Automatic on line preconcentration and determination of lead in water by ICP-AES using a TS-microcolumn

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Abstract

A simple, sensitive, low-cost and rapid, flow injection system for the on-line preconcentration of lead by sorption on a microcolumn packed with silica gel funtionalized with methylthiosalicylate (TS-gel) was developped. The metal is directly retained on the sorbent column and subsequently then eluted from it by EDTA. Five variables (sample flow rate, eluent flow rate, eluent concentration, pH and buffer concentration) were considered as factors in the optimization process. Interactions between analytical factors and their optimal levels were investigated using two-level factorial and Box–Behnken designs. The optimum conditions established were applied to the determination of lead by flow injection inductively coupled plasma atomic emission spectrometry (FI-ICP-AES). The proposed method has a linear calibration range from 10 to at least 500 ng ml⁻¹ of lead. At a sample frequency of 24 h⁻¹ and a 120 s preconcentration time, the enrichment factor was 41, the detection limit was 15.3 ng ml⁻¹ (S/N = 3) and the precision, expressed as relative standard deviation, was 0.9% (at 100 ng ml⁻¹). Validation of the developed method was carried out against electrothermal atomic absorption spectrometry analysis without statistically significant differences between the proposed method and the atomic absorption method.

Keywords: Lead; TS-gel; Flow-injection on-line preconcentration; ICP-AES; Water

1. Introduction

Environmental contamination of lead is widespread; the main anthropogenic source of this element is burning of leaded gasoline [1]. As result the lead is frequently found in surface water and, recently, in polar snow [2]. In humans, chronic lead poisoning is manifested by abnormalities such as encephalopathy, nervous irritability, kidney disease and altered heme synthesis and reproductive functions [3,4]. Such poisoning is associated with low to intermediate levels of chronic exposure to lead, with primary sources being intake of food, water and air. A clear example of lead poisoning by consumption of water is the French region “Les Vosges”, that is considered endemic zone of hydric saturnism [5]. In Spain zones with high lead concentration in the consumption water have been verified, whose indices reach about 6 mg l⁻¹ [6]. A complete discussion on lead with regard to sources of occupational exposure, including a summary of biological effects and methods of determination is contained in the National Institute of Occupational Safety and Health (NIOSH) revised criteria for recommended standards for occupational exposure [7].

The determination of low concentrations of lead in tap water samples requires powerful techniques and only a few techniques have sufficient sensitivity. Inductively coupled plasma mass spectrometry (ICP-MS) [8,9] has been used for the determination of lead; however, the cost of such instrumentation may be prohibitive to many laboratories. Likewise electrothermal atomic absorption spectrometry (ETAAS) is a very attractive option for the determination of trace amounts of lead in water samples [10]. Hydride generation coupled with inductively coupled plasma atomic emission spectrometry (ICP-AES) has been used for the determination of trace amounts of lead by Valdés-Hevia et al. [11]. Unfortunately, the method presents problems derived from the well-known characteristics of PbH₄ (instability at room temperature, slow kinetics and relatively poor generation efficiency) [12]. On the other hand, if conventional ICP-AES (without hydride generation) is used, the low level of lead in many water samples is not compatible with the detection limit of this technique. Consequently, the different methodologies

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of preconcentration developed have resulted of great usefulness as complement of this technique. Among known preconcentration methods, solid-phase extraction coupled on line with ICP-AES by means a flow injection system, seems to be the most advantageous [13]. The most important improvements are derived from the fact from working in closed systems whose requirements on the laboratory environment for trace analysis are much less stringent, reduced consumption of reagent and high sampling frequencies what justifies the current trend toward an increase in the use of these preconcentration techniques. Arpadjan and co-workers [14,15] applied column solid-phase extraction using diethiocarbamate-loaded polyurethane foam to the preconcentration of lead. Nevertheless, in addition to the need to introduce an organic solvent (which requires a careful control of the experimental parameters) to dissolve the lead–dithiocarbamate complex, this technique is time-consuming because a new column have to be prepared for each experiment. Fang et al. [16] obtained interesting results for lead determination using flame atomic absorption spectrometry (FAAS) coupled with on-line ion-exchange preconcentration. Spirling et al. [17] developed a sensitive and accurate method for lead determination in water samples by ETAAS with preconcentration of lead diethyldithiocarbamate in a knotted reactor (KR) and using ethanol as eluent. Unfortunately, this method cannot be applied to ICP-AES due to ethanol cause plasma instability or even its extinction. More recently, Spirling et al. [18] described a preconcentration method for lead using a microcolumn packed with corona ethers immobilized on silica gel; lead is adsorbed on the microcolumn at acid pH, and eluted with an EDTA solution, the enhancement factor was between 20 and 50. The accuracy of this method was evaluated through the analysis of various certified reference materials of environmental and biological origin. Kubova et al. [19] analyzed lead in digested hair samples by adsorption of lead at pH 6 on cellulose pearls modified with 8-hydroxyquinolina.

