

ATOMIC SPECTROMETRY

**DETERMINATION OF LEAD IN  
DRINKING WATER BY ICP-AES WITH  
ULTRASONIC NEBULIZATION AND  
FLOW-INJECTION ON-LINE  
PRECONCENTRATION USING AN  
AMBERLITE XAD-16 RESIN**

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**ABSTRACT**

An on-line lead preconcentration and determination system implemented with inductively coupled plasma atomic emission spectrometry (ICP-AES) associated to flow injection (FI) with ultrasonic nebulization (USN) was studied. For the retention of lead, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and Amberlite XAD-16 were used, at pH 9.2. The lead was removed from the microcolumn

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in counter flow with nitric acid. A total enhancement factor of 150 was obtained with respect to ICP-AES using pneumatic nebulization (15.0 for USN and 10.0 for column). The detection limit value for the preconcentration of 10 mL of aqueous solution of Pb was  $0.2 \text{ ng mL}^{-1}$ . The precision for 10 replicate determinations at the  $5 \text{ ng mL}^{-1}$  Pb levels was 2.8% relative standard deviation (RSD), calculated with the peak heights obtained. The calibration graph using the preconcentration system for lead was linear with a correlation coefficient of 0.9997 at levels near the detection limits up to at least  $100 \text{ ng mL}^{-1}$ . The method was successfully applied to the determination of lead in drinking water samples.

*Key Words:* Flow injection; ICP-AES; Preconcentration and determination; Lead in drinking water samples; 5-Br-PADAP

## INTRODUCTION

It is generally recognised that moderately increased blood lead levels may have adverse effects. The exposure level is strongly dependent on pollution, type of diet, country, and so forth. Lead reaches humans from natural as well as anthropogenic sources, e.g., drinking water, soils, industrial emission, car exhaust, contaminated food and beverages, etc.<sup>[1,2]</sup>

The determination of extremely low concentrations of lead in drinking water samples requires powerful techniques and only few of them have sufficient sensitivity. Inductively coupled plasma-mass spectrometry (ICP-MS)<sup>[3,4]</sup> has been used for the determination of lead, however, the cost of the required instrumentation may be prohibitive to many laboratories. Graphite furnace atomic absorption spectrometry (GFAAS) is a very attractive option to determine Pb in drinking water.<sup>[5]</sup> Besides, Burguera et al. have reported interesting approaches for lead determination using flow injection atomic absorption spectrometry.<sup>[6-8]</sup>

Hydride generation (HG) associated with inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used for the determination of lead traces.<sup>[9,10]</sup> However, instability at room temperature as well as slow kinetics and relatively poor generation efficiency are well-known characteristics of  $\text{PbH}_4$  and must not be disregarded.<sup>[10]</sup>

On the other hand, the low level of lead concentration in drinking water is not compatible with the detection limit of conventional ICP-AES (without hydride generation). When the concentrations of analyte elements in the original material or the prepared solution are too low to be determined directly by ICP-AES preconcentrations and separations are needed in order to achieve accurate, reliable and sensitive results.

Many preconcentration techniques for the determination of Pb have been proposed, including chelation and extraction, precipitation, coprecipitation, and ion-exchange resins. However, many of these methodologies are performed in batch, thus requiring great sample volumes in order to reach low detection limits. Besides, these systems present higher contamination risks.

When preconcentration techniques are applied in batch mode, the time of analysis increases and the operations usually become too tedious to be compatible with the ICP-AES measurements. Furthermore, these procedures are not practical for application in routine analysis. This situation has been significantly improved utilising flow injection (FI) associated with ICP-AES,<sup>[11,12]</sup> such that general drawbacks of batch preconcentration procedures have been largely eliminated, and currently the preconcentrations can be achieved almost as efficiently as simple ICP-AES determination. Reagent consumption is reduced usually to a little percent of that in batch procedures, and sample contamination decreases, which becomes important when trace concentrations are determined.

