

Improving the Design of a Water-cooled Atom Trap to Increase Sensitivity and Precision

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An improvement to the design of the dual-tube water-cooled atom trap is discussed. The shape of the tubes was altered from the flat type to what is described as a 'bent' tube. This enabled more of the tube to be exposed to the light beam compared with the earlier flat design which had an arm of the tube passing through the light beam. A sturdier clamping system is shown which prevented the tubes from bouncing in the beam after collection of the metal and during measurement. Parameters such as the cooling water pressure through the tubes were optimized, as well as the positioning of the tubes with respect to the flame and the light beam (horizontal alignment, or front to back movement parallel to the burner slot). The latter was found to be critical for optimum sensitivity. Figures are presented which show splitting of the signal on the recorder trace resulting from the effects of incorrect alignment. Sensitivities for the improved design were found to be 0.3579 and 2.994 ng ml⁻¹ for cadmium and lead, respectively, an increase in sensitivity over the earlier design, which was 0.8813 and 3.544 ng ml⁻¹, respectively, for cadmium and lead. It is believed that the same increase in sensitivity will be seen with other elements previously examined.

Keywords: Cadmium; lead; dual-tube water-cooled atom trap; flame atomic absorption spectrometry; sensitivity

The single silica-tube atom trap was first investigated by Lau *et al.*¹ and subsequently by Ure and co-workers.²⁻⁷ Hallam and Thompson⁸ and Brown *et al.*⁹, later described the use of the dual silica-tube atom trap for the determination of cadmium and lead levels present in potable waters. Further work by Roberts and Kahokola¹⁰ investigated the optimization of significant parameters using simplex optimization for the operation of the water-cooled atom trap and analytical sensitivities were discussed for 12 elements in river water samples.

The following work is concerned with increasing or improving the analytical sensitivity for the determination of cadmium and lead by investigating parameters such as the horizontal alignment (front to back movement) of the tubes over the flame and the cooling-water pressure. A more reliable and fairly inexpensive automated system is also described. The sensitivities obtained with use of this system coupled with flame atomic absorption spectrometry (AAS) were similar to those obtained by electrothermal AAS.

EXPERIMENTAL

Apparatus

A Philips SP9-800 flame atomic absorption spectrometer was used with a PU9090 data graphics system and a PM8251

linear chart recorder. An electronic box, as described in previous work¹⁰ was used with a modification to the circuit diagram (Fig. 1). This was used to control the passage of cooling water and argon through the silica tubes and the aspiration of the standard solutions. A new electronic relay circuit (Fig. 2) connected the electronic box directly to the PU9090 data graphics system and had the effect of starting peak height integration at exactly the same time as the argon gas was switched on and trapped atoms began to leave the tube surface. A new type of 'bent' dual silica-tube atom trap was designed and built which featured bends and a raised section in each tube (Fig. 3). When clamped in the flame, the raised section was the only part of the atom trap present in the flame cell which could obscure the light beam. The earlier flat design had a silica tube passing across in front of the beam which partially obscured the light. Results obtained from both the flat and 'bent' dual silica-tube atom traps, could then be compared. A more rigid metal clamping system (Fig. 3), was used so that the height of the atom trap could be raised and lowered with respect to the burner. Results obtained using this new clamp were compared with those obtained using the rubber lined clamping system used in previous work.¹⁰ It became apparent that the dimensions of the tubes and space between the tubes was important for reproducible work. The tubes used were 3 mm in diameter with a 1 mm gap between them. It was also important that the parallel tubes were level when placed on a flat surface. A 160 psi Budenberg water pressure gauge was inserted into the water 'in'-line, which enabled control and optimization of the water pressure passing through the silica tubes. Operating conditions were as shown in Table 1. Deuterium lamp background correction was used throughout the work.

Reagents

All stock solutions and acids were supplied by Merck. Dilute solutions were prepared by serial dilution of standards with de-ionized water produced using the Purite CM2 water de-ionizing unit. All standards were prepared in 5% v/v Analar-grade nitric acid.

Silica Tubing

The quartz tubing used throughout this work was supplied by GE Quartz, Cleveland, Ohio, USA. It is known as Type 214 and contains less than 0.1 ppm Cd. An impurity value for lead was not given.

