

Flow Injection Techniques for Determination of Molybdenum

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Abstract

Flow injection (FI) technique for the determination of molybdenum is reviewed. Highly sensitive automatic determinations with detection limits down to $0.01 \mu\text{g l}^{-1}$ levels can be performed by FI systems incorporated with ICP mass spectrometry (MS), absorption spectrophotometry using a catalytic reaction and adsorptive stripping voltammetry with a complexing agent. They are also possible by on-line preconcentration ICP atomic emission spectrometry and graphite furnace atomic absorption spectrometry (GF-AAS). Air-carrier FI systems are used for ICP-MS and GF-AAS. On-line standard addition, preconcentration, separation, etc. are used for various detection modes and different types of samples.

Keywords Molybdenum determination, flow injection, review

1. Introduction

Molybdenum compounds are industrially used as catalysts, corrosion inhibitors and additives to steels, alloys, lubricants, etc. Molybdenum is an environmental pollutant from the oil combustion process. For geochemists, it may be an important tracer for understanding igneous activities. In living organisms, it is an essential element which plays an important role as a cofactor in enzymes in humans and other species. For example, this element is related to the nitrogen metabolism of plants by bacteria and the biosynthesis of nucleic acids. On the other hand, the genotoxicity of molybdenum is suggested by the micronucleus assay in human lymphocytes [1]. A tolerable daily intake in humans is estimated as $9 \mu\text{g Mo kg}^{-1} \text{day}^{-1}$ [2], although data for molybdenum toxicity are limited. WHO suggested a guideline value of $0.07 \text{ mg Mo l}^{-1}$ in drinking water [3]. Therefore, sensitive, rapid and routine methods are required for the determination of molybdenum in various kinds of industrial, environmental, geological and biological samples.

The instrumentation and applications of flow injection (FI) analysis have been given in a recent book [4] published in 2000. However, in this book, only several papers published in and after 1985 were cited about the FI determination method for molybdenum. In the present work, the papers reviewed were selected from the on-line survey result of Chemical Abstracts (1985 - March 2002), except a few papers.

From the above-mentioned analytical requirement, the FI techniques reported with detection limit or determination limit and application data are mainly reviewed. These FI techniques were classified according to the detection mode; inductively coupled plasma mass spectrometry (ICP-MS), ICP atomic emission spectrometry (ICP-AES), ICP atomic fluorescence spectrometry (ICP-AFS), direct current plasma atomic emission spectrometry (DCP-AES), atomic absorption spectrometry (AAS) using flame burner (FL) and graphite furnace (GF), absorption spectrophotometry (ASP), chemi-

luminescence detection (CL) and electrochemical detection (EC). In the present review, the concentration range ($\mu\text{g l}^{-1}$) indicated is the linear range of calibration graph for determinable Mo. DL and SF indicate the detection limit (3σ , $\mu\text{g l}^{-1}$) for the sample solution injected and the sampling frequency (samples h^{-1}), respectively. Sample preparation is very important for the discussion of matrix effects; e.g., filtration eliminates solid matters in liquid samples, and acid decomposition, fusion and pH adjustment increase salt concentration (HF treatment decreases the concentration of Si). However, in this review, such discussion is not included because of a limited space.

2. ICP-MS, ICP-AES, ICP-AFS and DCP-AES methods

FI techniques used for ICP method, *i.e.*, ICP-MS, ICP-AES and ICP-AFS in this review, are generally used for multielement analysis. FI technique can be incorporated with the ICP method without any special interface, because this method is usually based on the suction-type sample introduction. Full automatic analysis can be performed by a commercially-available ICP-MS system with computer-controlled sampler and FI system [5]. Moreover, useful advantages of the FI technique are in the prevention of clogging of nebulizer and sampling cone and the minimization of spectroscopic interferences and matrix effects for sample solutions with high salt concentrations.

2.1. Standard addition method

To correct the matrix effects based on the generalized standard additions method, a three-channel FI system has been proposed for ICP-AES [6]. A single multielement standard solution was injected into a carrier stream and flowed through a coil producing a dispersed zone. After a pre-determined time interval, a part of the zone was sampled into another stream and mixed with a sample zone which was injected into the other stream. The injection of sample and the zone sampling were synchronized. Depending on the time interval, a different concentration of the standard can be produced in the FI system and therefore the preparation of standard solutions with different concentrations of analytes are not required. This method has been applied to rock standard samples. But

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no analytical result was reported for Mo.