In this work, a FI system coupled on line with ICP-AES that integrates separation, preconcentration and determination of lead was developed. The manifold used involves a microcolumn charged with a silica gel resin functionalized with methylthiosalycilate (TS-gel) where the preconcentration of lead takes place: the microcolumn is included within the sample loop of the injection valve. The accuracy of this automated method was examined by the analysis of sea water and waste water samples. In developing a FI preconcentration and matrix separation on solid sorbents procedure, one needs to adjust many variables (e.g., sample flow rate, eluent flow rate, eluent concentration, pH, buffer concentration) in order to establish optimum conditions for the analysis. A fruitful way to conduct experimental designs and optimization is according to surface-response methodology (SRM). In SRM, the experimental response $Y$ is taken as a function on several independent variables called factors ($X_i$) [20]. They occupy the called space of the factors and the plot of $Y$ on this space is the response surface. The region close to the extremum it is known as a “nearly stationary regions” intrinsically non linear that can be suitably described by using second order polynomials [21]:

\[ Y = a_0 + \sum_{i=1}^{f} a_i X_i + \sum_{i=1}^{f} \sum_{j=1}^{f} a_{ij} X_i X_j + \sum_{i=1}^{f} a_{i1} X_i^2 + b \]

where $f$ is the dimension of the factor space and $b$ the error associated to the $X_i$ variable, which is assumed to be normally distributed. The number $m$ of coefficients to be estimated in this equation, is $m = (f + 1) f / 2$. In case of two variable, $m = 6$ and $Y = a_0 + a_1 X_1 + a_2 X_2 + a_{11} X_1^2 + a_{12} X_1 X_2 + a_{22} X_2^2$.

In order to attain the optimum response, several approaches have been developed, thus, most authors have used the central composite design [22]. However, central composite designs usually have axial points outside the “cube” (unless alpha, the axial spacing needed to ensure orthogonality, is specified as less than or equal to one). Some authors have proposed a modification from the experimental procedure using Box–Behnken [23] designs. These designs do not have axial points, thus all design points fall within the safe operating zone and also ensure that all factors are never set at their high levels, simultaneously [24]. Furthermore, Box–Behnken designs have fewer design points. Also, each factor requires only three levels instead of the five required for central composite designs (unless alpha is equal to one), which may be experimentally more convenient and less expensive to run than central composite designs with the same number of factors. The application of Box–Behnken designs has been recorded in optimization of food technology processes [25], microbiological studies [26], pharmaceutical formulation development work [27], amongst others. However, the use of Box–Behnken experimental design does not appear to be reported in optimization work of atomic spectrometry metals determination.

In this work, the Box–Behnken [23,28] matrix design was applied to the optimization of the main variables involved in the preconcentration and matrix separation of lead from water samples. Five experimental variables were considered as factors in the optimization process: sample flow rate, eluent flow rate, eluent concentration, pH, and buffer concentration. Peak height were used as the analytical signal.

2. Experimental

2.1. Instrumentation

The ICP-AES system used was a Perkin-Elmer 40 sequential emission spectrometer equipped with a Perkin-Elmer AS90 autosampler and controlled by an IBM AT-486 personal computer. The spectrometer output was connected to a PE Nelson model 1020 personal integrator. Samples were introduced via a gem tip Meinhard nebulizer (Perkin-Elmer)
fitted to a Scott-type, double pass spray chamber. The plasma operating conditions used in this work were identical to those described previously[29] except for the wavelength (220.353 nm for Pb in this work). For sorption complexes, a microcolumn was made from 3 cm length of glass tubing of 3 mm internal diameter packed with the TS-gel chelating resin to a height of 0.7 cm. At both ends of the microcolumn, polyethylene frits (Omnifit) were fixed to prevent material losses. Transport lines were made using 0.8 mm id PTFE tubing. The microcolumn was initially flushed with 2 M nitric acid; subsequent use of the eluent in each operating cycle was sufficient to make it ready for re-use.

All glassware was washed with 10% nitric acid and rinsed with deionized water immediately before use.

