Study of tropical organic aerosol by thermally assisted alkylation-gas chromatography mass spectrometry

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Abstract

Fine (< 2.6 μm) and size-segregated aerosol samples collected at a tropical pasture site (Rondônia, Brazil) under various conditions have been analysed by thermally assisted hydrolysis and alkylation, coupled to GC/MS. Fatty acids, alkadioic acids, hydroxybenzoic acids, levoglucosan, and other compounds of polysaccharide origin have been identified as their methyl ester and ether derivatives among the products of thermally assisted methylation. The identity of the characteristic hydrolysed fragments and soluble components has been confirmed by butylation and silylation as well. To improve available chemical information, this analytical method has also been combined with a thermal pre-treatment. Seasonal variation of size-resolved distribution of the characteristic fragments of thermally assisted hydrolysis and methylation (THM) in the atmospheric aerosol is shown. Although the results presented in this paper are preliminary and based on a limited number of aerosol samples, they clearly demonstrate the sensitivity and potential of thermally assisted alkylation-GC/MS to

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provide unique chemical information on the bulk of organic matter in tropospheric aerosol to facilitate their source apportionment.

1. Introduction

Carbonaceous aerosol has been recently shown to play a key role in inadvertent climate modification [1], though its chemical composition, sources and properties are still poorly understood. The chemical characterisation of carbonaceous aerosol requires efficient sampling and highly sensitive and selective analytical techniques due to its low atmospheric concentration and extreme complexity. Thermal desorption coupled on-line to GC/MS or MS proved to be an adequate method analysing industrial pollutants in urban aerosol in which combustion-derived species predominate [2]. The study of fine (< 2.5 μm aerodynamic diameter) carbonaceous aerosol in rural and remote areas, which reportedly contain highly polar macromolecular compounds of low volatility [3,4], calls for the application of analytical pyrolysis techniques capable of elucidating the chemical composition and structure of organic macromolecules. However, pyrolysis-GC/MS analysis of aged rural or biomass burning aerosol samples collected on carbon-free substrates yields non-specific degradation products (H_2O, CO_2, SO_2, benzene, toluene, paraffins, olefins) and consequently poor structural information on the carbonaceous matrix. Water and carbon dioxide as pyrolysis products indicate the presence of thermally unstable functional groups, thus thermally assisted hydrolysis and methylation (THM), coupled to GC/MS has been performed for characterising the organic matter in fine tropospheric aerosol [5]. Py-GC/MS and THM-GC/MS have also been applied recently in other laboratories to study the composition of organic constituents in air particulate matter (PM10) [6,7], tracing components of biomacromolecules, namely lignin, carbohydrates, protein and lipids. THM-GC/MS or -MS have already been widely used for the determination of structural components of lignin [8,9], soil organic matter [10,11], sediments [12], and kerogens [13], as well as for the detection and differentiation of carbohydrates [14], bacteria, viruses [15,16], and for on-line analysis of fatty acid composition of various lipids and waxes in trace quantities [17,18].

The main objective of the present work was to demonstrate the ability of the THM-GC/MS method for the characterisation of organic matter in fine aerosol, which, contrary to the unlimited bulk mass of soil organic matter, is available only in trace amounts distributed on the surface of a collection substrate. In some instances, the sample mass was further reduced by size-resolved sampling or sample pre-treatment. Tracking the size-distribution of the characteristic fragments of organic matter or pre-existing organic compounds with reasonable time-resolution, which seems to be only feasible with this highly sensitive direct method, may facilitate

source apportionment of carbonaceous aerosol, thus improving our understanding of fundamental atmospheric processes.

2. Experimental

2.1. Samples and sample preparation

Aerosol sampling was conducted in the European contribution to the Large Scale Atmosphere-Biosphere Experiment in Amazonia (LBA-EUSTACH) and CLAIRE campaigns in September to October 1999 and July 2001 in the dry (biomass burning) and wet seasons, respectively, at Fazenda Nossa Senhora Aparecida (FNS) (10°45′44″ S, 62°21′27″ W, 315 m a.s.l.), a ground-based station (4.5 m above ground level) in a pasture site in the state of Rondônia, Brazil [19]. The study site was deforested by fire about 20 years ago. Fine (< 2.6 μm) particles were collected on pre-baked quartz filters (Pallflex Tissuquartz 2500 QAT-UP) using a high volume dichotomous sampler (HVDS) at Rebio Jaru, in a forest site mounted at approximately 53 m from the ground. The HVDS sampler allows the collection of particles in fine (D_p < ca. 2.6 μm) and coarse (D_p > ca. 2.6 μm) modes. The total flow was around 330 l min^{-1} and the sampling periods were 12 h day and/or night, 24 and 48 h. The size-segregated aerosol samples were collected on pre-cleaned and pre-weighted aluminium foils with a ten-stage Micro Orifice Uniform Deposit Impactor (MOUDI) with cutoff values of (1) 0.071, (2) 0.124, (3) 0.222, (4) 0.426, (5) 0.777, (6) 1.342, (7) 2.322, (8) 4.384, (9) 7.835 and (10) 13.349 μm. Detailed description of sample collection has been published elsewhere [20]; the sample collection periods and sample types are indicated in Table 1.

Hydrolysis and alkylation was carried out directly on the collection surface. 5 μl of tetramethylammonium hydroxide (15 wt.% in water, from Fluka, Switzerland) or 3 μl tetrabutylammonium hydroxide (40 wt.% in water, Fluka) was poured onto a spot of quartz filter or aluminium foil with an area of 0.8–1.2 cm^2, then left to dry at room temperature for an hour prior to introducing it into the pyrolysis sample

Table 1
Sampling details for aerosol collected at "Fazenda Nossa Senhora" (pasture site) and Rebio Jaru (forest site), Rondônia, Brazil

Sample code	Sampling date (dd.mm.yyyy)	Sample volume (m^3)
LBA661–670[a,c]	05.10.1999–06.10.1999	39.3
AM01–AM10[a,d]	22.07.2001–25.07.2001	112.2
JARU-32[b,c,e]	05.10.1999–06.10.1999	426.6

[a] Pasture site.
[b] Forest site.
[c] Dry season campaign.
[d] Wet season campaign.
[e] Also analysed after heat-treatment.

holder. Silylation was performed by dumping the filter or foil with *N,O*-bis(trimethylsilyl)-acetamide (BSA, from Pierce, Netherlands), then the sample was immediately introduced in to the preheated pyrolysis chamber without drying.

