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Microextraction based on solidification of a floating organic drop followed by electrothermal atomic absorption spectrometry for the determination of ultratraces of lead and cadmium in waters

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A procedure for the determination of ultratraces of lead and cadmium by liquid-phase microextraction based on solidification of a floating organic droplet (LPME-SFO) separation and electrothermal atomic absorption spectrometry (ETAAS) has been developed. For this purpose, 50 μL of pre-heated (50 $^{\circ}\text{C}$) undecanoic acid (UA) are added to 25 mL of aqueous sample solution at pH 5. The mixture, maintained at 50 $^{\circ}\text{C}$, is stirred at 1000 rpm for 10 min and then the vial is immersed in an ice-bath, which results in the solidification of the UA drop that is easily separated. Injection into the atomizer is carried out after a gentle heating. By impregnating the atomizer with tungstate as a permanent chemical modifier, the detection limits were 10 and 0.5 ng L^{-1} with enrichment factors of 380 and 420, for lead and cadmium, respectively. The relative standard deviation was in the 2.8–3.2% range ($n = 5$, 25–400 ng L^{-1} Pb(II) and 1–15 ng L^{-1} Cd(II)). The proposed method has been applied to the determination of lead and cadmium in bottled, tap and sea water samples, the reliability of the results being verified by means of recovery tests and by using ICP-MS.

Introduction

It is well known that lead and cadmium are two of the most hazardous elements to human health because they cause adverse effects on metabolic processes. As a result, the maximum allowable levels of these metals in drinking water have nowadays been severely restricted by international regulations on water quality. In fact, cadmium and lead concentrations in tap water samples are very low, and values in the 0.06–4.3 and 0.07–15.8 $\mu\text{g L}^{-1}$ ranges, respectively, have been reported among others.^{1–3} Consequently, reliable and sensitive analytical procedures are necessary to carry out the measurements. Leaving aside inductively coupled plasma mass spectrometry (ICP-MS), a powerful technique that can deal with the problem, another possibility is the use of electrothermal atomic absorption spectrometry (ETAAS), since ETAAS instrumentation is present in practically all laboratories worldwide. Despite the good sensitivity of ETAAS, and due to the very low levels present in waters, some type of preconcentration stage is required in order to carry out the measurement.

In recent years there has been a growing interest in the development of miniaturized preconcentration methods based on liquid–liquid or solid phase extraction,^{4,5} an approach that allows high preconcentration factors to be obtained, thus rendering the ETAAS determination feasible even at such low levels. There is a large diversity of closely related miniaturized techniques for the purpose of preconcentration, dispersive liquid–liquid microextraction (DLLME)^{6,7} being one of the most significant for inorganic ultratrace analysis. One of these

techniques is that termed liquid phase microextraction by solidification of a floating organic droplet (LPME-SFO).⁸ Here, a few microlitres of an organic solvent with a low melting point are used for extraction. The aqueous sample solution is stirred and maintained at such a temperature that the organic droplet remains melted in order so that the extraction occurs. Once the process is finished and the liquid cooled, the solidified extractant floats on the aqueous sample and can be easily separated by means of a spatula. This technique has been successfully applied using undecanol and dodecanol to concentrate substances like trihalomethanes,⁹ organochlorine¹⁰ and organophosphorus pesticides,¹¹ polycyclic aromatic hydrocarbons,⁸ pyrazoline derivatives¹² and some metals like lead,¹³ cobalt and nickel.¹⁴

Recently, a modification to this technique has been proposed, in which the extractant is mixed with a suitable amount of a dispersing agent, like in DLLME. Thus, the analyte extraction process has been reported to be very rapid, the emulsion being broken by centrifugation. This combination of DLLME with LPME-SFO has been named as dispersive liquid–liquid microextraction with solidification of a floating organic droplet (DLLME-SFO).^{15,16}

