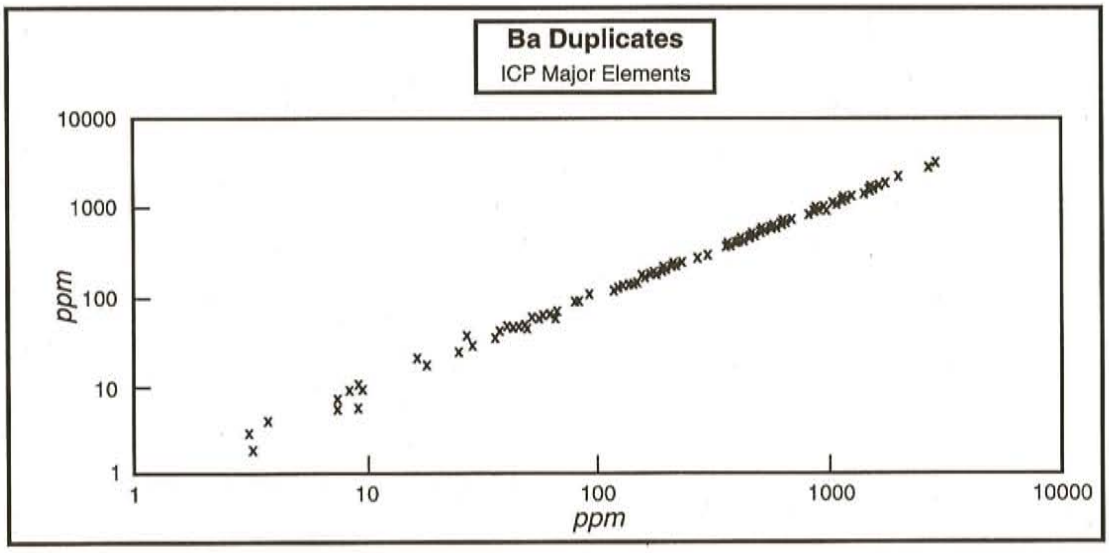


Figure 5. *Scatter plots of duplicate pairs for Ba by ICP-ES.*

Table 7. R^2 values and slopes for ICP-ES major and trace analysis SRM's

Reporting Name	R^2	Slope	Method	Reporting Name	R^2	Slope	Method
Al	0.9648	1.2476	Trace	Mn	0.9919	1.1255	Trace
Al_2O_3	0.9950	1.0365	Majors	MnO	0.9940	1.0327	Majors
Ba	0.9978	1.0325	Majors	Mo	0.9858	0.9542	Trace
Ba	0.9951	0.9127	Trace	Na	0.9909	0.8063	Trace
Be	0.9968	1.0135	Trace	Na_2O	0.9986	1.0106	Majors
Ca	0.9987	0.9768	Trace	Nb	0.9263	0.9578	Trace
CaO	0.9995	0.9943	Majors	Ni	0.9935	0.8057	Trace
Ce	0.9917	1.0254	Trace	P	0.9922	1.0307	Trace
Co	0.9950	0.9897	Trace	P_2O_5	0.9952	1.0438	Majors
Cr	0.9963	0.9163	Majors	Pb	0.9936	1.0272	Trace
Cr	0.9611	0.7315	Trace	Sc	0.9849	0.8918	Trace
Cu	0.9974	1.0657	Trace	SiO_2	0.9978	0.9676	Majors
Dy	0.9908	0.9805	Trace	Sr	0.9958	0.9344	Trace
Fe	0.9973	0.9879	Trace	Ti	0.9939	1.1672	Trace
Fe_2O_3	0.9993	1.0137	Majors	TiO_2	0.9995	1.0107	Majors
K	0.9939	0.9292	Trace	V	0.9990	0.9787	Trace
K_2O	0.9994	0.9664	Majors	Y	0.9681	1.0176	Trace
La	0.9878	0.9529	Trace	Zn	0.9975	0.9887	Trace
Li	0.9763	1.0234	Trace	Zr	0.1063	0.1376	Trace
Mg	0.9962	0.9170	Trace	Zr	0.9988	1.0394	Majors
MgO	0.9992	0.9965	Majors				

elements determined. At present, the laboratory is fully automated for the analysis and digital collection of data from both ICP-ES and AAS. The result of these changes over the years has been a six-fold improvement in productivity, and a broadened suite of analytical services that the lab provides to the geoscientists of the Geological Survey, while still maintaining the commitment to high accuracy and precision of all analysis performed.

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