In order to be used as packing in preconcentration columns for FI,<sup>[13]</sup> materials have to meet several requirements. Among these are: appropriate kinetic and mechanical conditions so that they can easily retain and elute the analyte and capacity to perform several retention and elution runs without exhaustion of column material. XAD resins meet many of these requirements and because they have good physical properties such as porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure, and good adsorbent properties for great amounts of uncharged compounds,<sup>[14]</sup> they have been used as supports for immobilisation of chelating agents and metal complexes.<sup>[15-20]</sup>

2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) forms stable complexes with numerous metal ions,<sup>[21,22]</sup> and is therefore a suitable reagent for lead preconcentration on a XAD resin.<sup>[23]</sup>

In the present work, a method for preconcentration and determination of lead using a microcolumn filled with a macroporous Amberlite XAD-16 resin is proposed. Lead was retained under the form of Pb-(5-Br-PADAP) complex. The determination was performed

using ICP-AES associated with an FI methodology and ultrasonic nebulization system.

## EXPERIMENTAL

### Reagents

The Amberlite XAD-16 resin (Rohm & Haas, PA, USA) was used. Particle size was between 20–50 mesh with a surface area of  $825\text{ m}^2\text{ g}^{-1}$ . Before use, the surface of the resin was activated by immersion in a mixture of methanol and  $4\text{ mol L}^{-1}$  HCl (1:1 v/v). Subsequently, metal impurities were removed by further washing with  $2\text{ mol L}^{-1}$  HCl solution.

A solution of 5-Br-PADAP ( $10^{-2}\text{ mol L}^{-1}$ ) was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

Lead standard solution was prepared dissolving the lead nitrate (99.999%, Aldrich, Milwaukee, WI, USA) in nitric acid (0.1% v/v).

A buffer solution was prepared by diluting a 3.0 M ammonium hydroxide solution adjusted to pH 9.2 with a hydrochloric acid solution.

Octylphenol poly(ethyleneglycol) ether (Triton X-100 Merck) solution. A 5% (v/v) surfactant solution in ultrapure water was prepared.

Ultrapure water ( $18\text{ M}\Omega\text{ cm}^{-1}$ ) was obtained from an EASY pure RF (Barnstedt, Iowa, USA).

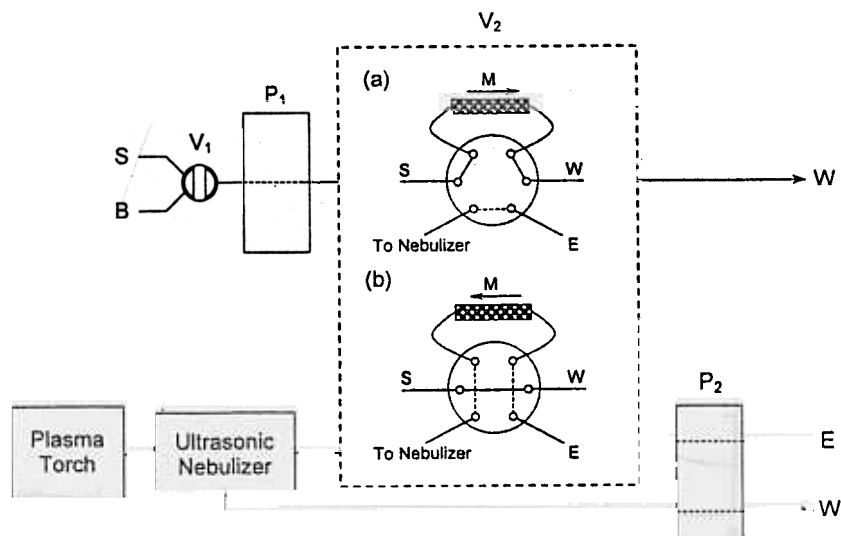
All the reagents were of analytical-reagent grade and the presence of lead was not detected in the working range.