2.2. Thermally assisted hydrolysis and alkylation- (THA-) and silylation-GC/MS

THA-GC/MS experiments were performed at 400 °C for 20 s in a Pyroprobe 2000 pyrolyser (Chemical Data System) equipped with a platinum coil and quartz sample tube interfaced to a gas chromatograph (Agilent 6890) coupled with a mass selective detector (Agilent 5973) operating in electron impact mode (EI) at 70 eV. The temperature of the GC/MS interface was held at 280 °C. Silylation-GC/MS was carried out under identical experimental conditions described for THA-GC/MS.

A helium carrier gas of 20 ml min^{-1} flow rate purged the pyrolysis chamber held at 250 °C. Splitless mode was applied at the GC inlet heated at 250 °C for the introduction of products from the pyrolysis chamber in to the GC column. The GC separation was carried out on a fused silica capillary column (Hewlett–Packard 5MS), 30 m × 0.25 mm. A temperature program from 50 to 300 °C at 10 °C min^{-1} was applied with an isotherm period of 1 min at 50 °C and of 4 min at 300 °C.

Identification of the GC/MS peaks was based in most cases on comparison to spectra of NIST 98 spectrum library. Relative amounts of the products were evaluated by relating peak areas of characteristic ion chromatograms. Total ion chromatograms or parent ion chromatograms could not used for this purpose, because of the contribution of occasionally unresolved peaks to the integrated counts of the compound under study.
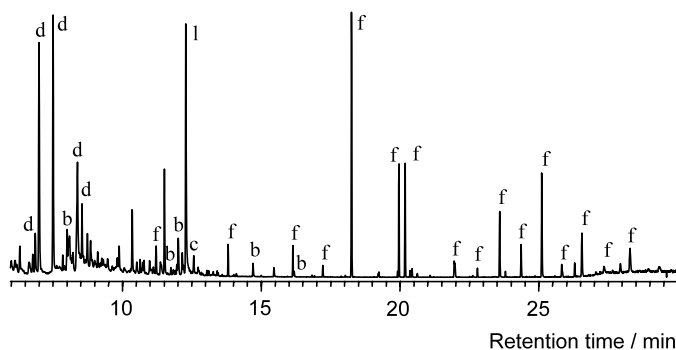

Fig. 1. THM-GC/MS total ion chromatogram of a tropical fine aerosol fraction (LBA666) collected in dry season. **b**, Benzoic acid methyl ester and methyl ether of hydoxybenzoic acid methyl ester; **c**, methyl ether of sugar alcohol; **d**, dimethyl ester of dioic acid; **l**, levoglucosan trimethyl ether; **f**, fatty acid methyl ester. List of the corresponding identified compounds is given in Table 1.

Table 2
THM-GC/MS products of fine tropical aerosol

Compound name	Retention time (min)	Symbol[a]
2-Butenedioic acid (*E*)-, dimethyl ester	6.89	**d**
Butanedioic acid, dimethyl ester	7.03	**d**
2-Methylbutanedioic acid, dimethyl ester	7.53	**d**
Butanedioic acid, 2,2-dimethyl-, dimethyl ester	7.89	
Benzoic acid, methyl ester	8.05	**b**
Pentenedioic acid, dimethyl ester	8.41	**d**
Pentanedioic acid, dimethyl ester	8.57	**d**
2-Methylpentanedioic acid, dimethyl ester	8.77	
Pentanedioic acid, 2-methyl-, dimethyl ester	9.14	
Nonanoic acid, methyl ester	9.85	
Benzene, 1,2,3-trimethoxy	11.14	
Decanoic acid, methyl ester	11.24	**f**
Benzoic acid, 3-methoxy-, methyl ester	11.54	**b**
Benzoic acid, 4-methoxy-, methyl ester	12.04	**b**
Levoglucosan trimethyether	12.32	**l**
2,3,4-Trimethyl-D-xylose	12.59	**c**
1,4-Benzenedicarboxylic acid, dimethyl ester	13.63	
Dodecanoic acid, methyl ester	13.84	**f**
Nonanedioic acid, dimethyl ester	14.13	
Benzoic acid, 3,4-dimethoxy-, methyl ester	14.72	**b**
Benzene, 1,2,3-trimethoxy-5-(2-propenyl)	15.40	
Tetradecanoic acid, methyl ester	16.17	**f**
Benzoic acid, 3,4,5-trimethoxy-, methyl ester	16.20	**b**
Pentadecanoic acid, methyl ester	17.24	**f**
7-Hexadecenoic acid, methyl ester, (*Z*)	18.05	
Hexadecanoic acid, methyl ester	18.28	**f**
Heptadecanoic acid, methyl ester	19.24	**f**
9-Octadecenoic acid (*Z*)-, methyl ester	19.99	**f**
Octadecanoic acid, methyl ester	20.21	**f**
Octadecadienoic acid, methyl ester	20.36	
Octadecadienoic acid, methyl ester	20.44	
Eicosanoic acid, methyl ester	21.97	**f**
Uncosanoic acid, methyl ester	22.80	**f**
Docosanoic acid, methyl ester	23.61	**f**
Tricosanoic acid, methyl ester	24.38	**f**
Tetracosanoic acid, methyl ester	25.13	**f**
Pentacosanoic acid, methyl ester	25.84	**f**
Hexacosanoic acid, methyl ester	26.57	**f**
Octacosanoic acid, methyl ester	28.29	**f**

[a] Symbol denoting peaks in Fig. 1.

3. Results and discussion

3.1. Identification of THM products

The main products of THM of the tropical fine aerosols investigated are fatty acid methyl esters, dimethyl esters of dioic acids, trimethyl ether of levoglucosan and

methyl ethers of hydroxybenzoic acid. A typical total ion chromatogram is displayed in Fig. 1, and the most important GC peaks identified are listed in Table 2. The sample (LBA666) subjected to THM-GC/MS was the fraction of the MOUDI impactor, in which most of the fine aerosol mass was found. Some minor peaks of the chromatogram are also included in Table 2, which may be of interest for the source apportionment of organic aerosol. Some methylated hydrolysis products of high volatility, originating from the aerosol sample-may be eluted at retention times lower than 6 min, but their identification could not be performed due to the co-eluting large peaks of the reagent by-products.

