**Towards the production of the first CRM for ions in PM2.5**

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Airborne particulate matter (PM) cannot be considered as a single pollutant, but rather a mixture of particles coming from different sources and containing different chemical species. These particles can be directly emitted into the atmosphere by anthropogenic activities, but they can also originate from natural events such as volcanic eruption, seismic and geothermal activities, wild-land fires, sea spray or high wind events with subsequent transport of particles from dry regions. The current Air Quality Directive 2008/50/EC gives the possibility to EU member states to provide evidence that the exceedances of PM are attributable to natural sources. Therefore, the Directive requires monitoring, among others, of Cl-, NO3-, SO42-, Na+, NH4+, K+, Ca2+ and Mg2+ in PM2.5, the finest fraction of PM, collected at rural background locations. It is also specified that member states are free to choose the methods to demonstrate where limits values are exceeded due to natural sources.

A sound approach for validation or performance assessment of analytical methods is to use certified reference materials (CRMs). While CRMs for some PM are commercially available, only a few consist exclusively of PM2.5 and none are certified for the ions listed in the Directive.

In developing a candidate CRM, it is fundamental to ensure that it behaves like a real sample when using established analytical methods, i.e. that it is commutable. Commutability is a property of reference materials whereby it responds comparable to a real sample in a given measurement procedure. A method for the measurement of anions and cations in PM2,5 has already been released by the European Committee for Standardization (CEN/TR 16269:2011). We have demonstrated that a dust collected in a road tunnel and previously used for the production of two CRMs of PM10 (Perez Przyk et al. 2008), is not commutable when using this method. The water soluble fractions of SO42-, NH4+, K+, Ca2+ and Mg2+ are only fully extracted after 3 hours sonication and not after 30 minutes, as stated in the method. Moreover, we found that the particle size of the test material produced from tunnel dust influenced the extraction yield of K+, Ca2+ and Mg2+, suggesting that these species are hidden inside the particles. Other particulate materials for CRM production suitable to support measurements made by the CEN method are under evaluation.

Perez Przyk E., Held A., Charoud-Got J., 2008. *Development of particulate matter certified reference materials (PM10 CRMs) - Final report*, EUR 23244 EN, ISBN 978-92-79-08347-1, European Communities, Luxembourg.