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Determination of palladium in airborne particulate matter in a German city

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Abstract The part of palladium in ambient urban air that is bound to particles and soluble in *aqua regia* was determined by means of sorbent extraction, coupled with graphite furnace atomic absorption spectrometry (GFAAS) and laser absorption fluorescence spectrometry (LAFS). Samples of about 200 m³ air were taken in a suburb of Berlin, Germany. The coupling of the selective and automated pre-concentration procedure for Pd as N,N-diethyl-N'-benzoylthiourea complex with the respective detection methods proved to be sufficiently sensitive. Severe interference with other matrix constituents, occurring mainly by direct LAFS detection, could be overcome and the detection limit was improved tremendously. The concentration of Pd in ambient air was determined to be in the range from 0.2 to 14.6 pg/m³.

Introduction

The extended use of palladium in automotive catalytic converters [1], in the chemical industry, and as constituents of dental and other alloys [2] has led to increasing concentrations of this metal in various parts of the environment [3]. Platinum group metals (PGMs) and other constituents are distributed as small particles in the stream of exhaust gases from automotive catalytic converters [4]. An increase of the palladium concentration in ambient air near frequently used roads is therefore expected. The average natural concentration of palladium in the continen-

tal earth crust is estimated to 15 pg/g [5]. Because palladium occurs mainly in mineral deposits, the palladium background in ambient air, with an average dust content of 100 µg/m³ [6], should therefore be far less than 15 pg/m³. In 1977 Schutyser et. al. [7] published average palladium concentration values in ambient air of 0.7 pg/m³.

Nevertheless, it is necessary to establish the present level of palladium in ambient air and to monitor possible future changes. For a quick and reliable determination, new methods must be developed, as previously used techniques, such as neutron activation analysis (NAA) [7] are too time consuming for routine analysis and also suffer from severe interferences.

The detection limits for palladium, using electrothermal atomization laser excited atomic fluorescence spectrometry (ETA-LAFA) and GFAAS, are in the pg range and are therefore suitable for palladium determination in airborne particulate matter. Complex matrices such as air particulate matter or road dust, however, cause an increase of the detection limit of several orders of magnitude [8]. A direct measurement of solutions derived from such matrices is therefore not possible. This also applies to other highly sensitive techniques such as ICP-MS [9] or NAA [10]. In response to these problems, several trace matrix separation procedures have been developed [11, 12]. The most successful separation procedure for ultra-trace levels of palladium appears to be the sorbent extraction of Pd(II) as a N,N-diethyl-N'-benzoylthiourea complex in a reversed phase micro column [13, 14]. The extraordinarily efficient and sensitive detection of palladium via coupling of this method with GFAAS (detection limits in the lower ng/L-range) and ETV-LAFA suggests that an air volume of approximately 100 m³ is sufficient for a successful determination of airborne palladium.

The enrichment procedure has been applied to a variety of complex matrices [15] such as road dust of different origin, sewage sludge ashes and plant material and has been validated by recovery functions and tracer experiments with the radioactive isotope ¹⁰⁹Pd [10]. Certified reference materials with complex matrices and environmentally relevant palladium concentrations are not avail-

Dedicated to Prof. Dr. D. Klockow on the occasion of his 65th birthday

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able to date and could therefore not be used for validation [9].

Experimental

Sampling. Sampling was performed using a micro filter device LVS 3 (Ströhlein, Kaarst, Germany). Glass fiber filters Nr. 10, diameter 50 mm, efficiency 99.97% (Schleicher und Schüll, Dassel, Germany) which are recommended by Ströhlein for the LVS 3 were used throughout the experiments. The filters were dried at 80°C to a constant weight. The dust content of the air was determined by weighing the filters before and after sampling. The sample volume was measured by a propeller anemometer which is built in the LVS 3. The error of the volume measurement is $\pm 2\%$. The throughput of air was approximately 2.4 m³/h and was supervised by a flowmeter.

Sample preparation. The loaded filters were treated with 2 mL of aqua regia in a high pressure asher (Paar, Graz, Austria). The applied time/temperature program is given in Table 1.