3.2. Products of butylation

The by-products from the decomposition of tetrabutylammonium hydroxide are of considerably higher molecular mass than those from tetramethylammonium hydroxide, hence they are eluted at higher GC retention times. In this way, the identification of the butyl esters of acetic and propanoic acids was possible among the hydrolysis butylated (THB) products, since their GC peaks are eluting before the by-products of the butylating reagent.

The main products of thermally assisted hydrolysis and butylation are similar to those of methylation, but butyl derivatives are obtained as expected. It has to be mentioned that the relative areas of the GC/MS total ion peaks also changed noticeably: the peaks of alkadioic acid diesters are higher than those of fatty acid butyl esters, moreover, tributyl ether of levoglucosan could not be identified among the THB products. This alteration may be attributed to the different reactivity of the reagents.

Butylation makes it easier to find the origin of the hydroxybenzoic acid derivatives (shown in Fig. 2), because the alkylated hydoxyl groups are clearly distinguished from the originally present methoxy substituents characteristic for the lignin type, since the last ones remained unchanged in the molecules of the butylated hydrolysis products. The molecular ion chromatograms of the corresponding butylated compounds derived from THB-GC/MS of sample LBA666 are displayed in Fig. 3. The nearly exclusive appearance of the methoxyphenolic compounds among the butylated products, which are expected from the basic lignin repeat units confirm the origin of these products. The only exception is 3-butoxybenzoic acid butyl ester, the molecular ion peak of which occurs in Fig. 3 at 17.79 min. The methylated analogue of this compound is also found among the THM products eluted at 11.54 min (one of the **b** peaks in Fig. 1). Mass spectra of butylated compounds presented in Fig. 2 are not included in the spectral library available, thus they are displayed in Figs. 4 and 5.

In addition to lignin-derived benzoic acids, similarly substituted benzaldehydes have been also detected among THM and THB products. The relative peak areas of the analogous methoxy-substituted benzoic acids to benzaldehydes are higher than 2, which may indicate an extended bacterial oxidation of the lignin-derived material [21]. Although oxidation of the side chain of the lignin decomposition product could have occurred also during combustion, the selective oxidation of the α-carbon
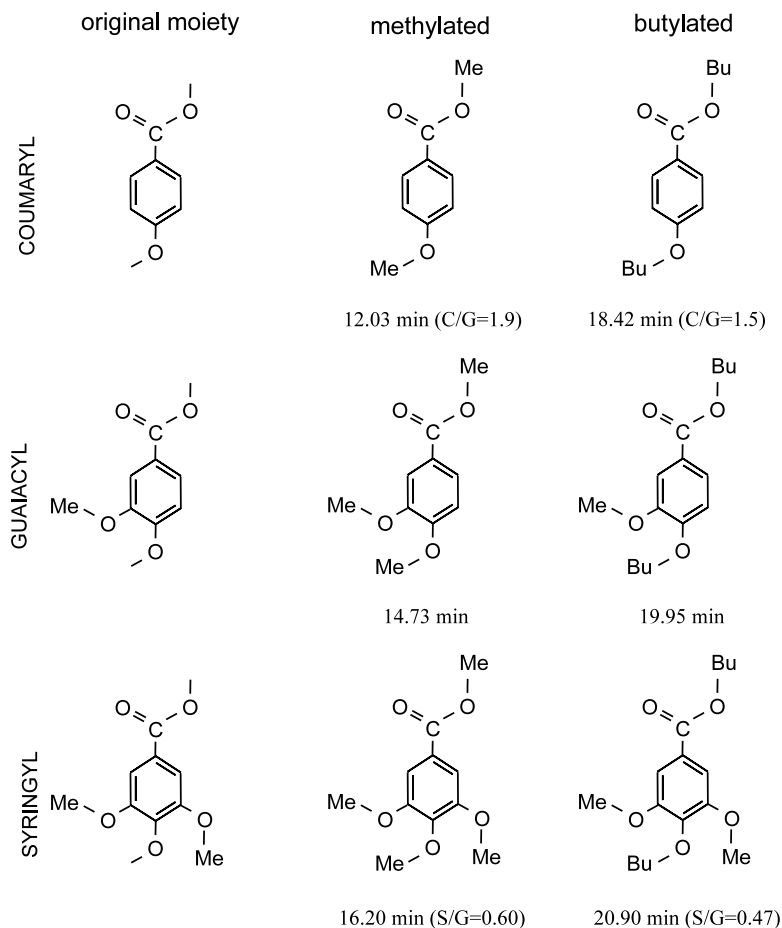
Fig. 2. Lignin derived products of thermally assisted hydrolysis alkylation of fine aerosol. Under the formulae the retention time of the corresponding GC peaks are also presented. The values in bracket shows the relative total ion peak area of the three selected compounds within the given column.

resulting in methoxy-substituted benzoic acid or methoxy-substituted benzaldehyde implies the contribution of microbial enzymes. Since the main source of organic aerosol was biomass combustion in the sampling period, these results may mean that microbial decomposition of the biomass had progressed by the time it was subjected to combustion. It follows that a large fraction of the biomass combusted was probably made of refuse or vegetation litter with rapid turnover time.

The ratios of coumaryl to guaiacyl (C/G) and syringyl to guaiacyl compounds (S/G) provides information on the origin of lignin. These values calculated from both methylation and butylation of aerosol are included in Fig. 2. The relatively high amounts of coumaryl compounds indicates lignins of grass and the low S/G ratio implies softwood origin [21]. Seemingly these results are in contrast with the
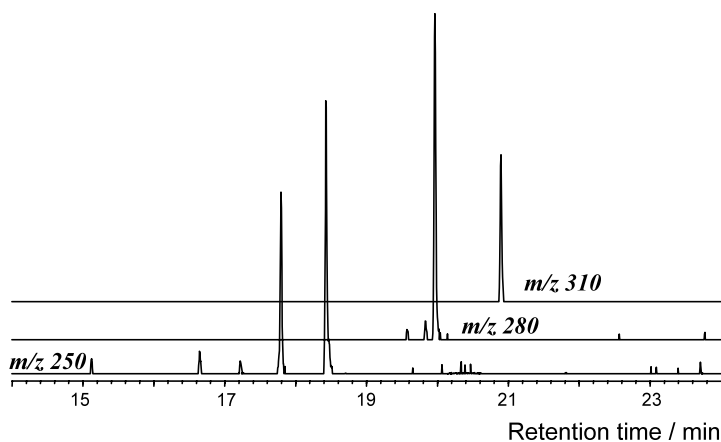
Fig. 3. Molecular ion chromatograms of butoxybenzoic acid butyl ester (*m/z* 250) methoxybutoxybenzoic acid butyl ester (*m/z* 280) and dimethoxybutoxybenzoic acid butyl ester (*m/z* 310) reconstructed from THB-GC/MS chromatogram of fine aerosol (sample LBA666).

