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Continuous flow system for lead determination by faas in spirituous beverages with solid phase extraction and on-line copper removal

Yaneira Petit de Peña [a,*], Boris Paredes [a], Wendy Rondón [a], Marcela Burguera [a], José Luis Burguera [a], Carlos Rondón [a], Pablo Carrero [a], Tarcisio Capote [b]

[a] *Departamento de Química, Facultad de Ciencias, Laboratorio de Espectroscopía Molecular, Universidad de Los Andes, La Hechicera, Mérida 5101-A, Venezuela*
[b] *Unidad de Análisis Instrumental, Decanato de Agronomía, Departamento de Química y Suelos, Universidad Centro Occidental Lisandro Alvarado, Barquisimeto, Venezuela*

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Abstract

A continuous flow system for the determination of lead in home made spirituous beverages was developed. The determination was based on the formation of a neutral chelate of the element with ammonium pyrrolidine dithiocarbamate, its adsorption onto a minicolumn packed with sodium faujasite type Y synthetic zeolite, followed by elution with methyl isobutyl ketone and determination by flame atomic absorption spectrometry. Ethanol and copper interfere strongly in the determination and therefore, must be separated prior to the analysis. Copper is removed by precipitation with rubeanic acid, while ethanol is eliminated by rotaevaporation. Sample solutions containing Pb^{2+} in the concentration range from 5 to 120 $\mu g\,l^{-1}$ at pH 2.5 could be analyzed, by using a preconcentration time of 3 min. Preconcentration factors from 80 to 140 were achieved for a sample volume of 6 ml and the detection limit varied from 1.4 to 3.5 $\mu g\,l^{-1}$, depending on the matrix composition. The relative standard deviations for 60 $\mu g\,l^{-1}$ Pb was 3.2% ($n = 10$) and the recovery of spikes (20, 40, 60 and 80 $\mu g\,l^{-1}$) added to the samples was estimated within 92–105% range, suggesting that lead can be quantitatively determined in such samples. Determining lead in several samples by an alternative technique further checked the accuracy. Finally, the concentrations of Pb^{2+} determined in 28 samples of Venezuelan spirituous beverages were in 12.6–370.0 $\mu g\,l^{-1}$ range, depending on the fermenting material based on different mixtures of agave, raw sugar cane and white sugar.

Keywords: Flame atomic absorption spectrometry; Continuous flow system; Synthetic zeolite; Lead; Alcoholic drinks; Copper removal; Spirituous beverages

1. Introduction

Lead manages to mix itself with food, contaminating it and therefore, turning it into a serious health hazard for everybody [1]. Lead is particularly harmful, even at levels considered innocuous in the past [2]. The diet is the main source of lead contamination for the general public. There has been a tendency to increase the beverage income, especially with regard to beers, wines, and soft drinks. Even though the lead quantity in these samples is low, its introduction in the daily diet may have, perhaps, significant physiological effects [3]. Alcoholic drinks may also be a significant source of lead in the daily diet [4]. The determination of lead traces in alcoholic drinks requires the use of highly sensitive analytical techniques [5]. Only few techniques have the sensitivity required to directly determine low quantities of analyte, such as electrothermal atomic absorption spectrometry (ETAAS) [6,7], or anodic stripping voltammetry with microelectrodes [8]. Flame atomic absorption spectrometry (FAAS) is available in most laboratories and is normally less subjected to interferences, but requires a preconcentration procedure in order to reach the lead concentration present in samples like spirituous beverages. Preconcentration and separation procedures coupled with FAAS offer the possibility of using a relatively simple and cheap detection system [9,10]. Lead concentrations in spirituous beverages are typically below the FAAS detection limit. The on-line flow injection (FI) coupled to preconcentration systems

* Corresponding author. Tel.: +58 274 2401390.
E-mail addresses: ypetit@ula.ve, ypetit69@hotmail.com (Y. Petit de Peña).

