

## Note

### Florisil® sorbent sampling and ion chromatographic determination of airborne aliphatic carboxylic acids

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Aliphatic monocarboxylic acids are industrial chemicals with a wide variety of applications. They are used in the preparation of polymers, resins, dyestuffs, in the manufacture of various esters for solvent purposes, in the food industry, in cosmetics and as chemical intermediates<sup>1</sup>.

The prominent physiological consequence of exposure to carboxylic acid functions is the primary irritation of eyes, skin or mucous membranes, short-chain acids (formic, acetic, propionic acids) being also responsible for burns<sup>2</sup>, and occupational standards have been set to limit the exposure to aliphatic acids.

Various methods are available for the sampling and analysis of airborne carboxylic acids<sup>3-5</sup>. The oldest and usual sampling method involves the bubbling of the air sample through an absorber solution<sup>3,4,6-8</sup>, which makes individual monitoring awkward; consequently, chemisorption methods have been developed and samplers consist of solid sorbents<sup>5,9-12</sup>. These sampling methods are generally associated with gas chromatography<sup>9,13</sup> and liquid chromatography<sup>10-12</sup>, with which a chemical derivatization step may be employed to lower the detection limit. However, there are few sampling and analytical methods which are applicable to the aliphatic carboxylic acid family, and the current procedures have the disadvantage of employing liquid traps<sup>6-8</sup> or an additional derivatization step<sup>13,14</sup>.

The aim of this work was to examine whether Florisil® is a general solid sorbent sampler for aliphatic carboxylic acids and can be used in conjunction with an easy and rapid method for the analysis of formic, acetic, propionic, monochloroacetic, acrylic and methacrylic acids. We have selected high-performance ion-exclusion chromatography with conductimetric detection as a relevant analytical method.

#### MATERIALS AND METHODS

##### *Reagents*

Benzoic, sulphuric and aliphatic carboxylic acids of analytical grade were obtained from Merck. Water for high-performance liquid chromatography (HPLC) was purified by passage through a Millipore Milli-Q water treatment system. Acetonitrile of chromatographic grade was obtained from Merck.

### Preparation of the sampling tubes

The sampling tubes, made of Pyrex (50 mm × 6 mm I.D.), were packed with about 0.8 g of Florisil (OSI 30–60 mesh) held between two glass-wool plugs.

### Standard and generation system

Acids were dissolved in acetonitrile and further diluted in order to form a series of four dilutions (Table I). A 10- $\mu$ l aliquot of each acid solution was injected in a Dynamic U-tube system. The dynamic U-tube system developed previously<sup>1,5</sup> to determine breakthrough and recovery consisted of a U-shaped tube as a flow chamber and sample container. One side arm was used as the air inlet, the other held the absorption tube and was connected to the pump. The U-tube assembly was immersed in a thermostated water-bath. Air was pumped through the Florisil tube at a flow-rate of 1 l/min. Relative humidities of 35, 65 and 100% were obtained by drawing air through saturated salt solutions.

TABLE I  
RECOVERY OF ACIDS FROM FLORISIL

Acid	Std. solutions (g/l)	% Recovery <sup>a</sup>	
		av. <sup>b</sup>	S.D. <sup>c</sup>
Formic acid	90.2	98.7	0.5
	45.1	100	1.2
	22.5	100	0.8
	4.5	97.7	1.7
Acetic acid	254.4	99	0.8
	127.2	101	1
	63.6	100	1.5
	12.7	100	1.5
Monochloroacetic acid	51.9	100	0
	25.9	100.5	1
	12.9	100.7	1
	2.6	98.7	1.5
Propionic acid	290	99.2	1
	148.5	101	0.8
	74.2	101.5	1.7
	14.8	96.5	2.9
Acrylic acid	378	99	1.4
	189	100.5	1
	94.6	97.5	2.6
	18.9	98.7	1.5
Methacrylic acid	852.4	97.7	1.9
	426.2	100.5	1
	213.1	97.2	2
	42.6	99.7	0.5

<sup>a</sup> Recovery for 10  $\mu$ l of acid standard solution placed in the Florisil tube.

