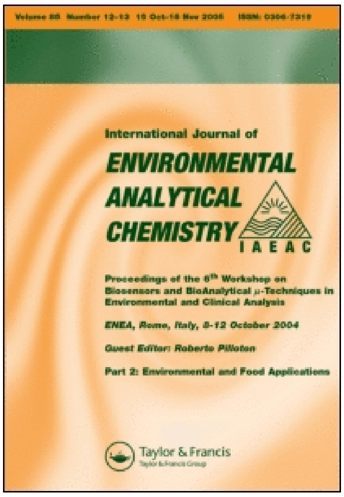

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Pyrolysis/Methylation: A Microanalytical Method for Investigating Polar Organic Compounds in Cultural Properties

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PYROLYSIS/METHYLATION: A MICROANALYTICAL METHOD FOR INVESTIGATING POLAR ORGANIC COMPOUNDS IN CULTURAL PROPERTIES

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The organic compounds present in weathered surfaces of building stones were investigated using simultaneous pyrolysis/methylation. The method consists of the derivatization of the sample with the alkylating reagent tetramethylammonium hydroxide. Tetramethylammonium salts of organic acids can be converted to methyl ester and the corresponding byproduct in the pyrolysis unit. Hydroxyl groups are also methoxylated. The protection of functional groups permits direct and complete analysis of samples by pyrolysis. No time-consuming solvent extractions, concentrations, derivatizations, and other manipulations which imply the possibility of cross-contamination, are required. The data obtained by solvent extraction and subsequent gas chromatography-mass spectrometry analysis are similar to those obtained by pyrolysis/methylation, proving that this method is an analytical procedure of great sensitivity for investigating organic compounds in inorganic matrices.

KEY WORDS: Pyrolysis/methylation, conventional pyrolysis, black crusts, polar compounds, aliphatic acids, aromatic acids, phenols.

INTRODUCTION

Deposition of airborne organic pollutants on historic buildings and monuments has been a matter of concern in recent years[1-3]. Previously, the effect of air pollutants on building stones was mainly focussed on the deposition of carbonaceous particles and the formation of gypsum crystals in the surface materials, causing the so-called black crusts[4-6].

Organic species present in weathered surfaces of building stones are complex mixtures of many classes of compounds entangled in the mineral matrix. This prevents direct analysis without previous extraction and separation. In order to eliminate mineral interferences the samples must be extracted with suitable organic solvents and analysed by an adequate technique.

Techniques used for the study of organic compounds deposited on building materials were solvent extraction, derivatization and gas chromatography-mass spectrometry analyses. Also, analytical pyrolysis was employed. The advantages and disadvantages of these methods have been previously reported[3,7]. Basically, solvent extraction requires an amount of black crusts (> 1 g) that is difficult to collect in cultural properties, mainly because of the aesthetic impact produced by the white or light area, left behind sample removal, over a black ground. The removal of high amounts of sample is especially critical in sculptures. Pyrolysis usually requires < 1 mg of sample, which minimizes such impact.

From all available analytical techniques, gas chromatography-mass spectrometry can be used to resolve the highest number of compounds, provided that sufficient quantity of sample can be obtained. Conversely, pyrolysis-gas chromatography-mass spectrometry probably increases the number of compounds resolved as some of them are also found as thermally modified products, but opposes the advantage that very minute amounts of samples are required. However, the information provided by analytical pyrolysis is far from complete, as demonstrated by the absence of fatty acids and other polar compounds identified in solvent extracts. It appears that pyrolysis induces a decarboxylation of fatty acids producing the corresponding alk-1-enes. This process could be catalysed by considerable amounts of inorganic materials present in the sample.

In a search for microanalytical methods able to provide as complete information as possible, the application of simultaneous pyrolysis/methylation to black crusts is investigated. These crusts were previously studied using solvent extraction procedures and conventional pyrolysis, therefore considerable amounts of data are available, permitting comparison between solvent extraction, conventional pyrolysis and pyrolysis/methylation.

MATERIALS AND METHODS

Samples

Details of samples, solvent extraction and conventional pyrolysis have been reported elsewhere[3,7]. Briefly, black crusts samples were removed during the restoration works, accomplished in 1988, on the Custom House, a historic building located in Dublin, Ireland, constructed in 1791 with Portland limestone.

