APPENDIX E

QUALITY CHECK OF THE TRACE ELEMENT ANALYSIS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) AT THE UNION COLLEGE GEOLOGY DEPARTMENT, SCHENECTADY, NY.

E.1 Introduction

In addition to the very good accuracy and precision of inductively coupled plasma mass spectrometry (ICP-MS) for trace element analysis, the detection limits are very low and are not easily matched by other analytical techniques (e.g., Longerich et al., 1990). ICP-MS is a suitable technique for the accurate measurement of low levels of incompatible elements in rock samples collected for this study. Yet, how capable is the ICP-MS, a VG PlasmaQuad2+, at the Union College Geology Department? The accuracy and precision of the ICP-MS as well as the sample preparation method by acid digestion have been tested and evaluated. Following the procedure for acid digestion routinely used at Union College, problems with Ta and Nb staying in solution became apparent. A modification of the routine procedure, adding 50 µl of 50% hydrofluoric acid to 15 ml analytical solutions, was found to be essential to stabilize Ta and Nb in solution.

ICP-MS results are only as good as sample preparation, i.e. the completeness of sample dissolution. Some of the analyzed rare earth and trace elements are partitioned into resistant minerals which are hard to dissolve by acid digestion, and can most easily be brought into solution using a fusion technique prior to dissolution. Hard to dissolve minerals include zircon, rutile, tourmaline, staurolite, and chromite. The fusion step is generally unnecessary for mafic subalkaline igneous rocks, because chemically resistant minerals such as zircon are not in equilibrium with subalkaline rocks of basaltic and andesitic composition. All of the collected basaltic and andesitic samples could be completely digested by a mixed acid attack in screw-top Teflon® vials using conventional heating. Samples that might contain well-crystallized zircon and other refractory minerals were sent off for analysis at Washington State University Geoanalytic Laboratory. This laboratory routinely decomposes samples with a lithium borate fusion attack.

The quality of trace element data obtained by ICP-MS is evaluated in this chapter. Precision and accuracy of the determination of 28 trace elements is presented and discussed as well as data that show the effectiveness of adding hydrofluoric acid as a complexing agent to the analytical solutions to stabilize Ta and Nb in solution. Evidence for incomplete dissolution using acid digestion has not been found; however, the possibility is discussed.

E.2 Sample preparation

E.2.1 Internal standards

Internal standards, which are added to all solutions for interference and drift correction (section E.3.2 and E.3.3), are prepared by mixing Spex® 1000 μg ml^{-1} single-element solutions and diluting to yield the desired element concentrations. To a 100 ml volumetric flask, 5 ml each of the Spex single-element solutions (1000 ± 2 μg ml^{-1}) of In, Re, and Bi and 15 ml of Ga were added with a high-precision pipette (pipette error is less than ± 2%). Then, 8 ml of high purity HNO_3 was added and the flask filled to volume with de-ionized H_2O. The concentration of Ga in the internal standard solution is 150 ± 3 μg ml^{-1} and of In, Re, and Bi 50 ± 1 μg ml^{-1}. The HNO_3 concentration is about 6%. This internal standard solution is enough for up to 650 samples.

E.2.2 Acid digestion procedure

Acid digestion has several advantages over flux fusion methods: it is less time consuming, it involves fewer steps reducing the risk of contamination, and analytical solutions have higher concentrations in the sample solution allowing better analytical precision and shorter run time. To keep the contamination at a minimum, only high purity (double distilled) acids and de-ionized H_2O were used. Disadvantages of acid digestion are: extremely hazardous hydrofluoric acid are used, and a number of chemically resistant minerals may not completely dissolve, especially zircon and rutile, but possibly also tourmaline, staurolite, and chromite.

E.2.1.1 Weighing and dissolution procedure

17 ml Teflon screw-top vials were cleaned by soaking the open vials and screw-top caps for several hours in boiling 20% HNO_3. Then, the Teflon vials were rinsed with de-ionized H_2O, filled with 9 ml high purity HF and capped. After about ten minutes, the Teflon vials (half-filled with HF) were turned over and left to soak for another ten minutes standing on the caps. Finally, the acid was discarded and the Teflon vials and caps were rinsed with de-ionized H_2O and placed in an oven to dry.

The following dissolution procedure was applied to prepare sample, standard and blank solutions for each analytical run. Blank solutions do not contain any dissolved solids; therefore, step (1) of the following was omitted preparing the acid blanks. The steps were as follows:

(1) 0.1000 ± 0.0002 g of rock powder was weighed in a clean Teflon vial. As illustrated in figure E.1, duplicates of standards and samples were prepared (i.e., 0.1g of sample powder were weighed in each of two Teflon vials per sample). Any sample dust adhering to the weighing paper could affect the accuracy of the weighing procedure. It was, therefore, necessary to pre-contaminate the weighing paper with the rock powder being weighed. Furthermore, the rim of the Teflon vials must be cleaned from any rock dust to avoid damage of the rim when the vials are capped. The cleaning of the rims also ensures that the caps seal properly.

(2) 0.5 ml of HNO_3 and 1.5 ml of HF were added to the rock powders in the Teflon vials. Five empty Teflon vials were also filled with 0.5 ml of HNO_3 and 1.5 ml of HF: these are the blanks (figure E1). All Teflon vials were capped, clamped into aluminum retainers and heated in an oven at 100°°C overnight. Even though the aluminum retainers ensure that the Teflon vials remain sealed when the pressure inside the vials rises, the oven must be under an exhaust hood in case any vapor escapes. Fast reacting silicates and glass are decomposed in this step. Further dissolution of hard to dissolve minerals are made in the following steps.

(3) Samples, standards and blanks were dried by placing the uncapped Teflon vials in a large Teflon bowl in which filtered hot air (~100°C) was pumped. Ventilation occurred through a conduit in the lid of the Teflon bowl. The evaporation apparatus was mounted beneath the exhaust hood.

(4) 0.5 ml of HNO_3 and 1.5 ml of HF were again added to the Teflon vials. Then, the Teflon vials were capped, clamped into aluminum retainers, and heated in an oven at 120°C overnight.

(5) Samples, standards and blanks were taken to dryness using the evaporation apparatus mounted in the hood (same as step 3)

(6) 1 ml of HNO_3 and 1 ml of de-ionized H_2O were added. The Teflon vials were capped, clamped into aluminum retainers, and heated in an oven at 100°C overnight.

(7) Samples, standards and blanks were again dried (same as step 3). During the last evaporation step, most fluoride escapes as HF and very little (or no) HF is retained. It is not desirable to dispel the complexing agent HF completely after the dissolution of aluminosilicate materials if Nb and Ta are to be kept in solution (Goguel, 1992). Because HF is almost completely driven out through step (7), it is necessary to add a certain amount of HF later (discussed in detail in sections 5.7.1.6 and 5.7.2.6).

(8) 2.1 ml HNO_3, 12.7 ml de-ionized H_2O, and 0.15 ml of the internal standard solution were added using high precision automatic pipettes. Teflon vials were capped, clamped into aluminum retainers, and heated in an oven at 100°C. After about two hours, the Teflon vials were taken out of the oven, shaken, then placed back in the oven and heated overnight.

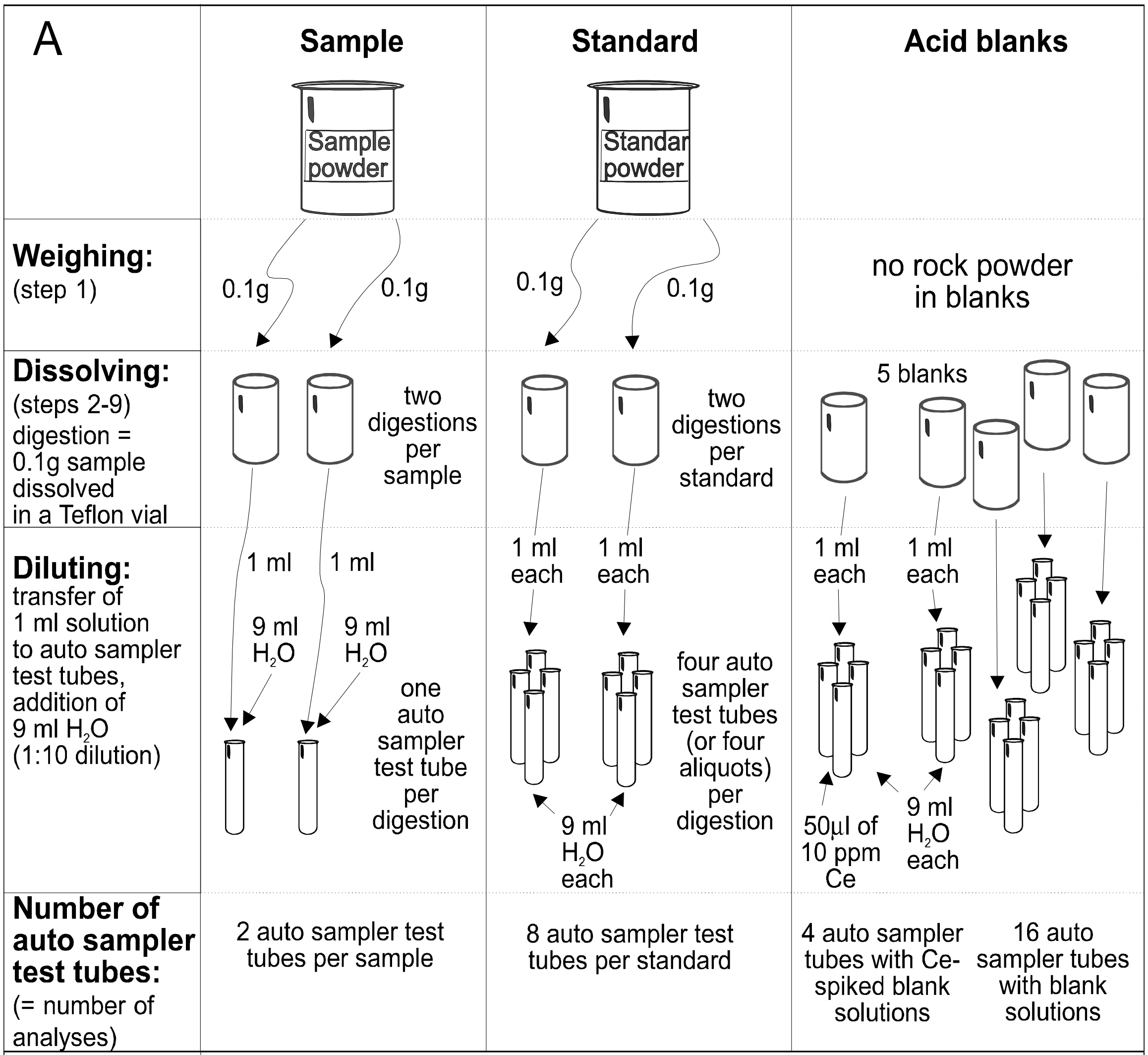
(9) All solutions were visually inspected for the completeness of dissolution. Precipitates or undissolved residue were not visually observed in any of the prepared solutions. Then, 0.05 ml of 50% HF was added to the solution in the Teflon vials.

Because 15 ml of solution was obtained by digesting 0.1g of rock powder in a screw-top Teflon vial (figure E.1a), the solution in the Teflon vial had a rock/solution proportion of 1:150 (except for the blanks which contained no dissolved solids). The final HNO_3 concentration was about 10% and HF concentration about 0.17%.

Figure E.1

a. Illustration of the main steps of the preparation of samples, standards and blanks. The term “a digestion of a sample” is defined as weighing of 0.1g of rock powder in a Teflon vial and dissolving the rock powder to obtain 15 ml of solution (rock solution ratio 1:150). Typically, samples and standards are prepared in duplicates (two digestions per sample or standard) and the blanks in quintuplets. Then, the solutions in the Teflon vials are transferred to the auto sampler test tubes and diluted, and as many aliquots as necessary are prepared.

b. Illustration of the sequence of the analysis. The aliquots of blanks and standards are arranged in four groups so that none of the aliquots in one group are from the same blank or the same digestion of a standard. All unknown samples are evenly distributed between the four groups of standards and blanks.



B

Sequence of test tubes in auto sampler:

For the analysis, the auto sampler test tubes should be arranged in the auto sampler tray as follows:

1. group of blanks and standards
Unknowns
*
*
Unknowns
2. group of blanks and standards
Unknowns
*
*
Unknowns
3. group of blanks and standards
Unknowns
*
*
Unknowns
4. group of blanks and standards
(end of analytical run)

arrangement of a group of blanks and standards

- Ce-spiked blank 1
- Blank 2
- Blank 3
- Blank 4
- Blank 5
- NIST-278
- NIST-278
- NIST-688
- NIST-688
- BCR-1
- BCR-1

E.2.1.2 Dilution procedure

The solutions in the Teflon vials were diluted prior to analysis by ICP-MS (figure E.1). 1 ml of solution was taken from the Teflon vials using a high-precision pipette and transferred to polypropylene auto sampler test tubes. Then, 9 ml of de-ionized H_2O was added using a high-precision pipette. The auto sampler test tubes were capped and shaken to homogenize the solutions. The analytical solution contained a rock/solution proportion of about 1:1500 (except for the blanks), an HNO_3 concentration of about 1%, and an HF concentration of about 0.017%. All sample and standard solutions should be transferred to the auto sampler tubes shortly before the analytical run because Ta and Nb may be lost in the dilute solutions when the solutions are stored for long periods of time in polypropylene.

E.3 ICP-MS instrument operation

E.3.1 Instrumentation

The results of the trace element analysis presented in this study were acquired with one single routine-procedure covering the complete element suite. The analyses were performed at the Union College Geology Department, Schenectady, NY, using a VG PlasmaQuad2+ ICP-MS instrument equipped with a VG multi-channel-analyzer. Kurt Hollocher is gratefully acknowledged for the set-up and operation of the ICP-MS instrument. The analyses were performed using a RF power of 1350 W, argon flow rates of 13 l min.$^{-1}$ (cooling), 0.6 l min.$^{-1}$ (auxiliary), and 0.78 l min.$^{-1}$ (nebulizer). For automatic sampling, an auto sampler was used. Liquid sample flow rates were controlled with a peristaltic pump, with a sample flow at 0.8 ml min.$^{-1}$. The glass Meinhard concentric nebulizer in a glass spray chamber was cooled to 15C. The scan range, skipped mass regions, dwell times, and the selected isotopes are listed in table E1. The detector of the ICP-MS instrument was always run in pulse counting mode.

Table E1: Plasmaquad element menu for analytical runs

Mass Range:	49.94 to 236.75 a.m.u.
Number of Channels:	2048
Number of Scan Sweeps:	100
Dwell Time (μs):	320
Points per Peak:	5
DAC Step between Points:	5
Number of Peak Jump Sweeps:	100
Collector type:	Pulse

Skipped mass regions:

PULSE COUNTING		ANALOG	
From	To	From	To
12.50	24.00	12.00	23.50
27.50	41.50	27.50	41.50
79.50	80.50	79.50	80.50

Analyzed elements/isotopes:

Elements selected	Symbol	Selected isotope	Peak Jump Dwell	Collector
Vanadium	V	51	2560	Pulse
Chromium	Cr	53	5120	Pulse
Gallium	Ga	71	1280	Pulse
Rubidium	Rb	85	10240	Pulse
Strontium	Sr	86	5120	Pulse
Yttrium	Y	89	5120	Pulse
Zirconium	Zr	90	2560	Pulse
Niobium	Nb	93	10240	Pulse
Indium	In	115	1280	Pulse
Cesium	Cs	133	20480	Pulse
Barium	Ba	137	5120	Pulse
Lanthanum	La	39	5120	Pulse
Cerium	Ce	140	2560	Pulse
Praseodymium	Pr	141	5120	Pulse
Neodymium	Nd	146	10240	Pulse
Europium	Eu	151	40960	Pulse
Samarium	Sm	152	10240	Pulse
Gadolinium	Gd	158	10240	Pulse
Terbium	Tb	159	20480	Pulse
Dysprosium	Dy	163	10240	Pulse
Holmium	Ho	165	10240	Pulse
Erbium	Er	166	10240	Pulse
Thulium	Tm	169	20480	Pulse
Ytterbium	Yb	174	10240	Pulse
Lutetium	Lu	175	20480	Pulse
Hafnium	Hf	178	10240	Pulse
Tantalum	Ta	181	10240	Pulse
Rhenium	Re	185	1280	Pulse
Lead	Pb	206	5120	Pulse
Lead	Pb	207	5120	Pulse
Lead	Pb	208	5120	Pulse
Bismuth	Bi	209	1280	Pulse
Thorium	Th	232	5120	Pulse
Uranium	U	238	10240	Pulse

E.3.2 Drift

The sensitivity for any element can and does vary with time, as a result of changes in instrument parameters (Riddle et al, 1988). Generally, there is a loss of sensitivity with time, but increase and sudden jumps were observed as well, especially at the beginning of a run. Also, the sensitivity changes across the mass spectrum: larger changes of the sensitivity have been observed for lighter elements than for heavier.

The changes of the sensitivity with time as well as the mass-dependent signal drift was monitored by analyzing the selected internal standard elements Ga, In, Re, and Bi in all sample, blank, and standard solutions. The effectiveness of internal standardization to correct for mass and time dependent signal drift has repeatedly been demonstrated using various internal standard elements (e.g., Doherty, 1989). The best internal standardization is achieved when internal standard elements satisfy four requirements. First, they have to be in low and/or constant concentration in the samples. Second, internal standard elements have to be stable in dilute acid solutions. Third, oxides or doubly charged ions of internal standard elements must not interfere with analyzed elements. Fourth, the ionization potential of the internal standard elements should be closely matched to that of the analyzed elements. These requirements were met with the selected internal standard elements in the analytical runs.

E.3.3 Interference

There are a variety of potential mass spectral interfernces possible, including isobaric (e.g., ^{144}Nd on ^{144}Sm), doubly charged ions (e.g., ^{138}Ba on ^{69}Ga), oxides (e.g., ^{135}Ba^{16}O on ^{151}Eu), hydrides (e.g., ^{85}RbH on ^{86}Sr), and fluorides (e.g., ^{138}Ba^{19}F on ^{157}Gd). Of these, oxide interferences are a significant problem for REE, Ta and Hf analysis (e.g., Jenner et al., 1990; Young-Sang et al., 1990).

In order to correct for these interferences, Ce was analyzed at mass 140 and Gd at mass 158. With the analysis of the Ce-spiked blanks, the production rate of ^{142}Ce^{16}O^{+} at mass 158 can be monitored throughout the run. The ratio ^{142}Ce^{16}O / ^{140}Ce served as a monitor of the production of all Ba oxides (BaO^{+}) and rare earths oxides (REO^{+}). The computer program VGFIX2, which was used to convert measured peak intensities to elemental concentrations, contains an empirical table of ratios of BaO^{+} and REO^{+} interferences on Ta, Hf, and the REE normalized to the ^{142}Ce^{16}O^{+} oxide. This table, however, does not contain a complete list of normalized ratios of all possible oxide interferences on all isotopes of Ta, Hf, and the REE. Therefore, the isotope masses of the REE, Ta and Hf listed in table E1 must be analyzed, so that interference corrections can be made using the correction factors contained in the VGFIX2 program.

E.4 Calibration

E.4.1 Sequence of analysis

The blanks, standards and samples must be analyzed in a certain sequence (figure E.1), in order that measured peak intensities can be accurately converted to elemental concentrations and that necessary drift and interference corrections can be made. The blanks and standards must always be in groups. Special solutions to monitor interferences, such as Ce-spiked blanks, must be included among the other acid blanks. If there are two sets of standards and blanks; they must be at the beginning and end of each run with all unknowns in between. If there are more than two sets of standards and blanks, one set must be at the beginning, one at the end and the others evenly spaced between approximately equal numbers of unknowns. Typically, four groups of standards and blanks were analyzed with unknown samples evenly distributed between these groups (figure E.1).

E.4.2 Standards

Three standards were used for the calibration of all analytical runs. The standards are BCR-1, NIST-278 and NIST-688. As described in section E.2.2, the standard solutions were prepared by acid digestion along with the samples and blanks. For each analytical run, two digestions of each of the standards were prepared and four aliquots of each digestion analyzed (figure E1).

The elemental concentrations of BCR-1, NIST-278 and NIST-688 are listed in tables E2, E3 and E4, respectively. For the calibration of the analytical runs, the recommended standard values of Govindaraju (1994) were adopted for BCR-1, whereas for NIST-278 and NIST-688, the in-house standard values (K. Hollocher, personal communication 1995) were used.

Table E2: Standard values of BCR-1

				BCR-1 analyzed as unknown using NIST-278 and NIST-688 as standards	
Element	recom-mended values [1]	ID-SSMS (n=10) [2]	method preferred values* [3]	Element	ICP-MS (n=32) [this study]
V	407	-	-	V	403
Cr	16	-	-	Cr	13.1
Rb	47.2	46.7	46.8	Rb	47.3
Sr	330	327	331	Sr	333
Y	38	37.9	36.8	Y	35.5
Zr	190	186	195	Zr	185
Nb	14	13.8	13.5	Nb	15.0
Cs	0.96	0.91	0.96	Cs	0.96
Ba	681	653	676	Ba	694
La	24.9	24.7	25.03	La	25.6
Ce	53.7	54	53.6	Ce	53.4
Pr	6.80	6.79	-	Pr	6.84
Nd	28.8	29.1	28.8	Nd	29.6
Sm	6.59	6.63	6.60	Sm	6.53
Eu	1.95	1.96	1.97	Eu	1.97
Gd	6.68	6.56	6.68	Gd	6.73
Tb	1.05	1.07	-	Tb	1.04
Dy	6.34	6.35	6.57	Dy	6.30
Ho	1.26	1.24	-	Ho	1.27
Er	3.63	3.77	3.64	Er	3.52
Tm	0.56	0.62	-	Tm	0.52
Yb	3.38	3.43	3.37	Yb	3.30
Lu	0.51	0.53	0.5	Lu	0.55
Hf	4.95	4.9	-	Hf	5.01
Ta	0.81	-	-	Ta	0.78
Pb	13.6	15.9	-	Pb	14.3
Th	5.98	6.02	6.02	Th	6.08
U	1.75	1.73	1.73	U	1.72

* Cs, Rb, Ba, and REE determined by ID-TIMS
U and Th determined by ID-SSMS
Nb, Zr, and Y determined by SSMS

[1] Govindaraju (1994), data underlined are recommended values; other values are proposed

[2] Jochum et al (1988)

[3] Jenner et al (1990)

Table E3: Standard values of NIST-278

Element	preferred in-house standard values	recom-mended values [1]	UA SSC-method ICP-MS [2]	error 1σ	UC SA-method ICP-MS [2]	error 1σ	ITNA/ XRF [3]	error 1σ	consensus values [4]	error 1σ
V	9	9	-	-	-	-	16	2	15	8
Cr	6.6	6.1	-	-	-	-	7.3	0.7	6.4	0.9
Rb	130	127.5	121	2	-	-	133	6	133	6
Sr	63.5	63.5	60	2	-	-	74	8	64	5
Y	39	39	35	1	-	-	42	4	39	5
Zr	290	290	276	9	-	-	338	30	290	30
Nb	21	18	22	4	-	-	22	2	18	5
Cs	5.2	5.5	5.3	0.2	-	-	5.2	0.3	5.2	0.2
Ba	947	1140	904	21	896	19	1000	90	970	60
La	31.3	32	30	1	31	2	31.9	1.7	32	2
Ce	61.8	62.2	65	2	61	2	68	3	60	6
Pr	7.2	7.2	-	-	7	0.2	-	-	7.0	1.3
Nd	28	30	27	1	26	1	33	3	30	3
Sm	5.6	5.7	5.6	0.3	5.6	0.1	4.73	0.22	5.9	0.5
Eu	0.78	0.84	0.67	0.07	0.8	0.04	0.74	0.04	0.78	0.03
Gd	5.7	5.3	5.7	0.1	5.8	0.1	-	-	5.5	0.4
Tb	0.97	1.0	1.01	0.04	0.92	0.02	0.99	0.09	1.06	0.14
Dy	6.2	6.3	-		6	0.1	6.1	0.5	6.3	0.4
Ho	1.33	1.26	1.31	0.04	1.29	0.02	-	-	1.26	0.17
Er	3.95	3.8	4.1	0.1	4.1	0.1	-	-	3.8	0.5
Tm	0.64	0.41	0.63	0.03	0.64	0.02	-	-	0.41	0.15
Yb	4.45	4.5	4.31	0.03	4.4	0.1	5.3	0.3	4.6	0.6
Lu	0.74	0.73	0.64	0.2	0.66	0.02	0.74	0.04	0.77	0.12
Hf	8.1	8.4	7.7	0.1	-	-	8.2	0.5	8.5	0.4
Ta	1.29	1.2	1.5	0.1	-	-	1.42	0.11	1.29	0.08
Pb	16.4	16.4	17.2	1	-	-	-	-	14	6
Th	12.6	12.4	12.1	0.8	-	-	12.8	0.5	12.6	0.6
U	4.55	4.58	4.7	0.3	-	-	4.89	0.18	4.55	0.18

[1] Govindaraju (1994); data underlined are recommended values, other values are proposed

[2] Hollocher (1993) UA ... University of Arizona UC ... Union College
SSC ... Standard solution comparisorSA ... Standard addition

[3] Bower et al. (1992)

[4] Gladney et al. (1987, supplement 1 issued in 1993)

Table E4: Standard values of NIST-688

Element	preferred in-house standard values	recom-mended values [1]	UA SSC-method ICP-MS [2]	error 1 σ	UC SA-method ICP-MS [2]	error 1 σ	ITNA/ XRF [3]	error 1 σ	consensus values [4]	error 1 σ
V	238	250	240	3	-	-	228	9	238	7
Cr	321	332	298	6	-	-	315	18	332	9
Rb	1.91	1.91	1.9	0.1	-	-	10	4	5	4
Sr	169	169.2	162	5	-	-	166	8	169	3
Y	18	19	16.9	0.4	-	-	8	6	19	3
Zr	59	59	49	0.1	-	-	62	6	59	3
Nb	5.6	5.7	-	-	5.2	0.05	7	2	5.7	1.2
Cs	0.26	0.26	-	-	-	-	<1.5	-	-	-
Ba	198	200	175	7	165	4	220	100	198	14
La	5.15	5.3	4.9	0.5	5.1	0.6	5	0.3	5.3	0.5
Ce	12.55	13.3	12	1	10.1	0.3	13.1	0.6	12.5	1.4
Pr	1.78	2.0	-	-	1.58	0.04	-	-	2.0	0.3
Nd	8.3	8.9	8.4	1.2	8	0.2	<35		8.9	1
Sm	2.4	2.79	2.17	0.01	2.3	0.1	2.2	0.1	2.4	2
Eu	0.98	1.07	0.89	0.02	0.94	0.03	0.85	0.04	1.00	0.06
Gd	2.9	3.2	2.9	0.3	2.6	0.1	-	-	3.2	0.4
Tb	0.50	0.45	0.46	0.02	0.47	0.01	0.36	0.09	0.52	0.04
Dy	3.25	3.3	-	-	3.1	0.1	3.2	0.4	3.3	0.4
Ho	0.70	0.75	0.66	0	0.72	0.02	-	-	0.75	0.1
Er	1.99	2.09	1.9	0.1	2.04	0.04	-	-	2.09	0.2
Tm	0.31	0.31	0.27	0.04	0.31	0.01	-	-	0.30	0.05
Yb	2.00	2.09	1.9	0.1	2.00	0.04	2.1	0.3	2.03	0.16
Lu	0.31	0.34	0.26	0.01	0.31	0.01	0.33	0.02	0.33	0.03
Hf	1.55	1.6	1.4	0.1	-	-	1.46	0.1	1.55	0.1
Ta	0.31	0.31	-	-	-	-	0.28	0.12	0.31	0.07
Pb	3.6	3.3	3.16	0.05	-	-	-	-	4.6	-
Th	0.32	0.33	-	-	-	-	0.28	0.08	0.33	0.02
U	0.32	0.37	-	-	-	-	0.32	0.06	0.31	0.02

[1] Govindaraju (1994); data underlined are recommended values, other values are proposed

[2] Hollocher et al. (1995) UA ... University of Arizona UC ... Union College
SSC ... Standard solution comparison SA ... Standard addition

[3] Bower et al. (1992)

[4] Gladney et al. (1987, supplement 1 issued in 1993)

In addition to the recommended standard values of BCR-1, two sets of values are listed in table E2 for comparison. The elemental concentrations determined by isotope-dilution spark-source mass spectrometry (ID-SSMS) represent the mean of ten independent measurements performed at the Max-Planck-Institut, Germany (Jochum et al., 1988). The method preferred values were compiled by Jenner et al. (1990): Cs, Rb, Ba, and the REE were determined by isotope-dilution thermal-ionization mass spectrometry (ID-TIMS) and Nb, Zr, and Y by spark-source mass spectrometry (SSMS). There is excellent agreement between the recommended standard values and the values determined by these highly accurate techniques. This clearly indicates that BCR-1 is a well-characterized standard.

The in-house standard values of NIST-278 and NIST-688 are listed in tables E3 and E4, respectively, and can be compared with five published sets of elemental concentrations arranged in the tables. The agreement between the in-house standard values and the other five sets of values is good, generally within indicated errors of the analytical techniques, or within the errors given for the compilation. Furthermore, there is very good evidence that the in-house standard values are very accurate: BCR-1 was analyzed in this study as unknown sample using NIST-278 and NIST-688 as standards for the calibration, and the recommended standard values of BCR-1 were accurately reproduced (table E2).

E.4.3 Blanks

As described in section E2.2, the blanks were prepared in five different Teflon vials for each analytical run together with the samples and standards. The blanks are dilute acid solutions which contain no dissolved solids except for the internal standard elements Ga, In, Re, and Bi. As illustrated in figure E1, four aliquots were taken from each of the five blanks and diluted. Then, four aliquots of one blank were spiked with 50 μl of 0.01 μg/ml Ce single-element solution.

The analysis of acid blanks is important for several reasons. First, the calibration curves are generated by calculating a regression line between the measured peak intensities and known concentrations of the standards plus the blanks (the “known” concentrations of the blanks are assumed to be zero). A “zero-intercept” model is used for the linear regression; accordingly, the measured peak intensities of the blanks are subtracted from the data (the blank level is so low that its subtraction from the data results in no significant change in the peak intensities). Second, the detection limits are determined from the analysis of the blanks. And third, possible contamination during sample preparation can be detected (unusually high blank levels would indicate that the blanks contain some amounts of dissolved solids). Contamination was not found to be a problem in all analytical runs performed at Union College. Only occasionally were blank solutions contaminated with Pb and very rarely with Rb.

E.5 Calculation of concentrations

The measured peak intensities were converted to elemental concentrations using VGFIX2, a computer program written by Kurt Hollocher, Union College, Schenectady, NY. This program was written in Turbo Pascal v. 6.0 and compiled for IBM-type personal computers running the DOS operating system, with or without a numeric coprocessor.

Prior to inputting data into the VGFIX2 program, the obtained peak intensities were read into spread-sheet format and arranged in the order in which the blanks, standards and samples were analyzed (see section E.4.1). The details on how to arrange the data table so it can be read by the VGFIX2 program are described in the unpublished program manual. For example, the type of analyzed solution, whether it is a blank, Ce-spiked blank, standard or unknown sample must be specified in the data table before the VGFIX2 program is put to use. The rows containing the elemental concentrations of the standards must be entered (in ppm) in the data table as well.

Two data tables per analytical run were arranged as outlined above. Both data tables contain the same measured peak intensities of the same analytical run. However, there are differences between the two tables. The information entered in the first data table tells VGFIX2 that BCR-1 is a unknown sample and NIST-278 and NIST-688 are the standards. The second data table is arranged so that NIST-278 and NIST-688 as well as BCR-1 are recognized as standards. Then, VGFIX2 was used to convert the peak intensities to elemental concentrations. The elemental concentrations of BCR-1 (treated as unknown sample) were calculated using NIST-278 and NIST-688 as standards. Then, the elemental concentrations of all other analyzed samples were calculated using NIST-278, NIST-688 and BCR-1 as standards.

The calculations performed by the VGFIX2 program are described in more detail in its program manual. Basically, linear calibration curves were calculated using the blank-subtracted peak intensities and known concentrations of standards and blanks. The unknown concentrations were calculated by comparing the blank-subtracted peak intensities of the samples to the (best-fit) calibration curves. Corrections were made by the program for internal standard drift, blank drift, calibration drift and interferences of BaO^+ and REO^+ on Hf, Ta and the REE.

