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LEAD PRECONCENTRATION WITH FLOW INJECTION FOR FLAME ATOMIC ABSORPTION SPECTROMETRY

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SUMMARY

The flow-injection preconcentration of lead with immobilised reagents under a variety of conditions is discussed. Timed sample loading and matrix removal without passing the matrix to the nebuliser were achieved simply with one valve. Reagent consumption and calibration time were reduced by the addition of further valves. A system design incorporating control of the timing of operations by a commercial autosampler is described. The effects of pH and interferent ions were examined. Water samples were analysed against aqueous standards and as standard additions solutions. For an analysis time of about 3 min a preconcentration factor of about 40 was obtained for both peak height and area measurements. Detection limits of down to 1.4 ng ml^{-1} were obtained.

The measurement of very low levels of environmental pollutants is becoming increasingly important. The determination of lead, a cumulative toxin, is a good example. The current maximum allowable concentration of lead in British drinking water, before it enters the distribution network, is 50 ng ml^{-1} [1]. Although electrothermal atomisation atomic absorption spectrometry (a.a.s.) can be used to measure this and lower concentrations, it suffers from the problems of slowness and of requiring considerable effort to ensure accurate results. Flames can provide simple and effective atom sources but, if samples are aspirated directly, do not provide sufficient sensitivity. Therefore, if a flame is to be used as the atom source, a preconcentration step is essential.

Various methods of achieving preconcentration have been applied, including liquid-liquid extraction, precipitation, immobilisation and electrodeposition. Most of these have been adapted to a flow-injection format for which retention on an immobilised reagent appears attractive. Solid, silica-based preconcentration media are easily handled [2–9], whereas resin-based materials tend to swell, depending on the material adsorbed by them, and may break up. Resins can be modified [10] by adsorption of a chelating agent to prevent this. Solids are easily incorporated into flow-injection manifolds as small columns [5,6,8,11,12]; 8-quinolinol immobilised on porous glass has often been used

[5,6,8]. The flow-injection technique provides reproducible and easy sample handling and the manifolds are easily interfaced with flame atomic absorption spectrometers.

The manifolds, which have been described previously, operate with injection of a large sample volume, either by timed flow-switching [5,8] or by using a large sample loop in an injection valve [6,11,12]. This second option allows only multiples of a discrete volume to be preconcentrated, unless the sample loop is changed. With timed injection, the preconcentration volume can, in theory, be infinitely varied. In many previous manifold designs, the column is placed just before the nebuliser of the atomic absorption spectrometer [5,6,11,12], so all the sample matrix and unadsorbed analyte will pass into the nebuliser during preconcentration. This could cause nebuliser or burner blockage or an unstable baseline. However, by diverting the stream away from the detector during preconcentration [8,12], these problems can be eliminated.

In this paper, the manifolds described for preconcentration involve a column included within the sample loop of an injection valve. This enables timed sample loading onto the column without the matrix components passing to the spectrometer. Elution is achieved by switching the valve to place the column into the carrier stream which contains eluent.

EXPERIMENTAL

Apparatus and reagents

A Philips Scientific SP9 atomic absorption spectrometer, with an air/acetylene flame, was optimized for the detection of lead. The conditions which gave the maximum signal to noise values were as follows: wavelength 283.3 nm, air flow setting 29, acetylene flow setting 15, burner height 4, lamp current 7.5 mA and bandpass 1 nm. Results were recorded with a chart recorder (Philips AR55).

Reagents were AristaR or Spectrosol grade (BDH). Water used was reagent grade obtained from a reverse osmosis/deionization unit.

All glassware was stored in dilute nitric acid and rinsed with water before use. To prevent adsorption of lead from the prepared solutions, one drop of nitric acid (s.g. 1.412) was added per 100 ml of final solution volume.

Diazo-coupling of various reagents (see Table 2) to silica gel was achieved by using the method described by Hill [2]. A 0.2–0.5-mm particle size silica gel (Kieselgel 100; Merck) was used in order that the columns would not induce significant back-pressure within the manifolds. These columns were constructed from glass tubing as shown in Fig. 1.