### Apparatus

The measurements were performed with a sequential inductively coupled plasma spectrometer [Baird (Bedford, MA, USA) ICP 2070]. The 1 m Czerny—Turner monochromator had a holographic grating with  $1800\text{ grooves mm}^{-1}$ . An ultrasonic nebulizer U-5000 AT [CETAC Technologies (Omaha, Nebraska, USA)] with desolvation system, was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table 1. The flow injection system used is shown in Fig. 1. A Minipuls 3 peristaltic pump [Gilson (Villiers Le-Bell, France)] was used. The sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four way rotary valve. A microbore glass column (50 mm length; 3 mm internal diameter) fitted with porous  $25\text{ }\mu\text{m}$  glass frits was used as the resin holder. Tygon type pump tubes (ismatec, Cole-Parmer Instrument

**Table 1.** ICP and Ultrasonic Nebulizer Instrumental Parameters

ICP conditions	
RF generator power	0.8 kW
Frequency of RF generator	40.68 MHz
Plasma gas flow rate	8.5 L min <sup>-1</sup>
Auxiliary gas flow rate	1.1 min <sup>-1</sup>
Observation height (above load coil)	15 mm
Analytical line: Pb	220.353 nm
Ultrasonic nebulizer conditions	
Heater temperature	140°C
Condenser temperature	5°C
Nebulizer gas flow rate	0.95 L min <sup>-1</sup>



**Figure 1.** Schematic diagram of the instrumental setup. S, sample; B, buffer diluted; E, eluent; W, waste; P<sub>1</sub> and P<sub>2</sub>, peristaltic pump; M, microcolumn; V<sub>1</sub>, two way valve; V<sub>2</sub>, load-injection valve ((a) Load position; (b) Injection position).

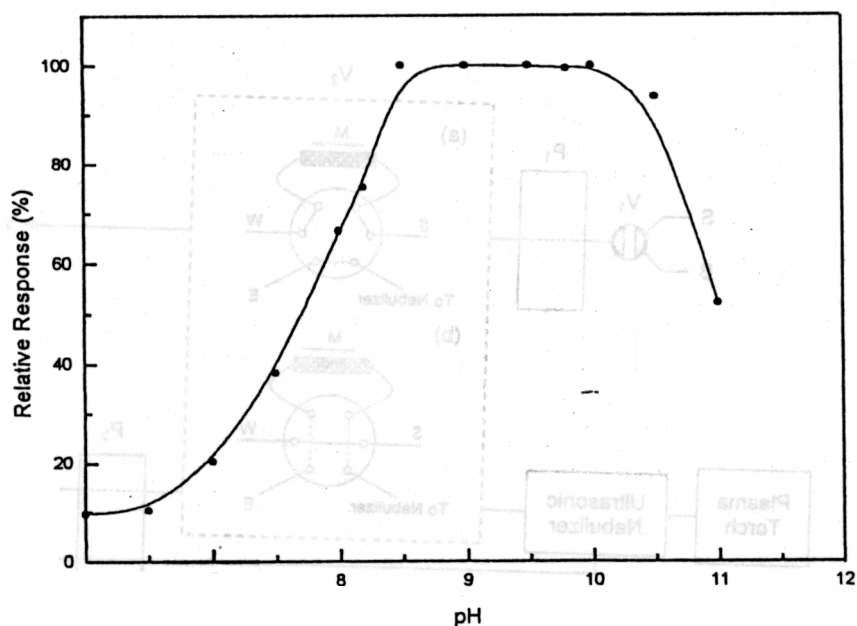
Company, Illinois, USA) were employed to propel the sample, reagent and eluent. The 220.353 nm spectral line was used and measurements of FI system were expressed as peak-height emission, which was corrected against the reagent blank.

