

## VALIDATION OF AN ALKALI REACTION, BORATE FUSION, X-RAY FLUORESCENCE METHOD FOR SILICON METAL

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### ABSTRACT

The value assignment of candidate Standard Reference Material (SRM<sup>®</sup>) 57b Silicon Metal provided an opportunity to develop an alkali reaction procedure as a precursor to borate fusion for the preparation of test specimens from the metal powder for X-ray fluorescence spectrometry (XRF). Suggested for this purpose by Blanchette (*Adv. X-Ray Anal.*, **45**, 415, 2002), the alkali reaction uses LiOH·H<sub>2</sub>O to convert Si to Li<sub>2</sub>SiO<sub>3</sub>. Lithium silicate is fused with lithium borate flux without damage to platinum ware. Once specimens are fused and cast as beads, calibration standards are prepared to closely match the compositions of the specimens allowing a linear calibration for each analyte. The XRF method yields results that are directly traceable to the mole through NIST SRM spectrometric solutions. The method was validated in two ways. First, the reaction was used on older SRMs for Si metal: SRM 57 and SRM 57a. Second, XRF results for candidate SRM 57b were compared to results obtained using prompt gamma-ray activation analysis (PGAA) and inductively coupled plasma optical emission spectrometry (ICPOES). Bias tests show the XRF results are accurate for the elements Al, S, Ca, Ti, Cr, Mn, Ni, Cu, and Zr. Levels of S, Ca, Cr, and Cu in candidate SRM 57b are near the limits of quantification of the borate fusion method. Iron results may be subject to a low bias. Phosphorus is not quantitatively retained during the alkali reaction and borate fusion. These elements, plus B which cannot be determined after borate fusion, are listed in manufacturing specifications for Si metal.

### INTRODUCTION

NIST maintains a Standard Reference Material (SRM<sup>®</sup>) for silicon metal due to the economic significance of silicon as a raw material for ferroalloys, used in the manufacture of specialty steels for high strength and electrical applications [1,2]. Silicon is used in the aluminum industry to improve weldability and castability. In the chemicals industry, silicon metal is the starting point for the production of silanes, silicone resins, lubricants, anti-foaming agents, hydraulic fluids, electrical insulators, and water-repellent compounds. Silicon materials are used in the production of advanced ceramic materials including silicon carbide, silicon nitride, and sialons. Fumed silica is used as filler for cement, grout, refractory materials, synthetic rubber, and polymers. The markets for many silicon-derived products continue to grow with strong price structures, e.g., approximately \$1,000 per ton for silicon and \$15,000 or more per ton for polycrystalline silicon of high purity for electronics applications.

The National Bureau of Standards (NBS) first certified an SRM for Refined Silicon on November 28, 1924 [3]. SRM 57 was certified for Si, Fe, C, Mn, P, S, Cu, Ni, Cr, V, Zr, Ti, Al, Ca, and Mg. At that time, eight industrial laboratories collaborated with NBS using a variety of classical test methods. In 1980, NBS certified SRM 57a [4] to replace SRM 57 and the name

was changed to Silicon Metal. The same elements were certified as in 1924 plus information values were listed for B, O, Zn, As, Sn, Sb, Pb, and Bi. In the 1980 certification, there were six collaborating laboratories in the U.S. and Canada.

The National Institute of Standards and Technology (NIST), with assistance from Globe Metallurgical, has completed certification measurements for SRM 57b Silicon Metal as a replacement for SRM 57a. SRM 57b is certified [5] for Fe, Mn, P, Ni, Al, Ti, and Zr. Reference values are assigned for B, Cu, Cr, and Ca. Information values are provided for C, S, V, O, and Co. The list of important elements has changed somewhat as compared to the list for SRM 57a. One reason for this change is that industry specifications contain fewer elements. According to one major supplier [6], the elements currently monitored in refined silicon are Si, P, Ca, Ti, and Fe. ASTM International Standard Specification A 922-93 [7] lists only Fe as an element to be reported for silicon metal, but calls for reporting other trace elements. A second reason for the change is that the composition of high-purity silicon metal has changed over time. If one were to compare the certificates of analysis of all three NIST SRMs for silicon metal, it would be immediately obvious that the number and mass fractions of elements have decreased over time. Iron is a good example because the value has dropped from a mass fraction of 0.65 % for SRM 57 to 0.50 % for SRM 57a and now 0.34 % for SRM 57b. Phosphorus has decreased markedly from 0.008 % in SRM 57 to 0.003 % in SRM 57a to only 0.00163 % in the new SRM 57b.

