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Abstract

Two manifold designs were evaluated. Water samples and wine digests in 10% nitric acid were pumped through a column containing a commercially available resin (Pb-Spec[®]), an immobilized crown ether with a cavity size selective for Pb²⁺. The column was rinsed with 2% HNO₃ and the eluent, 0.1 mol l⁻¹ ammonium oxalate was injected via a six-port rotary valve. The eluted lead was delivered to the flame atomic absorption spectrometer at 4.0 ml min⁻¹. The following flow-injection (FI) parameters were optimized: sample acidity and volume, loading and elution flow rates, and eluent composition and volume. The detection limit for the water samples, estimated from the noise on the signal obtained for 250 ml of 10 µg l⁻¹ loaded at 19.1 ml min⁻¹ was 1 µg l⁻¹. For 50 ml of wine digest loaded at 4 ml min⁻¹, the value was 3 µg l⁻¹. The roles of loading flow rate and sample volume were investigated in detail. The variation in retention efficiency with loading flow rate showed that the amount of lead retained (during a fixed loading time) increased with flow rate until the upper performance limit of the peristaltic pump was reached. The variation of detection limit with sample volume followed the expected hyperbolic relationship and showed that only small improvements in LOD were obtained for volumes greater than 50 ml. The method was evaluated through spike recovery for both water and wine. The lead contents of tap (0.24 µg l⁻¹), pond (0.40 µg l⁻¹), and river waters (not detected) were determined. The concentrations of lead in three Port wine samples ranged from not detected to 190 µg l⁻¹. No significant matrix suppression effects were observed.

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1. Introduction

Lead, even at low concentrations, is toxic to both animals and humans. As the primary sources include food, beverages, water, soil, and paint, analytical methods that are rapid and have low detection limits

are necessary [1–5]. Flame atomic absorption spectrometry (FAAS) generally cannot be used to determine trace heavy metals in water samples because of insufficient detection capability and/or matrix interferences. Preconcentration provides the dual advantages of increasing the analyte concentrations to measurable levels and removing the potentially interfering matrix. However, preconcentration in the batch mode can be time- and reagent-consuming, with a risk of sample contamination or analyte loss, whereas automated

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techniques such as flow-injection (FI) are rapid, economical, and may require only small volumes [6,7]. FI sample introduction has been coupled with FAAS for preconcentration and matrix removal [8], and several solid-phase extraction (SPE) procedures have been developed for the determination of lead [9–13]. The most commonly used procedure involves lead complexation with DDC, followed by retention on C-18 silica and Amberlite XAD-7 [5,12,13], though various other extractants, including silica treated with Aliquat 336 [4], alumina [14], cellulose [15], and Chromosorb 102 [16], have been used to retain the uncomplexed cation. These extractants have the disadvantage of being nonselective, and retain more elements than just lead. The preconcentration of lead would be more efficient with a more selective resin.

Many of the previously published procedures do not clearly describe the figure of merit for the optimization. It appears that a somewhat subjective figure of merit is used, which could be described as increased sensitivity with reasonable throughput. A primary goal of the development of a preconcentration procedure for the determination of lead by FAAS must be improved detection limit. Leaving aside considerations of the effect of the various relevant parameters on the magnitude of the noise, a major consideration is thus how the various operating parameters affect sensitivity. These parameters include the nature of the extractant, the composition of the carrier and elution solutions, the column dimensions, the loading and elution flow rates, and the sample volume. As many previous researchers have pointed out, sensitivity is directly proportional to sample volume. Thus, an obvious feature of a FI-SPE procedure is the requirement to process as much sample as possible. Clearly, increasing the sample volume decreases the throughput, unless the loading flow rate is also increased. However, at higher flow rates, the retention efficiency decreases below 100%. In the presence of matrix elements that could also bind to the extractant, this reduced retention efficiency may lead to inaccuracies due to variable retention for the samples and the standards.

In this paper, we present results of optimization studies of a procedure for which interferences are not an issue; Pb-Spec[®] is highly selective for lead over any other element likely to be encountered in environmental water or wine samples [17]. Thus, we have been able to evaluate the potential benefits of increas-

ing the sample volume without regard to the possible inaccuracies due to reduced retention efficiencies.

