The Analyst COMMUNICATION

Separation and enrichment of palladium and gold in biological and environmental samples, adapted to the determination by total reflection X-ray fluorescence

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Received 17th January 2000, Accepted 9th February 2000

The reductive co-precipitation of trace and ultra-trace elements together with mercury followed by complete evaporation of the mercury makes it possible to determine palladium and gold by total reflection X-ray fluorescence. Both elements can be detected without interferences at optimal sensitivity in the pg range. Thus, detection limits of, *e.g.*, 2.5 ng L^{-1} for palladium and 2.0 ng L^{-1} for gold, in urine, were obtained. The precision was determined to 0.04 at a palladium concentration of about 200 ng L^{-1} urine and to 0.19 at a gold concentration of only 18 ng L^{-1}. The recovery for a urine sample spiked with known amounts of palladium and gold amounted to >95%. Results of the combined procedure are given for the determination of palladium and gold in the urine of non-exposed and occupationally exposed persons and in some other environmentally relevant samples.

Introduction

The determination of traces and ultra-traces of palladium in the environment, as well as in body fluids of living species, at low concentrations is an urgent problem which is discussed controversially. Pd affects the environment to an increasing degree as pollution, especially by the technical use of catalysts containing active Pd metal. The production and recycling of Pd-containing materials, as well as the use of Pd as a constituent of dental restorative alloys, may be a source for toxic or allergic reactions of organisms.[1,2] A critical evaluation of possible risks for human health can only be given if reliable analytical data are available.

Inductively coupled plasma with mass spectrometry (ICP-MS) is generally capable of determining Pd down to the pg range. However, this technique suffers from spectral interferences, which can be eliminated in the high resolution mode by applying a mathematical correction.[3,4] This correction method is suitable for the determination of Pd in body fluids but not in environmental samples, such as road dust.[5] Other instrumental methods, such as graphite furnace atomic absorption spectrometry (GFAAS) or instrumental neutron activation analysis (INAA, detection limit 150 ng L^{-1} in urine[6]), are not sensitive enough for direct measurements in the lower ng kg^{-1} or ng L^{-1} range. Additionally, INAA is a high expenditure method available only to a few laboratories. Consequently, a direct determination of Pd in body fluids (urine, serum) or in solutions of digested biological or environmental samples is possible only in a few cases and an additional separation or enrichment step becomes necessary.[7–11] For that purpose, an effective combined procedure was developed by Schuster *et al.*[11,12] using a novel version of solid-phase extraction in a flow injection system. The element detection was performed by graphite furnace AAS (GFAAS), by laser atomic fluorescence spectrometry with electrothermal vaporization (ETV-LAFS), by ICP-MS or by INAA.

In this paper a procedure based on a reductive co-precipitation of the noble metals Pd and Au with mercury is presented. It is especially optimised for element determinations by total reflection X-ray fluorescence (TXRF). Au is included in the investigations because it is separated and enriched quantitatively together with Pd in contrast to the other noble metals.

Experimental

The whole procedure consists of decomposition of the sample, the separation of Pd and Au, and subsequent determination of the elements by TXRF. These steps are described here for urine as the sample material. Different sample matrices (*e.g.*, plant material and other biological tissues, airborne particulate matter, tunnel dust) can be treated according to the same procedure. Care has to be taken concerning the quality of the decomposition step, because a complete digestion is essential. Otherwise, lower recoveries of Pd and Au are to be expected.

Decomposition of the sample

For the decomposition, 20 mL of urine and 1 mL of nitric acid, 14 M, are mixed in a 70 mL quartz vessel and slowly heated up in order to concentrate the volume to about 2 mL. Afterwards, a further 4 mL of 14 M nitric acid and 0.5 mL of 12 M hydrochloric acid are added and this sample is digested in a high pressure asher (HPA®) for 50 min at a temperature of 320 °C and a pressure up to 130 hPa. In order to remove the excess of acids from the resulting solution the volume is finally reduced to about 0.5 mL. Evaporation to dryness has to be avoided, otherwise losses of the analytes may occur.

