Microchemical Journal 123 (2015) 237–242

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

New room temperature coacervation scheme for lead traces determination by solid surface fluorescence. Application to wines produced in Argentina

María C. Talio [b], Marcos Kaplan [a], Mariano Acosta [b], Raúl A. Gil [a,b], Marta O. Luconi [a], Liliana P. Fernández [a,b,*]

[a] Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina
[b] Instituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina

ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form 3 June 2015
Accepted 19 June 2015
Available online 6 July 2015

Keywords:
Lead traces
Rhodamine B
Solid surface fluorescence
Red and white wines

ABSTRACT

Lead traces were preconcentrated on paper filter discs using the coacervation phenomenon based on cationic and anionic surfactant reaction at room temperature. The increase in fluorescent signal of Rhodamine B dye was used for metal quantification by solid surface fluorescence. Experimental variables that influence on preconcentration step and fluorimetric sensitivity were optimized using uni-varied assays. The calibration graph using zeroth order regression was linear from 1.24×10^{-3} μg L^{-1} to 1.25 μg L^{-1} with a correlation coefficient of 0.997. At the experimental optimal conditions, a limit of detection of 3.73×10^{-4} μg L^{-1} and a limit of quantification of 1.24×10^{-3} μg L^{-1} were obtained. The method showed good sensitivity, adequate selectivity with good tolerance to foreign ions, and was applied to the determination of trace amounts of Pb(II) in red and white wines produced in Argentina with satisfactory results validated by ICP-MS. The proposed method represents an innovative application of paper filters to solid surface fluorescence methodology.

1. Introduction

In the last time, many efforts have been devoted in the development of faster, safer, and environmentally friendly techniques for analyte extraction. In this sense, surfactants have been widely used in analytical chemistry as extracting solvents, replacing conventional organic solvents in extraction methods [1–8].

Surfactants are substances non-volatiles and non-flammables that allow to implementing a safer sample handling with excellent analyte recuperations. The most well-known extraction technique, using surface-active compounds, is the cloud point extraction (CPE) technique. However, surfactants are also used in coacervative extraction technique, which is not as well-known and popular as the CPE [9]. Coacervation is a phenomenon in which a macromolecular aqueous solution separates into two immiscible liquid phases: a liquid rich in colloidal phase in equilibrium with another diluted liquid phase. Surfactant coacervation refers to phenomenon whose main components are surfactants with low molecular weights.

Anionic surfactants have been still scarcely used as potential extraction media with the analytical purposes. A micellar solution of sodium dodecyl sulfate (SDS) displays clouding phenomenon in micellar solution in the presence of symmetrical quaternary bromides like tetra-n-butyl ammonium/phosphonium and tetra-n-amyl ammonium bromides [10]. This remarkable behavior of SDS has been explained in light of van der Waals attractions, electrical repulsions, penetration effects and solvation [11]. Due to geometrical restrictions the quaternary alkyl bromide ion, R_4N^+, is oriented in two directions into SDS micellar solution: one, is toward the water phase, and the other, toward the micellar core [12].

On the other hand, among cationic surfactants, cetyltrimethylammonium bromide (CTAB) constitutes undoubtedly an example of self-assembled ordered medium as micelles, and other structures and phases, in function of its concentration and characteristics of the dissolvent, having been widely employed in analytical chemistry with different purposes [13–18].

Wine is a complex matrix which contains a great variety of inorganic components as well as organic. Its composition is influenced by many factors related to the production area [19,20]. Moderate wine consumption contributes to the daily intake of many essential metals as Ca, Co, Cr, Cu, and Fe, between others. The analysis of metals in wines is of great importance for authenticity purposes and quality control. The elements can influence the wine making process or change its taste and quality. Furthermore, the presence of heavy metal can be related not only to the natural soil content but also the addition of fertilizers and pesticides. It should be noted that the levels of such contaminants elements at different stages of the winemaking process are of great concern because of present legal requirements [21].

* Corresponding author at: Instituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina. Tel.: +54 02664 425385.
E-mail address: lfernand@unsl.edu.ar (L.P. Fernández).

http://dx.doi.org/10.1016/j.microc.2015.06.014
0026-265X/

The development of the analytical methods has become a basic prerequisite for laboratories that work in an official food and beverage control [22]. In particular, the complexity of matrix composition and low metal concentration levels in wine samples requires the implementation of separation and pre-concentration steps.

Lead is a human carcinogen that causes chronic poisoning manifested by disorders such as encephalopathy, nervous irritability, kidney disease and altered heme synthesis and reproductive functions [23–25]. This poisoning is associated with chronic lead exposure of low to intermediate, whose primary sources of intake are foods, water and air.

