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Talanta 69 (2006) 927–931
Talanta
www.elsevier.com/locate/talanta

An improved flow-injection system for spectrophotometric determination of molybdenum and tungsten in tool steels

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Received 11 November 2005; received in revised form 18 November 2005; accepted 18 November 2005
Available online 27 December 2005

Abstract

A flow-injection procedure for simultaneous spectrophotometric determination of tungsten and molybdenum in steel alloys is proposed. The method exploits the catalytic effects of Mo(VI) and W(VI) on the rate of iodide oxidation by hydrogen peroxide under acidic conditions. A novel strategy for ion-exchange separation of the potential interfering species is proposed, and an AG50W-X8 cationic resin mini-column is used. The sample is injected twice, originating two sequential plugs, citrate being added to one of them in order to suppress the W(VI) catalytic activity thus providing the kinetic discrimination.

The system handles 70 samples per hour and requires 1.6 mg KI per determination. A linear response is verified up to 10 mg l^{-1} Mo (or W) in the injectate, and signal additivity is 98–103%. Results are precise (R.S.D. < 0.04) and in agreement with ICP-OES. Running a standard reference material (IPT-50) assessed also accuracy.

Keywords: Flow analysis; Catalytic determination; Sample injection; In-line ion exchange; Spectrophotometry; Molybdenum; Tungsten

1. Introduction

For an efficient control of the steel making process, rapid analytical procedures are required. To this end, different techniques such as spark and X-ray fluorescence spectrometry [1], inductively coupled plasma optical emission spectrometry [2], atomic absorption spectrometry [3] and others, sometimes in connection with electrolytic dissolution [4–6], have been used. The related instrumentation is, however, high-priced, and skilled analysts are needed.

Molybdenum and tungsten are important refractory-forming elements in the production of tool and high-speed steels, and considered as expensive raw matter [7]. Consequently, fast analytical procedures yielding reliable and expedite results should be available for process quality control. Spectrophotometric methods involving reagents such as e.g. ammonium thiocyanate and dithiol [8,9] have been often used, especially in less equipped metallurgical industries. Separation steps are often needed [3,10], and this aspect may limit the applicability of these classical methods. Alternatively, catalytic methods can be used, and those involving iodide oxidation by hydrogen peroxide under acidic conditions followed by monitoring of the resulting tri-iodide complex should be highlighted [11,12].

With the advent of flow analysis, catalytic procedures experienced a boom [13], as precise timing is inherent to it. Regarding molybdenum determination, the above-mentioned method was firstly implemented to an air-segmented flow system [14]. Since then, the favorable characteristics of accuracy, sensitivity, selectivity and cost have been often reported in relation to the determination of molybdenum and/or tungsten in natural waters [15], rocks [16], steels [17,18], soil extracts [19], plant materials [20–22], etc.

Catalytic methods have also been proposed for simultaneous determinations, as the catalytic activity of W(VI) is selectively inhibited through addition of citrate, as emphasized by Alekseeva et al. [23] who reported the formation of the highly stable complex involving tungstate and citrate ions. Exploitation of this

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doi:10.1016/j.talanta.2005.11.042

feature allowed to the design of a flow-injection procedure for the determination of Mo(VI) plus W(VI) in rocks at the mg kg^{-1} level [16]. The sample was injected twice, and citrate was in-line added to only one of the two originated sample zones. However, optional addition of an extra confluent reagent stream led to a somewhat complex flow manifold including three sampling loops. This system cannot be readily applicable to steel alloys, as Mo(VI) and W(VI) are major constituents of the samples, and preliminary tests pointed out the occurrence of precipitation effects especially with regard to W(VI).

