

Analysis of polar aromatic biomass burning tracers in combustion aerosol using HPLC-MS

Motivation

Biomass burning produces several organic polar and non-polar compounds in the gas- and particle phase. Different substituted aromatic compounds (e.g. methoxyphenols) were formed in particular from the combustion of lignin^[1,2] (Figure 1). Due to the toxicity and phytotoxicity of these compounds, their chemistry and concentration in the particle phase is of note. Furthermore, they were used as tracer compounds for the contribution of biomass burning to the particle matter. For this reason, a suited analytical method is necessary for the analysis of several substituted aromatics. The analysis of environmental samples is commonly performed by GC-MS. However, the introduction of atmospheric pressure ionisation techniques (API) for HPLC-MS coupling offers new possibilities for the analysis of polar compounds. Especially the easy sample pre-treatment, the short analytical time and the high sensitivity makes the HPLC-MS coupling to an interesting tool. For this reason, an HPLC-MS method was developed for the routine analysis of substituted aromatics in combustion samples. Accurate yet fast analytical methods are necessary in order to understand combustion processes and to obtain input parameters for chemical models. In turn, such analytical technique can be also used for model validation.

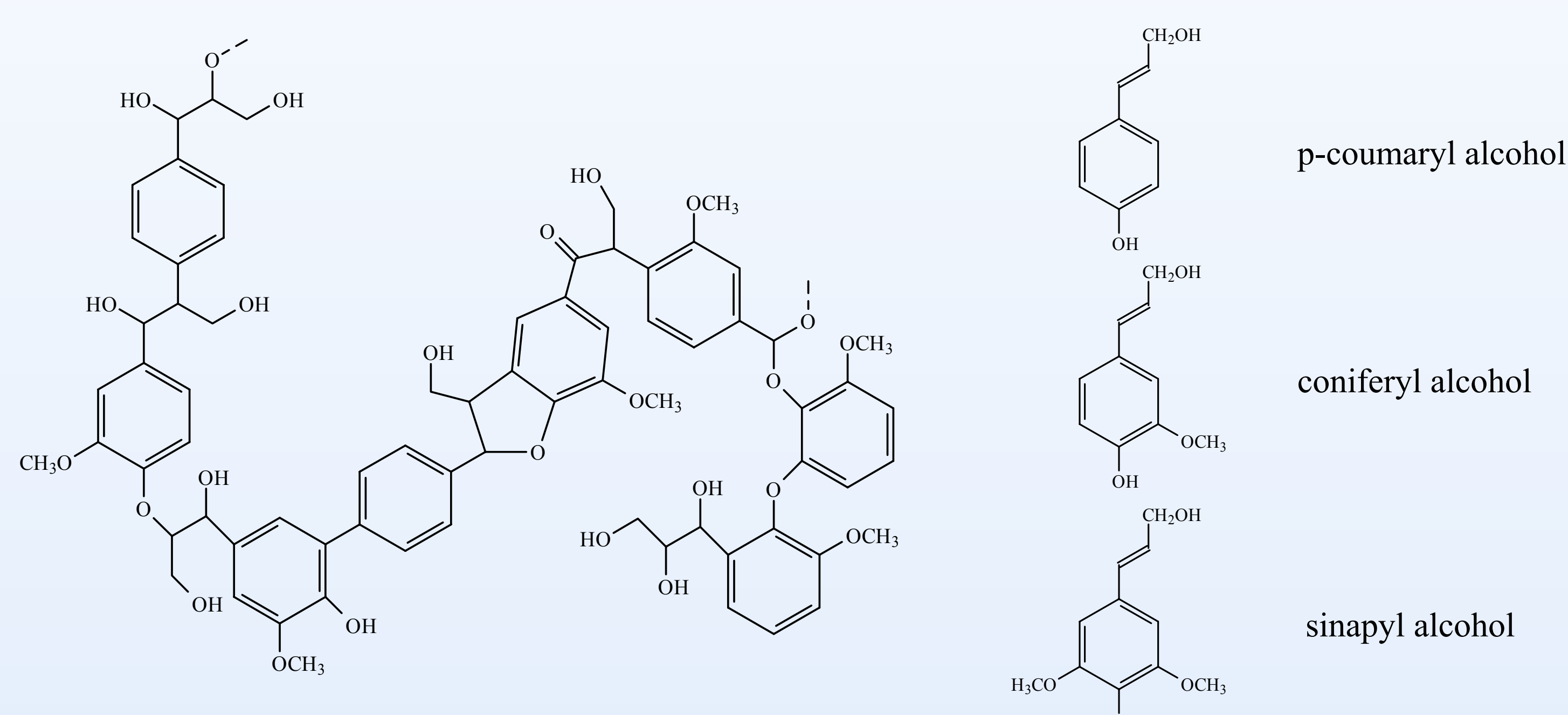
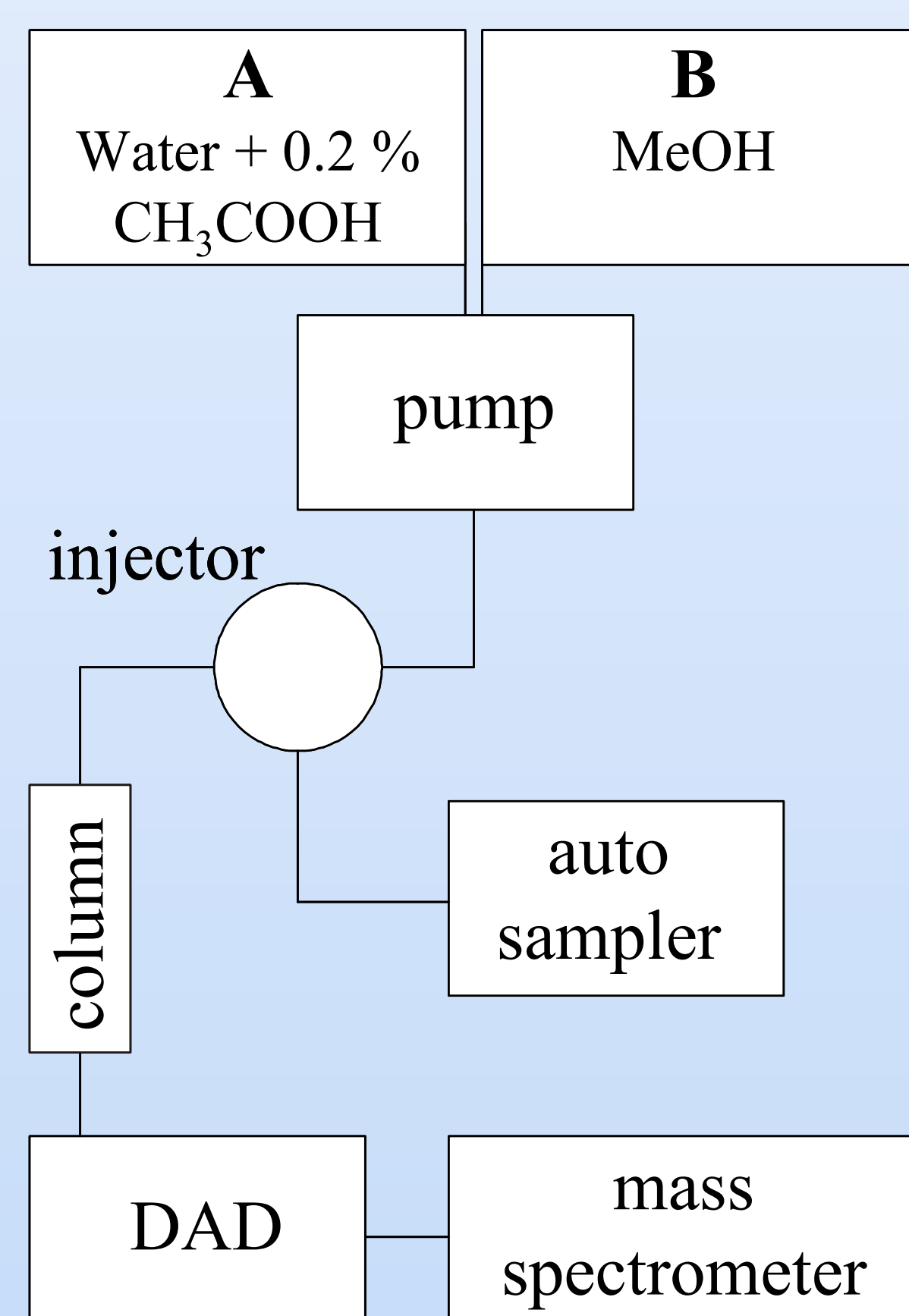


Figure 1: Partial lignin structure and phenolic breakdown products from the pyrolysis of lignin

Experimental



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 (3mm x 150mm x 3,5 µm) and a Zorbax SB-C18 (4,6mm x 30mm x 3,5 µm) by an isocratic elution with H₂O (0.2% CH₃COOH) and MeOH at a 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.

Figure 2: Experimental set-up HPLC-APCI-MS

Results

For a positive identification and quantification of the compounds, a standard solution (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.

