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# Slurry analysis after lead collection on a sorbent and its determination by electrothermal atomic absorption spectrometry

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**Abstract**

In this study, in order to eliminate the drawbacks of elution step and to reach higher enrichment factors, a novel preconcentration/separation technique for the slurry analysis of sorbent loaded with lead prior to its determination by electrothermal atomic absorption spectrometry was described. For this purpose, at first, lead was collected on ethylene glycol dimethacrylate methacrylic acid copolymer (EGDMA-MA) treated with ammonium pyrolidine dithiocarbamate (APDC) by conventional batch technique. After separation of liquid phase, slurry of the sorbent was prepared and directly pipetted into graphite furnace of atomic absorption spectrophotometer. Optimum conditions for quantitative sorption and preparation of the slurry were investigated. A 100-fold enrichment factor could be easily reached.

The analyte element in certified sea-water and Bovine-liver samples was determined in the range of 95% confidence level. The proposed technique was fast and simple and the risks of contamination and analyte loss were low. Detection limit ($3\delta$) for Pb was 1.67 $\mu g\,l^{-1}$.
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*Keywords:* Separation; Preconcentration; Lead; Electrothermal atomic absorption spectrometry; Slurry sampling

## 1. Introduction

The determination of heavy metals including lead are of considerable analytical interest particularly in biological and environmental samples including water, soil and plant, etc. Lead is an abundant toxic metal for biologically and environmental, have no function in body. Most significant lead sources are lead-based gasoline additives to improve the number of octane, lead-based dyes, lead-soldered canned boxes, pesticides, batteries, ceramic glazes and industrial pollution. Since lead is a non-essential and highly toxic element, its existence in any sample is never wanted at all concentrations even at ultra-trace levels. Thus, its determination at concentrations as low as possible is important and provides a basis for the diagnosis of clinical disorders and intoxication as well as for monitoring environmental pollution.

Electrothermal atomic absorption spectrometry (ETAAS) is an important tool for the determination of trace and heavy metals. However, when the concentration of the analyte is too low to be determined directly and/or interferences due to matrix cannot be eliminated, the use of a separation/preconcentration technique is a necessity. For this purpose, the most commonly and practically applied method is the collection of the analyte on a sorbent using different materials such as polymeric resins, silica, activated carbon with or without chelating groups and subsequently its elution by means of a convenient reagent [1–9]. Elution causes loss of time, contamination, high blank values and highly influences the quality of analytical data such as recovery, precision, enrichment of analytes, etc. It should be fast, complete and reproducible. The reagents used for elution may decrease the life time of graphite tubes. Therefore, the elution step determines the appropriateness of the method including fastness, easiness, accuracy (or recovery) and precision very strongly.

Nukatsuka et al. proposed a solid-phase extraction system in which cellulose nitrate resin after loaded with thallium was suspended in a small volume of aqueous solution and directly introduced into the furnace [10].

The introduction of solid samples as their suspensions directly into graphite furnace (slurry technique) has many advantages in AAS. In slurry method, solid samples are first finely ground, slurried with an appropriate liquid mostly adding sur-

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factants, e.g. Triton-X 100, homogenously mixed manually or using tools such as ultrasonic agitation and finally pipetted into the furnace by means of a micropipette or autosampler. In this technique, duration of sample preparation is very short and only very small amounts of reagents are used. In addition, the enrichment factor can be adjusted by modifying the volume of the suspension. The smaller the volume of suspension, the greater the enrichment factor are attained. Therefore, ultra-trace concentrations can be detected. However, to obtain a homogeneous and stable slurry, which influence directly accuracy and precision, many experimental parameters such as particle size, solid to total slurry volume, addition of stabilizing, etc. should be optimized [11–17].

