Simultaneous Determination of Sub $\mu\text{g g}^{-1}$ Levels of Impurities in High Purity Iron by Inductively Coupled Plasma-Atomic Emission Spectrometry after Circulation of Eluant through Anion Exchange Resin Mini-Column

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Boron, Mo, Nb, Sn, Ta, W and Zr were separated from an iron matrix using a horizontal mini-column of an anion exchange resin. The flow of solutions through the mini-column was controlled by a peristaltic pump. The elements adsorbed on the resin were simultaneously eluted by the circulation of an eluant and determined by inductively coupled plasma-atomic emission spectrometry. Quantitative recoveries were obtained for all 7 elements in the acid-soluble fraction and for 5 elements (not B or Sn) in the acid-insoluble fraction. A part of B in the acid-insoluble fraction was lost during the ashing and the fusion but the loss was compensated by using the calibration solutions prepared with the same procedure as that for the samples. A 500-fold enrichment was obtained using this preconcentration system compared with an ordinary sample solution of $0.5 \text{ g}/100 \text{ cm}^3$. The proposed method was applied to the simultaneous determination of sub $\mu\text{g g}^{-1}$ levels of impurities in high purity irons.

Keywords Inductively coupled plasma-atomic emission spectrometry, anion exchange resin, eluant circulation, boron, molybdenum, niobium, tin, tantalum, tungsten and zirconium, high purity iron, acid-soluble fraction, acid-insoluble fraction

Determination of traces of impurities in high purity iron has been demanded in connection with the studies of purification and physical properties of iron.^{1,2} Even in the certified reference materials of high purity iron from the Iron and Steel Institute of Japan (JSS CRMs), contents of many impurities at sub $\mu\text{g g}^{-1}$ levels have not been certified.³ Therefore, the accurate determination of these impurities is necessary. The present authors developed analytical methods of high purity irons for B⁴ and S⁵ by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Extraction of the iron matrix with 4-methyl-2-pentanone was used for the simultaneous determination of traces of impurities in high purity irons followed by total reflection X-ray fluorescence (TXRF) spectrometry⁶, ICP-AES⁶ and ICP-mass spectrometry.⁷ Relative standard deviations (RSDs) of TXRF spectrometry ranged from 12 to 29%.⁶ The solvent extraction method was, however, unsuitable for the separation of Cr^{VI}, Mo^{VI}, Sn^{IV}, V^V and W^{VI} from the iron matrix because these elements were coextracted with iron.^{8,9}

Though ICP-AES is relatively sensitive to such refractory metals, preconcentration is necessary for the determination of traces of these elements in high purity iron. Ion exchange separation is useful for refractory metals. Anion and anion plus cation exchange chromatography from hydrofluoric acid have been studied for

many elements.^{4,10-12}

In this paper, elution of refractory metals from a mini-column of an anion exchange resin was studied using a peristaltic pump and circulation of an eluant. This system has advantages over a vertical column method such as minimization of the eluant and eluate, decrease in detection limit (DL), decreased analysis time, accurate control of flow rate over a wide range and rapid change of the flow rate and flow direction. This system has the possibility of being used in the flow injection analysis.

Experimental

Apparatus

A Shimadzu (Japan) Model ICPV-1000 vacuum-type polychromator and a Model CTM-50 auxiliary monochromator were used with a sodium-treated hydrofluoric acid-resistant sample introduction system. The instrumentation used has been described elsewhere.¹³ Compromise operating conditions for the simultaneous determination are shown in Table 1. An Ismatec (Switzerland) Model MS-4 4-channel peristaltic pump was used to control the flow rates of the solutions. Four solutions were simultaneously processed with this peristaltic pump.

Table 1 Operating conditions

Frequency (MHz)	27.12	
Output power (kW)	1.2	
Reflected power (W)	<1	
Flow rate of Ar gas (dm ³ min ⁻¹)		
Outer gas	15	
Intermediate gas	1.5	
Carrier gas	1.1	
Purge gas	3.0	
Observation height above coil (mm)	12	
Sample uptake rate (cm ³ min ⁻¹)	1.6	
Integration time (s)	26	
Spectral lines used (nm)		
Al I 396.15	As I 193.76	B I 249.68 ^a
Ca II 393.37	Co II 228.62	Cr II 267.72
Cu I 327.40	Fe II 259.94	Ga I 294.36
Hf II 264.14	Mg II 279.55	Mn II 257.61
Mo II 202.03	Nb II 319.50	Ni II 231.60
P I 178.29	S I 180.73	Si I 251.61
Sn II 189.99	Ta II 248.87	Ti II 337.28
V II 311.07	W II 207.91	Zr II 343.82

a. Used for (N+1) channel auxiliary monochromator.

