Determination of Trace Elements in Iron and Steels by Graphite Furnace Atomic Absorption Spectrometry with Solution Samples of mg Order*

By Takeshi Kobayashi**, Kunikazu Ide** and Haruno Okochi**

An analytical method has been established for the determination of trace elements in very small samples by graphite-furnace atomic absorption spectrometry. Milligrams of samples of metal chips were dissolved in a pressure bomb using a definite volume of mixture of acids. The trace amounts of As, Sn, Co, Ni, Cr and Sb in those sample solutions were determined by atomic absorption spectrometry. When the samples were dissolved in a pressure bomb, the volume of evaporated sample solution was monitored by measurement of the whole mass before and after the dissolution. Gold was used as an internal standard. As a result, it was known that the pressure bomb used was excellent in maintenance of the solution volume, leading to high precision of the measurements. The analytical values of several standard samples (ca. 1 mg) used in this study were in good agreement with certified values of them. Therefore, it was found that even one milligram of them was able to sufficiently serve as standard reference materials. Detection limits (3σ of blank value) were 0.7, 0.8, 0.3, 0.3, 0.2, 0.3 and 0.3 ppm for As, Sn, Co, Ni, Cr, Sb and Au, respectively, when one milligram was used. The proposed method has a good accuracy and precision and is adequate to analysis of specimens of very small amount.

(Received February 5, 1987)

Keywords: graphite-furnace atomic absorption spectrometry, trace element analysis, arsenic, tin, cobalt, nickel, chromium, antimony, gold, small sample analysis, impurity determination in iron and steel

I. Introduction

Recently, the study for new materials such as ultra-fine particles, evaporated films, various compounds, whiskers and so on has been performed, and it is required to determine the analytes of a wide concentration range from trace to major with high accuracy and precision by using a small amount of samples.

This paper describes trace analysis using a small amount of samples by graphite-furnace atomic absorption spectrometry which is highly sensitive and precise. There are reports concerning the determination of rather many elements in metals(1)-(4), alloys(5)-(6) and ores(7)-(8) by graphite-furnace atomic absorption spectrometry with direct atomization of a solid sample. This method has excellent merits such as no need of pretreatment of samples, while it is necessary to prepare calibration curves with standard reference materials of which compositions are similar to those of samples. However, certified values of trace elements in the commercial standard reference materials have not so much been established yet. The analytical precision of this method is generally worse than those of the usual solution method(9)-(11), and the cause is not clear yet.

In this study, the solution method by dissolving very small samples of mg order with a small amount of acid was investigated. Important factors to be considered were to weigh a small amount of samples, to make a constant volume with a small amount of solution, to prevent loss of solution by evaporation at the dissolution of samples and to choose the optimum conditions for atomic absorption spectrometry. Accordingly, a very precise electric micro-balance was used. The pressure bomb which was designed by Bernas(12) was reported(13) to have an excellent air-tight structure and to be safe. This pressure bomb was ap-
plied for dissolving samples with a constant small amount of acids. The volume of evaporated sample solution was monitored by measurement of the whole mass before and after the dissolution, and by the determination of gold which was added as an internal standard. Various iron and steel standard reference materials were analyzed by ca. 5 mg or ca. 1 mg of a sample taken, and analytes under investigation were arsenic, tin and antimony which were apt to segregate on a grain boundary, and nickel, chromium and cobalt which were easy to be solid-soluble. The accuracy and precision of analytical values by the proposed method were compared with those by the usual method with 0.100 g of a sample taken. The proposed method showed a good accuracy and precision in the determination and was able to determine about ten analytes with 1 mg of specimens, calculating from the volume to be needed for analysis.

