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TRACE GOLD DETERMINATION BY ON-LINE PRECONCENTRATION WITH FLOW INJECTION ATOMIC ABSORPTION SPECTROMETRY

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Summary—A reverse-phase extraction column method has been employed as an on-line preconcentration technique for trace gold analysis by flame atomic absorption spectrometry. Di(methylheptyl)methyl phosphonate (DMHMP) loaded onto a macroporous resin was used as the immobilized phase. A thiourea–HCl solution was found successful in eluting the gold. The experimental parameters were optimized by Simplex Optimization, with 17 tests needed to obtain optimal conditions. Sensitivities of 5.2 μg/l. and 2.3 μg/l., with sample frequencies of 45/hr and 48/hr, were obtained by using single and dual-columns respectively. The recoveries for mixed composition samples were 93–110%.

On-line preconcentration techniques in flow injection, when combined with atomic absorption spectrometry (FI–AAS), have provided a sensitive and rapid method for the analysis of trace elements. In particular, successful trace heavy metal analysis has been performed after either ion exchange or chelating resin concentration.[1–4] Recently, Taylor[5] and Qi[6] presented alternative methods for trace gold analysis, the first by forming supported-liquid membranes, the second by using a fibre column with on-line preconcentration technique. Unfortunately, a troublesome organic solvent had to be used in the former method, while synthesis of the fibre containing the requisite functional group was needed in the latter.

In this study, we have adopted a method of reverse-phase extractive column chromatography for the determination of trace gold by FI–AAS. The extractant, di(methylheptyl)-methyl phosphonate (DMHMP), was loaded onto macroporous resin beads and used as the immobilized phase, with the aim of developing a stable, reusable system.

The introduction of columns into FI–AAS adds to the complexity of the experiments performed, and places a strong onus on optimization to achieve good elemental recovery. A simplex optimization method was applied to the parameters of the system. This method was initially proposed by Spendley[7] and used in analytical chemistry by Long,[8] and Morgan and Deming.[9] Some applications in FIA have also been reported.[10–12] We have developed software to simultaneously control both the calculation of the simplex, and the operation of the flow injection system. Thus, the experimental procedures have been significantly simplified.

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EXPERIMENTAL

Apparatus

The atomic absorption spectrometers used were a GBC 905 Flame Model (GBC Scientific Equipment Pty Ltd, Australia) for the determination of gold and a GBC 900 Graphite Furnace Model (GBC Scientific Equipment Pty Ltd, Australia) for comparison. The gold wavelength was 242.8 nm with a slit width of 0.5 nm. Deuterium background correction was used in gold determination. The flame type was air-acetylene. Two Minipuls pumps (Gilson, France) and an 8-way pneumatic valve (Home made) were controlled by an Intelligent Data Acquisition and Control System (IDACS, Psitek Pty Ltd, South Australia) linked to an IBM computer. The optimum flow rates were 7.7 ml/min in the sampling stage and 5.1 ml/min in the elution stage. A manual 3-way switch was used to select the path of the eluent. Two microcolumns of 4.0 (i.d) × 5.0 (l) mm were linked into the manifold for gold preconcentration.

Reagents

A 1.00 mg/ml gold solution (BDH Chemicals Ltd, Poole England) was used as the stock solution for gold standards. An organic phosphorus di(methylheptyl)methyl phosphonate (analytical grade, Chemicals Ltd, Innermongolia, China) was loaded onto a macroporous resin of 80–100 mesh (PSD X-5 adsorptive resin, Institute of Polymer Chemistry, Nankai University, China). The eluent was a 0.1*M* thiourea–0.1*M* HCl solution.[13]

Preparation of the column

Weighed amounts of DMHMP and macroporous resin were combined in a 1:1 (w/w) ratio by mixing and stirring DMHMP dissolved in CCl_4 with the resin beads, and then drying the beads under an infrared lamp. The resin, coated with DMHMP, was soaked in 1*M* HCl for 24 hr prior to use. A glass tube was used in experiments as a microcolumn. One end of the microcolumn was first blocked with a small piece of plastic foam, and the resin was then introduced onto the column by a glass pipette. Finally the other end of the column was again blocked with foam. Tygon inserts (Gilson, France) were used to hold the foam in place, and to provide a seal for the 0.8-mm teflon capillary tubes. The column length was measured by a ruler.