### Procedure

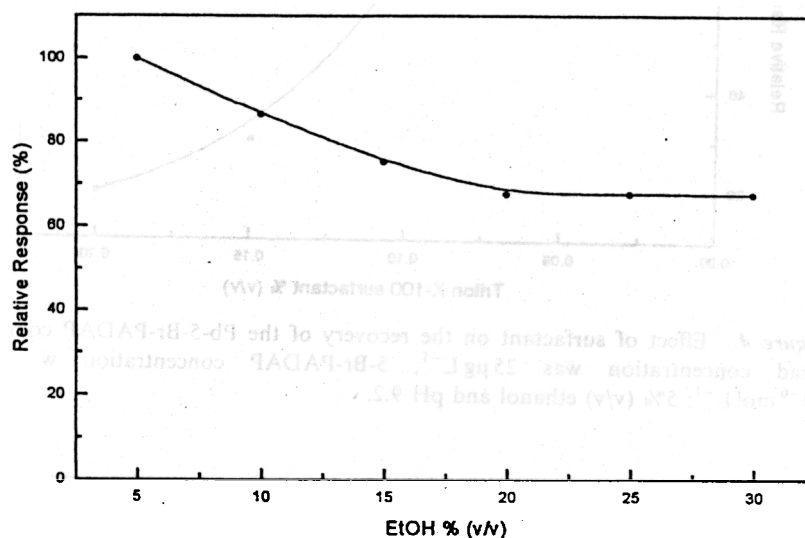
#### Study of the Retention Conditions

In order to optimise the retention of the metal complex on the column, the following variables were assessed: pH, ethanol and surfactant concentration, reagent-metal molar relation and loaded flow-rate.

Solutions were prepared with a known amount of lead and 30-fold excess in moles of 5-Br-PADAP to form the metal complex, and pH was varied by adding diluted HCl or NaOH solutions so that 100 mL of each solution were obtained at the corresponding pH and containing  $25 \mu\text{g L}^{-1}$  of lead. The final ethanol concentration was 5% (v/v). Each of the solutions was loaded on the XAD-16 resin and subsequently the retained metal complex was eluted with 5 mL of a 25% (v/v)  $\text{HNO}_3$  solution in a 10 mL volumetric flask taking to volume with water. Figure 2 shows the response at different solution pH values.



**Figure 2.** Dependence of retention of Pb-5-Br-PADAP complex on pH of loading solutions. Preconcentration of 10 mL of Pb-5-Br-PADAP complex. Pb concentration was  $25 \mu\text{g L}^{-1}$ ; ethanol concentration 5% (v/v); 5-Br-PADAP concentration was  $7 \times 10^{-6} \text{ mol L}^{-1}$ .



**Figure 3.** Effect of ethanol on the recovery of the Pb-5-Br-PADAP complex. Lead concentration was  $25 \mu\text{g L}^{-1}$ ; 5-Br-PADAP concentration was  $7 \times 10^{-6} \text{ mol L}^{-1}$  and pH 9.2.

The effect of ethanol concentration in the medium was studied by following the batch procedure above described, preparing solutions under the same conditions at pH 9.2 and containing different ethanol percentages. A similar procedure was used for determining the optimum surfactant concentration. Figures 3 and 4 show the effect of ethanol and surfactant percentage upon the complex retention on the resin.

The optimum molar relation between 5-Br-PADAP and the metal (Fig. 5) was determined by the same procedure, working at pH 9.2, 5% (v/v) of ethanol and 0.05% (v/v) of surfactant.

Assessment of the retention with respect to the loading flow rate of the solutions was performed at flow rates between  $5\text{--}20 \text{ mL min}^{-1}$ .

The concentration of lead was determined by ICP-AES. Recovery was calculated against the theoretical concentration. Figure 6 shows the Pb recovery.

#### Sample Collection and Preparation

To obtain the samples, tap water was allowed to run for 20 min and approximately 1000 mL of water were collected. The water samples were

