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SAMPLE PREPARATION FOR FLAME ATOMIC ABSORPTION SPECTROSCOPY: AN OVERVIEW

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ABSTRACT

Sample preparation is an important step in chemical analysis, from time and reagent consuming point of view and from the probability of errors. The present article gives an overview of recently most used techniques in sample preparation for flame atomic absorption spectroscopy. Wet and dry sample decomposition techniques, separation and pre-concentration methods of the target analyte(s) have been discussed.
Keywords: Sample preparation, FAAS, decomposition, separation, pre-concentration

INTRODUCTION

Elemental analysis of the majority of organic and inorganic matrices requires the partial or total dissolution of the sample prior to instrumental analysis.

Analysis by spectroscopic methods practically always necessitates a simple or more complex preparation of the sample. These steps are generally the most critical part of analysis because they are responsible for the most important errors.[1-3]

Only a few direct methods allow the introduction of the sample without any preparation. In these cases the lack of reliable calibration is the major problem. On the other hand, sample preparation allows the separation and/or pre-concentration of analytes and makes possible the use of several determination methods.

Sample preparations involve digestion, extraction and preparation of the analytes before the analysis, so this step is time limiting, requiring *ca*. 61% of the total time to perform the complete analysis, and is responsible for 30% of the total analysis error. Nowadays the goals to be reached are the best results, in the shortest time, with minimal contamination, low reagent consumption and generation of minimal residue or waste.[1]

Sample preparation was probably the single most neglected area in analytical chemistry relatively to the great interest in instruments. While the level of sophistication of the instrumentation for analysis has increased significantly, a comparatively low technical basis of sample preparation often remains.[4]

Sample preparation and development of methods have now became a growing field along with instrumental improvements. There are drastic improvements in the detection power of measurement techniques used. Consequently, the analyst also realizes that it is often no longer mandatory to resort to laborious, dubious and time-consuming separation or pre-concentration steps in the sample preparation procedures.[2]

It is normal in atomic spectroscopy for the sample to be found in one of two forms solid or liquid. The liquid case would seems to be the easiest form in which to handle the sample, with maybe a requirement for filtration being all that is required. However, the inherent lack of sensitivity of many spectroscopic techniques and the need to carry out determinations at lower and lower levels means that invariably some form of pre-concentrations is required. If the sample is in a solid form, the normal requirement is to covert it into the liquid form although it is possible to analyse solids directly by using the atomic spectroscopy, but this is not the preferred approach.[4]

The principal objectives of sample preparation for residue analysis are; isolation of the analytes of interest from as many interfering compounds as possible, dissolution of the analytes in a suitable solvent and pre-

concentration. In an analytical method sample preparation is followed by a separation and detection procedure.

EXPERIMENTAL

The selection of a preparation method is dependent upon: (1) the analyte(s), (2) the analyte concentration level(s), (3) the sample matrix, (4) the instrumental measurement technique, and (5) the required sample size.

Matrix

The term *matrix* refers to the collection of all of the various constituents making up an analytical sample. In addition to the analyte, the sample matrix includes all of the other constituents of the sample, which are sometimes referred to as concomitants.

Contamination and Losses

The major problem in preparing samples for trace analysis is the risk of contamination. Contamination is associated with several probable causes, i.e. the grade of reagents used, sample storage container, steps of digestion or dilution of the sample and their previous history, and human intervention.

Losses are a particularly significant problem in trace analysis. Container surfaces, for example, may present a significantly large area on which the analyte can be adsorbed. At higher levels such a small absolute loss would have little effect on the concentration but at trace levels a large proportion of the analyte may be stripped from the solution.[5]

Samples

Samples analyzed may be divided into those which are already in an aqueous solution (e.g. various water samples, beverages, blood, serum, and urine.), in other liquid form (e.g. oils, fuels, and organic solvents.) or in solid form (e.g. soils, sediments, plants, animal tissues, metals, and plastics.). Solid samples may contain a high proportion of organic matter (e.g. plants, animal tissues, and plastics.) or have more inorganic composition (e.g. soils, sediments, and metals.). For routine analysis by atomic spectroscopic techniques, which are all dedicated to work with aqueous samples, the analysis of other liquids must be adapted and the solids are generally converted into a solution by an appropriate dissolution method.[2]

Liquid Samples

Aqueous samples can be generally introduced for analysis directly and without any prior treatment. The only major problem associated with work with solutions is their collection and storage. Concerning atomic spectroscopic analysis itself, no particular precautions have to be taken. If measured concentrations satisfy the principal criteria of the spectroscopic method used (sensitivity, dynamic range) and possible interferences are under control, the analysis of solutions may be performed automatically with all modern atomic spectroscopic systems.