Fig. 1 Schematic diagram of preconcentration system.

Flow of sample solution, d to f; circulation of eluant, d to e; a, peristaltic pump; b, PFA mini-tube (resin volume 3 cm³); c, PTFE beaker.

Anion exchange resin mini-column

Strongly basic anion exchange resins, Dowex 1-X8 and Dowex 2-X8 (Dow Chemical Co., USA, particle size 0.15–0.30 mm, chloride form), were used. A resin mini-column was contained in a horizontal mini-tube which had been handmade from a piece of polytetrafluoroethylene (PTFE)-perfluoroalkylvinylether copolymer (PFA) tubing (8 mm i.d.). One side of the mini-tube was connected with the PTFE tubing (0.8–1.0 mm i.d.) and the other side was connected with the pump tubing. A schematic diagram of the preconcentration system is shown in Fig. 1. The resin mini-column was preconditioned by circulating 10 cm³ of 5 mol dm⁻³ hydrofluoric acid for 1 h twice and then passing 10 cm³ of 1 mol dm⁻³ hydrofluoric acid.

Reagents and solutions

Hydrofluoric acid (29.6 mol dm⁻³), nitric acid (13.0 mol dm⁻³) and hydrogen peroxide (9.7 mol dm⁻³) were of atomic absorption spectrometry grade (Kanto Chemical Co., Japan). Hydrofluoric acid (29.6 mol dm⁻³) of

semiconductor grade (Daikin Industries, Japan) was also used. The other reagents were of analytical reagent grade. Standard solutions were prepared by dissolving high purity metals or oxides.

Procedure

(a) *Acid-soluble fraction.* Weigh 5 g of high purity iron into a 500-cm³ PTFE beaker. Add 21 cm³ each of concentrated hydrofluoric acid and water. Cover the beaker with a PTFE lid. Heat the solution on a hot plate and add 5 mol dm⁻³ hydrogen peroxide until a clear solution is obtained. Filter the solution with a Toyo Roshi (Japan) No. 5C filter paper. Wash the filter paper with dilute hydrofluoric acid. Combine the filtrate with washings and dilute to 200 cm³ with water. Pass the solution through a horizontal Dowex 1-X8 mini-column (3 cm³) and wash the mini-column with 150 cm³ of 2 mol dm⁻³ hydrofluoric acid using a peristaltic pump at a flow rate between 3 and 7 cm³ min⁻¹. Elute adsorbed elements with 7 cm³ of a mixture of 8 mol dm⁻³ nitric acid and 0.1 mol dm⁻³ hydrogen peroxide at the same flow rate for 30 min and then elute 4 more times by using a new batch of the eluant at each elution. Evaporate the combined eluate to about 0.5 cm³. Add 1 cm³ of 5 mol dm⁻³ hydrofluoric acid and 200 mm³ of 200 µg cm⁻³ of Mn to monitor emission intensities of the elements. Dilute the solution to 2 cm³ with water. Prepare calibration solutions by matching the volume of the eluant and reagents and following the evaporation procedures. Analyze the sample solution by ICP-AES. (b) *Acid-insoluble fraction.* Transfer an acid-insoluble residue with the filter paper into a Pt crucible. Heat to dryness, add 2 cm³ of 20 mg cm⁻³ of sodium carbonate solution into the crucible and heat to dryness. Ash the filter paper and fuse the residue with 1 g of potassium hydrogen sulfate. Add 10 cm³ of 5 mol dm⁻³ hydrofluoric acid and water into the crucible and dissolve the melt by heating. Dilute the solution to about 100 cm³ with water. Follow the mini-column separation procedures in (a). Prepare calibration solutions by following the procedures mentioned in (b).

