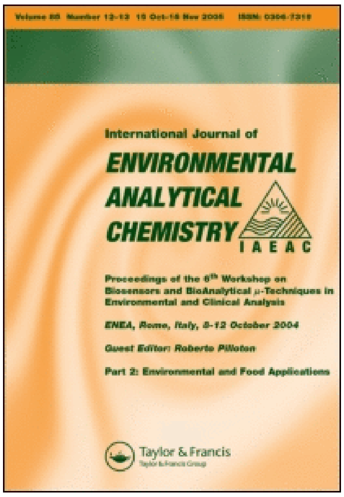

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Flame atomic absorption determination of lead through on-line preconcentration by surfactant mediated glass wool retention

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This work reports on the fabrication of a mini column packed with controlled pore glass and glass wool, and its application for the on-line preconcentration of lead with the aid of an anionic surfactant (sodium dodecyl sulphate, SDS) and AAS detection. Lead reacts with SDS in a high-ionic-strength environment, and the product is retained and preconcentrated on a high-surface-area substrate like glass wool. The intervention of controlled pore glass increases the active surface of glasswool and prevents its accumulation into a sticky mass after wetting. Washing the mini column with a methanolic solution of HNO_3, causes the retained micellar face to be eluted, and consequently the lead content can be determined with AAS. A preconcentration factor of 50 along with a signal enhancement due to the combined presence of SDS and methanol yields a detection limit of $1.5\,\mu g\,L^{-1}$. The correlation coefficient of the calibration curve is 0.999, and the linear range $5–500\,\mu g\,L^{-1}$. The method was used for the determination of lead in water and wastewater with good results.

Keywords: Controlled pore glass–glass-wool-packed minicolumn; High-surface-area substrate; Determination of lead; On-line surfactant mediated preconcentration; Atomic absorption spectrometry

1. Introduction

The analytical merits of surfactant mediated cloud-point extraction (CPE) for the preconcentration of organic and inorganic species were demonstrated several years ago as an environmentally benign alternative to the use of hazardous organic solvents [1–5]. Most recently, CPE was adjusted to a flow injection analysis (FIA) manifold for on-line preconcentration and determination of porphyrins [6]. The last innovation in this field of research is the mixed micelle CPE for the extraction of metals without the need for complex formation with an organic complexing agent [7]. In the latter paper, several metallic species were adsorbed on a mixed micellar aggregate of SDS and the non-ionic surfactant Triton X-114, which was clouded with the aid of a

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salting out agent (sodium sulphate) and retained on a cotton-packed column previously proposed by Fang *et al.* [6]. Evolving this approach, an attempt was made to preconcentrate metal species directly without the need for cloud formation, thus using the surfactants as complexing and adsorbing agents at the same time. In this respect, several surfactants were tested in order to examine their capacity to bind metallic species. Sodium dodecyl sulphate was proven to interact with several of them [7] and especially with heavy bivalent cations. Among those metals, lead has a greater affinity for SDS [8] ($K_{sp} = 1.9 \times 10^{-10}$), and it was expected to be physically and chemically sorbed on its micelles. The dense micellar aggregates are easily retained by filtration on a minicolumn which was fabricated for this purpose.

The already proposed cotton packed mini column [6] has a smaller retaining capacity, while glasswool is more porous and has a better filtering performance, allowing for the surfactant phase to remain on the filter without the need for cloud formation. With the additional help of a salting-out agent, the density of the surfactant aggregates is enhanced, and up to $500\,\mu g\,L^{-1}$ of lead can be preconcentrated and determined with AAS. A detection limit of $1.5\,\mu g\,L^{-1}$ and a quantification limit of $5.0\,\mu g\,L^{-1}$ along with a total time of analysis of 5.5 min and a sample throughput of 10/h render the above-mentioned approach an interesting alternative to current methods of surfactant-mediated preconcentration.

2. Experimental

2.1. *Reagents*

All reagents were of analytical reagent grade, free from lead traces. Working standard solutions of lead in the range of $5.0–500\,\mu g\,L^{-1}$ were prepared daily with appropriate dilutions of a $1000\,mg\,L^{-1}$ standard solution for atomic absorption (Merck) in 0.1 N nitric acid solution to prevent hydrolysis of lead. SDS (Fluka) was used, without further purification, to prepare a 4% w/v aqueous solution. Na_2SO_4 and CH_3COONa (Aldrich) solutions were prepared by dilution of the appropriate amounts in doubly distilled water. The solutions of various cations and anions used for the interference study were obtained from the respective inorganic salts (Aldrich) with proper dilution in distilled water. A certified reference material, IMEP9 surface water, purchased by the Institute for Reference Materials (IRMM), was used for method validation.