Pb-Spec[®], a commercially available resin, consists of an inert polymeric support impregnated with an isodecanol solution of bis-4,4'(5')-[*t*-butylcyclohexano]-18-crown-6, a crown ether which provides selectivity by retaining only those cations which can fit within the macrocycle cavity [17]. This characteristic of the resin has proven advantageous for the determination of trace lead in iron and steel [18], and the resin's high capacity for lead has been exploited for matrix removal for multielement determinations [19]. Recently, the procedure used for the analysis of iron and steel has been adapted [20] for the preconcentration and determination of lead in river and seawater materials by FI-FAAS and FI-ICP-MS.

2. Experimental

2.1. Apparatus

A Perkin-Elmer (Shelton, CT, USA) model 1100B atomic absorption spectrometer equipped with deuterium background correction was used. The Perkin-Elmer lead hollow cathode lamp current was 10 mA, otherwise the instrument was operated under the conditions recommended by the manufacturer. The position of the 10 cm air-acetylene burner head was optimized while aspirating a 20 $\mu\text{g ml}^{-1}$ Pb solution in 2% HNO₃. Prior to analysis, the position of the nebulizer capillary in the venturi throat was adjusted to obtain a sample uptake rate of zero. This ensured that the flow rate of the sample introduction was controlled by the FI manifold pumps. The spectrometer was operated in continuous mode, monitoring absorbance versus time. Data were recorded by an Epson Model LQ-850 printer, and peak height signals were measured.

Sample digestion was performed with a CEM Corporation (Matthews, NC, USA) model MDS-2100 microwave oven with advanced composite vessels.

The FI manifold for water ("manifold 1") is illustrated in Fig. 1. The manifold consisted of a two-position selection valve, a peristaltic pump (Ismatec), and a six-port rotary valve, all connected by appropriate tubing. The tubing was either 0.8 mm i.d. PTFE or for the pump, three-stop Tygon with an

Fig. 1. Schematic diagram of manifold 1, for the preconcentration of water samples. In the sample loading position: (a) the sample was pumped through the column into the flame atomic absorption spectrometer. After the sample was fully loaded, the selection valve was turned to the elute position and (b) the carrier solution briefly rinsed the column. The eluent was then injected into the carrier.

i.d. of 2.06 mm (purple-white). High flow rates were achieved by pumping through two Tygon tubes in parallel. The SPE column (4 mm i.d., 40 mm long glass tube, 51 mg resin) was located between the eluent six-port injection valve and the spectrometer. The tubing length between the column and the spectrometer was minimized.

The manifold for the wine analysis (“manifold 2”) is shown in Fig. 2. In this design, the Pb-Spec[®] column (3 mm i.d., 25 mm long Omnifit glass tube, 40 mg resin) was contained within the loop of a six-port rotary valve.

Fig. 2. Schematic diagram of manifold 2, used to preconcentrate wine. In the sample loading position (a) the sample was pumped through the column into the waste container. After the sample was fully loaded, the valve was turned to the elute position and (b) the carrier solution briefly rinsed the column. The eluent was then injected into the carrier.

tary valve. The sample solution was propelled through 0.8 mm i.d. PTFE tubing by a peristaltic pump (Ismatec) with 1.52 mm i.d. three-stop Tygon tubing (blue-yellow). The same pump was used to control the flow of carrier solution, and a second six-port rotary valve controlled the injection of eluent into the carrier.

A slurry of Pb-Spec[®] material was prepared by the addition of a few milliliters of 3% HNO₃ to 0.5–1.0 g of Pb-Spec[®] resin (Eichrom Technologies Inc., Darien, IL, USA). A small amount of glass wool was placed in one end of the column and the slurry introduced manually from a disposable plastic syringe. Once a sufficient amount of resin had been packed into the column, a plug of glass wool was inserted and the end fitting attached. The columns were cleaned by pumping 3% HNO₃ at 3 ml min⁻¹ for 5 min, followed by 0.1 mol l⁻¹ ammonium citrate for 5 min. After a final 5 min rinse with 3% HNO₃, the columns were ready for use. When the columns were not in use, they were stored wet to avoid the possibility of channeling.