<sup>b</sup> Average of four determinations.

<sup>c</sup> Standard deviation.

### *Desorption of samples*

The sorbent was transferred to glass vials with PTFE-lined screwcaps and 5 ml of water were added. The mixture was then mechanically shaken for 10 min, and 10  $\mu$ l of 1 N sulphuric acid was added prior to injection into the chromatographic system.

### *Apparatus*

A Waters Associates Model 590 chromatographic pump, a 20- $\mu$ l sample loop (Rheodyne Model 7125) and a conductivity detector (Perkin-Elmer LC-21 or Waters 430) were employed. An integrator (Hitachi D-2000) and a recorder (Sefram) were used to convert the peaks into quantitative data.

### *Column*

The Aminex HPX 87 H organic acid analysis column (300 mm  $\times$  7.8 mm) was obtained from Bio-Rad (France) and contains an 8% cross-linked cation-exchange resin ( $H^+$ ) consisting of totally porous 10- $\mu$ m particles.

### *Chromatographic analysis*

Samples free of particulate matter were injected directly into the chromatographic system. The eluent,  $2.5 \cdot 10^{-4}$  M sulphuric or benzoic acid, was pumped at a flow-rate of 0.8 ml/min through the cationic resin column. The retention times were compared with those of known standards, and the method of peak-height measurement with an external standard was used for qualitative and quantitative assessment, respectively.

## RESULTS AND DISCUSSION

Solid sorbents have previously been used to sample carboxylic acids in air, but they varied from one technique and test compound to another<sup>3,5,9-12,14</sup>. The Florisil sorbent used in this work was applied to six carboxylic acids. A static method was used to evaluate the adsorption-desorption efficiency of each acid at increasing levels (Table I). The standard solutions were directly injected into the Florisil tube and air was pumped through the tube at about 1 l/min for 60 min. For each acid, the amounts collected were in the concentration range of 0.52-85.2 mg/m<sup>3</sup>.

The sampling efficiency was investigated by generating the test atmospheres in the dynamic U-tube system. The results are summarized in Table II. In any case, the U-tube was rinsed with the extracting solution after sampling, and the washing liquid was analyzed to ascertain the transfer of the carboxylic acid in the collection tube.

For a vapour concentration equal to twice the ACGIH standard level<sup>a</sup>, no breakthrough of any of the compounds occurred when 120 l of air conditioned to 100% relative humidity were sampled. A 0.8-g amount of Florisil was quite sufficient to collect the totality of each acid. During preliminary experiments, silica gel (Merck Kieselgel 60, 30-70 mesh) was tested; the use of this support is not recommended for

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<sup>a</sup> American Conference of Governmental Industrial Hygienists: Threshold Limit Values and Biological Exposure Indices for 1988-1989. Time-weighted average values: formic acid, 9 mg/m<sup>3</sup>; acetic acid, 25 mg/m<sup>3</sup>; propionic acid, 30 mg/m<sup>3</sup>; acrylic acid, 30 mg/m<sup>3</sup>; methacrylic acid, 70 mg/m<sup>3</sup>.

TABLE II  
COLLECTION AND RECOVERY OF ACIDS USING THE DYNAMIC U-TUBE SYSTEM

Acids	Std. solutions (g/l)	% Recovery <sup>a</sup>	
		av. <sup>b</sup>	S.D. <sup>c</sup>
Formic acid	90.2	94.8	1.9
	45.1	94.8	4
	22.5	92.6	3.1
	4.5	97	2.1
Acetic acid	254.4	91.8	4.3
	127.2	94.6	2
	63.6	90.5	3.6
	12.7	101	4.7
Monochloroacetic acid	50	92.2	1.7
	22.4	98	1.7
	12.5	93	4.4
	2.5	94.3	2.6
Propionic acid	297	92.8	4
	148.5	97.3	1.8
	74.2	95.3	6.5
	14.8	94.3	2.6
Acrylic acid	378	96	3.8
	189	97.8	1.5
	94.6	99	1.1
	18.9	94	2.5
Methacrylic acid	852	99	1.8
	426	97.6	1
	213.1	100	1.5
	42.6	93	2.8

<sup>a</sup> Recovery for 10  $\mu$ l of acid standard solution placed in the U-tube system.

