METAL SPECIATION IN FLUE GASES AND WORK PLACE ATMOSPHERES

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The determination of metals in technical and ambient aerosols is a field of analytical chemistry related, e.g., to emission control, investigation of atmospheric processes, or to effects research. In this context not only the total content of a certain metallic element in a volume of air or in a dust sample, respectively, is of interest, but also its distribution between different phases or over different size ranges and its occurrence in definite chemical forms (species).

In aquatic chemistry the determination of dissolved and particulate metal species has been given considerable attention to for many years. In emission measurements or air quality studies, however, attempts towards metal speciation are scarce and have concentrated mainly on gaseous metal compounds.

Flue gases and work place atmospheres as well as ambient air are complex mixtures of several minor and major gaseous and particulate compounds, socalled aerosols, in which droplets and/or solid particles are suspended in a carrier gas. Consequently, metal compounds also may be present in gas, liquid or solid phase in such aerosols, their partitioning being a function of the aerosol generating process involved.

Taking ambient air as an example, sea spray, soil dust raised by winds, volcanic eruptions, or cement manufacturing are typical emission sources with primary particle production. In these cases material, through mechanical action, is emitted directly in particulate state (predominantly bigger or equal to 1 micron diameter).

During, e.g., fossil fuel combustion or ferrous and nonferrous metallurgical operations secondary particles (smaller than 1 micron diameter) are formed besides primary ones by condensation from vapour after its escape from high temperature sources. In technical as well as in ambient aerosols large fractions of typical heavy metals (Pb, Cd, Zn) may be found in this submicron size range, often enriched at surfaces of small primary particles.

Homogeneous or heterogeneous chemical transformations of airborne trace gases (gas-to-particle conversion) likewise lead to secondary particulate matter and are of particular relevance for a number of atmospheric compunds such as SO2, NO2, NH3 and also metal alkyl species.

A speciation scheme for characterization of a metal containing aerosol may be divided into a physical and a chemical part. The physical part includes investigation of the partitioning of the metal under study between the different phases or determination of the metal in different particle (droplet) size ranges. The chemical part deals with identification and quantification of well defined chemical forms of the respective metal in gas, liquid and solid phase.

Metal speciation in aerosols first of all requires proper sampling techniques which allow reliable separation and preconcentration of gaseous and particulate metal compounds without artifact formation. In principle such techniques are based on the interaction of inertial and viscous forces (impactors, filters), electrical forces (electrical mobility analyzers), and diffusion (diffusion batteries, denuders, filters). Especially, diffusion processing has found wide application in aerosol sampling and will be shown to be a promising approach to metal speciation in flue gases also.

In particulate matter collected from workplace air on a suitable substrate metal, speciation may be achieved by thermal or X-ray techniques. Among these, X-ray diffraction is the most straightforward and unambiguous method, because it yields not only compound but also phase (lattice) specific information.

Electron spectroscopy is well suited for particle surface analysis, whereas laser microprobe mass analysis (LAMMA) has been successfully applied to single particle characterization including depth profiling. A simple microchemical technique employing phase selective leaching procedures can be used for determination of Ni, Co or Cr species in microgram amounts of collected particulate matter. This will be shown using dust from metal plating workplaces and from a nickel refinery as examples.