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using columns packed with sorbent materials improved the signal 20–30 times with respect to that obtained by conventional FAAS [10–14]. Such systems improve the sensitivity and the selectivity of FAAS allowing the determination of traces of lead in spirituous beverages, and could represent an alternative to ETAAS [10]. Consequently, preconcentration techniques based on sorption procedures seem to be the more convenient, due to the high selectivity, speed of analysis, capability to eliminate undesirable matrix components and attain high preconcentration factors [11].

The present work aims to evaluate a new automated continuous flow system containing a synthetic zeolite sodium *faujasite* type Y, (Na-FAU) packed minicolumn for the determination of lead in spirituous beverages with on-line copper removal.

2. Experimental

2.1. Instrumentation

A Varian (Mulgrave, Vict., Australia) flame atomic absorption spectrometer model SpectrAA 110, with an air-acetylene flame was used throughout. Absorbance measurements were carried out at 217.0 and 324.8 nm using lead and copper hollow cathode lamps, respectively, both from Varian, operated at 4.0 mA with deuterium background corrector, and at 10 mA, respectively. The instrumental parameters were used according to the manufacturer's recommendations. All measurements were based on peak height. A Rota evaporator Buchi B-480 was used to separate ethanol portion from samples. An Oakton pH meter was also used.

The flow injection (FI) system (Fig. 1) performed on line the copper removal and the lead preconcentration. It consists of: (i) two Gilson Minipuls-3 peristaltic pumps (four channels) as liquid propulsion devices; one channel was used for the sample and three channels for the reagents; (ii) three reaction coils, assembled with politetrafluoroethylene (PTFE) tubing; (iii) a porous plaque filter (F), specially designed in the laboratory provided with removable porous plaques to retain the precipitate; (iv) two Rheodyne injection valves provided with fixed volume loops substituted by a reaction coil (C2) followed by a minicolumn in valve V1 and by another reaction coil (C3) filled with methyl isobutyl ketone (MIBK) in valve V2. The column was manufactured in the laboratory using politetrafluoroethylene (PTFE) tubing, sealed at the ends with little glass wool plugs to avoid material losses. They were washed with diluted nitric acid, before use. For the propulsion of the organic solvent used as eluent, a displacement bottle was used.

2.2. Chemicals

All chemicals used were of analytical–reagent grade and water from a Milli-Q (Barnstead NANOpure Infinity) was used to prepare all solutions. Laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with water. A stock of 1000 mg l^{-1} Pb^{2+} (Merck) solution was prepared by dissolving 1.0000 g of metal into a minimum volume of concentrated nitric acid and diluting to 1 l with 1% (v/v) nitric acid. A standard solution of 1000 mg l^{-1} copper (Merck) was similarly prepared.

The working standard solutions were 5–120 μg l^{-1} Pb, also 40% (v/v) ethanol plus 26 mg l^{-1} Cu. Both standards and samples were pretreated according to the procedures described below (Section 2.4). The pH of these solutions was adjusted to 2.5 with dilute nitric acid.

A 0.30% (w/v) aqueous solution of ammonium pyrrolidine dithiocarbamate APDC (Sigma), was used as chelating reagent. An 8×10^{-3} mol l^{-1} aqueous rubeanic acid (Ditiooxamide) (Sigma, analysis) solution was used to precipitate copper. As elution solvent, methyl isobutyl ketone (MIBK) (J.T. Baker) was used. As sorbent material, Na-FAU synthetic zeolite was used. This zeolite was synthesized following a procedure reported elsewhere [12,15,16].

Two commercially alcoholic drinks named aguardiente I and aguardiente II were used for matrix matching assays.

