UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

A Method of Quantitative Analysis of Trace Elements in Silicate Rocks by Energy-Dispersive X-Ray Fluorescence Spectroscopy

by

John C. Jackson and Robert A. Ayuso
U.S. Geological Survey
Reston, VA 22092

Open-File Report 88-432

1988

Abstract

Fourteen rock samples were analyzed to evaluate the precision and accuracy of an automated energy-dispersive x-ray fluorescence analytical method. The samples were prepared as loose powders, then analyzed for 14 trace elements (Rb, Sr, Ba, Zr, Nb, La, Ce, Y, Cr, Ni, Cu, Mo, Sn, Zn). Each sample was analyzed 10 times. Intensities for Ni, Cu, Zn and Sn were determined by integrating the net peak area; intensities for the remaining elements were determined using a gaussian-curve fitting routine. Resulting intensities were ratioed to either Compton or Compton and Rayleigh scatter intensity. Elemental concentrations were calculated by a least-squares fitting method using simple linear regressions derived from a variety of standard rock samples.

Overall analytical precision is estimated at ± 2% relative for elemental concentrations above 100 ppm. Our results are generally in agreement with data obtained by other methods of analysis and differ by $\leq$6% relative for Rb, Sr, Ba, Zr, Ce, Y, Cr, and Zn for concentrations $\geq$100 ppm. Estimates of the precision and relative agreement with other methods indicate that routine trace element analysis by energy-dispersive X-ray fluorescence is fast, reliable, and efficient.

Introduction

Many geologic studies rely on large-scale reconnaissance sampling. An example of this approach is the effort to assess the potential for economic concentrations of mineral deposits in large areas of the United States. Reconnaissance geochemical sampling in such studies requires analytical methods capable of producing multi-element analyses of large numbers of samples quickly and reliably.

Energy dispersive x-ray fluorescence spectroscopy (EDXRF) is ideally suited for such projects because in this method of analysis the time required from sample preparation to production of data is relatively short. In addition, this method is non-destructive, and has been shown to be relatively precise and accurate for quantitative analysis of geologic samples (Johnson 1984, 1987; Terashima 1987). EDXRF results can thus be used as a preliminary screening step to select samples for more detailed analytical work.

This report evaluates the precision of an automated trace-element analysis routine implemented on an energy dispersive x-ray fluorescence spectrometer and analyzer system (Kevex 0700/8000)*, at the Branch of Eastern Mineral Resources, Reston, Virginia. In this report, an analytical method is presented which is fast, efficient, and precise for screening economically and petrologically important elements from a wide variety of felsic rock compositions such as would be obtained during reconnaissance geochemical sampling. Comparison of this automated trace element technique demonstrates good agreement with analytical determinations by other techniques.

Summary of Sample Preparation and Analytical Method

Fourteen rock samples representing a diverse group of felsic rock types were selected to demonstrate that the method is widely applicable (table 1, see page 4). Each sample was analyzed 10 times for 14 elements. These data, along with the means and standard deviations, are shown in Appendix A. Also shown in Appendix A under the heading "other methods," are the analytical results for these samples as reported by several other methods.

---

* Any use of trade name or trademark in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Each sample was crushed to approximately 1mm to 3mm size pieces using a stainless steel jaw-crusher, then ground to a 100 mesh powder using an alumina-ceramic grinding dish on a shatterbox. Approximately 2 grams of powdered sample was hand pressed into a sample holder consisting of a 1 inch diameter aluminum ring with 0.00025 inch thick mylar stretched over one end by means of a teflon collar, fitting over the aluminum ring. Samples were prepared in duplicate, then five replicate analyses were performed on each specimen.

An energy dispersive x-ray fluorescence spectrometer (Kevex 0700/8000) employing secondary targets was used for the analysis of the samples. Different secondary targets were used depending on the groups of elements analyzed in order to optimize excitation efficiency (table 2). A Gd target was used to fluoresce Sn, Ba, La, and Ce; a Ag target was used to fluoresce Rb, Sr, Y, Zr, Nb, and Mo; a Ge target was used to fluoresce Ni, Cu, and Zn; and an Fe target was used to fluoresce Cr. The resulting spectra were acquired and processed to remove escape peaks, smooth the spectra, determine and subtract background, and in the case of certain elements, correct for interference of overlapping peaks.

Background interference was determined on spectra acquired from the Ge secondary target by recalling a previously stored background intensity, and normalizing it to the sample spectrum. Background was determined on spectra acquired from other secondary targets by recalling previously selected points (windows) along each spectrum, then modeling a fit between these points. The background as determined was then subracted from the sample spectrum.

Table 1. Description of Samples

Sample Number	ROCK TYPE
AQM-CL	Leucogranite
SLC-21-D	Diorite
SLC-66	Quartz diorite
WID-101-MI	Quartz diorite
AT-0-2	Leucogranite
84-AR-30	Leucogranite
J-17	Gneiss
83-PL-217	Granodiorite
84-AA-15	Leucogranite
83-D-192	Granodiorite
14-384-397	Granodiorite
82-D-185	Syenite
83-D-209	Syenite
83-PL-222	Granodiorite

Table 2. Excitation conditions

Element	Secondary Target	Kv	Ma	Acquisition Time(seconds)
Cr	Fe	25	2.0	200
Ni,Cu,Zn	Ge	20	1.5	300
Rb,Sr,Y,Zr,Nb,Mo	Ag	40	1.3	500
Sn,Ba,La,Ce	Gd	60	2.0	500

Spectral interference of the K-alpha line by the K-beta line of an element of lower atomic number was found for the following elements: Ni interfering with Cu, Ti with Cr, Rb with Y, Sr with Zr, and Y interfering with Nb. Interference of Ni on Cu spectra was corrected using a pure element strip process. This was done by recalling a spectrum of pure Ni, normalizing it to the sample spectrum and then subtracting the normalized pure Ni spectrum from the sample spectrum, resulting in a Ni-free Cu K-alpha peak. Other spectral overlap problems encountered during this study were corrected automatically by the deconvolution software provided by the Kevex Corporation using a gaussian curve fitting method. This method synthesizes gaussian shaped peaks, fitting them to the appropriate elemental peaks, and compensates for the K-beta on K-alpha overlap, if present, before determining analyte intensities.

Intensities were determined for Ni, Cu, Zn, and Sn by integrating the net peak area. For elements Cr, Rb, Sr, Y, Zr, Nb, Mo, Ba, La, and Ce, intensity determination was done using the gaussian curve fitting method described above, by extracting intensities and compensating for spectral overlap. The extracted peak intensities were then ratioed to the Compton or Compton and Rayleigh scatter intensity to correct for particle size and matrix absorption (Nielson 1979).

Data reduction was performed by a least squares fitting method which produced element concentrations from intensity ratios, using regression coefficients determined from calibration curves. These calibration curves were constructed by plotting intensity ratios determined from analyzing well known U.S. Geological Survey standards, as well as standards from other sources, against the known concentrations for these standards (table 3, see next page).

Table 3. Standards used for the calibration curves

Name of Standard	Source	Element Rb	Sr	Ba	Zr	Nb	La	Ce	Y	Cr	Ni	Cu	Mo	Sn	Zn
AGV-1	a	X	X	X	X	X	X	X	X		X	X		X	X
BCR-1	a	X	X	X	X	X	X	X	X					X	X
BHVO-1	a	X	X	X	X	X	X	X	X	X	X	X		X	X
BIR-1	a	X	X		X				X	X	X	X		X	X
DNC-1	a	X	X		X				X	X	X	X		X	X
DTS-1	a									X	X			X	
G-1	a		X		X	X	X	X	X	X		X			X
G-2	a	X	X	X	X	X	X	X	X		X	X		X	X
GSP-1	a	X	X	X	X	X	X	X	X		X	X		X	X
GXR-1	a			X				X							
MAG-1	a		X	X	X	X		X	X	X	X	X		X	X
MA-N	a	X		X											
MICA-Fe	a	X		X	X	X	X	X							
MICA-Mg	a	X	X	X	X	X					X			X	
PCC-1	a									X	X			X	
QLO-1	a	X	X	X	X	X	X	X	X		X	X		X	X
RGM-1	a	X	X	X	X	X	X	X	X		X	X		X	X
SCO-1	a	X	X	X	X	X	X	X	X	X	X	X		X	X
SDC-1	a	X	X		X	X	X	X	X	X	X	X		X	X
SG-1A	a	X					X	X							
SGR-1	a	X	X	X	X	X	X	X	X	X	X			X	
STM-1	a	X	X	X	X	X	X	X	X		X			X	X
W-1	a	X		X			X			X	X	X		X	X
W-2	a		X	X	X	X	X	X	X	X	X	X		X	X
AK-107	b		X	X					X						
AK-110	b								X						
AK-112	b		X	X											
LH-14	c	X	X												
LH-34	c	X	X												
MO580	d												X		
MO290	d												X		
MO145	d												X		
MO100	d												X		
MO70	d												X		
MO70	d												X		
MO35	d												X		
MO20	d												X		
MO10	d												X		
RJM-22	e		X	X											

Sources

a. from Abbey, 1984.

b. from Hudson and Arth 1983.

c. from Arth and others 1980.

d. Dilution series prepared as an in house molybdenum standard in 1985 by Jim Eckert of the U.S. Geological Survey, Reston, VA.

e. Rhyolitic pumice from Jemez Nountains, NM, prepared as an in house standard by David Gottfried, U.S. Geological Survey, Reston, VA.

Detection Limits

Minimum detection limit (MDL) calculations were estimated at the 2 sigma level for each element from the spectrum of a standard acquired using the excitation conditions shown in table 2. An extrapolated lower and upper limit of detection was determined for each element based on these MDL values, considering also the range of concentrations of the standards and the linearity (integrity) of each calibration (table 4).

Precision

In order to evaluate the precision for each element across the full range of concentrations covered by these 14 samples, the low, high, and median values and their respective standard deviations are shown (table 5). There is no median value for molybdenum since there were only two samples with detectible molybdenum.

For all elements, the standard deviation values, if taken as a percentage of the mean (these calculations are not shown), decrease from the lowest to highest elemental concentrations indicating a higher precision at higher concentrations. This is expected because that portion of the uncertainty due to statistical counting error depends upon the total accumulated count, and thus decreases as the number of counts increases (Bertin 1970). This suggests that the primary factor limiting precision in our study is counting error.

The average relative precision for each element was calculated both for concentrations greater than 100 ppm, and for concentrations less than 100 ppm. These values are at one sigma, and are shown in Table 5.

Table 4. MDL values, the standard from which each MDL was determined, the range of standards, and the extrapolated range of detection for each element. All values are in ppm.