<sup>b</sup> Average of six determinations.

<sup>c</sup> Standard deviation.

formic and acetic acids, as a breakthrough of these compounds appeared for a vapour concentration equal to the ACGIH standard level when 60 l of air at 65% relative humidity were sampled.

The stability of trapped samples was studied for vapour concentrations equal to half and a tenth of the ACGIH standard level for each acid; storing in the dark at 4°C for 9 and 21 days did not significantly hinder the recovery.

In order to prevent the polymerization of acrylic acid, Vincent and Guient<sup>9</sup> recommended the use of silica gel treated with *p*-methoxyphenol. During the assessment of the applicability of Florisil to acrylic and methacrylic acids, no decomposition of these monomeric substances was observed with the untreated sorbent. It should be noted, however, that the acids used in this evaluation contained 200 ppm of *p*-methoxyphenol.

Ion-exclusion chromatography (IEC) associated with conductivity or sometimes UV detection is commonly used for the separation and determination of car-

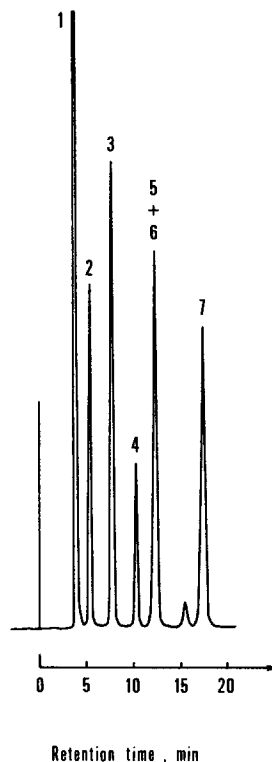
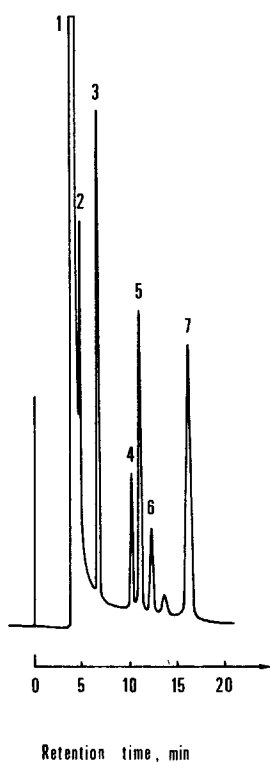


Fig. 1. Separation of acids on the Aminex HPX 87 H column with a  $2.5 \cdot 10^{-4} M$  benzoic acid mobile phase; flow-rate 0.8 ml/min; conductivity 20  $\mu S$  full scale. Peaks: 1 = sulphuric acid; 2 = monochloroacetic acid (400 ng); 3 = formic acid (360 ng); 4 = acetic acid (1000 ng); 5 = acrylic acid (2000 ng); 6 = propionic acid (1200 ng); 7 = methacrylic acid (4000 ng).

Fig. 2. Separation of acids on the Aminex HPX 87 H column with a  $2.5 \cdot 10^{-4} M$  sulphuric acid mobile phase; flow-rate 0.8 ml/min; conductivity 20  $\mu S$  full scale. Peaks as in Fig. 1.

boxylic acids<sup>6-8,10,12,16-18</sup>. According to Tanaka and Fritz<sup>16,17</sup>, high-performance separation of the six carboxylic acids can be obtained by using a strongly acidic cation-exchange resin ( $H^+$ ) with diluted aqueous solutions of sulphuric or benzoic acid as the eluents. Such eluents have a much lower background conductance than the strongly acidic eluents commonly used and permit a more sensitive detection of the sample acids.