The aim of this work was then to develop a simple and rugged flow-injection system for spectrophotometric determination of tungsten and molybdenum in tool steels. An improved sample injection process involving the insertion of two sequential sample plugs, one of them spiked with the citrate reagent is proposed. A novel strategy for ion exchange in flow analysis is presented. Analogously to chromatography, the interfering ions are delayed; after passage of the analytes through the ion-exchange mini-column, the column is inserted into another flowing stream with a similar matrix; the interfering ions are then eluted towards waste. As separation and elution are accomplished in similar media, Schlieren effects are avoided.

2. Experimental

2.1. Samples, standards, reagents

All solutions were prepared with chemicals of reagent-grade quality and deionized water.

For sample preparation, a procedure similar to that already described [5] was followed. The steel alloys were washed with a 0.1% (v/v) HNO_3 solution, dried and drilled. About 0.1 g of the resulting fillings were accurately weighed and placed into 250 ml Erlenmeyer flasks. Thereafter, 10 ml of an acidic solution (3:1:1, v/v/v, water:concentrated sulfuric acid:phosphoric acid) were added, and the flasks were heated on a hot plate (250 °C) during 10 min. Next, 10 ml of 7.0 mol l^{-1} HNO_3 were added, and the temperature was maintained at 250 °C during 45 min. About 4.0 ml of a 10 mol l^{-1} H_2O_2 solution were then added, the flasks were cooled to room temperature, and the volume was made up to 100 ml with water. Before analyses the sample solutions underwent a 10-fold dilution with 1.5 mol l^{-1} HNO_3.

Molybdenum and tungsten stock solutions (1000 mg l^{-1} Mo or W) were prepared by dissolving 920.3 mg $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ or 897.0 mg Na_2WO_4 in water and the volume was filled up to 500 ml with water. Single-analyte working standards were daily prepared in 1.5 mol l^{-1} HNO_3 and covered the 0.00–10.00 mg l^{-1} Mo (or W) range. The Mo(VI) working standards were also 4.0 mg l^{-1} W, 120 mg l^{-1} Fe^{3+}, 5.0 mg l^{-1} V^{5+}, plus 5.0 mg l^{-1} Cr^{6+}, whereas the W(VI) ones presented a similar matrix, yet without leveling off the tungsten concentrations. A 1.5 mol l^{-1} HNO_3 solution acted as sample carrier stream and as eluent (Fig. 1C and E).

The reducing reagent (R_1, Fig. 1) was a 0.005 mol l^{-1} iodide solution prepared by dissolving 0.83 mg KI in 100 ml of water. The oxidizing reagent (R_2) was daily prepared by diluting 0.3 ml of 10 mol l^{-1} H_2O_2 in 100 ml of water. The R_3 reagent was a 3.8×10^{-3} mol l^{-1} citric acid solution, daily prepared by dissolving 8.0 g of the acid in 100 ml of water.

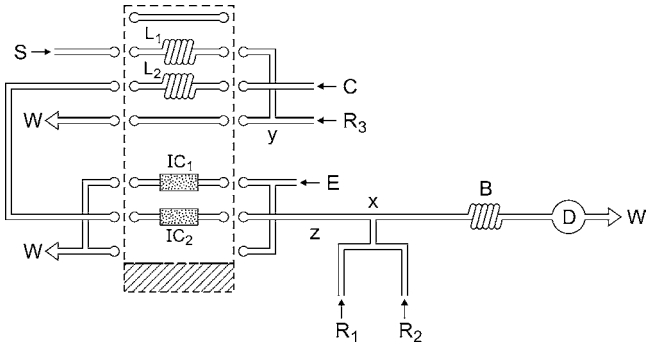

Fig. 1. Flow diagram. S: sample (2.4 ml min^{-1}); L_1 and L_2: sampling loops (5 and 40 cm, ca. 25 and 200 μl); C: carrier stream (1.5 mol l^{-1} HNO_3, 2.4 ml min^{-1}); R_1: reducing reagent (0.005 mol l^{-1} KI, 2.4 ml min^{-1}); R_2: oxidizing reagent (0.03 mol l^{-1} H_2O_2, 2.4 ml min^{-1}); R_3: discriminating reagent (3.8×10^{-3} mol l^{-1} citric acid, 0.3 ml min^{-1}); IC_1 and IC_2: ion-exchange mini-columns; E: eluent (1.5 mol l^{-1} HNO_3, 2.4 ml min^{-1}); B: coiled reactor (200 cm); x and y: confluence points; z: site where mini-column was placed for verifying interferent delays; D: detector (450 nm); W: waste.