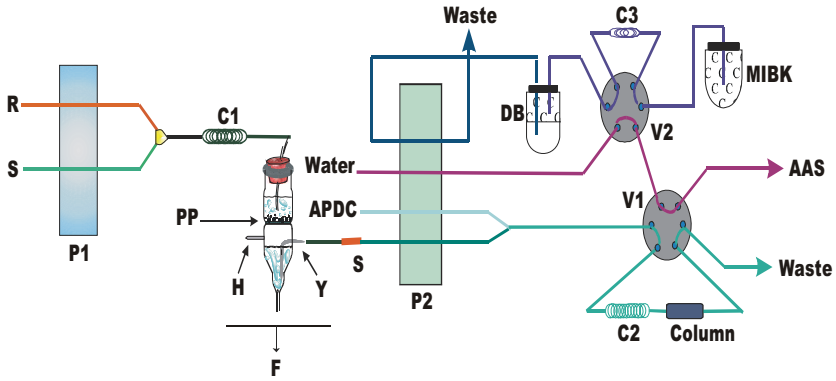

Fig. 1. Schematic diagram of the manifold for the on line elimination of copper interferences and automatic lead preconcentration. R: reagent; S: sample; C1, C2, C3: coils; DB: displacement bottle; F: filter; H: to the vacuum system; P: peristaltic pump; V1, V2: injection valves; Y: connection; PP: porous plaque; F: filter with porous plaque.

2.3. Samples

The alcoholic drinks were obtained by distillation of either agave ($n = 4$), white sugar ($n = 4$), raw sugar cane ($n = 4$), or mixtures of agave–white sugar ($n = 11$) and agave–raw sugar cane ($n = 5$). These samples, which contain about 40% (v/v) alcohol with about 60% (v/v) water, were provided by artisans from rural areas of the Urdaneta municipality in Lara state, Venezuela. Sampling process was really rough, since the producers are located in areas of difficult access. The manufacturing activity of these beverages is illegal and not controlled by sanitary authorities; they are elaborated on domestic distilleries (*alambiques*) entirely made of copper. The glass bottles with tight plastic cups containing aliquots of samples were stored in a cool, dry place until analysis was performed.

All the samples differ only on the fermenting base from which the liquors are obtained. In that sense, five types of samples were analyzed, in which the ethanol comes from the fermentation of: (i) agave Cocuy alone; (ii) a mixture of agave and white sugar; (iii) agave and raw sugar cane; (iv) white sugar alone and (v) raw sugar cane alone. This liquors are denominated "aguardiente de Cocuy de Penca", although not all are fabricated from agave. They are illicitly produced and named Cocuy to hoax customers.

2.4. Preliminary assays

A pool was prepared by mixing about 5 ml taken from each sample without previous treatment and a measurement of the lead signal was made using conditions reported in the literature [17–20]. No analytical signal was detected because an abundant precipitate was formed in the reaction coil in the concentration step, which altered the flow in the system and damaged the minicolumn. Since the distillation process is made using copper piping, and the APDC reagent is known to form metal complexes with copper [12,21,22], it was inferred that the samples contained high quantities of this metal. A test to detect copper in the pool was performed using conventional flame atomic absorption spectrometry [21]. The amount of copper was found to be $26\,\mathrm{mg\,l^{-1}}$. Presence of nickel, cadmium and cobalt were also tested since they also form APDC complexes under the same conditions, but no detectable signals were found for any of these metals. To remove the copper interference, attempts were made to separate it by selective precipitation using sodium pyrrolidine dithiocarbamate (NaDDC), 1,10-phenanthroline and rubeanic acid (ditiooxamide) as precipitating agents [23]. The assays were carried out in batch mode in aqueous solutions containing $26\,\mathrm{mg\,l^{-1}}$ of copper and $50\,\mu\mathrm{g\,l^{-1}}$ of lead, and then determining copper in the remaining solution by conventional FAAS and lead by preconcentration using a Na-FAU minicolumn and FAAS as detection system. The same assays were also performed on-line by using the manifold shown in Fig. 1. The three precipitating reagents were tested with samples containing either $26\,\mathrm{mg\,l^{-1}}$ Cu + $50\,\mu\mathrm{g\,l^{-1}}$ Pb or $50\,\mu\mathrm{g\,l^{-1}}$ Pb. The results shown in Fig. 2 indicates that NaDDC (Fig. 2A) is not a selective reagent for copper because forms a precipitate with lead too, which might coprecipitate copper under the same experimental conditions. On the other hand, in the presence of 1,10-phenanthroline (Fig. 2B) the copper interference is not completely circumvented as the curdy precipitate formed is difficult to separate by filtration. Rubeanic acid (Fig. 2C) was selected as the precipitating agent for further experiments because instantaneously reacts with copper forming an abundant precipitate, easily separated by filtration as previously reported [24,25]. The acid–base concept could explain this selectivity since the complex formation depends on the chemical specie size, electronic density and oxidation state [26]. According to Pearson rule [27], as the rubeanic acid contains an $(NS)^-$ active site which makes it an intermediate base [28], it would prefer to coordinate with Cu(II) which is considered an intermediate acid, instead of coordinating with Pb(II) which is a weak acid with a big size and consequently with a low electronic density. This behavior is shown in Fig. 3.

