



Determination of lead in environmental waters with dispersive liquid–liquid microextraction prior to atomic fluorescence spectrometry

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ABSTRACT

This paper established a new, rapid and sensitive method for the determination of lead in water samples preconcentrated by dispersive liquid–liquid microextraction (DLLME) prior to atomic fluorescence spectrometry. Dithizone was used as the chelating agent. In the DLLME procedure, lead formed lead–dithizone complex and migrated into the carbon tetrachloride micro-droplets. Important factors that would affect the extraction efficiency had been investigated including the kind and volume of extraction solvent and dispersive solvent, sample pH, the amount of chelating agent, extraction time and centrifugation time. The results showed that the coexisting ions containing in water samples had no obvious negative effect on the determination of lead. The experimental results indicated that the proposed method had a good linear range of 0.01–100 ng mL⁻¹ ($r^2 = 0.9990$). The precision was 2.12% (RSD, $n = 7$) and the detection limit was 0.95 ng L⁻¹. Proposed method was validated with four real environmental samples and the results indicated that the proposed method was excellent for the future use and satisfied spiked recoveries were in the range of 92.9–97.4%.

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1. Introduction

Trace levels of heavy metals are widely distributed in environment due to soil erosion, industrial and agricultural processes [1]. Nowadays the pollution by heavy metals from various environmental sources has absorbed much more attention [2]. Lead, cadmium, nickel, and mercury are heavy metals of unquestionable toxicity [3–5]. These metals are main sources of contamination for human being found in water and foods. Lead is one of the most hazardous elements to human health, because it can cause adverse effect on metabolic processes of human beings [6], and lead has been proved to be a carcinogenic agent. So many nations and international organizations have set an allowable level for lead. For example, the World Health Organization (WHO) has made a maximum allowable limit of 10 µg L⁻¹ for lead in drinking water [7].

The analytical methods of lead usually involves in using flame atomic absorption spectrometry (FAAS), electrothermal atomic

absorption spectrometry (ETAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) [8–12]. These instruments have sufficient sensitivity, however some of them are very expensive, and not available for a common analytical laboratory. Atomic fluorescence spectrometry is a relatively new and sensitive method for elemental analysis, and has been successfully used for the determination of cadmium, zinc, the speciation of mercury and arsenic [13–17]. Atomic fluorescence spectrometry has also reported for the determination of lead [18,19]. In this experiment, it is utilized because of its merits such as simplicity, easy to operate, low cost and high sensitivity. Moreover, it is often difficult to determine lead directly at very low concentrations because of the matrix interferences occurring in real samples. Hence a preliminary separation and preconcentration step are often needed.

Up to now, many sample preconcentration methods have been developed for the enrichment of lead in water samples, for example, knotted reactor [20], combination of flow injection and cloud point extraction [21], solid phase extraction [22,23], cloud point extraction [24], capillary microextraction [25], solid phase microextraction [26], and liquid phase microextraction [27]. Generally, solid phase extraction is the most widely used one because of its merits such as simplicity, rapidness, low cost, low consumption of organic solvents, and high enrichment factor. Solid phase

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microextraction is also an important technique with many merits, however a derivatization step is needed when it is used for the determination of lead [24]. Recently, liquid phase microextraction has become another popular enrichment method in analytical and environmental fields. Some valuable liquid phase microextraction methods have been developed and applied for the analysis of many analytes. One of them is dispersive liquid–liquid microextraction (DLLME), which has attracted increasing attention for its simplicity, easy to operate, rapidness, and high extraction efficiency. In this extraction procedure, two organic solvents having different characteristics are involved in use, one is hydrophilicity which performs as dispersive solvent such as methanol and acetone [28,29] and the other is hydrophobicity which performs as extraction solvent such as chlorobenzene and carbon tetrachloride [30,31]. The extraction solvent would form innumerable infinite small droplets, when it was rapidly injected into the sample solution. These droplets limitlessly enlarge the contact area between extraction solvent and analytes. Until now, this method has been successfully applied for the determination of heavy metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polyphenol-like compounds, polybrominated diphenyl ethers (PBDEs), pesticides and herbicides [32–41]. There are some reports on the application of DLLME for the determination of lead in water samples, but GFAAS and ETAAS are often used as the detection techniques. The extraction solvents were xylene and carbon tetrachloride, and the chelating agents were 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and ammonium pyrrolidine dithiocarbamate, and usually methanol and acetone were used as the dispersive solvents [12,42]. However, it has not found related reports on the combination of atomic fluorescence spectrometry and DLLME.