Element	MDL (standard)	Range of Standards	Extrapolated range of Detection
Rb	1 (AGV)	2-3600	2-4000
Sr	1 (AGV)	9-700	5-1000
Ba	4 (STM)	42-4000	10-5000
Zr	1 (AGV)	18-1300	10-1500
Nb	1 (AGV)	5-270	5-500
La	5 (STM)	10-195	10-500
Ce	6 (STM)	19-370	20-500
Y	1 (AGV)	11-172	10-500
Cr	3 (BHVO)	20-4200	20-5000
Ni	2 (SCO)	3-2400	5-3000
Cu	1 (SCO)	10-140	5-500
Mo	2 (AGV)	10-580	10-1000
Sn	1 (GSP)	2-70	2-500
Zn	1 (SCO)	36-240	18-1000

Table 5. Range of concentrations for each element including the high, low, and median values and their standard deviations. Analytical precision is shown for each element both for concentrations above 100 ppm and less than or equal to 100 ppm. All values are in ppm unless otherwise shown.

	Range of Concentrations						Relative Precision	
	high		low		median			
Element	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	<100ppm	>100ppm
Rb	910	4	5	1	119	2	8%	2%
Sr	1280	5	5	2	236	2	13%	1%
Ba	2036	8	23	3	592	7	11%	1%
Zr	596	5	61	1	201	1	2%	1%
Nb	40	1	5	2	15	1	10%	--
La	83	7	15	4	29	8	16%	--
Ce	176	7	40	6	55	6	11%	4%
Y	134	2	10	1	30	2	7%	2%
Cr	195	7	26	11	45	5	27%	3%
Ni	73	3	6	2	20	2	17%	--
Cu	202	3	5	1	14	2	14%	1%
Mo	83	1	11	1	--	--	5%	--
Sn	45	3	2	1	3	1	37%	--
Zn	132	3	31	1	63	1	2%	2%

Precision was determined by averaging the percent relative standard deviations for all values over 100 ppm, and for all values less than or equal to 100 ppm for each element. The elements Sr, Ba, Zr, and Cu have the highest precision above 100 ppm, with an average analytical uncertainty of ± 1% at one sigma, and Ce showed the lowest precision above 100 ppm with an average analytical uncertainty of ± 4% at one sigma. It should be noted that for elements Nb, La, Ni, Mo, and Sn, no samples have a concentration greater than 100 ppm, thus precision estimates could not be made in these cases at this level.

For elemental concentrations less than or equal to 100 ppm, precision ranges from ± 2% for Zr and Zn, to ± 27% for Cr and ± 37% for Sn. However, as the analysis of a given element nears the detection limit, the results are progressively less precise and may approach ± 50% of the concentration of the sample. Thus analysis of elements with contents at or near the limit of detection indicate that precision in this case is better shown in absolute terms as determined by averaging the standard deviations for all values less than 100 ppm for each element. In absolute terms, determinations of Zr, Nb, Mo, Sn, and Zn contents are the most precise below 100 ppm, showing an average analytical uncertainty of ± 1 ppm at one sigma; results for Cr, Ce, and La are the least precise below 100 ppm as they have average analytical uncertainties of ± 8 ppm, ± 6 ppm, and ± 5 ppm, respectively.

Relative agreement with other techniques

Analytical estimates determined for this group of felsic samples by other methods of analysis are included in Appendix A. We note that values determined by other methods of analysis are used in our report to indicate the relative agreement between our method and these other techniques. Thus the term "relative agreement" is used here instead of "accuracy."

Calculated values showing the percent relative agreement for each element are listed in table 6. These values represent the difference between the two methods, divided by the value obtained by other methods. Concentrations were separated into three categories: less than or equal to 10 ppm, from 11 ppm to 99 ppm, and greater than or equal to 100 ppm. Also shown in table 6 is the overall agreement for each element, obtained by calculating the average percent relative difference (a weighted average).

For concentrations above 100 ppm, agreement ranges between 4% and 6%, with the exception of Cu (26%), but the validity of this estimate is in question since it is based on only one sample. The relative agreement for concentrations from 11 ppm to 99 ppm ranges from 7% for Rb and Y, to 54% for Mo; values of 33% for Sn and 54% for Mo are based on only one sample each. Another factor which may limit the results for molybdenum is the lack of suitable standards (table 3).

For concentrations below 10 ppm the agreement is ± 1 ppm for Rb, Sr, Nb, and Sn, in terms of absolute difference.

In general, the relative agreement between the results obtained by our technique and those from other methods is better at higher concentrations, except for Cu, Sn, and Nb. The discrepancies for Cu and Sn may be explained by our limited data base, in which the relative agreement estimate for the highest concentration range for these elements is based on only one sample. Another possible explanation, however, may be unresolved matrix effects, which depend on the nature of the sample. For example, in the case of Nb, the four samples which exhibited the closest agreement between methods were all granodiorites, two of these being the only two samples in the less than 10 ppm concentration range. Thus for Nb, the relative agreement increased in the lower range.

Table 6. Relative agreement between EDXRF data by this study and analytical data as reported by other methods (Appendix A.). Values are in percent relative difference.

Element	Concentration Range ≤10 ppm	 11-99 ppm	 ≥100 ppm	 overall
Rb	17%	7%	6%	7%
Sr	25%	15%	4%	8%
Ba	--	30%	4%	8%
Zr	--	11%	5%	6%
Nb	9%	14%	--	13%
La	112% *	17%	--	24%
Ce	--	14%	4%	11%
Y	43%	7%	6%	9%
Cr	--	9%	5%	6%
Ni	110% *	22%	--	55%
Cu	30%	18%	26% **	22%
Mo	100% *	54% **	--	76%
Sn	27%	33% **	--	29%
Zn	--	26%	4%	24%

* determined from values at or near the detection limit.

** based on the analysis of one sample.

We also examined the relative agreement of our technique and other methods of analysis by calculating simple linear regressions (figures 1a-1m, see pages 16-28). No plot was done for molybdenum because there were only two data points. Also shown in figures 1a-1m is an estimate of the goodness of fit for each regression (R). Regressions for elements Rb, Sr, Ba, Zr, Ce, Y, and Cr, indicate low fitting errors, and thus they show close agreement between methods. La showed the poorest fit (figure 1f). Results for Cu and Sn show a tendency at higher concentrations to be high relative to emission spectrography data (figures 1k and 1l respectively), whereas most energy-dispersive XRF data for Ni are slightly lower relative to emission spectrography across the entire range of concentrations (figure 1j). Zinc was the only element to show a distinct analytical bias between energy-dispersive XRF data and other data (figure 1m), in this case results obtained by instrumental neutron activation analysis. As shown in figure 1m, nearly all energy-dispersive XRF Zn values are higher than those produced by instrumental neutron activation analysis. It is beyond the scope of this paper to speculate which Zn method is more accurate. However, we speculate that the discrepancy may reflect among other reasons, calibration errors in the XRF method due to unresolved matrix effects and lack of reliable standards.

Conclusions

1) The estimated precision of this energy-dispersive x-ray fluorescence spectrometry method is ± 2% for concentrations of Rb, Sr, Ba, Zr, Y, Cu, and Sn above 100 ppm; Ce and Cr are precise to about 3-4% at this level.

2) The best overall estimate of the relative agreement between this energy-dispersive x-ray fluorescence method and other methods of analysis

is ± 7% for elements Rb, Sr, Ba, Zr, and Cr; ± 14% for Nb, La, Ce, and Y; ± 33% for Ni, Cu, Sn, and Zn; and ± 76% for Mo.

3) The primary factor limiting precision is probably counting error; primary factors limiting accuracy are precision, calibration, and lack of standards.

4) For those elements which have the highest precision and best overall relative agreement with other methods energy-dispersive XRF spectrometry is clearly a useful petrologic tool. All elements analyzed in this study have high enough precision to demonstrate that energy-dispersive XRF spectrometry is a reliable method for the rapid screening of anomalous samples in preparation for more precise analyses and for reconaissance geochemical surveys.

Acknowledgements

The authors wish to gratefully acknowledge Robert Johnson and Terry Klein of the U.S. Geological Survey for their critical review of this paper. We wish to also thank Dave Gottfried and John Evans of the U.S. Geological Survey for helpful discussions concerning this work.

References

Abbey, Sydney, Studies in "Standard Samples" of Silicate Rocks and Minerals 1969-1982, Geological Survey of Canada, Paper 83-15, 1983.

Arth, J.G., Barker, F., and Stern, T.W., Geochronology of Archean Gneisses in the Lake Helen area, South-western Big Horn Mountains, Wyoming, Precambrian Research, 11, 11-22, 1980.

Baedecker. P.A., Methods for Geochemical Analysis, U.S. Geological Survey Bulletin 1770, 1987.

Bertin, E.P., Principles and Practice of X-Ray Spectrometric Analysis, New York, Plenum Press, 1970.

Hudson T., Arth, J.G., Tin Granites of Seward Penninsula, Alaska, Geological Society of America Bulletin, v. 94, p. 768-790, 1983.

Johnson, R.G., Trace Element Analysis of Silicates by Means of Energy-Dispersive X-Ray Spectrometry, X-Ray Specrometry, Vol. 13, p.64-68, 1984.

Johnson, R.G., Palmer, C.A., Dennon, K.O., and Hearn, P.P., Energy - Dispersive X-Ray Fluorescence Analysis of Trace Elements in Carbonate Rocks, Applied Spectroscopy, Vol. 40, p.76-79, 1986.

Kevex XRF Toolbox(TM) Software (RT-11XM) version 3.2, Kevex Corporation, 1101 Chess Drive, Foster City, CA 94404.

Nielson, K.K., Progress in X-Ray Fluorescence Corrections Methods Using Scattered Radiation, Advanced X-Ray Analysis, Vol. 22, P.303-315, 1979.

Terashima, S., X-Ray Fluorescence Determination of Chromium, Gallium, Niobium, Lead, Rubidium, Strontium, Yttrium, Zinc, and Zirconium in Rocks, Bull. of Geological Survey of Japan, Vol 28, p.43-49, 1977.