In this study, in order to eliminate the elution step and thereby to avoid its drawbacks, the slurry of the sorbent loaded with lead by batch technique was directly introduced into the graphite furnace. For this purpose, the analyte element was sorbed on ethylene glycol dimethacrylatemethacrylic acid copolymer (EGDMA-MA) treated with ammonium pyrolidine dithiocarbamate (APDC) by batch technique. After separation of the liquid phase, the sorbent loaded with analyte element was slurried appropriately and pipetted directly into graphite furnace. The effects of experimental parameters on the sorption of analytes as well as optimum conditions to obtain a homogeneous and stable slurry were investigated.

## 2. Experimental

### 2.1. Apparatus and reagents

A Perkin-Elmer 3030 Zeeman Atomic Absoption Spectrophotometer equipped with a HGA-600 graphite furnace was used for the determination of analyte element. Pyrolytic graphite coated tubes with pyrolytic L'vov platforms were used throughout this work. The wavelength was set to 283.3 nm. Nitrogen was used as the purge gas. Actually argon is more frequently used than nitrogen, because there is a possibility that nitrogen may produces CN bands which may cause recombination process with the analyte before or during atomization step. However, since the purge gas flow was interrupted during atomization step, there is no probability of analyte cyanide formation during atomization step. On the other hand, at low pyrolysis temperatures lead cyanide is not formed. Graphite furnace programme for the determination of lead is given in Table 1. As can be seen from the table, after the atomization step, a high temperature (2650 °C) was applied to clean the platform thermally and thereby to prevent any deposition of organic material from the organic material. In addition, during the analysis, absorbances for the empty furnace, standards and samples were re-checked often to see if there is a change.

The pH of the samples were adjusted by 0.01 mol $l^{-1}$ $NH_4OH$ or 0.01 mol $l^{-1}$ $HNO_3$ and controlled using WTW pH 340-A/SET2 pH meter.

All chemical were of analytical reagent grade (Merck, Germany). Stock solution (1000 mg $l^{-1}$) of Pb was prepared from Titrisol concentrates (Merck) and further diluted with distilled–deionized water daily. EGDMA-MA was synthesized in the laboratory as described elsewhere [18].

Ammonium pyrolidine dithiocarbamate was purchased from Fluka whereas sea-water (CRM-SW) and Bovine Liver (CRM-BL) certified reference materials were bought from High-Purity Standards (USA). Samples were introduced into graphite furnace manually as 10 μl with a Eppendorf micropipette. Results were given as the averages of at least three independent replicate analyses.

### 2.2. Procedure for slurry sampling

At first, EGDMA-MA, used as the sorbent, was finely ground and sieved as 50 mesh. The sorbent was washed three times with 0.1 mol $l^{-1}$ NaOH; then three times with 0.1 mol $l^{-1}$ HCl and finally three times with distilled water which was enough to obtain analyte-free washings and then dried at 100 °C overnight. We used 10 ml of each reagent for about 1 g of sorbent. After three times of washing with water, slurry blanks of the sorbent prepared were completely free from the analyte. Instead of preparing the stock of EGDMA-MA modified with APDC, we preferred to prepare the sorbent daily. For this purpose, 50 mg of sorbent was treated with 10 ml of 0.05% (w/v) APDC and the liquid phase was removed by vaporization. In order to collect the analyte elements by batch technique, 50 mg of sorbent treated with APDC was weighed precisely and mixed with 40 ml of sample solution containing minimum 0.001 mg $l^{-1}$ Pb. The pH of the solution was adjusted to 6.5 and shaken for 5 min. The solid part was precipitated by centrifugation for 5 min at 1000 rpm. The supernatant was removed by decantation. The sorbent, collecting the analyte element, was washed with water a few times to remove the matrix traces and washing water was removed by decantation, too. The slurry of the sorbent carrying analyte element (minimum 0.001 mg $l^{-1}$ Pb) was prepared in 400 μl of

Table 1
Graphite furnace programme for the determination of Pb

| Step no. | Furnace temperature (°C) | Time (s) | | Internal gas flow (ml $min^{-1}$) | Read |
|---|---|---|---|---|---|
| | | Ramp | Hold | | |
| 1 | 110 | 10 | 15 | 300 | – |
| 2 | 150 | 5 | 15 | 300 | – |
| 3 | 400 | 10 | 20 | 300 | – |
| 4 | 1800 | 0 | 6 | Stop | * |
| 5 | 2650 | 1 | 5 | 300 | – |
| 6 | 20 | 2 | 6 | 300 | – |

* Atomization step. Atomic absorption is read.