2.2. Manifold and procedure

This paper uses a previously described [30] FI assembly with on-line separation-preconcentration for cadmium determination. This FI system was operated as follow: during the first stage of sample loading period, with the valve in the “fill” position, a sample (standard or blank) buffered with boric acid–sodium borate at pH 9.2, was pumped at 6 ml min\(^{-1}\) (via pump P 2 ) through the microcolumn (located in the loop of the valve). The metal is adsorbed on the sorbent microcolumn and the sample matrix sent to waste. During preconcentration, a flow of eluent (2% EDTA) was being aspirated from the containers by the pump P1 to establish the baseline of the readout and to stabilize the plasma. At the beginning of the 30 s elution stage, the valve position was changed and the sample pump P2 was stopped. When the valve was in the “inject” position, the eluent passes through the column. Thus, the accumulated metal ions were eluted and transferred into the nebulizer of the ICP, and the emission signals were recorded. The injector system permitted continuous aspiration of the eluent to the nebulizer to wash and stabilize the plasma.

Calibration plots were constructed from five standards solutions within the concentration range 10–500 ng ml\(^{-1}\). Peak heights were used for analytical measurements within 30 s injection, the FI system was ready for the next injection.

2.3. Reagents and samples

High-purity reagents were employed in all experiments. For the synthesis of TS-gel the following were used: silica gel (particle size: 0.2–0.5 mm, 35–70 mesh ASTM), 3-aminopropyltrimethoxysilane and diglutaric aldehyde from Fluka (Buchs, Switzerland), methylthiosalycilate were supplied by Aldrich Chemie (Steinheim, Germany), ethanol, methanol and toluene from Carlo Erba (Milan, Italy). The synthesis and characterization of this resin was described in a previous paper[31].

A standard 1000 µg ml\(^{-1}\) Pb(II) solution (Fluka) was used. Standards of working strength were made by appropriate dilution as required, immediately prior to use. Water was deionized with a Milli-Q system. Buffers solutions of required pH were prepared from 0.5 M boric acid (Fluka) and 0.5 M sodium hydroxide solutions (Carlo Erba).

The water samples analysed to determine the accuracy of the proposed procedure were: Synthetic sea water (SSW), sea water (SW) and waste water (WW). The composition of the synthetic sea water was (in g l\(^{-1}\)): 27.9 of NaCl, 1.4 of KCl, 2.8 of MgCl\(_2\), 0.5 of NaBr and 2.0 of MgSO\(_4\), according to the specifications of Weast [32], spiked with 5.0 ng ml\(^{-1}\) of Pb. Sea and waste water samples were collected in polypropylene bottles previously cleaned by soaking in 2 M nitric acid. Samples were filtered by using a membrane of 0.45 µm pore size, acidified to 1% (v/v) with concentrated nitric acid and stored frozen until analysis.

The pH of the samples was adjusted to an optimum pH with concentrated NaOH and buffer solutions and, finally, the samples were diluted to 50 ml with deionized water in a calibrated flask. Samples were analysed, in triplicate, immediately after preparation, by introducing them into the manifold described previously [30].

2.4. Optimization strategy

The experimental variables were optimized by applying a factorial experimental design at two levels and with Box–Behnken design. The experimental data were processed following the scheme in Fig. 1, making use of the STATGRAPHICS program [33].

3. Results and discussion

3.1. Optimization of the preconcentration procedure

To optimize the system, efforts were focused on the conditions for sample loading and metal elution from the
Fig. 2. Influence of pH on the preconcentration of lead.

As is well known, strong acids are very efficient to liberate metallic ions from their complexes. The eluents assayed for this study were: hydrochloric acid, nitric acid and their mixtures at different concentrations; as well as EDTA, thiourea, ethylenediamine, tartaric acid, citric acid and their mixtures due to these acids make complexes with high stability constants. The results of these experiments are shown in Fig. 3. As can be noted that EDTA dissolution at concentrations higher than 3% was found to be the better eluent for the Pb–TS-gel complex.

A glass tube microcolumn (3 cm × 3 cm i.d.) packed with the chelating resin to a height of 0.7 cm was taken for this study because longer columns were more susceptible to back-pressure problems, owing to packing of the resin beads, and therefore need more frequent replacement.

The characteristics described above can be summarized to conclude that the variables to be optimized were: sample flow rate, eluent flow rate, pH, eluent concentration, and buffer concentration. The traditional “step-by-step” or “one variable at a time” approach for achieving the highest response, although widely used, involves a large number of independent runs and could not enable the researcher to establish the multiple interaction parameters. These drawbacks might result in missed important conclusions about the dependence of the effect of one factor on the level of another factor. Experimental design as an effective and efficient optimization strategy to overcome these drawbacks has found widespread application in all branches of analytical chemistry.

