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DETERMINATION OF FATTY ACIDS IN AIRBORNE PARTICULATE MATTER, DUST AND SOOT BY MASS CHROMATOGRAPHY

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SUMMARY

Extracts from airborne particulate matter, dust taken from an air filter and some soots were fractionated by alumina column chromatography. The solution eluted with ethanol-acetic acid (9:1) contained fatty acids and other polar substances. After heating the solution with a small amount of sulphuric acid, the esters of the fatty acids formed were extracted and separated from other polar substances by column chromatography. Identification and quantification were performed by mass chromatography at the molecular ion masses of the esters. Fatty acids from octanoic to tetratriacontanoic acid were determined in these samples and dotriacontanoic, triatriacontanoic and tetratriacontanoic acids were found for the first time.

INTRODUCTION

Organic components in airborne particulate matter are very complex and much information is available regarding the extractable compounds, although most of the investigations have been directed towards to analysis of polynuclear aromatic hydrocarbons such as benz[*a*]anthracene and benzo[*a*]pyrene because of their carcinogenic properties. Recently, some attention has been paid to polynuclear heteroaromatic compounds. Higher fatty acids in environmental samples such as airborne particulate matter are very interesting components as regards their origin and toxicity. Laseter and Valle² showed that many free fatty acids are contained in fungal spores, which constitute a significant proportion of the airborne particulate matter³. It is not known whether direct contact of fatty acids on respiratory tissue has any detrimental effects, but some epoxides of unsaturated fatty acids have been found to be carcinogenic⁴.

Analysis of higher fatty acids in airborne particulate matter has usually been performed by successive procedures of Soxhlet extraction, reverse extraction with an alkaline aqueous solution, neutralization, extraction, esterification with diazomethane and gas chromatography-mass spectrometry (GC-MS). Cautreels and Van Cauwenbergh⁵ determined linear chain fatty acids (dodecanoic acid to triacontanoic acid) in airborne particulate matter sampled in Antwerp by the procedures described above.

Also, they found that the separation of acidic and neutral components was not complete. Cautreels and Van Cauwenberghe⁶ measured major fatty acids (C_{12} and C_{14} – C_{22}) in crude extracts from airborne particulate matter by methylation with diazomethane and mass chromatography at m/z 74, omitting several extraction and separation steps in order to avoid time-consuming procedures and manipulation losses of the products. However, the analysis of minor fatty acids was very difficult using this method.

Airborne particulate matter sampled near the Chacaltaya Cosmic Ray Laboratory in Bolivia was analysed by Cautreels and Van Cauwenberghe⁷ in order to establish the natural background level of fatty acids and other components. Lunde *et al.*⁸ detected C_7 – C_{29} normal fatty acids (except C_{26}) and many branched-chain acids in rain and snow sampled in Norway. The distribution of organic pollutants containing fatty acids between airborne particulate matter and the corresponding gas phase has been investigated⁹. The results showed that lower fatty acids are more abundant in the gas phase and higher acids, from docosanoic acid up, are not detected in the gas phase. Some alternation of the distribution factors is observed for the even and odd carbon numbered fatty acids. This effect is known for several physico-chemical parameters of these compounds.

In this study, octanoic to tetratriacontanoic acids were determined by a combination of column chromatography and GC-MS and dotriacontanoic acid to tetratriacontanoic acid were found for the first time.

EXPERIMENTAL

Sample collection

Airborne particulate matter was collected with a Hi-Volume sampler, Model HVS-500, made by Sibata Chemical Apparatus Mfg. Co., near a bypass road at Ohomiya, Japan. A glass-fibre filter, 110 mm in diameter, was used to collect the sample by drawing the ambient air through it at a flow-rate of 610 l/min for 6 h.

As another airborne particulate matter sample, accumulated dust on the air conditioner filter used at the National Institute for Environmental Studies (Ibaraki, Japan) was used.

Soot was collected at the top of the chimney of a furnace in Hyogo Prefecture where firewood is burnt every day. Soot obtained by combustion of soybean oil and petroleum oil was prepared in the laboratory.