As has been pointed out, the solvent to be used for LPME-SFO should have a low volatility, as well as a low melting point¹⁴ and, up to date 1-undecanol (m.p. 11–14 $^{\circ}\text{C}$) and 2-dodecanol (m.p. 22–26 $^{\circ}\text{C}$) have been recommended.^{13,14} This manuscript reports our studies for lead and cadmium preconcentration by using undecanoic acid (UA), that acts both as the complexing and extracting agent. The physico-chemical properties of UA are similar to those of the reagents cited, but its use can be advantageous since no additional complexing agent is required. On the contrary, it is important to bear in mind that UA is a weak acid (pK close to 5) so that its solubility in water increases in alkaline medium hindering its use for the purpose here considered. Since

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the UA melting point is low (28–31 °C) it is suitable for extraction using the solidified organic drop approach. LPME-SFO proved to be more effective than DLLME-SFO for this purpose. After the preconcentration stage, final measurement was carried out by ETAAS and, since UA has a relatively low boiling point, its easy elimination during the heating cycle allowed low background values to be obtained. In this way, the optimized procedure makes available the measurement of very low levels of these elements to most of the laboratories worldwide.

Experimental

Apparatus

A model 939QZ atomic absorption spectrometer (ATI-Unicam, Cambridge, UK) equipped with a Zeeman-based correction device and a longitudinally-heated graphite furnace atomizer was used. Pyrolytic graphite platforms inserted into pyrolytically coated graphite tubes were used for atomization. Argon was used as the inert gas, the flow rate being 300 mL min⁻¹ during all the stages, except atomization when the flow was stopped. Measurements were carried out in the peak area mode using lead and cadmium hollow cathode lamps (Perkin-Elmer, Shelton, USA) operated at 10 mA and 283.3 nm and 4 mA and 228.8 nm, respectively. The instrumental parameters used are summarized in Table 1. For verification purposes, an ICP-MS instrument (Agilent 7500 ce, Agilent, Waldbronn, Germany) operated in the conditions recommended by the manufacturer was used.

To decrease the risk of lead and cadmium contamination, only plastic (polypropylene) vessels were used for preparing and storing the solutions. Pipette tips were also of polypropylene. All

plasticware was nitric acid-washed and rinsed with ultrapure water.

Reagents

High quality water, obtained using a Milli-Q system (Millipore, Bedford, MA, USA), was used exclusively. Stock solutions of lead and cadmium (1000 mg L⁻¹) were prepared by dissolving appropriate amounts of Pb(NO₃)₂ and CdO (Fluka, Buchs SG, Switzerland), respectively. Working solutions were obtained daily by stepwise dilution of the stock solutions. Undecanoic acid was obtained from Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, Germany). The rest of the chemicals used were obtained from Fluka. A 1 M acetic acid/sodium acetate solution was used to adjust the pH of the sample. For the study of pH, phosphate-based and ammonium/ammonia buffer solutions were also used.

Impregnation of the tubes and platforms with tungsten

Tungsten was used as a permanent modifier. To this purpose, as indicated elsewhere^{6,17} the tube and platform were immersed in a solution containing Na₂WO₄·2H₂O (1g L⁻¹) and left overnight. These graphite parts were subsequently dried in an oven at 120 °C for 4 h and finally submitted to a simple temperature programme¹⁸ for conditioning before the first use (Table 1).

Procedure

To 25 millilitres of sample placed in a 30 mL screw cap vessel vial with flat bottom, 0.25 mL of a 1 mol L⁻¹ acetate buffer solution of pH = 5 was added. The solution was heated at 50 °C using a thermostatic block placed on a magnetic stirrer and next stirred using a high speed (at least 1000 rpm). Then 50 µL undecanoic acid (UA), preheated to 50 °C, were incorporated with a micro-pipette and the stirring maintained for ten minutes. Next, the stirring speed was reduced to 300 rpm for 2 min in order to group all the droplets and the vial was cooled in an ice bath. The solidified UA was removed with a spatula placing it in a 2 mL Eppendorf vial. The vial was heated in a heat block at 50 °C, a 10 µL aliquot of the liquid was taken and injected into the atomizer and the programme given in Table 1 was run. Calibration was carried out using aqueous standards submitted to the same sample treatment.