The conventional instrumental methods widely recognized as suitable techniques for the metals determination are atomic spectroscopies [26,27]; in many cases, the low levels of toxic metal are incompatible with instrumental sensitivity. Added to this, high prices and expensive inputs of associate instrument constitute a major constraint for many control laboratories.

The main purpose of this work is to study a new alternative method for Pb(II) determination based in the formation of coacervate phase using a cationic surfactant (CTAB) and an anionic surfactant (SDS). The dye rhodamine B (RhB) is added as fluorophore reagent whose fluorescent signal is increased in the presence of Pb(II). The coacervate phase is collected on a filter paper disc and the solid surface fluorescence signal is determined in a spectrofluorometer. The experimental parameters that influence on separation and determination steps have been optimized and the new methodology has been applied to Pb(II) determination in five red wines and two white wines marketed in Argentina.

2. Materials and methods

2.1. Reagents

Filter papers (FP) blue ribbon (Whatman, England) 2–5 μm pore size and 4.5 cm diameter were used in sorption studies.

Stock solutions of Pb(II) 1×10^{-7} mol L^{-1} were prepared by dilution of 100 μg mL^{-1} standard solution plasma-pure (Leeman Labs, Inc.).

Buffer sodium tetraborate (Mallinckrodt Chemical Works, New York, Los Angeles, St. Louis, USA) 1 mol L^{-1} solution was prepared. The desired pH was obtained by adding $HClO_4$ (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works) solution, with the assistance of a pHmeter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940.

Stock of RhB solutions 1×10^{-7} mol L^{-1} (Fluka AG, ChemischeFabrik, Buchs SG, Switzerland) solution was weekly prepared by dissolution of the appropriate amount of each, in ultrapure water. The stability of solutions was checked by spectrophotometric measurements.

Sodium dodecylsulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Tokyo Kasei Industries (Chuo-Ku, Tokyo, Japan). Solution of CTAB 1×10^{-2} mol L^{-1} and SDS 2×10^{-2} mol L^{-1} was prepared by dissolution in ultrapure water of the respectively appropriate amounts.

Glass materials were previously washed with a 10% *v/v* HNO_3 solution and then with ultrapure water. All used reagent were of analytical grade.

2.2. Apparatus

Spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. A combined glass electrode and a pHmeter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940 was used for pH adjustments.

An Inductively Coupled Plasma Mass Spectrometer, PerkinElmer SCIEX, ELAN DRC-e (Thornhill, Canada) was used for validation measurements. The argon gas with minimum purity of 99.996% was supplied by Air Liquide (Córdoba, Argentina). An HF-resistant and high performance Teflon Nebulizer model PFA-ST, was coupled to a quartz cyclonic spray chamber with internal baffle and drain line cooled with the PC3 system from ESI (Omaha, NE, USA) (Table 1). Tygon black/black 0.76 mm i.d. and 40 cm length peristaltic pump tubing was used. The instrument conditions were: auto lens mode on, peak hopping measure mode, dwell time of 50 ms, 15 sweeps/reading, 1 reading/replicate, and 3 replicates [28].

2.3. General procedure

Adequate volume of sample/standard Pb(II) solution (1.24×10^{-3} μg L^{-1} to 1.25 μg L^{-1}), 1 mL RhB 1×10^{-7} mol L^{-1}, 200 μL CTAB 1×10^{-2} mol L^{-1}, 100 μL SDS 2×10^{-2} mol L^{-1} and 1 mL buffer solution 1×10^{-2} mol L^{-1} (pH = 11) were putt in a volumetric flask and the whole mixture was diluted to 10 mL with ultrapure water. The system was mechanically shaken (10 min) and filtered through disc of filter paper (FP) with the assistance of a vacuum pump. FP was dried at room temperature and reserved in dried ambient (20 °C–25 °C) to the following step. Pb(II) concentration was determined on FP by solid surface fluorescence at λ_{em} = 570 nm (λ_{exc} = 520 nm), using a solid sample holder (see Fig. 1).

2.4. Selection and treatment of samples

A group of commercially available wines were analyzed. Samples were opened, protected against sunlight and stored at 4 °C. With the aim of assuring the samples' representability, analyses were carried out within a few days. An aliquot was filtered through a 0.2 μm Nylon Millipore chromatographic filter, diluted when necessary and analyzed.

2.5. Interference study

Different amounts of ions which may be present in samples (1/100 and 1/1000 Pb(II)/interferent ratio) were added to the test solution containing 0.62 μg L^{-1} Pb(II) and general procedure was applied.