Results and Discussion

Sample treatment

High purity iron was dissolved with hydrofluoric acid and hydrogen peroxide. Nitric acid was not used as an oxidizing agent because it interfered with the adsorption of several elements to be determined on the resin column. Hydrofluoric acid was useful to prevent hydrolysis of refractory metals and as a solvent for the anion exchange separation. It is necessary to consider the acid-insoluble fraction in addition to the acid-soluble fraction for the complete determination of refractory metals in iron and steel. The acid-insoluble residue is ordinarily decomposed by fusion with potassium hydrogen sulfate or potassium disulfate. The former was chosen because purer reagent was obtained. Vapor-

ization of B, Mo and W during ashing was minimized by adding sodium carbonate solution to the residue before the ashing.⁴

Preliminary investigation of ion exchange separation by vertical column method

Recoveries of 1 mg each of 24 elements shown in Table 1 from the Dowex 1-X8 and 2-X8 columns (4 cm³ each, 9 mm i.d.) were investigated by the vertical column method. One, 2, 3, 5 and 7 mol dm⁻³ hydrofluoric acids containing these elements were passed through the columns. Adsorbed elements were eluted with 150 cm³ of a mixture of 2 mol dm⁻³ nitric acid and 0.1 mol dm⁻³ hydrogen peroxide at the flow rate of 1.5 cm³ min⁻¹. Boron, Mo, Nb, Sn, Ta, Ti, W and Zr were quantitatively recovered from both resin columns between 1 and 5 mol dm⁻³ hydrofluoric acids. More S which had been added as sulfate ion was found in the eluate from Dowex 2-X8 than in that from Dowex 1-X8. Sulfate ion which is derived from potassium hydrogensulfate decreased emission intensities of the elements to be determined as will be shown later. Therefore, Dowex 1-X8 was used in the following experiments.

Two grams of iron to which 1 mg each of the 8 elements had been spiked were dissolved and processed as above. Quantitative recoveries of the 8 elements were obtained in the eluate. When a large amount of iron was dissolved, fluoride ion which was combined with iron lowered the effective concentration of hydrofluoric acid. Therefore, the effective concentration of hydrofluoric acid as a solvent was calculated by subtracting the combined fluoride ion from the nominal concentration. About 2 mol dm⁻³ were chosen as the effective concentration of hydrofluoric acid for the anion exchange separation in consideration of the dissolution of high purity iron and recoveries of the elements.

Optimization of preconcentration system

A system composed of a horizontal resin mini-column and a peristaltic pump was studied for the separation of traces of the 8 elements from the iron matrix. Eight kinds of plastic tubes (polychlorotrifluoroethylene, polyethylene, PFA, polymethylmethacrylate, polypropylene, polystyrene, PTFE and polyvinylchloride) were tested as mini-tubes. These mini-tubes were washed with a strong mineral acid or a mixture of acids for several days. Then, impurity blanks from the mini-tubes without the resin were investigated by first passing 5 mol dm⁻³ hydrofluoric acid for 2 h and then the eluant composed of 8 mol dm⁻³ nitric acid and 0.1 mol dm⁻³ hydrogen peroxide for 2 h at the flow rate of 3 cm³ min⁻¹. The Ti blank detected from all the mini-tubes was between 0.1 and 10 µg and other impurities were low. The PFA mini-tube was adopted because it had a relatively small blank of Ti and could be easily processed and washed with a mixture of strong mineral acids by heating. However, traces of Ti in high purity iron could not be determined with this mini-tube because the Ti blank from the PFA mini-tube could not be controlled to

a constant value.

The following various eluants were investigated for the simultaneous elution of B, Mo, Nb, Sn, Ta, W and Zr; 2, 4 and 8 mol dm⁻³ nitric acids, 1 mol dm⁻³ hydrochloric acid plus 8 mol dm⁻³ nitric acid, 0.3 mol dm⁻³ perchloric acid plus 1.5 mol dm⁻³ hydrofluoric acid, and 0.5 mol dm⁻³ perchloric acid plus 0.5 mol dm⁻³ hydrofluoric acid plus 2 mol dm⁻³ nitric acid, all of which contained 0.1 mol dm⁻³ hydrogen peroxide. Eight mol dm⁻³ nitric acid plus 0.1 mol dm⁻³ hydrogen peroxide was the best eluant among them.