2.2. Reagents and samples

All reagents were at least of analytical reagent grade. High-purity deionized water (18 MΩ, E-Pure, Barnstead) was used throughout the experiments. The standards and samples were acidified with nitric acid (65%, Mallinckrodt). The eluents, ammonium oxalate (0.1 and 0.5 mol l⁻¹) and ammonium citrate (0.1, 1.0, and 2.0 mol l⁻¹) solutions, were prepared by dissolving the appropriate amount of solid reagent (J.T. Baker and Fisher, respectively) in deionized

Table 1
Programs used for microwave digestion of wine samples

	Stage					
	1	2	3	4	5	6
Temperature (°C)	120	140	160	180	120	160
Fan speed	100	100	100	100	100	100
Power (%)	25	40	40	40	25	100
Pressure (psi)	20	40	85	150	20	60
Time (min)	15	15	15	15	15	20
TAP (min)	5	5	5	5	5	10

The applied power was varied between 30 and 70% depending on the number of vessels. TAP stands for time at pressure. Stages 5 and 6 were performed after the vessels were cooled, vented and H₂O₂ was added.

water. Standard solutions of lead were prepared daily in the concentration range 0.1–1.0 mg l⁻¹ by the appropriate dilution with HNO₃ of a 1000 mg l⁻¹ atomic absorption standard solution (Aldrich).

Water samples were collected and stored in acid-washed polyethylene (Nalgene) bottles. Tap and pond waters were obtained on the campus of the University of Massachusetts, Amherst, while the river water was collected from the Connecticut River in Northampton, Massachusetts. The tap water was acidified with HNO₃ prior to analysis. The pond and river waters were filtered through Whatman 42 paper to remove any suspended solids, and acidified.

Wine samples were digested in the microwave oven using the program listed in Table 1. Five grams of sample were weighed into each vessel and combined with 5 ml concentrated HNO₃. The vessels were sealed after 15 min of predigestion. The samples were irradiated by the first four steps of the program, then removed from the oven and cooled to room temperature. One milliliter of 30% H₂O₂ (Mallinckrodt) was added to each sample, and then the vessels were resealed and subjected to the final two stages of the program. At the completion of the microwave digestion, the colorless samples were transferred to 50 ml volumetric flasks and made up to volume with deionized H₂O.

2.3. Method development

As the goal of the method development was the determination of lead in various matrices at concentrations below the detection limit of conventional FAAS, factors which affect the detection limit

and the separation from the matrix are important. The strategy adopted here was to consider how to increase the sensitivity, then evaluate the effect on the detection limit obtainable, and finally measure the accuracy by the analysis of spiked samples against aqueous standards.

There are two main issues governing preconcentration: the efficiency with which the analyte is removed from the sample on loading, and the efficiency with which the retained analyte is eluted. In addition, the response of the spectrometer as a function of the operating conditions needs to be considered.

Pb-Spec[®] is unlike other materials that have been used to retain metals from solution in that the chelating agent is not covalently bound to an inert resin support, but rather is dissolved in a water immiscible organic solvent (*n*-decanol) which impregnates the support material. It is thought that lead is retained by a mechanism which first involves extraction of the neutral Pb(NO₃)₂ species into the organic solvent followed by dissociation of this nitrate complex and formation of the lead–crown ether complex. Thus, the effect of the carrier and sample acidity is not easy to predict. The mechanism of elution is even more obscure, but presumably involves the reverse processes with the rapid complexation of the lead in the eluent solution by the oxalate or citrate anion.

It is expected that retention efficiency would decrease as loading flow rate increased; however, as the relevant parameter is the mass of analyte loaded, it may be better to load at a faster rather than a slower rate. The amount of analyte would then be set by the time which could be devoted to loading. It was decided that a loading time of 15 min per sample would be the maximum. For manifold 1, the loading flow rate for 5 ml of 1.0 µg ml⁻¹ solution was varied from 2.5 to 19.1 ml min⁻¹, and the absorbance during the loading step was monitored to determine breakthrough. For manifold 2, the loading flow rate was varied between 1 and 15 ml min⁻¹ for a 50 ml volume of 0.2 mg ml⁻¹ Pb. Peak height upon elution was evaluated for both systems.

