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Platinum, palladium, and rhodium in airborne particulate matter

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Measurable quantities of platinum, palladium, and rhodium, even in remote areas of the planet, evidence the global nature of pollution with these metals, mostly from catalytic converters of modern vehicles (other sources are jewellery production, chemical industry, and anticancer drugs). The amount of the platinum group metals (PGMs) emitted from automobile catalysts varies with the type, age, and condition of the engine and the catalyst, as well as the style of driving. Current literature suggests that the concentrations of these metals have increased considerably over the last twenty years, palladium concentrations in particular, as it has been proved more effective catalyst than platinum. However, whether and to what extent the emitted PGMs are toxic for people is still a controversy. The potential health risk from exposure to these elements is most likely for those living in urban environments with busy roads or along major highways. Because of the importance of PGMs and their trace levels in particulate matter, sensitive methods are required for reliable determination. This review discusses particular steps of analytical procedures for PGM quantification in airborne particulate matter and addresses the common preparation, detection, and determination methods.

KEY WORDS: automotive catalytic converter; ICP-MS; microwave digestion; platinum group metals; spectral interferences

Along with osmium (Os), iridium (Ir), and ruthenium (Ru), platinum (Pt), palladium (Pd), and rhodium (Rh) are transitional metals of the periodic system of elements that belong to the platinum group. Platinum was brought to Europe in 1735 from today's Colombia and was described in literature in 1748. English chemist W. H. Wollaston, who devoted his work to the study of natural platinum noted that there were metals of very similar nature to crude platinum. In 1803, he discovered palladium and rhodium. In 1804, S. Tennant, a friend of Wollaston's, discovered two more platinum group metals (PGMs): osmium and iridium. Osann, a chemistry professor, found a new residual element in natural platinum and called it ruthenium (Latin name for Russia). His former teacher Berzelius, however, expressed doubts, and Osann retracted his discovery. In 1844, a Russian chemist Klaus confirmed Osann's discovery of rhutenium in a larger sample of insoluble natural platinum residue (1).

Platinum, palladium, and rhodium are rare in the Earth's crust, with estimated concentrations of 0.06–0.4 µg/kg (2).

Platinum and its alloys are used in the glass industry to obtain very clean glass. Platinum is also used as a catalyst in many reactions such as hydrogenation, dehydrogenation, isomerisation, dehydration, cyclisation, oxidation (e.g. ammonia in nitric acid) (3). It is also used as a catalyst in reactions that increase the octane number of gasoline and various other fuels. Except as a combustion catalyst, platinum is also used as a catalytic converter for the removal of incomplete combustion residues in automotive exhaust systems. Large amounts of platinum are used in dentistry and the production of various medical tools and laboratory equipment (such as pots, pans, and tweezers). It is also used for making jewellery (3).

Palladium too has a widespread application. It is also used for electrical contacts, especially in telephones. Its alloys are used to produce resistant wire (Pd-Ag), thermocouples (Pd-Pt-Au), jewellery (Pd-Ru-Rh), and dental casts (4).

Rhodium is mainly used as an alloying addition of platinum and palladium, because it increases their hardness. Such alloys are used as shells of high temperature gas and electric laboratory furnaces and for welding electrodes in space technology. Due to corrosion resistance, good conductivity, and low transitional resistance, they are also used for making electrical contacts and switches. Rhodium alloys are also used by goldsmiths. Elementary rhodium is used for electroplating mirrors for various optical devices, because it gives a very hard and highly reflective layer. Rhodium powder is toxic and its soluble salts even more so. The maximum levels of rhodium and its salts in production plants are 0.1 mg/m^3 and 0.001 mg/m^3 respectively (4).

AUTOMOTIVE CATALYTIC CONVERTERS

The first automobile Pt–Pd catalytic converters from the 1970s gradually evolved to also utilise Rh (5, 6). These

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three-way converters consist of a metal box with a cordierite ceramic honeycomb coated with Pt, Pd and/or Rh (Figure 1) (7). Earlier two-way catalytic converters were called oxidation catalysts, as they oxidised carbon(II) oxide and hydrocarbons (unburnt and/or partly burnt fuel) into carbon(IV) oxide and water. They are still used in diesel engines.