Pyrolysis/methylation

The milled crusts (500 μg) were deposited in a Curie-point small hollow ferromagnetic cylinder (temperature 700°C) and wetted with 5 μl of a 25% w/w aqueous solution of tetramethylammonium hydroxide, according to Challinor[8]. The cylinder was slightly dried with a N_2 flow and immediately inserted in the pyrolyser. The analysis was performed in a Fisons instrument GC 8000/MD 800 coupled to a Fischer 0316 Curie-point pyrolyser, using a 30 m × 0.25 mm SPB-5 column (film thickness 0.25 μm). The GC oven was held at 25°C with a cryogenic unit and programmed to 280°C, at a rate of 5°C/min. The final temperature was held for 20 min.

The pyrolysis products were identified by comparison of their mass spectra with a self-collected data bank[2,3,7]. In some cases, identification was achieved by computer, with an NBS library of about 54000 spectra.

RESULTS AND DISCUSSION

Solvent extraction *vs* pyrolysis data was briefly discussed in a previous paper[7]. The major classes of compounds identified in solvent extraction and subsequent gas chromatography-mass spectrometry analysis *vs* conventional pyrolysis are shown in Table 1. From these data it has been concluded that analytical pyrolysis is a fast screening procedure for identification of organic compounds. The method provides basic information about most classes of compounds present in surfaces of building stones, but for a detailed study and specific search for polar compounds, solvent extraction and concentration should be employed. The disadvantage of pyrolysis with regard to solvent extraction is both the loss of information on polar compounds and the formation of thermal degradation products.

In a search for solving the bias of data in pyrolysis, a novel procedure, simultaneous pyrolysis/methylation, was tested. Basically, the method consists of the derivatization of samples containing carboxyl and/or hydroxyl groups with an alkylating reagent. Tetramethylammonium salts of organic acids can be converted to methyl esters and the corresponding byproducts in the pyrolysis unit, thus the functional groups are directly protected[8]. Previous papers demonstrated the feasibility of the method for analysis of polyesters, waxes, etc.[9,10], and aquatic fulvic acids[11]. The application of pyrolysis/methylation to the study of black crusts seems to be very promising as several series of polar compounds, not previously found in conventional pyrolysis, were identified in the pyrolysates. In fact, Table 1 also shows the major classes of compounds identified from a total of 250 in pyrolytic methylation. The carboxylic acids are recovered as the corresponding

Table 1 Main classes of compounds identified in the black crust of the Custom House, Dublin, according to the analytical procedure

Class of compounds	*Solvent extraction*	*Pyrolysis*	*Py/Methylation*
	Range[1]	*Range*	*Range*
n-Alkanes	C_{13}-C_{35}	C_5-C_{32}	C_9-C_{29}
n-Fatty acids	C_{10}-C_{32}	—	C_6-C_{26}
n-Dicarboxylic acids	+	—	C_7-C_{17}
(Alkyl)benzenes	+	C_6-C_{17}	C_6-C_{26}
(Alkyl)naphthalenes	C_{10}-C_{13}	C_{10}-C_{14}	C_{10}-C_{13}
(Alkyl)phenanthrenes	C_{14}-C_{16}	C_{14}-C_{17}	C_{14}-C_{16}
Diterpenoids	C_{18}-C_{20}	C_{18}	C_{18}-C_{20}
Triterpenoids	C_{27}-C_{34}	C_{27}-C_{35}	+
Polycyclic aromatic hydrocarbons	C_{10}-C_{22}	C_{10}-C_{24}	C_{10}-C_{18}

[1] Range denotes number of carbon atoms

+ Present, but range not determined,—not identified methyl esters and the hydroxyls as methoxyls. Throughout this paper they are referred to as acids and hydroxyls, their original forms, rather than as derivatized methyl esters and methoxyls.

The fatty acid series in pyrolysis/methylation is only limited by the resolution of the chromatographic column. This fatty acid series is absent in conventional pyrolysis. Fatty acids have been found extensively in aerosols[12]. Kawamura and Kaplan[13] detected C_5-C_{30} fatty acids in rain and snow samples in California, where it appears that lower acids have a microbial origin whereas higher acids are characteristic components of plant waxes.