II. Experimental

1. Apparatus

A Perkin-Elmer Model 4000 atomic absorption spectrophotometer was used, equipped with a Model HGA-500 graphite furnace. The graphite furnace was a Perkin-Elmer pyrolytically coated graphite furnace equipped with a L'vov platform (hereafter referred to as platform). A Perkin-Elmer Model AS-40 autosampler was used. The balances used were a Mettler Model M3 electric micro-balance (standard deviation <1 μg) and a Satorius Model 2003 MP I electric semimicro-balance. The data treatment was performed with NEC Model PC-8801mkII personal computer. The pressure bombs used for the dissolution of samples were a Parr pressure bomb (23 cm³) and a Uniseal one (5 cm³). The sample dissolution was performed in a ventilated thermostat drying oven (Showa Kagaku Kogyo, Tokyo, Japan). An Eppendorf Model 4710 micro-pipett was used. The other apparatuses were the same as those used in previous paper (15).

2. Reagent

Standard arsenic solution 1 kg/m³ (1 mg/mL): 1.320 g of arsenic trioxide (Merck) was dissolved with 4 g of potassium hydroxide and 20 cm³ of distilled water, and the solution was neutralized with 20 vol% sulfuric acid and diluted to 1000 cm³ with 1 vol% sulfuric acid. Standard gold solution 1 kg/m³: 0.500 g of high-purity gold (Johnson Matthey Chemicals) was dissolved by heating with 30 cm³ of aqua regia, and after cooling to room temperature the solution was diluted to 500 cm³ with hydrochloric acid (1 + 10).

Tin, cobalt, nickel, chromium and antimony stock standard solutions were prepared according to the JIS method (16). When using, those standard solutions were diluted with distilled water.

High-purity iron (99.999%, Spex Industries) was used. Super high-purity argon (99.999%) and hydrogen (99.5%) were used as purge gases. Acids and chemicals used were of super special grade or of analytical reagent grade.

Iron and steel standard reference materials used were JSSs 161-3 (trace element series A), 168-3, 169-3 and 171-3 (trace element series B), ECRMs 087-1 (low alloy steel), 097-1 (high-purity iron) and NBS SRM 361 (low alloy steel).

The mixture of acids used for the dissolution of samples were prepared as follows. Acid mixture (A): 415 cm³ of hydrochloric acid and 126 cm³ of nitric acid were mixed. Standard gold solution (Au: 500 μg) was added and the solution was diluted to 1000 cm³ with distilled water. Acid mixture (B): 185 cm³ of hydrofluoric acid and 252 cm³ of nitric acid were mixed. Standard gold solution (Au: 500 μg) was added and the solution was diluted to 1000 cm³ with distilled water. Furthermore, acid mixtures (A-2) and (B-2) were prepared by diluting acid mixtures (A) and (B) to one fifth concentration.

3. Procedure

Weigh 0.100 g of a high-purity iron into a 200 cm³ beaker. Add 20 cm³ of the acid mixture (A) and heat the solution on a hot-plate for the dissolution. After cooling, add a constant amount of arsenic, tin, cobalt, nickel, chromium and antimony stock standard solutions.

Transfer the solution into a 100 cm³ vol-
umetric flask and dilute to the mark with distilled water. On the other hand, when using 20 cm³ of the acid mixture (B), transfer the solution into a 100 cm³ PTFE beaker and a 100 cm³ polypropylene volumetric flask. Inject 20 mm³ (20 μL) of the solution into the graphite furnace by means of an autosampler. Operate the controller of the graphite furnace under the conditions summarized in Table 1 and measure the absorbances. The graphite furnace was equipped with a platform in which heating characteristics and reproducibility were excellently improved."\(^{15}\)(17)(18). Unless otherwise stated, the final concentrations of prepared solutions were 0.1 g/m³ (0.1 μg/mL) of arsenic, tin, cobalt, nickel, chromium, antimony and gold, and the concentrations of a sample and an iron were 1 kg/m³ (1 mg/mL). The mixture of hydrochloric acid—nitric acid was composed of 1 kmol/m³ of hydrochloric acid and 0.4 kmol/m³ of nitric acid and the mixture of hydrofluoric acid—nitric acid was composed of 1 kmol/m³ of hydrofluoric acid and 0.8 kmol/m³ of nitric acid.