Three-way catalytic converters, in turn, can also reduce oxides (NOx, x=1, 2) to elementary nitrogen and oxygen (8), as follows:

$$2NO \rightarrow N_2 + O_2$$

$$2NO_2 \rightarrow N_2 + 2O_2$$

$$2CO + O_2 \rightarrow 2CO_2$$

$$C_nH_{2n} + \frac{3n}{2}O_2 \rightarrow nCO_2 + nH_2O$$

For these processes to take place the operating temperature should be 300–800 °C. Hot toxic fumes from the engine pass through the honeycomb containing the catalyst layer, which reduces the activation energy and increases the speed of chemical reactions. However, catalysts wear out with time and enter the environment along with exhaust gases.

This emission of nanocrystalline PGM particles depends to a large extent on engine operating conditions, age and type of catalytic converter, PGM content, pH, and the type of fuel additive (9). PGM emissions can increase in unfavourable operational conditions like misfiring or excessive heating, which can destroy the converter. The emission mechanism and the form PGM takes in automobile exhaust are still unclear, but it is generally believed that the major cause is mechanical erosion of the converter surface. Mitra and Sen (10) suggest that more than 50 % of global Pt, Pd, and Rh is released through automobile catalytic converters. Other important anthropogenic sources are mining and fossil fuel burning.

PARTICULATE MATTER AND PGMs

Released Pt, Pd, and Rh attach to particulate matter (PM), which is a mixture of various organic and inorganic compounds (metals, organic compounds, ions, adsorbed gases, and carbon) suspended in the air. They vary in shape, size, density, and origin (natural and anthropogenic). Physical and chemical properties of PM affect their behaviour in the air, deposition, distribution, and transport (11). Primary particles are those emitted directly from the source, while secondary particles are generated in the atmosphere from gaseous precursors such as sulphur(IV) oxide (SO_2), nitrogen(IV) oxide (NO_2), ammonia (NH_3), and volatile organic compounds (VOC). Particulate matter is classified into fractions based on equivalent aerodynamic diameter, which is the diameter of a sphere with density of 1 g/cm^3. The PM_{10} fraction is a thoracic or inhalable fraction that includes all PM with aerodynamic diameter lower than 10 μm. The $PM_{2.5}$ fraction is called respirable and has aerodynamic diameter lower than 2.5 μm, whereas the PM_1 fraction includes all particles of aerodynamic diameter lower than 1 μm and can reach as deep into the lung as the alveoli (11, 12).

These PM fractions are often monitored for adverse effects on human health and are primarily associated with heart and lung diseases (13, 14). PGMs from catalytic converters are released into the environment as finely dispersed nanoparticles or washcoat particles (15, 16).

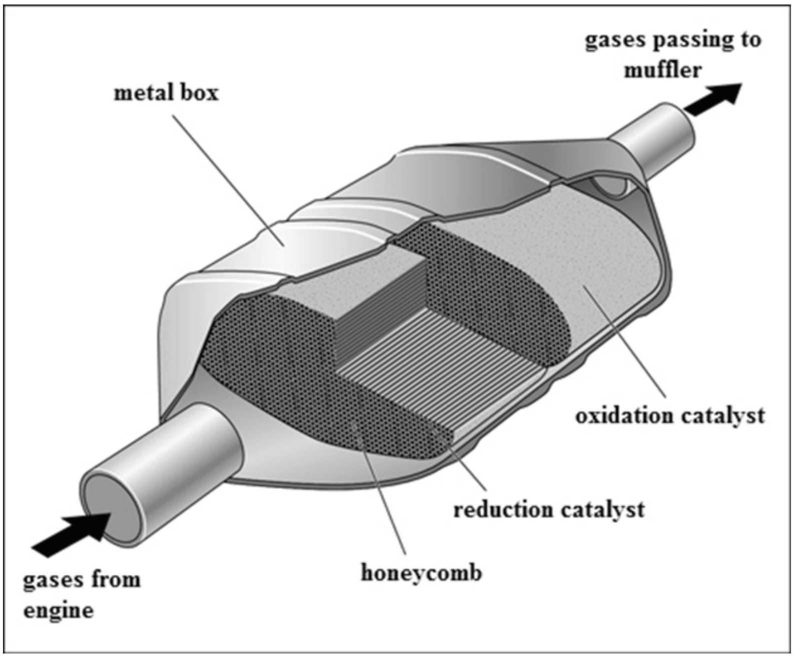

Figure 1 Parts of the automotive catalytic converter (adapted from https://www.dummies.com/wp-content/uploads/130970.image0.jpg)

METHODS FOR DETERMINING PGMs IN PM

Determination of PGMs requires analytical methods of high sensitivity and selectivity, especially if they need to be quantified. Quantification most often relies on atomic absorption spectrometry (AAS) (17–19), atomic emission spectrometry (AES) (19, 20), and mass spectrometry (MS) (21–34). Samples analysed by these methods must be in liquid state. Therefore, the key step is their preparation and efficient digestion.