Regeneration of the column

The gold retained on the column could be eluted completely with a solution of 0.1*M* thiourea–0.1*M* HCl by controlling the elution rate (See text). A microcolumn could be reused hundreds of times with the above regeneration method before performance deteriorated.

Manifold

The manifold is shown in Fig. 1. A computer program was developed to simultaneously control the FIA system and the simplex optimization. Two pumps (P1, P2) were used to carry the solution into the stream. An 8-way valve (V) allows two microcolumns (C1, C2) to be used if required in the experiment. One of the columns can be excluded by use of a 3-way switch (Sw) in the preliminary investigation of the system, and during the application of simplex optimization (See the section enclosed within the broken line). Tygon pump tubes were used (Gilson, France), while all other manifold tubes were 0.8 mm i.d. PTFE (J. R., Sweden). Since the pump tubes used in the sampling stage were much thicker than the PTFE capillary tubes delivering liquid to the column and AAS (the internal diameters were 2.06 mm for pump tubes and 0.8 mm for capillary tubes respectively), the samples were first taken up through capillary tubing, then through the columns, and finally through the pump tubes. This approach also reduces sample consumption and cross-contamination. Reverse-flow elution was also applied to further limit eluent dispersion.

Application of simplex optimization

We programmed the Basic Simplex Method (BSM) proposed by Spendley[7] and the Modified Simplex Method (MSM) proposed by Nelder and Mead.[14] We also merged another program by which the operations of the FIA system were controlled. The basic procedures of both the BSM and the MSM are as follows: (1) Choose the responses (R) and n relative factors (F), which must be continuous variables; (2) Choose the initial coordinate (I), step sizes (S), and the upper and the lower limits (U, L) of each factor;

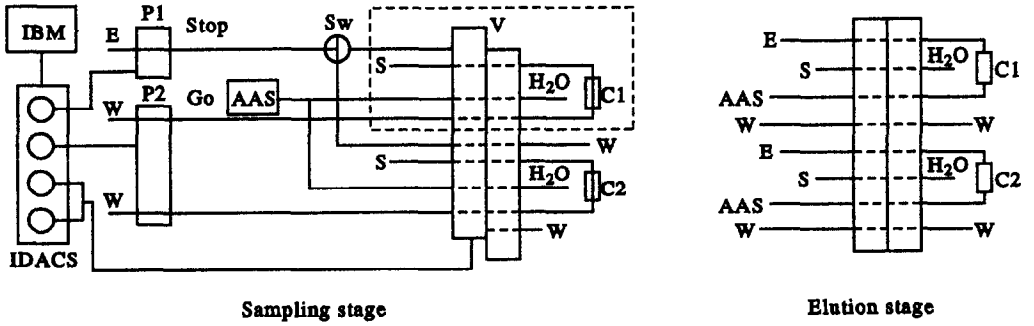

Fig. 1. The manifold design for single- and dual-microcolumn FI-AAS. P1 and P2: Gilson Minipuls Pumps; C1 and C2: Microcolumns; Sw: 3-way switch; V: 8-way rotating valve; S: Sample; E: Eluant; and W: Waste.