Sample extraction and separation procedure

Airborne particulate matter (33.9 mg), dust taken from a filter (15.61 g), soot from a chimney (13.57 g), soot from the combustion of soybean oil (6.70 mg) and soot from the combustion of petroleum oil (136.9 mg) were extracted with benzene (200 ml) in a Soxhlet apparatus for over 24 h. The extracts were concentrated with a vacuum rotary evaporator at room temperature and then column chromatography was carried out as shown in Fig. 1. The solution eluted with ethanol-acetic acid (9:1) was mixed with concentrated sulphuric acid (0.5 ml) and heated under reflux for 4 h. This solution was concentrated with a vacuum rotary evaporator to a third of its volume, then poured into an aqueous solution of sodium hydrogen carbonate. The ethyl esters of the fatty acids formed were extracted three times with dichloromethane

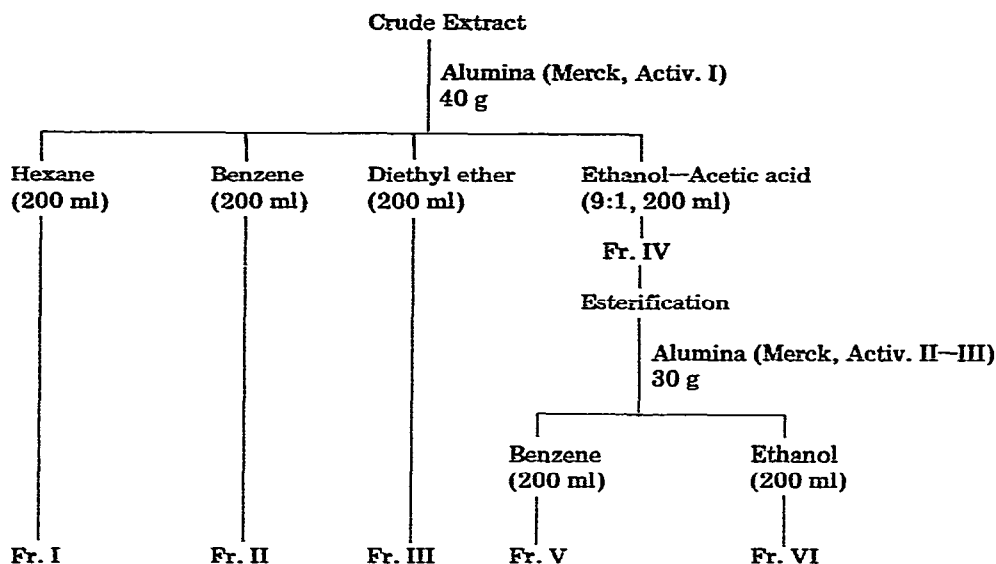


Fig. 1. Column chromatographic separation procedures.

(ca. 100 ml) and after concentration were chromatographed again as shown in Fig. 1. The corresponding fraction (V) was concentrated to ca. 1 ml for GC-MS and an internal standard (pyrene) amounting to 1 μg per millilitre of the solution was added.

Benzene, hexane, diethyl ether, ethanol and dichloromethane were distilled in all-glass apparatus from pesticide-grade solvents obtained from Wako (Osaka, Japan). Alumina was washed with diethyl ether in a Soxhlet apparatus for 15–20 h and then heated at 200°C under vacuum for 3–5 h before use. Acetic acid and sulphuric acid were of “super special” grade for trace analysis.

