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## DETERMINATION OF TRACE AMOUNTS OF HYDROGEN CHLORIDE BY DERIVATIZATION WITH EPOXIDES AND GAS CHROMATOGRAPHIC SEPARATION

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### SUMMARY

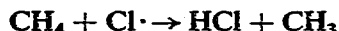
An investigation into the possibilities of determining hydrogen chloride in small quantities by derivatization with epoxides and the gas chromatographic measurement of the formed 2-chloroalcohols has been carried out.

For the gas chromatographic determination of the 2-chloroalcohols open tubular glass columns are used as well as packed glass columns with large inner diameters. The detection limits of the 2-chloroalcohols are in the lower picogram-range (flame-ionization or electron-capture detector). The possibilities for the separation of larger sample volumes on capillary columns (solvent evaporation, coupling of large pre-columns with capillary columns etc.) are discussed.

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### INTRODUCTION

A problem which gained more and more interest in the last years is the determination of the concentration of hydrogen chloride in the upper troposphere and the stratosphere. The reason is the probable destruction of the stratospheric ozone layer by fluorochlorohydrocarbons [Freons (Du Pont), Frigens (Hoechst)]<sup>1-5</sup>. The mechanism of destruction which is discussed for ozone<sup>6,7</sup> is a catalytical reaction with Cl radicals which are formed by photochemical decomposition of the "Freons". One of the possible important reactions which remove Cl radicals from the catalytical ozone destruction cycle is<sup>8</sup>:



Therefore, it is very important to determine the vertical and horizontal profiles of HCl in the stratosphere and upper troposphere. The expected concentrations are in the range of 0.1-1 nl/l (mixing ratio)<sup>9,10</sup>.

The current experimental methods for the analysis of HCl in air are only capable of determining HCl in the 1  $\mu\text{l/l}$  (mixing ratio) region<sup>11</sup>. Owing to the technical and practical conditions (remote-controlled balloon borne samplers) sample volumes of only 1-10 l (standard temperature and pressure) can be obtained from the strato-

sphere. Therefore the analytical problem is to determine HCl amounts of 10 ng or less in a very small sample, which contains other chlorinated species as well as other hydrogen halides. (The separation of nitrogen and oxygen from the air components of lower volatility is possible by freeze-out concentration or by adsorptive sampling, but the separation of such small amounts of HCl from the other trace constituents of the air is far more difficult.)

To our knowledge there is no existing analytical method which solves all the following requirements which result from this analytical problem: (1) the method must be sensitive enough to determine nanogram amounts of HCl in a small sample volume; (2) the method must be sufficiently selective, in order to avoid interferences from other hydrogen halides and organic chlorinated compounds. We have decided to use derivatization methods and gas chromatographic separation and determination for the following reasons: (1) the separation efficiency of gas chromatographic methods is so high, that interferences from other components can be excluded; (2) the sensitivity of gas chromatographic detectors is sufficient to allow the detection of amounts down below the nanogram region; (3) derivatization is necessary since a satisfying gas chromatographic separation of nanogram amounts (or less) of HCl is not possible without considerable losses of HCl due to the high reactivity and polarity of this component. Therefore, we have studied the derivatization of HCl with the aim of forming compounds with good separation efficiency and high detection sensitivity. Rüssel<sup>12</sup> derivatized  $5 \cdot 10^{-5}$  mol l<sup>-1</sup> with ethylene oxide. We have used some other epoxides that are more suitable with regard to reproducibility, ease of handling and lower detection limits.

We have found 7-oxabicyclo[4.1.0]heptane to be a very suitable derivatization reagent for HCl. The reasons are the ease of handling a liquid (in contrast to ethylene oxide), a sufficient rate of reaction of 7-oxabicyclo[4.1.0]heptane with HCl to give 2-chlorocyclohexanol, the formation of only one reaction product and a suitable detection sensitivity with a flame-ionization detector (FID).

