U. S. Department of the Interior
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Analysis of soil reference materials PL-1 and BPGM-1 for the Polish Committee on Standardization Measures and Quality Control

By

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INTRODUCTION

Under a cooperative agreement between the U.S. Geological Survey (USGS) and the National Institute of Standards and Technology (NIST) analyses were performed on two Polish soil reference materials identified as PL-1 and BPGM-1. This investigation is part of a continuing effort to carefully describe selected international reference materials prior to their distribution in the United States by NIST. The availability and use of diverse and well characterized reference materials provides the scientific community an opportunity to rigorously evaluate routine analytical procedures using reference materials that more closely match samples of interest.

ANALYTICAL PROCEDURES

Drying studies

Triplicate samples of PL-1, BPGM-1 and a single sample of NIST SRM 2704 were weighed into tared ground glass weighing bottles using a Mettler AE100 balance. With the container lids ajar, the bottles were transferred to a drying oven previously equilibrated to 110°C and dried for two hours. After drying, the bottles were capped and transferred to a desiccator to cool for approximately 30 minutes prior to reweighing. Calculation of percent moisture was based on the differences in sample weights divided by the original sample weight and then multiplied by 100.

WDXRF procedure

Prior to WDXRF analyses a Loss on Ignition (LOI) value is determined for each sample. In this step a 0.8000 ± 0.0002g sample is weighed in a tared platinum alloy crucible. The sample is ignited at 925°C for 45 minutes, cooled, reweighed, and the weight difference used to calculate LOI. After completing the LOI analysis a 8.0000 ± 0.0002 g charge (on a dry weight basis) of lithium tetraborate is added to the crucible and the contents thoroughly mixed. A 0.250 mL aliquot of a 50% LiBr solution is then added as a nonwetting agent and the crucible transferred to a specially designed fluxer. The fluxer, holding up to seven crucibles, is then transferred to a muffle furnace operating at 1,120° C. The samples are fused under continual agitation for 40 minutes and then poured into a platinum alloy mold and allowed to cool. The sample disc is analyzed using a Phillips PW1606 X-ray spectrometer. Major element concentrations routinely reported as their oxides were converted to their elemental form through the use of appropriate gravimetric factors. Precision for the method expressed as the percent relative standard deviation (%RSD) is generally <2%. Determination limits for the elements quantified

in this study are reported in table 1. A more detailed discussion of analytical procedures is available (Baedecker, 1989; Arbogast, 1990).

ICP-AES procedure

In the ICP-AES procedure a 0.200 g aliquot of sample is transferred to a Teflon container and 100 μL of a 500 ppm lutetium internal standard is added. The sample is digested at 100°C on a hot plate using a combination of concentrated nitric, hydrochloric, perchloric, and hydrofluoric acids. Following sample decomposition, contents of the teflon container are quantitatively transferred to a 60 mL polyethylene bottle and the final mass adjusted to 10.0 g with 1% v/v nitric acid. Solutions are then analyzed using a 63-channel Jarrell-Ash ICP-AES polychromator, model 1160 Plasma Atomcomp. The ICP-AES system quantifies up to 40 elements simultaneously using 219 inter-element corrections to adjust for spectroscopic interferences. Determination limits for elements quantified in this study are listed in table 1. Additional technical information is available (Baedecker, 1989; Arbogast, 1990).

RESULTS AND DISCUSSIONS

ICP and WDXRF results are reported on the dried weight basis using the drying protocol described above. Summary information for the drying studies, WDXRF, and ICP-AES analyses are reported in tables 2, 3, and 4. Original data is reported in appendices A and B for PL-1 and BPGM-1 respectively. Selected elements in Appendices A and B and tables 3 and 4 are reported with an extra significant figure (lower case) for statistical purposes. Users of these results are cautioned against using more than the appropriate number of significant figures outside the context of this study.

Drying experiments

Examination of table 2 reveals an average weight loss after drying for both soil reference materials of <0.6% with a % RSD of <1%. In the case of SRM 2704, the weight loss of 0.74% correlates closely with the recommend value of 0.8%.

WDXRF results

Results of within bottle analysis using WDXRF for PL-1 and BPGM-1 are reported in table 3. Concentrations are reported on the elemental rather than the traditional oxide basis to assist in subsequent inter-technique comparisons. Estimates of average total element concentration, standard deviation, and percent relative standard deviation are derived using established

statistical procedures and based on the sample population of n=3. In the case of Ca, K, Mg, Na in PL-1 and Ca, Na, and Mn in BPGM-1 observed element concentrations using WDXRF were identical using the rounding criteria established by the routine technique. For these elements, the standard deviation is estimated as <50% of the last significant concentration interval. The less than value reported for the %RSD also reflects this estimated standard deviation. In table 3 standard deviations for Ti, P, and Mn were determined using original data reported with an extra significant figure (lower case). Table 3 also list the average total oxides content (TOC) and LOI values for both reference materials using the original WDXRF data. Average TOC values >99% for both soils is indicative of a reliable quantitative analysis.

ICP-AES results

Results of within bottle determinations for PL-1 and BGPM-1 using ICP-AES analyses are reported in table 4 for 34 elements. Calculation of average, standard deviation and %RSD are based on a sample population of n=3 except in the case of Sc and P in BPGM-1, where the %RSD values are estimated at <50% of the last reporting concentration interval. Calculated standard deviations and %RSD values are determined using the original unrounded data presented in Appendices A and B. Average total element concentration have been corrected (rounded) to the appropriate number of significant figures based on method protocol.