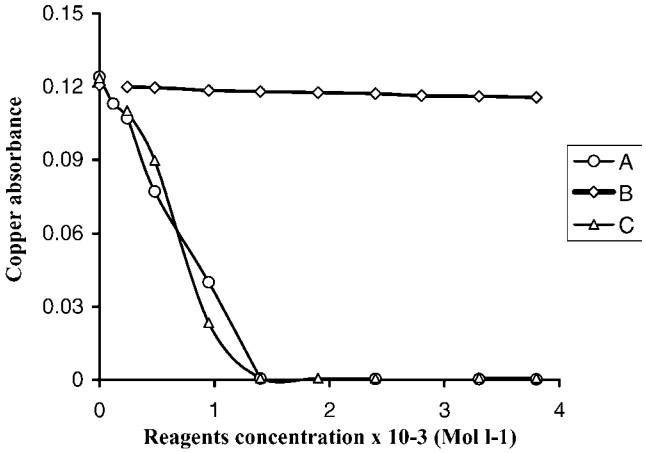

Fig. 2. Effect of copper precipitating reagents: sodium diethylditiocarbamate (A); 1,10 phenanthroline (B); and rubeanic acid (C) on copper ($26\,\mathrm{mg\,l^{-1}}$) absorbance. All experiments were performed in the presence of $50\,\mu\mathrm{g\,l^{-1}}$ Pb.

To confirm the on-line copper removal, the pool sample was analyzed by conventional FAAS and no copper signal was observed. However, when analyzed on-line using this configuration, no lead signal was observed neither. It was assumed that the hydroalcoholic matrix could be interfering with the lead analytical signal. Therefore, the effect of the concentration of ethanol between 0 and 50% (v/v) was investigated, and it was observed that as the ethanol concentration increases, the lead signal decreases. This behavior might be due to the solubility of Pb-$(PDC)_2$ in this matrix, which prevents its formation and therefore the lead preconcentration in the flow system. For this reason, previous to the lead preconcentration, the ethanol must be separated from samples. To remove the interference of ethanol, a procedure

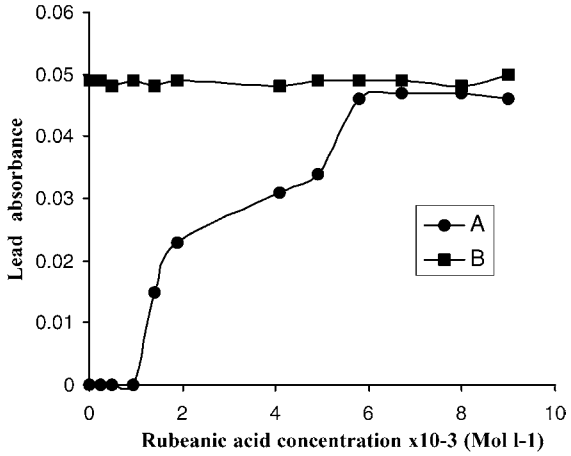

Fig. 3. Effect of the rubeanic acid concentration on the lead analytical signal using a solution of 50 μg l^{-1} of lead alone (A) and 50 μg l^{-1} Pb plus 26 mg l^{-1} of Cu (B).

previously used for wine analysis [29] was applied as described below.