The series of dicarboxylic acids was also absent in conventional pyrolysis, and evidenced in pyrolysis/methylation up to a range of C_{17}. Kawamura and Kaplan[14] analysed dicarboxylic acids up to C_{10} in Los Angeles air and auto exhausts. The study indicated that automobile emissions are the important primary source of atmospheric dicarboxylic acids, which due to their polar nature are associated with moisture and may form salts.

The identification of aromatic acids is to be noted. These included benzoic acid, methylbenzoic acids, benzenedicarboxylic acids, methylbenzenedicarboxilic acids, benzenetricarboxylic acids, and naphthalenecarboxylic acid (Table 2). Cautreels and van Cauwenberghe[15] identified alkanes, polycyclic aromatic hydrocarbons (PAH) and its alkylated derivatives, dialkyl phthalates, fatty acids, and aromatic acids in the gas phase of urban air. Aromatic acidic compounds included phenol, cresols, xylenols, benzoic acid, methylbenzoic acids, hydroxybenzoic acids, benzenedicarboxylic acids, and naphthalenecarboxylic acid. These compounds were also encountered in the pyrolytic methylation of the black crusts. Kawamura and Kaplan[13] suggested that benzoic acids and phenols originate from non-biogenic sources, such as fossil fuel combustion.

Table 2 Major compounds identified in the pyrolytic methylation of a black crust from Custom House, Dublin.

Peak	*Compound**
1	Styrene
2	Phenol
3	*n*-Hexanoic acid
4	Benzaldehyde
5	Ethylmethylbenzene
6	Trimethylbenzene
7	Benzonitrile
8	Trimethylbenzene + benzofuran
9	N,N-dimethylalkyl amide
10	Trimethylbenzene
11	*n*-Heptanoic acid
12	Indene
13	Methylbenzonitrile
14	Methylbenzonitrile
15	Benzoic acid
16	Methylbenzofuran
17	*n*-Octanoic acid
18	Methylindene
19	Methylindene
20	Methylindene + cresol
21	Naphthalene

Table 2 cont.

Peak	*Compound**
22	Benzothiophene
23	Methylbenzoic acid
24	*n*-Nonanoic acid
25	Dimethylbenzofuran
26	*n*-Hexylbenzene
27	Dimethylindene
28	Methylindole + methyldihydronaphthalene
29	Methylnaphthalene
30	Methylnaphthalene
31	*n*-Decanoic acid
32	Methylbenzoic acid
33	Methylbenzoic acid
34	Biphenyl
35	Dimethylnaphthalene
36	Dimethylnaphthalene
37	Dimethylnaphthalene
38	*n*-Octanedioic acid
39	Benzenedicarboxylic acid
40	Methylbiphenyl
41	*n*-Pentadecane
42	Benzenedicarboxylic acid
43	Dibenzofuran
44	*n*-Dodecanoic acid
45	*n*-Nonanedioic acid
46	Methylbenzenedicarboxylic acid
47	Fluorene
48	Methylbenzenedicarboxylic acid
49	*n*-Tridecanoic acid + methyldibenzofuran
50	Methyldibenzofuran
51	Naphthalenecarboxylic acid
52	*n*-Decanedioic acid + methyldibenzofuran
53	*n*-Heptadecane
54	*n*-Tetradecanoic acid
55	*n*-Undecanedioic acid
56	Phenanthrene
57	Anthracene
58	*n*-Pentadecanoic acid + benzenetricarboxylic acid
59	Benzenetricarboxylic acid
60	Methylpentadecanoic acid
61	Methylphenanthrene
62	Methylphenanthrene
63	*n*-Hexadecanoic acid
64	*n*-Tridecanedioic acid
65	Phenylnaphthalene + anthracenedione
66	Methylhexadecanoic acid + *n*-eicosane
67	*n*-Heptadecanoic acid + dimethylphenanthrene
68	Fluoranthene
69	*n*-Octadecadienoic acid
70	*n*-Octadecenoic acid + *n*-heneicosane
71	*n*-Octadecenoic acid
72	*n*-Octadecanoic acid

* Aromatic and fatty acids were recovered as methyl esters and phenols as methoxy derivatives