## EXPERIMENTAL

The derivatization reactions were carried out in small volumes (50–100  $\mu$ l) by adding a large excess of 7-oxabicyclo[4.1.0]heptane to solutions of acetone–water–HCl with varying concentrations of HCl. Acetone was used as a solvent to ensure that a homogeneous solution containing water and the epoxide is formed. Water was added as it is present in nearly all instances where HCl has to be analysed. For the gas chromatographic determination a Bodenseewerk Perkin-Elmer F-22 gas chromatograph was used with an FID and an electron-capture detector (ECD). The FID was used with 40–45 ml min<sup>-1</sup> of hydrogen 5.0\* and 400–500 ml min<sup>-1</sup> of synthetic air. With make-up gas the gas flow through the ECD chamber was maintained so that the flow-rate through the ECD was always about 60 ml min<sup>-1</sup> of argon–5% methane. For the separation, both packed and capillary columns were used. To increase the accuracy of the measurement we used *n*-pentadecane or *n*-octadecane as an internal standard. For the separation, the following stationary

\* Hydrogen 5.0: purity 99.999%; argon 5.0: purity 99.999%; nitrogen 5.5: purity 99.9995%.

phases were tested: Apiezon L, OV-101, OV-17, Carbowax 1500, Carbowax 20M and DEGS. The most satisfactory results were obtained with Carbowax 20M.

## RESULTS AND DISCUSSION

To obtain calibration graphs we first carried out the gas chromatographic investigations of the chosen derivatization reaction with suitable standard solutions to determine the sensitivity and reproducibility of the method.

In Fig. 1 the dependence of the relative peak height (2-chlorocyclohexanol to *n*-pentadecane) on the detected amount of 2-chlorocyclohexanol referred to HCl is shown. To examine the possibilities of HCl determination, the derivatizations were first carried out with known amounts of HCl and the results compared with the calibration graph prepared from known standard solutions.

Table I shows the results of this comparison, which demonstrates that the described method is suitable for HCl concentrations down to the lower micrograms

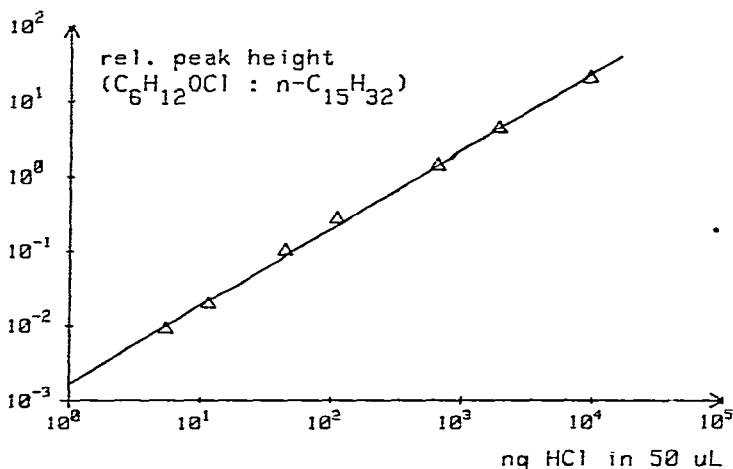


Fig. 1. Dependence of the relative peak height (2-chlorocyclohexanol to *n*-pentadecane) on detected amount of 2-chlorocyclohexanol referred to HCl in a volume of 50  $\mu$ l. Column, glass (6 m  $\times$  4 mm I.D.) packed with 5% Carbowax 20M on Chromosorb W HP; carrier gas, argon 5.0; detector, FID; FID gas,  $H_2$  5.0; synthetic air, volume injected, 5  $\mu$ l; flow-rate through column, ca. 20 ml  $min^{-1}$ ;  $T_{injection}$ , 240°;  $T_{detector}$ , 250°; isothermal pre-period, 16 min at 70°; isothermal after-period, 8 min at 190°. Temperature programme:  $\Delta T_1$ , 4°  $min^{-1}$  from 70° to 150°;  $\Delta T_2$ , 2°  $min^{-1}$  from 150° to 190°. Regression coefficient, 0.9990; intercept on y-axis,  $-2.75 \pm 0.05$ ; slope,  $1.03 \pm 0.02$ .

TABLE I

### COMPARISON OF HCl MEASUREMENTS WITH STANDARD SOLUTIONS

Experimental conditions as in Fig. 1.