The VGFIX2 program also calculated the “blank residuals”. In essence, the measured peak intensities of the blanks were compared to the calibration curves (similar to the calculation of concentrations of the unknown samples) deriving “concentrations” of the blanks given in “ppm”. These “concentrations" represent the blank residuals. The blank residuals calculated in this manner also indicate whether the calibration curves intercept the origin in plots of peak intensities vs. concentrations (mean of blank residuals ≅ 0) or intercept the y-axis at notable positive or negative values (mean of blank residuals < 0, or mean of blank residuals > 0). For instance, the absolute mean of the blank residuals of V, Cr, Zr and Ba typically indicate values between 0.5 ppm and 3 ppm. The absolute mean of the blank residuals calculated for all other elements is very close to zero.

E.6 Evaluation of data

E.6.1 Determination of detection limits

Limits of detection (LOD) are used as a measure of instrument performance. The ICP-MS instrument does not have a fixed LOD and must be calculated for each individual run with the formula:

$$LOD = \left|\overline{X}\right| + 3 \bullet \sigma \qquad (1)$$

The limits of detection are given in ppm. $\left|\overline{X}\right|$ is the absolute mean and σ the standard deviation of twelve blank residuals. As mentioned in section E.5, the elements V, Cr, Zr and Ba indicated generally higher absolute means (0.5-3 ppm) of the blank residuals than any other element (≅ 0 ppm). Consequently, the detection limits of V, Cr, Zr and Ba are relatively higher than those for all other elements.

The detection limits of the ICP-MS instrument, as determined in this study, are generally well below chondrite level, and for most elements several orders of magnitude lower than element concentrations in the samples. The detection limits, calculated for each individual run, are listed in tables E6, E8, E9, E10, E11 and E12.

E.6.2 Determination of precision

In geochemical analyses, it is common practice to run a series of determinations, or replicates, on a single sample to determine the precision of the analytical technique. The most frequently measure adopted to express the spread or dispersion about the mean is the *standard deviation* denoted by the Greek letter σ:

$$\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}} \qquad (2)$$

$\overline{X}$ is the mean of **n** determinations with X_i being the value of *i*th measurement. A small σ indicates that the measurements are clustered tightly around the mean, indicating the multiple determinations were realized with "high" or "excellent" precision.

Furthermore, the standard deviation is commonly normalized and presented as the percentage of the respective mean value. This is called the relative standard deviation (RSD). The RSDs are calculated for each element using the formula:

$$RSD = (\sigma/\bar{X}) \bullet 100\% \qquad (3)$$

Then, the RSDs are plotted using bar diagrams to illustrate the precision of the analysis for each run (e.g., figure E2). The classification of the precision as "excellent", "good", "acceptable", and "poor" based on the %-RSD was arbitrarily chosen, although it is comparable to the precision of ICP-MS analysis discussed elsewhere (e.g., Jenner et al., 1990; Longerich et al., 1990; Holmes et al., 1995).

E.6.3 Determination of accuracy

E.6.3.1 Comparison with standards

In order to evaluate the accuracy of the ICP-MS analysis at Union College, two standards (BCR-1 and Pal-889) were analyzed as unknowns in each of the analytical runs. The accuracy is then assessed by comparing the determined values with the recommended standard values. However, no absolute values for the standard materials are available, only a consensus of the most likely values and, occasionally, values obtained by highly accurate techniques (e.g., ID-SSMS). Accordingly, an exact measurement of the accuracy cannot be made, and the accuracy must be determined with this deficiency in mind.

To facilitate the comparison, measured values are plotted against the standard values in bivariate diagrams having logarithmic scale on both axes (e.g., figures E3 and E4). Ideally, all points should plot close to or on the solid line with slope = 1. Generally, the accuracy of the analysis is considered "good" when the range of the multiple determinations is within ±10% of the corresponding standard values. To illustrate ±10% deviation from the line with slope = 1, two dashed lines are drawn on the diagrams. The upper line, limiting the dark gray field, is a line with slope of 1.1, the lower line, limiting the light gray field, is a line with slope of 0.9. Note that lines with different slopes plot parallel on diagrams having logarithmic scales on both axes.

The standard values compiled by Govindaraju (1994) were selected as the reference values to which the analyses of BCR-1 were compared (e.g., figure E2). The standard values of BCR-1 are listed in table E2. Cr and Nb standard values are not as well-established as the other values. Accordingly, Cr and Nb values are "proposed" instead of "recommended" (Govindaraju , 1994).

Pal-889 is an in-house standard used at Cornell University, Uthica, NY. It was sampled from the Palisade Sill at the same locality as the U.S.G.S. standard W-1 (Wirth, 1991). As shown in table E5, most standard values of W-1 agree well with the in-house standard values of Pal-889. However, some elements, such as Cr and Cs, indicate significant differences, confirming that Pal-889 and W-1 are actually two different rock samples. Nonetheless, both standards agree sufficiently well and the concentrations of the elements Y, Zr, Nb, Pr, Gd, Dy, Ho, Er and Tm determined in W-1 were used to complement the in-house standard values of Pal-889 (table E5). Accordingly, the reference values used in the comparative plots

Table E5: Standard values of Pal-889 and W-1

Element	**W-1** recommended values [1]	**W-1** ID-SSMS (n=7) [2]	**Pal-889** in-house standard values [3]
V	257	-	-
Cr	119	-	314
Rb	21.4	21.6	-
Sr	186	193	183
Y	26	22.6	-
Zr	99	98.6	-
Nb	9.9	7.91	-
Cs	0.96	0.9	2.19
Ba	162	162	185
La	11	10.9	10.52
Ce	23.5	24	23.6
Pr	3.2	3.27	-
Nd	14.6	14.4	13
Sm	3.68	3.65	3.42
Eu	1.12	1.14	1.07
Gd	4.01	4.24	-
Tb	0.63	0.65	0.67
Dy	3.99	4.18	-
Ho	0.81	0.8	-
Er	2.3	2.25	-
Tm	0.34	0.33	-
Yb	2.03	2.17	2.18
Lu	0.32	0.34	0.3
Hf	2.5	2.68	2.56
Ta	0.48	-	0.63
Pb	7.5	7.83	-
Th	2.4	2.65	2.07
U	0.57	0.61	0.5

[1] Govindaraju (1994); data underlined are recommended values, other values are proposed

[2] Jochum et al. (1988)

[3] Wirth (1991)

(e.g., figure E4) are a blending of the in-house standard values of Pal-889 and elemental concentrations of W-1 determined by ID-SSMS (Jochum et al, 1988). The elemental concentrations determined by ID-SSMS are preferred over the recommended standard values of Govindaraju (1994), because there are indications of bias in the compilation of the standard values (e.g. Jochum et al, 1988; Jenner et al, 1990). For instance, the Y concentration in W-1, determined by ID-SSMS, is 22.6 ppm (table E5), whereas the recommended standard value is notably higher (Y = 26 ppm). The discrepancy in the Nb concentrations could be due to bias in the compilation of the standard values as well. Nevertheless, all other values determined by ID-SSMS agree well with the recommended standard values of W-1 (Govindaraju, 1994).

The agreement, or disagreement, between recommended standard values of W-1 and the ID-SSMS data may be considered as an "accuracy gauge". ID-SSMS is one of the most accurate methods of trace element analysis (Jochum et al, 1988), and the mean of seven independent analyses of W-1 agree within 2% to 10% of the recommended standard values of Govindaraju (1994), except for Y and Nb.

E.6.3.2 Inter-laboratory comparison

The comparison of results obtained at different analytical laboratories -- "inter-laboratory comparison" -- is another method to evaluate the accuracy of the analysis by ICP-MS. Accordingly, several samples analyzed at various laboratories were re-analyzed at Union College, and the different sets of data were compared. Similar to the comparison with standard values, the same type of bivariate diagrams are used for the inter-laboratory comparison (e.g., figures E5 and E6).

E.7 Test runs

E.7.1 First test run, 06/12/1995, synthetic standard used

E.7.1.1 Strategy and methods

Prior to analyzing any samples collected from the Snow Camp terrane, SW Oregon, the accuracy and precision of the analysis by ICP-MS were evaluated by analyzing three reference materials: BCR-1, Cou-IL-6 and Pal-889. For the calibration of the analysis, several aliquots of a synthetic standard solutions were analyzed along with the sample and blank solutions.

Three digestions per reference material were prepared in order to assess the precision and accuracy of weighing of the sample (i.e. weighing three times 0.1000g ± 0.0002g per sample), pipetting, and diluting. Also, the completeness of dissolution and whether contamination is a problem or not can be evaluated by analyzing aliquots of three separate digestions per sample. The rock powders were dissolved following the acid digestion procedure routinely used at the Union College Geology Department (see section E2.2 for detail). This, however, means HF was not added at the end of the digestion procedure, a step that was later added to keep Ta and Nb in solution (see section E7.2.6). As always, five blanks were prepared along with the samples.

The completeness of dissolution of the sample can be independently verified by using a standard which is already available in dissolved form. If a rock standard were used and the dissolution of the aluminoslicates and other minerals (e.g., oxides) were incomplete, an identical problem dissolving the samples may not be detected. Hence, a synthetic standard solution was prepared by mixing accurately measured volumes of 1000 μg ml^{-1} Spex single-element solutions into a 150 ml volumetric flask. Then, 21 ml high purity HNO_3 and 1.5 ml of the internal standard solution were added and the flask filled to volume with de-ionized H_2O. The synthetic standard solution was prepared four days in advance of the analysis by ICP-MS.

The following number of aliquots of each of the sample, standard and blank solutions were transferred from the Teflon vials to a total of 39 polypropylene auto sampler test tubes, diluted and analyzed: two aliquots of three digestions per sample (n=6 per sample), six aliquots of the synthetic standard solution, and three aliquots of five blanks (n=15, three of which were spiked with Ce). All but three sample solutions (n=15) and all blank (n=15) and standard solutions (n=6) were transferred to 36 polypropylene auto sampler tubes three days in advance of the run. The remaining three auto sampler tubes were filled shortly before the analysis, each of which contained a different sample (i.e. BCR-1, Pal-889, and Cou-IL-6).

E.7.1.2 Limits of detection

The limits of detection calculated for the first test run are listed in table E6. Generally, the detection limits are at ppb levels or lower. The comparatively high detection limits of Rb and Pb could be due to very small amounts of contamination of the blanks. Three out of twelve analyzed blank solutions indicated perceptibly higher blank levels for Rb and Pb. However, this amount of contamination in the blanks is negligible and does not affect the determination of the element concentrations as long as the concentrations in analyzed samples are well above the determined limits of detection. Pb and Rb contamination have been reported from other laboratories and may cause poor precision analyzing Rb and Pb (e.g., Jenner et al., 1990). Pb and Rb are apparently more prone to contamination than any other analyzed element.

E.7.1.3 Precision

The mean values and standard deviation of the measured elemental concentrations are listed in table E6. For the purpose of the illustration of the precision, the relative standard deviations were calculated from the data in table E6 and plotted in figure E2. Excluding Ta, Nb, and Pb, the overall precision of the ICP-MS analysis is excellent as indicated by less than 3% relative standard deviation for most elements. However, Pal-889 indicates significantly higher (though still "good") relative standard deviation for Rb, Y, and the light REE than BCR-1 and Cou-IL-6 (figure E2). This must be due to fluctuations in the performance of the ICP-MS instrument during the analytical run, because significant differences between the three separate digestions of Pal-889 were not found (table E7). Furthermore, notable differences among any of the three separate digestions of any of the samples do not exist, suggesting all samples were completely digested and no errors were made during weighing of the samples and subsequent dissolution.

The element Pb has been determined with excellent precision in BCR-1 and Pal-889 (figure E2) whereas the determination of Pb in Cou-IL-6 indicates poor precision. Because contamination with Pb can occur very easily, it is reasonable to conclude that the poor precision of the analysis of Pb in Cou-IL-6 is caused by various amounts of Pb contamination of the sample solutions (table E7). Also, three of the blank solutions analyzed in the test run indicated some Pb contamination supporting this hypothesis.

Table E6: Results of first test run, 12/6/95, synthetic standard used

	Detection Limits	BCR-1		Pal-889		Cou-IL-6	
Element	in ppm	mean (n=6)	error 1 σ	mean (n=6)	error 1 σ	mean (n=6)	error 1 σ
V	-	n.d.	-	n.d.	-	n.d.	-
Cr	-	n.d.	-	n.d.	-	n.d.	-
Rb	0.156	46.91	0.78	30.3	1.4	13.04	0.10
Sr	-	n.d.	-	n.d.	-	n.d.	-
Y	0.031	36.51	0.51	22.0	1.1	39.8	0.3
Zr	-	n.d.	-	n.d.	-	n.d.	-
Nb	0.039	15.7*	2.0	9.71*	1.97	5.73*	0.14
Cs	0.0046	0.905	0.009	1.91	0.03	2.77	0.01
Ba	0.11	674.5	3.1	174.4	2.3	57.1	0.3
La	0.013	24.50	0.16	10.62	0.95	6.28	0.05
Ce	0.025	52.9	0.3	22.8	1.0	17.07	0.03
Pr	0.0072	6.82	0.04	3.02	0.09	2.73	0.02
Nd	0.016	28.4	0.3	13.0	0.4	14.0	0.1
Sm	0.0069	6.39	0.05	3.27	0.11	4.31	0.04
Eu	0.0018	1.98	0.02	1.12	0.04	1.44	0.01
Gd	0.0087	6.64	0.08	3.70	0.13	5.59	0.07
Tb	0.0016	1.06	0.01	0.624	0.018	0.996	0.016
Dy	0.0061	6.15	0.07	3.71	0.07	6.25	0.09
Ho	0.0020	1.28	0.01	0.779	0.012	1.37	0.02
Er	0.0063	3.61	0.03	2.18	0.03	3.96	0.06
Tm	0.00073	0.564	0.005	0.342	0.004	0.634	0.007
Yb	0.0075	3.36	0.03	2.03	0.02	3.80	0.04
Lu	0.00093	0.508	0.005	0.279	0.003	0.532	0.006
Hf	0.011	4.93	0.06	2.51	0.03	3.18	0.03
Ta	0.0043	3.21*	1.70	2.47*	1.39	0.83*	0.06
Pb	0.44	13.9	0.1	4.68	0.11	0.87 ×	0.30
Th	0.0017	5.96	0.05	2.04	0.01	0.523	0.009
U	0.00085	1.77	0.01	0.513	0.004	0.185	0.003

* Ta and Nb unstable in solution

× Pb contamination detected

n.d. not determined

standard deviation:

$$\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively

see tables 14, 15 and 16 for compilation of analytical results
for BCR-, Pal-889, and Cou-IL-6, respectively

Table E7: %-Difference between three digestions per sample, first test run, 12/6/95

0.1g of sample powder were weighed in each of three Teflon vials per sample and dissolved (= three digestions per sample).
Two aliquots of each digestion were prepared and analyzed, accordingly, listed values are the mean of two analyses.

Sample:	**BCR-1**				**Pal-889**				**Cou-IL-6**			
Digestion:	no.1	no.2	no.3	%Diff.	no.1	no.2	no.3	%Diff.	no.1	no.2	no.3	%Diff.
Rb	47.9	46.3	46.5	3.2%	30.8	30.0	30.3	2.7%	13.1	13.0	13.0	1.2%
Y	36.8	36.7	36.1	2.0%	22.6	21.7	21.6	4.6%	40.1	39.5	39.7	1.5%
Cs	0.91	0.90	0.91	0.8%	1.94	1.89	1.89	2.3%	2.77	2.76	2.77	0.4%
Ba	676	673	674	0.4%	177	173	173	1.9%	57.0	57.1	57.2	0.3%
La	24.3	24.6	24.6	1.1%	11.03	10.8	10.0	9.1%	6.31	6.26	6.27	0.7%
Ce	53.0	52.8	53.1	0.5%	23.3	22.8	22.2	4.6%	17.0	17.1	17.1	0.2%
Pr	6.81	6.83	6.82	0.4%	3.07	3.00	2.98	2.9%	2.74	2.72	2.74	0.8%
Nd	28.6	28.4	28.2	1.4%	13.2	12.9	12.9	2.5%	14.0	14.0	14.0	0.5%
Sm	6.43	6.39	6.36	1.1%	3.33	3.23	3.24	3.0%	4.34	4.32	4.26	1.8%
Eu	1.99	1.98	1.97	1.1%	1.14	1.11	1.11	2.8%	1.45	1.44	1.42	1.6%
Gd	6.70	6.62	6.58	1.8%	3.78	3.65	3.68	3.3%	5.65	5.62	5.52	2.3%
Tb	1.06	1.06	1.05	1.3%	0.64	0.62	0.61	3.4%	1.01	1.00	0.98	2.4%
Dy	6.19	6.14	6.12	1.1%	3.76	3.66	3.70	2.6%	6.27	6.26	6.22	0.9%
Ho	1.29	1.28	1.28	1.1%	0.79	0.77	0.78	3.0%	1.38	1.37	1.36	1.1%
Er	3.61	3.61	3.60	0.2%	2.20	2.16	2.17	1.8%	3.99	3.97	3.91	1.9%
Tm	0.56	0.57	0.56	1.1%	0.35	0.34	0.34	2.0%	0.64	0.63	0.63	1.0%
Yb	3.38	3.36	3.35	1.1%	2.05	2.02	2.01	1.8%	3.80	3.80	3.82	0.5%
Lu	0.51	0.51	0.51	1.0%	0.28	0.28	0.28	2.0%	0.53	0.53	0.53	1.1%
Hf	4.94	4.92	4.93	0.5%	2.52	2.48	2.53	2.0%	3.19	3.17	3.18	0.7%
Pb	14.01	13.78	13.78	1.6%	4.75	4.75	4.55	4.2%	0.90 ×	1.23 ×	0.49	60%
Th	5.92	5.94	6.02	1.8%	2.04	2.04	2.02	0.9%	0.52	0.51	0.53	4.0%
U	1.76	1.77	1.78	0.7%	0.51	0.51	0.52	0.9%	0.19	0.18	0.19	3.1%
			average	1.1%			average	2.9%	average without Pb-value			1.3%

calculation of the %-Difference between the minimum and maximum value: $\%Diff = \frac{(\text{max.- min.})}{\text{max.}} \bullet 100\%$

×Pb contamination detected

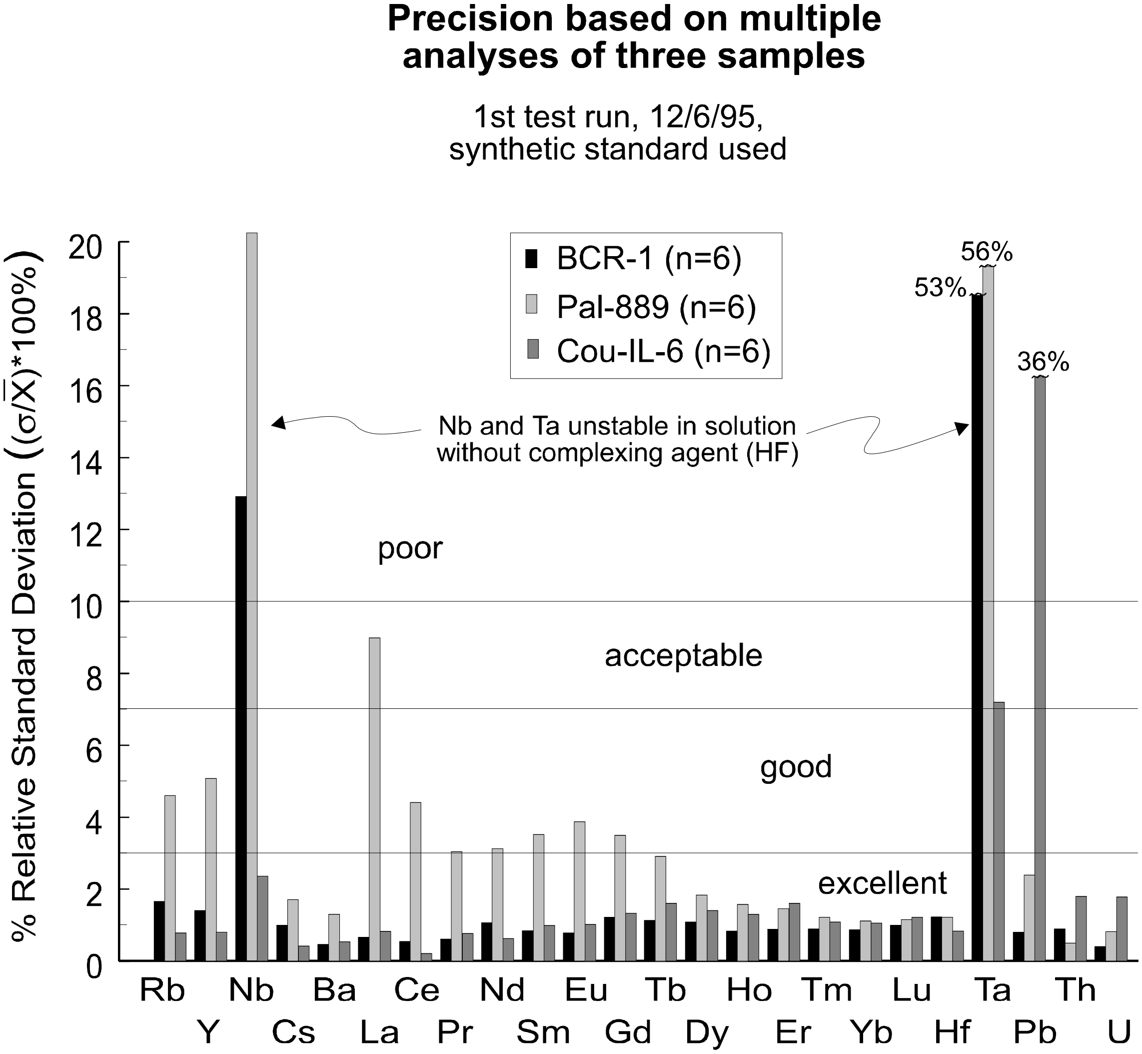


Figure E2

Diagram illustrating the precision of the analysis in the first test run. The analysis was performed by ICP-MS on two aliquots of three separate digestions per sample. Very low relative standard deviation indicate excellent precision of the determination of most elements. The poor precision of the determination of Ta and Nb is due to instability of these elements in solution (see text). Various amounts of Pb contamination were found in two of three digestions of Cou-IL-6, accordingly, large relative standard deviations were obtained (see table E6).

The poor precision of the analysis of Ta and Nb illustrated in figure E2 is interpreted as due to the instability of these elements in solution. This problem will be discussed below (section E7.1.6).

E.7.1.4 Accuracy

The elements Ta and Nb are excluded from the following discussion of the accuracy of the analysis, because Ta and Nb were apparently not stable in the analytical solutions and poor accuracy was the result. This problem was solved in the first analytical run and is discussed in more detail below (section E.7.1.6).

As illustrated in figure E3, very small differences between the measured and the recommended standard values of BCR-1 indicate that all trace elements were analyzed with very good accuracy. The results of the analysis of BCR-1 agree with the reference values within better than 5%.

The comparison of the analytical results of Pal-889 with the selected reference values reveals that some of the data points deviate more than 10% from the line with slope = 1 (figure E4). Perhaps because the reference values selected for Pal-889 are not as well-characterized as the recommended standard values of BCR-1, differences between the ICP-MS data and the reference values of Pal-889 are larger than 5% for many elements (compare figure E3 with figure E4). For example, Dy and Gd were analyzed in BCR-1 with excellent accuracy (figure E3), whereas in figure E4, the accuracy of the analysis of Pal-889 for Gd and Dy appears to be poorer, possibly due to the selection of the reference values (i.e., standard values of W-1 instead of Pal-889 were selected; see section E6.3 for more detail). Furthermore, lower precision for Y and the light REE result in slightly lower accuracy for Pal-889 as well (figure E4). Nonetheless, the mean of six analyses of Pal-889 are generally within ±10% of the reference values, indicating good accuracy of the analysis.

E.7.1.5 Inter-laboratory comparison

The samples Pal-889 (table E15) and Cou-IL-6 (table E16) were analyzed by ICP-MS at Washington State University Geoanalytical Laboratories. These ICP-MS data were used as reference values to which the results of the ICP-MS analysis at Union College (UC) were compared. Again, Ta and Nb are excluded from the discussion of the inter-laboratory comparison and discussed below (section E.7.1.6).

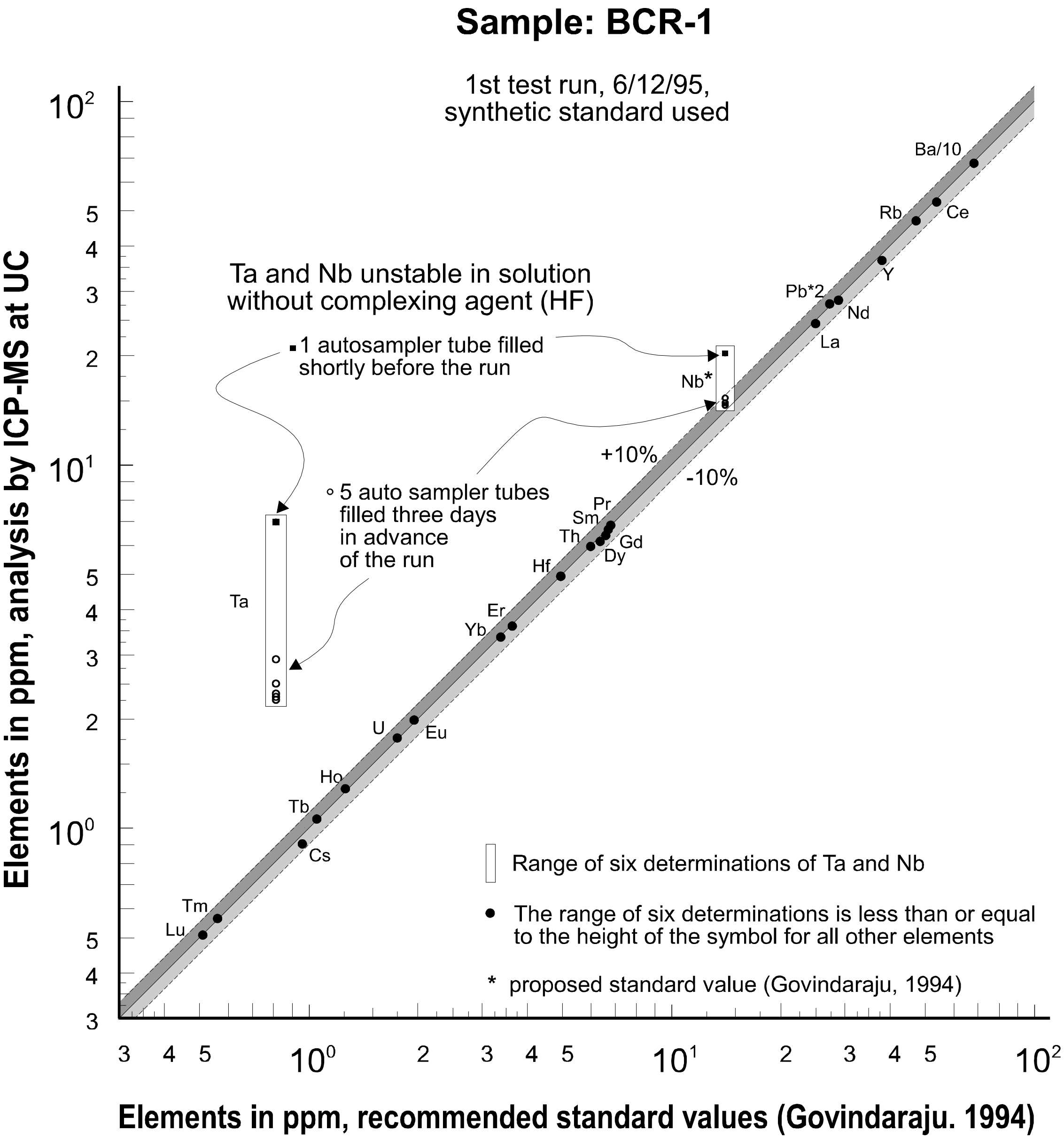


Figure E3

Comparative plot of the analytical data for BCR-1 versus the recommended standard values of Govindaraju (1994). All data points, except Ta and Nb, plot close to or on the line with slope = 1, indicating excellent accuracy of the analysis. The poor accuracy of Ta and Nb is due to the instability of these elements in solution. Three days in advance of the test run, BCR-1 solutions were transferred from the Teflon vials to five auto sampler test tubes and subsequently diluted. The sixth auto sampler tube was filled shortly before the test run and diluted. As illustrated, Ta and Nb concentrations apparently decreased with time of residence in the polypropylene auto sampler test tubes. This problem was resolved in subsequent runs.

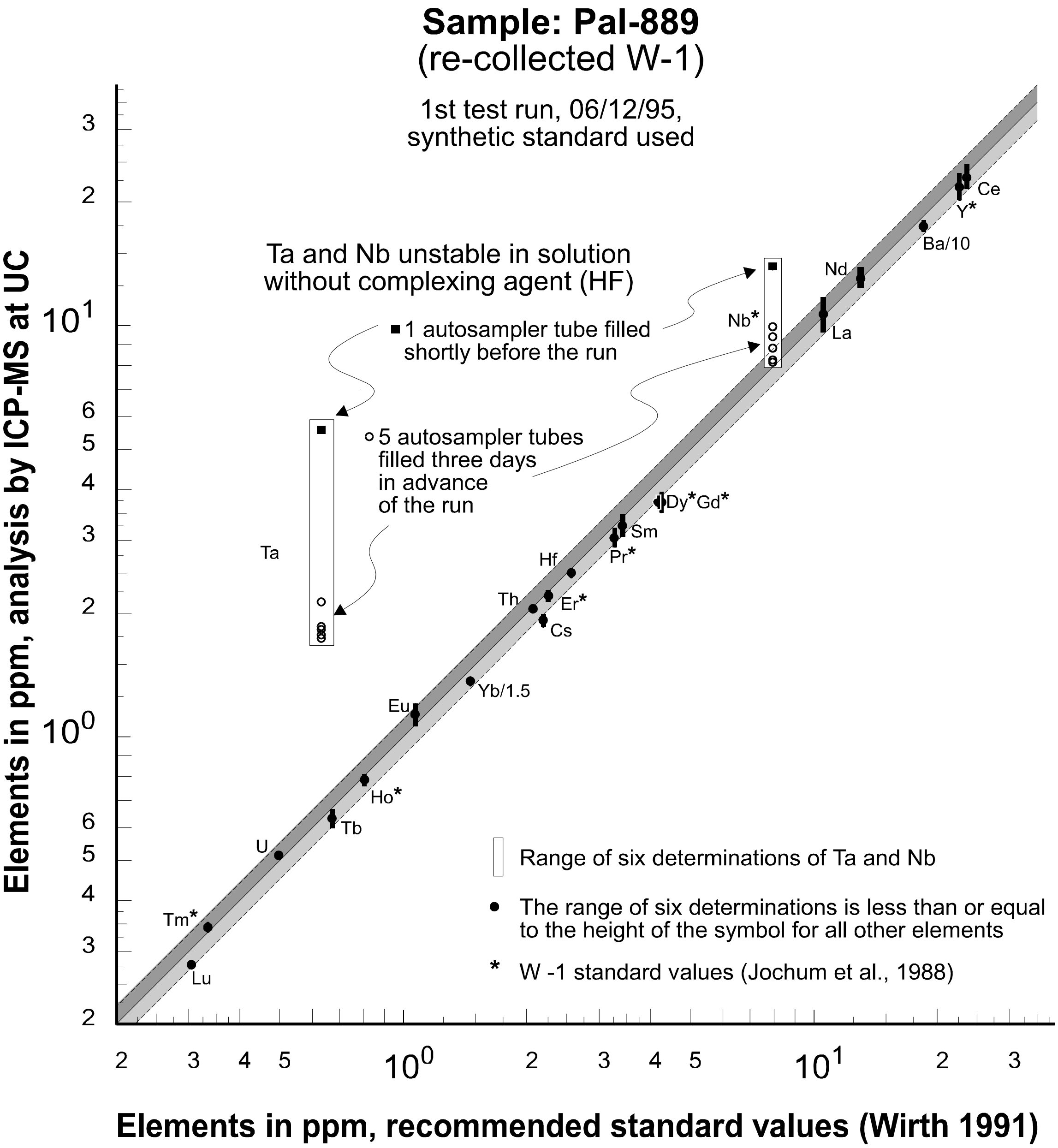


Figure E4

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. The agreement between the analytical results for Pal-889 and the selected standard values is very good, indicating good accuracy of the analysis (except Ta and Nb). The deviation of the data points from the line with slope = 1 are generally larger than in figure E3 (e.g. Dy and Gd), suggesting that the selected reference values could be somewhat inaccurate as well. Again, the solution in the auto sampler tube, that was filled last, was analyzed with the highest Ta and Nb concentrations. The problem with Ta and Nb was resolved in subsequent runs.