As it has been reported [17,19,21,22] that the sorption characteristics of the resin for lead are affected by the concentration of nitric acid, the concentration of nitric acid in the carrier solution was varied over a range. This range was 0–20% (v/v) for manifold 1, and 0–5% (v/v) for manifold 2. Sample solutions

($1.0\ \mu\text{g ml}^{-1}$ Pb for manifold 1, $0.2\ \mu\text{g ml}^{-1}$ Pb for manifold 2) containing 0–20% HNO_3 were prepared for both systems. Each sample solution was tested for each carrier solution. This experiment was performed twice with manifold 1. In the first experiment, 5 ml samples were loaded at $2.0\ \text{ml min}^{-1}$ and eluted with 0.5 ml of $0.1\ \text{mol l}^{-1}$ ammonium citrate. In the second, the 5 ml samples were loaded at $4.0\ \text{ml min}^{-1}$ and eluted with 2.5 ml of $0.1\ \text{mol l}^{-1}$ ammonium oxalate. The elution flow rate was $4.0\ \text{ml min}^{-1}$. When manifold 2 was tested, 50 ml of $0.2\ \mu\text{g ml}^{-1}$ Pb were loaded at $4\ \text{ml min}^{-1}$, and eluted with 0.5 ml of $0.1\ \text{mol l}^{-1}$ ammonium citrate. Again, the elution flow rate was held at $4.0\ \text{ml min}^{-1}$.

Two eluents, ammonium citrate and ammonium oxalate, were tested by manifold 1. Three concentrations of ammonium citrate were evaluated: 0.1, 1.0 and $2.0\ \text{mol l}^{-1}$. For ammonium oxalate, 0.1 and $0.5\ \text{mol l}^{-1}$ were used. The volume of the eluent was varied over the range of approximately 0.5–2.5 ml. The eluent flow rate, for 2.5 ml of $0.1\ \text{mol l}^{-1}$ ammonium oxalate, was varied from 4.0 to $13.1\ \text{ml min}^{-1}$. The effect of eluent flow rate was not evaluated in detail as this flow rate was also the sample introduction rate. This placed some restrictions on the eluent flow rates as the nebulizer only operated at maximum signal-to-noise ratio over a relatively narrow range.

An experiment was performed with manifold 1 to determine the relationship between detection limit and sample volume. It is believed [23] that there is a limit to the extent that increasing the sample volume will substantially improve the detection limit. Sample volumes between 10 and 1000 ml were preconcentrated for concentrations of 5, 10, and $15\ \mu\text{g l}^{-1}$. The detection limit was calculated as the concentration giving an absorbance equal to three times the standard deviation of the signal for the standard, assuming (a) the noise on the signal for a low standard is approximately the same as that for the blank and (b) a linear calibration.

2.4. Procedures and validation

When manifold 1 was used, the sample was pumped through the column while the loop of the eluent valve was loaded from a disposable syringe. The manifold design was chosen to allow any unretained analyte to be detected by connecting the column effluent directly to the nebulizer of the spectrometer, allowing

the evaluation of the lead retention efficiency. After the sample was loaded, the selection valve was moved to its alternate position, and the 2% HNO_3 carrier was pumped through the column for 45 s, removing any remaining matrix. During the elution step, the injection valve was switched to introduce the eluent, releasing the lead from the crown ether and delivering it to the spectrometer.

The loading process was similar for manifold 2. In this case, the sample was pumped through the column and into the waste container. At the same time, the 2% HNO_3 carrier solution was pumped into the spectrometer. After the sample was loaded, the valve containing the column was switched into its second position so that the carrier could rinse away any residual matrix. Finally, the eluent was injected into the carrier and propelled through the column in the direction opposite to that used for loading.

