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GAS CHROMATOGRAPHIC MONITORING OF THE CHLOROLYSIS PROCESSES OF SOME BY-PRODUCTS FROM VINYL CHLORIDE, ALLYL CHLORIDE AND EPICHLOROHYDRIN PRODUCTION

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SUMMARY

A method for the monitoring of the chlorolysis processes of some by-products from vinyl chloride, allyl chloride and epichlorohydrin production is reported, as well as a method for calculating the response correction factors for chlorinated hydrocarbons.

INTRODUCTION

Chlorinated hydrocarbons are important in providing the principal routes by which chlorine reaches the heavy chemical market¹. Chlorinated hydrocarbons are used extensively as solvents for the extraction of organic materials and are widely used as intermediates in the manufacture of silicones, tetraethyllead, glycerol, etc. Vinyl chloride and chloroprene are very important in the plastics and synthetic rubber industries.

In the analytical monitoring of processes for the manufacture of chlorinated light hydrocarbons (C_1 - C_3) by the chlorination or chlorolysis of alkanes, alkenes and some by-products obtained in the manufacture of vinyl chloride, allyl chloride, epichlorohydrin, etc., there is often a need to define the composition of some complex mixtures containing chlorinated hydrocarbon derivatives such as chlorinated methane, ethane, ethylene, propane and propylene.

We have developed a gas chromatographic (GC) method for separating mixtures of chlorinated C_1 - C_3 hydrocarbons in a conventional packed column². The application of this method for monitoring the chlorolysis processes of some by-products from vinyl chloride, allyl chloride and epichlorohydrin production is discussed.

EXPERIMENTAL

Apparatus and columns

Chromatographic analyses were performed using a ZDSO Model 577 (ZDSO, Kędzierzyn-Koźle, Poland) gas chromatograph equipped with a flame-ionization detector connected to an MKE-I recorder (VEB Messgerätewerk, Magdeburg, G.D.R.) with a chart speed of 1 cm/min.

Nickel-200 columns: (I) 3.6 m \times 1/8 in. O.D. and (II) 1.5 m \times 1/8 in. O.D., packed with a mixture of 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100–120 mesh) (Supelco, Bellefonte, PA, U.S.A.) were used.

Chemicals and reagents

Hexachloro-1,3-butadiene, hexachlorocyclopentadiene, pentachlorobenzene and hexachlorobenzene (all of analytical-reagent grade), obtained from Merck-Schuchardt (Hohenbrunn, G.F.R.), were used as standards. Other chemicals and reagents and their handling have been described previously².

Analytical conditions

The GC operating conditions for both columns I and II were as follows: initial temperature, 40°C; time at initial temperature, 4 min; programming rate, 5°C/min; final temperature, 160°C; injector and detector temperature, 250°C; and nitrogen carrier gas flow-rate, 15 ml/min.

The samples of the by-products obtained from vinyl chloride, allyl chloride and epichlorohydrin manufacturing plants were stored at 0–5°C.

The samples from the chlorolysis processes were collected in dark, ice-cooled flasks and analysed immediately in order to avoid possible further chlorination and photochlorination reactions. Samples of 1.0 μ l were injected using a 5- μ l microsyringe (SGE, Melbourne, Australia).

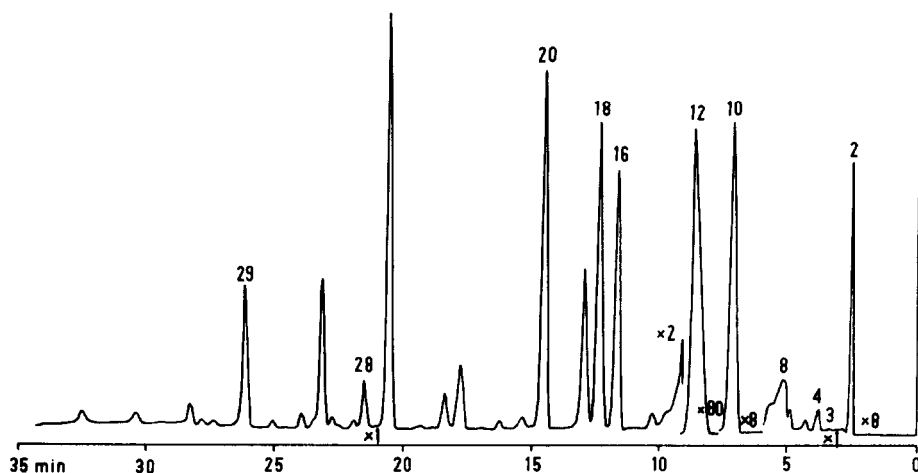


Fig. 1. Gas chromatogram of the by-products taken from a vinyl chloride manufacturing plant. Column I: 3.6 m \times 1/8 in. O.D. nickel-200 tube, packed with 5% SP-1200 + 1.75% Bentone-34 on Supelcoport (100–120 mesh). Column temperature: 4 min isothermal at 40°C, then programmed at 5°C/min to 160°C and kept isothermal at 160°C until the end of the analysis. Carrier gas: nitrogen at 15 ml/min. Flame-ionization detector. Injector and detector temperatures: 250°C. Peaks: 2 = vinyl chloride; 3 = chloroethane; 4 = 2-chloro-1-propene; 8 = vinylidene chloride; 10 = *trans*-1,2-dichloroethylene; 12 = 1,1-dichloroethane; 16 = chloroform; 18 = *cis*-1,2-dichloroethylene; 20 = 1,2-dichloroethane; 28 = 1,1,1,2-tetrachloroethane; 29 = 1,1,2,2-tetrachloroethane.

