

Accepted Manuscript

Lead preconcentration by solid phase extraction using oxidized carbon xerogel and spectrophotometric determination with dithizone

Ariel Maratta, Sandra Vázquez, Ayelén López, Miriam Augusto, Pablo H. Pacheco

PII: S0026-265X(16)30043-1
DOI: doi: [10.1016/j.microc.2016.04.017](https://doi.org/10.1016/j.microc.2016.04.017)
Reference: MICROC 2464

To appear in: *Microchemical Journal*

Received date: 15 March 2016
Revised date: 18 April 2016
Accepted date: 19 April 2016

Please cite this article as: Ariel Maratta, Sandra Vázquez, Ayelén López, Miriam Augusto, Pablo H. Pacheco, Lead preconcentration by solid phase extraction using oxidized carbon xerogel and spectrophotometric determination with dithizone, *Microchemical Journal* (2016), doi: [10.1016/j.microc.2016.04.017](https://doi.org/10.1016/j.microc.2016.04.017)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Lead preconcentration by solid phase extraction using oxidized carbon xerogel and spectrophotometric determination with dithizone.

Ariel Maratta^{1,3}, Sandra Vázquez^{2, 3}, Ayelén López², Miriam Augusto^{2, 3} and Pablo H. Pacheco^{1*}

¹Instituto de Química de San Luis, INQUISAL, Centro Científico-Tecnológico de San Luis (CCT-San Luis), Consejo Nacional de Investigaciones Científicas - Universidad Nacional de San Luis, Chacabuco y Pedernera, Ciudad de San Luis, 5700, Argentina

²Instituto de Ciencias Básicas, FFHA, Universidad Nacional de San Juan
Av. Libertador San Martín 1109 – Oeste, 5400 San Juan, Argentina.

³Departamento de Física y Química, FFHA, Universidad Nacional de San Juan
Av. Ignacio de la Roza 330 – Oeste, 5400 San Juan, Argentina.

***Corresponding author**

Pablo Pacheco

E-mail: ppacheco@unsl.edu.ar

Abstract

The proposed methodology is based on the preconcentration of Pb^{2+} on oxidized carbon xerogel, a porous material of low density and high surface area. Adsorbed Pb^{2+} was eluted with HCl, followed by complexation with dithizone in ethanol-water solution and determined by UV-visible spectrophotometry in a continuous flow system (FI). Variables such as pH, type of eluent, eluent concentration, type of complexing solvent, concentration of complexing reagent and flow rates were optimized. The proposed system reached an enrichment factor of 50, with 5 mL of sample. Detection limit was of $0.9 \mu\text{g L}^{-1}$, with a precision of 7.8% (n=10). The proposed system was successfully applied to the determination of Pb in tap water from San Juan city, Argentina.

Keywords: Lead; Carbon xerogel; Spectrophotometric determination; Dithizone

1. Introduction

Lead is a metal found in the environment, from both natural and anthropogenic sources. It is a toxic metal and its species and compounds dissolved in waters present a high risk to living organisms [1]. It has an accumulative effect, causing serious hematologic, brain and kidney malfunction problems [2].

In recent decades, the main source of lead in wastewater is industrial activity related to lead batteries manufacturing, electronics, paint, oil, as well as the cars emission and mining activity [3]. Furthermore, the presence of lead in drinking water, occurs as a result of corrosion and detachment of old lead pipes commonly used in homes [4, 5]. The presence of lead in natural waters is within a range of 2-10 $\mu\text{g L}^{-1}$, and the World Health Organization (WHO) establishes a recommended limit of 10 $\mu\text{g L}^{-1}$ in water corps for consumption [6].

From the above mentioned, there is growing interest to determine lead traces in water. However, most analytical techniques lack the sensitivity required for trace metals determination [7]. Despite the fact that there is a breakthrough in the development of modern instrumental techniques, there are economic difficulties for standard laboratories in acquiring the necessary equipment to determine traces of heavy metals found in environmental samples.

The UV-visible spectrometry has limitations because of low sensitivity compared with modern instrumental methodologies. However, even today it is widely used in different scientific fields worldwide, especially in biochemistry and analytical chemistry, because of its simplicity, flexibility, low cost and convenience. In recent years, a need to reduce the amounts of sample and/or reagents used in an analytical

determinations emerged [8, 9]. For these reason research was focused on coupling novel techniques of sample pretreatment with conventional spectrophotometry. In this way it is possible to improve sensitivity, and consequently expand applications.

In order to achieve determination of low concentrations of different heavy metals various sample pretreatment procedures have been designed as preconcentration techniques like solid phase extraction (SPE) [10, 11]. The principle of this technique is based on metals retention on a suitable sorbent contained in a minicolumn and subsequent elution with an specific solvent [12]. SPE represents advantages as short extraction times, high enrichment factors and recovery, simplicity and economy in the use of reagents [13].

The choice of absorbent material used in the SPE system is of great importance. They require some properties like high selectivity, stability and efficient extraction. Today there is a relatively new group of carbonaceous materials, carbon aerogel and xerogel, which can be obtained by polycondensation of resorcinol with formaldehyde, which is subsequently dried (for subcritical or supercritical xerogels for aerogels) and finally carbonized in an inert atmosphere [14, 15]. They are characterized by their porous texture, low density, high surface areas and excellent textural properties. It is common to use these materials in industries as agents for inorganic matter removal (heavy metals or halide ions) and organic matter (phenols or more colorants) from aqueous solutions [15-17].

The objective of this study is to determine the effectiveness of oxidized carbon xerogel as sorbent in SPE to preconcentrate lead from tap water samples. Lead complexation with dithizone allowed a spectrophotometric determination. To this end a FI system is proposed, decreasing reagents consumption and avoiding the implementation of organochlorine reagents commonly used as an extraction solvent for

dithizone metal complexes. The developed technique encompassed lead concentration in water samples regard sensibility according to WHO regulations.

