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Note

Determination of tropospheric phosgene and other halocarbons by capillary gas chromatography

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Large amounts of halogenated hydrocarbons have been released into the atmosphere in recent years. Since these compounds are responsible for the destruction of the stratospheric ozone layer and contribute to the "greenhouse effect", it is necessary to investigate the chemical reaction cycles in which the halocarbons are involved.

Phosgene has been identified as an atmospheric decomposition product of several chlorinated hydrocarbons, for example CH_2Cl_2, $CHCl_3$, CCl_3CH_3, C_2HCl_3 and C_2Cl_4[1]. Because of the well known high toxicity of phosgene and its role as a reactive intermediate product in the troposphere it is important to develop sensitive analytical detection methods. This compound is also assumed by some authors[1,2] to accumulate in the troposphere.

Most existing analytical methods are not suitable for measuring phosgene at concentrations relevant to tropospheric conditions. There are a few wet chemical methods using the reaction of phosgene with a suitable reagent solution to form a product for spectrophotometric detection. These methods were often used to monitor the threshold limit value (TLV) (0.1 ppmv) at industrial working places. However, due to interferences, lack of specificity and large sample volumes they are less favoured for tropospheric trace determination of phosgene[3]. Infrared spectrophotometry suffers from similar problems and provides satisfactory results only for concentrations above 0.025 ppmv phosgene[4].

Priestley *et al.*[5] reported the determination of phosgene in air with gas chromatography with electron-capture detection (GC–ECD) using an aluminium column packed with 30% dodecyl phthalate coated on GC 22 super support (100–120 mesh). Singh[2] improved the method and presented the first results of phosgene detection in the area of Los Angeles. He found phosgene concentrations between 21 and 61 pptv also using a gas chromatograph equipped with an aluminium column packed with 30% dodecyl phthalate coated on Chromosorb P (100–120 mesh). The main problem of the analysis is the heterogeneous decomposition of phosgene on the active column sites. In order to prevent losses of phosgene it is necessary to precondition or pretreat the column and to carry out frequent calibrations[6]. Additionally, Singh used a gas chromatograph specially equipped with dual electron-capture detectors in series and applied "pulsed flow coulometry" in order to extrapolate to the phosgene concentration for a zero retention time on the column[7].

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Recently Hendershott reported upon a solid sorbent sampling procedure for phosgene and other chloroformates in combination with a GC–flame ionization detection (FID) system. He collected these compounds on a di-*n*-butylamine coated solid sorbent, whereby a detection limit of 0.002 ppmv for phosgene was achieved (40 l sample). The drawbacks are the large sampling volume and the time-consuming collection process and sample preconditioning.

This investigation describes a method which avoids significant losses of phosgene by use of chemically inert tubes, a capillary column and a careful enrichment step and analytical procedure. The high resolution of the capillary column allows the separation and simultaneous detection of other ECD-sensitive compounds. The method can be adapted easily for collecting samples in the field.

EXPERIMENTAL

Apparatus

A Siemens gas chromatograph (Model Sichromat 1) equipped with an electron-capture detection was used and prepared for a low temperature gradient. The apparatus was fitted with a fused-silica capillary column (50 m × 0.32 mm I.D., 0.53-μm coating of SE-30 CB, Macherey and Nagel). The carrier gas was helium (99.996%, Messer Griesheim), additionally purified in cryo- and adsorption traps; flow-rate 2.5 ml/min. Nitrogen was used as the make-up gas to provide proper ECD operation.

The transfer of the air sample on to the column was accomplished by a six-port valve (Valco). The valve was connected to the column with a deactivated fused-silica capillary column (2 m × 0.32 mm I.D., Macherey and Nagel) and a zero dead volume fitting. The deactivated fused-silica capillary column was used to cryofocus the analytes at the temperature of liquid nitrogen before separation on the column. This is necessary to provide sharp peaks. Separation on the column was performed with a temperature programme (−30°C for 7 min, raised at 25°C/min to 200°C).

During our investigations a packed column was also tested: a Perkin-Elmer Model F 22 gas chromatograph was equipped with a PTFE column (1.6 m × 1/8 in. I.D.) packed with 30% dodecyl phthalate coated on Chromosorb P. The enrichment and transfer of the sample was as described.

