Fresenius Envir Bull 9: 322 - 327 (2000)

1018-4619/2000/5-6/322-06 DM 20 or 3.50/p

CHARACTERIZATION OF THE ORGANIC COMPOUNDS DEPOSITED ON MONUMENT SURFACES

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SUMMARY

Buildings and monuments act as repositories of airborne organic pollutants, which accumulate at the surfaces forming black crusts. The organic compounds present in the black crusts collected from monuments located in four European cities, Brussels, Dublin, Rome and Seville were investigated and compared with those extracted from a diesel soot. The methods used were evaporation/pyrolysis and simultaneous pyrolysis/methylation. A complex mixture of compounds was identified in the crusts, mainly *n*-alkanes, *n*-alkenes, acyclic isoprenoids, fatty acids, aliphatic dicarboxylic acids, alkylbenzenes, benzenepolycarboxylic acids, polycyclic aromatic hydrocarbons, thiophenes, furans, pyridines, quinolines, benzonitriles, etc. These compounds were produced from total or partial combustion of petroleum derivatives. Similar compounds were obtained from diesel soot indicating that traffic around the most outstanding monuments contributes to a continuous blackening of its walls.

Key words: Air pollution, black crusts, diesel soot, hydrocarbons, fatty acids, monument pollution

INTRODUCTION

Stone buildings, monuments, outdoors-exposed sculptures and objects of art have been deteriorated over the centuries by natural causes. Wind, rain, and frosts contribute to a gradual process of ageing and deterioration. The alteration of stone is not, therefore, a contemporary phenomenon, but was already known in ancient times, and was a cause of preoccupation to Greek and Roman writers. In the present century deterioration processes increased due to air pollution.

As stated by Simoneit and Mazurek (1) urban aerosols generally consist of a mixture of lipid materials emitted locally along the aged material that has been carried into the urban area by winds. Urban environments contain many organic pollutants which are related to incomplete fuel combustion in domestic heating, industrial plants, and vehicular exhausts. In addition to organic compounds, carbonaceous matter (mainly graphitic carbon) is common in urban environments. Buildings and monuments act as repositories of these airborne organic pollutants, which accumulate at the surfaces as black crusts.

Presented at the 10th International Symposium of MESAEP in Alicante, Spain, 2 - 6 Oct. 1999

In this paper the composition of black crusts from different European monuments is studied and compared with the components of a diesel soot.

MATERIALS AND METHODS

Sites investigated

The organic compounds present in the black crusts collected from monuments located in four European cities: Brussels (Belgium), Dublin (Ireland), Rome (Italy) and Seville (Spain) were investigated. To study the possible contribution of diesel soot to organic pollutants and blackening of building stones in urban environments, diesel soot collected from the exhaust of a 10-year-old Sevillian public bus was also analysed.

Analytical pyrolysis of black crusts

Pyrolysis was accomplished as described by Saiz-Jimenez (2). Briefly, a few mg of sample was needed for analysis. The sample was pyrolyzed for 10 s using a wire with a Curie temperature of 700 °C.

The analysis was performed in a Fisons intrument GC 8000/MD 800 coupled to a Fischer 0316 Curie-point pyrolyzer, using a 30 m x 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 temperature used was shown to be adequate for evaporation/pyrolysis of organic materials within mineral matrices (3). However, some changes in the thermal breakdown of molecules could be expected, as the crust contains high percentages of gypsum and other salts and it has been demonstrated that cations influence the thermal behaviour of organic materials. Furthermore, decarboxylation of organic acids was observed (2).

In a search for solving the bias of data in pyrolysis, mainly the missing of polar compounds, simultaneous pyrolysis/methylation was used. This 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.

For pyrolysis/methylation the milled crust was deposited of 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. The cylinder was slightly dried with a N_2 flow and immediately inserted in the pyrolyzer. The same instrument and analytical conditions, previously described for pyrolysis, were used. A description of the method and its advantages can be found elsewhere (4).

RESULTS AND DISCUSSION

The pyrolysis of black crusts yield a complex pyrogram dominated by a homologous series of *n*-alkenes in the range C_8-C_{28} together with the series of *n*-alkanes (C_8-C_{32}). However, whereas alkenes predominate over alkanes up to C_{20}, the opposite is true for alkanes from C_{21} with a considerable reduction in alkenes as the series progresses. Polycyclic aromatic hydrocarbons (PAH) up to 4 rings and alkylbenzenes up to C_{25} were other significant compounds (Table 1).

No fatty acids were detected in the pyrolysate. Several facts could contribute to this absence, such as the relatively high pyrolysis temperature and the presence of considerable amount of salts. Inorganic additives result in the production of unwanted thermal reactions, namely cyclization and aromatization reactions of unsaturated fatty acids. A decarboxylation process in fatty acids could be expected in the pyrolysis of black crusts, resulting in the formation of alkenyl compounds with one C atom less than the original fatty acid, together with the formation of some other artifacts. However, the fatty acid series in pyrolysis/methylation (C_6-C_{32}) is only limited by the resolution of the chromatographic column (Table 2). This fatty acid series is absent in conventional pyrolysis. The series of dicarboxylic acids was also absent in conventional pyrolysis, and evidenced in pyrolysis/methylation up to a range of C_{17}.