Tube Coating Procedure

Silica tubes were pre-coated by aspirating 5000 ppm solutions of the relevant tube coating material (Al(NO₃)₃·9H₂O or NH₄VO₃) for 5 min *via* the burner nebulizer. During aspiration,

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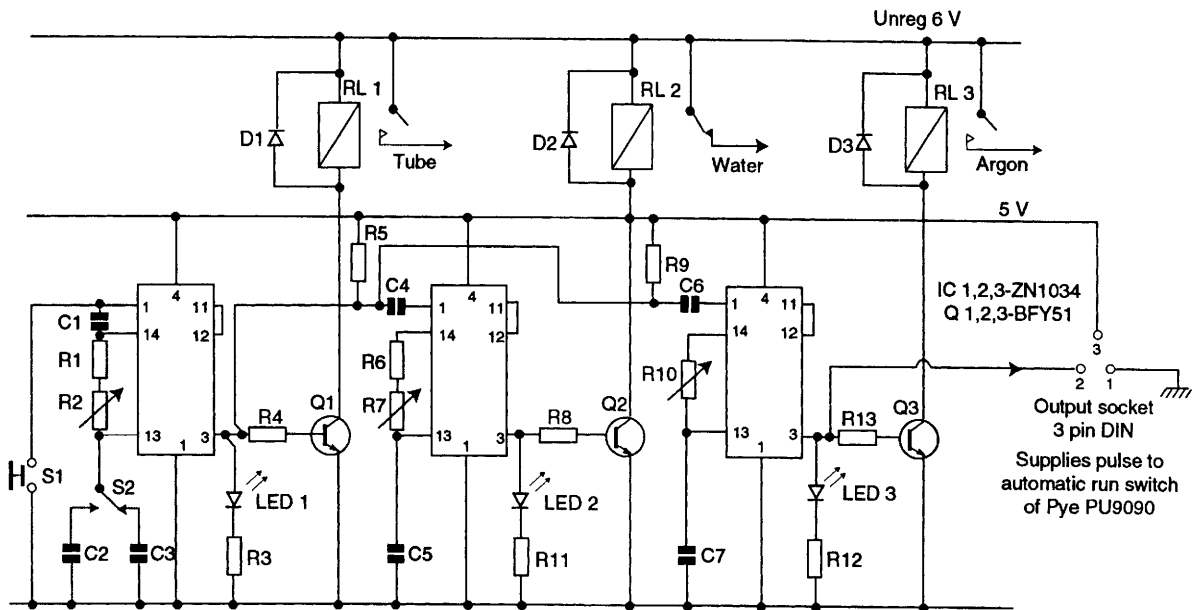


Fig. 1 Modified electronic circuit diagram of the electronic box for the automated atom trapping atomic absorption spectrometry system