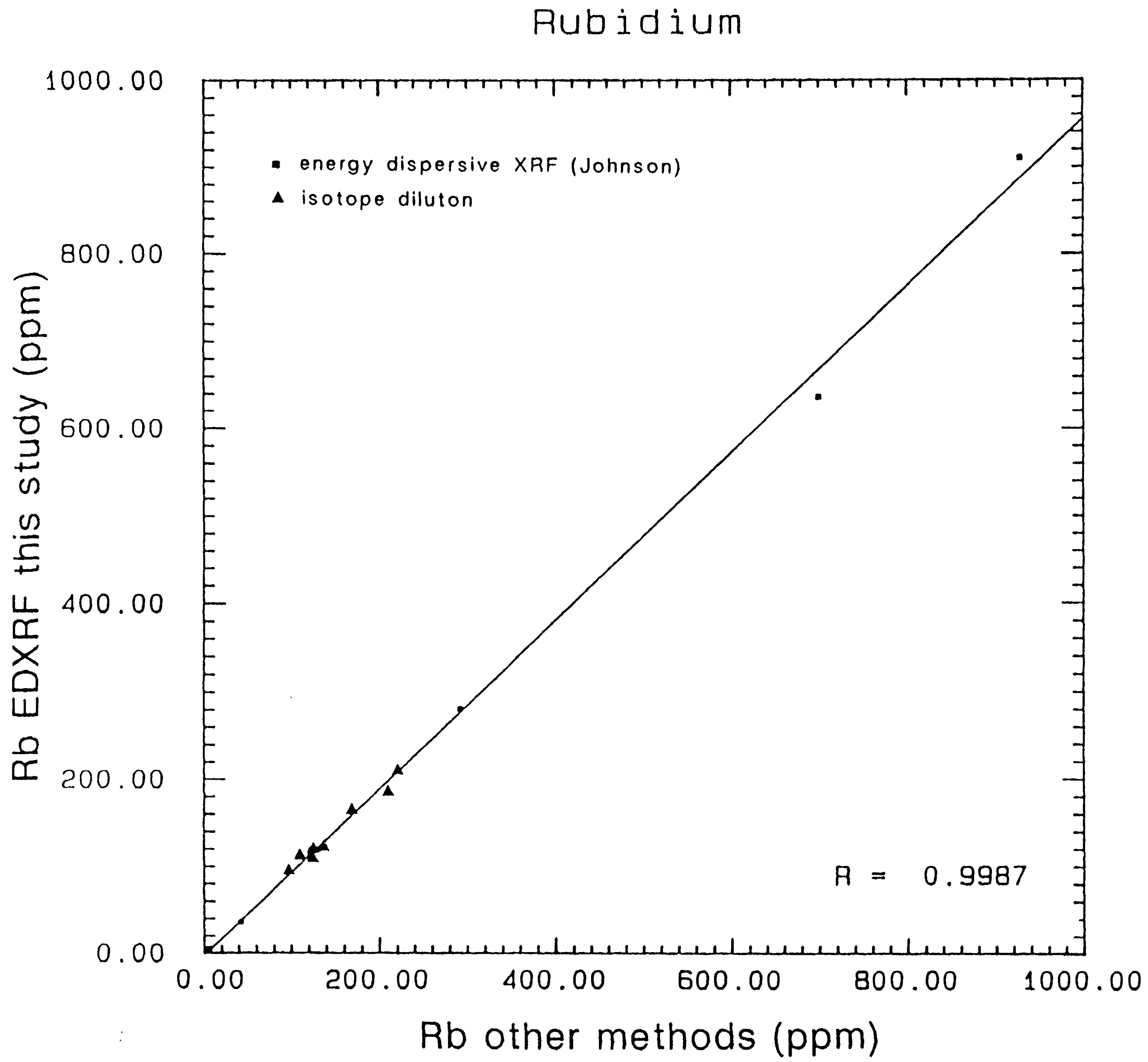

Figure 1a. Plot of Rb values by EDXRF (this study) and Rb values by other methods.

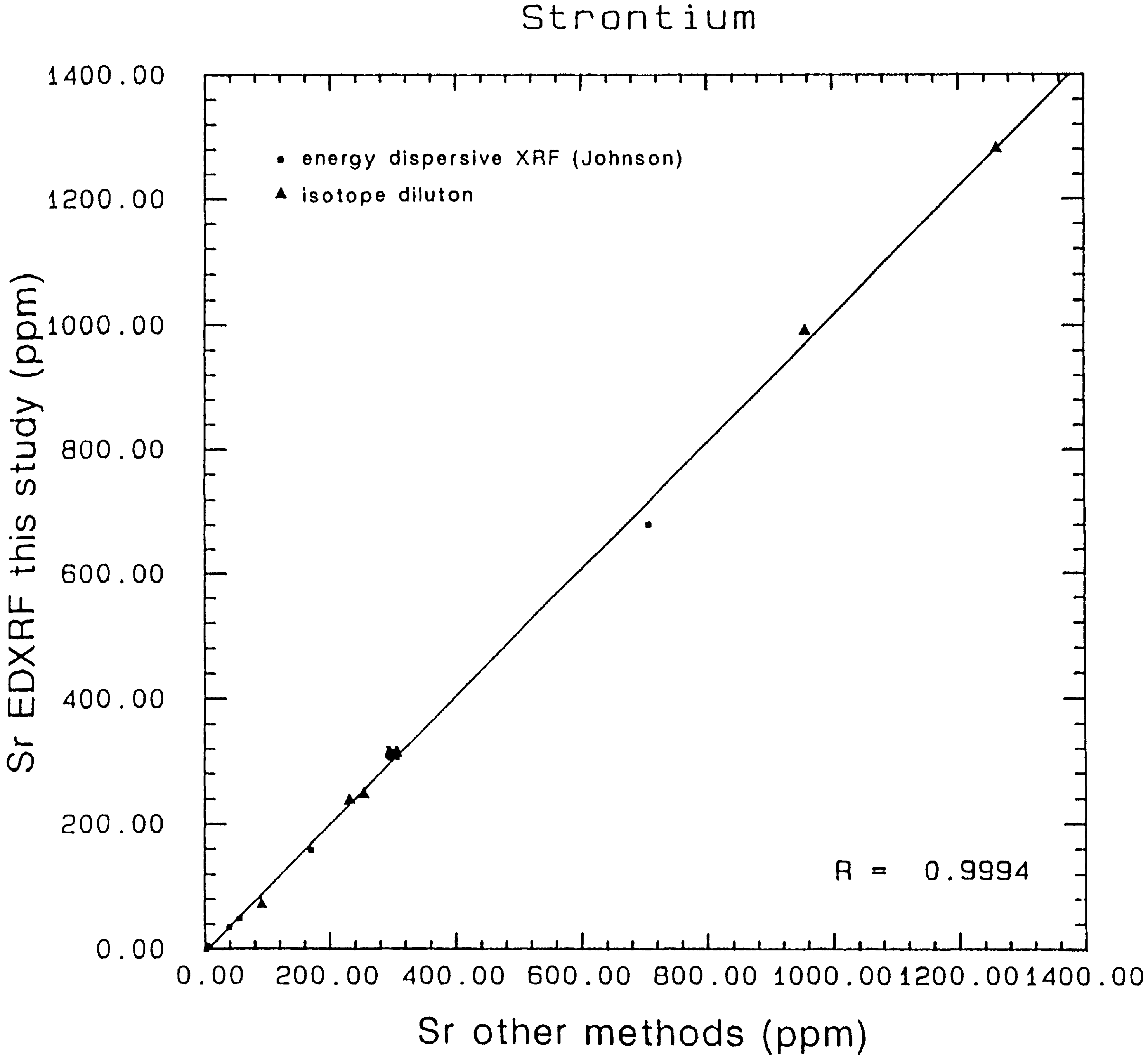

Figure 1b. Plot of Sr values by EDXRF (this study) and Sr values by other methods.

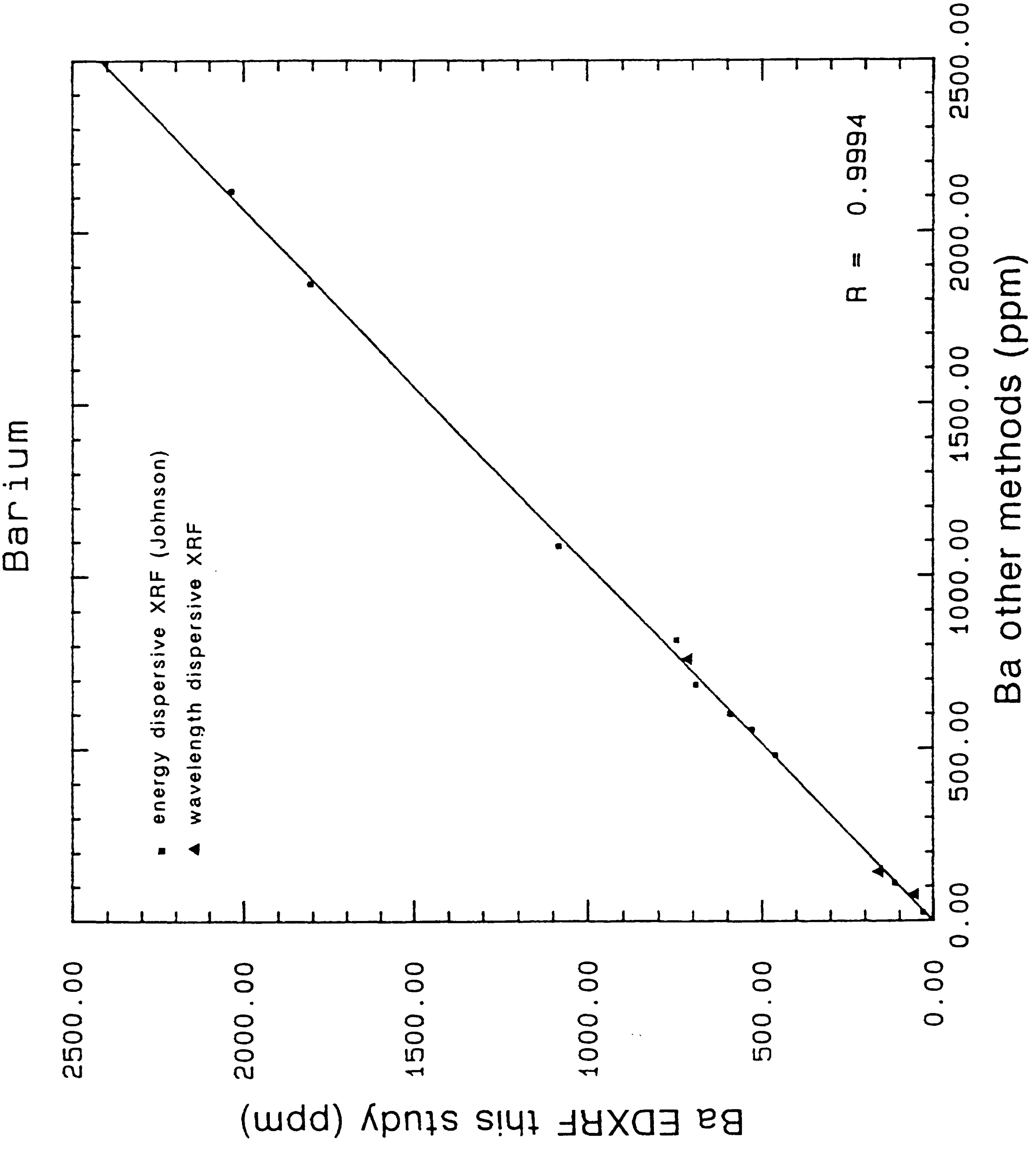

Figure 1c. Plot of Ba values by EDXRF (this study) and Ba values by other methods.