2 Experimental.

2.1 Instrumentation.

For Pb absorbance measurements, a spectrophotometer double beam UV-visible (UV-1800 PC Shimadzu, Kyoto, Japan) was used, equipped with cells for continuous flow (quartz windows, 70 μ L nominal volume, 10 mm pathlength, Starna Pty. Ltd, NSW, Australia). Gilson Minipuls 3 peristaltic pump (Villiers, Le-Bell, France) and Tygon tubes-type (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel sample, eluent and reagents in FI system. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. A conical minicolumn was used as sorbent support (40 mm long, 4.5 mm internal diameter greater and 1.5 mm internal diameter less). It was prepared by placing 30 mg of oxidized carbon xerogel in a conical tip by the empty packaging dry method. To avoid sorbent losses during analysis small amounts of quartz wool were placed at both ends.

2.2 Reagents.

Unless otherwise stated, the chemicals used were of analytical reagent grade and, therefore, no further purification was required. The stock standard solution [1.000 g L^{-1} , 4% HNO_3 (v v⁻¹)] of Pb^{2+} was obtained from Merck (Darmstadt, Germany) and was diluted with deionized water. Dithizone solution was prepared by dissolving an appropriate amount of dithizone from Merck (Darmstadt, Germany) in an ethanol-water

mixture (1:9). Buffer solutions with different pH were prepared by dissolving appropriate amounts of suitable salts purchased from Merck (Darmstadt, Germany) and Fluka (Switzerland) in deionized water. A 0.75 mol L^{-1} Tris (hydroxymethyl) aminomethane (TRIS)–HCl buffer solution (pH 6.0) was prepared from a reagent grade Trizma® hydrochloride (Sigma) and adjusted to pH 6.0 with NaOH. Sodium hydroxide and hydrochloric acid were purchased from Sigma–Aldrich. This solution was prepared daily.

Carbon xerogel was obtained by polycondensation of resorcinol and formaldehyde, with subsequent chemical activation with potassium hydroxide. Details and procedure have been reported by Stolarski *et al.* [18] and Łużny *et al.* [15]. Subsequently, the carbon xerogel was treated with concentrated nitric acid to clean and remove any residues from generation process. This procedure allows the generation of oxidized groups on the surface of carbon xerogel, improving sorbent properties. Then they were centrifuged, washed with milli Q water, filtered and dried [19].

2.3 Sample preparation

Water samples were taken from six different sampling points from San Juan city water system. Tap was left open for 15 minutes and the containers were filled and emptied three times. Before analysis water samples were filtered through membrane filters with 0.45 microns pores immediately after sampling. Samples were transported refrigerated at 5°C , once in the lab they were analyzed immediately.

2.4 Procedure

In Figure 1 the diagram of the FI system used for this purpose is shown. Before introducing the sample, a buffer solution was added to condition the sample pH. Next, sample **S** was loaded on minicolumn **M** with valve **V₁** in loading position **a** (pump **P₁**). Lead elution was achieved by passing the eluent **E** (pump **P₂**), injection valve **V₁** in position **b**. Then, it is merged first with **NaOH** (pump **P₃**) to neutralize eluent pH (valve **V₂**, position **NaOH**), and second with Tris-HCl buffer solution (**P₃** pump, valve **V₃**, position **B**) to stabilize eluate pH's. After the first reaction coil **RC** the complexing reagent dithizone is added (pump **P₃**, valve **V₄**, position **D**) entering in the second **RC**, and subsequently entering into **UV-visible spectrophotometer**. Once the operating conditions were established analyte determination was reached.

3 Results and Discussion

3.1 Study of micro-SPE.

Lead retention conditions on carbon xerogel, as pH, eluent; and sample and eluent flow rates were studied. For all conditions Pb^{2+} concentration was determined by UV-visible spectrophotometry previous complexation with dithizone. A Pb^{2+} concentration of $10 \mu\text{g L}^{-1}$ was used for optimization. Recoveries were calculated versus the theoretical concentration.

3.1.1 Effect of pH.

Sample pH was evaluated to identify optimal sorption conditions for lead retention on oxidized carbon xerogel. The study was performed by adding buffer solutions to Pb^{2+} standard solution in a pH range of 2-9, previous introduction to FI

system. A sample flow rate of 1.0 mL min^{-1} was used. Results obtained are shown in Figure 2. It is observed that Pb retention increases in a pH range of 5.0-7.0. This may be explain considering that at pH values lower than 5.0 Pb^{2+} is partially hydrolysed resulting PbOH^+ , competing with protons from the acid medium for adsorption sites on the surface of carbon xerogel [2, 20]. Furthermore, at pH values above 7.8, Pb begins to precipitate as hydroxide [21]. For these reasons, an optimal pH of 6.0 was used. At this pH value the Pb species that interacts with the sorbent is Pb^{2+} , which is very stable in aqueous media [20]. Pb^{2+} can interact with C-O groups generated on the surface of carbon (as carboxylic groups) that at pH 6.0 are negatively charged (pKa 4.7, carboxylic acid) [22]. In addition retention is enhanced by the large surface area available due to porosity developed in the carbon xerogel [23].

3.1.2 Sample flow

Sample loading flow rate through the minicolumn is a critical variable to achieve Pb^{2+} quantitative retention on oxidized carbon xerogel because it determines contact time of the analyte with the sorbent, affecting the time of analysis. The conditioned sample was passed through the column at flow rates ranging from 0.1 to 1.2 mL min^{-1} (Figure 3). The selected optimal flow rate was 0.4 mL min^{-1} because at higher flow rates Pb^{2+} contact time with the sorbent decreases, thus decreasing analyte retention. Lower speed affects the analysis time significantly.