2.5. Ethanol separation

In order to reduce this interference the ethanol was separated from the matrix, by a vacuum distillation, performed by rotaevaporation. Several assays were performed on solutions containing 50 μg l^{-1} of lead, and 40/60% (v/v) of ethanol/water attempting to simulate the alcohol content estimated by the manufactures. Therefore, the alcohol was evaporated at the boiling temperature of the azeotrope, until it stopped boiling, then the temperature was raised until the water boiling point was reached, allowing a little quantity of water to distill too. In this precise moment the rotaevaporation was stopped, while non-volatile substances remained in the distillation rounded bottom flask. These solutions were then taken to their original volume by adding deionized water, in order to restore the original lead concentration. The lead signal was in all cases 10% less than that from a standard aqueous solution of 50 μg l^{-1} Pb. The loss of analyte occurs in the same proportion for all the hydroalcoholic dissolutions. Due to these observations a matrix matching curve was constructed as specified below.

2.6. Flow-injection copper removal and lead preconcentration

The FI manifold is shown in Fig. 1. The operational sequence of the manifold is completed in two steps: preconcentration and elution. In the first step, a sample (after separating the ethanol) or standard solution containing 5–120 μg l^{-1} of lead and 26 mg l^{-1} of Cu (pH, 2.5) was introduced into the system through the sample channel S, while a 8×10^{-3} mol^{-1} rubeanic acid solution was introduced through the reagent channel, R, at a flow rate of 2 ml min^{-1}. A precipitate was immediately observed in the reaction coil C1 due to the formation of the chelate Cu–rubeanic acid, which was retained in filter F. Afterwards, the copper free solution, was transferred to the pre-concentration system through connection Y and vigorously mixed with an 0.3% (w/v) APDC solution to form the chelate lead pyrrolidine dithiocarbamate [Pb(PDC)$_2$] which was retained in the minicolumn located in the loop of the injection valve (V1), while the matrix of the sample was sent to waste. During this period, which lasted 3 min, a stream of water was continuously passed through the nebulizer, so that the matrix of the sample never reached the detector. Meanwhile, the coil (C3) located in the injection valve (V2) is charged with 100 μL of MIBK, and then, the injection valves were simultaneously inverted, so that the chelate adsorbed is eluted and the analyte is directed to the detector.

3. Results and discussion

3.1. Optimization of experimental parameters

The flow system parameters were optimized by varying the chemical and the flow conditions, in a univariate manner. The optimal conditions were selected considering the maximum signal and the best reproducibility for lead absorbance, using the matrix matching standard solution of 50 μg l^{-1} of lead. Chemical variables were studied first, so, this standard solution was continuously pumped in the flow system shown in Fig. 1 at a sample flow rate of 2 ml min^{-1} and a preconcentration time of 3 min.

The pH of the samples or standards might affect the formation and sorption of the Pb-(PDC)$_2$ chelate. Its effect was studied between 0.5 and 7.0 units, adjusted with HNO_3. The best results were obtained for pH between 2 and 3 units. The decrease of the lead signal below pH 2 is probably due to the fact that APDC earns a new proton, prevailing this fact over the formation of the complex Pb-(PDC)$_2$. At pH values higher than 3, lead hydrolysis might occur. Therefore, 2.5 was selected as the most favorable pH value.

The effect of the ADPC concentration was studied between 0.001 and 0.4% (w/v). The lead signal increases as APDC concentration increases up to 0.2% (w/v); thereafter, the signal tends to keep constant. Given these results, it was decided to choose 0.3% (w/v) as the most favorable concentration of complexing agent, so that enough reagent is guaranteed when higher analyte concentrations are used.