Results and discussion

Preliminary experiments were carried out using solutions containing 200 and 5 ng L⁻¹ Pb(II) and Cd(II), respectively, and devoted to test the use of UA for DLLME-SFO. It was verified that it allowed a good, very rapid extraction process, but the separation of the solidified UA after the cooling stage was difficult, since the fine droplets originated made necessary the solution to be centrifuged twice, which counteracted the advantage of the rapid extraction stage characteristic of DLLME methodology. So, the use of a disperser solvent was discarded and the efforts focused in LPME-SFO. In conventional LPME-SFO, the small volume of extracting solvent floats at the top of the aqueous sample solution during stirring so that the contact surface between the organic and aqueous phases is small and, consequently, a relatively long extraction time is required. To

Table 1 Instrumental parameters

Parameter	Pb	Cd
Lamp intensity, mA	14 (HCL)	4 (HCL)
Wavelength, nm	283.3	228.8
Slit, nm	0.5 nm	
Atomizer type	graphite tube with platform inserted	
Injection volume, µL	10	
Permanent modifier	Tungstate coating	
Background correction	Zeeman	

Recommended furnace heating programme

Step	Temperature, °C	Ramp, °C s ⁻¹	Hold, s
Injection with heating	80	0	20
Dry	300	10	20
Pyrolysis	500	10	30
Atomization ^{a,b}	1700 (Pb) and 1300 (Cd)	0	5
Cleaning	2300	0	3

^a Internal argon flow stopped. ^b Reading step.

Temperature programme for conditioning the impregnated atomizer

Step	Temperature, °C	Ramp, °C s ⁻¹	Hold, s
1	120	1	120
2	200	5	120
3	1200	5	30
4	2400	1	6

improve this, we propose to use a high stirring rate in the magnetic stirrer, so that a pronounced vortex is originated at the top-center of the solution. Thus, when UA is incorporated, the microdrop is broken into many small droplets that suffer repeated movements towards the bottom and the top of the sample solution as a consequence of the high stirring rate and the low density of the organic phase. The final result is that a large contact surface between the aqueous sample and the organic droplets is achieved, thus leading to a fast extraction process. This is a distinctive, advantageous characteristic of the procedure here proposed.

Optimization of the ETAAS measurement

Preliminary experiments proved that, in order to obtain well defined analytical signals and low background values during the atomization stage, a chemical modifier should be used. In the absence of a chemical modifier, losses of lead and cadmium were observed for pyrolysis temperatures above 500 and 300 °C, respectively. A suitable way of carrying out chemical modification in the case considered here that involves two immiscible phases is the use of “permanent” chemical modifiers, so that one single treatment of the graphite atomizer could be effective for a large number of firings. Molybdenum, iridium and tungsten salts were assayed for this purpose in two ways, namely, by injecting a concentrated solution of the modifier and by impregnation obtained by immersing the atomizer overnight in the solution. Ashing-atomizing curves were obtained in each case, and the results compared, looking for a low background value during the atomization stage, maximum sensitivity and repeatability of the analytical signal and duration in the effectiveness of the permanent modifier. The best results were obtained using impregnation of the pyrolytic material with a tungsten salt, as indicated in Experimental. This simple-to-use chemical modifier has already proved effective in the stabilization of these analytes when preconcentrated by means of DLLME.¹⁸ The optimal pyrolysis temperature was found to be 500 °C, the atomization temperatures being finally fixed at 1700 and 1300 °C for lead and cadmium, respectively.

Effect of the experimental conditions. Efficiency of the microextraction stage

The effect of the acidity of the medium was studied and the results, summarized in Fig. 1A, showed that the extraction reached a maximum at pHs close to 5. For pH values above 7 the repeatability of the measurements was poor, which could be attributable to the solubilization of the reagent. A pH 5 obtained by means of a 0.01 mol L⁻¹ acetic/acetate buffer solution is recommended.

An important aspect to be considered is the efficiency of preconcentration. To this purpose, the effect of varying the volume of the aqueous phase maintaining a 50 µL UA constant volume was studied. There was a linear behavior up to 50 mL which corresponded to an aqueous to organic volume ratio of 1000. However, this high volume ratio is not recommended since it requires more contact time between the two phases to reach an equilibrium, and so a ratio of 500 which corresponds to 25 mL of aqueous phase and 50 µL of organic phase was selected (Fig. 1B).

