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Journal of Chromatography B, 760 (2001) 237–245

JOURNAL OF CHROMATOGRAPHY B

www.elsevier.com/locate/chromb

Determination of palladium in human urine by high-performance liquid chromatography and ultraviolet detection after ultraviolet photolysis and selective solid-phase extraction

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Received 6 November 2000; received in revised form 25 May 2001; accepted 29 May 2001

Abstract

The high-performance liquid chromatographic method with UV detection described below permits the selective determination of traces of palladium in human urine. After UV photolysis, during which the complete organic matrix was destroyed, the palladium was selectively enriched by solid-phase extraction (SPE). The reversed-phase C_{18} SPE column material was loaded with the ligand *N*,*N*-diethyl-*N′*-benzoylthiourea (DEBT) which shows an excellent complexing capacity for palladium in acidic solutions and at room temperature. The $Pd(DEBT)_2$ complex was eluted with ethanol. After isocratic separation on the analytical column ($MeOH/H_2O$ 98:2 (v/v)), the complex was detected at 274 nm. The detection limit was 10 ng Pd/l. The relative standard deviations (RSD) of the within-series imprecision were in the range between 11% (75 ng Pd/l) and 7% (180 ng Pd/l). The between-day imprecision was 11% (75 ng Pd/l) and 5% (180 ng Pd/l). The recovery rates ranged between 94 and 96%. Using this method, urine samples of 44 persons from the general population were analysed. Only in one urine sample could palladium be detected. For comparison, 10 persons with occupational palladium exposure were examined. The urinary concentrations ranged from <10 to 2538 ng/l.

Keywords: Ultraviolet photolysis; Biological monitoring; Palladium

1. Introduction

Noble metals, especially platinum, rhodium and palladium, are widely used in industrialized countries. One large field of application are catalytic converters. Earlier types contained mainly platinum and rhodium, while nowadays palladium is increasingly being used in the new catalyst generation. With exhaust fumes, metallic particles are emitted into the environment. Platinum, rhodium and palladium can now be determined in tunnel or street dust and in grass near motorways [1,2].

Another field of application are dental restorative alloys. In addition to gold, these contain platinum and palladium in different portions. In earlier studies it was shown that dental alloys containing gold may increase the platinum level in urine of the general population [3,4].

In contrast to platinum, palladium is often used as

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0378-4347/01/$ – see front matter
PII: S0378-4347(01)00271-7

a catalyst in industrial chemical and pharmaceutical synthesis. Because of the allergenic potential of palladium, this metal is of great concern to environmental and occupational medicine. Since palladium traces (ppb/ppt range) might be released from the catalysts during industrial processes, specific and sensitive analytical methods for effective environmental and biological monitoring need to be elaborated.

This paper describes a method for determining palladium in human urine using high-performance liquid chromatography and UV detection. In order to minimize interference, which may occur from the accompanying compounds in urine, UV photolysis was carried out first. To achieve the required sensitivity, palladium was selectively bound to *N*,*N*-diethyl-*N′*-benzoylthiourea and the metal complex was concentrated using solid-phase extraction.

2. Materials and methods

2.1. Chemicals and materials

Methanol (HPLC grade), methanol (analytical grade), ethanol (Lichrosolv®), nitric acid (65%, Suprapur®), sulphuric acid (96–98%, analytical grade) and hydrogen peroxide (30%, Suprapur) were obtained from Merck (Darmstadt, Germany).

Palladium standard solution (1 g/l) was received from Sigma–Aldrich (Deisenhofen, Germany) and *N*,*N*-diethyl-*N′*-benzoylthiourea from Fluka (Deisenhofen, Germany).

Polyethylene reservoirs (empty, 4 ml) and polyethylene frits (20 μm, ∅ 9 mm) were obtained from ICT Handels-GmbH (Bad Homburg, Germany).

Bakerbond reversed-phase C_{18} material (for flash, 40–60 μm) was received from Baker–Mallinckrodt (Griesheim, Germany).

