Chemical Characterisation of Polar Organic Compounds in Ambient Aerosols by High Resolution Mass Spectrometry: A Non Target Approach

Christian Dye and Karl Espen Yttri

Norwegian Institute for Air Research, P.O. Box 100, NO-2027 Kjeller, Norway - www.nilu.no

Summary

In this work a High Performance Liquid Chromatograph (HPLC) was combined with a Time of Flight (TOF) high-resolution mass spectrometer (HRMS) and used as a tool in non-target chemical analysis of polar organic compounds in ambient aerosols. The experiments indicate that the complementary use of flow injection analysis FIA combined with HRMS (TOF), HPLC/HRMS(TOF) and HPLC/UV provides an efficient non target approach. The FIA/HRMS reveals a variety of classes of polar organic compounds.

Introduction

Why characterize ambient aerosols?

- The chemical composition of atmospheric aerosols influences the ability to act as a cloud condensation nucleus (CCN). The polar water-soluble organic compounds (WSOC) are of special importance regarding the CCN properties.
- The atmospheric aerosols may contain chemical compounds that have severe health effects.

Challenge

- Ambient aerosols contain a mixture of hundreds of organic compounds. A large fraction is still unidentified compounds. Therefore, an efficient non-target approach is needed.
- The aerosol sample contains a mixture of acids, bases, neutrals and salts.

Methodology

Strategy

1. FIA/HRMS provides a qualitative sample screening. This technique has a high sample throughput. Outcome example: See table 1.
2. Chemical class determination/ Isotope determination by use of model compounds, HPLC/HRMS and HPLC/UV. Combination of elemental composition, isotopic pattern, retention times and UV spectra.
3. Quantitative chemical analysis by HPLC/HRMS.

Instrumentation

- HP1100 HPLC equipped with diode array detector.
- Micromass LCT (Time-Of-Flight) HRMS.

Sample preparation

1. The aerosol samples are collected by exposing quartz fibre filters (47 mm diameter and a flow rate of 10 l/min).
2. The filters are extracted by immersing the filter in water and subsequent an ultrasonic bath.
3. The sample extract is drawn through a syringe filter (0.45 um) before injection.

Results

Table 1: Selected outcome of a FIA/HRMS (Negative electrospray ionisation) analysis of a $PM_{2.2}$ filter sample from Sofienbergparken in Oslo (November 2001)

Measured m/z (M-H)	Suggested elemental composition (M-H)	Theoretical m/z (M-H)	Possible interpretation
89.0237	$C_3H_5O_3$ (M-H) or $C_6H_{10}O_6$ (M-2H)	89.0239	Glucose/Fructose
115.0779	$C_6H_{11}O_2$	115.0756	Carboxylic acids/esters/ Hydroxy carbonyls
121.0297	$C_7H_5O_2$	121.0290	Benzoic acid, hydroxy benzaldehyde
129.0965	$C_7H_{13}O_2$	129.0912	Carboxylic acids/ esters/ Hydroxy carbonyls
130.0872	$C_6H_{12}NO_2$	130.0868	Leucine or aminobutyric acid or an isomer.
131.0361	$C_5H_7O_4$	131.0342	Hydroxyketoacid/unsaturated diacid
143.1053	$C_8H_{15}O_2$	143.1068	Carboxylic acids/ esters/ Hydroxy carbonyls
145.0501	$C_6H_9O_4$	145.0498	Diacid
159.0600	$C_7H_{11}O_4$	159.0654	Hydroxyketoacid/unsaturated diacid
161.0447	$C_6H_9O_5$	161.0450	Levoglucosan (MAs), Hydroxy diacid
164.0712	$C_9H_{10}NO_2$	164.0712	Phenylalanine or an isomer.
199.1647	$C_{12}H_{23}O_2$	199.1692	Carboxylic acids/ esters/ Hydroxy carbonyls
255.2388	$C_{16}H_{31}O_2$	255.2316	Carboxylic acidsr/ esters/ Hydroxy carbonyls
277.1529	$C_{15}H_{21}N_2O_3$	277.1552	Tolycaine
341.0961	$C_{12}H_{21}O_{11}$	341.1084	Sucrose

Acknowledgment

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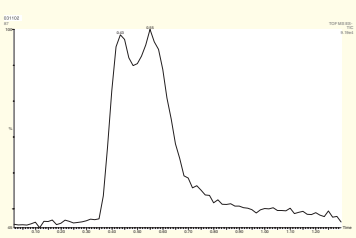

Figure 1: FIA/HRMS profile.