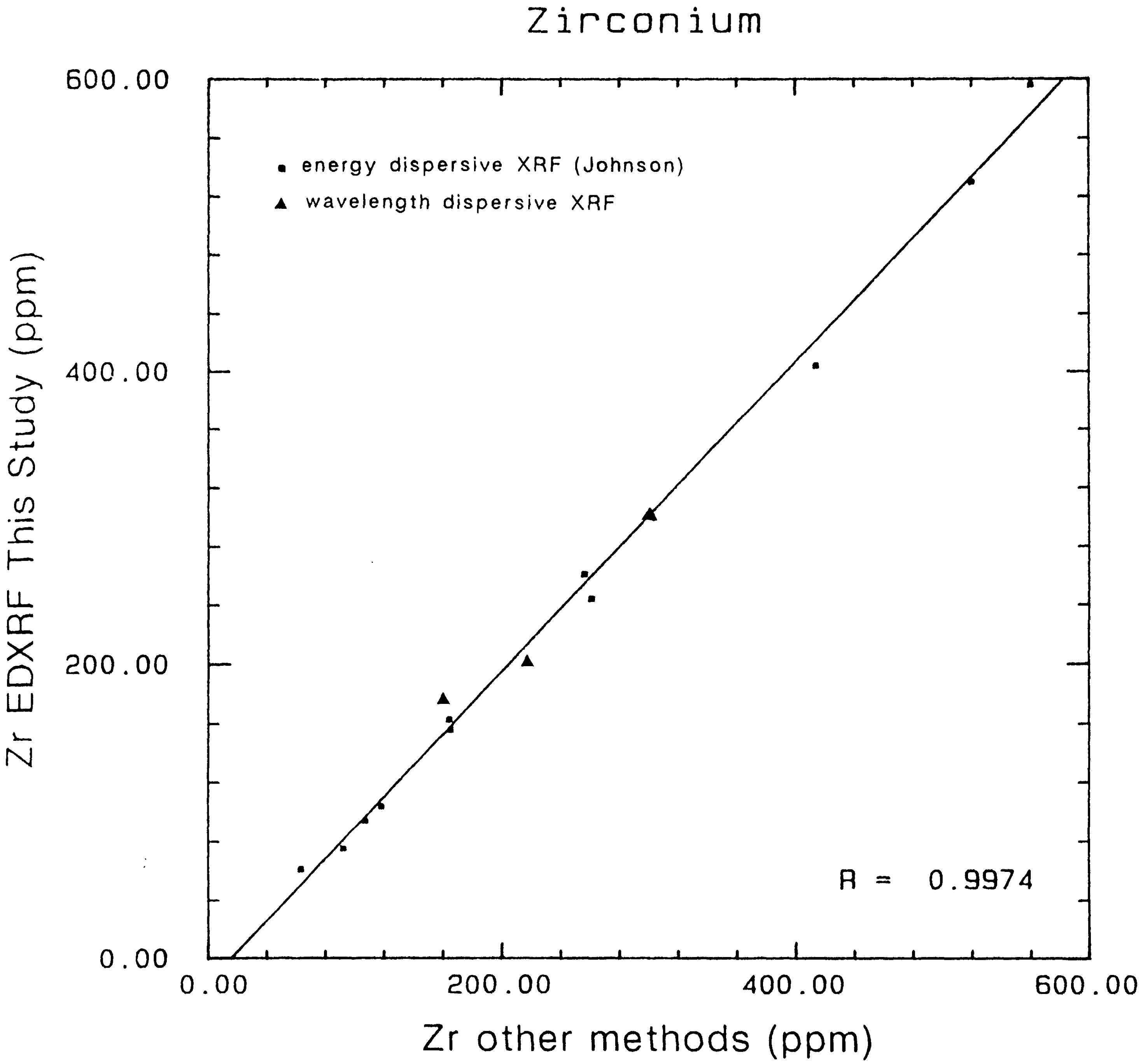

Figure 1d. Plot of Zr values by EDXRF (this study) and Zr values by other methods.

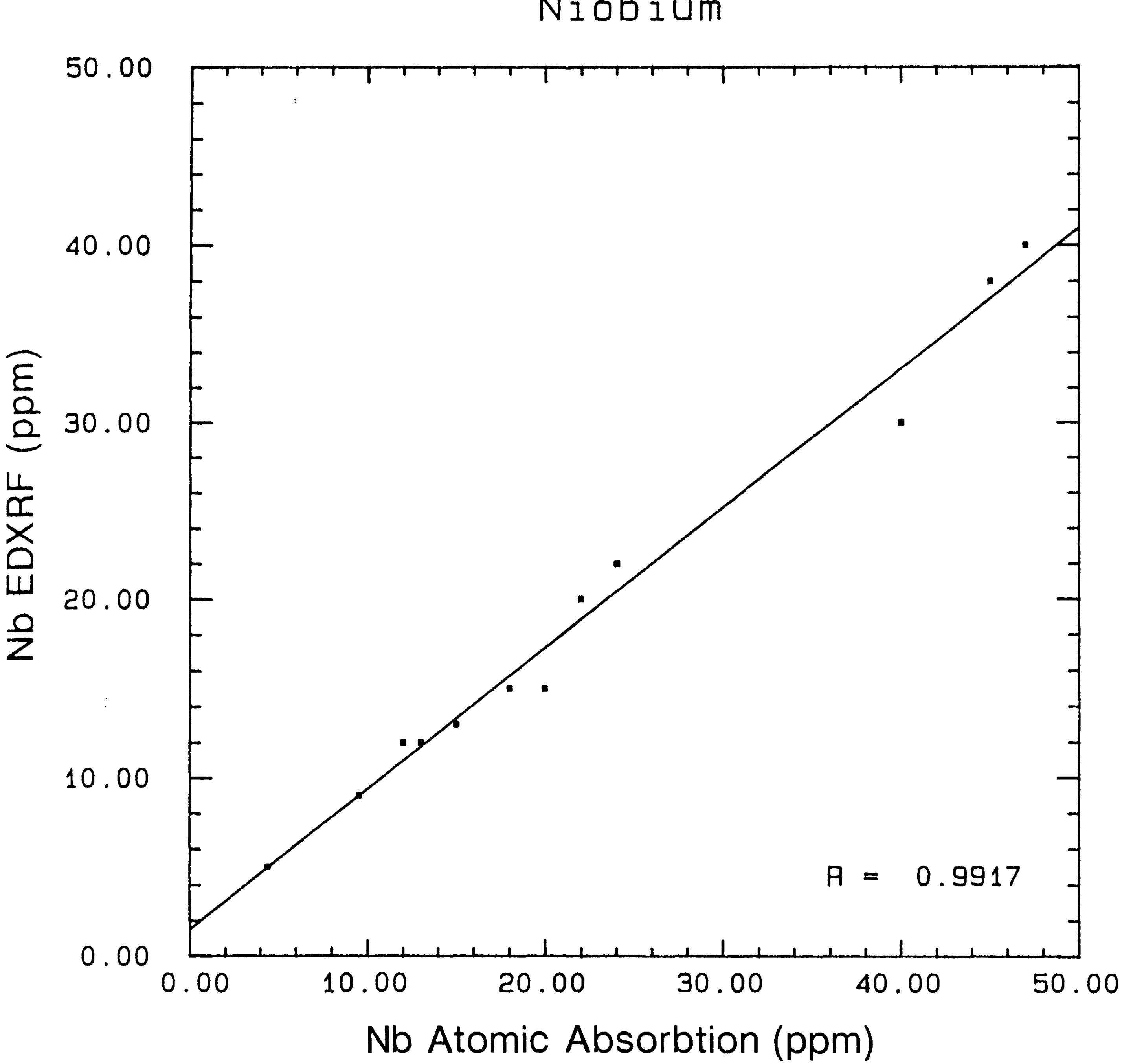

Figure 1e. Plot of Nb values by EDXRF (this study) and Nb values by other methods.

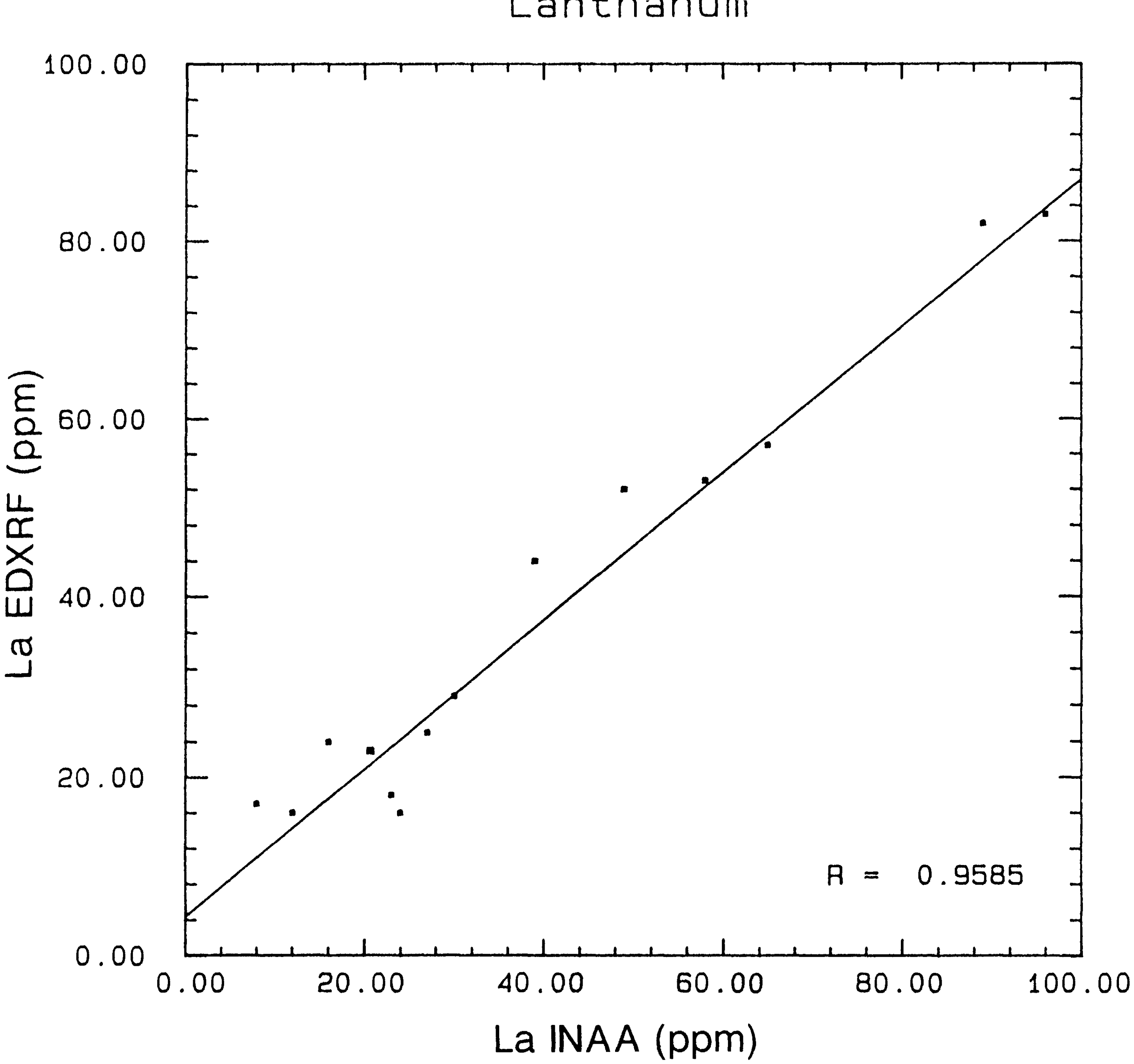

Figure 1f. Plot of La values by EDXRF (this study) and La values by other methods.