2.2. Dilution method

The problems caused by the high salt concentration can be minimized by the dilution of sample. The FI technique automatically performs the dilution by the dispersion of a sample zone injected and by an extra stream of diluent. For wine samples, 72 elements including Mo (DL=0.4) have been determined by FI/ICP-MS [7]. Analytical data obtained were used to differentiate the region of origin of wines. In ICP-MS determination of Mo (DL=0.09) and other 6 elements in human urine samples, on-line 16.5-fold dilution and standard addition by a three-channel FI system have been employed for the minimization of matrix effects [8]. In this method, ^{103}Rh was chosen as the internal standard. However, the internal standard correction did not contribute to the improvement in the precision and recovery of Mo (^{95}Mo). The FI dilution is very convenient for routine analyses, but it accompanies by the degradation of sensitivity.

2.3. Preconcentration method

For sensitive determination and elimination of matrix matter, on-line preconcentration/separation has been used in FI/ICP method. An anion-exchange microcolumn packed with Dowex 1-X8 has been used for the matrix separation in the analysis of tantalum materials by ICP-MS using a three-channel FI system (DL=0.06) [9]. An Chelating ion-exchange microcolumn (Dionex MetPac CC-1) has been developed for 50-fold preconcentration and matrix separation in the analysis of sea water by ICP-MS using a four-channel FI system [10]. Using a three-channel FI system, an anion-exchange microcolumn with Amberlite IRA-93 has been used for the ICP-AFS determination of Mo and W (SF=10) [11]. A reported DL (8) of Mo was improved about 8 fold compared to the conventional nebulization without the column. However, this method has not been applied to any real sample. For the ICP-AES determination of Mo, dual ion-exchange columns with Dowex 1 have been used for 50-fold preconcentration of Mo in tap water and soil extract (SF=12) [12]. Inorganic adsorbents have been also used for the on-line preconcentration of Mo and other elements. In ICP-AES, a ZrO_2 microcolumn was prepared and used for 100-fold preconcentration of 18 elements in river water (DL=0.036 for Mo) [13]. In the ICP-AES determination of Mo, a microcolumn packed with commercially-available activated-alumina has been used for 20-fold preconcentration of Mo from a sea water sample by a two-channel FI system [14]. On-line liquid-liquid extraction was reported for ICP-AES determination of Mo and other 6 elements in waste water (SF=20) [15]. For sea water sample, the matrix of chlorides has been eliminated by the electrothermal vaporization of FI/ICP-MS (DL=1.4) [16].

2.4. Air flow and air-segmented flow method

The use of air flow and air-segmented aqueous flow has been studied for highly sensitive determination [17, 18]. Analytical performances for air and water carriers have been compared in FI/ICP-MS for 14 elements [17]. For Mo, a DL (0.18) obtained using air carrier was lower than that (0.31) using water carrier, although the background level was increased. This study indicated that air-segmented water

carrier was useful to prevent the memory effect. However, a comparison among water, air and air-segmented water carriers indicated that sensitivity and DL of Mo were degraded for air-segmented carrier, although they were improved or not degraded for other elements [18]. Sequential flows of sample and rinse solutions separated by air bubbles using an autosampler was introduced into a nebulizer of ICP-MS [19 – 21]. For Mo, a DL of $0.03 \mu\text{g l}^{-1}$ was obtained using off-line preconcentration and separation using chitosan-based chelating resin. However, this value was comparable to DL obtained using water carrier [19] and higher than that in pneumatic nebulization mode [20, 21]. This method has been applied to freshwater samples. Nevertheless, from the results in the above several studies, the use of the air-segmented water carrier or the air-sandwiched sample/rinse flow promises narrower peak signal and thereby higher SF.