Gas chromatography-mass spectrometry

Mass spectra were measured with a JEOL Model JMS-DX 300 mass spectrometer connected with a JEOL GCG-05 gas chromatograph and a JEOL JMA-2000 mass data analysis system and stored on a 2.4-MW disk. The glass column (1 m \times 3 mm I.D.) was packed with Chromosorb W coated with 1% OV-17. The column temperature was set at 70°C for 2 min, increased to 300°C at 4°C/min, then held at 300°C until completion of analysis. The injector temperature was 340°C and the helium carrier gas flow-rate was 40 ml/min. The separator temperature for GC-MS was 250°C (the same results were obtained at higher temperatures). The mass spectrometric conditions were as follows: ionizing source pressure, $1 \cdot 10^{-6}$ – $2 \cdot 10^{-6}$ Torr; ionizing source temperature, 200°C; ionizing current, $3 \cdot 10^{-4}$ A; ionizing energy, 70 eV; accelerating voltage, 3 kV; scan range, m/z 10–600; scan speed, 1.3 sec per scan; scan interval, 3.0 sec. Identification was carried out by mass chromatography at the molecular ion masses of each fatty acid ethyl ester. Standard solutions were prepared for ethyl esters of C_{10} , C_{12} , C_{14} , C_{16} and C_{18} fatty acids. Quantification was performed by comparison of peak heights between each ester and the internal standard in the mass chromatogram. Compounds whose standard solutions were absent were tentatively analysed using calibration graphs of other esters, as follows:

- C₉-C₁₀ acid esters: calibration graph of ethyl decanoate;
 C₁₁, C₁₂ acid esters: calibration graph of ethyl dodecanoate;
 C₁₃, C₁₄ acid esters: calibration graph of ethyl tetradecanoate;
 C₁₅, C₁₆ acid esters: calibration graph of ethyl hexadecanoate;
 C₁₇-C₃₄ acid esters: calibration graph of ethyl octadecanoate.

RESULTS AND DISCUSSION

Column chromatography is a more desirable technique than using several extraction steps for the systematic separation of organic substances in airborne particulate matter, because with the latter technique separation is not complete and because it is almost impossible to fractionate neutral components. Fraction I in Fig. 1 contained aliphatic hydrocarbons; fraction II, polynuclear aromatic hydrocarbons and weakly polar compounds; fraction III, medium polar compounds such as phthalic acid esters; and fraction IV, strongly polar components. Alcohols such as methanol and ethanol could not elute fatty acids from the column, but a mixture of an alcohol and acetic acid (9:1) was successfully used to elute them. Ethanol was a better solvent than methanol because the solubility of fatty acids in methanol is lower than that in ethanol and because the esterification yield is higher in ethanol than in methanol, although Hill *et al.*¹⁰ found that methanol is more effective than cyclohexane for the extraction. By esterification and rechromatography, fraction V was composed of esters of fatty acids.

TABLE I
RECOVERY OF OCTADECANOIC ACID

Run No.	Recovery (%)
1	59.5
2	58.0
3	60.4
4	59.4
Mean (%)	59.4
Standard deviation (%)	1.0
Coefficient of variation (%)	1.7

Table I shows the overall results of the recovery test for octadecanoic acid using Soxhlet extraction, a first column chromatographic step, esterification and a second column chromatographic step. The mean recovery was relatively low, but the standard deviation was very small. Therefore, all subsequent analytical values were corrected by a recovery factor of 59.4%. Blank values were negligible in the overall analytical procedures.

Mass chromatogram plots were measured at m/z 88 (a McLafferty rearrangement ion), at the molecular ion masses of every fatty acid ethyl ester and at m/z 202 (molecular ion mass of pyrene internal standard). The precision of the mass chromatographic measurements is shown in Table II for five esters. The coefficients of variation were slightly higher in mass chromatography than in gas chromatography, but

TABLE II
PRECISION OF MEASUREMENT BY MASS CHROMATOGRAPHY

Solutions to be tested were prepared at concentrations of *ca.* 35 $\mu\text{g/ml}$ for all acids.