The goal of present study is to develop a new method for the sensitive determination of lead in water samples utilizing the merits of atomic fluorescence spectrometry and DLLME. Dithizone, an often-used chelating agent, is employed for forming complex with lead. Factors that would influence the efficiency of DLLME extraction and the determination of atomic fluorescence spectrometry were investigated.

2. Experimental

2.1. Reagents

Stock standard solution of lead with a concentration of 1000 mg L^{-1} was obtained by dissolving appropriate amount of lead nitrate obtained from Beijing Chemical Engineering technique Co. Ltd. (Beijing, China) in double-distilled water. Working standard solution was obtained by appropriate dilution of the stock standard solution. The solution of dithizone was prepared by dissolving an appropriate amount of dithizone purchased from Shanghai Reagent Factory (Shanghai, China) in ethanol. The double-distilled water was prepared in the lab using quartz–glass vaporization purchased from Shanghai Ya-rong Biochemistry Instrument Factory (Shanghai, China) and all the other solvents were analytical reagent grade unless otherwise stated. Concentrated ammonia and 1 mol L^{-1} hydrochloric acid were used for adjusting the sample pH. All glassware used in the experiments were cleaned with pure water, then soaked in 6 mol L^{-1} nitric acid over 24 h and then washed with ultra-pure water.

2.2. Apparatus

An AF-610B Atomic Fluorescence Spectrophotometer equipped with lead hollow cathode lamp was purchased from Beijing Ruili Analytical Instruments Co. Ltd. (Beijing, China). A model Anke TDL-40B centrifuge obtained from Shanghai Anting Scientific

Instruments Factory (Shanghai, China) was used for accelerating the phase separation. The main instrument parameters were listed as below. Negative high voltage of PMT, lamp current, atomizator height, flow rate Argon gas, flow rate of shielding gas and injection volume are 280 V, 80 mA, 11 mm, 700 mL min^{-1} , 800 mL min^{-1} , 2 mL, respectively.

2.3. Dispersive liquid–liquid microextraction

In the preconcentration procedure, 50 mL ultrapure water or water sample was added into a 50 mL plastic centrifuge tube. $20 \mu\text{L}$ $10 \mu\text{g mL}^{-1}$ of lead standard solution was spiked into the aqueous solution to give a spiked concentration of lead at 4 ng mL^{-1} . Sample pH was adjusted to pH 8.0 with 27% concentrated ammonia. 3 mL ethanol containing $250 \mu\text{L}$ tetrachloride carbon and reasonable amount of dithizone was rapidly injected into the aqueous solution with a 5 mL syringe, a turbid phase immediately was formed. Then the solution was centrifuged at 3000 rpm for 20 min. The upper aqueous phase was removed with a syringe, and the residue carbon tetrachloride was vaporized to dryness and further dissolved in 2.5 mL 1.5% HCl. The final solution was determined with the Atomic Fluorescence Spectrophotometer.

2.4. Real water sample analysis

In this experiment, four environmental samples from the exit of the effluent from three factories and a wastewater treatment factory in Xinxiang City, Henan Province (Xinxiang, China) were used to validate the proposed method. Before use all the water samples were filtered through $0.45 \mu\text{m}$ micro-pore membranes and stored in brown glass containers under low temperature.

3. Results and discussion

DLLME is a new mode of liquid phase microextraction, its principle is as the same of conventional liquid–liquid extraction. Compared with a conventional liquid phase microextraction such as a single drop microextraction, DLLME infinitely enlarges the surface area of the extraction solvent and the contact area between extraction solvent and analytes, which significantly enhance recoveries of analytes. In this enrichment procedure, some important parameters that would influence the enrichment performance and they were investigated for obtaining the optimal extraction conditions. The extraction recovery was calculated with the ratio between the determined sample concentration and the spiked sample concentration.

