HARDWOOD	SOFTWOOD
BIRCH	SPRUCE
SYRINGYL	GUAIACYL
PHENOLS	SMOKE
IDENTIFICATION	GC - MS

Gas chromatographic and mass spectrometric analysis of 36 lignin-related methoxyphenols from uncontrolled combustion of wood

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A subsequent similar study was made for
phenols from burning of forest plant materials
A preceding study reports
volatile hydrocarbons from domestic wood burning

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Gas chromatographic and mass spectrometric analysis of 36 lignin-related methoxyphenols from uncontrolled combustion of wood.

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Abstract

Eighteen 4-hydroxy-3-methoxyphenyl (guaiacyl) compounds in wood smoke from spruce, and eighteen 4-hydroxy-3,5-dimethoxyphenyl (syringyl) analogues in birchwood smoke were analysed. Smoke samples were taken by a gas syringe from wood burning under varying but more or less choked conditions in laboratory pot experiments. Retention index data for a methylsilicone column and basic mass spectral data are given for all compounds. Retention index in combination with molecular mass and structure-specific fragment ions greatly facilitates qualitative analysis. The syringyl and guaiacyl analogues differ by 240 units in retention index and the matching structure-specific ions in their mass spectra by 30 mass units.

The identified methoxyphenols differ in the structure of the sidechain, which may be lacking, an alkyl group, an alkenyl group, a carbonyl-containing group or an alcoholic moiety. The proportions between these groups of compounds varied strongly with combustion conditions whereas the proportions of phenols within them were quite specific for each group. The phenols with reactive olefinic linkages in the sidechain were present in larger proportions than reported in other studies of methoxyphenols.

Keywords: Phenols; GC/MS Data; Wood smoke; Biomass burning

1. Introduction

Air pollutants from wood combustion are of great concern both in wood fuel use by man and in natural and accidental fires. The nature of these pollutants and their environmental and

health effects are widely different compared with the better known pollutants from petroleum products and traffic. The methoxyphenols from lignin in wood stand out as particularly specific and prominent combustion-formed compounds. Their importance was pointed out and many of them were determined in studies of soot and smoke from stoves and fireplaces [1,2]. These and several additional methoxyphenols have been determined from controlled pyrolysis of wood [3,4]. Softwood gives rise to 4-hydroxy-3-methoxyphenyl (guaiacyl) compounds, whereas mainly 4-hydroxy-3,5-dimethoxyphenyl (syringyl) compounds are formed from hardwood [2-4].

With urban health hazards in view, several methoxyphenols have been determined in urban air [5] and in fog polluted by wood smoke [6]. Considering the dangers of wildland fires, methoxyphenols and other pollutants have been studied in wood smoke condensates [7] and in combustion emissions from different types of forest biomass [8].

The purpose of this study is to give analytical data for a comprehensive set of methoxyphenols formed from wood combustion under varying conditions. Previous studies have been made for volatile hydrocarbons from the burning of biomass [9] and wood [10], and for furans from wood burning [11].

2. Experimental

The wood burnt (0.5 - 2 g) was sticks of about the size of a match and thinner chips cut from sapwood. The wood was intended for residential heating and had been dried in the open air during the summer.

Conditions

Combustion pot	:	Ceramic, 1.5 l
Covering pot	:	Clay, 2l, with bottom hole
Sampling syringe	:	500 µl, gas-tight, SGE
Sample volume	:	100 - 500 µl

Gas chromatograph	:	Varian 3800 (MS-linked)
Injection	:	220 °C, splitless
Column	:	30 m FSOT, 0.25 mm i.d.
Stationary phase	:	DB-1, methylsilicone
Phase layer	:	0.25 µm
Temperature program	:	5 °C min^{-1} from 50 to 200 °C
Carrier gas	:	Helium, 1.1 ml min^{-1}, 12 psi

Mass spectrometer	:	Varian Saturn 2000
Ionization	:	EI, 70 eV
Ion trap	:	150 °C
Mass range	:	m/z 35 - 400
Scanning	:	1 spectrum s^{-1}
Spectra library	:	NIST

The identifications of the methoxyphenols were based on correlations between structure and retention, and on molecular weight and specific mass spectrometric fragmentations, as described below. The structural assignments were supported by comparisons between the matching guaiacyl and syringyl compounds. Data library spectra (NIST) were available for several of the guaiacyl species but only for a few syringyl species. Comparisons with published sets of mass spectra of phenols from pyrolysis [3,12,13] confirmed the identities of the methoxyphenols. The identifications were also checked against mass spectral and retention data in the other literature references on phenols.

