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Summary

Solvent extraction and pyrolysis of the black sulfated crusts obtained from the Custom House, a 18th century building located in Dublin, Ireland, revealed common products upon gas chromatography-mass spectrometry analysis. Both methods yielded aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and triterpanes. The differences were the presence of fatty acids and diterpenoids (as methyl esters) and dialkyl phthalates in the solvent extract. On the contrary, low molecular weight compounds were identified as pyrolysis products, as denoted by their absence in the solvent extract. The origin of the identified compounds is related to urban and industrial activities.

1. INTRODUCTION

Air pollution is a significant source of economic loss in urban areas. Damages to materials used in historic buildings and monuments such as stones, metals, bricks, tiles, stained glass windows, etc. are well documented (1).

Different types of pollutants (CO_2 , SO_2 , NO_x) affect stone materials. The formation of gypsum on the surface and within the surface zones of the stone is one of the most destructive forms of pollution related damage. In fact, black sulfated crusts are extensively distributed in European urban buildings.

Although the deterioration of historical buildings and monuments is, at present, object of extensive research, organic chemical studies have barely been applied to this field. The study and identification of organic compounds present in black and grey crusts is of great concern because the role of organic compounds in weathering processes is relatively unknown.

2. EXPERIMENTAL

The Custom House was completed in 1791. During two centuries, in addition to the damage to the fabric caused by the aggressive atmosphere of Dublin and by the corrosion of ferrous metals, the building has suffered greatly from the effect of three major fires.

Black crusts were obtained from the balustrade removed from the east front during the restoration works. The samples were collected in June 30th and July 2nd, 1988. A representative sample of black crust was pounded in an agate mortar and subjected to analysis.

For solvent extraction, 20 g of sample were extracted during 8 h in a Soxhlet apparatus with toluene and methanol consecutively, as described by Cautreels and van Cauwenberghé (2).

For pyrolysis, several hundred micrograms of sample were deposited on a ferromagnetic wire (Curie temperature 770°C). Methods and analytical conditions were thoroughly described elsewhere (3).

3. RESULTS AND DISCUSSION

The evaporate/pyrolysate chromatogram from the black crust showed a great complexity, with up to 400 identified compounds. However, the

chromatogram from the extract was relatively less complex. To avoid large tables, identified compounds were studied by multiple ion detection technique. The use of ions permitted several classes of compounds to be monitored, thus providing information on categories of compounds present in the black crusts. Only some of the most representative classes of compounds are described in this paper.

n-Alkanes. Typical distribution for the n-alkanes (mass chromatogram m/z 85) ranges from n-C₅ to n-C₃₆ in the evaporate/pyrolysate and from n-C₁₃ to C₃₆ in the extract (Figure 1). Crude petroleum contains n-alkanes ranging from C₁ to C₃₅. The C₁-C₂₀ homologs can be lost during distillation in the refining processes, evaporation in the environment or by the experimental procedure employed. Natural biogenic background of vascular plant wax can be superimposed in the range n-C₂₃ to n-C₃₅.

The carbon preference index (CPI), a diagnostic criteria to define the probable sources of compounds, is useful to determine plant wax or fossil fuel input. CPI typical for petroleum is 1.0, while for the extract is 1.3. A more sensitive method requires a split of the carbon range into low (C₁₂-C₂₅) and high (C₂₆-C₃₅) ends. In this case, CPI is 1.1 and 1.5, respectively.

The lower end is representative of anthropogenic input while the high end demonstrates a mixed input, in which a signature of higher plant wax is also evident, as confirmed the dominance of n-C₂₉.