Four manifolds (see Fig. 2) were used. Poly(tetrafluoroethylene) (PTFE) tubing (0.5 mm i.d.; Anachem) was used throughout. Manifolds 1–3 were used for preconcentration studies and were based on an autosampler (PS Analytical 20.080) which allowed the control and timing of external devices. Valves V_1 and V_2 (PS Analytical, T-series) were controlled by the autosampler. Valve V_1

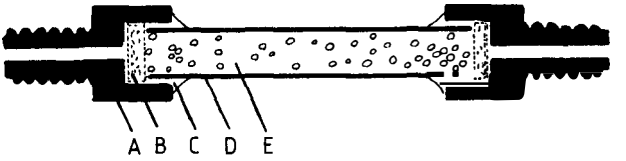

Fig. 1. Preconcentration column: A, $\frac{1}{4}$ UNF plastic connector (Anachem); B, porous PVC disc; C, epoxy glue; D, 40-mm glass tubing, 2.5 mm i.d.; E, packing material.

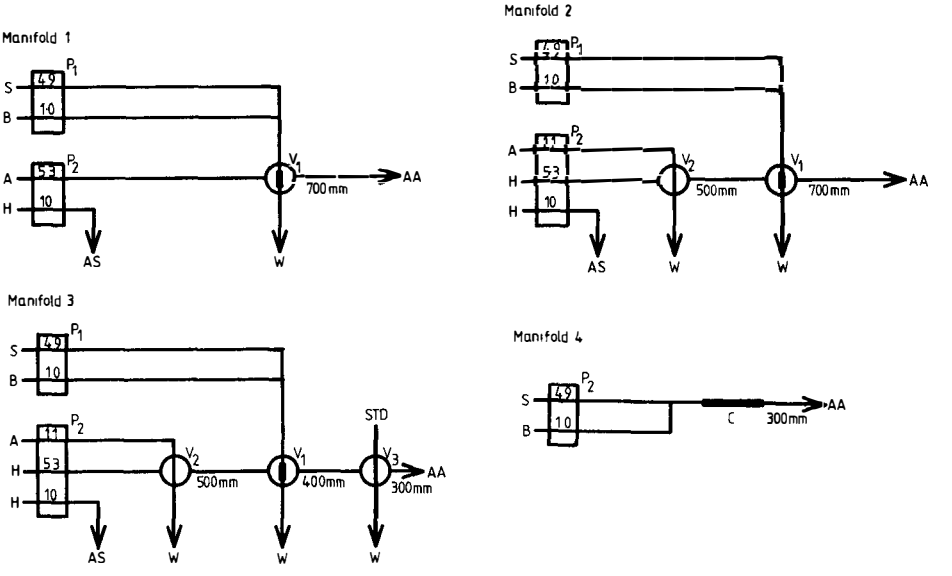

Fig. 2. Preconcentration manifolds: S, sample; B, buffer; A, acid; H, water; STD, standards; AS, autosampler probe wash-pot; W, waste; AA, spectrometer; C, column. Other symbols are explained within the text. Flow rates are in ml min^{-1}.

had the column connected within the sample loop by using two 250-mm lengths of tubing, so that sample loading was done in the opposite flow direction to elution. The injection valve V_3 (Rheodyne), incorporated a 287-μl sample loop. Pump P_1 (LKB Microperpex 2132) was switched off by the autosampler when the sample probe travels between the sample vial and probe wash-pot. This prevented air entering the column. Pump P_2 (Ismatec Mini-S 840) was run continuously at a fixed speed.

Procedures

Use of the manifolds. These manifolds were used in the following manner. Sample and buffer were merged before being pumped to the column for 150 s, whereupon valve V_1 was switched and the sample was eluted either by a continuous acid stream (manifold 1) or by an acid slug injected simultaneously via valve V_2 (manifolds 2 and 3). During elution, the sample probe resides in

the wash-pot which contains water. This water is merged with buffer and washes the sample from the connecting tubing for 40 s. Valve V_3 (manifold 3) allowed the injection of standards that had concentrations above the normal detection limit of the instrument, whilst preconcentration was proceeding. In these manifolds, the elution flow rate was selected to give maximum signal for solutions injected without preconcentration. Manifold 4 was used to monitor the column effluent during preconcentration.