2.6. Accuracy study

Adequate volume of wine samples was spiked with increasing amounts of Pb(II) (0.41 to 1.50 μg L^{-1}). Pb(II)concentrations were determined by proposed methodology.

2.7. Precision study

The repeatability (within-day precision) of the methodology was tested for replicate of samples ($n = 4$) spiked of Pb(II) and the contents were determined by proposed methodology.

2.8. Validation

Pb(II) contents in samples were determined by ICP-MS, using operational conditions previously consigned in apparatus item.

Table 1
Instrument settings and data acquisition parameters for ICP-MS.

Sample uptake rate (μL min^{-1})	200
Sample introduction	Nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with internal baffle and drain line, cooled with the PC^3 system from ESI (Omaha, NE, USA)
RF power (W)	1200
Nebulizer gas flow rates (mL min^{-1})	0.77
Interface	Ni cones (sampler and skimmer)
Isotope	^{208}Pb
Scanning mode	Peak hopping
Dwell time (ms)	50 in standard mode
Number of replicate	3

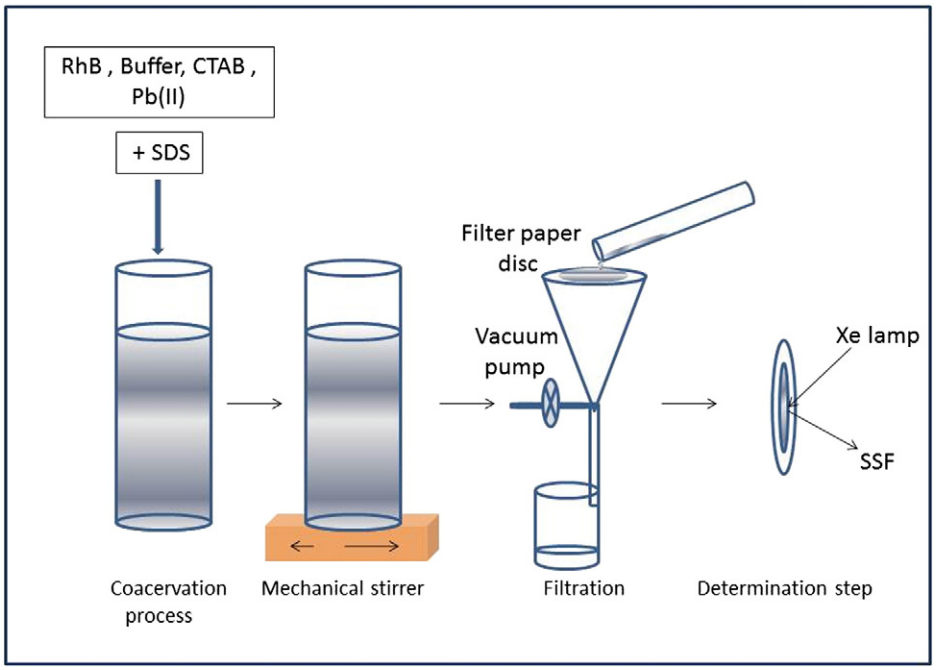

Fig. 1. Schematic representation of general procedure of developed methodology.

3. Results and discussion

Rhodamine dye is characterized as a highly selective and sensitive fluorescence probe for metals [29–33]. In order to study the fluorescent response of RhB in presence of Pb(II), aqueous systems were prepared maintaining constant the dye concentration and varying the metal. While the lower Pb(II) levels conducted to an increase in RhB fluorescent signal, when higher concentrations of Pb(II) were added, a decrease in the same signal was observed. Similar results were obtained when the system was prepared by adding CTAB cationic surfactant at micellar concentration.

With the aim of producing the coacervation separation phenomenon, RhB–Pb(II) systems were prepared in the presence of CTAB and SDS surfactants. So, turbidity was observed; systems were filtered through filter paper discs and coacervate phases were retained. When supports were dried, they were explored by solid surface fluorescence (SSF). Satisfactory results were obtained in the fluorescent response of RhB in the presence of increasing Pb(II) concentrations.

In order to assure quantitative retention of RhB–Pb(II) system, several filtering materials were tested. Among the solid supports assayed, filter paper (blue ribbon) showed a satisfactory retention and was chosen as optimal due to, between other advantages, its low cost. Quantitative analyte retention was proven to realize fluorescence measures in filtrate phase. For all supports, quantitative retention of coacervate phase was obtained and fluorescent signal of filtrate was similar to that of blank solution.

