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Hollow-fiber liquid–liquid–solid micro-extraction of lead in soft drinks and determination by graphite furnace atomic absorption spectrometry

Jeferson S. Carletto, Eduardo Carasek, Bernhard Welz*

Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-900, Brazil

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ABSTRACT

A novel hollow-fiber liquid–liquid–solid micro-extraction technique based on simultaneous liquid–liquid micro-extraction and solid phase micro-extraction using a polypropylene microporous membrane has been developed. The applicability of the proposed procedure was evaluated by extraction of Pb(II) from aqueous solutions and soft drinks. The parameters affecting the extraction efficiency were optimized using multivariate methodology, and the analytical features were established. Under optimized conditions, Pb(II) was concentrated for 20 min on three microporous membrane hollow fibers of 6 mm of length each, placed into 20 mL of sample containing 60 μL of toluene and ammonium O,O-diethyl dithiophosphate. The fibers were introduced directly into the graphite furnace as a solid sample, and the analyte was thermally desorbed from the fiber and atomized using ruthenium as a permanent modifier. A detection limit of 7 ng L^{-1} Pb was obtained for soft drink samples and good repeatability was found for all samples. The enrichment factor varied between 22 and 66, depending if only one or all three hollow fibers were used for the determination of lead. The results suggest that the proposed procedure represents a simple and low-cost micro-extraction alternative rendering adequate limits of quantification for the determination of Pb(II) in soft drink samples.

1. Introduction

Lead is a trace element of high interest, due to the toxicity of most of its compounds; lead poisoning adversely affects the central and peripheral nervous systems and the kidney [1], among others. However, its unique properties make it to be used as industrial material in a variety of fields, and hence it is released to the environment in considerable quantities.

Several analytical techniques, such as flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma-optical emission spectrometry and inductively coupled plasma mass spectrometry are available for the determination of lead with good sensitivity for a variety of applications [2–5]. Among these techniques, GF AAS is a very attractive option to determine trace amounts of lead in complex samples, as it is the most robust technique for this purpose. However, due to the low level of lead in many samples its direct determination with all of the above techniques, including GF AAS, is on occasions difficult, and major constituents, such as organic compounds and inorganic salts, could cause interferences. Consequently, separation and pre-concentration procedures might be necessary prior to the GF AAS determination of this element.

The most widely used techniques for separation and preconcentration of trace concentrations of lead include liquid–liquid extraction [6–8], cloud point extraction [3,9,10], and solid-phase extraction [11–14]. Another promising sample preparation technique which has attracted considerable attention in recent years is the hollow-fiber supported liquid membrane (HF-SLM) extraction. There are mainly two forms to work with hollow-fiber membranes, two-phase or three-phase configurations [15–19]. Especially in two-phase systems a back-extraction step is necessary to make the sample adequate for the analytical instrument. It might be possible to avoid the back-extraction by using a solid sampling module coupled with GF AAS, minimizing sample manipulation and increasing the analytical throughput and sensitivity.

The goal of this study has been to develop a new hollow-fiber liquid–liquid–solid micro-extraction (HF-LLSME) system. The chelating agent ammonium O,O-diethyl dithiophosphate (DDTP), which in acid medium forms a hydrophobic complex with Pb(II), was added into the sample. With further addition of an organic solvent the Pb-DDTP complex was extracted from the sample and sorbed on a porous polypropylene hollow-fiber membrane fixed at a stainless steel support. Finally, the membranes were placed onto a graphite platform and introduced into a graphite furnace for direct solid sample analysis. The validity of the HF-LLSME technique was

* Corresponding author. Fax: +55 48 3721 6850.
E-mail address: welz@qmc.ufsc.br (B. Welz).

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demonstrated by applying it for the determination of lead in soft drink samples.