conclusion of the studies of water-soluble organic compounds performed on the same biomass burning aerosol samples, in which the predominance of lignin of hardwood origin was found [20]. It should be noted, however, that THA-GC/MS yields information directly on the bulk of organic polymer releasing structural units, which are not accessible to aqueous extraction because they are bound to the polymeric network. Therefore, the results obtained by the two methods are not readily comparable, as aqueous extraction followed by derivatisation GC/MS determines only the water-soluble, "free" organic compounds, which, according to a parallel study on the same samples [22], represents a minor fraction of such aromatic structures in biomass burning aerosol.

3.3. Products of silylation

The single main silylated product of fine aerosol samples collected in the dry season at tropical site is trimethylsilyl (TMS) ether of levoglucosan. Among the several minor components TMS derivatives of sugars, sugar alcohols, other anhydrosugars, methoxyphenolic compounds, fatty acids, keto and hydroxy acids, di- and tri-carboxylic acids have been identified. This product distribution is very similar to that obtained in the water-soluble fraction of aerosols from the same site, admittedly because only the compounds having active hydrogen-containing functional groups are silylated, and no pyrolysis–silylation occurs [23] under the given conditions. However, the relative quantities of lignin-derived TMS ether methoxy benzoic acid TMS esters (C/G = 0.8, S/G = 0.6 evaluated analogously to the values in Fig. 2) obtained by silylation of sample LBA666 are nearer to the ratios obtained by THA of the same sample than to those evaluated in the water-soluble fraction in which syringyl units predominated among the methoxyphenolic compounds [20].
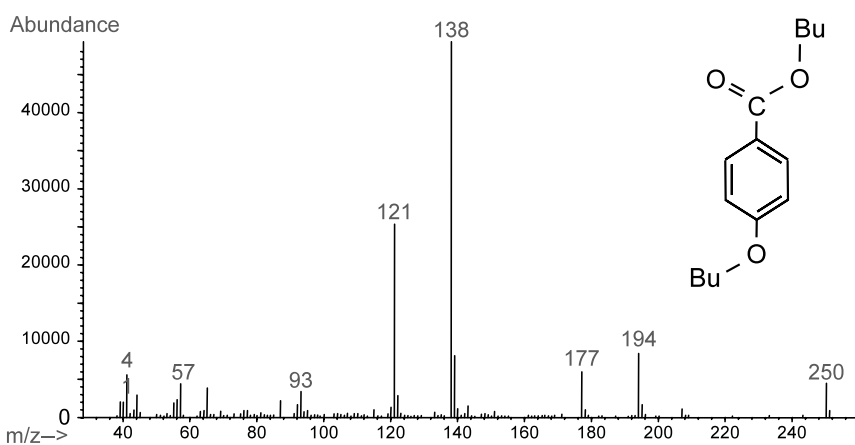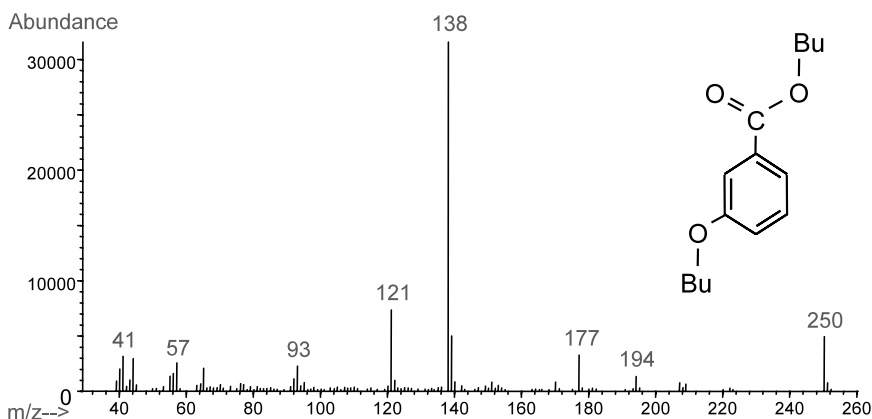
Fig. 4. Mass spectrum of butoxybenzoic acid butyl ester isomers.

The amount and number of silylated products of fine aerosol samples collected in the wet season at the same tropical site is considerably lower than of those from the dry season. Mainly TMS ethers of various sugar alcohols (xylitol, mannitol, D-glucitol) have been identified. Only traces of levoglucosan were detected.

It should be emphasised that no hydrolysis occurs in the reaction with silylating reagents even at 400 °C, but full esterification and etherification of carboxyl and hydroxyl groups are achieved only by BSA without chlorosilane catalyst.