In addition, the extract shows a unresolved hump centered at the relative retention time of the carbon number range n-C₂₀ to n-C₃₀, which was also reported for the hydrocarbon fraction of vehicle exhaust emission (4).

n-Fatty acids. Mass chromatogram (m/z 74) for the extract (Figure 2) shows the presence of fatty acids (as methyl esters) in the range n-C₁₀ to n-C₃₂, a high even-to-odd carbon preference index (CPI ~ 2.5) and maxima at n-C₁₆ and n-C₂₄. The distribution pattern seems characteristic of a biogenic origin, where the homologs <n-C₂₀ and probably in part <n-C₂₄ are derived from microbial sources and the homologs >n-C₂₂ are derived from vascular plant wax. A similar distribution pattern for atmospheric particles from two slash burns, with a strong even CPI and maxima at n-C₂₂ and n-C₂₄ was reported (5). The fatty acids, in this case, showed a pattern characteristic of plant wax signature. For the lower end a microbial input is expected, because algae and fungi are common inhabitants of the black crust environment (6).

Triterpanes. Figure 3 shows the evaporate/pyrolysate hopane signature (m/z 191), which is similar to those obtained for the extract. Table 1 list the identified compounds. The 17 α (H),21 β (H)-hopanes are the geologically mature isomers of the 17 β (H),21 β (H)-hopanes (produced by microorganisms and some higher plants) and are evidence of petroleum input. The C₃₁ to C₃₅ hopanes consist of nearly equivalent amounts of 22S and 22R isomers. This distribution can be attributed to the presence of lubricating oil in vehicular exhaust of gasoline and diesel engines (5).

Diterpenoids. The abietane-type diterpenoids are predominant resin components of conifers and they rapidly dehydrogenate to yield more stable hydrocarbons and acids. Various intermediates along the pathway of thermal degradation of abietic acid to retene have been detected in smoke particles (5). Retene, 16,17-bisnordehydroabietic acid and dehydroabietic acid (the last two as methyl esters) were identified in the black crust extract. These compounds were also found in aerosols over rural areas (4). The thermally altered products of abietane compounds and specifically retene have been considered as a molecular marker of residential wood combustion (7).

Polycyclic aromatic hydrocarbons. Unsubstituted rings system ranging from two aromatic rings to six fused rings were the primary components of both evaporate/pyrolysate and extract. Some of the most abundant compounds were indene, naphthalene and its C₁-C₃ derivatives, fluorene and methylfluorenes, phenanthrene, fluoranthene, pyrene and benzopyrene. Enrichment of polycyclic aromatic hydrocarbons in black crusts can readily be attributed to anthropogenic input and combustion sources, because these compounds are known to be originated during fossil fuel combustion and fires (8).

Pyrolysis vs solvent extract. Both types of analysis yield similar classes of compounds. n-Alkanes, triterpenoids and polycyclic aromatic hydrocarbons represent the vast majority of compounds identified in the evaporate/pyrolysate. The advantage of pyrolysis is the very minute amount of sample required, which does not cause any mechanical or visual discontinuity on the building surface. The disadvantage is lost of information on polar compounds and the formation of some thermal degradation products.

Solvent extraction is a tedious and time-consuming method. In addition, very large amounts of sample are required, which creates patches and negative aesthetic effects on the building surface. This method evidences both fatty acid and abietic acid derivatives (as methyl esters) and dialkyl phthalates. The presence of phthalates could be explained by concentration of compounds as they were found in the gas phase of urban air (2), although a contamination during the experimental procedure cannot be ruled out. Probably, the advantage of the method is the concentration of different classes of compounds and the identification of polar compounds.

4. CONCLUSIONS

Flash evaporation and pyrolysis-gas chromatography-mass spectrometry of black crusts is a fast screening procedure for identification of organic compounds. The method is the choice when minute amounts of samples need to be analysed and provides basic information about most classes of compounds present. For a more detailed work and specific search of certain compounds solvent extraction and concentration should be employed.

Hydrocarbon fractions of black crust lipids contain molecular markers that are characteristic of petroleum derivatives. The evidences are the homologous series of n-alkanes with CPI ~ 1, the presence of a moderate unresolved hump, of triterpenoids and of polycyclic aromatic hydrocarbons.

The identification of diterpenoids and fatty acids with a maximum at n-C₂₄ point to the presence of smoke particles from wood combustion, whereas the distribution pattern of fatty acids with maximum at n-C₁₆ is characteristic of microbial input.