Non-aqueous samples can sometimes be run directly, but this depends significantly on their viscosity. In flame atomic absorption spectroscopy (FAAS) analysis, the viscosity should be similar to that of water for which most nebulizers are designed. Only some organic solvents, such as ethanol or methyl isobutyl ketone, fulfill this condition and are consequently often used for dilution of organic liquids, the major drawback, encountered with these techniques is the dilution factor, which reduces the metal content per unit volume.[6] Standards can be prepared in the pure solvent. Elements in organic solvents usually give an FAAS analysis response similar to that given by the same element in aqueous solution.

Solid Samples

In this case, many steps are required, including sampling, sub-sampling, grinding, and dissolution. The risk of contamination is higher than the case of liquid samples.

RESULTS AND DISCUSSION

Sample preparation techniques

    A. Decomposition techniques

Decomposition involves the libration of the metal of interest from an interfering matrix by using a reagent and/or heat. The utilization of reagents or acids may cause contamination or loss of the analytes.

Acid digestion or wet decomposition

Acid digestion involves the utilization of mineral or oxidizing acids and an external heat source to decompose the sample matrix. The choice of the acid or the combination of the acids depends upon the nature of the matrix to be decomposed.

Wet decomposition has been performed in open systems for many years: Teflon beakers when using HF or glass tubes or beakers on hot plates or aluminum blocks. Open systems are useful for relatively "easy" samples such as food or agricultural, but generally unsuitable for some samples that require lengthy dissolution times of 1–24 h. Other concerns are that they tend to be time consuming and tedious and result in evaporative loss of volatile metals and the risk of contamination.[7]

In general, nitric acid is used as oxidant alone or in combination with other acids (e.g., sulfuric and hydrochloric acids) or sometimes with hydrogen peroxide.[8-10] In addition, hydrofluoric acid can be used in combination with nitric acid for the total decomposition of silica containing organic matrices.[11] Nitric acid is popular because of its chemical compatibility, oxidizing ability, availability, purity, and low cost.[12]

For samples that are not highly aromatic and/or contain a high -OH functionality, it is preferred to use nitric acid followed by perchloric acid.

The ability of nitric acid to react with alcohols and aromatic rings forming explosive compounds calls for caution when using nitric acid alone or in combination with other reagents in the decomposition of organic matrices. If the sample contains high -OH functionality it is best to pre-treat the sample with concentrated sulfuric acid which will act as a dehydrating agent. The use of nitric acid is not recommended for digestion of highly aromatic samples.[5]

Digestion may be performed in open or closed vessels using classical heating blocks or microwave radiation.[13-15] The closed vessels have been currently used in order to improve the oxidation efficiency and to reduce the time of digestion, and it has been successfully used for digestion of a variety of samples. Closed systems allow high pressures above atmosphere to be used. This allows boiling at higher temperatures and often leads to complete dissolution of most samples.[7, 12]

The advantages of the closed system, as compared with the open system are: No volatilization of elements, reduced reagent quantities, and no contamination from external sources.[16]

Microwave digestion

Microwave-assisted sample preparation techniques are becoming widely used in analytical laboratories all over the world.[17]

Microwave radiation can greatly speed up the extraction and the so-called microwave-assisted extraction (MAE) is thus established.[18,19] In principle, only samples or solvents containing dipolar materials or microwave absorbents can be affected by microwaves which heat the extraction body from inside to outside in a very short time, much different from the common heating methods. The acceleration is resulted from the fast and uniform heating feature. MAE can be conducted with an open or closed microwave system. A closed-vessel offers a special way to regulate the extracting temperature by simply adjusting the vessel pressure. Although almost all reported MAE methods were conducted off-line, on-line approaches have been shown to be possible.[20-22] The main advantage of MAE lies in its wide applicability for fast extractions of analytes including some thermally instable substances.

The closed digestion technique involves placing the sample in a vial (or bomb), usually constructed of a fluorinated polymer, such as polytetrafluoroethylene (PTFE) or perfluoro alkoxy (PFA). After adding the digestion reagents, the bomb is tightly sealed and placed in the microwave oven for irradiation by microwave energy.[23-25]

Although digestion using closed vessels may also employ conventional heating, most of the recent applications have been performed using microwave radiation in view of the relatively short time involved and also to allow specific applications where high purity reagents and matrix removal are necessary.