Examination of ICP-AES major element results reveals that estimates of precision (%RSD) coincide with values observed in WDXRF analyses. The good precision for major element analysis (<4%RSD) indicates that both reference materials should be considered homogeneous with respect to within bottle major element concentrations. Graphical comparisons of ICP-AES versus WDXRF major element results for the two reference materials are presented in figures 1 and 2. Calculated slopes and correlation coefficients for the best fit lines obtained using linear regression analysis are both >0.9 indicating no general bias between the two techniques. A possible exception to this trend is Ti, which shows a lower average concentration by ICP-AES in both materials. This lower average concentration may be attributed to the incomplete dissolution of certain acid resistant Ti mineral species.

Evaluation of ICP-AES trace element data in table 4 reveals precision values generally less than 10%. Notable exceptions include Th in both reference materials, Co and Ga in PL-1, and Cu in BPGM-1.

Comparison of trace and major elements results with values for United States soils (Schacklett, H., and Boerngen, J., 1984) reveal that concentrations of most major elements and all trace elements are below the mean (geometric) value for U.S. soils.

Most notable are the lower concentrations of Fe, Nd, Sr, V, and Y. The lower concentrations of major and trace elements in both reference materials is compensated by a higher average silicon concentration compared to United States soils.

Quality Control

NIST's Buffalo River Sediment (SRM 2704) was used as a control sample in this study. Observed values are reported in table 5 along with NIST certified and information values. Comparison of USGS WDXRF results and NIST certified values reveals that all nine major elements lie within the 95% confidence interval (CI) reported by NIST, with an average percent difference (APD) of only 0.8%. A graphical comparison of the two data sets is presented in figure 3 along with a calculated best fit line based on linear regression results. Values for the slope (1.00) and correlation coefficient (0.999) confirm the excellent agreement between USGS WDXRF and NIST certified values.

Major element analysis by ICP-AES reveals that observed Al, K, Mg, and P concentrations also fall within the 95% CI for NIST certified values. The observed concentration values for Ca lie outside the NIST CI boundaries, but previous ICP investigations (Briggs, 1993) involving SRM 2704 reveal that the ICP-AES 95% CI overlaps NIST's CI and is inclusive of the current ICP results. The overlap of CI's is a second criteria established by NIST to evaluate intermethod comparability. Only Na and Ti show a statistically significant bias in the ICP-AES data relative to the NIST value. In the case of Ti this bias correlates with previous studies (Briggs, 1993) utilizing SRM 2704 and is again attributed to the incomplete dissolution of Ti mineral material. Calculation of the APD for the USGS and NIST major element data sets yields a value of <1.3%.

Comparisons of ICP-AES trace element data and NIST certified values are presented in figures 4 and 5 for different element concentration ranges. Best fit lines determined using linear regression analysis reveal slopes and correlation coefficients close to 1, indicating no general bias between ICP-AES and NIST certified values. Calculation of the APD for NIST certified and observed ICP-AES yields a value of 5.7%. A comparison of NIST information values and observed USGS data shows poorer agreement which is reflected in an APD value of 10%. The lack of agreement is especially noticeable for Sr and Ce.

CONCLUSIONS

Polish soil reference materials PL-1 and BPGM-1 were analyzed for their trace and major element constitutes at the U.S. Geological Survey laboratories under a cooperative arrangement with the National Institute of Standards and Technology. Results of major elements analysis for both reference materials using WDXRF and ICP-AES reveal an average %RSD of <1.3% suggesting that the reference materials are homogeneous with respect to within bottle determinations. Statistical analysis of average trace element data for PL-1 and BPGM-1 by ICP-AES reveals a similar trend with an average %RSD of 6.6%.

Comparison of trace element data in the Polish reference materials and average United States soils indicate that the Polish reference materials contain lower major and trace element concentrations. Higher concentrations of silicon in the Polish reference materials compensate for the lower element concentrations. Analysis of control sample SRM 2704 by WDXRF and ICP-AES shows good agreement with NIST certified and information values.

ACKNOWLEDGEMENT

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Appendix A Analytical results for Polish soil reference material PL-1

ICP-AES

ID	Al, %	Ca, %	Fe, %	K, %	Mg, %	Na, %	P, %	Ti,%
A	2.89	0.313	0.886	1.54	0.161	0.561	0.049	0.234
B	2.84	0.309	0.876	1.53	0.157	0.556	0.048	0.237
C	2.84	0.311	0.883	1.53	0.156	0.554	0.048	0.231

ID	Ag, ppm	As, ppm	Ba, ppm	Be, ppm	Cd, ppm	Ce, ppm	Co, ppm
A	<2	<10	369	<1	<2	45.1	3.6
B	<2	<10	364	<1	<2	43.3	4.5
C	<2	<10	364	<1	<2	44.9	3.5

ID	Cr, ppm	Cu, ppm	Ga, ppm	La, ppm	Li, ppm	Mn, ppm	Mo, ppm
A	22.1	5.1	6.3	22.5	10.4	433	<2
B	23.7	4.4	5.7	21.4	10.3	429	<2
C	21.4	4.2	7.1	21.0	10.4	432	<2

ID	Nb, ppm	Nd, ppm	Ni, ppm	Pb, ppm	Sc, ppm	Sr, ppm	Th, ppm
A	5.9	16.2	8.5	19.2	3.8	71.3	6.9
B	5.7	15.8	7.3	19.3	3.8	70.4	5.7
C	5.7	17.3	8.0	19.4	3.8	70.2	6.0

ID	U, ppm	V, ppm	Y, ppm	Yb, ppm	Zn, ppm
A	<100	22.8	11.1	1	28.9
B	<100	22.4	10.7	<1	28.7
C	<100	22.5	10.8	1	28.3

WD-XRF

ID	Si, %	Al, %	Fe, %	Mg, %	Ca, %	Na, %	K, %	Ti, %	P, %	Mn,%
A	40.39	2.81	0.87	0.14	0.29	0.50	1.55	0.348	0.053	0.044
B	40.29	2.81	0.85	0.14	0.29	0.49	1.55	0.344	0.051	0.043
C	40.39	2.79	0.85	0.14	0.29	0.49	1.55	0.345	0.051	0.044