Recovery studies for manifold 1 were performed with water samples from different sources: tap, pond and river water. These acidified samples were spiked to yield a final added concentration of $10\ \mu\text{g l}^{-1}$. Similar studies were performed for manifold 2, with a California Merlot (12% alcohol) that was spiked with varying lead concentrations prior to sample digestion (12.5 , 25 , 50.1 , $100\ \mu\text{g l}^{-1}$ Pb).

External calibration for water was performed with lead standard solutions in the concentration range 0.5, 1.0 and $2.5\ \mu\text{g l}^{-1}$. For wine, the calibration standards spanned the range of 5 – $50\ \mu\text{g l}^{-1}$. Analytical blanks (2 and 10% of nitric acid) were measured in the same way as the samples and standard solutions. Peak height absorbance was measured, and three replicate measurements for each standard and sample were made. The calibration data were then processed on a personal computer using Microsoft Excel (version 5.0) to obtain the calibration curve and the equation.

3. Results and discussion

3.1. Factors affecting sample loading

When the nitric acid content of the sample was varied, optimal loading occurred with the sample containing 10% HNO_3 . Optimal loading was defined as those sample introduction conditions resulting in maximum Pb retention, indicated by the largest peak

heights upon elution. The samples containing 10% HNO_3 demonstrated the greatest retention regardless of whether ammonium citrate or ammonium oxalate was used as the eluent. This result was identical for both manifolds. The carrier acidity that produced the best Pb retention for samples with 10% HNO_3 was 2% HNO_3 . Again, this result was observed with both eluents. Although the absorbance was higher for manifold 1 when the carrier was simply deionized water, the error bars for this absorbance point were larger than those for 2% HNO_3 , and also included the mean absorbance for the 2% HNO_3 point within their range. The water peak heights were also highest for manifold 2, but the precision of the absorbance signals was improved so the performance of this carrier was clearly better than 2% HNO_3 . The carrier concentration for manifold 1 was therefore 2% HNO_3 for use with samples containing 10% HNO_3 . The carrier for manifold 2 was water, also for use with samples containing 10% HNO_3 .

The results of changing the sample loading flow rate are shown in Fig. 3, from which it can be seen that increasing the loading flow rate resulted in diminished sample absorbance. In addition, a small

absorbance during loading was observed for higher flow rates with manifold 1, indicating sample breakthrough. The trend shown in Fig. 3 indicates that if the loading time is limited to 15 min, the maximum analyte mass will be loaded at the maximum flow rate. Although the retention efficiency was higher at the slower flow rates, the time limit of 15 min per sample only allowed the preconcentration of about 35 ml. At a faster flow rate, although a small amount of Pb would not be retained, the overall sensitivity would be improved by preconcentrating a much larger volume (up to 250 ml). Water samples were therefore preconcentrated at 19.1 ml min^{-1} to maximize the volume of sample that was processed, while the wine samples were loaded using a more conventional flow rate of 4 ml min^{-1} to maximize analyte retention.

3.2. Factors affecting analyte elution

The best signal-to-noise ratio was obtained for a 0.1 mol l^{-1} ammonium oxalate eluent solution. The smallest volume of eluent that completely stripped the retained lead for manifold 1 was 2.5 ml. Volumes smaller than 2.5 ml also enabled quantitative recovery

Fig. 3. Effect of sample loading flow rate on absorbance for both manifolds (Pb solution: 10 ml of $1.0 \mu\text{g ml}^{-1}$; eluent: 2.5 ml of 0.1 mol l^{-1} of ammonium oxalate; eluent flow rate: 4.0 ml min^{-1}). Each point represents the mean of three replicates, and the error bars show two standard deviations.

of lead, but multiple injections were required. Larger volumes were not tested, since the goal of the preconcentration experiment was to use the minimum amount of eluent that would completely remove the adsorbed material. An eluent volume of 2.5 ml of 0.1 mol l^{-1} ammonium oxalate was therefore chosen for subsequent work with this system. For manifold 2, however, the minimum eluent volume that completely desorbed the analyte was 0.5 ml. The elution volume for manifold 2 was smaller than that required by manifold 1 primarily because of the different designs. The lead was eluted in manifold 2 by backflushing the column, therefore requiring a smaller volume of eluent. In the case of manifold 1, however, the eluent flushed the analyte through the entire length of the column to effect complete desorption.

