

# ETAAS Determination of Palladium in Tunnel Dust after Flow Injection Separation and Preconcentration Using a Cyclic Polyether

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Received: August 24, 2004

Accepted (in revised form): September 29, 2004

## Résumé

Une méthode d'injection en flux continu en ligne fut développée pour la préconcentration et la détermination du palladium. La spectrométrie d'absorption atomique électro-thermique (ETAAS) fut employée à la détection du Pd élué. La préconcentration et la séparation du palladium de la matrice furent faites au moyen de polyéther cyclique hexaoxacyclooctadecane-1,4,7,10,13,16 (18-crown-6). Le  $\text{Pd}(\text{SCN})_4^{2-}$  chargé négativement formé dans la solution de l'échantillon réagit avec le  $\text{K}^+ \cdot 18\text{-crown-6}$  chargé positivement qui fut préalablement immobilisé sur les parois internes du réacteur noué. Le rôle du KSCN dans le processus de préconcentration est discuté. Un facteur d'augmentation de 29 et une fréquence d'échantillonnage de  $14 \text{ h}^{-1}$  furent obtenus pour un temps de préconcentration de 90 s et un débit d'échantillonnage de  $4.4 \text{ mL min}^{-1}$ . La limite de détection (3s) était  $16 \text{ ng L}^{-1}$  et la précision (RSD) pour  $0.4 \mu\text{g L}^{-1}$  Pd était 2.3 %. La concentration du Pd dans un échantillon de poussière de tunnel était  $58 \pm 3 \text{ ng g}^{-1}$  telle que déterminée par la présente méthode.

## Abstract

An on-line flow injection method for palladium preconcentration and separation from dust matrix was

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developed. ETAAS was used for the detection of Pd in the eluate. The preconcentration and separation of palladium from the matrix were performed by means of the cyclic polyether 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). The negatively charged  $\text{Pd}(\text{SCN})_4^{2-}$  formed in the sample solution reacted with the positively charged  $\text{K}^+ \cdot 18\text{-crown-6}$  previously immobilized onto the inner walls of the knotted reactor. The role of KSCN in the preconcentration process was discussed. An enhancement factor of 29 and a sampling frequency of  $14 \text{ h}^{-1}$  were obtained for a preconcentration time of 90 s and a sampling flow rate of  $4.4 \text{ mL min}^{-1}$ . The detection limit (3s) was  $16 \text{ ng L}^{-1}$ , and the precision (RSD) for  $0.4 \mu\text{g L}^{-1}$  Pd was 2.3 %. The concentration of Pd in a tunnel dust sample determined by the present method was  $58 \pm 3 \text{ ng g}^{-1}$ .

**Keywords:** Palladium, preconcentration, crown ether, ETAAS, tunnel dust.

## Introduction

A large amount of research has been conducted on the determination of traces of palladium in a variety of sample types. Pd is used in jewelry, dentistry applications, fine instruments, such as watches and some surgical tools, for electrical contacts and for the purification of hydrogen gas (1). However, the largest application of palladium is in the catalytic field. The extensive use of Pd in automotive catalytic converters and in chemical industry has led to increasing concentrations of this metal in the

environment. The accumulation of Pd has already been detected in road dust (2-4), airborne particulate matter (4-6), car exhaust fumes (7), plants (2) and urban water (8), and it correlates with traffic density and distance from the road. The effect of environmental concentrations of Pd on humans is still unknown, but hypersensitivity and allergic reactions have been observed in susceptible individuals following chronic occupational exposures (9). Thus the determination of this pollutant in environmental matrices is of considerable importance for human exposure assessment and for the investigation of correlations with health effects.

Currently, cisplatin is mainly used as an anticancer agent for several human cancers. Side effects, especially nephrotoxicity, of this drug limit its use in high dose (10). The need to develop new complexes with reduced nephrotoxicity and higher activity has stimulated the synthesis of many new complexes. As such, complexes of Pd with amino acids (10,11) and peptides (11) have been synthesized and studied as alternative anticancer drugs. Some of these complexes displayed antitumor properties against some human lymphocytic leukaemia cells (10), showing activity similar to cisplatin.