Elution of 20 µg each of the 7 elements which had been adsorbed on the mini-column was first investigated by using a continuous flow of the eluant. The elution showed tailing and recoveries of the 7 elements were between 80 and 95% with 100 cm³ of the eluant. Recovery was the highest for Mo and the lowest for Zr. Therefore, circulation of the eluant was carried out to complete the elution of the 7 elements and to minimize reagent blanks with a limited volume of the eluant. One circulation of the eluant was carried out for 30 min with 7 cm³ of the eluant at the flow rate of about 5 cm³ min⁻¹. A new batch of the eluant was used at each circulation and this promoted the rapid elution because of the effective elimination of fluoride ion from the mini-column. The minimum number of circulations of the eluant was 3 or 4 for the complete elution of Nb, Sn, W and Zr and 5 for B, Mo and Ta. Elution behavior for the continuous flow and that for the circulation of the eluant were different. The 7 elements were quantitatively and simultaneously eluted by 5-time repetition of the circulation of the eluant. The eluate thus obtained was a simple acid solution and could be evaporated to a small volume. Dryness of the eluate was unsuitable due to the vaporization of B.⁴

Resin volume was varied from 1 to 5 cm³. Adsorption of 20 µg each of the 7 elements from 100 cm³ of 2 mol dm⁻³ hydrofluoric acid and the circulation of the eluant were investigated. Eluant volume was 7 cm³ and its flow rate was 3 cm³ min⁻¹. Recovery of Mo is shown in Fig. 2 as an example. Increase in the resin volume made the elution of Mo more difficult. However, the recovery of Mo became complete with increasing the number of the circulations of the eluant. Quantitative adsorption was not obtained with a small volume of the resin. Three cubic centimeters of the resin volume were chosen in consideration of the complete adsorption and easy elution of the 7 elements. The resin was used at least 10 times.

A batch method was also tried instead of the circulation of the eluant through the mini-column. The resin (3 cm³) on which 20 µg each of the 7 elements had been adsorbed was removed from the mini-tube and 7 cm³ of the eluant were added. The mixture was stirred with a magnetic stirrer for 30 min. Then the equilibrated eluate was removed. Recoveries of the 7 elements measured were between 45 and 80%. A new batch of the eluant was mixed with the resin and the batch method was repeated. As a result, it was found that

Fig. 2 Effect of resin volume and elution time on recovery of molybdenum. Period for one circulation of eluant, 30 min; number of circulations of eluant: a, once; b, twice; c, 3 times; d, 4 times; e, 5 times.

equilibriums of 4 to 5 times were necessary for the quantitative recoveries of the 7 elements. These results were similar to those obtained by the circulation of the eluant. The procedures in the batch method were troublesome, time-consuming and difficult to automate. Therefore, the batch method was not adopted.

Acid-soluble fraction and acid-insoluble fraction

We investigated the effect of the iron concentration in the acid-soluble fraction on the adsorption of the 7 elements in the effective concentration of 2 mol dm^{-3} hydrofluoric acid. The iron solutions from which the 7 impurities had been eliminated by passing once through the mini-column were used for the experiments. Average recoveries ($\bar{x}$) and standard deviations (σ) are shown in Table 2. Quantitative adsorption of the 7

elements was obtained irrespective of the iron concentration from 3 to 5 g/200 cm^3 . The iron remaining on the mini-column after passing 5 g of iron was decreased to less than $10 \mu\text{g}$ by washing with 150 cm^3 of 2 mol dm^{-3} hydrofluoric acid. Then, the effect of the flow rates of the sample, washing and circulation of the eluant was studied on the recoveries of the 7 elements in 5 g/200 cm^3 of iron solutions as shown in Table 2. Quantitative recoveries of the 7 elements were obtained at all the flow rates studied. Thus, 5 g/200 cm^3 of iron solutions and a flow rate between 3 and $7 \text{ cm}^3 \text{ min}^{-1}$ were used for the separation of the 7 elements from the iron matrix in the acid-soluble fraction. Analysis time of the acid-soluble fraction was within 6 h from the sample loading on the mini-column to the end of evaporation.

The acid-insoluble fraction which contained a fusion flux was unsuitable for the ICP-AES determination of traces of elements due to high viscosity and difficult evaporation to a small volume. Separation of traces of the 7 elements from the flux was investigated by using the preconcentration system.

