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Note

Liquid chromatographic determination of trace amounts of low-molecular-weight fatty acid vapours in industrial emissions

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Low-molecular-weight fatty acids have received much attention as odorous substances around painting workshops and dairy establishments. As they generate odour at parts per trillion (ppt) (v/v) levels, specific techniques are required in order to determine trace amounts of these vapours.

Such fatty acid vapours have been sampled in alkaline solution[1] and on solid particles[2]. However, a large volume of sample needs to be sampled in order to compensate for the detector response in chromatographic analysis. High analytical accuracy is difficult to achieve in trace determinations because of their reactivity and/or adsorption on solid surfaces.

Fatty acids reacts with phenacyl bromides under the catalytic effect of crown ethers to produce ultraviolet-absorbing[3–5] or fluorescent[5] derivatives that can be detected by liquid chromatography (LC)[6,7]. Trace amounts of fatty acids such as are present in air are difficult to determine, however, because of the limited response.

Several convenient methods have been developed for the determination of trace amounts of aldehydes[8], amines[9,10], alkanethiols[11] and phenols[12] in air by using a Sep-Pak C_{18} (SP-18) cartridge. Recently, the application of LC for introducing a large volume of sample has been used to compensate for the detector response in determining ultra-trace levels of phenols in environmental samples[12,13].

In this paper, a convenient method is presented for the determination of trace levels of gaseous and aerosol-adsorbed C_3–C_6 fatty acids in industrial emissions. The fatty acids were sampled by the use of an SP-18 cartridge impregnated with sodium hydroxide and derivatized with *p*-bromophenacyl bromide (PBPB). The derivatives were introduced into a liquid chromatograph on a large scale through an ODS mini-column sampling loop. The method may be useful for determining fatty acids at parts per billion (ppb) (v/v) or ppt levels, such as those found in industrial emissions or ambient air, especially in field research.

EXPERIMENTAL

Reagents and materials

Propionic acid, *n*-butyric acid, *n*-valeric acid and *n*-caproic acid were of special grade and methanol and acetonitrile were of chromatographic grade from Wako (Osaka, Japan). PBPB and 18-crown-6-(1,4,7,10,13,16-hexaoxacyclooctadecane)

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(18-crown-6-ether) were of special grade from Dojindo Labs. (Kumamoto, Japan) and Tokyo Kasei (Tokyo, Japan), respectively.

A standard solution was prepared to contain 1 mg/ml of the individual fatty acids in methanol. PBPB solution was prepared by dissolving 0.4 g of PBPB and 0.04 g of 18-crown-6-ether in 100 ml of acetonitrile. The Sep-Pak C_{18} cartridge was obtained from Waters Assoc. (Milford, Ma, U.S.A.).

Apparatus

A Waters Assoc. ALC/GPC 244 liquid chromatograph was employed, equipped with a mini-column sampling loop system and an M440 UV absorbance detector adjusted to 245 nm. The mini-column, attached to a Rheodyne (Cotati, CA, U.S.A.) 7125 six-way switching valve, was a 10.0 mm × 4.0 mm I.D. stainless-steel tube packed with 15–30 μm ODS silica particles (Nomura Kagaku, Aichi, Japan). The loop was washed with 5 ml of methanol prior to use. The analytical column used was a 15 cm × 4.6 mm I.D. tube packed with Develosil ODS-3 (3 μm) (Nomura Kagaku). The mobile phase was acetonitrile–methanol–water (55:10:35) at a flow-rate of 1.0 ml/min.

Preparation of sampling cartridge

An SP-18 cartridge was washed with 2 ml of methanol prior to use. A 2-ml volume of 0.1% sodium hydroxide in methanol was forced through the cartridge, which was then dried for 1 h under reduced pressure in a stream of nitrogen and subsequently dried further by passing nitrogen (99.999%) at 70–100 ml/min for 30 min. The cartridge was closed with glass plugs, sealed in a vial and stored in a cool place in the dark until use.

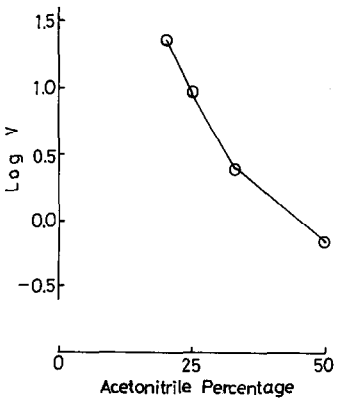
Analytical procedure

A 1–100-l volume of air sampled was sampled at 0.5–1.5 l/min through a coated SP-18 cartridge. The absorbed substances in the cartridge were eluted with 2 ml of acetonitrile in the opposite direction to that used in sampling. The eluate was mixed with 0.1 ml of 1% sodium hydroxide solution in distilled water and 0.1 ml of the PBPB solution and allowed to stand for 15 min at 80–90°C. The sample volume was then adjusted to 6 ml with distilled water. A 0.1–1.5-ml aliquot of the sample was injected into the mini-column sampling loop. The adsorbed substances were introduced into the liquid chromatograph with the carrier in the opposite direction to that used in the injection and determined by LC. Identification was made on the basis of capacity factors (k') and the quantitation was performed by measuring the peak heights. The cartridges could be used repeatedly at least five times by washing them with 3–5 ml of methanol each time.