### III. Results and Discussion

#### 1. Operating conditions

Ashing temperature curves and atomizing temperature curves of arsenic, tin, cobalt, nickel, chromium, antimony and gold were obtained using hydrochloric acid—nitric acid or hydrofluoric acid—nitric acid solutions of iron containing each standard solution. A constant absorbance was obtained at 973–1273 K–2Os using argon as a purge gas for the elements with the exception of tin. However, as for tin, the ashing temperature range giving a high and constant absorbance was not obtained. This fact was caused by the evaporation of tin as stannic tetrachloride or stannic tetrafluoride. Accordingly, reductive hydrogen was applied as a purge gas and the mixture of hydrofluoric acid was used for the dissolution, so that an ashing stage might be successfully performed at 773 K–30s. This result was the same as those obtained in a previous report."\(^{19}\)

\[\text{Table 1 Operating parameters.}\]

| Element | Light source (mA) | Wavelength (nm) | Spectral band-width (nm) | Background correction | Calibration mode | Integration time (s) |
|---------|-------------------|----------------|-------------------------|----------------------|-----------------|----------------------|
|         | HCL:12            | 193.8          | 0.7                     | D₂                   | Peak area       | 7                    |
|         | HCL:12            | 286.3          | 0.7                     | D₂                   | Peak area       | 5                    |
|         | HCL:15            | 240.7          | 0.2                     | D₂                   | Peak area       | 10                   |
|         | HCL:12            | 231.8          | 0.2                     | W                    | Peak area       | 10                   |
|         | HCL:12            | 357.7          | 0.7                     | D₂                   | Peak height     | (4)                  |
|         | HCL:12            | 217.5          | 0.2                     | D₂                   | Peak area       | 5                    |
|         | EDL:8W            | 242.8          | 0.7                     | D₂                   |                 |                      |

\[a)\text{ Pyrocoated tube-platform.} \ b) \text{Ashing-2: Temperature: 773 K, Ramp time: 1s, Hold time: 14s, Internal gas: Ar, 5 cm³/s.}\]
concerning the analysis of nickel-based superalloys. However, when using mixture of hydrochloric acid, hydrogen was ineffective. 0s of ramp time at atomization was the maximum power mode, in which the elevating temperature rate was ca. 2000 K/s. The integration time was decided to be 1s plus the time when absorption cures ended, and those for the analytes are summarized in Table 1. The cleaning condition was 2773 K-3s for all the elements, at which there was no memory effect and no effect of the residue of iron.

2. Sensitivity, detection limit and limit of firing numbers of a graphite furnace

The quantity of an injection was 50 mm³ and a purge gas flow was interrupted at the atomizing stage.

Sensitivity was defined as the equivalent concentration to 1% absorption (absorbance 0.0044) obtained from the slope of a calibration curve. Detection limits were calculated from the equivalent concentration to 3σ of twenty measurements of a blank solution. Table 2 summarizes the results of each analyte.

The relation between firing numbers of a graphite furnace and sensitivity or precision was examined. The RSDs of twenty measurements of absorbances were calculated and the number of injections in which the RSD was less than 2% was defined as a suitable number of firing of a graphite furnace. The result of gold is illustrated in Fig. 1. Table 2 shows the limit of firing numbers of a graphite furnace for each analyte.

3. Analysis of standard reference materials

Standard reference materials of JSSs 161-3, 168-3, ECRMs 087-1, 097-1 and NBS SRM 361 were analyzed.