1% Triton X-100 and further homogenized manually in a vial by stirring with micropipette tip just before each sampling. The slurry was then pipetted manually with 10 μl of pipette into the graphite furnace and atomized applying the graphite furnace programme given in Table 1.

## 3. Results and discussion

In the proposed technique, the slurry of sorbent collecting the analyte element was introduced into ETAAS without elution. First of all, quantitative sorption of analyte element 0.1 mg $l^{-1}$ for Pb onto the sorbent is a prerequisite which depends on the pH of the sample, sample volume, amount of sorbent, shaking time, addition of chelating agent (if necessary), etc. In addition, the success of the slurry technique necessitates a careful selection of solid-phase material, convenient mixing and addition of surfactants, optimization of particle size and the slurry concentration (solid mass to slurry volume ratio). Thus, in order to obtain quantitative recovery and high precision, both sorption and slurry parameters were carefully optimized.

In this study, the slurries were pipetted manually which is actually not common in graphite furnace applications, once that the autosampler is used just for avoiding losses in precision as well as to precisely delivery the drop on the platform surface. Manual sampling into graphite tube really needs care, experience and skilfulness so that the absorbances and peak shapes of repetitive pipettings for the same solution are always as good as those obtained using autosamplers. This may be seen even more problematic with slurry injection. Therefore, the many slurry conditions (particle size of the solid material, the volume of the slurry and the ratio of the slurry volume to solid-phase amount, etc.) were carefully optimized to obtain a homogenous and durable slurry as well as its perfectly and repetitively pipettings.

After each injection we controlled the place of sample drop in the platform and observed its drying with a special mirror. In case of any problem during injection, the furnace programme was stopped and injection was repeated after thermally cleaning the tube. However, since the injections in previous studies were performed manually, above-mentioned problems were hardly occured [19]. In addition, the depth of the injection hole of graphite furnace used in this study is appropriate to the manual pipettings successfully which is not appropriate at recent instruments. Due to the risk of clogging of autosampler tip and its capillar tubes, we preferred manual pipetting rather than using an autosampler for slurry analysis. In addition, special tools for the homogenization.

### 3.1. Optimization of parameters for sorption

#### 3.1.1. Effect of pH and chelating agent

One of the most important parameters for the quantitative sorption is the pH of sample. In order to improve the sorption properties of a sorbent, it is mostly modified with a chelating agent. For this purpose, EGDMA-MA was treated with APDC as described in Section 2. Although the sorption of 0.1 mg $l^{-1}$ analyte element on untreated EGDMA-MA was not complete, quantitative retention for the analyte was obtained after modifying the sorbent with APDC. As can be seen from Fig. 1, when the pH of solution was adjusted at pH ≥ 6.5, the analyte element could be quantitatively retained on the sorbent.

