3.12 Palladium in Environmental Matrices: A Review

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3.12.1 Introduction

Palladium is one of the Platinum Group Elements (PGEs) and it is present on the Earth Crust (EC) at very low concentrations. Background concentrations of these noble elements in the range 0.06-0.40 mg/kg were reported by Taylor (1985), Wedepohl (1995) and Rauch et al., (2000) while a Pd average concentration of 0.015 mg/kg in the Upper Continental Crust (UCC) was proposed by Greenwood and Earnshaw (1989) and Hartley (1991). In the last two decades the use of cars equipped with VECs (Vehicle Exhaust Catalyst) was strongly implemented in order to reduce the gaseous pollutants from vehicle exhausts. PGEs are present in catalyst owing to their chemical and physical properties. In fact, at the high operational temperatures of these systems (450-550°C), they facilitate the reactions that permit the transformation of about 90% of NOx, CO and HCs in the less dangerous products as N₂, water and CO₂. In modern three-way catalytic converters (TWCs), PGEs are dispersed in the honeycomb structure of the catalyst. However, notwithstanding the evident benefit, the continuous release of PGEs in the environment, following the deterioration of TWCs, produces some concerns. In fact in some urban areas the PGEs concentration in soils, sediments and dusts is slightly but continuously increasing, reaching in some cases values that are one or two order of magnitude higher than the natural background ones. In addition, the small particles of PGEs mainly are in the PM₁₀ fraction where the < 3 µm breathable fraction could reach 35-40% of the emissions.

These concerns arise also considering recent data on PGEs demand for industrial use. In fact, since the introduction of catalytic converters a constant increase of these noble metals demand for application in auto catalysts has been observed. In Europe from 1992 to 2002 the total demand for Pt and Pd is grown of the 94.2% and 150% respectively, while their application for auto catalyst required the 75% and 84% of the total production. Worldwide data show that in the year 2000 rather 98% of the total mined Rh (16200 kg) has been used in car industry while the percentage for Pt and Pd was 31% and 61% respectively [WHO (1991, 2002), Johnson Matthey (2001), Ravindra et al., (2004)].
From when catalytic converters were first introduced, to comply with new legislation guidelines and thanks to technologic developments, catalysts have become increasingly efficient. Recently the importance of Pd has been hampered by the fact that the new three-way catalyst employ preferentially Pd and Rh instead of Pt which cost results too high for the market. So in the next future an increase on Pd emission can be reasonably expected and, cause to its highest mobility among PGEs a deeply investigation on Pd in environmental matrices should be promoted.

3.12.2 Palladium in Airborne Particulate Matter

Airborne Particulate Matter (APM) is characterized by very low levels of Pd which general range is <1-10 pg g\(^{-1}\) in extra urban sites, while in urban and heavy traffic areas the concentrations range from 10 to 300 pg g\(^{-1}\). A paucity of data results for Pd in APM owing to detection limit of the proposed analytical procedures and for the presence of many interferences hampering the analysis of Pd at the very low concentrations. A further difficulty arises from differences in sampling methodologies and strategy (sampling time, sample volume, etc), that do not permit an immediate and easy data comparison. A data collection of Pd in airborne particulate matter is reported in Table 3.12.1.

Very high concentration values of Pd in APM have been found in Chernivtsi (Ukraine), where an ambient air study was done in 1990 following on ongoing occurrence of childhood illness evidenced that the pollutants involved were mainly present in airborne (Scheff \textit{et al.} 1997). Analysis of total particulate matter evidenced elevated concentration of Pd (mean concentration of 56600 pg m\(^{-3}\)), with an enrichment factor of more than 200000. These data exceed also those measured in ambient air of heavy polluted cities as Chicago where a mean concentration of 12700 pg m\(^{-3}\) of Pd has been measured in 1990. Until today these results are the highest values reported in literature.

A range from 30 to 280 pg m\(^{-3}\) for Pd in APM for six different meteorological sites in Czech Republic has been reported by Vlašankova \textit{et al.} (1999) in a methodological study where Pd was analysed with different methodologies by selective separation and preconcentration as Pd-chloro-complexes.

Petrucci \textit{et al.} 2000, in a study on PGEs concentration in APM in Rome, compare data of Pd levels from samples collected in different periods of the year in urban (high traffic) and remote (low traffic) sites. The study evidenced appreciable differences between urban (21.2-85.7 pg m\(^{-3}\)) and