Other experimental variables for optimum generation of RhB–Pb(II) association were studied using uni-varied assays. Taking into account that the interaction of metal with RhB is pH-dependent, the experimental parameter equilibrium pH was optimized. The effect of this parameter was evaluated preparing systems with varying pH from 7.5 to 13.8, maintaining constant the Pb(II) concentration and other parameters. Fig. 2 shows the found results. The SSF signal began to increase at pH higher than 7. The maximum emission was shown between pH 10 and 12. For pH very alkaline, the emission begins to fall again. So, a pH value of 11 was chosen as optimal.

With the objective of assuring the quantitative analyte recuperation, the fluorophore reagent concentration was also varied from 1×10^{-8} to 1×10^{-5} mol L^{-1}, maintaining constant other experimental parameters in the prepared systems. The best results with respect to Pb(II) quantitative retention and reproducibility were obtained when a dye concentration of 1×10^{-7} mol L^{-1} was used. This value was assumed as optimal considering sensitivity and repeatability (Fig. 3).

The effect of the nature and concentration of the buffer on the analytical signal was also evaluated. The best results were obtained using sodium tetraborate (1×10^{-3} mol L^{-1}).

Regarding surfactant concentration, considering that coacervation phenomenon will take place when negative charges of SDS are totally neutralized by positive charges of CTAB, that is to say situation electro-neutrality, systems were prepared maintaining constant other experimental variables, using the same final concentration of SDS and CTAB. In order to achieve quantitative recuperation of RhB–Pb(II) association, a great excess of micellar system is desirable. So, systems with 2×10^{-4} mol L^{-1} of each surfactant were prepared and results were satisfactory with respect to the appearance of coacervation phenomenon and quantitative analyte retention proved by fluorescence measures in filtration phase. Then these levels of surfactant concentration were chosen for the following assays.

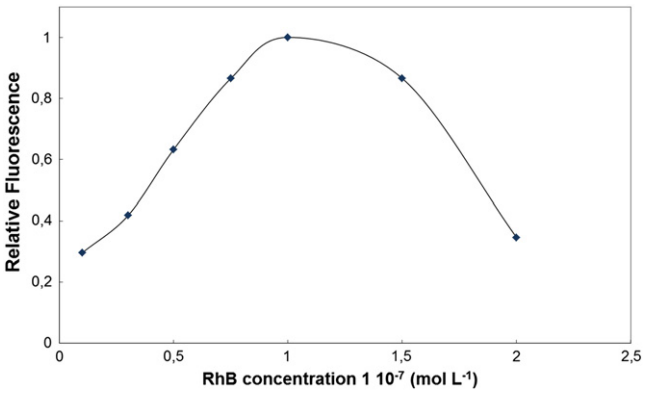

Fig. 2. Influence of RhB concentration on Pb(II) determination. Conditions: $\lambda_{em} = 568$ nm; $\lambda_{exc} = 520$ nm; $C_{CTAB} = 2 \times 10^{-4}$ mol L^{-1}; $C_{SDS} = 2 \times 10^{-4}$ mol L^{-1}; $C_{buffer\ borax} = 1 \times 10^{-3}$ mol L^{-1}, pH 11; $C_{Pb(II)} = 0.62$ μg L^{-1}. Other experimental conditions are described under procedure.

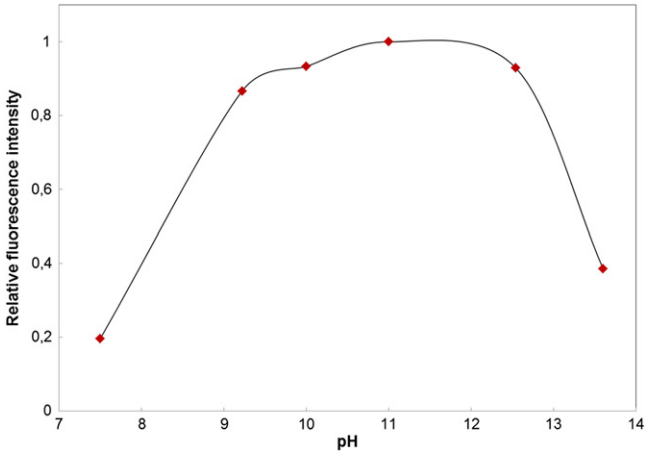

Fig. 3. Influence of pH on Pb(II) quantification. Conditions: $\lambda_{em} = 568$ nm; $\lambda_{exc} = 520$ nm; $C_{CTAB} = 2 \times 10^{-4}$ mol L^{-1}; $C_{SDS} = 2 \times 10^{-4}$ mol L^{-1}; $C_{buffer\ borax} = 1 \times 10^{-3}$ mol L^{-1}, pH 11; $C_{Pb(II)} = 0.62$ μg L^{-1}. Other experimental conditions are described under procedure.

