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Ion chromatographic determination of carboxylic acids in air with on-line liquid membrane pretreatment

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ABSTRACT

A method for the determination of low-molecular-mass carboxylic acids in air is reported. The method is based on impinger sampling in sodium hydroxide, selective enrichment across a liquid membrane and determination by ion-exclusion chromatography. The membrane enrichment is carried out in an automated continuous-flow system coupled to the chromatographic column. By impregnation of the membrane with 10% tri-*n*-octylphosphine oxide in di-*n*-hexyl ether, extraction efficiencies in the range 30–100% for C_1–C_4 carboxylic acids were achieved. Formic and acetic acid were measured in the range 17–300 nmol/m^3 and some other carboxylic acids were detected in air samples taken in southern Sweden.

INTRODUCTION

The occurrence of various carboxylic acids in the atmosphere, measured in the gas phase, in precipitates or in particles, has been reported in many papers. Relatively low concentrations (2–100 nmol/m^3) of formic and acetic acid have been found over oceans [1,2]. Model experiments and field investigations have shown that photochemical oxidation of hydrocarbons is an important source of gaseous organic acids in non-polluted areas [2]. Jacob and Wofsy [3] proposed isoprene emitted from biomass as a significant source of pyruvic, formic and methacrylic acid. This theory was supported by several studies carried out in the Amazon forest by Andreae and co-workers [4,5]. Direct emission of formic and acetic acid from vegetation has also been measured [6]. Anthropogenic sources such as motor exhausts [7,8] are reported to be the main origin of organic acids in urban areas. The average emission of monocarboxylic acids from motor vehicles in southern California basin was estimated to 15 000–20 000 kg/day, and gaseous formic acid and acetic acid in the range 50–800 nmol/m^3 were found in this area [9].

The contribution from organic acids to the total acidity in the atmosphere is important to air quality issues but has not been sufficiently studied. Grosjean [10] measured organic and inorganic acids (as Cl^- and NO_3^-) in ambient southern California air and found that 73.5% (mole basis) of the total gas-phase acids consisted of formic and acetic acid.

Long-path IR measurements are commonly used for various gaseous molecules including formic and acetic acid [11]. It is a rapid method that gives instantaneous results, but the sensitivity is lower than that of chromatographic techniques.

A number of sampling methods for gaseous and particle-bound formic and acetic acid have been compared in a comprehensive study [12]. It was concluded that only the mist chamber [13] and NaOH-coated denuders were free from

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significant interferences. In another recent study, various other collection devices, such as alkaline filters and solvent traps, have been found to give considerable interferences due to reactions with other compounds present in air (*e.g.*, aldehydes), while microimpingers were free from these interferences [14]. Thus, absorption in an alkaline solution appears to be the safest principle for air sampling of acids. The mist chamber is a recently developed device for wet absorption of gaseous components and it has been successfully used for the collection of formic and acetic acid [4,5,15]. The advantage is that this collector over a conventional impinger is that it allows a higher air flow-rate (up to 8 l/min), but a drawback is that it is not commercially available.

For the determination of acetic and formic acid in air, further preconcentration of the absorbing solution is usually not necessary, but the determination of other acids present in very low concentrations would require some treatment prior to the determination step. A range of organic acids (C_1–C_7) have been measured in rain and fog samples by GC after concentrating the sample using a rotary evaporator [16]. For analysis of antarctic ice an anion exchanger was used as a precolumn in order to improve the detection limits for formic, acetic, propanoic and butanoic acid [17].

An efficient technique for the selective enrichment of various classes of compounds using supported liquid membranes has been developed at our laboratory [18,19]. With this technique, the required enrichment of acids in aqueous absorbing solutions can be made in a closed automated system, with on-line connection to chromatographic instrumentation. Interfering compounds (non-acidic, particulate, etc.) are simultaneously rejected.

Carboxylic acids are most often determined by ion-exchange or ion-exclusion chromatography [5,7,8,17]. Generally, lower detection limits can be achieved with open-tubular column GC after derivatization of carboxylic acids to *p*-bromophenacyl esters [16,20]. This method in combination with mass spectrometry has been used for the determination of nineteen dicarboxylic acids in ambient air [21]. However, the difficulty of automating the derivatization and extraction procedures, the introduction of additional operations and chemicals and the long analysis times are disadvantages of the described GC methods compared with LC.