In the determination of trace or ultra-trace amounts of Pd in environmental and pharmaceutical samples, a preconcentration/separation procedure is required even when relying on the high sensitivity and selectivity of modern instrumental techniques, such as electrothermal atomic absorption spectrometry (ETAAS) (5,6), inductively coupled plasma atomic emission spectrometry (ICP-AES) (3) and inductively coupled plasma mass spectrometry (ICP-MS) (2,4,7,8), because of their very complex sample matrices. Conventional off-line procedures for preconcentration and separation, although effective, are usually tedious and time-consuming, require large quantities of sample and reagents, and are vulnerable to contamination and losses of analyte. Flow injection techniques have played an important role in the automation, acceleration and miniaturization of solution handling in sample pretreatment. Several on-line preconcentration and separation methods, such as ion exchange (3) and sorption (6,8) have been adopted for the flow injection analysis of palladium.

Cyclic polyethers, better known as crown ethers, have drawn much interest since their synthesis in 1967 by Pedersen (12). Crown ethers are a unique class of compounds with a hydrophilic interior and lipophilic exterior capable of metal ion transport across non-aqueous

barriers, but they require the co-extraction of an anion to maintain electroneutrality (13). Due to their selective complexation of alkali metal ions, crown ethers have been widely utilized for the separation of these species (14). The stability of the alkali metal complex with the crown ether is a function of the correspondence between the ionic radius of the metal and the radius of the crown ether cavity. The stability of the alkali metal complexes with 18-crown-6 increases in parallel with the increase in the ionic radius of the metal, exhibits a maximum at potassium and then decreases (15). Crown ethers are also used for preconcentration/separation of many other metal ions by ion-pair formation followed by liquid-liquid extraction (13,14) or micro-column sorption (16). Formation of an ion-pair between palladium and dicyclohexyl-18-crown-6 has been reported by Hossain and Honjo (13) for the liquid-liquid extraction separation/preconcentration of palladium. The method is, however, time consuming, requires large quantities of reagents and involves sample manipulations that predispose it to contamination and losses.

In the present work, crown ether was used for on-line preconcentration and separation of palladium from the tunnel dust matrix with a view to its subsequent determination by ETAAS. The method is based on the on-line formation of an ion-pair between the palladium thiocyanate anion and the cationic potassium complex of 18-crown-6. The accuracy and selectivity of the method were demonstrated by recovery measurements of spiked road dust samples. The method was applied to the determination of palladium in tunnel dust.

## Experimental

### Instrumentation

The ETAAS measurements were performed on the Perkin Elmer (Norwalk, CT, USA) model AAnalyst 300 atomic absorption spectrometer equipped with a deuterium background corrector and a HGA-800 graphite furnace and were computer-controlled using the AAWinlab software, version 2.61. A palladium hollow cathode lamp (Z-tek, Amsterdam, The Netherlands) was used as a light source at 247.6 nm with a spectral bandpass of 0.20 nm. Pyrolytic graphite-coated standard tubes (Z-tek) were employed. The graphite furnace temperature/time program used for Pd determination in the eluate is summarized in Table 1. The integrated absorbance ( $A_{int}$ ) values obtained with an integration time

Table 1. Graphite furnace temperature/time program for the determination of Pd in the eluate after FI on-line sorption preconcentration

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (mL min <sup>-1</sup> )
Drying	90	10	20	250
	120	5	10	250
Pyrolysis	1100	15	30	250
Intermediate cooling	20	1	15	250
Atomization	2300	0	4	0
Cleaning	2600	1	5	250

Table 2. Operating sequence of the FI on-line sorption preconcentration of Pd using a KR precoated with 18-crown-6/KSCN, coupled with ETAAS