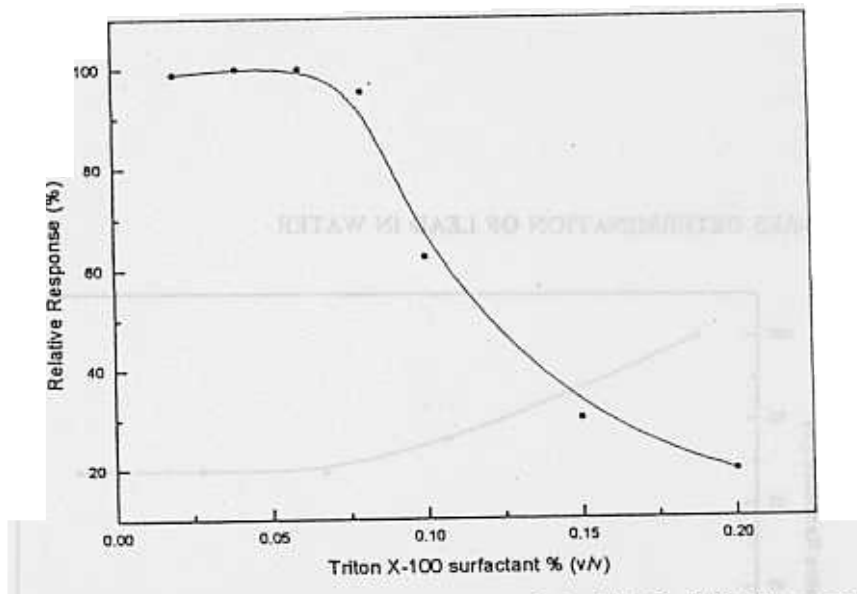


Figure 4. Effect of surfactant on the recovery of the Pb-5-Br-PADAP complex. Lead concentration was  $25 \mu\text{g L}^{-1}$ ; 5-Br-PADAP concentration was  $7 \times 10^{-6} \text{ mol L}^{-1}$ ; 5% (v/v) ethanol and pH 9.2.

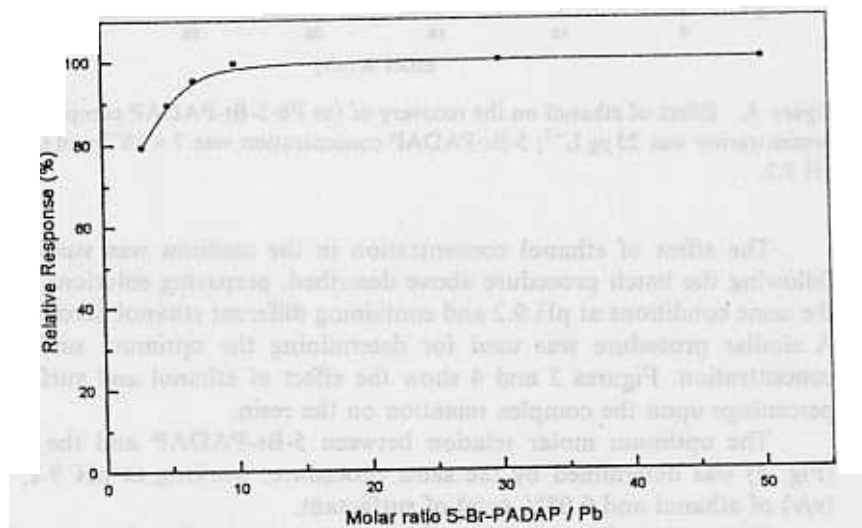


Figure 5. Dependence of retention of the Pb-5-Br-PADAP complex with the 5-Br-PADAP/lead molar ratio.



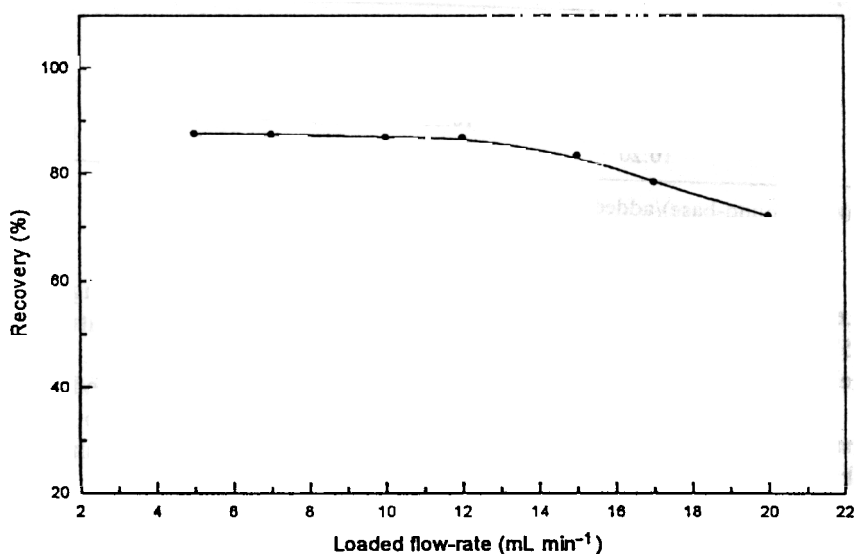


Figure 6. Dependence of recovery of metal complex on sample flow rate.

