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Platinum in indoor settled dust matter (homes and cars)

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ABSTRACT

This paper presents a method for Pt analysis in indoor (homes and cars) settled dust, used as passive samplers, and the results relative to samples collected in the Sicilian area are used to evaluate the magnitude and distribution of concentrations inside common environments and the possible origins of the considered contaminant. The concentrations of platinum in settled indoor dust were measured by differential pulsed voltammetry (DPV). Concentrations of Pt in homes are in the range from 30 to 1460 μg kg^{-1} d.w. while, in the vehicles from 30 to 1750 μg kg^{-1} d.w. Considering the geoaccumulation index (I_{geo}), 42% of the settled dust sampled in homes could be classified as *extremely contaminated*. Only in two cases, the I_{geo} indicates *extremely contaminated* and the analyzed settled dust sampled in the cars, about 11% corresponds to *practically unpolluted*. Considering the Pt concentrations found by us in apartments and cars, it is possible to estimate a daily total uptake of 10 and 4 ng respectively. Compared to the dietary PGE intake, which is estimated about μg per day level, or uptake by drinking water, the amount uptake by the indoor dust (homes and cars) may be considered negligible.

1. Introduction

Different statistics on the European people's way of living [1] show that they spend 90% of their time indoors, 6% outdoors and 4% in transportation (car, bus, train or plane, etc). As a consequence, indoor air quality has a preponderant role in evaluation of people exposure to air hazardous substances for assessing total exposure to them. Several researchers studying inorganic (metals, etc) [2] and organic (PAHs, pesticides, etc.) indoor pollutants [3–8] have hypothesized that particulate matter may be directly linked with health effects, especially in children and adults with chronic lung disease [9,10]. However, while organic pollutants can be reduced by photochemistry [11,12] or biologic mechanism, inorganic pollutants are persistent in the environment with resulting environmental and human harms [13,14]. Some of these metals are mutagens and carcinogen and are associated with various disorders (cardiovascular, nervous system, blood and bone diseases, kidney failure, gingivitis, tremors, etc.) [15]. In 2011, International Agency for Research on Cancer (IARC, 2011) [16] categorize some heavy metals based on their potency to cause cancer. People may be exposed to metals through oral ingestion, inhalation and or dermal contacts and also, significantly, through indoor dust inhalation and ingestion (EPA, 2011) [17].

Generally, indoor environments can be contaminated by platinum dust in several ways: as infiltration from outdoor sources majorly from vehicle emissions; transfer of particles by wind or shoes and; rarely from indoor sources. About vehicle emissions, catalytic converters for cars containing PGEs (platinum-group elements) were largely used in all new car models produced in European countries since 1993 to remove or reduce pollutant substances as carbon monoxide, hydrocarbons, NO_x, etc. from exhaust gas. Unfortunately, during their use, the catalytic converters are chemically and physically stressed by speedy changing oxidative/reductive conditions, high/low temperatures and mechanic abrasion of the Al_2O_3 washcoat causing the emission in various particulate forms (PM_{10}, $PM_{2.5}$, PM_1) of a part of metals of the catalyst that are transferred into the environment [18–20]. At present, it is well known that car converter use is the major source of emission of platinum into the environment, with a probable release of 0.5–1.4 ton per year [21–23]. Platinum, once released to the air, travels short distances, due to its mass and is deposited along bordering traffic routes. Higher concentrations of Pt in environment are clearly correlated with a higher traffic density and with time since the introduction of catalytic converters. Platinum once released by exhaust pipes is deposited along roadways, on adjacent building, soils and then might enter the vegetation and, hence, the food cycle [6,24–26]. The settled amount is a function of concentrations of Pt in air [24]. Since this metal may be also dispersed in silt, soil, water and accumulated in plants [27], a rapid accumulation in the environment was observed: in German soils a distinct increase of Pt concentrations, between 1999 and 2005, nearly alongside heavy traffic roads was observed [28], with enrichment factors between 2.1 and 8.9, once even a factor of 15 was found. Studies on road dust of a highway tunnel in the north of Graz, (Styria, Austria) showed that during four years the average concentration of Pt increased from 56 to 82 ng/g

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[19]. Parallel to these findings, especially Pt and Rh concentrations were found to be elevated in airborne dust [29,30].

These data made concern arise about potential environmental and health risks [31]: there are experimental evidences that after ingestion and inhalation of Pt compounds, the metal can be found in various body organs [32]. People exposed to exhaust gas from heavy automobile traffic showed a quantifiable increase of platinum in the urine compared with subjects exposed to low-traffic environments [33]. Although Pt is mostly released in elemental and oxide form, also it can be transformed into soluble compounds by complex formation with natural and or environmental ligands and can enter in organisms and in the food chain [9,25].

Inhalation of dust can occur when it is suspended by activities such as cleaning, playing or walking through a room. Contaminant levels in house dust are generally higher than in yard and soil because indoor they are protected from environmental degradation and losses; compounds associated with dust persist for long periods.