(3) Establish an initial simplex with $n+1$ coordinates (X_i) by using Long's coefficient table;[8] (4) Determine the responses under the $n+1$ coordinates; (5) Reject the coordinate X_w for which the response is considered to be worst; (6) Calculate a new coordinate X_r either by equation (1) for the BSM or by equation (2) for the MSM, where G is a coefficient of the expansion or the contraction for the progress of the MSM.

$$X_r = \frac{2}{n}\sum_{\substack{i=1 \\ i\neq w}}^{n+1} X_i - X_r \qquad (1)$$

$$X_r = \frac{1+G}{n}\sum_{\substack{i=1 \\ i\neq w}}^{n+1} X_i - GX_w \qquad (2)$$

We chose $G = 2$ in the simplex expansion when the new response was the best one, $G = 0.5$ in the contraction when the new response was better than the worst but worse than the others, and $G = -0.5$ in the inter contraction when the new response was even worse than the worst one. (7) The calculations continue until the deviation of the best response (R_b), and the worst response (R_w), is smaller than a convergence coefficient E. The value of E is arbitrarily chosen as required by each system. E is then related to R_b and R_w by equation 3:

$$\left|\frac{R_b - R_w}{R_b}\right| < E \qquad (3)$$

The area defined by the last simplex is the area where the optimum response can be expected. (8) When a new coordinate is calculated, which is beyond the upper or the lower boundary limits, the program will force it to equal the boundary value.

RESULTS AND DISCUSSION

Preliminary study of the system performance

The performance of the system and the parameters required for AAS detection were preliminarily investigated with the single-column. The loading capacity of the column was first determined to be 23 mg Au/g DMHMP. Less than 10 mg of DMHMP was needed, and organic solvent was only involved in the column preparation. The column could be regenerated by elution with $0.1M$ thiourea–$0.1M$ HCl, which has been found to be efficient in previous research,[13] and reused for several hundred tests before the performance deteriorated. There is a linear relationship between absorbance and sample time when the latter is less than 3 min for a Au solution of 1.0 mg/ml. In this system a faster sample flow rate leads to an improved sensitivity. In some ion exchange methods for heavy metals, decreased flow rates are often needed, due to the influence of coexisting ions.[15] Obviously, DMHMP possesses excellent selectivity, and very fast reaction speed for gold.

Four size ranges of the resin, 80–100, 100–120, 120–140 and 140–160 mesh, were tested. Good absorbance could be obtained using larger resin particle size due to the relative low flow resistance in the system which allowed more gold to pass through the column. The effect of column dimension on the sensitivity was also studied by comparing the performance of a longer column (40 mm) and a shorter column (5 mm). The flow resistance was again an important factor in deciding the sensitivity. A shorter column seemed to be beneficial to the analysis. Further investigations on the system parameters were carried out by simplex optimization methods, column length being included.

Simplex optimization

Both the BSM and the MSM were applied in this study. We chose the peak height of atomic absorption as the response. The four selected relative factors were the column length (F1), the pump rate in the sample stage (F2), the pump rate in the elution stage (F3), and the aspiration rate of the AAS (F4). Generally, the flow rate of a system is selected as a parameter in FIA systems. Since a microcolumn was introduced into the manifold in this study, it is relatively hard to control flow rate, or to use it as a factor in the simplex optimization method. We have thus selected the pump rate as our preferred factor, despite the arbitrary units employed. Janse *et al.*[11] used the % maximum pump rate in their phosphate study for a similar reason. Some representative flow rates are, however, listed in the Table 1 for reference. The upper and lower limits (U, L), the step sizes (S), and the initial coordinates of each factor (I), and the convergence coefficients E are also listed in Table 1.

The optimization processes are shown in Fig. 2. It can be seen that the larger step sizes of the MSM are more favourable for optimization progress (17 tests needed), than the smaller step sizes of the BSM (23 tests needed). This is because an expansion of the simplex in the area far away from the optimum and a