The identification of aromatic acids is to be noted. These included benzoic acid, benzenedi-, tri- and tetracarboxylic acids, etc. Also, some phenols and quinones were found in the pyrolysate mixture. They encompass phenol (as methoxybenzene), cresol (as methoxymethylbenzene) and benzenediol (as dimethoxybenzene), etc. In addition, fluorenone and anthracenedione were identified.

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 carbonaceous particles from fossil fuel combustion (5). Basically, species from two to four aromatic rings are distributed in the pyrolysate, the same compounds being previously identified in the solvent extracts (6). In urban environments lower PAHs up to benzofluorenes are abundant in the gas phase, whereas higher PAHs are found predominantly in the particulate fraction.

Table 1. Main classes of compounds identified in evaporation/pyrolysis of black crust and diesel soot

	European black crusts average range	Diesel Soot range
n-Alkanes	C_8-C_{32}	C_9-C_{32}
n-Alkenes	C_8-C_{28}	C_9-C_{26}
Saturated acyclic isoprenoids	C_{19}, C_{20}	C_{15}, C_{20}
Saturated fatty acids	C_{14}-C_{16}	-
Alkylbenzenes	C_6-C_{25}	C_6-C_{26}
Alkylcyclohexanes	-	C_{14}-C_{23}
Polycyclic aromatic hydrocarbons	C_{10}-C_{18}	C_{10}-C_{17}
Thiophene and derivatives	+	+
Pyridine and derivatives	+	+
Furan and derivatives	+	-
Benzonitriles	+	-
Quinoline and derivatives	+	-

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, some alkylated pyrrols and indoles were representative of nitrogen-containing compounds.

Lee et al. (7) identified similar PAHs in the combustion of three common fuels. The sulphur-containing species were related to coal combustion products. However, Williams et al. (8) identified these compounds in diesel fuels. Sicre et al. (9) 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. Bayona et al. (10) found indoles in coal tar fractions, and Ramdahl (11) identified polycyclic aromatic ketones in diesel exhaust, wood and coal combustion samples.

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 previously identified in both solvent extraction and conventional pyrolysis studies (2).

All classes of compounds shown in Tables 1 and 2 have been previously identified in gas phase, aerosols, and particulate matter in urban atmospheres. A study of Sagebiel et al. (12) illustrates the importance of diesel vehicles in the production of particulate emissions, as it was reported that 31 diesel vehicles whose age averaged 22 years showed average emissions of 944 mg/km, with one vehicle emitting at a rate of 10,500 mg/km. For comparison, emission rates of total particles were below 6 mg/km for most production catalyst vehicles. Diesel soot has a considerable influence in the blackening of urban monuments, which is of particular concern in Mediterranean countries where old vehicles are used for public transport and freight.

Table 2. Main classes of compounds identified in pyrolysis/methylation of black crusts and diesel soot

	European black crusts average range	Diesel Soot range
n-Alkanes	C_8-C_{32}	C_8-C_{32}
n-Alkenes	C_8-C_{30}	C_9-C_{25}
Saturated acyclic isoprenoids	C_{19}, C_{20}	C_{18}, C_{20}
Saturated fatty acids	C_6-C_{30}	C_5-C_{25}
Unsaturated fatty acids	C_4-C_{18}	C_{18}
Dicarboxylic acids	C_7-C_{17}	-
Alkylbenzenes	C_6-C_{26}	C_6-C_{27}
Alkylcyclohexanes	-	C_{15}-C_{24}
Benzoic acid and derivatives	+	+
Benzenedicarboxylic acids	+	+
Benzenetricarboxylic acids	+	+
Benzenetetracarboxylic acids	+	-
Polycyclic aromatic hydrocarbons	C_{10}-C_{18}	C_{10}-C_{17}
Thiophene and derivatives	+	+
Pyridine and derivatives	+	-
Furan and derivatives	+	+
Benzonitriles	+	+
Quinoline and derivatives	+	-

Grimalt et al. (13) reported the close similarity between the organic composition of black crusts from the Holy Family church in 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 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.

From the data, it was concluded that the black crusts from different European monuments and buildings contain molecular markers that are characteristic of petroleum derivatives and generated by the traffic. The overprint of some biogenic components of aerosols over petroleum components from anthropogenic emissions (mainly vehicular) can be illustrated by the dominance of hydrocarbons around n-C_{29} (plant waxes) and fatty acids in the range n-C_{12}-C_{19} (microorganisms and plant waxes).

Acknowledgement

This work was supported by the Junta de Andalucia, Research Group RNM-201.

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Received for publication: November 03, 1999
Accepted for publication: May 08, 2000