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DETERMINATION OF LOW-MOLECULAR-WEIGHT OXYGENATED HYDROCARBONS IN AMBIENT AIR BY CRYOGRADIENT SAMPLING AND TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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SUMMARY

A highly sensitive and accurate method for the quantitative analysis of a wide range of low-molecular-weight oxygenated hydrocarbons in ambient air is described. Samples were collected on cryogradient sample tubes, transferred to the gas chromatograph by gentle heat desorption and analyzed by two-dimensional gas chromatography. The samples were separated on a packed column [1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W AW], then refocused on-line in a fused-silica capillary cold-trap, followed by on-line splitless reinjection into a fused-silica capillary column (50 m × 0.3 mm I.D., non-polar stationary phase). The detection limit for a typical oxygenate was 0.1 $\mu g/m^3$ using a 3-l sample volume. The precision of the method was better than 12% relative standard deviation for compounds in the low $\mu g/m^3$ range.

INTRODUCTION

An increasing interest in the sources and fates of individual organic compounds in urban air has stimulated intense efforts toward the development of new analytical methodologies. Despite the many successful applications of gas chromatographic (GC) techniques in this area, the identification and quantitation of polar compounds, such as volatile oxygenated hydrocarbons is still a matter of great uncertainty. This important group of chemicals (referred to below as oxygenates) is formed both in fuel-burning processes, and in the atmosphere by photochemical oxidation of hydrocarbons[1,2]. The adverse effects of oxygenates in the environment are mainly due to their toxic properties, many being strong irritants[3–5] and /or suspected carcinogens[6–8], and to their ability to form highly toxic and reactive oxidants upon exposure to sunlight[9]. Thus, detailed knowledge of the occurrence and distribution of oxygenates in the atmosphere is of great importance for the understanding of the chemical processes involved in photochemical smog formation. Furthermore, measurement and

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surveillance of these compounds should be important factors in emission control strategies.

Difficulties incurred in the sampling and analysis of oxygenates derive mainly from their high reactivities and polarities, making quantitative sample treatment difficult. This reactivity has been taken advantage of in several analytical applications. Hence, the solute is allowed to react with a reagent to form a stable derivative that is more easy to separate chromatographically than the original oxygenate. Thus, aldehydes and some ketones were allowed to react with 2,4-dinitrophenylhydrazine[10,11] or an oxime[12] prior to gas or liquid chromatographic analysis. However, these methods are limited to certain functional groups and often do suffer from low sensitivity and background interference. Sample enrichment on a solid adsorbent prior to GC analysis is widely used for the analysis of hydrocarbons and halocarbons in air[13–15]. However, oxygenates may be irreversibly adsorbed on adsorbents, giving low, non-reproducible sample recovery. In addition, GC detectors are not selective towards oxygenates; thus, the detector signal from these compounds is often obscured by the signal from the more abundant hydrocarbons. Due to these difficulties, few data have been reported on ambient levels of oxygenates.

Kaiser[16] demonstrated a powerful technique for enriching volatile compounds in air by using a temperature gradient along a sorbing bed. The technique has several advantages for oxygenates, compared to ambient temperature enrichment on solid adsorbents: (1) the temperature gradient leads to a rough separation between compounds of different volatility, thus reducing the risk for chemical reactions within the sample, this risk is further reduced by the low temperature; (2) due to the low temperature, quantitative enrichment can be accomplished by using a relatively weak sorbent, thus minimizing losses due to irreversible adsorption; also, sample transfer of enriched compounds can be accomplished by using a flowing inert gas during mild warming of the sorbent bed, which minimizes the risk of thermal reactions; (3) the temperature gradient prevents aerosol formation, which might be encountered when sample components are rapidly cooled to very low temperatures in a cryogenic trap.

The thermogradient sampling technique has been used by Dulson[17] for the analysis of volatile organic compounds in air. However, chromatographic separation was accomplished for only a few oxygenated hydrocarbons by using packed and capillary column GC. Better separation of individual oxygenates can be achieved by using two-dimensional chromatography. This technique was used by Bellar and Sigsby[18] and later by Seizinger and Dimitriades[19] for the analysis of oxygenated hydrocarbons in emissions. In these particular applications the first column was highly polar, providing a group separation of oxygenates from the main part of the hydrocarbons. The oxygenates were then transferred to the second analytical column by means of intermediate cryogenic trapping and "on-line" sample transfer.

We have adopted the thermogradient sampling technique, combined with two-dimensional GC, in our efforts to solve the problems involved in ambient air measurements of volatile polar organics. For this purpose, a two-dimensional gas chromatograph was constructed in our laboratory. The system is equipped with two separate GC ovens, with independent temperature-programming facilities, linked by an interface. The heart of the interface is the intermediate trap, made of fused silica. The trap and trap enclosure were designed to allow for total transfer of sample components from the first (packed) column to the trap, followed by splitless injection

into the second (capillary) column. Thus, the flexibility of the two-dimensional GC, combined with quantitative sample transfer and high-resolution separation allows for highly sensitive and accurate measurement of a wide range of trace compounds in a complex sample matrix. Details of the chromatographic system will be published elsewhere[20]. This paper describes the evaluation and application of the sampling and analytical system. The integrity of the complete analytical procedure was evaluated by using a series of model substances. The precision, accuracy, detection limit and background interferences are reported. The coupling of the gas chromatograph to a double-focusing mass spectrometer is demonstrated and, finally, examples are given of measurements in city air.

EXPERIMENTAL

Cryogradient sample tubes

Cryogradient sample tubes were made of Pyrex glass tubing (380 × 6 mm O.D., 3 mm I.D.). They were thoroughly cleaned, silanized and filled to a length of 300 mm with sorbent material, the sorbent bed being held in place by small plugs of silanized glass wool. The sample tubes were then conditioned overnight under a stream of high-purity helium at 200°C, and were finally sealed with Swagelock caps and nylon ferrules.