Table 1. Parameters of the simplex optimization

	Factors	*U*	*L*	*S*	*I*	*E*
	F1*	40	5.0	10.0	15.0	
BSM	F2†	1000	200	200	850	
	F3†	1000	200	300	700	0.08
	F4*	9.0	3.0	1.5	5.0	
	(SFR‡	7.7	1.3	—	6.0)	
	(EFR‡	7.7	1.3	—	4.8)	
	F1*	40	5.0	20.0	20.0	
	F2†	1000	200	400	500	
MSM	F3†	1000	200	500	500	0.08
	F4*	9.0	3.0	3.0	3.5	
	(SFR‡	7.7	1.3	—	3.3)	
	(EFR‡	7.7	1.3	—	3.3)	

*The units of F1 and F4 are mm and ml/min respectively.
†The pump rate (given in arbitrary units, 100–1000, as designated by the manufacturer).
‡SFR: sample flow rate (ml/min); EFR: elution flow rate (ml/min).

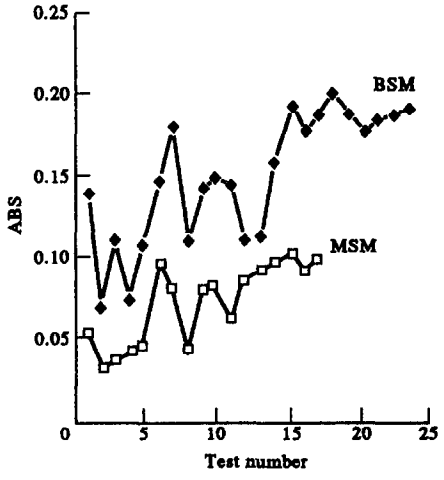

Fig. 2. Mean absorbance during the optimization. For discussion of BSM and SMS, see text. Au solution: BSM: 1.0 mg/l; MSM: 0.5 mg/l.

contraction of the simplex in the area close to the optimum have been taken into account in the MSM. The use of larger step sizes is, therefore, able to accelerate the optimization process without missing the optimum. It should be mentioned that the optimization condition obtained is an area rather than an exact value. This area is defined by the last simplex. The optimal areas obtained by both the BSM and the MSM are listed in Table 2, and checks of the optimal conditions by the conventional methods are shown in Fig. 3. The optimization procedure was obviously simplified, with only seventeen tests required by the MSM.

Retention efficiency and interference

Retention efficiency (%*E*) was determined at the different sample flow rates. %*E* is high for gold if the sample flow rate is not higher than 12 ml/min (Fig. 4).

Interference was generally small for the following cations, K^+, Na^+, Ni^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+} and Cr^{3+}, with Au recoveries being above 95% except in the case of Al^{3+} where it was 91%. Cation to gold ratios were in the range 200–1000. A small decrease in the recovery of the gold was, however, found in a nitrate–chloride solution compared with that in a sulphate–chloride solution. An effect due to anions was observed (Fig. 5). The monovalent anions followed the sequence, $H_3C.COO^- > NO_3^- > Cl^-$. This probably results from the competitive extraction of the larger anions with the $AuCl_4^-$. SO_4^{2-} is not easily associated with a monovalent protonated DMHMP.

Table 2. The optimal areas obtained by BSM and MSM

Methods	Column length (*mm*)	Pump rate* (sample)	Pump rate* (elution)	Aspiration rate of AAS (*ml/min*)
BSM	5.0–6.5	935–1000 (SFR: 7.0–7.7)†	450–700 (EFR: 3.2–5.1)†	5.0–7.0
MSM	5.0	835–1000 (SFR: 6.2–7.7)†	835–1000 (EFR: 6.2–7.7)†	4.0–7.0

*Same as in Table 1.
†SFR: Sample flow rate (ml/min); EFR: elution flow rate (ml/min).