For all aqueous solutions, Ultrapur water was used (Milli Q-plus, Millipore, Eschborn, Germany).

2.2. Solutions

HNO_3 (1.2 mol/l) was prepared as follows: 82 ml HNO_3 65% Suprapur was filled up to the mark with Ultrapur water in a 1000-ml glass volumetric flask.

Palladium (10 μg/l) working standard was prepared as follows: 1 ml of a 1 g/l palladium stock solution was filled up to the mark with 1.2 mol/l HNO_3 in a 100-ml glass volumetric flask to produce a 10 mg Pd/l solution; 100 μl of the 10 mg/l palladium solution was filled up to the mark with 1.2 mol/l HNO_3 in a 100-ml glass volumetric flask to produce a 10 μg Pd/l solution. This solution was freshly prepared every week.

N,*N*-diethyl-*N′*-benzoylthiourea (DEBT) solution (2.5 mg/l) was prepared as follows: 5 mg DEBT was dissolved with 1 ml methanol and the flask was filled up to the mark with Ultrapur water in a 100-ml glass volumetric flask to produce a 50 mg DEBT/l solution; 5 ml of this solution was taken and the flask was filled up to the mark with 1.2 mol/l HNO_3 in a 100-ml glass volumetric flask to produce a 2.5 mg DEBT/l solution. All solutions containing the ligand were freshly prepared every day.

2.2.1. Mobile phase

The composition of the mobile phase for the isocratic separation was 98:2 MeOH/H_2O (v/v). The solvent was degassed using an ultrasonic unit.

2.3. Sample preparation

2.3.1. UV photolysis

The aim of this procedure was to destroy all dissolved organic matter in the urine. The interfering background was completely removed which was necessary for the sensitivity of the following high-performance chromatographic step.

A UV digester 705 from Metrohm (Herisau, Switzerland) was used. The UV digester was equipped with a 500 W Hg lamp. The quartz vessels were arranged concentrically around the Hg lamp with a distance of 2.5 cm.

Ten milliliters of urine calibration standards and real samples were placed in quartz vessels; 500 μl H_2SO_4 and 500 μl H_2O_2 were added. The pH of the solution was about 1. The solution was irradiated with UV light for about 6 h. During this period amounts of 500 μl H_2O_2 were added until the solutions stayed clear (ΣH_2O_2: 3 ml).

After cooling to room temperature (overnight), the whole solution was applied to the enrichment step.

2.3.2. Solid phase extraction (SPE)

In each SPE cartridge a frit was inserted and filled with 80 mg C_{18} reversed-phase material. Another frit was inserted on the top. The cartridges were conditioned with 3 ml methanol and 3 ml 1.2 mol/l HNO_3. Then 3 ml of a 2.5 mg/l DEBT solution was passed through the column. After that the sample solution was loaded on the column. The cartridges were dried in a vacuum for 5 min using a Vak-Elut™ Station (Varian, Darmstadt, Germany). The $Pd(DEBT)_2$ complex was eluted with 450 μl ethanol.

2.4. High-performance liquid chromatographic analysis

Analysis was carried out using a liquid chromatograph (Vista 5500 Varian, Darmstadt, Germany), an isocratic pump (LaChrom L-7110 Merck Hitachi, Darmstadt, Germany), a guard column (Lichrosper® 100 RP 18-e, 5 μm, 4×4 mm I.D., Merck, Darmstadt, Germany), an analytical column (Lichrosper 100 RP 18-e, 5 μm, 250×4 mm I.D., Merck, Darmstadt, Germany) and a UV detector (L-4000 Merck Hitachi, Darmstadt, Germany). The chromatograms were plotted with an integrator (4290 Varian, Darmstadt, Germany). The attenuation was set to 0.5.

Two hundred microliters of the ethanolic eluate were injected into the HPLC system. After isocratic separation on the analytical column, the complex was quantified using UV detection at 274 nm. The flow-rate of the mobile phase was 1 ml/min.

