On-line ion-exchange matrix separation and inductively coupled plasma mass spectrometric determination of trace impurities in high-purity aluminium

A.-G. Coedo, M. T. Dorado and I. Padilla

Centro Nacional de Investigaciones Metalúrgicas, Avda Gregorio del Amo, 8, 28040 Madrid, Spain

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The feasibility of using an anion-exchange resin for on-line separation of trace amounts of Fe, Cu, Mn, Mg, Cr, Ni, Zn, Co, Pb, and Cd from pure aluminium was investigated. A test portion of 50 mg of aluminium drillings was dissolved with 6 ml of a buffer solution, 2.64% m/v NaOH–0.91% m/v KCl (pH = 13.4 ± 0.1). An aliquot of 500 μ l of the solution obtained was passed through a micro-column, included in a flow injection (FI) manifold, packed with a 2 + 1 mixture of Metalfix Chelamine and Hyphan Cellulose (the micro-column volume was about 150 μ l). The retained trace elements were eluted in the back-direction with 200 μ l of a 3 + 1 mixture of 1 mol l⁻¹ HCl–1 mol l⁻¹ HNO₃ and then determined using flow injection inductively coupled plasma mass spectrometry. The operating parameters and operational scheme of the manifold of the FI on-line ion-exchange assembly are given. The accuracy of the proposed method was tested by analysing a pure aluminium standard sample (Aluminium Pechiney, CODE 566). Recoveries from 50 mg test portions of a high-purity aluminium (99.999%) spiked with 2.5 and 25 ng each of the studied analytes were close to 100%, and the relative standard deviations ranged from 1 to 3%. Determination limits (10s) were in the ng g⁻¹ range.

1 Introduction

Aluminium has recently gained prominence due to its classification as a low activation material. Aluminium compounds are important materials for various purposes in the production of electronic components as well as for their use as advanced reactor materials. The permissible concentrations of trace elements in high-purity aluminium used for these purposes generally range between 0.1 and 1 μ g g⁻¹. Since the presence of trace elements in high-purity aluminium may significantly affect some special properties of the products, production of high quality aluminium base materials is required and quality control should receive maximum attention, employing the most advanced available methodology and instrumentation. The determination of microgram amounts of various elements in high-purity aluminium poses problems which are not easily solved by conventional analytical techniques. Raouf and Popova¹ presented a review of the available methods for the determination of impurities in high-purity aluminium and aluminium oxide by flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS). Ishizuka *et al.*² applied inductively coupled plasma atomic emission spectrometry (ICP-AES) to determine Ca, Cu, Mg, Mn, Na and Si in high-purity alumina. Saleem *et al.*³ studied the matrix effects on the determination of trace elements in aluminium, using ICP-AES. A round-robin analysis of a high-purity (99.99%) aluminium sample using glow discharge mass spectrometry (GD-MS) has been presented by Venzago *et al.*⁴ Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for trace and ultratrace element determination⁵ and it is widely used for the determination of impurities in materials of high-purity grade. Nakane *et al.*⁶ determined trace impurities in high-purity aluminium oxide by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), using the standard additions method for quantitative analysis. To separate analytes from the aluminium matrix and therefore to eliminate the matrix effect, many different techniques have been applied.

Ammonium pyrrolidinedithiocarbamate (APDC) has been widely used as a complexing agent. Elci and Dogan⁷ absorbed the chelates in activated carbon and after mixing the carbon with spectral graphite the mixture was analysed by optical emission spectrometry. Berndt and Messerschmit⁸ used FAAS after membrane filtration of the APDC complexes. The same complexing agent was used by Coedo *et al.*⁹ to determine trace elements in high-purity aluminium by AAS after extraction with IBMK. Berndt and Schaldach¹⁰ applied the same system to the on-line preconcentration–matrix separation of trace elements in aluminium solution, using high-performance ETAAS. However, one of the most satisfactory approaches that can be applied, without decreasing the maximum analyte signal intensities, is the use of ion-exchange separation techniques. Burba and Willmer¹¹ described the multi-element separation from high-purity aluminium by means of a chelating ion exchanger; the aluminium solution (pH 13.3–13.5) was treated with Cellulose Hyphan and, after filtering and drying the solid phase at 90 °C, the adsorbed trace elements were extracted into 2 M HCl and determined by FAAS. An interesting alternative is the retention of the analyte elements on resin columns, while interfering matrix ions are not retained. For this purpose flow injection (FI) systems provide a successful approach to on-line sample preconcentration–matrix removal using ion-exchange separation procedures with multi-element detection techniques. A wide variety of papers describing the incorporation of micro-columns into an FI system have been published. Ebdon *et al.*¹² applied this procedure to determine some metals in biological samples. Coedo *et al.*¹³ used the system to determine Nb, Ta, W, Zr and Hf in high-purity iron. Benkhedda *et al.*¹⁴ described the trace metal analysis of natural waters and biological samples with FI on-line adsorption preconcentration using a knotted reactor. In the present work the simultaneous determination of Fe, Cu, Mn, Mg, Cr, Ni, Zn, Co, Pb and Cd in high-purity aluminium by FI-ICP-MS is presented. The FI system incorporates an ion-exchange micro-column packed with a 2 + 1 mixture of Metalfix Chelamine and Cellulose Hyphan. The effects of