2. Experimental

2.1. Instrumentation

An AAS 5 EA atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with deuterium background correction, equipped with a transversely heated graphite tube atomizer, was used for all measurements. The lead hollow cathode lamp (Hitachi, Mitorika, Ibaraki, Japan) was operated at 7.5 mA, and the analytical line at 283.3 nm was used with a spectral bandwidth of 0.8 nm. Integrated absorbance (peak area) was used exclusively for signal evaluation. An SSA 5 manual solid sampling (SS) accessory (Analytik Jena), consisting of a pre-adjusted pair of tweezers and a guide rail, was used for introduction of the SS platforms (Analytik Jena, Part No. 407-152.023) into the SS graphite tube (Analytik Jena, Part No. 407-A81.303). An MQAMA 301 stirrer (Microquímica, Santa Catarina, Brazil) was used to agitate the solutions. A Q 3/2 accurel polypropylene hollow-fiber membrane, 600 μm inner diameter, 200 μm wall thickness and 0.2 μm pore size (Membrana GmbH, Wuppertal, Germany) was used throughout. The hollow fiber was cleaned in 5% (v/v) nitric acid for 48 h before use. 400 μg of ruthenium was deposited on the solid sampling platforms as a permanent modifier using a previously established temperature program [20]. The graphite furnace temperature program has been optimized and is show in Table 1.

2.2. Reagents

Ultrapure water from a Milli-Q® water purification system (Millipore, Bedford, MA, USA) was used to prepare all solutions. All chemicals were of analytical grade and were used without prior purification, except for DDTP. The laboratory glassware was kept overnight in a 2% (v/v) Extran® solution (Merck, Darmstadt, Germany) and then again overnight in a 10% (v/v) hydrochloric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment. Lead(II) working standard solutions were prepared daily by dilution of a 1000 mg L^{-1} Pb(II) stock solution (atomic absorption grade, Carlo Erba, Italy). Toluene, hexane and chloroform (Tedia, Fairfield, OH, USA) were used as extractor solvents. Ammonium O,O-diethyl dithiophosphate (DDTP, Aldrich, Milwaukee, WI, USA) was further purified by passing it through a silica gel C18 column (Merck). The working solutions were prepared by the addition of a proper amount organic solvent, 10% (v/v) nitric acid (Merck) and 0.3 mol L^{-1} DDTP solution to 20 mL of a working standard solution containing 2 μg L^{-1} Pb(II). Cola soft drinks, low sugar, regular and regular with lemon, low sugar and regular soda and regular Guarana, were purchased in a local supermarket and used to verify the applicability of the proposed method for real samples.

Table 1
Graphite furnace temperature program for the determination of Pb(II) after HF-LLSME with polypropylene membrane using SS-GF AAS.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)	Ar flow-rate (L min^{-1})
Drying	100	10	5	1.0
Pyrolysis	900	50	20	2.0
Auto Zero	900	50	1	0
Atomization	1800	500	6	0
Cleaning	2300	1000	3	2.0

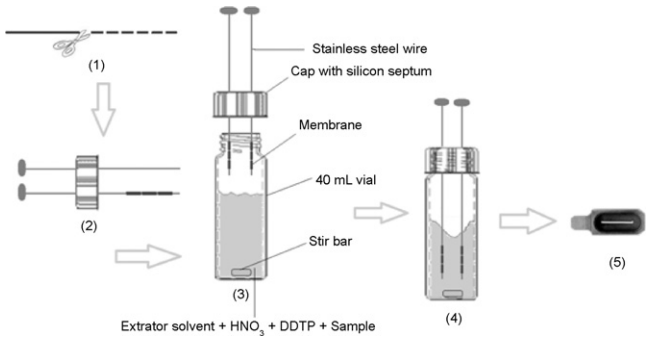

Fig. 1. Schematic representation of the steps for the proposed procedure to extract lead from aqueous solution using HF-LLSME with porous polypropylene membranes followed by SS-GF AAS. (1) The hollow fibers are cut into segments of 6 mm length; (2) two stainless steel wires are inserted through the septum of the screw cap and the hollow fiber segments slid on it; (3) the glass vial with sample and reagents is sealed with the screw cap; (4) the mixture is agitated for 20 min to transfer the complexed analyte to the hollow fiber membrane; (5) the hollow fiber membranes are transferred to a solid sampling platform and analyzed directly by SS-GF AAS.

