NMR AEROSOLOMICS AS A TOOL TO DISTINGUISH VARIOUS TYPES OF AEROSOLS

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Keywords: NMR, Aerosolomics, WSOC, Organic composition

INTRODUCTION

Water-soluble organic compounds represent up to 80% of all organic compounds present in atmospheric aerosols (Duarte, 2011). Unlike composition of inorganic compounds or volatile organic compounds, which seems to be well explored, the knowledge about WSOC composition is still rather limited. The most frequently used method for WSOC analysis is GC-MS, which is a very sensitive technique (Pietrogrande, 2011). However, the analysis of polar compounds via GC-MS requires derivatization and the quantification is extremely time consuming. The second widely used technique is ion chromatography (IC). Nowadays, IC is routinely used for analysis of specific groups of organic compounds such as carboxylic acids, amines or carbohydrates (Tsai, 2008). On the other hand, there is NMR spectroscopy as a fully quantitative but rather insensitive method. NMR spectroscopy was for the purpose of aerosol chemistry employed only recently (Decesari, 2000) as this technique has undergone rapid development and sensitivity gain of late. So far, the use of NMR spectroscopy is mainly restricted to so-called Functional Group Analysis, of which main interest lies elsewhere than in identification of individual compounds.

EXPERIMENTAL SETUP

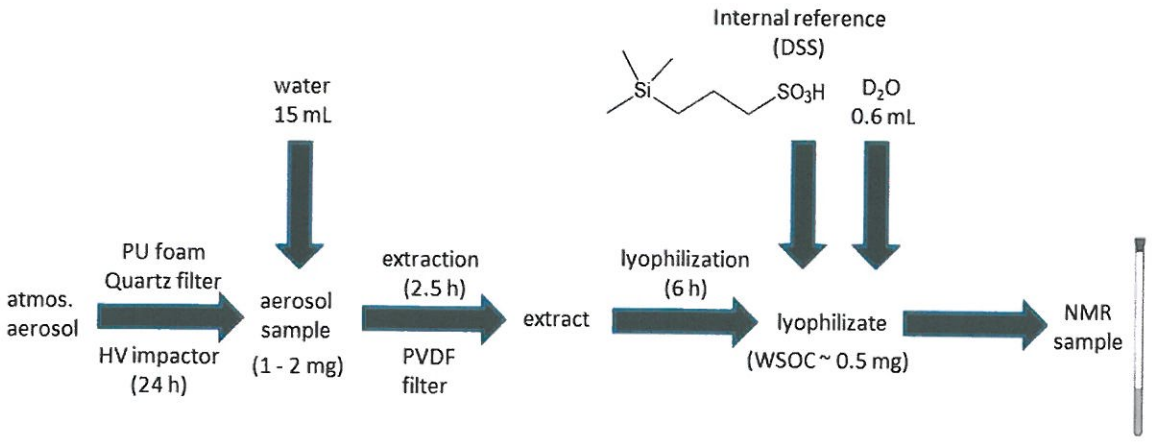

Fig. 1: Scheme of a NMR sample preparation

Aerosol samples were collected during two campaigns in years 2008 and 2009 in Prague-Suchdol. First campaign was focused on summer samples and ran from June 25th, 2008 to September 5th, 2008. Second campaign was conducted between November 6th, 2008 and March 28th, 2009 and winter samples were collected. Both $PM_{2.5}$ and PM_{10} samples were collected during both campaigns.

The quartz filter was cut into pieces and extracted into 15 mL of deionized water. The extraction was run for 30 minutes in an ultrasonic bath and for 2 hours on a shaker. The extract was then filtered and freeze-dried. Subsequently, the obtained matter was dissolved in deuterated water (99.96% D) containing a known amount of DSS (dimethyl-silapentane-sulfonate, 0.5 mM) as a chemical shift and line shape reference. Finally, the sample was transferred into a 5 mm NMR tube after dissolution and immediately inserted into the NMR spectrometer.

RESULTS AND CONCLUSIONS

The suitability of NMR aerosolomics method was tested on summer and winter samples collected in summer 2008 and winter 2009 in Prague-Suchdol. In order to obtain sufficient amount of particulate matter, 2-3 samples had to be combined together according to similar weather conditions, which led to the formation of 21 samples (10 summer and 11 winter). The method exploits a comprehensive ^1H NMR library consisting of ca. 150 compounds present in WSOC fraction of particulate matter. Around 50 – 60 compounds were identified in each aerosol spectrum owing to the extensive database. The profile of 85 compounds identified in the samples altogether served as an input data for statistical analysis. Multivariate statistical analysis clearly discriminates between summer and winter samples. Separation of the samples based on their particle size was also tentatively performed and showed some trends in composition. Furthermore, the most significant compounds varying between seasons were determined by the means of univariate statistical analysis. These compounds were subjected to the further analysis of their possible sources. Among 85 compounds identified, eight compounds were found for the first time as part of particulate matter best to our knowledge and four compounds were predicted by the literature in theory, but have never been directly identified in ambient aerosol.

ACKNOWLEDGEMENT

This work was supported by Technology Agency of the Czech Republic project (TK02010035) and by Large Research Infrastructures project of the MEYS of the Czech Republic ACTRIS-CZ, project No. LM2015037.

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