Preparation of sorbent material

3,3,3-Trifluoropropyl(methyl)cyclotrisiloxane (b.p. 126°C, 10 mmHg) was prepared by hydrolysis of 3,3,3-trifluoropropyl(methyl)dichlorosilane according to Pierce *et al.*[21]. Chromosorb W AW (30–60 mesh) (Johns-Manville, Denver, CO, U.S.A.) was acid-washed according to Aue and Wickramanayake[22], dried and deactivated with the cyclic siloxane according to the following procedure: 5 g of the acid-washed and thoroughly dried Chromosorb and 0.5 g of the siloxane were transferred to a 70-ml Pyrex glass ampoule. After flushing the ampoule with helium, the pressure was reduced to 10^{-1} Torr, and the ampoule was sealed with a torch. It was slowly heated to 360°C and maintained at this temperature for 15 h. The Chromosorb bed was then Soxhlet-extracted with toluene for 4 h, washed with methanol, dried and coated with 5% SP-2401 (Supelco, Bellefonte, PA, U.S.A.).

Sampling

The cryogradient sampling device, purchased from AMA Analysentechnik (AMA PN 721; AMA, Hilden, F.R.G.), is shown schematically in Fig. 1. The sampling train consists of a cryogradient sample tube (4) enclosed in a cooling-mantle (5), a sampling pump (8), a needle valve (9) and a rotameter (10), coupled in series. A pump (12) forces a stream of nitrogen through a 5-l liquid nitrogen Dewar vessel (13) into the cooling-mantle and back again to the pump; excess of nitrogen is vented. In this way, a negative temperature gradient is created along the sample tube in the direction of the sample path. At the low-temperature side of the cooling-mantle, the temperature is monitored with a thermocouple, mounted at point 14a. The flow of cooling gas, and thus the temperature, can be adjusted by regulating the input power to the recirculating pump.

In our laboratory, the following parts of the sample device were modified. An

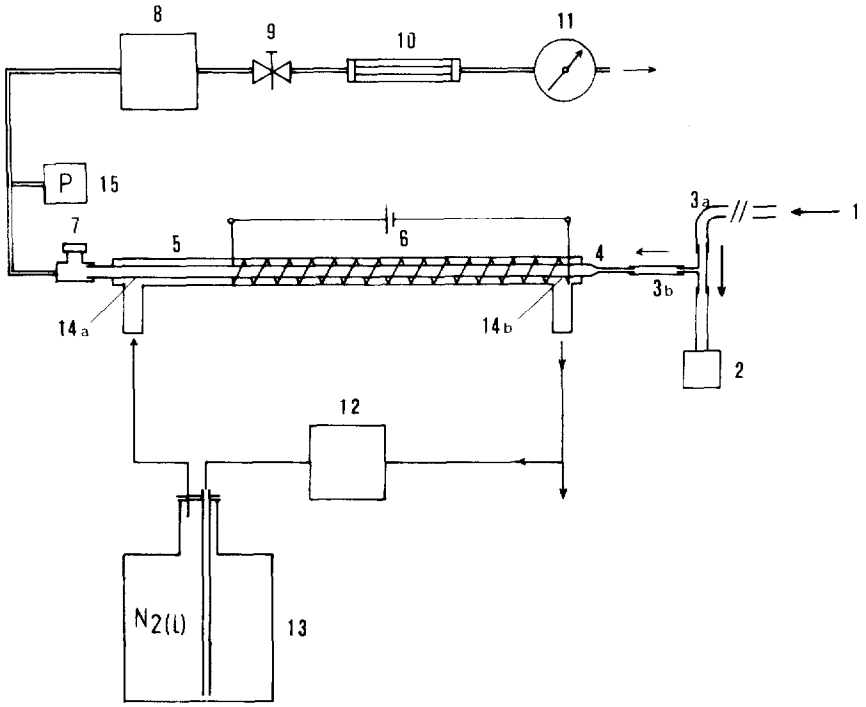

Fig. 1. Cryogradient sampling system. 1 = Sample inlet; 2 = sample bypass pump; 3 = sample probe; 4 = sample tube; 5 = cooling-mantle; 6 = heating coil; 7 = septum nut; 8 = sample pump; 9 = needle valve; 10 = flow meter; 11 = wet-gas meter; 12 = cooling nitrogen pump; 13 = liquid nitrogen Dewar; 14 = fixed-temperature measuring points; 15 = pressure gauge.

additional sample pump (Type G12/02; Brey, Memmingen, F.R.G.) (2, in fig. 1) was occasionally used to sample air through a probe (3a) (polyethylene/aluminium tubing, 6 mm O.D.), at a rate of 3 l/min. From this probe, a small portion of the air (40–300 ml/min) was allowed to enter the sample tube via a short piece of PTFE tubing (3b). A piece of heating-wire (6) (1.5 m, 6.93 Ω/m) was coiled and mounted inside the cooling-mantle, as shown in Fig. 1. During sampling, the wire was connected to the 12-V battery source, giving a heating power of 14 W. A Swagelock Union Tee with a septum nut (7) was soldered to the stainless-steel tubing between the sample tube and sample pump (8). Here, samples were withdrawn with a gas-tight syringe during the breakthrough studies, which will be discussed below. A high-precision wet-gas meter (11) (Size 00; 2–200 dm^3/h; Elster-Handel, Mes- und Regeltechnik, Mainz-Kastel, F.R.G.) was connected to the sampling train after the rotameter. For better control of the thermogradient, an additional thermocouple was inserted inside the cooling-mantle at point 14b.