For compositional value assignment of SRM 57b, NIST performed the majority of the determinations using X-ray fluorescence spectrometry (XRF), prompt gamma-ray activation analysis (PGAA) [8], and radiochemical neutron activation analysis (RNAA) [9, 10]. One collaborating industry laboratory, Globe Metallurgical, Inc., provided analytical results from inductively coupled plasma optical emission spectrometry (ICPOES). The four test methods represent independent means of sample preparation and measurements ranging from no preparation for PGAA to borate fusion for XRF and chemical separations for RNAA. This is important for test method validation because there is a low probability that the same bias is present in results from independent test methods.

X-Ray fluorescence and borate fusion have been used together since 1956 [11, 12] as the basis of test methods for elemental analyses of a wide variety of materials. Borate fusion offers the ability to synthesize beads having compositions that match the compositions of unknown materials. When high-purity materials and spectrometric solution reference materials are used in the preparation of such beads, a set of calibration standards is established with calculated values that are directly traceable to the amount of substance, i.e., the mole. If the set of calibration standards is carefully designed to closely bracket the composition of the fused unknown for all constituents, the calibration function can be simplified to a line plus corrections for spectral line overlaps. The utility of this approach for high-accuracy determinations has been demonstrated for zeolite materials [13], portland cement [13, 14], low alloy steel [15], and a Ti-Al aerospace alloy [15]. In these examples, the material was fused and measured to determine the nominal composition of the borate beads. For reduced materials (metals), an acid digestion must precede the borate fusion. To apply an acid digestion procedure to silicon would require a large quantity of HF, which is impractical for safety reasons as well as because HF promotes loss of constituents by formation of volatile fluoride compounds. An alternative approach is found in the work by Blanchette [11, 16] using an alkaline reaction to digest silicon metal. It follows

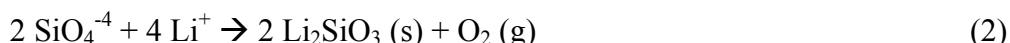
logically that quantitative analysis of silicon metal may be possible through a combination of alkaline reaction with borate fusion of the products. The validation of just such a method is discussed in this paper.

## ALKALINE REACTION

Silicon metal reacts with LiOH in solution according to Eq. 1.



When the products of Eq. 1 are allowed to react, solid lithium silicate forms as shown by Eq. 2.



In the laboratory, the reactions were carried out in a 150 mL Teflon beaker. First, 1.0 g Si powder was weighed to the nearest 0.00001 g into the beaker by difference from weighing paper. Next, 3.0 g LiOH·H<sub>2</sub>O was added, followed by 25 mL filtered, deionized H<sub>2</sub>O. A Teflon-coated stirring bar was added to the beaker before it was placed on a stirring hotplate set to a surface temperature of approximately 100 °C. The beaker was covered with a Teflon watch cover and the reaction proceeded with stirring for at least 4 h. As the reaction progressed, gas was evolved as expected from both equations 1 and 2. Once gas evolution ceased, stirring was stopped and the cover was removed. Heating was continued to take the beaker contents to dryness. The reaction products were a mixture of mostly white solids with some gray particles throughout. The solid products agglomerated and required a combination of crushing and rinsing to remove them to the Pt crucible for borate fusion. The gray particles were not separated and tested because borate fusion appeared to dissolve all solid reaction products.

## BORATE FUSION

Borate fusion was carried out using an induction-heated machine, a Perl'x3<sup>1</sup> (PANalytical, Almelo, The Netherlands). The platinum ware included a 100 g crucible of approximately 30 mL capacity and a 100 g casting dish designed to produce a 40 mm diameter bead. The fusion program consisted of nine steps enumerated below. Steps 6 and 7 must be done manually; the rest are automated.

Fusion program:

- 1) Heat to 200 °C for 2 min.
- 2) Heat to 600 °C for 6 min.
- 3) Heat to 975 °C for 3 min.
- 4) Heat to 975 °C for 5 min with mixing by rocking the crucible.
- 5) Cool to room temperature.
- 6) Manually rotate crucible 90° in ceramic sleeve.
- 7) Manually add several drops of a 20% LiI (aq) non-wetting agent.