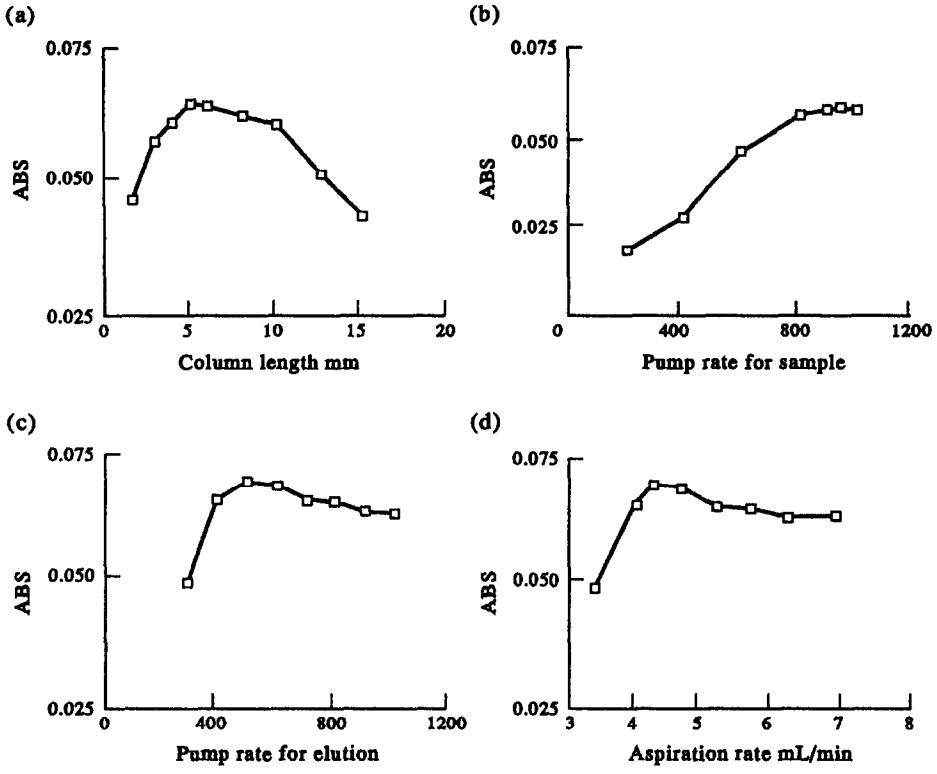

Fig. 3. Checks on optimal conditions obtained by simplex optimization. The selected parameter is altered, the others being maintained at their optimum values. Au solution is 0.35 mg/l.

A dual-column system

Two-fold improvement in either sensitivity or sample frequency was achieved using a dual-column system. However, a slight reduction in the peak height from the second column was observed due to the longer residence time of the gold on this column. Fortunately, this difference could be eliminated by restricting the elution time for the first eluted column to no longer than 10 sec. The final replicates are shown in Fig. 6.

Comparison of the sensitivity

Table 3 shows a comparison of the sensitivities, the precisions, the concentration factors

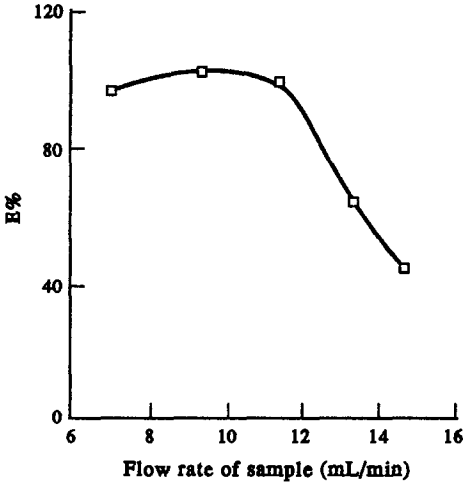

Fig. 4. Effects of the sample flow rate on the retention efficiency. The sample flow rate was controlled by changing the column length. The concentration of gold was 1 mg/l. All the other parameters were optimal.