The effects of the flow variables were also studied. To examine the effect of the sample flow rate, 6.0 ml of a solution containing 50 μg l^{-1} lead was pumped into the system at flow rates from 0.5 to 6.0 ml min^{-1}. There is an increase in the analytical signals up to 2 ml min^{-1}; probably to sample dispersion is very little affected by variations in flow rate. Between 2.5 and 6 ml min^{-1} the analytical signal decreases, as a result of an increase in the sample dispersion and a decrease in the analyte residence time in the reaction coil. The effect of the complexing reagent flow rate was studied

within the 0.20–1.4 ml min^{-1} range. Increasing the APDC flow is equivalent to increasing its concentration; however, simultaneously the sample dilutes in the reagent leading to a drastic decrease of the signal. There is a zone of maximum absorbance, between 0.3 and 0.5 ml min^{-1}, then, the signal gradually decreases, since the dilution of the sample in the reagent is bigger. As a result, an optimum APDC flow of 0.4 ml min^{-1} was selected.

The length of the reactor C2 was varied from 50 to 500 cm. Teflon piping of 0.8 mm internal diameter were used throughout. The maximum adsorption of the chelate was achieved with a length of the reactor of 200 cm, indicating that the chelate is completely formed with a residence time of 16 s. With reactors longer than 250 cm, the chelate would probably be adsorbed on the internal walls of the Teflon piping, distributing itself over a large superficial area, and subsequently not dissolving completely in the volume of MIBK used, with resulting in a decrease of the analytical signal.

The effect of the eluent volume was studied by varying the MIBK volumes from 30 to 500 μl. The maximum attained signal corresponded to 100 μl of MIBK, which was considered optimum and was used in further experiments. Volumes of MIBK lower than 90 μl give rise to the lowest analyte responses due to incomplete elution. For volumes higher than 100 μl the signal decreases, probably due to the dilution of the analyte in the dissolvent.

The optimized operation conditions for lead determination are shown in Table 1.

Table 1
Optimal experimental conditions

System	Parameter	Conditions
Flame (AAS)	Wavelength (nm)	217
	Lamp current (mA)	4
	Slit width (nm)	1
	Air/acetylene (l min^{-1})	2/10
Precipitation–filtration	Sample pH and RA reagent[a]	2.5
	Rubeanic acid concentration (mol l^{-1})	8×10^{-3}
	Sample and reagent flow rate (ml min^{-1})	1
	Coil length (cm)	50
Preconcentration–elution	Sample pH[a]	2.5
	APDC concentration (%) m/v	0.3
	Sample flow rate (ml min^{-1})	2
	APDC flow rate (ml min^{-1})	0.4
	Carrier flow (water) rate (ml min^{-1})	4
	MIBK volume (μl)	100
	Reaction coil length (cm)	200
	Preconcentration time (min)	3
	Elution time (s)	20
	Quantity of zeolite Na-FAU (mg)	20

[a] Adjusted with HNO_3—RA: rubeanic acid, APDC: ammonium pyrrolidine dithiocarbamate, MIBK: methyl isobutyl ketone.

3.2. Interferences study

The influence of other metals that might replace lead in the original APDC chelate was investigated with the purpose of identifying potential interferents. The following cations Al^{3+}, Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Bi^{3+}, might be present in the real samples and are capable of forming APDC chelates under the same conditions as lead.

Tolerance levels, defined as the maximum concentration of interferent that causes a change in the analytical signal no higher than 10% when compared with the signal of 50 μg l^{-1} lead alone were: 5000, 50, 50, 50, 200, 100, 50, 50, 50 mg l^{-1} for Al^{3+}, Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Bi^{3+}, respectively. In all cases, the presence of the interferent decreased the lead signal. This effect can be attributed to: (i) the complexing agent concentration is insufficient to form the lead and the interferent chelates (chelating competition) or (ii) the volume of eluent used (100 μl) might be inadequate to completely elute all the chelates from the minicolumn. None of these elements are present in the spirituous beverages above these tolerance levels.