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<sup>1</sup> Certain commercial equipment and commercial laboratories were named in this paper for the purpose of adequately specifying the experimental conditions and the sources of analytical results. Such descriptions do not constitute endorsement by the National Institute of Standards and Technology, nor do they imply that the equipment and services are necessarily the best for the purpose.

- 8) Heat to 975 °C for 5 min with mixing by rocking.
- 9) Cast into Pt dish with slow cooling followed by forced-air cooling from under the dish.

The above fusion program was specifically designed for the induction-heated, Perl'x3 automatic bead machine. The first step at 200 °C is used to remove remaining moisture before the temperature is elevated for fusion. The fusion program is stopped part way through to allow manual rotation of the crucible because the machine does not rotate the crucible. Mixing is achieved by simple rocking. After the crucible is reheated, the molten mixture will lap more of the inside of the crucible for more complete incorporation of all ingredients. While the crucible is cool, the LiI non-wetting solution is added. Doing this late in the program allows the use of a smaller quantity of iodine. Iodine is the preferred non-wetting agent in the NIST XRF laboratory because it is the most efficient halogen for the purpose. Under borate fusion conditions, iodine is the most volatile halogen used and only a few milligrams per kilogram remain in the glass. Iodine complicates measurement of Ti due to a line overlap. However, the alternative is to use a Br compound. Bromine is less volatile and Br lines overlap Al and Mn lines. Therefore, Br is a less attractive choice.

The following stepwise procedure was used to prepare each bead from the  $\text{Li}_2\text{SiO}_3$  reaction products.

- 1) Weigh a Pt(5 % Au) crucible and accurately record the mass.
- 2) Add 4.6 g of pre-fused flux (67 %  $\text{Li}_2\text{B}_4\text{O}_7$ /33 %  $\text{LiBO}_2$ ) and accurately record the mass.
- 3) Crush the  $\text{Li}_2\text{SiO}_3$  reaction products in the Teflon beaker and transfer them to a Pt(5 % Au) crucible with rinsing using distilled, de-ionized  $\text{H}_2\text{O}$ .
- 4) Dry the contents of the crucible at 110 °C for  $\geq 2$  h until all visible liquid is gone.
- 5) Weigh an empty Pt(5 % Au) casting dish and accurately record the mass.
- 6) Run the borate fusion program shown above.
- 7) Weigh the (crucible + residual glass) and the (casting dish + bead) and accurately record the mass values.

Note that in step 3 no mixing of flux and  $\text{Li}_2\text{SiO}_3$  is required prior to fusion.

The resulting borate beads contain 1.0 g of silicon in a total bead mass of 7.7 g to 8.1 g. The range of bead masses shows the level of control exercised over the addition of flux. Some variation is acceptable as long as the ranges of measured count rates for the elements in the unknowns are no greater than the ranges for the synthetic calibration standards. Except for the  $\text{LiOH}\cdot\text{H}_2\text{O}$ , all mass values were recorded to the nearest 0.00001 g and corrected for buoyancy prior to use in calculations [17].

## QUANTITATIVE APPROACH

The calibration approach for this method is the preparation of synthetic calibration standards to bracket the fused samples [13, 14, 15]. In this work, the primary reference materials used to prepare the synthetic calibrants are NIST single-element spectrometric solution SRMs. Spectrometric solution SRMs are solutions containing element concentrations of 10 mg/g in dilute acid and are prepared from NIST primary materials. The three main advantages of this

approach are 1) the direct traceability to the mole provided by using primary reference materials as ingredients, 2) the low uncertainty of the assigned values for the spectrometric solution SRMs, and 3) the control of matrix effects obtained by having the calibration standards so closely match the samples that the corrections for matrix effects would amount to 0.1 % relative or less for each analyte. With close matching of calibrants and specimens, matrix effects to be ignored.

The matrix effects can be simulated using alpha coefficients derived from first principles for a nominal material composition obtained using a fundamental parameters XRF method such as IQ+ (PANalytical). Using the derived alpha coefficients, the analyst can estimate the ranges of mass fractions for calibration of each analyte. Equation 3 is an example of a matrix correction algorithm based on constant alpha coefficients.

$$C_i = D_i + E_i R_i (1 + \sum_j \alpha_{ij} C_j) \quad (3)$$

where  $C_i$  = the concentration of the analyte,

$D_i$  = the intercept,

$E_i$  = the slope of the linear model,

$R_i$  = the measured count rate for the analyte,

$\alpha_{ij}$  = alpha-type, constant correction coefficient

$C_j$  = the concentration of each interfering element

The term  $\sum_j \alpha_{ij} C_j$  is the total matrix correction for elements  $j$  on element  $i$ .