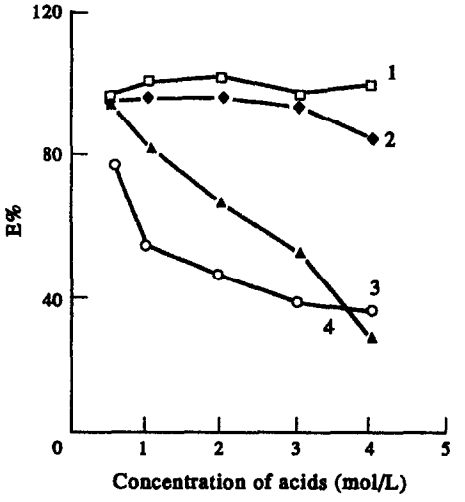

Fig. 5. Effects of acid anions on the retention efficiencies of gold. 1 mg/l Au solution. 1. HCl; 2. H_2SO_4; 3. HNO_3; and 4. H_3CCOOH.

Table 3. Comparison of the sensitivities, the precisions and the concentration factors observed using conventional AAS and on-line preconcentration methods

Parameters	Flame AAS Std.*	GF AAS Std.†	GF AAS Mix.‡	On-line preconc. AAS (S–C) Std.†	On-line preconc. AAS (S–C) Mix.†	On-line preconc. AAS (D–C) Std.†
Sensitivities (μg/l/1%A)	170	1.8	10.6	5.2	5.0	2.3
RSD (%)	—	2.8	3.0	3.1	3.8	4.2
Concentration factors	—	—		33		74
Sample frequency (s/hr)	—	—		45		48

*200 μg Au/l solution; †20 μg Au/l solution; ‡125 μg Au/l solution; Sample time: 60 sec; Sample volume in the GFAAS: 10 μl; S–C: single column; D–C: dual-column. All the other parameters are optimal (See Table 2).

Table 4. Recoveries of gold from the mixed composition samples

Sample No.	Anions added	Gold added ($\mu g/l$)	Gold detected ($\mu g/l$)	Recovery (%)
1	Chloride-sulphate	20.0	22.0 ± 0.7	110 ± 3
2	Chloride-sulphate	50.0	52.3 ± 1.2	104 ± 2
3	Chloride-nitrate	20.0	18.5 ± 0.5	92 ± 2

and the sample frequencies produced by different methods. A 33-fold or 74-fold improvement in sensitivity has been achieved over the conventional AAS methods with either the single-column or the dual-column system.

Sample analysis

The gold content was determined in mixed composition samples of K^+, Na^+, Ni^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, Cr^{3+}, and Al^{3+} with metal to gold ratios of 1000 or more (Table 4). Recoveries obtained were 93–110% for known amounts of gold added.

CONCLUSION

The use of reverse-phase extractive columns in on-line preconcentration is particularly suited to systems where both extractants and eluents possess good performance. Compared to earlier methods, column preparation was simple, and faster reaction speed and lower interference were observed. Advantages over other methods of sorbent extraction[16] include freedom from organic solvents, and a lower consumption of the extractant, especially useful with expensive compounds.

Use of the simplex optimization method significantly simplified the experimental procedure. The Modified Simplex Method with larger step sizes was found to be efficient in the present study.

A 33-fold or 74-fold improvement in the sensitivity has been achieved by either the single-column or the dual-column system with the sample frequency of 45 hr or 48 hr. Recoveries of gold analytically were found satisfactory.

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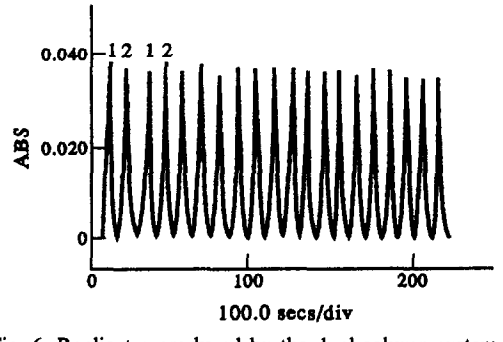

Fig. 6. Replicates produced by the dual-column system. 1. Peaks produced by C1; 2. Peaks produced by C2. Au solution is 20 μg/l; sample time is 30s; and RSD% obtained is 4.2%.

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