# Graphite furnace atomic absorption spectrometric determination of some noble metals using flow injection on-line clean-up

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In this paper, a flow injection on-line clean-up system was developed for determination of trace Pt, Pd and Au in the presence of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> by electrothermal atomic absorption spectrometry (ETAAS). A column packed with strongly acidic cation-exchange resin (Type 732) was used as a clean-up column. As  $Pt^{2+}$ ,  $Pd^{2+}$  and  $Au^{3+}$  can form strong complex anions with  $Cl^-$  in HCl medium, they can be separated from coexisting cations by passing through the clean-up column. The experimental results obtained for trace amounts of gold in reference materials were in good agreement with the certified values.

Electrothermal atomic absorption spectrometry (ETAAS) is one of the most sensitive techniques for determination of trace elements. Although ETAAS has very low detection limits for a large number of elements, the direct determination of trace amounts of elements in complicated matrices is usually difficult due to interferences and/or insufficient detection power.<sup>1</sup> Thus, separation of analytes from the matrix is undoubtedly effective in avoiding matrix interferences.

Flow injection (FI) provides a flexible approach to the elimination of interferences caused by the concomitant elements.<sup>2–6</sup> In general, strong acidic cation- and basic anion-exchange resins are less used in on-line preconcentration because of their poor selectivity. However, these resins can be used to adsorb interference ions with the opposite charge to the tested ions, and allow the analyte to pass through freely. This procedure is often termed "on-line clean-up" of the sample. Kamson and Townshend<sup>7</sup> and Marshall and Van Staden<sup>8</sup> used this technique to eliminate the matrix effects in the determination of calcium and selenium, and arsenic, respectively. Liang *et al.*<sup>9</sup> used this technique to eliminate some concomitant cations in the determination of silicon.

 $Pt^{2+}$ ,  $Pd^{2+}$  and  $Au^{3+}$  can form strong complex anions with  $Cl^{-}$  in solution, and the stability constants of these complexes are all very high.<sup>10</sup> This ability has been widely used for concentrating these noble metal complex anions with an anion-exchange resin.<sup>11</sup> However, the elution of these complexes is usually very difficult. In this study, this ability was used not for concentration, but for passing noble metals through the cation-exchange resin in order to separate them from coexisting cations.

In the present work, a new FI on-line clean-up procedure was developed for ETAAS for the determination of trace platinum, palladium and gold in the presence of alkali metals, alkaline earth metals, iron and aluminum. A strong cation-exchange resin column was used as the clean-up column. The concomitant cations are exchanged and adsorbed on the cation resin, the analytes (Pt, Pd and Au), which can form complex anions with  $Cl^-$  in HCl medium, are passed through the clean-up column, and then introduced into the graphite furnace atomizer for determination. The feasibility and accuracy of the proposed method were demonstrated by the determination of Au in two kinds of certified ore reference samples.

## Experimental

### Instrumentation

A Hitachi Model 180-50 atomic absorption spectrometer equipped with a Hitachi GA-3 graphite furnace atomizer was used throughout this work. Deuterium arc background correction and pyrolytic graphite-coated graphite tubes were used for all experiments. Argon (99.99%) was used as the purge gas at a flow rate of 150 ml min<sup>-1</sup>. Integrated absorbance was used for evaluating the results. An FI clean-up system containing an LZ-1010 peristaltic pump and an LZ-1010 multifunctional valve (Shenyang Zhaofa Institute of Automatic Analysis) was used. The injection volume was 40  $\mu$ l, and the ion-exchange column was made of glass of 2 mm id and 25 mm length. Both ends of the column were plugged with poly-urethane plastic foam as end caps.<sup>12</sup> A newly packed column should be washed with deionized water to condition the column and to remove trace amounts of analyte from the ion-exchange material and the plastic foam. Small bore (0.35 mm id) PTFE tubing was used for all connections.

## **Reagents and samples**

All chemical reagents were at least of analytical-reagent grade. Doubly deionized water was used throughout. The resin used in this study was a strongly acidic cation-exchange resin (Type 732, produced in China) with sulfonic acid groups as functional groups (particle size 16–50 mesh). Before using, the resin was washed with water and immersed in 2 mol  $1^{-1}$  HCl overnight to connvert it into the H<sup>+</sup> form. When used, the resin was washed with deionized water until the eluant was neutral. The standard stock solutions of Pd, Pt and Au (1 mg ml<sup>-1</sup>) were prepared using standard methods. The standard working solutions were prepared daily by stepwise dilution of standard stock solutions with HCl (0.2% v/v). The geological certified ore reference materials used in this work were MG<sub>1</sub>-Au-01 (obtained from Geological Research Institute of Beijing) and J<sub>Au-2</sub> (obtained from the Bureau of Geological Minerals of Jilin province).