For the elements determined in silicon metal, there are no spectral line overlaps. One overlap is introduced by the use of LiI as the non-wetting agent during borate fusion. The I L<sub>3</sub>-N<sub>5</sub> X-ray line directly overlaps the Ti K-L<sub>2,3</sub> line. The I L<sub>3</sub>-M<sub>4,5</sub> line is measured and a correction is applied by adding a term to Eq. 3 to subtract a fraction of the I L<sub>3</sub>-M<sub>4,5</sub> count rate from the Ti count rate,  $R_{Ti}$ . The overlap factor is calculated during the regression analysis for Ti using the empirical data.

For each interfering element  $j$ , uncertainty in either  $\alpha_{ij}$  or  $C_j$  will result in uncertainty in  $C_i$ . This relationship can be written as Equation 4, where the symbol  $\Delta$  indicates a small difference between the value in use and the true value. As defined,  $\alpha_{ij}$  is constant over small ranges of  $C_i$ ; therefore, Eq. 4 can be rearranged to get Eq. 5.

$$\Delta C_i = \Delta(\alpha_{ij} C_j) \quad (4)$$

$$\Delta C_i = \alpha_{ij} \Delta C_j \quad (5)$$

If the maximum allowed difference in  $C_i$  is 0.1 % relative, substitution into Eq. 5 and rearrangement yields Eq. 6, which defines how wide the range of  $C_j$  can be to ensure the calibration data will fit the equation of a line.

$$\Delta C_j = 0.001 C_i / \alpha_{ij} \quad (6)$$

Matrix effects can be ignored if all values of  $C_j$  lay within the range  $C_j \pm 0.5\Delta C_j$ . A maximum allowed difference of 0.1 % relative was chosen because that value is smaller than the uncertainty estimates for assay values of most primary reference materials. If the conditions imposed on all analytes and interfering elements by Eq. 6 are met by the calibration standards, the equation of the calibration function, Eq. 3, can be simplified to Eq. 7. Target compositions of the calibration standards were calculated on the basis of Eq. 6 and the nominal composition obtained as described previously.

$$C_i = D_i + E_i R_i \quad (7)$$

All elements, except Si, were calibrated using this approach. The actual calibrations are not discussed in this paper. The performance criteria were met for all elements. Estimates of uncertainty are discussed below with the root-mean-square (RMS) deviation between chemical and calculated concentrations serving as the primary measure of fit of the measured data for the calibrants to Eq. 7.

Silicon was not calibrated, but it must be used to represent the matrix in the fused synthetic calibrants. SRM 3150 Silicon Standard Solution cannot be used for this purpose because it contains a Si concentration of only 10 mg/g and the required quantity of solution does not fit inside the Pt crucible. Several commercial, high-purity silica and silicon materials were evaluated for use. Each source of silica or silicon was free of most, but not all, contaminants. Even the silica with the lowest measurable contamination still contained one or more analytes at trace levels. Therefore, all sources of high-purity silica and silicon were used to prepare beads containing only Si to serve as blanks for the minor and trace analytes. That way, it was possible to choose one or more as blanks and create an unbiased calibration for each analyte.

### **XRF RESULTS FOR CANDIDATE SRM 57b**

Homogeneity testing was carried out on the bottled powder prior to acceptance of the material for certification analyses. Two briquettes were prepared from each of 16 bottles selected at random from the entire population. For Si metal, the powder was carefully mixed in a 50/50 ratio with boric acid as a binder to form stable briquettes. XRF measurements were collected under conditions that provided counting statistical imprecision of less than 1 % relative, and as low as 0.25 %. A one-way analysis of variance was used to test for within-bottle variance and between-bottle variance in compliance with ISO Guide 34 [18]. The material was accepted with a recommended minimum quantity per sample of 250 mg.

