



# Identification of platinum nanoparticles in road dust leachate by single particle inductively coupled plasma-mass spectrometry

Karel Folens<sup>a</sup>, Thibaut Van Acker<sup>b</sup>, Eduardo Bolea-Fernandez<sup>b</sup>, Geert Cornelis<sup>c</sup>, Frank Vanhaecke<sup>b</sup>, Gijs Du Laing<sup>a</sup>, Sebastien Rauch<sup>d,\*</sup>

<sup>a</sup> Laboratory of Analytical Chemistry and Applied Ecochemistry, Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

<sup>b</sup> Department of Analytical Chemistry, Faculty of Sciences, Ghent University, Campus Sterre, Krijgslaan 281 S12, 9000 Ghent, Belgium

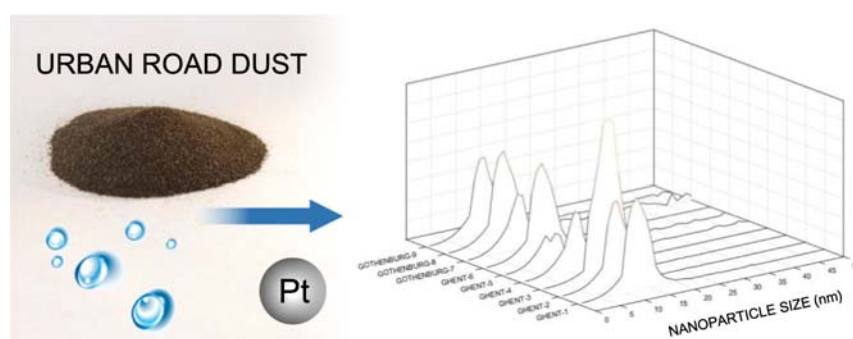
<sup>c</sup> Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, 75007 Uppsala, Sweden

<sup>d</sup> Water Environment Technology, Department of Architecture and Civil Engineering, Chalmers Institute of Technology, Sven Hultingsgata 8, 412 96 Göteborg, Sweden

## HIGHLIGHTS

- Platinum in road dust of Ghent and Gothenburg is comparable to other medium cities.
- Single particle ICP-MS can detect Pt nanoparticles as small as 7.4 nm in solution.
- Contact with stormwater causes the leaching of small platinum nanoparticles.
- With no soluble fraction, Pt is solely present as nanoparticles between 9 and 21 nm.
- Though a small fraction (3.3%), it is important in terms of bioavailability.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 24 April 2017

Received in revised form 25 September 2017

Accepted 26 September 2017

Available online xxxx

### Keywords:

Platinum  
Nanoparticles  
Road dust  
Single particle ICP-MS  
Catalytic converters  
ICP-MS/MS

## ABSTRACT

Elevated platinum (Pt) concentrations are found in road dust as a result of emissions from catalytic converters in vehicles. This study investigates the occurrence of Pt in road dust collected in Ghent (Belgium) and Gothenburg (Sweden). Total Pt contents, determined by tandem ICP-mass spectrometry (ICP-MS/MS), were in the range of 5 to 79 ng g<sup>-1</sup>, comparable to the Pt content in road dust of other medium-sized cities. Further sample characterization was performed by single particle (sp) ICP-MS following an ultrasonic extraction procedure using stormwater runoff for leaching. The method was found to be suitable for the characterization of Pt nanoparticles in road dust leachates. The extraction was optimized using road dust reference material BCR-723, for which an extraction efficiency of 2.7% was obtained by applying 144 kJ of ultrasonic energy. Using this method, between 0.2% and 18% of the Pt present was extracted from road dust samples. spICP-MS analysis revealed that Pt in the leachate is entirely present as nanoparticles of sizes between 9 and 21 nm. Although representing only a minor fraction of the total content in road dust, the nanoparticulate Pt leachate is most susceptible to biological uptake and hence most relevant in terms of bioavailability.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Catalytic converters, which were first introduced in the 1970s and are now required in all new vehicles in many countries worldwide,

\* Corresponding author.