City air sampling

For sampling of city air, the sample probe inlet was mounted on the roadside edge of the pavement at a height varying from 1.5 to 3 m. The following operating procedure was routinely used for sampling: a cryogradient sample tube was inserted

into the cooling-mantle (5) and connected to the sample pump via the Swagelock union (7) and to the sample probe (3). The bypass pump (2) and the cooling pump (12) were started and the heating circuit (6) was connected to the 12-V source. When the readout of the thermocouples showed a cryogradient from −100°C (at 14a) to −50°C (at 14b), the speed of the cooling pump was adjusted to steady-state conditions. At point 14b the temperature fluctuated by ±5°C for a 15-min period, and it was necessary to adjust the cooling pump speed once or twice during 1-h sampling period in order to keep the temperature within this range. The wet-gas meter (11) was set to zero, and the sample pump was started. The sample flow was adjusted to 40–50 ml/min by means of the needle valve (9). Sample periods were typically 1 h, thus 2–3 l of air were sampled.

During sampling, the initial pressure drop over the sorbing bed was 20–25 mbar at 50 ml/min, measured by the pressure meter (15). Because water condensed in the sample tube, this pressure drop increased progressively for high sample volumes, and the tube finally became plugged. The maximum sample volume which retained a low pressure drop, and, thus, a stable sample flow, was 2.5–3 l during the warm season. At the end of a sampling period, the cryogradient sample tube was sealed, stored in a Dewar vessel with solid carbon dioxide (−79°C) and transported to the laboratory for analysis.

Analysis

Technical details of the two-dimensional GC system are described elsewhere[20] and will only briefly be discussed here. The chromatographic column used for the first separation (column I) was made of glass tubing (2 m × 1.8 mm I.D.), silanized and packed with 5% 1,2,3-tris(2-cyanoethoxy)propane (Alltech, Deerfield, IL, U.S.A.) on deactivated Chromosorb W AW (100–120 mesh). The packing was deactivated by the procedure described above for the sorbent material. Separation of compounds trapped after column I was performed on wall-coated fused-silica columns (50 m × 0.3 mm I.D.). Two different stationary phases were tested, OV-101, 0.17 μm (column IIa) and UCON-50 HB-5100, 0.25 μm (column IIb). Column IIa was purchased from Hewlett-Packard (Palo Alto, CA, U.S.A.), and column IIb from

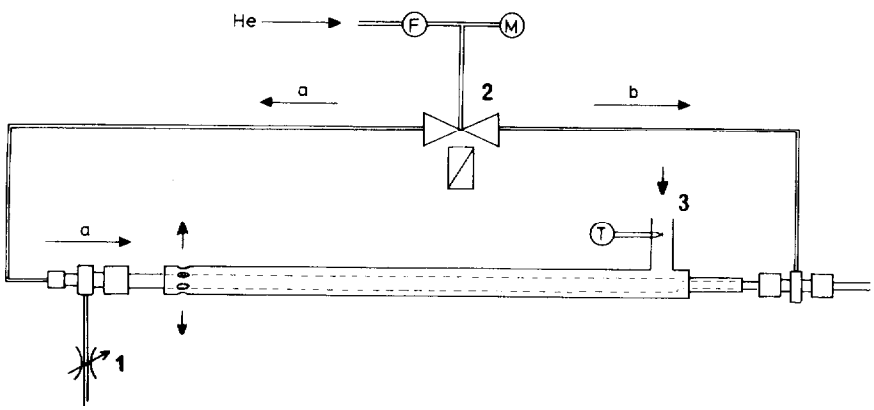

Fig. 2. Thermal desorption injection system. 1 = Needle valve; 2 = three-way solenoid valve; 3 = hot-air inlet; F = flow regulator; M = pressure gauge; T = thermocouple; a, injection mode; b, normal mode.

Orion (Espoo, Finland). Column IIa had 2600 theoretical plates per m at $k = 6.5$, and column IIb had 2500 theoretical plates per m at $k = 6.3$.

The thermal desorption injection system is shown schematically in Fig. 2. Injection into the first column is made by switching over the three-way solenoid valve (2), so that the carrier gas flow is forced to pass through the gradient tube. Injection time is typically 30 sec. The connecting T-pieces are made from Swagelock unions by drilling a hole in the centre part of the unions and brazing to this a 1/16 in. O.D. × 0.5 mm I.D. tube. Needle valve 1 is used for reducing the inlet pressure before the sample tube is removed. It can also be used for purging air from the sample tube before desorption. Carrier gas is controlled with a flow regulator (F). Thus, some time will elapse before the pressure builds up after the system has been vented, *e.g.*, for changing tubes. This pressure is monitored by a gauge (M), which indicates when the correct pressure has been reached; the gauge also indicates leaks in the injection system. The gradient tube is enclosed in a 35-cm long, 11-mm O.D., 10-mm I.D. stainless-steel tube. This tube is connected to a heating gun (Leister Triac) by a length of flexible metal tubing. The temperature of the incoming air is monitored by a thermocouple, positioned 2 cm from the sample tube. Before heating is started, the pressure in the injector must be allowed to settle, otherwise the sample is forced backwards in the sample tube, and this could cause irreproducible retention times and increased peak widths. On injection, the sample tube is heated to 150°C; the time necessary for heating was evaluated by installing a thermocouple inside one sample tube.

The effluent from column I is split in two parts, *i.e.*, 5% is continuously led to a photoionization detector and 95% either to a laboratory-made flame ionization detector or to a capillary trap by means of "flow switching". Thus, the photoionization detector monitors the effluent, even during trapping. Trapped fractions are then reinjected onto column II by means of heating the trap with a thermogradient. Flame ionization detection (FID) is used for quantitative analysis. Data recording and peak processing are made with an integrator (Shimadzu Chromatopac C-R1A). The various chromatographic parameters and their usual settings are shown in Table I.