Quantitative results from the borate fusion/XRF procedure are given in Table 1. All individual measurements are shown for duplicate specimens from each of six bottles. The entire uncertainty budget is provided in Table 1 with the components of uncertainty described in Table 2. For quality assurance, samples of SRM 57 and SRM 57a were prepared and analyzed using the same procedures and calibrations as the samples of candidate SRM 57b. Interesting aspects of method performance are discussed below.

Phosphorus was not detected in the fused specimens and appears to have been lost during sample preparation. An analysis of the Si powder using a fundamental parameters method showed P

content of approximately 30 mg/kg prior to reaction with LiOH. Similarly, SRM 57 and SRM 57a lost nearly all P during sample preparation.

The results for the QA samples were subjected to a bias test [19], which indicated the Fe results are biased low with respect to the certified values for both SRM 57 and SRM 57a. For additional information on Fe, the measured results from NIST PGAA analyses were compared to the XRF results for candidate SRM 57b. The average Fe value from PGAA is 3386 mg/kg ( $s = 84$  mg/kg for  $n = 7$  determinations) compared to the XRF result of 3178 mg/kg ( $s = 96$ ,  $n = 12$ ). The XRF Fe result for SRM 57a (4648 mg/kg,  $U_{k=2} = 310$  mg/kg) and the assigned Fe value for SRM 57a (5000 mg/kg,  $U_{k=1} = 100$  mg/kg) were used to calculate a correction ratio for the XRF results. SRM 57 is considered less reliable due to age and was not used. The correction ratio of 1.076 from SRM 57a values compares well to the ratio of PGAA to XRF results of 1.065. The corrected Fe result for candidate SRM 57b is 3418 mg/kg. This corrected value must be accompanied by a revised expanded uncertainty,  $U$ , estimated at the 95 % confidence level, that includes the contribution of the estimated uncertainty of the correction ratio. The estimate of  $U_{k=2} = 91$  mg/kg shown in Table 1 for Fe becomes 166 mg/kg after combination with the uncertainty of the correction [20,21].

**Table 1. Quantitative Results from the XRF/Borate Fusion Method for Proposed SRM 57b (Results are mg/kg determined on an as-received basis.)**

Sample	Al (mg/kg)	P (mg/kg)	S (mg/kg)	Ca (mg/kg)	Ti (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zr (mg/kg)
3-1	1648	-0.01	36	17	386	13.5	80.0	3162	17.3	16.9	18.76
3-2	1747	-0.89	33	25	402	15.0	82.0	3311	14.7	15.9	18.64
46-1	1692	1.66	72	20	385	19.5	82.1	3248	20.8	29.7	18.28
46-2	1706	2.49	73	63	386	34.0	82.7	3277	17.9	16.4	17.82
254-1	1676	0.83	27	69	370	15.5	80.0	3188	15.9	13.8	18.13
254-2	1680	1.05	43	18	382	30.4	79.9	3196	16.4	4.7	18.13
388-1	1651	0.23	42	35	391	14.7	76.8	3082	12.5	3.5	17.86
388-2	1667	0.00	41	21	368	12.9	76.7	3100	13.4	11.1	17.74
415-1	1678	1.25	32	12	396	15.8	86.9	3063	17.9	9.2	18.19
415-2	1639	1.27	19	16	368	21.2	77.9	3098	14.7	4.2	17.93
694-1	1691	1.26	45	15	402	15.8	77.1	3077	16.0	10.7	17.80
694-3	1678	0.44	27	20	398	16.6	81.2	3329	19.1	21.8	19.19
Average	1679	0.80	41	28	386	18.8	80.3	3178	16.4	13.2	18.21
$s$	29	0.90	17	19	12	6.8	3.0	96	2.4	7.7	0.45
$n$	12	12	12	12	12	12	12	12	12	12	12
$u_f$	21	2.3	9.4	2.3	11	3.9	0.86	40	1.6	1.6	0.23
$p$	5	8	7	7	9	5	10	4	9	6	7
$u_m$	21	2.3	9.4	2.3	11	3.9	0.86	40	1.6	1.6	0.23
$u_s$	3.0	0.0016	0.082	0.055	0.77	0.038	0.16	3.2	0.033	0.026	0.036
$u_b$	0.25	0.00012	0.020	0.0041	0.058	0.0028	0.012	0.48	0.0025	0.0020	0.0027
$u_c$	19	1.7	8.3	5.7	8.4	3.7	1.0	46	1.3	2.5	0.22
$U_{k=2}$	38	3.3	17	11	17	7.5	2.1	91	2.6	5.0	0.43

Symbols:  $s$  = standard deviation of the measured values,  $n$  = number of specimens,

$u_f$  is the root-mean-square (r-m-s) deviation of known versus fit values of calibration standards,

$p$  = number of calibration standards,  $u_m = u_f$  used as an estimate of uncertainty due to choice of calibration model,

$u_s$  = standard uncertainty of assay of primary calibrant,  $u_b$  = standard uncertainty of basis weight,

$u_c$  = combined uncertainty,  $U_{k=2}$  = expanded uncertainty using  $k = 2$  as the expansion factor to achieve an approximate 95 % level of confidence.