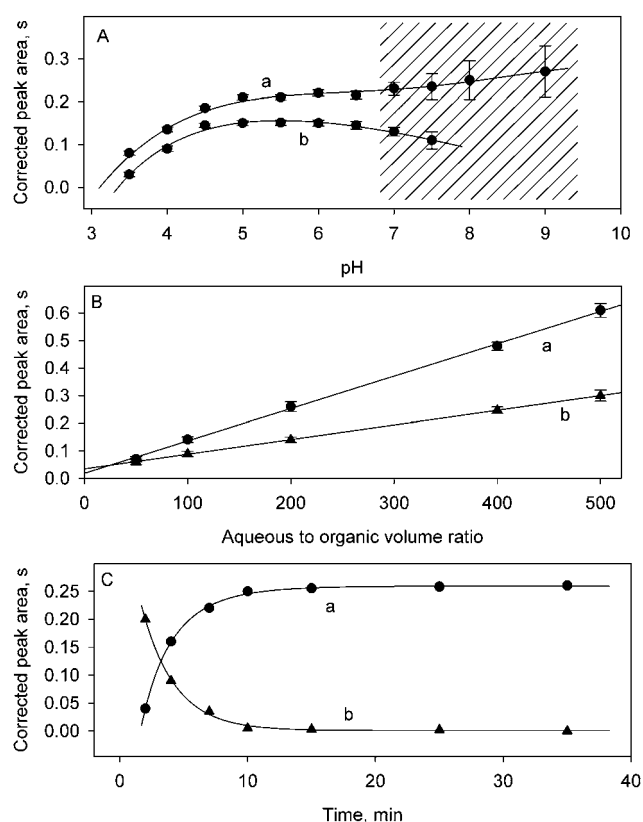


Fig. 1 Effect of some experimental parameters. Graph A: Effect of pH on the signal obtained using the recommended conditions of solutions containing 200 and 5 ng L⁻¹ lead and cadmium (curves a and b), respectively; Graph B: Volumetric ratio of aqueous to organic phase for lead (curve a) and cadmium (curve b), respectively; the volume of the organic phase was fixed at 50 µL; Graph C: Effect of the extraction time for both first and second extraction (curves a and b, respectively) of a solution containing 200 ng L⁻¹ lead.

In these conditions, an apparent efficiency of preconcentration of 380 and 420 times for lead and cadmium, respectively, was obtained indicating a high extraction percentage. These values were calculated by dividing the calibration slope obtained from aqueous solutions submitted to the microextraction process by the calibration slope obtained for aqueous solutions that were not extracted. In the latter case, the heating programme shown in Table 1 was slightly modified by using 130 °C as the drying temperature. No significant differences in sensitivity were noted when the measurements were carried out in the aqueous solutions or UA extracts.

Table 2 Tolerance limits of coexisting ions

Coexisting ions	Tolerance limits (mg/L) ^a
Cl ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	5000
Ca ²⁺ , Mg ²⁺ , Ba ²⁺	1000
Cu ²⁺ , Co ²⁺ , Zn ²⁺ , Mn ²⁺	50
Ni ²⁺	10
Fe ³⁺ , Al ³⁺ , Cr ³⁺	5

^a maximum amount tested.

The volume of UA used as the extractant was also studied in the 15 to 50 μL range. Very small volumes are not advisable because a part of UA dissolves in the aqueous solution during the process. In the conditions recommended in Experimental, it was found that when 50, 40 and 30 μL UA were used, the amounts of organic phase recovered after the cooling stage (18–20 $^{\circ}\text{C}$) were approximately 40, 30 and 20 μL , respectively, that is, about 10 μL UA passed to the aqueous phase. In order to have a suitable volume of organic phase to be transferred to the atomizer in a safe way, the recommendation is to use 50 μL UA.

The effect of the extraction time was studied for both analytes and the results for lead are shown in Fig. 1C. As can be seen, the signal obtained (curve a) was practically constant and reached a maximum after 10 min. Similar results were found for cadmium. On the other hand, to verify the high percentage of extraction, each solution was extracted twice, the analytical signal being also obtained after the second extraction. The results for lead shown in Fig. 1C (curve b) prove that although the extraction was not complete, the percentage of analyte extracted was very high. The values calculated, that taking into account the way in which they were obtained have to be considered as indicative, were 92 and 94% for lead and cadmium, respectively.