In this approach, an experimental design methodology to optimize the preconcentration of lead has been developed. In the following section, the statistical techniques which are used in this methodology that is based on full factorial and Box–Behnken designs are described.

3.1.1. Factorial design

Two level factorial designs have many advantages in analytical procedures. In this method, there are comparisons available for each main effect on the experimental results. The total number of runs in factorial design is much less as compared to the “one variable at a time” approach. Estimation of the interaction of effects is an additional advantage over the “one variable at a time” approach.

Two levels full factorial design requires an experiment to be carried out at all possible combination of the two levels of each of the \( k \) factors considered. In general the necessary number of experiments is \( 2^k \), where \( k \) is the number of factors. The levels can be represented in different ways. To calculate the effect of factors the design matrix of experiment should be drawn. Then by the total combination of factor levels and corresponding responses for every combination in experiment \( Y \) the effect should be calculated as:

\[
\text{Effect} = \frac{\sum \text{treatments of higher level}}{2^k-1} - \frac{\sum \text{treatments of lower level}}{2^k-1}
\]

For estimating the interaction of factors, the sign of these effects should be detected.

In this work, a two level full factorial design \[34,35\], \( 2^k \), involving 32 runs was used as the first approximation to the response surface of the preconcentration process. The factors and their levels are shown in Table 1. Table 2 shows the experimental design matrix developed and the results obtained for the net emission signal. The sign \((-\)\) is for low level and \((+)\) is used to show the high level for each factor.
The significance of the effects was checked by analysis of the variance (ANOVA) and using $P$-value significance levels [29]. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the $P$-value is less than 5%, the effect of the corresponding factor is significant. The ANOVA results for lead produced were not statistically significant. We should note the positive effect of the pH ($B$) and sample flow rate ($E$) in Fig. 4. The lines indicate the magnitude and sign (increase or decrease) of the variation of the peak height with the factor level (from low to high).

and with this aim was chosen the Box–Behnken statistical design.

3.1.2. Box–Behnken design

In this design, three factors were performed $B$, $E$ and $D$. The buffer concentration is included as a third factor for investigate the characteristics of the response on the retention of Pb by the TS-gel. The levels for the factors using in this design are shown in Table 3. Therefore, 15 experiments were carried out for the combinations [23,28]. Details of the Box–Behnken experiments (matrix and the experimental results obtained for the net emission signal) were represented in Table 4.

The results obtained fit the equation:


(1)

where $Y$ is the net emission signal and $B$ and $E$ are pH of the sample and sample flow rate in ml min$^{-1}$, respectively. There was a significant interaction between the factors $B$ and $E$. The predicted values by this equation were in accordance with the peak height values obtained experimentally (coefficient of determination $R^2 = 0.989$). The response surface for this equation is shown in Fig. 5.

The critical point of the Eq. (1) is located from applying the Lagrange’s criterion [29]. It is based on calculating the

The levels for factors using Box–Behnken design

<table>
<thead>
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<th>Levels</th>
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<tr>
<td>$-1$</td>
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<td>$0$</td>
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<td>$+1$</td>
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Table 2

<table>
<thead>
<tr>
<th>Design matrix and response values obtained in the factorial design</th>
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<td>Experiment number</td>
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Table 3

<table>
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<th>Levels</th>
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<tr>
<td>$B$ (pH)</td>
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<tr>
<td>$D$ (buffer concentration, mol l$^{-1}$)</td>
</tr>
<tr>
<td>$E$ (sample flow rate, ml min$^{-1}$)</td>
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</tbody>
</table>
The application of Lagrange’s criteria to the Eq. (1) indicates the presence of a maximum, located at the position B and E, which can be seen, fall within the experimental domain. As a result of these observations, the following working conditions were chosen: A = 8.5 ml min⁻¹; B = 9.2; E = 6 ml min⁻¹; C = %; and D = 0.055 mol l⁻¹ for latter experiments.

The effects of samples loading times on the emission signal of 100 ng ml⁻¹ Pb was studied at a sample flow rate of 6.0 ml min⁻¹. The results showed that the signal increased almost linearly up to a 20 min preconcentration time, after which the slope decreased gradually. Sensitivity enhancements increased by increasing the sample loading time; however, a loading time of 120 s was selected in order to achieve high sampling frequency with a reasonable degree of sensitivity. A longer loading time can be employed for samples with low concentrations of metal.

4. Performance of the method

Under the optimum conditions, with the use of a 120 s preconcentration time, a sample flow rate of 6.0 ml min⁻¹ and an elution flow rate of 8.5 ml min⁻¹, a linear calibration graph was obtained from 10 to at least 500 ng ml⁻¹ of Pb(II) with a regression coefficient of 0.9997. The signal appeared 30 s after sample injection, the overall time required for each measurement was 2.5 min; the throughput was 24 samples h⁻¹.