The GC set-up was connected to a double-focusing mass spectrometer (JEOL

TABLE I

OPERATING PARAMETERS FOR THE GC SYSTEM

First separation	*Interface*	*Second separation*
Temp. program: isothermal at 60°C	Interface temp.: 120°C	Temp. program: 25°C isothermal for 14 min then raised at 5°C/min to 150°C, held for 10 min
Injector: 150°C	Trap temp.: trapping, −150°C; reinjection, 120°C	
Detection: PID, 150°C FID, 150°C		Detection: FID, 190°C
Carrier gas (He): 20 ml/min Column inlet pressure: 2.2 bar		Carrier gas (He): 0.2 m/sec Column inlet pressure: 0.71 bar

JMS-D300) by a fused-silica open-split interface. Although direct coupling of the fused-silica capillary column to the ion source is simpler, the open-split interface was preferred, because the latter allows for direct comparison of retention times between GC–FID and GC–MS analyses. The mass spectral resolution was adjusted to 700. Mass spectra were produced by electron impact at 70 eV. Data acquisition, storage and processing were carried out by an Incos 2400 data system, which was also used to control the magnet and the high voltage of the mass spectrometer. During analysis, the mass spectrometer was set at the repetitive scan mode. The following parameters were selected: mass range, 24–150 m.u.; scan cycle time, 1.1 sec (0.8 sec upscan, 0.2 sec downscan, 0.1 sec hold bottom); temperatures of open-split interface and ion source, 180°C.

Standards and calibration

Methyl nitrite was synthesized, as described previously[23,24]. Formic acid methyl ester was synthesized by mixing equimolar amounts of methanol and formic acid, followed by fractional distillation at atmospheric pressure. GC analysis of the reaction product (b.p. 31.5°C) gave a single peak and showed no traces (< 1%) of methanol. All other compounds used were purchased from Merck-Schuchardt (Hohenbrunn bei München, F.R.G.) or from Fluka (Buchs, Switzerland). The purity of the compounds was 95–99.7%; the ethyl nitrite concentration in ethanol was 15%.

For calibration and for validation of the analytical procedure in the ppb range, a gas-phase standard of five volatile aldehydes, three ketones and benzene was prepared by means of diffusion tubes and dynamic gas-phase dilution. Fig. 3 schematically shows the laboratory-made standard gas generator. This equipment was specially constructed to give highly stable diffusion rates and accurate dilution of the

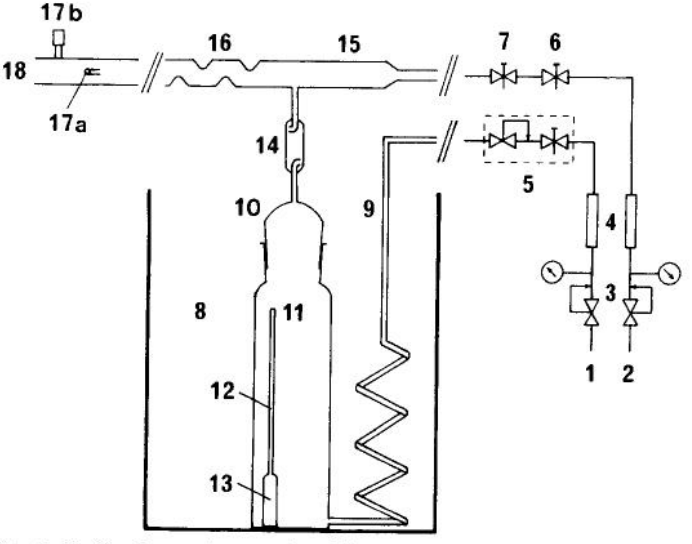

Fig. 3. Calibration equipment. 1 = Nitrogen inlet; 2 = air inlet; 3 = pressure reducer; 4 = trap; 5 = flow regulator; 6 = toggle valve; 7 = needle valve; 8 = thermostatted water-bath; 9 = glass tubing; 10 = diffusion chamber; 11 = diffusion tube; 12 = capillary; 13 = liquid reservoir; 14 = mixing chamber; 15 = dilution tunnel; 16 = mixing orifice; 17a = sampling probe; 17b = septum nut; 18 = to vent.

primary gas standard from the diffusion chamber. Also, since polar and reactive compounds were to be used, the system was designed for high chemical inertness.

The insulated water-bath (Fig. 3) was thermostatted with a high-precision (±0.01°C at 70°C) immersion thermostat (MGW Lauda, Type Thermostar; Lauda, Königshofen, F.R.G.). In order to keep the thermostat within an optimal working range, the water-bath was cooled by a coil with circulating tap-water; the temperature of the diffusion chamber was held at 25.5°C. The diffusion tubes, diffusion chamber and dilution tunnel were made of glass, and all surfaces that come in contact with the standard compounds were deactivated with dimethyldichlorosilane. The diffusion tubes were constructed to give a diffusion rate of a few hundred nanograms per minute at 25.5°C. This was achieved for all nine compounds by using two different capillary diameters (0.35 and 0.5 mm I.D.). The length of the capillaries was varied from 15 to 137 mm. Diffusion rates were determined by repeated weighing of the diffusion tubes during a period of 1 month. Loss in weight was plotted against time, and linear regression analysis of the data gave straight lines with correlation coefficients from 0.996 to 0.9999. The diffusion rate for each compound was determined from the slope of the corresponding regression line.

The nitrogen gas flow through the diffusion chamber was held constant (20 ml/min) by a high-precision flow regulator (Porter VCD 1000 ss, Porter, Hatfield, PA, U.S.A.). The concentration of the primary gas standard was thus in the low ng/ml range. This standard was used to calibrate the GC set-up by direct injection with a gas-tight syringe. It could be further diluted in the dilution tunnel to the low ppb range by using purified air at flow-rates up to 50 l/min. Accurate determination of the dilution air flow-rate was made with a high-precision dry-gas meter (size 3; 1–100 l/min; Elster-Handel, Mainz-Kastel, F.R.G.). This low-concentration gas standard was used to evaluate the analytical procedure in terms of sample recovery, sampling and analytical precision.

