

Analytical methods for quantification and characterization of HULIS (Humic Like Substances) in atmospheric aerosol

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Introduction

HULIS (Humic Like Substances) belong to OC (Organic Carbon) fraction of atmospheric particulate matter, where OC represents about 30-40% of PM mass. **Atmospheric HULIS are ubiquitous pollutants** regarded as a polymeric material with poly-acidic properties and as optically active substances (yellow-brown coloured). HULIS are involved in the CCN (cloud condensation nuclei) forming processes and influence the optical properties of the aerosol particles. In the literature they have been characterized by means of different analytical methods (1, 2, 3). Most of these methods consist of solid phase extraction (SPE) followed by Total Organic Carbon (TOC) analysis.

Methods

Here we propose the use of UV-VIS spectroscopy and TOT (Thermal Optical Transmittance) for their quantification.

TOT analysis is usually employed in order to quantify OC (Organic Carbon) and EC (Elemental carbon) (4).

In this work, samples were prepared by means of SPE extraction of PM10 samples collected in two sites of Lombardy region.

HULIS have been analyzed by means of:

- TOT (Thermal Optical Transmittance)
- UV-VIS
- FT-IR/ATR

Experimental

water soluble HULIS separation:

- ❖ Portions of the aerosol filter were extracted with Milli-Q water for 72 hours. The ratio filter area/water volume was between 1 and 3 cm² mL⁻¹ depending on the carbon load of the sample.
- ❖ The pH of samples was adjusted to 2 by the addition of HCl 0.1 M (1.5-2 mL)
- ❖ Samples were filtered through a syringe filter of 0.45 μm pore size
- ❖ Extraction with SPE columns (OASIS HLB, Waters)
- ❖ Methanol elution
- ❖ Evaporation to dryness and followed by dissolution in water (UV-Vis analysis) or in methanol (for the other analyses)

References

- 1) Feczko, T., Puxbaum, H., Kasper-Giebl, A., Handler, M., Limbeck, A., Gelencsér, A., Pio, C., Preunkert, S., Legrand, M., (2007) *J. Geophys. Res.*, 1123, D23S10
- 2) Graber, E. R., Rudich, Y., (2006) *Atmos. Chem. Phys.*, 6, 729 – 753
- 3) Salma, I., Ocskay, R., Lång, G. G., (2008), *Atmos. Chem. Phys.*, 8, 2243 – 2254
- 4) Birch, M.E., Cary, R.A., (1996) *Aeros. Sci. & Technol.*, 25, 3, 221-241

Analytical methods: quantification

1. UV-VIS

HULIS quantification using for the calibration a fulvic acid (IHSS); absorbances corresponding to the spectrum maximum have been considered and the corresponding molar absorptivity calculated

2. TOT

HULIS quantification using punches of quartz fiber filter as a support for the sample solution (the analysis is performed after solvent evaporation)

Analyzed samples: a sampling of two weeks carried out in **Milan** during September 2008; a sampling of one week in **Mantova** during the same period; in both cases a high volume sampler was employed

Analytical performance:

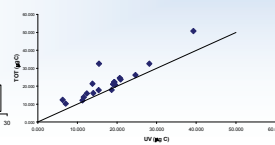
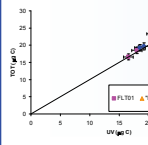
Reproducibility

3 filters have been chosen and for each filter 3 portions have been extracted and analyzed

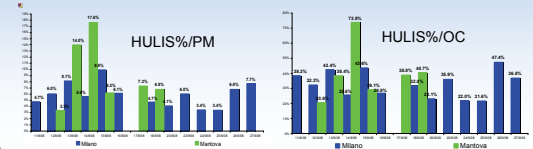
Comparison TOT/UV-Vis:

Results on the two sampling campaigns carried out in Milan and Mantova

Comparison UV/TOT



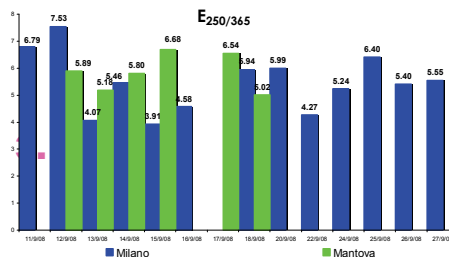
HULIS determination in aerosol samples: %HULIS/OC and %HULIS/PM



Analytical methods: characterization

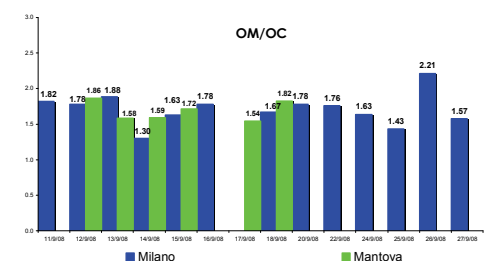
3. UV-VIS: aromaticity

The ratio E_{250}/E_{365} has been found to be inversely correlated with molecular weight and aromaticity (1). The examined samples show values mainly in the range 4-6; so high values are more similar to the ratio encountered for fulvic acids which are less aged than humic acids. Information on particulate matter ageing processes can so be acquired.

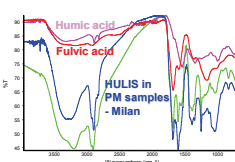


4. TOT: OM/OC evaluation

Evaluation of OM/OC ratio allows to convert OC (organic carbon) % into OM (organic matter) %. At the moment a direct experimental estimation of this ratio doesn't exist in the literature. A correct knowledge of this conversion factor allow to have a correct PM mass closure.



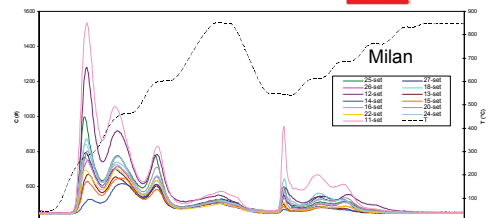
4. FT-IR



- 1712 and 1619 cm⁻¹
 - v C=O (-COOH)
 - v C-C (aromatic)
 - v C=O (conjugated)
- 2850 - 2950 cm⁻¹
 - v -CH₂ e -CH= (aliphatic chains)
- 1088-1036 cm⁻¹
 - v C=O (polysaccharides)

The extracted HULIS samples have been analyzed also by ATR spectroscopy. In this way it has been possible to distinguish the two components, i.e. fulvic and humic acids. It can be observed that HULIS in PM are more similar to fulvic acids. The presence of the absorption at about 1088-1036 cm⁻¹ indicates a more biogenic origin of these HULIS.

4. TOT: thermograms



Differences have been encountered also for the thermograms obtained during TOT analysis; work is in progress in order to assign the different peaks to the species identified by infrared spectroscopy.

Two methods for HULIS quantification in particulate matter aerosol samples have been proposed and it has been demonstrated that are both suitable. In particular UV-Vis, until now used just for HULIS characterization, is quite advantageous since this technique is commonly available in many analytical laboratories. Furthermore OM/OC has been determined experimentally.