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Determination of trace amounts of carboxylic acids in ambient air by capillary gas chromatography–mass spectrometry

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ABSTRACT

A method for the determination of organic acids in ambient air using an ion-exchange resin in a bifunctional manner is presented. The ion-exchange resin is used as an adsorbent for sampling and subsequently as catalyst for the methylation of the adsorbed acids by methyl formate. The methyl esters are analysed by gas chromatography or gas chromatography–mass spectrometry. This method can be used to monitor workplace atmospheres and to analyse other ambient air samples.

INTRODUCTION

Organic acids are important compounds in chemical industry and are encountered in solvents, plastics and food processing. They are known as ubiquitous odour pollutants with a very low odour threshold (below 1 ppb in air). Moreover, fatty acids are released in considerable amounts into the atmosphere by biogenic sources. Hence methods for the determination of trace amounts of organic acids in the gaseous phase with low detection limits are desirable.

Some methods for the determination of carboxylic acids in ambient air have been reported. All these methods have in common that they require specialized analytical techniques and instrumentation or, if gas chromatography (GC) is used, special column phases. Simon *et al.* [1] reported a method using Florisil as adsorbent for sampling followed by ion chromatographic detection. Brocco and Tappa [2] also used ion chromatography, but collected airborne acids using filters impregnated with potassium hydroxide. The "scrubber" technique has been described in combination with ion chromatography [3]. Alternative approaches utilized liquid chromatographic procedures for detection. Samples have been collected on charcoal tubes, desorbed by sodium hydroxide with subsequent injection into a liquid chromatograph using a cation-exchange resin and a sulphuric acid mobile phase [4]. This technique has been termed ion-moderated partition chromatography [5]. For high-performance liquid chromatography with UV detection, derivatization by *p*-bromophenacyl bromide has been proposed, where sampling is achieved again by adsorption on charcoal [6]. An 18-crown-6 ether was useful for improvement of the conversion of the corresponding alkali metal salts into their bromophenacyl derivatives [7]. Liquid chromatographic approaches may also include ion-exclusion columns [8]. The GC determination of free organic acids was performed using analytical columns packed with 0.3% FFAP + 0.3% H_3PO_4 [9,10].

If a FFAP column is not available, derivatization of the acids will be necessary, and different methods have been reported [11–15]. Boron trifluoride in

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TABLE I

CONDITIONS FOR THE DETERMINATION OF VOLATILE ORGANIC ACIDS BY MASS SPECTROMETRY

Time (min)	Ion monitored (m/z)	Methyl esther of	Abbreviation
5 –8	88	Propionic acid	C_3
8 –10.2	74	Butanoic acid	C_4
	100	Metyhacrylic acid	METH
10.2–13.5	74	Methoxyacetic acid	MEAC
	74	Pentaoic acid	C_5
13.5–15.5	74	Hexanoic acid	C_6
	117, 119	Trichloroacetic acid	TRIC
>15.5	74	Heptanoic acid	C_7
	74	Octanoic acid	C_8
	74	Nonanoic acid	C_9

methanol is a common derivatization reagent but with the disadvantage of column degradation if the methylation solution is injected without removal of the boron trifluoride. Another drawback is the relatively high boiling point of the solvent methanol, thus not allowing for the baseline GC separation of the lower homologues of fatty acid esters.

In this paper, a method is proposed in which the acids are adsorbed on different adsorbents and determined by GC after derivatization with methyl formiate in the presence of a cation-exchange resin in the protonated form. The cation-exchange resin acts as an acidic catalyst to drive the methylation of the acids. GC can be carried out using common columns with methyl- or methyl/phenylsilicone phases.