RESULTS AND DISCUSSION

Breakthrough volume

The breakthrough volume of the sampling tube, *i.e.*, the maximum allowable sample volume with negligible sample loss (breakthrough), was determined for nine volatile oxygenates with different functional groups. Of the compounds tested (Table II), one or two were of the most volatile in each group; however, formaldehyde was excluded. In order to examine the limits of the sampling procedure for volatile compounds, the test parameters were selected to simulate unfavourable field conditions. Thus, high concentrations were used (40–1000 ppm). Two different techniques were employed to generate the test gases for breakthrough studies: (1) purified air, containing approximately 100 ppm each of ethanal, propanal, acrolein and acetone, was generated by the dynamic dilution procedure described by Gold *et al.*[25]; (2) a static mixture of methyl nitrite (MN), ethyl nitrite (EN), methanol, ethanol, ethylene oxide and methyl formate in purified air was prepared by injecting known amounts of the compounds into a Tedlar sampling bag, filled with 10 l of air.

In order to determine the breakthrough volume, the following procedure was used. For each experiment, a freshly conditioned sample tube was installed in the cryogradient sampling device and connected to the gas mixture with a short piece of

TABLE II

BREAKTHROUGH TEST FOR VOLATILE OXYGENATES

Cryogradient: −50 to −100°C. Sampling flow-rate: 100 ml/min. Pressure drop over sorbent: 30–80 mbar. 1 ppm = 10^{-6} by volume.

Substance	*Concentration (ppm)*	*Breakthrough volume (l)*
Ethanal	100	9
Propanal	110	>12
Acrolein	80	>12
Acetone	110	>12
Methanol	50	> 5
Ethanol	1090	> 5
Methyl nitrite	100	0.5
Ethyl nitrite	100	> 5
Methyl formate	40	> 5
Ethylene oxide	100	> 5

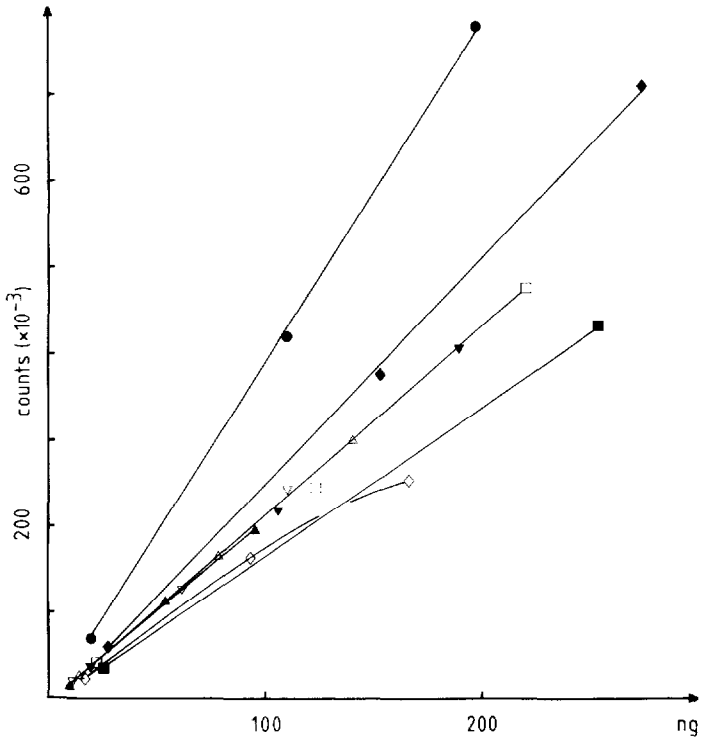

Fig. 4. Plot of peak area (integrator counts) *versus* sampled amount (nanograms). The symbols represent average peak areas for three different concentration levels. Sample volume: 1 l. ■, Acrolein; □, acetone; ▲, methacrolein; △, 3-buten-2-one; ▼, crotonaldehyde; ▽, isovaleric aldehyde, ●, benzene; ◆, methyl isobutyl ketone; ◇, hexanal.

TABLE III

EVALUATION OF THE TOTAL SAMPLE RECOVERY FOR SAMPLING AND ANALYSIS OF A LOW-CONCENTRATION GAS STANDARD

Sample volume: 1 l. Sample matrix: dry air. 1 ppb = 10^{-9} by volume.

Compound	*Concentration*		*Average peak area (counts)*	*S.D. (%, n = 3)*	*Recovery (%)*
	μg/m³	*ppb*			
Acrolein	25	11	36,700	7	92 ± 6
Acetone	22	9.3	43,400	9	101 ± 9
Methacrolein	9.5	3.3	16,700	11	98 ± 10
3-Buten-2-one	14	4.9	25,200	9	97 ± 10
2-Butenal	19	6.6	36,700	4	106 ± 5
3-Methylbutanal	11	3.1	20,600	12	95 ± 12
Benzene	20	6.2	69,300	7	100 ± 7
Methyl isobutyl ketone	27	6.7	61,100	9	96 ± 9
Hexanal	17	4.1	23,000	3	102 ± 3

PTFE tubing. The sampling was started, using the sampling parameters as described above. The sampling rate was 100 ml/min. Samples were collected every 5 min at the septum port (7 in Fig. 1) with a 500-μl gas-tight syringe. The sample was immediately injected into a gas chromatograph, where the individual compounds were separated and quantified. The breakthrough volume was thus determined with an accuracy of ±0.5 l. The results in Table II show that all compounds, except methyl nitrite, have a breakthrough volume larger than 5 l, which is also the upper practical limit for the sampling device due to plugging by water during field sampling.

Calibration and sample recovery

In order to evaluate the linearity and sample recovery for the whole analytical procedure, the following experiment was set up. Three different concentrations, ranging from 10 to 270 μg/m³, of the nine test substances were generated by using the system in Fig. 3. Three replicate 1-l samples were taken at each of the three concentration levels. The samples were then stored in a Dewar vessel with dry-ice for at least 1 h before analysis by two-dimensional GC. In Fig. 4, the mean peak area at each concentration level is plotted *versus* amount of substance. The curves are not true regression curves, but illustrate the linearity of the analytical method.

The sample recovery at the lowest concentration was calculated by dividing the specific peak area (area per weight of substance) for each compound by the corresponding specific peak area obtained when a 1.0-ml sample of the undiluted gas standard is injected directly into the gas chromatograph. The results (Table III) indicate quantitative sample recovery for all substances, with standard deviations ranging from 3 to 12%.