In this paper, we present an automated method for the determination of carboxylic acids at low concentrations, involving impinger sampling, liquid membrane enrichment and ion-exclusion chromatography. With this combination, a convenient and selective technique is obtained for the determination of carboxylic acids in air with few interferences and sufficient sensitivity.

EXPERIMENTAL

Equipment

Analyses were performed on a Dionex 4000i ion chromatograph connected on-line to a liquid membrane enrichment flow system. An HPICE-AS1 ion-exclusion column with 2 m*M* HCl as eluent was used. The recommended eluent, 1 m*M* octanesulphonic acid, was also tested. The eluent and NaOH solution (for the flow system) were kept in helium-pressurized bottles in the Dionex eluent degas module. An anion micro membrane suppressor (AMMS-ICE) with 5 m*M* tetrabutylammonium hydroxide as regenerant was used. The regenerant flow control valve (Dionex) was replaced with a three-way slider valve (Model 5301; Reodyne, Cotati, CA, USA) for on–off regulation of the regenerant solution. The chromatograms were collected and handled with a personal computer (Victor V386A; Victor Technologies, Stockholm, Sweden), using a JCL6000 chromatography data system (Jones Chromatography, Hengoed, UK), which also controlled the time sequence for the operation of the valves in the flow system.

The flow system is shown in Fig. 1. The three pneumatic valves in the Dionex chromatography module (injection valve, column-switching valve and regenerant flow control valve) were used for the flow system, which was constructed inside the chromatography module. A Minipuls 3 peristaltic pump (Gilson, Villers-le-Bel, France) with PVC pump tubes (Elkay, Shrewsbury, MA, USA) was used. The confluences, where the channels meet at a 60° angle, were made of PTFE. Reagents were mixed in a knotted tube

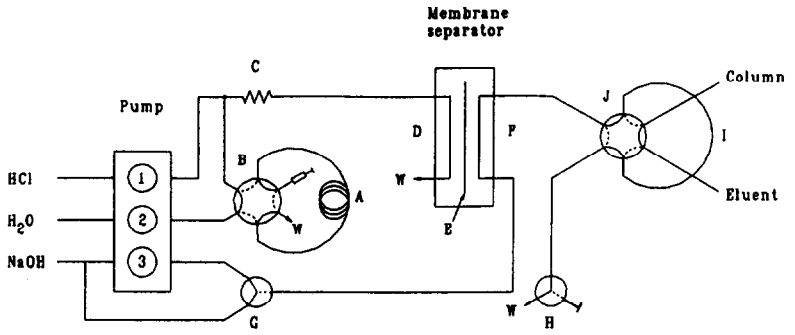

Fig. 1. Flow system for enrichment of organic acids. A = Sample loop; B and J = injection valves; C = knitted tube reactor; D = donor channel; E = liquid membrane; F = acceptor channel; G and H = valves; I = injection loop.

reactor (0.5 mm I.D., six knots). PTFE tubing, flange-free fittings (Alltech, Deerfield, IL, USA) and Dionex standard fittings were used to connect the various parts of the flow system.

The membrane used was a porous PTFE membrane (TE 35 membrane filter, Schleicher & Schüll, Dassel, Germany) with a pore size of 0.2 μm and cut to 36×77 mm^2. The membrane was held between two blocks of PTFE (outer dimensions $85 \times 55 \times 15$ mm^3), with meander channels facing each other (Fig. 2). Each channel was 0.1 mm deep, 2.5 mm wide and 750 mm long, giving a calculated volume of 188 μl. The PTFE blocks were tightened together with eight screws (see Fig. 2).

The solutions for impregnating the membrane were prepared by adding 10 ml of di-*n*-hexyl ether to the desired amount of tri-*n*-octylphosphine oxide and sonicating it for *ca.* 1 h. The membrane was immersed in the organic liquid in a petri dish for a few minutes (the time is not critical). After mounting the membrane, excess of solvent was washed out from the separator by pumping acceptor and donor solutions through the channels for about 30 min. A membrane prepared in this way can be used for several hundred enrichments.