In the present work we used the method of Tanaka and Fritz; a satisfactory separation of the six acids studied was obtained with an aqueous solution of benzoic acid ( $2.5 \cdot 10^{-4} M$ ) or sulphuric acid ( $2.5 \cdot 10^{-4} M$ ) as the eluent (Figs. 1 and 2). With benzoic acid, a weak resolution between sulphuric and monochloroacetic acids was obtained, but separation of acrylic and propionic acids was achieved with  $R_s > 1.25$ . Conversely, with sulphuric acid as the eluent, sulphuric and monochloroacetic acids were separated while acrylic and propionic acids had the same retention time.

The detection limits (signal/noise ratio  $> 3$ ) were approximately 0.2, 0.3, 3, 5, 2 and 5  $\mu g/ml$  for monochloroacetic, formic, acetic, propionic, acrylic and methacrylic

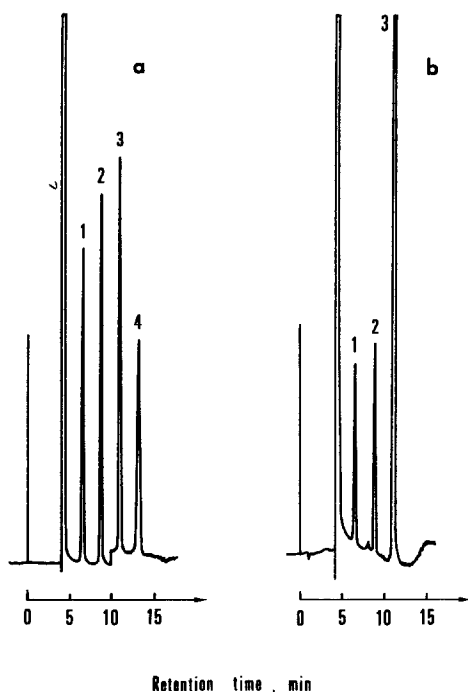


Fig. 3. Ion-exclusion chromatograms of standard acid and acid vapours from the air of a pickling workshop with a  $2.5 \cdot 10^{-4}$  M sulphuric acid mobile phase; flow-rate 0.8 ml/min; conductivity  $5 \mu\text{S}$  (0–10 min),  $2 \mu\text{S}$  full scale (10 min). (a) Acid standard. Peaks: 1 = monochloroacetic acid (100 ng); 2 = formic acid (180 ng); 3 = acetic acid (500 ng); 4 = propionic acid (600 ng). (b) Air sample (96 l). Peaks: 1 = monochloroacetic acid ( $0.02 \text{ mg/m}^3$ ); 2 = formic acid ( $0.05 \text{ mg/m}^3$ ); 3 = acetic acid ( $0.47 \text{ mg/m}^3$ ).

acids corresponding to concentrations of 0.1, 0.15, 1.5, 2.5, 1 and  $2.5 \text{ mg/m}^3$  in an air sample of 10 l, respectively.

The method has been successfully used to measure low levels of airborne aliphatic carboxylic acids in a metal sheet pickling workshop; Fig. 3b shows a liquid chromatogram of acids from this source. Monochloroacetic, acetic and formic acids were detected at the respective levels of  $0.02$ ,  $0.47$  and  $0.05 \text{ mg/m}^3$  in the air sample (96 l pumped). Dichloromethane present in the atmosphere ( $63 \text{ mg/m}^3$ ) did not interfere with the determination of acids. One possible disadvantage of this sampling method in an industrial environment is the positive interference from acyl chlorides. Acyl chlorides are hydrolysed in humid air to carboxylic and hydrochloric acids on solid sorbents and in solution. Therefore, the sampling method may overestimate the carboxylic acid level.

The Florisil sorbent seems to be a well adapted support for the sampling of many aliphatic carboxylic acids. This solid adsorbent is compatible with ion-exclusion analysis, which is not liable to known interferences except from acyl chlorides. The method is rapid, easy and appears suitable for the determination of aliphatic carboxylic acids at ppm (v/v) or ppb levels, such as those found in industrial emissions.

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