RESULTS AND DISCUSSION

Adsorption and desorption of fatty acids on and from the cartridge

A 100-l volume of air sample containing 0.2–5.0 μg of the fatty acids, prepared by using a Yuasa (Osaka, Japan) KS-04C standard-gas generation apparatus[12], was passed at 1.5 ml/min through two coated SP-18 cartridges in series. The fatty acids were detected only on the first cartridge and none was found on the second at any relative humidity (20–80%) of the air samples. The adsorbed substances were



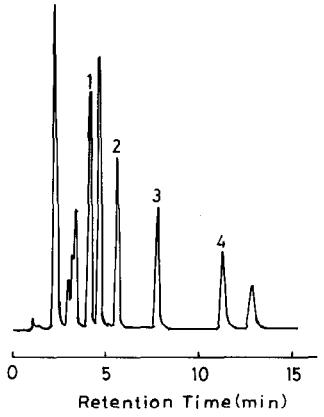


Fig. 1. Retention volume of propionic acid–PBP derivative *vs.* percentage of acetonitrile in acetonitrile–water eluent. V = retention volume (ml).

Fig. 2. Liquid chromatogram of fatty acid–PBP derivatives: (1) propionic acid; (2) *n*-butyric acid; (3) *n*-valeric acid; (4) *n*-caproic acid. Amount of the individual fatty acids introduced, 200 ng; sample volume introduced, 1.5 ml.

completely eluted with 1.0 ml of acetonitrile. As a result, the maximum sampling volume of air and the elution volume of methanol were set to 100 l and 2.0 ml, respectively.

Derivatization of fatty acids with PBPB in the organic medium

The fatty acids couple with PBPB to form a *p*-bromophenacyl (PBP) derivatives in the presence of the crown ether in a weakly alkaline medium[3–5]. In the reaction medium, the absorbance of the PBP derivatives reached a maximum within 10 min at 80–90°C, as reported earlier[3–5].

Sample introduction by the mini-column loop system

The reversed-phase mini-column was used in order to concentrate the sample and to introduce it on a large scale into the liquid chromatograph to compensate for

TABLE I

RECOVERY OF LOW-MOLECULAR-WEIGHT FATTY ACID VAPOURS IN AIR SAMPLES

*Fatty acid vaporized (μg)**	*Average recovery ± S.D. (%)***			
	C_3***	C_4***	C_5***	C_6***
0.2	101.5 ± 1.5	97.7 ± 2.5	98.6 ± 2.9	101.2 ± 3.1
1.0	99.1 ± 2.2	99.3 ± 2.2	96.3 ± 2.8	98.3 ± 4.4
5.0	98.0 ± 2.3	97.6 ± 2.6	99.3 ± 3.0	97.2 ± 5.0

* Fatty acids were vaporized at 180°C in an air stream and introduced into an air stream at 1.0 l/min.

** Average of six runs.

*** C_3, propionic acid; C_4, *n*-butyric acid; C_5, *n*-valeric acid; C_6, *n*-caproic acid.

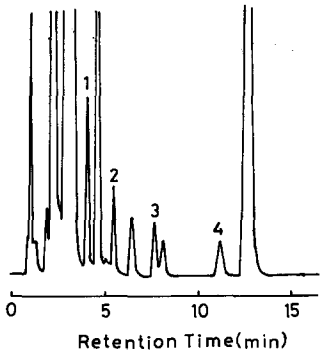


Fig. 3. Fatty acids in emission from a baking finish in painting work: (1) propionic acid, 3.6 ppb; (2) *n*-butyric acid, 2.6 ppb; (3) *n*-valeric acid, 0.3 ppb; (4) *n*-caproic acid, 0.2 ppb. Air sample volume, 60 l; sample volume introduced after the derivatization procedures, 1.5 ml.

the low response of detector. The breakthrough behaviour of the propionic acid–PBP derivative, which eluted first among the C_3–C_6 fatty acid–PBP derivatives, was investigated on the mini-column by varying the acetonitrile content in the acetonitrile–water eluent. Fig. 1 shows the retention volume of the derivative *versus* percentage of acetonitrile in the eluent. The acetonitrile concentration in the sample after the derivatization procedure was adjusted to 25% in order to give a large breakthrough volume and to minimize the effects of the eluent on the analysis. The retention volume of the derivative could be more than 10 ml under the conditions used. The sampling volume was 0.1–1.5 ml in order to suppress the effects of coexisting substances that appeared with larger sampling volume. In calibration, excellent linearity was obtained for the fatty acids in the range 0.2–1.6 μg in 0.1–1.5 ml of sample. Fig. 2 shows a typical chromatogram for the fatty acid–PBP derivatives with mini-column introduction.

Analytical accuracy and detection limits for fatty acid vapours

To investigate the analytical accuracy for fatty acid vapours, a 100-l volume of air sampling containing 0.2–5.0 μg of the fatty acids was generated by using the standard-vapour generation apparatus. The air sample was sampled with a coated SP-18 cartridge and analysed for the individual fatty acids. Table I indicates that the recovery of the fatty acids was 96.3–101.5% with standard deviations of 1.5–5.0% at these levels. The detection limit of the fatty acids was defined as the amount or concentration corresponding to a response of three times of noise level on a chromatogram. The estimated detection limits of the acid vapours were 2–3 ppt for 100 l of air sample.

Stability of the sample

The fatty acids placed on the cartridge were recovered without loss after the cartridge had been stored for 7 days at room temperature. The PBP derivatives were stable for at least 2 weeks in the sample solution.

Application

The method was applied to the determination of low-molecular-weight fatty acids in an emission sample from painting work. Fig. 3 shows a typical chromatogram of fatty acids in the emission from a baking finish, which is one of the most complex samples, containing solvent vapours, synthetic resins and their decomposition products. Low-molecular-weight fatty acids were easily determined at the levels involved without any effects from coexisting substances.

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