Precision and sensitivity

An important factor to evaluate is the precision of the whole analytical procedure during realistic conditions, *i.e.*, field sampling. For this purpose, a 10-l city air sample was collected at a busy road. Four replicate 1-l samples were collected

TABLE IV

EVALUATION OF THE TOTAL SAMPLING AND ANALYTICAL PRECISION USING A FIELD SAMPLE (CITY AIR)

Sample volume: 1 l.

No.	*Compound*	t_R	*S.D. (%, n = 4)*	t_R *(stand.)*	*Calc. concn.*		*S.D. (%, n=4)*
					μg/m³	*ppb*	
1	Methanol	4.84	0.2	4.86	61	45	11
2	Ethanol	5.48	0.1	5.49	13	7.7	4
3	Acrolein	5.64	0.1	5.66	12	5.6	9
4	Acetone	5.74	0.1	5.77	30	13	3
5	2-Propanol	6.09	0.2	6.09	6.6	2.3	5
10	Methacrolein	7.60	0.2	7.62	0.84	0.29	6
11	3-Buten-2-one	8.16	0.2	8.17	0.92	0.32	6
20	3-Methylbutanal	12.01	0.3	12.03	0.46	0.13	37
22	Benzene	13.08	0.3	13.12	53	17	5
26	Toluene	21.54	0.1	21.49	133	35	4

from the Tedlar bag by using the sampling device, the samples were then stored for at least 1 h under dry-ice before analysis by GC. It is evident from the data in Table IV that the total analytical precision is good, even at the very low μg/m³ level (< 11% S.D.). However, 3-methylbutanal was just above the detection limit (300 pg at a

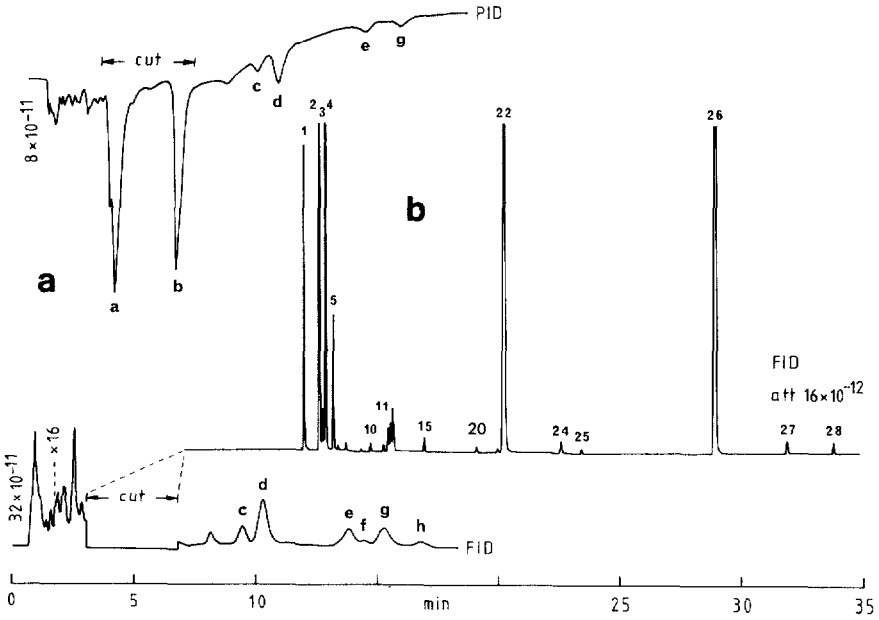

Fig. 5. "Two-dimensional" chromatogram of an air sample from central Stockholm. Sample volume: 2.49 l. Sampling time: 70 min. Chromatogram a: a = benzene + oxygenates; b = toluene (+ oxygenates); c = ethylbenzene; d = *m/p*-xylene; e–h = alkylbenzenes. Chromatogram b: Column IIa (OV-101). Maximum sensitivity: 1×10^{-12} A/mV. Peak identification as in Table IV. Recorder attenuation: a, 10 mV full-scale deflection; b, 1 mV f.s.d.

signal-to-noise level of 3:1), resulting in a poorer precision than the above.

For a typical oxygenate, *i.e.* 3-methylbutanal, the detection limit of 300 pg corresponds to 0.1 $\mu g/m^3$ in a 3-l sample. The background in the analytical system gives a slightly lower detectability for the common solvents, *i.e.*, acetone, methanol, ethanol and benzene. However, these compounds are ubiquitous in urban air, and the system background does not interfere with their quantitation.

Analysis

A "two-dimensional" chromatogram of a 2.5-l air sample from central Stockholm is shown in Fig. 5. Here, the cut was from 2.95 to 6.75 min, *i.e.*, compounds within this retention window in the first column were transferred to the second column. Due to the high selectivity of the packed column, C_1–C_{10} aliphatic hydrocarbons were eluted within 1.5 min, *i.e.*, a major part of the atmospheric aliphatic hydrocarbons were eluted prior to acetaldehyde, which had a retention time of 1.8 min. Water was strongly retarded on the packed column and started to emerge after *ca.* 8.5 min. This is observed as a negative baseline drift of the photoionization detector trace (Fig. 5).