Effect of the hydrofluoric acid concentration (0.5 to 3 mol dm^{-3}) was investigated on the adsorption of the 7 elements. One gram of potassium hydrogen sulfate was added to each hydrofluoric acid solution. The adsorption was decreased with increasing concentration of hydrofluoric acid. Quantitative adsorption of the 7 elements was obtained from 0.5 mol dm^{-3} hydrofluoric acid; the results are shown on the left column in Table 3. The amount of sulfate ion found in the eluate was about 15 mg (2.1% against 1 g of the flux) and sulfate ion suppressed the emission intensities of the elements due to the increase in the viscosity of the eluate. Matching of sulfate ion was necessary.

Effect of the ashing and fusion of the acid-insoluble residue was investigated on the recoveries of the 7 elements. Mixed standard solutions of Mo, Nb, Sn, Ta, W and Zr were fused with sulfuric acid in a Pt crucible. This procedure was necessary to eliminate hydrofluoric acid in order to avoid the vaporization of B as boron trifluoride. Then, boron standard solution, prepared by dissolving boric acid with water, a filter paper and 2 cm^3 of 20 mg cm^{-3} of sodium carbonate solution were

Table 2 Effect of iron concentrations and flow rates on recoveries of 7 elements ($\%, \bar{x} \pm \sigma, n=6$)

	Concentration of iron (g/200 cm^3) ^a			Flow rate of sample, washing and eluant (cm^3/min) ^b		
	3	4	5	3	5	7
B	99.8 ± 1.3	99.1 ± 1.3	98.8 ± 1.6	101.8 ± 2.5	99.8 ± 1.6	101.7 ± 1.4
Mo	100.1 ± 2.3	99.0 ± 1.3	98.6 ± 1.5	99.8 ± 1.7	97.5 ± 0.9	97.2 ± 1.3
Nb	101.1 ± 2.2	99.4 ± 1.1	99.6 ± 1.6	101.2 ± 1.8	99.8 ± 0.9	101.3 ± 1.6
Sn	101.4 ± 2.9	99.1 ± 1.2	99.7 ± 1.6	101.0 ± 2.2	100.0 ± 1.0	100.8 ± 1.7
Ta	99.3 ± 2.4	98.0 ± 1.4	98.6 ± 1.1	100.4 ± 2.2	99.1 ± 1.2	100.3 ± 1.6
W	100.6 ± 2.9	99.6 ± 1.6	99.2 ± 1.5	100.8 ± 1.8	100.0 ± 1.1	100.8 ± 1.8
Zr	101.2 ± 2.7	99.9 ± 1.4	99.4 ± 1.6	101.0 ± 1.7	100.1 ± 1.1	101.9 ± 2.4

a. Twenty micrograms each of 7 elements was spiked. Flow rates of sample, washing and eluant were $3 \text{ cm}^3 \text{ min}^{-1}$. b. Twenty micrograms each of 7 elements was spiked in 5 g/200 cm^3 of iron solution.

added into the crucible. The mixture was dried and ashed. The residue was fused with the flux. The melt was dissolved with 0.5 mol dm^{-3} hydrofluoric acid and the 7 elements were separated by the preconcentration system. The recoveries of Mo, Nb, Ta, W and Zr were 95% or more, as shown on the right column in Table 3, and those of B and Sn were low. A part of B and Sn seems to have been lost during the fuming of the solution and the fusion of the residue. It will, however, be no problem for Sn because the acid-insoluble residue has been discarded¹⁴ for the determination of Sn in iron and steel. For the accurate simultaneous determination of the 6 elements other than Sn in the acid-insoluble fraction, calibration solutions have to be prepared according to the above-mentioned procedures following the fuming of the standard solutions.

Table 3 Effect of ashing and fusion on recoveries^a of 7 elements in acid-insoluble residue (%), $\bar{x} \pm \sigma$, $n=6$)

	Without ashing and fusion	With ashing and fusion
B	99.1 $\pm$ 1.3	86.4 $\pm$ 2.4
Mo	98.6 $\pm$ 1.6	95.2 $\pm$ 2.8
Nb	99.9 $\pm$ 1.4	97.0 $\pm$ 2.5
Sn	100.3 $\pm$ 2.1	67.6 $\pm$ 5.6
Ta	99.3 $\pm$ 1.6	96.7 $\pm$ 2.4
W	99.1 $\pm$ 1.7	95.2 $\pm$ 3.0
Zr	100.1 $\pm$ 1.6	97.9 $\pm$ 1.6

a. Twenty micrograms each of 7 elements was spiked. Flow rate was $4 \text{ cm}^3 \text{ min}^{-1}$.