solution pH, the eluting acid concentration, the micro-column dimensions, the volume loops, and the sampling and elution flow rates are considered. The method was verified using a pure aluminium reference material from Pechiney and recoveries of the tested elements were calculated at two concentration levels from spiked aluminium samples.

2 Experimental

2.1 Instrumentation

A PerkinElmer SCIEX Elan 6000 ICP-MS (PerkinElmer SCIEX Instruments, Concord, Ontario, Canada) equipped with a glass cyclonic spray chamber, a concentric glass nebuliser, and platinum cones, in conjunction with an FIAS 200 (PerkinElmer) was used. The FI system was connected to the Elan nebuliser and the measurement step was fully computer-controlled by the ICP-MS software. The ICP-MS operating conditions, the FI programme, and the operating parameters used to perform the FI measurements are presented in Table 1. A flow diagram of the manifold is shown in Fig. 1.

2.2 Ion-exchange resin and columns

A mixture of Metalfix Chelamine (tetraethylenepentamine polymer bound, particle size 40–80 μm , Sigma–Aldrich) and Cellulose Hyphan (H^+ form, microcrystalline, Sigma–Aldrich), in a 2 + 1 proportion, was loaded into two types of column: vertical mini-columns with an internal diameter of 15 mm (containing a volume of resin of about 2.0 ml), and horizontal micro-columns of internal diameter 2.5 mm and length 30 mm (containing a volume of resin of about 150 μl). The resin bed was held in position by PTFE membranes. The columns were cleaned with 5 mol l^{-1} HNO_3 and equilibrated with alkaline buffer solution ($\text{pH} = 13.4 \pm 0.1$).

2.3 Reagents and standards

All chemicals used were from Sigma–Aldrich: 32% m/v hydrochloric acid, 70% m/v nitric acid (both doubly distilled),

Fig. 1 Flow injection manifold steps and solution paths. Sample (S); eluent (E); carrier (C); HNO_3 (A); buffer (B); waste (W).

sodium hydroxide (99.998%), potassium chloride (99.999%) and pure aluminium foil (99.999%). De-ionised water of 18 $\text{M}\Omega\text{ cm}^{-1}$, obtained from an Elga Maxima ultrapure water system, was used throughout. A multi-element standard solution (Multielement Verification Standard II, PerkinElmer) containing 10 $\mu\text{g ml}^{-1}$ of each of the considered analytes was used to prepare the multi-element standard calibration solutions. A pure aluminium standard sample from Aluminium Pechiney Research Centre (France), CODE 566, was used to verify the method. A 0.5% v/v HNO_3 solution was used as the carrier in FI experiments.

2.4 Sample treatment and calibration solutions

A 0.0500 g amount of fine drilling sample was digested in a PTFE vessel using 6.0 ml of a $\text{pH} = 13.4 \pm 0.1$ buffer solution (2.64% m/v NaOH + 0.91% m/v KCl), heating gently until complete dissolution. After cooling, the volume was completed to 10 ml with the alkaline buffer solution ($\text{pH} 13.4$). This solution containing 5 mg ml^{-1} of sample was used for resin treatment and ICP-MS measurements.