EXPERIMENTAL

Instruments

A Hewlett-Packard Model 5890 gas chromatograph coupled with a Hewlett-Packard MSD 5970 mass spectrometer and a modified thermal desorption unit (Chrompack, Middelburg, Netherlands) was used. Baseline GC separation was achieved using an RTx-Volatiles capillary column (30 m × 0.25 mm I.D., 1.0-μm film thickness) (Restek). Other columns with methyl- or methyl/phenylsilicone phases can also be used. The temperature was maintained at 35°C for 5 min and then raised at 10°C/min to 200°C. The gas chromatograph was equipped with a thermal desorption unit (Chrompack) modified as described previously [16]. The mass spectrometer was operated in the total-ion mode (33–175u) and in the selected ion monitoring (SIM) mode (low-resolution option). The ions monitored under SIM conditions are listed in Table I.

Sampling

Gaseous samples were collected by adsorption on silica gel, activated charcoal and Amberlyst or their combinations. Fig. 1 shows the apparatus used for the generation of gaseous samples of the acids, consisting of a mass flow controller, a humidifier, a heated injector and a thermostated adsorption tube. The recovery experiments were carried out with gaseous samples of the acids produced as described in Fig. 1 with the exception of methoxyacetic acid and trichloroacetic acid, which were injected directly onto the adsorption tube.

Derivatization

Volumes of 2 ml of methyl formate were placed in glass vials (160 mm × 16 mm O.D.), which were closed by a screw-cap sealed with a silicone-rubber septum. The adsorbent loaded with organic acids

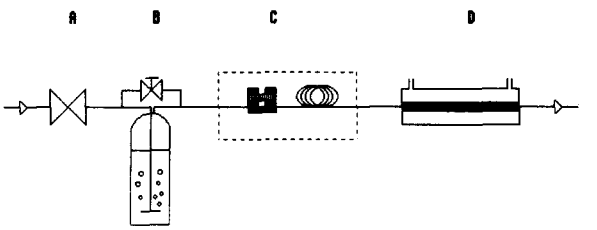

Fig. 1. Arrangement of standard gas and sampling equipment. A = Mass flow controller; B = humidifier; C = heated injector; D = thermostat for the sampling tubes.

and the Amberlyst cation-exchange resin (400 mg) was added to these vials. The tightly closed vials were heated at 90°C for 30 min by immersing them 40 mm deep in a stirred oil-bath. Before opening the vials they were chilled with water to prevent losses of the volatile esters. Volumes of 1–100 μl of the solution were injected into a stainless-steel tube filled with Tenax TA. The compounds were transferred to the gas chromatograph by thermal desorption after purging the solvent.

Thermal desorption

To purge the solvent, the oven of the thermal desorption unit was kept at 50°C for 8 min, maintaining a helium flow of 5 ml/min through the Tenax tube [160 mm × 6 mm I.D., containing 120 mg of Tenax TA (60–80 mesh)]. Thermal desorption was carried out by heating at 250°C for 10 min while a cryotrap capillary arranged in series was kept at −100°C. The analytes, now cryofocused, were then transferred to the analytical column by heating the cryotrap ballistically at 15°C/min to 200°C.

Chemicals

The acids, methyl formiate and the Amberlyst R 15 ion-exchange resin [17] were purchased from Aldrich (Steinheim, Germany). All reagents were of special grade. Before use the ion-exchange resin was washed several times with methanol until the methanol phase remained colourless and then extracted with methanol overnight using a mechanical shaker.

Silica gel (type G) and charcoal adsorption tubes (type B) were obtained from Dräger (Lübeck, Germany). Tenax TA (60–80 mesh) was purchased from Chrompack.

RESULTS AND DISCUSSION

Methylation

A mixture of ten organic acids (listed in Table I) consisting of 200 or 2000 μg of each compound (not dissolved in any solvent) was methylated as described above (eight consecutive methylations were carried out). Methoxyacetic acid was added to the acid mixture immediately before the addition of the methylation suspension. Thus, the concentrations of the acids in 2 ml of the methylation solution were 0.1 and 1.0 mg/ml, respectively. A typical chromatogram is shown in Fig. 2a for the total-ion mode and in Fig. 2b for the SIM mode. Recoveries were determined by external calibration. Within the reproducibility of the experiment the yield of the methylation step for each organic acid tested is >80%, with the possible exception of trichloroacetic acid, showing a slightly lower recovery. As chloroform was identified by GC–mass spectrometry (MS) in the methylation suspension, it is assumed that the lower recovery in the case of trichloroacetic acid is due to the formation of chloroform as a competitive process. According to Christensen *et al.* [18], trichloroacetic acid decomposes to chloroform when heated. The temperature and depth of immersion of the vial in the oil-bath have to be chosen carefully in order to control this competitive effect. As the methylation was performed with two different concentrations of the acids (four times at each concentration), it was found that the methylation was nearly independent of the acid concentration, which is explained by the excess of ion-exchange resin and methyl formiate (the results are summarized in Table II).