2.5. Calibration

2.5.1. In urine

Calibration standards were prepared by spiking urine with 0, 50, 100, 150, 200, 250 and 500 ng Pd/l; 10 ml of each standard underwent UV digestion as described in Section 2.3.1. After mineralization the enrichment step was carried out as described in Section 2.3.2; 200 μl of the ethanolic eluate were injected into the HPLC.

2.5.2. In 1.2 mol/l HNO_3

Calibration standards containing 0, 50, 100, 150, 200, 250 and 500 ng Pd/l were prepared by appropriate dilution of the working standard (10 μg Pd/l) with 1.2 mol/l HNO_3. No UV photolysis was carried out before; 10 ml of each standard underwent the enrichment step described in Section 2.3.2; 200 μl of the ethanolic eluate were injected into the HPLC.

For urine and aqueous (1.2 mol/l HNO_3) calibration, a linear addition calibration curve with zero intercept was chosen. The peak areas were plotted as a function of the concentration. These graphs were used to ascertain the unknown concentrations of palladium in urine samples from unexposed and exposed persons.

2.6. Biological monitoring

2.6.1. Environmental

We investigated 44 persons (24 women, 20 men) from the general population. We divided this group of persons into those who had dental alloys containing gold ($n=24$) and those who had none ($n=20$). We collected 24-h urine in pre-cleaned polyethylene bottles. Aliquots of the 24-h urine from each person were stored in disposable cups (polypropylene (100 ml), Sarstedt, Nürmbrecht, Germany) at −20°C until analysis.

2.6.2. Occupational

Spot urine samples ($n=10$) of persons occupationally exposed to palladium were analysed. The samples were stored in polypropylene tubes (13 ml, Sarstedt, Nürmbrecht, Germany) at −20°C until analysis.

3. Results and discussion

It was our aim to elaborate a specific and sensitive analytical procedure which at least should be able to quantify occupational exposures of palladium and to reach a limit of detection like other procedures described in literature (Table 1). Therefore, the development of the new method presented here had to meet the requirements of an adequate clean-up procedure and an effective enrichment step.

Minimizing interference resulting from sample matrix, the urine samples underwent UV photolysis which is known as a powerful mineralization procedure. Since small amounts of acids were used and

Table 1
Results of biological monitoring compared with the latest literature data

Reference	Method	Detection limit (ng Pd/l)	General population (ng Pd/l)	Occupationally exposed persons (ng Pd/l)
Schramel et al. [19]	ICP-MS after dilution	30	30–200 (n=14)	
Begerow et al. [25]	ETAAS after liquid–liquid extraction (APDC)	20	<20–80 (n=9)	
Begerow et al. [20–22]	SF-ICP-MS after UV-photolysis	0.2	32.7–219.7 (n=21)	
			9.5–133.7 (n=17)	
			27.3–82.5 (n=17)	
			5.8–91.1 (n=262)	
Krachler et al. [24]	SF-ICP-MS after microwave digestion	5	<5–21 (n=30)	
Schuster et al. [17]	On-line enrichment and FI-GFAAS	36	<36 (n=6)	<80–3400 (n=12)
Messerschmidt et al. [18]	Total reflection X-ray fluorescence after reductive co-precipitation of Pd with mercury	2.5	<2.5 (n=5)	200–1000 (n=7)
Philippeit and Angerer (this paper)	HPLC–UV after UV photolysis and solid-phase extraction	10	<10–28 (n=44)	<10–2538 (n=10)

the added hydrogen peroxide was of Suprapur grade, sample contamination was very low. Sulphuric acid was chosen because it is known that acids, like hydrochloric acid for example, may decrease the oxidation potential of hydrogen peroxide [5]. Since sulphuric acid does not show this effect, less hydrogen peroxide was necessary for complete mineralization. Even the reaction of hydrogen peroxide with the organic matter in the sample was less vigorous using sulphuric acid. The solution was irradiated with UV light for about 6 h. Such long irradiation times for large volumes of difficult matrices like urine were described elsewhere [5]. Irradiation times <6 h led to insufficient mineralization of the samples. Carrying out the following enrichment step with poorly mineralized samples, chromatograms with high background level were obtained and the palladium signal was completely suppressed.