Step	Function	Pumped medium	Pump active	Valve position	Time (s)	Flow rate (mL min <sup>-1</sup> )
1	KR precoating	Reagent	1	Inject	30	4.4
2	Reagent removing	Air	2	Inject	30	1.9
3	Preconcentration	Sample	1	Fill	90	4.4
4	KR rinsing	Reagent	1	Inject	15	2.2
5	Reagent removing	Air	2	Inject	40	1.9
6	EL filling	Eluent	2	Fill	8	1.0
7	Elution	Air	2	Inject	45	1.0
8	DT withdrawing	-	-	Inject	2	-

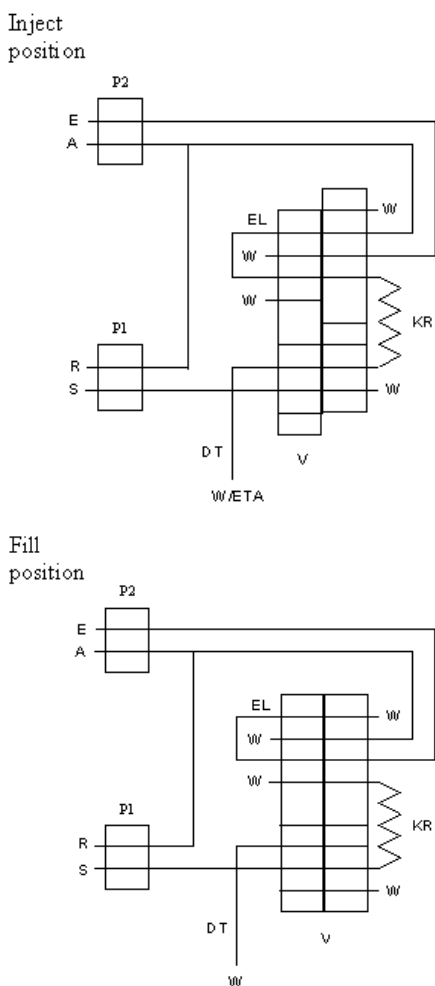


Figure 1. FI manifold for the on-line sorption preconcentration of Pd in a KR precoated with 18-crown-6/KSCN coupled with ETAAS. P1, P2 – peristaltic pumps; S – sample; R – reagent; E – eluent; A – air; KR – knotted reactor; W – waste; EL – eluent loop; V – valve; DT – delivery tube; ETA – electrothermal atomizer. Valve positions: (a) inject, (b) fill.

of 4 s were used for evaluation.

The on-line separation and preconcentration were performed with a Perkin Elmer Model FIAS-400 accessory equipped with a Perkin Elmer 2x4 channel 16-port double layer rotary injector valve. The two peristaltic pumps and the injector valve were programmed and controlled using the Perkin Elmer AAWinlab version 2.61 software. The scheme of the FI manifold is presented in Figure 1 (this is a representation for the convenience of drawing and is not an accurate depiction of the real valve). A knotted reactor (100 cm length), laboratory-made from PTFE tubing (0.5 mm i.d.) by tying interlaced knots with ca. 5 mm diameter loops, was used. PTFE tubing (0.5 mm i.d.) of 50 µL volume was used as an eluent loop. Ismaprene pump tubes (Ismatec, Wertheim, Germany) were employed for propelling the reagent, sample, eluent and air. All connections were made of PTFE tubing (0.35 mm i.d.). A 30 cm delivery tube was used to connect the FI system with the ETA unit. The operation sequence is presented in Table 2. The preconcentration procedure consisted of the following steps: (a) with pump 1 active and the valve in the inject position, the reagent solution was directed to the KR while the sample solution filled the tubing before the valve and went to waste; (b) with the valve still in the inject position and pump 2 running, the reagent solution was removed from the KR by an air flow; (c) with the valve in the fill position and pump 2 active, the sample solution was directed to the KR to form the ion-pair between the analyte and the immobilized reagent; (d) with pump 1 still running and the valve in the inject position, the KR was washed with the reagent solution; (e) with the valve