2.3. Extraction procedure

The various stages of the extraction procedure are illustrated in Fig. 1. The tubular porous polypropylene membrane was cut into segments of 6 mm length; two stainless steel wires with a diameter equal to the inner diameter of the hollow fiber were inserted through the silicone septum of the polypropylene screw cap of a 40-mL extraction vial. The segments of the polypropylene hollow fiber membrane were slid over the stainless steel wire, so that only the outer surface and the pores in the walls of the polypropylene hollow membrane were available for extraction of the analyte. The screw cap with the wires and the membrane tubes was used to seal the glass vials containing the sample, the chelating agent, the extractor solvent and the acid. The whole system was kept in a thermostatic bath on a magnetic stirrer, making possible controlled temperature and agitation during the extraction procedure. After the extraction, the membranes were removed from the sample and then from the stainless steel wire and introduced as solid samples into the graphite furnace, individually or together.

3. Results and discussion

The optimum Pb(II) extraction conditions for the proposed system have been determined using multivariate methods. Organic solvent (extractor) composition, extraction procedure, extractor volume, extraction time and number of membrane segments to be used for extraction and final determination have been optimized. Values for sample pH and DDTP concentration have been taken from the literature [3]. Analytical figures of merit were obtained using the optimized extraction conditions. In addition, the proposed method was applied for the determination of Pb(II) in six soft drink samples.

3.1. Optimization of the extractor solvent composition

As the liquid–liquid micro-extraction is an equilibrium process, it is advisable to use solvents with the highest extraction capability for the Pb-DDTP complex. In other words, it is recommended to choose a solvent or a mixture of solvents that results in a high partition coefficient of the complex formed between the solvent (or a mixture of solvents) and the sample. Another necessary characteristic is a low solvent solubility in the sample medium (water), so that the polypropylene membrane can extract the maximum amount of analyte-loaded solvent from the sample.

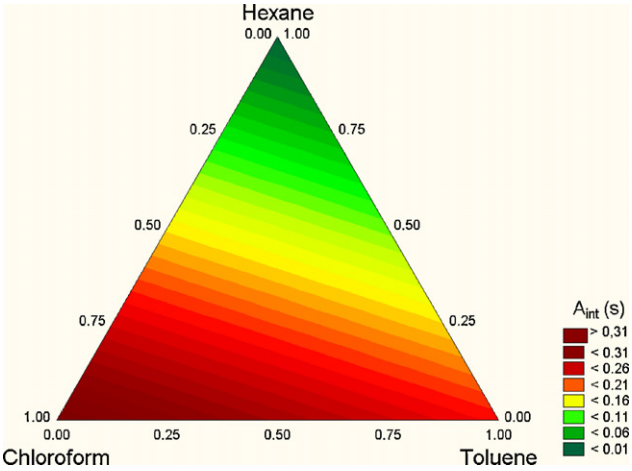

Fig. 2. Optimization of extractor solvent and solvent composition using triangular mixture surface for Pb(II) extraction by HF-LLSME and determination by SS-GF AAS. Experimental conditions: 0.1% (v/v) HNO_3, 0.01% (m/v) DDTP, 10 min extraction time, liquid–solid extraction (membrane extraction) only during the last minute of liquid–liquid extraction, 2 μg L^{-1} Pb(II), 200 μL solvent volume and 2 segments of membrane (12 mm length).