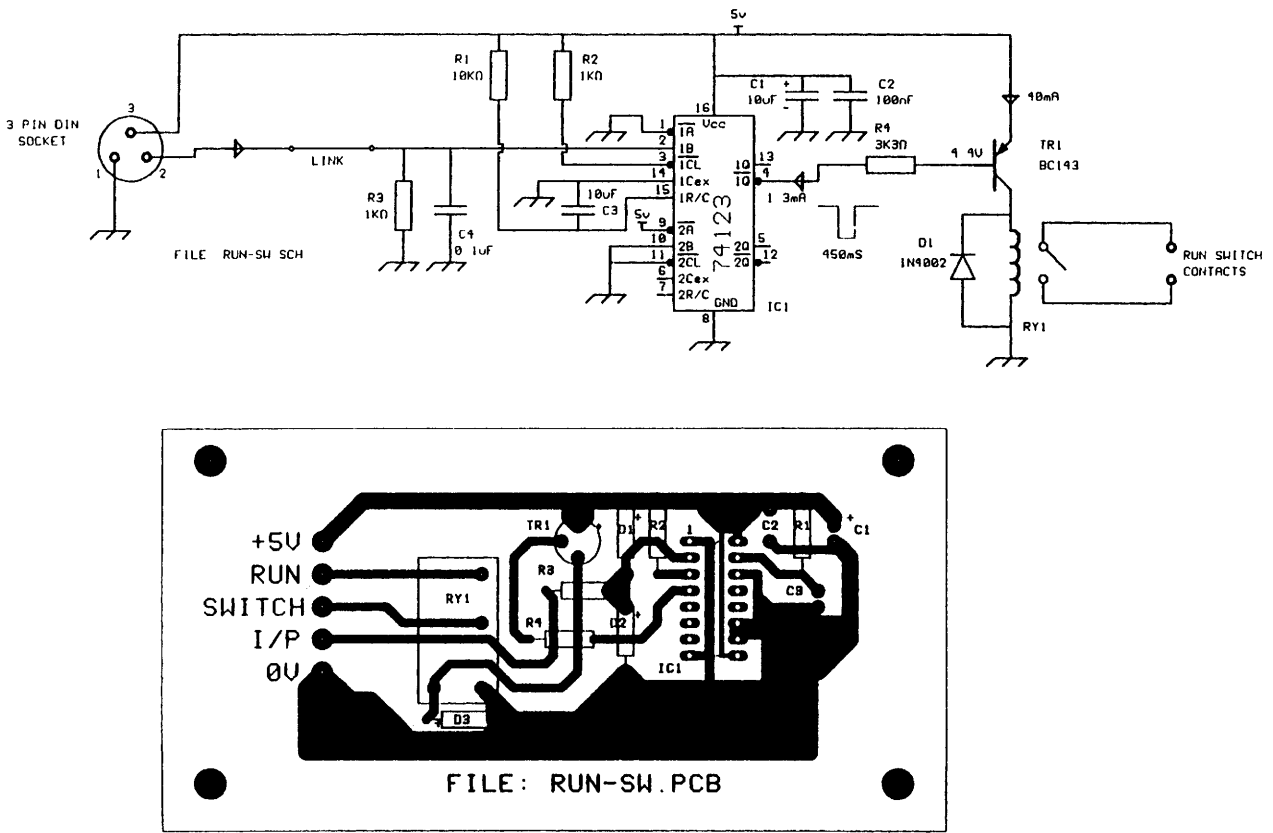


Fig. 2 Automatic (remote) circuit diagram of run switch for Pye Unicam PU9090 computer

Table 1 Operating conditions for the analysis of cadmium and lead

Element	Wavelength/ nm	Spectral bandpass/nm	Lamp current/ mA	Tube coating material
Cadmium	228.8	0.5	4	NH ₄ VO ₃
Lead	217.0	0.5	5	Al(NO ₃) ₃ ·9H ₂ O

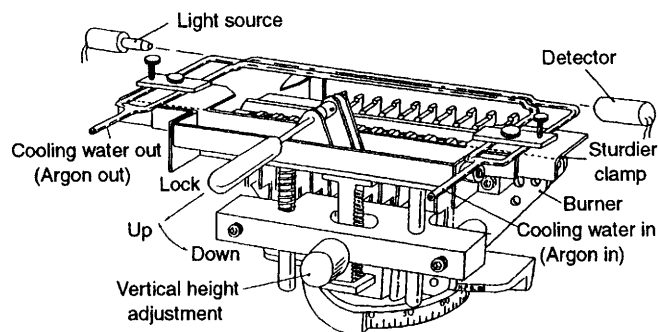


Fig. 3 'Bent' tube water-cooled atom trap with sturdier clamping device

the water-cooled atom trap (WCAT) was present in the flame with cold water passing through the tubes. The tubes were then conditioned by removing the water with argon gas at 40 psi ($1 \text{ psi} \approx 6.894757 \times 10^3 \text{ Pa}$) and allowing the tube to heat up for 20 s in the flame. The tubes were re-coated after approximately 50 runs and checks were made on performance sensitivity using 50 ppb cadmium and 100 ppb lead standard solutions.

Atom Trapping Procedure

Solutions were aspirated *via* the nebulizer/burner into the flame for 2 min. Water flowing through the silica tubes kept the tubes cool, allowing atoms to condense on the surface of the tubes. After collection, argon gas blown through the tubes removed the coolant allowing the tubes to rapidly heat up in the flame. Trapped atoms were then volatilized from the tubes surface, generating a transient atomic absorption signal.

Parameter Optimization

The various parameters optimized for both types of dual-tube atom trap were: (1) height of the silica tubes above the burner (tube height); (2) percentage obscuration of the light beam by the dual silica-tube assembly; (3) flow rate of the fuel; and (4) pressure of coolant water flowing through the silica tubes.

