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DETERMINATION OF TRACE AMOUNTS OF HYDROGEN HALIDES IN THE ATMOSPHERE BY COLLECTION IN SAMPLING TUBES AND SUBSEQUENT DERIVATIZATION AND GAS CHROMATOGRAPHY

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SUMMARY

The determination of low concentrations of hydrogen chloride in the atmosphere by derivatization with 7-oxabicyclo(4.1.0)heptane and gas chromatographic separation and detection of the reaction product 2-chlorocyclohexanol is described. The detection limit is in the nanogram per gram region. For a further increase in sensitivity solvent extraction and/or solvent evaporation is used.

INTRODUCTION

The problem of the influence of anthropogenic and natural halogen-containing trace components on the atmosphere has caused considerable concern during the last few years. The main problem is the probable disturbance of the ozone layer by catalytic reaction cycles in the stratosphere¹⁻⁶. One of the possible important reactions that interfere with the chlorine-catalysed ozone destruction cycle is the reaction of methane or other hydrocarbons with chlorine radicals to give hydrogen chloride^{7,8}. To judge the importance of this reaction, it is useful to determine stratospheric vertical profiles of hydrogen chloride.

For the solution of this problem we collected the hydrogen chloride in the atmosphere but carried out the subsequent measurements in the laboratory. The advantage is that the measurements themselves can be made under optimal conditions.

EXPERIMENTAL AND RESULTS

For the determination of the hydrogen halides, derivatization with 7-oxabicyclo(4.1.0)heptane and gas chromatographic separation and detection of the reaction product, 2-chlorocyclohexanol, was employed. Reagents are listed in Table I. A Bodenseewerk Perkin-Elmer F22 gas chromatograph equipped with a flame-ionization detector (FID) was used. The flow-rates in the detector were as follows: hydrogen (purity 99.999%), 40-45 ml/min; and synthetic air, 400-500 ml/min. The separation column (6 m × 4 mm I.D.) was packed with 3-5% Carbowax 20M on

TABLE I
REAGENTS USED

Reagent	Purity	Manufacturer
7-Oxabicyclo(4.1.0)heptane	p.a., 98 % 95-97 %	Merck-Schuchardt (Hohenbrunn, G.F.R.) EGA-Chemie (Steinheim/Albuch, G.F.R.)
2-Chlorocyclohexanol	95-97 %	EGA-Chemie
HCl	Titrisol	Merck (Darmstadt, G.F.R.)
Acetone	Nanograde	Promochem (Wesel, G.F.R.)
<i>n</i> -Pentadecane	99 %, GC standard	WGA (Griesheim b. Darmstadt, G.F.R.)
<i>n</i> -Octadecane	p.a., 99 %	Merck

Chromosorb W HP (80-100 mesh), as it was the most suitable of a number of different columns⁹.

The gas chromatographic separation and detection of 2-chlorocyclohexanol was first tested with appropriate standard solutions in order to determine the sensitivity and reproducibility of the measurements. Calibration graphs of peak height *versus* concentration (expressed as HCl) are shown in Fig. 1 for injection volumes of 5 and 10 μ l.

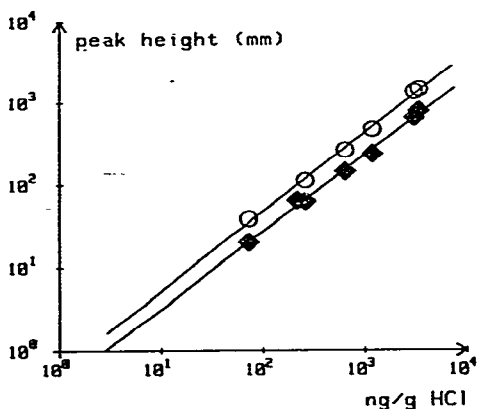


Fig. 1. Dependence of the peak height of 2-chlorocyclohexanol on the concentration of 2-chlorocyclohexanol (expressed as HCl). Volume injected: \blacklozenge , 5 μ l; \circ , 10 μ l. Flow-rate through column: ca. 25 ml/min (N_2). Injector temperature, 200°C; detector temperature, 240°C. Temperature programme: 140°C (16 min), 2°C/min to 173°C (4 min), 4°C/min to 185°C (8 min). Detector: FID. Regression coefficients: 0.9972 (5 μ l); 0.9984 (10 μ l). Intercepts with *y*-axis: -0.42 ± 0.09 (5 μ l); -0.23 ± 0.08 (10 μ l). Slopes: 0.93 ± 0.03 (5 μ l); 0.96 ± 0.03 (10 μ l).