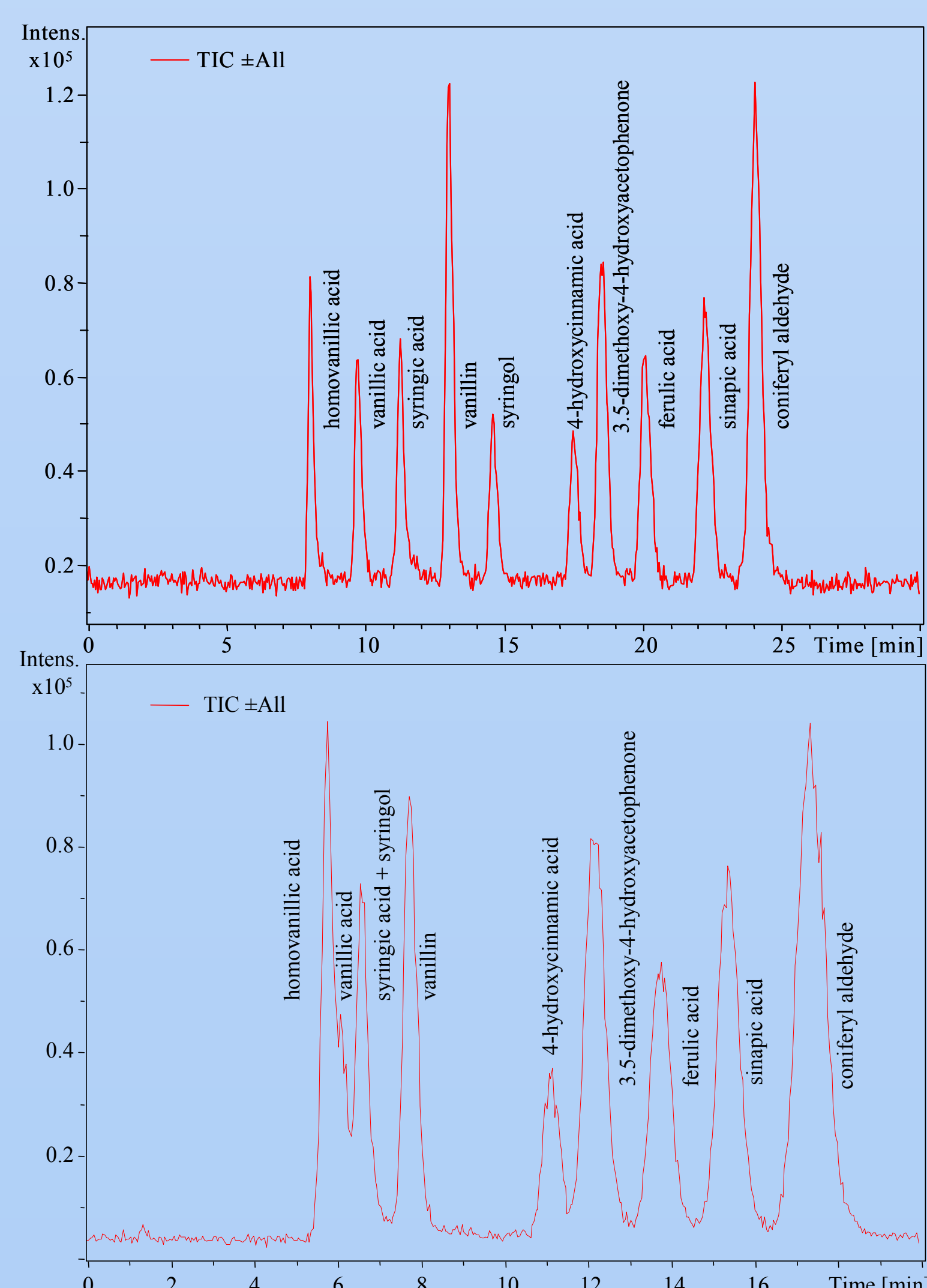


Table 1: Composition, LOD (S/N=3) and correlation coefficients of the biomass burning standard

Standard - biomass burning	MW	m/z	calibration curve corr. coeff.	detection limit µM
vanillin	152.2	153	0.995	0.6
vanillinic acid	168.2	183	0.997	3.3
homovanillinic acid	182.2	137	0.999	0.4
eugenol	164.2	-	n.d.	n.d.
cinnamic acid	148.2	-	n.d.	n.d.
ferulic acid	194.2	177	0.996	0.8
coniferyl aldehyde	178.2	179	0.990	0.3
sinapic acid	224.2	207	0.993	0.7
guaiacol	124.1	-	n.d.	n.d.
3,5-dimethoxy-4-hydroxyacetophenone	196.2	197	0.998	1.1
syringol	154.2	155	0.999	6.4
syringic acid	198.2	213	0.99	1.6
4-hydroxycinnamic acid	164.2	147	0.988	0.8