3.1. Effect of the concentration of dithizone

Dithizone was a good chelating agent for lead extraction and its chelating ratio was 2:1. Enough dithizone was needed to assure that lead would be extracted completely. Therefore, the concentration of dithizone was investigated over the range of $0.0025\text{--}0.1 \text{ mmol L}^{-1}$. Fig. 1 exhibited that when the concentration of dithizone was up to $0.009 \text{ mmol L}^{-1}$, lead would be extracted completely, and with the further increase of the concentration of dithizone, the extraction efficiency had no significant increase. In order to assure the complete extraction of the lead, 0.01 mmol L^{-1} of dithizone was used in the subsequent experiments.

3.2. Selection of extraction solvent and its volume

In conventional liquid phase extraction and liquid phase microextraction, the kind of extraction solvent and its volume are crucial parameters, which significantly influence the extraction efficiency of the analytes. Generally, the selection of extraction

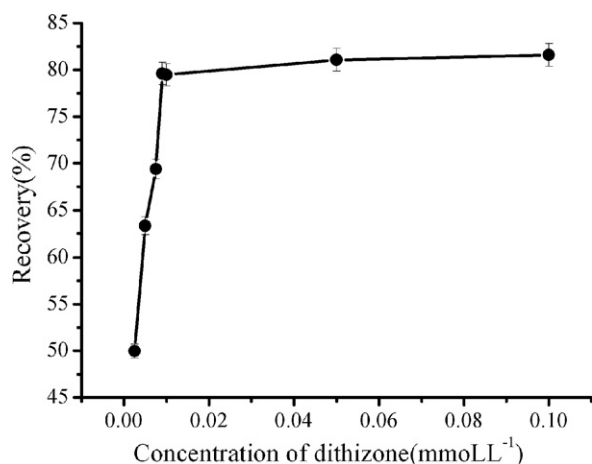


Fig. 1. The effect of concentration of dithizone. Concentration of lead, 4 ng mL⁻¹; volume of carbon tetrachloride, 250 μ L; concentration of dithizone, 0.01 mmol L⁻¹; volume of ethanol, 3 mL; sample pH, pH 8.0; extraction time, 5 min; centrifugation time, 15 min; centrifugation rate, 3000 rpm.

solvent is based on the physical and chemical properties of the solvents. In most cases, the ideal extraction solvent has two properties, one is hydrophobicity, the other is to have higher solubility for the analytes in which than that in water. In this experiment, four organic solvents such as dichloromethane, trichloromethane, carbon tetrachloride, and chlorobenzene were checked. The experimental results demonstrated that very little sedimented phase was found after centrifugation when dichloromethane and trichloromethane were used as the extraction solvents. The recovery of lead was very low at about 8.4% when chlorobenzene was used as the extraction solvent. The recovery of lead reached 79.4% with carbon tetrachloride as the extraction solvent. So carbon tetrachloride was used as the extraction solvent in further experiments. In DLLME, the volume of extraction solvent may change in a relative wide scope. In this experiment, the volume of carbon tetrachloride was optimized between 50 and 450 μ L and the results were exhibited in Fig. 2. As can be seen, the recovery of lead increased along with the increase of volume of carbon tetrachloride from 50 μ L to 250 μ L, and then decreased when the volume of carbon tetrachloride further increased. The increase of recoveries were due to the increase of volume of carbon tetrachloride which can dissolve more lead complex. But when the volume is over 250 μ L, some of carbon

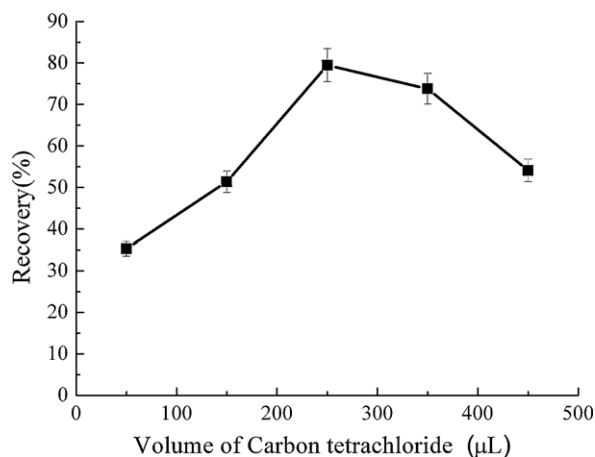


Fig. 2. The effect of the volume of carbon tetrachloride. Concentration of lead, 4 ng mL⁻¹; concentration of dithizone, 0.01 mmol L⁻¹; volume of ethanol, 3 mL; sample pH, pH 8.0; extraction time, 5 min; centrifugation time, 15 min; centrifugation rate, 3000 rpm.