The effect of the elution flow rate was investigated with an ammonium oxalate concentration of 0.1 mol l^{-1} . The optimum sensitivity and precision were obtained when the elution flow rate was approximately 4.0 ml min^{-1} regardless of which manifold was in place. This parameter was instrument-dependent, since the flame AA spectrometer has an optimum flow rate yielding the best sensitivity. Flow rates higher than 4.0 ml min^{-1} also gave quantitative recovery, but the analytical signal decreased due to the sub-optimal conditions for the spectrometer.

3.3. Analytical performance

Lead was determined using manifold 1 in the range $0.5\text{--}15 \mu\text{g l}^{-1}$ with sample volumes of 10–250 ml. Linear calibrations were obtained over the concentration ranges $0.5\text{--}2.5$ and $2.5\text{--}15 \mu\text{g l}^{-1}$. The calibration graph for the first range had the least squares fit equation $A = 0.0057 [\text{Pb } (\mu\text{g l}^{-1})] + 0.0003$, where A represents the peak height absorbance. The correlation coefficient ($n = 4$) was 0.9988. For the second range, the calibration equation was $A = 0.0010 [\text{Pb } (\mu\text{g l}^{-1})] + 0.0120$, with a correlation coefficient ($n = 4$) of 0.9989. When the slopes of these curves were compared to the slope of the calibration for a standard flow-injection system (0.5 ml sample with no preconcentration), a ratio of between two and three orders of magnitude was obtained. For manifold 2, with 50 ml of sample, the ratio of slopes before and after preconcentration was 30.

The variation of detection limit as a function of sample volume for manifold 1 is shown in Fig. 4. It can be clearly seen that the detection limit decreased with increasing sample volume. Further increase in sample volume beyond 250 ml did not improve the LOD. The general shape of the plot is in line with that predicted by the flow-injection detection limit equation [23], that is, a hyperbolic relationship between preconcentrated

Fig. 4. The effect of increasing sample volume on detection limit for manifold 1. Each point represents the mean of the three replicate measurements of the detection limits for each of three Pb concentration, so $n = 9$ for each point. Extra replicates were collected for the 250 ml volume of $10 \mu\text{g l}^{-1}$, so $n = 14$ for this point. The error bars show one standard deviation.

sample volume and LOD. The best LOD, obtained with the $10 \mu\text{g l}^{-1}$ lead solution ($n = 8$), was found to be $1 \mu\text{g l}^{-1}$ for a 250 ml sample volume. This value is included in Fig. 4 as one of the three lead concentrations averaged to obtain the mean LOD for the 250 ml point.

The limit of detection for manifold 2, based on three times the standard deviation of the blank ($n = 10$), was calculated to be $3 \mu\text{g l}^{-1}$. This would be consistent with about $30 \mu\text{g l}^{-1}$ in an undiluted wine sample. However, in practice, it was possible to measure lower concentrations: for example a $12.5 \mu\text{g l}^{-1}$ predigestion spike was recovered with good precision.

Previously reported LOD for the determination of lead by FI-SPE-FAAS range from 0.04 [15] to $10 \mu\text{g l}^{-1}$ [4]. These values were obtained with 200 and 5 ml, respectively. One reason for these differences in LOD may be the contribution from the analyte contamination in the reagent blank. In the procedure described by Naghmush et al. [15], the sample pH was adjusted to 2.5 ($3.2 \times 10^{-3} \text{ mol l}^{-1}$) by the addition of nitric acid, whereas in the procedure described here, samples are acidified to 1.6 mol l^{-1} . Thus, for equal purity of nitric acid with respect to lead, the Pb-Spec[®] procedure involves the addition of 500 times more analyte from the reagents, however the LOD is only 25 times greater. Both Rodriguez et al. [14] and Naghmush et al. [15], report variations of LOD with

sample volume in agreement with that predicted by the flow-injection detection limit equation [23]. Other LOD reported previously [14,16,24] for water determinations are 0.4, 2 and $4 \mu\text{g l}^{-1}$ for sample volumes of 25, 4.4 and 4.5 ml, respectively; and $3 \mu\text{g l}^{-1}$ for the analysis of wine [25] (sample volume not given).