3. Results and discussion

The phenols reported in Table 1 were identified as characteristic components in wood smoke from uncontrolled burning under differing conditions. The basic substitution pattern of the aromatic ring was found to be uniform and characteristic of the phenols from wood. The phenols from spruce (Picea abies) contained the guaiacyl (4-hydroxy-3-methoxyphenyl) unit. Birchwood gave rise mainly (about 80%) to phenols containing the syringyl (4-hydroxy-3,5-dimethoxyphenyl) unit, but also (about 20%) to the same guaiacyl compounds as spruce. These differences between spruce and birch reflect the structural differences of lignin between softwood and hardwood species. Comparative studies of wood smoke from pine and several hardwood species confirmed this difference in phenol composition, which has also been reported for products from pyrolysis [3,4,14].

Some twenty experiments were performed with deliberately varied conditions with respect to combustion and wood fuel. The phenolic carbonyl and alcohol compounds reported in Table 2 were identified in some of the experiments. Most of these phenols differ from those in Table 1 by strongly fluctuating proportions, more polar properties, lower volatility, and longer

Table 1

Basic analytical data for methoxyphenols regularly occurring in wood smoke from birch (4-hydroxy-3,5-dimethoxyphenyl or syringyl compounds) and spruce (4-hydroxy-3-methoxyphenyl or guaiacyl compounds).

Birch Sy: Syringyl	Proportions %, approximate	Retention index Methylsilicone	Molecular ion		β-Cleavage ions			Further data
			m/z	%	Bond	m/z	%	
SyH	5	1304	154	100	O–C	139	60	a b c d
SyCH$_3$	10	1403	168	100	O–C	153	60	b c d
SyCH$_2$CH$_3$	5	1490	182	50	C–C	167	100	b c
SyCH$_2$CH$_2$CH$_3$	2	1568	196	40	C–C	167	100	b c
SyCH=CH$_2$	20	1517	180	100	O–C	165	60	c d
SyCH$_2$CH=CH$_2$	5	1558	194	100	O–C	179	20	a b c d
SyCH=CHCH$_3$ (Z)	3	1604	194	100	O–C	179	20	b c d
SyCH=CHCH$_3$ (E)	30	1652	194	100	O–C	179	20	b c d
Sy(CO)H	10	1595	182	100	C–H	181	80	a b c d
Sy(CO)CH$_3$	3	1671	196	40	C–C	181	100	a b c d
SyCH$_2$(CO)H	2	1642	196	30	C–C	167	100	c d
SyCH$_2$(CO)CH$_3$	5	1707	210	40	C–C	167	100	b c

Spruce Gu: Guaiacyl	Proportions %, approximate							
GuH	5	1057	124	80	O–C	109	100	a b c d
GuCH$_3$	10	1160	138	100	O–C	123	100	a b c d
GuCH$_2$CH$_3$	5	1247	152	40	C–C	137	100	a b c d
GuCH$_2$CH$_2$CH$_3$	2	1334	166	30	C–C	137	100	a b c
GuCH=CH$_2$	20	1277	150	100	O–C	135	100	c d
GuCH$_2$CH=CH$_2$	5	1321	164	100	O–C	149	40	a b c d
GuCH=CHCH$_3$ (Z)	3	1370	164	100	O–C	149	40	a b c d
GuCH=CHCH$_3$ (E)	30	1411	164	100	O–C	149	40	a b c d
Gu(CO)H	10	1346	152	80	C–H	151	100	a b c d
Gu(CO)CH$_3$	3	1435	166	40	C–C	151	100	a b c d
GuCH$_2$(CO)H	2	1406	166	30	C–C	137	100	c d
GuCH$_2$(CO)CH$_3$	5	1478	180	30	C–C	137	100	a b c

[a]Available in the NIST library of mass spectra.

[b]Determined in extracts of filter-sampled stove emissions [2] and urban air [5].

[c]Reported as products of wood pyrolysis, with retention data and mass spectra [3,12,13].

[d]Determined from controlled pyrolysis of wood and pulp from birch and spruce [4].