Analytical results by ICP-AES

Spectral interferences between the elements in the eluate were investigated using 50 mg cm^{-3} of the standard solutions. Tungsten interfered with the Ta II 248.87 nm line and the interference was corrected by the calculation. Sulfur interfered strongly with the B I 182.64 nm line when the polychromator was used and the interference could not be corrected by the calculation. Therefore, the B I 249.68 nm line was measured with the auxiliary monochromator.

The DL, defined as the concentration equivalent to 3 times the standard deviation ($n=10$) of the reagent blank, is shown in Table 4, here 5 g of the sample and 2 cm^3 of the final volume were used. The DLs for the elements in the acid-insoluble fraction were slightly higher than those in the acid-soluble fraction. The DL for B was improved by about 4-fold compared with that by the previous method.⁴

Traces of the 7 impurities in the JSS CRMs 002-2 and 003-3 of high purity iron were determined by the proposed method. Average values ($\bar{x}$), σ and RSDs of 6 separately dissolved samples are shown in Table 4. However, content at sub $\mu\text{g g}^{-1}$ levels is not certified for any of the 6 elements except B. The certified value for B in the CRM 002-2 is $0.5 \mu\text{g g}^{-1}$ and the non-certified value for B in the CRM 003-3 is $0.3 \mu\text{g g}^{-1}$.³ Analytical values for B were in good agreement with these values. Concentrations of the 6 impurities in the acid-insoluble fraction were less than the DLs in both CRMs. Accuracy of the proposed method was confirmed by the recoveries of spikes as shown in Table 4. Ten micrograms each of the 7 and 6 elements without Sn were

Table 4 Analytical results ($\mu\text{g g}^{-1}$, $\bar{x} \pm \sigma$, $n=6$) of high purity irons, RSDs (%), $n=6$), recoveries (%), $\bar{x} \pm \sigma$, $n=6$) and DLs ($\mu\text{g g}^{-1}$, $n=10$)

JSS 002-2	Acid-soluble fraction			Acid-insoluble fraction	
	$\bar{x} \pm \sigma$	RSD	DL	$\bar{x}$	DL
B	0.532 $\pm$ 0.007	1.3	0.012	<0.018	0.018
Mo	0.351 $\pm$ 0.004	1.1	0.006	<0.010	0.010
Nb	<0.018		0.018	<0.029	0.029
Sn	0.082 $\pm$ 0.004	4.9	0.011		
Ta	<0.032		0.032	<0.077	0.077
W	0.078 $\pm$ 0.005	6.4	0.017	<0.038	0.038
Zr	0.013 $\pm$ 0.003	23	0.007	<0.010	0.010

JSS 003-3	Acid-soluble fraction		Acid-insoluble fraction	Recoveries ^a ($\bar{x} \pm \sigma$)	
	$\bar{x} \pm \sigma$	RSD		Acid-soluble fraction	Acid-insoluble fraction
B	0.221 $\pm$ 0.010	4.5	<0.018	103.3 $\pm$ 1.2	102.1 $\pm$ 2.2
Mo	0.159 $\pm$ 0.005	3.1	<0.010	99.9 $\pm$ 0.5	101.4 $\pm$ 1.7
Nb	0.071 $\pm$ 0.006	8.5	<0.029	99.8 $\pm$ 1.0	98.7 $\pm$ 2.0
Sn	0.088 $\pm$ 0.004	4.6		99.6 $\pm$ 0.5	
Ta	<0.032		<0.077	100.7 $\pm$ 1.1	97.4 $\pm$ 1.8
W	0.138 $\pm$ 0.010	7.3	<0.038	100.0 $\pm$ 0.4	99.2 $\pm$ 2.3
Zr	0.009 $\pm$ 0.005	55	<0.010	99.9 $\pm$ 0.8	99.6 $\pm$ 1.8

a. Ten micrograms each of the elements was spiked.

spiked, respectively, to the acid-soluble fraction and acid-insoluble residue of the CRM 003-3. Quantitative recoveries were obtained for all the spikes. Small RSDs for the 4 or 5 elements (B, Mo, Nb, Sn and W) in the acid-soluble fractions showed good precision of the proposed method.

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(Received December 22, 1992)

(Accepted March 11, 1993)