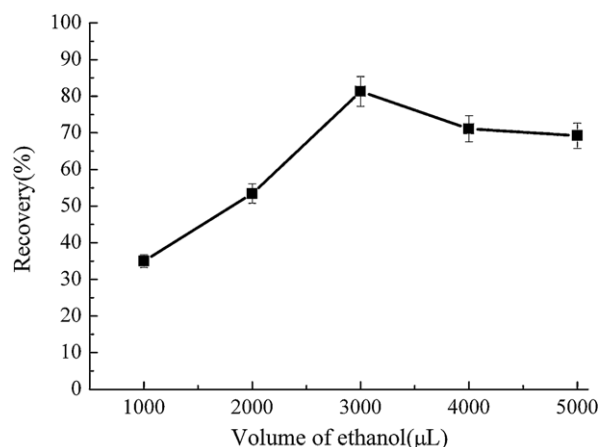


Fig. 3. The effect of the volume of ethanol. Concentration of lead, 4 ng mL⁻¹; volume of carbon tetrachloride, 250 μ L; concentration of dithizone, 0.01 mmol L⁻¹; sample pH, pH 8.0; extraction time, 5 min; centrifugation time, 15 min; centrifugation rate, 3000 rpm.

tetrachloride could not be dispersed into the aqueous solution as infinitesimal drops, and existed as larger drops which decreased the contact area between lead complex and organic drops, that is to say, which reduced the transfer of lead complex into the carbon tetrachloride phase. On the basis of these facts, 250 μ L carbon tetrachloride was selected.

3.3. The selection of kind and volume of dispersive solvent

In DLLME procedure, the kind of dispersive solvent and its volume play important roles in the enrichment of analytes. In order to achieve better dispersing, methanol, ethanol, acetone, and acetonitrile were tested. The results exhibited that the use of methanol and acetonitrile gave much lower enrichment efficiencies. When ethanol and acetone were used as the dispersive solvents, much higher enrichment efficiencies were achieved, and the difference between them was very small. Because ethanol is nontoxic, hence it was used in the followed experiments. The volume of dispersive solvent was also an important factor for achieving good extraction performance. So the volume of ethanol was optimized over the range of 1000–5000 μ L and the results were exhibited in Fig. 3. When the volume of ethanol was small, carbon tetrachloride could not be dispersed completely and cloudy solution could not form. When the volume of ethanol was over 3000 μ L, the solubility of the complex in water would increase with the increase of the volume of ethanol. Meanwhile, parts of carbon tetrachloride was dissolved in ethanol and migrated into aqueous phase. These parts of carbon tetrachloride could not be sedimented down, which accounted for the decrease of the enrichment performance. Therefore, 3000 μ L ethanol was used.

3.4. Effect of sample pH

The sample pH plays an important role in a DLLME extraction procedure. In general, lead ion should be converted into the complex form to make the extraction procedure available. For this propose, the effect of sample pH was investigated systematically in the range of pH 6–10 with dithizone as the chelating reagent, which ensured that lead ion could be extracted as a chelate complex. The results exhibited in Fig. 4 and showed that the recovery of lead increased significantly when the sample pH increased from pH 6 to 8, and decreased when pH was over pH 8. The highest recovery was achieved at pH 8. Thus, the sample pH was set at pH 8 in the following experiments.

Table 1
Effect of coexisting ions.

Coexisting ions	Concentration ratio of existing ions to lead	Enrichment efficiency (%)
Na ⁺	1000	99.20
K ⁺	800	96.90
Ca ²⁺	1000	103.9
Cl ⁻	1000	103.9
Mg ²⁺	600	94.35
SO ₄ ²⁻	600	94.35
Al ³⁺	100	91.67
Zn ²⁺	100	91.52
Fe ³⁺	50	93.01
Ni ²⁺	25	100.6
Cd ²⁺	50	97.65
Cu ²⁺	25	90.12

3.5. Effect of extraction time

In this experiment, extraction time was another parameter for DLLME. The effect of extraction time was optimized over 1–20 min and the results indicated that the recovery of lead increased when the extraction time was changed from 1 to 5 min and decreased slightly when the extraction time was longer than 5 min because of the adsorption onto the wall of the conical tube. According to these, 5 min was chosen in the following study in order to reduce the analytical time of this experiment.