Figure 3: Total Ion Chromatogram of the biomass standard
(up) Zorbax SB-C8; H₂O/MeOH 70/30; 0,3 ml/min; APCI(+)
(down) Zorbax SB-C18; H₂O/MeOH 75/25; 0,3 ml/min; APCI(+)

Linear calibration curves ($R^2 > 0.98$) were obtained for all standard compounds in the range of 5-50 µM. The detection limits in Table 1 are comparable to the results obtained with CE/ESI-MS^[3] (0.1-1 µM) but higher than the detection limits obtained by Simpson et al. with GC-MS^[4].

To characterise the combustion aerosol of different biofuels, several kinds of wood (hard- and softwood) were combusted. Subsequently, the combustion aerosol was collected, extracted with MeOH, and analysed with the HPLC-APCI/MS. The following figures show two samples from oak and spruce, respectively.

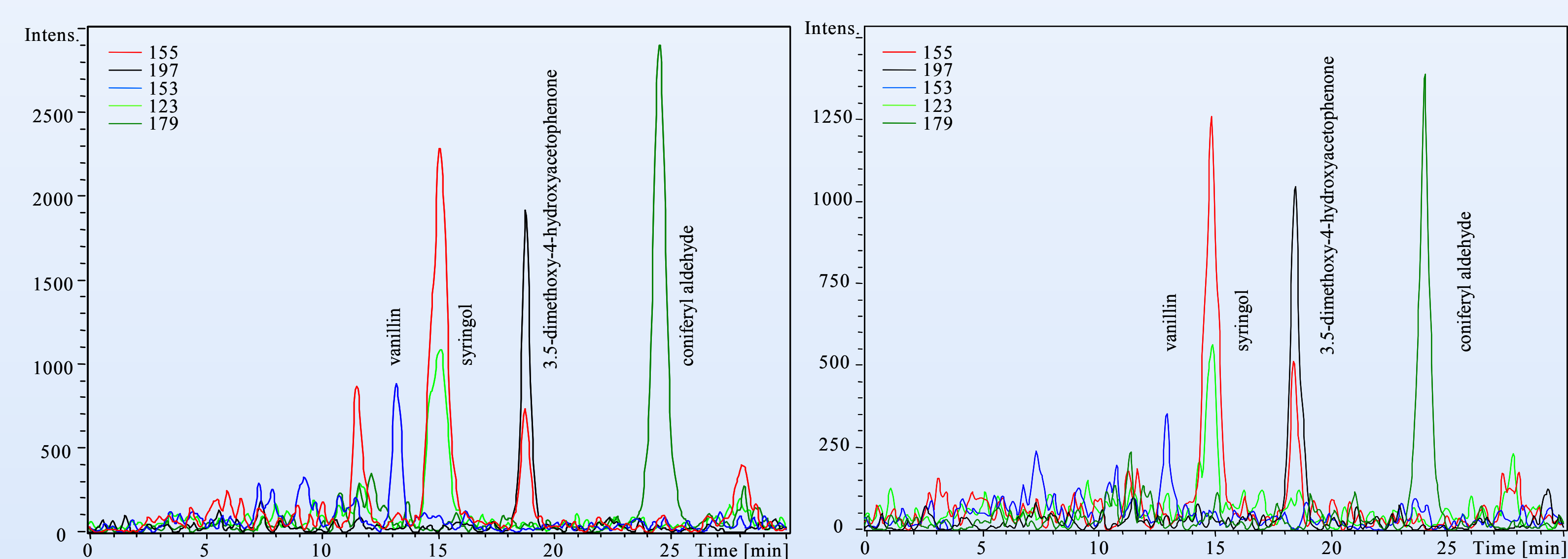
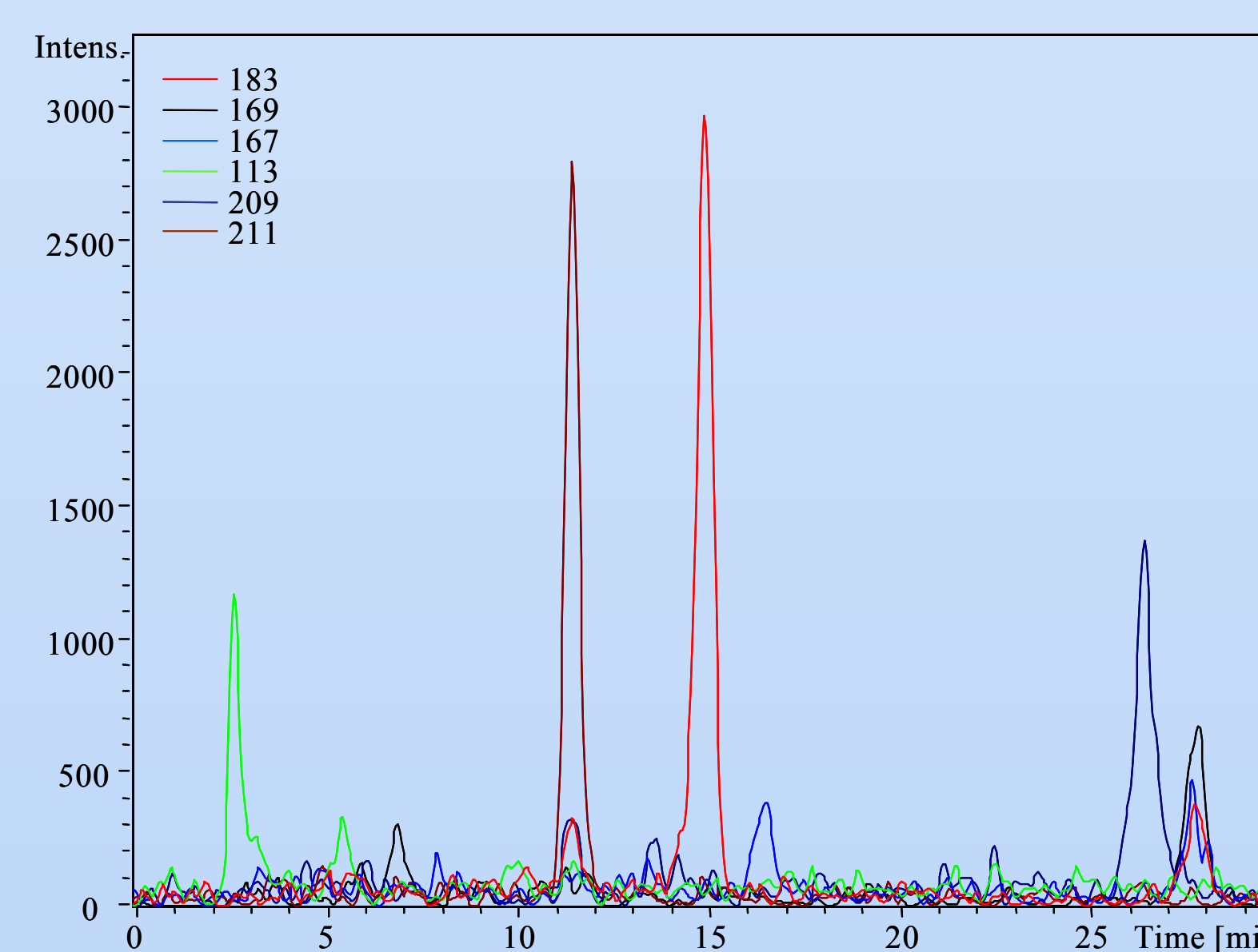