3.4. Study on the refractory organic residue of biomass burning fine aerosol

Fine aerosol samples collected on quartz filter have been heat treated at 250 °C for 2 h in air to determine the chemical structure of the refractory organic residue in aerosol. This residue corresponds to the class of "apparent black carbon" (BC$_{app}$), the nomenclature and rationale of which are described in detail elsewhere [22].
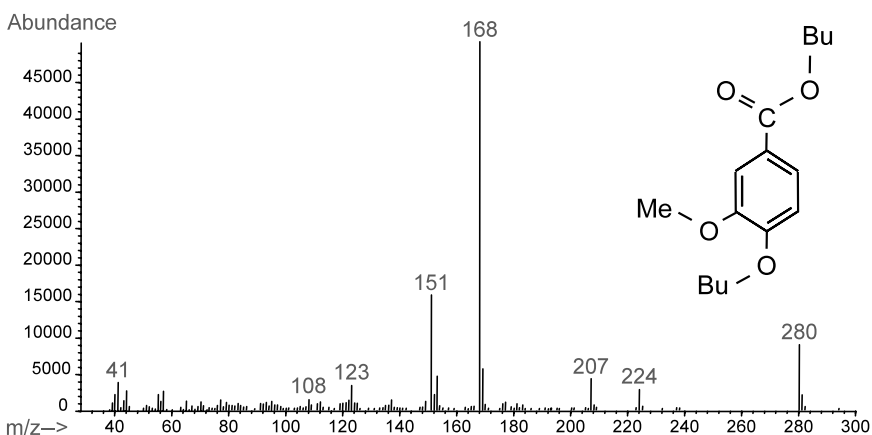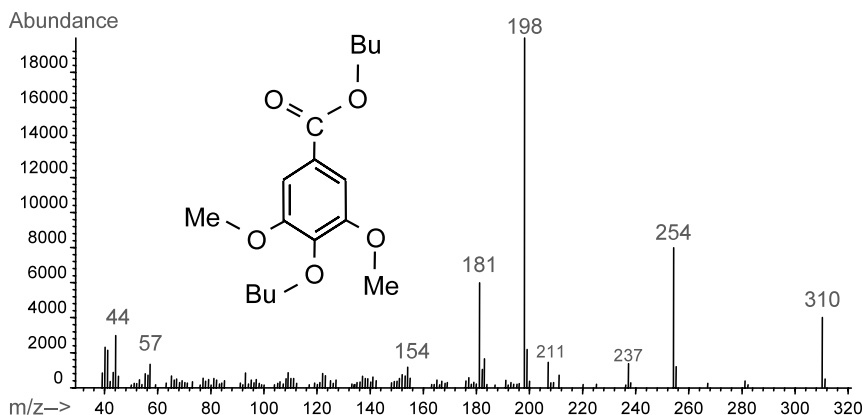
Fig. 5. Mass spectrum of 3-methoxy-4-butoxybenzoic acid butyl ester (upper) and of 3,5-dimethoxy-4-butoxybenzoic acid butyl ester (lower).

Although heat treatment reduced the total organic carbon considerably, THM-GC/MS experiments revealed that the refractory organic residue still contains more or less the same constituents as the original aerosol. Mass chromatograms of characteristic products evolved from the original and the heat-treated JARU-32 sample by THM are displayed for comparison in Figs. 6 and 7. Only traces of butane- and pentanedioic acid dimethyl esters are found among the THM products of heat treated aerosol, while dimethyl ester of hexanedioic acid (peak of 10.13 min retention time) is present without significant change. The fatty acid methyl esters of $> C_{20}$ carbon number could not be detected in the treated sample. Molecular mass peaks of lignin-derived methoxy benzoic acid methyl esters are lower in intensity but still non-negligible in the residue, except for 4-methoxy benzoic acid methyl ester which was left behind only in trace amounts. Probably this compound may not be
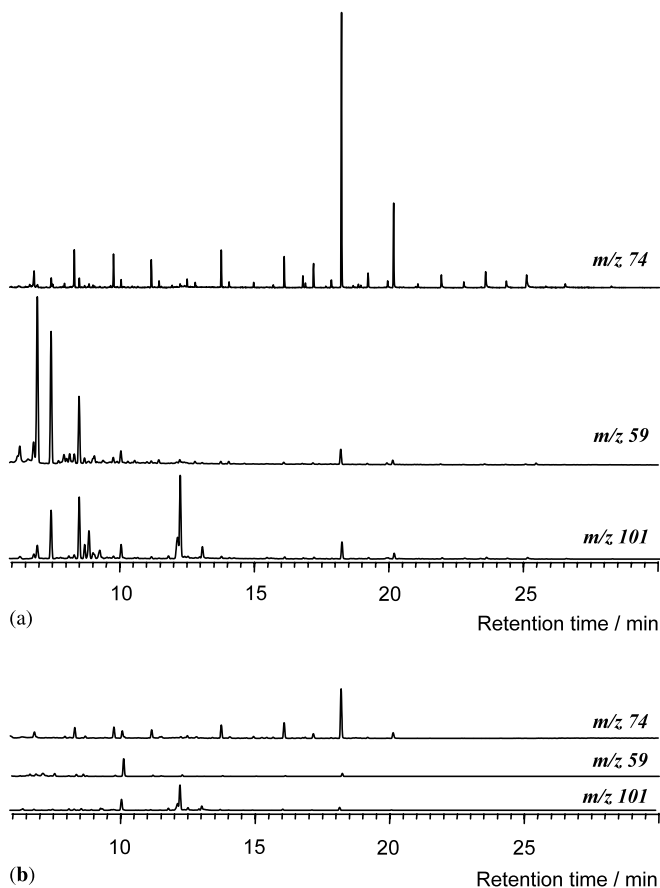
Fig. 6. Fragment ion chromatograms of methylated cellulose-derived compounds (m/z 101), dioic acid dimethyl esters (m/z 59), and fatty acid methyl esters (m/z 74) reconstructed from THM-GC/MS chromatogram of untreated (a), and heat treated (b) fine aerosol (JARU-32).

derived primarily from grass lignin but from a more easily volatilisable moiety of the aerosol particle.