To increase the accuracy of the measurement, *n*-pentadecane or *n*-octadecane is used as an internal standard. Chromatograms of solutions with 2-chlorocyclohexanol (expressed as HCl) concentrations of 1 μ g/g and 62 ng/g are shown in Fig. 2a and b, respectively. This indicates that HCl concentrations as low as 50 ng/g should be detectable with good reliability, provided that the derivatization reaction causes no problems. This was checked by reaction of known amounts of hydrogen chloride with

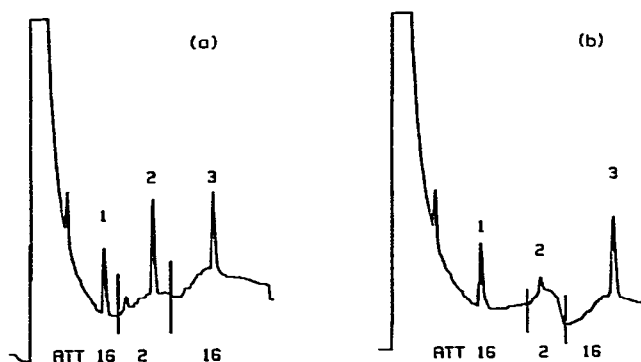


Fig. 2. Chromatograms of standard solutions. Flow-rate through column: *ca.* 30 ml/min. Injector temperature, 200°C; detector temperature, 240°C. Temperature programme: 130°C (16 min), 2°C/min to 158°C (4 min), 4°C/min to 175°C (16 min). Recorder speed: 200 mm/h. (a) 1 ppm of 2-chlorocyclohexanol (expressed as HCl); (b) 60 ppb of 2-chlorocyclohexanol (expressed as HCl). 1, *n*-Pentadecane; 2, 2-chlorocyclohexanol; 3, *n*-octadecane.

7-oxabicyclo(4.1.0)heptane in solution [50 μ l of acetone containing 10% of water, plus 5 μ l of 7-oxabicyclo(4.1.0)heptane]. The dependence of the peak height of 2-chlorocyclohexanol on the concentration of hydrogen chloride is shown in Fig. 3, which demonstrates that the method described is suitable for the determination of hydrogen chloride at the nanogram per gram level in solution.

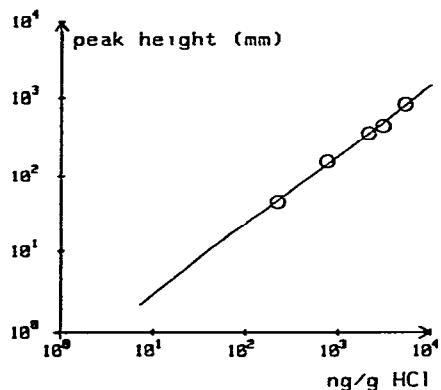


Fig. 3. Dependence of the peak height of 2-chlorocyclohexanol on the concentration of HCl. Volume injected: 5 μ l. Separation conditions as in Fig. 1. Regression coefficient: 0.9980. Intercept with y-axis: -0.42 ± 0.10 . Slope: 0.89 ± 0.03 .