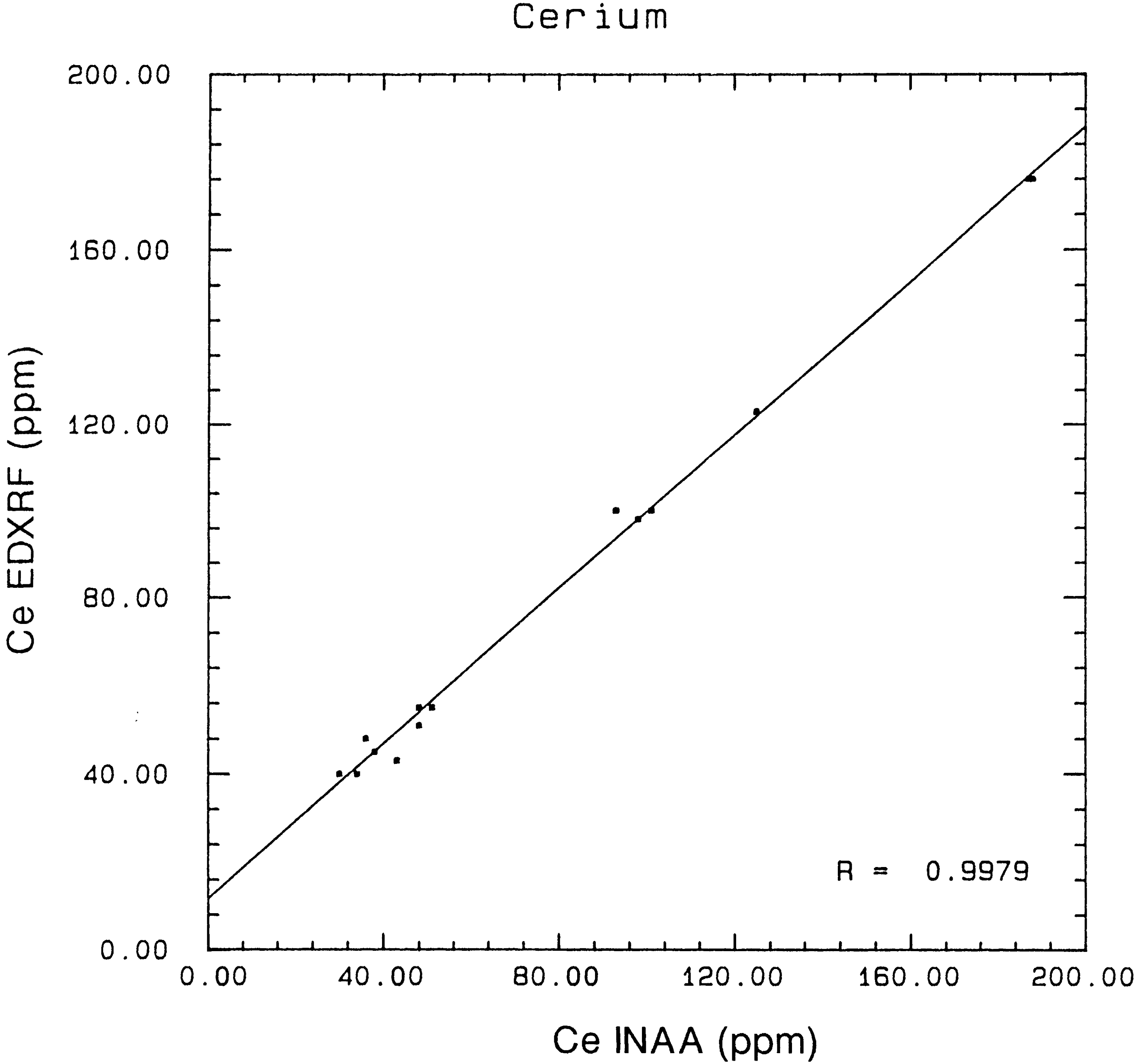

Figure 1g. Plot of Ce values by EDXRF (this study) and Ce values by other methods.

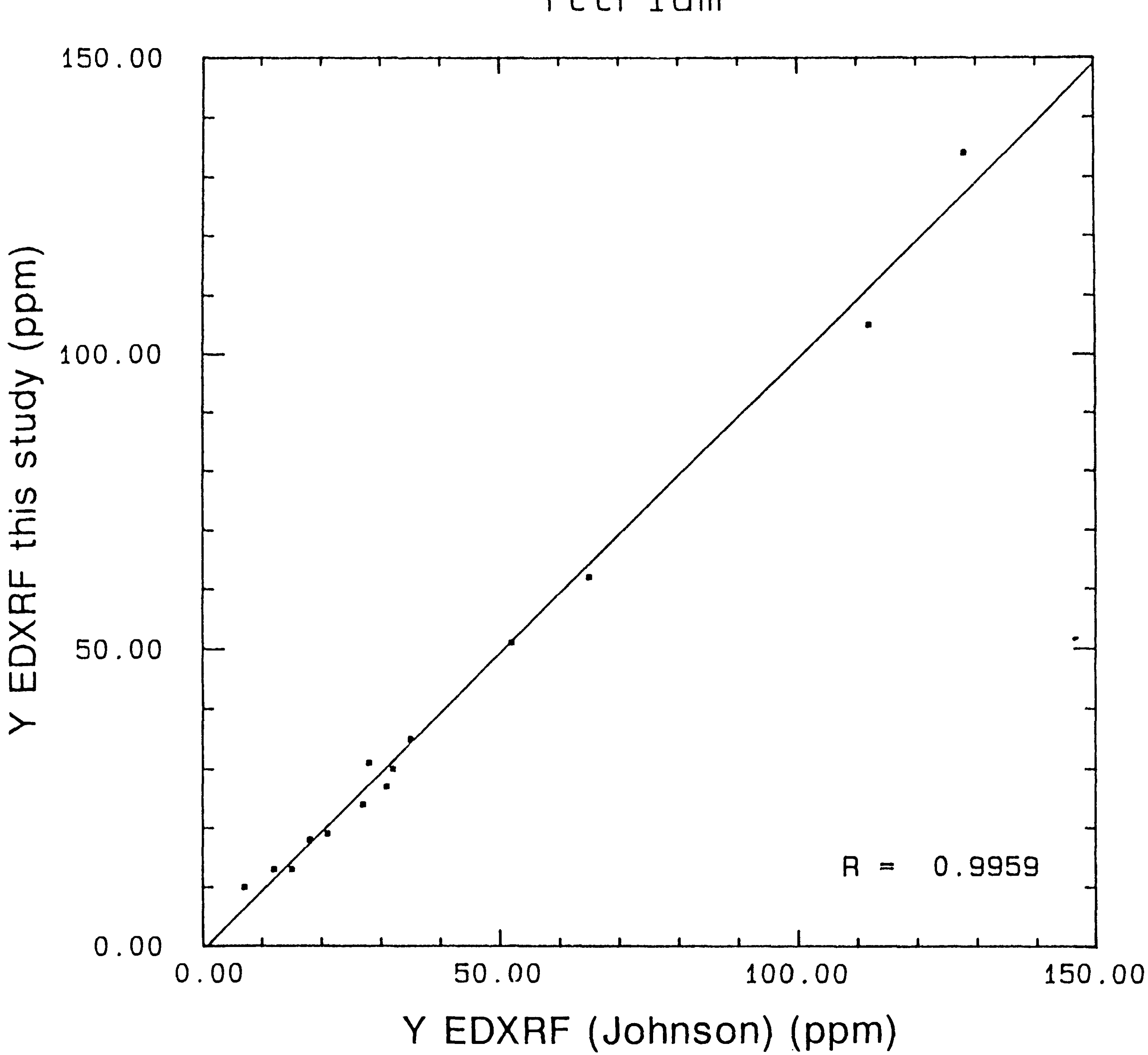

Figure 1h. Plot of Y values by EDXRF (this study) and Y values by other methods

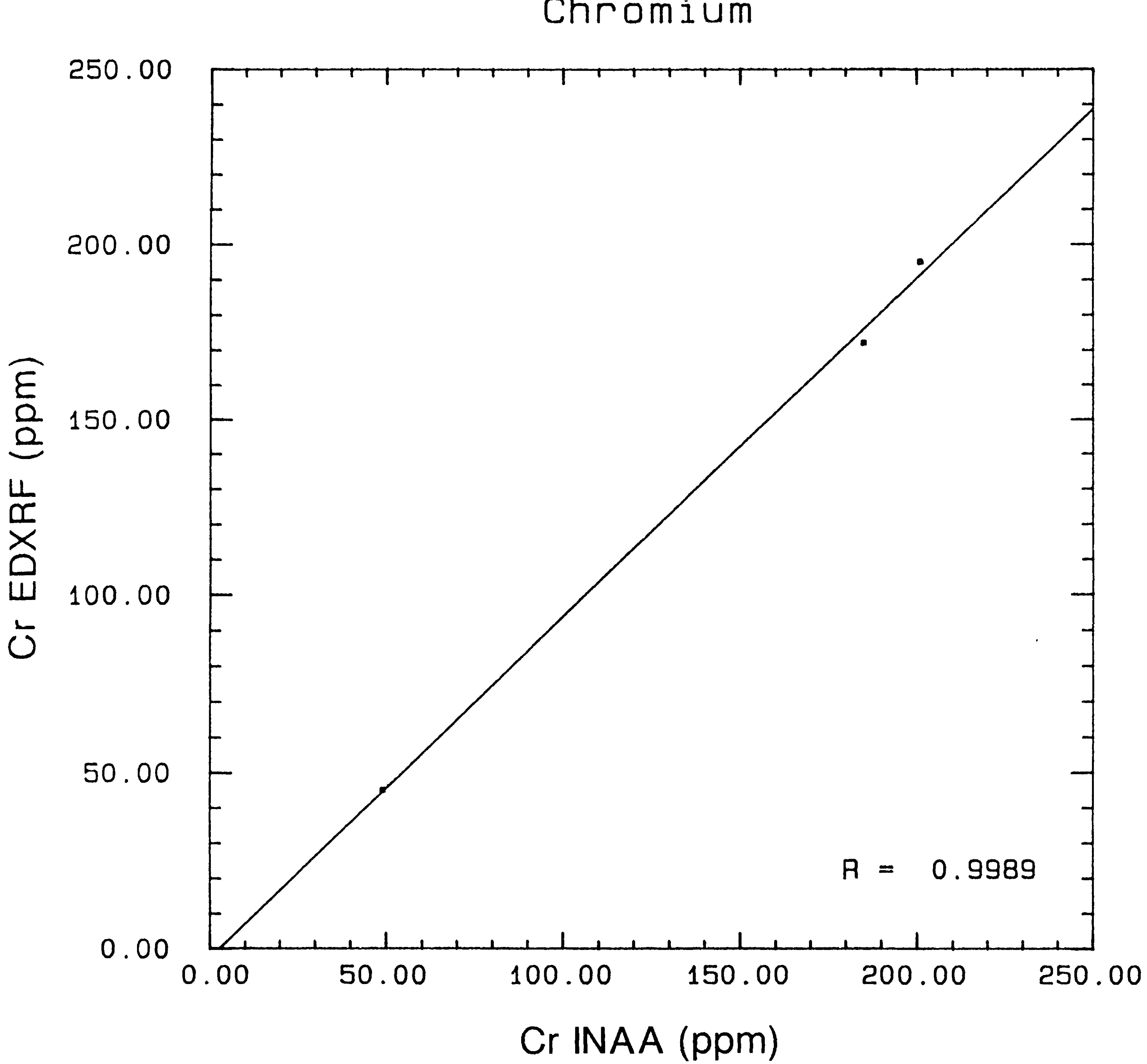

Figure 1i. Plot of Cr values by EDXRF (this study) and Cr values by other methods.

