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Evaporative light scattering: A novel detection method for size exclusion chromatographic quantification of humic like substances on aerosols

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The chemical nature of a large fraction of organic aerosols is not known. It has been shown that high molecular weight compounds make up a significant fraction (20-50%) of the water-soluble organic carbon (WSOC) fraction of aerosols. The term humic like substances (HULIS) was suggested, as their chemical characteristics are similar to humic acids, which are found in natural waters and soil. HULIS, have been analyzed and characterized using spectroscopic methods such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), UV, Fluorescence measurements or by size exclusion (SEC) chromatography. Using liquid chromatography combined with electrospray ionization mass spectrometry (HPLC-ESI-MS) or laser desorption ionization mass spectrometry (LDI-MS), an upper mass limit is ranged in the 500-700 Dalton region.

A quantification of HULIS remains difficult because the chemical structure is still unknown. All of the above mentioned detection methods for liquid chromatography require identical or at least structurally similar standards in order to obtain reliable quantitative results, because optical or ionization properties can vary by orders of magnitudes between classes of compounds. However, for HULIS there are no true standards available. We present a new technique to quantify the HULIS fraction from atmospheric aerosol particles: SEC coupled with Evaporative Light Scattering Detection (ELSD).

In a first step water-soluble compounds with humic-like properties were isolated by the application of solid-phase extraction from e.g. inorganic salts. In a second step we used size exclusion chromatography for the separation of higher molecular weight compounds coupled with ELSD for quantification. The operation principle of this detection method consists of three stages: (1) nebulization, (2) mobile-phase evaporation, and (3) detection. A nebulizer combines a gas flow of nitrogen with the column effluent to produce small droplets. The droplets are introduced into a heated drift tube in which the mobile phase evaporates, leading to a particulate form of the analyte. Finally, light scattering is used to detect the amount of analyte in real time. The molecular size range of the quantified HULIS is further determined by electrospray ionization mass spectrometry.

A series of ambient high-volume filter samples (PM 1) have been collected at a suburban site in Dübendorf, Switzerland and characterized. First results show that ELSD measurements are by a factor of two higher in concentration compared to a quantification with UV detection using fulvic acid as quantification standard, a method often used in the literature.