3.1.3 Elution

In literature describing columns filled with carbon based substrates for metal retention, authors agree that elution is achieved with acidic solutions, instantaneously

and with high recoveries, through a process of ion exchange between metal and H^+ [20]. In this paper, ethanol, nitric acid and hydrochloric acid were tested, obtaining higher recoveries with HCl. A concentration range of 0.12 - 1.2 mol L^{-1} was evaluated. As shown in Figure 4, a minimum concentration of 0.6 mol L^{-1} is sufficient for Pb^{2+} quantitative elution.

A very important parameter to optimize was elution flow rate, because it is related to analyte desorption kinetics and enrichment factors. Flow rates from 0.4 to 1.6 mL min^{-1} were tested and results are shown in Figure 5, where a flow rate of 0.4 mL min^{-1} exhibited quantitative elution.

3.2 Study on the colorimetric determination

The developed method for Pb^{2+} analysis involves adsorption on carbon xerogel, complexation with dithizone and determination by UV-visible spectrophotometry in a FI system. To optimize complexation with dithizone and determination, different variables such as pH, type of solvent, dithizone concentration, and reagents flow rate and measurement wavelength were evaluated.

3.2.1 Study of the complexing reagent Dithizone

Dithizone (Diphenylthiocarbazone) it is known as one of the most important chelating reagents introduced to form metal complexes referred as metal dithizonates. Dithizone is commonly represented in its neutral form as H_2Dz because it has two exchangeable protons. It is recognized as a sensitive method for Pb determination in colorimetric methods, properly described by Fries and Getrost [24].

In order to frame this technique with green chemistry standards, use of highly toxic organic solvents was avoided, and solvents such as acetone, acetic acid, ethanol and ethanol-water mixture were evaluated to dilute dithizone. Best responses were obtained with ethanol-water mixture (1:9).

Previously the optimum wavelength was determined by treating the eluted solution with dithizone, where Pb^{2+} formed a colored complex (Dithizone- Pb^{2+}) (Figure 6). The maximum absorbance of this complex was at a wavelength of 544 nm, proportional to Pb^{2+} concentration.

Dithizone is known to form complexes with metals in 2:1 ratio [24, 25]. However it was decided to study a concentrations range according to established optimal complex formation. Concentrations tested oscillated in values from $1.43 \cdot 10^{-5}$ mol L^{-1} to $5.72 \cdot 10^{-5}$ mol L^{-1} , being injected at a flow rate of 0.45 mL min^{-1} . Figure 7 shows the effect of dithizone concentration where above $4.29 \cdot 10^{-5}$ mol L^{-1} an optimum colorimetric response was achieved. For subsequent analysis a dithizone concentration of $4.29 \cdot 10^{-5}$ mol L^{-1} concentration was selected.

3.2.2. Effect of Buffer Solution

The sample acidity is an important factor to optimize, since at low pH values, protons excess present in acidic solutions can protonate binding sites of chelating molecules like dithizone. At high pH values hydroxides from alkaline solutions can precipitate metals or metal complexes. To stabilize eluate pH's first the acidity is reduced with a NaOH solution 0.6 mol L^{-1} and a flow rate of 0.3 mL min^{-1} . Thus, it was possible to evaluate the effect of buffer solutions.

To evaluate this parameter, citrate-citric and TRIS buffer solutions were merged with eluate at pH range of 5.0 – 9.0 at a flow rate of 0.7 mL min⁻¹ according to the optimum pH complex formation, corresponding to pH 6.0 - 7.0. TRIS was selected for future assays since it maintains pH at 7.0 values at flow rates of 0.7 mL min⁻¹.

3.3 Interferences

It is known that dithizone form colored complexes with Bi, Sn²⁺ and Tl⁺ and weak ammoniacal cyanide solution (pH 8.5 to 9.5) [26]. However these complexes are formed in chloroform media, and at different pH values compared to pH 7.0 and ethanol-water media employed in this research, decreasing the possibilities of spectral interferences. Nevertheless dithizone complexation under these conditions was evaluated for these elements and others to evaluate possible interferences. Pb²⁺ determinations at concentrations range close to LOD to 30.0 mg were not interfered in presence of 20 mg L⁻¹ Tl⁺, 100 mg L⁻¹ Sn²⁺, 200 mg L⁻¹ In³⁺, and 1000 mg L⁻¹ of each of the following: Ba²⁺, Co²⁺, Cd²⁺, Cu²⁺, Mg²⁺, Mn²⁺, Hg²⁺, Sr²⁺, Zn²⁺, Al³⁺, Sb³⁺, As³⁺, Cr³⁺, Fe³⁺, V³⁺, PO₄³⁻ and SO₄²⁻.

3.4 Analytical performance

Once all variables were optimized, it was found that under the working conditions the proposed methodology was selective for Pb²⁺ determination, achieving an enrichment factor of 50 when 5 mL of 1 µg L⁻¹ Pb²⁺ solution were injected through the column loaded with 60 mg of oxidized carbon xerogel. Once Pb²⁺ was adsorbed, it was eluted with 0.3 mL of HCl 0.6 mol L⁻¹. The detection limit (DL), calculated as the amount of Pb²⁺ required to generate a signal equal to three times the standard deviation

of the background signal (3σ), was equal to $0.9 \mu\text{g L}^{-1}$. The limit of quantification (LOQ) of the proposed method was $3 \mu\text{g L}^{-1}$, calculated as 10 times the amount of Pb^{2+} required to generate a signal which was equal to three times the standard deviation of the background signal (3σ , $n=3$). The precision, calculated as the relative standard deviation (RSD), corresponds to 7.8% ($n = 10$). Calibration curves using the proposed system were linear with a correlation coefficient of 0.9983 from the limit of quantification until at least $2000 \mu\text{g L}^{-1}$. The retention percentage of the column at these concentration levels was of 99.86%. Oxidized carbon xerogel maintained its Pb^{2+} preconcentration performance for at least 60 cycles.

