Simple off-line flash pyrolysis procedure with in situ silylation for the analysis of hydroxybenzenes in humic acids and coals

Daniele Fabbri[a,*], Ivano Vassura[a], Colin E. Snape[b]

[a]*Department of Chemistry 'G. Ciamician' and Laboratorio di Chimica, c/o ITIS, CIRSA - Università di Bologna, Via Marconi 2, I-48100 Ravenna, Italy*
[b]*School of Chemical, Environmental and Mining Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK*

Abstract

A simple device consisting of a glass pyrolysis chamber fitted for a commercial resistively heated pyrolysis probe and connected to a solvent desorption tube for air monitoring was applied to off-line pyrolysis under silylating conditions of humic acids (soil, lake) and coals. Samples were flash pyrolysed at 700 °C in the presence of excess hexamethyldisilazane, and evolved products were swept off by a nitrogen stream and trapped onto a charcoal filter from where they were desorbed with dichloromethane and analysed by gas chromatography (GC)–mass spectrometry. Humic acids afforded trimethylsilyl (TMS) ethers of phenols, 2-methoxyphenols (guaiacols), 2,6-dimethoxyphenols (syringols), and dihydroxy and trihydroxybenzenes as major products. TMSoxy benzenes were the principal products observed from pyrolysis/silylation of coals. In comparison with conventional pyrolysis, the in-situ derivatisation process enhances the levels of phenols with respect to hydrocarbons and improves the GC separation of isomers (e.g. *meta-* from *para*-cresol). With respect to tetramethylammonium hydroxide thermochemolysis, pyrolysis/silylation operates under milder conditions and permits discrimination between free and methylated hydroxy groups. The performance of the method for the quantitative determination of evolved product is described. Yields of evolved silylated mono and dihydroxybenzenes occur in the mg/g range with relative standard deviations generally between 16 and 30%.
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Keywords: Pyrolysis; Coal; Derivatization, GC; Humic acids; Hydroxybenzenes; Benzenes; Hexamethyldisilazane

1. Introduction

Pyrolysis in combination with gas chromatography and mass spectrometry (Py–GC–MS) is a well-established analytical technique for the structural analysis of coals [1–5] and related humic acids [6]. In conventional Py–GC–MS, the organic sample is thermally decomposed in an inert atmosphere to give volatile fragments amenable to GC–MS analysis. Benzenes bearing hydroxy and carboxylic groups are important structural units of humic substances which could be preserved in the coal. To improve their detection thermal treatment is conducted in the presence of the methylating reagent tetramethylammonium hydroxide (TMAH), a procedure known as thermally assisted hydrolysis and methylation (THM) or more briefly as thermochemolysis [7]. The procedure has been largely applied to humic acids

*Corresponding author. Tel.: +39-0544-400-870; fax: +39-0544-275-134.

E-mail address: dfabbri@ambra.unibo.it (D. Fabbri).

[8–13] and to a lesser extent to whole coals [14]. Two principal techniques have been adopted: flash pyrolysis in the presence of TMAH with a pyrolytic device connected on-line to the GC–MS apparatus [8–10] and off-line thermochemolysis in sealed glass tubes at sub-pyrolysis temperatures (e.g. 300 °C) [11]. The latter procedure is more time consuming and has the disadvantages of prolonged thermal treatment, but overcomes some of the problems due to the injection of TMAH excess into a Py–GC–MS apparatus (overloading, column deterioration, disturbing smell of trimethylamine, memory effects), and is better suited for quantitative analyses.

Whatever the adopted procedure is, there still remain drawbacks in the TMAH thermochemolysis of humic substances and related materials, difficult to circumvent as they are inherent to the chemical reactivity of TMAH. Methyl esters of benzene(poly)carboxylic acids are relevant THM products of humic substances and their detection has important implications for the interpretation of the humic structure and how it evolves during transformation into coal [8,9,15]. However, side chains of aromatic units can be oxidised by the hydroxide ion of the derivatising reagent giving rise to aldehydic and carboxylic groups not originally present in the sample [16]. It has been shown that TMAH produces methylated benzenecarboxylic acids from aromatic aldehydes through a Cannizzaro reaction [17]. A similar behaviour has been reported for tetrabutylammonium hydroxide (TBAH) [18]. This degradative oxidation is related to the alkaline environment created by TMAH and TBAH, and its elimination requires the use of less basic derivatising reagents during thermal treatment. The following non-alkaline reagents have been used in pyrolysis: tetramethylammonium acetate [19], tetraethylammonium acetate [13], dimethylformammide acetal [20], *N,N*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) [21], and hexamethyldisilazane (HMDS) [22,23]; however, with the exception of tetraethylammonium acetate, their effectiveness in Py–GC–MS analysis of humic substance and coal has not been evaluated. One of the primary objectives of this work is to assess the potential of HMDS as a mild derivatising reagent in pyrolysis for the characterisation of humic acid and coal.