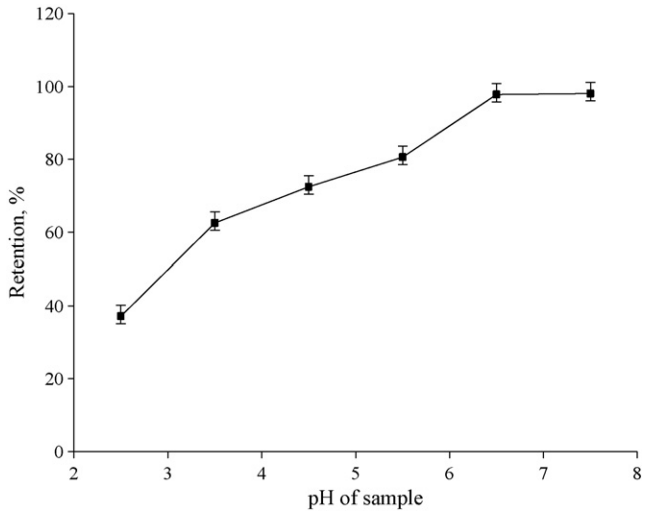



Fig. 1. Effect of pH of sample on the sorption of lead with APDC (analyte concentration: 0.1 mg $l^{-1}$; sample volume: 40 ml; sorbent: 50 mg).

#### 3.1.2. Effect of amount of sorbent

In order to optimize the sorbent amount, the effect of different amounts of EGDMA-MA on the sorption of analyte element was investigated. From a series of experiments, it was found that the analyte (0.1 mg $l^{-1}$ Pb) was quantitatively sorbed using 50 mg of EGDMA-MA treated with APDC (Fig. 2). This value was also chosen critical parameter throughout the experimental works.

#### 3.1.3. Effect of sample volume

The effect of sample volume on the sorption of analyte element using 50 mg of EGDMA-MA treated with APDC at pH 6.5 was investigated between 20 and 100 ml. If the sample volume were between 20 and 40 ml, quantitative sorption was obtained whereas at sample volumes higher than 40 ml, sorption was decreased. Prolonged shaking time was not helpful in this matter. On the other hand, if the amount of sorbent is higher than

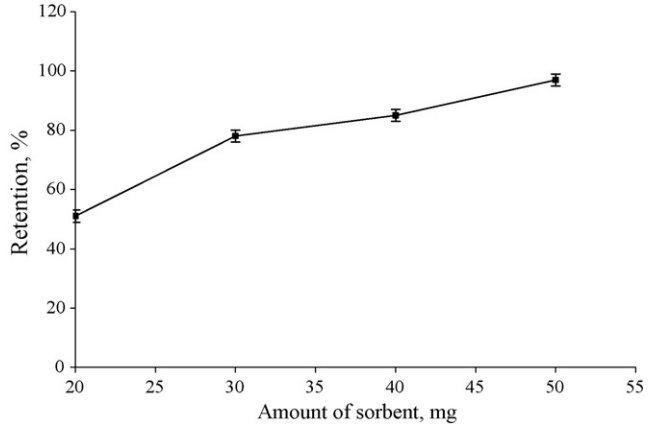



Fig. 2. Effect of amount of sorbent (EGDMA-MA) on the sorption of lead with APDC (analyte concentration: 0.1 mg $l^{-1}$; sample volume: 40 ml; pH: 6.5).

Table 2
Effect of foreign ions on the sorption of Pb (analyte concentration: 0.1 mg $l^{-1}$; sorbent: 50 mg; sample volume: 40 ml; pH: 6.5; number of repetitions: 3)

| Species | Added as | Concentration of the diverse ion (mg $l^{-1}$) | Retention (%) |
|---|---|---|---|
| $Na^+$ | NaCl | 4800 | 100 |
| | $NaNO_3$ | 400 | 98 |
| | $Na_2SO_4$ | 1950 | 108 |
| $K^+$ | KCl | 325 | 105 |
| $Mg^{2+}$ | $MgCl_2$ | 380 | 108 |
| $Ca^{2+}$ | $CaCl_2$ | 220 | 100 |
| $Fe^{3+}$ | $Fe(NO_3)_3$ | 35 | 105 |
| $Cu^{2+}$ | $CuSO_4$ | 25 | 100 |
| $Cl^-$ | NaCl | 7200 | 100 |
| | KCl | 275 | 105 |
| | $CaCl_2$ | 380 | 100 |
| | $MgCl_2$ | 1120 | 108 |
| $NO^{3-}$ | $NaNO_3$ | 1100 | 98 |
| | $Fe(NO_3)_3$ | 115 | 105 |
| $SO_4^{2-}$ | $Na_2SO_4$ | 4050 | 108 |
| | $CuSO_4$ | 35 | 100 |

50 mg, a durable homogeneous suspension for slurry analysis could not be obtained using Triton X-100 and by stirring. In this case, a better mixing for homogenization with special tools is needed. Consequently, in all experiments, sample volume did not exceed 40 ml.