Run No.	Measured concentration ($\mu\text{g/ml}$)				
	C_{10} acid	C_{12} acid	C_{14} acid	C_{16} acid	C_{18} acid
1	32.5	36.5	37.0	37.2	43.0
2	41.0	32.7	33.0	33.2	36.4
3	46.0	38.0	38.0	34.7	38.0
4	36.0	33.0	32.7	30.5	34.8
5	37.8	33.0	34.9	31.6	37.0
Mean ($\mu\text{g/ml}$)	38.7	34.6	35.1	33.4	37.8
Standard deviation ($\mu\text{g/ml}$)	5.1	2.4	2.4	2.6	3.1
Coefficient of variation (%)	13	7	7	8	8

mass chromatography has a higher selectivity and sensitivity than gas chromatography. Although selected ion monitoring (SIM) has a greater sensitivity than mass chromatography, it was not effective in practice because the number and mass range of the selected ions in each run were strictly limited in the magnetic-type mass spectrometer used. Also, in mass chromatography the sensitivity of this instrument was satisfactory and it was very convenient to confirm entire mass spectra of peaks because all data in the full range were stored. Detection limits were 10, 5, 5, 2 and 1 ng for decanoic, dodecanoic, tetradecanoic, hexadecanoic and octadecanoic acid, respectively.

Mass chromatograms of ethyl esters of fatty acids in airborne particulate

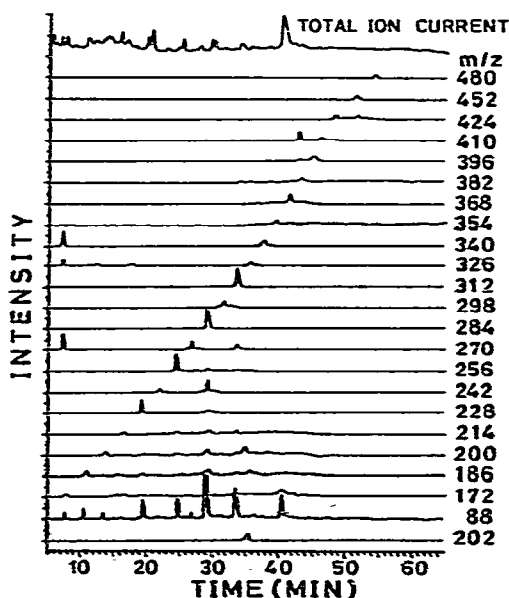


Fig. 2. Mass chromatograms of fatty acid (ethyl esters) in airborne particulate matter.

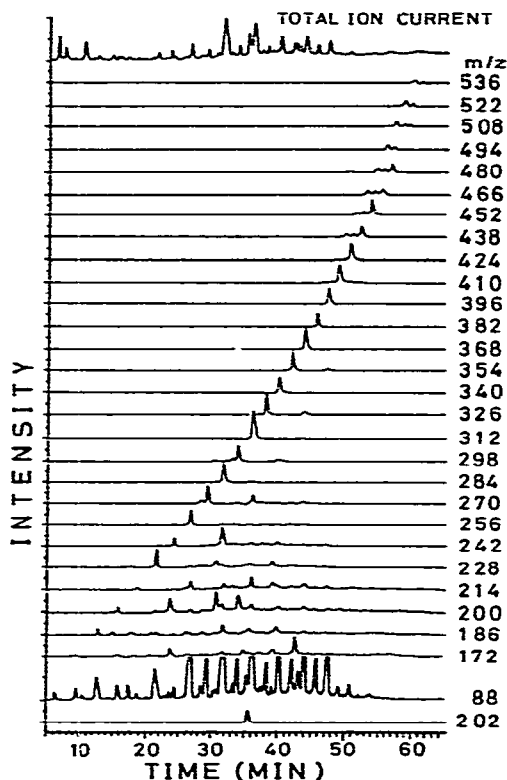


Fig. 3. Mass chromatograms of fatty acid ethyl esters in dust taken from an air conditioner filter.