Characteristic TMAH thermochemolysis products

of terrestrial humic acids are permethyl ethers of di and trihydroxybenzenes, which are related to two primary aromatic units of lignin: 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol). However, the same compounds could be produced by the methylation of cathecol (1,2-dihydroxybenzene) and 1,2,3-trihydroxybenzene moieties originally occurring in the sample, for instance, by natural demethylation of methoxy groups of guaiacols and syringols during diagenesis/coalification or as remnants of other biopolymers (e.g. tannins). In order to differentiate between free and methylated hydroxybenzenes in the original sample, it is necessary to cap the hydroxylic function with a group other than simple methyl. TBAH [24] and ^{13}C-labeled TMAH [25] have been employed for this purpose in the reactive pyrolysis of lignins. An other possibility is the insertion of a trimethylsilyl (TMS) group using a silylating reagent. Kuroda has shown that pyrolysis of lignin in the presence of BSTFA yields TMS derivatives of guaiacyl units [21]. As an alternative to BSTFA, hexamethyldisilazane (HMDS) can be used as a silylating reagent in pyrolysis and TMS ethers of (di, tri)hydroxybenzenes have been found as pyrolysis/silylation products of carbohydrates [23]. We show in this work that the use of HMDS enables the differentiation of free and methylated hydroxybenzene units in humic acids.

Finally, with few exceptions (e.g. Refs. [26,27]), studies which made use of on-line pyrolysis report at best semiquantitative data on the distribution of evolved products. Quantitative inspections have been mainly conducted using off-line thermochemolysis. In this study we describe the analytical performances of a simple off-line pyrolytic procedure under silylating conditions for the quali-quantitative analysis of hydroxylated compounds in humic acids and coals.

2. Experimental

2.1. Samples

The two humic acids examined in this study are extracted from soil and lake sediments according to the procedure recommended by the International Humic Substances Society (IHSS). Details of extraction procedure and structural characteristics of

the soil humic acid are described in a previous study [28]. The carbon content of soil humic acid and lake humic acid is 53.0 and 49.8%, respectively. Three coals, named coal 1, 2 and 3, have been analysed. Most of the work is conducted on coal 1, which is a high volatile bituminous coal from Gedling (Nottingham, UK), with the following characteristics: ash 2.0%, volatile content 34.5%, carbon 81.6%, hydrogen 5.2%, oxygen 10.3% and nitrogen 1.7%. Two North American bituminous coals, namely coal 2 (Buchanan, 29.5% volatile matter) and coal 3 (Ramsey, 24.4% volatile matter) were provided by CPL industries (Chesterfield, UK). Silylated standard compounds for identification purposes are obtained by treating the compound of interest dissolved in pyridine with HMDS and trimethylchlorosilane at 60 °C for 30 min (or overnight at room temperature). The solvent and excess HMDS are evaporated off and the residue dissolved in dichloromethane is analysed by GC–MS. All standards, HMDS and Orbo solvent desorption tubes were purchased from Sigma–Aldrich.