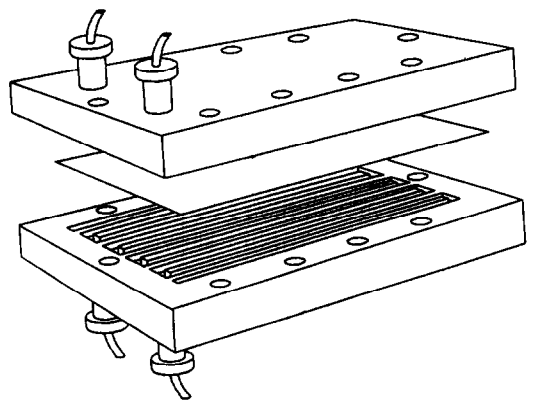

Fig. 2. Membrane separator unit.

Operation of the liquid membrane enrichment system

Referring to Fig. 1, the operation can be described as follows (for a detailed description of the liquid membrane extraction technique, see refs. 18 and 19). The sample is introduced through a 3.0-ml loop (A) into the aqueous carrier stream (channel 2, 0.17 ml/min) using valve B. The pH is decreased to *ca.* 1.4 by mixing with 1 *M* HCl (channel 1, 0.02 ml/min) in a knitted tube reactor (C). From the donor side of the membrane separator (D) the organic acids are extracted into the liquid membrane (E). On the other side of the membrane, the acids are trapped in a stagnant NaOH solution (acceptor phase, F). After the whole sample has passed the separator, valves G and H are switched. The enriched sample plug (*ca.* 200 μl) is then pushed by the acceptor solution into a 300-μl injection loop (I) and injected into the ion-exclusion separation column by switching valve J. A typical enrichment time is 20 min, during which time a previously extracted sample is chromatographed. Between the enrichment cycles the sample loop and the separator are washed with the donor and acceptor solutions, respectively, for 3 min to reduce memory effects. Only very

small losses (due to adsorption) of the free acids were observed during the transport from the membrane unit to the injection loop.

Determination of extraction efficiency

The enrichment efficiency for each acid was calculated in the following way. Calibration graphs for direct injections (without enrichment) were constructed in the range 10–320 μM. A 20-μM solution was enriched as described above and the corresponding concentration after enrichment was evaluated using the calibration graph. The extraction efficiency, E, is defined by $E = n_A/n_D$, where n_A is the number of moles of analyte collected in the acceptor phase and n_D is the number of moles pumped into the donor phase. Here n_A is given by the evaluated concentration after enrichment times the volume of the injection loop (300 μl) and n_D by the concentration before enrichment (20 μM) times the sample loop volume (3.0 ml).

Air sampling

Midget impingers with glass joints were used for collection of the air samples. The 20 mM NaOH absorption solution was prepared freshly every day and also analysed as a blank. The impingers were wrapped in aluminum foil to avoid photochemical reactions of the acids during sampling in daylight. Two parallel samples were collected simultaneously in most instances. The pumps were portable programmable air sampling pumps (Model 224-30, SKC) and 480 or 960 l were collected with a flow-rate of 2 ml/min. All connections were made of glass except that a PVC tube used between the outlet of the impinger and the pump.

The sampling recovery was determined by bubbling nitrogen through three impingers connected in series, the first containing a 20 mM solution of seven carboxylic acids (pH < 2) and the second and third containing 20 mM NaOH, followed by analysis of the contents of the second and third impingers [22]. Sources of contamination were identified by soaking plastic caps, screw-caps, tubing and filters in the sampling solution for 2 h. The samples were stored in a refrigerator and analysed within 2 days.

Chemicals

Formic, acetic, oxalic, succinic and hydrochloric acid and chloroform were obtained from Merck (Darmstadt, Germany), propanoic acid from Aldrich Chemie (Steinheim, Germany), butanoic acid and lactic acid from BDH (Poole, UK), malic acid, sodium pyruvate and di-*n*-hexyl ether from Sigma (St. Louis, MO, USA), glycolic acid (70% in water) from Kebo (Stockholm, Sweden), sodium hydroxide from EKA (Bohus, Sweden), tri-*n*-octylphosphine oxide and tetrabutylammonium hydroxide (1.5 M) from Fluka (Buchs, Switzerland) and octanesulphonic acid (0.1 M) from Fisons Scientific (Loughborough, UK). Analytical-reagent grade chemicals were used when available. Water was purified with a Milli-Q/RO-4 unit (Millipore).