Recovery including sampling

Activated charcoal tubes, silica gel tubes and ion-exchange resin tubes (Pasteur pipettes containing 800 mg of Amberlyst R 15 ion-exchange resin) were tested. A 1-ml volume of the mixture of ten acids was used to generate a gaseous sample of vaporized acids employing the apparatus shown in Fig. 1. Ten litres of humidified nitrogen (relative humidity 45%) were drawn through the tubes, maintaining a flow-rate of 150 ml/min. The contents of the tubes were then transferred into vials containing the methylation suspension (see Experimental). The reference solution was prepared by direct injection of 1 μl of the acid mixture into a second vial also containing the methylation suspension. The methylation of both solutions was carried out as described under Experimental. The experiment was repeated three times. The recoveries, shown in Fig. 3, depend on the individual adsorbent and acid under investigation. The recovery is ⩾85% for the organic acids containing four or five carbon atoms, independent of the adsorbent chosen (standard deviation <14%). For the higher homologues a decrease in recovery was found with increasing boiling point, the decrease being greater for activated char-

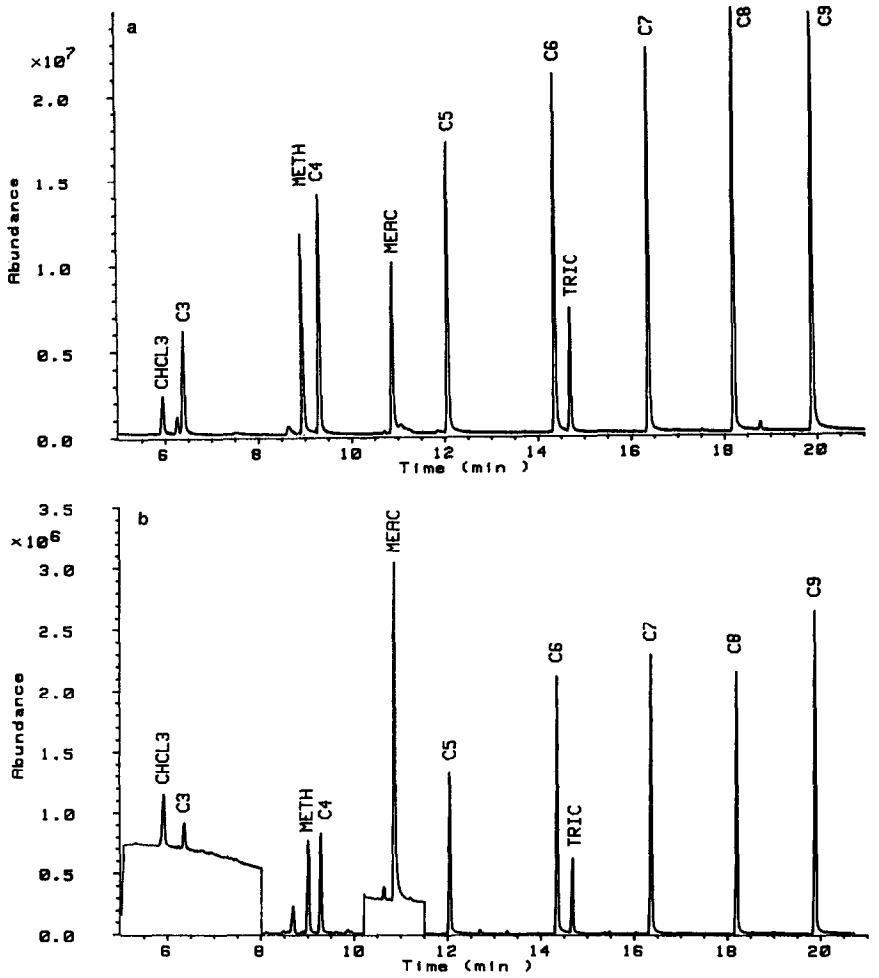

Fig. 2. (a) Typical total-ion chromatogram and (b) typical SIM chromatogram. For abbreviations, see Table I.

coal than for silica gel or Amberlyst. This decrease in recovery is also observed, if activated charcoal is added to the reference suspension after methylation of the acids and an additional heating period, thus leading to the conclusion that this reduced recovery is due to irreversible adsorption of esters of the higher homologues.