RESULTS AND DISCUSSION

The parameters used for the optimization of the WCAT for the determination of cadmium and lead, are shown in Table 2. In accordance with previous work,¹⁰ tube height above flame, % obscuration of light beam and fuel flow rate were found to be highly significant in order to obtain optimum analytical sensitivity. The measurement and maintenance of water pressure was also found to be highly significant (see Fig. 4). A water pressure of approximately 60 psi was found to give maximum sensitivity and maximum precision. This pressure gave a constant flow rate of 440 ml min^{-1} , the optimum cooling rate to collect atoms. At this flow rate, the water pressure was low enough for the argon gas to quickly and completely evacuate all the water from the silica tubes and at the same time high enough to successfully re-enter and cool the red-hot tube after the atom release. The graph (Fig. 4) shows that any deviation

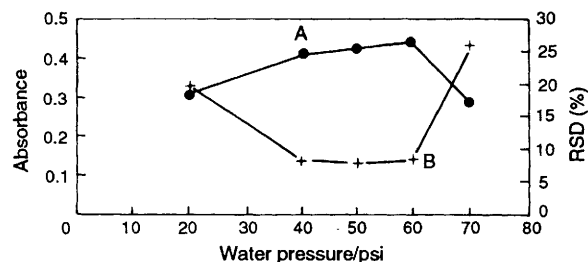


Fig. 4 Effect of water pressure on sensitivity and precision of Cd analysis, where: A, absorbance and B, RSD

from this optimum value results in a very significant drop in sensitivity and a large increase in RSD. Therefore, the installation and use of the standard water pressure gauge was found to have very significant effects on the overall analysis.

Measurements taken using an earlier design with rubber insulators on the clamping system were found to have high levels of random errors, even with the introduction of automation as discussed.¹⁰ These errors, shown by high RSD values, were reduced with the introduction of the new electronic relay and, more importantly, the more rigid metal clamping system. The new metal clamp was seen to hold the silica tubes more rigidly in the flame, so the tube remained in the same position in the flame for each subsequent measurement. The conditions in which trapping and releasing occurred were then much less variable, resulting in much lower RSD values. The absorbance values (peak heights) obtained from ten successive runs using the flat dual-WCAT with the rubber-lined clamp and ten runs using the 'bent' dual-WCAT with the new metal clamping system are presented in Table 3. The higher random errors found in the first instance are thought to be mainly due to movement in the rubber-lined clamp rather than in the atom trap itself. An RSD value of 3.1% obtained in earlier work¹⁰ using the same set-up, indicated that the rubber-lined clamp deteriorated with use. The metal clamp combined with the new 'bent' dual-WCAT resulted in much lower levels of random errors. This is thought to be mainly due to the much sturdier and more rigid design of the new clamp (Fig. 3). The absorbance values obtained from five successive runs for lead using the flat dual-WCAT with rubber-lined clamp and five runs using the bent dual-WCAT with the new clamping system are presented in Table 4. As for cadmium (Table 3) there was an improvement in RSD from 9.37% with the rubber-lined system to 2.0% with the sturdier design. More importantly, an improvement in sensitivity was observed.

Peak Splitting

Typical chart recorder traces obtained by previous workers, have shown the transient signals to be typical Gaussian-shaped peaks. However, in this work, the chart recorder speed was increased to 600 mm h^{-1} and showed the presence of multiple peaks. Experiments were therefore conducted to determine the nature of this peak splitting. The random nature of the peak splitting obtained with use of the old rubber-lined clamping system is shown in Fig. 5. Measurements obtained with the new metal clamp showed less variation during successive runs,

Table 2 Optimized conditions for cadmium and lead analysis using the flat and bent dual silica-tube water-cooled atom traps

Parameter	Flat dual-WCAT		Bent dual-WCAT		Previous work (ref. 10)	
	Cd	Pb	Cd	Pb	Cd	Pb
Tube height/mm	10	8	7	8	8	7
Tube obscuration(%)	50	50	40	50	32	47
Fuel flow/ l min^{-1}	1.0	1.0	1.0	1.0	1.0	1.0

Table 3 Comparison of precision obtained (50.0 ng ml^{-1} of Cd) using the flat dual-WCAT held with the rubber-lined clamping system and the 'bent' dual-WCAT held with the new metal clamp