The detection limit, defined as the concentration of analyte giving a signal equivalent to three times the standard deviation of the blank signal plus the net blank intensity, was measured to be 15.3 ng ml⁻¹. The precision of the method for aqueous standards (evaluated as the relative standard deviation obtained after analysing 10 series of 10 replicates) was 0.9% at the 100 ng ml⁻¹ level of Pb(II). The enrichment factor (EF), defined as the ratio of the slopes of the linear section of the calibration graph before and after the preconcentration, was 41.17. The concentration efficiency (CE), defined as the product of the EF and the sampling frequency in number of samples analysed per hour was 16.47 min⁻¹ and the consumptive index, defined as the volume of sample, in millilitres, consumed to achieve a unit EF, was 0.29 ml.

In order to evaluate the selectivity of the proposed on-line system, the interference of various elements was investigated on the determination of 100 ng ml⁻¹ Pb(II), taking as a criterion for an interference the deviation of the percentage recovery more than ±5%. High concentrations of alkali and alkaline earth metals, which are usually found at high concentrations in natural waters and other samples. A number of common cations and anions like Na⁺ (NaCl), K⁺ (KCl), Ca²⁺ (CaCl₂), Mg²⁺ (MgCl₂), Br⁻ (NaBr), SO₄²⁻ (Na₂SO₄), Cl⁻ (NaCl), and F⁻ (NaF) were tested and found that they did not interfere at high concentrations. On the other hand, the preconcentration of lead on TS-gel was reduced in the presence of high concentration of Ni(II), Cu(II) and Mn(II) (50 mg l⁻¹), Cd(II) (40 mg l⁻¹) and Zn(II) (30 mg l⁻¹), because these elements can be chelated by the column and compete with lead for active sites.
As it can be seen, high value of lead level (57.1 ng ml

The results, shown in Table 5, indicated excellent recovery.

ing Pb(II) were added to natural and synthetic sea waters.

mination of lead in sea waters, standard solutions contained

significant differences between both methods.

these results demonstrated that there was not statistically

equal to the unit and an intercept statistically equal to 0,

with a correlation coefficient of 0.9992, a slope statistically


G.P.E. Box, D.W. Brakenk, Technometrics 2 (1968) 455.

5. Application to the analysis of samples

In order to test the accuracy and applicability of the pro-
posed method to the analysis of real samples, three residual
waters were analysed. The results, as the average of three
separate determinations, are shown in Table 5. These results
show that the proposed automated system provides analyti-
cal results in good agreement with those obtained by ele-
ctrothermal atomic absorption spectrometry.

The representation of the obtained data for residual wa-
ters by mean the proposed method (Y) in front to those ob-
tained by ETAAS (X) lead to the following linear regression
equation:

\[ Y = 0.9959X + 1.0306 \]

with a correlation coefficient of 0.9992, a slope statistically
equal to the unit and an intercept statistically equal to 0,
these results demonstrated that there was not statistically
significant differences between both methods.

In view of the application of the method to the deter-
mination of lead in sea waters, standard solutions contain-
ing Pb(II) were added to natural and synthetic sea waters.

the results, shown in Table 5, indicated excellent recovery.

As it can be seen, high value of lead level (57.1 ng ml

the ability of TS-gel and its performance for on-line determi-
nation of other metals with other detection techniques more
sensitive than ICP-AES technique with a neumatic nebulizer.

Acknowledgements

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References


Table 5

Results for the determination of lead in water samples, n = 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference or added (ng ml⁻¹)</th>
<th>Found value* (ng ml⁻¹)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water (WW₁)</td>
<td>28.5 ± 2.3</td>
<td>29.2 ± 0.8</td>
<td>2.46</td>
</tr>
<tr>
<td>Waste water (WW₂)</td>
<td>26.5 ± 0.3</td>
<td>27.6 ± 0.4</td>
<td>4.15</td>
</tr>
<tr>
<td>Waste water (WW₃)</td>
<td>39.4 ± 1.1</td>
<td>40.3 ± 1.4</td>
<td>2.28</td>
</tr>
<tr>
<td>Sea water (SW)</td>
<td></td>
<td>57.1 ± 2.3</td>
<td></td>
</tr>
<tr>
<td>Synthetic sea water (SSW)</td>
<td>0</td>
<td>4.8 ± 0.2</td>
<td>-4</td>
</tr>
</tbody>
</table>

* Mean ± S.D. for three replicate measurements.

** Added value.