The resulting extracts were diluted with nitric acid (c HNO₃ = 0.7 mol/L) and subsequently filtered. The filtrate was evaporated to dryness and redissolved in nitric acid (c HNO₃ = 0.7 mol/L). The sample volume was adjusted to 10 mL. Transportation and storage of the samples were performed in glass tubes, which were steamed with nitric acid prior to use.

Blank values were tested by analysis of 4 unused filters, the average blank value was (3 pg \pm 3 pg)/filter. Calibration standards were prepared by stepwise dilution of a 1000 mg/L stock solution (Merck, Darmstadt, Germany) with nitric acid (c HNO₃ = 0.7 mol/L).

Determination of palladium. Palladium determination was performed using a laboratory built apparatus for ETV-LAFS [16] and a Perkin-Elmer 4100 ZL GFAAS spectrometer, equipped with Zeeman effect background correction, a transversally heated graphite atomizer (THGA), and an AS-70 furnace autosampler.

Table 1 Time/temperature program for the high pressure ashing of filters

Step	Temperature [°C]	Time [min]	Pressure [Mpa]
1	110	60	8
2	185	240	8
3	20	60	8

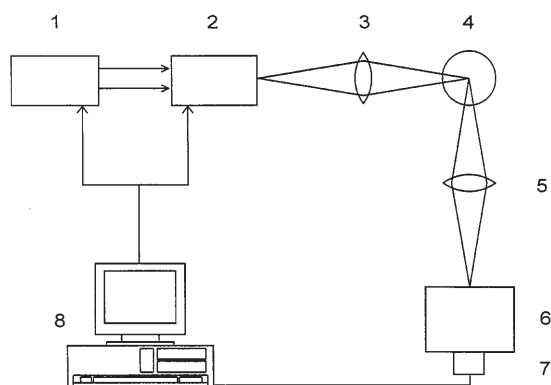


Fig. 1 Block diagram of the main parts of the ETA-LAFS setup. 1 – XeCl-laser, 2 – dye-laser and SHG-setup, 3,5 – quartz lenses, 4 – cup atomizer, 6 – monochromator, 7 – photo multiplier, 8 – system computer

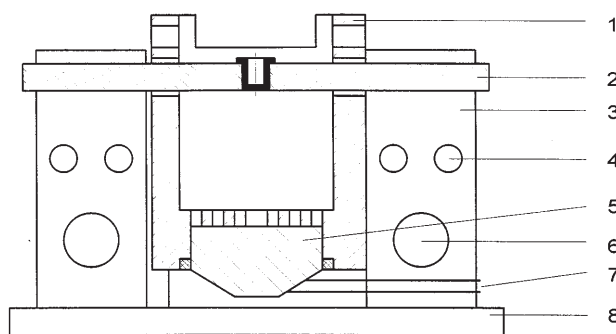


Fig. 2 Scheme of the cup atomizer. 1 – shield made from electro graphite, 2 – graphite cup between graphite rods, 3 – water cooled electrodes, 4 – cooling water inlet/outlet, 5 – graphite felt, 6 – electrical connection, 7 – argon inlet, 8 – ground plate made from insulating material

Table 2 Time/temperature program for the determination of palladium with ETV-LAFS

Step	Temperature [°C]	Ramp [s]	Hold [s]	Function
1	72	11.4	0	Drying
2	100	28.0	5	Drying
3	1000	4.5	5	Ashing
4	1000	0.0	15	Ashing/Laser activation
5	2100	1.8	3	Atomization/Measurement
6	2400	5.2	1	Cleaning

Figures 1 and 2 show the experimental setup of the ETV-LAFS device. Atomization was performed in a small pyrolytically coated graphite vessel, which was heated by a computer-controlled electric current of max. 500 mA. Table 2 shows the time/temperature program for the ETV-LAFS detection.

The detection was performed at an excitation wavelength of 276.310 nm and a fluorescence emission line at 351.694 nm. Standard addition as well as external calibration were used for quantification. The detection limits were calculated by the 3 σ method. σ is the standard deviation of a repeated measurement ($n = 10$) of the unspecific background fluorescence.