2.2. Off-line pyrolysis/silylation

The apparatus employed for off-line pyrolysis experiments is sketched in Fig. 1. It consists of a glass tube (pyrolysis chamber) designed for the probe of a CDS 1000 pyroprobe equipped with a resistive heated platinum filament. During the analysis the apparatus is flushed with a nitrogen stream regulated at 100 ml/min with a flow control valve. The exit is connected to an activated charcoal trap (Orbo 32 solvent desorption tube). A quartz tube containing the sample (an exactly weighed amount of less than 4 mg) is inserted into the platinum coil of

Fig. 1. Off-line pyrolysis device.

the probe, and the sample is evenly spread with 0.01 ml HMDS. Once the probe is inserted into the glass tube fluxed with nitrogen, the mixture is pyrolysed at 700 °C (set temperature) for 30 s at the maximum heating rate. The evolved products are retrieved from the charcoal filter and the glass tube by dissolution into dicholoromethane. Stepwise elution experiments have shown that 4 ml of solvent suffice to withdraw quantitatively the analytes. The solution is spiked with 0.04 ml of an internal standard solution (100 mg/l triphenylmethane in hexane) and analysed by GC–MS.

After pyrolysis the probe and quartz tube are washed with DCM and the obtained solutions analysed by GC–MS. No pyrolysis/silylation products are detected in the GC–MS traces indicating they are efficiently swept off the probe. Procedural blank analyses are performed by pyrolysing 0.01 ml HMDS under the same conditions of the samples. The obtained solutions do not reveal any presence of interfering silylated hydroxybenzenes.

2.3. GC–MS analysis

Solutions are injected under splitless conditions into a Varian 3400 gas chromatograph connected to a Varian Saturn 2000 mass spectrometer. Analytes are separated with an MDN-5S (Supelco) fused-silica capillary column (stationary phase: poly(5% diphenyl–95% dimethylsiloxane), 30 m×0.25 mm, 0.25 μm film thickness) with the following temperature program: from 50 °C (held for 2 min) to 300 °C at 5 °C/min. Mass spectra are recorded under electron impact (70 eV) at 1 scan/s in the m/z 45–500 range.

2.4. Quantitation

Peak areas (A_q) of selected compounds evolved from pyrolysis/silylation are determined in the mass chromatogram mode using an intense and characteristic ion in the mass spectrum, the ($M^{+\cdot}$-15) ion is generally chosen as target ion. The total area (A_t) is hence calculated by dividing A_q to a factor (F) which is the ion intensity (I_q) of the target ion with respect to the summed intensities of the top five ions (ΣI_x) in the mass spectrum of the quantified compound ($F = I_q/\Sigma I_x$). The yield Y of the evolved
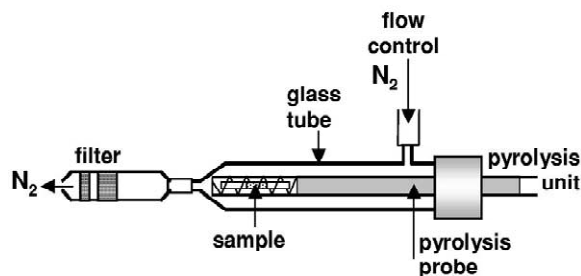
compound is calculated from the weight W_{is} and total peak area A_{is} of the added internal standard, and the quantity Q of pyrolysed sample: $Y = W_{is}A_t\ f/A_{is}Q$, where f is the response factor of the given compound with respect to the internal standard. Given the difficulty in establishing f for all the silylated products, f was determined for 1-TMSoxy-3-methyl-benzene and assumed to be the same for TMS ethers of phenol and monosubstituted phenols. Similarly, f was determined for 1,3-bisTMSoxybenzene and assumed to be the same for 1,2 and 1,4-bisTMSox-ybenzenes. Standard solutions of 1-TMSoxy-3-methylbenzene and 1,3-bisTMSoxybenzene, were prepared by silylating standard solutions of *m*-cresol and resorcinol, respectively, as previously described.

Reproducibility of the quantitation procedure was expressed as estimated standard deviation (SD) of the yields obtained from four replicate analyses of the same sample performed on different days by two different operators.

3. Results and discussion

3.1. Humic acids

Figs. 2 and 3 show the GC–MS traces of products

Fig. 3. GC–MS trace of the products obtained from off-line pyrolysis with HMDS of lacustrine humic acid. Peak numbers refer to Table 1. C: perTMS ether of levoglucosan; L: TMS ester of fatty acids. Asterisks: probably contaminants.

evolved from soil and lacustrine humic acid, respectively, when pyrolysed with excess HMDS. Compounds assigned to the numbered peaks are listed in Table 1. The identified compounds are all silylated derivatives, principally TMS ethers of hydroxy-benzenes besides TMS esters of fatty acids. It is noteworthy that free hydroxybenzenes are not detected indicating the virtually quantitative yield of the silylation process in the off-line procedure. On-line pyrolysis/silylation-GC–MS experiments (data not shown) resulted in the production of both silylated and underivatised hydroxybenzenes. The greater excess of added HMDS and the lower temperature of the pyrolytic chamber which reduces HMDS volatilisation prior to pyrolysis are probably responsible for the higher silylation yields in the off-line system compared to on-line.