Table 2

Basic GC-MS data for late-eluting syringyl (4-hydroxy-3,5-dimethoxyphenyl) and guaiacyl (4-hydroxy-3-methoxyphenyl) compounds occurring under specific inefficient combustion conditions.

Hardwood Sy: Syringyl	Proportions Relative	Retention index Methylsilicone	Molecular ion		β-Cleavage ions			Further data
			m/z	%	Bond	*m/z*	%	
Sy(CO)CH$_2$CH$_3$	minor	1764	210	20	C–C	181	100	b c
SyCH$_2$CH$_2$(CO)H	minor	1753	210	40	C–C	167	100	
SyCH=CH(CO)H (*E*)	significant	1909	208	100	O–C	193	10	c d
SyCH=CHCH$_2$OH (*Z*)	minor	1856	210	80	(C–C)^e	167	100	c d
SyCH=CHCH$_2$OH (*E*)	significant	1928	210	100	(C–C)^e	167	100	c d
SyCH$_2$CH$_2$CH$_2$OH	minor	1833	212	60	C–C	167	60	b c
Softwood Gu: Guaiacyl								
Gu(CO)CH$_2$CH$_3$	minor	1529	180	20	C–C	151	100	b c
GuCH$_2$CH$_2$(CO)H	minor	1515	180	60	C–C	137	100	
GuCH=CH(CO)H (*E*)	significant	1668	178	100	O–C	163	20	c d
GuCH=CHCH$_2$OH (*Z*)	minor	1623	180	60	(C–C)^e	137	100	c d
GuCH=CHCH$_2$OH (*E*)	significant	1683	180	80	(C–C)^e	137	100	a c d
GuCH$_2$CH$_2$CH$_2$OH	minor	1597	182	60	C–C	137	100	c d

[a]Available in the NIST library of mass spectra.

[b]Determined in extracts of soot from wood burning [1].

[c]Reported as products of wood pyrolysis, with retention data and mass spectra [3,12,13].

[d]Determined from controlled pyrolysis of wood and pulp from birch and spruce [4].

[e]β-Cleavage after rearrangement of the molecular ion.

gas chromatographic retention times. The results indicated that they are more likely to occur from pyrolysis and smouldering than from flame combustion and fires.

3.1 Gas chromatography

Retention data are given in Tables 1 and 2 as retention index for linear temperature-programmed analysis on a capillary column with a methylsilicone as the stationary phase. Methylsilicone phases are well defined and widely used and therefore suitable for reference data. Polar compounds normally tend to give somewhat asymmetrical and tailing peaks when separated on non-polar stationary phases. Although the phenols are more or less polar in nature, satisfactory chromatographic behaviour was observed on the non-polar methylsilicone column for most of them. Columns with appropriate polar stationary phases [3,12] are recommended for the carbonyl and especially the alcoholic compounds when quantitative accuracy is critical. Polar columns are also needed when anhydrosugars, such as 1,6-anhydroglucose, and other very polar pyrolysis products from wood polysaccharides are to be analysed simultaneously [4].

The retention index of the reported phenols ranges from 1000 to 2000, and increases with molecular weight and to some extent with the polarity of the species. The index of structural homologues increases with approximately 100 units for each carbon atom in the sidechain. For each of the eighteen pairs of guaiacyl and syringyl compounds, the retention index increment is between 230 and 250, which must be regarded as a very narrow range. The systematic relationships between structure and retention index are useful in qualitative gas chromatographic analysis of the phenols.

Retention index data for many of the methoxyphenols have been given for a 5% phenylmethylsilicone [1,2]. The reported values are between 30 and 80 units higher than those

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given here for a methylsilicone. As anticipated, the difference tends to increase with the polarity of the compounds.

3.2 Mass spectrometry

Mass spectra were recorded, interpreted and used in identifications for all the reported phenols.

The molecular ion is abundant for these phenols, and normally the most abundant ion in the whole spectrum, if there are no favoured fragmentation paths in the sidechain. The selected molecular ion chromatograms in Fig. 1 demonstrate the presence and separation of all twelve syringyl compounds reported in Table 1 from birchwood burning. The total ion chromatogram illustrates the predominance and the quantitative proportions of the methoxyphenols. Guaiacyl compounds give rise to the small early peaks, and the major product from cellulose, 1,6-anhydroglucose, to the unresolved bulky peak. Similar chromatograms were obtained for the guaiacyl compounds from softwood. For the later eluting, somewhat more complex phenols, reported in Table 2, the presence of an abundant molecular ion is especially useful for identification purposes.