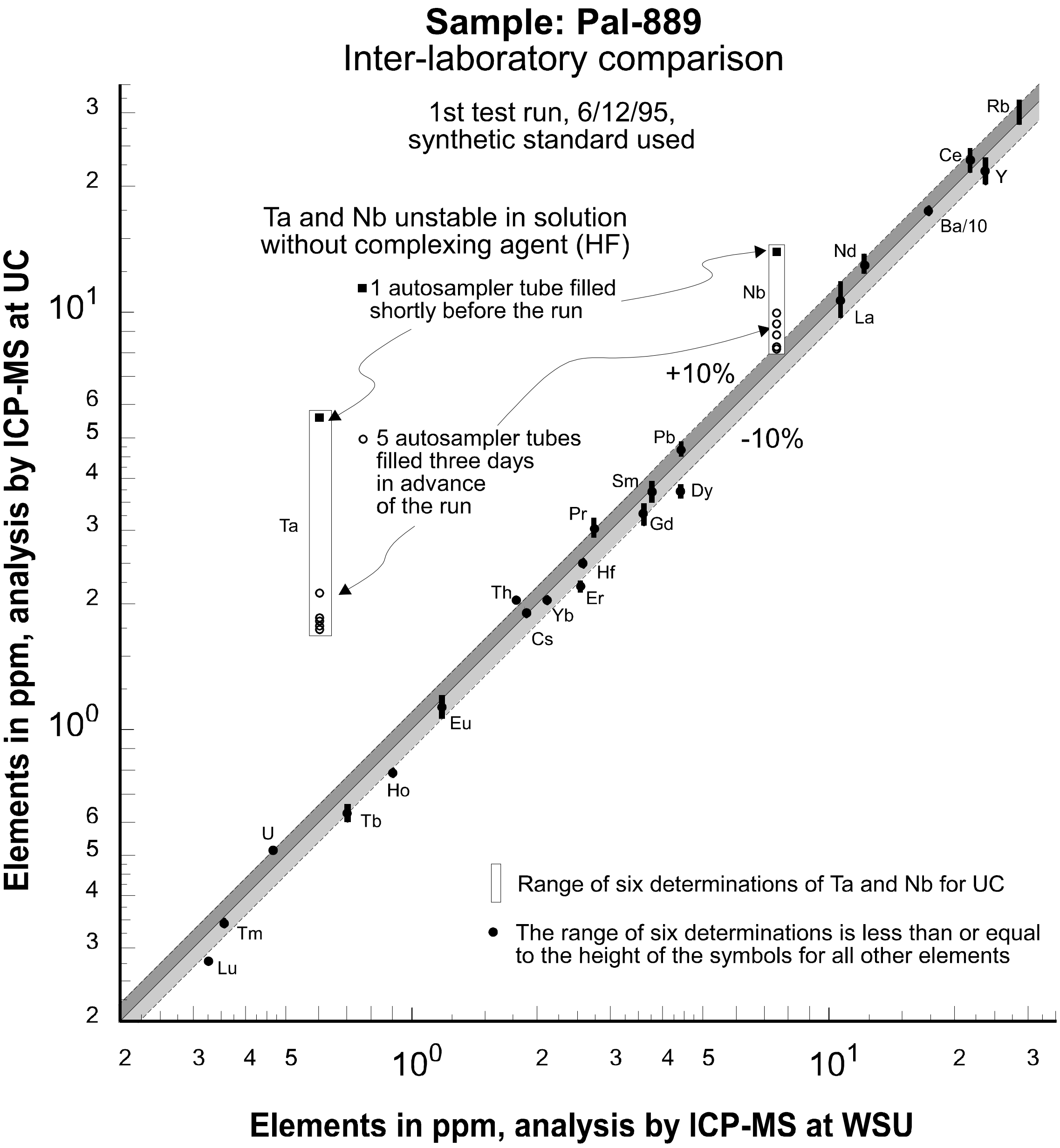


Figure E5

Comparative plot of analytical data for Pal-889 obtained at Union College (UC) versus the analytical data obtained at Washington State University (WSU). Most of the analytical results agree within 10%, indicating good accuracy of the analysis at UC as well as at WSU. The accuracy of Ta and Nb at UC is poor due to instability of Ta and Nb in solution. The sample preparation by acid digestion, routinely used at UC, does not include the addition of hydrofluoric acid (HF) to the analytical solutions. However, it is common practice at WSU to add couple drops of HF to the analytical solutions in order to stabilize Ta and Nb in the solutions. This procedure was used in later runs at UC (see section 7.1.6) resulting in good accuracy.

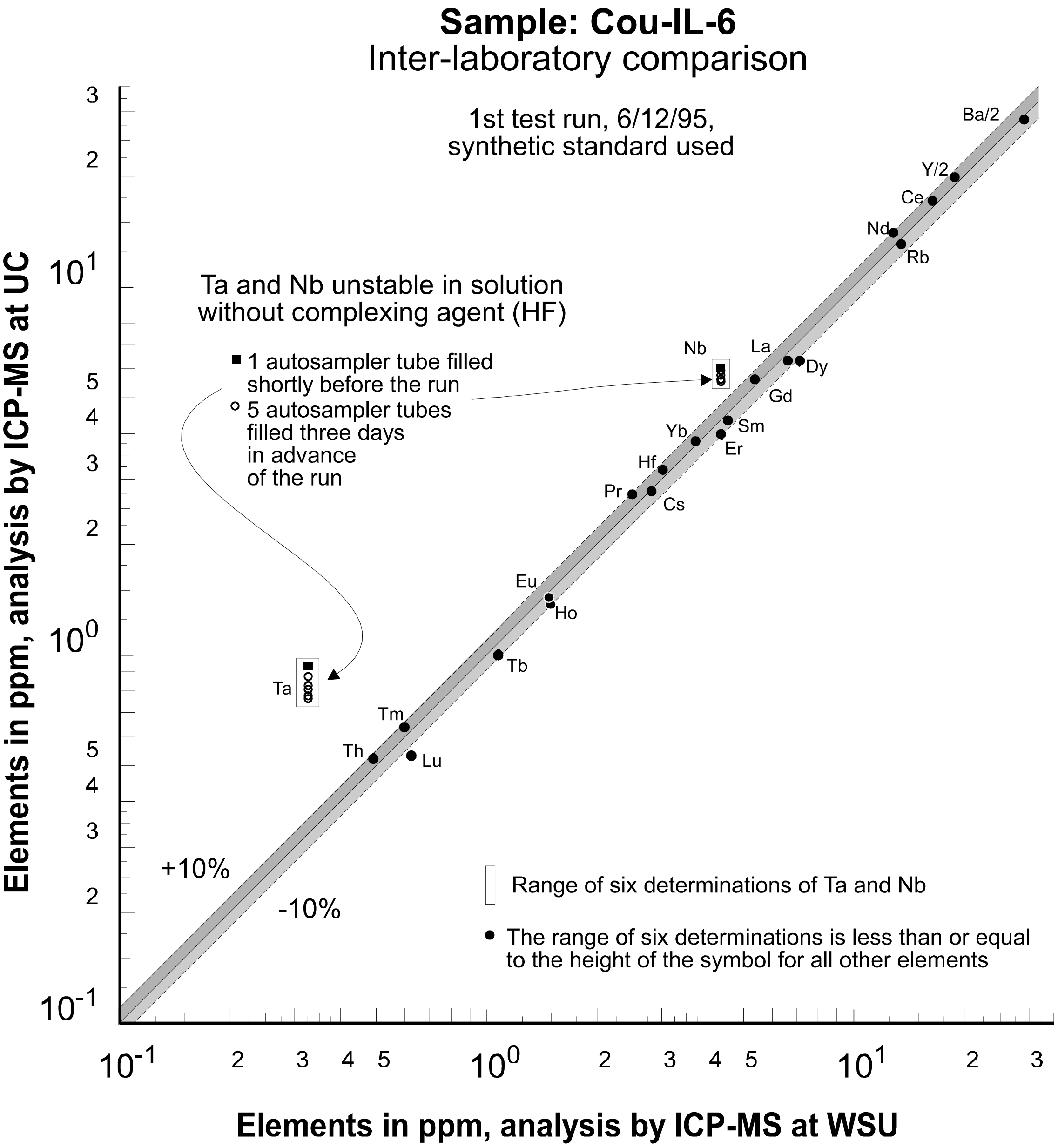


Figure E6

Comparative plot of analytical data for Cou-IL-6 obtained at Union College (UC) versus the analytical data obtained at Washington State University (WSU). Similar to the comparative diagram in figure 5, all analytical data, except for Ta, Nb and Lu, agree within 10%. Ta and Nb were determined with poor accuracy at UC because Ta and Nb were not stable in solution (the complexing agent HF was not added to the analytical solutions). The differences in the Lu values is insignificant considering the low levels of Lu in the sample.

There is generally good agreement between the two laboratories as illustrated for Pal-889 in figure E5. Most elemental concentrations, with view exceptions, agree within ±10%. The average of six determinations of Lu, Er, and Dy plot below the line with slope = 0.9 (-10%), and the averages of Th and Pr above the line with slope = 1.1 (+10%). Differences of this kind are apparently not uncommon comparing results of different laboratories (e.g., ICP-MS, INAA and SSMS data compiled in Ewart et al., 1994a,b) differ as much as 15 - 20 % depending on the element). Using the standard values of Pal-889 in table E15 as reference values for the data obtained at WSU, the accuracy of the analysis at WSU can be assessed as well. For instance, Lu, Er and Dy concentrations measured at UC are 3% to 11% lower than the standard values, and the concentrations obtained at WSU are 5% to 14% higher than the standard values. Both laboratories determined Lu, Er and Dy with very similar accuracy; however, WSU measurements were too high and those for UC too low. Basically, the errors of both laboratories accumulate in the comparative diagram (figure E5). Furthermore, the Th and Pr concentrations determined at WSU are 16% lower than the standard values, whereas the Th data obtained at UC match exactly the standard value and Pr is only 6% lower. Consequently, the determinations of the Th and Pr concentrations are apparently more accurate at UC.

The results for Cou-IL-6 obtained at UC agree with the data obtained at WSU within ±10% (figure E6). Similar to the comparative diagram for Pal-889, Lu and a few other elements indicate larger than 10% variations from the 1:1 line (figure E6). As discussed above, such differences are probably the sum of the errors of both laboratories accumulating in the comparative diagram. However, such differences are inconsequential for petrogenetic interpretations.

E.7.1.6 Problems with Ta and Nb

The variations in the analytical results for BCR-1, Pal-889 and Cou-IL-6 suggest that Ta and Nb were not stable in the sample and standard solutions. Two observations were made supporting this hypothesis:

(1) Ta and Nb were determined with consistently higher concentrations in the three auto sampler tubes filled shortly before the test run, whereas all other sample solutions, which were transferred from the Teflon vials to the polypropylene auto sampler tubes three days in advance of the run, are up to 40% lower in Nb

and up to 70% lower in Ta (figures E3, E4, E5 and E6). Evidently, the concentrations of Ta and Nb in solution decreased with time of residence in the polypropylene auto sampler tubes. Possibly, Ta and Nb adhere to polypropylene when the solutions are stored in the auto sampler tubes, while Ta and Nb remain stable in solution when stored in Teflon vials (generally, polypropylene is chemically less inert than Teflon).

(2) The analytical results of Ta and Nb for BCR-1, Pal-889 and Cou-IL-6 are systematically higher than the corresponding reference values (figures E3, E4, E5 and E6), suggesting the synthetic standard solution lost relatively more Ta and Nb than the sample solutions. The elemental concentrations (= standard values) of the synthetic standard solution are accurately known as long as the elements remain stable in solution. However, Ta and Nb were apparently not stable in solution, and the concentrations may have decreased with time of residence in the polypropylene volumetric flask (1 day) and in the auto sampler tubes (3 days). Perhaps, Ta and Nb concentrations decreased more in the synthetic standard solution than in the sample solutions due to longer contact with polypropylene. As a result, the synthetic standard solution contained much less Ta and Nb in solution than originally added, and thus the standard values were much too high when applied to calibrate the analysis. Ultimately, the analytical results of Ta and Nb for BCR-1, Pal-889 and Cou-IL-6 derived from this calibration would be much higher than the corresponding reference values as observed (figures E3, E4, E5 and E6). Conversely, if Ta and Nb would have been stable in the synthetic standard solution, or would have lost relatively less Ta and Nb than the sample solutions, the analytical results for BCR-1, Pal-889 and Cou-IL-6 would be lower than the corresponding reference values.

As soon as the problem with Ta and Nb was recognized, other ICP-MS laboratories were contacted, and it was found that the instability of Ta and Nb in solution had been a problem at Washington State University (WSU) as well. The analysts at WSU solved this problem with addition of HF to the sample and standard solutions (C. Knaack, personal communication, 1995), which apparently keeps Ta and Nb in solution as fluorine complexes. This procedure, adding HF to the solutions (section E.2.2.1), was used with success at Union College beginning with first analytical run (section E8.2).

The instability of Ta and Nb in solution, however, had not been reported from the Union College Geology Department before, and Ta and Nb had been analyzed with good accuracy and precision (K. Hollocher, personal communication, 1995). The good results had apparently been obtained without adding

HF to sample and standard solutions. Presumably, the problem with Ta and Nb occurred in the first test run, because the test run was arranged in a different way than most analytical runs performed at Union College. The main differences were the following: a synthetic standard solution was used instead of rock standards, and all but three solutions were stored in the auto sampler tubes for three days instead of minimizing the exposure to polypropylene.

The hypothesis outlined below might explain why these differences could be critical. Perhaps, Ta and Nb were not stable in solution due to deficiency of HF in the synthetic standard solution (HF was not added). In contrast to the synthetic standard solution, which was prepared by mixing and diluting single-element solutions, the samples were dissolved by acid digestion and might have retained HF during the dissolution procedure (section E.2.2.1). Perhaps, not all HF was driven out in the last evaporation step (step 7 in section E.2.2.1). Provided that HF was retained, the amount of HF was probably insufficient to stabilize Ta and Nb in the sample solutions that were stored in the polypropylene auto sampler tubes for three days. However, the amount of retained HF might have been sufficient to stabilize Ta and Nb in the sample solutions that were stored in Teflon vials until transferred to polypropylene auto sampler tubes just prior to analysis.

Rock standards were used in a second test run, and the exposure of solutions to polypropylene was minimized as described in "Strategy and Methods" for the second test run (section E.7.2). Potentially, standards as well as samples might retain enough HF so that Ta and Nb are stable in solution for the duration of the analysis by ICP-MS (~7 hours). The second test run was designed to determine whether it is really necessary to add HF to the sample and standard solutions to stabilize Ta and Nb.

E.7.1.7 Evaluation of dissolution

High precision (figure E2) and accuracy (figures E3, E4, E5 and E6) were demonstrated in the first test run where 24 trace elements were determined for BCR-1, Pal-889 and Cou-IL-6. Several potential problems, such as incomplete digestion of the samples, weighing errors, poor instrumentation, or flawed calibration can be ruled out, because the test run was set up in a manner such that any of these would be indicated by poor precision and/or accuracy. In fact, the test run proved to be very successful, revealing a major problem with Ta and Nb, which were apparently unstable in solution.

As argued below, it is well-constrained that incomplete digestion is not a problem dissolving samples of basaltic to andesitic composition using the sample preparation method described in section E.2.2. A synthetic standard prepared from Spex® single element solutions was used for the calibration. Therefore, the elemental concentrations in the synthetic standard solution do not depend on the complete dissolution of any mineral phases. If samples were not completely dissolved, then systematically lower values for the elements partitioned into chemically resistant minerals would have been observed. However, all elements (except Ta and Nb) were determined very accurately. Consequently, the complete dissolution of the samples was verified using a synthetic standard.

E.7.2 Second test run, 11/17/95, NIST-278 and NIST-688 used as standards

E.7.2.1 Strategy and methods

The second test run was set up similar to a typical analytical run: 16 samples from the Oregon Coast Range ophiolite and four samples from the Josephine ophiolite were analyzed, and two rock standards (NIST-278 and NIST-688) were used for the calibration. Five blanks and two digestions of each of the samples and standards were prepared using the acid digestion method described in section E.2.2. However, HF was not added to any of the solutions as done in following runs to stabilize Ta and Nb. The sequence of the analysis of solutions is similar to that of the analytical runs (figure E1). However, the four groups of blanks and standards in the second test run contained only aliquots of NIST-278, NIST-688, and blanks but none of BCR-1 (i.e., BCR-1 was not used as standard). Furthermore, the exposure of solutions to polypropylene was minimized: all blank, standard, and sample solutions were transferred to the auto sampler tubes and diluted within 3-9 hours of being analyzed. Two additional elements (Cr and Zr) were analyzed in the second test run.

Three reference materials (Z-83a, BCR-1 and Pal-889) were analyzed together with blanks standards and samples for the purpose of evaluating the accuracy and precision for the second test run. Two aliquots of two digestions of Z-83a (n=4) were evenly spaced throughout the run to test whether or not Ta and Nb are stable in solution for the duration of the second test run (about 7 hours). If not, one would expect to see Ta and Nb values changing throughout the run. Additionally, these four analyses of Z-83a enable to evaluate drift corrections which the VGFIX2 program automatically performs. In contrast to the four auto sampler tubes containing Z-83a spaced throughout the run, two aliquots of two digestions of BCR-1 (n=4) and Pal-889 (n=4) were analyzed in series. If drift corrections were incorrect, the precision of the analysis would be significantly lower for Z-83a than for BCR-1 and Pal-889.

E.7.2.2 Limits of detection

Using equation (1), the detection limits were determined from the blank residuals of the second test run and are listed in table E8. The detection limits of Cr, Zr, and Ba are generally higher than those of the other elements (see section E.5 and E.6.1 for more detail). Nonetheless, all elemental concentrations determined in the samples are well above the calculated detection limits.

E.7.2.3 Precision

The mean values and standard deviations (1 σ) of four analyses of BCR-1, Pal-889 and Z-83a are listed in table E8. To illustrate the precision of the analysis, the relative standard deviations of analyzed elements are plotted in figure E7. Generally, the precision is very good as suggested by the analytical results of BCR-1, Pal-889 and Z-83a, except for Ta. The problem with Ta (and Nb) is discussed separately in section E.7.2.6.

The four sample solutions of Z-83a were evenly spaced throughout the test run in order to evaluate the drift corrections performed by the VGFIX2 program. In general, the sample Z-83a does not indicate significantly higher relative standard deviations than BCR-1 and Pal-889 which were analyzed in series (figure E6). This shows clearly that the drift corrections, performed by the VGFIX2 program, are sufficient to compensate for instrument drift, even for very long analytical runs (7 hours).

Cr concentrations determined in the four Z-83a solutions do not change systematically with time; but vary randomly. Therefore, the marginally acceptable precision of determining Cr is most likely due to real limitations of the analysis and not due to any instability of Cr in solution.

Table E8: Results of second test run, 11/17/95, NIST-278 and NIST-688 used as standards

Element	**Detction Limits** in ppm	**BCR-1** mean (n=4)	error 1 σ	**Pal-889** mean (n=4)	error 1 σ	**Z-83a** mean (n=4)	error 1 σ	**Z-83a** ***XRF***/INAA [1]	error 2 σ
V	n.d.	n.d.	-	n.d.	-	n.d.	-	***416***	-
Cr	0.66	12.0	0.5	283	11	283	30	***254*** 293	-
Rb	0.019	52.6	2.2	31.5	0.4	2.05	0.11	-	-
Sr	n.d.	n.d.	-	n.d.	-	n.d.	-	***598***	-
Y	0.034	37.0	0.2	23.0	0.2	26.3	0.8	***25***	-
Zr	5.5	190	4	97.3	1.7	75.0	1.9	***84***	-
Nb	0.014	17.8*	0.4	9.9*	0.19	8.3*	0.52	-	-
Cs	0.0040	1.037	0.027	2.19	0.06	0.06	0.00	-	-
Ba	0.62	684.4	17.9	185.0	3.2	11.7	0.7	-	-
La	0.010	26.83	1.24	11.27	0.19	7.09	0.10	6.89	0.15
Ce	0.031	57.3	1.7	23.7	0.6	16.85	0.46	18.36	1.19
Pr	0.0037	7.17	0.12	3.15	0.04	2.72	0.08	-	-
Nd	0.017	29.5	1.3	14.3	0.3	13.7	0.3	-	-
Sm	0.0048	6.44	0.27	3.45	0.09	3.90	0.12	3.82	0.05
Eu	0.0013	1.97	0.05	1.14	0.03	1.38	0.04	1.25	0.03
Gd	0.0047	7.17	0.19	3.87	0.08	4.69	0.23	-	-
Tb	0.0008	1.05	0.04	0.623	0.014	0.737	0.019	0.81	0.1
Dy	0.0043	6.33	0.16	3.86	0.09	4.60	0.12	-	-
Ho	0.0014	1.33	0.03	0.787	0.015	0.96	0.03	-	-
Er	0.0030	3.41	0.13	2.15	0.08	2.53	0.06	-	-
Tm	0.00088	0.521	0.010	0.314	0.006	0.373	0.012	-	-
Yb	0.0031	3.44	0.14	2.07	0.05	2.39	0.03	2.34	0.24
Lu	0.00080	0.575	0.014	0.322	0.006	0.370	0.008	0.35	0.3
Hf	0.006	5.31	0.12	2.63	0.03	2.51	0.07	2.37	0.24
Ta	0.0045	0.89*	0.11	0.77*	0.06	0.45*	0.15	0.43	0.19
Pb	0.03	15.3	0.3	5.59	0.13	1.843	0.02	-	-
Th	0.0031	6.32	0.15	2.25	0.04	0.709	0.003	0.76	0.19
U	0.0022	1.80	0.05	0.516	0.007	0.255	0.012	-	-

* Ta (and Nb) unstable in solution

[1] unpublished data from Harper (pers. comm., 1995)

n.d. not determined

ICP-MS analysis; standard deviation: $\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively

see tables 14 and 15 for compilation of analytical results for BCR-1 and Pal-889, respectively

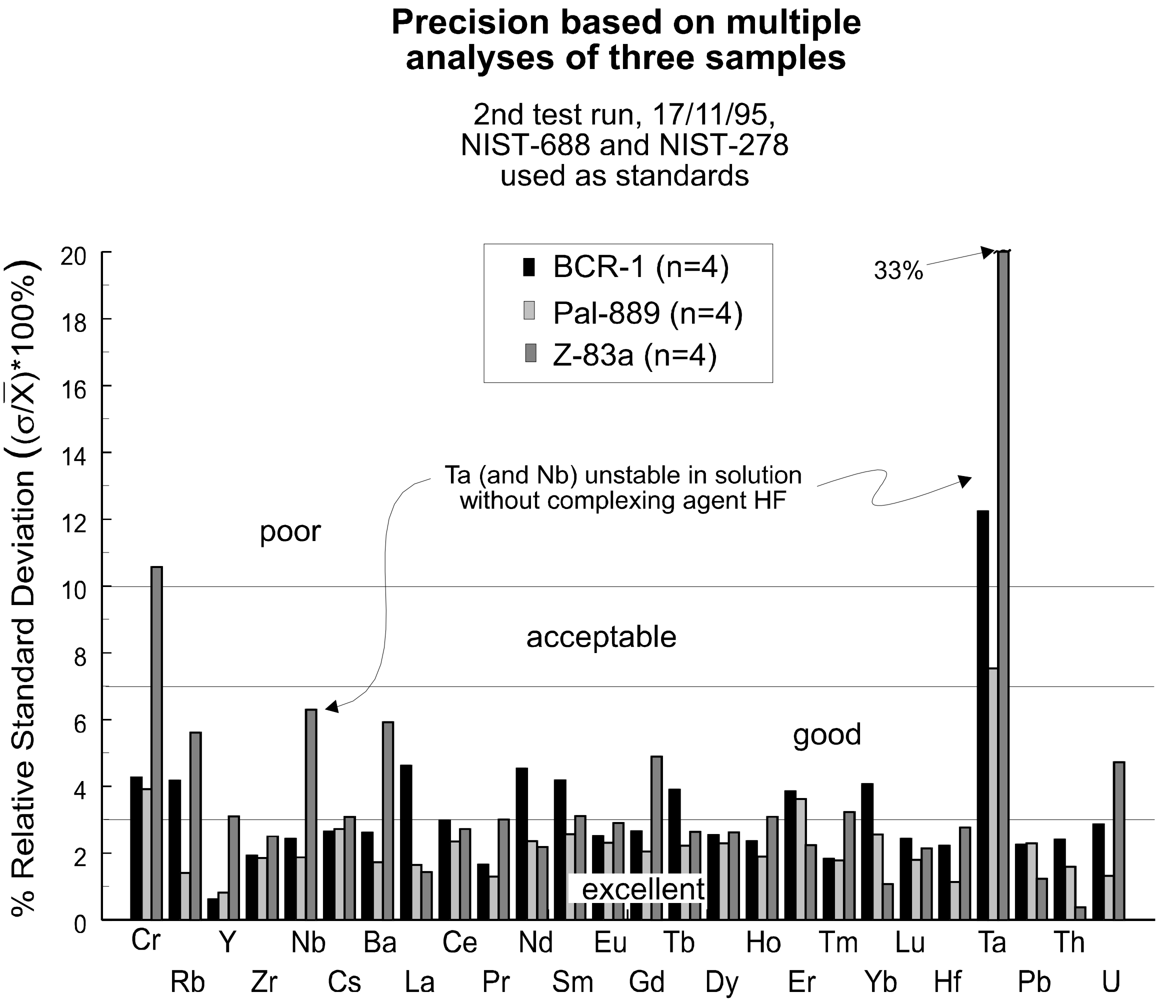


Figure E7

Diagram illustrating the precision of the analysis of the second test run. Two aliquots of two separate digestions per sample were analyzed. Except for the element Ta, good to excellent precision of the analysis is indicated by 2% to 5% relative standard deviation. In contrast to BCR-1 and Pal-889 which were analyzed in series, the four auto sampler tubes of Z-83a were evenly spaced throughout a ~7 hour run. The extremely poor precision of Ta for Z-83a is interpreted as due to the decrease of Ta concentrations with time of residence in the polypropylene auto sampler tubes.

E.7.2.4 Accuracy

The accuracy of the second test run is assessed by comparing the analytical results of BCR-1 and Pal-889 with the corresponding reference values. As illustrated in figures E8 and E9, the analytical results agree with the recommended standard values generally within 10%, and most points plot with very little departure from the line with slope = 1. However, the data points of Ta, Nb and Cr in figure E8 (BCR-1) and of Ta and Nb in figure E9 (Pal-889) indicate significant disagreement between the ICP-MS analysis and the corresponding standard values. Evidently, the problem with Ta and Nb was still not resolved in the second test run and is discussed in a separate section below (section E7.2.6).

The Cr concentration in BCR-1 was determined with seemingly poor accuracy as illustrated in figure E8. Perhaps, the standard value of Cr is not very good (it is “proposed’ rather than “recommended”, table E2). The Cr values obtained by ICP-MS may be more accurate than the proposed standard value of Govindaraju (1994). Regardless, the difference of 25% between the standard value (16 ppm) and the analytical results (12 ppm) is inconsequential for petrogenetic interpretations considering the low level of Cr in the sample. Furthermore, the analytical results for samples with higher Cr concentrations are in good to acceptable agreement with the reference values (figures E9 and E10).

E.7.2.5 Inter-laboratory comparison

The analytical data of Z-83a obtained by XRF and INAA are listed in table E8, and the corresponding comparative plot is shown in figure E10. Generally, the analytical data agree within the errors of the analyses. The indicated mean values plot close to or on the line with slope = 1.

Cr is determined with much higher precision by XRF analysis and INAA than ICP-MS analysis (figure E10). Nonetheless, there is a notable difference between the Cr data obtained by INAA (293 ppm) and XRF analysis (254 ppm), and these Cr values do not overlap within 2σ error. The mean of the ICP-MS analysis of Cr (283 ppm) agrees best with the INAA data (table E8).

The analytical results for Y indicate good agreement between ICP-MS and XRF analyses (figure E10). Yet, the ICP-MS data for Zr are more than 10% lower than the XRF values, even though Zr concentrations in BCR-1 and Pal-889 were determined very accurately (figures E8 and E9). Probably, Zr

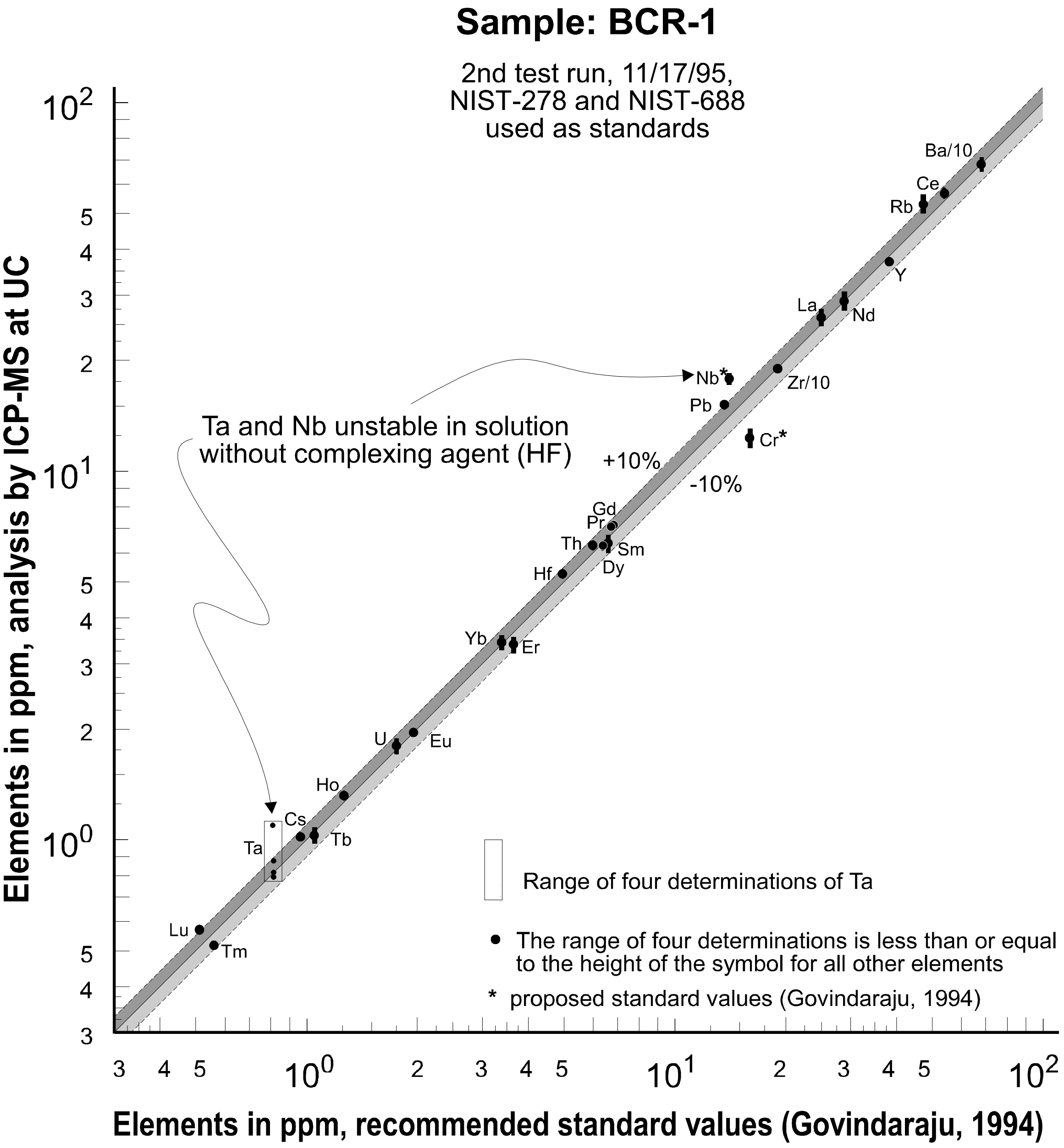


Figure E8

Comparative plot of the analytical data of the second test run versus the recommended standard values of BCR-1 (Govindaraju, 1994). Most data points plot close to or on the line with slope = 1, indicating excellent accuracy of the analysis. The analytical results of Ta and Nb suggest once again that Ta and Nb are unstable in solution, although accuracy was improved over the first test run (compare with figure 3). Note that the analytical results of Cr are notably lower than the proposed standard value of Cr. Either the standard value is too high, or the analysis by ICP-MS is too low for samples with low levels of Cr.