3.5. Size-resolved distribution of characteristic fragments of carbonaceous aerosols

The pyrolysis products of tropospheric aerosols show various concentration profiles as a function of particle aerodynamic diameter. It should be noted that although absolute concentrations were not available, peak areas of carefully selected characteristic fragment ions of individual organic compounds in size-resolved aerosol samples provide proxies for the reconstruction of mass size distribution of the compounds. The size distribution of the most abundant alkadioic acids in water extracts of tropospheric aerosol has already been evaluated applying capillary electrophoresis [24] and ion chromatography [25]. According to these observations,
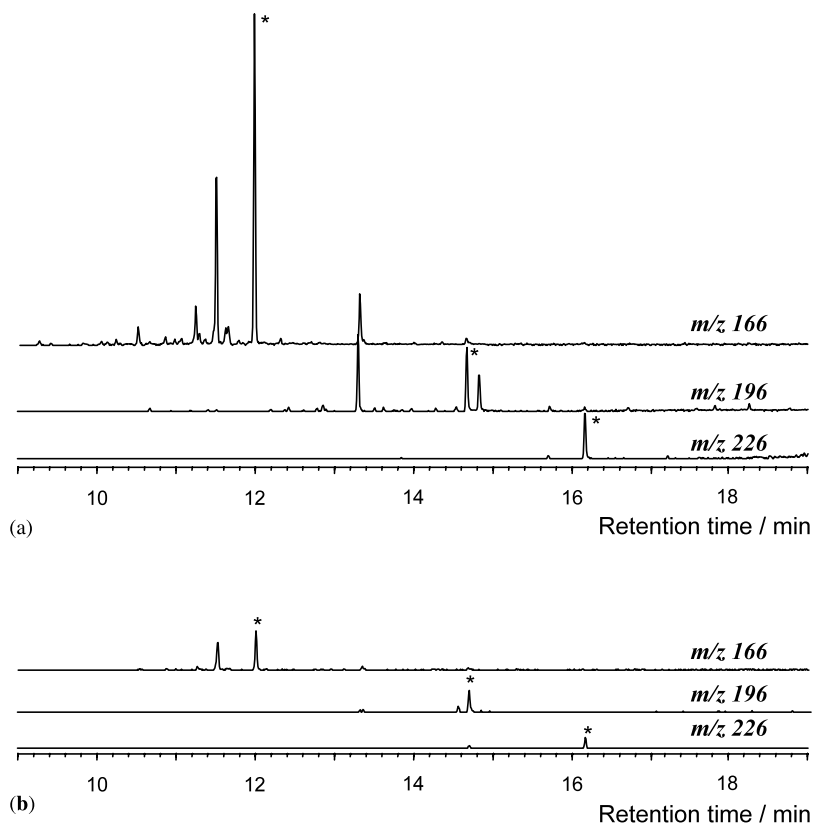
Fig. 7. Molecular ion chromatograms of methoxybenzoic acid methyl ester (*m/z* 166), dimethoxybenzoic acid methyl ester (*m/z* 196), and trimethoxybenzoic acid methyl ester (*m/z* 226) reconstructed from THM-GC/MS chromatogram of untreated (a), and heat treated (b) fine aerosol (JARU-32 sample). The peaks corresponding to methylated lignin-derived compounds are marked with an asterisk.

succinic acid had a maximum in the accumulation mode and in some cases also in the coarse mode at a coastal Arctic site.

3.5.1. Samples collected during the dry season (LBA661–670)

Among the THM products of tropical aerosols from the dry season, C_3–C_6 dioic acids exhibit bimodal mass size distributions with maxima in the accumulation and the coarse modes. The profile of butanedioic (succinic) acid dimethyl ester is plotted in Fig. 8, in which counts of the peak area of the fragment ion chromatogram of *m/z* 59 at 7.03 min represent the quantity of the compound. (The unit of *y*-axis is indicated as common in atmospheric sciences, although it refers in fact only to the numerator of the *y* variable, i.e. mass/volume.) The mass (counts of fragment ion peak of *m/z* 73 at 11.13 min) distribution of butanedioic acid bis-trimethylsilyl ester is plotted also in Fig. 8. The two fragment ion profiles are semi-quantitatively comparable, because both fragment ions represent about 20% of the total ion
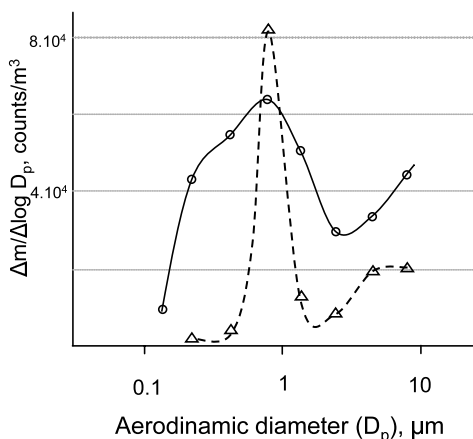
Fig. 8. Mass size distribution of butanedioic (succinic) acid in aerosol samples (LBA661–670) collected at a Brazilian tropical site in dry season. Solid line, measured as dimethyl ester obtained by hydrolysis and methylation; dashed line, measured as bis-trimethylsilyl ester obtained by silylation.

abundance in the mass spectrum of the corresponding compound. As it was mentioned earlier, in contrast to THM, no hydrolysis occurs by silylation, thus the deviation of the two profiles in Fig. 8 may reflect the differences of the involvement of alkadioic acids in the organic macromolecular matrix in fine aerosols.

The size-resolved distribution of fatty acid methyl esters plotted in Fig. 9 has been evaluated from fragment ion peaks of m/z 74. All the members of the homologous series of methylated n-alkanoic acids from C_9 to C_{18} exhibit similar profiles as palmitic acid, while the distribution of methylated fatty acids $> C_{22}$ is similar to that of tetracosanoic acid methyl ester displayed in Fig. 9. The concentration of unsaturated 16:1, 18:1 fatty acids and isomers of 18:2 are also decreasing with increasing particle size similarly to palmitic acid, but these compounds could not be
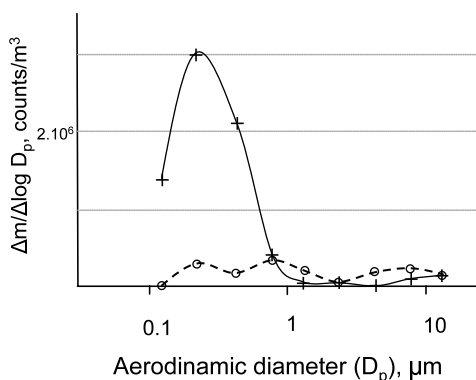