Separation by co-precipitation

The separation of Pd and Au is based on a reductive co-precipitation with mercury. A 2 mL volume of de-ionised water is added to the clear digestion solution and the whole solution is transferred into a 10 mL centrifuge tube. Next, 0.2 mL of a mercury solution (corresponding to 30 mg of mercury) and 0.5 mL of formic acid are added and the tubes are heated up to 80–85 °C in an aluminium block. After about 5 min, a dark precipitate of finely dispersed mercury appears. About 10 min later, a second addition of 0.5 mL formic acid becomes necessary to complete the reduction step. If large amounts of gases are produced during this step the vessel has to be taken out of the heating block to avoid frothing of the solution. After further heating for 30 min at 80–85 °C, the solution becomes clearer while the mercury is collected as a dark precipitate or as droplets at the bottom of the vessel. Subsequently, the temperature of the heating block is increased to 115–120 °C and after 10 min of weak boiling the reduction step is finished.

The residual solution containing one or two mercury droplets is decanted, *i.e.*, the supernatant is removed and the droplets are

DOI: 10.1039/b000471p

washed with 3 mL of 0.4 M hydrochloric acid and centrifuged to promote the formation of one mercury droplet. Subsequently, this droplet and the clear solution are filtered, the droplet is washed with water and finally with propan-2-ol. The droplet of metallic mercury containing the Pd and Au from the sample is transferred onto a siliconized quartz-glass target suitable as a sample carrier for TXRF. The mercury is evaporated by heating the carrier on a hot plate at about 300 °C. A mercury absorber, *e.g.*, iodized activated carbon or zinc chips, must be used for that step. Thus, an environmental contamination by mercury is avoided. After 10–15 min a residue remains which is hardly visible but contains the elemental Pd and Au of the sample.

Reagents

For the decomposition of the samples, sub-boiled nitric acid, 14 M, and hydrochloric acid, 12 M, were used. For the co-precipitation step, a mercury solution was prepared as described below: 3 g of mercury (analytical grade for polarography) were dissolved in a volumetric flask in 4.5 mL of dilute nitric acid (2.5 mL sub-boiled nitric acid, 14 M, and 2 mL of de-ionised water). After dissolution of the mercury, the solution was diluted up to 20 mL with de-ionised water. As the reducing agent, formic acid (98–100%) was used. For cleaning and drying of the mercury droplet de-ionised water and propan-2-ol were used. All reagents were purchased from Merck (Darmstadt, Germany) and were at least of analytical grade, if not stated otherwise. Water was de-ionised by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Apparatus

A high pressure asher (HPA®, Kürner, Rosenheim, Germany) with 70 mL quartz-glass vessels was used for the decomposition of the samples (closed system). A hot plate and an aluminium heating block were applied for evaporation of the digestion solution. For the reductive co-precipitation 10 mL tapered vessels and an aluminium heating block were used. Furthermore, a centrifuge and a filtration apparatus with folded filters (Nr. 595 ½, id 9 cm, Schleicher und Schüll, Dassel, Germany) were employed.

Element determination was performed by use of a TXRF-spectrometer Extra II (R. Seifert & Co, Ahrensburg, Germany) and a detector/analyser system QX 2000 (Link Systems, Oxford Instruments, High Wycombe, Buckinghamshire, UK).

TXRF analyses

The residues on the siliconized quartz-glass carriers were spiked with a standard solution containing 2 ng of yttrium. After drying the solution this element served as internal standard for the quantification of Pd and Au. For the excitation of the sample, X-ray tubes with a Mo and W anode were chosen and operated at 50 kV and 38 mA. The acquisition time for each spectrum was adjusted to 200 s. General informations about TXRF analysis are given in the literature.[13,14]

Results

The efficiency of the separation and enrichment procedure was studied by its application to a urine sample of an occupationally exposed person. The residues of some matrix elements (K, Ca, Fe and Zn) and some trace elements (Ti, Cr, Mn, Ni, Cu, Sn, Pb and noble metals) are listed in Table 1. Mercury, which was added to the test solution as a reagent, showed a residual amount of ~5 ng. This is a fraction of 1.7×10^{-7} in relation to the initial amount of 30 mg added to the test solution. Other elements were found at the ng or sub-ng level. A few elements were not detected because their masses were below the detection limit. Therefore, the recovery for matrix elements is of the order of 10^{-8}. For the noble metals it is expected to be > 90%.