Effect of pH of preconcentration. Various universal buffer solutions [13] were merged with three lead solutions (0.1, 0.4 and 1.0 $\mu g\ ml^{-1}$) preconcentrated on immobilised 8-quinolinol in manifold 1 and eluted with a 1 M hydrochloric acid carrier stream.

Effect of buffer constituents. A solution consisting of 0.05 M disodium tetraborate decahydrate (borax) was acidified with citric and boric acids to produce two buffers of pH 8. These were merged with a 10 $\mu g\ ml^{-1}$ lead solution and preconcentrated on immobilised 8-quinolinol in manifold 4. The borax/boric acid buffer was used for all the following experiments.

Eluent concentration. Solutions containing 0.1, 0.4 and 1.0 $\mu g\ ml^{-1}$ lead were preconcentrated on immobilised 8-quinolinol in manifold 1. Elution was done with carrier streams of 0.25, 0.5, 0.75 and 1.0 M hydrochloric acid.

Detection limits. Solutions containing 0, 10, 20 and 30 $ng\ ml^{-1}$ lead were preconcentrated on immobilised 8-quinolinol in manifold 2, and eluted by injection of a 1.0 M hydrochloric acid solution. Detection limits were calculated from the resultant calibration curve [14].

Peak-height and peak-area calibrations. Duplicates of three samples of solutions containing 0, 20, 60, 100, 120 or 200 $ng\ ml^{-1}$ lead were preconcentrated on immobilised 2-methyl-quinolinol in manifold 3 and eluted by the injection of 1.0 M hydrochloric acid via valve V_2. Solutions containing 2, 5, 10 or 20 $\mu g\ ml^{-1}$ lead were injected six times via valve V_3. Peak heights and areas were measured by using the SP9 computer, each measurement cycle being started manually when either preconcentrated or non-preconcentrated lead was injected. In order to record the whole peak, an integration time of 20 s was required for preconcentration injections and 7 s for normal injections.

Analysis of water samples. Samples (500 ml) were collected from an outhouse supplied via a lead pipe. No water was drawn for approximately two weeks before 500 ml was run to waste and six samples were collected. These were acidified with the appropriate quantity of concentrated nitric acid (0.5 ml) and, if they could not be analysed immediately, stored in a refrigerator. These samples were analysed against aqueous standards by using manifold 2 with 2-methyl-8-quinolinol column, and by direct nebulisation. Standard additions were also made to the samples and the solutions were re-examined by both techniques.

RESULTS AND DISCUSSION

The flow rate and preconcentration time used resulted in the consumption of approximately 12 ml of sample per determination. This enabled duplicate determinations to be done on the contents of each vial.

The results of preconcentration of lead from buffers of different pH, are presented in Fig. 3. The 8-quinolinol column is most effective at pH $\geqslant$ 8.0. A pH of 8.0 was therefore used in subsequent systems because, at this pH, the solubility product for lead hydroxide is not exceeded until the lead concentration is greater than 500 μg ml^{-1}. This ensured that preconcentration occurred by chelation rather than precipitation. The difference in the optimum pH range from that observed by Malamas et al. [5] may be due to the preconcentration being done at higher flow rate in these experiments, so that the efficiency of preconcentration at lower pH values was reduced.

It was hoped that the interference by iron could be suppressed by the use of a buffer containing citrate, but when the borax/citric acid buffer was used, the effluent from the column gave a large and erratic signal compared with that obtained with the borax/boric acid buffer (Fig. 4). This indicates that citrate competes with the immobilised reagent for the lead. If this were the sole reason for the change in signal, a larger effluent signal would be observed rather than a very erratic signal. The erratic behaviour is probably due to poor mixing of the buffer with the sample, which is only apparent when a component of the buffer competes for the lead.

When the eluent concentration was increased from 0.25 M to 1.0 M, a steady increase in peak height of 3.25% was observed for manifold 1. The peaks were all sharp and the widths were not significantly reduced. This indicates that the lead is eluted by the acid and, if continuous elution is employed, a 0.25 M acid solution will give acceptable sensitivity. The dispersion of an acid slug injected into manifold 2 will cause dilution of the acid. If a 1.0 M acid solution is injected, the dilution will not greatly reduce sensitivity.