Stock standard solutions of the acids (20 mM) were prepared in water; 0.5 ml of $CHCl_3$ (Merck) per 100 ml was added as a biocide. The stock standard solutions were stored in a refrigerator, and fresh working standard solutions were prepared every day. To minimize the carbonate content of the NaOH solution, it was prepared by dissolving prewashed NaOH pellets in water. The concentration was determined by titration with H_2SO_4. The solution was then kept in a Dionex eluent bottle under helium pressure.

RESULTS AND DISCUSSION

Membrane extraction efficiency

Choice of membrane solvent. The first experiments were carried out with a membrane impregnated with pure di-*n*-hexyl ether (DHE). The extraction coefficient was reasonably high for propanoic and butanoic acid but low for formic and acetic acid, and for the more polar acids (pyruvic, malic and lactic) no extraction was obtained. The extraction efficiency and the precision were substantially improved incorporating tri-*n*-octylphosphine oxide (TOPO) in the membrane solvent. Table I shows the differences in extraction efficiency and relative standard deviation for a 20 μM solution of seven acids in DHE without and with 10% of TOPO.

TOPO is a reagent that has been used for facilitating liquid membrane extraction of carboxylic acids [23]. It acts as a carrier molecule

TABLE I

EXTRACTION EFFICIENCY AND PRECISION WITH 10% TOPO IN DHE IN THE MEMBRANE

Acid	Extraction efficiency (%)		R.S.D. (%)[a]	
	DHE	10% TOPO in DHE	DHE	10% TOPO in DHE
Pyruvic	–	69	–	3.1
Malic	–	29	–	5.8
Lactic	–	34	–	2.1
Formic	5.1	77	41	2.2
Acetic	16	63	8.2	6.0
Propanoic	46	99	9.6	7.0
Butanoic	81	93	4.8	2.6

[a] Relative standard deviation ($n = 4$).

which by hydrogen bonding to the acid forms an apolar species, more soluble in the membrane liquid than the free acid. In general, the extraction efficiency for the investigated acids increases with increased TOPO content in the membrane. The effect was more pronounced for the more polar hydroxy acids [24]. Extraction of HCl became disturbing at TOPO concentrations over 10%, as the chloride peak increased markedly with increasing TOPO concentration. The optimum membrane solvent was considered to be 10% TOPO in DHE.

Choice of acceptor solution. One of the most important parameters for controlling the enrichment across the membrane is pH. The pH of the stagnant acceptor solution is critical, as a high pH is essential in order to obtain enrichment of the acids. The initial pH of the acceptor solution (20 m*M* NaOH) before enrichment starts is *ca.* 12, but as the organic acids and hydrochloric acid accumulate in the acceptor phase, the pH decreases. The critical contribution was found to originate from HCl, especially at high TOPO concentrations. Extraction of carbonic acid generated from CO_2 also contributes to this pH drop. The CO_3^{2-} peak increased with increasing NaOH concentration in the acceptor, but the pH of the acceptor stabilized at *ca.* 8, owing to buffering. Different concentrations (10–100 m*M*) of NaOH in the acceptor solution were compared for extraction of six carboxylic acids (20 μM) with 5% TOPO in the membrane. The extraction efficiency was similar with 10 and 20 m*M* NaOH, but decreased markedly with 50 and 100 m*M* NaOH as the acceptor [24]. The reason for this is not fully understood but the phenomenon will be further investigated.

As an alternative to NaOH solution, various buffer systems could be considered, but the anions of a buffer are very likely to interfere with the analyte ions in the chromatogram. A borate and a phosphate buffer were tried but rejected owing to the large interfering peaks that arose. A tris(hydroxymethyl)aminomethane (Tris) buffer has been tried with promising results [24].

Air sampling

As the sampling procedure is a common source of errors, various experiments were performed in order to investigate suspected artifacts. Keene *et al.* [12] concluded that there are significant systematic and episodic artifacts among many currently developed measurement systems for formic and acetic acid.