The resin mini-column was made by packing a Tygon tube (i.d. = 3.0 mm, h = 1.0 cm) with an AG50W-X8 cationic exchanger (50–100 mesh, H^+ form, 1.7 meq ml^{-1} nominal capacity). Glass wool plugs were placed at the column ends in order to avoid resin losses during system operation.

2.2. The flow-injection system

A model USB 2000 UV–vis Ocean Optics spectrophotometer furnished with a Z-shaped flow cell (inner volume = ca. 10 μl, optical path = 10 mm), a model IPC 8R Ismatec peristaltic pump, a manually operated injector-commuter [24], and accessories were used. The manifold was build-up with polyethylene tubing (i.d. = 0.8 mm) of the non-collapsible wall type.

The flow system (Fig. 1) was designed with two sampling loops. Every switching of the injector-commuter intercalated a different sample plug into the sample carrier stream, and interchanged the resin mini-columns. R_3 reagent was added to the sample prior to L_2 sampling loop; therefore, composition of the established plugs were different from each other, depending on whether L_1 or L_2 loop was concerned.

When the injector-commuter rested in the position specified in Fig. 1, the sample was aspirated through L_1 loop (5 cm, ca. 25 μl), whereas L_2 loop (40 cm, ca. 200 μl) and IC_2 mini-column were inserted into the carrier stream, and IC_1 column was intercalated into the eluent stream. In this position, baseline was proportional to the extent of the non-catalyzed reaction.

After switching the injector-commuter, the established sample plug was pushed forwards by C carrier stream, flowing through IC_1 mini-column. Molybdate and tungstate anions did not interact with the cation-exchanger, whereas potential interfering species such as e.g. ferric ions were sorbed and slowly displaced along the mini-column by the action of H^+ ions from the flowing medium (HNO_3). These delayed species are further eluted in reversed flow towards waste. After leaving the

mini-column, the analytes merged with R_1 and R_2 reagents at the x confluence point and their catalytic influence on the indicator reaction manifested itself inside the following B coiled reactor. Details of the involved chemical reactions are given elsewhere [15]. Passage of the sample through the flow cell, led to a transient increase in the monitored absorbance (450 nm), proportional to the catalytic activity of both analytes. This transient signal was recorded as a peak proportional to the Mo(VI) plus W(VI) contents in the sample. At the sample time, sample plus citrate solutions filled the L_2 loop.

Next switching of the injector-commuter introduced the sample aliquot selected by L_2 loop into C carrier stream, and promoted another resin interchange. Potential interferents inside IC_1 mini-column then were eluted, and the established sample plug was handled similarly as above described. As R_3 reagent was added to the sample prior to the sampling loop (point y, Fig. 1), the recorded peak was proportional to the Mo(VI) content in the sample, and the W(VI) content was calculated by difference.

As sensitivity was not critical, and improved mixing conditions were aimed, equal flow rates (2.4 ml min^{-1}) were chosen for the sample carrier stream, R_1 and R_2 reagents. In order to avoid excessive sample dilution at y confluence (Fig. 1), a high sample/R_3 reagent flow rate ratio was fixed. Sample aspiration and R_3 flow rate were then set as 2.4 and 0.3 ml min^{-1}, respectively. As a compromise between mixing conditions and sampling rate, length of the B coiled reactor was fixed as 200 cm.