In agreement with previous data arising from conventional pyrolysis, showing the relevance of phenolic, guaiacyl and syringyl units in these humic acids [28], TMS ethers of simple phenols and those bearing methoxy groups in ortho positions are found as major products in pyrolysis/silylation.

In contrast with the behaviour observed for TMAH thermochemolysis, where the most abundant compounds released from soil humic acid were the methyl esters of 3,4-dimethoxybenzoic acid and
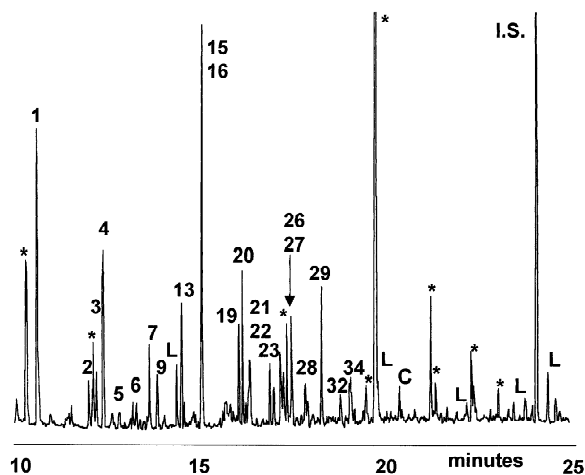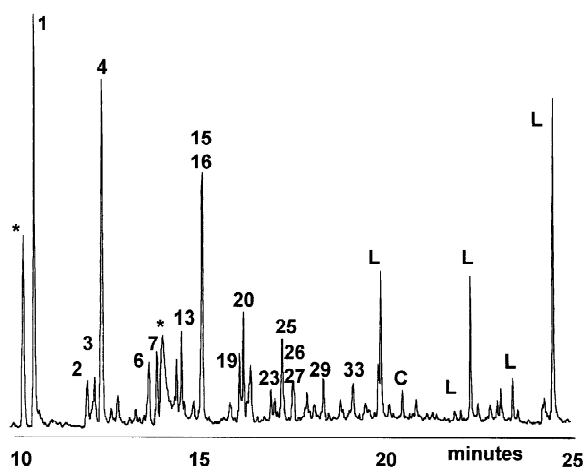

Fig. 2. GC–MS trace of the products obtained from off-line pyrolysis with HMDS of soil humic acid. Peak numbers refer to Table 1. C: perTMS ether of levoglucosan; L: TMS ester of fatty acids. Asterisks: probably contaminants.

Table 1
Products released from off-line pyrolysis with HMDS of coals and humic acids