The relevance of using a high stirring rate to fragment the UA drop into droplets, thus speeding up the extraction process should be emphasized. Using a 29 mm outer diameter vial containing 25 ml of aqueous solution, the height of the liquid column is about 50 mm. When the solution is stirred (1000 rpm) by means of a 10×3 mm stir bar, a vortex that extends down to the base of the vial is obtained. In this way, the 50 μL UA drop is easily fragmented into small droplets that easily regroup when the stirring speed is reduced to 300 rpm. On the other hand, the extraction temperature has to be high enough to allow UA to be in the liquid form. However, high temperatures lead to excessive UA solubility in the aqueous phase, while the global process slows down because more time is needed for cooling the solution after extraction. The recommended value is 50 $^{\circ}\text{C}$.

Table 3 Summary of analytical characteristics

Characteristic	Pb(II)	Cd(II)
Linear dynamic range (ng L^{-1})	25–400	1–15
Detection limit ^a (ng L^{-1})	10	0.5
Calibration function (5 standards, $n = 3$)	$A_{\text{int}} = 0.034 + 0.0011 \cdot C_{\text{Pb}}$	$A_{\text{int}} = 0.025 + 0.041 \cdot C_{\text{Cd}}$
Correlation coefficient	0.9985	0.9978
Relative standard deviation ($n = 5$) (%)	2.8	3.2
Sampling frequency (samples h^{-1})	3	3
Sample volume (mL)	25	25
Preconcentration factor ^b	380	420

^a Calculated on the basis of $3s_{y/x}$. ^b Compared with direct injection of aqueous solutions.

Table 4 Characteristics of similar microextraction procedures for the determination of lead and cadmium in water samples

Extraction method	Analyte	Detection technique	Preconcentration factor	Extraction time (min)	Sample volume (mL)	Linear range ($\mu\text{g L}^{-1}$)	Ref.
DLLME ^a	Pb	FAAS	450	0	25	1–70	19
SI-DLLME ^b	Pb	FAAS	265	2	12	2.3–260	20
SDME ^c	Pb	ETAAS	16	20	1	0–40	21
CF-SDME ^d	Pb	ETAAS	45	15	7.5	0–60	22
IL-SDME ^e	Pb	ETV-ICP-MS	60	10	1.5	0.05–40	23
IL-SDME	Pb	ETAAS	76	7	1.75	0.025–0.8	24
IL-USA-DLLME ^f	Cd	ETAAS	67	2	10	0.02–0.15	25
LPME ^g	Cd	ETAAS	390	15	2	0.01–1	26
LPME-SFO	Cd	FL-FAAS	640	15	160	0.08–30	27
SDME	Cd	ETAAS	65	10	5	0.01–1	28
SDME	Pb, Cd	ETC-ICP-MS	190, 140	15	0.2	0.01–50	29
HF-LPME	Pb, Cd	ICP-MS	73, 29	15	2.5	0.02–30	30
CPE ^h	Pb, Cd	FL-FAAS	~18	5	15	25–2000, 2.5–500	31
DLLME	Pb, Cd	ETAAS	115	0	5	0.03–1, 0.01–0.3	18
LPME-SFO	Pb, Cd	ETAAS	380, 420	10	25	0.025–0.4, 0.001–0.015	This work

^a Dispersive liquid–liquid microextraction. ^b Sequential injection dispersive liquid–liquid microextraction. ^c Single drop microextraction. ^d Continuous flow single drop microextraction. ^e Ionic liquid single drop microextraction. ^f Ionic liquid ultrasound assisted dispersive liquid–liquid microextraction. ^g Liquid-phase microextraction. ^h Cloud point extraction.