3.6. Effect of centrifugation time

Centrifugation time was another parameter that influenced the separation of carbon tetrachloride from water phase. And the centrifugation time was optimized between 5 and 25 min. The results exhibited that when the centrifugation time was up to 20 min, lead was enriched completely. When the centrifugation time was shorter or longer, the recoveries were both lower than 94.4%. The short centrifugation time could not insure the preferable phase separation, and longer centrifugation time would generate heat which may enhance the dissolving of lead complex into the aqueous phase, which also resulted in the decrease of dissolved lead complex, and all these would lead to the decrease of sedimented amount of Pb complex. On the other hand, the generated heat would make lead to the evaporation of some carbon tetrachloride which enter into the gas phase over the liquid phase. This part of carbon tetrachloride also resulted in the lost of carbon tetrachloride in aqueous solution, which also lead to the decrease of dissolved lead complex. That is to say longer centrifugation time resulted

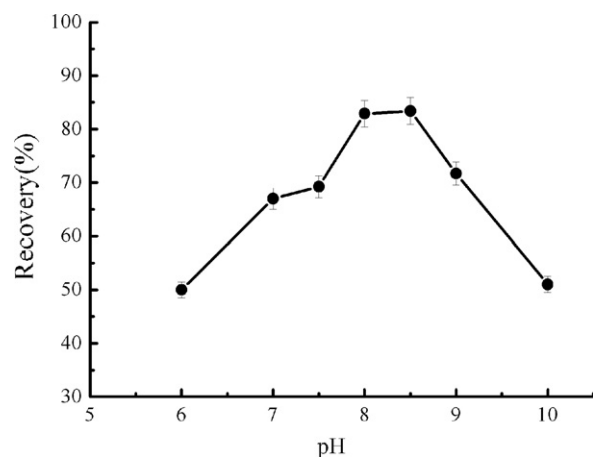


Fig. 4. Effect of sample pH. Concentration of lead, 4 ng mL⁻¹; volume of carbon tetrachloride, 250 μL; concentration of dithizone, 0.01 mmol L⁻¹; extraction time, 5 min; centrifugation time, 15 min; centrifugation rate, 3000 rpm.

in the decrease of extraction efficiency. So 20 min was selected for further use.

3.7. Effect of coexisting ions

Many metal ions existing in environmental waters would form stable chelating complexes with dithizone within a wide pH range and may be co-extracted along with the analytes. Moreover, this competitive chelating effect coupled with co-extracted effect would influence the chelating degree between lead and dithizone and make the extraction efficiency of lead decrease. Therefore, a series of experiments have been designed using a standard solution of 4 ng mL⁻¹ lead under the above-optimized conditions. The results were given in Table 1. The obtained results indicated that the presence of large amounts of cation and anion including Na⁺, K⁺, Mg²⁺, and SO₄²⁻ had no obvious influence on the recovery of lead.

3.8. Analytical performance

The analytical performance of DLLME coupled with atomic fluorescence spectrometry for the pre-concentration and determination of lead from environmental samples was systematically investigated under optimized experimental conditions. The results exhibited that there was an excellent linear range over 0.01–100 ng mL⁻¹ ($r^2 = 0.9990$). The precision of this method was 2.12% (RSD, $n = 7$) at the spiked concentration of 4 ng mL⁻¹. And the detection limit (calculated as the concentration corresponding to three times the standard deviation of 17 runs of the blank samples) of proposed method for lead was 0.95 ng L⁻¹.

3.9. Analysis of real water samples

In order to demonstrate the applicability and reliability of the proposed method for realworld samples, four environmental samples were collected. Three spiked and two blank experiments for each real water sample were carried out according to the above-mentioned procedure. Subsequently extractions of four samples spiked with lead at 4 ng mL⁻¹ were processed as described above. The concentration of lead was determination by atomic fluorescence spectrometry and the results were given in Table 2. The recoveries of lead were in the range of 92.9–97.4%. Certi-

Table 2
The results from real water samples.