Fig. 9. Mass size distribution of fatty acids measured as methyl esters obtained by hydrolysis and methylation in aerosol samples (LBA661–670) collected at a Brazilian tropical site in dry season. Solid line, hexadecanoic (palmitic) acid; dashed line, tetracosanoic acid.
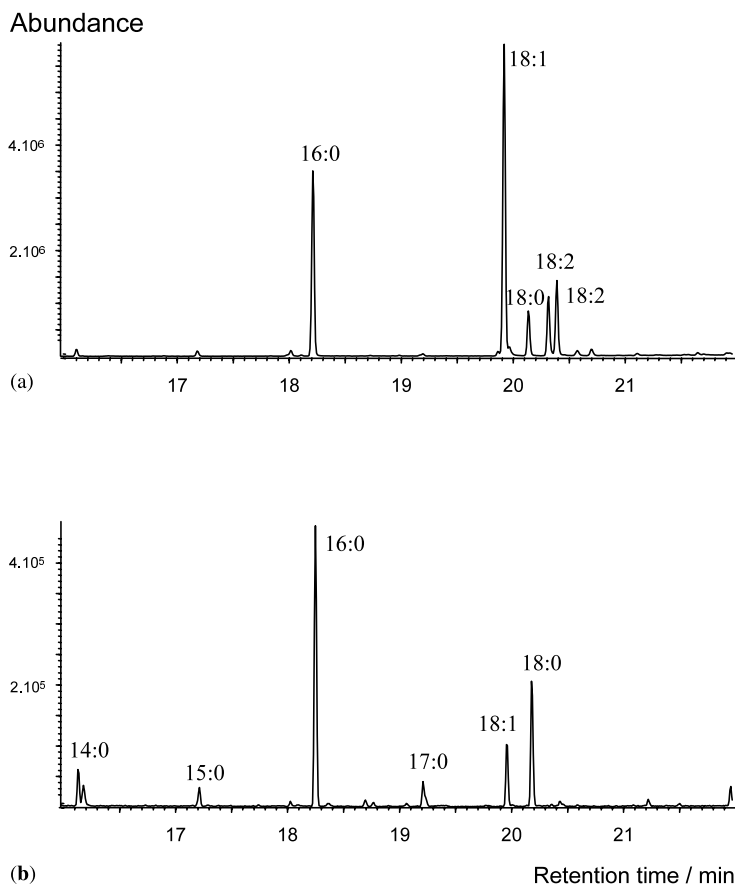
Fig. 10. THM-GC/MS total ion chromatogram details (retention time range of C_{14}–C_{20} fatty acids) of a tropical fine aerosol fraction collected in the dry season. (a) Size fraction of 0.2 μm, LBA663; (b) size fraction of 7.8 μm, LBA669.

detected in the coarse mode. Total ion chromatograms in the retention time region of predominant fatty acid methyl esters are presented in Fig. 10. The substantial differences of the relative occurrence of fatty acids in the size fractions corresponding to the two maxima of the distribution may be attributed to different origin. The accumulation mode observed for fatty acids $< C_{22}$ suggests a microbiological lipid origin [16,17,26], while the coarse mode indicates plant wax sources. Small amounts of palmitic and stearic acid trimethylsilyl esters were detected also by silylation, but only in the coarse mode, indicating the presence of some free fatty acids.

Organic tracers from biomass burning in atmospheric particulate matter have been extensively studied by Simoneit and Elias [26]. They assumed that levoglucosan, one of the main pyrolysis products of cellulose, remained unchanged in the tropospheric aerosol, since its trimethylsilyl derivative was the major product of silylation in all size ranges. The size-resolved distribution of levoglucosan tris-
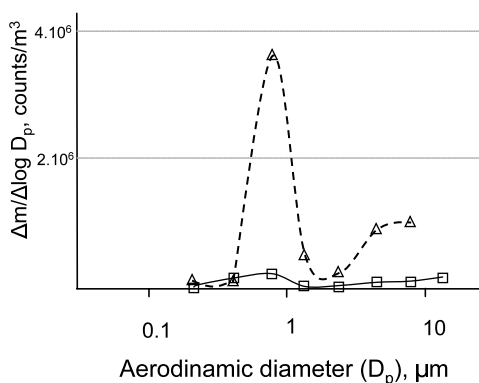
Fig. 11. Mass size distribution of levoglucosan measured as tris-trimethylsilyl ether and trimethyl ether obtained by silylation- and THM-GC/MS, respectively, in aerosol samples (LBA661–670) collected at a Brazilian tropical site in the dry season. Solid line, levoglucosan trimethyl ether; dashed line, levoglucosan tris-trimethylsilyl ether.

trimethylsilyl ether and trimethyl ether is plotted in Fig. 11. The basis of the concentration evaluation was the fragment ion peak area of *m/z* 204 at 16.15 min for the trimethylsilyl, and that of 101 at 12.32 min for the methyl ether derivative. The contribution of the above fragment ions are 15 and 20% of the total ion abundance of the corresponding compound, respectively. The much higher amount tris-trimethylsilyl ether compared with trimethyl ether of levoglucosan could be due to the low methylation efficiency of TMAH for free alcohols [27].
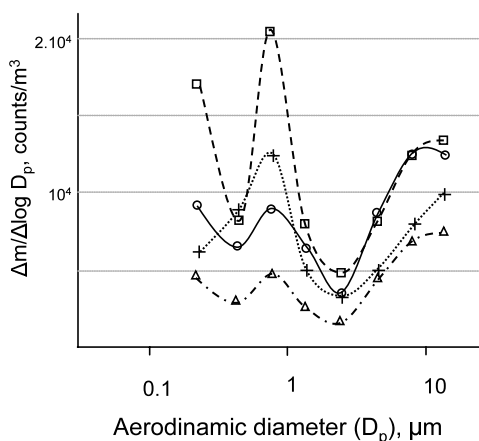

Fig. 12. Mass size distribution of hydroxybenzoic acids measured as methylated derivatives obtained by hydrolysis and methylation in aerosol samples (LBA661–670) collected at a Brazilian tropical site in the dry season. Solid line, 3,4-dimethoxy benzoic acid methyl ester; dashed line, 4-methoxy benzoic acid methyl ester; dashed–dotted line, 3,4,5-trimethoxy benzoic acid methyl ester; dotted line, 3-methoxy benzoic acid methyl ester.

4-Hydroxy benzoic acid, 3-methoxy-, and 3,5-dimethoxy-4-hydroxy benzoic acids are tracers of lignin burning. The size-resolved distribution of the methylated hydroxy benzoic acids are shown in Fig. 12. Molecular ion peaks of *m/z* 166 at 11.54 and 12.04 min have been considered for 3-methoxy- and 4-methoxy benzoic acid methyl ester, molecular ion peak of *m/z* 196 at 14.73 min for 3,4-dimethoxy benzoic acid methyl ester, and that of *m/z* 226 at 16.20 min for 3,4,5-trimethoxy benzoic acid methyl ester. The distribution exhibits two maxima for all the four compounds, however, the relative importance of the accumulation mode is more pronounced for the methoxy benzoic acid methyl esters (dashed and dotted line profiles in Fig. 12), indicating a possible non-lignin source not only for 3-hydroxy benzoic acid, but also for 4-hydroxy benzoic acid, which, belonging to the class of coumaryl compounds, could be a tracer for the burning of grass lignin.