Although in the past platinum has been considered inert and harmless for human health, risks of platinum species have been recently investigated: as metal, Pt is non-toxic and non-allergenic, but some of its compounds, especially the chlorinated ones, are very toxic and allergenic [34,35]. There is evidence that, in the environment, metallic platinum can be transformed into soluble species by complex formation with natural ligands which can enter the food chain [36,37]. A research on exhaust gases and road particulate to simulated lung fluids established possible health risks due to the likely formation of Pt-chloride complexes in the respiratory tract [19]. Information of the acute toxicity of some Pt-chlorinated salts and evidence of DNA damage due to Pt exposure have been observed both in vitro and in vivo [38]. Only few compounds (cisplatin, and carboplatin, etc) are used as antineoplastic agents in the medical treatment of several tumors [39,40].

Cars represent a micro-environment with potentially high levels of traffic-related pollutants which can flow into indoor cabin with passenger. This is associated with the highest levels of exposure among commuting vehicles because of the low body position and the low intake point of the ventilation system that results in a close contact with the exhaust of other vehicles.

Elevated hazardous material levels in cars were related to locations with high traffic volumes and combustion engine emissions from other vehicles [41]. Several researchers have reported that drivers were exposed to higher levels of traffic-related PM and endured higher health risks than the general population [42,43].

Indoor air quality is usually investigated by means of automatic instruments that sample and analyze various substances. As a result, times, costs and difficulty in managing the monitoring of a great number of indoor stations are obvious; therefore, in the majority of case, indoor pollution monitoring is partial to few stations, located in area at risk. Also, a realistic difficulty in analyzing environmental pollutants is either near very low concentration or below the detectable analytical limits at which they often occur.

There are very few studies [5] engaged in evaluating the distributions of Pt in homes and no data are available on Pt in car settled dust. Until now, no previous work in literature had assessed the potential human health risks posed by platinum from indoor environments (homes, cars, etc.). The purpose of this work is to extend the voltammetric analytic method of Pt to the indoor settled dust samples, used as passive sampler, and to use results from samples collected in the Sicilian area to evaluate the magnitude and distribution of concentrations inside common environments and the possible origins of the considered contaminant. Other objectives of this study were to investigate the degrees of contamination of indoor settled dust by platinum trace using geo-accumulation index and to evaluate the potential health risk to people of this element.

Indoor dust in buildings and car interiors consists in particles settled onto objects, surfaces, floors, and carpeting and including also soil particles that have been tracked or blown into the indoor environment from outdoors as well as organic matter.

The ingestion of settled dust is a possible route of exposure for both adults and children to pollutants. Children, in particular, may ingest considerable quantities of settled dust due to their tendency to play on the floor indoors and their tendency to mouth objects or their hands. Children may ingest settled dust through deliberate hand-to-mouth movements, or unintentionally by eating food that has dropped on the floor. Adults may also ingest settled dust that adheres to food, cigarettes, or their hands. Thus, understanding settled dust composition is an important part of estimating overall exposures to environmental chemicals.

There are many advantages of using settled indoor dusts as passive accumulators [3,7]. The settled dust are certainly efficient for determining exposure, they essentially give information on the average variation in time and space of the concentrations of contaminants in the considered area.

This investigation characterizes human real exposure to Pt indoor stations and compares indoor levels to the corresponding outdoor levels. Our study has been carried out in the Sicilian area which is considered to be a tourist and commercial region with a population about 5 million.

Chemical monitoring plays an important role in assessing the human being exposure to platinum and the health risks associated with the exposure. Through suitable researches and full performance of analytical quality control, specific concentration ranges for Pt can be obtained, which can be used to distinguish between background, environmental and occupational exposure.

Analysis of Pt in environmental matrices is often complicated by a number of other compounds present in the environmental samples.

Several analytical techniques, such as atomic absorption spectrometry (AAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP–AES) [44,45], inductively coupled plasma mass spectrometry (ICP–MS) [46–48] and high performance liquid chromatographic (HPLC) analysis [49] were applied for the determination of platinum in different matrices. An ordinary problem when analyzing environmental samples is that, some methods suffer from severe matrix effects, especially at ppb or lower concentration levels of analytes in complex matrices [46]. A direct determination of Pt using ICP–MS, for instance, is difficult [46], due to interfering signals and problems related to isolating this metal from the matrix.

In this work, we used the differential pulsed voltammetry (DPV) to measure the concentrations of platinum in settled indoor dust. In acidic solution, formaldehyde and hydrazine can be condensed to produce the corresponding hydrazone, which forms a complex with Pt(II). At potential as −0.8 V versus Ag/AgCl it reduces overvoltage related to the hydrogen formation giving a peak whose intensity is directly proportional to Pt concentration.

2. Experimental part

2.1. Quality control and quality assurance

All the laboratory glassware was cleaned before use by rinsing three times with HNO_3 (2%) and three times with water purified by Milli Q System. The reproducibility of the sampling was preliminarily checked by analyzing for Pt three different samples of settled dust collected at different points of the same indoor environment. The standard deviation on sampling (about 10%) with respect to that of the analytical process was similar. All the analyses of Pt in indoor dust were repeated three times and the relative standard deviation results ranged from 1 to 7%.

Quantification limit for Pt in the indoor settled dust, calculated on the basis of 10 determinations of the blanks as ten times the standard deviation of the blank is 30 μg kg^{-1} d.w. The Pt coefficient of variation (as a measure of analytical precision) was within 5%, based on three