#### Sample digestion

Certified ore samples (0.1 g) were first heated in a porcelain crucible at  $650 \,^{\circ}$ C in a muffle furnace for 2 h.<sup>13</sup> Then the

J. Anal. At. Spectrom., 2001, 16, 1341–1343 1341

JAAS www.rsc.org/jaas crucible was taken out and cooled down to room temperature. The sample was transferred into a beaker with about 12 ml HCl (36% v/v) and 4 ml HNO<sub>3</sub> (65% v/v), and boiled for about 1 h with regular stirring until the sample was completely decomposed. The dissolved sample was then filtered and the residue was washed with doubly deionized water, transferred into a volumetric flask and diluted to the mark with deionized water.

#### Procedure

The schematic diagram of the FI on-line clean-up system is shown in Fig. 1(a) and (b). In step 1 [Fig. 1(a)], the pump was active and the valve was in the filling position. The sample was hoisted by the pump and filled the 40  $\mu$ l sample loop. In step 2 [Fig. 1(b)], the valve was turned to the injection position while the pump was still active. The air pushed the sample through the cation-exchange resin column to remove most of the cations and the analytes passed into the graphite tube for determination.

In this study, the weight of the resin used was about 0.15 g. Due to the small exchange capacity of the resin, it is necessary to regenerate the column about every 1–2 hours. This can easily be done by washing the resin 3–5 times with 3 mol  $L^{-1}$  HCl for the on-line clean-up procedure, and then 2–3 times with deionized water.

## **Results and discussion**

#### Effect of sample solution acidity

Using the traditional sampling mode a phenomenon was observed; the interference caused by potassium was quite significant when determining Pt, Pd and Au.

In order to study the effect of sample solution acidity, an amount of K<sup>+</sup> that could cause interference was added to the solution of an analyte, and the analyte standard solutions were prepared with hydrochloric acid of different concentrations. Fig. 2 shows the effect of acidity of the sample solution on the relative absorbances. It can be seen that when the HCl concentration is low,  $Pt^{2+}$  (50 µg 1<sup>-1</sup>),  $Pd^{2+}$  (80 µg 1<sup>-1</sup>) and  $Au^{3+}$  (10 µg 1<sup>-1</sup>) cannot efficiently form complex anions with  $Cl^-$ . They are exchanged and adsorbed on the cation resin, so the relative absorbance is very small. When the HCl concentration is in the range of 0.02–0.6 mol 1<sup>-1</sup>, the relative absorbances of the test elements approach 1.0 (compared to the



**Fig. 1** Schematic diagram of the FI on-line clean-up system: (a) filling position and (b) injecting position.



**Fig. 2** The effect of acidity of sample solution on the relative absorbance of Au, Pt and Pd. Conditions: Pt, 265.9 nm,  $50 \ \mu g \ l^{-1}$  with 75 mg  $l^{-1}$  K; Pd, 247.6 nm,  $80 \ \mu g \ l^{-1}$  with 120 mg  $l^{-1}$  K; Au, 242.8 nm,  $10 \ \mu g \ l^{-1}$  with 15 mg  $l^{-1}$  K; sample loading flow rate,  $1.5 \ ml \ min^{-1}$ .

value without K). In other words, the interference caused by  $K^+$  is almost completely eliminated with the on-line clean-up technique. With lower acidity, the H<sup>+</sup> in the resin can be easily replaced by the interfering cation K<sup>+</sup>. With higher acidity, the K<sup>+</sup> exchange efficiency becomes poorer because the concentration of H<sup>+</sup> is much higher than that of the interfering cation to be separated, and thus the partition ratio of the interfering cation between the sample solution and resin is lowered. To prevent hydrolysis of some concomitant cations (such as Fe and Al), 0.05 mol l<sup>-1</sup> HCl was chosen as the separation medium.