The advantage of destroying all dissolved organic matter in the sample was that no matrix effect occurred. This was verified by comparing the mean slopes of the calibration curves carried out in aqueous solutions (1.2 mol/l HNO_3) and in urine. No significant difference between the slopes could be established. Likewise, with both 1.2 mol/l HNO_3 and urine all calibration points varied within the same prediction band (P=95%), as shown in Fig. 1. Consequently, calibration was carried out using palladium standard solutions in 1.2 mol/l HNO_3. This also saved time because UV photolysis was not needed for aqueous calibration standards. Further, no analyte loss was observed by UV photolysis. The mean peak area (n=10) of all calibration standards in urine and in 1.2 mol/l HNO_3 are compared in Table 2. No significant difference between the mean values of urine calibration standards after UV photolysis and aqueous calibration standards without UV photolysis could be detected. Using a chromatographic method, mineralization of the organic matter was the best way to achieve the lowest analytical background which was possible.

The use of *N*,*N*-diethyl-*N′*-benzoylthiourea (DEBT) for the chelation of palladium and simultaneous solid-phase extraction of the palladium complex is based on a study by Schuster and Schwarzer [6,7]. They described that DEBT and its palladium complex ($Pd(DEBT)_2$) are strongly adsorbed to apolar stationary phases such as C_{18} modified silica gel. They also investigated that the adsorption of the $Pd(DEBT)_2$ complex is much stronger than that of the ligand. Therefore, leaching of the palladium

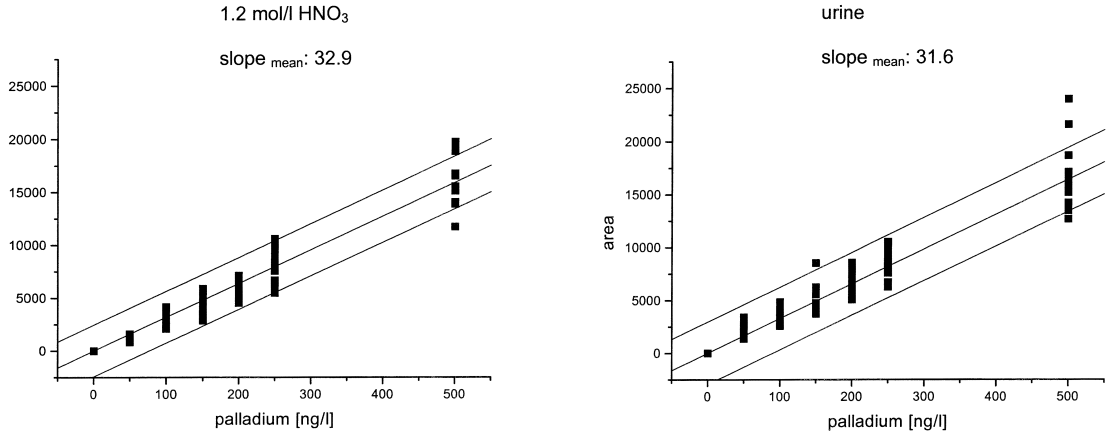

Fig. 1. Comparison of the slopes of calibration curves for palladium in 1.2 mol/l HNO_3 ($n=17$) and in urine ($n=17$).

Table 2
Comparison of the mean peak areas ($n=10$) of all calibration standards in 1.2 mol/l HNO_3 and in urine. No significant analyte loss occurred during UV photolysis

	Mean peak area of calibration standard 50 ng Pd/l	Mean peak area of calibration standard 100 ng Pd/l	Mean peak area of calibration standard 150 ng Pd/l	Mean peak area of calibration standard 200 ng Pd/l	Mean peak area of calibration standard 250 ng Pd/l	Mean peak area of calibration standard 500 ng Pd/l
In 1.2 mol/l HNO_3	1328	3268	4810	6064	8043	16 728
In urine	1667	3376	4775	6401	8341	16 166

complex and the associated loss of analyte is not observed. Schuster and Schwarzer also pointed out that the ligand *N*,*N*-diethyl-*N′*-benzoylthiourea provides an extraordinary chemical resistance against oxidation and hydrolysis and a striking selectivity for palladium.