No.	t_R (s)	m/z[a]	Assigned compound	ID[b]
1	636	77, **151**, 166	Phenol, TMS ether	ST
2	721	135, **165**, 180	2-Methylphenol, TMS ether	ST
3	732	91, **165**, 180	3-Methylphenol, TMS ether	ST
4	745	91, **165**, 180	4-Methylphenol, TMS ether	ST
5	803	105, **179**, 194	2-Ethylphenol, TMS ether	T
6	816	105, **179**, 194	Dimethylphenol, TMS ether	L
7	819	**166**, 181, 196	2-Methoxyphenol, TMS ether	L
8	820	105, 179, **194**	2,4-Dimethylphenol, TMS ether	ST
9	833	73, **179**, 194	3,5-Dimethylphenol, TMS ether	L
10	841	105, **179**, 194	2,3-Dimethylphenol, TMS ether	ST
11	853	105, **179**, 194	2,6-Dimethylphenol, TMS ether	L
12	861–925	73, **193**, 208	C3-Phenols, TMS ether	L
13	871	151, **177**, 192	4-Vinylphenol, TMS ether	T
14	876	151, **181**, 196	3-(or 4)-Methoxyphenol, TMS ether	L
15	905	**73**, 239, 254	1,2-Dihydroxybenzene, bisTMS ether	ST
16	907	**180**, 195, 210	4-Methyl-2-methoxyphenol, TMS ether	T
17	930–990	73, 207, 222	C4-Phenols, TMS ether	T
18	951	73, **195**, 210	Methylmethoxyphenol, TMS ether	T
19	965	73, **239**, 254	1,3-Dihydroxybenzene, bisTMS ether	ST
20	971	73, **253**, 268	4-Methyl-1,2-dihydroxybenzene,bisTMS ether	T
21	981	**196**, 211, 226	2,6-Dimethoxyphenol, TMS ether	T
22	983	73, **239**, 254	1,4-Dihydroxybenzene, bisTMS ether	ST
23	1014	73, **192**, 222	4-Vinyl-2-methoxyphenol, TMS ether	T
24	1021	73, **253**, 268	1-Methyl-3,5-dihydroxybenzene,bisTMS ether	L
25	1032	**73**, 267, 282	4-TMSoxybenzoic acid, TMS ester	U
26	1051	**73**, 269, 284	1,2-Dihydroxy-6-methoxybenzene, bisTMS ether	T
27	1052	**210**, 225, 240	4-Methyl-2,6-dimethoxyphenol, TMS ether	T
28	1073	**73**, 192, 280	Unknown	U
29	1098	73, **239**, 342	1,2,3-Trihydroxybenzene, triTMS ether	L
30	1106	185, 201, **216**	1-Naphthalenol, TMS ether	L
31	1128	145, **201**, 216	2-Naphthalenol, TMS ether	L
32	1129	73, **253**, 356	5-Methyl-1,2,3-trihydroxybenzene,triTMS ether	T
33	1145	73, **222**, 252	4-Vinyl-2,6-dimethoxyphenol, TMS ether	T
34	1147	**73**, 239, 342	1,2,4-Trihydroxybenzene, triTMS ether	T
35	1147	282, **297**, 312	4-TMSoxy-3-methoxybenzoic acid, TMS ester	L

[a] Characteristic abundant ion in the mass spectrum; base peak in bold.

[b] Identification based on: L: match with mass spectrum of NIST92 library with FIT greater than 900; ST: injection of a silylated standard compound; T: interpretation of mass fragmentation; U: unidentified or library FIT less than 900.

3,4,5-trimethoxybenzoic acid [10], pyrolysis/silylation produces low levels of silylated derivatives of guaiacol and syringol with a carboxylic group. The difference might be due to a biased excess of carboxylic acids in pyrolysis/methylation associated to TMAH induced degradative oxidation [16] and/or a lower efficiency of pyrolysis/silylation in protecting carboxylic groups. As the latter aspect is concerned, it is known that HMDS/pyrolysis is effective in producing TMS esters of carboxylic acids, at least as far as aliphatic acids are concerned

[22]. An other possibility is that TMAH favours the thermal production of carboxylic acids through the hydrolytic breakdown of esters.

A remarkable feature of the chromatograms of Figs. 2 and 3 is the relatively high abundance of silylated 1,2-dihydroxybenzene constituents (peaks 15, 20). TMS ethers of 1,3 and 1,4-dihydroxybenzenes (peaks 19, 22, 24) along with trihydroxybenzenes (29, 32, 34) are also detected at significant levels. Underivatised di and trihydroxybenzenes exhibit poor chromatographic behaviour in the most

utilised non-polar GC stationary phases, and their detection is difficult to achieve in conventional pyrolysis where they are released as such from the sample. On the other hand, the conversion of di and trihydroxybenzenes into the corresponding methyl ethers by TMAH thermochemolysis precludes the individuation of the pre-existing methylated forms, and as a consequence the contribution of free hydroxy groups cannot be properly evaluated. In this respect, pyrolysis/silylation presents advantages over both conventional and methylating pyrolysis. It enhances the detection of (poly)hydroxybenzenes due to the improved GC behaviour of the corresponding silylated derivatives, and meantime makes possible the distinction between free and methylated forms.