Environmental samples	Blank (ng mL ⁻¹)	Spiked (ng mL ⁻¹)	Recovery (%)
Sample 1	0.51	4	97.4 ± 5.0
Waste water	0.13	4	96.1 ± 8.6
Sample 2	0.30	4	92.9 ± 1.7
Sample 3	0.16	4	95 ± 1.9

fied reference water sample (GSB 07-1183-2000) was also used for validation of proposed method, and the standard value was $0.593 \mu\text{g mL}^{-1}$. The mean determined value with proposed method was $0.577 \mu\text{g mL}^{-1}$ and the recovery was 97.3%.

3.10. Comparison with present methods

Recently, a review on the trace level of metals with liquid phase microextraction was presented [43]. From this review, three DLLME methods for the determination of lead were mentioned, the extraction solvent was the CCl_4 , the dispersive solvents were acetone, ethanol, methanol, and the chelating agents were diethyldithiophosphoric acid 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, diethyldithiophosphoric acid. However the linear range was very small, and they 0.05–1, 0.1–20, and 1–70 $\mu\text{g L}^{-1}$, and the LODs were 20, 39, and 500 ng L^{-1} . The enhancement factor the three methods were 150, 78, and 450. The linear range and LOD of present method were 0.01–100 $\mu\text{g L}^{-1}$ and 0.95 ng L^{-1} , and the volume enhancement factor is 20. Hence, the proposed method would be a good alternative for the determination of trace lead in environment.

4. Conclusions

A simple and sensitive method was developed for the pre-concentration and determination of lead in water samples in combination of DLLME and atomic fluorescence spectrometry. The experimental results demonstrated that proposed method had many merits such as excellent enrichment performance, simplicity, sensitivity, easy to operate, cost-effective and low consumption of organic solvents. The results indicated that proposed method had high tolerance to coexisting ions and perfect analytical performance and proved that proposed method was a good alternative for the determination of lead in environmental samples.