External calibration was used to perform the on-line ICP-MS measurements. Solutions containing Fe, Cu, Mn, Mg, Cr,

Table 1 Operating conditions for the Elan 6000, working parameters used to perform the FI analysis, and FIAS manifold control programme

Elan 6000 parameters—							
Rf power/W	1000	Dwell time per amu/ms	150				
Plasma Ar flow/l min ⁻¹	15	Sweeps per reading	1				
Nebuliser Ar flow/l min ⁻¹	0.85	Readings per replicate	50				
Lens voltage/V	7.8	Number of replicates	3				
Analog stage voltage	−1900	Est. replicate time/s	62				
Pulse stage voltage	1350	Scanning mode	Peak hopping				
Running pressure/Pa	3.68 × 10 ^{−5}	Data treatment	Peak height				
Isotopes measured	⁵⁷ Fe, ⁶³ Cu, ⁵⁵ Mn, ²⁴ Mg, ⁵² Cr, ⁶⁰ Ni, ⁶⁶ Zn, ⁵⁹ Co, ²⁰⁸ Pb, ¹¹¹ Cd						
FI working conditions—							
Micro-column	2.5 mm id and 30 mm length (1 ~ 50 µl)						
Sample solution	0.050 g in 6 ml buffer: 0.66 mol l ^{−1} NaOH + 0.12 mol l ^{−1} HNO ₃ (pH = 13.4)						
Eluent	3 + 1 mixture of 1 mol l ^{−1} HCl–1 mol l ^{−1} HNO ₃						
Washing solutions	Water and buffer solution (pH = 13.4)						
Carrier	0.5% v/v HNO ₃						
Loop volumes	500 µl (sample), 200 µl (eluent)						
Flow rates	Loading loops (filling step): 2 ml min ^{−1} ; ion exchange and measurement steps: 0.9 ml min ^{−1}						
FIAS manifold control program—							
Step	Time/s	Pump P ₁ /rev min ^{−1}	Pump P ₂ /rev min ^{−1}	Valve position			Function
				a	b	c	
1	25	40	40	1	1	1	Fill loops and resin conditioning
2	20	0	40	2	1	1	Ion-exchange process
3	25	0	40	2	2	2	Elution and
	40	0	80	2	2	2	measurement

Ni, Zn, Co, Pb and Cd in the range 2.5–250 ng each in 10 ml of alkaline buffer solution, pH = 13.4 (without aluminium matrix matching), were submitted to the ion-exchange process, in the same way as the test samples. By using these calibration solutions aluminium samples containing the analytes in the range from 50 ng g⁻¹ to 5 µg g⁻¹ can be analysed from test sample portions of 50 mg in 10 ml.

It is recommended that the analysis be performed as soon as possible after the samples and calibration solutions have been prepared.

3 Results and discussion

3.1 Optimisation of the ion-exchange procedure

Preliminary experiments of ion-exchange separation testing different ion-exchange media, were carried out by the vertical mini-column method. The retention of the impurities normally present in pure aluminium was studied on Chelex 100, Metalfix Chelamine, Cellulose Hyphan, Dowex 50W-X8, and C₁₈ (retaining the elements as APDC complexes). All these preliminary experiments were carried out using 0.050 g portions of pure aluminium foil, spiked with 50 ng of each of the analytes (added from the multi-element standard solution), and using mini-columns with an internal diameter of 15 mm (containing a volume of resin of about 2.0 ml). The best retention capability (>95%) for the majority of the foreseen analytes was obtained with Cellulose Hyphan in a pH = 13.4 ± 0.1 medium. This medium was also found to be the best when using Chelex 100, Dowex 50W-X8 and Metalfix Chelamine, but these three ion exchangers provided lower retention factors for some elements. The calculated recovery factors (RFs) are shown in Table 2. The retention of the APDC complexes on C₁₈ was also found to be lower than 90% for the majority of the tested analytes.

As the Cellulose Hyphan was in a microcrystalline form, it was very difficult to circulate solutions through columns packed only with this material, even when using a peristaltic pump to try to favour the flow circulation. To solve this problem, mixtures containing different proportions of Cellulose Hyphan and one of the other cation-exchange resins (Chelex 100, Dowex 50W-X8 and Metalfix Chelamine) were tested. The best results were provided by a 2 + 1 mixture of Metalfix Chelamine and Cellulose Hyphan: recoveries close to 100% were obtained for Fe, Mn, Mg, Cr, Ni, Zn, Co, Pb and Cd; for Cu the recovery was 95 ± 2%. Sample treatment was carried out using different reagents in order to find a final pH value of 13.4 ± 0.1. For this purpose samples were dissolved either by using HCl and raising the pH value with different alkaline solutions (NaOH solutions or buffer NaOH-based

mixtures) or by direct dissolution in an alkaline medium. The easiest way to obtain directly an adequate pH medium was to dissolve the sample using a 2.64% m/v NaOH + 0.91% m/v KCl buffer solution (pH = 13.4 ± 0.1) as attacking reagent.