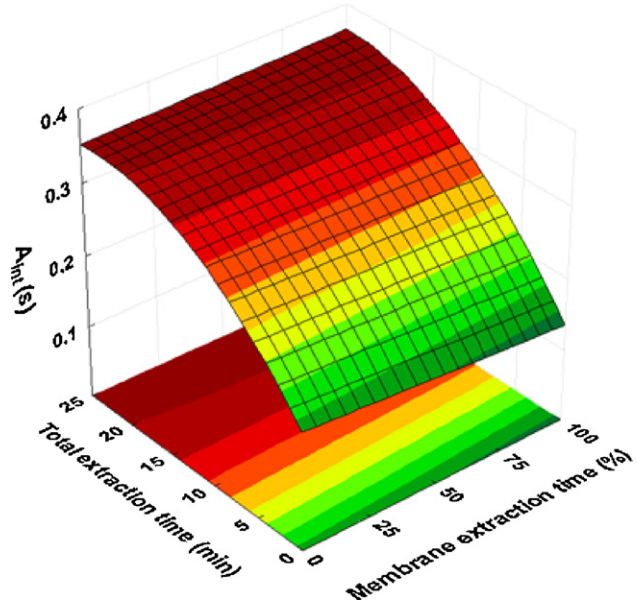

Fig. 3. Integrated absorbance (A_{int}) for Pb as a function of total extraction time (liquid–liquid extraction) and membrane extraction time (fraction of the total extraction time that the membranes are immersed into the emulsion, as percentage of the total extraction time) using HF-LLSME and determination by SS-GF AAS. Experimental conditions: 0.1% (v/v) HNO_3, 0.01% (m/v) DDTP, toluene volume 100 μL, lead concentration of 2 μg L^{-1}, membrane length 12 mm.

The studied solvents were hexane, chloroform and toluene. A triangular mixture surface was used, where each solvent was evaluated alone, in mixtures with 33.3% (v/v) and 66.7% (v/v) of a pair of solvents and a ternary mixture of 33.3% (v/v) of each one. The result of this study, which is shown in Fig. 2, indicates a significant increase of the analytical signal when chloroform was used as solvent for any proportion studied. It is also clear that hexane cannot be used alone to extract the Pb-DDTP complex. Toluene showed a good extraction capacity, but lower than chloroform. However, although the best sensitivity was obtained with chloroform, its use is not recommended because of the inferior repeatability of the results, most likely due to the high volatility of this solvent. Another aspect is the toxicity of organic solvents; although both, chloroform and toluene are considered highly toxic, the former one is more toxic and was banned from many laboratories, even in small quantities. Another reason to avoid the use of chloroform as solvent was the need to use a volume of about 150 μL for the extraction, whereas only 25 μL of toluene was necessary when 12 mm of membrane was used (two segments of 6 mm each).

Two aspects can be qualitatively considered to know if the solvent was sorbed on the porous membrane during the extraction or not. The first is that, when the membrane adsorbs the solvent, its visual aspect changes from white to limpid colorless (toluene) or to cloudy colorless (chloroform). For hexane the visual aspect did not change. The second aspect to be considered is the smell of the membrane after the extraction procedure, where the membrane should exhale the characteristic smell of the solvent.

Taking into account the aforementioned observations, toluene was chosen as the solvent in this study. Obviously, because of the toxicity of the solvent, all sample preparation had to be carried out under a fume hood and an efficient exhaust system had to be mounted at the graphite furnace in order to avoid any risk for the lab personnel.

3.2. Multivariate optimization of extraction times

One of the limiting factors for the extraction efficiency of the Pb-DDTP complex is its partition between the aqueous phase and the extractor solvent. It might therefore be advantageous to introduce the membrane only some time after the addition of the extractor solvent in order to reach partition equilibrium before sorption. This way, the extractor solvent containing the complex could be adsorbed very quickly in the pores of the membrane. In this case, when the membrane is immersed at the end of the extraction procedure, there might be a higher amount of the solvent available to extract the complex from the aqueous phase than when introducing it at the beginning of the process.

A multivariate study using response surface methodology was used to check the above hypothesis, taking into consideration the total extraction time versus the fraction of the total extraction time during which the tubular membrane is immersed in the sample. According to the response surface obtained in this study, which is shown in Fig. 3, there is no significant difference in Pb(II) extraction efficiency in relation to the time at which the membrane is immersed into the solution after adding the extractor solvent. That means the extractor solvent adsorbed in the porous membrane is in equilibrium with the emulsion, leading to a continuous renewal of the membrane surface as reported previously [14,15]. It also indicates that the polypropylene membrane is an inert material and it does not interfere in the extraction process. This has been further supported by carrying out an extraction without an extractor solvent, where no signal at all was obtained. Independent on the point in time when the membrane is immersed into the liquid, the total extraction time is highly significant and it is determined by the Pb-DDTP liquid–liquid micro-extraction process as the critical parameter. Fig. 3 shows a maximum analytical signal after 20 min. of extraction, and no significant further increase for longer extraction times. To simplify the method the next experiments were carried out with the membrane immersed in the liquid during the whole extraction procedure, and the extraction time was fixed at 20 min.