2.3. Optimization procedure

Initially, batch-wise experiments involving addition of Fe(III), Cr(VI), V(V) and Mo(VI) at different concentrations to the W(VI) standards were carried out in order to investigate the stability of the working standards. The main parameters involved in the system design were then investigated by injecting in triplicate either Mo(VI) or W(VI) standard solutions into the flow system in Fig. 1. Optimization was based on the one-parameter-at-a-time approach [25].

The present method usually involves reaction development at a pH value of 1.6 [14,15,20]. In view of the high acidity inherent to the sample preparation step, and considering that sensitivity was not critical, it was decided to develop the indicator reaction at higher acidity. Influence of HNO_3 concentration was then studied and, to this end, standard solutions and sample carrier stream prepared in 0.5–2.0 mol l^{-1} HNO_3 were used.

Concentrations of R_1–R_3 reagents were investigated within the 0.6×10^{-3} to 6.0×10^{-3} mol l^{-1} KI, 0.02–0.10 mol l^{-1} H_2O_2 and 1.0–5.0 $\times 10^{-3}$ mol l^{-1} citric acid ranges, respectively. In these experiments, the extent of development of the indicator reaction was considered both under catalyzed and non-catalyzed conditions. Possibility of occurrence of synergistic effects was also evaluated by running mixed W–Mo standard solutions.

For selectivity evaluation, the standard and blank solutions were prepared to contain also 0.0–10.0 mg l^{-1} V or Cr, or 50–300 mg l^{-1} Fe single-handedly or in combination. Concerning ion exchange, flow rate of the E solution was investigated within 1.6 and 3.9 ml min^{-1} for different mini-column lengths (1–3 cm).

After system design, the main figures of merit of the proposed procedure were evaluated. Running some samples already analyzed by ICP-OES [26] assessed accuracy. For getting an additional accuracy assessment, an IPT-50 tool steel reference material with certified contents of W, Mo, V, Cr, Co, Ni, Mn and C (6.40, 5.54, 2.00, 4.49, 0.26, 0.33, 0.28 and 0.916%, w/w) was used. Thereafter, the flow system was applied to large-scale analyses.

3. Results and discussion

3.1. Sample preparation

When hydrogen peroxide was not added during the sample preparation step, measurements were erratic (R.S.D. > 20%) and accuracy of the results was impaired. This can be explained in terms of the different oxidation states of the dissolved analytes. In fact, molybdenum and tungsten can be present at lower oxidation states even after complete sample dissolution, confirmed by the establishment of a clear solution. It was therefore necessary to add an oxidizing agent for quantitative conversion to Mo(VI) or W(VI). This aspect proved to be a limiting factor when <2 ml of 10 mol l^{-1} H_2O_2 aliquots were added during the step of sample preparation. For a 4 ml aliquot, results were precise and in agreement with certified values.

3.2. Preparation of the standard solutions

Although Na_2WO_4 is a primary standard, polymerization effects after dissolving it have been reported [27]. The phenomenon is not well understood, and is likely to occur in relation to W(VI) acidic solutions, where formation of the slightly soluble tungstic acid may lead to undesirable settlement effects. This drawback was noted during preparation of the standard solutions, and became more pronounced for higher W(VI) concentrations.

Preliminary experiments revealed that the stability of acidic W(VI) solutions increased in the presence of Cr(VI) and V(V), and decreased in the presence of high Fe(III) contents. This is a beneficial aspect in relation to tool steel analyses, as the samples present tungsten, vanadium, chromium, molybdenum and iron as their major constituents [7]. When sample dissolution is carried out under acidic conditions, the resulting solution is stable for at least 1 day, as confirmed in the present work. This is the reason why the working standards were prepared with similar matrix as the samples.