### 3.1.4. Effect of foreign ions

The effect of various foreign ions on the sorption of analyte element was investigated. For this purpose, eight different chemical species were added to the test solution containing Pb and the retention of analyte element was found. The results are shown in Table 2. Obviously, EGDMA-MA could be successfully used for the determination of Pb in the presence of foreign ions at their concentrations given in the table. The concentrations of foreign ions are above of those in most commonly studied samples having very heavy matrices, e.g. sea-water, serum.

## 3.2. Effects of total slurry volume on homogeneity of slurry

The effects of total slurry volume on the analytical results were investigated and the results in the presence of Triton X-100 are given in Table 3. Since the slurry was not stable in the absence of dispersant, Triton X-100 was necessarily added into

Table 3
The effect of total slurry volume on recovery of Pb (final analyte concentration: 0.1 mg $l^{-1}$; sorbent: 50 mg; sample volume: 40 ml; pH: 6.5; number of repetitions: 3; the slurry was prepared in 1% of Triton X-100)

| Total slurry volume (μl) | Recovery (%) |
|---|---|
| 200 | 67 |
| 400 | 97 |
| 600 | 91 |
| 800 | 62 |
| 1000 | 55 |

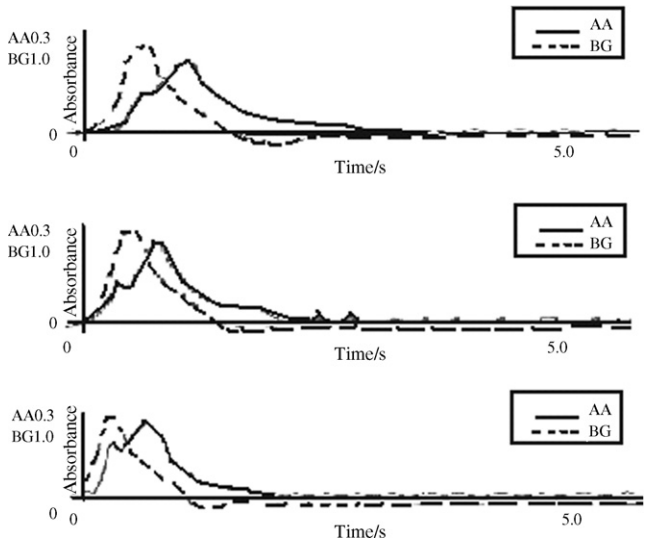



Fig. 3. Atomic absorption (—) and background (- - -) profiles for 1.0 ng of lead in 10 μl slurry pipetted three times manually.

the all solutions. When the slurry was prepared in 400 μl of 1% Triton X-100, quantitative recoveries (>97%) was obtained. By considering these results, all samples were prepared in 1% Triton X-100 as 400 μl. As mentioned previously when the sample volume was taken up to 40 ml and final slurry volume was 400 μl, an enrichment factor of 100 was obtained. Although the addition of universal modifier of the mixture of 0.2 mg $NH_4H_2PO_4$ and 0.01 mg $Mg(NO_3)_2$ for Pb was hardly improved the analytical data, all analyses were performed using modifiers to prevent any possible interference.

