ANALYSIS OF ATMOSPHERIC RELEVANT SUBSTITUTED PHENOLS IN AQUEOUS SOLUTION USING HPLC-APCI-MS

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Motivation

Substituted phenols may be emitted directly or they are formed by the atmospheric oxidation of aromatic hydrocarbons. Beside anthropogenic processes the combustion of biomass is one of the biggest direct sources of phenolic compounds in the atmosphere - particularly cresols, substituted guaiacols, and substituted syringols were found in the gas and/or particle phase. Nitro containing phenols are often phytotoxic and are suspected to contribute to the forest decline. The reaction with free atmospheric radicals, such as OH- and NO_3-radicals, can be the predominant sink process for such compounds. The products of these oxidation reactions are also important to understand the chemistry of these compounds in the atmosphere. For this reason, an analytical method is necessary for the analysis of several substituted phenols and their oxidation products in the atmosphere. Routinely, the biomass burning samples were analyzed by GC-MS. However, the introduction of atmospheric pressure ionization techniques (API) for the HPLC-MS coupling, offers new possibilities for the analysis of atmospheric samples. Numerous publications report the applicability of this analytical method to environmental samples. Particularly the easy sample pre-treatment, the short analytical time and the high sensitivity make the HPLC-MS coupling to an interesting tool for qualitative and quantitative measurements.

Experimental

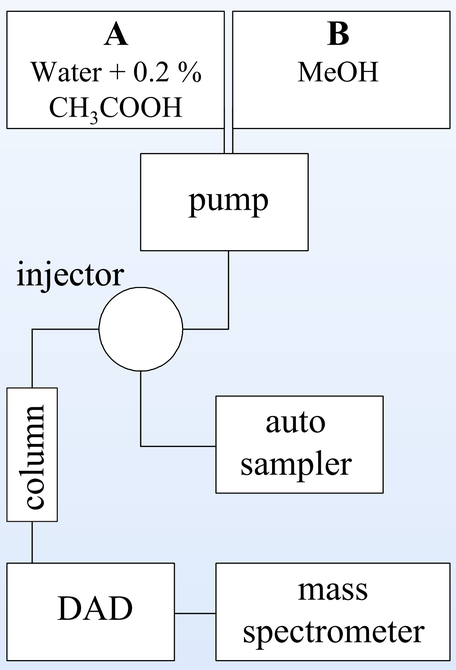

Figure 1: Experimental set-up HPLC-APCI-MS

All the measurements were carried out with a HPLC-MS system consisting of a HP 1100 liquid chromatography system and Esquire 2000 Ion Trap mass detector. The HPLC system consists of a binary pump, degasser unit, DAD detector and an auto sampler. The mass detector was equipped with an APCI interface. Chromatographic separations were performed on a Zorbax SB-C8 column (3mm x 150mm x 3,5 µm) by an isocratic elution with 70% water (0.2% CH_3COOH) and 30% MeOH at flow rate of 0.3 ml/min. Analytes were detected in positive mode at 4000 V capillary voltage, 20 p.s.i. vaporizer gas pressure, 10 l/min dry gas flow, 290 °C dry gas temperature and 410 °C vaporizer temperature. Corona current was set to 7.5 µA.

Results and Discussions

For a positive identification and quantification of the compounds, standard solutions (5mM) with known biomass burning tracers have been prepared. The standard compounds were obtained from Fluka or Sigma Aldrich and dissolved in methanol. Before measurement, the standard solutions were diluted (1:50) in water.

Table 1: Composition of the standard solutions

Standard 1	MW	m/z
vanillin	152.2	153; 125
vanillinic acid	168.2	169; 183
homovanillinic acid	182.2	153; 137
eugenol	164.2	-
cinnamic acid	148.2	-
ferulic acid	194.2	177; 151
coniferyl aldehyde	178.2	171; 161
sinapic acid	224.2	207; 181
guaiacol	124.1	-
3,5-dimethoxy-4-hydroxyacetophenone	196.2	197; 155
syringol	154.2	155; 123
syringic acid	198.2	213; 169
4-hydroxycinnamic acid	164.2	179; 147

Standard 2	MW	m/z
2-fuoric acid	112.1	-
3-fuoric acid	112.1	-
3-hydroxybenzoic acid	138.1	-
veratric acid	182.2	197; 183
homoveratric acid	196.2	167; 151
trimethylgallic acid	212.2	227; 213
3-methoxysalicylic acid	168.2	169; 151
4-vinylbenzoic acid	148.2	-
4-nitroguaiacol	169.1	170; 153

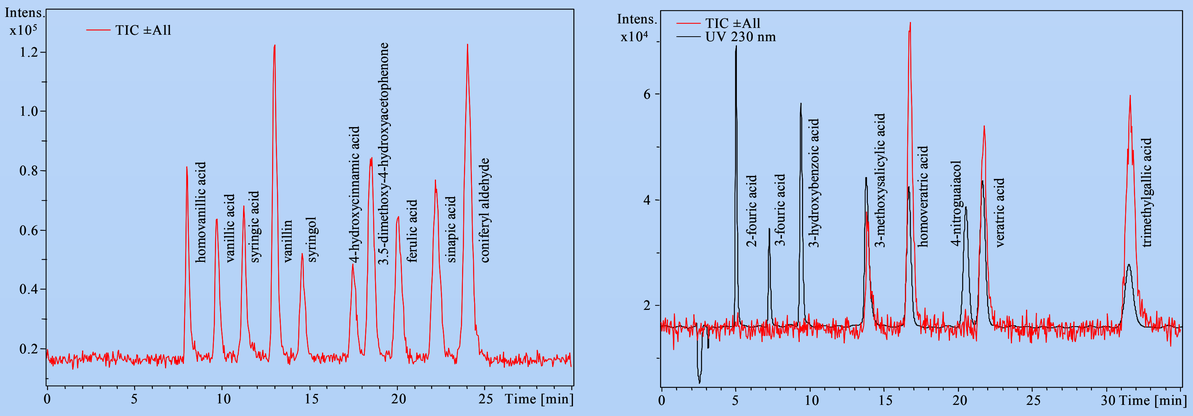

Figure 2: Chromatogram of both standards; standard 1 (left); standard 2 (right)