Moisture

ID	% weight loss on drying
A	0.557
B	0.567
C	0.564

Appendix B Analytical results for Polish soil reference material BPGM-1

%, percent; ppm parts per million; ID, sample replicate identification code; -, data not reported

ICP-AES

ID	Al, %	Ca, %	Fe, %	K, %	Mg, %	Na, %	P, %	Ti, %
A	2.88	0.313	0.886	1.54	0.161	0.561	0.049	0.145
B	2.84	0.309	0.876	1.53	0.157	0.556	0.048	0.143
C	2.84	0.311	0.883	1.53	0.156	0.554	0.049	0.147

ID	Ag, ppm	As, ppm	Ba, ppm	Be, ppm	Cd, ppm	Ce, ppm	Co, ppm
A	<2	<10	369	<1	<2	27.6	2.6
B	<2	<10	364	<1	<2	26.3	2.8
C	<2	<10	364	<1	<2	30.1	2.9

ID	Cr, ppm	Cu, ppm	Ga, ppm	La, ppm	Li, ppm	Mn, ppm	Mo, ppm
A	14.8	3.9	4.8	13.6	7.7	248	<2
B	15.6	4.2	4.8	13.4	7.9	249	<2
C	15.5	4.9	5.5	14.1	8.1	246	<2

ID	Nb, ppm	Nd, ppm	Ni, ppm	Pb, ppm	Sc, ppm	Sr, ppm	Th, ppm
A	3.9	11.3	5.1	15.2	2.7	55.2	4.3
B	4.0	11.0	5.8	15.4	2.7	54.9	2.9
C	3.2	12.3	5.6	14.4	2.7	55.6	3.8

ID	U, ppm	V, ppm	Y, ppm	Yb, ppm	Zn, ppm
A	<100	15.9	7.1	<1	22.2
B	<100	15.9	6.9	<1	23.1
C	<100	16.4	7.0	<1	-

WD-XRF

ID	Si, %	Al, %	Fe, %	Mg, %	Ca, %	Na, %	K, %	Ti, %	P, %	Mn, %
1A	41.70	2.27	0.64	0.12	0.26	0.35	1.31	0.191	0.051	0.028
1B	41.65	2.25	0.65	0.11	0.26	0.35	1.30	0.195	0.052	0.028
1C	41.79	2.28	0.65	0.11	0.26	0.35	1.32	0.192	0.051	0.028

Moisture

ID	% weight loss on drying
A	0.408
B	0.406
C	0.399

Table 1 Determination limits for ICP-AES and WDXRF methods

-, element not determined using this procedure; ppm, parts per million concentration, μg/g; %, percent concentration,

Element	ICP-AES	WD-XRF[1]
Al, %	0.005	0.05
Ca, %	0.005	0.01
Fe, %	0.005	0.03
K, %	0.05	0.02
Mg, %	0.005	0.06
Na, %	0.005	0.11
P, %	0.005	0.02
Ti, %	0.005	0.01
Si, %	-	0.05
Ag, ppm	2	-
As, ppm	10	-
Ba, ppm	1	-
Be, ppm	1	-
Cd, ppm	2	-
Ce, ppm	4	-
Co, ppm	1	-
Cr, ppm	1	-
Cu, ppm	1	-
Ga, ppm	4	-
Ho, ppm	4	-
La, ppm	2	-
Li, ppm	2	-
Mn, ppm	4	80
Mo, ppm	2	-
Nb, ppm	4	-
Nd, ppm	4	-
Ni, ppm	2	-
Pb, ppm	4	-
Sc, ppm	2	-
Sr, ppm	2	-
Th, ppm	4	-
U, ppm	100	-
V, ppm	2	-
Y, ppm	2	-
Yb, ppm	1	-
Zn, ppm	2	-

[1] WDXRF element determination limits based on oxide values multiplied by the appropriate gravimetric factor

Table 2. Summary results for moisture determinations in Polish soil reference materials PL-1 and BPGM-1 and NISTS's SRM 2704

%, percent; RSD, relative standard deviation; -, value not calculated, only a single measurement made

Sample	Average moisture content, %	Standard Deviation	%RSD
PL-1	0.56	0.004	0.73
BPGM-1	0.40	0.004	0.88
SRM 2704	0.72	-	-

Table 3 Major element concentrations in Polish soils PL-1, BPGM-1, and NIST SRM 2704 as determined by Wavelength Dispersive X-ray Fluoresence.

Avg., arithmetic average; Std. Dev., standard deviation; %RSD, percent relative standard deviation; %, percent of total element concentration; TOC, total oxide content; LOI, loss on ignition.

	PL-1			BPGM-1		
Element	Avg.	Std. Dev.	%RSD	Avg.	Std. Dev.	%RSD
Si, %	40.39	0.05	0.13	41.71	0.05	0.13
Al, %	2.81	0.01	0.33	2.27	0.02	0.70
Fe, %	0.86	0.01	0.94	0.65	0.004	0.6
Mg, %	0.14	<0.005	<3.6	0.12	0.004	3.0
Ca, %	0.29	<0.005	<1.7	0.26	<0.005	<1.9
Na, %	0.49	<0.005	<1.0	0.35	<0.005	<1.4
K, %	1.55	<0.005	<0.3	1.31	0.01	0.63
Ti, %	0.35	0.002	0.6	0.19	0.002	1.0
P, %	0.05	0.001	2.0	0.05	0.001	2.0
Mn, %	0.04	<0.0005	<1.2	0.03	<0.0005	<2.0
TOC, %	99.5	0.15	0.15	99.6	0.18	0.18
LOI, %	2.68	0.02	0.78	2.05	0.01	0.49