Added (ppm)	Found (ppm)
3.9	3.7
2.1	2.3
1.1	1.1

per gram level (corresponding to amounts down to 50 ng of 2-chlorocyclohexanol referred to HCl in volumes of 50  $\mu$ l).

It is important to keep the volume of the original sample as small as possible, because the volumes that can be separated on gas chromatographic columns are in the microlitre range for packed columns. We have found that a volume of 50  $\mu$ l for the derivatization of the original sample is appropriate to the problem for two reasons: (1) the problems of handling volumes much smaller than 50  $\mu$ l are considerable and the reliability and reproducibility decrease for too small volumes; (2) a volume of 50  $\mu$ l allows several measurements of this sample, which is very important since the collection of stratospheric samples is expensive and difficult.

For even lower concentrations two problems arise: (1) the blank value caused by the chloride content of the reagents can no longer be neglected, and (2) samples

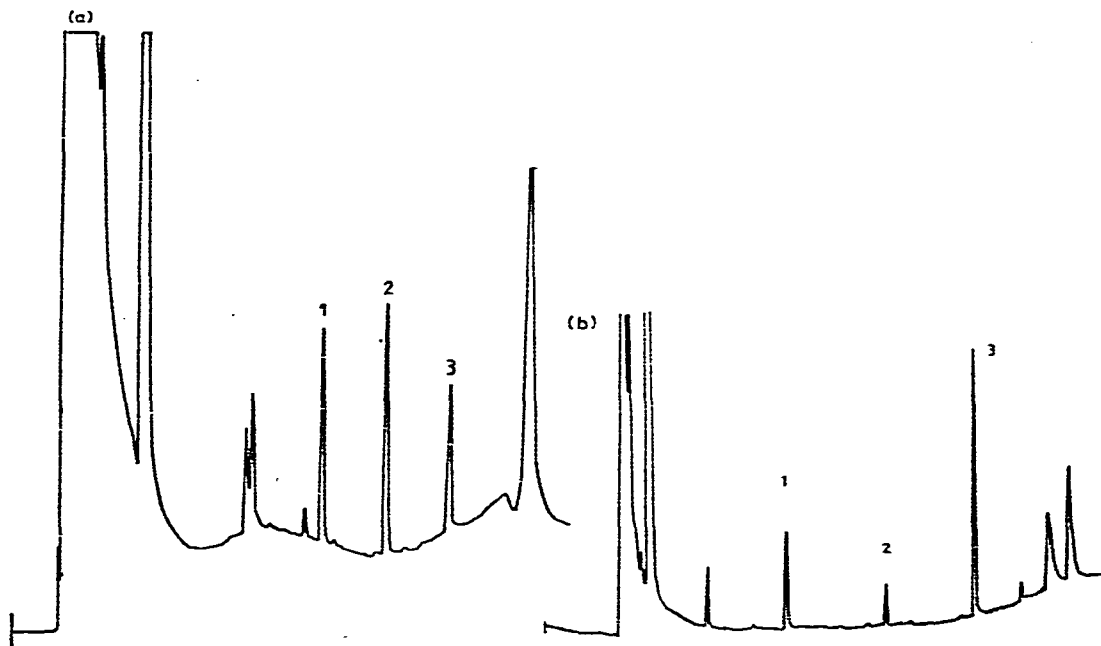


Fig. 2. (a) Chromatogram of a standard solution that contains  $1.49 \cdot 10^{-2} \text{ mol l}^{-1}$  of 7-oxabicyclo[4.1.0]heptane,  $7.1 \cdot 10^{-4} \text{ mol l}^{-1}$  of cyclohexanediol-1,2,  $7.9 \cdot 10^{-5} \text{ mol l}^{-1}$  of 2-chlorocyclohexanol,  $3.6 \cdot 10^{-5} \text{ mol l}^{-1}$  of *n*-pentadecane and  $3.9 \cdot 10^{-5} \text{ mol l}^{-1}$  of *n*-octadecane. Solvent acetone. Column, glass (6 m) packed with 5% Carbowax 20M on Chromosorb W HP; carrier gas, nitrogen 5.5; detector, FID; volume injected, 5  $\mu$ l; recorder speed, 200 mm h<sup>-1</sup>; flow-rate through column, 30 ml min<sup>-1</sup>;  $T_{\text{injector}}$ , 200°;  $T_{\text{detector}}$ , 220°; isothermal pre-period, 16 min at 100°; isothermal after-period, 8 min at 190°. Temperature programme:  $\Delta T_1$ , 4° min<sup>-1</sup> from 100° to 164°;  $\Delta T_2$ , 2° min<sup>-1</sup> from 164° to 190°. Attenuation, 32. Peaks: 1 = *n*-pentadecane; 2 = 2-chlorocyclohexanol; 3 = *n*-octadecane. (b) Chromatogram of a standard solution that contains  $4.8 \cdot 10^{-2} \text{ mol l}^{-1}$  of 7-oxabicyclo(4.1.0)heptane,  $1.5 \cdot 10^{-3} \text{ mol l}^{-1}$  of cyclohexanediol-1,2,  $6.1 \cdot 10^{-5} \text{ mol l}^{-1}$  of 2-chlorocyclohexanol,  $6.3 \cdot 10^{-5} \text{ mol l}^{-1}$  of *n*-pentadecane and  $1.2 \cdot 10^{-4} \text{ mol l}^{-1}$  *n*-octadecane. Solvent acetone, Column, glass capillary (50 m) coated with Carbowax 20M; carrier gas, argon 5.0; detector, FID; volume injected, 0.5  $\mu$ l; splitting ratio, 1 : 10.1; recorder speed, 1 cm min<sup>-1</sup>; flow-rate through column, 1.1 ml min<sup>-1</sup>;  $T_{\text{injector}}$ , 230°;  $T_{\text{detector}}$ , 200°; isothermal pre-period, 8 min at 90°; isothermal after-period, 8 min at 180°. Temperature programme: 6° min<sup>-1</sup> from 90 to 180°. Attenuation, 1. Peaks: 1 = *n*-pentadecane; 2 = 2-chlorocyclohexanol; 3 = *n*-octadecane.

which have to be analysed for HCl may contain impurities that may interfere with the chromatographic determination of the 2-chloro-alcohol. The blank value can be reduced by careful purification of the reagents and handling all samples in clean air free of gaseous HCl or chloride aerosols (glove-box, clean bench). The second problem can be eliminated or at least considerably reduced if the separation efficiency is sufficiently high, which means if capillary columns are used.

In Fig. 2 separations on (a) a packed and (b) a capillary column are shown. The advantages of the capillary column are the better separation efficiency and the shorter time of analysis. The drawback is that only small sample volumes (*ca.* 0.1  $\mu\text{l}$ ) can be analysed whereas the large packed column permits sample volumes of 5–10  $\mu\text{l}$ . In spite of these different sample volumes the minimal detectable concentrations are approximately the same on both columns (about 20–40 ng/g). The reason is the lower minimal detectable amount of HCl with a capillary column (see Fig. 3), owing to the narrower peaks and the lower bleeding of the capillary column. The question is whether the advantages of capillary and packed columns can be combined. Therefore, we investigated different possibilities for the separation of larger sample volumes (in this context this means several microlitres) on capillary columns.

#### *Increasing the volume injected*

We found that volumes up to 0.5  $\mu\text{l}$  (5  $\mu\text{l}$  injected, splitting ratio 1:10) can be separated sufficiently by temperature-programmed gas chromatography on a capillary column<sup>13</sup>. The disadvantage of this method is a substantial decrease in the lifetime of the capillary column.