Experiments to evaluate the effectiveness of different reagents in eluting all the analytes were performed. The following eluents were investigated: 0.1–8 mol l⁻¹ nitric acid, 0.1–6 mol l⁻¹ hydrochloric acid, mixtures of nitric and hydrochloric acid with different concentrations, and the same eluents containing 0.1 mol l⁻¹ hydrogen peroxide. A 3 + 1 mixture of 1 mol l⁻¹ HCl and 1 mol l⁻¹ HNO₃ was found to be the best eluent. The elution recoveries were close to 100% for all the considered analytes, with the exception of Cu for which the elution was about 92%.

The optimised procedure consisted in dissolving the test sample with 6.0 ml of alkaline buffer solution of pH = 13.4 ± 0.1 (2.64% m/v NaOH + 0.91% m/v KCl), and, after circulating the solution through a mini-column loaded with a 2 + 1 mixture of Metalfix Chelamine and Cellulose Hyphan, the adsorbed elements were eluted with 2 ml of a 3 + 1 mixture of 1 mol l⁻¹ HCl and 1 mol l⁻¹ HNO₃. The eluate was diluted to 10 ml with water to perform the ICP-MS measurements using continuous nebulisation.

As high-purity blanks are necessary for ultratrace determinations, the alkaline buffer solution (pH = 13.4) used to dissolve the samples was purified by passing it through a 2 + 1 Metalfix Chelamine–Cellulose Hyphan column. The effectiveness of this purification system was evaluated by using the purified solutions as test solutions. After being submitted to the entire load–elution process and performing the ICP-MS measurements it was found that all the analytes provided values lower than the corresponding detection limits.

3.2 Optimisation of the flow injection parameters

After operating the method by using vertical mini-columns the procedure was transferred to the FI system. Sample load and elution flow rates, sample and eluent volumes and micro-column dimensions were considered to be important factors in the design of the on-line ion-exchange FI manifold.¹⁵ Micro-columns with different dimensions, from 2 to 4 mm id and from 10 to 50 mm in length, were tested. They were all packed with a 2 + 1 mixture of Metalfix Chelamine and Cellulose Hyphan (volumes between 30 and 600 µl), loaded with sample volumes ranging from 100 to 500 µl of a 10 ng ml⁻¹ multi-element standard solution in a pH = 13.4 ± 0.1 buffer medium, and eluted with volumes of the eluent ranging also between 100 and 500 µl of a 3 + 1 mixture of 1 mol l⁻¹ HCl and 1 mol l⁻¹ HNO₃. Concerning the sample and eluent flow rates it was proved that at low sample flow rate a large breakthrough capacity can be obtained for all the analytes, whereas the acid flow rate for elution does not significantly affect the elution process, influencing only the response times. The relative signals were estimated against direct similar injection volumes of solutions in the same acidic medium. A careful evaluation of these parameters led to the conclusion that the best recoveries together with well-shaped elution peaks were obtained from a 150 µl micro-column (2.5 mm id, and 30 mm length) loaded with 500 µl of the pH = 13.4 ± 0.1 buffered sample solution (at a flow rate of 0.9 ml min⁻¹) and eluted with 200 µl of a 3 + 1 mixture of 1 mol l⁻¹ HCl and 1 mol l⁻¹ HNO₃ (at a flow rate of 2.0 ml min⁻¹).

Fig. 2 shows the transient peak signals corresponding to a 5 ng ml⁻¹ multi-element standard solution after applying the complete developed process. As the computer program only presents six peaks at the same time, signals from ⁵⁵Mn, ⁵⁹Co, ⁵²Cr, ⁶³Cu, ¹¹¹Cd and ⁶⁰Ni were chosen; the remainder of the elements presented similar peak shapes.

Table 2 Recovery factors (RFs) for the tested resins in a pH = 13.4 ± 0.1 medium

Element	RF ^a			
	Chelex-100	Dowex 50W-X8	Metalfix Chelamine	Cellulose Hyphan
Fe	82	90	95	98
Mn	61	92	63	100
Mg	90	95	100	99
Cr	75	89	72	99
Ni	80	91	100	98
Zn	94	83	82	100
Co	73	100	40	98
Pb	90	85	73	99
Cd	75	100	90	100
Cu	62	93	89	95
Al	10	<1	15	<1

^aPercentage ratio between the eluted and the loaded mass.

Fig. 2 Peak shape of the transient signals of a 5 ng ml⁻¹ multi-element solution eluted from the micro-column.