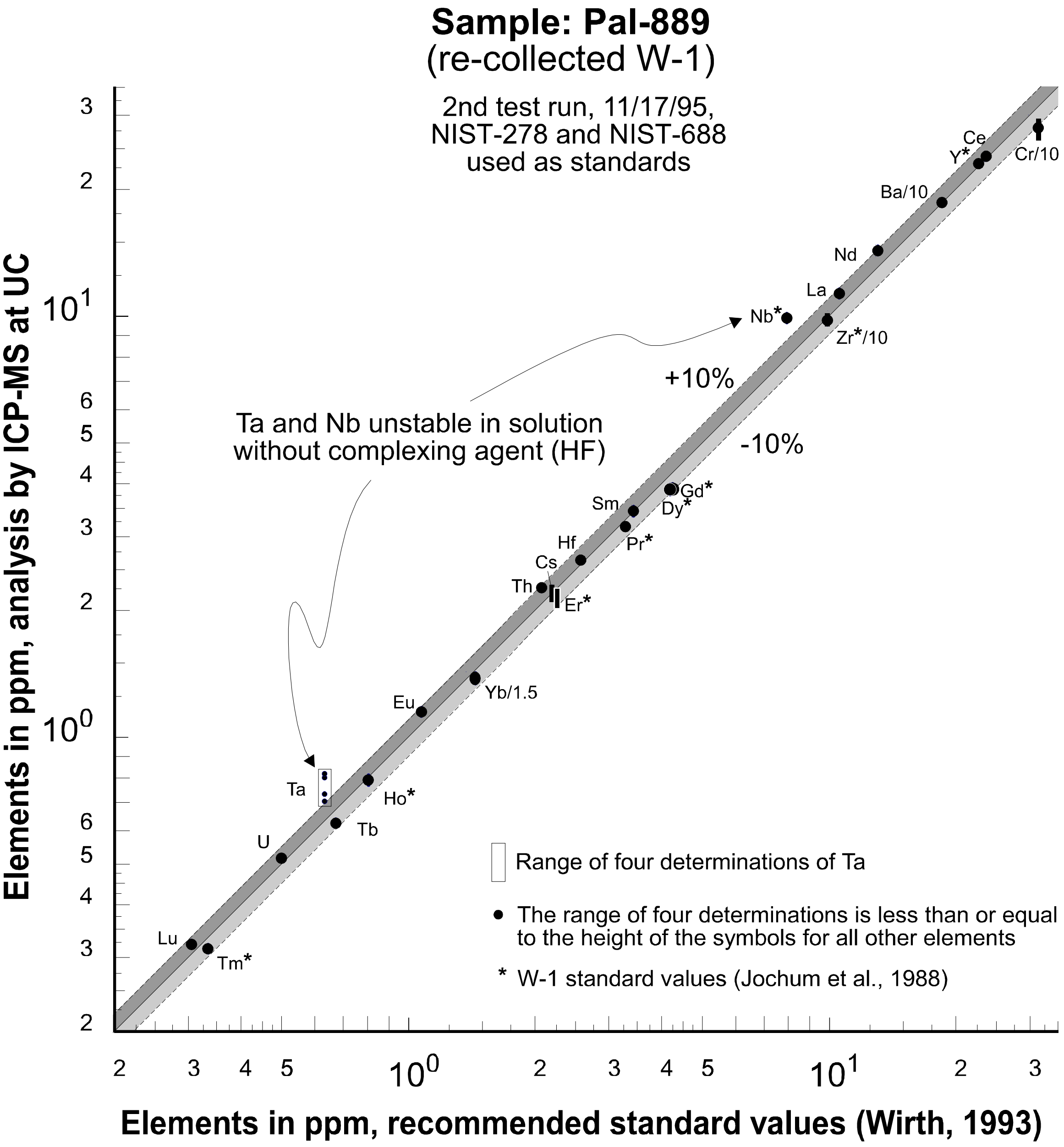


Figure E9

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. All analytical results agree with the reference values within 10%, indicating very good accuracy of the analysis. Also in this diagram, Ta and Nb data plot at notably higher values than the corresponding standard values, indicating that the standard solutions (NIST-278 and NIST-688) lost some amount of Ta and Nb.

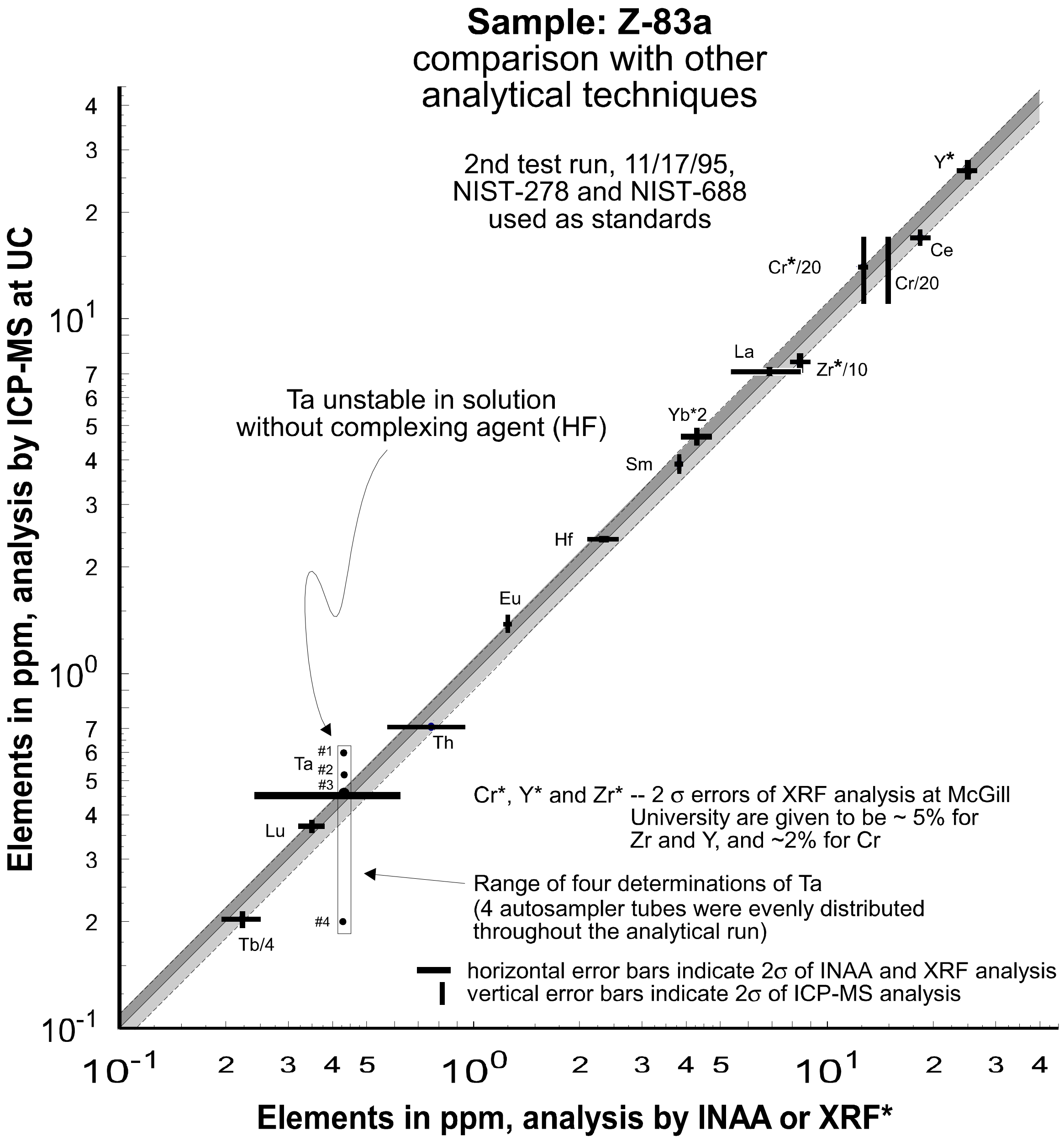


Figure E10

Comparative plot of analytical data for Z-83a obtained at Union College (UC) versus the analytical data obtained by XRF analysis and INAA. All of the analytical results agree within 10%, indicating good accuracy of the analysis at UC as well as by INAA and XRF analysis. The four auto sampler tubes containing Z-83a solutions were evenly distributed throughout the run. The first analyzed solution (#1) indicates the highest concentration and the last analysis (#4) the lowest, suggesting that Ta was not stable in solution for the duration of the test run. This problem was resolved with beginning of the first analytical run.

was determined at higher than standard concentration in the XRF analyses and lower than standard concentration using ICP-MS, therefore resulting in >10 % differences between the two techniques. For example, the XRF analysis of Pal-889 (table E.15) determined at the University of Massachusetts (Zr = 101.6 ppm) matches very closely the standard value of 98.6 ppm whereas five analyses by XRF at McGill University indicate significantly higher Zr values (116 ± 5 ppm). The ICP-MS data for Pal-889 show generally lower Zr concentrations (90.6 to 99.3 ppm) than the recommended standard value.

Evidently, the precision of La, Ce, Tb, Yb, Lu, Hf, and Th was better by ICP-MS analysis than by INAA as indicated by smaller 2σ errors calculated for the ICP-MS data. Only Eu and Sm were determined with better precision by INAA than by ICP-MS analysis. Generally, the agreement between the two techniques is very good (within 10%, figure E10), giving further evidence of good accuracy of the ICP-MS analysis.

E.7.2.6 Problems with Ta and Nb

Apparently, Ta and Nb were not stable in the sample and standard solutions analyzed in the second test run, in spite of the changes with respect to the first test run. Two observations support the hypothesis that Ta and Nb were not stable in solution:

(1) The concentrations of Ta in Z-83a solutions, which were dispersed thought the run, decreased with time of residence in the auto sampler tubes, resulting in the high relative standard deviation of 33% (figure E7). The Z-83a solution analyzed earliest in the run gave the highest Ta concentration (#1, figure E10). Subsequently, Ta concentrations decreased with time (#2 - #4, figure E10). Consequently, such variations in the analytical results are interpreted as due to the instability of Ta in solution (i.e., increased loss of Ta with time is possibly due to adherence to walls of polypropylene auto sampler tubes).

(2) Similar to the first test run (figures E3 and E4), the Ta and Nb concentrations determined in the second test run are higher than the recommended standard values (figures E8 and E9). This suggests that the standard solutions (NIST-278 and NIST-688) must have lost relatively more Ta and Nb than the sample solutions, further indicating that the problem with Ta and Nb was still not solved.

Nonetheless, the accuracy and precision of Ta and Nb were clearly improved (figures E7, E8 and E9) compared to the first test run (figures E2, E3, and E4). Apparently, the use of rock standards instead of a synthetic standard solution and minimizing the exposure of the solutions to polypropylene were effective measures to improve the accuracy and precision of Ta and Nb. However, the analytical results of Ta and Nb were still not acceptable and had to be further improved. It was believed that further improvement might be achieved by adding HF to all solutions prior to analysis as done at Washington State University Geoanalytical Laboratories (C. Knaack, personal communication 1995)

In conclusion, the analytical results of the second test run suggest that the samples and standards probably retained some HF during acid digestion. However, this amount of retained HF was apparently not enough to stabilize Ta and Nb in all analytical solutions for the duration of the test run. The observed decrease of the Ta and Nb concentrations in analytical solutions during the 7 hour run could be partly due to the deterioration of the solutions when in prolonged contact with polypropylene. Consequently, some HF must be added to the sample and standard solutions in the Teflon vials before the solutions are transferred to the polypropylene auto sampler tubes and subsequently diluted. It appears that by adding a sufficient amount of HF to the solutions in the chemically inert Teflon vials, all of the Ta and Nb in solution form soluble complexes before the solutions are transferred to the chemically less inert polypropylene auto sampler tubes. This procedure was successfully used for all samples and standards in subsequent analytical runs, and excellent accuracy and precision were obtained for Ta and Nb in all samples.

E.8 Analytical runs

E.8.1 Introduction

A complete description of the sample preparation procedure, the acquisition of the data, and the methods of data evaluation are described above in sections E2 through E6. Nonetheless, some remarks regarding the procedure are made in order to emphasize parts of it (or differences with the test runs) which enhanced the accuracy and precision of the analysis, or at least provided the means to detect any problems with the analysis.

The unknown samples were prepared in duplicate, which means two separate solutions were prepared by weighing and dissolving 0.1g of the sample powder in each of two Teflon vials (figure E1). The accuracy may be improved with the analysis of duplicates, and errors during sample preparation, such as weighing errors, pipetting errors, contamination and incomplete dissolution can be detected. In the analytical runs, the relative standard deviation of the analysis of four separate digestions for a number of samples were generally less than 5% (table E13), indicating no errors were made preparing the samples, and all samples were completely dissolved. Similar consistency of the analytical results of three separate digestions per sample were demonstrated in the first test run (table E7). The results of ICP-MS analyses reported in appendix A represent averages of the duplicate analyses. Note that two additional elements (V and Sr) were analyzed in all analytical runs.

The well-characterized U.S.G.S. standard BCR-1 was always included in the analytical runs, and obtained data for each analytical run were used in two ways (section E5). First, BCR-1 was treated as unknown sample, and the elemental concentrations of BCR-1 were calculated with NIST-278 and NIST-688 as standards. Obtained analytical results of BCR-1 were then used to asses the accuracy and precision of the analysis. Treating BCR-1 as an unknown sample has the additional benefit that any problems with the preparation of the standard solutions (NIST-278, NIST-688 and BCR-1), such as weighing errors, pipetting errors, or contamination, can be detected before the elemental concentrations of all other unknown samples are calculated. Second, NIST-278, NIST-688 and BCR-1 were used as standards in order to calculate the elemental concentrations of Pal-889, Cou-IL-6 and all other samples. The analytical results are most likely more accurate when all three standards, instead of only the two NIST-standards, are put to use. In other words, the accuracy of the analytical results of Pal-889, Cou-IL-6 and all other samples (derived from a calibration with three standards) is considered better characterized than the analytical results of BCR-1 (derived from a calibration with only two standards).

Finally, 0.05 ml of 50% HF was added to all blank, standard and sample solutions prior to transferring aliquots of the solutions to polypropylene auto sampler tubes. Any indications of instability of Ta and Nb in solution were not observed in any of the analytical runs. Ta and Nb were analyzed with excellent accuracy and precision in all analytical runs. Thus, the Ta and Nb problems were resolved. Of course, new sample solutions for all unknown samples analyzed in the second test run were prepared again using acid digestion, and HF was added to the solutions. Thus, all samples analyzed in the second test run were re-analyzed in order to obtain accurate Ta and Nb values.

E.8.2 First analytical run, 02/23/96

E.8.2.1 Limits of detection

The detection limits were determined as described in section E.6.1 and are listed in table E9. None of the detection limits indicate problems with the analysis, and as usual, V, Cr, Zr and Ba have relatively higher detection limits than other elements. This is not a problem in that all determined elemental concentrations of the samples (appendix F) are well above the detection limits.

E.8.2.2 Precision

The precision of the analysis is based on multiple analyses of BCR-1 (treated as an unknown), Pal-889 and Cou-IL-6. The relative standard deviation is smaller than 7% for most elements in all three samples (figure E.11), indicating good precision of the analysis.

Cr and V show slightly higher relative standard deviations than the other elements (figure E11). This was also observed for Cr in the second test run (figure E7). Perhaps, the precision of Cr and V is in general not as good as for the other elements indicating limitations of ICP-MS for accurate analysis of Cr and V.

The poor precision for Pb in Cou-IL-6 may be related to the low levels of Pb in Cou-IL-6: samples with low Pb concentrations are affected by even very small amounts of Pb contamination whereas similar amounts of contamination would have no effect on samples with high Pb concentrations.

E.8.2.3 Accuracy

The accuracy is evaluated by comparing the analytical results of BCR-1 and Pal-889 (table E9) with the corresponding standard values. As illustrated in figure E12, the range of eight determinations of most

Table E9: Results of first analytical run, 02/23/96

Element	Detection Limits in ppm	BCR-1 mean (n=8)	error 1 σ	Pal-889 mean (n=4)	error 1 σ	Cou-IL-6 mean (n=8)	error 1 σ
V	0.35	411	26	269	16	501	28
Cr	1.27	14.5	1.3	310	21	89	5
Rb	0.035	47.2	0.7	29.7	1.1	12.8	0.2
Sr	0.18	342	9	174	4	273	5
Y	0.016	35.5	1.0	21.4	0.7	38.9	1.0
Zr	8.3	183	4	90.9	2.5	119	2
Nb	0.035	15.5	0.5	8.68	0.32	5.71	0.24
Cs	0.0062	0.96	0.02	1.95	0.02	2.82	0.13
Ba	0.60	686	17	169	8	53.5	3.4
La	0.028	25.7	0.5	10.1	0.3	6.11	0.26
Ce	0.056	52.5	1.1	21.8	0.8	15.9	0.8
Pr	0.0068	6.76	0.16	2.93	0.08	2.57	0.11
Nd	0.020	29.8	0.502	13.1	0.4	13.4	0.6
Sm	0.0038	6.52	0.15	3.26	0.10	4.18	0.22
Eu	0.0014	2.00	0.03	1.09	0.04	1.34	0.06
Gd	0.0040	6.73	0.22	3.69	0.12	5.31	0.30
Tb	0.00035	1.03	0.03	0.620	0.018	0.912	0.041
Dy	0.0025	6.29	0.11	3.82	0.11	6.06	0.19
Ho	0.00086	1.29	0.02	0.768	0.033	1.30	0.05
Er	0.0023	3.51	0.07	2.13	0.08	3.77	0.12
Tm	0.00080	0.506	0.017	0.319	0.011	0.575	0.023
Yb	0.0028	3.26	0.10	2.01	0.03	3.65	0.15
Lu	0.00052	0.563	0.014	0.305	0.004	0.557	0.014
Hf	0.0044	4.97	0.11	2.56	0.09	3.15	0.07
Ta	0.013	0.751	0.011	0.600	0.043	0.301	0.009
Pb	0.25	14.5	0.2	4.52	0.27	0.582	0.075
Th	0.017	6.22	0.09	2.07	0.06	0.541	0.012
U	0.0021	1.71	0.05	0.494	0.008	0.180	0.005

standard deviation : $\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively
see tables 14, 15 and 16 for compilation of analytical results
for BCR-, Pal-889, and Cou-IL-6, respectively

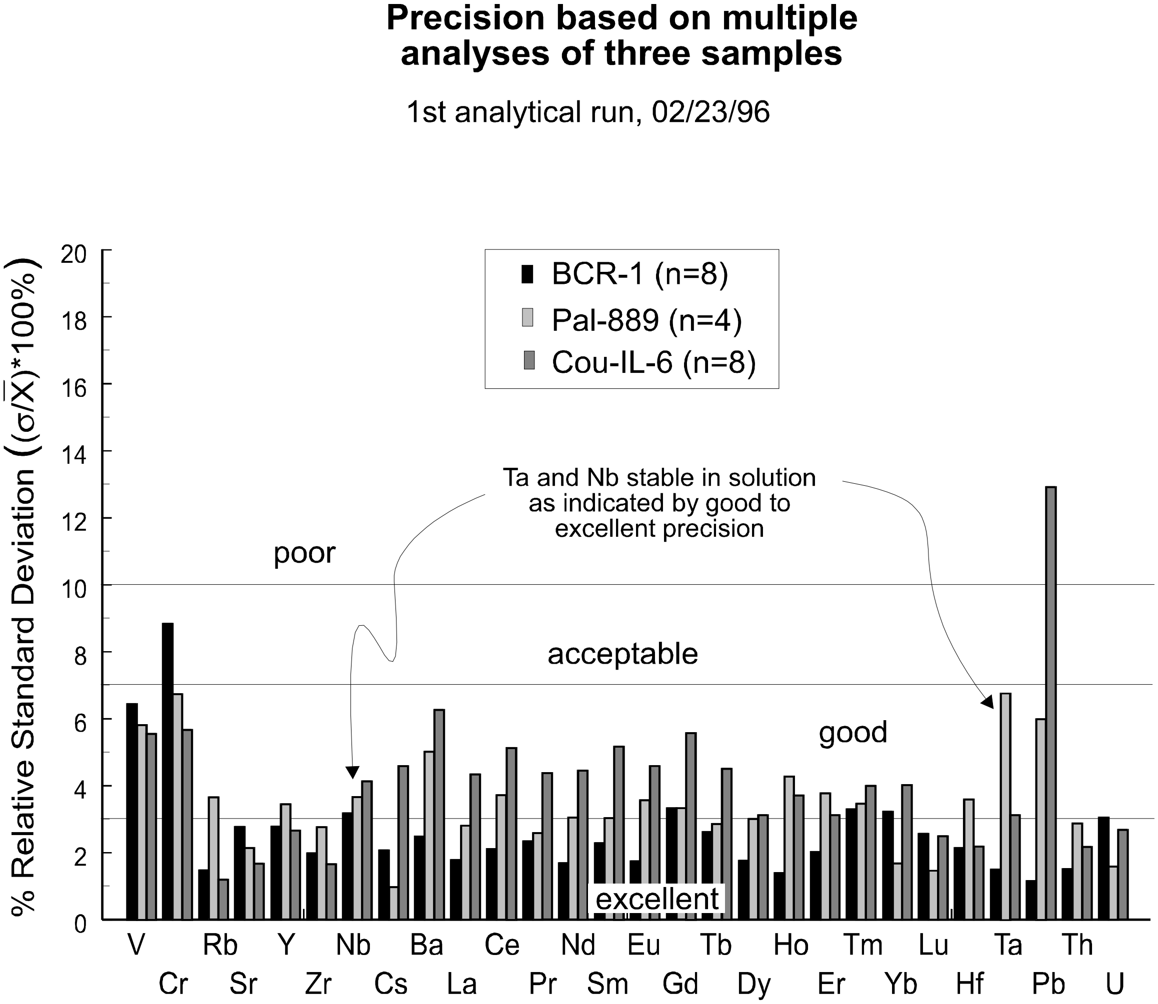


Figure E11

Diagram illustrating the precision of the analysis of the first analytical run. Four aliquots of two digestions of BCR-1 and Cou-IL-6 and two aliquots of two digestions of Pal-889 were analyzed. Except for Pb determined in Cou-IL-6, good to excellent precision of the analysis is indicated by 2% - 5% relative standard deviation on average. V and Cr have slightly higher relative standard deviations (~7%).

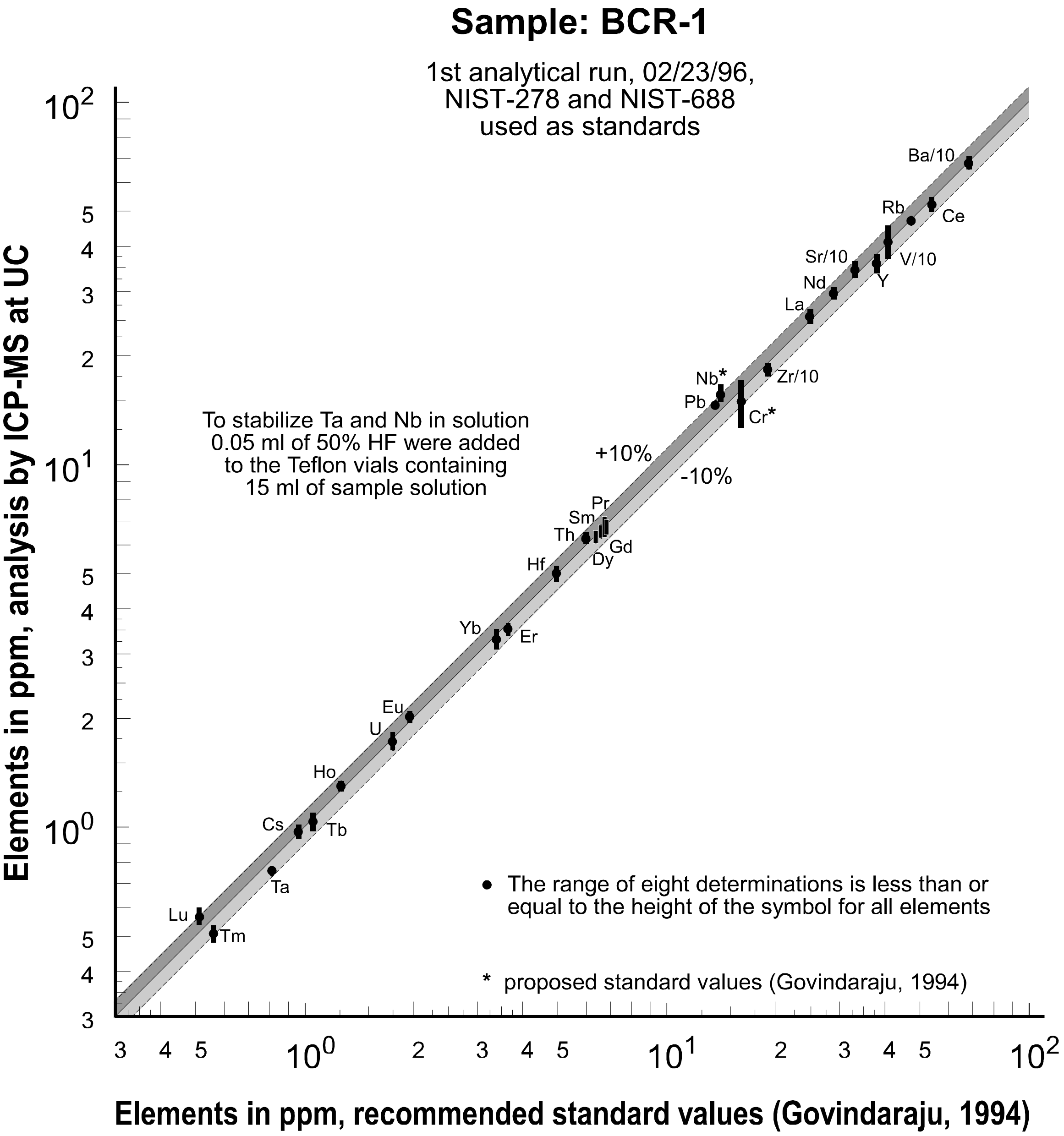


Figure E12

Comparative plot of the analytical results of the first analytical run versus the recommended standard values of BCR-1 (Govindaraju, 1994). All data points plot close to or on the line with slope = 1, indicating excellent accuracy of the analysis. The analytical results generally agree with the standard values within 10% (most within 5%). Furthermore, good analytical results obtained for Ta and Nb suggest that Ta and Nb are stable in solution. Similar to the second test run (figure 8) the analytical results of Cr are somewhat lower than the proposed standard value.

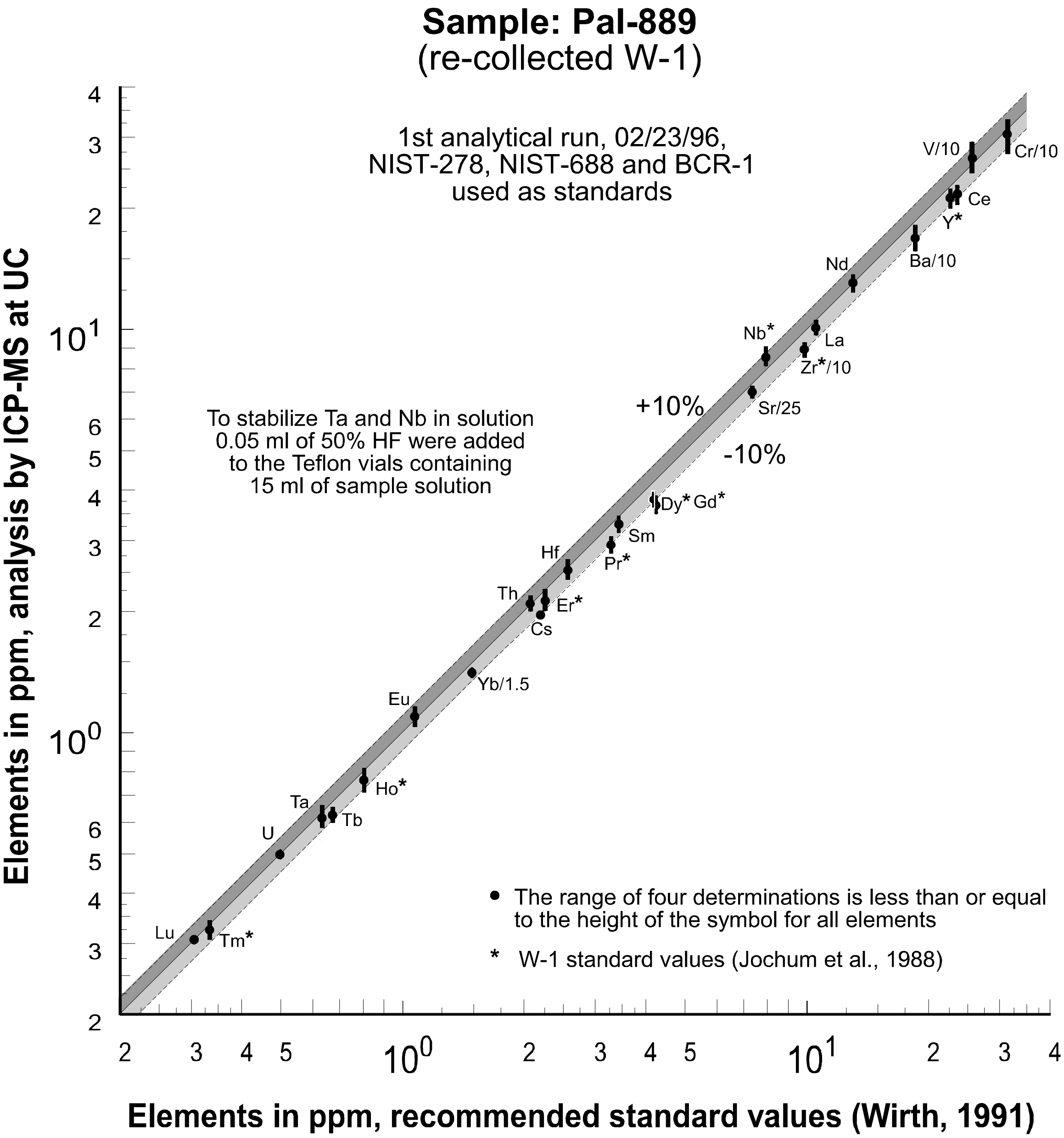


Figure E13

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. The agreement between the analytical results for Pal-889 and the selected standard values is very good, indicating good accuracy of the analysis, including Cr. Also in this diagram, data points of Ta and Nb plot within 10% of the standard values, suggesting Ta and Nb are stable in solution and, therefore, could be analyzed with very good accuracy and precision.

elements is within ± 10% of the recommended standard values of BCR-1. Only two determinations of Lu and Nb deviate more than +10% from the corresponding standard values, and two determinations of Tm and three determinations of Cr deviate more than -10%. Nonetheless, the average of eight determinations of all elements of BCR-1 agrees within ± 10% of the recommended standard values. Furthermore, good agreement exists between the four determinations of Pal-889 and the recommended standard values (figure E13). The standard values of W-1 for Pr and Gd, used to supplement missing standard values of Pal-889, are more than 10% higher than the measured values of Pr and Gd. Possibly, this is due to real differences between Pal-889 and W-1 (table E5). As pointed out in section E.6.3.1, real differences do exist between Pal-889 and W-1 based on significantly different Cr and Cs values.

The eight determinations of Cou-Il-6 agree well with the results from the first test run and also with the analysis at WSU (table E16), confirming good accuracy of the analysis.