Particulate matter sampling

Samples of particulate matter are collected by passing a known volume of air through various types of filters such as membrane, quartz, Teflon, and glass fibre. There are two types of sampling devices: high volume samplers (HVS) and low volume samplers (LVS) (35, 36). Depending on the type used and fractions of particulate matter collected, sampling time can vary from a few hours to a week.

Preparation of PM samples containing PGMs

Filters with collected samples of particulate matter are digested with acids by microwave-assisted digestion (at high pressure and temperature) or thermal digestion. Various acids or acid mixtures and various high pressure instruments are used for digestion of samples. For example, Zereini et al. (22) report adding aqua regia and the standard of a selected metal isotope (high percentage of purity) to samples to accelerate preparation and in order to accelerate the preparation time, they used microwave digestion. When aqua regia is evaporated nearly to dryness hydrofluoric acid is added and then nitric acid is added several times to fully eliminate fluoride. Other authors have also reported using this preparation method to determine PGMs in particulate matter (21, 29, 30). Other authors (15, 16, 31), in turn, report using the NiS fire assay with isotope dilution. Rinkovec et al. (28) report using high temperature and pressure microwave digestion system with acid digestion for PM_{10} samples.

Instrumental methods for determining PGMs in the environment

The most common method for determining PGMs in particulate matter is inductively coupled plasma mass spectrometry (ICP-MS). However, it is quite demanding due to spectral interferences from the matrix, which is rather complex (see Table 1 for interferences for Pt, Pd and Rh). In order to remove them, samples are often prepared using methods of isotope dilution and various types of purification (cationic and anion exchange). Sometimes they can be removed with special mathematical equations, such as the one reported by Gómez et al. (37). Molecular interferences can also be efficiently removed by collision or dynamic reaction gases (29, 38, 39). Bozlaker et al (40) reported using a dynamic reaction cell (DRC-q-ICP-MS) to detect metals in the PM_{10} and $PM_{2.5}$ fractions collected in an underwater tunnel with two traffic lanes. Zereini et al. (22) used isotopic dilution (ID-ICP-Q-MS) for more accurate quantification of Pt, Pd, and Rh. Other authors (15, 21, 27), in turn, used sector field SF-ICP-MS in high resolution mode. Among them, Hays et al. (27) reported detection limits of 0.01-2 $\mu g/m^3$ but did not specify to which type of filter they applied. Pan et al. (23) reported ICP-MS detection limits for Pt, Pd, and Rh on quartz filters of 3.49 pg/m^3, 60.6 pg/m^3 and 0.44 pg/m^3, respectively, explaining the high Pd detection limit with filter contamination with Zn, which may generate additional spectral interference with chlorides in solution ($^{70}Zn^{35}Cl$, $^{68}Zn^{37}Cl$). A similar explanation was proposed by Rinkovec et al. (28) for Pt, Pd, and Rh limits of detection on quartz, cellulose nitrate membrane, and glass fibre filters.

LEVELS OF PGMs IN THE AIR

Table 2 lists average mass concentrations of Pt, Pd, and Rh in particulate matter reported across the world. Most of these studies focused on the PM_{10} fraction and to a smaller degree on the $PM_{2.5}$ fraction in cities with high traffic density such as Gothenburg, Sweden (37, 41), Rome, Italy (42), Mexico City, Mexico (15, 30), Buenos Aires, Argentina (43), Vienna, Austria (21), Houston (40) and Raleigh (27), USA, Zagreb, Croatia (32), Frankfurt, Germany (22, 44, 45), and Beijing (23, 29), Guangzhou (23), and Xinjiang (33), China. Only one focused on rural locations in Germany (Deuselbach, Neuglobsow) (22).