Analytical procedure

Air samples were collected by a system of two pumps as shown in Fig. 1. Ambient air (60 ml/min) was sucked through the PTFE loop at the trapping temperature of −196°C. The resulting sub-atmospheric pressure avoided condensation of oxygen. The volumes of air sampled during the enrichment procedure varied between 0.3 and 1 l, depending on the amount of trace compounds present in the air.

The humidity of the atmosphere has to be removed to avoid possible interferences of the electron-capture detector; furthermore, water shortens the lifetime of the deactivated capillary column used to cryofocus the analytes. Drying was performed in a glass tube (13 cm × 1.5 cm I.D.) filled with magnesium perchlorate (Fluka).

Cryogenic enrichment of the trace compounds was realized in a stainless-steel covered PTFE loop (70 cm × 1/8 in. O.D., 1/16 in. I.D.) at −196°C. Resistance heating of the stainless-steel cover was used for regulating the desorption process. After flushing the cryogenic trap with helium to remove oxygen, the carrier gas was

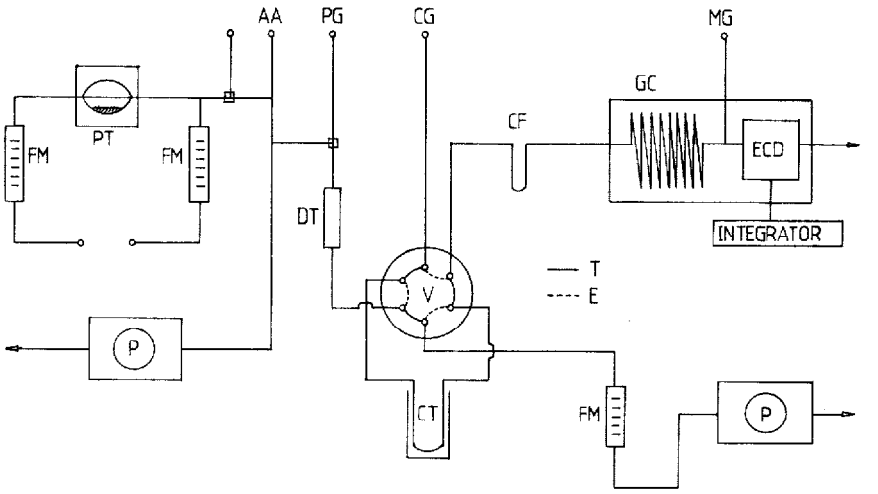

Fig. 1. Analytical system: FM = flow-meter; PG = purge gas (N_2); PT = permeation tube; AA = ambient air; CG/PG = carrier gas/purge gas (He); DT = drying tube; V = six-port valve; P = pump; CT = cold trap; CF = cold focussing; T = transfer; E = enrichment; GC = gas chromatographic system; MG = make-up gas.

conducted by the six-port valve through the PTFE loop. Analytes were vaporized by resistance heating of the stainless-steel cover. Before separation and detection the compounds were cryofocused at −196°C as mentioned above.

Calibration

The calibration had to be carried out completely identically to the sample collection procedure in order to compensate for possible losses of phosgene during the analysis. The phosgene standard was generated with a PTFE permeation tube kept at constant temperature. The purge gas was purified nitrogen at a flow-rate of 11 ml/min. All gas flows were controlled by flow meters. The content of phosgene in the nitrogen was determined with ion chromatography (IC) as a reference method. Phosgene was hydrolysed in impingers filled with water and determined as the chloride.

For GC calibration the purge gas was diluted in ambient air which was conducted through a trap filled with sodium hydroxide-coated charcoal (Merck) in order to decompose phosgene. So the phosgene concentration of the whole gas flow was reduced to the levels expected in the troposphere.

Enrichment and analysis were carried out analogous to the analysis of air samples described above. The amounts of phosgene were varied by changing the sampling volume.

Field measurement

Sample collection in the field was realized in a PTFE loop at the temperature of liquid nitrogen. Dried ambient air was sucked with a flow-rate of 60 ml/min through the cryogenic trap, then the loop was closed by two PTFE stop-cocks. The sample was kept under liquid nitrogen until it was subjected to GC analysis in the usual way.

RESULTS AND DISCUSSION

Fig. 2 presents two chromatograms containing characteristic compounds in air samples. In Fig. 2a trace compounds were separated using a capillary column, in Fig. 2b using a packed column.