Impingers were chosen for the sampling owing to their simplicity and high efficiency. Dilute NaOH was chosen as the absorption solution as water was found to be less efficient. The pH of the NaOH solution decreased (owing to collection of CO_2) from 12 to 9.4 in both the first and second impinger, regardless of the air volume sampled (480 or 960 l). The sampling recovery in NaOH was found to be >95% for the seven acids tested. The same recovery was achieved with a buffer solution (20 m*M* $NaHCO_3$ + NaOH) at pH 9.5, indicating that the pH drop of the NaOH solution during sampling is not a problem.

A particulate filter was not used as we found no significant difference between parallel samples with and without a filter. It has been shown in a study carried out in Virginia, USA, that ≥98% of atmospheric acetic and formic acid occur in gaseous form [15]. Significant contamination from various materials such as PVC and silicone-rubber tubing, polypropene caps, PTFE-faced screwcaps and polycarbonate filters was revealed when soaked in NaOH. Therefore, all

sample containers and connections used were made of glass or PTFE except between the outlet of the impinger and the pump. The risk of contamination of the sampling solution by vapour in the indoor air was observed by leaving an impinger with sampling solution exposed to the air in the laboratory via the inlet and outlet for 2 days. Small amounts of formic and acetic acid were found in the solution when analysed. The sampling solution was always prepared fresh in a separate room to circumvent contamination from sources in the laboratory. Similar problems with contamination from plastics and indoor air have been reported by others [25].

Addition of chloroform to the samples in order to prevent microbiological activity in the samples has been recommended by several workers [1,9]. Chloroform has also been added to the sampling solution before impinger collection [14]. However, it is known (and observed by us) that chloroform can be photochemically converted into formic acid. As the samples were analysed within 2 days after sampling, no chloroform was used for the samples.

Suppression of carbonate

The high level of carbon dioxide in air caused a large tailing carbonate peak, interfering with propanoic acid in the chromatogram. It was possible to separate the peaks with a weaker eluent (30 μM HCl, pH 4.5), but then the other acids were not sufficiently resolved.

An attempt was made to remove the carbonate with a gas membrane (an "empty" PTFE membrane) by letting the carbon dioxide diffuse from the acidified sample through the membrane into an acceptor phase consisting of 10 m*M* NaOH. The method could have been incorporated on-line in the flow system, but the loss of carboxylic acids was 10–30% and this method was rejected.

A more successful technique was to bubble nitrogen through the air samples after decreasing the pH to 2–3 by adding 1 *M* HCl. The carbonate peak disappeared from the chromatogram after bubbling for only 1 min. In order to check the stability of the carboxylic acids, a standard solution of 200 μM was treated with nitrogen for 0.5–10 min. The solutions were injected directly into the column (without membrane enrichment). In Fig. 3 it can be seen that there is no loss of acids, even with longer bubbling times. However, after membrane enrichment of any sample or blank, there was still a small carbonate peak originating from CO_2 dissolved in the acceptor solution and the carrier.

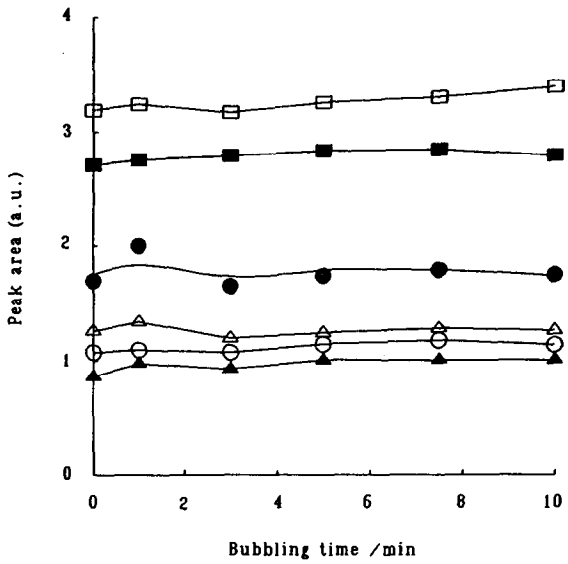

Fig. 3. Stability of a 200 μM solution of organic acids in 1 m*M* HCl after bubbling with nitrogen for 0–10 min. ○ = Lactic; ● = formic; □ = malic; ■ = pyruvic; △ = acetic; ▲ = butanoic acid.