Dry ashing

Dry ashing or oxidation is usually performed by placing the sample in an open vessel and destroying the combustible (organic) portion of the sample by thermal decomposition, normally in the presence of an ashing aid, using a muffle furnace. Typical ashing temperatures are 450 to 550°C at atmospheric pressure, and the ash residues are dissolved in an appropriate acid. The degree of volatilization loss is a limiting factor and depends on (i) the applied temperature, (ii) the form in which the analyte is present in the

sample, and (iii) the chemical environment in the ashing stage. Oxidizing reagents may be used as ashing aids in order to prevent the volatilization of analytes and also to speed up the ashing process. High-purity magnesium nitrate and magnesium oxide are commonly used for that purpose.[26] Low-temperature ashing involves treatment of the sample at about 120 °C using activated (singlet state) oxygen.

The most important advantages of the ashing are the ability to decompose large sample sizes and dissolving the resulting ash in a small volume of acid, and the need for little or no reagents.

A.   Trace element separation and pre-concentration

The direct determination of metals frequently proves to be insufficiently sensitive therefore, in many cases pre-concentration is necessary.[27] Efficient and selective separation of metal ions is gaining more importance because of the increasing demand for high purity products and also for environmental concerns. There are various separation methods such as precipitation, solvent extraction, cloud point extraction, solid phase extraction, and ion-exchange are widely used to solve these problems.

Liquid- liquid extraction

Solvent extraction separation is based on the differences in the solubility of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is an aqueous solution and the second phase is an organic solvent immiscible with water. Extraction is usually fast and simple process; it demands only very simple equipments. Stripping (re-extraction, back-extraction or scrubbing) involves bringing the element from the organic extract back to the aqueous phase.

After extraction the concentration of the metallic complex in the organic phase can then be directly determined by atomic absorption spectrophotometric methods. The use of organic solvents in flame atomic absorption spectrometry (FAAS) increases the efficiency of the atomization, as the viscosity and surface tension of most organic solvents are lower than those of water, resulting in smaller drops and larger volumes of sample entering the flame.[28,29]

Organic solvents containing chlorine are not recommended in FAAS since they generate toxic products and some times extinguish the air/acetylene flame.[30] The most common chelate used in atomic spectroscopy is ammonium pyrrolidine dithiocarbamate (APDC), with methyl isobutyl ketone as the organic solvent.[4] Solvent extraction is convenient both for group and selective concentration of heavy metals. [27, 31-34]

The main disadvantage of liquid- liquid extraction is the large consumption of solvents which is not environmentally friendly aspect. There is an urgent necessity to evaluate employed analytical procedures not only in respect to the reagents, instrumental costs and analytical parameters but also on the basis of their negative influence on the environment.[35]

Chromatography

The most common type of chromatography for metal separation and pre-concentration is ion exchange chromatography. This process can be achieved in two ways, batch, or column.

The term 'ion chromatography' does not refer to a specific technique defined by the nature of the stationary and mobile phases, but rather to a group of related liquid chromatographic methods that are applicable to a particular group of analytes. These analytes include inorganic anions and cations, as well as low-molecular-mass organic acids and bases.[36]

Different types of ligands or groups of compounds are suitable for HPLC such Schiff base chelates, hydrazones, dithizonates, and metal dithiocarbamates. For these groups of substances principally reversed-phase and adsorption systems are suitable; separations by reversed- phase systems are very well reproducible.[37-41]

Solid phase extraction

The solid phase typically consists of small, porous particles of silica with a bonded organic phase or of an organic polymer, such as crosslinked polystyrene. The extraction can take place in a batch mode in which the solid extractant is intimately mixed with liquid sample solution. In chemical analysis it is more common to pack the solid extractant into a small tube and pass the liquid sample through the tube.[41]

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology.

Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first case, a chemical bond is formed between the solid support surface groups and those of the organic compound (*functionalized sorbent*). In the second approach, the organic compound is directly adsorbed on the functional groups of the solid support surface (*impregnated* or *loaded sorbent*), either by passing the reagent solution through a column packed with the adsorbent, or by soaking the adsorbent in the reagent solution.[42-45]

This method is simple and convenient to apply, and has the major advantage of ease of automation. Further, high enrichment factors are achieved and the technique is less prone to sample contamination effects than other methods.

A variety of solid materials such as modified polyurethane foam (PUF)[46], cellulose[47], activated carbon[48], silica gel[49] and micro crystalline naphthalene[50] have been used for pre-concentration of metals.