19 of 22 standard compounds could be detected with this analytical method. Standard 2 clarifies, that the DAD represents a useful complement of the mass spectrometer. Eugenol, cinnamic acid and vinylbenzoic acid couldn't be detected at all. Therefore, other experimental conditions as well as the electrospray interface (ESI) are to be tested.

Further, it's noticeable, that even with this soft ionization technique nearly all the standard compounds show fragmentation. It supports the positive identification of compounds with a known retention time and fragmentation pattern.
To characterise the smoke of different biofuels, several kinds of wood were combusted. Subsequently, the resulting aerosol was collected, extracted with MeOH, and analysed with the APCI-MS. The following figures show two samples from oak and spruce, respectively.

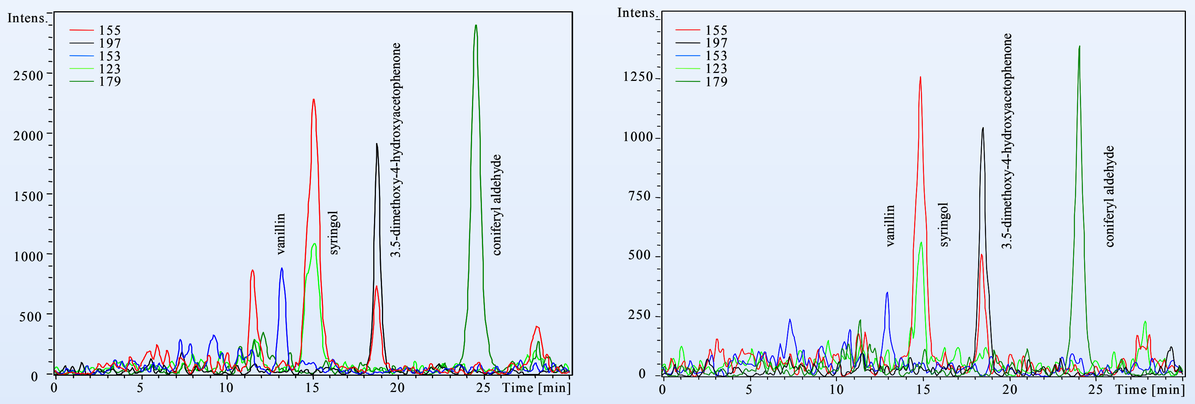

Figure 3: Extracted Ion Chromatograms of biomass burning samples; left side: ; right side:

Four compounds (coniferyl aldehyde, syringol, vanillin and 3.5-dimethoxy-4-hydroxyacetophenone) were positively identified in both biofuels by the help of the retention time and the fragmentation pattern. Additional certainty for the identification can be reached by MS^n experiments like in Figure 4. Emissions rates of substituted phenols are about 2 - 50 mg/kg for the oak sample and approximately two times smaller for the spruce. However, further unknown compounds could be detected in the oak and the spruce sample (see Figure 5).

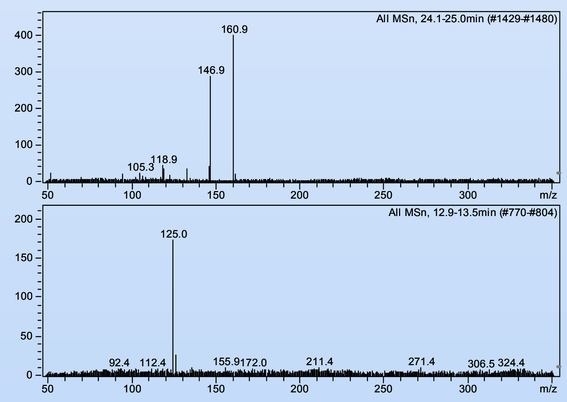

Figure 4: MS^n-chromatograms of coniferyl aldehyde (top) and vanillin (bottom)

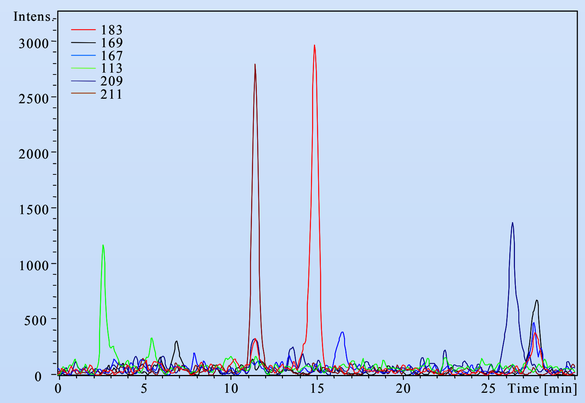

Figure 5: Extracted Ion Chromatograms of biomass burning samples

To characterize this analytical method, the limits of detection for all detectable compounds were determined. The limits of detection were about 1 up to 3 µM for nearly all the compounds in the standard and therefore sufficient enough for the investigation of biomass burning samples.

Summary/Outlook

- suited and complementary method for the analysis of biomass samples
- sufficient limits of detection
- identification of unknown compounds
- testing of ESI-MS

References

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Acknowledgments

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