Mass spectra of alkylbenzenes are characterised by abundant ions formed by "β-cleavage" of the bond between the carbon atoms in α and β positions relative to the benzene ring. From the data given in Tables 1 and 2, it is seen that methoxyphenols which can be fragmented by single-bond C-C β-cleavage typically have the corresponding ion as the most abundant in their spectra. Although less favoured, β-cleavage of the O-C bond of the methoxy group appears to give rise to prominent ions for other phenols. Other prominent peaks in the spectra of these phenols can be ascribed to further loss of carbon monoxide (28 mass units). Vanillin (4-hydroxy-3-methoxybenzaldehyde) and the corresponding syringyl aldehyde are
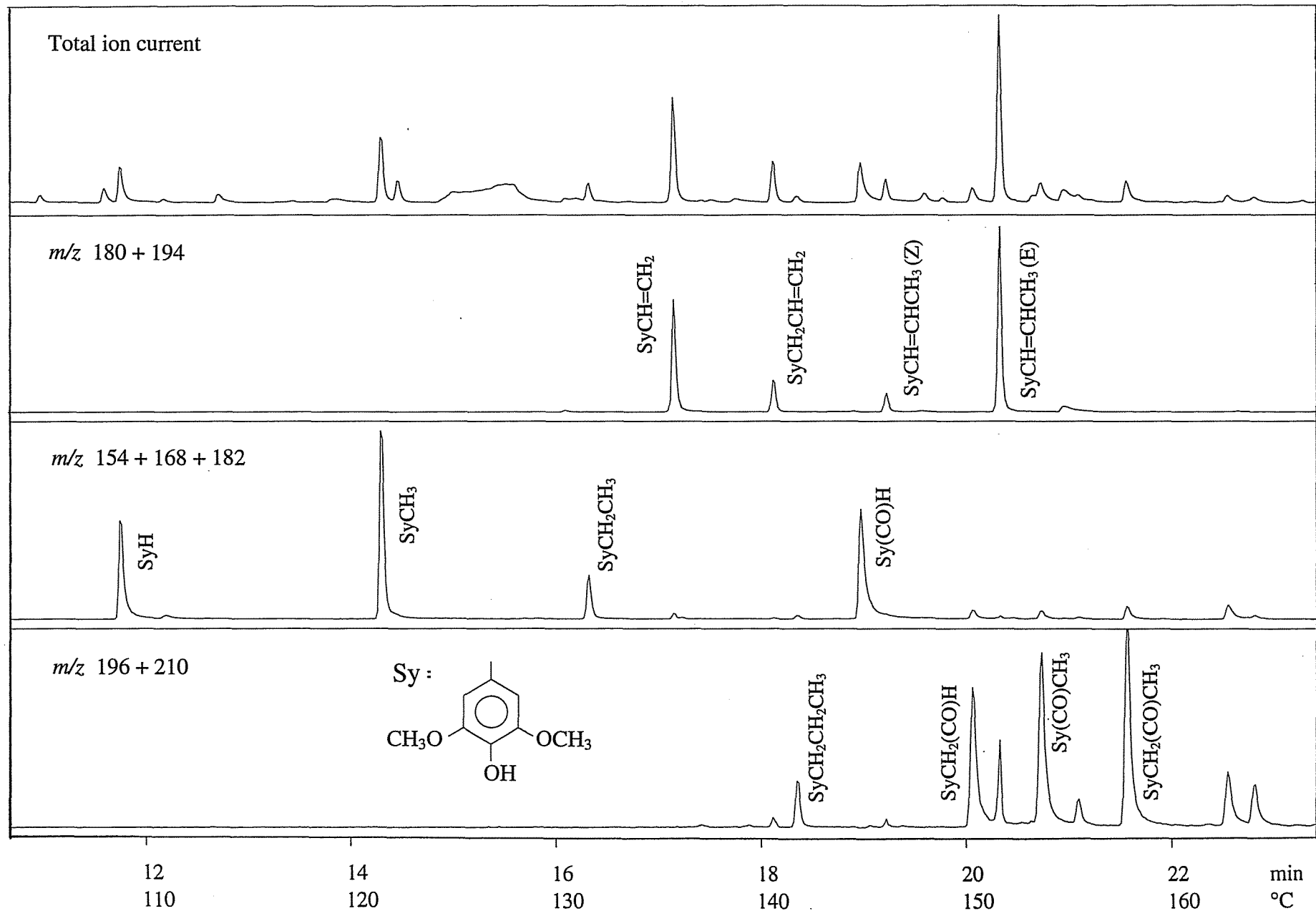
Fig.1. Ion chromatograms from GC-MS analysis of 4-hydroxy-3,5-dimethoxyphenyl
(syringyl) compounds in smoke from birchwood burning (total ion current and ion currents
corresponding to the molecular ions m/z 180 + 194, 154 + 168 + 182 and 196 + 200).