Regarding the time required to analyze a sample with the proposed system, for preconcentration of 5 mL of sample (12.5 min at a flow rate of 0.4 mL min^{-1}), elution (0.75 min at a flow rate of 0.4 mL min^{-1}), bufferization (0.7 min), complexation with dithizone (0.75 min at a flow rate of 0.4 mL min^{-1}), determination by UV-Vis spectrophotometry (0.3 min) and washing and conditioning (3 min) was of approximately 17.5 minutes.

The proposed methodology was compared with similar research for lead determination (FI-SPE-UV visible) reported in literature and it can be observed in Table 1. This work reaches the highest EF, with a minimal sample volume, achieving low detection limit.

3.5 Validation study

In order to validate the proposed methodology, a recovery study was performed using the standard addition method. The method was evaluated by analyzing water samples from the water distribution system of San Juan city, Argentina. Three portions

of the sample were analyzed, they were previously diluted 1:100, because samples correspond to tap water from local ancient houses with lead pipes. Pb^{2+} concentration of each sample was taken as base value. Lead quantities were increased in all samples in values of 10, 20 and 50 $\mu\text{g L}^{-1}$. As shown in Table 2, the recovery values ranged from 94.25 to 107.02% for Pb^{2+} .

As a second validation method, water samples were analyzed by Electrothermal Atomic Absorption Spectrometry (ETAAS), previous 1:10 dilution of samples. Results obtained between both methodologies were compared with the *t*-test and no significant differences were observed at 95% confidence level.

3.6 Application

The developed method was applied to Pb^{2+} determination in tap water samples from different local domestic houses. They were split in two groups, ancient and modern, depending on the type of water pipes system, lead pipes and polypropylene pipes respectively. Samples were diluted according to the concentration range of the method. The concentration values obtained are shown in Table 2. As can be observed, in antique properties Pb concentration values exceeded almost 200 times the concentration limit set by the WHO (10 $\mu\text{g L}^{-1}$). However in modern properties, values are close to the limit. From these results it can be concluded that the type of pipe significantly affects the quality of drinking water. These results are correspondent with results reported in literature [5, 27, 28].

4 Conclusion

This paper describes the introduction of oxidized carbon xerogel as sorbent in a minicolumn for Pb^{2+} SPE. Adsorption was quantitative in the $\mu\text{g L}^{-1}$ levels, previous optimization of different FI parameters. FI system introduced an UV-visible spectrophotometer for Pb^{2+} determination, previous complex formation with dithizone in ethanol-water. The introduction of this type of detector turn this technique into a valuable tool for most laboratories were more sophisticated techniques for Pb^{2+} analysis are unavailable. A thoughtful study established the lack of interferences from concomitants ions and metals.

A good desorption kinetics of Pb^{2+} from oxidized carbon xerogel allowed obtaining high enrichment factors with subsequent low detection limits, compatible with minimum Pb^{2+} concentration in drinking water established by WHO. Carbon xerogel showed a superior performance compared to similar FI-SPE-UV methodologies reported in literature for Pb analysis. FI system allowed a reduction of sample volume and time of analysis, increasing throughput sample. The method was applied to Pb^{2+} determination in tap water, allowing a clear distinction of waters from old lead pipes systems and modern propylene pipes.

5. Acknowledgements

This work was supported by Universidad Nacional de San Juan (Argentina). Special acknowledge to Universidad Nacional de San Luis (Argentina) for the instrumentation.

References

- [1] Y. Huang, A.A. Keller, EDTA functionalized magnetic nanoparticle sorbents for cadmium and lead contaminated water treatment, *Water Res.*, 80 (2015) 159-168.
- [2] A.A. Ensafi, A.Z. Shiraz, On-line separation and preconcentration of lead (II) by solid-phase extraction using activated carbon loaded with xylenol orange and its determination by flame atomic absorption spectrometry, *J. Hazard. Mater.*, 150 (2008) 554-559.
- [3] J. Duruibe, M. Ogwuegbu, J. Ekwurugwu, Heavy metal pollution and human biotoxic effects, *Int. J. Phys. Sci.*, 2 (2007) 112-118.
- [4] S.H. Frisbie, E.J. Mitchell, B. Sarkar, Urgent need to reevaluate the latest World Health Organization guidelines for toxic inorganic substances in drinking water, *Environ. Health-Glob.*, 14 (2015) 63.
- [5] C. Cartier, S. Nour, B. Richer, E. Deshommes, M. Prévost, Impact of water treatment on the contribution of faucets to dissolved and particulate lead release at the tap, *Water Res.*, 46 (2012) 5205-5216.
- [6] W.H. Organization, Guidelines for drinking-water quality: recommendations, World Health Organization, 2004.
- [7] A. Apha, WEF. (2012). Standard methods for examination of water and waste water. 22nd American Public Health Association (Eds.). Washington. 1360 pp, 2014.
- [8] F. Pena-Pereira, I. Costas-Mora, V. Romero, I. Lavilla, C. Bendicho, Advances in miniaturized UV-Vis spectrometric systems, *TrAC-Trend Anal. Chem.*, 30 (2011) 1637-1648.