3.3. Multivariate optimization of extractor volume, number of membrane segments and extraction time

Keeping in mind that HF-LLSME is an equilibrium process and an excess of solvent is used for extraction, it is reasonable to consider that the volume of extractor solvent (carrying the complex Pb-DDTP) per millimeter of membrane could be constant. Thus, the

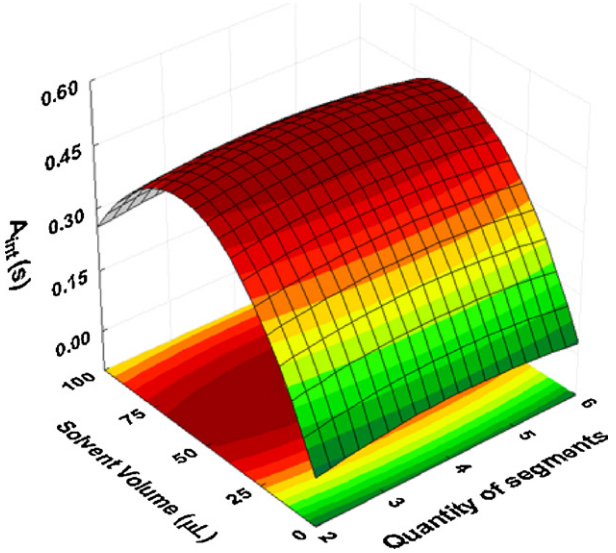

Fig. 4. Mean integrated absorbance (A_{int}) for Pb per membrane section as a function of total membrane length (number of membrane sections) and the extractor solvent volume using HF-LLSME and determination by SS-GF AAS. Experimental conditions: 0.1% (v/v) HNO_3, 0.01% (m/v) DDTP, toluene as extractor solvent, 2 μg L^{-1} Pb, extraction time 20 min.

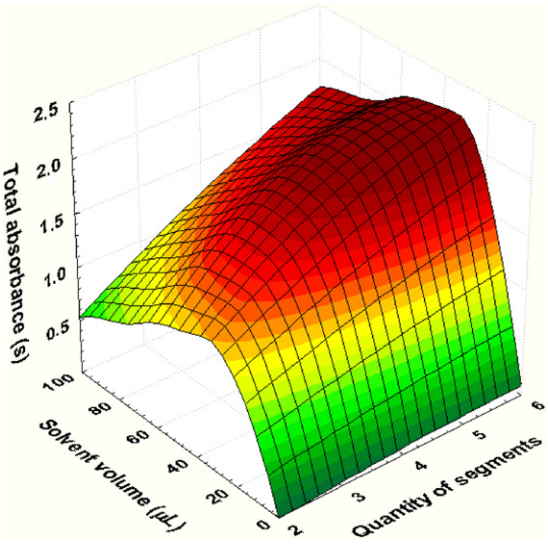

Fig. 5. Total integrated absorbance (A_{int}) for Pb as a function of the number of membrane segments analyzed and the extractor solvent volume using HF-LLSME and determination by SS-GF AAS. Experimental conditions: 0.1% (v/v) HNO_3, 0.01% (m/v) DDTP, toluene as extractor solvent, 2 μg L^{-1} Pb, extraction time 20 min.

variables membrane length (number of membrane segments) and extractor solvent volume were optimized using response surface methodology. The analytical signal was the average absorbance per segment used for each set of experiments. Fig. 4, which shows the result of this study, indicates that there is no loss of analytical signal per membrane section when using a greater length of membrane (more segments). However, when a lower volume of extractor solvent (25 μL) and a greater membrane length (6 segments of 6 mm = 36 mm) was used, it was observed through the analytical signal of each segment that not all membranes had adsorbed the same quantity of solvent containing the Pb-DDTP. The four lower segments (24 mm) presented good agreement of the absorbance values, but the two upper segments (12 mm) showed an absorbance very close to zero. In this particular set of experiments the average absorbance of 4 membrane segments was used to feed the response surface in Fig. 4. This figure also shows that, when no solvent is used, the Pb-DDTP is not extracted, confirming that the membrane is an inert material. A maximum in the analytical signal was obtained when the volume of extractor solvent was 65 μL, whereas higher volumes resulted in a decrease in the response, probably because of the increasing dilution of the Pb-DDTP complex in the organic phase.