3.3. Analytical features and analysis of real samples

The analytical features obtained for 3 min of preconcentration time and 6 ml of sample and different matrix matching solutions (water, water–ethanol, water–ethanol–copper, and commercial *aguardiente I and aguardiente II*) are shown in Table 2. The experimental preconcentration factor, (calculated as the ratio of the slopes of the calibration curves, obtained with and without preconcentration), for water–ethanol–copper mixture matches better with that obtained for the alcoholic pool sample, considering it the best choice for the calibration graphs before the analysis of real

Table 2
Analytical characterization of the system

Matrix	Analytical equation	Correlation factor (R^2)	Linear range (μg l^{-1} Pb^{2+})	PCF	SF (h^{-1})	DL (μg l^{-1})	R.S.D. (%)
Water	$A = 0.0021X + 0.0021$	0.9994	5–120	140	18	1.4	1.5
Water–ethanol	$A = 0.0018X + 0.0138$	0.9991	5–120	122	18	2.5	2.4
Water–ethanol–copper	$A = 0.0013X + 0.0135$	0.9990	5–120	87	18	3.1	2.8
Aguardiente I	$A = 0.0012X + 0.0179$	0.9976	5–120	80	18	3.5	3.6
Aguardiente II	$A = 0.0014X + 0.0120$	0.9985	5–120	94	18	2.7	3.2

A: absorbance; *X*: concentration of Pb^{+2} (μg l^{-1}); PCF: preconcentration factor compared to the conventional introduction of aqueous sample ($A = 0.0015X + 0.0079$, $R^2 = 0.9993$); SF: sampling frequency; DL: detection limit; R.S.D.: relative standard deviation.

Table 3
Analytical applications reported for on-line preconcentration of lead compared with this work

Element	Matrix	Technique	Reagent	Average concentration ($\mu g l^{-1}$)	Detection technique	DL ($\mu g l^{-1}$)	R.S.D.	Reference
Pb	Wine, juice, fruit, other drinks	Flow injection-hydride generation	$NaBH_4$	40	Atomic absorption spectrometry	10 wine 1 in juice	5–6% in wine 3–8% in juice	[3]
Pb	Spanish wines and other alcoholic drinks	Flow injection-hydride generation	$NaBH_4$	97	Atomic absorption spectrometry	10	5–6%	[5]
Pb and Cu	Italian wine	Different techniques of pretreatment	HCl, H_2O_2 radiation UV, HCl–UV	5–300	Anodic stripping-voltammetry		Cu 0.5% Pb 1.3%	[8]
Pb	Port wine	Flow injection-preconcentration with resins of ionic exchange	Malachite green, iodine like chelating reagent	73	UV–vis compared with ETAAS	12	2.6%	[30]
Pb	Alcoholic drinks	Direct determination with an atom trapping		52	Atomic absorption spectrometry		2.7–5.1%	[31]
Pb	White, rosy and red wine	Flow injection-hydride generation	$NaBH_4$	85 123 155	Atomic absorption spectrometry	24	2.4%	[32]
Pb	Homemade spirituous beverages (Cocuy)	Flow injection-preconcentration with Na-FAU	APDC	12.6–370[a]	Atomic absorption spectrometry	1.4–3.5	3.2%	This work

[a] Range.

Table 4
Concentration of lead in six different samples determined by ETAAS and the proposed procedure

Sample code	Concentration of lead ($\mu g\,l^{-1}$)	
	ETAAS	This procedure
2	60.8 ± 1.1	59.1 ± 1.2
8	248.5 ± 2.9	246.8 ± 3.1
14	13.2 ± 0.5	12.6 ± 0.8
17	38.4 ± 0.8	37.5 ± 1.0
24	56.3 ± 1.1	55.7 ± 1.4
27	16.4 ± 0.6	15.9 ± 0.5

samples. Therefore, in order to determine the lead content in real samples, linear calibration curves within the concentration range from 5 to 120 $\mu g\,l^{-1}$ Pb^{2+} with 26 $mg\,l^{-1}$ of Cu^{2+} and 40% (v/v) ethanol were selected.

Samples volumes beyond 6 ml (equivalent to more than 3 min of preconcentration time) can be used and thus, higher preconcentration factors can be achieved, with consequent decrease in the sampling throughput.

The results shown in Table 3 indicate that the sensitivity and precision of the proposed procedure is comparable to those obtained by other authors [3,5,30–32]. The detection limits (3σ), are lower when compared to those obtained in other experiments using FAAS [3,32], and, in one case, even lower than those obtained with ETAAS [6].