Amberlyst gave recoveries >80% for all acids, with the exception of propionic acid, the most volatile acid studied. Keeping this in mind, a combination of two adsorbents is recommended if quantitative sampling of all organic acids listed in Table I is desired. To test this, a combination of 500 mg of Amberlyst and 100 mg of activated charcoal arranged in series was investigated. The recoveries with both adsorbents were determined separately. As Table III reveals, only short-chain acids break through the Amberlyst adsorbent, leading to low recoveries if only Amberlyst is used. If the recoveries from both adsorbents determined separately are added, a value close to 100% is achieved also for the very volatile acids.

Detection limits, blanks

Detection limits (signal-to-noise ratio = 3) are shown in Table IV. If detection occurs by mass

TABLE II

RECOVERY (%) AND REPRODUCIBILITY OF METHYLATION USING METHYL FORMATE AND AN ION-EXCHANGE RESIN AS REAGENTS

Concentration of each acid in the methylation solution = 0.1 or 1 mg/ml.

Compound	0.1 mg/ml acid						1 mg/ml acid					
	Replicate No.				Mean	R.S.D. (%)[a]	Replicate No.				Mean	R.S.D. (%)
	1	2	3	4			1	2	3	4		
Propionic acid	100.0	99.7	99.8	98.1	99.4	0.9	98.0	96.4	101.3	105.2	100.2	3.9
Methacrylic acid	97.1	104.4	99.1	96.4	99.3	3.6	102.3	98.4	97.6	95.5	98.7	2.5
Butanoic acid	105.9	114.4	107.2	98.4	106.5	6.6	105.1	96.3	99.1	103.8	96.3	7.7
Methoxyacetic acid	100.4	103.3	101.0	99.7	101.1	1.6	106.1	97.3	86.4	97.2	96.8	8.1
Pentanoic acid	109.8	114.4	105.0	101.0	107.6	5.8	97.9	95.4	103.9	103.1	100.0	4.1
Hexanoic acid	95.4	96.6	100.0	102.3	98.6	3.2	105.0	101.6	103.8	99.8	102.6	2.3
Trichloroacetic acid	80.1	79.2	85.3	86.1	82.7	3.5	77.1	78.4	82.7	85.3	80.9	3.8
Heptanoic acid	87.6	86.7	87.1	89.2	87.7	1.1	84.5	89.2	85.4	90.2	87.3	2.8
Octanoic acid	81.3	80.8	81.7	82.5	81.6	0.7	86.2	80.9	84.5	89.1	85.2	3.4
Nonanoic acid	82.6	85.5	83.4	84.3	84.0	1.2	84.7	85.3	81.3	87.6	84.7	2.6

[a] R.S.D. = relative standard deviation.