Oxygenated compounds with retention times shorter than that of acetaldehyde on the packed column, *e.g.*, methyl nitrite, ethyl nitrite and ethylene oxide, may not

TABLE V

RETENTION CHARACTERISTICS OF LOW-MOLECULAR-WEIGHT COMPOUNDS TYPICALLY FOUND IN CITY AIR, ON 50-m FUSED-SILICA CAPILLARIES, COATED WITH A NON-POLAR (COLUMN IIa) AND A POLAR (COLUMN IIb) STATIONARY PHASE

Compound	*OV-101*		*UCON-50 HB-5100*	
	Rel. ret.	*k*	*Rel. ret.*	*k*
Ethanal	–	–	0.364	0.206
Propylene epoxide	–	–	0.437	0.452
Methanol	0.368	0.156	0.703	1.33
Ethanol	0.416	0.307	0.889	1.95
Acrolein	0.428	0.345	0.566	0.878
Acetone	0.437	0.372*	0.519	0.722
Propanal	0.437	0.372*	0.487	0.608
2-Propanol	0.482	0.512	0.920	2.05*
2-Methylpropanal	0.558	0.757	0.574	0.906
Methacrolein	0.579	0.817	0.736	1.44
3-Buten-2-one	0.621	0.951	0.922	2.06*
n-Butanal	0.641	1.02	0.753	1.50
2-Butanone	0.656	1.06	0.824	1.74*
Ethyl acetate	0.753	1.37	0.837	1.78*
3-Methylbutanal	0.918	1.88	0.945	2.14
Benzene	1.000	2.14	1.000	2.32
n-Pentanal	1.21	2.80	1.15	2.82
Trichloroethylene	1.28	3.03	–	–
Methyl isobutyl ketone	1.44	3.53	1.28	3.25
Toluene	1.60	4.02	1.37	3.54
Tetrachloroethylene	1.94	5.12	–	–

* Unresolved peak.

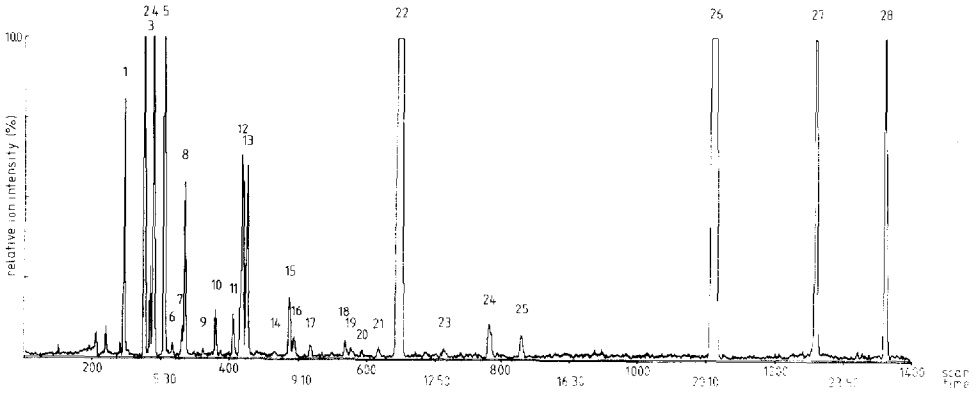

Fig. 6. Two-dimensional GC–MS of an air sample from central Stockholm. Sample volume: 3 l. Sampling time: 20 min. Peak identification as in Table VI.

be separated from the large amount of aliphatic hydrocarbons present in a city air sample. On the other hand, compounds that are eluted after 8.5 min may not be trapped at all, due to immediate plugging of the trap by water. These limitations are, of course, only valid for the analytical conditions given in this text. The two-dimensional GC is very flexible, so that different columns and chromatographic parameters may be selected almost independently for the first and second separation. If, for instance, higher-molecular-weight oxygenates are to be analyzed, a less polar packed column, from which water is eluted earlier, should be selected.

The retention characteristics on columns IIa and IIb of 21 volatile compounds (mainly oxygenates), typically found in ambient air, are summarized in Table V. The polar column is more selective towards the oxygenated volatiles; hence, compounds with similar boiling points but with different functional groups, such as propanal and acetone, are fully resolved on column IIb but not at all on column IIa. However, in order fully to utilize the high resolving power of the two-dimensional GC there should be a large polarity difference between the first and the second separation stage. Therefore, in this experimental set up with a polar first column, the capillary column should preferably have a non-polar stationary phase. This is illustrated by the data in Table V, which show that despite the higher selectivity there are more overlapping peaks on the polar capillary column than on the non-polar one.

A reconstructed total ion chromatogram of a two-dimensional GC–MS analysis of a 3.0-l air sample from central Stockholm is shown in Fig. 6. 28 peaks were detected and all but one could be tentatively identified by using the Incos mass spectra library search system. The identities of the compounds of primary interest were confirmed on the basis of retention data (see Table VI). In the confirmed cases, no misinterpretation of the library search system occurred, even though some peaks represented less than 1 ng of the compound. The possibility of reliable MS identification even in the picogram range, exists thanks to the high resolving power of the two-dimensional GC, which gives very pure peaks and, consequently, very pure mass spectra. The high quality of the MS data of trace compounds is illustrated in Fig. 7a, which shows a background-subtracted mass spectrum of peak 6 in the air sample, containing 0.5 ng of acrylonitrile.

TABLE VI

TWO DIMENSIONAL GC–MS IDENTIFICATION OF LOW-MOLECULAR-WEIGHT COMPOUNDS IN A CITY AIR SAMPLE

Identification based solely on the mass spectrum is considered tentative (T); it is considered positive (P) when both the mass spectrum and retention time confirm the identity.

Peak No.	*Compound identified*	*Identification*	*Peak No.*	*Compound identified*	*Identification*
1	Methanol	P	16	Trichloromethane + methylfuran	T
2	Ethanol	P			T
3	Acrolein	P	17	Tetrahydrofuran	T
4	Acetone	P	18	Unknown	–
5	2-Propanol	P	19	2-Methyl-2-butanol	T
6	Propene nitrile	P	20	3-Methylbutanal	P
7	Unknown	–	21	3-Methyl-2-butanone	T
8	Dichloromethane	T	22	Benzene	P
9	2-Methylpropanal	P	23	Isopropyl nitrate	T
10	Methacrolein	P	24	*n*-Pentanal	P
11	3-Buten-2-one	P	25	Trichloroethylene	P
12	Trimethylsilanol*	T	26	Toluene	P
13	2-Butanone	P	27	Tetrachloroethylene	P
14	Butan-2-ol	T	28	Hexamethylcyclotrisiloxane*	T
15	Ethyl acetate	P			

* Suspected artefact.