- [9] X. Wen, Q. Yang, Z. Yan, Q. Deng, Determination of cadmium and copper in water and food samples by dispersive liquid–liquid microextraction combined with UV–vis spectrophotometry, *Microchem. J.*, 97 (2011) 249-254.
- [10] A.R. Türker, New Sorbents for Solid-Phase Extraction for Metal Enrichment, *Clean–Soil Air Water*, 35 (2007) 548-557.
- [11] A. Stafiej, K. Pyrzynska, Solid phase extraction of metal ions using carbon nanotubes, *Microchem. J.*, 89 (2008) 29-33.
- [12] R.A. Gil, P.H. Pacheco, S. Cerutti, L.D. Martinez, Vapor generation–atomic spectrometric techniques. Expanding frontiers through specific-species preconcentration. A review, *Anal. Chim. Acta*, 875 (2015) 7-21.
- [13] N. Ozkantar, E. Yilmaz, M. Soylak, M. Tuzen, Solid-phase extraction of iridium from soil and water samples by using activated carbon cloth prior to its spectrophotometric determination, *Environ. Monit. Assess.*, 187 (2015) 1-7.
- [14] S. Álvarez, R. Ribeiro, H. Gomes, J. Sotelo, J. García, Synthesis of carbon xerogels and their application in adsorption studies of caffeine and diclofenac as emerging contaminants, *Chem. Eng. Res. Des.*, 95 (2015) 229-238.
- [15] R. Łużny, I. Małgorzata, Walendziewski J., Stolarski M., Heavy metal ions removal from aqueous solutions using carbon aerogels and xerogels, *Chemik*, 68 (2014) 544–553.
- [16] J. Figueiredo, J. Sousa, C. Orge, M. Pereira, J. Órfão, Adsorption of dyes on carbon xerogels and templated carbons: influence of surface chemistry, *Adsorption*, 17 (2011) 431-441.

- [17] P. Veselá, V. Slovák, N-doped carbon xerogels prepared by ammonia assisted pyrolysis: Surface characterisation, thermal properties and adsorption ability for heavy metal ions, *J Anal. Appl. Pyrol.*, 109 (2014) 266-271.
- [18] M. Stolarski, J. Walendziewski, M. Steininger, B. Pniak, Synthesis and characteristic of silica aerogels, *Appl. Catal. A-Gen.*, 177 (1999) 139-148.
- [19] A. Maratta, M. Acosta, L.D. Martinez, P.H. Pacheco, R.A. Gil, Ultratrace arsenic determination through hydride trapping on oxidized multiwall carbon nanotubes coupled to electrothermal atomic absorption spectrometry, *J. Anal. Atom. Spectrom.*, 28 (2013) 916-922.
- [20] F. Burriel, F. Lucena, S. Arribas, J. Hernández, *Química analítica cualitativa*, Editorial Paraninfo, SA, 2006.
- [21] S.S.H. Davarani, N. Sheijooni-Fumani, A.M. Najarian, M.-A. Tabatabaei, S. Vahidi, Preconcentration of Lead in Sugar Samples by Solid Phase Extraction and Its Determination by Flame Atomic Absorption Spectrometry, *Am. J. Anal. Chem.*, 2 (2011) 626.
- [22] N.A. Fathy, M.S. Rizk, R.M. Awad, Pore structure and adsorption properties of carbon xerogels derived from carbonization of tannic acid-resorcinol-formaldehyde resin, *J. J. Anal. Appl. Pyrol.*, (2016).
- [23] N.A. Fathy, I.Y. El-Sherif, Equilibrium removal of Pb (II) Ions from aqueous solution onto oxidized-KOH-activated carbons, *Carbon Lett.*, 12 (2011) 1-7.
- [24] J. Fries, H. Getrost, D.E. Merck, *Organic reagents trace analysis*, E. Merck, 1977.

- [25] K. Zargoosh, F.F. Babadi, Highly selective and sensitive optical sensor for determination of Pb²⁺ and Hg²⁺ ions based on the covalent immobilization of dithizone on agarose membrane, *Spectrochim. Acta A*, 137 (2015) 105-110.
- [26] A. Apha, WEF (1998) Standard methods for the examination of water and wastewater, American Public Health Association, Washington, DC, 1998.
- [27] F.R. Spellman, Handbook of water and wastewater treatment plant operations, CRC Press, 2013.
- [28] S. Gonzalez, R. Lopez-Roldan, J.-L. Cortina, Presence of metals in drinking water distribution networks due to pipe material leaching: a review, *Toxicol. Environ. Chem.*, 95 (2013) 870-889.
- [29] N. Rajesh, S. Manikandan, Spectrophotometric determination of lead after preconcentration of its diphenylthiocarbazone complex on an Amberlite XAD-1180 column, *Spectrochim. Acta A*, 70 (2008) 754-757.
- [30] M.a.S. Di Nezio, M.E. Palomeque, B.S.F. Band, A sensitive spectrophotometric method for lead determination by flow injection analysis with on-line preconcentration, *Talanta*, 63 (2004) 405-409.
- [31] Q. Hu, G. Yang, Y. Zhao, J. Yin, Determination of copper, nickel, cobalt, silver, lead, cadmium, and mercury ions in water by solid-phase extraction and the RP-HPLC with UV-Vis detection, *Anal. Bioanal. Chem.*, 375 (2003) 831-835.
- [32] J. Klamtet, S. Sanguthai, S. Sriprang, Determination of lead in aqueous samples using a flow injection analysis system with on-line preconcentration and spectrophotometric detection, *NU. Int. J. Sci.*, 4 (2008) 122-131.

Table 1. Comparison of some methods published with FI-SPE and spectrophotometric determination of lead.

Solid phase adsorbent	Sorbent mass (mg)	Chelating agent	Solvent	Sample volume (mL)	Elution volume (mL)	Sample throughput (h ⁻¹)	Enrichment factor	Detection limit (µg L ⁻¹)	Reference
Amberlite XAD-1180	1500	Dithizone	Acetone	250	10	-	25	3.5	[29]
Poly(d-glucosamine)	-	Dithizone	Triton X-100 aqueous solution	3	-	15	8.2	5.0	[30]
C18	30	Tm-APP	THF	100	2.5	-	100	0.003	[31]
Amberlite XAD-7	50	PAR	Water	3.6	-	12	3	11	[32]
Oxidized Carbon Xerogel	60	Dithizone	Ethanol-water mixture	5	0.3	4	50	0.9	This work

Table 2. Determination of Pb²⁺ in tap water and Recovery study.