In Germany, annual mass concentrations (averaged for 2008 and 2009) in the PM_{10} fraction in Frankfurt were significantly higher than at the rural station in Neuglobsow. Yet, even though mass concentrations are lower in rural

Table 1 Spectral interferences for Rh, Pd, and Pt (34, 35)

Isotope	Abundance (%)	Interference	Abundance (%)
^{103}Rh	100	$^{87}Rb^{16}O$	27.91
		$^{206}Pb^{2+}$	24.10
		$^{63}Cu^{40}Ar$	68.91
		$^{68}Zn^{35}Cl$	21.00
^{105}Pd	11.14	$^{40}Ar^{65}Cu$	30.71
		$^{88}Sr^{16}O^{1}H$	82.37
		$^{89}Y^{16}O$	99.76
^{195}Pt	33.80	$^{179}Hf^{16}O$	13.64

Table 2 PGM mass concentrations in particulate matter in cities around the world

City, country	Sampling period	Location	Fraction	γ(Pt) (pg/m^3)	γ(Pd) (pg/m^3)	γ(Rh) (pg/m^3)	Ref.
Frankfurt, Germany	1988−1998	roadside	PM$_{10}$	0.9–246		0.2–15	(44)
Rome, Italy	1998/1999	urban	PM$_{10}$	15.5	56.7	3.1	(42)
Gothenburg, Sweden	1999	high traffic	PM$_{10}$	14.1	4.9	2.9	(41)
			PM$_{2.5}$	5.4	1.5	1.6	
		low traffic	PM$_{10}$	2.1	1.8	0.6	
			PM$_{2.5}$	2.7	1.4	0.5	
Rome, Italy	1999/2000	downtown	PM$_{10}$	8.1	42.7	2.2	(37)
		ring-road		8.6	54.9	3.0	
Gothenburg, Sweden		downtown	PM$_{10}$	13.1	4.6	2.7	
		ring-road		4.1	1.6	0.8	
Madrid, Spain		downtown	PM$_{10}$	7.3		2.8	
		ring-road		17.7		4.6	
Buenos Aires, Argentina	Mar 2001	urban, traffic	PM$_{10}$	2.3–47.7		0.3–16.8	(43)
Frankfurt, Germany	2001/2002	main street	PM$_{10}$	23	15	4	(45)
		side street		6	6	1	
		rural area		5	3	1	
Boston, USA	2002/2003	main street	PM$_{10}$	9.4	11.0	2.2	(16)
		side street		6.2	7.1	1.3	
Mexico City, Mexico	2003	urban traffic	PM$_{10}$	9.3	11.0	3.2	(15)
Raleigh, USA	Oct – Dec 2006	near highway	PM$_{10}$	20.0	29.0	1.0	(27)
Beijing, China	Oct – Dec 2007	urban, traffic	PM$_{10}$	6.22–24.3		1.16–8.60	(23)
Guangzhou, China		urban, traffic	PM$_{10}$	7.68–12.2		2.15–5.15	
Frankfurt, Germany	2008/2009	roadside, urban, traffic	PM$_{10}$	12.4	43.9	3.2	(22)
			PM$_{2.5}$	9.4	16.1	1.8	
Deuselbach, Germany		rural area	PM$_{10}$	2.0	2.1	1.2	
Neuglobsow, Germany		rural area		1.9	2.6	0.3	
Vienna, Austria	2009 – 2011	main street	PM$_{10}$	9.9	10.6		(21)
			PM$_{2.5}$	2.3	4.9		
Mexico City, Mexico	2011	urban traffic	PM$_{2.5}$	45.8			(30)
Houston, USA	Nov 2012 – Jan 2013	fan room ambient air	PM$_{10}$	15.1	23.1	3.8	(40)
			PM$_{2.5}$	4.5	11.1	1.5	
		tunnel ambient air	PM$_{10}$	61.1	214.4	36.3	
			PM$_{2.5}$	30.1	91.1	12.5	
Zagreb, Croatia	Apr 2015 – Mar 2017	background	PM$_{10}$	0.49	3.86	0.44	(32)
		low traffic		0.93	5.4	0.64	
		high traffic		1.05	5.6	0.75	
Beijing, China	Oct – Nov 2014	high traffic	PM$_{2.5}$	9.35	76.92	1.31	(29)
Kolkata, India	Dec 2013 – Jan 2014	traffic junction	PM$_{10}$	6.27*	10.8*	0.70*	(46)
			PM$_{2.5}$	6.45*	9.79*	0.62*	

*values are shown in ng/m^3

areas, they are still measurable, which suggests that PGMs can cross great(er) distances. A case in point is the finding of PGMs at higher altitudes, far from high-traffic roads in Greenland and Alps (34).

To my knowledge, the highest PGM concentrations, however, were measured at road junctions of Kolkata, India by Diong et al. (46). These were 10 to 1,000 times higher than in other parts of the world and confirmed road junctions as sites with the highest exposure but also pointed to industrial emissions as no lesser environmental polluters.