0.25 g of a sample was dissolved with 50 cm³ of an acid mixture(A) or (B) and the solution was diluted to 250 cm³. For the calibration, 0.100 g of a high-purity iron was dissolved by precisely adding 20 cm³ of an acid mixture(A)

![Fig. 1 Influence of aging of the pyrolytically coated tube-platform on absorbance and precision (n=20).](image)

---: Au absorbance
-----: Au relative standard deviation

| Element | Sample treatment | Sensitivitiesᵇ (pg) | Detection limitsᶜ (pg) | Limits of number of firings |
|---------|------------------|---------------------|------------------------|---------------------------|
| As      | HCl + HNO₃      | 28                  | 36                     | 550                       |
|         | HF + HNO₃       | 31                  | 42                     |                           |
| Sn      | HCl + HNO₃      | 110                 | 44                     | 440                       |
|         | HF + HNO₃       | 38                  | 39                     |                           |
| Co      | HCl + HNO₃      | 20                  | 16                     | 600                       |
|         | HF + HNO₃       | 20                  | 16                     |                           |
| Ni      | HCl + HNO₃      | 14                  | 15                     | 400                       |
|         | HF + HNO₃       | 13                  | 15                     |                           |
| Cr      | HCl + HNO₃      | 4                   | 12                     | 550                       |
|         | HF + HNO₃       | 4                   | 10                     |                           |
| Sb      | HCl + HNO₃      | 8                   | 15                     | 550                       |
|         | HF + HNO₃       | 9                   | 14                     |                           |
| Au      | HCl + HNO₃      | 17                  | 12                     | 750                       |

a) Calculated for N=20 and 50 mm³ (µL) injections.
b) Concentration giving 1% absorption (0.0044 absorbance unit).
c) Concentration giving 3σ of blank value.
or (B) and heating. After cooling, standard solutions (0–30 μg of each analyte) were added, and the solutions were diluted to 100 cm³. The analytical values were obtained for an average of four repetitive measurements of absorbance for the same sample solution. They were in good agreement with the certified values as shown in Table 3.

4. Accuracy in making a constant small volume and loss of solution at dissolution

When analyzing with a constant small volume the accuracy of the volume of volumetric glasswares is important, therefore, those of a pipet(5 cm³) and a micropipet(1 cm³) were examined by the JIS method of “General Rules for Chemical Analysis”(20). The results were satisfactory, that is, the accuracies obtained were within the allowable error of volumes which the JIS of “Volumetric Glassware”(21) provided. Next, each mg amount of ten replicating samples was dissolved with 5 cm³ or 1 cm³ of the mixture of acid at 363 K–60 min in a pressure bomb. The loss of the solutions during the dissolution was below the standard deviation (R: 0.0003 g) of repetitive weighing (n=10) of a PTFE container itself. The same result was obtained, even if the dissolution conditions were 403 K–30 min which temperature was over the boiling point of water at one torr. Consequently it was proved that a pressure bomb was superior in maintenance of the solution volume.

5. Effect of concentration of acid for dissolution

A slow reaction at the dissolution of samples is desirable in this method, in order to prevent the distillation of analytes. In addition, the concentration of acid for the dissolution is advisable to be more diluent mixture of acids than usual ones taking account of acid concentration for atomic absorption spectrometry. However, the distillation of analytes or the formation of insoluble substances might occur during a dissolution process with some kinds of acids or a certain concentration of acids. Accordingly, dissolution conditions were examined by dissolving samples with hydrochloric acid-nitric acid or hydrofluoric acid-nitric acid at 363 K–60 min in a pressure bomb. As for the analytes under investigation tin (JSS 168–3), antimony (ECRM 097–1) and arsenic (JSS 168–3) were selected, since they were apt to form hydrides and make hydrolysis. Figure 2 illustrates the effect of hydrochloric acid concentration in hydrochloric acid-nitric acid medium. When the concentration of hydrochloric acid varied from 0 to 1.2 kmol/m³ in 0.8 kmol/m³ of nitric acid, no effect on the absorbances of arsenic and antimony were observed, while the absorbance of tin decreased with the increase in a hydrochloric acid concentration. The same phenomenon was also observed with the synthetic solutions, and