E-mail address: [Sebastien.Rauch@chalmers.se](mailto:Sebastien.Rauch@chalmers.se) (S. Rauch).

are devices mounted in the exhaust system to alleviate the emission of harmful contaminants from the engine. The catalytic converters are composed of a honeycomb ceramic structure coated with an active alumina washcoat. Platinum group elements (PGEs, i.e. Pt, Pd and Rh) are homogeneously deposited onto the alumina surface at around 0.1% (Ravindra et al., 2004). The PGEs possess the unique catalytic properties required for the oxidation of carbon monoxide and hydrocarbons and for the reduction of nitrogen oxides. The most common three-way catalysts operate under strict reaction conditions, precisely steered by an air-fuel ratio near the stoichiometric optimum (Twigg, 2011).

PGE particles on the catalyst surface are expected to have diameters of <10 nm, but sintering can lead to their aggregation and formation of larger particles. PGE particles with diameters of 50–400 nm have for instance been observed in a catalyst aged for 60,000 km (Palacios et al., 2000). Mechanical abrasion and chemical reactions at the catalyst surface are responsible for the emission of PGEs through exhaust gasses (Moldovan et al., 2003). The Pt emission rate is expected to be in the  $\text{ng km}^{-3}$  rate (Palacios et al., 2000; Moldovan et al., 2002) and emitted particles might include PGE particles or PGE-containing washcoat particles. Characterization of the emitted particles revealed that 11–36% of the nominal number of particles was found to have a diameter smaller than  $3.14 \mu\text{m}$  (Artelt et al., 1999) and that the soluble fraction represents <10% of the original PGE content (Moldovan et al., 2002). PGE emissions have led to the dispersion and accumulation of these elements in the environment. Elevated concentrations have been observed in airborne particles, road dust and in neighboring roadside soil (Ravindra et al., 2004; Zereini and Wiseman, 2015; Rauch and Morrison, 2008). Pt is present in both coarse (<10  $\mu\text{m}$ ) and fine (<2.5  $\mu\text{m}$ ) airborne particles, including particles with diameters <0.45  $\mu\text{m}$  (Gomez et al., 2002; Kanitsar et al., 2003). Observations of single airborne particles by electron microscopy supports that Pt is present in different types of particles in urban air, including washcoat particles (Al/Si-rich particles with Pt as minor component), soot (C-rich particles with Pt as minor component) and Pt particles (particles in which Pt is the main component) (Rauch et al., 2005). During rain events, Pt can eventually be transported to aquatic compartments (Laschka and Nachtwey, 2000). Since the introduction of the catalytic converters in vehicles, significant increases have been observed for Pt concentrations in lake sediments (Rauch et al., 2004).

Although it was originally believed that the catalyst derived Pt occurs in a non-bioavailable metallic form ( $\text{Pt}^0$ ), research to date supports that at least some of the Pt present in the environment is in soluble or bioavailable forms (Nachtigall et al., 1997). The composition of different environmental compartments can affect Pt speciation (Rauch et al., 2002). pH has been reported to have a strong influence on Pt oxidation and solubilisation, while the effect of ligands such as phosphate, chloride, citric acid or fulvic acid are demonstrated to be less determinative in the activation of PGEs (Šebek et al., 2011). Dissolution can favor the bioavailability, as metal ions can be subject of binding to small proteins,

e.g. metallothioneins (Rauch et al., 2000a). It was shown that  $\text{Pt}^{\text{IV}}$  concentrations of  $14 \mu\text{g L}^{-1}$  can induce a 16% increase in reproductive impairment in *Daphnia magna*, while loss in organism weight was already observed below this exposure level (Biesinger and Christensen, 1972). Pt concentrations up to  $119 \text{ng g}^{-1}$  were found in *Asellus aquaticus* macroinvertebrates collected in an urban river. Accumulation of Pt in *Asellus aquaticus* was also found as a result of laboratory exposure and exposure to automobile catalyst and road dust particles (Moldovan et al., 2001).