3.5.2. Samples collected during wet season (AM01–AM10)

The total mass size distribution of the particles collected in the wet season differs considerably from that of aerosols collected in the dry season (plotted in Fig. 13). The mass size distributions of C_3–C_6 dioic acids exhibit maxima in the accumulation mode also in the wet season, as displayed in Fig. 14. For comparison see the analogous distribution measured in the dry season in Fig. 8.

The size-resolved distribution of fatty acid methyl esters of particles collected in the wet season are quite similar to that in the dry season already shown in Fig. 9. Moreover, the relative contributions of the dominant fatty acids to the organic particles are also analogous in both the accumulation and coarse modes. However, in the aerosol collected in the wet season only traces of fatty acids of $> C_{22}$ were observed.

Organic tracers from biomass burning are expected to be much less abundant in the wet season, when no deforestation burning takes place and fires are limited to domestic burning and wood-processing activities in the region. Accordingly,
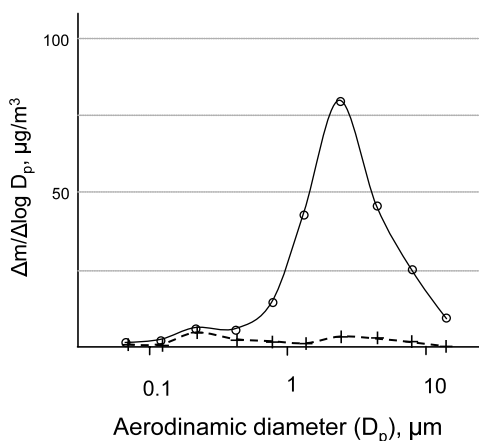

Fig. 13. Total mass size distribution of the particles collected at a Brazilian tropical site. Solid line, dry season (LBA661–670); dashed line, wet season (AM01–AM10).
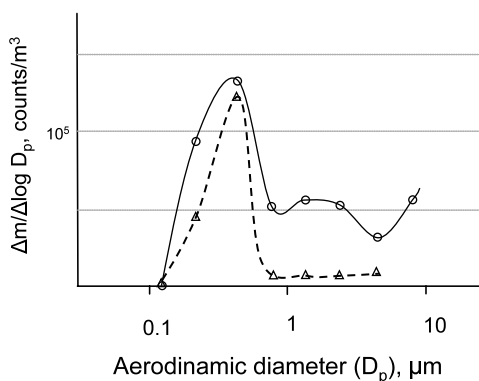
Fig. 14. Mass size distribution of butanedioic (succinic) acid in aerosol samples (AM01–AM10) collected at a Brazilian tropical site in the wet season. Solid line, measured as dimethyl ester obtained by hydrolysis and methylation; dashed line, measured as bis-trimethylsilyl ester obtained by silylation.

levoglucosan was detected in nearly all size fractions, but in amounts of two to three orders of magnitude lower than in the dry season. The maximum of the size-resolved distribution was found in AM04 of 0.4 μm diameter.

Most of lignin-derived hydroxybenzoic acids were also found in the accumulation mode, and in similar concentrations as in the dry season. The size-resolved distribution of the methylated hydroxybenzoic acids in the aerosol collected in the wet season is displayed in Fig. 15.
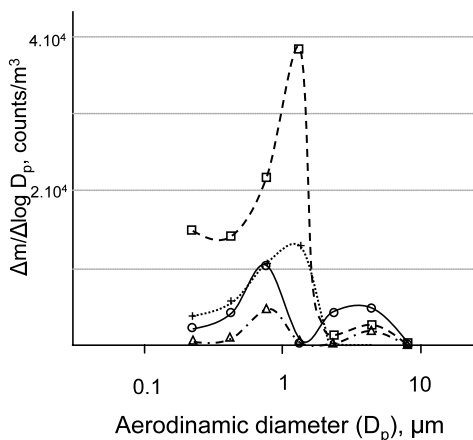

Fig. 15. Mass size distribution of hydroxybenzoic acids measured as methylated derivatives obtained by hydrolysis and methylation in aerosol samples (AM01–AM10) collected at a Brazilian tropical site in the wet season. Solid line, 3,4-dimethoxy benzoic acid methyl ester; dashed line, 4-methoxy benzoic acid methyl ester; dashed–dotted line, 3,4,5-trimethoxy benzoic acid methyl ester; dotted line, 3-methoxy benzoic acid methyl ester.

4. Conclusions

The method of thermally assisted alkylation-GC/MS was shown to be a highly sensitive and informative direct method for the analysis of the bulk of organic compounds in tropospheric aerosol samples. Compared with the off-line aqueous extraction and derivatisation followed by GC/MS analysis this method is applicable to much smaller amount of sample, less laborious and could provide information not only on the water-soluble "free" organic species but also on the compounds already incorporated into a polymeric matrix, which, according to recent studies, makes up most of the total organic carbon in tropospheric aerosol. The application of two alkylating reagents helps establish the chemical identity of the pyrolysis degradation products, especially of the substituted aromatic species of lignin origin. Although the method is by no means quantitative and could not be calibrated, the relative peak areas provide proxies for the concentration ratios of various organic species, which serve as indicators for the possible sources of the aerosol. In the case of the selected aerosol samples collected in the dry season at a tropical site influenced by biomass burning, this approach implied the burning of partially decomposed grass and softwood based on the relative ratios of coumaryl, syringyl and guaiacyl units.

Similarly, peak areas of carefully selected characteristic fragment ions of individual organic compounds in size-resolved aerosol samples provide proxies for the reconstruction of mass size distribution of the compounds. This information facilitates source apportionment of the species and might also indicate in which form they are likely present in the particulates.

Although the results presented in this paper are admittedly preliminary and based on a rather limited number of aerosol samples, they clearly demonstrate the potential of thermally assisted alkylation-GC/MS to provide valuable chemical information on the bulk of organic matter, the refractory polymeric substances which are not directly accessible by any other known analytical technique in the amount and form they are present. It can be foreseen that in the future this method will be widely applied, in combination with other off-line separation methods to reveal the chemical nature of hitherto unknown macromolecular organic compounds in tropospheric aerosol.

Acknowledgements

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