E.8.2.4 Resolution of problem with Ta and Nb

The auto sampler tubes containing solutions of BCR-1, Pal-889 and Cou-IL-6 were evenly distributed throughout the entire run. If Ta and Nb were not stable in solution for at least the duration of the analytical run, poor precision and/or accuracy would have been the result. Apparently, addition of HF to all sample and standard solutions in this analytical run stabilized Ta and Nb as indicated by the good precision (figure E11) and accuracy (figures E12 and E13) for Ta and Nb. This clearly demonstrates the effectiveness of adding a complexing agent to the analytical solutions to stabilize Ta and Nb in solution. This technique, adding HF to the solutions, was developed at Washington State University and has been applied to subsequent runs with great success. It is also important to note that the HF concentration in the analytical solutions is so low, that damage to the glass spray chamber of the ICP-MS instrument has never been observed even after several years of applying this technique (C. Knaack, personal communication, 1995).

E.8.3 Second analytical run, 08/19/96

E.8.3.1 Limits of detection

The limits of detection for the second analytical run are presented in table E10 together with the mean values of twelve analyses of BCR-1 and of two analyses of Pal-889 and Cou-IL-6. Two digestions of each sample were analyzed once, and the average of obtained elemental concentrations are presented in appendix F. Similar to previous runs, the detection limits of Cr, Zr, Ba, and Pb are relatively higher than of the other elements. However, this is not a problem in that all determined elemental concentrations are well above the detection limits.

E.8.3.2 Precision

Four auto sampler tubes were filled with solutions of BCR-1 left from the first analytical run and analyzed in addition to four aliquots of two new digestions of BCR-1. Accordingly, each of the four sets of standards and blanks (figure E1) consisted of the two NIST-standards, and two new and one old BCR-1 solution (stored in a Teflon vial). Consequently, twelve determinations of elemental concentrations in BCR-1 were made as indicated in figure E14. The old solution of BCR-1 was used to test the long-term stability of Ta and Nb in solution.

The precision is based on twelve analyses of BCR-1 (treated as unknown), and excellent precision are indicated by less than 3% relative standard deviations for all elements (figure E14). There was no systematic difference observed between new and old BCR-1 solutions suggesting that all elements, including Ta and Nb, are stable in solution stored in Teflon vials for long periods of time (>1/2 year). Both analyses of Pal-889 and Cou-Il-6 indicate very good reproducibility (table E10), confirming the excellent precision achieved in the second analytical run.

4.8.3.3 Accuracy

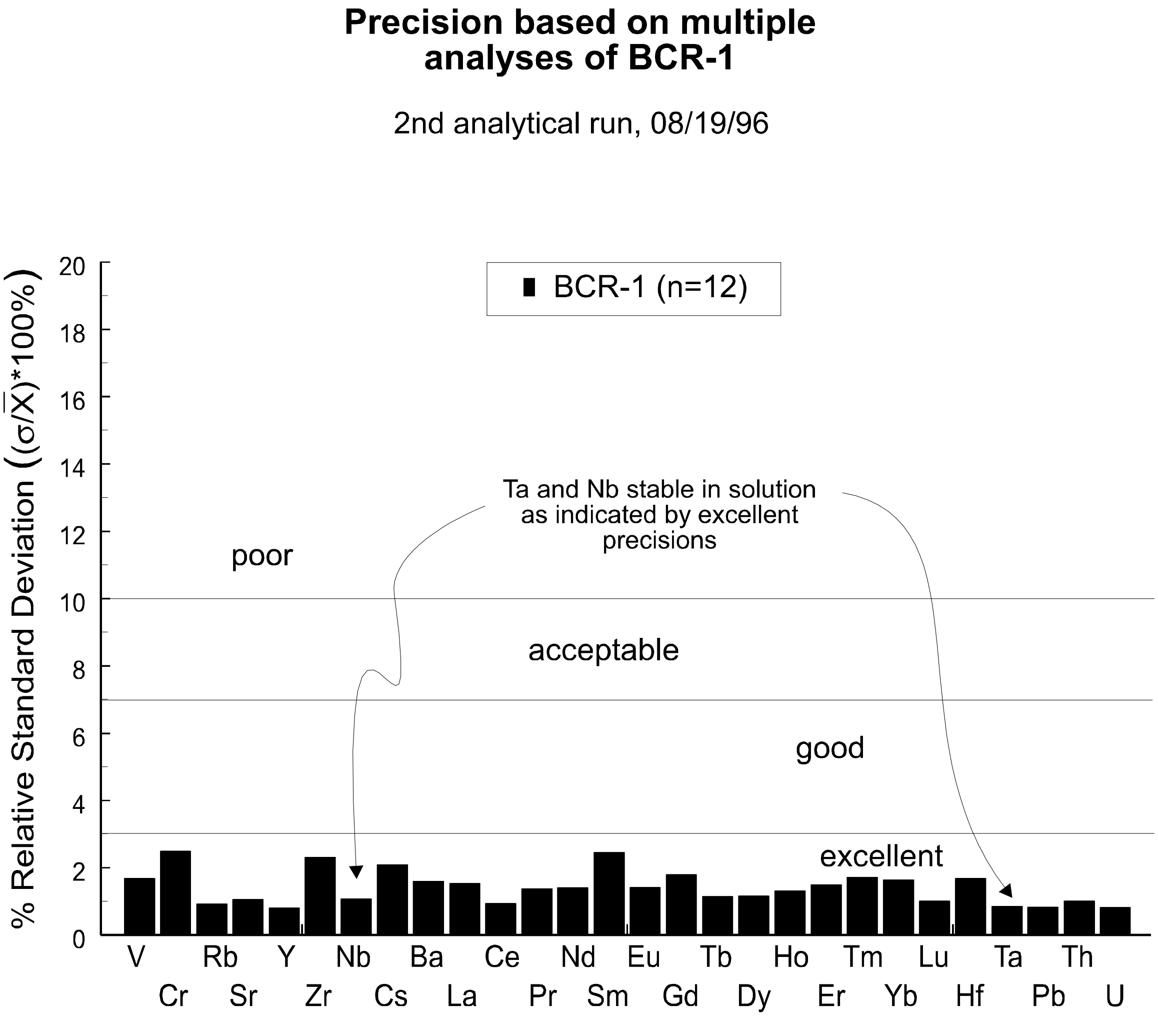
As illustrated in the comparative plot in figure E15, all elements, except Lu and Cr, were determined within ±10% (most within ±5%) of the recommended standard values of BCR-1 indicating very

Table E10: Results of second analytical run, 08/19/96

	Detection	**BCR-1**		**Pal-889**		**Cou-IL-6**	
	Limits	mean	error	doublicate analysis		doublicate analysis	
Element	in ppm	(n=8)	1 σ	no.1	no.2	no.1	no.2
V	0.092	398	7	261	264	492	493
Cr	0.34	10.4	0.3	292	297	81	81
Rb	0.037	47.3	0.4	30.5	30.8	12.7	12.5
Sr	0.07	329	3	181	181	268	266
Y	0.028	34.6	0.3	21.9	22.1	38.1	38.0
Zr	4.8	184	4	92.9	93.0	117	116
Nb	0.012	15.4	0.2	8.77	8.70	5.60	5.55
Cs	0.0062	0.97	0.02	2.04	2.01	2.96	2.92
Ba	0.42	714	11	180	181	59.7	57.9
La	0.0059	26.5	0.4	10.2	10.3	6.56	6.46
Ce	0.020	54.7	0.5	22.3	22.4	17.2	16.9
Pr	0.0058	7.02	0.09	2.94	2.92	2.72	2.66
Nd	0.011	30.8	0.427	12.7	13.1	13.7	13.9
Sm	0.0069	6.51	0.16	3.37	3.32	4.30	4.22
Eu	0.0015	1.98	0.03	1.08	1.13	1.35	1.36
Gd	0.0036	6.86	0.12	3.71	3.77	5.60	5.47
Tb	0.0012	1.07	0.01	0.619	0.599	0.957	0.951
Dy	0.0034	6.40	0.07	3.72	3.80	6.30	6.20
Ho	0.0013	1.29	0.02	0.751	0.773	1.32	1.31
Er	0.0032	3.51	0.05	2.16	2.26	3.81	3.89
Tm	0.0011	0.512	0.009	0.319	0.320	0.597	0.598
Yb	0.0046	3.32	0.05	2.00	2.02	3.77	3.76
Lu	0.0012	0.578	0.006	0.301	0.304	0.581	0.572
Hf	0.028	5.15	0.09	2.48	2.51	3.24	3.22
Ta	0.003	0.764	0.006	0.600	0.606	0.314	0.315
Pb	0.31	14.2	0.1	4.37	4.48	0.661	0.574
Th	0.0046	6.12	0.06	2.06	2.06	0.526	0.554
U	0.0036	1.72	0.01	0.494	0.483	0.186	0.183

standard deviation : $\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively
see tables 14, 15 and 16 for compilation of analytical results
for BCR-, Pal-889, and Cou-IL-6, respectively


Precision based on multiple analyses of BCR-1

2nd analytical run, 08/19/96

Figure E14

Diagram illustrating the precision of the analysis of the second analytical run. Four aliquots of two new digestions of BCR-1 and four aliquots of an old BCR-1 solution were analyzed. The old BCR-1 solution left from the first analytical run was stored in a Teflon vial. Excellent precision of the analysis is indicated by < 3% relative standard deviation for all elements. This suggests, that all elements, including Ta and Nb were stable in solution for long periods of time (~ 1/2 year). Furthermore, extremely good run performance of the ICP-MS instrument is demonstrated as well as high reproducibility preparing samples by acid digestion (i.e., there are no systematic differences between new and old BCR-1 solutions).

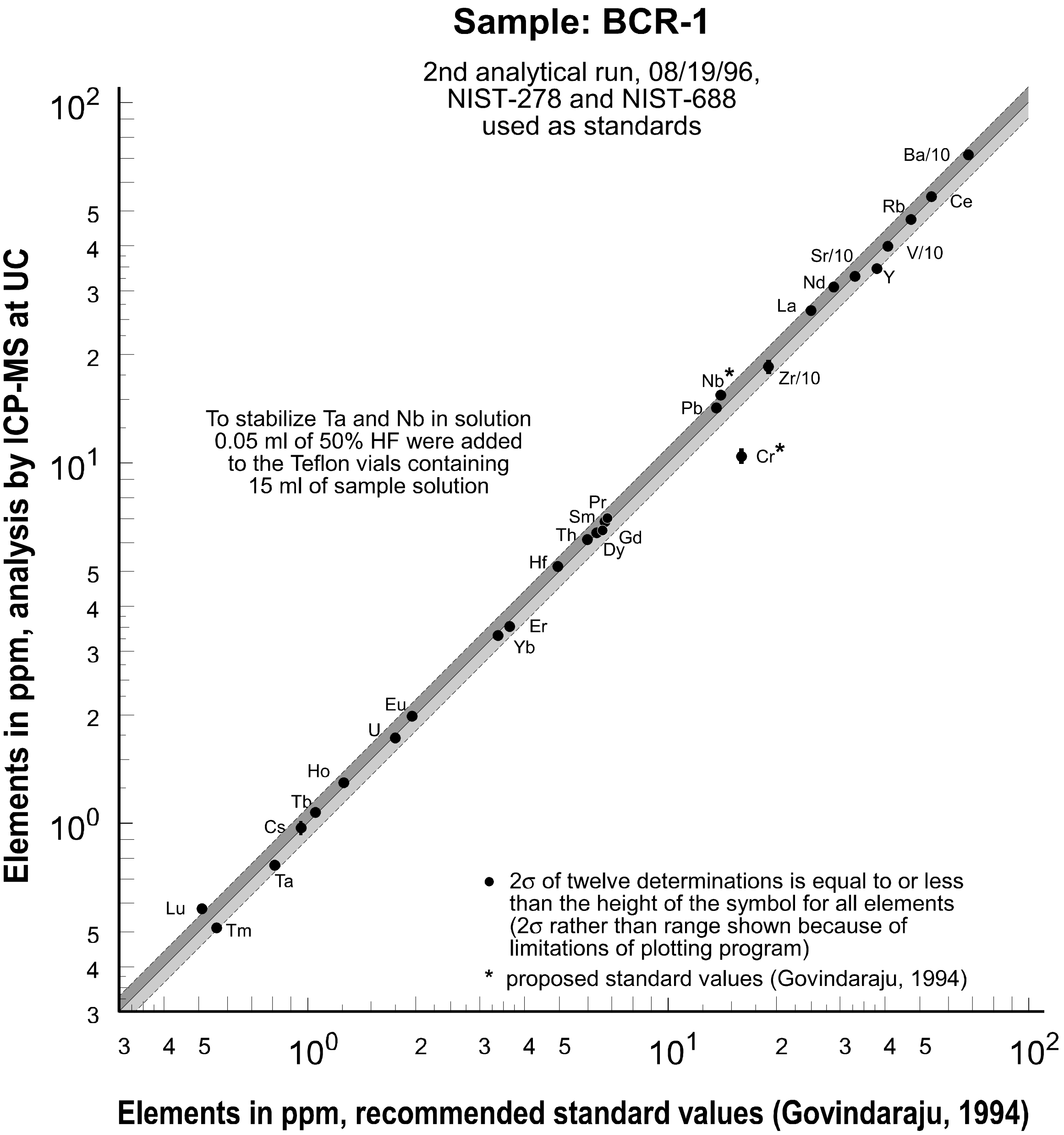


Figure E15

Comparative plot of the analytical results of the second analytical run versus the recommended standard values of BCR-1 (Govindaraju, 1994). The mean values of twelve analyses of BCR-1 plot close to or on the line with slope = 1, indicating excellent accuracy of the analysis. Generally, the analytical results agree with the standard values within 10% (most within 5%). Furthermore, good accuracy of Ta and Nb was obtained verifying Ta and Nb were stable in solution. The analytical results of Cr are once again lower than the standard value suggesting the standard value of Cr might be too high.

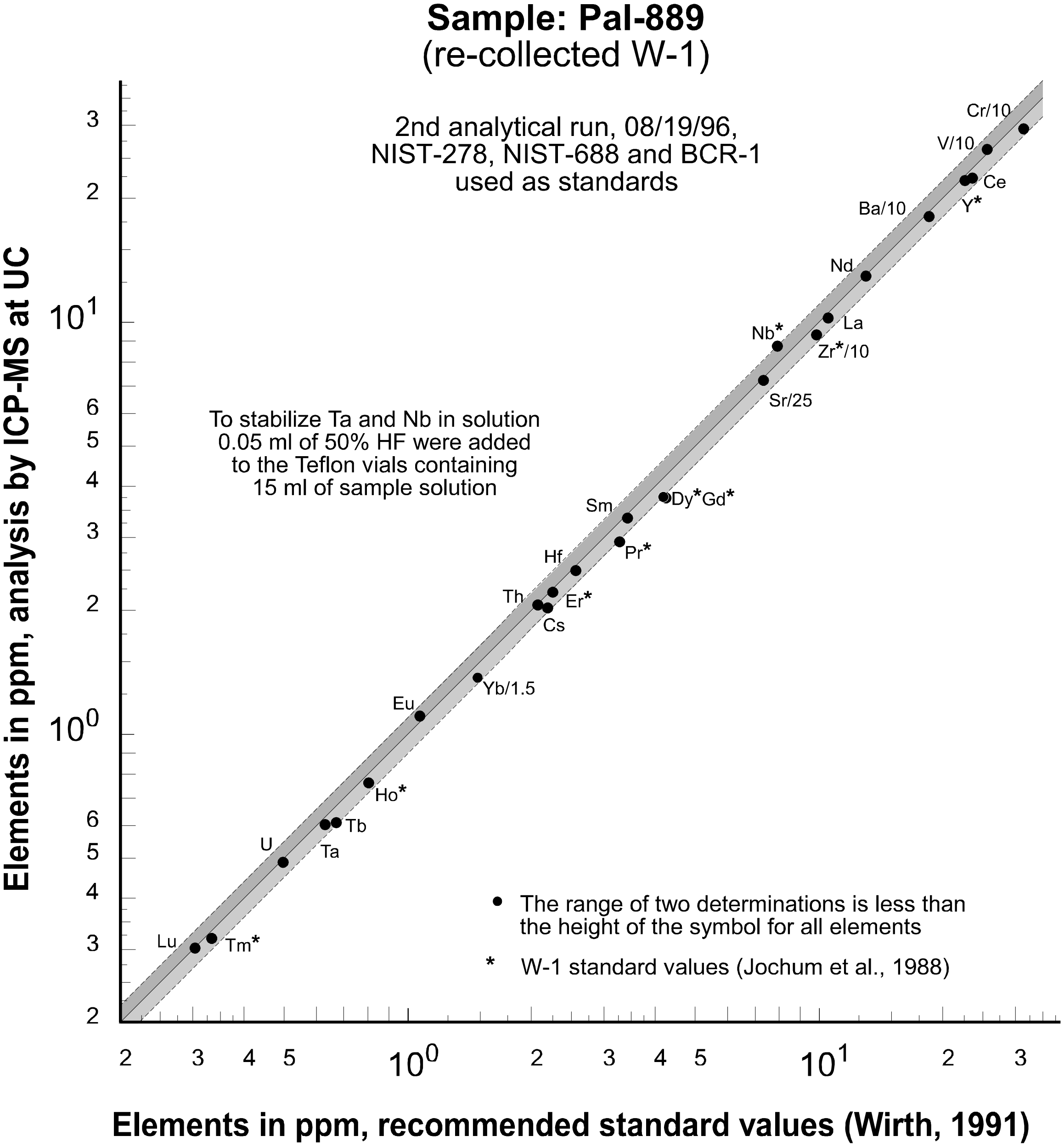


Figure E16

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. The agreement between the analytical results for Pal-889 and the selected standard values is very good, indicating good accuracy of the analysis, including Cr. Also in this diagram, data points of Ta and Nb plot within 10% of the standard values, suggesting Ta and Nb are stable in solution and, therefore, could be analyzed with very good accuracy and precision.

good accuracy. It appears that either the determination of Cr using ICP-MS is not very accurate in samples with low Cr concentrations or the reference value of BCR-1 is high. Note that consistently lower Cr values were obtained for BCR-1 in previous runs (12 ppm and 14.5 ppm), suggesting the proposed value of Govindaraju (1994) is indeed high. Also similar to previous runs, the Cr concentration in Pal-889 was analyzed with good accuracy (figure E16), suggesting there are no significant problems analyzing Cr using ICP-MS.

In contrast to BCR-1, Lu was determined in Pal-889 matching exactly the recommended standard value (figure E16). This suggests that the results for Lu are more accurate when three rock standards were used for the calibration instead of only the two NIST-standards. Furthermore, all other elements in Pal-889 were analyzed with good accuracy as indicated by small or no disagreement between measured and recommended standard values (figure E16). The discrepancies between analytical results for Pal-889 and W-1 standard values (e.g. Pr, Dy and Gd) are very similar to the differences observed in earlier runs (figures E4, E9, and E13). Most likely, the discrepancies are due to actual differences between Pal-889 and W-1.

Both analyses of Cou-IL-6 agree well with earlier analyses at Union College and at WSU (table E16) giving further evidence for the good accuracy achieved in the second analytical run.

E.8.3.4 Evaluation of dissolution

It was demonstrated in the first test run that incomplete dissolution of samples is not a problem in this study (section E.7.1.7). This observation is also in agreement with the study of Jarvis (1990) showing that Y, Zr, Nb, Hf, Ta, Pb, Th, U, and the REE can be measured with good accuracy in a range of silicate (i.e., basalt, dolerite, andesite, norite) and carbonate (i.e. limestone, dolomite) matrices, both in samples brought into solution by acid digestion and lithium metaborate fusion. Jarvis (1990) observed poor agreement between reference values of Zr, Ta, Nb, and HREE and the analytical results only when rock samples containing refractory minerals, such as zircon and rutile (i.e. granite, syenite, shale), were brought into solution by acid digestion. Evidently, zircon and rutile did not dissolve using open acid digestion. Since samples analyzed in this study (i.e. subalkaline basalts and andesites) do not contain refractory minerals such as zircon and rutile, inaccurate determination of elemental concentrations due to incomplete dissolution of samples is very unlikely.

Possibly, further evidence for complete dissolution of samples in this study was obtained through repeating the duplicate analysis of samples analyzed in the second test run. Two separate digestions of 20 samples were prepared and analyzed in the second test run (section E.7.2.1). Duplicates of 19 of these 20 samples were prepared and analyzed in the first and second analytical runs (11 and 8 samples, respectively), because of problems with Ta and Nb in the second test run (section E.7.2.6). Thus, a total of four separate digestions of each of these 19 samples were prepared and analyzed. Supposing four 0.1g-units of a sample weighed in four different Teflon vials would not dissolve completely, systematic and relatively large variations in the analytical data of the four digestions of this sample should be expected (this is based on the assumption that four 0.1g-units of a sample would dissolve differently if incomplete dissolution would occur). The analytical results for all samples, however, indicate high reproducibility suggesting that incomplete dissolution was not a problem. The relative standard deviations of the multiple analyses of the 19 samples are presented in table E13. As shown, the variations in the analytical results are generally less than 5% on average, indicating very good precision of the ICP-MS analysis as well as completeness of dissolution of the samples.

E.8.4 Third analytical run, 09/10/97

E.8.4.2 Limits of detection

As before, BCR-1 solutions left from the second analytical run were re-analyzed together with two new digestions of BCR-1. Consequently, twelve determinations of elemental concentrations in BCR-1 were made. The limits of detection for the third analytical run are listed in table E11 together with the mean values of twelve analyses of BCR-1 and of four analyses of Pal-889 and Cou-IL-6. Compared to previous runs, the detection limit of Ta is about ten times higher than normal, which is still rather low (0.013 ppm). The reason for the higher detection limit is not known and was still significantly below values in most samples. The results of the third analytical run are presented in appendix F, and the listed concentrations represent the mean value of duplicate analysis made for two digestions per sample (note that the Ta values obtained in the fourth analytical run are preferred over the Ta data of the third analytical run, see section 8.5.4).

E.8.4.3 Precision

The precision, based on the multiple analyses of BCR-1 is excellent for most elements as indicated by ≤3% relative standard deviations (figure E17). Only Cr is determined with poor precision in BCR-1 possibly due to difficulties analyzing low levels of Cr. Similar to the second analytical run, there are no systematic differences observed between stored BCR-1 solutions and the new solutions of BCR-1. The good reproducibility between old and new solutions of BCR-1 not only indicates a high degree of consistency preparing the samples, but also that all elements are stable in solution stored in Teflon containers for more than a year.

E.8.4.4 Accuracy

The comparison of the analytical results of BCR-1 with recommended standard values indicates that all elements (except Cr) were accurately determined (figure E18). The mean values as well as $\pm 2\sigma$ of twelve determinations plot within 10% of the recommended standard values.

It was noted in previous runs that the analytical results of Cr for BCR-1 are consistently lower than the proposed standard value (16 ppm). Also in this analytical run, the mean value is significantly lower than the reference value suggesting the proposed standard value is high.

As illustrated in figure E19, Pal-889 was analyzed with good accuracy as well, including Cr. All elements, except Nb, were determined within ±10% of the recommended standard values. Measured Nb concentrations of Pal-889 from this and previous runs are higher by about 0.5 to 1 ppm than the adopted reference value of 7.91 ppm (compare figures E13, E16 and E19) suggesting that the selected reference value could be too low. Actually, an alternative standard value of Nb is listed in table 5 (9.9 ppm recommended by Govindaraju, 1994) which is significantly higher than the selected reference value (ID-SSMS). Consequently, depending on the selection of the reference value, analytical data of Nb for Pal-889

Table E11: Results of third analytical run, 09/10/97

	Detection	BCR-1		Pal-889		Cou-IL-6	
	Limits	mean	error	mean	error	mean	error
Element	in ppm	(n=12)	1 σ	(n=4)	1 σ	(n=4)	1 σ
V	0.77	393	18	275	17	476	16
Cr	1.3	10.6	1.3	312	11	85	1
Rb	0.018	47.6	1.0	30.1	0.1	13.1	0.2
Sr	0.45	335	8	173	2	273	4
Y	0.045	35.3	1.0	22.1	0.2	40.2	0.9
Zr	3.8	194	6	100.5	4.4	131	5
Nb	0.020	14.5	0.5	8.51	0.34	5.70	0.20
Cs	0.0046	0.96	0.01	2.15	0.03	2.96	0.04
Ba	0.78	688	11	193	1	59.7	0.6
La	0.012	24.6	1.0	10.9	0.1	6.51	0.09
Ce	0.096	53.6	1.4	23.6	0.0	17.7	0.1
Pr	0.0042	6.79	0.24	3.15	0.01	2.81	0.02
Nd	0.016	28.4	0.982	13.2	0.2	14.2	0.2
Sm	0.0048	6.59	0.19	3.46	0.05	4.45	0.07
Eu	0.0015	1.94	0.04	1.12	0.02	1.41	0.02
Gd	0.0049	6.58	0.15	3.89	0.09	5.68	0.12
Tb	0.00082	1.04	0.02	0.649	0.022	0.984	0.019
Dy	0.0053	6.20	0.14	4.01	0.09	6.47	0.09
Ho	0.00094	1.25	0.03	0.811	0.016	1.37	0.02
Er	0.0030	3.48	0.06	2.35	0.07	3.99	0.07
Tm	0.00077	0.531	0.011	0.360	0.010	0.623	0.010
Yb	0.0034	3.29	0.07	2.12	0.04	3.84	0.07
Lu	0.00055	0.517	0.010	0.314	0.007	0.552	0.006
Hf	0.015	4.95	0.07	2.62	0.04	3.27	0.04
Ta	0.037	0.821	0.009	0.677	0.008	0.330	0.006
Pb	0.18	14.0	0.4	4.75	0.23	0.598	0.013
Th	0.013	5.87	0.23	2.02	0.01	0.520	0.005
U	0.00088	1.71	0.05	0.492	0.006	0.181	0.003

standard deviation : $\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively
see tables 14, 15 and 16 for compilation of analytical results
for BCR-, Pal-889, and Cou-IL-6, respectively

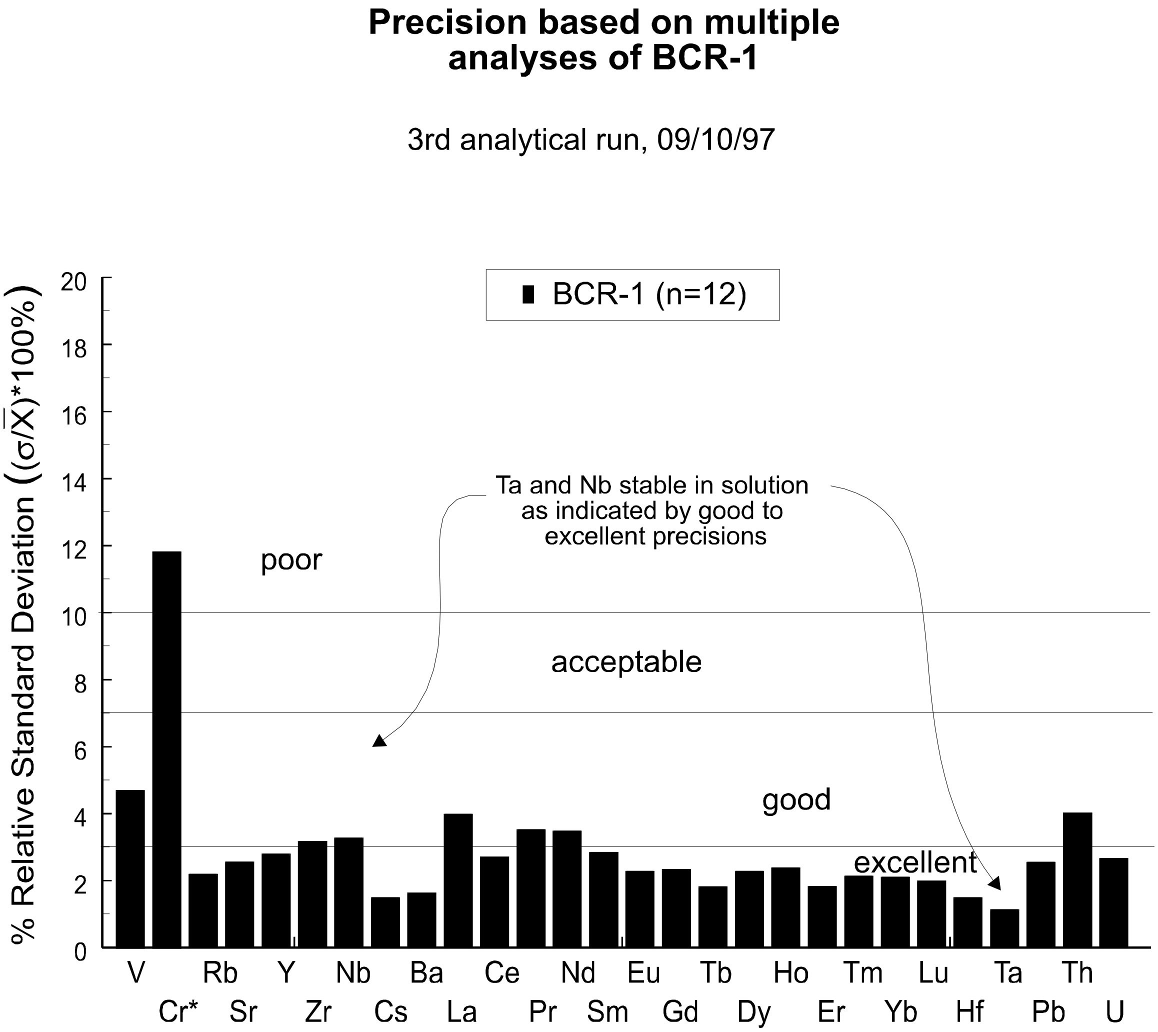


Figure E17

Diagram illustrating the precision of the analysis of the second analytical run. Four aliquots of two new digestions of BCR-1 and four aliquots of an old BCR-1 solution were analyzed. The old BCR-1 solution left from the second analytical run was stored in a Teflon vial. Excellent precision of the analysis is indicated by ~3% relative standard deviation for most elements. Good run performance of the ICP-MS instrument is demonstrated as well as high reproducibility preparing samples by acid digestion (i.e., there are no systematic differences between new and old BCR-1 solutions).

* The high relative standard deviation for Cr is misleading in that the Cr level in BCR-1 is very low (proposed standard value of 16 ppm). The precision of Cr for samples with higher levels of Cr is very good as demonstrated with the duplicate analyses of Pal-889 and Cou-IL-6 (table E11).