An enhancement of the sensitivity of the proposed method could be obtained by using the total absorbance of all membrane segments instead of the average absorbance per membrane segment. The result of this study is shown in Fig. 5, from which it is clear that the more membrane segments are added, the higher the analytical signal, due to the higher volume of solvent containing Pb-DDTP that has been extracted. There is a region of maximum extraction efficiency (maximum response), beyond which an increase in the number of membrane segments does not improve the analytical signal, considering a solvent volume in the range of 30–60 μL. That happens because all the extractor solvent has already been extracted to the membrane, and further increase in the number of membrane segments only results in a deterioration of the repeatability between the individual segments due to a competition for the extractor solvent. Fig. 5 also shows a clear relationship between the extractor solvent volume and the number of membrane segments; while for two segments the maximum response is obtained around 30 μL of solvent, the optimum solvent volume for six segments is around 80 μL.

The effect of the extractor solvent volume on the extraction kinetics was studied using response surface methodology, as is shown in Fig. 6. According to this study, the effect of extraction time is more pronounced when lower volumes of extractor solvent are used. For higher volumes of extractor solvent the extraction of Pb-DDTP is facilitated due to the higher superficial area of contact between the solvent and the aqueous phase, whereas for small volumes of solvent a longer extraction time is necessary to reach equilibrium.

In conclusion, the optimum extraction condition for the proposed method was an extraction time of 20 min, 60 μL of toluene, and 18 mm length of membrane (3 membrane segments), which

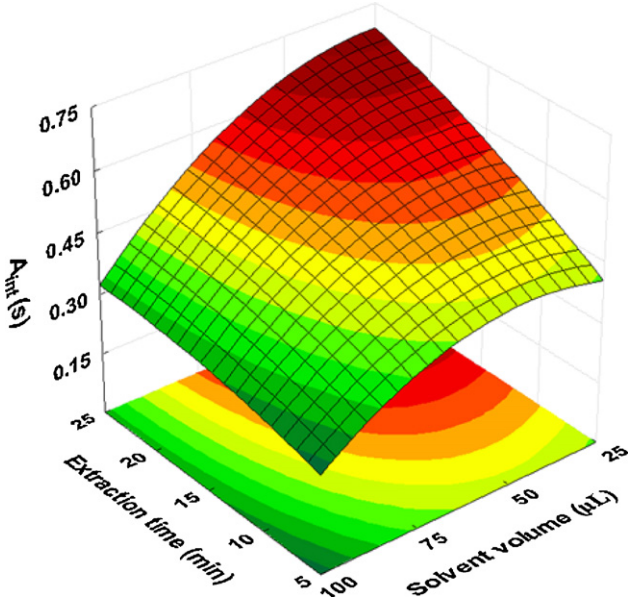

Fig. 6. Integrated absorbance (A_{int}) for Pb as a function of extractor solvent volume and extraction time using HF-LLSME and determination by SS-GF AAS. Experimental conditions: 0.1% (v/v) HNO_3, 0.01% (m/v) DDTP, toluene as extractor solvent, 2 μg L^{-1} Pb, and four membrane segments (24 mm total length).

Table 2
Analytical figures of merit for the determination of Pb(II) using SS-GF AAS after HF-LLSME with one segment of polypropylene hollow-fiber membrane.

Limit of detection (LOD)	0.007 μg L^{-1}
Limit of quantification (LOQ)	0.024 μg L^{-1}
RSD (0.25 μg L^{-1}, n = 6)	6%
Linear range (μg L^{-1})	0.024–1.00
Linear correlation coefficient (R)	0.99998
Slope (L μg^{-1})	0.2302 ± 0.0009
Enrichment factor (EF)	22 (1 membrane)–66 (3 membranes)

could be placed onto the graphite platform individually or together to introduce the solid samples into the graphite furnace. The highest sensitivity is obtained in the latter case, whereas in the former case three replicate measurements can be made in case that highest sensitivity is not required.