2.5. Other methods

Other types of FI techniques have been proposed for ICP method. A FI system with a commercial membrane dryer tube has been used to minimize the amount of organic solvents introduced into ICP mass spectrometer [22]. The dryer tube consists of an inner membrane tube and an outer tube. The sample dissolved in organic solvent (diethyl ether) was injected into a nitric acid carrier and introduced into the inner tube. In the dryer tube, the organic solvent was dried by argon gas flowing through the outer tube. This method has been applied to the determination of Mo and other 7 elements in organometallic compounds. The FI technique incorporated with ICP-MS has been effectively used for on-line preconcentration and field-flow fractionation of various elements [23]. This method allowed the injection of maximum 50 ml of sample and gave a DL of $0.01 \mu\text{g l}^{-1}$ for Mo. The application result indicated that Mo was present as dissolved molybdate in a creek water. The FI technique incorporated with ICP-AES or ICP-MS has also been applied to other geological and environmental samples [24], concentrated mineral acids [25], steels [26, 27], oils [28] and human hair [29]. A FI/ICP-AES method for the determination of Mo and other 4 elements performed DL=42 for Mo dissolved in 4-methyl-2-pentanone (MIBK) and then injected into an acetic acid carrier [30]. This method has not been applied to real sample.

3. AAS method

In AAS, for sensitization of the determination and elimination of matrix effects, the FI technique has been used for on-line preconcentration (and separation) of Mo, as described below. Using a three-channel FI system, on-line complexation of Mo with 8-quinolinol and adsorption of the complex on C18 sorbent packed in a microcolumn has been used for the FL-AAS analysis of sea water [31]. Ammoniacal methanol was pumped into the microcolumn to elute the adsorbed Mo. The sensitivity was improved 100-fold and SF=30. Molybdenum ($10 \mu\text{g l}^{-1}$) in sea water samples has been determined with an error of $0.5 \mu\text{g l}^{-1}$. Using a four-channel FI system, automatic preconcentration for GF-AAS determination of Mo in sea water has been developed using a chelating ion-exchange microcolumn packed with Muromac A-1 [32]. Sample, eluent and washing solutions (50 – 200, 50 and 103 μl , respectively) were injected into an air-carrier stream through valve-type injectors. In the introduction of

the eluate into a graphite furnace, the capillary outlet of FI system was positioned at the furnace by the arm operation of autosampler. A DL of $0.06 \mu\text{g l}^{-1}$ is obtainable for $200 \mu\text{l}$ of sample injected. Using a five-channel system, on-line complexation of Mo with dithiocarbamate and adsorption of the complex on C18 sorbent packed in a microcolumn has been used for the GF-AAS analysis of sea and river water samples [33]. The highest concentrated portion ($40 \mu\text{l}$) eluted with ethanol was introduced into an air-carrier stream. A DL of $0.027 \mu\text{g l}^{-1}$ was performed for 1.35 ml of sample injected. Using a four-channel FI system, on-line coprecipitation of Mo with Fe(II)-pyrrolidinedithiocarbamate and its collection on the inner wall of a reactor (knitted PTFE tube) has been used for the preconcentration and GF-AAS determination of Mo (DL=0.04, SF=15) [34]. In this method, before analysis, Fe(II) and L-ascorbic acid solutions were added to a sample solution. Volumes of sample and eluent (MIBK) injected were controlled by their pumping times. The sample solution stream was mixed with an ammonium pyrrolidinedithiocarbamate (APDC) stream, the precipitate was formed in the reactor, and it was dissolved in the eluent. Finally the outlet of FI system was inserted into the GF-AAS atomizer and a $50\text{-}\mu\text{l}$ portion of eluate containing Mo was introduced into the atomizer by pumping APDC solution. The method has been applied to analyses of tap and sea water, human hair and high purity NaCl samples.

4. ASP method

ASP method promises good cost-performance compared to the methods described in the above sections. FI/ASP methods can be classified by two types, as described below.

4.1. Non-catalytic method

Several FI/ASP methods are based on the formation of color complex of Mo with organic reagents: thiocyanate used in the analysis of steels with on-line electrolytic dissolution of sample (four-channel FI system, SF=40) [35] and without it (four-channel FI system, SF=270) [36]; thiocyanate, Malachite Green and mixed surfactants in the analysis of well water near Mo-Fe ores, iron and steel (stopped flow system, $40 - 200 \mu\text{g l}^{-1}$, SF=24) [37]; thiocyanate and Rhodamine B in the analysis of plants (DL=20) [38]; carminic acid and cetyltrimethylammonium bromide (CTAB) in the analysis of steel and pharmaceutical samples (four-channel reverse FI system, DL=330) [39]; Pyrocatechol Violet and Crystal Violet in the analysis of steels ($20 - 500 \mu\text{g l}^{-1}$ in the presence of polyvinyl alcohol) [40]; 2,3,7-trihydroxy-9-(6'-hydroxyphenyl)-6-fluorone (Salicyl Fluorone I) and CTAB for the determination of Mo (SF=150) [41] and simultaneous determination (multi-standard additions method) of Mo ($50 - 350 \mu\text{g l}^{-1}$), Ti and W in steels (three-channel FI system) [42]. An indirect FI determination method using a three-channel FI system has been proposed [43]. This method is based on the reduction of Mo(VI) in a microcolumn reductor packed with copperized cadmium powder, the reduction of Fe(III) with the reduced Mo and the production of color complex of the resulting Fe(II) with Ferrozine. (DL= 1×10^2 , a maximum SF of 75 samples l^{-1}).