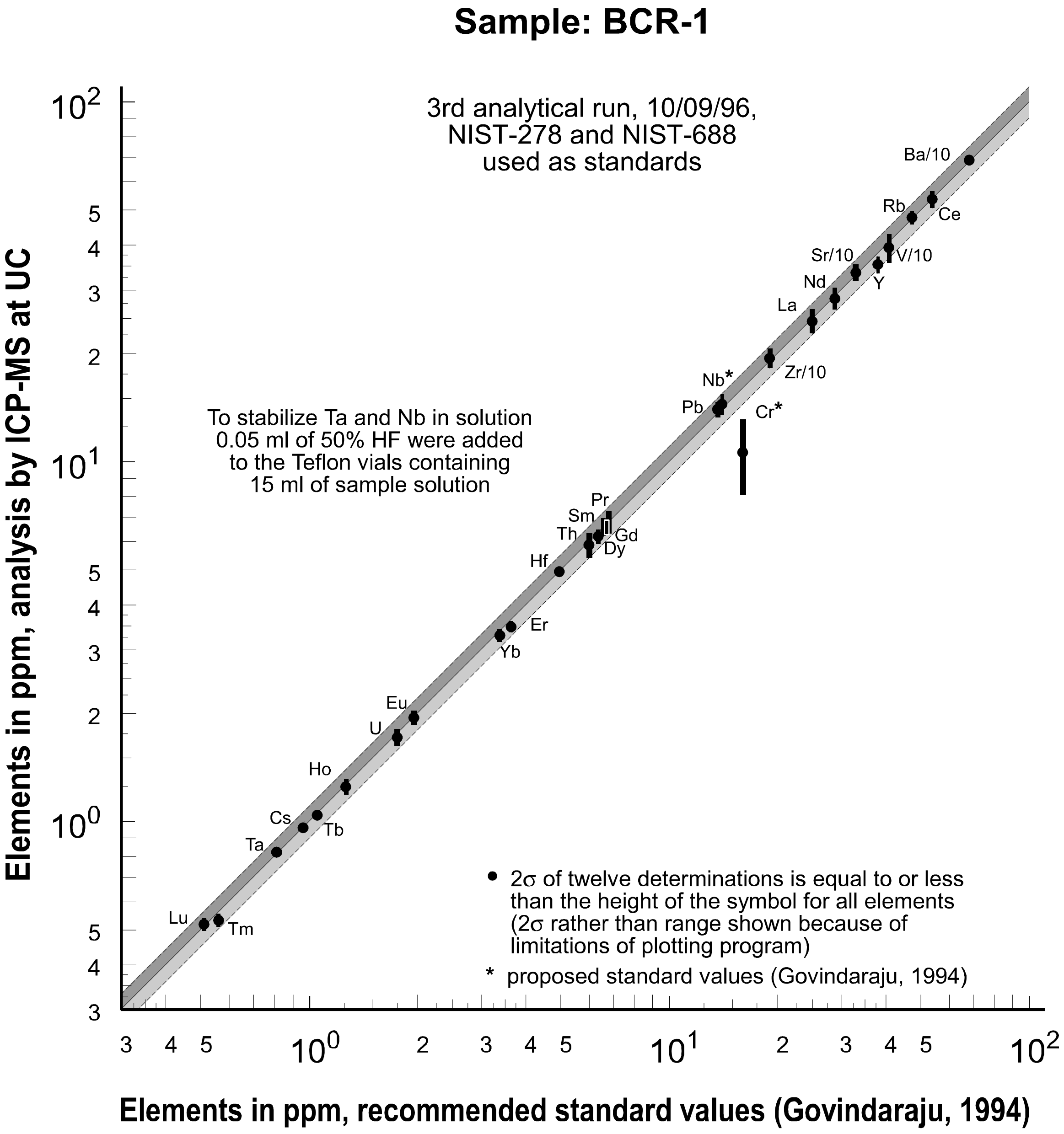


Figure E18

Comparative plot of the analytical results of the third analytical run versus the recommended standard values of BCR-1 (Govindaraju, 1994). All data points plot close to or on the line with slope = 1, indicating excellent accuracy of the analysis. The analytical results generally agree with the standard values within 10% (most within 5%). Furthermore, good analytical results obtained for Ta and Nb suggest that Ta and Nb are stable in solution. The analytical results of Cr are once again lower than the standard value, suggesting the proposed standard value of Cr might be too high.

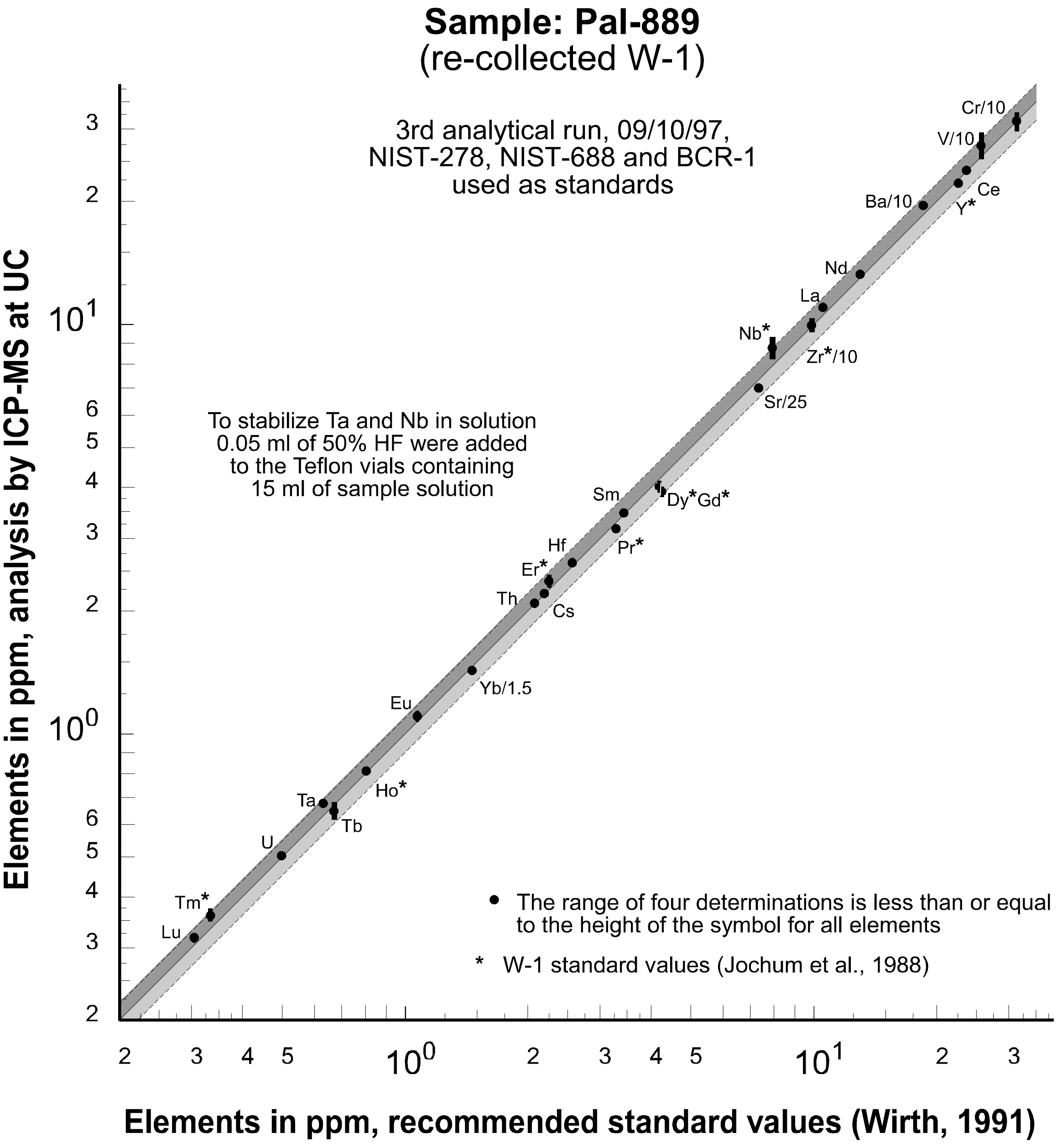


Figure E19

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. The agreement between the analytical results for Pal-889 and the selected standard values is very good, indicating good accuracy of the analysis, including Cr. Note that the analytical data of Nb obtained in all analytical runs are consistently higher than the standard value of Nb (see figures E12 and E15), suggesting the selected W-1 standard value is too low (see text).

(8.40 to 8.74 ppm) would either plot significantly above the line with slope = 1 (reference value of 7.91 ppm selected) or significantly below the line with slope = 1 (reference value of 9.9 ppm selected).

E.8.5 Fourth analytical run, 09/19/97

E.8.5.1 Limits of detection

The analysis of some samples analyzed in the third analytical run was repeated, because the detection limits of Ta were approximately ten times higher in the third analytical run (table E11) than those in the preceding runs (tables E9 and E10). Samples with Ta concentrations near or below the unusually high detection limits were re-analyzed. New solutions of the samples and standards were not prepared for the fourth analytical run; that is, the same standard and sample solutions were analyzed as in the third analytical run.

In the fourth analytical run, lower detection limits of Ta were obtained (table E12), providing accurate values for the re-analyzed samples (Appendix F). The Ta values obtained in run 3 were replaced by Ta values obtained in run 4 in the data table in appendix F.

E.8.5.2 Precision

The precision is based on 6 analyses of BCR-1 treated as unknown. Unlike the other analytical runs, the light REE and medium REE were determined with poor to acceptable precision (figure E20). All other elements were analyzed with good to excellent precision. The generally poor precision obtained for the fourth run must be due to a decline of the performance of the ICP-MS instrument, because the same solutions were analyzed with much higher precision in the third analytical run (figure E17). Apparently, a vacuum leak occurred in the ICP-MS instrument that was repaired between third and fourth analytical run. Nonetheless, Ta was determined with excellent precision, not only in BCR-1 (figure E19), but also in Cou-Il-6 and Pal-889 (table E12).

Table E12: Results of fourth analytical run, 09/19/97*

(partial repeat of third analytical run: same sample and standard solutions re-analyzed)

Element	**Detection Limits** in ppm	**BCR-1** mean (n=6)	error 1 σ	**Pal-889** doublicate analysis no.1	no.2	**Cou-IL-6** doublicate analysis no.1	no.2
V	0.143	370	13	246	265	467	476
Cr	0.71	13.3	3.0	302	325	84	83
Rb	0.112	47.0	3.2	27.4	29.5	12.0	12.4
Sr	0.22	331	16	178	188	269	281
Y	0.024	34.5	1.9	23.0	24.9	37.3	37.5
Zr	0.4	185	5	97.7	99.5	118	119
Nb	0.019	15.3	0.4	8.15	8.66	5.59	5.58
Cs	0.0059	1.05	0.04	2.26	2.12	2.86	2.81
Ba	0.71	738	55	192	177	60.3	57.1
La	0.0109	27.4	2.6	11.0	10.0	6.63	6.28
Ce	0.033	56.0	5.7	24.6	22.5	17.9	16.5
Pr	0.0036	7.20	0.82	3.32	3.07	2.75	2.58
Nd	0.029	31.2	4.448	13.7	12.3	14.2	13.1
Sm	0.0078	6.58	0.90	3.61	3.21	4.41	4.04
Eu	0.0069	1.92	0.13	1.13	1.00	1.34	1.23
Gd	0.0079	6.78	0.85	4.24	3.73	5.70	5.22
Tb	0.0018	1.05	0.12	0.710	0.625	1.005	0.920
Dy	0.0155	6.36	0.67	4.18	3.78	6.48	6.09
Ho	0.0022	1.28	0.12	0.841	0.776	1.39	1.30
Er	0.0030	3.47	0.32	2.42	2.17	4.02	3.79
Tm	0.0011	0.508	0.040	0.355	0.324	0.609	0.582
Yb	0.0041	3.29	0.18	2.24	2.12	3.88	3.76
Lu	0.0021	0.568	0.026	0.314	0.293	0.592	0.576
Hf	0.009	4.96	0.17	2.63	2.48	3.33	3.22
Ta	0.0029	0.753	0.020	0.633	0.626	0.295	0.299
Pb	0.06	13.6	0.2	4.59	4.24	0.677	0.597
Th	0.0045	6.06	0.19	2.03	2.11	0.549	0.542
U	0.0017	1.70	0.03	0.492	0.502	0.184	0.177

standard deviation : $\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively

see tables 14, 15 and 16 for compilation of analytical results
for BCR-, Pal-889, and Cou-IL-6, respectively

* only Ta values for samples used

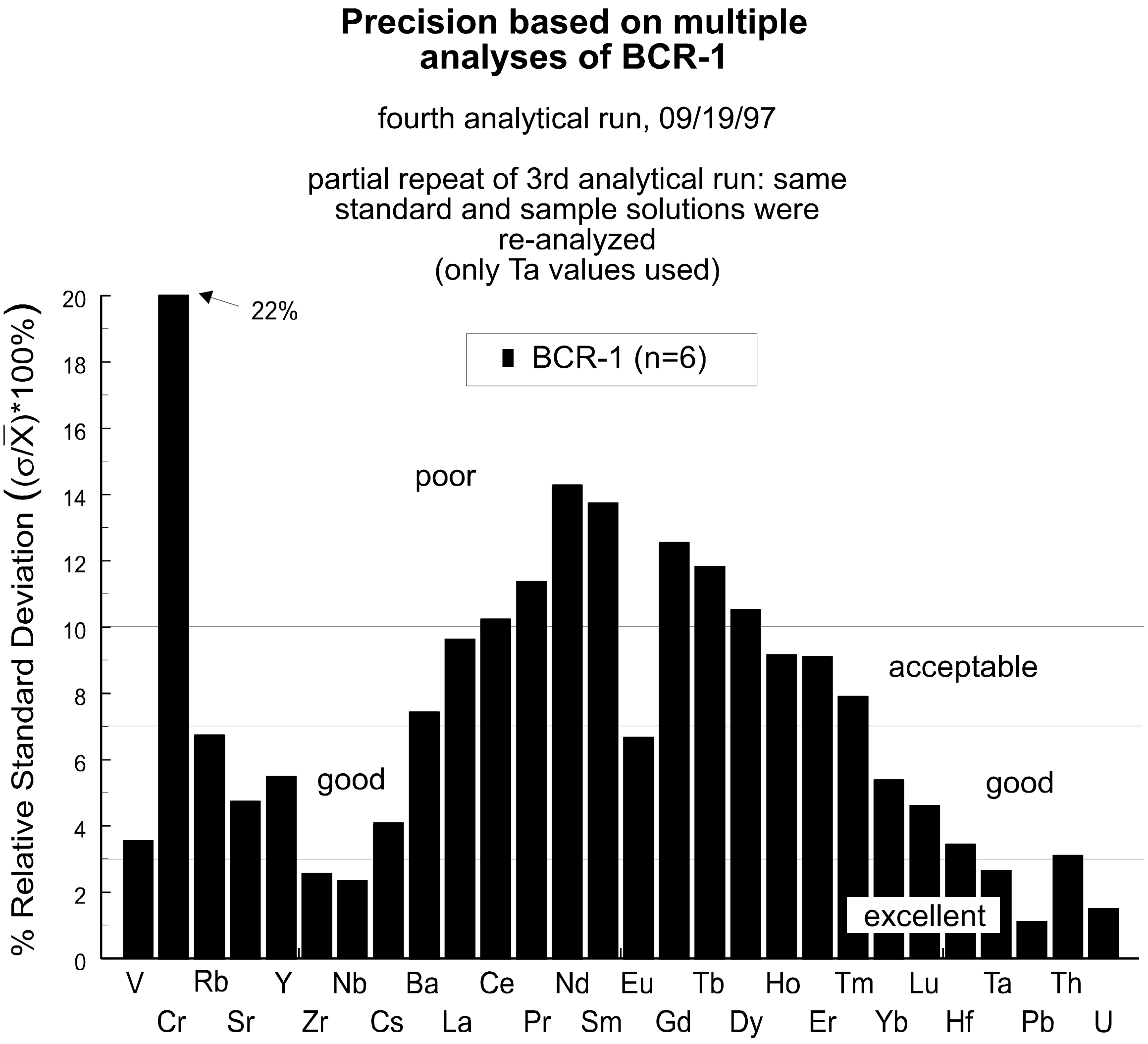


Figure E20

Diagram illustrating the precision of the analysis of the fourth analytical run. The standard and sample solutions prepared for the third analytical run were stored in Teflon vials and re-analyzed in the fourth analytical run (i.e., the samples with very low levels of Ta, near or below detection of third analytical run, were re-analyzed). Compared to the third analytical run (figure 17), the overall precision of the fourth analytical run is notably worse suggesting that a decline of the performance of the ICP-MS instrument occurred (see text). Nonetheless, the analytical results of Ta obtained in the fourth analytical run are very good as indicated by very low detection limits (table 12), good accuracy (figures 21 and 22) , and excellent precision (< 3% relative standard deviation).

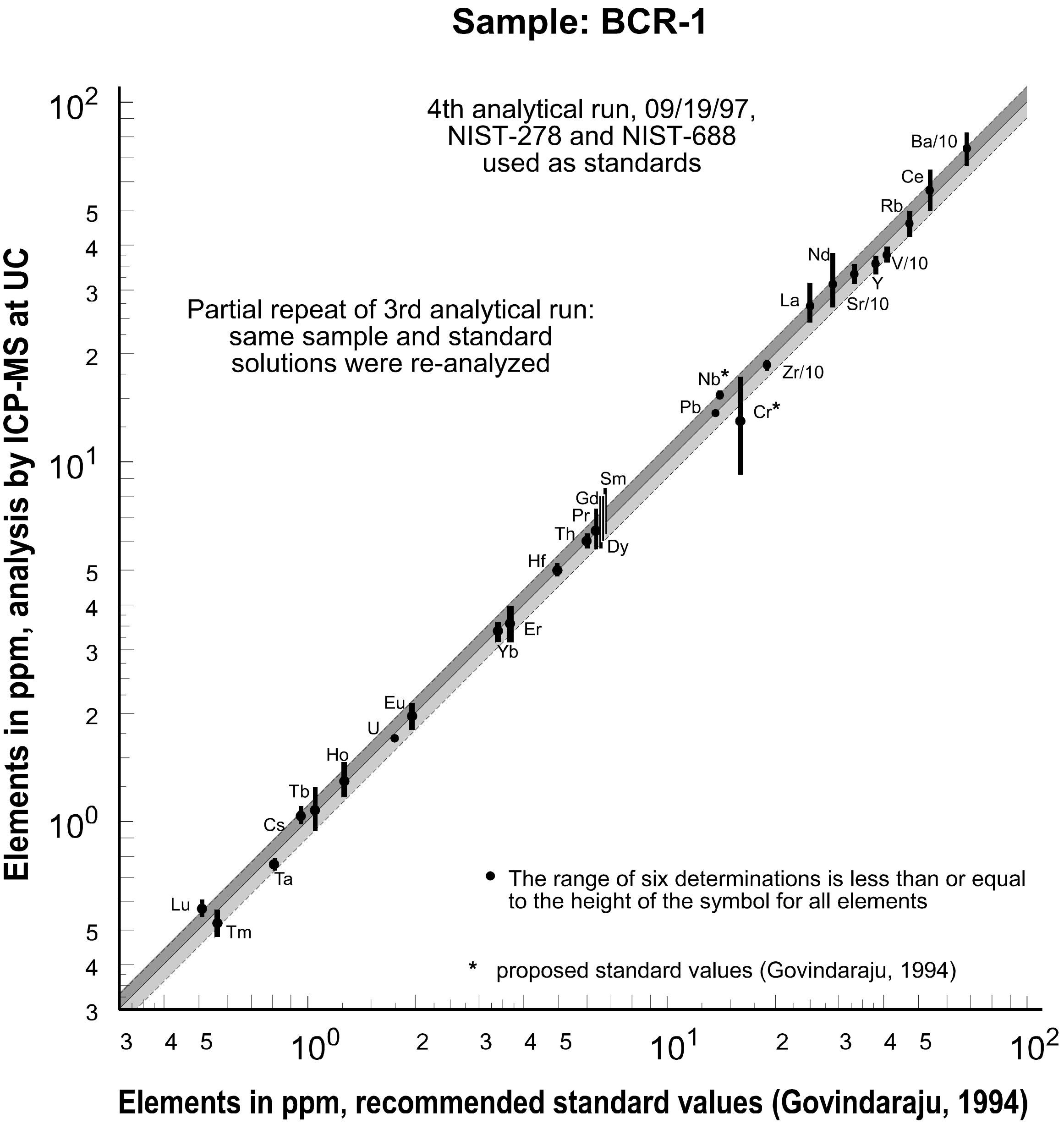


Figure E21

Comparative plot of the analytical results of the fourth analytical run versus the recommended standard values of BCR-1 (Govindaraju, 1989). Many data points deviate significantly from the line with slope = 1, indicating poor accuracy of La, Ce, Pr, Nd, Sm, Gd, Tb, and Dy (elements analyzed with poor precision). For the other elements, the analytical results generally agree with the standard values within 10%. Furthermore, good analytical results obtained for Ta and Nb suggest that Ta and Nb are stable in solution. Even though the precision of Cr is extremely poor in this run, the analytical results of Cr are once again lower than the reference value, suggesting the proposed standard value of Cr might be too high.

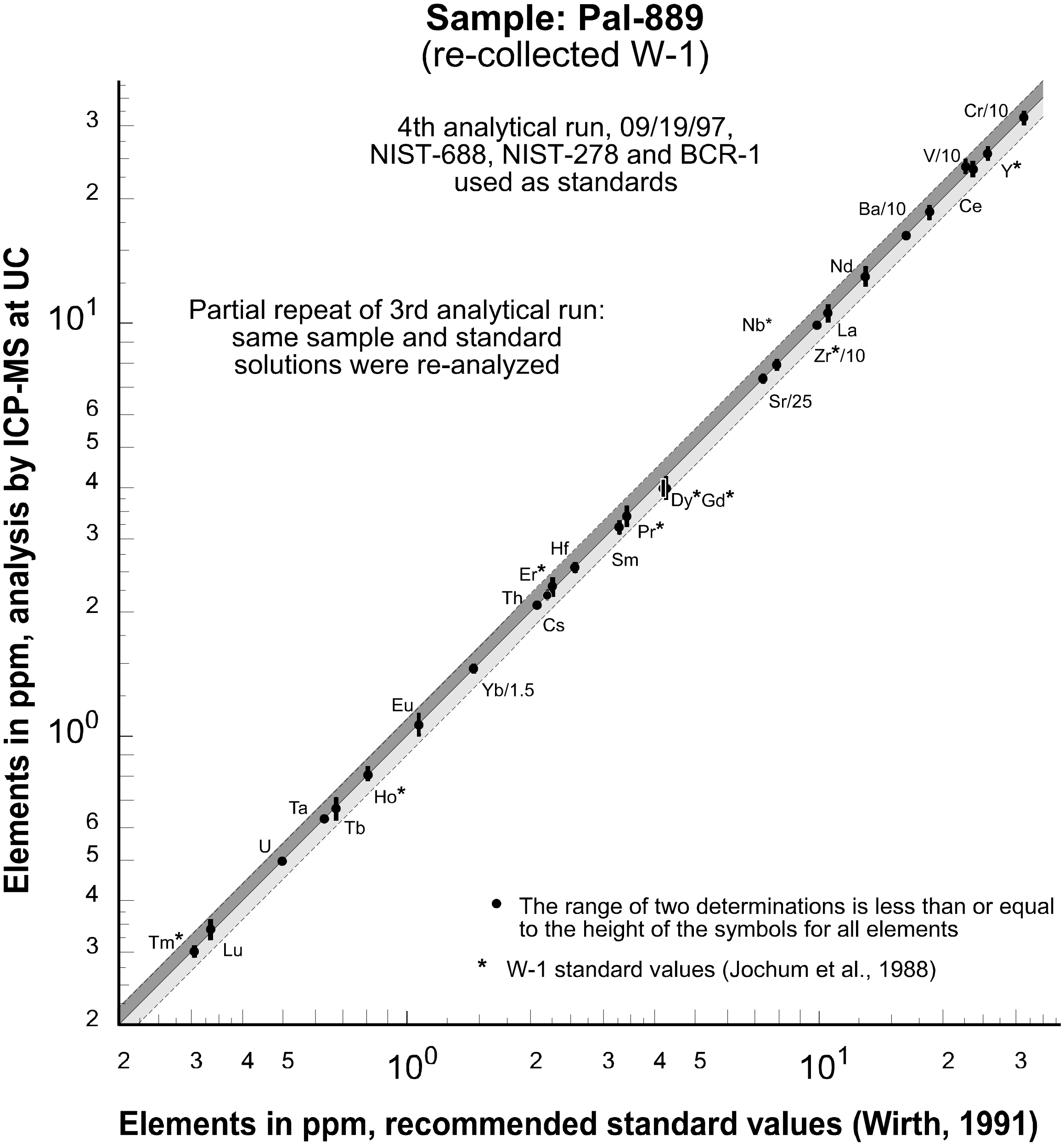


Figure E22

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. The agreement between the analytical results for Pal-889 and the selected standard values is surprisingly good considering the poor precision of some elements analyzed in the fourth run (figure 20). Ta was analyzed with excellent precision (figure 20), good accuracy (figure 21 and 22) and low detection limits (table 12). The Ta values obtained with fourth analytical run are preferred over those of the third run because of relatively high detection limits for Ta in the third analytical run.

E.8.5.3 Accuracy

The agreement between recommended standard values and the average of measured values of BCR-1 is good (figure E21). Generally, two or three of the twelve determinations of the light REE and medium REE for BCR-1 are significantly higher than the corresponding standard values due to the poor precision for these elements. It is surprising that both analyses of Pal-889 agree very well with the recommended standard values (figure E22), considering the large variations for BCR-1. Also, both analyses of Cou-Il-6 agree well with the results obtained earlier at UC and also with the analysis at WSU (table E16).

E.8.5.4 Selection of data

Because of the poor accuracy and precision determining the light REE and medium REE in BCR-1 (figure E20 and E21), only Ta values obtained in the fourth analytical run are used, and all other analytical data of this run are not reported in appendix F. The detection limits of Ta were ten times lower than in the third analytical run (table E12) and Ta was also determined with good accuracy (figure E21) and precision (figure E20). Therefore, the Ta concentrations obtained in the fourth analytical run are preferred over those of the third analytical run; that is, the Ta values obtained in run 3 were replaced by the Ta values obtained in run 4 (appendix F).

E.9 Comments on use of ICP-MS at Union College and conclusions

It was demonstrated in preceding sections that the analytical results obtained by ICP-MS at Union College are of high quality. Overall, high accuracy, very good precision and low detection limits were realized analyzing samples from the Oregon Coast Range ophiolite (and samples from the Josephine ophiolite). The following summary outlines the main points of the sections E7 and E8:

- Multiple analyses of solutions prepared from separate digestions (weighing of 0.1g of sample in a Teflon vial and dissolving is defined as a digestion of a sample, figure E1) show that sample preparation errors are very small, in general < 3% (table E7). Thus, sample preparation errors are within the precision of the analysis by ICP-MS.

- The complete dissolution of samples was verified using a synthetic standard in the first test run (section E.7.1.7). Furthermore, absence of chemically resistant minerals in analyzed samples (section E.8.3.4) and high reproducibility of analytical data (i.e., multiple analyses of solutions prepared from separate digestions) suggest that incomplete dissolution of the samples did not occur (tables E7 and E13).
- Ta and Nb were accurately analyzed in this study, only when HF was added to all sample and standard solutions to stabilize Ta and Nb in solution (section E.8.2.4). The problem with Ta and Nb has not been detected previously at Union College (K. Hollocher, personal communication 1995), even though HF has not been added to the solutions.
- The analysis of BCR-1 as an unknown sample is extremely accurate as indicated by comparing the analytical results for BCR-1 (obtained in analytical runs 1, 2 and 3) with the recommended standard values: V, Rb, Sr, Cs, Ba, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Hf, Th and U were analyzed within better than 2%; Zr, La, Nd, and Yb within better than 3%; Er, Ta, and Pb within better than 5%; and Y, Nb, Tm, and Lu within better than 8% of the recommended standard values of BCR-1.
- The precision analyzing the samples might be obtained from the average relative standard deviations listed in table E13 in addition to the relative standard deviations shown in figures E11, E14, and E17. The average relative standard deviation (1σ) for Dy, Ho, Er and Tm is estimated to be smaller than 3%; for Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm Eu, Gd, Tb, Yb, Lu, Hf, Ta and Th smaller than 4%; for V, Cr, Rb and U smaller than 8% and for Pb smaller than 10%.
- The analytical results obtained at Union College agree well with the ICP-MS data of the Washington State University Geoanalytical Laboratories (tables E15 and E16). Furthermore, the agreement is very good between the ICP-MS data obtained at Union College and the data obtained by other analytical techniques (figure E10, tables E15 and E16).
- Much poorer precision was obtained in the fourth analytical run than in the third analytical run (compare figures E17 and E20), even though the same solutions stored in Teflon vials were analyzed in both runs. Consequently, observed differences in precision (and accuracy) are interpreted as due to machine problems in the fourth analytical run. As discussed in section E.8.4, the third analytical run was repeated because of relatively high detection limits of Ta (table E12). Therefore, only Ta values

were needed in the fourth analytical run. Fortunately, good accuracy, excellent precision, and low detection limits of Ta were obtained. Thus, the analytical results of Ta in the fourth run are given for those samples in appendix A rather than the Ta data of the third run.

- Multiple analyses of standards as unknowns is essential to evaluate accuracy and precision, and thus, evaluate performance of the ICP-MS instrument at the Union College Geology Department. The machine performance may change drastically from one run to another (e.g., third and fourth analytical run). The cause of varying machine performance is unknown.

  Nonetheless, very good results can be obtained with the ICP-MS instrument at the Union College Geology Department (e.g., table E14). The accuracy and precision of the presented data of this study is similar to that of published ICP-MS data (Jenner et al., 1990). For example the analytical results for BCR-1 of the study of Jenner et al. (1990) are very similar in precision (figure E23) and accuracy (figure E24) to the results obtained at Union College (precision figures E11, E14, and E17; accuracy figures E12, E15, and E18).
- Occasionally, small amounts of Pb and Rb contamination affected accuracy and precision of the analysis of samples with low levels of Pb (< 1 ppm) and Rb (< l ppm) as indicated in table E13.
- Low precision and accuracy was obtained analyzing low levels of Cr in some samples (e.g., figures E17 and E18). The relatively large differences observed between the analytical results for BCR-1 and the proposed standard value of 16 ppm (Govindaraju, 1994) is partly due to large uncertainty of the proposed standard value. Generally, the precision of Cr is better than 5% relative standard deviation for samples with > 35 ppm Cr (table E13), and Cr concentrations of Pal-889 were determined within 10% of the reference values (e.g., figures E13, E16 and E19). Nonetheless, the accuracy and precision of Cr by XRF analysis might be better than by ICP-MS analysis (e.g., results for Z-83a shown in figure E10). Additionally, Cr concentrations in many samples exceed the highest standard of 321 ppm. For that reason, the analysis of Cr by XRF is preferred over the ICP-MS values (note: the differences between XRF and ICP-MS values is inconsequential for petrogenetic interpretations).

To summarize, the high precision and accuracy achieved for analytical runs 1, 2 and 3 (and for Ta in run 4), as well as the duplicate digestion and analyses of each unknown sample, which agree within 3% (e.g., table E7), leads to the conclusion that ICP-MS analytical data reported for samples in this study (appendix A) are very accurate.

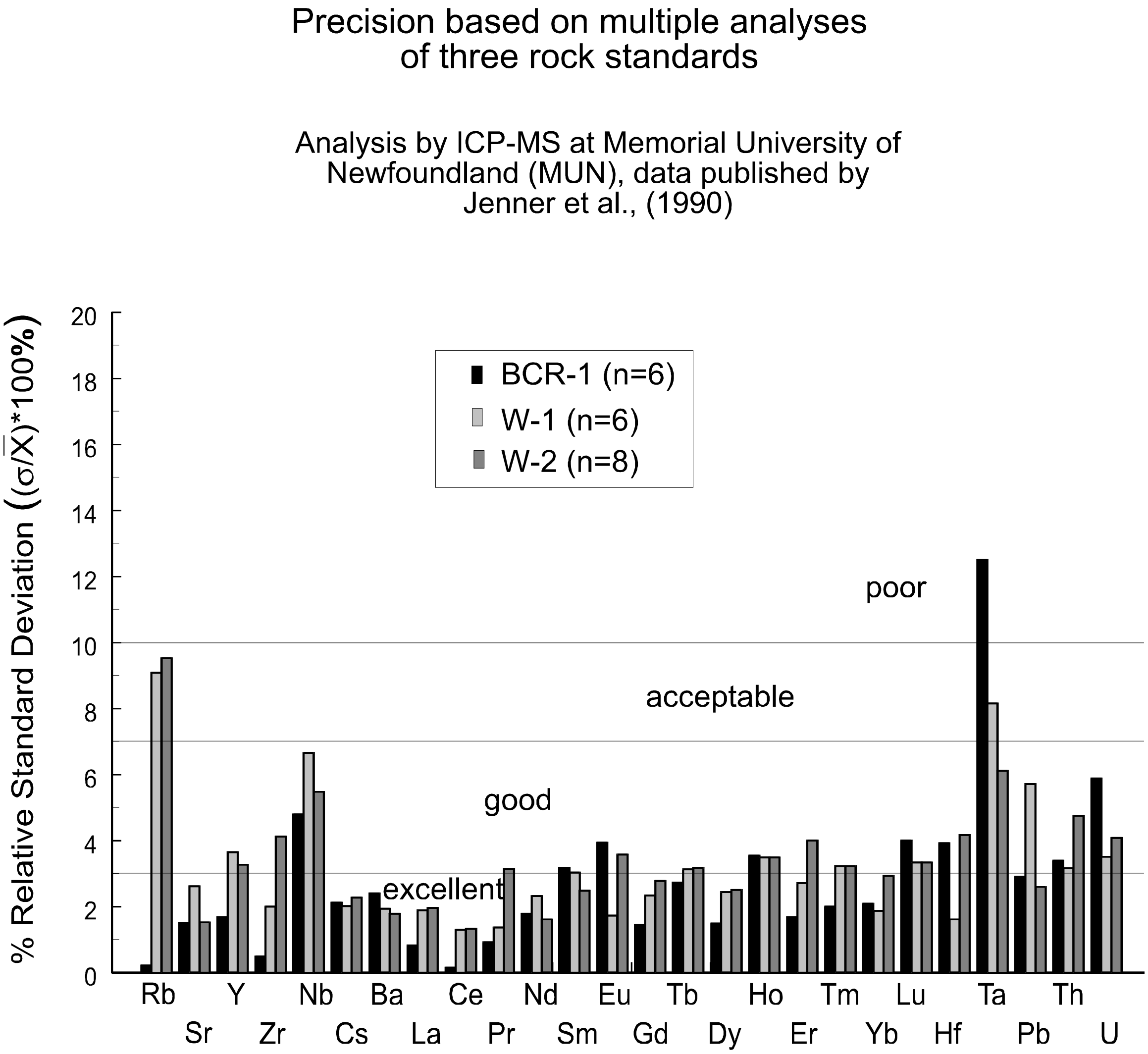
E.10 Supplement: Evaluation of the fifth analytical run; analysis of samples from the Coast Range ophiolite remnants at Llanada and Black Mountain

E.10.1 Introduction

The samples from the Coast Range ophiolite remnant at Black Mountain and Llanada were supplied by Glenn MacPherson for re-analysis by ICP-MS at Union College. The samples from these CRO remnants were previously analyzed by XRF and INAA, and these analytical data are reported in Giaramita et al., (1998). In this section, the analysis of these samples by ICP-MS is evaluated and compared to the XRF and INAA data in Giaramita et al., (1998).