Run no.	Absorbance (peak height)	
	Flat WCAT/ rubber clamp	'Bent' WCAT/ metal clamp
1	0.241	0.572
2	0.305	0.582
3	0.305	0.583
4	0.284	0.579
5	0.293	0.592
6	0.300	0.591
7	0.276	0.589
8	0.290	0.589
9	0.289	0.570
10	0.265	0.586
Mean	0.285	0.583
Standard deviation	0.0198	0.007689
RSD (%)	6.97	1.32

Table 4 Comparison of precision obtained (100.0 ng ml^{-1} of Pb) using the flat dual-WCAT held with the rubber-lined clamping system and the 'bent' dual-WCAT held with the new metal clamp

Run no.	Absorbance (peak height)	
	Flat WCAT/ rubber clamp	'Bent' WCAT/ metal clamp
1	0.268	0.327
2	0.301	0.314
3	0.253	0.322
4	0.248	0.334
5	0.301	0.324
Mean	0.274	0.324
Standard deviation	0.0255	0.00648
RSD (%)	9.37	2.0

but very definite multiple peaks were still observed. A new parameter of 'horizontal alignment' (HA) was defined, with $\text{HA}=0$ corresponding to the light beam from the hollow cathode lamp running along the exact centre of the atom trap. Adjustment of HA means a fine adjustment of the silica trap by moving the tubes either side of the slot and parallel to the slot. A + sign indicates a movement to the front and a - indicates a movement to the back of the burner slot. Measurements were taken at various settings of HA and were found to give the corresponding peak shapes and absorbance values as shown in Figs. 6 and 7, respectively. Therefore, with an analogue chart recorder running, observed peak splitting was found to indicate a deviation from $\text{HA}=0$ resulting in a drop in analytical sensitivity.

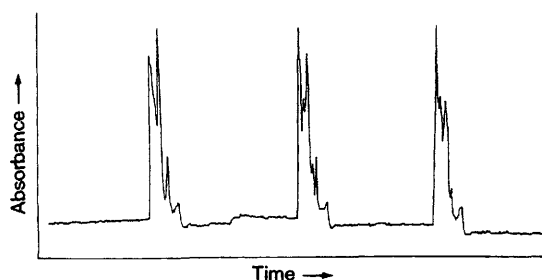


Fig. 5 Changes in peak shape during successive runs using Cd (50 ng ml^{-1}) with 40% tube obscuration

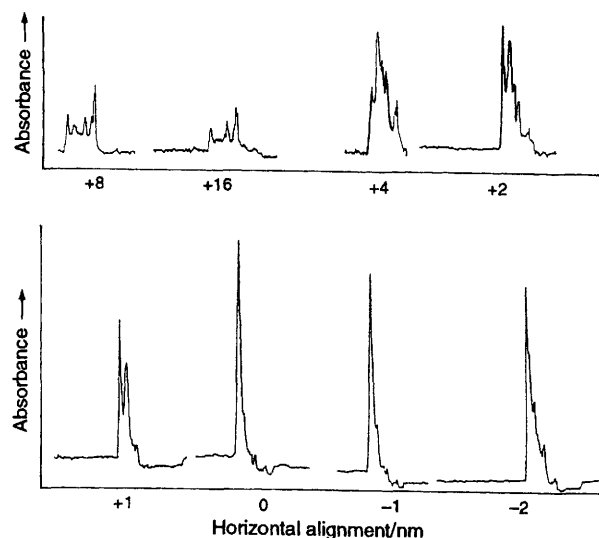


Fig. 6 Effect of horizontal alignment (HA) on peak shape for cadmium standard solution (50 ng ml^{-1}) in 5% nitric acid with 50% tube obscuration at each setting of HA. Tube coated with vanadium. At $\text{HA}=0$, mean absorbance = 0.506. Mean absorbance = 0.007 for an air blank

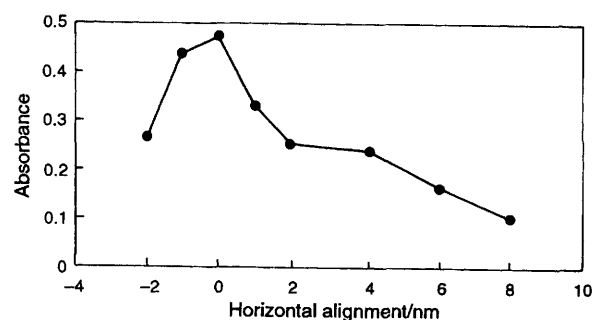


Fig. 7 Optimization of horizontal alignment (HA) for cadmium standard solution (50 ng ml^{-1}) in 5% nitric acid with 50% tube obscuration at each setting of HA. Tube coated with vanadium. At $\text{HA}=0$, mean absorbance = 0.506. Mean absorbance = 0.007 for an air blank