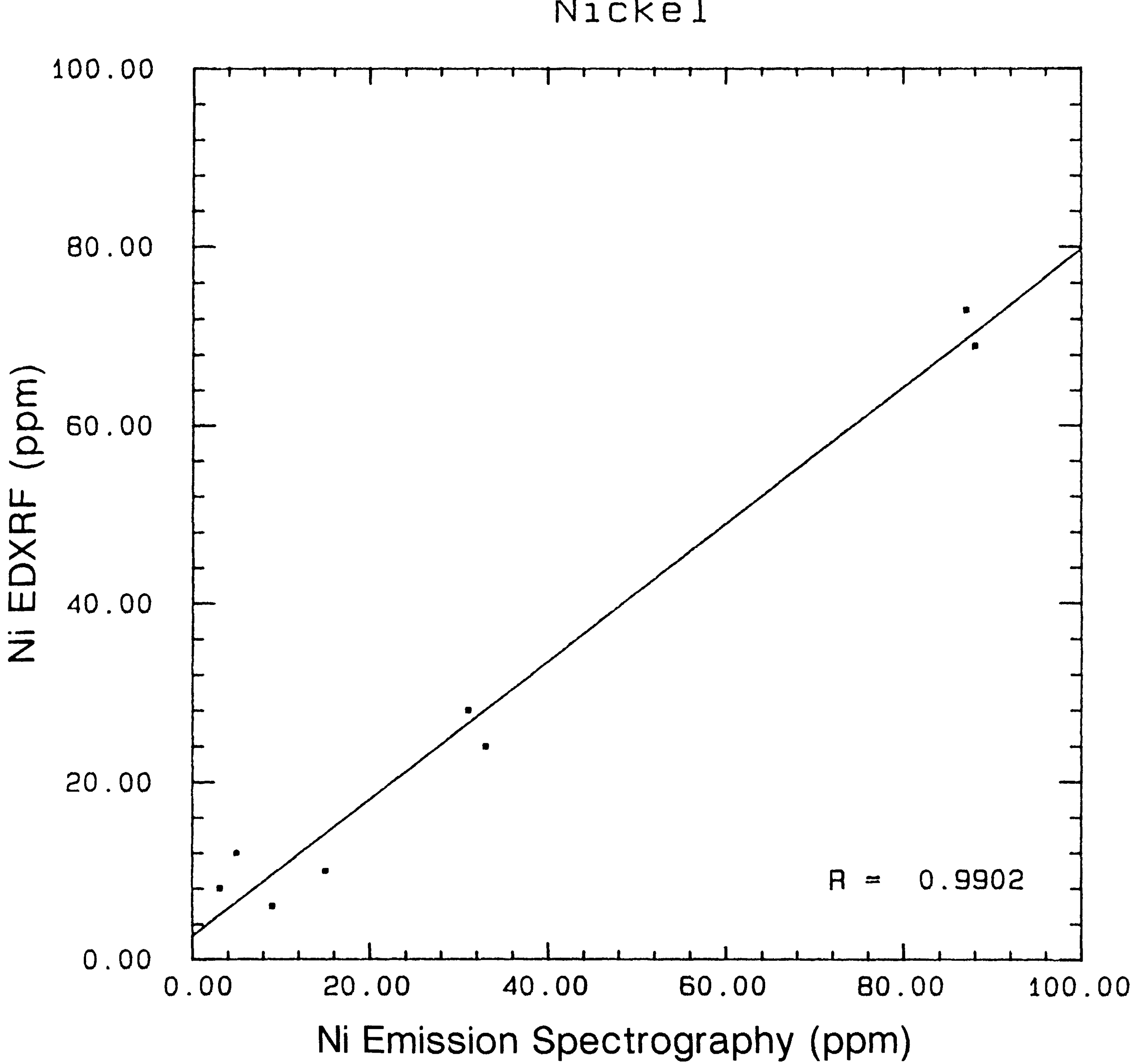

Figure 1j. Plot of Ni values by EDXRF (this study) and Ni values by other methods.

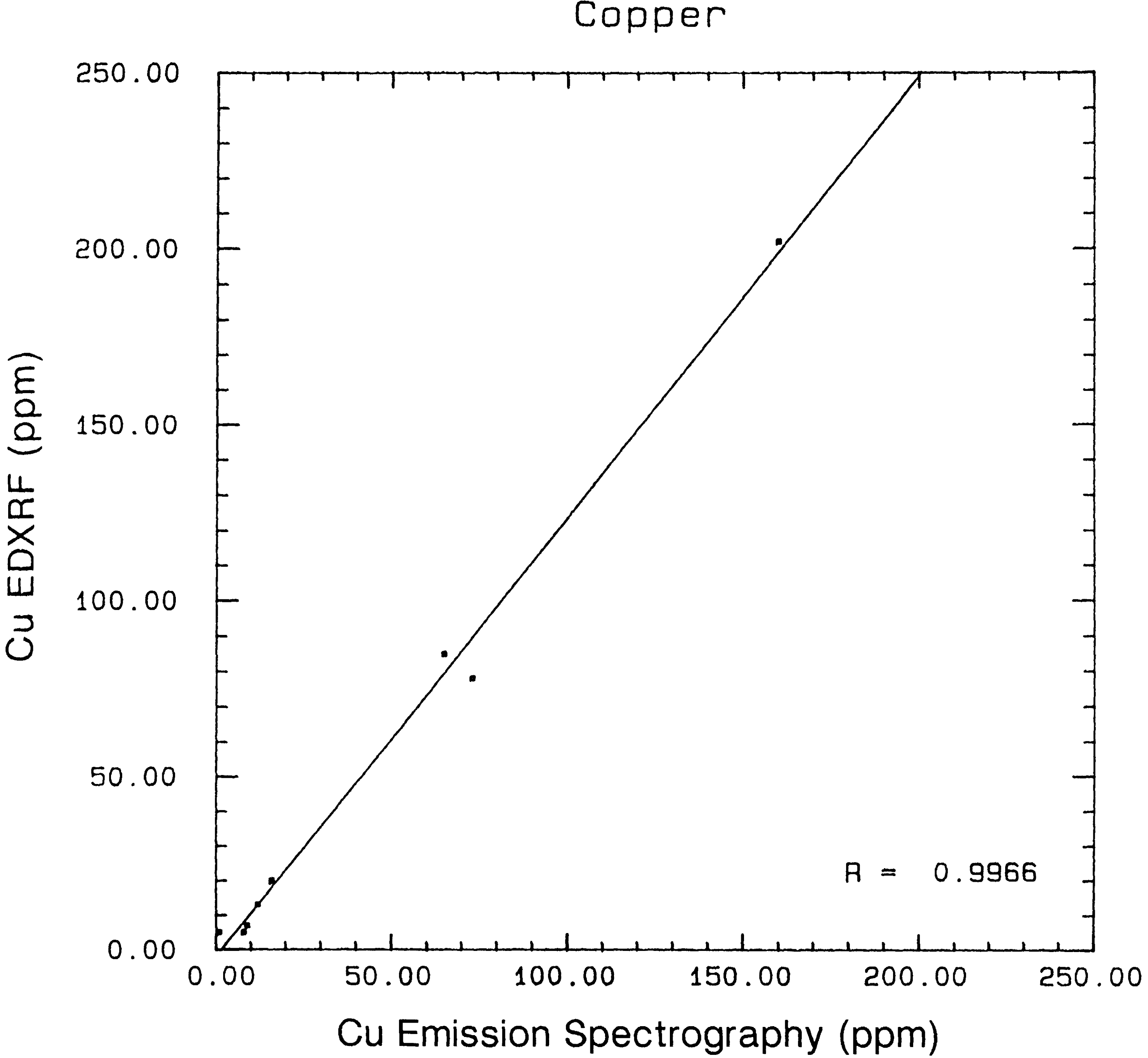

Figure 1k. Plot of Cu values by EDXRF (this study) and Cu values by other methods.