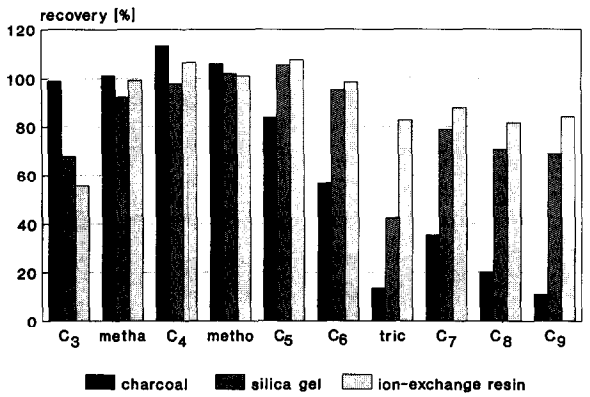

Fig. 3. Recoveries using different adsorbents. For abbreviations, see Table I.

spectrometry in the total-ion mode, detection limits from 0.1 to 2.4 μg/l are achieved. They are lower by a factor of 5–10 if the mass spectrometer is operated under SIM conditions. The detection limit depends on the molecular weight, *i.e.*, higher homologues exhibit lower detection limits, which is due to a higher detector response. The detection limits can be further reduced by applying an additional preconcentration step (*i.e.*, by injecting larger volumes of the methylation solution onto Tenax adsorbent followed by thermal desorption after purging the solvent as described under Experimental). This procedure exhibits a high reproducibility for most of the methyl esters, with the exception of methyl propionate, which shows a lower recovery due to a

TABLE III

RECOVERY USING A COMBINATION OF AMBERLYST AND ACTIVATED CHARCOAL

Compound	Recovery (%)					
	Replicate 1			Replicate 2		
	Amberlyst	Charcoal	Total	Amberlyst	Charcoal	Total
Acetic acid	31.3	62.2	93.5	40.1	60.4	90.5
Propionic acid	55.4	42.5	97.9	57.4	42.9	100.3
Butanoic acid	85.1	13.5	98.6	89.8	8.6	98.4

TABLE IV

DETECTION LIMITS

Compound	Total ion mode: without additional preconcentration		SIM			
			Without additional preconcentration		With additional preconcentration	
	ng/μl[a]	ng/l[b]	pg/μl[a]	ng/l[b]	pg/μl[a]	ng/l[b]
Propionic acid	4.3	861	850	170	11.5	2.3
Methacrylic acid	3.4	672	880	176	10.1	2.0
Butanoic acid	4.7	948	900	180	13	2.6
Methoxyacetic acid	12.3	2464	1020	204	18	3.6
Pentanoic	3.4	696	905	181	11	2.2
Hexanoic acid	2.6	520	157	31.5	1.7	0.3
Trichloroacetic acid	n.d.[c]	n.d.[c]	282	56.4	4.3	0.8
Heptanoic acid	1.2	232	16	3.2	0.3	0.06
Octanoic acid	0.70	142	6.5	1.3	0.09	0.02
Nonanoic	0.56	112	4.2	8.4	0.05	0.01

[a] In methylation suspension.
[b] In air sample.
[c] Not determined.

TABLE V

RECOVERY AND REPRODUCIBILITY OF REPLICATE PRECONCENTRATIONS

Methyl ester of	Recovery (%)						
	Replicate No.					Mean	R.S.D. (%)
	1	2	3	4	5		
Propionic acid	73.8	69.9	61.6	58.4	60.4	64.8	6.7
Methacrylic acid	115.8	90.1	88.7	97.3	95.9	97.6	10.8
Butanoic acid	119.8	86.5	116.7	84.2	84.3	98.3	9.0
Methoxyacetic acid	118.7	93.4	92.4	91.2	90.2	97.2	12.1
Pentanoic acid	113.8	97.7	96.7	96.2	95.1	99.9	7.8
Hexanoic acid	114.7	112.7	103.3	103.9	113.3	109.6	5.5
Trichloroacetic acid	91.9	89.9	73.6	75.2	78.1	81.7	8.5
Heptanoic acid	105.6	97.7	98.1	101.2	101.6	100.8	3.2
Octanoic acid	98.8	101.3	105.4	96.7	97.1	99.8	3.6
Nonanoic acid	100.9	110.9	101.9	103.4	104.4	104.3	3.9