Peak splitting mechanisms

It seems likely that significant peak splitting occurs when the silica tubes are out of alignment with the burner head resulting in uneven release of metal atoms. The different environments in which the two sides of a dual silica-tube atom trap will occupy when this alignment is not central are shown in Fig. 8. The two sides of the WCAT will then be expected to heat up at different rates, the first transient signal therefore coming from the more rapidly heated tube, located in the hotter environment.

It therefore seems apparent that both HA (between atom trap and light beam) and the silica tube–burner head alignment must be centralized in order to achieve even rates of heating and atom release over the whole atom trap. Once the alignment was centralized, large single transient peaks of maximum sensitivity were obtained and a low air blank of 0.007 absorbance units was achieved.

Comparison of sensitivities obtained using 'bent' and flat dual silica-tube atom traps.

The significant parameters of both the flat and 'bent' dual silica-tubes were set to their optimum values and calibration graphs were obtained using cadmium and lead standards prepared in the laboratory. The characteristic concentrations calculated from each linear calibration are presented in Table 5.

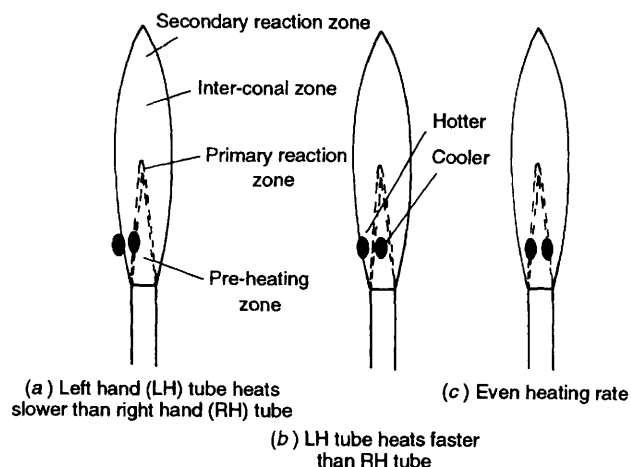


Fig. 8 Flame structure showing various positions of dual silica tube atom trap within the flame

Table 5 Comparison of characteristic concentrations obtained from flat and 'bent' dual-silica tube atom traps

Element	Concentrations/ng ml ⁻¹	
	Flat dual-silica tube	'Bent' dual-silica tube
Cadmium	0.8813	0.3579
Lead	3.544	2.994

It is clear that with use of the new 'bent' model, the overall analytical sensitivity for both cadmium and lead is significantly improved. This is thought to have occurred due to the reduction in the percentage of the light beam obscured by the parts of the atom tube not directly involved in the atom trapping procedure.

REFERENCES

- 1 Lau, C., Held, A., and Stephens, R., *Can. J. Spectrosc.*, 1976, **21**, 100.
- 2 Khalighie, J., Ure, A. M., and West, T. S., *Anal. Chim. Acta*, 1979, **107**, 191.
- 3 Khalighie, J., Ure, A. M., and West, T. S., *Anal. Chim. Acta*, 1980, **117**, 257.
- 4 Khalighie, J., Ure, A. M., and West, T. S., *Anal. Chim. Acta*, 1981, **131**, 27.
- 5 Khalighie, J., Ure, A. M., and West, T. S., *Anal. Chim. Acta*, 1982, **134**, 271.
- 6 Lau, C. M., Ure, A. M., and West, T. S., *Anal. Chim. Acta*, 1982, **141**, 213.
- 7 Lau, C. M., Ure, A. M., and West, T. S., *Anal. Chim. Acta*, 1983, **146**, 171.
- 8 Hallam, C., and Thompson, K. C., *Analyst*, 1985, **110**, 497.
- 9 Brown, A., Roberts, D. J., and Kahokola, K. V., *J. Anal. At. Spectrom.*, 1987, **2**, 201.
- 10 Roberts, D. J., and Kahokola, K. V., *J. Anal. At. Spectrom.*, 1989, **4**, 185.

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