

Determination of alkyl phenols in atmospheric aerosols by gas chromatography–ion trap mass spectrometry

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In recent years there is increasing interest in atmospheric emissions from biomass burning, one of the largest sources of accumulation mode particles globally.

Specific molecular markers have been identified for tracing biomass combustion, in particular carbohydrates (predominately levoglucosan and other anhydrosugars) produced by thermolysis of cellulose and hemicellulose and alkoxyphenols, as thermally decomposition products of lignin, one of the main components in wood. As the basic structure of lignin derives from p-coumaril, coniferyl and synapil alcohols, its burning releases in atmosphere molecules similar to their precursors, such as p-coumaric acid, vanillin, vanillic acid, acetovanillone ferulic acid, syringol, syringaldehyde, syringic acid and acetosyringone.

Different kinds of woods contain different percentage of the three monomers, so that their combustion releases different amounts of alkoxyphenols: diagnostic ratios of syringic/vanillic acids (S/V) and cinnamic/vanillic acids (C/V) have been proposed to identify emissions from specific plant tissue combustion, i.e., hard woods (oak, beech and walnut) or soft woods (conifers) and grass and soft plant tissues (Kuo *et al.*, 2011).

GC–MS is the most widely applied technique for the characterization of organic aerosols since it provides multi-residue methodologies for the simultaneous analysis of several compounds with excellent separation efficiency, sensitivity and high number of species analyzed. Due to their high polarity, lignin phenols have to be converted into volatilizable and stable derivatives: trimethylsilyl derivatives are produced by using BSTFA (N,O-bis(trimethylsilyl)-trifluoroacetamide) as silylation reagent (Pietrogrande *et al.*, 2011).

Due to small concentration of alkoxyphenols in environmental samples, very sensitive analytical methods like GC/MS/MS are needed. The present paper describes a gas chromatography tandem mass spectrometry method using an ion trap system, as a further development of the previous GC/MS method (Pietrogrande *et al.*, 2013), providing the low detection limits and the high reproducibility required by environmental monitoring.

All the compounds were monitored in multiple reaction mode (MRM). For each target analyte the precursor ion and collision-induced dissociation (CID) voltage were carefully selected to optimize CID efficiency to produce daughter ion(s) and minimize interference during the analysis. The MS detection conditions for each target compound are listed in Table 1.

Five-point calibration curves were prepared to quantify the target analytes in the concentration range of 0.2ngm^{-3}

to 5ngm^{-3} using standard solutions. The limits of detection (LOD) of the proposed method were determined by three times the signal to noise ratio S/N (Table 1).

Table 1: MS/MS detection parameters for each target compound: precursor and parent ions. Comparison between sensitivity (LOD) of MS/MS and MS detection procedures.

Analyte	Precursor ion (m/z)	Parent ions (m/z)	MS/MS LOD (ngm^{-3})	MS (SIM) LOD (ngm^{-3})
Catechol	254	239, 166	0,76	1,24
Syringol	196	153, 181	0,51	0,94
Pyrogallol	239	133, 151, 211	0,45	3,53
Vanillic acid	267	223, 225	0,58	1,82
p-Coumaric acid	293	253, 255, 223	1,75	4,56
Syringic acid	297	243, 233, 219	0,57	3,26

As expected, compared to MS detection operating in the selected ion monitoring (SIM) mode, the MS/MS method is characterized by higher specificity and sensitivity due to the effective exclusion of interfering matrix compounds.

The applicability of the developed method to air quality monitoring was verified by application to $\text{PM}_{2.5}$ filters collected under different seasons (summer vs. winter) in different sampling sites (urban vs. rural) in the Emilia Romagna region (Northern Italy).

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