Table 4 Total element concentrations in Polish soils PL-1 and BPGM-1 determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy

Element	PL-1 Avg.[1]	PL-1 STDV[2]	PL-1 %RSD[3]	BPGM-1 Avg.[1]	BPGM-1 STDV[2]	BPGM-1 %RSD[3]
Al, %	2.9	0.03	1.0	2.3	0.003	0.13
Ca, %	0.31	0.002	0.6	0.28	0.003	1.1
Fe, %	0.88	0.005	0.6	0.66	0.003	0.4
K, %	1.5	0.01	0.6	1.3	0.005	0.4
Mg, %	0.16	0.003	1.9	0.13	0.001	0.8
Na, %	0.56	0.004	0.7	0.39	0.003	0.8
P, %	0.05	0.001	2.0	0.05	<0.005	<2.0
Ti, %	0.23	0.003	1.2	0.14	0.002	1.4
Ag, ppm	<2	-	-	<2	-	-
As, ppm	<10	-	-	<10	-	-
Ba, ppm	360	3.1	0.8	280	0.7	0.2
Be, ppm	<1	-	-	<1	-	-
Cd, ppm	<2	-	-	<2	-	-
Ce, ppm	44.	0.9	2.1	28	2	7.0
Co, ppm	4	0.5	14	3	0.14	5.2
Cr, ppm	22	1.1	5.2	15	0.4	2.9
Cu, ppm	5	0.4	9.9	4	0.5	12
Ga, ppm	6	0.7	11.	5	0.4	7.4
La, ppm	22	0.7	3.5	14	0.4	2.8
Li, ppm	10	0.1	1.	8	0.2	2.9
Mn, ppm	430	1.8	0.4	250	1.3	0.5
Mo, ppm	<2	-	-	<2	-	-
Nb, ppm	6	0.1	1.8	4	0.1	3.4
Nd, ppm	16	0.7	4.6	11	0.6	5.8
Ni, ppm	8	0.6	7.8	6	0.4	6.4
Pb, ppm	19	0.1	0.5	15	0.6	3.7
Sc, ppm	4	<0.05	<1.3	3	<0.03	<1.3
Sr, ppm	70	0.6	0.9	55	0.3	0.5
Th, ppm	6	0.6	10	<4	-	-
U, ppm	<100	-	-	<100	-	-
V, ppm	23	0.2	0.9	16	0.3	1.9
Y, ppm	11	0.2	2.2	7	0.1	1.4
Yb, ppm	<1	-	-	<1	-	-
Zn, ppm	29	0.3	1.2	23	0.7	2.9

[1] arithmetic average
[2] standard deviation of sample population
[3] percent relative standard deviation

Table 5 Comparison of U.S. Geological Survey ICP-AES and WDXRF values to National Institute of Standards and Technology's SRM 2704 recommended or certified values.

-, value not reported; (#), values in parenthese are NIST information value; ppm, parts per million concentration, μg/g; %, percent concentration; <, less than.

Element	USGS WD-XRF	USGS ICP-AES	NIST Value	NIST Confidence Interval
Al, %	6.14	6.1	6.11	± 0.16
Ca, %	2.62	2.7	2.60	± 0.03
Fe, %	4.13	4.0	4.11	± 0.10
K, %	1.99	2.0	2.00	± 0.04
Mg, %	1.19	1.2	1.20	± 0.02
Na, %	0.55	0.61	0.547	± 0.014
P, %	0.10	0.10	0.0998	± 0.0028
Ti, %	0.46	0.30	0.457	± 0.018
Si, %	29.1	-	29.08	± 0.13
Ag, ppm	-	<2	-	-
As, ppm	-	20	23.4	± 0.8
Ba, ppm	-	410	414.	± 12
Be, ppm	-	2	-	-
Cd, ppm	-	3	3.45	± 0.22
Ce, ppm	-	60	(72)	-
Co, ppm	-	16	14.0	± 0.6
Cr, ppm	-	140	135	± 5
Cu, ppm	-	99	98.6	± 5.0
Ga, ppm	-	15	(15)	-
La, ppm	-	31	(29)	-
Li, ppm	-	47	(50)	-
Mn, ppm	500	560	555	± 19
Mo, ppm	-	<2	-	-
Nb, ppm	-	8	-	-
Nd, ppm	-	30	-	-
Ni, ppm	-	45	44.1	± 3.0
Pb, ppm	-	150	161	± 17
Sc, ppm	-	12	(12)	-
Sr, ppm	-	140	(130)	-
Th, ppm	-	7	(9.2)	-
U, ppm	-	<100	3.13	± 0.13
V, ppm	-	93	95	± 4
Y, ppm	-	22	-	-
Yb, ppm	-	2	(2.8)	-