Table 5 Determination of lead and cadmium in water samples

Sample	Added (ng L ⁻¹)		Found ^a (ng L ⁻¹)		ICP-MS values ^b (ng L ⁻¹)	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)
Tap water 1	0	0	320 ± 4	64 ± 0.8	307 ± 9	56 ± 2
	200	5	513 ± 5 (96.5)	68.9 ± 0.9 (98)		
Tap water 2	0	0	85 ± 2	16.2 ± 0.7	91 ± 5	19 ± 3
	200	5	286 ± 3 (100.5)	21.1 ± 0.6 (98)		
Tap water treated with a domestic inverse osmosis system	0	0	52 ± 2	3.1 ± 0.5	50 ± 6	5 ± 1
	200	5	251 ± 3 (99.5)	8.2 ± 0.6 (102)		
Sea water 1	0	0	67 ± 2	13.5 ± 0.6	60 ± 5	11 ± 2
	200	5	261 ± 3 (97)	18.4 ± 0.6 (98)		
Sea water 2	0	0	158 ± 5	27 ± 0.9	167 ± 8	32 ± 3
	200	5	357 ± 6 (99.5)	32.1 ± 0.8 (102)		

^a Mean of five determinations ± standard deviation, values in brackets indicate relative recovery (%). ^b Mean of three determinations ± standard deviation.

The ionic strength was varied by incorporating potassium nitrate in the 0.01–1 mol L⁻¹ range, and no effect was observed. The effect of potential interferences was also examined (Table 2). In these experiments, solutions of 200 and 5 ng L⁻¹ Pb(II) and Cd(II), respectively, containing the added interfering ions were treated according to the recommended procedure under the optimal conditions. The common cations and anions present in natural water possess no adverse effects (maximum amounts tested 5 g L⁻¹). The presence of more than 10 mg L⁻¹ of Ni²⁺, Fe³⁺, Al³⁺ and Cr³⁺ led to a decrease of 10% in the analytical signal. This is not a serious drawback since the sensitivity is so high that the sample may be diluted, if necessary.

Figures of merit and analytical results

Table 3 summarizes the results obtained using 25 mL for the aqueous phase and 50 µL for the organic phase (UA). The detection limits were calculated on the basis of three times the standard error from calibrating regression (s/x). The very low detection limits are the consequence of both the high pre-concentration factor and the low standard deviation of the blank. The preconcentration or enrichment factors were calculated as mentioned before. The values obtained for both analytes were very similar, the difference being mainly attributable to the experimental error. In any case, these values confirm that, although extraction is not total, most of the metals are transferred to the organic phase. Table 4 shows the main characteristics of the microextraction procedures for cadmium and lead reported up to date. As can be seen, the procedure here studied is particularly sensitive. To this favourable feature should be added the fact that is very simple to be carried out, only requiring a single reagent, which together with the use of an easy-to-apply chemical modifier results in an excellent relative standard deviation of the measurements.

The proposed procedure was applied to the determination of cadmium and lead in twelve samples, namely seven bottled mineral waters of different brands, three tap waters and two sea waters obtained near of the shore but faraway of a small

harbour. In all cases, recovery tests were carried out to check the reliability of the measurements (Table 5). The results for the mineral waters, that are not shown for shortening, provided values in the 16–180 and 2.5–9 ng L⁻¹ ranges for lead and cadmium, respectively. Despite the very low DLs of the procedure, no cadmium nor lead could be detected in two of these samples. The differences found between the samples labeled as tap water 1 and 2 are noteworthy. The first sample was obtained in a 25-years old lab, while the second correspond to a building provided with a modern water supply system. The reliability of the procedure was checked, in addition, by comparing the results with those obtained by means of ICP-MS (Table 5), and the application of a common comparison test (Wilcoxon test) did not reveal significant differences at the 95% confidence level.

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References

- N. Burham, S. M. Abdel-Azeem and F. El-Shahat, *Int. J. Environ. Anal. Chem.*, 2008, **88**, 775–789.
- P. P. Mumba, B. Q. Chibambo and W. Kadewa, *Int. J. Environ. Res.*, 2008, **2**, 61–64.
- L. A. Portugal, H. S. Ferreira, W. N. L. dos Santos and S. L. C. Ferreira, *Microchem. J.*, 2007, **87**(1), 77–80.
- F. Pena-Pereira, I. Lavilla and C. Bendicho, *Spectrochim. Acta*, 2009, **64B**, 1–15.
- C. Nerin, J. Salafranca, M. Aznar and R. Batlle, *Anal. Bioanal. Chem.*, 2009, **393**(3), 809–833.
- R. E. Rivas, I. Lopez-Garcia and M. Hernandez-Cordoba, *Spectrochim. Acta*, 2009, **64B**(4), 329–333.
- Y. Liu, E. C. Zhao, W. T. Zhu, H. X. Gao and Z. Q. Zhou, *J. Chromatogr. A*, 2009, **1216**(6), 885–91.
- M. R. Khalili-Zanjani, Y. Yamini, S. Shariati and J. A. Jönsson, *Anal. Chim. Acta*, 2007, **585**(2), 286–293.