The samples from the Coast Range ophiolite remnant at Black Mountain and Llanada were prepared using acid digestion and analyzed as outlined in sections E2 through E5. Duplicates of the standards as well as of the samples were prepared. Thus, the presented analytical results for the samples (appendix F) are the average of two analyses by ICP-MS.

The analytical results of the fifth analytical run are perhaps not as good (i.e., accuracy and precision) as the results of the analytical runs 1, 2 and 3 (section E8.2, E8.3, and E8.4). However, the data obtained with the fifth analytical run are of much higher quality than the data obtained with the fourth analytical run (section E.8.5). Furthermore, the precision and accuracy of most elements appear to be good so that the analytical results can be used for meaningful petrogenetic interpretations. The analytical results for standards analyzed as unknowns generally agree within 10% of the corresponding reference values. Additionally, the agreement between the available XRF / INAA data and the ICP-MS values is good as well.


Precision based on multiple analyses of three rock standards

Analysis by ICP-MS at Memorial University of Newfoundland (MUN), data published by Jenner et al., (1990)

Figure E23

Diagram illustrating the precision of the analysis by ICP-MS at the Memorial University of Newfoundland. The precision of the analysis indicated by the relative standard deviation is very similar to the typical precision achieved in this study using the ICP-MS instrument at the Union College Geology Department (compare figures E11, E14 and E17).

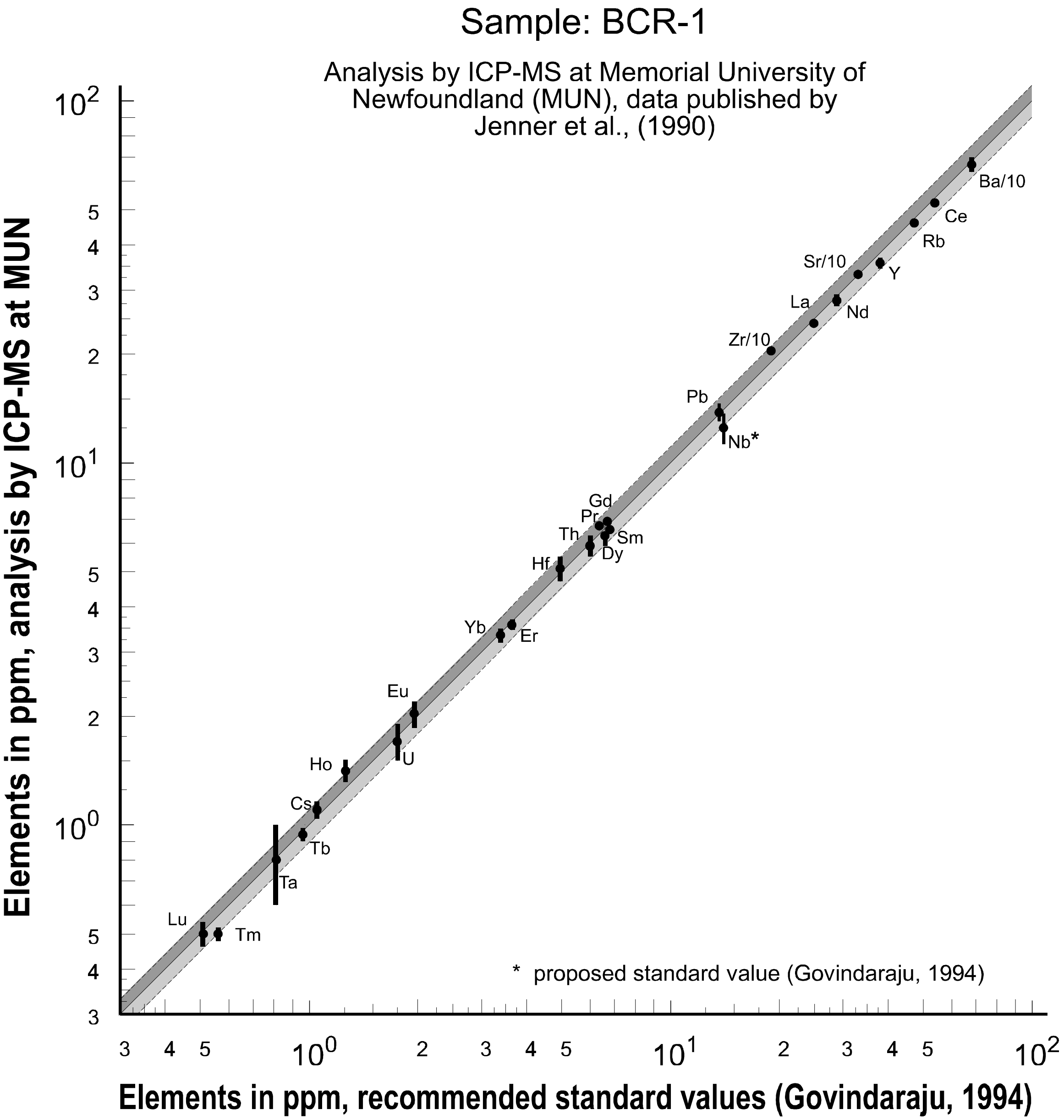


Figure E24

Comparative plot of the analytical data for BCR-1 obtained at MUN versus the recommended standard values of Govindaraju (1994). Similar accuracy is achieved using the ICP-MS at the Union College Geology Department (compare with figures E12, E15 and E18).

Table E13: Relative standard deviation (RSD) of multiple analyses of 19 samples
(table continued on next page)

Sample:	**Z-91a**	**Z-91b**	**Z-94**	**MRH-45a**	**MRH-45b**	**MRH-111**	**OC-1-S1**	**OC-1-S2**	**OC-5-S4**	**OC-6-S5**
Analyzed in runs:	(2),[1]	(2),[1]	(2),[1]	(2),[2]	(2),[1*]	(2),[1*]	(2),[2]	(2),[2]	(2),[1*]	(2),[2]
Total no. of analyses:	4	4	4	4	6	6	4	4	6	4
Cr	6.4%	3.7%	3.1%	2.6%	2.9%	10.1% +	2.8%	5.0% +	4.3%	4.8%
Rb	4.8%	2.8%	1.3%	3.0%	1.8%	2.6%	17.4% ×	1.0%	8.9% ×	2.1%
Y	3.2%	1.3%	3.8%	3.7%	1.5%	4.3%	1.3%	1.0%	2.2%	3.6%
Zr	3.4%	1.1%	2.3%	3.5%	1.7%	2.7%	1.9%	4.9%	3.8%	4.8%
Nb ◁	3.0%	1.9%	16.7%	1.2%	3.5%	4.6%	5.7%	3.0%	3.7%	2.8%
Cs	2.5%	2.5%	7.3%	1.0%	2.3%	3.0%	4.3%	2.8%	2.7%	2.7%
Ba	5.4%	4.0%	8.8%	1.4%	3.2%	2.7%	1.8%	1.7%	4.2%	3.7%
La	5.1%	2.2%	5.9%	1.9%	0.9%	1.8%	3.7%	3.8%	1.3%	6.4%
Ce	4.0%	2.9%	6.1%	1.4%	1.5%	2.5%	1.5%	0.9%	2.8%	3.1%
Pr	4.6%	2.8%	4.9%	1.3%	1.3%	1.6%	2.9%	3.5%	1.4%	3.8%
Nd	4.6%	2.0%	6.0%	3.5%	1.5%	2.3%	3.9%	4.0%	1.2%	4.1%
Sm	1.4%	0.2%	6.0%	4.5%	2.4%	5.1%	1.4%	3.1%	0.8%	3.8%
Eu	2.4%	1.4%	5.4%	4.8%	1.8%	1.8%	2.9%	3.7%	1.1%	4.8%
Gd	1.8%	1.0%	6.8%	3.7%	2.8%	4.0%	1.3%	1.6%	1.6%	3.3%
Tb	1.1%	2.6%	5.3%	3.9%	1.6%	2.1%	1.9%	2.4%	1.7%	2.4%
Dy	1.9%	2.5%	3.9%	3.7%	1.5%	2.1%	1.7%	2.5%	1.5%	2.5%
Ho	1.1%	0.6%	3.5%	2.6%	1.2%	3.3%	2.1%	1.9%	2.3%	3.0%
Er	0.3%	1.8%	4.2%	1.9%	1.5%	4.0%	1.3%	2.1%	1.2%	1.9%
Tm	2.3%	1.8%	3.2%	1.3%	2.7%	5.9%	3.0%	1.9%	1.5%	1.3%
Yb	6.7%	2.0%	7.6%	3.1%	2.7%	3.2%	4.0%	2.5%	4.2%	3.5%
Lu	3.1%	0.8%	8.3%	5.2%	3.8%	1.0%	3.3%	5.4%	5.2%	5.2%
Hf	0.9%	1.9%	7.9%	3.3%	2.9%	1.2%	3.4%	8.4%	7.4%	9.1%
Pb	9.1%	9.6%	4.8%	11.1%	8.6%	3.2%	9.2%	4.9%	25.2% ×	11.7%
Th	2.6%	3.1%	3.8%	2.6%	3.6%	2.9%	4.7%	3.4%	4.7%	5.4%
U	5.7%	7.6%	6.1%	6.7%	9.0%	6.7%	14.1%	7.6%	10.0%	8.7%
Average	3.5%	2.6%	5.7%	3.3%	2.7%	3.4%	3.5%	3.3%	3.0%	4.3%

Relative standard deviation:

$$RSD = (\sigma/\bar{X}) \bullet 100\%$$

Note that the solutions of four separate digestions per sample were analyzed:

(2) dublicate analyses of sample in second test run (n=2)
[1] dublicate analyses of sample in first analytical run (n=2)
[1*] analysis of two aliquots of two digestions (n=4)
[2] dublicate analyses of sample in second analytical run (n=2)
[1,2] dublicate analyses in first analytical run,
analyzed once in second analytical run (n=3)

Table E13 cont.

Sample:	**OC-58**	**OC- 113**	**OC-186**	**OC-224**	**OC-227a**	**OC-227b**	**OC-379**	**OC-380**	**PB-1**	**Aver-age of 19 samples**
Analyzed in runs:	(2),[1,2]	(2),[1]	(2),[1]	(2),[2]	(2),[2]	(2),[1]	(2),[2]	(2),[1]	(2),[2]	
Total no. of analyses:	5	4	4	4	4	4	4	4	4	
Cr	3.9%	1.6%	17.0% +	4.9%	4.8%	5.4%	9.3% +	24.7% +	3.7%	6.4%
Rb	3.3%	2.3%	2.4%	4.5%	3.3%	1.2%	22.3% ×	5.9%	17.3% ×	2.8%
Y	2.7%	2.8%	4.9%	3.6%	0.8%	2.5%	2.6%	3.3%	3.1%	2.7%
Zr	1.1%	4.2%	5.4%	4.5%	3.2%	2.6%	3.2%	4.0%	1.7%	3.2%
Nb ◁	2.8%	3.6%	0.8%	3.1%	5.3%	3.8%	3.0%	2.7%	3.4%	3.9%
Cs	3.9%	2.8%	6.5%	6.5%	7.2%	7.3%	4.7%	3.6%	14.5%	4.6%
Ba	4.6%	2.3%	8.0%	1.5%	1.3%	6.7%	4.0%	2.4%	2.5%	3.7%
La	3.2%	0.8%	9.4%	3.7%	7.2%	7.5%	2.8%	3.4%	2.0%	3.9%
Ce	4.0%	2.8%	7.4%	2.2%	3.9%	7.0%	2.9%	2.4%	2.1%	3.2%
Pr	4.3%	2.4%	8.5%	2.3%	0.7%	4.7%	2.0%	3.3%	1.1%	3.0%
Nd	4.2%	1.2%	9.0%	5.5%	5.7%	6.7%	2.6%	4.1%	1.5%	3.9%
Sm	3.6%	3.0%	6.1%	6.2%	2.9%	5.5%	3.7%	1.4%	2.3%	3.3%
Eu	4.0%	1.0%	7.5%	6.9%	3.7%	5.0%	2.6%	2.6%	1.9%	3.4%
Gd	3.8%	1.5%	8.0%	5.6%	3.3%	5.2%	2.6%	2.6%	0.9%	3.2%
Tb	3.5%	1.2%	8.2%	4.4%	2.8%	4.6%	3.3%	2.9%	1.4%	3.0%
Dy	2.7%	1.8%	6.1%	3.4%	1.9%	3.4%	3.5%	2.3%	0.9%	2.6%
Ho	2.1%	1.2%	4.3%	4.3%	2.3%	2.3%	2.4%	2.7%	2.4%	2.4%
Er	2.5%	0.4%	4.0%	3.7%	1.6%	3.4%	4.6%	1.9%	1.7%	2.3%
Tm	2.1%	2.0%	1.9%	1.5%	2.1%	2.6%	3.8%	2.7%	2.4%	2.4%
Yb	3.6%	1.4%	4.8%	4.0%	3.3%	5.4%	3.6%	5.2%	0.5%	3.8%
Lu	4.9%	1.7%	5.4%	3.0%	3.5%	5.5%	3.8%	2.4%	2.1%	3.9%
Hf	4.4%	0.6%	2.5%	6.7%	1.4%	2.5%	1.8%	2.3%	2.0%	3.7%
Pb	59.5% ×	7.0%	3.5%	4.2%	5.1%	7.0%	2.3%	8.2%	3.1%	6.6%
Th	5.4%	4.4%	3.1%	2.9%	8.2%	2.5%	4.6%	2.0%	2.7%	3.8%
U	11.2%	3.2%	7.1%	9.5%	5.5%	6.8%	2.3%	4.4%	4.1%	7.2%
Average	3.8%	2.3%	6.1%	4.3%	3.6%	4.7%	3.4%	4.1%	3.3%	

× Samples with very low levels (< 1 ppm) of Rb or Pb which are affected by small amounts of Rb or Pb contamination have high relative standard deviations
(average relative standard deviation of Rb and Pb calulated without marked values)

\+ In general, samples with the lowest levels of Cr have the highest RSDs (e.g., OC-380 with 8 ppm Cr)

◁ The accuracy and precision of Nb were improved with second test run;
Nb values of second test run agree well with those of the first and second analytical run.

Table E14: Compilation of analytical results, BCR-1 analyzed as unknown

	recom-mended values	Analysis by ICP-MS at Union College:						
		test 1	test 2	anly.1	analy.2	analy.3	analy.4	analy.5 ×
		(n=6)	(n=4)	(n=8)	(n=12)	(n=12)	(n=6)	(n=8)
Element	[1]	[---------------------------- this study						----------------------------]
V	407	n.d.	n.d.	411	398	393	370	373
Cr	16	n.d.	12.0	14.5	10.4	10.6	13.3	26
Rb	47.2	46.91	52.6	47.2	47.3	47.6	47	47.7
Sr	330	n.d.	n.d.	342	329	335	331	336
Y	38	36.51	37.0	35.5	34.6	35.3	34.5	34.7
Zr	190	n.d.	190	183	184	194	185	184
Nb	14	15.7*	17.8*	15.5	15.4	14.5	15.3	15.3
Cs	0.96	0.905	1.04	0.96	0.97	0.959	1.05	1.04
Ba	681	674.5	684	686	714	688	738	727
La	24.9	24.50	26.8	25.7	26.5	24.6	27.4	26.5
Ce	53.7	52.9	57.3	52.5	54.7	53.6	56.0	55.2
Pr	6.8	6.82	7.17	6.76	7.02	6.79	7.20	7.03
Nd	28.8	28.4	29.5	29.8	30.8	28.4	31.2	30.3
Sm	6.59	6.39	6.44	6.52	6.51	6.59	6.58	6.58
Eu	1.95	1.98	1.97	2.00	1.98	1.94	1.92	1.93
Gd	6.68	6.64	7.17	6.73	6.86	6.58	6.78	6.79
Tb	1.05	1.06	1.05	1.03	1.07	1.04	1.05	1.05
Dy	6.34	6.15	6.33	6.29	6.40	6.20	6.36	6.20
Ho	1.26	1.28	1.33	1.29	1.29	1.25	1.28	1.25
Er	3.63	3.61	3.41	3.51	3.51	3.48	3.47	3.40
Tm	0.56	0.564	0.52	0.506	0.512	0.531	0.508	0.50
Yb	3.38	3.36	3.44	3.26	3.32	3.29	3.29	3.21
Lu	0.51	0.508	0.575	0.563	0.578	0.517	0.568	0.56
Hf	4.95	4.93	5.31	4.97	5.15	4.95	4.96	4.98
Ta	0.81	3.21*	0.89*	0.751	0.764	0.821	0.753	0.76
Pb	13.6	13.9	15.3	14.5	14.2	13.97	13.61	13.6
Th	5.98	5.96	6.32	6.22	6.12	5.87	6.06	5.81
U	1.75	1.77	1.80	1.71	1.72	1.71	1.70	1.59

[1] Govindaraju (1994), data underlined are recommended values, other values are proposed

* Ta and Nb unstable in solution

× analytical run for MacPherson (11/11/97)

Table E15: Compilation of analytical results for Pal-889
(table continued on next page)

	selected	**Analysis by ICP-MS at Union College**						×	**WSU**	**UM**	**McGill**	**McGill**		**Cornell**	
	reference	test 1	test 2	analy.1	analy.2	analy.3	analy.4	analy.5	ICP-MS	XRF	XRF	XRF	error	INAA	error
	values	(n=6)	(n=4)	(n=4)	(n=2)	(n=4)	(n=2)	(n=3)	(n=2)	(n=1)	(n=1)	(n=5)	1 σ	(n=13)	1 σ
	[1]	[---------------------------- this study ------------------------------]							[2]	[2]	[2]	[3]		[3]	
V	***254***	n.d.	n.d.	269	263	275	256	285	-	252.4	260	249	21	-	-
Cr	314.0	n.d.	283	310	294	312	313	310	-	284.4	310	-	-	312	5
Rb	-	30.3	31.5	29.7	30.7	30.1	28.5	30.6	28.5	-	-	32	3	-	-
Sr	183.0	n.d.	n.d.	174	181	173	183	172	180.5	181.8	177	179	8	-	-
Y	22.6	22.0	23.0	21.4	22.0	22.1	24.0	21.4	23.7	-	-	22	1	-	-
Zr	98.6	n.d.	97.3	90.9	93.0	100.5	98.6	94.9	-	101.6	110	116	5	-	-
Nb	7.91	9.71*	9.9*	8.68	8.74	8.51	8.41	8.53	7.47	7.3	[15]	9	1	-	-
Cs	2.19	1.91	2.19	1.95	2.03	2.15	2.19	2.04	1.88	-	-	-	-	-	-
Ba	185.0	174.4	185.0	169	180	193	185	184	173.1	195.5	231	-	-	183	4
La	10.52	10.62	11.27	10.1	10.2	10.9	10.5	10.4	10.64	[6.5]	-	-	-	10.51	0.09
Ce	23.6	22.8	23.7	21.8	22.4	23.6	23.6	22.9	21.73	23.8	-	-	-	23.9	0.7
Pr	3.27	3.02	3.15	2.93	2.93	3.15	3.19	2.97	2.73	-	-	-	-	-	-
Nd	13.0	13.0	14.3	13.1	12.9	13.2	13.0	13.2	12.11	-	-	-	-	12.2	0.6
Sm	3.42	3.27	3.45	3.26	3.34	3.46	3.41	3.23	3.60	-	-	-	-	3.44	0.07
Eu	1.07	1.12	1.14	1.09	1.11	1.12	1.07	1.06	1.18	-	-	-	-	1.04	0.02
Gd	4.24	3.70	3.87	3.69	3.74	3.89	3.98	3.68	3.76	-	-	-	-	-	-
Tb	0.67	0.624	0.623	0.620	0.609	0.649	0.667	0.614	0.70	-	-	-	-	-	-
Dy	4.18	3.71	3.86	3.82	3.76	4.01	3.98	3.79	4.40	-	-	-	-	-	-
Ho	0.8	0.779	0.787	0.768	0.762	0.811	0.809	0.768	0.90	-	-	-	-	-	-
Er	2.25	2.18	2.15	2.13	2.21	2.35	2.29	2.15	2.54	-	-	-	-	-	-
Tm	0.33	0.342	0.314	0.319	0.319	0.360	0.339	0.327	0.36	-	-	-	-	-	-
Yb	2.18	2.03	2.07	2.01	2.01	2.12	2.18	2.03	2.11	-	-	-	-	-	-
Lu	0.3	0.279	0.322	0.305	0.303	0.314	0.304	0.304	0.33	-	-	-	-	-	-
Hf	2.56	2.51	2.63	2.56	2.49	2.62	2.56	2.60	2.58	-	-	-	-	2.58	0.05
Ta	0.63	2.47*	0.77*	0.600	0.603	0.677	0.630	0.596	0.60	-	-	-	-	0.65	0.02
Pb	-	4.68	5.59	4.52	4.43	4.75	4.41	4.69	4.42	-	-	-	-	-	-
Th	2.07	2.04	2.25	2.07	2.06	2.02	2.07	2.05	1.78	-	-	-	-	1.98	0.05
U	0.5	0.513	0.516	0.494	0.489	0.492	0.497	0.417	0.47	-	-	-	-	0.5	0.04

Table E15 cont.

[1] data underlined are in-house standard values of Pal-889 used at Cornell University (Wirth, 1991)
other values are from the analysis of the U.S.G.S. standard W-1 using ID-SSMS (Jochum et al., 1988)
***V* - reference value:** average of XRF analyses at McGill and UM

[2] unpublished data (Harper pers. com., 1995)

[3] Wirth (1991)

WSU ... Washington State University Geoanalytical Laboratories

UM ... University of Massachusetts

* Ta and Nb unstable in solution

× analytical run for MacPherson (11/11/97)

Table E16: Compilation of analytical results for Cou-IL-6

	Analysis by ICP-MS at Union College:						×	**WSU**	**WSU**
	test 1	test 2	analy.1	analy.2	analy.3	analy.4	analy.5	ICP-MS	XRF
	(n=6)	(n=0)	(n=8)	(n=2)	(n=4)	(n=6)	(n=3)	(n=2)	(n=2)
Element	[----------------------------			this study			---------------------------]	[1]	[1]
V	n.d.		501	493	476	472	492	-	472
Cr	n.d.		89	81	85	83	99	-	-
Rb	13.04		12.8	12.6	13.1	12.2	13.5	13.5	11
Sr	n.d.		273	267	273	275	279	-	257
Y	39.8		38.9	38.0	40.2	37.4	38.8	37.6	39
Zr	n.d.		119	117	131	119	122	-	120
Nb	5.73*		5.71	5.57	5.70	5.59	5.87	4.33	5.9
Cs	2.77		2.82	2.94	2.96	2.83	2.99	2.80	-
Ba	57.1		53.5	58.8	59.7	58.7	63	58.0	31
La	6.28		6.11	6.51	6.51	6.46	6.65	6.60	3
Ce	17.1		15.9	17.1	17.7	17.2	17.7	16.3	18
Pr	2.73		2.57	2.69	2.81	2.67	2.75	2.48	-
Nd	14.0		13.4	13.8	14.2	13.6	14.2	12.8	-
Sm	4.31		4.18	4.26	4.45	4.23	4.17	4.51	-
Eu	1.44		1.34	1.36	1.41	1.28	1.34	1.48	-
Gd	5.59		5.31	5.53	5.68	5.46	5.32	5.37	-
Tb	0.996		0.912	0.954	0.984	0.962	0.946	1.08	-
Dy	6.25		6.06	6.25	6.47	6.29	6.16	7.09	-
Ho	1.37		1.30	1.32	1.37	1.35	1.31	1.49	-
Er	3.96		3.77	3.85	3.99	3.90	3.76	4.35	-
Tm	0.634		0.575	0.598	0.623	0.596	0.581	0.60	-
Yb	3.80		3.65	3.76	3.84	3.82	3.76	3.70	-
Lu	0.532		0.557	0.577	0.552	0.584	0.58	0.62	-
Hf	3.18		3.15	3.23	3.27	3.27	3.23	3.02	-
Ta	0.83*		0.301	0.314	0.330	0.297	0.31	0.33	-
Pb	0.87 ○		0.582	0.617	0.598	0.637	0.82	2.04	-
Th	0.523		0.541	0.540	0.520	0.545	0.54	0.49	-
U	0.185		0.180	0.185	0.181	0.181	0.17	0.13	-

[1] unpublished data (G. Harper, pers. com., 1995)

* Ta and nb unstable in solution

○ contamination detected

× analytical run for MacPherson (11/11/97)

E.10.2 Fifth analytical run, 11/11/97

E.10.2.1 Limits of detection

Using equation (1) in section 6.1, the detection limits were determined from the blank residuals of the fifth analytical run and are listed in table E17. The detection limits of V, Cr, Rb, Sr, Zr, Ba and Pb are relatively higher than those of the other elements. Overall, the detection limits of the fifth analytical run are very similar to previous analytical runs (see tables E9, E10, E11 for comparison) and do not indicate problems with the performance of the ICP-MS instrument (i.e., back ground levels were very low as usual). Most importantly, all elemental concentrations determined in the samples (appendix F) are well above the detection limits (table E17).

E.10.2.2 Precision

The analytical results for BCR-1, Pal-889 and Cou-Il-6 are listed in table E17 as well as the standard deviation of the multiple analyses of these reference materials. The precision is based on eight analyses of BCR-1 treated as an unknown sample and three analyses of Pal-889 and Cou-IL-6 (figure E25). The overall precision achieved in the fifth analytical run is poorer than the precision of analytical runs 1, 2 and 3 (figures E11, E14, and E17, respectively), however, notably better than for the fourth analytical run (figure E20). As shown in figure E25, the precision of light REE and medium REE is acceptable to good, and the precision of Nb, Cs, heavy REE, Hf, Ta, Pb, Th and U is good to excellent based on the % relative standard deviation. The precision of the remaining elements (i.e., V, Cr, Rb, Sr, Y and Zr) might be unacceptable as indicated by high relative standard deviations. Overall, the precision of the fifth analytical run is poorer than usual which might be related to a decline of the performance of the ICP-MS instrument (see section E.10.2.4).

E.10.2.3 Accuracy

The agreement between the recommended standard values of BCR-1 and the mean of measured values is good (figure E26). Generally, the mean values agree within ±10% of the reference values, except

Table E17: Results of fifth analytical run 11/11/97

Element	Detection Limits in ppm	BCR-1 mean (n=8)	BCR-1 error 1 σ	Pal-889 mean (n=3)	Pal-889 error 1 σ	Cou-IL-6 mean (n=3)	Cou-IL-6 error 1 σ
V	0.36	373	42	285	17	492	27
Cr	1.29	26.2	4.1	310	40	99	16
Rb	0.111	47.7	4.5	30.6	2.7	13.5	1.2
Sr	0.60	336	31	172	7	279	20
Y	0.038	34.7	3.5	21.4	1.8	38.8	3.8
Zr	0.3	184	17	94.9	8.1	122	14
Nb	0.022	15.3	0.7	8.53	0.35	5.87	0.50
Cs	0.0105	1.04	0.05	2.04	0.10	2.99	0.21
Ba	2.41	727	54	184	8	63.4	1.6
La	0.084	26.5	2.0	10.4	0.6	6.65	0.54
Ce	0.159	55.2	4.2	22.9	1.2	17.7	1.5
Pr	0.0206	7.03	0.49	2.97	0.18	2.75	0.25
Nd	0.068	30.3	2.242	13.2	0.8	14.2	1.1
Sm	0.0117	6.58	0.40	3.23	0.14	4.17	0.27
Eu	0.0037	1.93	0.11	1.06	0.05	1.34	0.09
Gd	0.0075	6.79	0.38	3.68	0.16	5.32	0.26
Tb	0.00119	1.05	0.04	0.614	0.032	0.946	0.051
Dy	0.0110	6.20	0.25	3.79	0.19	6.16	0.33
Ho	0.00199	1.25	0.05	0.768	0.032	1.31	0.08
Er	0.0047	3.40	0.09	2.15	0.10	3.76	0.22
Tm	0.00115	0.500	0.012	0.327	0.011	0.581	0.024
Yb	0.0032	3.21	0.07	2.03	0.06	3.76	0.07
Lu	0.00083	0.564	0.012	0.304	0.008	0.576	0.021
Hf	0.0048	4.98	0.08	2.60	0.06	3.23	0.06
Ta	0.002	0.761	0.014	0.596	0.014	0.312	0.008
Pb	0.39	13.6	0.4	4.69	0.21	0.818	0.026
Th	0.021	5.81	0.34	2.05	0.02	0.539	0.003
U	0.0062	1.59	0.12	0.417	0.014	0.167	0.002

standard deviation : $\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n^2}}$

see tables 2 and 5 for recommended standard values of BCR-1 and Pal-889, respectively
see tables 14, 15 and 16 for compilation of analytical results
for BCR-, Pal-889, and Cou-IL-6, respectively

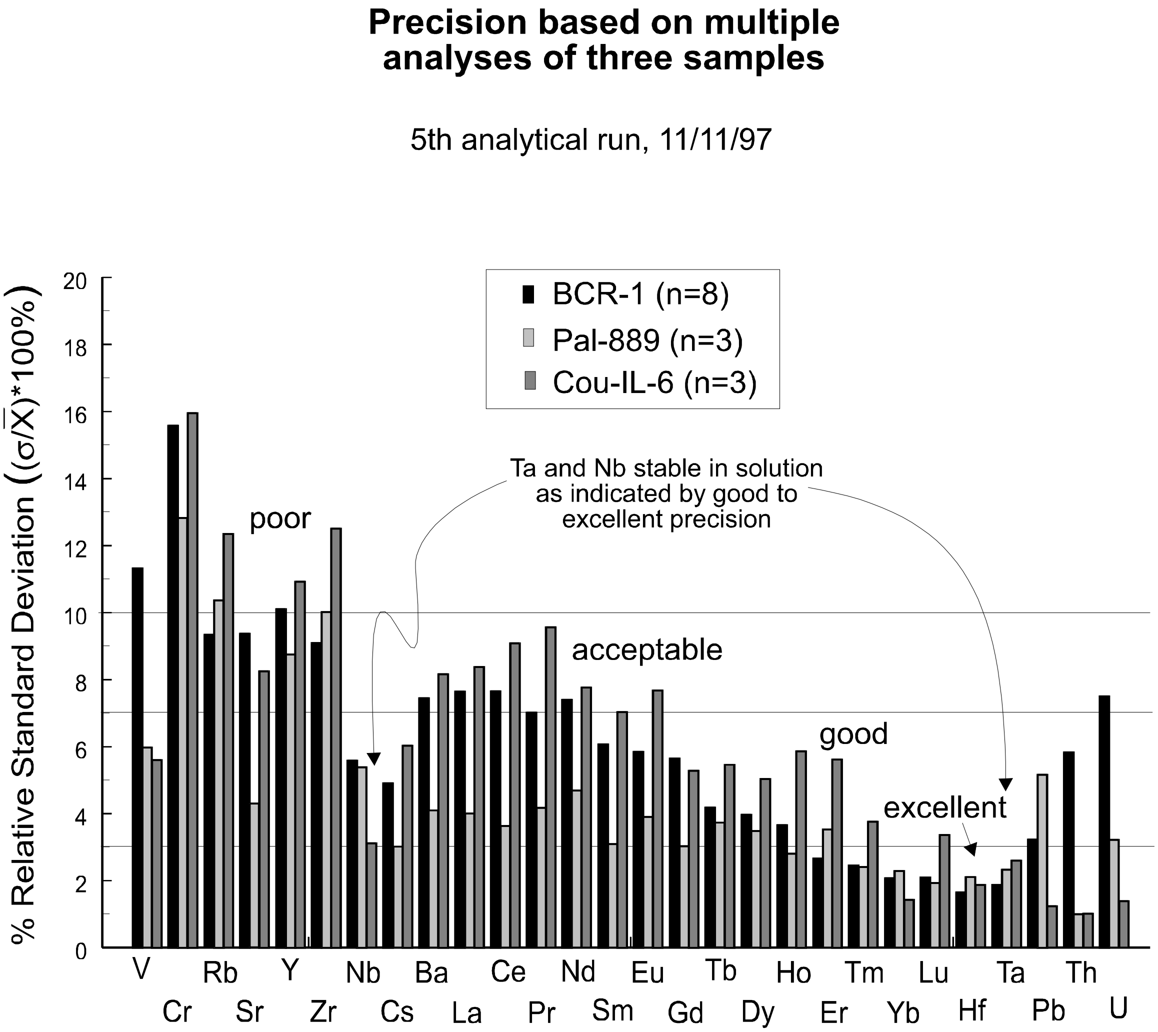


Figure E25

Diagram illustrating the precision of the analysis of the fifth analytical run. Four aliquots of an old BCR-1 solution and four aliquots of a new BCR-1 solution were analyzed. The old BCR-1 solution left from the third analytical run was stored in a Teflon vial. Systematic differences between the old and new BCR-1 solutions were not observed. Poor precision of V, Cr, Rb, Sr (compared to previous runs), and Zr is indicated by ≥10% relative standard deviation. Acceptable to good precision of Sr, Ba and the light REE is indicated by 5% to 9% relative standard deviation. The remaining elements were analyzed with good to excellent precision (1% to 5% relative standard deviation).