Some phenols and quinones were encountered in the pyrolysate mixture. They encompass phenol, cresol or benzenediol as the dimethoxybenzene recovered could be assigned to one or another, ethoxybenzoic acid ethyl ester, probably as such in the sample, 3-methoxy-4-hydroxybenzoic acid (vanillic acid), phenylprop-2-enoic acid and 4-hydroxyphenylprop-2-enoic acid (*p*-coumaric acid), hydroxybiphenyl, fluorenone, and anthracenedione. The 4-hydroxyphenylprop-2-enoic acid could be considered as a tracer of conifer pollen, as *Pinus* pollen contain sporopollenin which comprises *p*-coumaric acid[9], whilst the phenylprop-2-enoic acid is probably a pyrolysis product of the original acid, in which a dehydroxylation was produced. Vanillic acid can be traced as a product of residential wood stoves[16].

The PAH mixtures encountered in black crusts are complex because of the presence of their alkylated derivatives. These compounds derive from combustion-generated airborne particulate matter and have been identified, amongst other sources, in smoke from plant burning[17] and carbonaceous particles from fossil fuel combustion[12,18]. Basically, species from two to four aromatic rings are distributed in the pyrolysate (Table 2), the same compounds being previously identified in the solvent extracts[3]. In urban environments lower PAHs up to benzofluorenes are abundant in the gas phase, whereas higher PAHs are found predominantly in the particulate fraction.

Sulphur-, and oxygen-containing polycyclic aromatic species, including polycyclic aromatic ketones, were found in the pyrolysate, thiophene, benzothiophene, dibenzothiophene, benzonaphthothiophene, benzofuran, dibenzofuran, benzonaphthofuran and some of their alkylated derivatives being the identified compounds. Methylthiobenzothiazole and some alkylated pyrrols, indoles, were representative of nitrogen-containing compounds.

Lee *et al.*[19] identified similar PAHs in the combustion of three common fuels. The sulphur-containing species were related to coal combustion products. However, Williams *et al.*[20] identified these compounds in diesel fuels. Sicre *et al.*[21] reported that dibenzothiophenes are common in crude oils and coal emissions, therefore their presence is not indicative of a specific origin. Benzofurans are probably related to wood or coal combustion[19]. Bayona *et al.*[22] found indoles in coal tar fractions, and Ramdahl[23] identified polycyclic aromatic ketones in diesel exhaust, and wood and coal combustion samples.

Diterpenoids were observed in all three analytical procedures. However, in conventional pyrolysis only retene, an incomplete combustion product with the abietane skeleton, was identified. This compound is used as an indicator of residential coniferous wood combustion[17]. Dehydroabietic acid derivatives were identified in both solvent extraction and pyrolytic methylation, which further support a coniferous wood origin.

Triterpenoids were also present in pyrolytic methylation, but due to the absence of molecular ions in the mass spectra, they could not be individualized. However, the series of hopanes were identified in both solvent extraction and conventional pyrolysis studies with a more powerful mass spectrometry instrument[7].

All classes of compounds shown in Table 1 have been previously identified in gas phase, aerosols, and particulate matter in urban atmospheres. This is of interest as Grimalt *et al.*[1] reported the close similarity between the organic composition of black crusts from the Holy Family church (Barcelona, Spain), and airborne particulates, collected by glass fibre filtration, and gas-phase organic compounds, obtained by polyurethane foam adsorption. These facts and the finding of carbonaceous particles entrapped in the voids of gypsum