still in the inject position and pump 2 active, an air flow expelled the residual solution from the EL, KR and DT before elution; (f) with pump 2 still active and the valve in the fill position, the EL was filled with the eluent while the DT was manually inserted into the dosing hole of the graphite tube of the ETA unit; (g) with the valve in the inject position and pump 2 still running, an air flow drove the eluent from the EL through the KR and DT to elute the analyte and deliver the eluate into the graphite tube; (h) with the two pumps stopped, the DT was withdrawn from the ETA. The preconcentration was carried out in parallel with the ETAAS determination of the previous preconcentrated sample. For calibration, aqueous standard solutions were subjected to the preconcentration procedure. Linear least-squares regression was used to establish the calibration function. pH adjustment was performed with a Schott (Hofheim, Germany) CG820 pH meter using a combined glass-calomel electrode.

### Reagents

All reagents were of the highest available purity. Doubly de-ionized (MQ) water (18.2 M $\Omega$  cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout. Nitric acid (65 %), hydrochloric acid (30 %), perchloric acid (70 %) and hydrofluoric acid (40 %), all suprapur from Merck (Darmstadt, Germany), were used for sample digestion and for the adjustment of sample, reagent and eluent acidity. 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) and potassium thiocyanate (KSCN) were purchased from Fluka (Buchs, Switzerland). A reagent solution containing 0.05 % (m/v) 18-crown-6 and 0.05 % (m/v) KSCN was prepared daily by dissolving weighed portions of the reagents in 0.5 mol L<sup>-1</sup> HCl. 1 % (v/v) HNO<sub>3</sub> in methanol (Merck) was used as an eluent. Palladium intermediate solutions were prepared from 1000 mg L<sup>-1</sup> Pd standard stock solution (Z-tek) by stepwise dilution. The analytical solutions, containing Pd (0.05-0.6  $\mu$ g L<sup>-1</sup>) and 0.05 % (m/v) KSCN at pH 2 were prepared just before use.

### Sample preparation

The tunnel dust samples were taken from the walls of emergency call boxes in the Craeybeckx tunnel, Antwerp, Belgium, using a small brush and a plastic pan. The samples were dried in an oven at 100 °C for 24 h. Sieving of the material was not required, as only small dust particles settle on the walls of the boxes.

0.2 g of dust (tunnel dust or road dust BCR-723) sample was weighed in a PTFE vessel. 3 mL of *aqua regia* were added. The mixture was heated almost to dryness. After addition of 3 mL *aqua regia* and 1 mL 40 % HF, the mixture was heated again for 2 h. Then, 2 mL of 65 % HNO<sub>3</sub> were added, and the mixture was heated to dryness. The last step was repeated twice to ensure total elimination of HF. The residue was diluted to 50 mL with MQ water. The digest was centrifuged for 20 min at 3000 r min<sup>-1</sup> in order to separate the solid residue. The sample acidity was adjusted to pH 2 with HNO<sub>3</sub>.

A blank solution characterizing the procedure was prepared in the same way.

## Results and Discussion

### Method development

The FI manifold used for method development (Figure 1) is similar to that proposed in our previous work (17). The integrated absorbance (peak area) was taken as the output with simultaneous consideration of precision (aiming at <3% RSD) and efficiency.

The present system is based on the on-line formation of an ion-pair between K<sup>+</sup>.18-crown-6/SCN<sup>-</sup> precoated on the KR and Pd(SCN)<sub>4</sub><sup>2-</sup> formed in the sample solution. The benefits of using reagent precoating and subsequent on-line formation of an ion-pair instead of the conventional preconcentration scheme involving on-line merging of the sample and reagent solutions are discussed in a previous work (17). In order to achieve good performance of the FI system and to better understand the processes involved in the preconcentration procedure, a number of optimization studies were made.