3.3. System dimensioning

Increasing the nitric acid concentrations from 0.5 to 2.0 mol l^{-1} decreased the analytical signal in about 50%, yet maintaining the signal-to-baseline ratio and improving selectivity. For 0.5 mol l^{-1} HNO_3, presence of V(V) and Cr(VI) at concentrations > 2 mg l^{-1} caused pronounced interfering effects

that were minimized by increasing the acidity of the reaction medium. For >1.5 mol l^{-1} HNO_3, interference effects were not observed up to 6 mg l^{-1} V(V) or Cr(VI); therefore, this concentration was selected. Under these conditions, variations in sample acidity inherent to the sample preparation step were minimized.

Increasing the KI or the H_2O_2 concentration led to an asymptotic increase in sensitivity, similarly as already reported [16]. These parameters were fixed as 0.005 mol l^{-1} KI and 0.03 mol l^{-1} H_2O_2. In this situation, no synergistic effects were noted, additivity was estimated as 96–102% and the analytical curves were linear ($r > 0.999$; $n = 6$).

Regarding R_3 reagent, quantitative inhibition of the W(VI) catalytic activity was attained only for >3.5×10^{-3} mol l^{-1} citric acid. This concentration, however, cannot be increased at will, in order to avoid an excessive inhibition of the Mo catalytic activity. It was selected as 3.8×10^{-3} mol l^{-1} citric acid. In this situation, the Mo analytical signal underwent an 80% decrease when citric acid was added. In order to compensate the differences in sensitivity due to addition of citric acid, thus obtaining analytical signals within similar ranges, lengths of sampling loops L_1 and L_2 were set as 5 and 40 cm, respectively. Addition of citric acid influenced also the indicator reaction development under non-catalyzed conditions, and a lessening in monitored absorbance was always noted after processing the blank solution (see also the inverted peaks in Fig. 2).

Interference Fe(III) was circumvented by exploiting cation exchange; ferric ions and other potential interfering cationic species were delayed when along the AG50W-X8 resin mini-column whereas Mo(VI) and W(VI) did not interact with it [20]. With the flow system in Fig. 1, of up to 300 mg l^{-1} Fe could be tolerated. This figure is much higher that the concentration expected in the injectate considering the iron contents in typical steels and the procedure for sample preparation. Regarding V(V) and Cr(VI), concentrations < 6 mg l^{-1} can be tolerated. Interference effects due to the presence of these species did not manifest themselves as these ions were present in the injectate at concentrations lower than that value.

Eluent flow rate was not a critical parameter in the system design and any value beyond 2 ml min^{-1} could be set. It was selected as 2.4 ml min^{-1}, the same value of the other stream flow rates. In this way, applicability of the proposed procedure is enhanced. It is important to recall that elution should be done in counter flow conditions. In order to verify the efficiency of interfering ions separation, an additional experiment involving replacement of both mini-columns by 5 cm loops and placement of a single mini-column at point z (Fig. 1) was carried out. After injecting a W(VI) standard solution, the typical analytical signal was recorded, followed by a broader and lower peak reflecting the delayed interfering ion that was slowly displaced through the mini-column.