The surface can be modified chemically by chemical reaction or physically by means of adsorption, in order to enhance the selectivity toward certain metal ion or certain group of elements.[51-54]

Co-precipitation

The pre-concentration purpose is achieved by the formation of insoluble compounds. The co-precipitation is used when direct precipitation can not separate the desired metallic species due to its low concentration in sample solution. The co-precipitation can be associated with metal adsorption on the precipitate surface or due to metal incorporation onto the precipitate structures.

Inorganic or organic substances can be used as co-precipitation agents. The organic agents usually chosen are those able to originate neutral chelates with metallic species.

The carrier element, is precipitated to co-precipitate trace elements in sample solutions, copper and zinc are popular, because of their limited negative effects for environment.

After precipitation the precipitate can be removed by centrifugation and dissolved in acids to be measured by FAAS.

Many metal ions from water samples have been pre-concentrated by co-precipitation with hydroxides of iron (III)[55], indium(III)[56], and zirconium[57]. Organic co-precipitants, generally dithiocarbamates of bismuth and copper have been widely used as efficient collectors of trace elements.[58,59] A separation/pre-concentration procedure based on the co-precipitation of Pb(II), Fe(III), Co(II), Cr(III) and Zn (II) ions with copper(II)-N-benzoyl-N-phenyl-hydroxylamine complex (Cu BPHA) has been also developed.[60]

Cloud point extraction

Cloud point extraction (CPE) is an attractive technique that reduces the consumption of the solvent, extraction time and the disposal costs. Cloud point methodology has been used for the extraction and pre-concentrations of metal ions after the formation of sparingly water soluble complexes.[61]

The CPE of metal ions involves the formation of sparingly water soluble chelates with suitable reagents. The method is based on the entrapment of uncharged moiety within a micelle formed by heating the surfactant solution above the cloud point temperature.

The application of CPE offers an attractive alternative to conventional liquid-liquid extraction by reducing the consumption of and exposure to the solvent, disposal cost, and extraction time.

The main parameter to attain a surfactant monomer agglomeration in a micelle-rich phase is the surfactant concentration at the cloud point temperature. The temperature-concentration phase diagram is specific for each surfactant. The effect of additives such as salts and other surfactants also has to be considered. The first application of cloud point extraction for analytical purposes described the micelle aggregation of hydrophobic anionic metal complexes.[62,63]

The generation of the metal chelates is a main step in the process of CPE. Several ligands, have been listed by Sun et. al. such as 1-(2- thiazolylazo)-2-naphthol (TAN), ammonium pyrrolidinedithiocarbamate (APDC), 8-hydroxyquinoline (Oxine), dithizone, diethyldithiocarbamate (DDTC), 2-(5-bromo-2- pyridylazo)-5-diethylaminophenol (5-Br-PADAP),18 and 1-(2- pyridylazo)-2- naphthol (PAN), have been used in cloud point extraction of metal ions.[64]

Many metal ions have been determined by atomic absorption spectrometry such as Pb, Mn, Fe, Ag, Ni, Cu, Zn, Pd, Cr and Cd, after CPE in different kinds of samples.[65-67]

CONCLUSION

There are many different techniques in for sample preparation for FAAS. Selection of the sample preparation method depends mainly upon the analyte concentration, matrix, instrument operation conditions, costs and the environmental considerations.