On-line liquid-liquid extraction of Mo with 8-quinolinol into CHCl_3 using a two-channel FI system has been applied to the determination of Mo in alloy steel and mild steel samples (DL=110, SF=20) [44]. In this case, 8-quinolinol was added

into the sample solution before analysis to avoid clogging at the connectors of FI system. A flow-cell packed with QAE-Sephadex A-25 anion-exchanger has been used for the collection and determination of Mo (two-channel FI system, DL=0.22 (22 ng) for maximum 100-ml sample, SF=3 or 4) [45]. In this method, Mo in a sample solution was collected in a off-line microcolumn packed with Sephadex G-25 gel. This column was combined with a FI system and the adsorbed Mo was eluted by an EDTA carrier pumped. The eluate zone with Mo-EDTA was mixed with a Tiron solution by the merging-zones technique. Molybdenum(VI)-Tiron complex formed was collected in the flow-cell. This method has been applied to the analysis of river water, sea water and rock samples.

4.2. Catalytic method

In principle, the catalytic method based on molybdenum-catalyzed indicator reaction has a power to increase analytical sensitivity dramatically, compared to the non-catalytic method. On the other hand, the catalytic method requires the control of kinetic factors, e.g., reaction time and temperature. FI technique can control such factors automatically and thereby low DL is respected. Several methods [46 - 53] are based on molybdenum-catalyzed oxidation of iodide with H_2O_2 and absorbance measurement of iodine (with or without starch) or triiodide formed. This reaction has been used for food, soil and human hair samples (DL=3.2 with starch) [46]. By the standard addition technique, some fruits have been analyzed (three-channel FI system, DL=6, SF=90) [47]. Leaves and soya flour have been also analyzed (five-channel FI system, DL=0.6, SF=100) [48]. In this case, the interference of Fe (as sulfosalicylate complex) can be corrected spectroscopically. Plant samples have been analyzed by a mono-segmented FI system with five-channel flow (DL=1, maximum SF=120) [49]. Interferences were eliminated by on-line solvent extraction with α -benzoin oxime and HCl-saturated CHCl_3 . A cation-exchange microcolumn packed with Dowex 50W-X8 has been used for on-line separation of interfering ions and applied to leaf samples ($1 - 40 \mu\text{g l}^{-1}$, SF=40) [50]. The simultaneous determination of Mo and W in mineral samples has been carried out by selective masking of W with citric acid (four-channel FI system, DL=4 with starch) [51]. A tolerable ratio of interfering Fe(III) to Mo was 150 as mole ratio (88 as mass ratio). Based on kinetic-dual standard additions method, a three-channel stopped flow FI system has been constructed for the simultaneous determination of Mo and W in steel samples [52]. In this method, interfering Fe was eliminated by off-line anion-exchange separation. Ion-chromatographic separation incorporated with FIA has been also studied for such simultaneous determination (SF=25) [53].

As other types of catalytic reactions, only two reactions have been used for FI/ASP [54, 55]. A highly sensitive method (DL=0.06, SF=20) for the analysis of fresh water has been developed using molybdenum-catalyzed oxidation of L-ascorbic acid with H_2O_2 and formation of yellow quinoxaline derivatives by coupling of the resulting dehydroascorbic acid with *o*-phenylenediamine in a five-channel FI system [54]. A tolerable ratio of interfering Fe(III) to Mo was 50 as mass ratio in the presence of CyDTA. Simultaneous determination method for Mo ($(0.5 - 15) \times 10^3 \mu\text{g l}^{-1}$) and Fe has been proposed on the base of molybdenum-catalyzed oxidation of

o-aminophenol with H₂O₂ and the measurement of differential reaction rate by stopped flow FI system [55].