Aliquots	Base value ($\mu\text{g L}^{-1}$)	Quantity of Pb ²⁺ added ($\mu\text{g L}^{-1}$)	Quantity of Pb ²⁺ found ($\mu\text{g L}^{-1}$)	Recovery (%) ^a
Ancient Pipes	66.30	0.00	66.30±3.9	-
	66.30	10.00	76.42±2.5	101.20
	66.30	50.00	116.24±8.8	99.88
	66.30	100.00	173.40±12.9	107.10
	-	0.00	198.90±14.1	-
	198.90	100.00	301.94±19.0	103.04
	198.90	200.00	412.95±25.3	107.02
	198.90	500.00	690.66±41.1	98.35
	-	0.00	178.00±9.5	-
	178.00	100.00	187.95±13.0	99.50
	178.00	200.00	388.54±20.5	105.27
	178.00	300.00	461.12±29.2	94.37
Modern Pipes	-	0.00	10.41±0.6	-
	10.41	5.00	15.68±0.9	105.40
	10.41	10.00	20.33±1.1	99.20
	10.41	20.00	29.26±1.7	94.25
	-	0.00	9.33±0.7	-
	9.33	5.00	14.17±1.0	96.80
	9.33	10.00	19.21±1.1	98.80
	9.33	20.00	29.87±1.5	102.70
	-	0.00	8.9±0.5	-
	8.9	5.00	14.12±0.9	104.40
	8.9	10.00	19.56±1.0	106.60
	8.9	20.00	27.95±1.1	95.25

^a 100×[(found-base)/added]. Samples analyzed pH range 6.8-7.4

Figure captions

Figure 1. Schematic diagram instrumental configuration. S, sample; E, eluent; NaOH, sodium hydroxide solution; B, buffer; D, complexing reagent; V₁, injection valve, valve positions: (a) sample loading; (b) injection; V₂, V₃ and V₄, valves; RC, reaction coil; P₁, P₂ and P₃, peristaltic pumps; GLS, gas-liquid separator; RC, reaction coil; W, waste; M, mini-column filled with oxidized carbon xerogel.

Figure 2. Influence of the sample pH in Pb adsorption on oxidized carbon xerogel. Preconcentration of 5 mL of 10 µg L⁻¹ Pb²⁺ solution; Dithizone concentration, 4.29x10⁻⁵ mol L⁻¹.

Figure 3. Influence of sample flow rate on complex Dithizone-Pb²⁺ signal during the loading step. Preconcentration of 5 mL of 10 µg L⁻¹ Pb²⁺ solution; Dithizone concentration, 4.29x10⁻⁵ mol L⁻¹; eluent, HCl 0.6 mol L⁻¹; elution flow rate, 0.5 mL min⁻¹; eluent volume, 0.3 mL.

Figure 4. Influence of HCl concentration in Pb²⁺ elution from carbon xerogel. Preconcentration of 5 mL of 10 µg L⁻¹ Pb²⁺ solution; Dithizone concentration, 4.29x10⁻⁵ mol L⁻¹; loading flow rate, 0.4 mL min⁻¹; elution flow rate, 0.5 mL min⁻¹; eluent volume, 0.3 mL.

Figure 5. Influence of eluent flow rate on complex Dithizone-Pb²⁺ signal during the elution step. Preconcentration of 5 mL of 10 µg L⁻¹ Pb²⁺ solution; Dithizone concentration, 4.29x10⁻⁵ mol L⁻¹; eluent, HCl 0.6 mol L⁻¹; loading flow rate, 0.4 mL min⁻¹; eluent volume, 0.3 mL.

Figure 6. UV-Vis spectra. Comparison of absorbance spectrum between dithizone and the metal complex (Dithizone-Pb²⁺); Dithizone concentration, 1.5×10^{-5} mol L⁻¹; Pb concentration, 500 μ g L⁻¹.

Figure 7. Effect of Dithizone concentration in the formation of Dithizone-Pb²⁺ complex. Pb concentration, 500 μ g L⁻¹.