3.4. Accuracy of the proposed method

As there are not known alcoholic drinks certified for lead, the accuracy of the proposed method was verified by an alternative [6] method and through recovery studies. The results obtained by ETAAS are in good agreement with those obtained by the proposed procedure, as shown in Table 4. The Student's *t*-test at 95% confidence level confirmed that the results obtained by the two methods are similar. Several samples were reinforced with 20, 40, 60, 80 $\mu g\,l^{-1}$ of Pb^{2+} and then submitted to the procedure described for the removal of ethanol. Under the optimal conditions given in Table 1 and using the flow system configuration shown in Fig. 1, recoveries ranging between 91.3 and 104.7% were obtained. This proves that a quantitative recovery of lead can be obtained from all the samples analyzed.

The determination of lead in a total of 28 *Cocuy* samples was accomplished applying the pretreatment and preconcentration procedures described in this paper. From the result shown in Table 5, it can be appreciated that lead concentration in the different samples ranges 12.6 and 370.0 $\mu g\,l^{-1}$, with an average value of 78.9 $\mu g\,l^{-1}$. Although the samples are produced from the same fermenting base it is important to point out that the data obtained are very disperse, probably due to the intrinsic distillation process carried out by independent artisan producers. A significant number of samples contain high lead levels, which might become a public health problem, in view of the high toxicity of this metal.

Table 5
Concentration of lead in homemade alcoholic drinks

Sample code	Lead found ($\mu g\,l^{-1}$)	Range ($\mu g\,l^{-1}$)
Agave–white sugar[a]		
1	136.1 ± 0.9	
2	59.1 ± 1.2	
3	18.8 ± 1.2	
4	22.2 ± 1.1	
5	22.2 ± 0.4	
6	22.2 ± 1.2	22.2–354.5
7	354.5 ± 9.3	
8	246.8 ± 3.1	
9	31.1 ± 2.0	
10	75.7 ± 2.6	
11	131.2 ± 6.8	
Agave–raw sugar cane[a]		
12	108.3 ± 1.9	
13	19.6 ± 0.5	
14	12.6 ± 0.8	12.6 – 108.3
15	59.1 ± 1.1	
16	25.3 ± 1.3	
Agave[a]		
17	37.5 ± 1.0	
18	16.0 ± 0.8	16.0 – 194.2
19	194.2 ± 4.6	
20	22.5 ± 0.7	
White sugar[a]		
21	32.6 ± 2.3	
22	21.8 ± 1.3	12.9 – 55.7
23	12.9 ± 0.4	
24	55.7 ± 1.4	
Raw sugar cane[a]		
25	49.9 ± 2.3	
26	35.0 ± 1.5	15.9 – 370.0
27	15.9 ± 0.5	
28	370.0 ± 6.2	

[a] Fermenting base.

The method developed here would be useful to monitor artisan and commercial alcoholic beverages for lead levels and alert the producers about the harm that might cause to humans. Since there are not national laws to regulate the level of heavy, toxic metals present in the sort of beverages analyzed in this work, the following references were adopted: the Office International de la Vigne et du Vin (OIV) [33] in Europe, establishes that the highest permissible lead level is 300 $\mu g\,l^{-1}$ and 100 and 200 $\mu g\,l^{-1}$ in the USA and Canada, respectively [34]. The European Union or the national authorities of each country imposed these levels. When these international regulations are applied to the results given in Table 5, 7% of the samples exceed the permissible limits in Europe, 11% exceed the Canadian rules, while 25% of the samples exceed the American rules.

4. Conclusions

The results obtained in this work demonstrate the applicability of the proposed procedure to the separation,

preconcentration and determination of traces of lead in spirituous beverages. The ethanol separation from the hydroalcoholic matrix by rotaevaporation has demonstrated to be effective, while rubeanic acid proved to be a selective agent for the precipitation of high amounts of copper present in the samples analyzed in this work. Its on line removal is an additional performance of the continuous system described here.

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