For the determination of lead in wine by electrothermal atomic absorption spectrometry (ETAAS), an LOD of $6 \mu\text{g l}^{-1}$ has been reported [26]. By flow-injection hydride generation AAS, however, a value of $10 \mu\text{g l}^{-1}$ was obtained [27].

The Pb-Spec[®] resin exhibited a long lifetime suggesting a high degree of resin stability. Hundreds of sample retention and elution cycles were made over a period of several months without a measurable loss of analytical performance.

3.4. Application to water samples

The results for the analyses of the water samples are shown in Table 2. Recoveries of the lead spikes between 100 and 116% were obtained, demonstrating the absence of signal suppression due to the matrix in these sample materials. It is possible that the tap water value is slightly low: the sample was not collected as a “first flush” of the pipes, and the lead content of drinking water is known to vary as a function of contact time with lead-contaminated plumbing [2].

3.5. Application to wine samples

The digestion of the wine samples was critical to their determination. Because the crown ether in Pb-Spec[®] is dissolved in decanol as part of the manufacturing process, the crown ether can be leached from the resin if it comes into contact with alcohol. The complete decomposition of the wine was therefore necessary for two reasons: to destroy the ethanol, thereby preserving the integrity of the resin, and also to release the lead from its various organic ligands [28–30].

Table 2 shows the results for the spike recovery of lead from a red table wine. The recoveries spanned from 94 to 104% over a range of spike concentrations. The accuracy and precision of these results demonstrate the lack of matrix interferences in the samples, suggesting complete decomposition of the wine samples, i.e. the performance of the Pb-Spec[®] resin was

Table 2

Analysis of water samples spiked with $10 \mu\text{g l}^{-1}$ Pb and California red wine samples spiked with varying $\mu\text{g l}^{-1}$ Pb ($n = 3$)

Sample	Added ($\mu\text{g l}^{-1}$)	Found ^a ($\mu\text{g l}^{-1}$)	Recovery (%)
Tap water	0	0.24 ± 0.06	
	10.0	11 ± 2	108
Pond water ^b	0	0.4 ± 0.1	
	10.0	12 ± 2	116
River water	0	ND ^c	
	10.0	10 ± 2	100
California red wine	0	0	
	12.5	12 ± 1	94 ± 9
	25	26 ± 3	104 ± 10
	50.1	50 ± 6	100 ± 10
	100	100 ± 10	100 ± 10

^a Uncertainty term is the 95% confidence interval.

^b Average of eight replicates.

^c ND: not detected.

Table 3
Lead concentration in port wines ($\mu\text{g l}^{-1}$)

Port wine sample	Ethanol (%)	Lead found
White	19.5	60 ± 6
Rufby	19	ND ^a
Tawny, aged 30 years ^b	20	190 ± 20

Uncertainty term represents the 95% confidence interval ($n = 3$).

^a ND: not detected.

^b Matured in wood.

not affected by the presence of ethanol in the original samples.

Results for the determination of lead in three Port wine samples are shown in Table 3. These findings indicate that the oldest wine contained the largest amount of lead, a result which is consistent with previously published reports [30,31].

The overall uncertainty, obtained from the variation in replicate determinations, was about 10% at the concentrations of analyte encountered. It is speculated that the major sources of uncertainty, at concentrations well above the detection limit, are the variations due to the kinetics of the processes in the column responsible for the retention and elution of the analyte.

4. Conclusions

It is concluded that better LOD are obtained by the strategy in which the loading flow rate is maximized. However, the selection of the values of the relevant operating parameters based on an examination of the dependence of LOD on sample volume leads to the conclusion that little is to be gained by preconcentrating volumes greater than about 50 ml. It is also concluded that there are no advantages of loading at low flow rates, and thus it is suggested that in the interest of maximizing throughput, higher values should be used. For example, at a loading flow rate of about 20 ml min^{-1} , 50 ml would be loaded in approximately 150 s corresponding to a sample throughput of 24 h^{-1} .

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