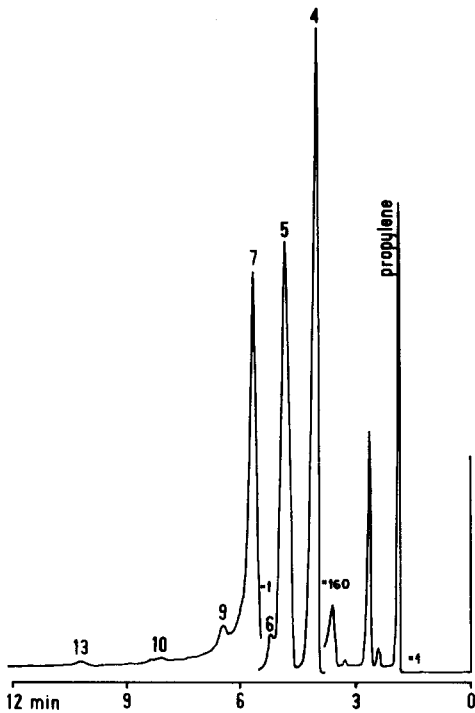


Fig. 2. Gas chromatogram of the by-products taken from an allyl chloride manufacturing plant. Conditions of analysis as in Fig. 1. Peaks: 4 = 2-chloro-1-propene; 5 = 2-chloropropane; 6 = *cis*-1-chloro-1-propene; 7 = *trans*-1-chloro-1-propene; 9 = 3-chloro-1-propene; 10 = *trans*-1,2-dichloroethylene; 13 = 2,2-dichloropropane.

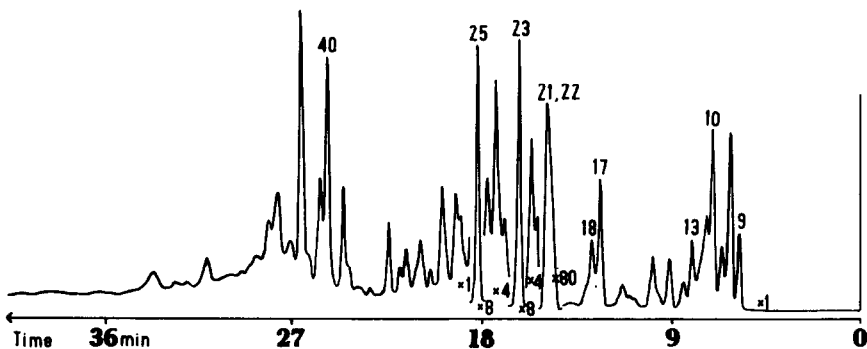


Fig. 3. Gas chromatogram of the by-products taken from an epichlorohydrin manufacturing plant. Conditions of analysis as in Fig. 1. Peaks: 9 = 3-chloro-1-propene; 10 = *trans*-1,2-dichloroethylene; 13 = 2,2-dichloropropane; 17 = 1,1-dichloro-1-propene; 18 = *cis*-1,2-dichloroethylene; 21 = 1,2-dichloropropane; 22 = 2,3-dichloro-1-propene; 23 = *trans*-1,3-dichloro-1-propene; 25 = *cis*-1,3-dichloro-1-propene; 40 = 1,2,3-trichloropropane.

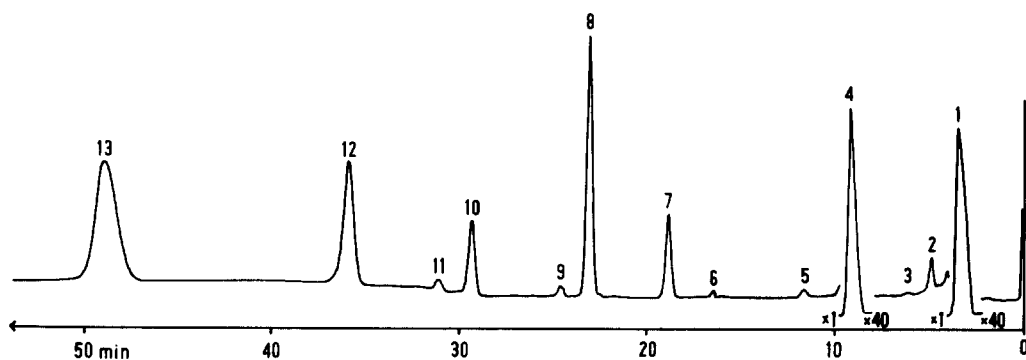


Fig. 4. Gas chromatogram of a sample taken from the chlorolysis process. Column II: 1.5 m \times 1/8 in. O.D. nickel-200 tube, packed with 5% SP-1200 + 1.75% Bentone-34 on Supelcoport (100-120 mesh). Other conditions as in Fig. 1. For peak identification, see Table I.