| Sample   | Element (ppm) |
|----------|---------------|
|          | As  | Sn  | Co  | Ni  | Cr   | Sb   | Au³ |
| JSS 168–3 Certified value | 9₂  | 6₀  | —   | 12₀ | 11₀  | —   | 100 |
| JSS 168–3 This method      | 9₂  | 6₂  | —   | 11₂ | 10₂  | —   | —   |
| JSS 161–3 Certified value  | 10₀ | 12₀ | 20₀ | —   | —    | —   | 100 |
| JSS 161–3 This method      | 10₁ | 11₁ | 20₁ | —   | —    | —   | —   |
| ECRM 087–1 Certified value | 2₄₀ | 1₇₀ | 1₅₀ | —   | —    | 4₆  | 101 |
| ECRM 087–1 This method      | 2₃₄ | 1₆₇ | 1₅₃ | —   | —    | 4₅  | —   |
| ECRM 097–1 Certified value | 5₁  | 10  | 3₆  | 2₅  | 1₆   | 1₀  | 100 |
| ECRM 097–1 This method      | 5₂  | 6   | 3₂  | 2₄  | 1₅   | 1₀  | —   |
| NBS 361 Certified value    | 1₃₀ | 1₉₀ | 3₀₀ | —   | —    | —   | 4₁  |
| NBS 361 This method         | 1₃₁ | 9₈  | 3₇₀ | —   | —    | —   | 4₀  |

a) Internal standard (Addition of 10 μg of Au corresponds to 100 ppm in sample).
b) Average of 10 replicates (master solution).
therefore, it was estimated that a tin compound might evaporate at the early stage of the ashing or atomizing process. In this medium, nitric acid concentration showed on effect. Figure 3 illustrates the effect of hydrofluoric acid concentration in a hydrofluoric acid-nitric acid medium. When the concentration of hydrofluoric acid varied from 0 to 1.5 kmol/m$^3$ in 0.8 kmol/m$^3$ of nitric acid, no effect on the absorbances of tin and antimony were observed, while the absorbance of arsenic was largely affected by the presence of hydrofluoric acid. As for synthetic solutions, the absorbance of arsenic was not influenced by the presence of hydrofluoric acid. Even if samples were dissolved below 293 K using a ultrasonic cleaner, lower absorbances were obtained. Accordingly, each 1 g of JSS 171–3 (As: 0.045%) and JSS 169–3 (As: 0.005%) was dissolved with 1.5 kmol/m$^3$ of hydrofluoric acid and 0.8 kmol/m$^3$ of nitric acid with an argon flow, and the exhausted argon was introduced into a quartz cell for hydride generation-atomic absorption spectrometry for measuring the absorbance of arsenic. Consequently, arsenic was detected, resulting in confirmation of generating arsine. Figure 4 presents the effect of the concentration of nitric acid in the same acid medium. Tin and antimony were not affected by 0–3.2 kmol/m$^3$ of nitric acid, while as for arsenic, lower absorbances were obtained in the presence of nitric acid in hydrofluoric acid medium. It was impossible to prevent evaporation of gaseous compounds such as arsine even when using a pressure bomb. The optimum mixture of acids for the dissolution to determine arsenic and antimony was the mixture of hydrochloric acid-nitric acid (A-2) which consisted of 1 kmol/m$^3$ of hydrochloric acid and 0.4 kmol/m$^3$ of nitric acid, and that for the determination of tin and antimony was the mixture of hydrofluoric acid-nitric acid (B-2) which consisted of 1 kmol/m$^3$ of hydrofluoric acid and 0.8 kmol/
IV. Analysis Using mg Amount of Sample Taken

