Characterization of Water-Soluble Organic Carbon in Atmospheric Particles: Recent Approaches and Methods

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ABSTRACT

▪Carbonaceous species, organic carbon (OC) and elemental carbon (EC), constitute a major, sometimes dominant, fraction of fine particulate matter (PM).

▪ OC represents a large variety of organic compounds. Hundreds of non- or semi-polar organic compounds have been quantified using GC-MS.

▪ However much less information is available on the water-soluble organic compounds (WSOC). Their molecular composition still remains poorly known. The major obstacle encountered in the molecular characterization of WSOC is the huge complexity of this fraction with hundreds of different compounds [1].

▪Over the past few years several research groups have proposed different strategies to obtain new information related to the characteristics of WSOC [2-4].

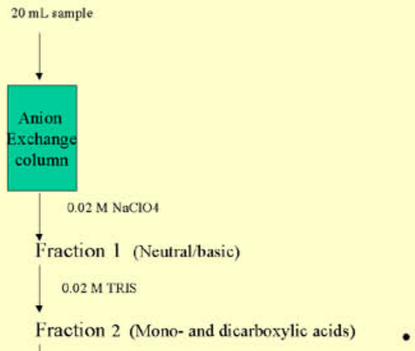
▪This poster overviews recent approaches proposed for the chemical characterization of WSOC.

Chemical Characterization of Fractions

The isolated fractions were characterized by using various analytical techniques such as:

- **Elemental analysis:** to determine elemental composition (C, N, H, and S) **[3]**
- **Total Organic Carbon (TOC)** : to determine OC [**3,4**]
- **FTIR and NMR spectroscopy**: to study molecular structure **[2, 3]**
- **Capillary electrophoresis (CE):** to determine LMW organic acids, acidic strength and the electrophoretic behavior of HULIS **[3, 5].**
- **HPLC-MS:** to obtain information on the probable molecular weight of organic compounds **[3].**
- **GC-MS (derivatization)**

Separation by Anion Exchange Chromatography [2]



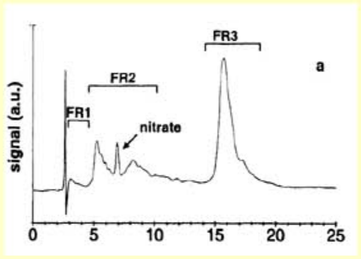
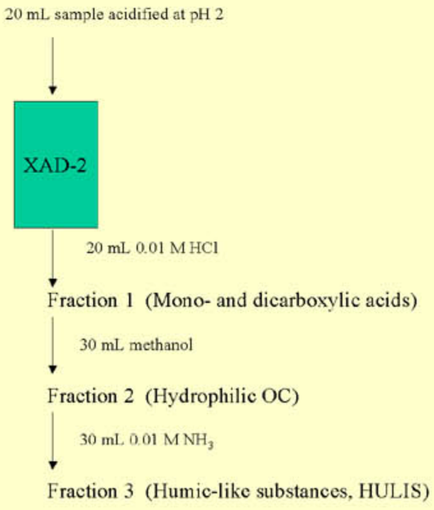


Figure 1. HPLC chromatogram at 254 nm of aerosol extract.

- Characterization by **HNMR** spectroscopy showed that
  - **Fraction 1** is mainly composed of polyols
  - **Fraction 2** is mainly composed of hydroxylated aliphatic acidic compounds
  - **Fraction 3** is composed of highly unsaturated polyacidic compounds of predominantly aliphatic character, with a minor content of hydroxyl- groups.

Fractionation on XAD-2 resin [4]



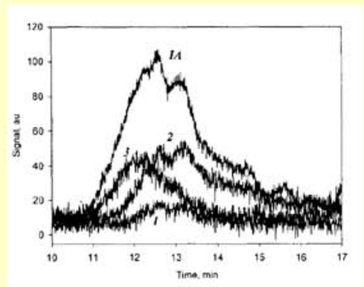
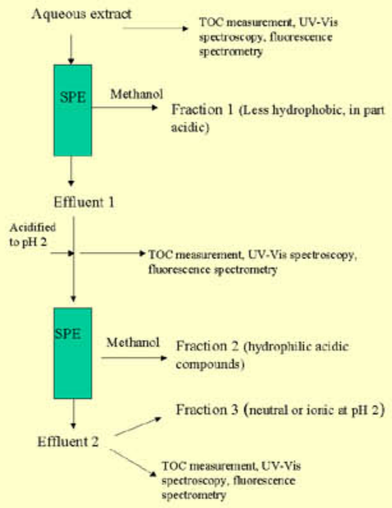


Figure 2. Size exclusion chromatograms (SEC), detected at 254 nm, of an aqueous extract, unfractionated, of interstitial aerosol (trace IA) and the three fractions collected after adsorption and elution on XAD-2 resin.

- The method proved particularly useful both in providing information on the organic content of the samples and for the characterization of the macromolecular compounds (HULIS) in the samples.
- The carbon content in the third fraction was estimated both by TOC and by means of the correlation between TOC and SEC area.

Fractionation on RP-18 SPE [3]



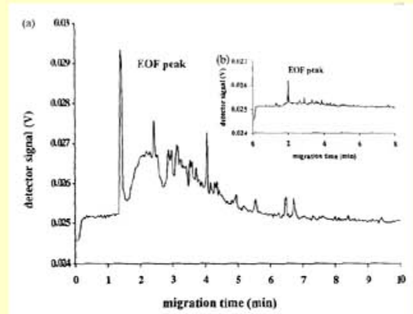


Figure 3. CE electropherogram for the ionic organic substances in the aqueous extract of the fine aerosol (plot (a)); and for the effluent from the second SPE cartridge (Fraction 3) (plot (b)).

- ✓ Separation into individual components was impossible either by HPLC or CE which indicates the presence of a high number of chemically similar but not identical species.
- ✓ Results obtained by ultrafiltration and HPLC-MS have shown that the molecular weights are of the order of several hundreds.
- ✓ Most of the protonation constants for the acidic compound determined by CE were in the range 10^4-10^7.

SUMMARY

- A general chemical characterization of WSOC with the purpose of characterizing of WSOC composition as a whole, through the elucidation of the type and concentration of functional groups characterizing the organic mixture has been proposed in the literature.
- This novel approach combines: (1) isolation of the organic carbon into several fractions on the basis of specific chemical properties by using various chromatographic or solid phase extraction schemes; (2) characterization of the collected fractions with respect to their relative size distribution, chemical characterization and/or hydrophilicity /hydrophobicity; and (3) estimation of the organic carbon of the isolated fractions by means of direct and indirect measurements of the total organic carbon.
- Although it is sometimes difficult to compare the subgroups isolated through different approaches, the fractionation steps effectively removed inorganic salts and enriched the organic material from dilute aqueous solutions. Therefore, the reported methods enable the characterization of the isolated WSOC by numerous analytical techniques (NMR spectroscopy, FTIR spectroscopy), which were not applicable or were less effective before. However, separation into individual components was impossible either by HPLC or capillary electrophoresis, which indicates the presence of a high number of chemically similar but not identical species.
- From these reports it follows that majority of the WSOC cannot be attributed to the individual low-molecular weight compounds analyzed so far, and new classes of organics as cellulose, protein or humic-like substances should be looked for.
- These biopolymers were detected in the aerosol samples collected at both the rural and the polluted sites.

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