3.4. Analytical figures of merit and accuracy

The analytical figures of merit for the HF-LLSME procedure, obtained under optimized conditions, are shown in Table 2, based on the analysis of one segment only of the hollow-fiber membrane. The limit of detection (LOD), calculated as $3\sigma/B$, where σ is the standard deviation of the linear coefficient of the calibration curve and B is the slope of the calibration curve submitted to HF-LLSME, was determined as 7 ng L^{-1} Pb, and the limit of quantification (LOQ), defined as $10\sigma/B$ was 24 ng L^{-1} Pb. The calibration curve was obtained using 20 mL of the working solutions containing between 0 and 2 μg L^{-1} Pb(II). The equation of the curve was $A_{int} = 0.23024c_{Pb} + 0.05424$, where A_{int} is the integrated absorbance and c_{Pb} is the lead concentration in μg L^{-1}. The enrichment factor was calculated as the ratio of the slopes of the calibration curves with and without pre-concentration; the enrichment factor increased linearly with the number of hollow fiber segments introduced into the graphite furnace from 22 for one segment to 66 for three segments. Nevertheless, LOD and LOQ did not improve to the same extent due to the increased baseline noise when more than one segment was used.

Table 3 shows a comparison with published data, which demonstrates that the LOD obtained in this study, is in most of the cases significantly better than that obtained in other work using GF AAS. In addition, the HF-LLSME technique is competitive in terms of sensitivity when compared with widely employed sample preparation techniques, such as solid-phase extraction and cloud-point extraction.

The calibration curves with and without pre-concentration were plotted in function of the analyte mass. The pre-concentration equation for one membrane segment is $A_{int} = 11.512\, m_{Pb} + 0.0542$, where A_{int} is the integrated absorbance and m_{Pb} is the mass of lead in μg. The equation for the curve without pre-concentration is $A_{int} = 213.426\, m_{Pb} + 0.0430$. Using the ratio of the curves with and without pre-concentration in function of the analyte mass it is possible to determine the analyte extraction fraction. Using only one membrane segment it is possible to extract 5.4% of the total analyte mass from the sample; for three membrane segments this value increases to 16.2%. Using Fig. 5 as a reference, where a maximum integrated absorbance of approximately 2.3 s was obtained for a 2 μg L^{-1} solution of Pb(II) under conditions where there was no lack of solvent and all the efficiency was liquid–liquid extraction dependent, we could estimate this efficiency to be approximately 26.5% of mass extraction.

Table 3
Comparison between the results obtained in this study and those published in the literature using separation techniques for GF AAS.

Matrix	Separation	LOD (ng L^{-1})	Ref.
Water	CPE[a]	80	[6]
Water	SPE[b]	9.5	[13]
Cetacean Dolphinidae tissue	GF AAS	500	[21]
Urine	CPE[a]	40	[3]
Soft drinks	HF-LLSME	7	This study

[a] CPE = cloud point extraction.
[b] SPE = solid phase extraction.

Table 4
Results for the analysis of soft drinks and recovery tests for Pb(II) extraction by HF-LLSME with polypropylene membrane and determination by SS-GF AAS.

Sample	Found (μg L^{-1})	Slope (L μg^{-1})	Recovery (%)
Low-sugar Cola	0.31 ± 0.02	0.229 ± 0.009	99
Regular Cola	0.64 ± 0.02	0.198 ± 0.006	86
Regular Cola with lemon	0.71 ± 0.03	0.195 ± 0.010	85
Regular Soda	0.40 ± 0.04	0.229 ± 0.021	100
Regular Guaraná	0.27 ± 0.04	0.216 ± 0.028	94
Low-sugar Soda	0.21 ± 0.03	0.226 ± 0.032	99

3.5. Application of the proposed method

The optimized HF-LLSME system was used to determine the Pb(II) concentration in several soft drinks. As no certified reference material is available that would come close to the samples analyzed in this study, recovery tests were performed using the ratio between the slopes of the calibration curve obtained by analyte addition and the calibration curve with aqueous standards in order to check the accuracy of the method. The results are shown in Table 4. Good recoveries of between 85 and 100% were obtained for the soft drink samples, although the two regular Cola samples with high sugar content appeared to give slightly lower recovery, indicating some interference of some matrix component of these drinks with the sorption process. Nevertheless, calibration using aqueous standard solutions submitted to the HF-LLSME procedure resulted in satisfactory accuracy for all samples.