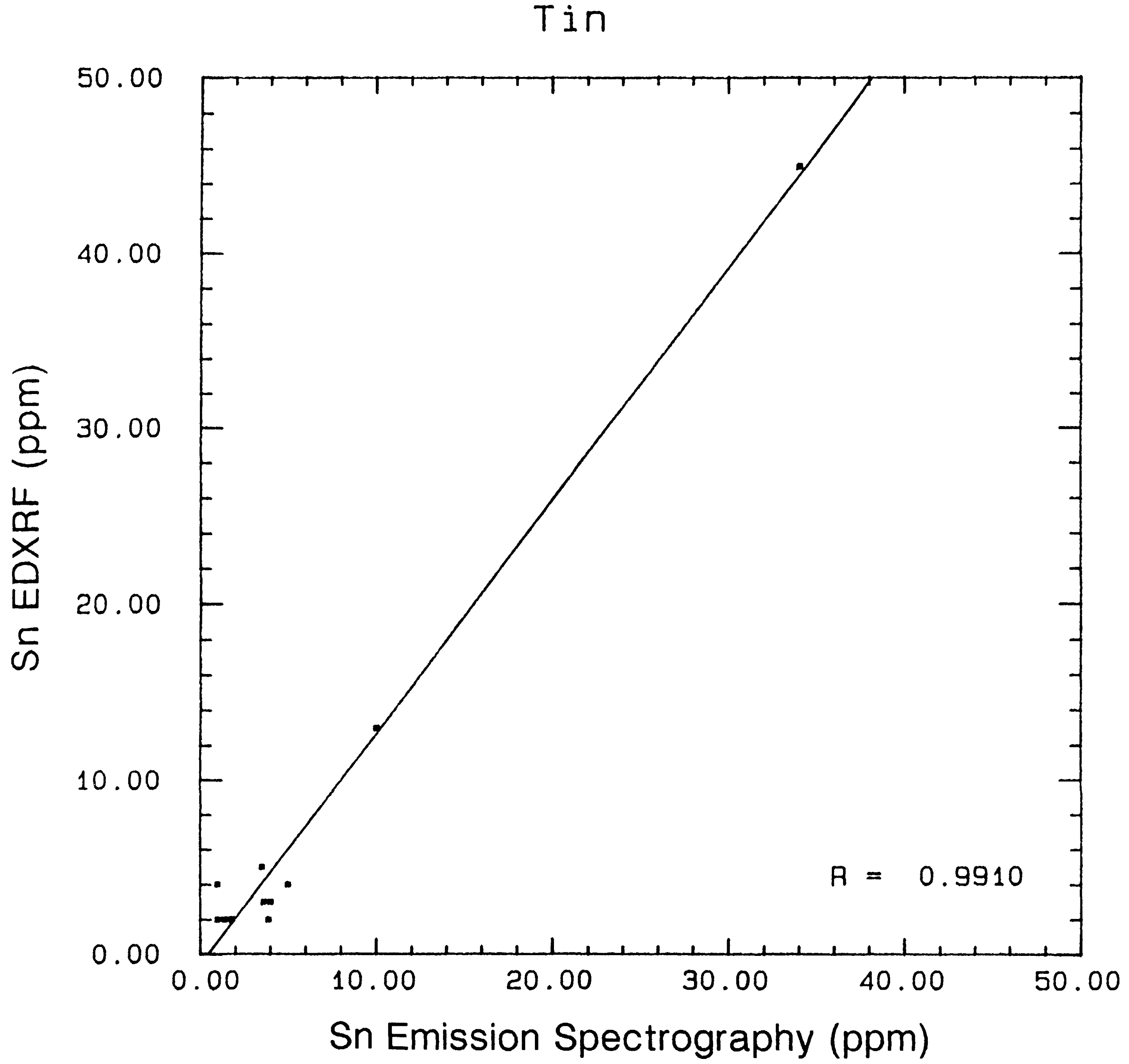

Figure 11. Plot of Sn values by EDXRF (this study) and Sn values by other methods.

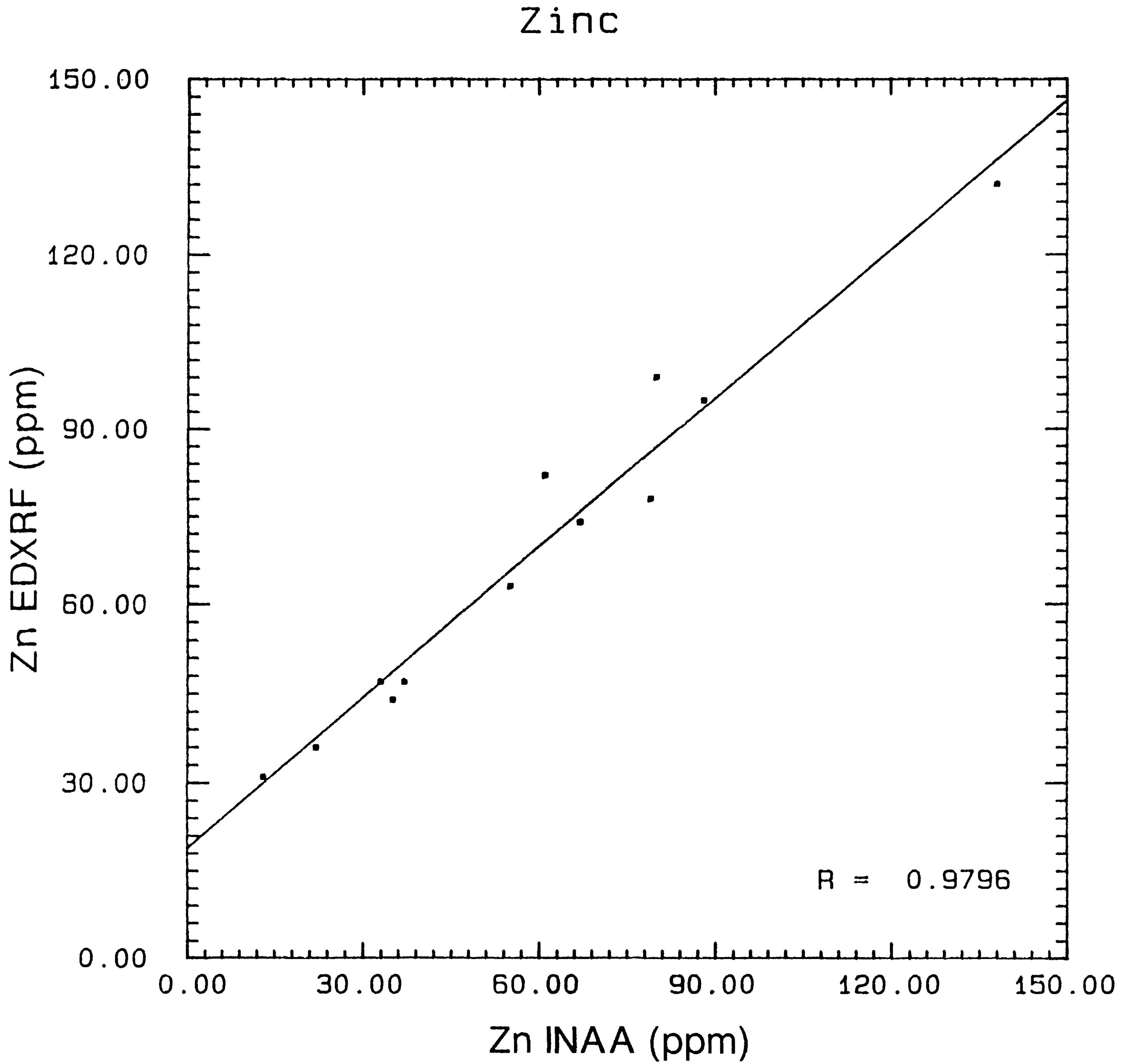

Figure 1m Plot of Zn values by EDXRF (this study) and Zn values by other methods.

Appendix A. Values in parts per million for 14 elements compiled during 10 separate analyses, the means and standard deviations determined from these values, and results in parts per million by other methods, for each of 14 rock samples.

Where qualified values are present, the mean for an element was calculated by averaging the intensity ratios from all ten runs. This average intensity ratio was then reduced to the average elemental concentration using the appropriate regression coefficients for that element. These intensity ratios are not shown. If no qualified values are present the mean for an element was calculated by averaging the values in parts per million.

Under the heading "other methods," for elements Rb, Sr, Ba, and Zr, subscript (ED) indicates values by energy-dispersive x-ray fluorescence (Johnson and King 1987, in Baedecker, 1987). For Ba and Zr, subscript (WD) indicates values by wavelength-dispersive x-ray fluorescence (Ayuso unpublished data). For Rb and Sr, subscript (ID) indicates values by isotope dilution (Ayuso unpublished data). For elements La, Ce, Cr, and Zn, values are by instrumental neutron activation analysis (Baedecker and Mckown, 1987, in Baedecker, 1987). For elements Ni, Cu, and Sn, values are by direct-current arc emission spectrography (Golightly and others, 1987 in Baedecker, 1987). For elements Nb, and Mo, values are by Atomic Absorption (Aruscavage and Crock, 1987, in Baedecker, 1987). Values for Y are by energy-dispersive x-ray fluorescence (Johnson and King, 1987, in Baedecker, 1987).

Sample AT-0-2

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	279	282	285	282	278	282	282	284	280	280	281	2	292 (ED)
Sr	46	49	49	50	47	48	47	49	46	49	48	1	55 (ED)
Ba	527	524	527	531	531	531	527	527	527	531	528	3	555 (ED)
Zr	75	73	77	76	76	77	74	76	75	74	75	1	92 (ED)
Nb	10	10	11	11	10	12	10	11	11	9	11	1	-
La	19	12	15	15	16	24	15	12	16	17	16	3	24
Ce	46	47	29	40	43	53	30	36	36	38	40	8	30
Y	13	14	14	15	11	12	12	13	12	13	13	1	12
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	3.4
Ni	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	-	3.7
Cu	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	-
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	0.13
Sn	<2	<2	<2	2	<2	<2	<2	2	<2	2	<2	-	2.5
Zn	46	45	47	46	48	47	47	47	47	48	47	1	33

Appendix A (continued)

Sample SLC-21-D

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	121	124	119	114	111	114	116	118	126	117	118	5	123 (ID)
Sr	315	311	309	303	303	306	310	306	314	307	308	4	301 (ID)
Ba	450	470	458	458	462	462	458	462	462	462	460	5	480 (ED)
Zr	409	405	402	395	402	399	409	409	412	402	404	5	414 (ED)
Nb	31	31	30	30	33	28	30	29	29	27	30	2	40
La	50	61	60	57	56	60	56	51	60	57	57	4	65
Ce	119	128	132	122	122	122	118	123	122	123	123	4	125
Y	56	53	48	48	48	50	53	52	55	50	51	3	52
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	5.7
Ni	25	28	33	30	40	26	27	28	29	18	28	6	31
Cu	<5	<5	6	<5	6	<5	<5	<5	<5	<5	<5	-	9
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	-
Sn	2	4	2	2	2	4	2	2	2	3	3	1	4
Zn	128	132	136	133	134	129	133	131	134	129	132	3	138

Sample WID-101-MI

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	119	120	119	116	117	119	118	121	121	122	119	2	126 (ID)
Sr	237	237	233	234	234	235	233	236	237	241	236	2	230 (ID)
Ba	159	153	163	159	152	156	161	158	153	158	157	4	143 (WD)
Zr	175	175	174	176	174	176	175	175	171	175	175	1	160 (WD)
Nb	14	16	15	16	14	17	15	15	13	16	15	1	18
La	25	17	25	21	18	24	21	26	25	30	23	4	21
Ce	51	48	53	50	47	49	46	52	50	59	51	4	48
Y	28	32	28	29	29	30	27	31	29	34	30	2	32
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	-
Ni	15	7	14	14	14	11	6	11	11	13	12	3	5
Cu	8	<5	<5	9	9	5	<5	6	<5	7	5	1	8
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	<0.5
Sn	4	6	4	4	3	3	5	3	4	5	4	1	4.7
Zn	96	95	92	97	96	94	96	96	95	93	95	2	88

Sample SLC-66

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	107	105	110	107	106	110	110	110	108	103	108	2	122 (ID)
Sr	246	245	252	242	246	248	248	247	248	241	246	3	252 (ID)
Ba	720	708	708	708	708	708	708	712	708	708	710	4	760 (WD)
Zr	304	301	300	299	300	301	303	301	300	298	301	2	302 (WD)
Nb	16	16	16	14	15	15	17	16	14	15	15	1	20
La	50	53	59	61	50	54	52	53	50	45	53	5	58
Ce	98	100	104	106	96	97	100	103	104	90	100	5	101
Y	29	31	32	32	31	32	31	32	29	29	31	1	28
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	11
Ni	5	<5	<5	5	7	7	5	6	9	8	6	2	9
Cu	<5	<5	<5	<5	5	<5	5	<5	8	6	<5	-	<10
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	0.9
Sn	3	3	2	<2	3	2	2	2	<2	2	2	1	3.9
Zn	63	62	62	64	64	63	63	65	64	64	63	1	55