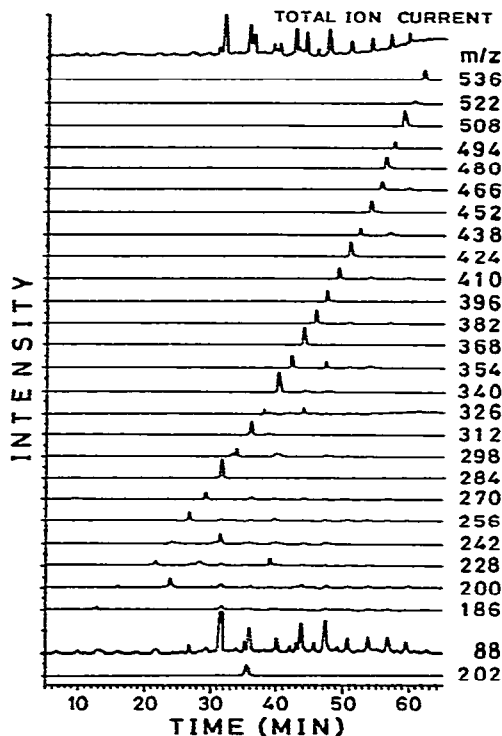


Fig. 4. Mass chromatograms of fatty acid ethyl esters in soot obtained from a chimney.

matter, dust taken from the filter and soot from the chimney are shown in Figs. 2, 3 and 4, respectively. Each chromatogram intensity was suitably magnified in order to make the peaks distinct. Normal and branched-chain fatty acid ethyl esters were clearly observed. Esters of normal acids appeared in constantly increasing order of retention time and esters of branched-chain acids were eluted faster than those of the corresponding normal acids. The structures of the branched-chain fatty acids were not investigated in detail.

It was observed in the mass spectra measured with this instrument that the relative intensity of molecular ions in the normalized mass spectra of esters increased with increasing molecular weight. Therefore, esters of fatty acids of high molecular weight were easily detected by mass chromatography at the molecular ion masses, although it was relatively difficult to detect them by mass chromatography at the McLafferty ion (m/z 88). Intensity ratios of molecular ions with respect to the McLafferty ion are shown in Fig. 5. There was a clear distinction between even and odd carbon numbered fatty acid ethyl esters.

The concentration patterns of the C_8 - C_{34} fatty acids were dependent on the origins of the samples. Fig. 6 shows the concentration patterns obtained in this study. Air particulate matter and soot from the combustion of soybean oil had fatty acids at

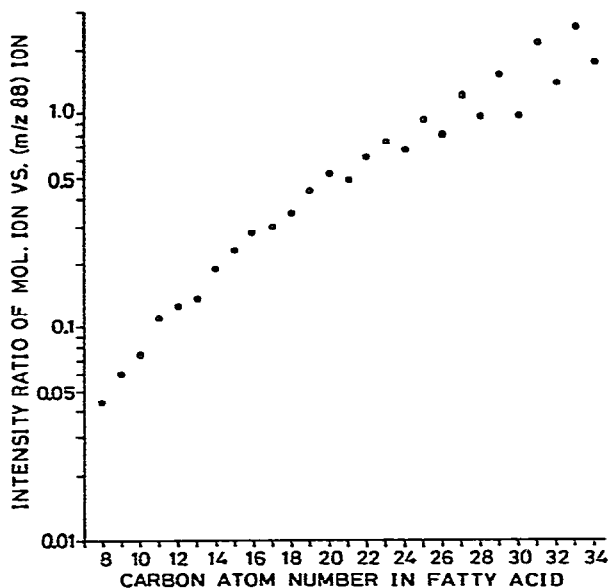


Fig. 5. Intensity ratios of molecular ions with respect to the McLafferty ion in mass spectra of fatty acid ethyl esters. ●, Fatty acids possessing an even carbon number; ○, fatty acids possessing an odd carbon number.