REFERENCES

1. E. de Oliveira., *J. Braz. Chem. Soc*., **14(2),** 174 (2003).
2. M. Hoenig, and A.-M. de Kersabiec., *Spectrochimica Acta Part B: Atomic Spectroscopy*, **51(11),** 1297 (1996).
3. M. J. Cal-Prieto, M. Felipe-Sotelo, A. Carlosena, J. M. Andrade, P. López-Mahía, S. Muniategui and D. Prada, *Talanta*, **56(1**), 41 (2002).
4. J. R. DEAN, Atomic Absorption and Plasma Spectroscopy, Second edition, John Wiley and Sons, Ltd., (1997).
5. A. G. Howard and P. J. Stathm, Inorganic trace analysis, philosophy and practice. John Wiley and sons Ltd. (1997)
6. F. Anwar, T.G. Kazi, R. Saleem and M.I. Bhanger., *Grasas y Aceites*, **55(2)**, 160 (2004).
7. J. Sneddon, C. Hardaway, K. K. Bobbadi, and A. K. Reddy, *Applied Spectroscopy Reviews,* **41,** 1 (2006).
8. R. Bock, Handbook of Decomposition Methods in Analytical Chemistry, Willey, New York, (1979), translated and revised by I.L. Marr.
9. F. Barbosa Jr., C. Palmer, F.J. Krug, P.J. Parsons, *J. Anal. At. Spectrom.* **19**, 1000, (2004).
10. J.A. Nóbrega, M.C. Santos, R.A. Sousa, S. Cadore, R.M. Barnes, M. Tatro, *Spectrochim. Acta Part B*, **61,** 465 (2006).
11. R. Anderson, Sample Pretreatment and Separation, John Wiley and Sons, New York, (1987).
12. É. M. Flores, J. S. Barin, M. F. Mesko, G. Knapp, *Spectrochimica Acta Part B*, **62**, 1051 (2007).
13. H. Matusiewicz, Wet digestion methods, in: Z. Mester, R.E. Sturgeon (Eds.), Elsevier, Amsterdam, pp. 193 (2003).
14. J.A. Nóbrega, L.C. Trevizan, G.C.L. Araújo, A.R.A. Nogueira, *Spectrochim. Acta Part B,* **57,** 1855 (2002).
15. D.D. Link, H.M. "Skip" Kingston, *Anal. Chem.* **72**, 2908 (2000).
16. G. Knapp, *Mikrochemica Acta*, **II**, 445 (1991)
17. F. E. Smith, E. A. Arsenault, *Talanta*, **43**, 1207 (1996).
18. J.M.R. B´elanger, J.R.J. Pare, *Anal. Bioanal. Chem.* **386**,1049, (2006).
19. J.L. Luque-Garcia, M.D. Luque de Castro, *Trends Anal. Chem.* **22**, 90, (2003).
20. M. Ericsson, A. Colmsjo, *Anal. Chem.*, **75**, 1713, (2003).
21. M. Ericsson, A. Colmsjo, *J. Chromatogr. A* **964 (1-2)**, 11 (2002).
22. A. Serrano, M. Gallego, *J. Chromatogr. A* **1104 (1-2**), 323 (2006).
23. K. J. Lamble and S. J. Hill, *Analyst,* **123***, 103R* (1998).
24. K. I. Mahan, T. A. Foderaro, T. L. Garza, R. M. Martinez, G. A. Maroney, M. R. Trivisonno, E. M. Willging *Anal. Chem.*, **59 (7)**, 938 (1987).
25. Q. Jin, F. Liang, H. Zhang, L. Zhao, Y. Huan and D. Song, *TrAC Trends in Analytical Chemistry*.**, 8(7)**, 479 (1999)
26. M. Korna, E. Mortea, D. Batista dos Santosa, J. Castroa, J. P. Barbosaa, A. Teixeiraa, A. Fernandesa, B. Welza, W. Carvalho dos Santosab, E. Nunes dos Santosc, M. Korn, *Applied Spectroscopy Reviews*, **43**,67 (2008).
27. Y. A. Zolotov, G.I. Malofeeva, O.M. Petrukhin and A.R. Timerbaev, *Pure & Appl. Chem.*, **59(4)**, 497 (1987).
28. Hill, S. J. *Chem. Soc. Rev.,* **26**, 291, (1997).
29. B. Welz, M. Sperling, M. *Atomic Absorption Spectrometry*, (Wiley. VCH. Weinheim) 3/e, (1999).
30. R. Laus, A. dos Anjos, R. Osório, A. Neves, M. Laranjeira and V. T. de Fávere, *Pak. J. Anal. Environ. Chem*. **9(2)**, 58 (2008).