3.3 On-line flow injection manifold

The operational principle of the manifold, including the sample filling, the ion-exchange and elution process step and the injection step, is illustrated in Fig. 1. The on-line operation procedure was performed in three fundamental steps: filling loops and resin conditioning (step 1), ion-exchange process (step 2), elution and measurement (step 3).

During step 1 (programmed for 25 s), pump 1 (P₁) pumps sample (S) and eluent (E) at a flow rate of 2.0 ml min⁻¹ (40 rpm and 1.14 mm id tubing). The sample solution enters valve V₁ to fill loop L₁, and the eluent enters valve V₂ filling loop L₂. Both excesses are discharged as waste (W). Simultaneously, pump 2 (P₂) pumps carrier C (0.5% m/v HNO₃) at a flow rate of 2.0 ml min⁻¹ (40 rpm and 1.14 mm id tubing) and washing and conditioning resin solutions A and B (A: 5 mol l⁻¹ HNO₃; B: alkaline buffer pH = 13.4 ± 0.1) at a flow rate of 0.9 ml min⁻¹ (40 rpm and 0.76 id tubing). The carrier (C) is directly transported to the ICP torch (ICP) through valves V₂ and V₃. The washing and conditioning resin solutions (A and B), encountering a dual injection rotary valve (k), enter V₁ and V₃ (first solution A for 10 s, and then solution B for 15 s) cleaning and equilibrating the resin of the micro-column (R), and the excess of both is discharged as waste.

In step 2, programmed for 20 s, pump 1 (P₁) is stopped and pump 2 (P₂) propels the alkaline buffer solution (B) to push the sample plug out of the loop L₁ into the micro-column, resulting in the adsorption of the analytes. The carrier stream continues as in step 1. After a pre-established time, allowing the sample solution to pass through the column and to wash the resin with solution B, the system is switched to the elution and measurement step.

In step 3, programmed for a total time of 65 s, during the first 25 s the carrier stream (C) pushes the eluent plug out of the loop L₂ into the micro-column counter-currently at a flow rate of 2.0 ml min⁻¹ (40 rpm), causing the release of analytes trapped mostly in the initial portion of the resin, then the flow rate is increased to 3.0 ml min⁻¹ for 40 s to remove completely the eluted analytes. In each complete cycle the micro-column, before loading with the aluminium sample, is washed with 5 mol l⁻¹ HNO₃ and equilibrated with alkaline buffer solution (pH = 13.4). Under such conditions the stability of the micro-column was evaluated; it was observed that after 30 separation cycles the sorption and desorption operations still performed satisfactorily.

The developed method was applied to the analysis of a high-purity aluminium standard sample (CODE 566) from Pechiney (France). Complementary recovery tests to evaluate the accuracy of the method at the sub-μg g⁻¹ level of impurities were performed. These tests were carried out using high-purity aluminium (99.999%). Two test portions of 0.0500 g were dissolved according to the sample treatment procedure; the obtained solutions were circulated directly (without any dilution) through a 2 + 1 Metalfix Chelamine–Cellulose Hyphan resin mini-column to be cleansed of possible analyte impurities. After this cleansing process they were spiked with 2.5 and 25 ng of each of the considered analytes and diluted to 10 ml with the alkaline buffer solution, then they were subjected to the described on-line FI process. The analysis results are given in Table 3. As can be seen, the developed method is suitable for the determination of impurities in aluminium samples with contents as low as 50 ng g⁻¹. The lower limits of quantitative analysis, expressed as limits of quantification (LOQs), were estimated from multiple blanks (*n* = 6), submitted to the entire methodology, and then determining the concentrations equivalent to ten times the standard deviations of the analyte signals. The values obtained ranged between 10 and 30 ng g⁻¹ and the precision (RSD) at concentration levels of 10 times the LOQ was between 1 and 3%. A further improvement in the LOQs is possible by increasing the sample loop volume.