1. Analytical procedure

Weigh 5 mg (±0.5 mg) of a chip of samples by an electric micro-balance and put it into a PTFE container (23 cm³) of a pressure bomb, which has been weighed beforehand. Precisely add 5 cm³ of the mixture of acids (A-2) or (B-2) using a pipette. Weigh the PTFE container again and calculate the amount of injection of the mixture of acids. Put it into a pressure bomb and heat at 363 K for 60 min in a ventilated thermostat drying oven. After cooling, take out the PTFE container from the pressure bomb, weigh it for monitoring the amount of loss of the solution. When weighing 1 mg (±0.1 mg) or 0.5 mg (±0.1 mg) of a chip of samples, add 1 cm³ or 0.5 cm³ of an acid mixture (A-2) or (B-2) into a PTFE container (5 cm³) using a micropipette, respectively, and perform the same procedures as those above-mentioned. Shake the PTFE container in order to uniform the concentration of the solution and measure the absorbances of analytes.

2. Analytical result

A very small chip of the standard reference materials used at par. III. 3 was analyzed. Table 4 summarized the analytical values of JSS 168-3. Consequently there was little difference between those analytical values and those determined by the usual sample taken described at par. III. 3. JSS 161-3, ECRMs 087-1, 097-1, and NBS SRM 361 were also analyzed. Table 5 summarized the analytical results by 1 mg of a sample taken. They were in good agreement with those determined by generally prepared solutions (master solutions) described at par. III. 3. Furthermore, these results show that there was little segregation of the analytes in those standard reference materials, and therefore, only one mg of them was able to sufficiently serve as standard reference materials. In addition there was no difference in analytical values of nickel, cobalt, chromium and antimony between the dissolution with the mixture of hydrochloric acid (A-2) and that with the mixture of hydrofluoric acid (B-2). Even if the amount of the acid mixtures was changed among 5 cm³, 1 cm³ and 0.5 cm³, it had no effect on the determination of gold which was added as an internal standard.

Table 4 Determination of arsenic, tin, nickel and chromium in JSS 168-3 standard reference material.

| Sample treatment | Element | As | Sn | Ni | Cr | Au
|------------------|---------|----|----|----|----|-----|
|                  |         |    |    |    |    |     |
| Master solution  |         | 1.35 | 1.52 | 1.40 | 0.80 |
| (100 mg/100 cm³) | RSD (%) |     |     |     |     |     |
| Dissolution 1    | Ratio² | 1.01 | 1.02 | 1.01 | 1.00 |
| (5 mg/5 cm³)     | RSO (%) | 2.11 | 1.27 | 2.21 | 1.24 |
| Dissolution 2    | Ratio² | 0.99 | 1.01 | 1.00 | 1.00 |
| (1 mg/1 cm³)     | RSD (%) | 3.47 | 2.62 | 1.75 | 1.46 |
| Dissolution 3    | Ratio² | 1.01 | 1.05 | 1.01 | 1.02 |
| (0.5 mg/0.5 cm³) | RSD (%) | 4.96 | 2.87 | 2.83 | 1.97 |
| HCl (1M) + HNO₃ (0.4M) |         |      |     |     |     |     |
| Master solution  |         | 1.48 | 1.45 | 1.68 | 0.92 |
| (100 mg/100 cm³) | RSD (%) |     |     |     |     |     |
| Dissolution 1    | Ratio² | 1.02 | 1.01 | 0.99 | 1.00 |
| (5 mg/5 cm³)     | RSD (%) | 1.79 | 1.80 | 1.90 | 1.30 |
| Dissolution 2    | Ratio² | 1.01 | 1.00 | 0.99 | 1.01 |
| (1 mg/1 cm³)     | RSD (%) | 3.29 | 2.13 | 2.33 | 1.56 |
| HCl (1M) + HNO₃ (0.8M) |         |      |     |     |     |     |

a) Internal standard (Concentration of 0.1 g/cm³).
b) Mean of 10 determinations.
c) Ratio=mg soln. value/master soln. value.
The amounts of loss of solutions observed by weighing PTFE containers before and after the dissolution were below 0.003 g, so that it was negligible taking the quantities of sample solutions into consideration.