As no suitable reference materials with certified contents of Pd and Au in the relevant concentration range are available, recovery experiments were carried out. Urine of non-exposed persons, showing element concentrations below the detection limit of the procedure, were spiked before the decomposition with known amounts of Ag, Au, Pd, Pt and Rh (corresponding to a concentration range of 10 ng L^{-1}–5 μg L^{-1}) and treated by use of the whole procedure as described above. For Pd and Au only total recoveries > 95% were obtained; Pt showed non-reproducible results of about 50%, whereas Ag and Rh were recovered up to a level of < 5%. Therefore, the method was validated only for Pd and Au (*cf.* Table 2). A possible loss of the analytes Pd and Au during the separation and evaporation step could be neglected because of the good recoveries. Detection limits were determined corresponding to absolute amounts of about 50 pg. In relation to 20 mL of urine, the relative detection limits are about 2 ng L^{-1} (ppt level), which is remarkably low. The precision of the method was investigated by analysing five aliquots of a urine sample of an exposed person (c_{Pd} = 203 ng L^{-1}, c_{Au} = 18 ng L^{-1}). The relative standard deviations (RSD) of the results were 0.04 for Pd and 0.19 for Au. These values are acceptable considering the low concentrations in the ppt range.

Several urine samples from non-exposed and occupationally exposed persons were analysed according to the procedure described above. The results are given in Table 3. In cases of normal exposure no Pd could be detected in the urine samples. The Au values generally were near to the detection limit. For the group of occupationally exposed persons significant concentrations of Pd and Au in urine were detected. Several other groups

Table 1 Typical amounts (ng) of some matrix and trace elements after separation by reductive co-precipitation and evaporation of the mercury. Pd and Au are the analytes, Hg is the trace collector. Sample: urine of an occupationally exposed person

K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn
1.2	1.4	0.4	< 0.05	< 0.02	0.37	0.04	0.17	< 0.03
Rh	**Pd**	**Ag**	**Sn**	**Pt**	**Au**	**Hg**	**Pb**	
< 0.1	3.39	1.45	0.8	0.43	0.21	~5	< 0.02	

Table 2 Validation of the method. Test material: urine of non-exposed and occupationally exposed persons

	Pd	Au
Recovery (10 ng L^{-1}–5 μgL^{-1})	> 95%	> 95%
Detection limit (absolute amount)	50 pg	40 pg
Detection limit (for 20 mL urine)	2.5 ng L^{-1}	2 ng L^{-1}
Precision	0.04	0.19
(RSD for *c*)	(203 ng L^{-1})	(18 ng L^{-1})

Table 3 Pd and Au in different sample materials: urine (non-exposed persons and occupationally exposed persons in a catalyst recycling factory), poplar roots (hydroponic cultivation), air dust (sampled near a high traffic road in Frankfurt/Main, Germany), road dust (European project PACE-PAC). *n* = number of different samples

	n	Pd	Au
Urine (normal exposure)	5	< 2.5 ng L^{-1}	< 2–20 ng L^{-1}
Urine (occupational exposure)	7	200–1000 ng L^{-1}	18 ng L^{-1} (n = 1)
Poplar roots	10	< 1–15 μg kg^{-1}	2–28 μg kg^{-1}
Air dust	1	140 μg kg^{-1}	440 μg kg^{-1}
Road dust	1	3.4 ± 0.9 μg kg^{-1}	—

of occupationally exposed persons have been investigated to determine the Pd content in urine samples. The results of these investigations will be published in a separate paper.[15]

In addition, some other sample materials could be analysed successfully (*cf.* Table 3). The investigated materials came from different projects which will not be discussed in detail here. A summary of the results is given here in order to demonstrate the suitability of the procedure presented. The contents for Pd and Au were found on the μg kg^{-1} level.