The identification of ring position for several compounds of Table 1 is based on the ortho-effect rearrangement in the mass fragmentation pattern. In fact, the mass spectra of TMSoxy benzenes with a substituent in the ortho position generally exhibit an intense even-mass ion produced by the loss of a neutral fragment from the molecular ion indicative of the ortho-substituent. Thus, assignment of peak 26 to 1,2-bisTMSoxy-6-methoxybenzene is accomplished on the grounds of the ions at m/z 254 and 196, corresponding to the loss of neutral fragments, respectively, with 30 (CH_2O) and 88 (C_3H_8OSi) amu, from the molecular ion (m/z 284).

Understanding the relevance of hydroxylated benzenes as building blocks of humic acids is important for several reasons. Structural data inferred from analytical pyrolysis when associated with computational chemistry contribute to the development of structural models [29], useful for better comprehension of chemical properties of humic acids (e.g. complexing capacity) at a molecular level. Hydroxybenzenes may provide information about the nature of the biological precursors and the degree of diagenesis (e.g. demethylation). Regarding the the latter, the occurrence of the silylated form of 1,2-dihydroxy-6-methoxybenzene is worth noting (peak 26). If the structural assignment is correct, this compound can be regarded as representative of an intermediate degree of demethylation of syringyl moieties, the final stage of the demethylation process being the 1,2,3-trihydroxybenzene. The detection of phenolic derivatives not related to guaiacyl and

syringyl moieties points to the participation of precursors other than lignins in the humic structure. Carbohydrate derivatives are probably responsible for the release of 1,2,4-triTMSoxybenzene [23], while 1,3,5-triTMSoxybenzene might be associated with cutans [30].

3.2. Coal

A representative GC–MS trace obtained from pyrolysis/silylation of coal samples (expanded in the region of phenols) is presented in Fig. 4B for coal 1 (Gedling high volatile bituminous coal). Coals 2 and 3 exhibited similar GC profiles. For comparison with conventional pyrolysis, the GC trace obtained from simple off-line pyrolysis (no HMDS added) of coal 1 is presented in Fig. 4A. It is apparent how the introduction of the silylating reagent during pyrolysis affects the product distribution. In the absence of the reactant, analysed coals yield a pyrolysate dominated by aromatic hydrocarbons, while with the addition of HMDS silylated phenolic constituents become the principal products. Clearly, the introduction of the
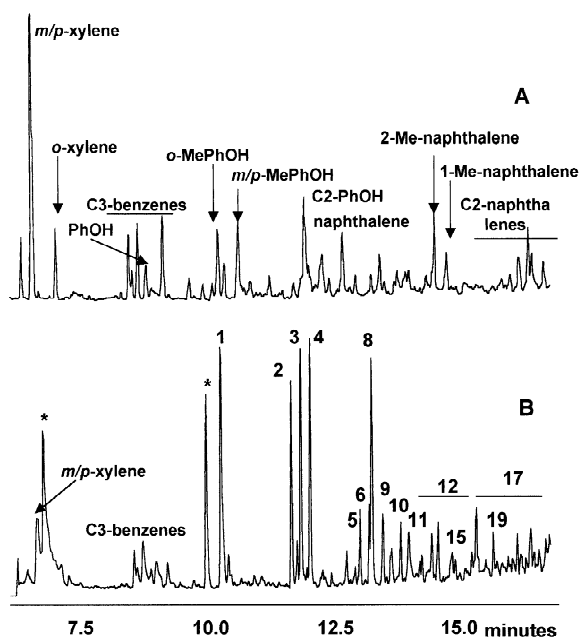

Fig. 4. GC–MS traces of the products obtained from off-line pyrolysis of coal 1 without (A) and with HMDS (B). Peak numbers in B refer to Table 1.

reactant has the benefit of enhancing the response of the phenolic compounds with respect to hydrocarbons. TMSoxybenzene and its alkyl derivatives are the principal oxygenated compounds. Silylated di and trihydroxybenzenes are detected at lower levels, while only the TMS ethers of naphthalenols are positively identified among hydroxylated polycyclic compounds. Polyhydroxybenzenes and naphthalenols are barely detected in the pyrolysates obtained in the absence of HMDS.