Figure 4: Extracted Ion Chromatograms of biomass burning samples; left side: oak; right side: spruce (Zorbax SB-C8; H₂O/MeOH 70/30; 0,3 ml/min; APCI(+))

Coniferyl aldehyde, vanillin, syringol and 3,5-dimethoxy-4-hydroxyacetophenone could be positively identified in both samples by the retention time and the fragmentation pattern. Additional certainty for the identification can be reached by MSⁿ and TOF-MS experiments. The measured emissions rates of the four identified compounds are about 2 - 50 mg/kg for the oak sample (hardwood) and approximately two times smaller for the spruce (softwood).



Besides this, further unidentified compounds could be detected in the oak and the spruce sample as well (see Figure 5). The identification of the unknown compounds in Figure 5 shall be done by further TOF-MS and MSⁿ experiments.

Figure 5: Extracted Ion Chromatograms of unidentified compounds in the biomass burning sample

Summary/Outlook

- Suited and complementary method for the analysis of biomass combustion samples
- Sufficient limits of detection
- Identification of unknown compounds by the help of TOF-MS and MSⁿ.

References

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Acknowledgments

This work was supported by BMBF within an AFO2000 framework under contract No. 07ATF25 "Impact of Vegetation Fires on the Composition and Circulation of the Atmosphere (EFEU)".