For the GFAAS detection of palladium, Perkin-Elmer hollow cathode lamps were employed as primary sources; the wavelength was set to 247.6 nm; the lamp current to 30 mA; the slit width (low) to 0.7 nm. (Perkin-Elmer, Überlingen, Germany).

Pre-concentration procedure. The detection devices were coupled to a previously developed fully automated selective pre-concentration procedure for palladium, which has been described in detail elsewhere [13, 14]. This procedure starts with the loading of N,N-diethyl-N'-benzoylthiourea [17] as a selective complexing agent for palladium onto a reversed phase C18 microcolumn (volume 10.2 μ L). Subsequently, the sample solution is passed over the column. After complex formation, a rinsing step with diluted nitric acid 6.5% (v/v) is performed to remove interfering matrix constituents from the pore volume of the column. The palladium complex and excess ligand are then eluted with 50 μ L of ethanol and directly introduced into the graphite vessel (ETV-LAFS) or the graphite furnace (GFAAS). The pre-concentration and separation procedure provides some exceptional advantages: independence of the sample acidity (up to 2.4 mol/L), sample and rinsing volume; easy removal of other metal ions: alkaline, alkaline earth, base metals, and even other PGMs do not interfere with the palladium pre-concentration up to a concentration of 10 g/L. The method is suitable for the measurement of ultra-trace levels of palladium even in solutions with high contents of interfering matrix con-

Table 3 Detection limits for palladium in different matrices

Method	Matrix		
	Aqueous solution [ng/mL]	Sample solution [ng/mL]	100 m ³ air [pg/m ³]
ETV-LAFS (10 µL sample solution)	0.1	1.6	160
SPE-ETV-LAFS (4 mL sample solution)	0.001	0.002	0.2
GFAAS (10 µL sample solution)	1	10	1000
SPE GFAAS (4 mL sample solution)	0.013	0.013	1.3

stituents. In addition to the removal of the matrix constituents, detection limits can be improved significantly. Table 3 shows the detection limits for GFAAS and ETV-LAFS with and without pre-concentration and trace/matrix-separation.

Results and discussion

The air samples were taken 5 m over the ground at a 1.5 m distance to the building of the Institut für Spektrochemie und angewandte Spektroskopie (ISAS) in Berlin-Adlershof. Table 4 shows the date of sampling, the sampled air volume, the dust content of the air and the determined palladium concentrations.

All measured concentrations of palladium were found to be significantly above the detection limits. Complete recovery of palladium in the enrichment procedure was proved by a recovery function ($c_{Pd} = 0-0.3 \mu\text{g/L}$), which showed a recovery rate of $100 \pm 6\%$. The precision of the palladium measurements was in the range of $\pm 15\%$. Due to the high palladium content, sample Nr. 14 was, in addi-

Table 4 Results of the palladium determination in ambient air

Nr. of sample	Date of sampling	Volume [m ³]	Content of dust [g/m ³]	Concentration of Pd in dust [ng/g]	Concentration of Pd in air [pg/m ³]
11	4/97	186.3	42.1	21.3	0.9
12	4/97	179.9	111.0	8.1	0.9
13	4/97	174.7	100.0	15.0	1.5
14	4/97	253.1	66.0	221.2	14.6
15	4/97	163.1	132.0	16.6	2.2
21	6/97	248.5	45.0	26.7	1.2
22	6/97	115.5	45.9	56.6	2.6
23	6/97	229.9	38.3	36.1	1.4
24	6/97	172.1	90.6	8.8	0.8
31	11/97	175.7	63.7	< 3.2	< 0.2
32	11/97	171.3	116.9	9.4	1.1
33	11/97	239.6	43.1	4.6	0.2
41	12/97	176.4	31.2	11.9	3.7
42	12/97	174.1	74.5	9.9	7.5
43	12/97	253.6	45.5	4.4	2.0

tion to the enrichment procedure, directly determined by ETV-LAFS and ETV-ICP-MS by means of standard addition. The conformity of the results was gratifying ($210 \pm 16 \text{ ng/g}$) and attests to the reliability of the proposed method.