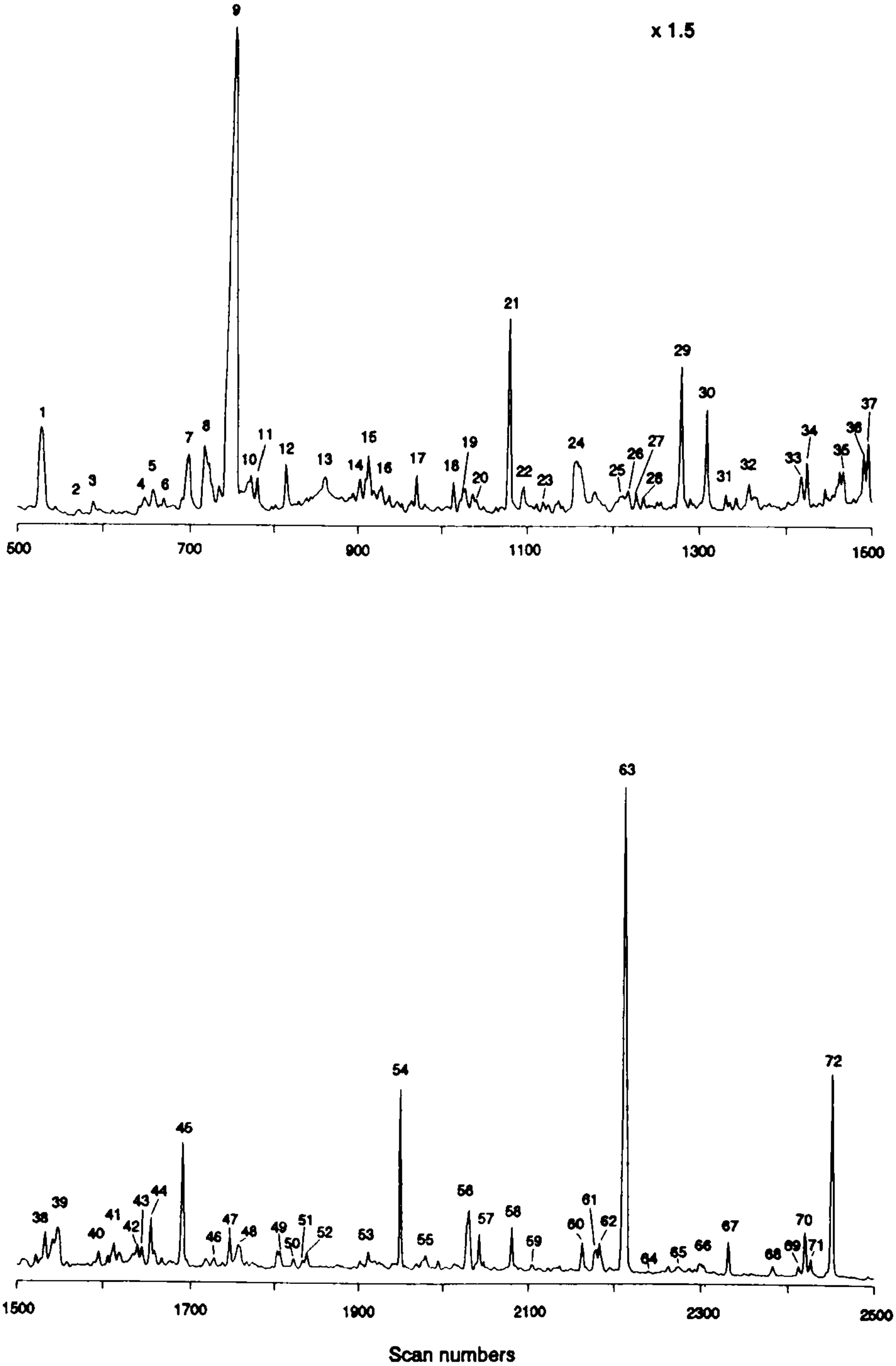

Figure 1 Major compounds identified in the pyrolytic methylation of a black crust from Custom House, Dublin. Peaks refer to Table 2.

crystals demonstrated that the organic compounds present in the black crusts, covering the building stones in urban environments, are the result of a direct input of air pollutants, the buildings acting as non-selective surfaces passively entrapping all deposited aerosols and particulate matter, from whose analysis a source can be traced.

CONCLUSIONS

The series of aliphatic and aromatic acids found in the pyrolysis/methylation mixture clearly indicate that pyrolysis/methylation protects carboxylic groups through the formation of methyl esters, and hydroxyl groups through the formation of methoxyls. This reveals that conventional pyrolysis is a strongly biased method for the identification of compounds containing oxygenated functional groups. This report demonstrates that pyrolysis/methylation is an analytical procedure of great sensitivity for investigating organic compounds in inorganic matrices. No time-consuming solvent extractions, concentrations, derivatizations, and other manipulations which imply the possibility of cross-contamination are required to obtain similar data to those obtained by solvent extraction and subsequent gas chromatography-mass spectrometry analysis.

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