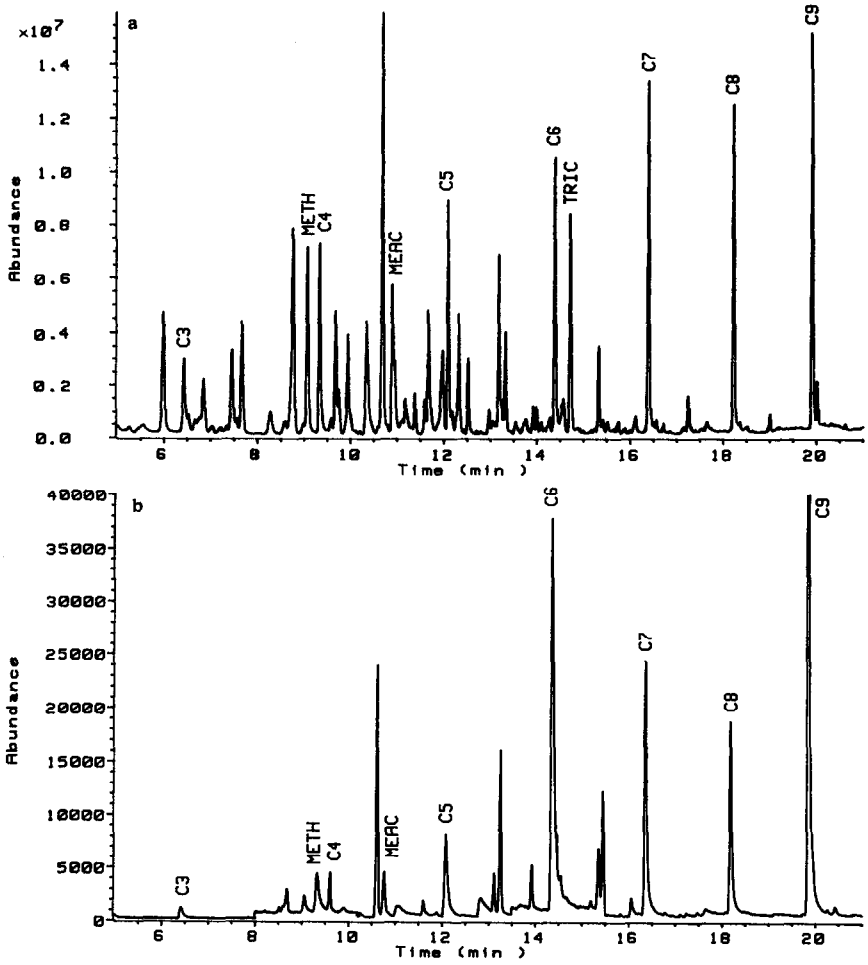

Fig. 4. (a) Typical total-ion chromatogram and (b) typical SIM chromatogram obtained after preconcentration in the thermal desorption unit. For abbreviations, see Table I. Additional peaks are due to impurities in the methylation reagent.

higher volatility, and trichloroacetic acid, due to thermal instability (see Table V). Two chromatograms obtained after preconcentration are shown in Fig. 4a (total-ion mode) and Fig. 4b (SIM mode). A further increase in sensitivity is also achievable by on-column injection of larger volumes using the retention gap technique [19]. Blank values were below the detection limit for the acids under investigation.

CONCLUSIONS

The method described for sampling and determining trace amounts of gaseous carboxylic acids shows a high repeatability and high recovery. The sample volume required is $\leqslant 10$ l. The acids are collected on an adsorbent (Amberlyst cation-exchange resin), which also catalyses the methylation of the acids. Derivatization and GC separation of the carboxylic acids require no special equipment and are completed within 50 min. Damage to the analytical column by a derivatization reagent is eliminated as the solid catalyst settles at the bottom of the vial after the derivatization step. Detection limits reach the lower ppt level.

Further simplification of the procedure is suggested by carrying out the derivatization directly in an adsorption tube containing the bifunctional adsorbent, followed by thermal desorption into the GC–MS system.

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