characterised by β-cleavage loss of a hydrogen atom. The specificity of the ions from β-cleavage makes them valuable for structural assignments of the phenols.

The four phenols in Table 2, with 3-hydroxy-1-propenyl sidechains, gave rise to deviating spectra with a mass of the most abundant ion corresponding to an unlikely β-cleavage of the double bond. This fragmentation is probably explained by favoured hydrogen rearrangements within the molecular ion before it is fragmented [3]. The spectra are actually similar to those attributed to the corresponding methoxyphenols with a 3-oxopropyl sidechain. The spectra of the cis (Z) and trans (E) isomers differed somewhat in relative peak intensities whereas, as expected, the spectra of the other pairs of geometric isomers were very similar.

3.3 Quantitative proportions

All reported methoxyphenols can be derived from the basic phenylpropenol units of lignin. The three-carbon side chain is kept intact, fragmented, oxidized or reduced to varying degrees, depending on the combustion conditions. The phenols in Tables 1 and 2 are arranged into several structurally similar groups. Particularly within these groups, characteristic quantitative ratios were observed.

Among the phenols with saturated hydrocarbon sidechains, the propyl compounds were less prominent than the compounds with fewer carbon atoms. In contrast, the trans-1-propenyl phenols were normally major components. The ethenyl phenols were also prominent and more so than the 2-propenyl and cis-1-propenyl analogues. Among the carbonyl compounds, the formyl and 2-oxopropyl species tended to be the most prominent. The proportions of these and other reported carbonyl phenols increased strongly under certain conditions such as glowing combustion. The alcohols in Table 2 are likely to be reactive intermediates during combustion, and their occurrence varied strongly with the nature of

wood fuel and combustion. The predominance of the *trans* isomer for the unsaturated phenols is in accordance with experience from the chemistry of these compounds.

The approximate proportions given in Table 1 for choked burning of small wood sticks and chips from birch and from spruce compare well with results from residential burning of American hardwood and softwood as determined in chimney smoke plumes [2]. Significant differences were higher proportions in the chimney smoke of guaiacol, syringol and their methyl and ethyl analogues, and lower proportions of the alkenyl derivatives. Controlled pyrolysis of wood from spruce and birch [4] gave rise to higher proportions of the carbonyl compounds and lower proportions of the alkenyl compounds. Some of the compounds in Table 2 were obtained in high proportions from spruce wood [4]. In our study, the proportions of the compounds in Table 2 were variable but for choked burning altogether about 10% of those in Table 1.

3.4 Sampling aspects

The method for combustion and sampling was designed to reflect the highly varying conditions during wildland fires and small-scale burning for heating and cooking. Typically, the wood material in the pot was aflame and about half of it burnt when the fire was choked by an upside-down pot. Syringe samples were normally taken within one minute through the bottom hole with extinguished flames but more or less glowing wood. The sample therefore reflects emissions on the scale from flaming to smouldering at different temperatures and differing oxygen supply. The small volume inside the pots causes concentrations more than high enough for detailed GC-MS analysis of syringe gas samples. The methoxyphenols obtained include those previously determined in residential wood smoke [2] as well as most of those obtained from controlled pyrolysis of wood [3,4].

Most of the methoxyphenols are easily condensed on particles and occur on particles at ambient temperature [2]. Analysing the still warm gas sample very soon after taking it minimized potential problems with condensation in the syringe. The alcohols and aldehydes in Table 2 are likely to condense rapidly because of their high polarity and low volatility.

An advantage of the applied sampling method is that losses are avoided for the easily oxidized olefinic compounds. Oxidative losses may cause severe problems when sampling on different kinds of filters [5]. More oxidative combustion conditions and higher decomposition rates in air are also important reasons why reported proportions of the olefinic phenols in ambient air [5,6] are much lower than in this study.

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