4. Conclusions

The HF-LLSME which consist of simultaneous liquid–liquid micro-extraction and polypropylene microporous membrane solid phase micro-extraction procedures to determine Pb(II) in aqueous solution and soft drink samples provided low limits of detection and good precision and linearity. The proposed method presents advantages as it is simple, effective, of low cost, uses microliters of organic solvents only, is almost free of matrix effects, and completely avoids problems associated with carry-over. Furthermore, the proposed combination of extraction systems results in improved extraction efficiency. To the best of our knowledge, this constitutes the first study that applies simultaneous LLME and polypropylene microporous membrane SPME as a preconcentration procedure to determine metal ions. It might be assumed that this system could be used for the extraction of other trace elements from a variety of other matrices.

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References

[1] S.E. Manahan, Environmental Chemistry, CRC Press, Boca Raton, 1994.
[2] W. Qi, Z. Sun, R. Li, Shanghai Environ. Sci. 21 (2002) 32.
[3] T.A. Maranhão, E. Martendal, D.L.G. Borges, E. Carasek, B. Welz, A.J. Curtius, Spectrochim. Acta B 62 (2007) 1019.
[4] A.S. Souza, G.C. Brandão, W.N.L. dos Santos, V.A. Lemos, E.M. Ganzarolli, R.E. Bruns, S.L.C. Ferreira, J. Hazard. Mater. 141 (2007) 540.
[5] B. Welz, M. Sperling, Atomic Absorption Spectrometry, 3rd ed., Wiley-VCH, Weinheim, New York, 1999.
[6] K.Z. Hossain, T. Honjo, Fresenius J. Anal. Chem. 361 (1998) 451.
[7] J.L. Manzoori, M. Amjadi, J. Abulhassani, Anal. Chim. Acta 644 (2009) 48.
[8] H. Bai, Q. Zhou, G. Xie, J. Xiao, Talanta 80 (2010) 1638.
[9] J.R. Chen, S.M. Xiao, X.H. Wu, K.M. Fang, W.H. Liu, Talanta 67 (2005) 992.
[10] Y. Surme, I. Narin, M. Soylak, H. Yuruk, M. Dogan, Microchim. Acta 157 (2007) 193.
[11] M.G. Pereira, E.R. Pereira-Filho, M.A.Z. Arruda, Spectrochim. Acta B 59 (2004) 515.
[12] M. Tuzen, K. Parlar, M. Soylak, J. Hazard. Mater. 121 (2005) 79.
[13] S. Wang, R.F. Zhang, Anal. Chim. Acta 575 (2006) 166.
[14] R. Liu, P. Liang, J. Hazard. Mater. 152 (2008) 166.
[15] J.S. Carletto, R.M. Luciano, G.C. Bedendo, E. Carasek, Anal. Chim. Acta 638 (2009) 45.
[16] R.M. Luciano, G.C. Bedendo, J.S. Carletto, E. Carasek, J. Hazard. Mater. 177 (2010) 567.
[17] R. Romero, J.A. Jonsson, Anal. Bioanal. Chem. 381 (2005) 1452.
[18] J.F. Peng, R. Liu, J.F. Liu, B. He, X.L. Hu, G.B. Jiang, Spectrochim. Acta B 62 (2007) 99.
[19] C. Zeng, X. Wen, Z. Tan, P. Cai, X. Hou, Microchem. J. 96 (2010) 238.
[20] A.F. da Silva, B. Welz, A.J. Curtius, Spectrochim. Acta B 57 (2002) 2031.
[21] M.G.A. Korn, G.L. dos Santos, S.M. Rosa, L.S.G. Teixeira, P.V. de Oliveira, Microchem. J. 96 (2010) 12.