The study of Rinkovec et al. (32), carried out in Zagreb, Croatia was the first to report airborne PGM measurements in Southeast Europe. Palladium had the highest and Rh the lowest means. The ratio of measured mass concentrations at all monitoring stations was similar to the Pt, Pd, and Rh content in automobile catalytic converters (47). Mass concentrations of Pt, Pd, and Rh varied significantly with seasons, peaking in the winter, which was explained by more intense traffic and adverse weather conditions that slow down air exchange, so pollution stays lower to the ground.

The behaviour and bioavailability of PGMs in the environment imply higher health risks, as they can be transformed into toxic compounds once they enter the organism. There are reports of the formation of chloric complexes with Pt, Pd, and Rh in the lungs that can be seriously damaging (15, 30). Zereini et al. (49) and Wiseman et al. (50) investigated the mobility of PGMs using simulated lung fluids and showed that significant fractions of PGMs are physically and chemically bioaccessible in the human lung, which is important because of known toxicological and allergenic effects of soluble forms of PGMs.

TOXICITY OF PLATINUM, PALLADIUM, AND RHODIUM

Health risks from environmental exposure to PGMs have long been considered minimal. However, recent toxicity studies suggest that exposure to these metals can cause asthma, allergies, and other serious health problems (51, 52). Most data on Pt toxicity come from chemotherapy studies (53, 54), but less is known about Pd, Rh, and the toxicity and behaviour of particle-bound PGMs emitted from catalytic converters.

As for occupational exposure of workers at catalytic converter plants, Petrucci et al. (55) observed low presence of Rh and Ir, because these two elements are rarely used in production. The highest reported concentrations were those of Pt in the hair, blood, and urine samples of workers in the final coating and drying sections, and of Pd in those working in the old catalyst recycling section. One study (56) investigated exposure of traffic policemen to Pt, Pd, and Rh in the city of Hyderabad, India and verified their levels in policemen's blood and urine. These policemen complained of symptoms such as dermatitis, eye irritation, and respiratory tract problems, which are often associated with toxic metal activity.

In vitro, Migliore et al. (57) reported that Pd salts were less genotoxic than Pt or Rh salts, probably because the latter two induce higher oxidative damage.

CONCLUSION

Mainly due to the widespread use as automotive catalysts for emission control since the 1970s, Pt, Pd, and Rh have been reported in ever increasing concentrations on airborne particulate matter, which has risen environmental and health concerns. While PGMs emitted from automobile exhausts are primarily deposited locally, long-range atmospheric transport cannot be excluded. Despite increase, however, current environmental PGM levels remain low, and the risks for environment and people are deemed minimal. Even so, currently available data are too scarce to assess the risks. Future studies should take into account that PGMs appear as nanoparticles, which increases their bioavailability, of Pd in particular. Research should also focus on chronic effects at low concentrations.

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Platina, paladij i rodij u lebdećim česticama u zraku

Mjerljive količine platine, paladija i rodija, čak i u udaljenim područjima našega planeta, dokaz su globalne prirode problema. Katalitički pretvarači suvremenih vozila, uz neke druge primjene (npr. proizvodnja nakita, kemijska industrija, lijekovi protiv raka), smatraju se glavnim izvorom kontaminacije metalima platinske skupine (PGM). Poznato je da količina PGM-ova koja se emitira iz automobilskih katalizatora varira ovisno o tipu, starosti i stanju motora i katalizatora te o brzini i uvjetima vožnje. Pregled postojeće literature pokazuje da se koncentracija tih metala značajno povećala u posljednjih dvadeset godina, osobito paladija, jer se pokazao učinkovitijim katalizatorom od platine. Još se raspravlja jesu li, i u kojoj mjeri, emitirane količine PGM toksične za ljude. Potencijalni rizik za zdravlje zbog izloženosti tim elementima treba uzeti u obzir za one koji žive u urbanim sredinama s prometnim cestama ili duž glavnih autocesta. Zbog važnosti PGM-ova i njihovih razina u lebdećim česticama, za pouzdano određivanje potrebne su osjetljive metode. Raspravljalo se o specifičnim koracima analitičkih postupaka za kvantifikaciju PGM-ova u lebdećim česticama. Opisane su i najčešće korištene metode priprave, kao i metode detekcije i određivanja PGM-ova.

KLJUČNE RIJEČI: ICP-MS, katalitički pretvornik, mikrovalna razgradnja, platinska skupina metala, spektralne interferencije