The physicochemical characteristics of PGEs in the environment and the processes that lead to the occurrence of soluble and bioavailable species still remain poorly understood (Cobelo-García et al., 2015). In addition, solubility has been widely defined based on the 0.45  $\mu\text{m}$  pore size ultrafiltration and might in part be explained by the occurrence of platinum as  $\text{Pt}^0$  nanoparticles instead of truly dissolved (ionic) Pt species such as  $\text{Pt}(\text{OH})^+$  or  $\text{PtCl}_6^{2-}$  (Azaroual et al., 2001). Common speciation techniques struggle with the analytical detection of colloidal  $\text{Pt}^0$  as it is neutral and, moreover, has a meta-stable state (Zereini et al., 1997). Characterization of Pt nanoparticles in the environment is indeed a challenging task, for it requires the distinction of a broad range of sizes at low concentrations (Leśniewska et al., 2015). Different models have been developed, aiming at obtaining a more profound insight in the distribution of nanomaterials and environmental processes such as dissolution, agglomeration and sedimentation (Nowack et al., 2015). However, the development of novel analytical methodologies able to provide reliable information are indispensable for a complete understanding, which is highly desired for e.g. risk assessment.

Single particle inductively coupled plasma-mass spectrometry (spICP-MS) provides opportunity means to study the occurrence of metal or metal oxide nanoparticles at environmentally relevant concentrations. This analytical methodology makes use of recent advances in ICP-MS instrumentation to directly provide information on the size, particle number density and mass concentration of nanoparticles in solution. The method is based on the monitoring of fast transient signals and the registration of signal bursts recorded by the detector when individual metal or metal oxide nanoparticles are introduced in the plasma. The size of this burst is proportional to the mass of Pt per particle and the frequency of these burst is proportional to the particle number concentration. Together with information on the composition, shape and mass density of the particles, e.g. obtained via microscopy, the particle size distribution (PSD) of nanoparticles can thus be derived on condition that the nebulization efficiency has been calibrated (Peters et al., 2015). Hence, spICP-MS is a powerful tool for simultaneous quantification of the particle number density, mass concentration and size of nanoparticles (Lee et al., 2014) selectively and in natural environments with typically low concentrations of the target analyte and in the presence of matrix compounds (Mitrano et al., 2014).

**Table 1**  
Overview of the road dust sampling locations in Ghent, Belgium and Gothenburg, Sweden and circumstantial conditions as distance to the nearest road, precipitation for 3 and 5 days prior to sampling and the prevalent speed of circulating traffic.

Location	#	Coordinates		Description	Sampling date	Distance from the roadside verge (m)	Precipitation before sampling (mm)		Prevalent speed ( $\text{km h}^{-1}$ )
							3 days	7 days	
Ghent	1	N 51° 2' 33"	E 3° 44' 1"	B401 next to Zuidparklaan and G. Callierlaan	11-02-2015	0	0.1	2.9	50
	2	N 51° 3' 13"	E 3° 40' 34"	Deinsteenweg	11-02-2015	1	0.1	2.9	70
	3	N 51° 2' 8"	E 3° 42' 14"	Valentin Vaerwyckweg	11-02-2015	0	0.1	2.9	50
	4	N 51° 2' 23"	E 3° 40' 51"	Crossing Sneppenbrugstraat and R4	07-04-2015	0	0.0	9.8	90
	5	N 51° 1' 23"	E 3° 42' 45"	De Pintelaan	07-04-2015	0	0.0	9.8	50
	6	N 51° 2' 21"	E 3° 43' 27"	Charles De Kerckhovelaan	07-04-2015	0	0.0	9.8	50
Gothenburg	7	N 57° 39' 8"	E 11° 54' 18"	Roundabout underneath E6.20 highway bridge	11-06-2016	0	0.0	0.0	40
	8	N 57° 39' 13"	E 11° 54' 11"	Middle of E6.20 highway ramp	11-06-2016	2	0.0	0.0	60
	9	N 57° 39' 14"	E 11° 54' 45"	Covered parking lot	11-06-2016	-	0.0	0.0	20

Download English Version:

<https://daneshyari.com/en/article/5749841>

Download Persian Version:

<https://daneshyari.com/article/5749841>

[Daneshyari.com](https://daneshyari.com)