With the purpose of assuring quantitative analyte recuperation, systems prepared at optimal experimental conditions were undergoing mechanical stirring during a varied period of times from 2 to 20 min. A time of 10 min was enough for quantitative RhB–Pb(II) extraction and was adopted as optimal.

Table 2 shows analytical parameters studied for the proposed methodology and the chosen values as optimal.

3.1. Analytical figures of merit

The limit of detection (LOD) of the proposed method was studied under optimal experimental conditions by applying the procedure for blank solutions. The detection limits based on three times the standard deviations of the blank (N = 15) were 3.73×10^{-4} μg L^{-1}.

The calibration graphs are linear in the range 1.24×10^{-3} to 1.25 μg L^{-1} for Pb(II). Table 3 summarizes the main characteristics of calibration plot of proposed methodology and of other instrumental conventional methodologies for quantification of Pb(II) traces [34–37]. As can be seen, the figures of merit of the new method are the same or better than conventional methods, with the additional advantages such as:

- Its simple procedures;
- The use of non-toxic reagents;
- Low waste generation;
- The use of an economic instrument as spectrofluorometer.

3.2. Interferences study

The effect of foreign ions on the recovery of Pb(II) was tested. Different amounts of ions commonly present in samples were added to the test solution containing 0.62 μg L^{-1} of Pb(II), and the developed procedure was applied. An ion was considered as interferent, when it caused a variation in the fluorescent signal of the test system greater than ±5%. The tolerance limits of various foreign ions are given in Table 4. These results demonstrate that some common cations and anions do not interfere on the determinations of the analyte, putting in evidence the adequate selectivity of the developed methodology.

Table 2
Experimental conditions for lead determination by SSF.

Parameters	Studied range	Optimal conditions
Support	Cellulose acetate, nylon, teflon, filter paper	Filter paper (blue ribbon)
pH	4.0–12.5	11.00
Buffer sodium tetraborate	1×10^{-4}–0.5 mol L^{-1}	1×10^{-3} mol L^{-1}
RhB concentration	1×10^{-8}–1×10^{-5} mol L^{-1}	1×10^{-7} mol L^{-1}
CTAB concentration	1×10^{-5}–1 10^{-2} mol L^{-1}	2×10^{-4} mol L^{-1}
SDS concentration	1×10^{-5}–1×10^{-2} mol L^{-1}	2×10^{-4} mol L^{-1}
Stirring time	2–20 min	10 min

Table 3
Analytical parameters of methodologies for Pb(II) determination in wines samples.

Method	Comments	Reference
TS-FF-AAS	RSD = 2.6%. LOD = 5.3 μg/L LOQ = 17.5 μg/L LOL = 200 μg/L $R^2 > 0.999$ Applied to wines and grape juices	[34]
AAS-TXRF	LOD = 1 μg/L Applied to wines and alcoholic distillates samples	[35]
ETAAS USN-ICP-OES	LOD = 0.28 μg/L Range lead determinate = 50–90 μg/L Applied to red and white wines samples	[36]
ICP-MS	$R^2 > 0.999$ LOD = 0.006 μg/L Applied to wine and slightly alcoholic beverages.	[37]
This method	LOD = 3.73×10^{-4} μg L^{-1} LOQ = 1.24×10^{-3} μg L^{-1} LOL = 1.25 μg L^{-1} $R^2 = 0.997$ Recovery (%) = 95.12–104.87 Applied to red and white wines samples.	–

3.3. Applications

The usefulness of the proposed method was evaluated for the determination of the analyte in Argentinian wines. The accuracy of the methodology was performed using the standard addition method and validated by ICP-MS. Sample aliquots (0.100 mL) were spiked with increasing amounts of Pb(II). Obtained results showed satisfactory agreement with adequate precision. The reproducibility of the method was evaluated repeating the proposed methodology, 4 times ($n = 4$) for each sample. Table 5 shows the recovery results achieved for each sample. Obtained results indicate that the proposed method is suitable for determination of this analyte in such studied samples. However, a wide variability of results was observed, not only between the different types of wine (red and white), but also in each type, even for samples that were from the same region.

Samples 2 and 5 had the highest values of Pb(II) contents; at the last stage of its production the metal presence depends on different factors, both natural and exogenous. Natural factors include soil type and its composition, grape variety, climate, etc. Exogenous factors can be

Table 4
Study of interferences.