Chromatography

In the first experiments, 1 m*M* octanesulphonic acid containing 2% of 2-propanol was used as the eluent, according to the recommendation of Dionex. The separation of seven carboxylic acids (pyruvic, malic, lactic, formic, acetic, propanoic and butanoic acid) was satisfactory but some acids occasionally eluted as negative peaks. With 1 m*M* HCl the separation of these acids was equally good and no peaks were negative. In order to improve the separation of pyruvic acid from the chloride peak (*i.e.*, the front peak), the eluent concentration was increased to 2 m*M*. The drawback was a slightly deteriorated resolution between lactic and formic acid. Other acids that unfortunately co-eluted in this system were glycolic, lactic and succinic acid. Fig. 4 shows chromatograms of a standard solution of

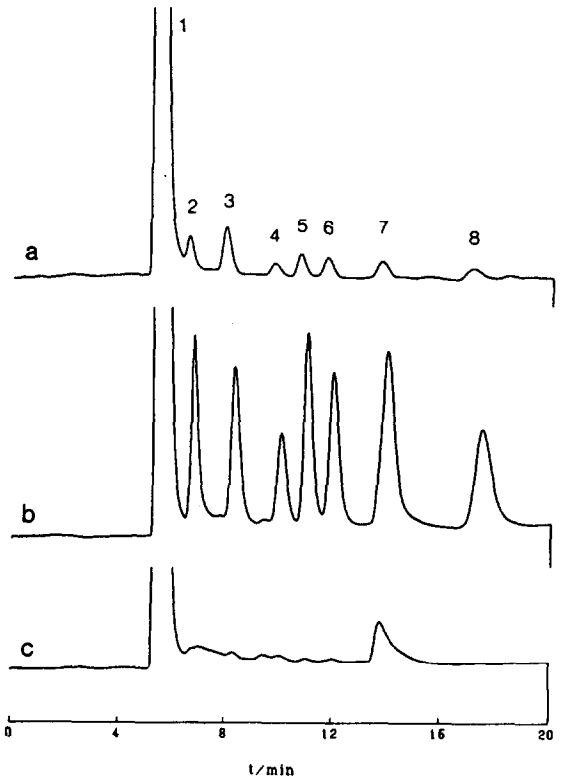

Fig. 4. Chromatograms of organic acids: (a) 24 μM standard solution in 1 mM HCl without enrichment; (b) after membrane enrichment; (c) blank (water). Peaks: 1 = Cl^-; 2 = pyruvic; 3 = malic; 4 = lactic; 5 = formic; 6 = acetic; 7 = propanoic (and CO_3^{2-}); 8 = butanoic acid.

seven organic acids (24 μM) injected with and without membrane enrichment and an enriched blank (water). This blank was injected directly after the enrichment of the standard solution showing also the overall memory effects. The blank peaks corresponded to 2–6% of the peaks of the standard solution. The contribution of carbonate to the propanoic acid peak in the chromatogram of the enriched solution (Fig. 4b) is revealed in the blank chromatogram (Fig. 4c). The interference from carbonate in the chromatogram of the directly injected solution (Fig. 4a) is negligible.

Quantification

Calibration graphs for the seven carboxylic acids after membrane enrichment were measured in the range 0.1–24 μM (Table II). The graphs

TABLE II

CALIBRATION GRAPHS AND PRECISION FOR VARIOUS ACIDS

Acid	Concentration range (μM)	Slope[a]	Intercept[a]	r
Pyruvic	1–24	10 ± 0.6	0.3 ± 8	0.9994
Malic	0.5–24	9 ± 0.5	−6 ± 6	0.9992
Lactic	0.5–24	7 ± 2	−0.9 ± 24	0.9911
Formic	0.1–24	12 ± 1	−3 ± 18	0.9966
Acetic	0.1–24	12 ± 0.6	−2 ± 7	0.9990
Propanoic[b]	1–24	15 ± 2	129 ± 30	0.9965
Butanoic	0.5–24	15 ± 0.4	−5 ± 4	0.9999

[a] Arbitrary units, 95% confidence interval.
[b] Including carbonate peak.

were linear with insignificant intercepts (95% confidence intervals) for all acids except propanoic acid, which has an intercept corresponding to the carbonate peak. The precision (Table I) is not significantly worse than for the other acids. The determination of pyruvic acid is limited by the front peak.