filtered through 0.45  $\mu\text{m}$  pore size membrane filters immediately after sampling. All the glass instruments used were previously washed with a 10% (v/v)  $\text{HNO}_3$  aqueous solution and then with ultrapure water.

Reagent 5-Br-PADAP was added to 10 mL of sample in a molar relation of approximately 30 times that of the metal, and the sample pH was adjusted at 9.2 with 4 mL of buffer solution. The water samples were immediately analysed. The standard solutions were prepared by the same procedure.

#### Preconcentration and Determination

Before loading, the column was conditioned for the preconcentration at the correct pH with buffer diluted solution, valve  $V_1$  in position B (Fig. 1). The complex was then loaded on the XAD-16 resin at a flow rate of  $12 \text{ mL min}^{-1}$ , with valve  $V_1$  in position S and valve  $V_2$  in load position (a). After the loading time, the sample still present in the lines and the column was removed by further washing with buffer diluted solution, with valve  $V_1$  again in position B. Finally, valve  $V_2$  was switched to the injection position (b) and the retained metal complex was eluted in counterflow

Table 2. Method Validation

Aliquots	Base Value ( $\mu\text{g L}^{-1}$ )	Quantity of Pb Added ( $\mu\text{g L}^{-1}$ )	Quantity of Pb Found ( $\mu\text{g L}^{-1}$ )	Recovery (%) <sup>a</sup>
		0.00	10.20 $\pm$ 0.30	–
2	10.20	3.00	13.07	95.6
3	10.20	6.00	16.07	97.9
	10.20	10.00	20.17	99.7
	10.20	20.00	30.20	100.0

<sup>a</sup>100  $\times$  [(found-base)/added].

(i.e., reversal of the flow direction with respect to sample loading) with 25% (v/v)  $\text{HNO}_3$  at a flow rate of  $1.5 \text{ mL min}^{-1}$ , directly into the ultrasonic nebulizer and subsequently the plasma.

Since the metal complex Pb-5-Br-PADAP is not totally retained on the resin (approximately 85%) the standard solution must be also passed through the microcolumn. The operating conditions were established and the determination was carried out.

#### Method of Validation

In order to demonstrate the validity of this method, 100 mL of sample water was collected and divided in 10 portions of 10 mL each. The proposed method was applied to six portions and the average quantity of lead obtained was taken as a base value. Then, increasing quantities of lead were added to the other aliquots of sample and lead was determined by the same method (Table 2).

Additionally, the proposed method was applied to a standard reference material, NIST SRM 1640 Trace Elements in Natural Water, with a lead content of  $27.89 \pm 0.14 \mu\text{g kg}^{-1}$ , the density of SRM 1640 at  $22^\circ\text{C}$  is  $1.0015 \pm 0.0005 \text{ g mL}^{-1}$ . Using the proposed method the content of lead determined in this SRM was  $28.23 \pm 0.21 \mu\text{g kg}^{-1}$ .

## RESULTS AND DISCUSSION

The preconcentration of lead from drinking water was necessary because its concentration can be too low to be compatible with ICP-AES

detection limits. This preconcentration, performed prior to the ICP-AES measurement, permitted to obtain accurate and precise analytical results.

The retention conditions of the metal complexes were optimised and lead signal was monitored by measuring it with ICP-AES while changing the pH of the solution that passes through the sorption microcolumn. Figure 2 shows that the optimal pH values were in the 8.5–10.3 range. This phenomenon is understandable, since better complexation occurs within this range. Considering these results, the selected pH was 9.2.