Advantages resulting from the use of the capillary column are as follows. (1) High resolution; simultaneous detection of other chlorinated hydrocarbons is possible. (2) Analysis can be carried out using low temperatures (−30°C) during separation to prevent losses of phosgene. (3) Small sample volumes are required, therefore short sampling times are possible. (4) Conditioning or pretreatment of the column is not necessary. The careful enrichment and analytical procedure as well as

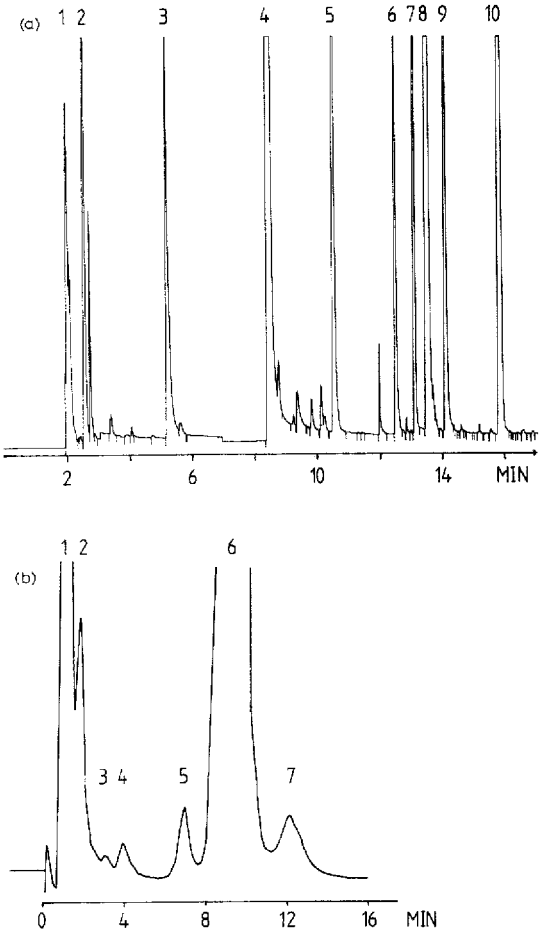

Fig. 2. (a) Gas chromatogram of an air sample (0.6 l, Darmstadt) on a capillary column with a temperature programme. Peaks: 1 = O_2/$CHClF_2$; 2 = CCl_2F_2; 3 = $COCl_2$; 4 = CCl_3F; 5 = CCl_2F–$CClF_2$; 6 = $CHCl_3$; 7 = CCl_3–CH_3; 8 = CCl_4; 9 = CCl_2 = $CHCl$; 10 = CCl_2 = CCl_2. (b) Gas chromatogram of an air sample (12 l, Darmstadt) on a packed column, 20°C isothermal. Peaks: 1 = O_2; 2 = $CHCl_2F$; 3 = $CHCl_3$; 4 = unknown; 5 = $COCl_2$; 6 = CCl_3F; 7 = CCl_2F–$CClF_2$.

the use of the chemically inert capillary column avoid significant losses of phosgene.

Cryogenic preconcentration of the trace compounds at −196°C proved to be an excellent method for trapping phosgene. PTFE loops filled with silylated glass balls (40–60 mesh) caused heterogeneous decomposition of phosgene on the glass surface. Detection was possible only when an empty PTFE loop was used. The efficiency of the method was tested with two traps in series. The second loop did not contain any compounds. Phosgene could be kept for several hours at −196°C without losses due to decay or adsorption.

Magnesium perchlorate used for drying proved to be inert to phosgene. No loss of phosgene during drying was observed. About 25 air samples were collected before a change of the magnesium perchlorate was necessary. A nafion dryer (Perma Pure, Model MD 250-48 F) was also tested. Its drying capacity was sufficient only for one sample. Due to adsorption of aldehydes and ketones on the nafion membrane, water was no longer removed effectively. A tedious cleaning procedure consisting of heating and outgassing the dryer while purging with purified nitrogen was necessary. If the cryogenically trapped compounds contained water the column was blocked temporarily by ice until the starting column temperature of −30°C was increased.

The separation on the column was obtained by a temperature programme. Phosgene should pass through the column in a short time at low temperatures.

The peak identities of the several compounds were determined by comparison of their retention times with those obtained of standard compounds. The standard deviation of the retention times was less than ± 0.01 min for most compounds (Table I). Additional chromatograms obtained with simultaneous ECD/FID detection were employed.