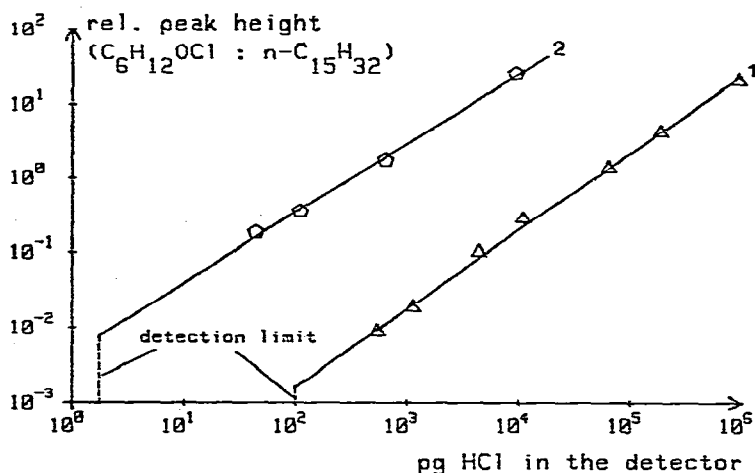


Fig. 3. Dependence of the relative peak height (2-chlorocyclohexanol to *n*-pentadecane) on detected amount of 2-chlorocyclohexanol referred to HCl in the detector. Carrier gas, argon 5.0; detector, FID. (1), 6 m  $\times$  4 mm I.D. glass column packed with 5% Carbowax 20M on Chromosorb W HP; detection limit, 100 pg of 2-chlorocyclohexanol referred to HCl; experimental conditions as listed in Fig. 1; regression coefficient, 0.9990; intercept on *y*-axis,  $-2.75 \pm 0.05$ ; slope,  $1.03 \pm 0.02$ . (2), 50-m glass capillary column coated with Carbowax 20M; detection limit, 2 pg of 2-chlorocyclohexanol referred to HCl; experimental conditions same as in Fig. 2b; regression coefficient, 0.9988; intercept on *y*-axis,  $-2.33 \pm 0.09$ ; slope,  $0.93 \pm 0.03$ .

### Solvent pre-evaporation

We have modified a commercially available solid injector (WGA, Griesheim, G.F.R.) for use with capillary columns (Fig. 4). The results indicate that sample volumes of 10  $\mu$ l with a splitting ratio of 1:10 can be used without peak broadening or a reduction in the column lifetime.

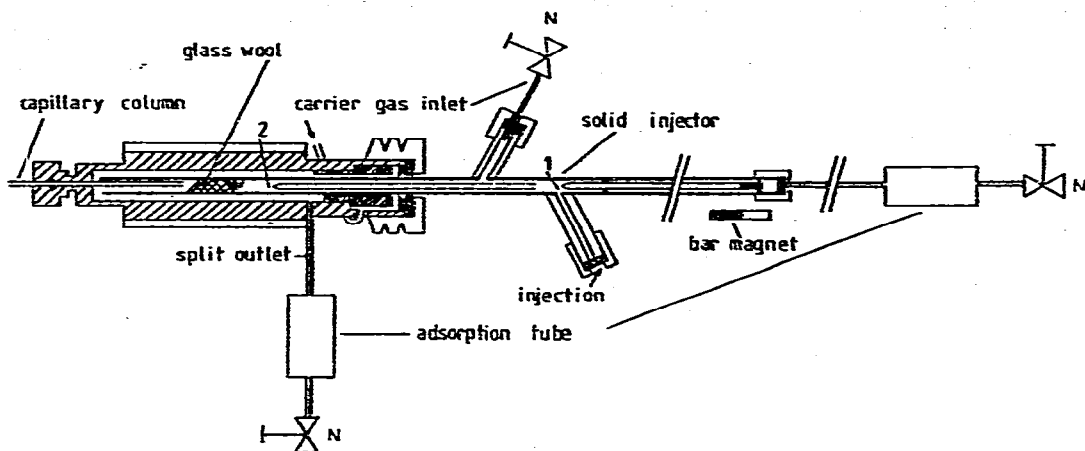


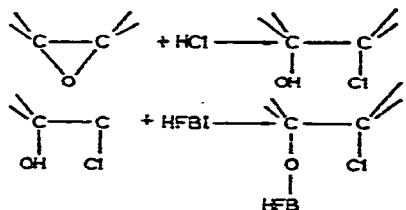
Fig. 4. Solid-injector. 1 = Position of the glass rod during injection; 2 = position of the glass rod during analysis. N = needle valve.

### Coupling of a packed column with a capillary column

The flow scheme for the Deans switch is shown in Fig. 5. So far we have only preliminary results, which allow no conclusions to be drawn about the separation efficiency or detection limit.