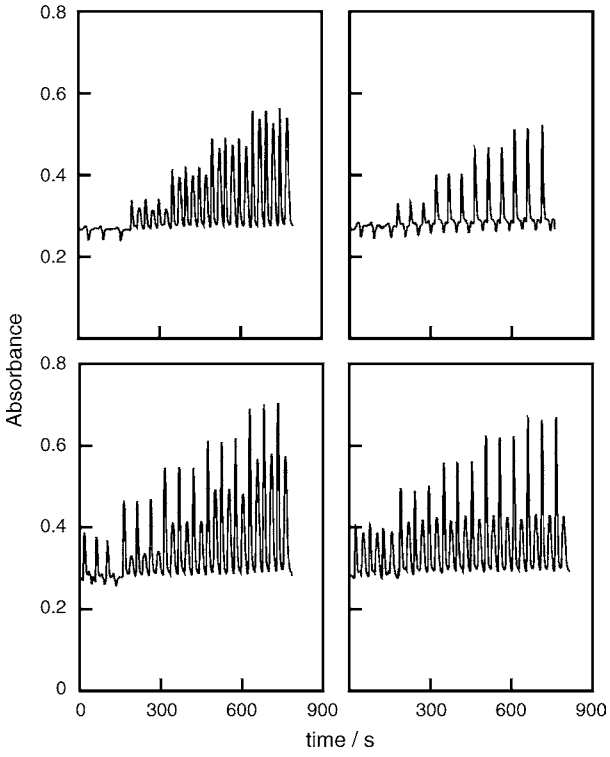

Fig. 2. Recorder tracings: 0.00–8.00 mg l^{-1} Mo (upper, left), 0.00–8.00 mg l^{-1} W (upper, right), 0.00–8.00 Mo plus 4.00 W (lower, left) and 0.00–8.00 W plus 4.00 Mo (lower, right) standard solutions injected in triplicate into the proposed flow system.

3.4. Application

The proposed system is rugged and stable, yielding precise results. After 10-fold running of typical samples, relative standard deviations of results were estimated as <0.7 and <5.0% for Mo(VI) and W(VI). The slightly worse precision relatively to W(VI) results is a consequence of error propagation effects, as subtraction of experimental data is involved.

Table 1
Comparative results of iron, vanadium and chromium in tool steel samples determined by ICP-OES [26]

Sample	ICP-OES					FIA	
	Fe	V	Cr	Mo	W	Mo	W
1	93.1 (1.7)	0.55 (5.5)	3.28 (1.8)	2.33 (2.1)	2.43 (1.2)	2.18 (0.3)	2.49 (4.4)
2	82.7 (0.5)	0.76 (1.3)	3.35 (0.6)	5.00 (1.4)	5.95 (0.6)	5.53 (*)	5.38 (1.1)
3	87.3 (0.4)	0.89 (1.1)	2.31 (0.9)	7.59 (0.2)	1.30 (0.6)	7.37 (0.4)	1.13 (0.5)
4	88.0 (0.9)	1.25 (0.8)	3.36 (0.6)	4.71 (0.2)	5.28 (0.4)	4.69 (0.6)	5.04 (1.6)
IPT-50	81.5 (0.4)	2.00 (1.2)	4.49 (1.1)	5.54 (0.5)	6.40 (0.5)	5.53 (*)	6.14 (0.6)

Molybdenum and tungsten determined by ICP-OES and by the proposed system (FIA). Data expressed in % (w/w) dry basis. Estimates of relative standard deviations (based on five replications, expressed in %) are specified in brackets. (*) Not observable.

Typical recorder tracings of diluted samples are shown in Fig. 2. Precise amounts of W and Mo were added to typical samples and the recovery values were calculated as 98–103. This is an additional assessment of the good additivity of analytical signals.

The system handles 70 samples per hour and requires only 1.6 mg KI and 96 μg of citric acid per determination. Baseline drift has not been observed during extended (4 h) system operation.

Regarding accuracy, analyses of Table 1 permits one to infer that there are no significant differences between methods at the 95% confidence level. Regarding the standard reference materials, deviations of 7.2 and 0.18% were found for tungsten and molybdenum, respectively.

4. Conclusions

The tool steels subjected to this investigation can be considered as complex samples to be analyzed [3]. The proposed flow system can be utilized for large-scale analyses of such samples without restrictions. It is a good alternative for quality control of the tool steel making process, especially in relation to the W(VI) determination.

The novel strategy for ion-exchange separation proved to be suitable, as Schlieren effects are avoided. Moreover, the interferent species are discarded without flowing through the detector.

Regarding the proposed procedure for sample injection, the feasibility of intercalating two different sample plugs into the main carrier stream was demonstrated, and precise results were obtained. The injection process can be also accomplished by using conventional six-way rotary valves.

Acknowledgements

Financial support from FAPESP, CAPES and CNPq is greatly appreciated.