4 Conclusion

The above results show the good properties of the Metalfix Chelamine–Cellulose Hyphan ion-exchanger mixture for the separation of Fe, Cu, Mn, Mg, Cr, Ni, Zn, Co, Pb and Cd from an aluminium matrix. The dissolution of the sample with an alkaline buffer solution allows one to obtain directly the optimum pH for the ion-exchange process. With the present manifold design, the micro-column, inserted in the manifold path, is cleaned and preconditioned before loading with a new

Table 3 Certified values and found results for sample Aluminium Pechiney, CODE 566 (*n* = 4), and recoveries from standard additions (*n* = 3) to high-purity aluminium (99.999%)^a

Element	Sample CODE 566		Recovery	
	Certified/μg g ⁻¹	Found/μg g ⁻¹	Added: 50 ng g ⁻¹	Added: 0.5 μg g ⁻¹
Fe	7.5 ± 0.6	7.83 ± 0.22	52.3 ± 2.5	0.491 ± 0.015
Cu	2.20 ± 0.15	2.05 ± 0.10	46.8 ± 2.2	0.470 ± 0.012
Mn	0.07 ± 0.01	0.056 ± 0.002	50.9 ± 1.2	0.513 ± 0.017
Mg	3.5 ± 0.3	4.02 ± 0.05	52.0 ± 2.1	0.507 ± 0.009
Cr	0.07 ± 0.01	0.052 ± 0.003	49.2 ± 1.2	0.520 ± 0.013
Ni	0.08 ± 0.02	0.10 ± 0.05	50.3 ± 0.9	0.501 ± 0.010
Zn	0.70 ± 0.05	0.62 ± 0.06	51.7 ± 1.8	0.489 ± 0.015
Co	0.007 ± 0.001	<0.01	49.4 ± 0.7	0.500 ± 0.008
Pb	<4	<0.01	52.0 ± 2.5	0.497 ± 0.018
Cd	—	<0.01	49.2 ± 0.8	0.502 ± 0.010

^aAccording to the information provided by Pechiney's Research Centre the certified values are mean values obtained by more than one method wherever this is feasible, or based on the method which experience has shown to be the most reliable. The range established with a 95% level of confidence refers to the average of six sparking tests carried out on a standard sample.

aluminium sample. The rapid uptake of the above elements without aluminium retention, the almost instantaneous release of adsorbed analytes during the elution phase, and the stability of the resin mixture (a micro-column that had been used for more than 100 preconcentration cycles still performed satisfactorily), are ideal properties for its application in an on-line FI-ICP-MS system. Using a sample loop volume of 500 μl and 200 μl of eluent, analyte concentrations from 50 ng g^{-1} to 5 $\mu\text{g g}^{-1}$ can be determined from test sample portions of 0.0500 g in 10 ml. The obtained results indicated that the analytes were quantitatively retained on the resin, with the exception of Cu, for which the retention was $95 \pm 2\%$. Elution proved to be quantitative at the tested concentration levels. The application range of the method can be modified by an appropriate change of the sample and eluent loop volumes.

References

- 1 A. Raouf and S. Popova, *Anal. Lab.*, 1998, **7**, 59.
- 2 T. Ishizuka, Y. Uwamino and A. Tsuge, *Anal. Chim. Acta*, 1984, **161**, 285.
- 3 M. Saleem, K. Anwar and D. Mohammad, *Anal. Lett.*, 1996, **29**, 1871.
- 4 C. Venzago, L. Ohanessian-Pierrad, M. Kasik, U. Collisi and S. Baude, *J. Anal. At. Spectrom.*, 1998, **13**, 189.
- 5 K. E. Jarvis, A. L. Gray and R. S. Houk, *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie, London, 1992.
- 6 K. Nakane, Y. Uwamino, H. Morikawa, A. Tsuge and T. Ishizuka, *Anal. Chim. Acta*, 1998, **369**, 79.
- 7 L. Elci and M. Dogan, *Fresenius' Z. Anal. Chem.*, 1988, **330**, 610.
- 8 H. Berndt and J. Messerschmit, *Fresenius' Z. Anal. Chem.*, 1979, **299**, 28.
- 9 A. G. Coedo, M. T. Dorado and J. L. Jimenez Seco, *Metallurgia*, 1972, 343.
- 10 H. Berndt and G. Schaldach, *J. Anal. At. Spectrom.*, 1994, **9**, 39.
- 11 P. Burba and P. G. Willmer, *Fresenius' Z. Anal. Chem.*, 1985, **322**, 266.
- 12 L. Ebdon, A. S. Fisher and P. J. Worsfold, *J. Anal. At. Spectrom.*, 1994, **9**, 611.
- 13 A. G. Coedo, T. Dorado and F. Alguacil, *Anal. Chim. Acta*, 1995, **315**, 331.
- 14 K. Benkhedda, H. Goenaga Infante, E. Ivanova and F. C. Adams, *J. Anal. At. Spectrom.*, 2000, **15**, 1349.
- 15 Z. Fang and B. Welz, *J. Anal. At. Spectrom.*, 1989, **4**, 543.