The extraction solution consisted of SDS ($0.25\,g\,L^{-1}$), Na_2SO_4 ($0.5\,mol\,L^{-1}$) and CH_3COONa ($0.5\,mol\,L^{-1}$) buffered to pH 12.5 with NaOH. The carrier was a methanolic solution containing $1\,mol\,L^{-1}$ of HNO_3.

2.2. *Apparatus*

The FIA manifold designed for the on-line preconcentration and subsequent determination of lead is shown in figure 1. This consisted of a four-way pneumatically actuated injection valve (Rheodyne, type 50 Teflon, Cotati, CA), a multi-channel peristaltic pump (Ismatec, Glattburg-Zurich, Switzerland), a 4 cm minicolumn packed with controlled pore glass–glasswool and an atomic absorption spectrometer (GBC Australia). The operating conditions for AAS measurements were: wavelength 283.3 nm; lamp current 4 mA. Deuterium background correction was also employed

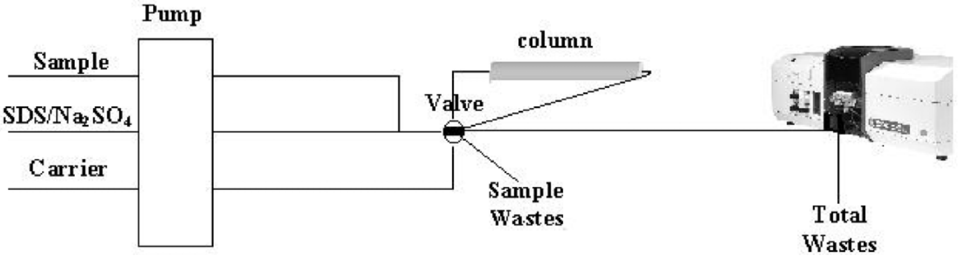

Figure 1. Schematic representation of the flow-injection manifold employed for the preconcentration and determination of lead on-line with AAS.

throughout the AAS measurements. pH measurements were carried out using a pH meter (PHM83 Radiometer, Copenhagen).

2.3. *Procedure*

With the sample valve set at the filling position, 25 mL of a standard or sample solution was pumped with the aid of the peristaltic pump and merged with the reagent solution in front of the column, which acted as the FIA sample loop. The Pb-containing SDS aggregates were retained on the filament of the mini-column. After the loading of the sample was completed, the valve was switched in the injection mode allowing for the methanolic solution to flow through the column washing the micelle and conveying it to the nebulizer of the AAS. The signal was recorded at the peak height mode.

3. Results and discussion

3.1. *Study of parameters affecting the preconcentration step*

The efficiency of the preconcentration was shown to be controlled by the following parameters: pH, surfactant type and concentration, Na_2SO_4 concentration, column length, and amount of glass wool.

In detail, the pH of the extraction was tested covering the range of 1–14. Also, different concentrations of HNO_3 and NaOH were examined so as to have a full range assessment of the effect of acidity.

As can be seen from figure 2 (open circle line), the efficiency of the extraction is greatly enhanced at pH values exceeding 10. This behaviour is attributed to several effects. In strongly acidic conditions, the SDS monomers are protonated and neutralized [9, 10], thus reducing their ability to interact with lead. In solutions of modest pH (5–9.5), lead is precipitated in the form of its hydroxide, while at higher pH values (pH > 9.5), the insoluble $Pb(OH)_2$ is transformed into the reactive $HPbO_2^-$ [11]. At pH values higher than 12.5, the extraction efficiency decreases rapidly because of strong repulsions between the SDS monomers that prevent them from aggregation [12]. To make the pH profile uniform, the reagent solution is made to $0.5\,\mathrm{mol\,L^{-1}}$ with respect to CH_3COONa. Lead is known to form stable complexes with acetate, regardless of pH conditions [11]. Thus, for the entire pH area (6.5–12.5), a more smooth profile is obtained. Still, a pH of 12.5 is maintained in order to alleviate