No Pd was preconcentrated in the absence of 18-crown-6, and very low signal was obtained when only 18-crown-6 was present in the precoating solution. This may be related to the fact that the palladium cation cannot be accommodated in the cavity of 18-crown-6 because of the difference in their radii. The only possibility for complexation of Pd with 18-crown-6 could be the formation of an ion-pair between a preformed cation of 18-crown-6 and a complex anion of Pd. According to the literature (15), 18-crown-6 forms very stable complexes with alkali metal cations, especially with potassium, which fits best into the 18-crown-6 cavity by forming the positively charged complex K<sup>+</sup>.18-crown-6. For the efficient sorption of this complex on the inner walls of the KR, a compensation of its electric charge

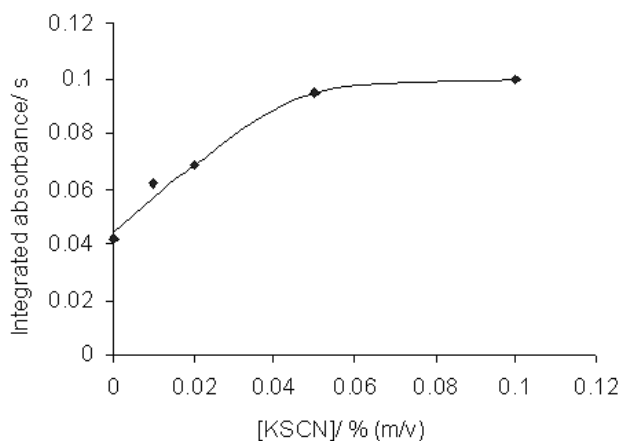


Figure 2. Effect of KSCN concentration in the precoating solution on the integrated absorbance of  $0.4 \mu\text{g L}^{-1}$  Pd

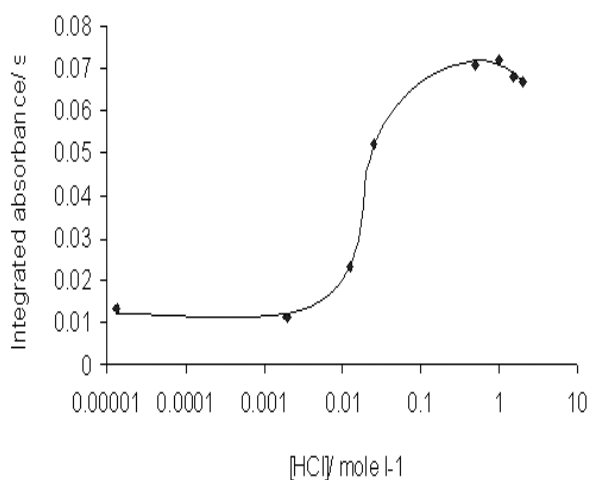


Figure 3. Influence of the acidity of the precoating solution on the integrated absorbance of  $0.4 \mu\text{g L}^{-1}$  Pd

by a suitable anion is necessary. In this work, chloride and thiocyanate were tested as counter-anions. A better performance was obtained with the larger thiocyanate anion. In further experiments, the KR was precoated with a solution containing 18-crown-6 and KSCN. The concentrations of 18-crown-6 and KSCN in the coating solution were varied between 0.01 and 0.1 % (m/v). As optimum concentrations, 0.05 % (m/v) 18-crown-6 and 0.05 % (m/v) KSCN were considered (Figure 2). The effect of the acidity of the coating solution on the integrated absorbance of palladium preconcentrated at pH 2 is shown in Figure 3. As can be seen, HCl concentrations between 0.5 and 2 mol L<sup>-1</sup> favor the formation and immobilization of K<sup>+</sup>.18-crown-6 onto the KR. As the optimum acidity of the precoating solution,