Ion	Tolerated interferent/Pb(II) ratio	Relative fluorescence	ER%	%CV
CO_3^{2-}	100/1	1.006	1.09	0.03
SO_4^{2-}	100/1	0.999	−0.49	0.03
NO_3^-	1000/1	0.993	−0.41	0.02
Cl^-	1000/1	0.994.	0.34	0.09
K^+	1000/1	1.002.	0.99	0.02
Na^+	100/1	1.003	0.31	0.10
Cd^{2+}	100/1	1.001	0.02	0.05
Ca^{2+}	100/1	1.005	0.66	0.04
Mg^{2+}	100/1	1.002	0.15	0.06
Ni^{2+}	100/1	0.9975	−0.18	0.07
Cu^{2+}	100/1	0.989	−0.62	0.06
Mn^{2+}	100/1	0.984	−0.25	0.05
Fe^{3+}	100/1	0.992	−1.01	0.04
Hg^+	100/1	0.996	−0.58	0.10

Table 5
Recuperation and validation studies by lead determination in wines samples.

Sample	Pb(II) added (μg L^{-1})	Proposed methodology			ICP-MS	
		Pb(II) found ± CV (μg L^{-1})	Recovery (%, n = 4)	Pb(II) content ± SD (μg L^{-1})	Pb(II) found ± SD (μg L^{-1})	ER%
1	−0.41 0.62	0.78 ± 0.04 1.20 ± 0.03 1.42 ± 0.08	−102.44 103.22	311.4 ± 0.07	324.9 ± 0.57	4.16
2	−0.41 0.62	0.69 ± 0.02 1.11 ± 0.09 1.29 ± 0.09	−102.44 96.77	1380 ± 0.10	1397 ± 0.05	1.22
3	−0.41 0.62	1.13 ± 0.03 1.56 ± 0.02 1.73 ± 0.06	−104.87 96.77	450.73 ± 0.13	450.7 ± 0.23	1.77
4	−0.41 0.62	ND	–	–	ND	–
5	−0.41 0.62	0.70 ± 0.04 1.09 ± 0.10 1.30 ± 0.08	−95.12 95.77	1391 ± 0.08	1352 ± 0.04	2.81
6	−0.41 0.62	0.71 ± 0.03 1.12 ± 0.12 1.31 ± 0.02	−100.00 96.77	282.5 ± 0.10	290.22 ± 0.1	2.66
7	−0.41 0.62	0.66 ± 0.06 1.09 ± 0.05 1.31 ± 0.07	−104.87 104.83	263.5 ± 0.09	251.5 ± 0.05	4.77

1 Classic red wine. (Mendoza, Argentina).
2 Red wine, tetra brik. (Mendoza, Argentina).
3 White wine, tetra brik. (Mendoza, Argentina).
4 Sweet white wine, tetra brik. (Mendoza, Argentina).
5 Cabernet Sauvignon (2012). (Mendoza, Argentina).
6 Cabernet Sauvignon (2012). (San Juan, Argentina).
7 Tempranillo-Malvec-Cabernet Sauvignon (2013). (Mendoza, Argentina).

derived from the fermentation process, the wine-making system or from different kinds of contamination.

The high concentration of Pb(II) found in some wine samples could be due to the use of pesticides or fertilizers which contained salts of this metal, but the application of these products is not systematic. Therefore, the levels of this metal depend, among other factors, on the chemical composition and the amounts of products used in a particular vineyard, the length of time between their application and the vintage period, and the amount of rain during this period, as water washes away part of these compounds from grapes.

The differences between Pb(II) levels in white and red wines were significant, with higher content in some samples of white wine, probably due to the fact that grape residues are in contact with must for a longer period for these wine types.

As there were not available Certified Materials, in order to check the accuracy of the proposed method, a comparative analysis by ICP-MS was carried out using the conditions published in previous works [28]. Results obtained for replicate of samples ($n = 4$) with proposed method and ICP-MS technique were statistically compared (t-test) and no significant differences ($p = 0.05$, $DF = 3$) were observed.

4. Conclusions

An alternative methodology simple, economical, rapid, and precise for Pb(II) traces determination using RhB dye has been developed. The coacervation scheme was carried out at room temperature and was used for retention/preconcentration of analyte on filter paper being a powerful tool for sensitive determination of metal in studied samples. The good tolerance at high levels of regular foreign constituents put in evidence the high selectivity and versatility of the new methodology. Precision and accuracy were tested and validated by ICP-MS with good agreement. The reached sensitivity was comparable at those arrived with atomic spectroscopies employing a simple and inexpensive instrumental. The developed methodology was successfully applied to red and white wines samples from Argentina.