Discussion

The possibility of separation of Pd and Au from a sample matrix by means of a reductive co-precipitation with mercury has been known for a long time.[16,17] In principle, all elements that are more electropositive than mercury should be collected in mercury. Besides Pd and Au, also Ag, Rh and Pt belong to this type of element. However, the feasibility of the applied procedure is also dependent on the solubility of the reduced trace elements in mercury. The solubilities of Pd and Au are high (0.06 %m/m and 0.13 %m/m, respectively, at room temperature) and increase with rising temperatures, whereas the solubility of Pt is much lower (< 0.001 %m/m). Pt is deposited as a layer on the surface of the mercury droplet, which results in poor reproducibility of its recovery. The poor recovery for Ag is possibly caused by the fact that it is not reduced to the element under the working conditions. Otherwise, the solubility of Ag in mercury would be good enough (0.03 %mm at room temperature). Similar reasons may be encountered for the difficulty to determine rhodium.

Another critical point is the selection of a suitable reducing agent. The following conditions are essential for the agent: it should perform a selective reduction of mercury and noble metals from solutions containing other trace and matrix elements; it should form at least volatile reaction products; it should be available in high purity, *i.e.*, free from blanks of noble metals. A series of investigations with different agents proved formic acid as the most suitable compound, which reacts with formation of only H_2O and CO_2. When applying ascorbic acid yellow oxidation products were formed, which were surface active and prevented the formation of a mercury droplet.

Further difficulties might be caused by nitric acid and hydrochloric acid. Both acids are necessary for sample decomposition and are removed after digestion as far as possible by evaporation. Residual nitric acid fortunately is decomposed by formic acid during the reduction step. Thus, the passivation of the surface of the mercury droplet by nitrous oxides is prevented, which would otherwise affect the solubility of the noble metals. Chloride ions have to be removed, otherwise they would prevent the reduction of mercury by formation of non-dissociated $HgCl_2$ or poorly soluble Hg_2Cl_2. In this case a mercury droplet would not be formed.

Conclusion

The separation and enrichment procedure presented in this paper was successfully developed for biological and environmental samples. It was especially optimized for detection by TXRF, and led to extremely low detection limits of about 2 ng L^{-1} for Pd and Au in urine samples. Its main advantage is the almost complete separation of the analytes from the matrix and the high degree of enrichment, thus enabling a determination without interferences at highest sensitivity. Both metals form a thin layer on the quartz glass target used for the determination by TXRF. Corrections are not necessary, in contrast to the determination of Pd by ICP-MS even in the high resolution mode. On the other hand the presented method is time consuming in comparison with direct instrumental techniques. Thus, it may serve mainly as an independent method in order to control other analytical techniques. The procedure may offer some further possibilities. The mercury droplet with the separated and enriched Pd and Au can be evaporated in a quartz vessel. After that, the residue can be dissolved in a nitric acid–hydrochloric acid mixture and both elements can be determined using other sensitive instrumental methods, *e.g.*, ICP-MS or ETV-LAFS without matrix interferences. On the other hand, it may be possible to place the mercury droplet into the graphite tube of a GFAAS system. After evaporation of the mercury Pd and Au could be atomized and determined by GFAAS with high sensitivity. At the moment both possibilities are under investigation.

Acknowledgements

The authors thank the 'Bundesministerium für Bildung und Forschung (BMBF)' and the 'Ministerium für Schule und Weiterbildung, Wissenschaft und Forschung (MSWWF) des Landes Nordrhein-Westfalen' for financial support. They are also indebted to Dipl. Ing. K. H. Schaller (Institut für Arbeits-, Sozial- und Umweltmedizin, Universität Erlangen), PD Dr. H.-J. Ballach (Botanisches Institut, Universität Frankfurt) and PD Dr. F. Zereini (Institut für Mineralogie, Universität Frankfurt) for making the appropriate samples available.

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Paper b000471p