

Development of diffusive gradients in thin films (DGT) passive samplers for simultaneous measurement of Platinum, Palladium, Rhodium and Mercury in surface water

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Increasing anthropogenic activity often has detrimental effects on human health and the environment due to the accompanying emissions of toxic compounds. The increased application of Platinum Group Elements (PGEs) (Pt, Pd, Rh, Ru, Os and Ir) in the last decades, especially as car catalysts but also in other applications, makes it necessary to monitor the concentration of these elements in the environment, investigate their environmental transformations and bioavailability. Mercury (Hg) is also recognized as one of the most toxic trace elements, whose natural cycle has been altered by anthropogenic activities. Complex biogeochemical transformations result in different chemical species, with varying toxicities and mobility, which need close monitoring. The concentration of these elements usually extremely low in the aquatic environment, which makes the analysis challenging.

As the toxicity, bioavailability and the cycle of environmental contaminants can strongly be influenced by their chemical speciation, in recent years, the importance of speciation analysis has been recognized by the environmental monitoring and assessment community, leading to the development of an increasing number of speciation techniques. The in situ passive sampling technique diffusive gradients in thin films (DGT) as a speciation tool is based on the binding of labile metal species on a resin gel layer via the diffusion through a diffusive hydrogel (agarose or polyacrylamide) using Fick's Law. The concentration gradient built between the bulk solution and the resin gel makes pre-concentration of solutes possible. Using Fick's law, the time-weighted average concentrations of labile metal species can be obtained in situ. This technique has been widely used to assess trace elements such as Cd, Cu, Ni, Pb, Co, Zn in aquatic systems, but never been applied to test PGE elements until now.

The aim of this study was to develop the DGT technique for the assessment of PGE and Hg using two novel resins R14 and R20, which were designed specifically for above elements. This implies that the binding of the PGEs to the resin is strong, irreversible, almost instantaneous and the accumulated metals amounts are well below the capacity of the resin. The method development involves several different steps: 1) selection of an appropriate diffusive gel 2) the selection of an appropriate resin or binding phase for the PGEs and Hg, 3) development of an efficient elution method for the PGEs and Hg from the resin gel, 4) evaluation of the linear response in function of the deployment time, 5) determination of diffusion coefficients for the PGEs and Hg in the diffusive gel, 6) study the selectivity of the tested resins gels, 7) the accumulated metal amount is well below the capacity of the binding gel, 8) fast kinetics of the resins gels.

Agarose diffusive gel (AGA) (1.5% agarose) was chosen for lower interaction with PGEs and Hg, adequate blank values and linear response ($R^2 = 0.99$) in function of the time were obtained for the new resins gels and diffusion coefficients could be determined. An aqua regia and thiourea in hydrogen chloride elution methods gave a recovery for PGEs and Hg over 90% and 80% for the R20 and R14 resins gels, respectively. The selectivity test showed these two resins have higher selectivity to PGE and Hg than other trace elements even though they are at very high concentration level and the analysis of PGEs and Hg by sector field ICP-MS optimized. The new resin gels showed capability of accumulation concentration of PGEs and Hg of each hundred times higher than their reported concentrations in the aquatic environments.

Preliminary deployments in the Zenne River and UZ hospital effluent, Brussels, Belgium, showed that Pt, Pd, Rh and Hg can be quantified by the DGT technique using both evaluated resins in fresh water.

Keywords: DGT; PGEs; Hg; SF ICP-MS; diffusive coefficient; surface water; speciation