5. ACKNOWLEDGEMENT

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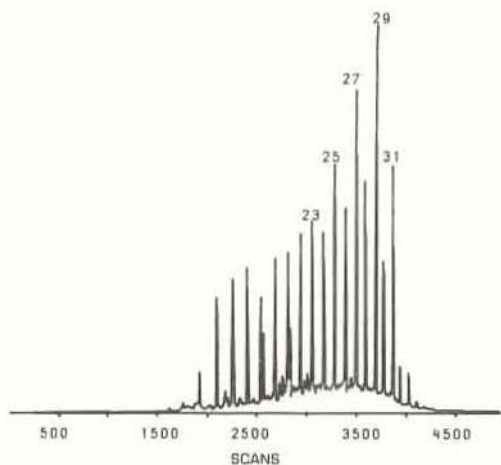


Figure 1. Mass fragmentogram (m/z 85) showing n-alkanes in solvent extract. Numbers above peaks indicate carbon numbers of series

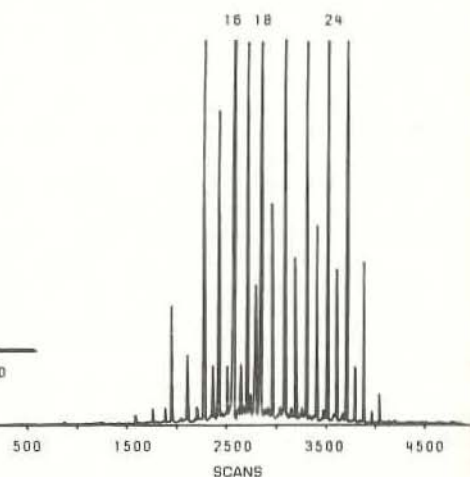


Figure 2. Mass fragmentogram (m/z 74) showing fatty acids (as methyl esters) in solvent extract. Numbers above peaks indicate carbon numbers of series

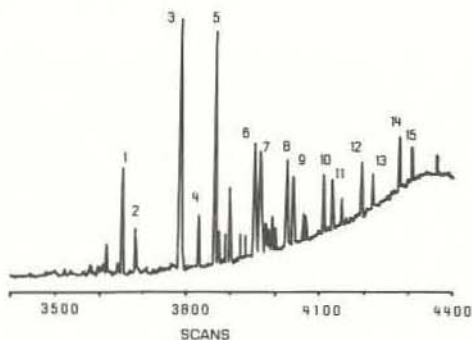


Figure 3. Mass fragmentogram (m/z 191) showing triterpanes in evaporate/pyrolysate. Identification of peaks in Table 1

TABLE 1

HOPANES IDENTIFIED IN THE BLACK CRUSTS FROM THE CUSTOM HOUSE, DUBLIN,

Compounds	Compounds
1 $17\alpha(H)$ -22,29,30-trisnorhopane	9 $17\alpha(H)$, $21\beta(H)$ -bishomohopane 22R
2 $17\beta(H)$ -22,30,30-trisnorhopane	10 $17\alpha(H)$, $21\beta(H)$ -trishomohopane 22S
3 $17\alpha(H)$, $21\beta(H)$ -30-norhopane	11 $17\alpha(H)$, $21\beta(H)$ -trishomohopane 22R
4 $17\beta(H)$, $21\beta(H)$ -30-norhopane	12 $17\alpha(H)$, $21\beta(H)$ -tetraquishomohopane 22S
5 $17\alpha(H)$, $21\beta(H)$ -hopane	13 $17\alpha(H)$, $21\beta(H)$ -tetraquishomohopane 22R
6 $17\alpha(H)$, $21\beta(H)$ -homohopane 22S	14 $17\alpha(H)$, $21\beta(H)$ -pentaquishomohopane 22S
7 $17\alpha(H)$, $21\beta(H)$ -homohopane 22R	15 $17\alpha(H)$, $21\beta(H)$ -pentaquishomohopane 22R
8 $17\alpha(H)$, $21\beta(H)$ -bishomohopane 22S	