The detection limit with membrane enrichment of a 3-ml sample was 100 nM for formic and acetic acid and 500 nM for pyruvic, malic, lactic and butanoic acid. For propanoic acid the interfering carbonate peak resulted in a detection (and quantification) limit of *ca.* 6 μM, which is about the same as for direct injection of a carbonate-free solution without enrichment. The limit of quantification determined from the calibration graph was in the range 1–3 μM for all acids in Table II except propanoic acid. This corresponds to 20–60 nmol/m^3 in air with sampling of 480 l of air and enrichment of 3 ml. The detection limit can be lowered at the cost of time by prolonging the sampling time or by enriching larger volumes of the absorbing solution.

Measurement of acids in air

To demonstrate the applicability of the described technique to real air samples, some samples were collected at various sites in southern Sweden, giving the results presented in Table III. This was not intended as a detailed investigation of the occurrence of organic acids in air. Formic and acetic acid were detected in all

TABLE III

CARBOXYLIC ACIDS IN AMBIENT AIR IN SOUTHERN SWEDEN

Site	Date (May 1993)	Time	T (°C)[e]	Wind direction[f]	Concentration (nmol m^{-3})		
					Formic acid	Acetic acid	Propanoic acid[g]
Lund[a]	14	11.15	23	S	28	17	nd
Lund[a]	17	14.18	16	SE	26	18	nd
Lund[a]	18	11.15	18	E	48	20	nd
Lund[a]	18	13.21	15	E	35	19	tr
Lund[a]	18–19	22.02	10	E	43	25	tr
Lund[b]	17	20.24	12	E	44	36	tr
Sandhammaren[c]	20	13.17	20	E	300	140	tr
Vallby[d]	21	00.08	13	E	140	150	tr
Vallby[d]	21	11.15	22	E	170	120	tr

[a] *ca.* 3 km from city centre.
[b] City centre.
[c] Rural, 50 m from the sea.
[d] Rural, 10 km from the sea.
[e] Mean temperature.
[f] Predominant wind direction.
[g] nd = Not detected; tr = traces.

samples in the range 17–300 nmol/m^3. An interesting observation is that the concentrations were considerably higher in rural areas with intense plant growth [2] than in the city of Lund. The increased level of acetic acid in the city centre compared with the other city location may be attributed to the denser traffic (including ethanol-fuelled buses) in the centre.

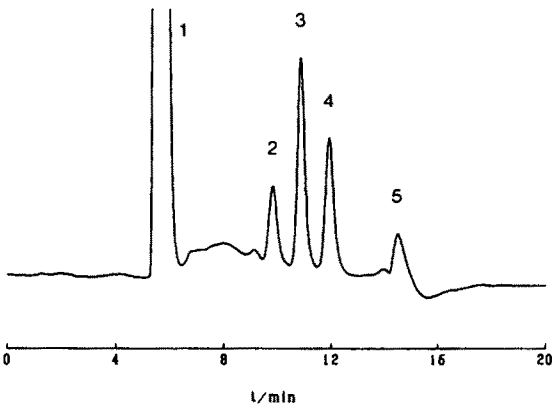

Fig. 5. Chromatogram of an air sample taken on May 21st in Vallby, S.E. Sweden. A 480-l volume of air was sampled with an impinger and 3 ml were enriched and analysed as described in the text. Peaks: 1 = Cl^-; 2 = unknown; 3 = formic acid; 4 = acetic acid; 5 = propionic acid and CO_3^{2-}.

In some samples traces of propanoic acid were found. In Fig. 5, a chromatogram is shown of an air sample taken at a rural site in the south east of Sweden. The unidentified peak could be lactic, succinic or glycolic acid or a mixture of them. Unfortunately, these acids are difficult to separate by ion-exclusion chromatography. Succinic acid up to 2.4 nmol/m^3 has been measured in Los Angeles with a GC method [21]. The concentrations of formic and acetic acid in two samples taken simultaneously with parallel impingers were the same (within 4%).

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