References

[1] T.R. Dulski, Anal. Chem. 67 (1995) 21R.
[2] P.W.J.M. Boumans, Inductively Coupled Plasma Emission Spectroscopy, Part 2: Applications and Fundamentals, John Wiley & Sons Ltd., New York, 1987.
[3] American Society for Testing and Materials, Annual Book of ASTM Standards, ASTM, Philadelphia, United States, 1991.
[4] R.C. Chirnside, H.J. Cluley, P.M.C. Proffitt, Analyst 82 (1957) 18.
[5] A.P.G. Gervasio, G.C. Luca, A.A. Menegario, B.F. Reis, H.B. Filho, Anal. Chim. Acta 405 (2000) 213.
[6] D. Yuan, X. Wang, P. Yang, B. Huang, Anal. Chim. Acta 251 (1991) 187.
[7] S.A. Souza, Composição Quimica dos Aços, Edgard Bluecher, Sao Paulo, Brazil, 1989.
[8] H. Onishi, Photometric Determination of Trace of Metals, Part IIB: Individual Metals, Magnesium to Zirconium, fourth ed., John Wiley & Sons Ltd., New York, 1989.
[9] Z. Marczenko, Separation and Spectrophotometric Determination of Elements, Ellis Horwood Ltd., Chichester, England, 1986.
[10] M. Soylak, L. Elci, M. Dogan, Talanta 42 (1995) 1513.
[11] K.B. Yatsimirskii, L.P. Alfanasena, J. Anal. Chem. U.S.S.R. 11 (1956) 327.
[12] T.P. Hadjiioannou, Anal. Chim. Acta 35 (1960) 360.
[13] H. Ukeda, J. Flow Injection Anal. 22 (2005) 45.
[14] R. Fuge, Analyst 95 (1970) 171.
[15] Z.-L. Fang, S.-K. Xu, Anal. Chim. Acta 145 (1983) 143.
[16] R.-M. Liu, D.-J. Liu, A.-L. Sun, G.-H. Liu, Analyst 120 (1995) 565.
[17] J. Wang, R. He, Talanta 43 (1996) 391.
[18] Z.-L. Zhu, C.-Q. Han, Z.-C. Gu, R.-M. Chen, Analyst 119 (1994) 2251.
[19] M. Trojanowicz, A. Hulanicki, W. Matuszewski, M. Palys, A. Fuksiewicz, T. Hulanicka-Michalak, S. Raszewski, J. Szyller, W. Augustyniak, Anal. Chim. Acta 188 (1986) 165.
[20] L.C.R. Pessenda, A.O. Jacintho, E.A.G. Zagatto, Anal. Chim. Acta 214 (1988) 239.
[21] P.M.I. Reguera, M.A. Diaz, M.L.F. Córdova, L.F.C. Vallvey, Microchim. Acta 112 (1994) 225.
[22] E.N.V.M. Carrilho, F.J. Krug, E.A.G. Zagatto, Talanta 42 (1995) 2021.
[23] I.I. Alekseeva, L.P. Ruzinov, E.G. Khachaturyan, L.M. Chernyshova, J. Anal. Chem. U.S.S.R. 60 (1980) 43.
[24] F.J. Krug, H.B. Filho, E.A.G. Zagatto, Anal. Chim. Acta 179 (1986) 103.
[25] H. Martens, T. Naes, Multivariate Calibration, John Wiley & Sons Ltd., New York, 1989.
[26] A.O. Jacintho, B.R. Figueiredo, B.F. Reis, E.A.G. Zagatto, F.J. Krug, M.F. Gine, M.C.U. Araujo, N.M. Pereira, R.E. Bruns, Análise Química de Rochas por ICP-AES, Ed. Unicamp, Campinas, Brazil, 1985.
[27] D.C. Harris, Quantitative Chemical Analysis, W.H. Freeman, New York, 1987.