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References

- [1] M. Tuzen, M. Soylak, K. Parlar, Cadmium and lead contamination in tap water samples from Tokat, Turkey, *Bull. Environ. Contam. Toxicol.* 75 (2005) 284–289.
- [2] E. Melek, M. Tuzen, M. Soylak, Flame atomic absorption spectrometric determination of cadmium(II) and lead(II) after their solid phase extraction as dibenzylthiocarbamate chelates on Dowex Optipore V-493, *Anal. Chim. Acta* 578 (2006) 213–219.
- [3] M.G.A. Korn, J.B. de Andrade, D.S. de Jesus, V.A. Lemos, M.L.S.F. Bandeira, W.N.L. dos Santos, M.A. Bezerra, F.A.C. Amorim, A.S. Souza, S.L.C. Ferreira, Procedures of separation and preconcentration for the determination of lead using spectrometric techniques: a review, *Talanta* 69 (2006) 16–24.
- [4] A.C. Davis, P. Wu, X.F. Zhang, X.D. Hou, B.T. Jones, Determination of cadmium in biological samples, *Appl. Spectrosc. Rev.* 41 (2006) 35–75.
- [5] Z. Grahek, M.R. Macefat, S. Lulic, Isolation of lead from water samples and determination of Pb-210, *Anal. Chim. Acta* 560 (2006) 84–93.
- [6] E.M. Gama, A.S. Lima, V.A. Lemos, Preconcentration system for cadmium and lead determination in environmental samples using polyurethane foam/Me-BTANC, *J. Hazard. Mater.* 136 (2006) 757–762.
- [7] World Health Organization, Guidelines for Drinking-Water Quality Health Criteria and Other Supporting Information, vol. 2, 2nd ed., WHO, Geneva, 1996, p. 973.
- [8] J.L. Manzoori, M. Amjadi, J. Abulhassani, Ultra-trace determination of lead in water and food samples by using ionic liquid-based single drop microextraction electrothermal atomic absorption spectrometry, *Anal. Chim. Acta* 644 (2009) 48–52.
- [9] L.A. Portugal, H.S. Ferreira, W.N.L. dos Santos, S.L.C. Ferreira, Simultaneous pre-concentration procedure for the determination of cadmium and lead in drinking water employing sequential multi-element flame atomic absorption spectrometry, *Microchem. J.* 87 (2007) 77–80.
- [10] J. Biasino, J.R. Domínguez, J. Alvarado, Hydrogen peroxide in basic media for whole blood sample dissolution for determination of its lead content by electrothermal atomization atomic absorption spectrometry, *Talanta* 73 (2007) 962–964.
- [11] P.F. Marchisio, A. Sales, S. Cerutti, E. Marchevski, L.D. Martinez, On-line pre-concentration/determination of lead in *Ilex paraguariensis* samples (mate tea) using polyurethane foam as filter and USN-ICP-OES, *J. Hazard. Mater.* B124 (2005) 113–118.
- [12] P. Liang, H. Sang, Determination of trace lead in biological and water samples with dispersive liquid-liquid microextraction preconcentration, *Anal. Biochem.* 380 (2008) 21–25.
- [13] R. Więtecha, P. Koscielniak, T. Lech, T. Kielar, Simple method for simultaneous determination of selenium and arsenic in human hair by means of atomic fluorescence spectrometry with hydride generation technique, *Microchem. Acta* 149 (2005) 137–144.
- [14] T. Frentiu, E. Darvasi, M. Senila, M. Ponta, E. Cordos, Preliminary investigation of a medium power argon radiofrequency capacitively coupled plasma as atomization cell in atomic fluorescence spectrometry of cadmium, *Talanta* 76 (2008) 1170–1176.
- [15] T. Frentiu, M. Ponta, M. Senila, A.I. Mihaltan, E. Darvasi, M. Frentiu, E.A. Cordos, Evaluation of figures of merit in atomic fluorescence spectrometry for Zn determination in environmental and biological samples using a new radiofrequency capacitively coupled plasma, *J. Anal. At. Spectrom.* 25 (2010) 739–742.
- [16] C. Lu, L. Liu, H. Dong, X. Li, Hydrochloric acid extract-mercury speciation analysis by high performance liquid chromatography coupled atomic fluorescence spectrometry, *Chin. J. Anal. Lab.* 29 (2010) 64–68.
- [17] L. Yang, H. Kang, D. Zhang, N. Li, L. Gao, Determination of As (III) and As (V) in water samples by hydride generation atomic fluorescence spectrometry with ion exchange technique, *Chin. J. Anal. Lab.* 23 (2004) 44–47.
- [18] K. Li, C. Liu, Determination of Pb in blood by hydrogen generation-atomic fluorescence spectrometry, *Henan J. Prev. Med.* 18 (2007) 279–280 (in Chinese).
- [19] Z. Shen, G. Dong, J. Shen, Determination of trace Pb in foods by VA-90 hydride generation-atomic absorption spectrometry, *Spectrosc. Spectral Anal.* 20 (2000) 390–392 (in Chinese).
- [20] A.S. Souza, G.C. Brandão, W.N.L. dos Santos, V.A. Lemos, E.M. Ganzarolli, R.E. Bruns, S.L.C. Ferreira, Automatic on-line pre-concentration system using a knotted reactor for the FAAS determination of lead in drinking water, *J. Hazard. Mater.* 141 (2007) 540–545.
- [21] E.L. Silva, P. dos Santos Roldan, Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry, *J. Hazard. Mater.* 161 (2009) 142–147.
- [22] Z. Li, Y. Yang, J. Tang, J. Pan, Spectrophotometric determination of trace lead in water after preconcentration using mercaptosephadex, *Talanta* 60 (2003) 123–130.
- [23] M. Karve, R.V. Rajgor, Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry, *J. Hazard. Mater.* 141 (2007) 607–613.
- [24] E.L. Silva, P.D. Roldan, Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry, *J. Hazard. Mater.* 161 (2009) 142–147.
- [25] F. Zheng, B. Hu, MPTS-silica coated capillary microextraction on line hyphenated with inductively coupled plasma atomic emission spectrometry for the determination of Cu, Hg and Pb in biological samples, *Talanta* 73 (2007) 372–379.
- [26] T. Gorecki, J. Pawliszyn, Determination of tetraethyllead and inorganic lead in water by solid phase microextraction/gas chromatography, *Anal. Chem.* 68 (1996) 3008–3014.
- [27] L. Xia, X. Li, Y. Wu, B. Hu, R. Chen, Ionic liquids based single drop microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for determination of Co, Hg and Pb in biological and environmental samples, *Spectrochim. Acta Part B: At. Spectrosc.* 63 (2008) 1290–1296.
- [28] R. Montes, I. Rodríguez, E. Rubí, R. Cela, Dispersive liquid-liquid microextraction applied to the simultaneous derivatization and concentration of triclosan and methyltriclosan in water samples, *J. Chromatogr. A* 1216 (2009) 205–210.
- [29] H. Farahani, P. Norouzi, R. Dinavand, M.R. Ganjali, Development of dispersive liquid-liquid microextraction combined with gas chromatography-mass spectrometry as a simple, rapid and highly sensitive method for the determination of phthalate esters in water samples, *J. Chromatogr. A* 1172 (2007) 105–112.
- [30] E. Zhao, W. Zhao, L. Han, S. Jiang, Z. Zhou, Application of dispersive liquid-liquid microextraction for the analysis of organophosphorus pesticides in water-melon and cucumber, *J. Chromatogr. A* 1175 (2007) 137–140.
- [31] A.P. Birjandi, A. Bidari, F. Rezaei, M.R.M. Hosseini, Y. Assadi, Speciation of butyl and phenyltin compounds using dispersive liquid-liquid microextraction and gas chromatography-flame photometric detection, *J. Chromatogr. A* 1193 (2008) 19–25.
- [32] P. Liang, E. Zhao, F. Li, Dispersive liquid-liquid microextraction preconcentration of palladium in water samples and determination by graphite furnace atomic absorption spectrometry, *Talanta* 77 (2009) 1854–1857.
- [33] M.T. Naseri, P. Hemmatkhan, M.R.M. Hosseini, Y. Assadi, Combination of dispersive liquid-liquid microextraction with flame atomic absorption spectrometry using microsample introduction for determination of lead in water samples, *Anal. Chem. Acta* 610 (2008) 135–141.
- [34] F. Rezaei, A. Bidari, A.P. Birjandi, M.R.M. Hosseini, Y. Assadi, Development of a dispersive liquid-liquid microextraction method for the determina-