5. CL method

CL method is very sensitive, but it requires rapid detection, because CL is instantaneous phenomenon. FI technique is suitable to detect such transient signal. However, for the FI determination of Mo, only two reports were found out. A DL of 0.02 µg l⁻¹ was performed by CL reaction of Mo(III) with lucigenin [56, 57]. Mo(VI) was reduced to Mo(III) using an on-line Jones reductor microcolumn prepared. Iron(III), V(V) and Cr(VI) seriously interfered with the determination. Therefore, their elimination by off-line separation with anion-exchange resin has been used to analyze fresh water and steel samples using a three-channel FI system [57].

6. EC method

FI systems have been incorporated with various types of electrochemical detection modes. Molybdenum can be determined (DL=30, SF=15) on the basis of the catalytic oxidation of iodide with H₂O₂ and on-line monitoring of iodide by the potential difference between two tubular ion-selective electrodes (Ag₂S/AgI solid membrane electrodes) in a three-channel FI system [58]. This method has not been applied to real samples. Using this catalytic reaction, more sensitive and rapid FI/EC method has been proposed (three-channel FI system, DL=1.8, SF=100) and applied to soil extracts [59]. This method is based on the amperometric monitoring of triiodide in a flow cell with two platinum wire electrodes.

A sensitive amperometric FI method has been studied using a wall jet flow cell with a glassy carbon electrode and a single-channel FI system [60]. A molybdenum solution buffered with phosphate was injected into a stream of a phosphate buffer. The electrode covered with the reduction product of molybdophosphate increased molybdenum signals. However, this method is susceptible to the pH of the injected solution and has the calibration graph with a narrow linear range.

A flow cell with a hanging mercury drop electrode has been designed for the adsorptive stripping voltammetry (AdSV) to determine Mo (three-channel FI system, 1–20 µg l⁻¹) and Ti in the presence of mandelic acid [61]. In an electrode compartment (about 2.5 ml), water carrier with 500 µl of sample injected was fed onto the mercury drop through a capillary nozzle. The compartment has a hole and through it contacts an outer overflow vessel with a reference electrode and an auxiliary electrode. Nitrogen gas passes over the solution in the vessel in order to prevent oxygen influences. The analytical performances were evaluated for a brine model solution. Another type of flow cell has been incorporated with a flow system for the AdSV determination of Mo [62]. The lowest DL (0.073) was performed by chloranilic acid among different complexing agents tested. This method has been successfully applied to the analysis of tap and sea water samples.

7. Conclusion

For elemental determination of Mo, ICP-MS incorporated with FI system is the most powerful tool which performs sensitive detection down to 0.01 µg l⁻¹ levels. Air-segmented liquid-flow system is seemed to be principally useful for

minimizing the dispersion of sample injected and the reagent consumption, compared to the traditional liquid-flow system. The FI determination at the above concentration levels is also possible by on-line preconcentration ICP-AES and GF-AAS, direct ASP based on molybdenum-catalyzed oxidation of L-ascorbic acid with H₂O₂ in the presence of *o*-phenylenediamine and direct AdSV with chloranilic acid. The arm operation of autosampler permits the incorporation of FI technique with GF-AAS. For the automatic analysis by various detection modes, FI technique is obviously essential for the dilution or elimination of matrix matters, the correction of matrix effects and the preconcentration/separation in order to perform the reliable and sensitive determination of Mo. For speciation of Mo, FI/ICP-MS with the on-line field fractionation channel is a unique method. In future, the FI technique based on catalytic method or AdSV may be used for the speciation of Mo species (ions, inorganic and organic complexes, coprecipitates, etc.), because they are sensitive to chemical forms of Mo.