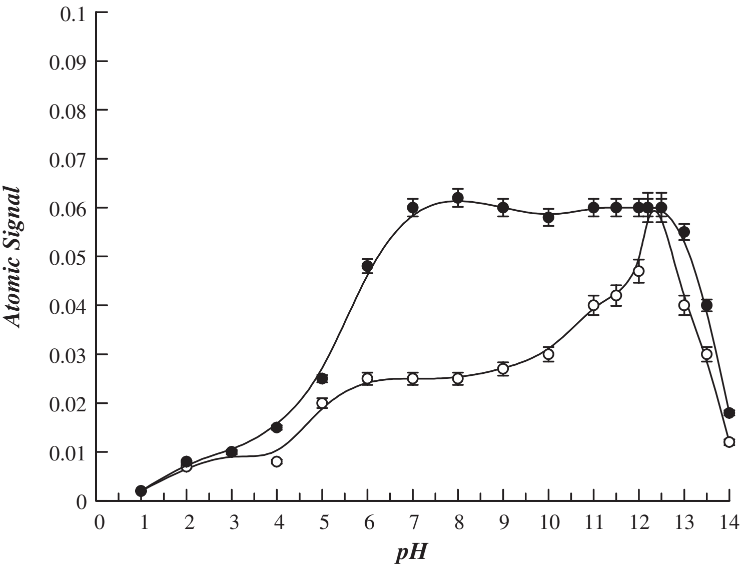

Figure 2. Effect of pH on the preconcentration and determination of 20 µg/L of lead: (•) in the presence of acetate; (○) in the absence of acetate. Points represent average values of five runs. Other parameters are as stated in the text.

interferences from other metals in the real sample which would otherwise compete with SDS for complexation.

Under these conditions, safe conclusions cannot be deduced on the actual mechanism of retainment or the nature of the complex retained on the column filament. According to the literature published so far regarding the behaviour of metallic species in surfactant solutions [2, 12–14], the product could very easily be in the form of a binary, ternary, or even quaternary complex among Pb^{2+} and the SDS, sulphate, and acetate anions that infest the solution. SDS certainly plays a key role in the whole process, acting as complexing agent and sorbent, because without its presence, no retention on the column is observed, and no signal on the AA is produced.

The type and the concentration of the surfactant used were also important. Various non-ionic, cationic, and anionic surfactants were tested with respect to assessing their capability of binding and preconcentrating lead directly without any prior complexation. Among them, sodium dodecyl sulphate (SDS) was the most effective. This outcome is expected because of the affinity of lead for SDS [8]. From previous experiments [7], it was demonstrated that surfactants and surfactant mixtures are able to extract metal species at concentrations up to $0.2\,\mu g\,L^{-1}$. For greater values such as those encountered in this work (5–$500\,\mu g\,L^{-1}$), this possibility was not revealed. The concentration of SDS in the extraction mixture was also important, since it is the critical reagent for both the complexation of lead and its extraction on the reactor. It is proven that for a sample volume of 25 mL containing up to $500\,\mu g\,L^{-1}$ of lead, a SDS concentration of 0.1–$0.3\,g\,L^{-1}$ was adequate for the proposed scheme. Smaller values are not sufficient for complete extraction, while greater concentrations increase the viscosity of the sample creating blockages of the extraction manifold and difficulties in the washing of the surfactant from the glasswool reactor.

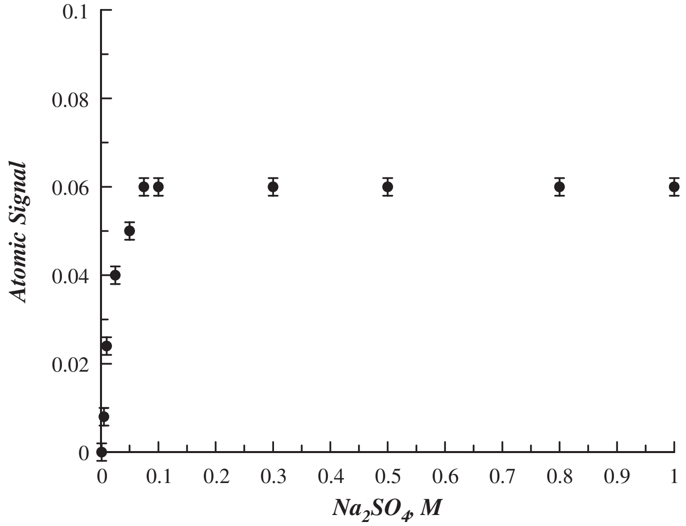

Figure 3. Effect of the concentration of Na_2SO_4 (salting-out reagent) on the preconcentration and determination of 20 µg/L of lead. Points represent average values of five runs. Other parameters are as stated in the text.