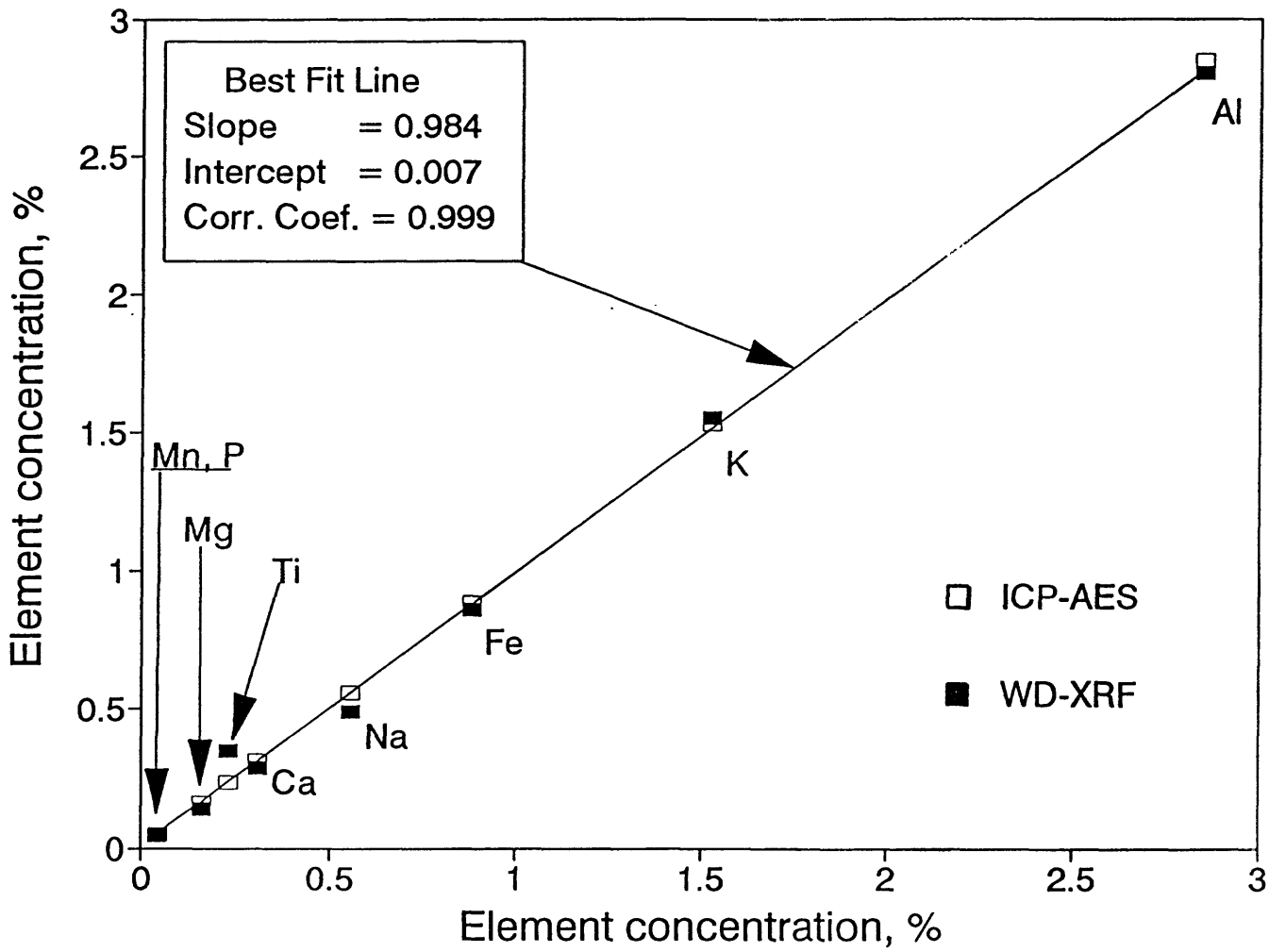

Figure 1. Comparison of major element concentrations in PL-1 by ICP-AES and WDXRF