Sample 82-D-185

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	209	206	211	212	206	210	208	210	209	206	209	2	221 (ID)
Sr	996	986	991	1001	977	991	991	991	991	986	990	6	955 (ID)
Ba	1810	1814	1803	1806	1806	1810	1810	1810	1795	1803	1807	5	1849 (ED)
Zr	588	598	591	595	591	595	604	598	601	595	596	5	560 (ED)
Nb	19	24	22	23	20	23	23	22	24	20	22	2	24
La	85	90	73	72	88	88	79	82	79	90	83	7	96
Ce	170	181	160	173	181	179	181	178	181	173	176	7	187
Y	23	24	22	25	23	25	25	25	25	20	24	2	27
Cr	170	169	168	172	168	172	173	181	172	176	172	4	185
Ni	71	71	72	75	78	74	68	75	71	75	73	3	87
Cu	84	84	81	86	88	84	86	87	89	84	85	2	65
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	4
Sn	4	5	6	5	4	6	4	9	5	3	5	2	3.5
Zn	74	75	72	73	75	71	74	75	74	74	74	1	67

Appendix A (continued)

Sample 14-384-397

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	111	107	110	111	112	107	110	117	116	111	111	3	108 (ID)
Sr	70	69	71	70	71	68	69	74	72	72	71	2	90 (ID)
Ba	747	747	743	747	747	743	747	751	759	747	748	5	815 (ED)
Zr	93	93	92	93	94	94	94	96	97	94	94	2	107 (ED)
Nb	<5	<5	<5	5	5	<5	6	<5	5	6	5	2	4.4
La	14	18	17	23	17	19	13	21	17	22	18	3	23
Ce	42	43	46	54	43	41	43	44	44	48	45	4	38
Y	11	8	11	10	11	9	9	12	12	11	10	1	7
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	6.3
Ni	<5	<5	6	<5	<5	<5	<5	<5	<5	<5	<5	-	5
Cu	200	205	207	201	198	202	208	199	203	201	202	3	160
Mo	79	83	83	83	83	83	83	83	83	83	83	1	54
Sn	<2	<2	2	<2	3	<2	3	2	<2	<2	<2	-	-
Zn	97	100	98	96	99	98	101	98	100	99	99	2	80

Sample 84-AR-30

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	912	900	912	912	912	906	906	912	912	912	910	4	928 (ED)
Sr	5	<5	6	<5	<5	<5	<5	<5	<5	<5	<5	-	3 (ED)
Ba	19	21	23	21	17	26	26	24	24	28	23	3	<2 (ED)
Zr	60	59	61	63	61	62	61	60	62	60	61	1	63 (ED)
Nb	38	38	38	40	40	39	39	35	39	37	38	2	45
La	11	13	19	17	14	20	20	18	13	26	17	4	8
Ce	40	35	42	50	36	45	43	46	37	56	43	7	43
Y	136	134	137	134	135	132	130	135	136	135	134	2	128
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	-
Ni	7	5	10	5	8	7	11	9	8	6	8	2	3.1
Cu	14	15	16	12	13	15	17	14	14	10	14	2	-
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	<0.5
Sn	43	46	46	44	43	43	50	43	47	42	45	3	34
Zn	46	46	46	45	49	47	49	46	48	46	47	1	-

Appendix A (continued)

Sample AQM-C1

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	3	7	4	5	6	6	6	4	5	3	5	1	6 (ED)
Sr	33	36	35	34	37	38	36	32	36	33	35	2	40 (ED)
Ba	50	50	50	50	54	50	55	57	49	51	52	3	75 (WD)
Zr	198	202	201	201	200	203	199	201	206	200	201	2	217 (WD)
Nb	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	-	4.6
La	27	21	25	22	24	20	26	30	19	25	24	3	16
Ce	49	48	50	45	49	50	45	51	41	53	48	4	36
Y	61	64	62	62	62	65	62	61	64	61	62	1	65
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	-
Ni	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	-	1
Cu	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	-	-
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	0.9
Sn	2	2	2	<2	<2	2	2	<2	2	<2	<2	-	0.9
Zn	31	31	31	30	32	31	32	33	32	30	31	1	-

Sample 84-AA-15

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	634	634	634	634	640	640	640	634	640	634	636	3	700 (ED)
Sr	5	4	7	3	7	5	5	1	5	4	5	2	4 (ED)
Ba	30	32	27	35	34	25	28	33	30	36	31	4	24 (ED)
Zr	101	104	104	103	107	105	107	101	105	105	104	2	118 (ED)
Nb	37	38	40	39	40	40	41	38	41	41	40	1	47
La	12	19	<10	16	21	<10	14	17	12	26	16	5	12
Ce	33	46	40	38	43	32	36	47	37	50	40	6	34
Y	103	106	107	104	103	109	107	104	104	107	105	2	112
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	-
Ni	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	-	2
Cu	<5	5	8	6	5	<5	<5	<5	<5	6	5	1	<1
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	0.7
Sn	15	12	13	12	14	15	9	12	13	14	13	2	10
Zn	37	37	37	37	37	36	35	36	37	38	37	1	-

Appendix A (continued)

Sample 83-D-209

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	187	180	187	183	186	189	182	182	180	180	184	3	209 (ID)
Sr	1284	1274	1279	1284	1279	1289	1284	1274	1274	1279	1280	5	1260 (ID)
Ba	2049	2034	2026	2030	2041	2045	2041	2038	2034	2026	2036	8	2120 (ED)
Zr	533	533	529	533	529	533	526	529	529	529	530	3	520 (ED)
Nb	22	21	19	18	18	21	20	19	19	18	20	1	22
La	88	78	73	81	79	96	72	90	84	79	82	8	89
Ce	180	180	174	176	176	184	170	179	177	163	176	6	188
Y	30	26	27	26	25	29	27	27	27	28	27	1	31
Cr	202	192	184	197	202	207	188	197	190	195	195	7	201
Ni	68	71	70	71	66	70	62	71	67	69	69	3	88
Cu	78	77	76	77	75	82	74	84	78	78	78	3	73
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	<1
Sn	2	<2	<2	4	4	4	2	6	8	2	3	2	3.6
Zn	80	78	78	75	76	79	74	81	76	79	78	2	79

Sample 83-PL-222

	Values in ppm												Other
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	Methods
Rb	163	162	165	158	160	162	165	164	165	165	163	2	167 (ID)
Sr	313	304	310	307	305	311	307	308	313	314	309	4	293 (ID)
Ba	689	697	693	689	693	689	685	689	693	697	691	4	685 (ED)
Zr	156	153	157	152	156	156	158	156	160	159	156	2	165 (ED)
Nb	12	10	11	11	11	11	13	12	14	13	12	1	13
La	28	34	25	27	18	11	21	36	28	22	25	7	27
Ce	51	65	51	63	48	42	52	71	59	45	55	9	48
Y	19	15	15	14	16	20	20	17	19	20	18	2	18
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	13
Ni	<5	5	8	<5	<5	<5	6	<5	7	6	<5	-	<10
Cu	10	14	16	10	11	9	15	13	14	13	13	2	12
Mo	12	10	11	10	11	10	10	10	11	11	11	1	5.5
Sn	3	<2	2	4	2	<2	3	3	5	3	2	1	1.8
Zn	35	37	37	36	35	36	37	36	34	37	36	1	22

Appendix A (continued)

Sample J-17

	Values in ppm												Other Methods
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	
Rb	38	37	35	37	37	33	34	36	36	36	36	2	42 (ED)
Sr	160	159	158	161	161	154	156	158	160	156	158	2	170 (ED)
Ba	113	111	114	113	108	118	116	112	110	116	113	3	110 (ED)
Zr	245	243	244	246	248	244	242	243	243	246	244	2	261 (ED)
Nb	12	13	15	14	14	13	14	13	11	12	13	1	15
La	48	41	38	44	45	47	47	43	39	48	44	4	39
Ce	105	98	91	100	100	98	99	101	96	96	98	4	98
Y	36	36	35	37	35	34	34	34	35	34	35	1	35
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	5
Ni	<5	<5	<5	<5	<5	5	<5	<5	<5	5	<5	-	6
Cu	9	5	5	8	7	8	7	5	5	9	7	2	9
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	-
Sn	4	4	4	4	5	5	3	3	5	4	4	1	5
Zn	84	81	80	83	81	81	81	81	81	83	82	1	61

Sample 83-PL-217

	Values in ppm												Other Methods
Element	1	2	3	4	5	6	7	8	9	10	Mean	s	
Rb	96	96	93	96	91	92	95	90	93	93	94	2	96 (ID)
Sr	313	317	312	309	308	309	310	306	312	311	311	3	303 (ID)
Ba	585	589	600	604	597	593	585	585	597	589	592	7	601 (ED)
Zr	160	161	158	161	158	166	164	166	169	166	163	4	164 (ED)
Nb	7	8	9	10	9	9	8	9	8	8	9	1	9.5
La	29	24	33	37	39	19	24	17	37	27	29	8	30
Ce	63	51	59	61	62	42	51	52	55	56	55	6	51
Y	18	20	19	18	20	18	20	16	19	18	19	1	21
Cr	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	20
Ni	10	11	11	10	7	12	10	14	8	11	10	2	15
Cu	<5	<5	<5	<5	<5	<5	<5	8	<5	<5	<5	-	3
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	<1
Sn	3	3	3	<2	<2	<2	<2	2	2	<2	2	1	1.4
Zn	47	44	48	46	48	48	46	49	47	46	47	1	37

Appendix A (continued)

Sample 83-D-192

Element	Values in ppm 1	2	3	4	5	6	7	8	9	10	Mean	s	Other Methods
Rb	120	121	120	122	126	119	125	119	121	121	121	2	136 (ID)
Sr	684	679	684	688	679	674	679	679	674	684	680	5	707 (ID)
Ba	1082	1101	1086	1082	1093	1074	1082	1074	1086	1071	1083	9	1087 (ED)
Zr	264	265	260	271	264	253	255	259	256	261	261	5	256 (ED)
Nb	14	11	12	14	12	12	10	10	10	10	12	2	12
La	47	52	47	50	53	52	48	59	55	55	52	4	49
Ce	96	93	95	104	106	101	98	108	97	104	100	5	93
Y	13	12	13	17	11	12	15	13	11	13	13	2	15
Cr	43	51	53	46	47	45	39	40	43	41	45	5	49
Ni	27	26	23	24	26	23	25	20	19	23	24	3	33
Cu	19	19	18	17	19	25	25	19	18	21	20	3	16
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	-	1.5
Sn	3	2	3	2	3	2	1	2	1	2	2	1	1.5
Zn	45	44	44	44	46	43	44	43	46	43	44	1	35