The presence of Na_2SO_4, or of another salting-out reagent is also of great importance. It is known that in typical cloud-point experiments, the presence of several salts induces clouding at temperatures far lower than the actual cloud-point temperature because of salting-out phenomena [13, 14]. In the present experimental methodology, the addition of Na_2SO_4 increases the extraction efficiency because of the increase in ionic strength, which drives more of the lead to the micellar aggregates. Moreover the retainability of the surfactant face on the glasswool column is also increased because of the increase in aggregation number of the surfactant monomers, leading to more bulky and viscous micelles. It is proved (figure 3) that a Na_2SO_4 concentration of 0.075 M is adequate for quantitative extraction of up to $0.5\,\mathrm{mg\,L^{-1}}$ of lead. Although lead also forms precipitates with sulphates, its affinity for SDS is greater ($K_{sp} = 1.9 \times 10^{-10}$ over $K_{sp} = 3.8 \times 10^{-8}$ for sulphate)[11]. Moreover, the micellar environment enhances the solubility of inorganic precipitates by acting like an organic solvent. Therefore, under the prevailing conditions and the presence of acetate, no precipitation as sodium sulphate occurs.

The nature of the salt was also examined. Of the different salts tested, Na_2SO_4 was chosen, as it produces the desired outcome with fewer amounts compared with $NaNO_3$, NaCl, KBr, etc. This outcome is in concurrence with the literature where sodium sulphate is used as the most effective salting-out reagent in cloud-point experiments [13, 14].

The length of the column was another parameter optimized for its effect on the preconcentration of lead. Columns 2, 4, 10, 15, and 20 cm in length were tested. A 4-cm-long column was finally adopted throughout the experiments giving the highest AAS signal. The 2 cm column was inadequate for retaining the whole of the surfactant phase, while for longer columns the signal decreased because of insufficient washing and blockage of the flow tubes.

With the selected column, the amount of glasswool was also optimized. It was found that up to 0.01 g of glasswool was sufficient for quantitative extraction as long as the column was filled uniformly. This is achieved by mixing glass wool with controlled pore glass, which prevents glasswool from forming bulky aggregates and allows it to spread inside the column. Exceeding the value of 0.01 g leads to the blockage of FIA.

The optimized column shows no memory effect, as can be deduced by the minimal tailing of the peaks and their reproducibility. Its performance is maintained unaffected for up to 50 consecutive runs. Thereafter, some problems in the optimum flow rates are observed due to the build-up of surfactant inside the cotton threads. Washing the column three times with methanol and subsequent air drying would regenerate the column.

3.2. *Study of the detection step*

The study of the flow rate of the methanolic solution is also of interest as it should lead to complete washing out of the retained surfactant phase while matching the aspiration rate from the nebulizer. From a range of 0.5–8.0 mL min^{-1} tested at an interval of 0.25, a flow rate of 4.0 mL min^{-1} was finally selected for producing optimum results.

The atomic parameters were also optimized with regard to the methanolic solution containing nitric acid and surfactant that carries the measured lead to the flame. Although washing with methanol would seem suitable for the complete elution of lead, the presence of nitric acid was proved to enhance the signal probably because the acidic environment in conjunction with SDS produces smaller droplets but prevents the formation of lead basic oxides in the nebulizer.

4. Evaluation of the method

4.1. *Figures of merit*

The reproducibility of the procedure and sample throughput was evaluated by repeated injections of a 20 μg L^{-1} standard lead solution (25 mL). The relative standard deviation was found to be 2.3% ($n = 5$). A linear working curve in the range of 5–500 μg L^{-1} of lead was obtained by measuring the peak height after applying the proposed method to standard solutions containing 10, 25, 50, 100, 200, 300, 400, and 500 μg L^{-1} of lead. The respective regression equation was $A = 0.004 + 0.003$ [C_{Pb}, μg L^{-1}] with a correlation coefficient $r = 0.999$. The limit of detection, defined as three times the signal-to-noise ratio ($3\sigma/a$), was 1.5 μg L^{-1}, while the limit of quantification, defined as 10 times the signal-to-noise ratio was 5.0 μg L^{-1}. The sample throughput was 10 measurements per hour. Compared with direct lead analysis by AAS, a 50-fold enhancement of the signal is observed due to preconcentration. Therefore, analysis of lead in water samples at the μg L^{-1} level is feasible without the need for hydride generation or electrothermal atomization.

4.2. *Interference study*

Several metals were tested to examine their interfering effect on the determination of 20 μg L^{-1} lead with the proposed methodology. Particular attention was paid to the

Table 1. Effect of possible interfering species in the determination of 20 µg/L of lead with the proposed methodology.