The dust content of the air was between $31.2-132 \mu\text{g/m}^3$. This is the expected range for urban air samples [6, 18]. The palladium content in air was between 0.2 and 14.6 pg/m^3 . Weather and seasonal conditions, which were also monitored, did not seem to have had a noticeable influence on the results. The palladium concentrations are in the same range as comparative values for platinum, determined in 1991/92 by Alt et. al. [18]. Those were in the range of 0.02 to 5.1 pg/m^3 . Also the dust content of the air was comparable. Noticeable was the high concentration of palladium in sample Nr. 14. This may have been due to single particles with a high palladium content. A single spherical particle of palladium with a diameter of $10 \mu\text{m}$ would cause a palladium concentration of about 64 pg/m^3 in an air sample of 100 m^3 . Particles of precious metals of this size can be found in automotive exhaust gases [4] and cause variations in metal concentrations of some orders of magnitude, as Alt et. al. proved for platinum [18].

Conclusions

The introduction of palladium in catalytic converters for automotive exhaust gases has caused an increase of palladium concentrations in urban ambient air. Although the use of palladium catalysts in 1997 was still small compared to platinum and rhodium based catalysts, the concentration of palladium in air is similar to the platinum concentration at the beginning of the decade. A further increase is expected. Similar observations have been made with the determination of palladium in road dust. Dust samples collected in tunnels of the "Mittlerer Ring" in Munich, Germany, show an increase in palladium concentration from $21.8 \pm 3.5 \text{ ng/g}$ in 1994 to $100.5 \pm 15.1 \text{ ng/g}$ in 1997/98 [15]. This increase is much higher than the increase of the traffic density in the same period of time.

References

1. Rickert G, Rabinowitz H (1994) Neue Katalysatorentechnologien. Engelhard Technologies, Hannover
2. Reuling N (1992) Biokompatibilität dentaler Legierungen. Hanser Verlag, München
3. Helmers E, Schwarzer M, Schuster M (1998) Environ Sci & Poll Res 5(1):44
4. Lüdke Ch, Hoffmann E, Skole J Artelt S (1996) Fresenius J Anal Chem 355:261
5. Handbook of Chemistry and Physics (1993) 74th edit. CRC Press, Boca Raton, p 9
6. Hupfer P, Chmielewski F-M (1990) Das Klima von Berlin. Akademie Verlag, Berlin
7. Schutyser P, Govaerts A, Dames R, Hoste J (1977) J of Radiochemistry 37:651
8. Tilch J, Lüdke C, Hoffmann E (1996) Fresenius J Anal Chem 355:913

9. Lustig S, Schramel P, Quevauviller Ph (1999) Anthropogenic Platinum-Group Element Emissions. Their Impact on Man and Environment. Zereini F, Alt F (eds) Springer-Verlag Berlin Heidelberg New York, p 153
10. Schwarzer M, Schuster M, von Hentig R (2000) Fresenius J Anal Chem (in press)
11. Mizuike A (1983) Enrichment Techniques for Inorganic Trace Analysis. Springer, Berlin Heidelberg New York
12. König K-H, Schuster M (1994) Platinum Group Metals, Handbook on Metals in Clinical and Analytical Chemistry. Seiler HG, Seiler A, Sigel H (eds) Marcel Dekker, New York, Basel, Hong Kong, p 521
13. Schuster M, Schwarzer M (1996) Anal Chim Acta 328:1
14. Schuster M, Schwarzer M (1998) Atomic Spectroscopy 19(3): 121
15. Schuster M, Schwarzer M, Risse G (1999) Anthropogenic Platinum-Group Element Emissions. Their Impact on Man and Environment. Zereini F, Alt F (eds) Springer-Verlag Berlin Heidelberg New York, p 173
16. Tilch J (1993) CANAS'93, Hrsg. Dittrich K, Welz B. Universität Leipzig, p 909
17. Schuster M (1992) Fresenius J Anal Chem 342:791
18. Alt F, Bambauer A, Hoppstock K, Mergeler B, Tölg G (1993) Fresenius J Anal Chem 346:693