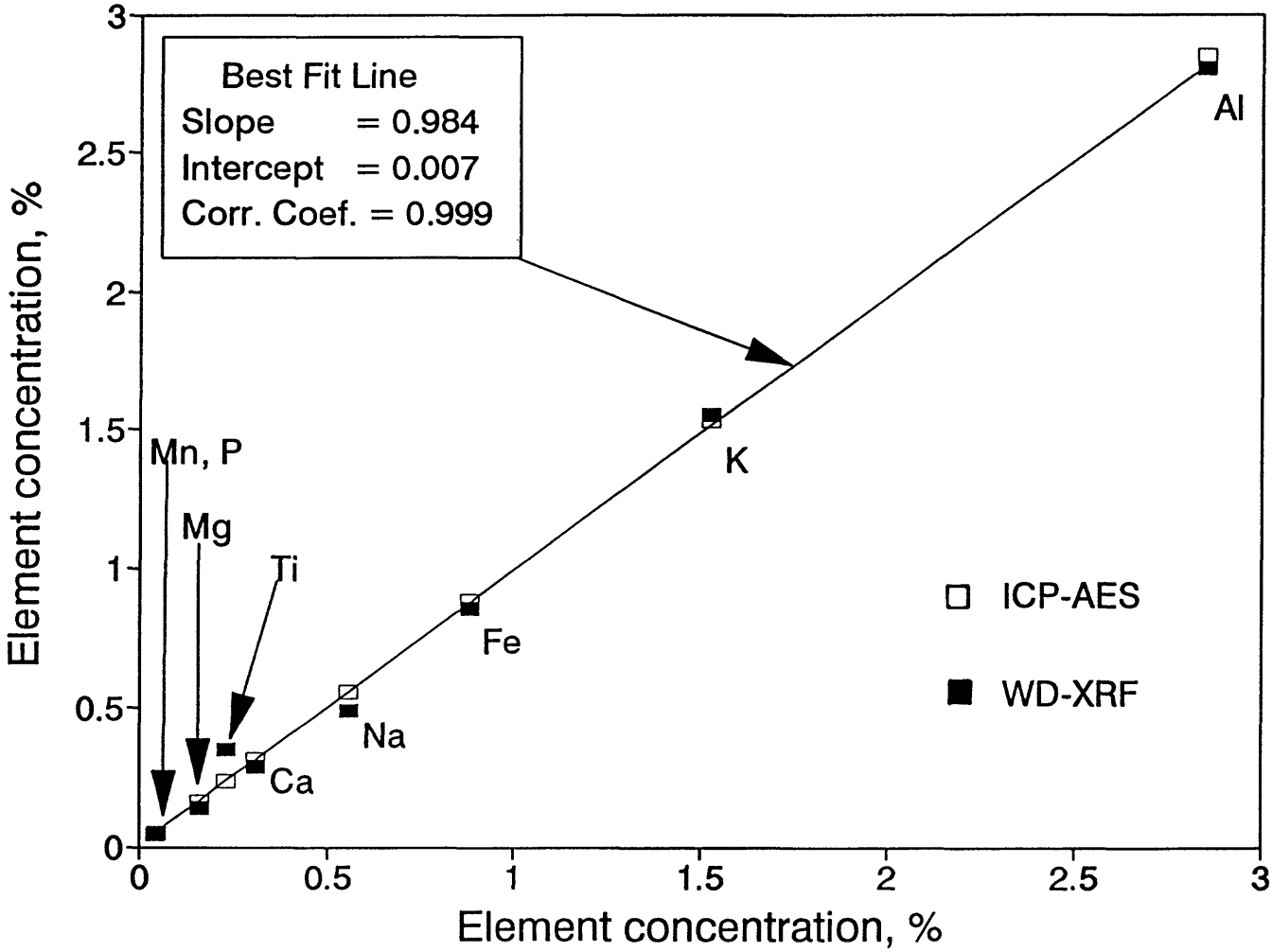

Figure 2. Comparison of major element concentrations in BPGM-1 by ICP-AES and WDXRF