The yields of evolved phenols and their degree of alkyl substitution are important structural parameters related to rank, maceral composition, vegetal precursors, depositional environment, and history of the coal [4,5,26,27]. The introduction of the TMS group has the advantage of improving the separation of structural isomers, increasing the detail of structural information. In fact, in commonly used non-polar stationary phases, like that utilised here, 4-methyl and 3-methylphenol coelute, while the corresponding TMS ethers are well separated. Seven peaks of C2-alkylTMSoxybenzenes are resolved after pyrolysis with HMDS, against five peaks associated with C2-alkylphenols found from simple pyrolysis,.

3.3. Quantitation

The performance of the proposed procedure for quantitative analysis of the evolved pyrolysis/silylation products has been investigated by replicate analyses of soil humic acid and bituminous coal 1. The results are presented in Table 2 where the yields and corresponding standard deviations of the principal silylated products are reported.

The yields of single products evolved from both humic acid and coal are very small, being in the part per thousand range even for the most abundant members. Nonetheless, yields can be considered comparable to those typically observed in analytical pyrolysis of similar materials. Poerschmann et al. [26] have reported a total yield of 5% for phenols (a dozen species quantified) evolved from pyrolysis of a peat humic acid, corresponding to an average yield for each phenol of 4 mg/g. Grasset et al. [13] reported a 3.3% total yield of pyrolysis products from a peat humic acid treated with TMAH at 400 °C for 1 h, which is consistent with single product yields in the mg/g range. As a further example, the amounts of methylated lignin phenols produced from TMAH thermochemolysis of a peat humic acid have been found to fall between 0.04 and 1.3% TOC [11]. It is well recognised that, although structurally important pyrolysis products are evolved with low yields from humic matter, they are of highly diagnostic value [26].

The precision of the whole procedure is not particularly good, as standard deviations (Table 2), expressed as percentages, are generally between 16 and 30%. Nevertheless, it can be considered still satisfactory in view of the characteristics of the analysis, that is the small sample size of extremely complex ethereogeneous materials, fast derivatisation in a solid non-homogeneous system, trapping and elution of products released at low yields. Table 3 compares the results obtained from the pyrolysis/silylation of two different coals. Data show that the procedure is well fitted for comparative purposes, as significant differences in the total amount of quan-

Table 2

Yields of products evolved from off-line flash pyrolysis/silylation of soil humic acid and coal 1 (Gedling high volatile bituminous)

Compound	Soil humic acid (mg/g)	Coal 1 (mg/g)
Phenol, TMS ether	3.19±0.63	0.57±0.14
2-Methylphenol, TMS ether	0.39±0.10	0.36±0.08
3-Methylphenol, TMS ether	0.49±0.15	0.47±0.09
4-Methylphenol, TMS ether	1.70±0.42	0.43±0.09
2-Methoxyphenol, TMS ether	0.65±0.23	n.d.
4-Vinylphenol, TMS ether	0.86±0.22	n.d.
1,2-Dihydroxybenzene, bisTMS ether	2.45±0.39	0.032±0.02
1,3-Dihydroxybenzene, bisTMS ether	0.62±0.18	0.047±0.02
1,4-Dihydroxybenzene, bisTMS ether	0.23±0.09	0.011±0.01

Mean±SD from four replicate analyses; n.d., not detected.

Table 3
Yields (mg/g) of TMS ethers of hydroxybenzenes evolved from
off-line flash pyrolysis/silylation of two different coal samples
(North American bituminous)

Compound	Coal 2	Coal 3
Phenol, TMS ether	0.54	0.10
2-Methylphenol, TMS ether	0.29	0.032
3-Methylphenol, TMS ether	0.56	0.12
4-Methylphenol, TMS ether	0.46	0.068
1,2-Dihydroxybenzene, bisTMS ether	0.022	0.001
1,3-Dihydroxybenzene, bisTMS ether	0.11	0.015
1,4-Dihydroxybenzene, bisTMS ether	0.024	0.005

tified silylated hydroxybenzenes are observed for two coals of different origin.

The good chromatographic separation of methylphenols in the silylated form enables evaluation of the contribution of each isomer in the starting macromolecular structure. The *para*-methylphenol is the dominant isomer in humic acid, in agreement with the occurrence of lignin building blocks, while its abundance in coal is similar to that of the meta isomer. Catechol is the principal dihydroxybenzene released from soil humic acid, whereas its content is similar or even lower than that of 1,3-dihydroxybenzene in coal samples.

Acknowledgements

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