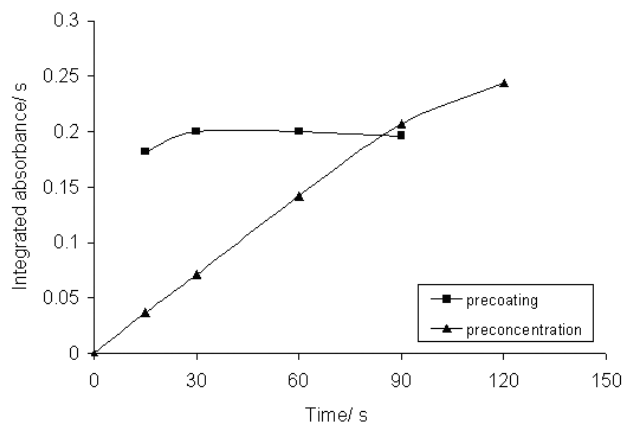


Figure 4. Effect of the times of precoating and preconcentration on the integrated absorbance of  $0.4 \mu\text{g L}^{-1}$  Pd

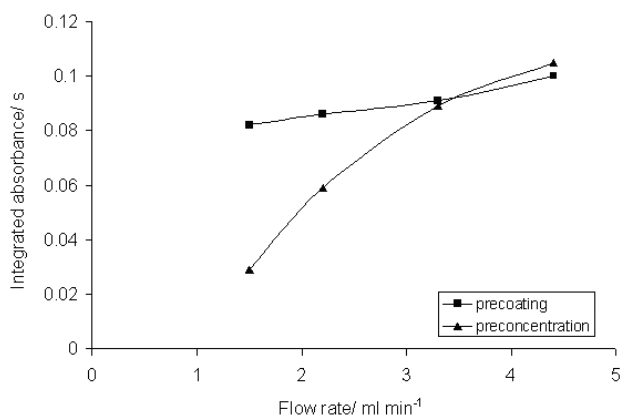


Figure 5. Influence of the flow rates of precoating and preconcentration on the integrated absorbance of  $0.4 \mu\text{g L}^{-1}$  Pd

0.5 mol L<sup>-1</sup> HCl was considered. The effects of the time and flow rate of KR coating on the analytical signal are shown in Figures 4 and 5, respectively. Effective KR coating is achieved within 30 s at a flow rate of 4.4 mL min<sup>-1</sup>.

As mentioned above, the ionic radius of Pd strongly differs from the radius of the 18-crown-6 cavity, and the only possibility for the immobilized K<sup>+</sup>.18-crown-6 to react with Pd would be the formation of an ion-pair with a complex Pd anion. It was found that Pd is most efficiently preconcentrated as the anion Pd(SCN)<sub>4</sub><sup>2-</sup>, which was assumed to replace the smaller SCN<sup>-</sup> anions in the outer coordination sphere of the immobilized K<sup>+</sup>.18-crown-6. The Pd(SCN)<sub>4</sub><sup>2-</sup> complex was formed by the addition of KSCN to the sample solution. As the optimum working concentration, 0.05 % KSCN was selected. The effect of sample acidity on the efficiency of Pd preconcentration

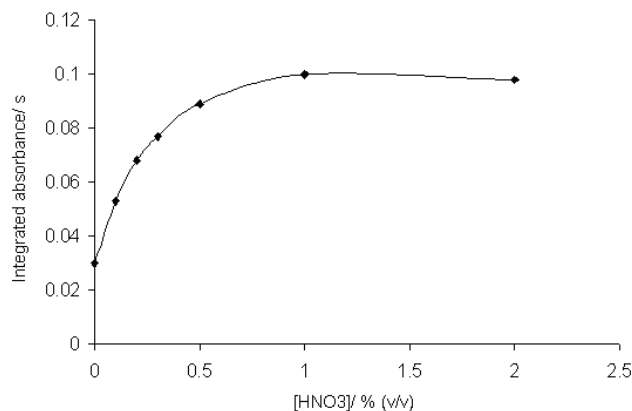


Figure 6. Influence of HNO<sub>3</sub> concentration in the eluent on the integrated absorbance of 0.4 µg L<sup>-1</sup> Pd.