Acknowledgments

Authors wish to thank the Instituto de Química San Luis—Consejo Nacional de Investigaciones Científicas y Técnicas (INQUISAL-CONICET), National University of San Luis (Project 22/Q228) for the financial support.

References

[1] A.S. Yazdi, Surfactant-based extraction methods, Trends Anal. Chem. 30 (2011) 918–929.
[2] K. Madej, Microwave-assisted and cloud-point extraction in determination of drugs and other bioactive compounds, Trends Anal. Chem. 28 (2009) 436–446.
[3] E.K. Paleologos, D.L. Giokas, M.I. Karayannis, Micelle-mediated separation and cloud-point extraction, Trends Anal. Chem. 24 (2005) 426–436.
[4] J.J. Santana-Rodríguez, Z. Sosa-Ferrera, D. Vega-Moreno, M.E. Torres-Padrón, C. Mahugo-Santana, Recent trends in the use of organized molecular systems combined with chromatographic techniques in environmental analysis, Anal. Bioanal. Chem. 391 (2008) 725–733.
[5] M.C. Talio, M.O. Luconi, A.N. Masi, L.P. Fernandez, Determination of cadmium at ultra-trace levels by CPE–molecular fluorescence combined methodology, J. Hazard. Mater. 170 (2009) 272–277.
[6] G. Acosta, M.C. Talio, M.O. Luconi, W.L. Hinze, L.P. Fernández, Fluorescence method using on-line sodium cholate coacervate surfactant mediated extraction for the flow injections analysis of Rhodamine B, Talanta 129 (2014) 516–522.
[7] M.C. Talio, M.O. Luconi, A.N. Masi, L.P. Fernandez, Cadmium monitoring in saliva and urine as indicator of smoking addiction, Sci. Total Environ. 408 (2010) 3125–3132.
[8] M. Alesso, G. Bondioli, M.C. Talio, M.O. Luconi, L.P. Fernández, Micelles mediated separation fluorimetric methodology for Rhodamine B determination in condiments, snacks and candies, Food Chem. 134 (2012) 513–517.
[9] A. Melnyk, L. Wolska, J. Namiesnik, Coacervative extraction as a green technique for sample preparation for the analysis of organic compounds, J. Chromatogr. A 1339 (2014) 1–12.
[10] S. Kumar, D. Sharma, D. Kabir-ud, Cloud point phenomenon in anionic surfactant + quaternary bromide systems and its variation with additives, Langmuir 16 (2000) 6821–6824.
[11] P. Mukherjee, S.K. Padhan, S. Dash, S. Patel, B.K. Mishra, Clouding behavior in surfactant systems, Adv. Colloid Interf. Sci. 162 (2011) 59–79.
[12] M. Almgren, S. Swarup, Size of sodium dodecyl sulfate micelles in the presence of additives. Multivalent and hydrophobic counterions, cationic and nonionic surfactants, J. Phys. Chem. 87 (1983) 876–881.
[13] H.L. Su, M.T. Lan, Y.Z. Hsieh, Using the cationic surfactants *N*-cetyl-*N*-methylpyrrolidinium bromide and 1-cetyl-3-methylimidazolium bromide for sweeping–micellar electrokinetic chromatograph, J. Chromatogr. A 1216 (2009) 5313–5319.
[14] C. Quiñones-Torrelo, Y. Martín-Biosca, S. Sagrado, R.M. Villanueva-Camañas, M.J. Medina-Hernández, Determination of amobarbital and secobarbital in plasma samples using micellar liquid chromatography, Biomed. Chromatogr. 14 (2000) 287–292.
[15] Y. Xia, X. Zhi, X. Wang, M. Chen, J. Cheng, Ultrasound-enhanced surfactant-assisted dispersive liquid-liquid microextraction and high-performance liquid chromatography for determination of ketoconazole and econazole nitrate in human blood, Anal. Bioanal. Chem. 402 (2012) 1241–1247.
[16] A. García-Prieto, L. Lunar, S. Rubio, D. Pérez-Bendito, Hemimicelle-based solid-phase extraction of estrogens from environmental water samples, Analyst 131 (2006) 407–414.
[17] E. Feitosa, K.T. Catelam, F.A. Hasmann, H.O. Johansson, I.C. Roberto, A. Pessoa Jr., Phase diagrams of a CTAB/organic solvent/buffer system applied to extraction of enzymes by reverse micelles, J. Chromatogr. B 862 (2008) 58–63.
[18] P.K. Tarafder, R. Thakur, Surfactant-mediated extraction of iron and its spectrophotometric determination in rocks, minerals, soils, stream sediments and water samples, Microchem. J. 80 (2005) 39–43.
[19] J. Sperkova, M. Suchanek, Multivariate classification of wines from different Bohemian regions (Czech Republic), Food Chem. 93 (2005) 659–663.
[20] S. Catarino, A.S. Curvelo-Garcia, R. Bruno de Sousa, Measurements of contaminant elements of wines by inductively coupled plasma-mass spectrometry: a comparison of two calibration approaches, Talanta 70 (2006) 1073–1080.
[21] Compendium of International Methods of Analysis – OIV 2007 **2** MA-E-C1-01-LIMMAX.
[22] S. D'Ilio, F. Petrucci, M. D'Amato, M. Di Gregorio, O. Senofonte, N. Violante, Method validation for determination of arsenic, cadmium, chromium and lead in milk by means of dynamic reaction cell inductively coupled plasma mass spectrometry, Anal. Chim. Acta 624 (2008) 59–67.
[23] M. Jakubowski, Low level environmental lead exposure and intellectual impairment in children—the current concepts of risk assessment, Int. J. Occup. Med. Environ. Health 24 (2011) 1–7.