Metal tested	Concentration ($mg\,L^{-1}$)	Atomic signal[a]
Pb(II)	0.02	0.060
Fe(III)	0.5	0.060
Fe(III)	5	0.058
Cu(II)	0.5	0.061
Cu(II)	5	0.058
Ca(II)	20	0.060
Ca(II)	100	0.062
Mg(II)	10	0.059
Mg(II)	50	0.062
Zn(II)	0.5	0.060
Zn(II)	5	0.062
Cr(III)	0.1	0.060
Cr(III)	0.5	0.060
PO_4^{3-}	0.5	0.060
PO_4^{3-}	10	0.060
NO_3^-	0.5	0.060
NO_3^-	10	0.060
Cl^-	0.5	0.060
Cl^-	10	0.060
Humic	5	0.060
Humic	25	0.055
Fulvic	5	0.062
Fulvic	25	0.055

[a] Average of five runs.

most abundant metals like calcium and magnesium, which in natural waters appear in concentrations of 20–100 $mg\,L^{-1}$ and also have an affinity for SDS. From the results presented in table 1, it is clear that no interference is produced, even by these high concentrations. In the case of calcium and magnesium, the on-line reaction with SDS is of particular use, since the formation of the respective Ca-SDS and Mg-SDS salts, although thermodynamically favoured, is kinetically controlled. When SDS is added to the sample, under steady-state conditions, the originally transparent solution becomes turbid within a couple of minutes, and milky-white precipitates appear, as a result of the reaction between Ca or Mg cations with SDS. Several anions that usually appear in natural waters were also tested for their interfering effect on the preconcentration of lead. Anionic forms like phosphates, nitrates, chloride, and humic and fulvic substances at concentrations as high as those appearing in natural waters were not found to impair the performance of the method.

4.3. *Method validation*

Lake water, river water, and wastewater from the region of Epirus in north-western Greece were analysed with the proposed methodology to assess their lead content. Prior to analysis of wastewater the sample was treated with a 0.01 M solution of $KMnO_4$ to reduce the high organic matter content and then filtered through a Whatman No. 2 filter paper to remove the MnO_2 formed. Spiked samples were also analysed. A certified reference material was also analysed for method validation. For further validation, the real samples were also analysed with GFAAS using deuterium background correction. The results are presented in table 2.

Table 2. Results from the analysis of CRM, real, and spiked samples for Pb.

Sample	Concentration[a] ($\mu g\,L^{-1}$)	Added ($\mu g\,L^{-1}$)	Found[b] ($\mu g\,L^{-1}$)	Recovery (%)
Tap water	n.d	6.5 ± 0.2	6.3 ± 0.2	97
	n.d	15.0 ± 0.4	14.8 ± 0.4	99
River water (Louros River)	16.2 ± 0.4	0	15.9 ± 0.4	98
		3.8 ± 0.1	19.9 ± 0.3	97
River water (Kalamas River)	23.8 ± 0.5	0	24.0 ± 0.5	101
		10.0 ± 0.2	34.1 ± 0.5	103
Lake water	16.0 ± 0.3	0	16.1 ± 0.4	101
		2.5 ± 0.2	18.5 ± 0.4	100
Wastewater	124 ± 0.8	0	123 ± 0.8	99
		25.0 ± 0.4	148 ± 0.7	99
IMEP[c]	10.5 ± 0.1	0	10.1 ± 0.4	96

[a]Determined with ETAAS in the original (not preconcentrated) sample. [b]Average of three experiments. [c]Certified value.

5. Conclusions

This work reports on the utilization of the interactions between anionic surfactants and metal species and the on-line preconcentration of the latter on a minicolumn filled with suitable materials as appropriate. This approach stands as a successful, quick, and reproducible alternative to the typical extraction and CPE procedures. Although the proposed method seems to have no numerical advantages over the conventional preconcentration techniques utilizing organic complexing agents and extraction solvents, it can be regarded as a new proposal towards the use of surface active species as complexants. This attempt is constantly gaining in popularity because of surfactants' environmental compatibility and easy degradation. As can be deduced by the analysis of real samples, the proposed method can be used safely at concentrations near the $\mu g\,L^{-1}$ level, but not for freshwater samples where concentrations range between 0.5 and $5\,\mu g\,L^{-1}$ (and for which Zeeman ET-AAS and ICP-MS remain the most trustworthy techniques).

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