Table 3. Effect of interferences on the percent relative signal of 0.4 µg L<sup>-1</sup> Pd under the optimum preconcentration conditions

Interferent	Concentration (mg L <sup>-1</sup> )	Interferent-to-analyte ratio	Percent relative signal
Cd <sup>2+</sup>	0.04	102	103
	0.4	103	99
Cu <sup>2+</sup>	0.4	103	101
	4	104	81
Fe <sup>3+</sup>	0.4	103	99
	4	104	94
Mn <sup>2+</sup>	0.4	103	99
	4	104	103
Ni <sup>2+</sup>	0.4	103	98
	4	104	101
Pb <sup>2+</sup>	0.4	103	100
	4	104	94
Pt	0.02	50	97
	0.04	102	94
Rh	0.02	50	105
	0.04	102	110
Zn <sup>2+</sup>	0.4	103	101
	4	104	99

was studied in the pH range from 0 to 4. The optimal pH of preconcentration was found to be 1.5 - 2.2. As shown in Figures 4 and 5, the analytical signal of palladium gradually increases with time and flow rate of preconcentration. 90 s of preconcentration at a sample flow rate of 4.4 mL min<sup>-1</sup> were chosen for the further work.

15 s rinsing of the system at a flow rate of 2.2 mL min<sup>-1</sup> was found sufficient to wash out the sample matrix from the KR and connecting tubing without affecting the sorption of palladium.

Ethanol and methanol were tested as eluents of the ion-pair from the KR. Ethanol showed unsatisfactory elution characteristics. The elution efficiency of methanol was further improved by acidification. The effect of HNO<sub>3</sub> concentration in the methanol on the analytical signal of Pd is illustrated in Figure 6. With a longer KR, both the sensitivity and the eluent volume needed for quantitative elution increase. As a compromise between sensitivity and eluent volume, a 100 cm KR and a 50 µL eluent loop were chosen. Best sensitivity and precision were achieved with an elution flow rate of 1 mL min<sup>-1</sup>.

The effect of potential interferences present in environmental samples on the determination of palladium was studied under the optimum chemical and FI conditions given in the experimental section. The results presented in Table 3 illustrate the relatively good tolerance to interferences. Particular attention was paid to Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup>, since these metal ions form stable complexes with KSCN. Pt and Rh were also considered as potential interferences because they have similar properties to Pd and might compete with its preconcentration.

The calibration function (4 standards, n=3, C in µg L<sup>-1</sup>) was 0.3188C-0.0046 with a correlation coefficient of 0.999. The linear concentration range was between 0.05-0.6 µg L<sup>-1</sup>. The enhancement factor, determined as the ratio between the slopes of the calibration curves with and without preconcentration, was 29. The sampling frequency was 14 h<sup>-1</sup>. The RSD was 2.3 % for 0.4 µg L<sup>-1</sup> Pd. The detection limit, based on 3σ of the blank, was 16 ng L<sup>-1</sup>.

#### Method validation

No reference materials with Pd concentration within the detectable range of the present method were available. Therefore, the accuracy of the method was demonstrated by recovery measurements of road dust

Table 4. Results of Pd determination in dust samples (mean  $\pm$   $\sigma$  of three replicate determinations)

Sample	Content ( $\mu\text{g L}^{-1}$ )	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Road dust	< DL	0.2	0.18 $\pm$ 0.01	90
(BCR CRM 723)		0.4	0.36 $\pm$ 0.01	90
Tunnel dust	0.23 $\pm$ 0.01	0.2	0.40 $\pm$ 0.01	93
		0.4	0.59 $\pm$ 0.02	94
	(58 $\pm$ 3*)			

\*ng g<sup>-1</sup>

(BCR CRM 723) spiked with Pd. The results (Table 4) show satisfactory recoveries. The method was applied to the determination of palladium in tunnel dust collected from the walls of emergency call boxes in the Craeybeckx tunnel, Antwerp, Belgium, which is characterized by high automobile traffic. The Pd content in the tunnel dust, determined by the standard addition method, was found to be 58  $\pm$  3 ng g<sup>-1</sup>.

### Acknowledgements

B. Dimitrova thanks the European Commission for a Marie Curie Training Site fellowship (EC-HPMT-CT-2001-00310). E. Ivanova thanks the British Royal Society of Chemistry for an RSC Journals Grant.

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