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- 9 H. Farahani, P. Norouzi, R. Dinarvand and M. R. Ganjali, *J. Sep. Sci.*, 2009, **32**(2), 314–320.
 - 10 H. Farahani, Y. Yamini, S. Shariati, M. R. Khalili-Zanjani and S. Mansour-Baghahi, *Anal. Chim. Acta*, 2008, **626**(2), 166–173.
 - 11 M. R. Khalili-Zanjani, Y. Yamini, N. Yazdanfar and S. Shariati, *Anal. Chim. Acta*, 2008, **606**(2), 202–208.
 - 12 H. R. Sobhi, Y. Yamini, A. Esrafil and M. Adib, *J. Pharm. Biomed. Anal.*, 2008, **48**(4), 1059–1063.
 - 13 S. Dadfarnia, A. M. Salmanzadeh and A. M. H. Shabani, *Anal. Chim. Acta*, 2008, **623**(2), 163–167.
 - 14 M. S. Bidabadi, S. Dadfarnia and A. M. H. Shabani, *J. Hazard. Mater.*, 2009, **166**(1), 291–296.
 - 15 H. Xu, Z. Q. Ding, L. L. Lv, D. D. Song and Y. Q. Feng, *Anal. Chim. Acta*, 2009, **636**(1), 28–33.
 - 16 M. I. Leong and S. D. Huang, *J. Chromatogr., A*, 2008, **1211**(1–2), 8–12.
 - 17 H. Fritzsche, W. Wegscheider, G. Knapp and H. M. Ortner, *Talanta*, 1979, **26**, 219–226.
 - 18 R. E. Rivas, I. Lopez-Garcia and M. Hernandez-Cordoba, *Microchim. Acta*, 2009, **166**(3–4), 355–361.
 - 19 M. T. Naseri, P. Hemmatkhah, M. R. M. Hosseini and Y. Assadi, *Anal. Chim. Acta*, 2008, **610**, 135–141.
 - 20 A. N. Anthemidis and K. I. G. Ioannou, *Talanta*, 2009, **79**, 86–91.
 - 21 P. Liang, R. Liu and J. Cao, *Microchim. Acta*, 2008, **160**, 135–139.
 - 22 J. Cao, P. Liang and R. Liu, *J. Hazard. Mater.*, 2008, **152**, 910–914.
 - 23 L. B. Xia, X. Li, Y. L. Wu, B. Hu and R. Chen, *Spectrochim. Acta*, 2008, **63B**, 1290–1296.
 - 24 J. L. Manzoori, M. Amjadi and J. Abulhassani, *Anal. Chim. Acta*, 2009, **644**, 48–52.
 - 25 S. Q. Li, S. Cai, W. Hu, H. Chen and H. L. Liu, *Spectrochim. Acta*, 2009, **64B**, 666–671.
 - 26 S. Nazari, *Microchem. J.*, 2008, **90**, 107–112.
 - 27 S. Dadfarnia, A. M. H. Shabani and E. Kamranzadeh, *Talanta*, 2009, **79**, 1061–1065.
 - 28 Z. F. Fan and W. Zhou, *Spectrochim. Acta*, 2006, **61B**, 870–874.
 - 29 L. Li, B. Hu, L. B. Xia and Z. C. Jiang, *Talanta*, 2006, **70**, 468–473.
 - 30 L. B. Xia, Y. Wu and B. Hu, *J. Mass Spectrom.*, 2007, **42**, 803–810.
 - 31 E. L. Silva and P. S. Roldan, *J. Hazard. Mater.*, 2009, **161**, 142–147.