The detection limits were calculated for several calibration curves and ranged from 2.8 ng ml^{-1} to 1.4 ng ml^{-1}. Although these detection limits are similar to

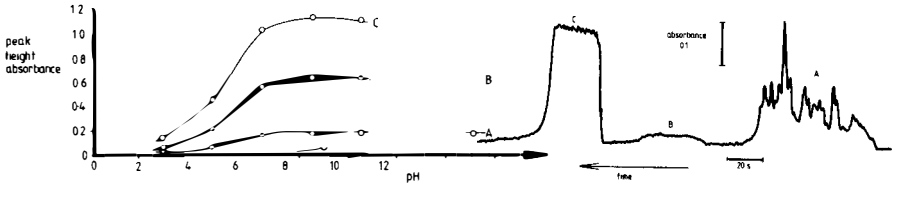

Fig. 3. Effect of pH on lead preconcentration on an 8-quinolinol column: A, 0.2 μg ml^{-1}; B, 0.4 μg ml^{-1}; C, 1.0 μg ml^{-1}.

Fig. 4. Signal produced when the column effluent of manifold 4 was monitored: A, borax/citric acid buffer; B, borax/boric acid buffer; C, buffer replaced by water and column removed.

those obtainable with an electrothermal atomiser, an improvement can be obtained simply by increasing the volume of sample pumped through the column. The decreased detection limits must then be traded against an increase in time.

The results of including significant levels of possible interferents are presented in Table 1. Interference by sodium chloride is low even at the 2% level, because the system was optimised for use with a sodium borate buffer which is merged with, and therefore present in, every sample. The elements which can be chelated by the column will compete with lead for the active sites. If the interferent is more strongly chelated on the column, or in a sufficiently high concentration, the adsorption of lead will be reduced. It is interesting to note that calcium and magnesium at the 10 μg ml^{-1} level significantly enhance the preconcentration of lead. How this is achieved is unclear. Inclusion of a reagent which competes for the interferent (e.g., fluoride in the case of iron) reduces the effect of the interferent.

The results obtained by using different columns (Table 2) indicate that, under the conditions used, there is no significant difference between column materials. If any column material was less selective for lead than for sodium, the signal would be reduced because the sodium in the buffer would displace

TABLE 1

The effect of interferents on the preconcentration of a 100 ng ml^{-1} lead solution[a]

Interferent	Concentration	Change in peak height (%)	Interferent	Concentration	Change in peak height (%)
Ca	50 μg ml^{-1}	−98.3	Fe	10 μg ml^{-1}	−92.9 (−49.1[b])
Ca	10 μg ml^{-1}	+11.4	Mg	10 μg ml^{-1}	+24
Cu	10 μg ml^{-1}	−60	NaCl	2%	−6.1

[a]The solution containing the interferent was preconcentrated on immobilised 8-quinolinol in manifold 2 and eluted with 1.0 M hydrochloric acid. [b]With 1% NaF added.

TABLE 2

Results of the preconcentration of a 100 ng ml^{-1} lead solution for different columns

Column material[a]	Peak height	Column material[a]	Peak height
8-Quinolinol	0.065	Pyrocatechol violet	0.059
2-Methyl-8-quinolinol	0.064	Silica gel[b]	0.063
4-(2-Pyridylazo)resorcinol	0.056	Borosilicate glass[b,c]	0.060

[a]Immobilised on silica gel. [b]Without immobilised reagent. The column materials were placed, in turn, in the loop of valve V_1 in manifold 2; 1.0 M HCl was used for elution. [c]0.5 mm diameter.

lead from the column during preconcentration. When plain silica gel or borosilicate glass beads were used, it was expected that the lack of an immobilised chelate would reduce the resultant lead signal. In these cases, the hydroxyl groups on the surface must themselves bind lead. The silica-based columns were mechanically stable and could be used without degradation for several months.