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References

- [1] N. Titenko-Holland, J. Shao, L. Zhang, L. Xi, H. Ngo, N. Shang M. T. Smith, *Environ. Mol. Mutagen.*, **32**, 251 (1998).
- [2] A. Vyskčil, C. Viau, *J. Appl. Toxicol.*, **19**, 185 (1999).
- [3] WHO, *Guidelines for Drinking-water Quality*, Vol. 1, 2nd ed., WHO, Geneva, 1993, p. 52.
- [4] M. Trojanowicz, *Flow Injection Analysis, Instrumentation and Applications*, World Scientific, Singapore, 2000.
- [5] Preplab Integrated Liquid Handling System, Catalog No. S359TB, Issue 1, Thermo Elemental, Winsford, Cheshire, UK, 2001.
- [6] M. F. Giné, F. J. Krug, H. Bergamin F°, B. F. Reis, E. A. G. Zagatto, R. E. Bruns, *J. Anal. At. Spectrom.*, **3**, 673 (1988).
- [7] M. J. Baxter, H. M. Crews, M. J. Dennis, I. Goodall, D. Anderson, *Food Chem.*, **60**, 443 (1997).
- [8] J. Wang, E. H. Hansen, B. Gammelgaard, *Talanta*, **55**, 117 (2001).
- [9] S. Kozono, R. Takashi, H. Haraguchi, *Anal. Sci.*, **16**, 69 (2000).
- [10] L. Ebdon, A. Fisher, H. Handley, P. Jones, *J. Anal. At. Spectrom.*, **8**, 979 (1993).
- [11] S. Greenfield, T. M. Durrani, S. Kaya, J. F. Tyson, *Analyst*, **115**, 531 (1990).
- [12] L. Guo, G. Zhang, Z. Fang, *Guangpuxue Yu Guangpu Fenxi*, **13**, 73 (1993); [Chem. Abstr., **121**, 25756 (1994)].
- [13] E. Vassileva, N. Furuta, *Fresenius' J. Anal. Chem.*, **370**, 52 (2001).
- [14] N. Furuta, K. R. Brushwyler, G. M. Hieftje, *Spectrochim. Acta*, **44B**, 349 (1989).
- [15] X. Cheng, J. Zhou, H. Liu, Z. Tang, Q. Shuai, Z. Ji n, *Fenxi Shiyanshi*, **15**, 66 (1996); [Chem. Abstr., **126**, 255137 (1997)].
- [16] E. Rosland, W. Lund, *J. Anal. At. Spectrom.*, **13**,