TABLE I
RETENTION DATA OF COMPOUNDS FROM CHLOROLYSIS PRODUCTS

Column dimensions, conditions and peaks as in Fig. 4.

| Peak No. | Compound | Retention time (min) | Relative retention |
|----------|---------------------------|----------------------|--------------------|
| 1 | Carbon tetrachloride | 3.23 | 0.36 |
| 2 | 1,2-Dichloroethane | 4.53 | 0.51 |
| 3 | Unidentified | 5.85 | 0.66 |
| 4 | Tetrachloroethylene | 8.93 | 1.00 |
| 5 | 1,1,1,2-Tetrachloroethane | 11.28 | 1.26 |
| 6 | 1,1,2,2-Tetrachloroethane | 16.33 | 1.83 |
| 7 | Hexachloroethane | 18.58 | 2.08 |
| 8 | Hexachloro-1,3-butadiene | 22.73 | 2.55 |
| 9 | Unidentified | 24.23 | 2.71 |
| 10 | Hexachlorocyclopentadiene | 28.93 | 3.24 |
| 11 | Unidentified | 30.73 | 3.44 |
| 12 | Pentachlorobenzene | 34.98 | 3.92 |
| 13 | Hexachlorobenzene | 48.08 | 5.38 |

TABLE II
COMPARISON OF CALCULATED RESPONSE CORRECTION FACTORS WITH THE CORRESPONDING EXPERIMENTAL VALUES

| Compound | Correction factor | | | | | $f_{\text{calcd.}}^*$ | Difference (%) |
|--------------------------|-------------------|------|------|------|------|-----------------------|----------------|
| | $f_{\text{exp.}}$ | | | | | | |
| | I | II | III | IV | Mean | | |
| Tetrachloroethylene | 0.56 | 0.59 | 0.60 | 0.57 | 0.58 | — | — |
| Hexachloroethane | 0.90 | 0.82 | 0.82 | 0.85 | 0.85 | 0.84 | 1.18 |
| Hexachloro-1,3-butadiene | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.46 | 8.00 |
| Hexachlorobenzene | 0.39 | 0.39 | 0.38 | 0.41 | 0.39 | 0.34 | 12.82 |

* The method of calculation is given in the text.

RESULTS AND DISCUSSION

All samples of the by-products obtained from industrial vinyl chloride, allyl chloride and epichlorohydrin manufacturing plants were analysed using column I packed with 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100–120 mesh). Figs. 1–3 show typical chromatograms obtained on this column. Identifications of the peaks were based on retention data of the standard².

The samples obtained from the above chlorolysis processes by-products were determined using column II packed with 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100–120 mesh). Fig. 4 shows the chromatogram of a sample taken from the chlorolysis process, and the analytical results are given in Table I.

Our studies indicated that a mixed stationary phase, 5% SP-1200 + 1.75% Bentone-34, has a good resolving power for chlorinated hydrocarbons.

Calculations were made by the internal standardization method according to the equation

$$x_i = \frac{A_i f_i}{\sum_{n=1}^n A_i f_i} \cdot 100 \quad (1)$$

where x_i = content of the i th component in the sample (wt.-%), A_i = peak area of the i th component and f_i = response correction factor of the i th component.

In order to determine response correction factors, standard mixtures with compositions similar to the analysed sample were prepared. For compounds of high volatility and/or with standards of insufficient purity, response correction factors were calculated. The calculations assumed that for chlorinated hydrocarbons the response of the flame-ionization detector is proportional to the mass fraction of the carbon atoms in the chlorinated hydrocarbon molecule. These calculations were made according to eqn. 2, considering the experimentally determined response correction factor for tetrachloroethylene:

$$f_i = \left(\frac{nM_{C(C_2Cl_4)}}{M_{(C_2Cl_4)}} \right) / \left(\frac{nM_{C(i)}}{M_{(i)}} \right) f_{C_2Cl_4} \quad (2)$$

where $nM_{C(C_2Cl_4)}$ = atomic weight of n carbon atoms in C_2Cl_4 ($n = 2$), $nM_{C(i)}$ = atomic weight of n carbons in the i th component, $M_{(C_2Cl_4)}$ = molecular weight of C_2Cl_4 and $M_{(i)}$ = molecular weight of the i th component.

A comparison of some calculated response correction factors with the corresponding experimental values is given in Table II.

REFERENCES

- 1 D. W. F. Hardie, in A. Standen (Editor), *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 5, Wiley-Interscience, New York, 2nd ed., 1964, pp. 85–92.
- 2 P. Kusz, A. Andrysiak, W. Czelakowski and J. Bobiński, *J. Chromatogr.*, 254 (1983) 163.