In the present work a bead size of resin of 20–50 mesh was considered adequate for the preconcentration procedure in the microcolumn. Smaller resin particles could have improve retention capacity, but this would have increased back-pressure of the microcolumn, and the flow rate ought to have been reduced, with the subsequent increase in preconcentration time.

Our choice of the Amberlite XAD-16 resin was motivated by the fact that it is highly stable in both acidic and basic solution and exhibits an adequate surface area. This allows the use of the microcolumn for an indefinite number of samples without degradation of performance, after using 25% (v/v) HNO<sub>3</sub> as eluent. Besides, many researchers have studied the behaviour of Amberlite XAD resins as adsorbents of organic substances and as supports for chelating agent-impregnated resins.<sup>[14,23,24]</sup> Parrish<sup>[24]</sup> considered the greater water regain of Amberlite XAD as the most important factor for a better exchange rate, independently of the surface area and pore diameter. Lee et al.<sup>[14]</sup> pointed out that in spite of having lower distribution coefficient for XAD-16 than that obtained for XAD-4, XAD-16 can be swelled in aqueous solution and is better for use in column.

The dimensions of the microcolumn used here were optimised by us in previous works.<sup>[25–27]</sup>

It is well known that complex retention on XAD resins is modified by the concentration of organic solvents.<sup>[23]</sup> Furthermore, the formation of metal complexes with 5-Br-PADAP is also affected by the solvent. Therefore, it was necessary to perform a study on the optimisation of ethanol in order to achieve maximum complex retention. Figure 3 shows the effect of the ethanol percentage on complex retention by the resin. Higher retention was observed for lower ethanol percentages. The value selected was 5% (v/v) of ethanol.

Due to the strong precipitating tendency both of the complex and the reagent excess,<sup>[22]</sup> it was necessary to introduce a surfactant agent into the reaction medium in order to solve the solubility difficulties.

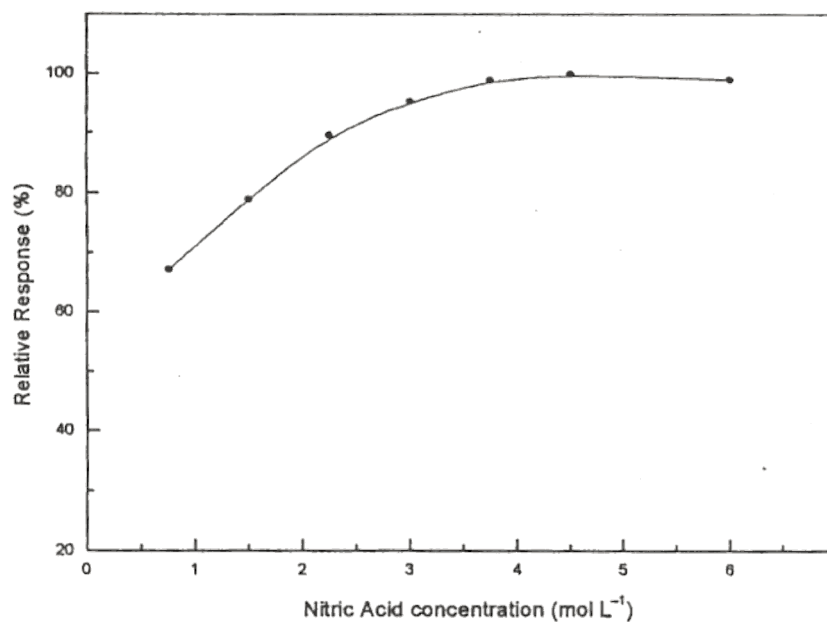
Figure 4 shows that the optimal surfactant concentration was in the 0.02–0.07% (v/v) range. Below 0.02% (v/v), serious precipitation risks arise and above 0.07% (v/v) retention in the microcolumn starts to decrease

probably because of a competition effect between the surfactant and the complex.

As regards the variation of response with the molar relation between reagent 5-Br-PADAP and lead (Fig. 5), the signal remained constant between 10/1 and at least 50/1.