To obtain a further increase in detection sensitivity we use solvent extraction and/or solvent evaporation. For our problem trichloromethane is a very useful extraction agent; a single extraction step gives a recovery of 80–90% and three extractions gives yields of nearly 100%. The dependence of the peak height of 2-chlorocyclohexanol on concentration (expressed as HCl) for single extractions are shown in Fig. 4. A two- to three-fold enrichment can be obtained by this extraction. For further

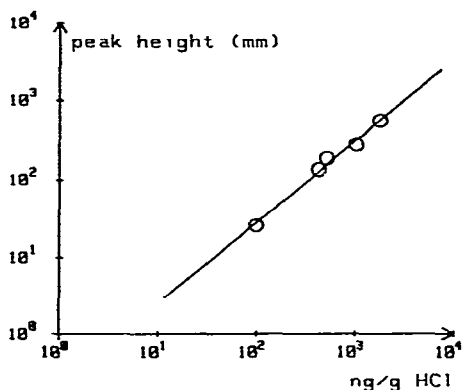


Fig. 4. Dependence of the peak height of 2-chlorocyclohexanol on the detected concentration of 2-chlorocyclohexanol (expressed as HCl) for single extractions. Volume injected: 5 μ l. Separation conditions as in Fig. 1. Regression coefficient: 0.9938. Intercept with y-axis: -0.64 ± 0.18 . Slope: 1.04 ± 0.07 .

enrichment, solvent evaporation is employed, using a procedure similar to that described by Düniges for other applications¹⁰. With this procedure a quantitative ten- to twenty-fold enrichment of 2-chlorocyclohexanol is possible. However, with smaller concentrations (less than *ca.* 500 ppb) some problems arise, indicated by a recovery of more than 100%, which means that the blank value is not negligible. This blank value can be determined by concentrating ten-fold 7-oxabicyclo(4.1.0)heptane-acetone solutions. By this enrichment a peak belonging to 2-chlorocyclohexanol not seen before concentration becomes clearly visible (Fig. 5a and b). These blank values correspond to 50 ppb of hydrogen chloride detected as 2-chlorocyclohexanol. Therefore, the detection limit for the determination of hydrogen chloride is determined not by the detection sensitivity of the system but by the blank value.

To reduce the blank values, careful purification of all reagents, especially 7-oxabicyclo(4.1.0)heptane, is necessary. Double distillation through a packed distillation column (glass Raschig rings) under slightly reduced pressure is sufficient for 7-



Fig. 5. Chromatogram of an acetone-1% 7-oxabicyclo(4.1.0)heptane solution. Volume injected: 5 μ l. Flow-rate through column: *ca.* 30 ml/min (N_2). Injector temperature, 220°C; detector temperature: 250°C. Temperature programme: 140°C (16 min), 2°C/min to 190°C (16 min). Detector: FID. Attenuation: 32. Recorder speed: 200 mm/h. (a) Before and (b) after ten-fold enrichment. The position of 2-chlorocyclohexanol is marked with an arrow.

cm \times 4 mm I.D.) were used. The collected hydrogen chloride was removed from the sampling tubes either by washing out or by thermal desorption¹¹.

The washing out was carried out with acetone-7-oxabicyclo(4.1.0)heptane solution or with water. In the latter instance the derivatization was effected in a second stage. If the washing out procedure was carried out with water, the derivatization product, 2-chlorocyclohexanol, was extracted from the aqueous solution with trichloromethane to prevent difficulties during gas chromatographic separation (possible decomposition of the stationary phase). This also allowed sample concentration by solvent evaporation. Preliminary results indicate that the described procedure is very useful for the determination of hydrogen chloride in air.

For automatic sampling, *e.g.*, by airplane, a twelve-fold adsorptive air sampler was built (Fig. 6). The sampling tubes can be exchanged and subsequently analysed in the laboratory.

This method has been tested in the laboratory but not with field measurements. Therefore, it is not possible to give precise detection limits or the reproducibility under realistic field conditions. We have tested the method for interferences from other hydrogen halides and found that the reaction product of 7-oxabicyclo(4.1.0)-heptane with different hydrogen halides can be separated from each other. However, possible interferences from other reactive trace components in air remain to be investigated.

CONCLUSION

The determination of hydrogen chloride by reaction with 7-oxabicyclo(4.1.0)-heptane and gas chromatographic measurement of the reaction product seems to be a very suitable method for the determination of hydrogen chloride in the lower microgram per gram and upper nanogram per gram regions. The detection limit seems to be sufficient for the determination of hydrogen chloride in tropospheric and stratospheric air. The procedure can also be used for the analysis of hydrogen chloride in solutions, *e.g.*, in rain water.

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