- 1239 (1998).
- [17] D. Beauchemin, *Analyst*, **118**, 815 (1993).
- [18] J. M. Craig, D. Beauchemin, *Analyst*, **119**, 1677 (1994).
- [19] K.-H. Lee, M. Oshima, T. Takayanagi, S. Motomizu, *J. Flow Injection Anal.*, **16**, 255 (1999).
- [20] K.-H. Lee, M. Oshima, S. Motomizu, *Bunseki Kagaku*, **49**, 529 (2000).
- [21] K.-H. Lee, M. Oshima, T. Takayanagi, S. Motomizu, *Anal. Sci.*, **16**, 731 (2000).
- [22] S. J. Hill, J. Hartley, L. Ebdon, *J. Anal. At. Spectrom.*, **7**, 895 (1992).
- [23] M. Hassellöv, B. Lyvén, C. Haraldsson, W. Sirinawin, *Anal. Chem.*, **71**, 3497 (1999).
- [24] I. B. Brenner, M. Liezers, J. Godfrey, S. Nelms, J. Cantle, *Spectrochim. Acta*, **53B**, 1087 (1998).
- [25] H. Klinkenberg, T. Beeren, W. Van Borm, *Spectrochim. Acta*, **49B**, 171 (1994).
- [26] A. G. Coedo, T. Dorado, *J. Anal. At. Spectrom.*, **10**, 449 (1995).
- [27] A. P. G. Gervasio, G. C. Luca, A. A. Menegário, B. F. Reis, H. B. Filho, *Anal. Chim. Acta*, **405**, 213 (2000).
- [28] M. P. Granchi, J. A. Biggerstaff, L. J. Hilliard, P. Grey, *Spectrochim. Acta*, **42B**, 169 (1987).
- [29] S. Qin, C. Yang, J. Yao, Y. Zhang, P. Yang, X. Wang, *Guangpu Shiyanshi*, **14**, 47 (1997); [Chem. Abstr., **130**, 206938 (1999)].
- [30] M. C. Brennan, G. Svehla, *Fresenius' J. Anal. Chem.*, **335**, 893 (1989).
- [31] C. S. P. Iyer, T. P. Rao, T. Kartikeyan, A. D. Damodaran, *At. Spectrosc.*, **15**, 234 (1994).
- [32] Y.-H. Sung, Z.-S. Liu, S.-D. Huang, *J. Anal. At. Spectrom.*, **12**, 841 (1997).
- [33] X.-F. Yin, M. Liu, *Gaodeng Xuexiao Huaxue Xuebao*, **15**, 1766 (1994).
- [34] H. Chen, S. Xu, Z. Fang, *J. Anal. At. Spectrom.*, **10**, 533 (1995).
- [35] H. Bergamin F°, F. J. Krug, B. F. Reis, J. A. Nobrega, M. Mesquita, I. G. Souza, *Anal. Chim. Acta*, **14**, 397 (1988).
- [36] J. F. Krug, O. Bahia F°, E. A. G. Zagatto, *Anal. Chim. Acta*, **161**, 245 (1984).
- [37] W. Qi, X. Chen, *Yejin Fenxi*, **12**, 17 (1992); [Chem. Abstr., **120**, 152429 (1994)].
- [38] Q. Xu, X. Yuan, *Fenxi Huaxue*, **20**, 319 (1992); [Chem. Abstr., **117**, 43793 (1992)].
- [39] T. Pérez-Ruiz, C. Martínez-Lozano, V. Tomás, C. Paredes, *Mikrochim. Acta*, **118**, 203 (1995).
- [40] X. Song, *Lihua Jianyan, Huaxue Fence*, **29**, 35 (1993); [Chem. Abstr., **121**, 314736 (1994)].
- [41] H. Shen, Y. Liu, X. Wang, L. Liu, *Yejin Fenxi*, **13**, 1 (1993); [Chem. Abstr., **122**, 45185 (1995)].
- [42] W. Jianhua, H. Ronghuan, T. Yuehong, *Chem. Anal. (Warsaw)*, **41**, 577 (1996).
- [43] A. M. Almuaibed, A. Townshend, *Microchem. J.*, **49**, 56 (1994).
- [44] D. T. Burns, M. Harriott, P. Pornsinlapatip, *Anal. Chim. Acta*, **281**, 607 (1993).
- [45] K. Yoshimura, S. Matsuoka, *Anal. Chim. Acta*, **225**, 313 (1989).
- [46] D. Liu, A. Zhang, *Yingyang Xuebao*, **13**, 68 (1991); [Chem. Abstr., **115**, 269443 (1991)].
- [47] K.-L. Lu, Y.-M. Chen, *Proc. Natl. Sci. Counc., Repub. China, Part A*, **8**, 85 (1984).
- [48] E. N. V. M. Carrilho, F. J. Krug, E. A. G. Zagatto, *Talanta*, **42**, 2021 (1995).
- [49] J. C. de Andrade, R. E. Bruns, S. P. Eiras, *Analyst*, **118**, 23 (1993).
- [50] L. C. R. Pessenda, A. O. Jacintho, E. A. G. Zagatto, *Anal. Chim. Acta*, **214**, 239 (1988).
- [51] R. Liu, D. Liu, A. Sun, G. Liu, *Analyst*, **120**, 565 (1995).
- [52] J. Wang, R. He, *Talanta*, **43**, 391 (1996).
- [53] T. Yamane, Y. Aruga, T. Ogawa, *Memoirs of the Faculty of Liberal Arts and Education, Yamanashi University*, **44**, Part II, 20 (1993).
- [54] S. Kawakubo, R. Fukasawa, M. Iwatsuki, *J. Flow Injection Anal.*, **14**, 25 (1997).
- [55] J. Li, Y. Chen, *Fenxi Kexue Xuebao*, **14**, 148 (1998); [Chem. Abstr., **128**, 330508 (1998)].
- [56] Z. Zhu, *Yejin Fenxi*, **19**, 42 (1999); [Chem. Abstr., **131**, 27185 (1999)].
- [57] Z. J. Zhu, *Chinese Chemical Letters*, **11**, 427 (2000).
- [58] H. Müller, V. Müller, *Anal. Chim. Acta*, **180**, 30 (1986).
- [59] M. Trojanowicz, A. Hulanicki, W. Matuszewski, M. Pałys, A. Fuksiewicz, T. Hulanicka-Michalak, S. Raszewski, J. Szyller and W. Augustyniak, *Anal. Chim. Acta*, **188**, 165 (1986).
- [60] R. Zhao, S. P. Scullion, A. G. Fogg, *Anal. Proc.*, **26**, 363 (1989).
- [61] A. Romanus, H. Müller, D. Kirsch, *Fresenius' J. Anal. Chem.*, **340**, 371 (1991).
- [62] S. Sander, *Fresenius' J. Anal. Chem.*, **365**, 435 (1999).

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