## 3.3. Validation of the method

The peaks of the three repetitive pipettings for the slurry of the sorbent loaded with lead were given in Fig. 3. Obviously, the peak shapes are smooth and reproducible as well as the precisions throughout this study were satisfactory which shows that the manual injection was successful and free of problems. To validate the method in different matrices, the lead was determined in sea-water (CRM-SW) and Bovine-liver (CRM-BL) certified reference materials after suitable enrichment. The analytical results are given in Table 4. For the samples having lower concentrations of analytes, the much higher enrichment factors needed can be obtained by using higher sample volumes and lower slurry volumes. However, it should be noted that the simplicity of this method without needing special tools is

Table 4
Recoveries for Pb in sea-water (CRM-SW) and Bovine-liver (CRM-BL) certified reference materials (sorbent: 50 mg; sample volume: 40 ml; pH: 6.5; number of repetitions: 3; the slurry was prepared in 1% of Triton X-100)

| Sea-water (μg $kg^{-1}$) | | Bovine-liver (μg $l^{-1}$) | |
|---|---|---|---|
| Certified value | Found[a] | Certified value | Found[a] |
| 4.0 | 3.9 ± 0. 2 | 3.0 | 2.9 ± 0.1 |

[a] Mean ± 95% confidence limits.

valid only in a limited range of experimental parameters given above. If the conditions had to be changed significantly for much higher enrichment factors, e.g. much more sample volumes and lower slurry volumes had to be applied, experimental parameters proposed in this study might not be sufficient for quantitative sorption and successful slurry analysis. In this case, the experimental factors for higher sample volumes and lower slurry volumes should be re-arranged such as using special tools for much effective mixing of slurry (ultrasonic blades, etc.), prolonged shaking time for quantitative sorption, higher concentrations of surfactants for the durability of a homogeneous slurry, etc. Almost no background value was observed which indicates that the matrix was successfully separated as well as the sorbent itself does not cause any spectral interference. There are no significant differences between mean values of the analyte element found as the average of three replicate determination and their certified values in the 95% confidence level. This obviously shows that after optimization of experimental conditions, the analyte element in different heavy matrices was quantitatively sorbed on EGDMA-MA treated with APDC and the sorbent collecting the analytes was successfully analyzed with slurry analysis. The calculated detection limit for lead using sample-matching blanks was $1.67\,\mu g\,l^{-1}$, according to the $3\sigma$ concept for the described method. It can be seemed that the lead quantification in sea-water is questionable, once that such result is lower than the LOQ, which is $5.6\,\mu g\,l^{-1}$, according to the $10\sigma$ concept However, we enriched the sample, the concentration of the analyte in the final concentrated slurry was much higher than LOQ.

## 4. Conclusion

The described method using EGDMA-MA as a sorbent and its directly introducing into the furnace as slurry without elution combines the advantages of batch enrichment/separation method and slurry analysis. The proposed technique is simple, fast and cheap. The elimination of elution step reduces the time required for analysis. The risk of contamination from eluents especially acids, apparatus and the laboratory atmosphere is lower. The last but not least, superior preconcentration factors can be achieved by adjusting the volume of the suspension, appropriately. For the samples studied, the enrichment factor could be easily increased up to 100 times. In fact, if necessary, much higher enrichment factors can be easily obtained for lower analyte concentrations.

On the other hand, since the described method is combination of sorption and slurry techniques, in the beginning, many experimental parameters had to be necessarily optimized for precise and quantitative sorption of analytes as well as preparation of homogeneous slurry and its reproducibly pipetting. Therefore, the choice of sorbent is very critical with respect to sorption and slurry analysis. EGDMA-MA after treated with APDC is suitable both for sorption and slurry analysis. It does not cause any spectral and non-spectral interferences, easily dispersed in dilute Triton-X solution, a homogeneous and durable slurry can be obtained without using special tools and extra effort.

In spite of various parameters to be optimized, it can be concluded that the proposed technique can be effectively and practically used for the preconcentration and separation of lead prior to their determination by ETAAS.