Peaks 12 and 28 (trimethylsilanol and hexamethylcyclotrisiloxane) are not likely to be present in ambient air at high concentrations. Thus, the fact that they sometimes show up in the chromatograms in substantial amounts indicates that they might be system artefacts. The absence of the two peaks in blank runs or during re-analysis of sample tubes further indicates that they might be produced by the action of some sample component(s) on silanized surfaces in the sample tubes and/or in the chromatograph. The origin of these silicon compounds will be further investigated. Fortunately, the possible formation of silicon artefacts does not interfere with the quantitation of the oxygenates, with one exception, which is illustrated below. The formation of artificial oxygenates by ozonolysis of trapped olefins might be a serious problem. Experiments indicate, however, that ozone (up to 220 ppb) does not interfere when a 1-l sample volume is used. These investigations will be published in forthcoming papers.

A reconstructed ion chromatogram, together with selected mass chromatograms of an expanded portion of the total chromatogram from scans 350–500, are shown in Fig. 8. The arrow indicates a non-resolved peak at scan 416. Here, by selecting appropriate mass numbers for reconstruction of mass chromatograms, the two peaks were "fully resolved". Fig. 7b shows an enhanced mass spectrum of the non-resolved peak at scan 416. A library search suggested *n*-butanal as the "best fit" (fit: 974) candidate. The identity was confirmed by retention data. The molecular ion (m/z = 72), $C_2H_5CHO^+$ (m/z = 57), CH_2CHOH^+ (m/z = 44), CH_2CHO^+ (m/z = 43), $CHCO^+$ (m/z = 41), CHO^+ (m/z = 29) and $C_2H_3^+$ (m/z = 27) are all due to ionization and fragmentation of *n*-butanal. Only a few interfering peaks are present.

The two-dimensional GC is currently being used for the quantitative analysis

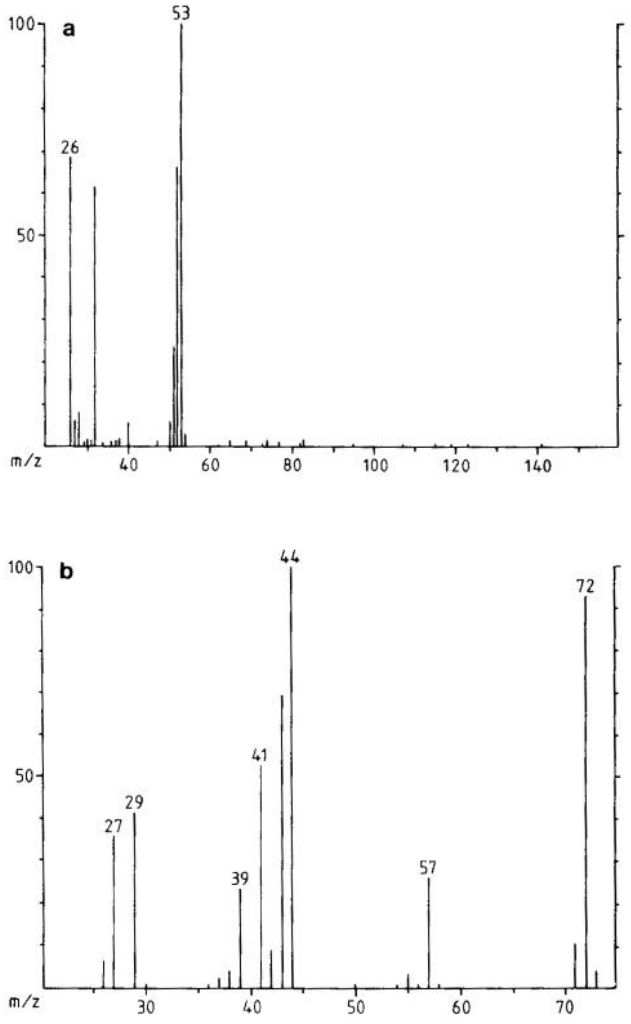

Fig. 7. a, Mass spectrum of peak 6 in Fig. 6. Compound: acrylonitrile; amount *ca.* 0.5 ng. Base peak intensity: 1360, background subtracted. b, Enhanced mass spectrum of unresolved compound (*n*-butanal) in peak 12.

of volatile oxygenated, aromatic and chlorinated hydrocarbons in Stockholm air. More than 200 city air samples have been analyzed during a 10 month period. During this period, the GC set-up has performed well, and no deterioration of the columns or changes in relative retention times have been detected.

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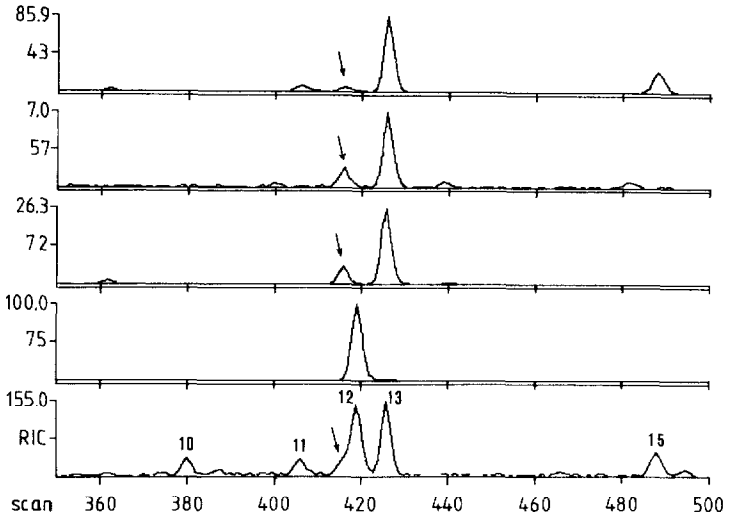

Fig. 8. Reconstructed selected ion chromatogram of expanded portion of the chromatogram in Fig. 6.

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