**Table 2. Components of Uncertainty of X-Ray Fluorescence Analysis of Silicon Metal**

Uncertainty	Basis	Type	DF
Uncertainty of Balance Calibration, $u_b$ ,	0.2 mg across range of masses. Tested using NIST-traceable weights set. Estimate expressed as a relative uncertainty. A uniform distribution was assumed.	B	$\infty$
Assay of Primary Material, $u_s$	$u_s = U_{k=2}/2$ , where $U_{k=2}$ = expanded uncertainty (an approximate 95 % level of confidence) for each spectrometric solution SRM.	B	$\infty$
Variability of Sample Preparation and Measurement, $s$	Standard deviation of the mean of calculated mass fractions for $n$ specimens.	A	$n - 1$
Variability of Calibrant Preparation and Measurement, $u_f$	RMS deviation of calculated values from chemical values for fit of calibration model (linear equation).	A	$p$
Uncertainty due to Calibration Model, $u_m$	Asserted to be no larger than $u_f$ , the RMS deviation of the calibration model.	B	$\infty$
Uncertainty of Correction Ratio for Fe, $u_r$	Based on the combined uncertainty of the found value for SRM 57a and the combined uncertainty of the certified value for SRM 57a.		

For all elements in SRM 57 and SRM 57a except P and Fe, the XRF results are greater than the estimated minimum quantifiable value,  $L_Q \equiv 10\sigma_Q$ , where  $\sigma_Q$  is the standard deviation of the concentration at the minimum quantifiable value [22], estimated by the value of  $s$  in Table 1. This performance indicates the test method can be used to determine the elements Al, S, Ca, Ti, Cr, Mn, Ni, Cu, and Zr. Results for S, Ca, Cr, Ni, and Cu in candidate SRM 57b are less than  $L_Q$ , but greater than the minimum detectable value,  $L_D \equiv 3\sigma_D$  [22]. The comparisons shown in Table 3 provide evidence that the XRF method is accurate at concentrations in the range of 10 mg/kg to 30 mg/kg for the elements tested.

## CONCLUSIONS

This work, demonstrates that an alkali reaction quantitatively converts Si metal powder to  $\text{Li}_2\text{SiO}_3$ , which can be fused with Li borates. The process can be used as the basis of a test method that is quantitative for Al, S, Ca, Ti, Cr, Mn, Ni, Cu, and Zr. Quantitative limits for some elements are in the range of 10 mg/kg to 30 mg/kg with a borate fusion dilution of 8. Phosphorus appears to be lost during the alkali reaction. The determination of Fe is biased low. A small amount of metallic Fe in the Si powder may be lost into the Pt crucible during fusion. This hypothesis remains to be tested.



**Table 3. Summary of Results for Candidate SRM 57b**

Element	Method	Results (mg/kg)	$U_{k=2}$ (Result) (mg/kg)
Al	XRF	1679	38
	PGAA	1880	80
	ICPOES	1498	41
B	PGAA	14.3	0.2
	ICPOES	10.6	0.4
Ca	XRF	20	11
	ICPOES	24.5	2.5
Cr	XRF	18.8	7.5
	ICPOES	15.9	7.0
Cu	XRF	13.2	5.0
	ICPOES	21.2	4.9
Fe	XRF	3418	166
	PGAA	3386	80
Mn	XRF	80.3	2.1
	PGAA	83.1	4.6
	ICPOES	71.2	3.3
Ni	XRF	16.4	2.6
	ICPOES	14.2	4.3
P	RNAA	17.5	0.7
	ICPOES	15	5.8
Ti	XRF	396	17
	PGAA	332	40
	ICPOES	310	15
Zr	XRF	18.21	0.43
	ICPOES	17.4	0.5

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