Figure 2

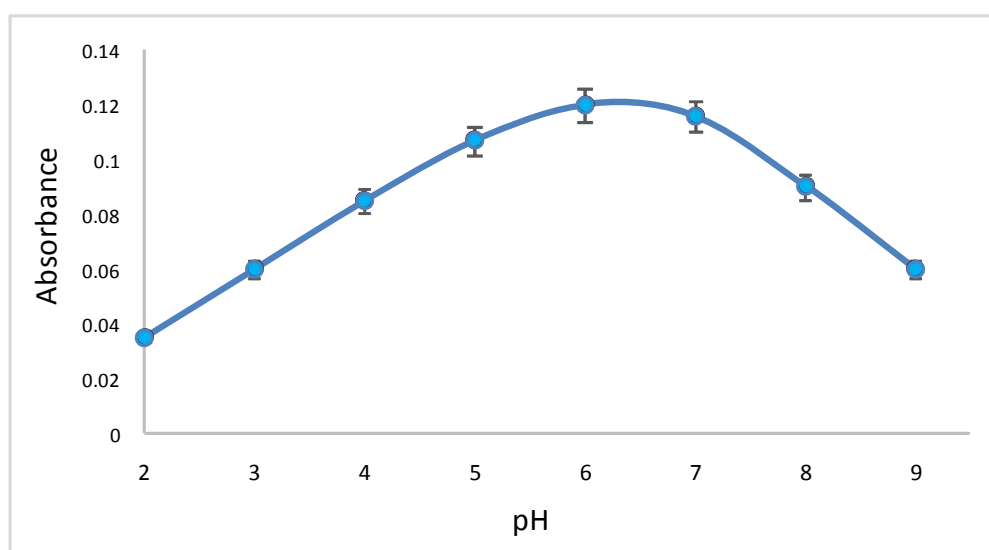


Figure 3

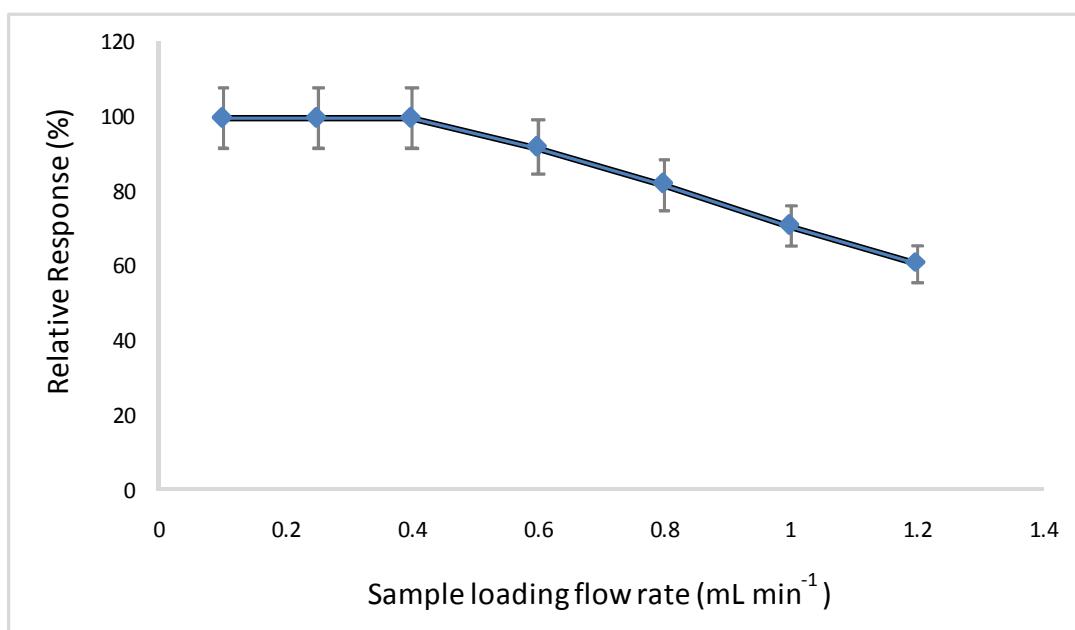


Figure 4

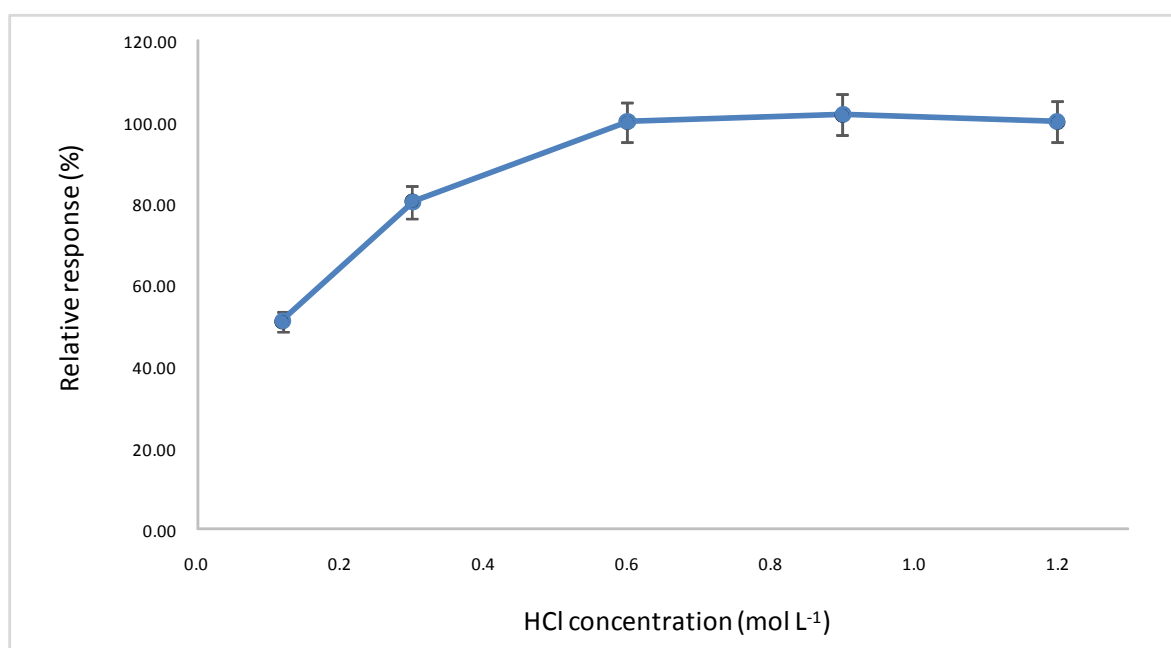


Figure 5

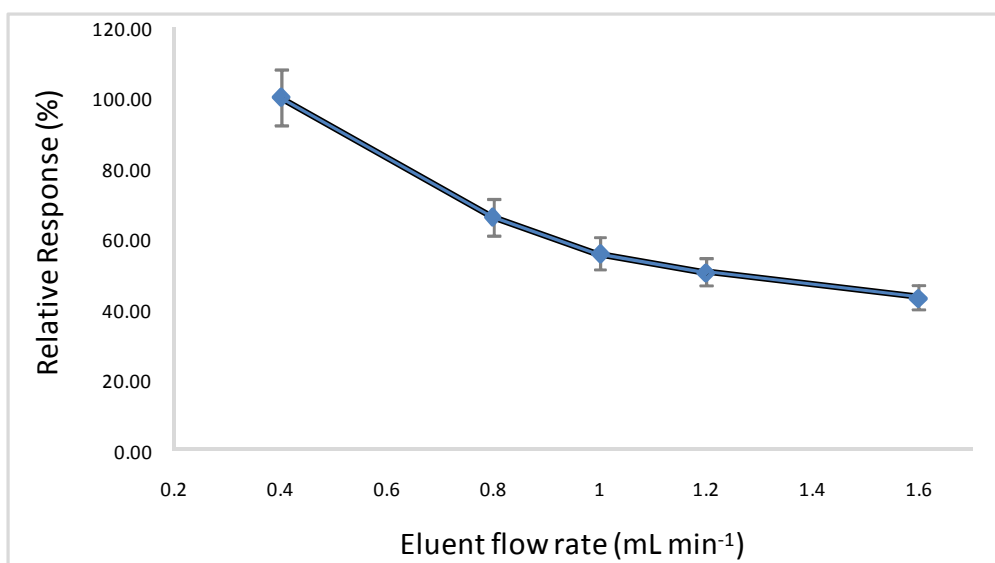


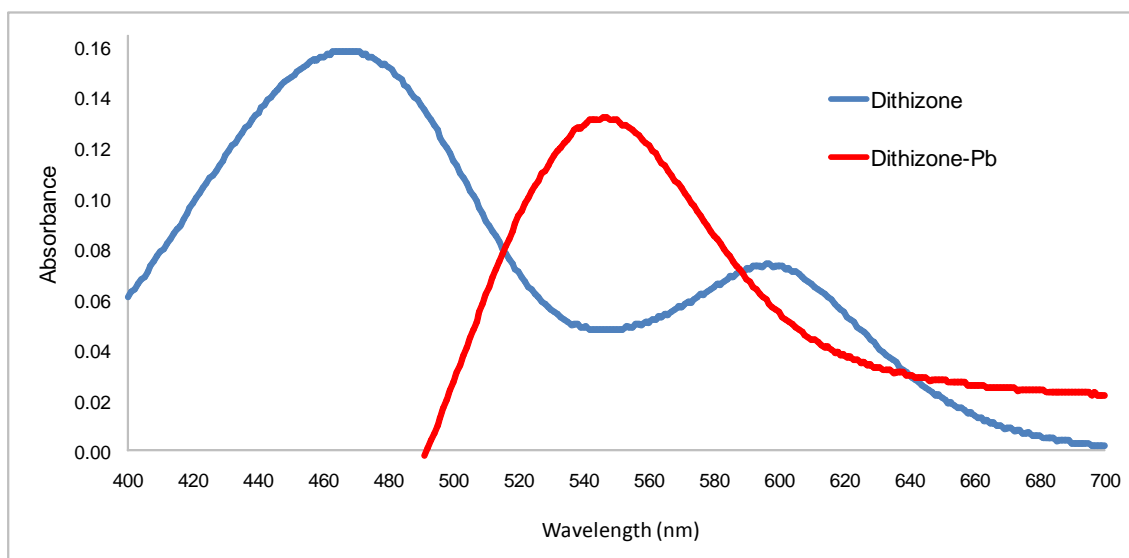
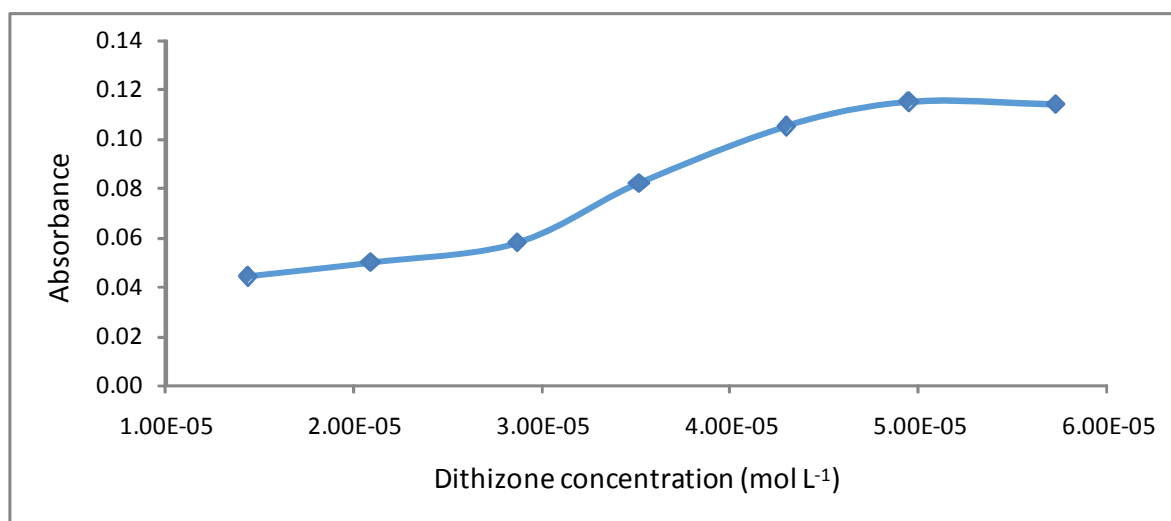
Figure 6

Figure 7



Highlights

- A FI-SPE-UV system has been design for Pb determination.
- Oxidized carbon xerogel is introduced for the first time in on line SPE procedures.
- Oxidized carbon xerogel showed quantitative Pb retention.
- Good Pb kinetic desorption from carbon xerogel allowed high enrichment factors.
- Method sensibility was compatible with maximum Pb concentrations in waters stablished by WHO.