[24] 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.
[25] D.C. Bellinger, The protean toxicities of lead: new chapters in a familiar story, Int. J. Environ. Res. Public Health 8 (2011) 2593–2628.
[26] Q. He, Z. Hu, Y. Jiang, X. Chang, Z. Tu, L. Zhang, Preconcentration of Cu(II), Fe(III) and Pb(II) with 2-((2-aminoethylamino)methyl)phenol-functionalized activated carbon followed by ICP-OES determination, J. Hazard. Mater. 175 (2010) 710–714.
[27] U. Divrikli, A.A. Kartal, M. Soylak, L. Elci, Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations, J. Hazard. Mater. 145 (2007) 459–464.
[28] F. Moyano, E. Verni, H. Tamashiro, S. Digenaro, L.D. Martinez, R.A. Gil, Single-step procedure for trace element determination in synovial fluid by dynamic reaction cell-inductively coupled plasma mass spectrometry, Microchem. J. 112 (2014) 17–24.
[29] X. Chen, J. Jia, H. Ma, S. Wang, X. Wang, Characterization of rhodamine B hydroxylamide as a highly selective and sensitive fluorescence probe for copper(II), Anal. Chim. Acta 632 (2009) 9–14.
[30] L. Balint, I. Vedrina-Dragojevic, M. Horvati, I. Mnrati, Spectrofluorometric method for determination of the total mercury content in natural waters, Z. Lebensm. Unters. Forsch. 198 (1994) 29–32.
[31] J.Y. Kwon, Y.J. Jang, Y.J. Lee, K.M. Kim, M.S. Seo, W. Nam, J. Yoon, A highly selective fluorescent chemosensor for Pb^{2+}, J. Am. Chem. Soc. 127 (2005) 10107–10111.
[32] B. Bag, A. Pal, Rhodamine-based probes for metal ion-induced chromo-/fluorogenic dual signaling and their selectivity towards Hg(II) ion, Org. Biomol. Chem. 9 (2011) 4467–4480.
[33] X. Bao, X. Cao, X. Nie, Y. Jin, B. Zhou, RBAP, a rhodamine B-based derivative: synthesis, crystal structure analysis, molecular simulation, and its application as a selective fluorescent chemical sensor for Sn^{2+}, Molecules 19 (2014) 7817–7831.
[34] D. Schiavo, J.Y. Neira, J.A. No′ brega, Direct determination of Cd, Cu and Pb in wines and grape juices by thermospray flame furnace atomic absorption spectrometry, Talanta 76 (2008) 1113–1118.
[35] S. Galani-Nikolakaki, N. Kallithrakas-Kontos, A.A. Katsanos, Trace element analysis of Cretan wines and wine products, Sci. Total Environ. 285 (2002) 155–163.
[36] R. Lara, S. Cerutti, J.A. Salonia, R.A. Olsina, L.D. Martinez, Trace element determination of Argentine wines using ETAAS and USN-ICP-OES, Food Chem. Toxicol. 43 (2005) 293–297.
[37] C. Voica, A. Dehelean, A. Pamula, Method validation for determination of heavy metals in wine and slightly alcoholic beverages by ICP-MS, J. Phys. Conf. Ser. 182 (2009) 1–6.