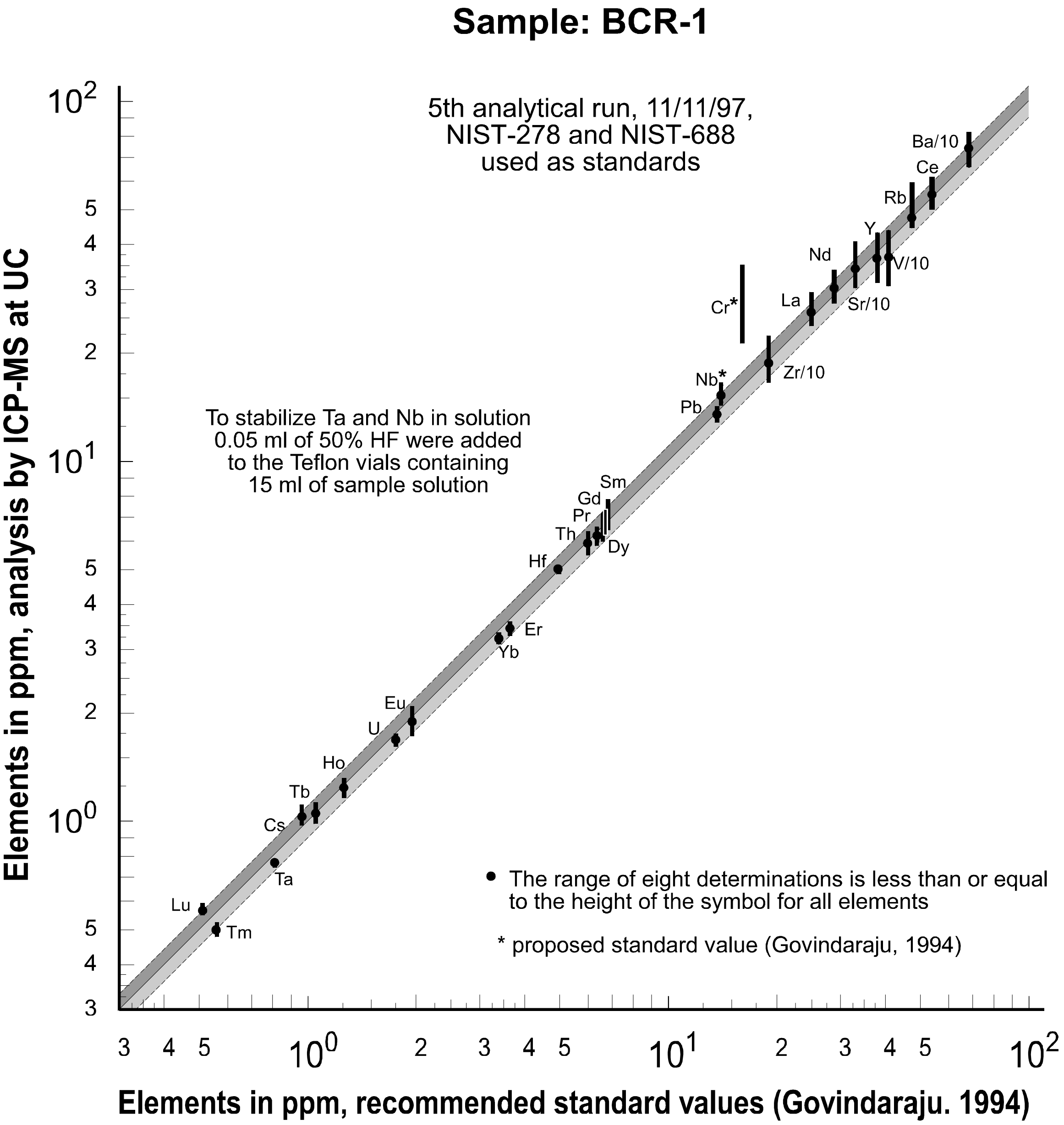


Figure E26

Comparative plot of the analytical results of the fifth analytical run versus the recommended standard values of BCR-1 (Govindaraju, 1994). The mean values of eight analyses of BCR-1 plot close to or on the line with slope = 1. However, due to poor precision of V, Cr, Rb, Sr, Y, and Zr, several data points plot outside the shaded fields indicating some analytical results differ more than 10% from the standard values. Nonetheless, most elemental concentrations were determined within ±10% of the standard values indicating good accuracy of the analysis.

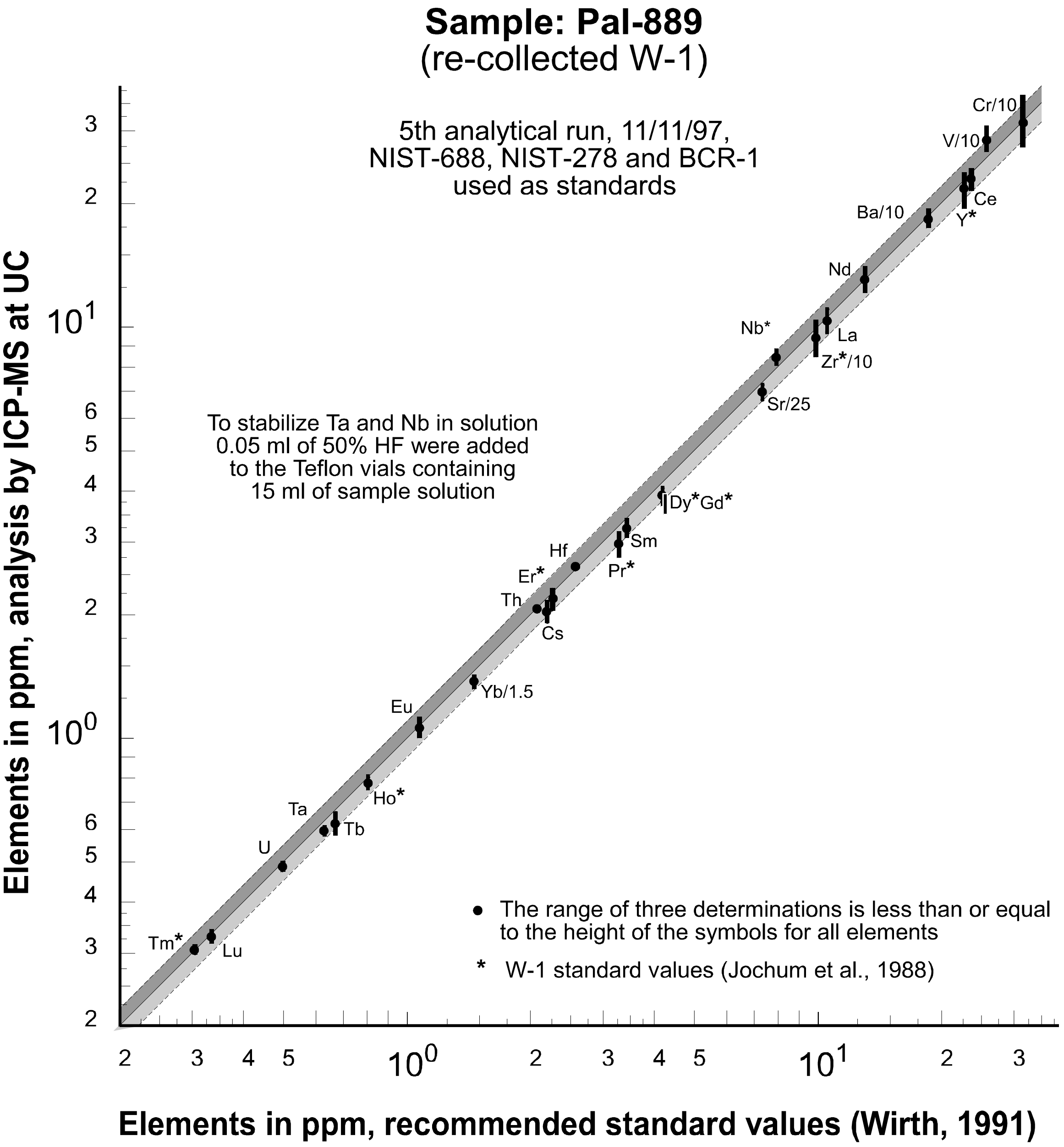


Figure E27

Comparative plot of the analytical data for Pal-889 versus the standard values of Pal-889 and W-1. The agreement between the analytical results for Pal-889 and the selected standard values is very good, indicating good accuracy of the analysis. In the fifth analytical run, the accuracy of V, Cr, Y and Zr may not be as good as for all other elements due to poor precision (figure E25). Note that the analytical data of Nb obtained in all analytical runs are consistently higher than the standard value of Nb (see figures E12 and E15), suggesting the selected W-1 standard value is too low (see section E.8.4.4).

for Cr. The analytical data of Cr are significantly higher than the proposed standard value (16 ppm). This is rather unusual because much lower Cr values (10-14 ppm) were obtained in all other analytical runs (table E14). This possibly indicates a problem analyzing low levels of Cr in the fifth analytical run.

Two or three of eight determinations of V, Rb, Sr, and Y and one of eight determinations of Zr, Ba, La and Nd do not agree within 10% of the corresponding reference values (figure E26). Thus, the accuracy (and precision) of the fifth analytical run is apparently not as good as the accuracy (and precision)of analytical runs 1, 2 and 3. Nonetheless, most data points agree within ± 10% of the recommended standard values suggesting that the analytical results are acceptably accurate.

The analytical results for Pal-889 agree well with the selected standard values (figure E27), indicating good accuracy of the analysis. As observed in previous comparative plots (e.g., figure E13), the analytical results for Pal-889 differ more than 10% from the W-1 standard values (i.e., Nb, Pr, Dy, and Gd), however, agree well with the Pal-889 standard values (most analytical results agree within 5-6% of the Pal-889 standard values). Furthermore, the three analyses of Pal-889 and Cou-Il-6 agree well with the results obtained earlier at Union College and also with the ICP-MS analysis at Washington State University (tables E15 and E16, respectively).

E.10.2.4 Varying performance of the ICP-MS instrument or incomplete dissolution ?

Poor precision of the fifth analytical run (figure E25) is interpreted as due to a decline of the performance of the ICP-MS instrument. Such decline of the performance was observed before: aliquots of the same sample, standard, and blank solutions (stored in Teflon vials) were analyzed in the third and fourth analytical run. If there would have been no change in the performance of the ICP-MS instrument, very similar precision of the analyses of the same solutions should have been obtained. However, the precision of the fourth analytical (figure E20) run is much poorer than that of the third analytical run (figure E17) indicating varying machine performance. Probably, the fifth analytical run was affected by similar problems with the ICP-MS instrument (i.e., a vacuum leak apparently occurred several times during 1997).

Furthermore, it has been demonstrated in this study that samples of basaltic to andesitic composition are completely dissolved using the mixed acid attack as described in section E2 (see also sections E.7.1.7 and E.8.3.4). Also, duplicates of the samples (i.e. weighing of 0.1g sample in each of two Teflon vials per sample and dissolving using acid digestion) were analyzed in the fifth analytical run. Systematic differences between the two digestions of a sample were not observed suggesting incomplete dissolution is not a problem in the fifth analytical run.

To summarize, poorer than usual precision of the fifth analytical run is most likely due to a decline of the performance of the ICP-MS instrument and not due to incomplete dissolution of the samples.

E.10.3 Comparison with XRF and INAA data

E.10.3.1 Comparison with XRF data

The precision of XRF as well as of ICP-MS analysis should be given for a meaningful comparison of the analytical results. The precision of ICP-MS analysis is given in figure E25. In lack of more detailed information, the precision of XRF analysis was roughly estimated using data obtained at McGill University and the University of Massachusetts. The relative standard deviation (1σ) was estimated as follows: Sr ~4.5%; V ~8.5%; Y ~4.5%; Zr ~4.5%; Ba ~50% to ~12% for concentrations ranging from 20 ppm to 100 ppm). Evidently, the precision of Sr, V, Y, and Zr is better by XRF than by ICP-MS analysis. Thus, the XRF data for these elements are preferred over the ICP-MS data. However, the precision of Ba by ICP-MS analysis (figure E25) is much better than by XRF analysis, especially at low levels of Ba (detection limit at ~20 ppm, figure E28a).

Overall, the analytical results agree within errors of the analyses (most data agree within 1σ and all data within 2σ). Nonetheless, a systematic difference between ICP-MS and XRF data can be seen in figure 28d (element Y). Unusual low and/or variable count rates analyzing Y in the standards (due to varying machine performance?) probably affected the calibration of the ICP-MS analysis. As a result, Y concentrations obtained by ICP-MS in the fifth analytical run are lower than the XRF values.

E.10.3.2 Comparison with INAA data

The comparative diagrams are shown in figures E29, E30 and E31. In general, the analytical results obtained by ICP-MS analysis and INAA agree fairly well: the agreement is within errors of the analyses, and differences are usually not larger than 10% (except for Cr, Rb, Cs, Ta and U).

Probably, the analysis of elements with very low concentrations is more accurate by ICP-MS than by INAA, because the detection limits of ICP-MS are 1 to 3 orders of magnitude lower than the detection limits of INAA. Consequently, more accurate results for Rb (figure E29b), Cs (figure E29c), Ta (figure E31c) and U (figure E31e) were obtained by ICP-MS. Considering the large uncertainty analyzing low levels of Th by INAA (figure E10), the Th data obtained by ICP-MS is probably more accurate as well.

Systematic differences between the two analytical techniques observed for Sm (figure E30b) and Yb (figure E30e) is possibly due to differences in the standardization (calibration) of the analyses. Documentation of accurate calibration of the analytical runs using ICP-MS is given in table E2: recommended standard values of BCR-1 (Govindaraju, 1994) were accurately reproduced analyzing BCR-1 as an unknown sample (NIST-278 and NIST-688 used as standards). Note that all samples were analyzed using BCR-1, NIST-278 and NIST-688 as standards.

E.10.4. Summary

Precision and accuracy of Nb, Cs, Ba, REE, Hf, Ta, Pb, Th and U are good to acceptable as shown in figures E25, E26 and E27. The analytical results of V, Cr, Sr, Y, and Zr obtained in the fifth analytical run are less than adequate compared to the data obtained by XRF analysis. In spite of poor precision of Rb, the analytical data of Rb obtained by ICP-MS are more accurate than by INAA. Overall, the ICP-MS data represent a valuable addition to previous data (mainly because of the low detection limits of ICP-MS) and may prove to be useful for petrogenetic interpretations. Nonetheless, petrogenetic interpretations of the geochemical data should be made within the limits of the precision and accuracy achieved in the fifth analytical run (figures E25, E26, and E27).

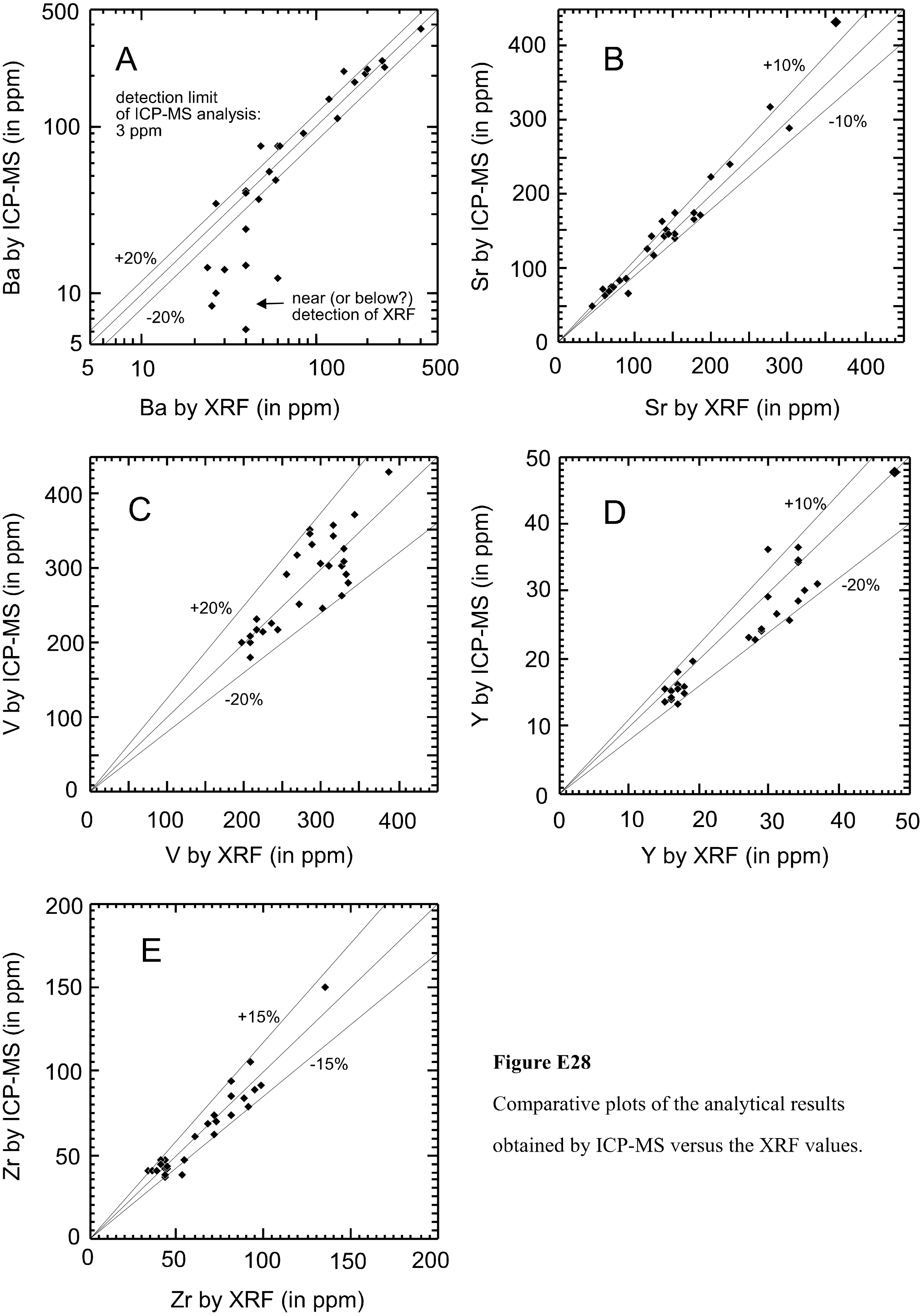


Figure E28

Comparative plots of the analytical results obtained by ICP-MS versus the XRF values.

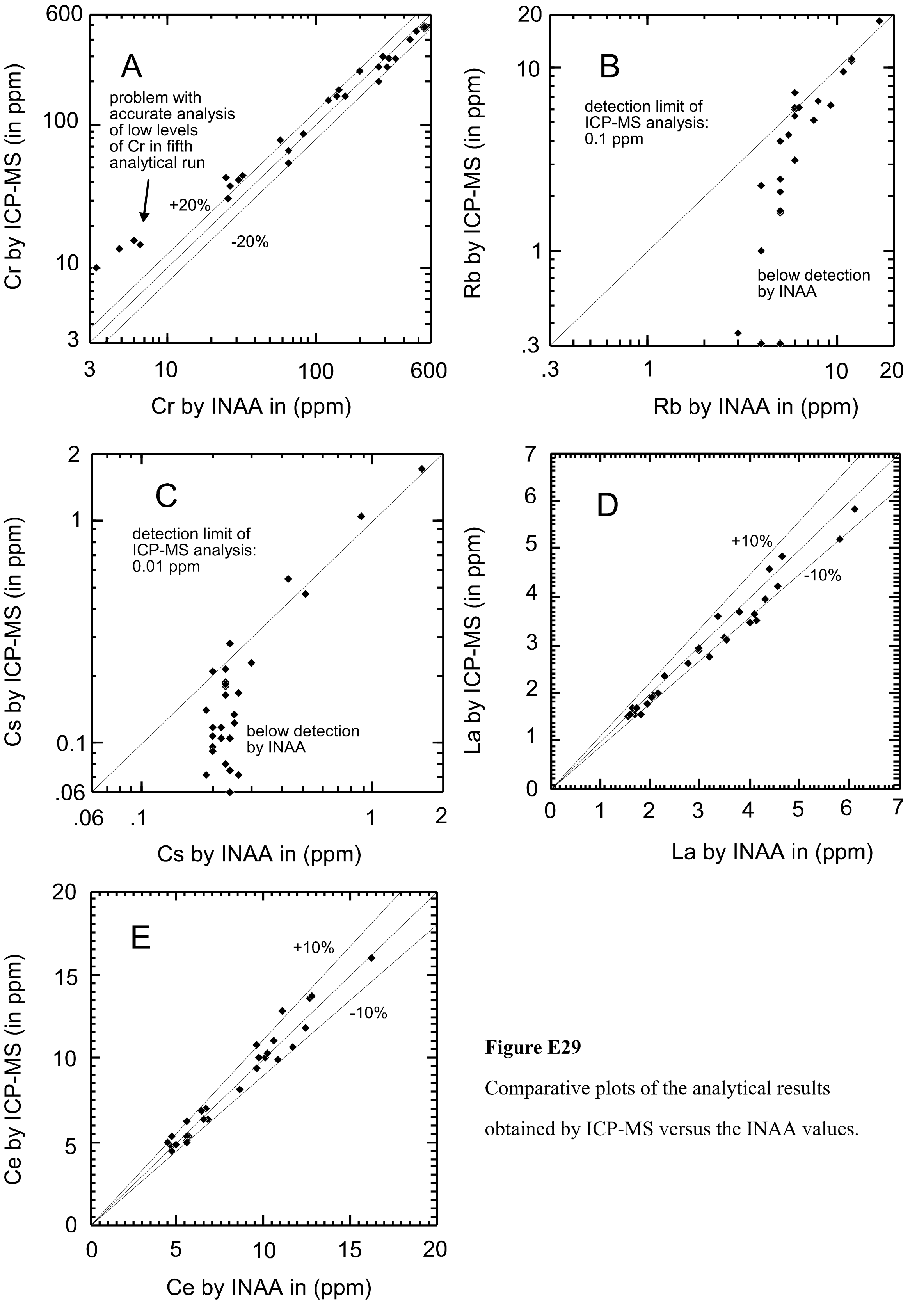


Figure E29

Comparative plots of the analytical results obtained by ICP-MS versus the INAA values.

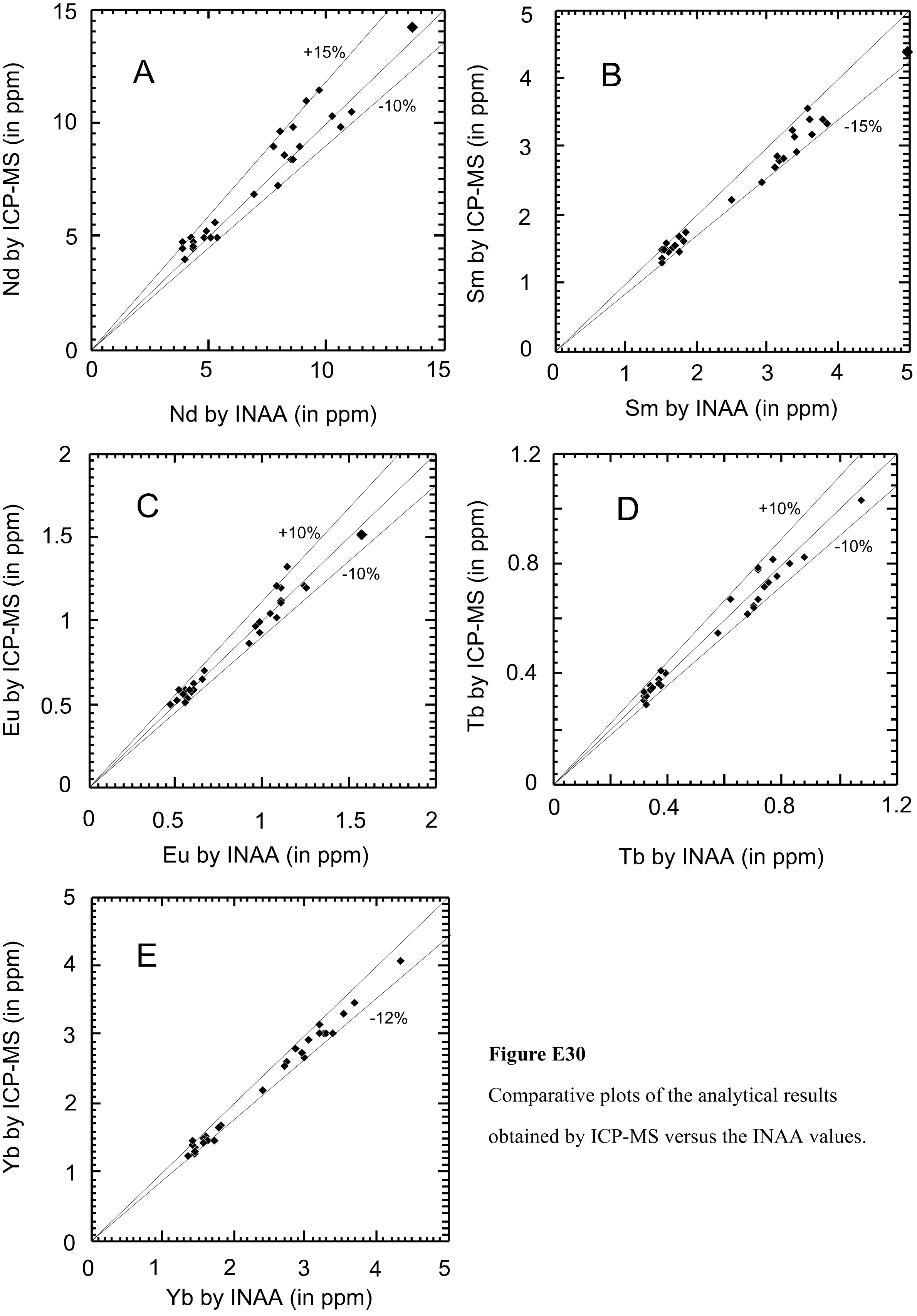


Figure E30

Comparative plots of the analytical results obtained by ICP-MS versus the INAA values.

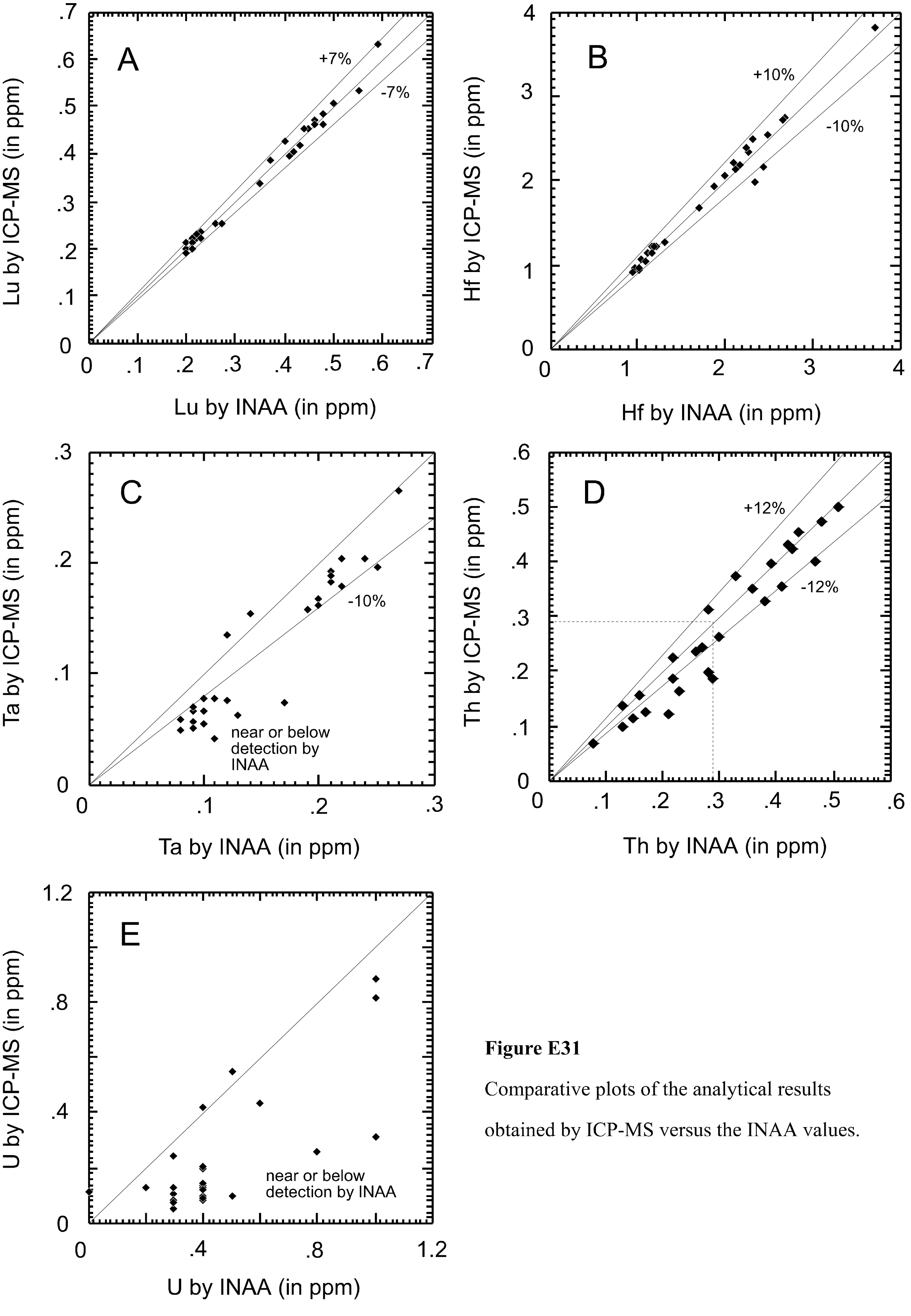


Figure E31

Comparative plots of the analytical results obtained by ICP-MS versus the INAA values.