The selectivity of DEBT for palladium was shown in numerous studies by Schuster et al. [8–10]. The essential part of all studies was that thioureas, in general, act as selective complexing agents for the enrichment of platinum metals even from strongly interfering matrices. Complexometrically the benzoylthioureas are members of the 1,3-dichalcogen group of ligands like the classical β-diketons. The specific arrangement of the heteroatoms of the thiourea group leads to significant changes in the chemical properties. They show a strong selectivity for b-type acceptor metal ions like Pd(II) and an unusual high redox stability for sulphur ligands. In acidic solutions (pH 1), as in the sample solutions after UV photolysis or in standard solutions, only ruthenium, osmium, platinum, palladium, gold, silver, rhodium and iridium are complexed as a result of their specific acceptor properties as shown in Fig. 2.

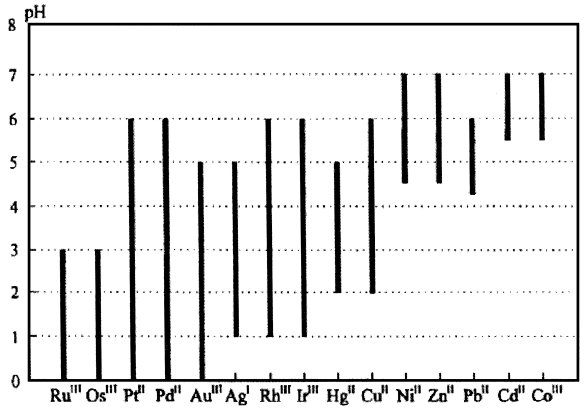

Fig. 2. pH-dependent complexation range of *N*,*N*-diethyl-*N′*-benzoylthiourea [11].

Since Pd(II) shows no kinetic inhibition [12] and cannot be oxidized to higher oxidation states under normal conditions, it is preferably complexed by DEBT in acid solutions. Another advantage is that palladium reacts at room temperature. This allows it to be separated from other noble metals such as platinum and rhodium. Both metals, which are also very important in occupational and environmental medicine, react to metal–DEBT complexes only at higher temperatures (about 60°C). Less stable chelates like Au(III) and Ag(I) dissociate in organic solvents before they can be determined chromatographically [13].

Considering the facts mentioned above about selectivity and stability, the ligand DEBT seemed to be the optimal chelating agent for Pd(II).

During the enrichment step of our method an appropriate amount of DEBT was loaded onto reversed-phase C_{18} material. After that the sample solution was applied and the complexation of palladium with DEBT took place on the column (Fig. 3). Eighty milligrams of the reversed-phase material were sufficient because, in this special case, the solid-phase extraction represented only an enrichment procedure. It did not serve for separation because of using sample solutions which were free from interfering matrix components.