- tion of polychlorinated biphenyls in water, *J. Hazard. Mater.* 158 (2008) 621–627.
- [35] M. Rezaee, Y. Assadi, M.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid–liquid microextraction, *J. Chromatogr. A* 1116 (2006) 1–9.
- [36] M. Rezaee, Y. Yamini, S. Shariati, A. Esrafilii, M. Shamsipur, Dispersive liquid–liquid microextraction combined with high-performance liquid chromatography–UV detection as a very simple, rapid and sensitive method for the determination of bisphenol A in water samples, *J. Chromatogr. A* 1216 (2009) 1511–1514.
- [37] N. Fattahi, Y. Assadi, M.R.M. Hosseini, E.Z. Jahromi, Determination of chlorophenols in water samples using simultaneous dispersive liquid–liquid microextraction and derivatization followed by gas chromatography–electron–capture detection, *J. Chromatogr. A* 1157 (2007) 23–29.
- [38] L. Fariña, E. Boido, F. Carrau, E. Dellacassa, Determination of volatile phenols in red wines by dispersive liquid–liquid microextraction and gas chromatography–mass spectrometry detection, *J. Chromatogr. A* 1157 (2007) 46–50.
- [39] Y.Y. Li, G.H. Wei, J. Hu, X.J. Liu, X.N. Zhao, X.D. Wang, Dispersive liquid–liquid microextraction followed by reversed phase–high performance liquid chromatography for the determination of polybrominated diphenyl ethers at trace levels in landfill leachate and environmental water samples, *Anal. Chim. Acta* 615 (2008) 96–103.
- [40] Y. Liu, E. Zhao, W. Zhao, H. Gao, Z. Zhou, Determination of four heterocyclic insecticides by ionic liquid dispersive liquid–liquid microextraction in water samples, *J. Chromatogr. A* 1216 (2009) 885–891.
- [41] D. Nagaraju, S.D. Huang, Determination of triazine herbicides in aqueous samples by dispersive liquid–liquid microextraction with gas chromatography–ion trap mass spectrometry, *J. Chromatogr. A* 1161 (2007) 89–97.
- [42] A.N. Anthemidis, K.-I.G. Ioannou, Development of a sequential injection dispersive liquid–liquid microextraction system for electrothermal atomic absorption spectrometry by using a hydrophobic sorbent material: determination of lead and cadmium in natural waters, *Anal. Chim. Acta* 668 (2010) 35–40.
- [43] S. Dadfarnia, A.M.H. Shabani, Recent development in liquid phase microextraction for determination of trace level concentration of metals—a review, *Anal. Chim. Acta* 658 (2010) 107–119.