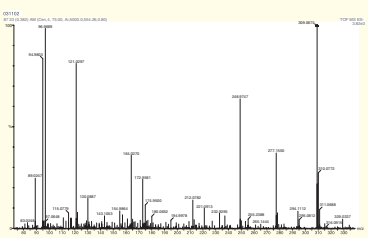

Figure 2: FIA/HRMS mass spectrum.

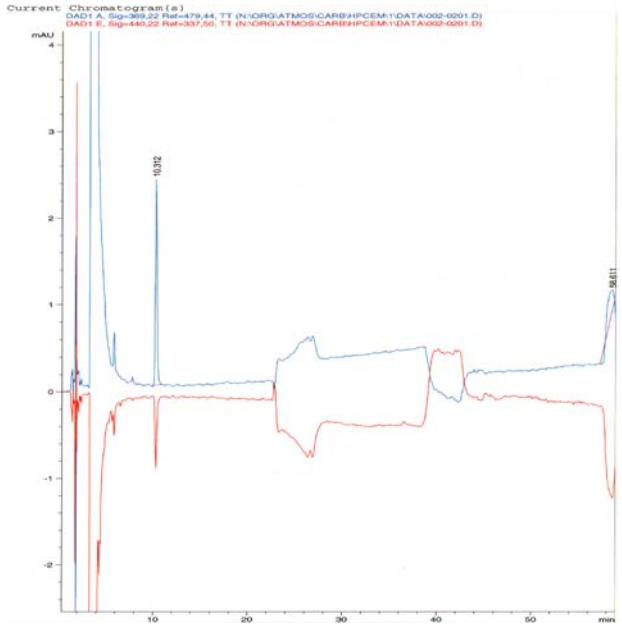

Figure 3: HPLC/UV chromatogram of carbonyl-2,4-Dinitrophenylhydrazones.

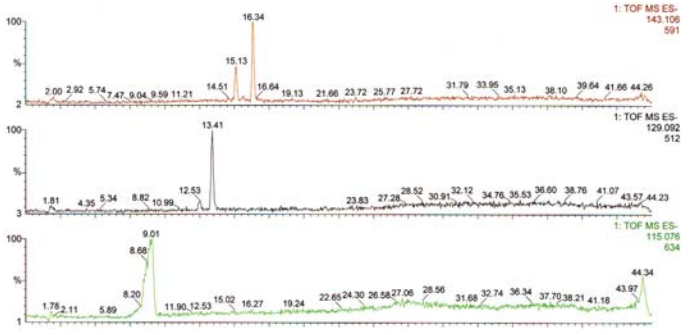

Figure 4: HPLC/HRMS ion profiles of carboxylic acids.

Example of Chemical Class Determination

The measured m/z 129.0965 indicates Carboxylic acids/ esters/ Hydroxy carbonyls.

- The sample is derivatised with acidified 2,4-Dinitrophenylhydrazine in order to analyse with respect to hydroxy carbonyl compounds. No hydroxy carbonyl compound was found in the sample with HPLC/UV (Figure 3).
- The sample is analysed with respect to organic acids by using HPLC/HRMS. Two isomers of organic C_7 carboxylic acid are identified (figure 4, retention time 12.53 and 13.41).

Conclusions

- The experiments show that the complementary use of flow injection analysis FIA combined with HRMS (TOF), HPLC/HRMS (TOF) and HPLC/UV provides an efficient non-target approach.
- The non-target approach has been tested with success in electrospray ionisation +/- mode and in Atmospheric Pressure Chemical Ionisation +/- mode.
- FIA/HRMS should not be used for quantification due to matrix dependent ionistion yield of the single compound.
- The non-target approach has been useful in sample screening of WSOC compounds as monosaccharide anhydrides and sugars.