31. S. Abe, T. Sone, K. Fujii and M. Endo. *Analytica Chimica Acta,* **274(1**), 141 (1993)
32. S. Abe, K. Fujii and T. Sono. *Analytica Chimica Acta*, **293(3)**, 325 (1994).
33. S. Abe, J. Mochizuki and T. Sone *Analytica Chimica Acta, 319(3)*, 387 (1996)
34. Yi Chena, Zhenpeng Guoa,b, Xiaoyu Wang a,b, Changgui Qiu *Journal of Chromatography A*, **1184**, 191 (2008).
35. J. Curyło, W. Wardencki, J. Namieśnik, *J. of Environ. Stud.* **16(1)**, 5 (2007).
36. P. R. Haddad, P. Doble, M. Macka, *Journal of Chromatography A*, **856**, 145 (1999).
37. P. C. Uden, D. M. Parees and F. H. Walters, *Anal. Lett.* **8**, 795 (1975).
38. E. F. Hilder, M. Macka and P. R. Haddad, *Analyst*, **123**, 2865 (1998).
39. J. M. Daud and I. M. Alakili *Malaysian Journal of Analytical Sciences,* **7(1)**, 113 (2001).
40. H. S.Rathore, M. Kumar, K. Ishratullah. *Indian Journal of Chemical Technology*, **13**, 84 (2006).
41. Nabil Ramadan Bader, *RASAYAN J. Chem.,* **3(4),** 660 (2010).
42. J. S. Fritz, *Analytical Solid Phase Extraction*, John Wiley and Sons, 8, (1999).
43. M. Ganjali, M. Pourjavid and L. Babaei,.*Quim. Nova*, **27(29)**, 213 (2004)
44. F. Shemirani, A. Alsadat, M. Niasiri and R. Kozani,. *Journal of Analytical Chemistry*, **59(3)**, 228 (2004).
45. M. H. Mashhadizadeh, A. Moatafavi, H. Allah-Abadi, and M. R. Zadmehr, *Bull. Korean Chem. Soc.*, **25, 9**, 1309 (2004).
46. Gama, E. M.; Lima, A. S.; Lemos, V. A. *J. Hazard. Mater.,* **136**, 757 (2006).
47. V. Gurnani, A. K. Singh, B. Venkataramani, *Anal. Chim. Acta.,* **485**, 221 (2003).
48. S. Xingguang, W. Meijia, Z. Yihua, Z. Jiahua, Z. Hanqi, J. Qinhan, *Talanta*, **59,** 989 (2003).
49. A. Goswami, A. K. Singh, *Talanta*, **58**, 6692002).
50. M. A. Taher, B. K. Puri, R.K. Bansal, *Microchem. J.*, **58**, 21 (1998).
51. M. H. Mashhadizadeh, A. Moatafavi, H. Allah-Abadi, and M. R. Zadmehr, *Bull. Korean Chem. Soc.*, **25(9)**, 1309 (2004).
52. D. Budziak, E. Luiz da silva, S. Denofre da Campos, and Eduardo Carasek *Michrocimica Acta,* **141**, 169 (2003).
53. M. Mashhadizadeh, M. Pesteh, Mahzad Talakesh, I. Sheikhshoaie, M. Ardakani, M.Karimi. *Spectrochimica Acta Part B* **63**, 885 (2008).
54. M. H. Mashhadizade, M. S. Azimi, M. Pesteh, I. Sheikhshoaei,M. M. Ardakani, M. A. Karimi. *Spectrochimica Acta Part B* **63**, 889 (2008).
55. Y. Kashiwagi, E. Kokufuta, *Anal Sci*. **16**, 1215 (2000).
56. M. Hiraide, Z. Chen, H. Kawaguchi, , Anal Sci **7**, 65 (1991).
57. Y.Tamari, R. Hirai, H. Tsuji, Y Kusaka, *Anal Sci*. **3**, 313 (1987)
58. H. Sato, J. Ueda, *Anal Sci.*,**17**, 461 (2001).
59. S. Tokalıoğlu, T. Oymak, S. Kartal, *Microchim Acta*, **159**:133 (2007).
60. Ş. Saçmacı, and Ş. Kartal, *Microchim Acta*, **170**, 75 (2010).
61. L. M. Jamshid and G. Karim-Nezhad, *Iran. J. Chem. Chem. Eng.,* **24**, 4, (2005)
62. M. F. Giné, A. F. Patreze, E. L. Silva, J. S. Sarkis, M. H. Kakazu, *J. Braz. Chem. Soc.*, **19(3)**, 471 (2008).
63. C. B. Ojeda, F. S. Rojas, J. C. Pavón. *American Journal of Analytical Chemistry*, **1**, 127, (2010).
64. Z. Sun, P. Liang, Q. Ding, J.Cao, *ANALYTICAL SCIENCES*, **22**, 911 (2006).
65. N. Dalali, N. Javadi, Y. Kumar Agrawal, *Turk J Chem*, **32**, 561 (2008).
66. M. Ghaedi, K. Niknam, E. Niknamb and M. Soylak, *Journal of the Chinese Chemical Society*, **56**, 981 (2009).
67. P. Liang, J. Li, and X. Yang, *Microchim Acta*, **152**, 47 (2005)
68. M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soylak, *Journal of Hazardous Materials*, **168,** 1022 (2009).
69. G. D. Matos, E. B. dos Reis, A. C.S. Costa, S. L.C. Ferreira, *Microchemical Journal,* **92**, 135 (2009).

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