## References

[1] N. Tokman, S. Akman, Determination of bismuth and cadmium after solid-phase extraction with chromosorb-107 in a syringe, Anal. Chim. Acta 529 (2004) 87–91.
[2] N. Tokman, S. Akman, C. Ozeroglu, Determination of lead, copper and manganese by graphite furnace atomic absorption spectrometry after separation/concentration using a water-soluble polymer, Talanta 63 (2004) 699–703.
[3] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta Part B 58 (2003) 1177–1233.
[4] Y. Bakircioglu, D. Bakircioglu, S. Akman, Solid phase extraction of bismuth and chromium by rice husk, J. Trace Microprobe Tech. 21 (2003) 467–478.
[5] M. Tuzen, E. Aydemir, H. Sari, Investigation of some physical and chemical parameters in the River Yesilirmak in Tokat region, Turkey, Fresenius Environ. Bull. 11 (2002) 202–207.
[6] G. Seren, Y. Bakircioglu, F. Coban, S. Akman, Investigation on the preconcentration of trace elements on activated bentonite, Fresenius Environ. Bull. 10 (2001) 296–299.
[7] R.G. Wuilloud, J.A. Salonia, J.A. Gasquez, R.A. Olsina, N.D. Martinez, On-line pre-concentration system for vanadium determination in drinking water using flow injection-inductively coupled plasma atomic emission spectrometry, Anal. Chim. Acta 420 (2000) 73–79.
[8] Q. Zhang, H. Minami, S. Inoue, I. Atsuya, Preconcentration by coprecipitation of chromium in natural waters with Pd/8-quinolinol/tannic acid complex and its direct determination by solid-sampling atomic absorption spectrometry, Anal. Chim. Acta 401 (1999) 277–282.
[9] M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of $Pb^{2+}$, Chem. Anal. 51 (2006) 593–602.
[10] I. Nukatsuka, H. Seitoh, K. Ozeki, Solid-phase extraction with slurry injection of the resin into ETAAS for trace determination of thallium in natural water, Microchim. Acta 148 (2004) 177–182.
[11] G. Gentscheva, A. Detcheva, I. Havezov, E. Ivanova, Slurry sampling electrothermal atomic absorption spectrometric determination of sodium and iron impurities in optical crystals of rubidium titanyl phosphate, Microchim. Acta 144 (2004) 115–118.
[12] E.C. Lima, F. Barbosa, F.J. Krug, Lead determination in slurries of biological materials by ETAAS using a W-Rh permanent modifier, Fresenius J. Anal. Chem. 369 (2001) 496–501.
[13] P. Vinas, M. Pardo-Martinez, M. Cordoba-Hernadez, Rapid determination of selenium, lead and cadmium in baby food samples using electrothermal atomic absorption spectrometry and slurry atomization, Anal. Chim. Acta 412 (2000) 121–130.
[14] S.J. Huang, S.J. Jiang, Determination of lead in fish samples by slurry sampling electrothermal atomic absorption spectrometry, Analyst 125 (2000) 1491–1494.
[15] M.M. Silva, M. Goreti, R. Vale, E.B. Caramao, Slurry sampling graphite furnace atomic absorption spectrometry: determination of trace metals in mineral coal, Talanta 50 (1999) 1035–1043.
[16] Y.X. Tan, W.D. Marshall, J.S. Blai, Slurry preparation by high-pressure homogenization for cadmium, copper and lead determination in cervine liver and kidney by electrothermal atomic absorption spectrometry, Analyst 121 (1996) 483–488.
[17] M.G.R. Vale, N. Oleszczuk, W.N.L. dos Santos, Current status of direct solid sampling for electrothermal atomic absorption spectrometry—A critical review of the development between 1995 and 2005, Appl. Spectrosc. Rev. 41 (2006) 377–400.
[18] C. Ozeroglu, G. Keceli, Removal of strontium ions by a crosslinked copolymer containing methacrylic acid functional groups, J. Radioanal. Nucl. Chem. 268 (2006) 211–219.
[19] N. Tokman, The use of slurry sampling for the determination of manganese and copper in various samples by electrothermal atomic absorption spectrometry, J. Hazard. Mater. 143 (2007) 87–94.