When analyzing major components, a larger quantity of an acid mixture is able to be used for the dissolution because of the higher concentration of analytes, so that making a constant volume would be more accurate.

V. Conclusion

A chip of samples of mg order was dissolved with small quantity of the mixture of acids in a pressure bomb and graphite furnace-atomic absorption spectrometry was applied to the determination. The pressure bomb was able to maintain the constant volume of sample solutions without the loss of solutions during the dissolution. However, when the mixture of hydrofluoric acid-nitric acid was used for the dissolution, arsenic in iron and steels formed arsine and even a pressure bomb could not prevent evaporation of a volatile compound, while when the mixture of hydrochloric acid-nitric acid was used, tin evaporated as stannic tetrachloride at an ashing stage, while when the mixture of hydrofluoric acid-nitric acid was used, it was possible to prevent its evaporation and good analytical values were obtained.

The detection limits (3σ) of the analytes for 1 mg of a sample taken were 0.7, 0.8, 0.3, 0.3, 0.2, 0.3 and 0.3 ppm for arsenic, tin, cobalt, nickel chromium, antimony and gold, respectively. The pyrolytically coated graphite furnace equipped with a platform made it possible to determine the analytes very sensitively and accurately, and in addition many repeated firing with one graphite furnace became possible.

The iron and steel standard reference materials used in this study are usually analyzed with a sample weighing over 100 mg, while by the proposed method it was possible to determine the analytes under investigation by using only ca. 1 mg of a chip of samples. It should be noted that to the analysis of the standard reference materials except those used in this study the proposed method can not be applied without investigation in a special concern with segregation of analytes.

Furthermore, the proposed method will be able to be applied to the analysis of new materials by examining the optimum condi-
tions concerning acids for the dissolution, their suitable concentrations and so forth, and it will be helpful for the material evaluation technique such as a macro-segregation.

REFERENCES
(1) S. Backman and R. W. Karlsson: Analyst, 104 (1979), 1017.
(2) E. Lundberg and W. Frech: Anal. Chim. Acta, 108 (1979), 75.
(3) W. Frech, E. Lundberg and M. Barboottl: Anal. Chim. Acta, 131 (1981), 45.
(4) K. Takada and K. Hirokawa: Spectrochim. Acta, part B, 39 (1984), 1113.
(5) J. Y. Marks, G. G. Welcher and R. J. Spellman: Appl. Spectrosc., 31 (1977), 9.
(6) J. B. Headridge and R. A. Nicholson: Analyst, 107 (1982), 1200.
(7) F. E. Munoz, A. Calvo and L. E. León: Analytical Letters, 16 (1983), 835.
(8) F. J. Langmyhr and S. Rasmussen: Anal. Chim. Acta, 72 (1974), 79.
(9) F. Shaw and J. M. Ottaway: Analyst, 100 (1975), 217.
(10) B. Welz, V. Voellkopf and Z. Grobenski: Anal. Chim. Acta, 136 (1982), 201.
(11) J. Yu and Z. Cui: Fenxi Huaxue, 11 (1983), 612.
(12) B. Bernas: Anal. Chem., 40 (1968), 1682.
(13) C. Iida, T. Uchida and I. Kojima: Anal. Chem., 113 (1980), 486.
(14) R. Nakajima, E. Kamata, K. Goto and S. Shibata: Bunseki Kagu, 32 (1983), T93.
(15) T. Kobayashi, O. Kujirai, F. Hirose and H. Okochi: J. Japan Inst. Metals, 48 (1984), 542.
(16) JIS G 1257-1975.
(17) B. V. L’vov: Spectrochim. Acta, part B, 33 (1978), 153.
(18) W. Slavin and D. C. Manning: Anal. Chem., 51 (1979), 261.
(19) T. Kobayashi, O. Kujirai, F. Hirose and H. Okochi: J. Japan Inst. Metals, 47 (1983), 676.
(20) JIS K 0050-1983.
(21) JIS R 3505-1983.