The flow rate sample through the microcolumn is a very important parameter, since this is one of the steps that controls the time of analysis. It could be verified that with flow rates up to  $12 \text{ mL min}^{-1}$  there is no effect on the analyte recovery, which in optimum conditions is approximately 85%. Figure 6 shows that at higher flow rates, recovery decreases.

In order to elute lead adsorbed on the resin,  $\text{HNO}_3$  in counterflow (i.e., reversal of the flow direction with respect to sample loading) was used as eluent. Figure 7 shows that the minimum concentration of  $\text{HNO}_3$  to achieve best results was 25% (v/v). Counterflow elution substantially improves the elution profiles as compared to unidirectional flow. Lead was completely eluted from the resin with 1.0 mL of 25% (v/v)  $\text{HNO}_3$ . The optimum flow rate of eluent was  $1.5 \text{ mL min}^{-1}$ . The elution profile for Pb is shown in Fig. 8.



*Figure 7.* Effect of eluent concentration on the relative response. The elution flow rate was  $1.5 \text{ mL min}^{-1}$ .

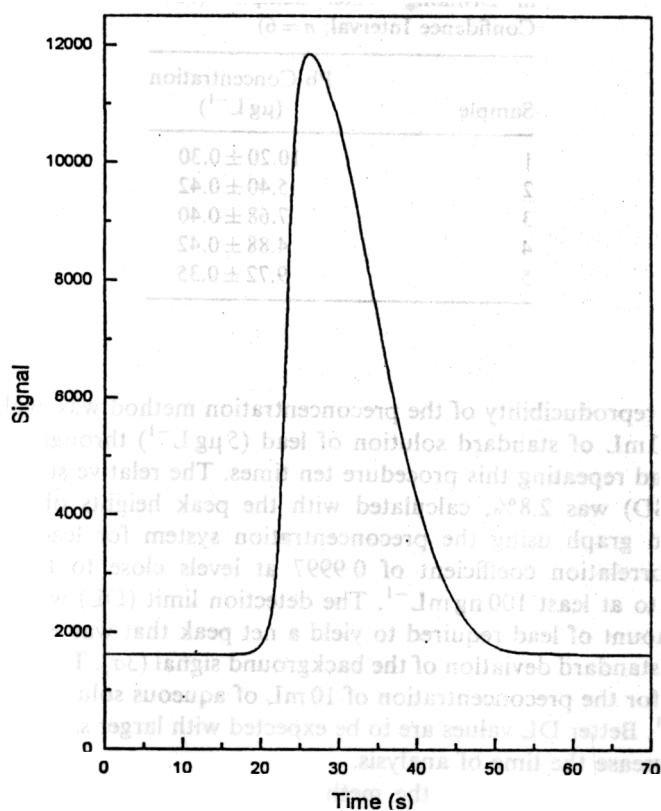


Figure 8. Peak profile obtained by pre-concentration of 10 mL of Pb-5-Br-PADAP complex using the system depicted in Fig. 1. Loaded flow rate was  $12 \text{ mL min}^{-1}$ ; the elution flow rate was  $1.5 \text{ mL min}^{-1}$ . Lead concentration was  $25 \text{ ng mL}^{-1}$ ; 5-Br-PADAP concentration was  $7 \times 10^{-6} \text{ mol L}^{-1}$ .

The effects of representative potential interfering species (at the concentration levels at which they may occur in the sample studied) were also tested. Thus,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Mn}^{+2}$  and  $\text{Fe}^{+3}$  could be tolerated up to at least  $2500 \mu\text{g L}^{-1}$ . Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the resin.

The overall time required for pre-concentration of 10 mL of sample (0.8 min, at flow rate of  $12 \text{ mL min}^{-1}$ ), washing (0.2 min), elution (0.7 min) and conditioning (0.3 min) was about 2.0 min; hence, the throughput was approximately  $30 \text{ samples h}^{-1}$ .

A recovery of 85% of the Pb-5-Br-PADAP complex from the microcolumn was obtained.

This system of preconcentration associated with ICP-AES and ultrasonic nebulization allowed for lead determination in drinking water samples at concentrations of the order of the  $\mu\text{g L}^{-1}$ . The determination procedure shows good reproducibility and accuracy.

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