During calibration of phosgene an average reproducibility of ±8% of the single values (four repeat determinations) was achieved. Bearing in mind that the variation of the permeation rate lies in the same range, the reproducibility is acceptable[9,10]. Concentrations of phosgene down to 7 pptv are detectable in a sample volume of 1 l air (STP). The absolute detection limit is 30 pg phosgene (resulting from three times the standard deviation). Fig. 3 shows the calibration graph for phosgene.

The sample volume cannot be increased due to the fact that higher amounts of

TABLE I

STABILITY OF RETENTION TIMES

Compound	*Retention time (min)*	*Standard deviation, n = 10 (min)*
$O_2/CHClF_2$	2.243	0.013
CCl_2F_2	2.766	0.007
$COCl_2$	5.506	0.009
CCl_3F	8.562	0.008
$CCl_2F–CClF_2$	10.600	0.004
$CHCl_3$	12.521	0.003
$CCl_3–CH_3$	13.122	0.003
CCl_4	13.495	0.002
$CCl_2=CHCl$	14.112	0.003
$CCl_2=CCl_2$	15.622	0.003

TABLE II

CALIBRATION DATA FOR PHOSGENE

Amount of phosgene (pg)	*Area*	*Standard deviation, n = 4 (%)*
36.5	3426	11.3
46.8	7379	11.5
54.3	15 344	10.8
62.3	18 677	8.3
77.7	42 457	9.1
93.2	79 621	6.0
108.7	95 609	5.4
139.1	182 201	5.8
217.3	417 861	7.5

atmospheric CO_2 will block the column. In this case the retention times vary over a wide range and the chromatograms are not interpretable.

During our investigations the concentrations of phosgene found in air samples varied between 8 and 87 pptv during daytime, whereas night-time concentrations up to 143 pptv were determined. From the varying phosgene concentrations we measured over several days/nights, a tropospheric lifetime of a few months has to be assumed. Until now, lifetimes of a few years have been stated. Fig. 4 shows the diurnal variation of the concentrations of phosgene.

The analytical procedure described is a sensitive, simply applicable quantitative method for the determination of phosgene and other haloorganic compounds present in ambient air. This method is suitable for continuous monitoring of these compounds in the troposphere.

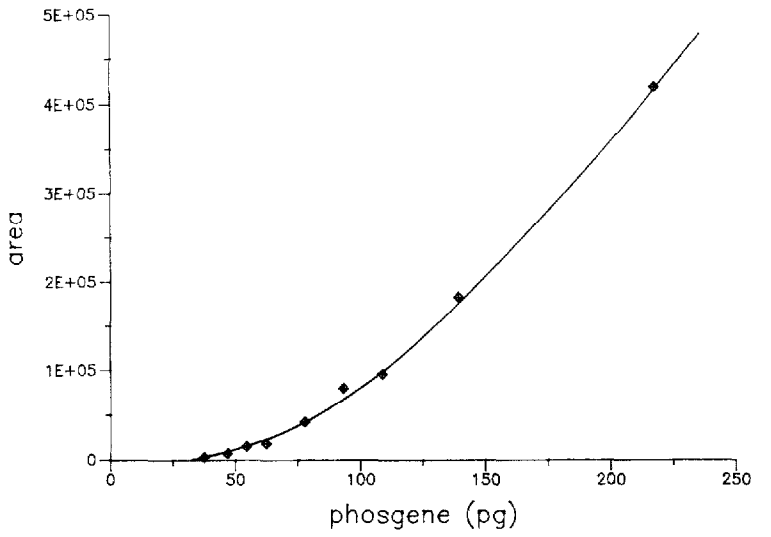

Fig. 3. Calibration graph for phosgene.

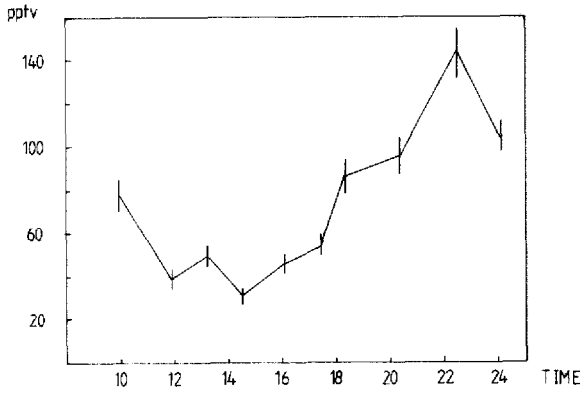

Fig. 4. Diurnal variation of phosgene.

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