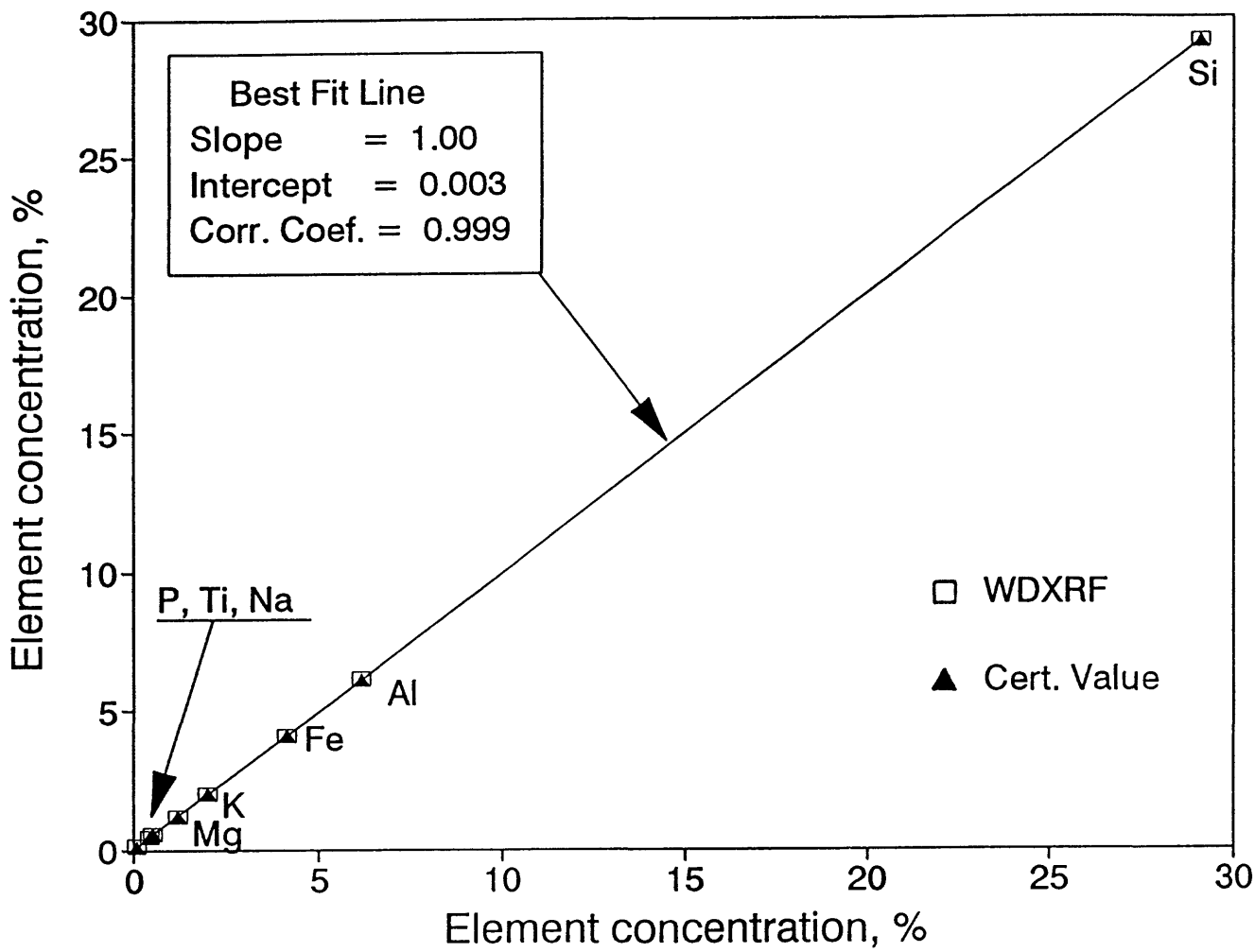

Figure 3. USGS WDXRF results versus NIST certified values in SRM 2704

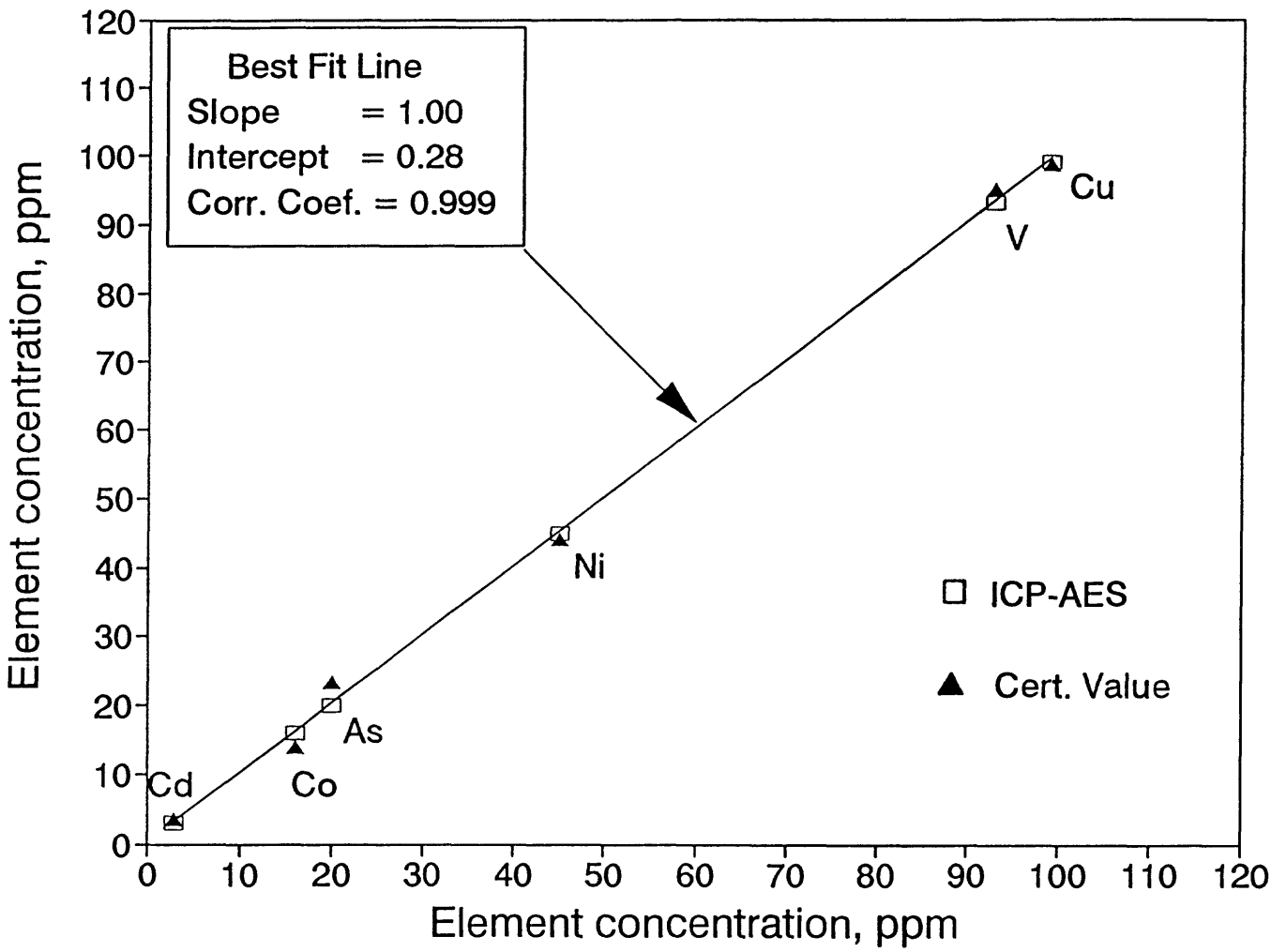

Figure 4. USGS ICP-AES results versus NIST certified values in SRM 2704 for element with total element concentration <200ppm