#### Effect of sample flow rate

In order to study the effect of sample flow rate on the relative absorbance, an amount of  $K^+$  that interferes under conditions without a clean-up column was added into the solution of an analyte. The results are shown in Fig. 3. It can be seen that the relative absorbances are almost all over 0.95 at lower flow rates. When the flow rate is higher than 2.5 ml min<sup>-1</sup>, the cation-exchange efficiency becomes poor. Obviously, a higher flow rate causes incomplete exchange between the sample and the resin. In this study, a sample flow rate of 1.5 ml min<sup>-1</sup> was selected for Pt, Pd and Au determination.



**Fig. 3** The effect of sample flow rate on the relative absorbance of Au, Pt and Pd. Conditions: Pt, 265.9 nm,  $50 \ \mu g \ l^{-1}$  with 75 mg  $l^{-1}$  K; Pd, 247.6 nm,  $80 \ \mu g \ l^{-1}$  with 120 mg  $l^{-1}$  K; Au, 242.8 nm,  $10 \ \mu g \ l^{-1}$  with 15 mg  $l^{-1}$  K; acidity of sample solution, 0.05 mol  $l^{-1}$ .

**Table 1** Effect of concomitant ions on the recoveries of Au, Pt and Pd; relative absorbances of Au, Pt and Pd taking the value without concomitant ions as 100

	Concomitant ion	Concentration/ mg l <sup>-1</sup>	Relative absorbance	
Element			Traditional sampling	On-line cleaning-up
Au	None	0	100	100
	Na	15	79	105
	Κ	15	58	96
	Ca	15	74	102
	Mg	15	84	93
	Fe	15	70	92
	Al	15	84	103
Pt	None	0	100	100
	Na	75	59	107
	K	75	53	96
	Ca	75	69	101
	Mg	75	70	95
	Fe	75	61	94
	Al	75	72	95
Pd	None	0	100	100
	Na	120	76	99
	Κ	120	60	94
	Ca	120	67	101
	Mg	120	75	92
	Fe	120	65	94
	Al	120	81	93

#### Interferences caused by concomitants

As the main matrix elements in natural samples are usually alkali metals, alkaline earth metals, iron and aluminum, the effects caused by these elements on the recoveries of Pt, Pd and Au were investigated in detail.

The on-line clean-up technique was compared with the traditional sampling mode, whereby the sample is introduced into the graphite furnace atomizer directly. Interferences from co-existing ions were evaluated under two operational conditions and the results are listed in Table 1. It is obvious that, by using the on-line clean-up procedure, the determination of Pt, Pd and Au is almost free from interference of the most common matrix constituents.

#### Analytical performance of the FI on-line clean-up system

The analytical performance of the FI on-line clean-up procedure proposed for the determination of Pt, Pd and Au by ETAAS is summarized in Table 2. With the injection of 40  $\mu$ l of sample solution, the characteristic concentrations were 2.7, 1.8 and 0.5  $\mu$ g l<sup>-1</sup> and the detection limits (3*s*, *n*=10) were 2.5, 1.4 and 0.4  $\mu$ g l<sup>-1</sup> for Pt, Pd and Au, respectively.

#### Analysis of certified reference samples

The accuracy of the developed method was checked by the determination of Au in two kinds of certified ore samples. The

 
 Table 2
 The analytical performance of FI on-line clean-up ETAAS for the determination of Pt, Pd and Au

Element	Characteristic concentration/µg l <sup>-1</sup>	Detection limit/µg l <sup>-1</sup>	RSD (%, <i>n</i> =6)
Pt	2.7	2.5	3.5
Pd	1.6	1.4	3.8
Au	0.5	0.4	3.3

 Table 3 Analytical results of Au in certified reference materials

 obtained by using FI on-line clean-up procedure

Sample	Certified/g t <sup>-1</sup>	Determined/g $t^{-1}$	RSD (%, $n = 5$ )
MG <sub>1</sub> -Au-01	3.59	3.48	3.8
J <sub>Au-2</sub>	4.40	4.27	3.2

analytical results are listed in Table 3. The results show that, for the two certified samples investigated, the Au concentrations determined with the proposed method are in good agreement with the certified values.

## Conclusion

The results presented in this work demonstrate the feasibility of selective determination of trace Pt, Pd and Au by ETAAS using the FI on-line clean-up procedure. This technique offers a novel and attractive method, in which the tested ions can form complex anions in an acidic medium, and most of the coexisting ions exist in the form of cations.

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