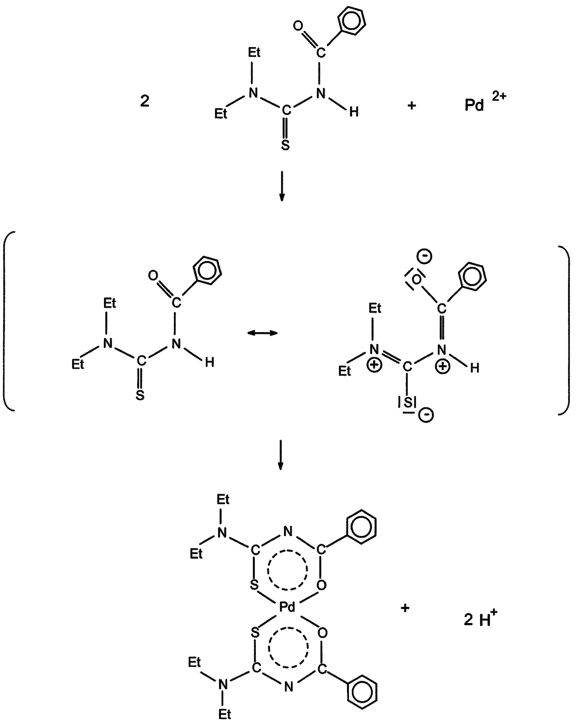

Fig. 3. Formation of a neutral complex between *N*,*N*-diethyl-*N*′-benzoylthiourea and palladium (II) [14,15].

Ethanol was found to be the best solvent for eluting the $Pd(DEBT)_2$ complex from the column. Because of the good solubility of the $Pd(DEBT)_2$ complex in ethanol, only a small volume (450 μl) was necessary. By eluting the column three times and analysing each fraction it was proven that the amount of solvent was enough for elution. Only in the first fraction was palladium detected. The whole enrichment step resulted in an enhancement factor of 22 which was necessary to reach a low limit of detection.

Since *N*,*N*-diethyl-*N*′-benzoylthiourea and its palladium complex were both eluted with ethanol, they had to be separated using high-performance liquid chromatography with UV detection. It was shown in earlier studies that UV guarantees a sensitive detection method. In the UV range (λ=274 nm), the $Pd(DEBT)_2$ complex shows considerable absorption with a molar extinction coefficient ϵ of about 50 000 [16].

An analytical HPLC column filled with reversed-phase C_{18} (endcapped) material was used for separation of the free ligand and its palladium complex. Although the level of methanol in the mobile phase was very high (98%) the resolution of both peaks was sufficient. Fig. 4 shows two representative chromatograms obtained with urine samples from an unexposed and an exposed person.

The reliability of this newly elaborated method was checked under the given conditions for sample preparation and HPLC–UV detection. As adequate certified standard reference material for palladium was not available, urine samples were spiked with 75 and 180 ng Pd/l. The within-series imprecision was determined by sixfold analysis (relative standard deviations (RSD) 5–11%) and the between-day imprecision on 10 different days (relative standard deviations (RSD) 7–11%). The recovery was checked by analysing urine samples spiked with 75 and 180 ng Pd/l sixfold. The recovery varied from 94 to 96%. Taking into consideration a threefold signal-to-noise ratio, a detection limit of 10 ng Pd/l

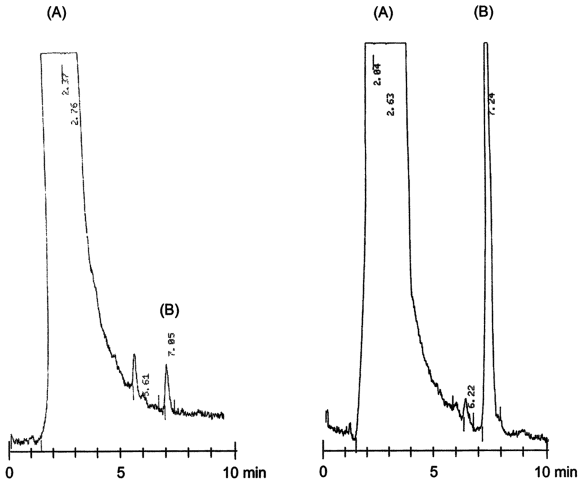

Fig. 4. Left: Chromatogram of a urine sample from a person without occupational exposure to palladium (28 ng Pd/l); (A) free ligand DEBT (retention time 2.37/2.76 min), (B) $Pd(DEBT)_2$ complex (retention time 7.05 min). Right: Chromatogram of a urine sample from an occupationally exposed person (2538 ng Pd/l); (A) free ligand DEBT (retention time 2.04/2.63 min), (B) $Pd(DEBT)_2$ complex (retention time 7.24 min). Time of analysis: 10 min. Attenuation: 0.5. Mobile phase 98:2 $MeOH/H_2O$. Wavelength 274 nm.

was determined. Concerning the low concentrations which can be detected using this method, the reliability data summarised in Table 3 can be regarded as good.