Normal injection of standards (0–20 $\mu g\ ml^{-1}$ lead) via valve V_3 in manifold 3 produced the expected results. The calibrations were linear with correlation coefficients of 0.9999 and 0.9999 and detection limits of 0.30 and 0.28 $\mu g\ ml^{-1}$ based on peak height and area, respectively. The precision of the peak areas was better than that obtained for peak heights, because the constant quantity of material injected is measured rather than the maximum amount passing into the flame at one time, which depends on injection technique. The results obtained for preconcentration (Table 3) also gave linear calibrations (for 0–200 ng ml^{-1} lead), with correlation coefficients of 1.0000 and 0.9992 and detection limits of 1.3 and 6.4 ng ml^{-1} based on peak height and area, respectively. For these results, the precision was poorer for peak areas than for peak heights, probably because of integration of a considerable portion of the baseline, the resultant error being reflected in the negative intercept.

The factors by which the solutions were concentrated were calculated for each preconcentrated solution, by using the calibration curve generated from standards injected normally. A mean value of 43 with a relative standard deviation (r.s.d.) of 4% was obtained for peak heights and a value of 42 (r.s.d. 2%) for peak areas.

The results obtained for the water samples (Fig. 5) confirm the effects of interferents on the preconcentration of lead. When samples were analysed without additions, the preconcentration results obtained were low, indicating the presence of competing species. But the use of the standard additions was

TABLE 3

Results obtained for preconcentration of lead solutions with manifold 3

Solution concn. (ng ml^{-1})	Peak height		Peak area	
	Mean	R.s.d. (%)	Mean	R.s.d. (%)
200	0.0932	1.57	0.2152	3.40
120	0.057	1.42	0.1205	5.98
100	0.048	2.79	0.0969	10.5
60	0.029	3.13	0.0489	22.2
20	0.011	10.8	0.0119	39.9
0	0.002	-	−0.0124	-

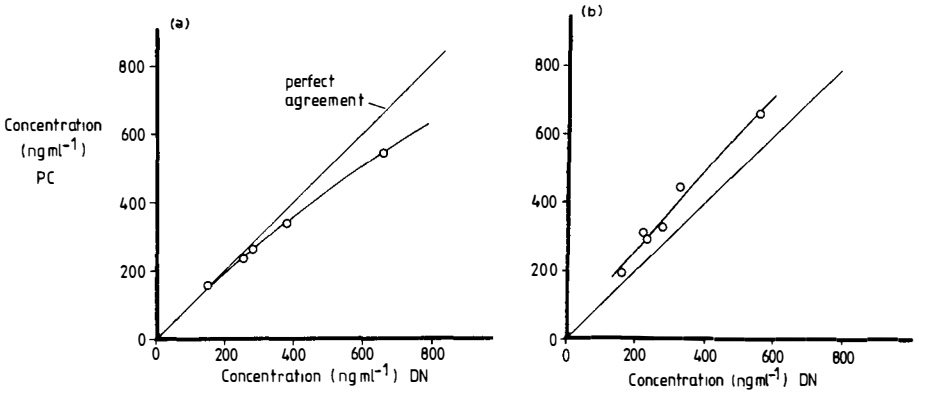

Fig. 5. Comparison of result for lead by direct nebulisation (DN) and preconcentration (PC): (a) raw water samples; (b) samples with standard addition.

inappropriate; the results were then high when the solutions were preconcentrated.

Conclusion

These manifolds enable accurate and precise preconcentration of lead, enabling the detection limits of flame a.a.s. to be reduced by a factor dependent on preconcentration time. Placing the column within the sample loop enables a simple and effective manifold to be constructed without the sample matrix passing into the nebuliser. Manifold 1 is simple and effective but consumes a considerable quantity of acid at the nebulisation flow rate. When a second valve is included (manifold 2), the consumption of acid is reduced. When a third valve is included (manifold 3), other solutions can be injected during a preconcentration. Indeed, if a calibration is generated from the normal injection of standards and the preconcentration factor is evaluated from one preconcentration standard, the system can quickly be calibrated. Each preconcentration of a standard takes a total of 190 s, compared with 7 s for a normal injection. The immobilized reagents used appear to be inselective for lead so that other species can compete for the reagent.

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