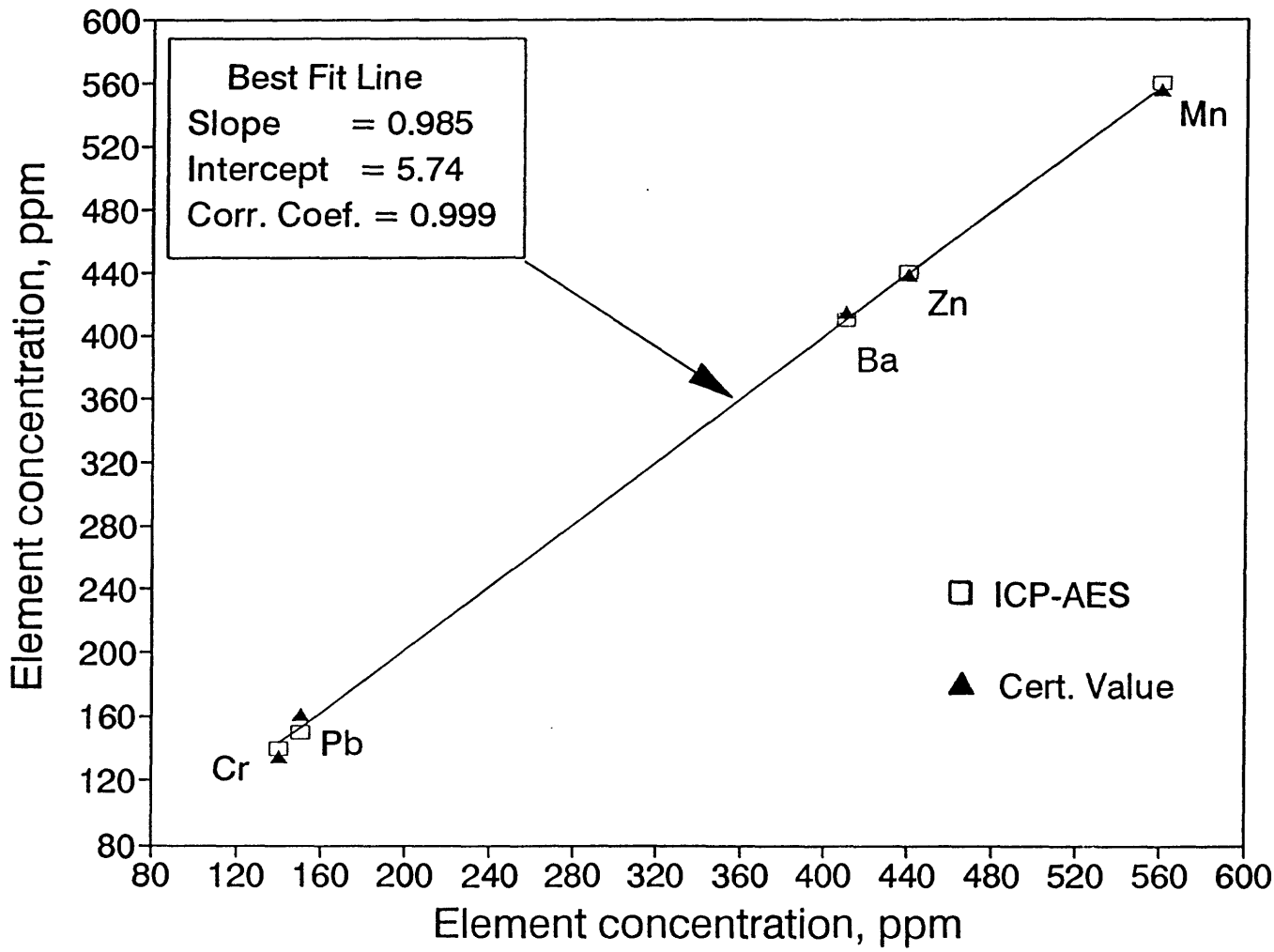

Figure 5. USGS ICP-AES results versus NIST certified values in SRM 2704 for elements with total element concentratrions between 200 and 600 ppm

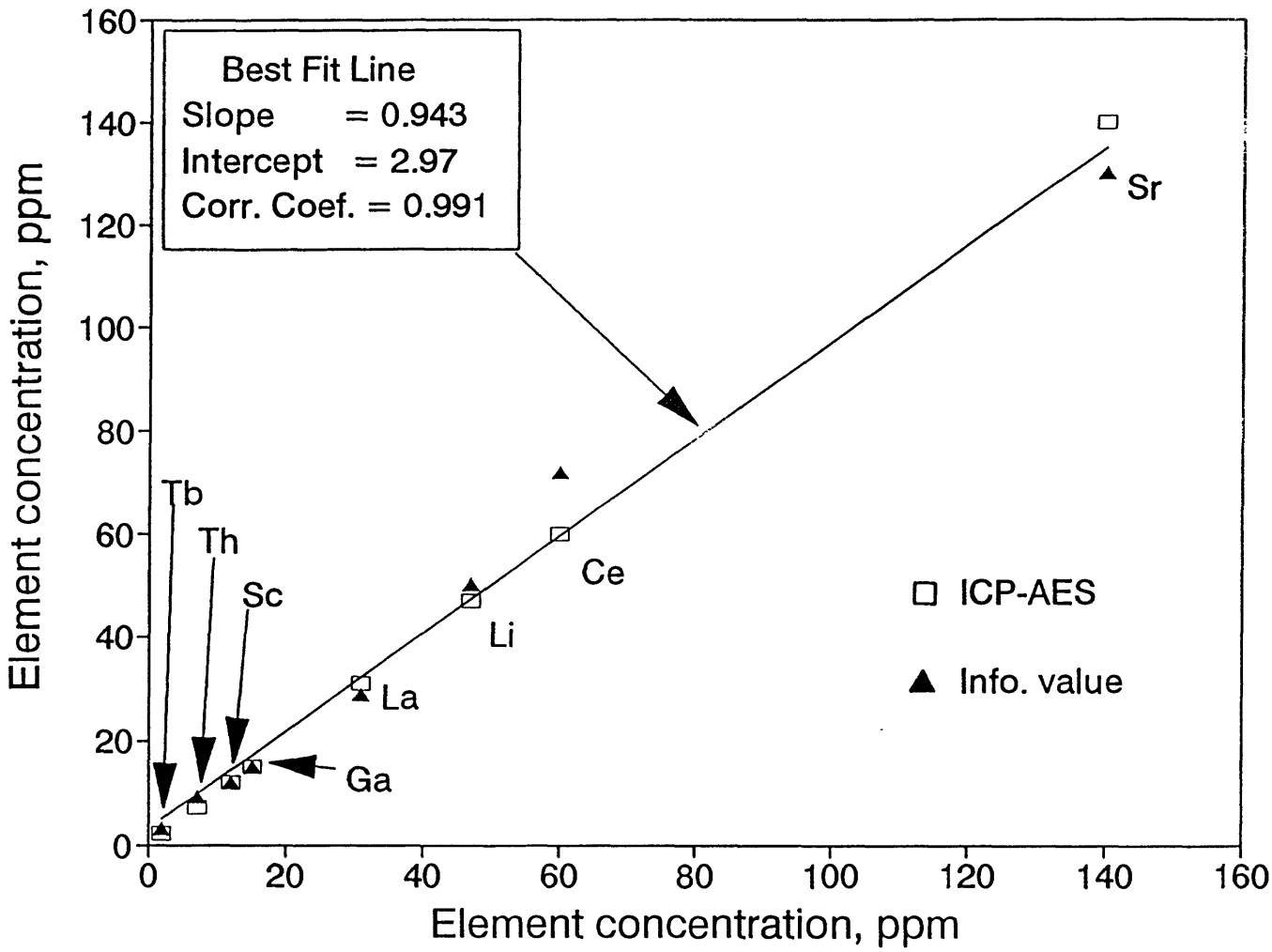

Figure 6. USGS ICP-AES results versus NIST information values in SRM 2704