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Determination of Pt in urine of tram drivers by sector field inductively coupled plasma mass spectrometry

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Abstract

The Platinum Group Elements (PGEs) used in automotive catalytic converters are partly emitted into the air during use and can enter the human respiratory system. Due to the increasing use of automotive catalytic converters, the importance of this problem cannot be overlooked.

The goal of this investigation was to determine the concentration of Pt in the urine of individuals occupationally exposed to urban air with heavy traffic. Sector field inductively coupled plasma mass spectrometry (SF–ICP–MS) was used for determination of Pt in the urine of tram drivers. 38 and 34 subjects were investigated in Vienna and Budapest, respectively. Samples were taken from the tram drivers both before and after the shift.

The results for Pt were compared to those from a previous study performed by our team. The comparison showed that the concentration medians were 4 times higher than the previous ones. Moreover, the values in Budapest were about twice as high as those from Vienna. A partly significant change could be observed between the two sets of data: before, and after the shift.

Keywords: Platinum; Urine; Sector field inductively coupled plasma mass spectrometry; Tram drivers; Urban settings

1. Introduction

Platinum has been well known for being an important metal for catalyst production. The so-called three-way car catalytic converters contain Pt, Pd and Rh at different concentrations, with the Pt/Rh ratio varying from 10/1 to 5/1. The conventional three-way catalysts contain noble metals in bulk concentration of 0.10–0.15% (w/w).

Due to the thermal and mechanical deterioration of the catalyst structure, these noble metals are released and emitted into the air. In the framework of the CEPLACA project [1,2], the concentration of Pt in the exhaust fumes of Ford and Seat cars equipped with different catalysts amounted to approximately 43–133 ng/km in case of the new cars and 5.7–162 ng/km for cars with at least 80 000 km. It should be emphasized, however, that the water-soluble part was in all cases less than 10%. Another important observation made during this investigation was that the emission of Pt increased with prolonged operation time, particularly in case of diesel cars.

In order to follow the fate of inhaled Pt in the human body, Caroli et al. [3] analysed the urine samples of 310 schoolchildren aged between 6 and 10 years from urban and suburban areas of Rome. Analyses were performed by sector field inductively coupled plasma mass spectrometer (SF-ICP-MS) after the UV irradiation and oxidation of the samples. The mean concentration values of Pt were found to be 1.1±1.1 ng/L (the Pt concentration related to creatinine amounted to 0.9±1.1 ng/g). No correlation

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between Pt concentration in urine and traffic density was found. Presumably, this may be the consequence of the long-range transportation of fine particles (respirable fraction) of car exhaust fumes.

Schierl [4] presented the urinary Pt concentrations of 29 bus drivers, 10 taxi drivers, 13 car mechanics, 12 members of scientific staff, and 12 industry workers without occupational exposure to Pt and 86 employees of hospital pharmacies. Spot urine samples were analysed by adsorptive voltammetry technique following the decomposition of organic compounds by UV photolysis in the presence of H_2SO_4 and H_2O_2. Data obtained for 178 individuals showed a mean value of 6.5 ng/g creatinine and exhibited a non-normal distribution. 96% of the individuals had a Pt concentration of less than 20 ng/g creatinine. All of the seven persons with urinary Pt concentrations above 20 ng/g had dental gold alloys, which can be an important (but not unique) source for human Pt exposure.

In a previous study of ours [5], Pt was determined in urine samples of 100 subjects from Budapest and 100 subjects from Vienna. The subjects were chosen from hospital patients without having regard to occupational background. The median values for Budapest and Vienna were 7.8 and 3.2 ng/g creatinine, respectively. The upper range of the analytical results was as high as 40 ng/g creatinine.

The determination of Pt traces using inductively coupled plasma mass spectrometry (ICP-MS) was partly hampered because of the spectral overlap caused by HfO^+. This interference, however, can be either mathematically corrected in case of environmental samples [6] or can be neglected in case of biological samples [7]. It is possible to eliminate the matrix through column separation [8] or electrothermal vaporisation [9]; however, the reported investigations were carried out at the μg/L to sub-μg/L concentration level. The method described by Dong et al. [8] has a detection limit of 3.2 ng/L, that of Fan et al. [9] could not detect Pt in urine at the normal concentration at all; the detection limit was 5400 μg/L.

Due to the observations and results mentioned above, as well as the fact that in Hungary the age of cars equipped with catalytic converters is about twice of those in western European countries, the aim of this investigation was to compare the two urban settings of Vienna and Budapest as regards exposure to Pt through the analysis of urine samples of tram drivers working on routes with high automotive traffic density, and to assess the variations in Pt concentration caused by the work shift.

2. Experimental

2.1. Sampling of urine

In Vienna and Budapest, 34 and 38 tram drivers, working on tram routes with high automotive traffic density, were chosen for sampling, respectively. Two (before and after the shift) urine samples were taken from each tram driver in Vienna and Budapest. The samples were placed into 15-mL polypropylene tubes, which had been previously rinsed with 2 mol/L HNO_3 and subsequently with high purity water. Samples were stored at −20 °C prior to analysis. Each sample consisted of three 15 mL-subsamples, one for the Pt determination, one for the creatinine determination, and one as spare sample.

2.2. Sample preparation

The method described is a modified version of that published by Caroli et al. [3]. After thawing, the samples were homogenised by means of a Vortex shaker at 3000 rpm for 5 min. In order to decompose the organic matrix, 5-mL aliquots of urine were subsampled from each vial, transferred into another chemically decontaminated polypropylene tube and added with 2.0 mL of 30% H_2O_2 (Suprapur grade, Merck, Darmstadt, Germany) and 1.0 mL of 65% HNO_3 (Suprapur grade, Merck, Darmstadt, Germany). The latter was previously purified in an all-PTFE sub-boiling distillation unit (Maassen, Germany). The specimens were subsequently heated at 75 °C for 16 h, resulting in clear sample solutions. Finally, to each 1.00 mL aliquot of these solutions 10 μL of a 50 mg/L Au internal standard and 8.99 mL high-purity water with 16.8 MΩ cm specific resistivity (PUR1TE still plus) were added. Three blank solutions were also prepared using the same procedure. Calibration solutions were prepared daily from single element stock solution of 1000 mg/L of Pt (Merck, Darmstadt, Germany).

The creatinine determination was carried out in clinical laboratories of both cities, according to well established routine analytical methods.

2.3. Pt determination

The determination of Pt was carried out by means of sector field (SF) ICP-MS (Element 2, ThermoFinningan, Bremen, Germany). The operating conditions are summarized in Table 1.

2.4. Quality control

As there is a lack of fit-for-purpose certified reference materials for the determination of Pt in urine only the recovery of Pt could be checked. To this end, a pooled urine sample was spiked with known amounts of the element and analyzed as the normal samples. The spiked concentrations were 10, 20, and 30 ng/L. The spiked solution was prepared from single element standard (Merck).

Table 1
Operating conditions of the SF–ICP–MS

Forward power	1180 W
Outer gas (Ar)	1.00 L/min
Intermediate gas (Ar)	16.0 L/min
Aerosol carrier gas (Ar)	0.83 L/min
Sample uptake	0.3 mL/min
Nebuliser	Meinhard
Spray chamber	Double pass
Sampler cone	Ni, 1.0 mm orifice
Skimmer cone	Ni, 0.7 mm orifice
Analytical isotopes	Pt-195, Internal standard Au-197
Data acquisition	Peak jumping
Dwell time	0.1 s
Replicates	15