However, the selective and effective enrichment procedure was not sufficient to detect palladium in the urine of persons from the general population. Only in one out of 44 urine samples was palladium found. Taking into consideration that 24 persons had gold containing dental alloys we could not confirm if this kind of restorative dental alloy increased the urinary palladium level of the general population. At this moment there is no evidence either that other sources like drugs, food, catalytic converters, etc., influence the palladium concentrations in urine of the general population. Occupational exposures, however, caused palladium concentrations in urine up to the μg/l range. When we analysed the urine samples of 10 persons with occupational exposure to palladium we found concentrations between <10 and 2538 ng Pd/l (Table 4).

A comparison of these results and data obtained in recent literature is shown in Table 1. Our results agree with those of Schuster et al. [17] and Messerschmidt et al. [18]. With regard to the detection limits, the sensitivity of the three methods is comparable. Schuster et al. increased the sensitivity of graphite furnace atomic absorption spectroscopy (FI-GFAAS) using first an on-line enrichment procedure according to the pre-concentration step described here. Messerschmidt et al. used a separation and enrichment method for palladium in biological sam-

Table 3
Reliability data of the method

	n	Palladium (ng/l)	RSD (%)	(%)
Within-series imprecision	6	75	11	
	6	180	5	
Between-day imprecision	10	75	11	
	10	180	7	
Recovery	6	75		96
	6	180		94
Detection limit		10		

Table 4
Results of biological monitoring in urine ($n=44$)

Palladium	Range (ng/l)	Persons with dental alloys (ng/l; $n=24$)	Persons without dental alloys (ng/l; $n=20$)	Results above detection limit
General population ($n=44$)	<10–28	<10	<10–28	1
Occupationally exposed persons ($n=10$)	<10–2500	–	–	9

ples which included reductive co-precipitation with mercury followed by determination using total reflection X-ray fluorescence (TRXF).

In the last few years, ICP-MS has often been used for determination of platinum group metals [19–22]. Especially, in the case of palladium, spectral interference strongly affected the accuracy. To eliminate this spectral interference, mass resolutions greater than 10 000 were necessary. Even with high resolution (HR)-ICP-MS it was not possible to solve these problems till now. Therefore, most of the palladium results obtained with this technique are nowadays considered to be too high [19–22]. Being a powerful and sensitive analytical method for metal analysis, however, attempts were made to make ICP-MS suitable for palladium determination. Müller and Heumann [23] eliminated interfering elements using an anion-exchange resin before they determined palladium with isotope dilution (ID)-ICP-Q-MS. Krachler et al. [24] applied a mathematical correction method and it was then possible to determine palladium in urine with HR-ICP-MS. Their results are comparable with ours and the results in the latest literature [17,18]. An electrothermal atomic absorption spectroscopic method after liquid–liquid extraction was also applied for the determination of palladium in human urine [25]. The authors used Pyrrolidinecarbodithioic acid Ammonium salt (APDC) as complexing agent. However, like all thiocarbamates, APDC is labile to hydrolysis and oxidation. Even low concentrations of ubiquitous elements might cause serious interference in the enrichment procedure [26]. Therefore, the data obtained for palladium in urine have to be considered carefully.

4. Conclusions

The analytical method presented here for the determination of traces of palladium in human urine with HPLC–UV detection after UV photolysis and solid-phase extraction is reproducible, sensitive and specific. It is practical because few instruments are needed. The reliability data of the method, such as within-series imprecision, between-day imprecision, detection limit and recovery, can be regarded as good and are comparable with the reliability data of other analytical methods [6,18]. This analytical method is suitable for analysing urine samples from persons occupationally exposed to palladium. In the case of low external exposures, such as found in the environment or in dental alloys, the excretion of palladium is usually too low to be detected with this newly elaborated method. This is also the case with other analytical methods available to date, such as FI-GFAAS [17] and TRXF [18].

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