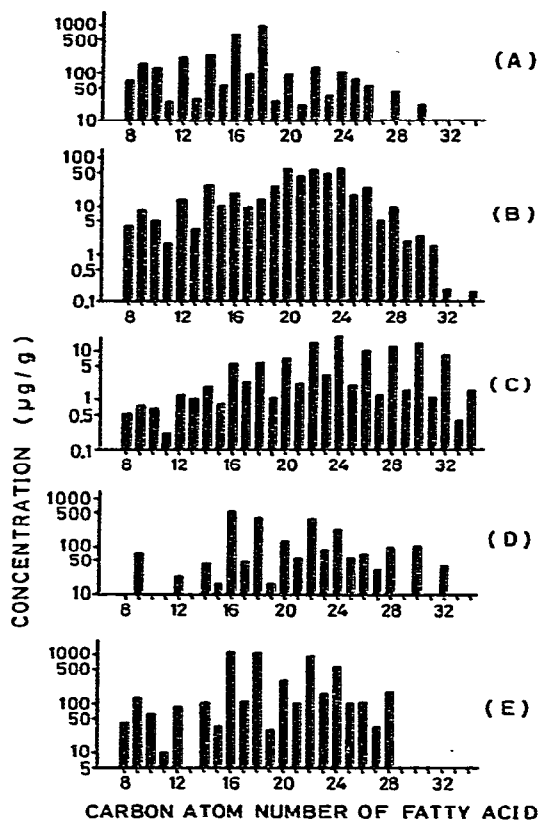


Fig. 6. Concentration patterns of fatty acids. (A) Airborne particulate matter; (B) dust taken from an air conditioner filter; (C) soot obtained from a chimney; (D) soot obtained by combustion of petroleum oil; (E) soot obtained by combustion of soybean oil.

similar concentrations. Contents of fatty acids in the dust taken from the filter were fairly low compared with those in airborne particulate matter, probably because the dust contained a significant amount of soil. It was interesting that the concentrations of fatty acids were extremely low in the soot from the chimney compared with the soot obtained by combustion of petroleum oil or soybean oil. The reason may be the disappearance of the acids during long-term heating of the soot in the chimney. It was characteristic that the concentration patterns were significantly different between airborne particulate matter and the dust taken from the filter. The origins of the fatty acids in the two samples might be different. Octadecanoic acid was the most abundant acid in airborne particulate matter. Hexadecanoic acid was the most abundant acid in the soot obtained by combustion of petroleum oil or soybean oil, and tetracosanoic acid in the dust taken from the filter or soot from the chimney. Fatty acids above hentriacontanoic or nonacosanoic acid could not be detected in airborne particulate matter or soot obtained by combustion of soybean oil because the amount of the

samples was inadequate. Dotriacontanoic, tritriacontanoic and tetratriacontanoic acids were detected for the first time in the dust taken from the air conditioner filter, soot obtained from the chimney and soot obtained by combustion of petroleum oil.

The concentrations of fatty acids in airborne particulate matter were comparable to the values reported by other investigators⁷. In all instances except for the dust taken from the filter, even carbon numbered fatty acids were always present in considerably higher concentrations than the odd carbon numbered acids.

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REFERENCES

- 1 F. W. Karasek, D. W. Denney, K. W. Chan and R. E. Clement, *Anal. Chem.*, 50 (1978) 82.
- 2 J. L. Laseter and R. Valle, *Environ. Sci. Technol.*, 5 (1971) 631.
- 3 S. M. Prady, *Mycologia*, 49 (1957) 399.
- 4 R. Cortesi and O. S. Privett, *Lipids*, 7 (1972) 715.
- 5 W. Cautreels and K. Van Cauwenberghe, *Atmos. Environ.*, 10 (1976) 447.
- 6 W. Cautreels and K. Van Cauwenberghe, *J. Chromatogr.*, 131 (1977) 253.
- 7 W. Cautreels and K. Van Cauwenberghe, *Sci. Total Environ.*, 8 (1977) 79.
- 8 G. Lunde, J. Gether, N. Gjøs and M. S. Lande, *Atmos. Environ.*, 11 (1977) 1007.
- 9 W. Cautreels and K. Van Cauwenberghe, *Atmos. Environ.*, 12 (1978) 1133.
- 10 H. H. Hill, Jr., K. W. Chan and F. W. Karasek, *J. Chromatogr.*, 131 (1977) 245.