An alternative to the use of large sample volumes is the application of detectors with a higher detection sensitivity such as an FID. For suitable compounds, ECDs have detection sensitivities several orders of magnitude better than FIDs. Unfortunately, 2-chlorocyclohexanol does not have a high ECD sensitivity. The direct use of epoxides, which yielded compounds with a high electron-capture ability after reaction with HCl, was not successful because electron-attracting groups which increase the ECD sensitivity decrease the rate of reaction of the epoxides with HCl to such an extent that the reaction time is unacceptably long<sup>14</sup>.

A possibility for combining the fast rates of reaction of the unsubstituted epoxides with HCl and the high ECD sensitivity is a second derivatization of the hydroxy groups of the reaction products ( $\alpha$ -chloro-alcohols) with heptafluorobutryl-imidazole (HFBI) or a similar reagent:



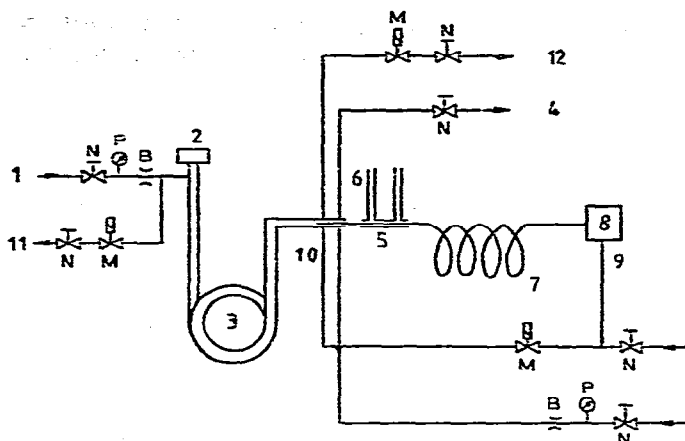


Fig. 5. Flow-scheme of the Deans switch for coupling a packed and a capillary column. 1 = Carrier gas inlet; 2 = injection port; 3 = packed pre-column; 4 = split outlet; 5 = trap position; 6 = inlet for cooling gas; 7 = capillary column; 8 = ECD; 9 = make-up gas for the ECD; 10 = back-flush; 11 = outlet for back-flushing components from the pre-column; 12 = outlet with cut-operating. M = magnetic valve; N = needle-valve; P = pressure gauge; B = micro-blend.

The results of investigations of the reaction of butylene oxide with HCl and subsequent derivatization of the  $\alpha$ -chloro-alcohol with HFBI showed that owing to the more complicated reactions and the resulting difficulties, the minimal detectable concentrations are of the same order of magnitude as for detection with an FID.

We have also used an ECD as gas chromatographic detector for the determination of 2-chlorocyclohexanol (reaction product of cyclohexene oxide and HCl), but the results indicated no advantage over the use of an FID<sup>15</sup>. As has been mentioned above the direct gas chromatographic separation of such small amounts of HCl is not possible.

We are currently trying to find more promising reactions for the derivatization of HCl. Apart from examining other epoxides that form reaction products with HCl that can be further derivatized with electron-attracting compounds, we are also studying the reaction of phenylmercury nitrate with HCl and the detection of the phenylmercury chloride formed by gas chromatography with an ECD. The first results indicate that this reaction is fast and complete.

## CONCLUSION

The determination of HCl by reaction with 7-oxabicyclo[4.1.0]heptane and gas chromatographic measurement of the reaction product appears to be suitable for the determination of HCl at the lower micrograms per gram level. Detection limits in the hundreds of nanograms per gram range are possible (corresponding to 1–10 ng of 2-chlorocyclohexanol referred to HCl in a volume of 50  $\mu$ l). This is sufficient to solve the analytical problem connected with the determination of HCl in the stratosphere. The application of more refined injection methods or column-switching techniques should decrease the detection limit by an order of magnitude. The use of other derivatization reagents has so far not been as successful as we had originally

expected. The most promising reagent is phenylmercury nitrate, which may also be detected by methods other than gas chromatography, e.g., atomic-absorption spectrometry.

#### ACKNOWLEDGEMENT

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