CHROM. 3407

Gas chromatographic determination of impurities in vinyl chloride

Monomers of very high purity are extremely important in polymer formation since it is well known that the quality of the monomers has a great influence on the polymerisation and on the characteristics of the polymer obtained. It is therefore necessary to know the quality and the quantity of the impurities present, taking into account the fact that their presence is strictly related to the purity of the starting materials and to the type of process used to produce the monomers.

Vinyl chloride, one of the most important monomers, is mainly produced nowadays by two processes, *viz.* synthesis from acetylene and hydrochloric acid, and cracking of 1,2-dichloroethane. In the first process, the impurities present in the acetylene used are a determining factor, while the acetylene obtained from calcium carbide is practically pure, and that obtained by cracking of hydrocarbons is relatively impure due to the presence of paraffinic hydrocarbons, particularly ethylenic and acetylenic hydrocarbons.

Hydrochloric acid may also contain other impurities if it is a by-product of other processes, while that obtained by direct synthesis is practically pure. In the cracking of dichloroethane the formation of vinyl chloride, which is carried out at a high temperature, is accompanied by secondary reactions, which give rise to saturated and unsaturated chlorinated hydrocarbons. The two processes are often integrated with the aim of using the hydrochloric acid obtained as a by-product in the dichloroethane cracking process; typical impurities of both the processes can therefore be found in the finished product.

Today, however, highly efficient purification methods make it possible to obtain a monomer in which the impurities are very low and therefore difficult to detect by the usual analytical methods. Gas chromatography, therefore, for both its high separating power and its high detection sensitivity, has a fundamental importance as a means of controlling the quality of vinyl chloride.

MIKKELSEN[1] described a gas chromatographic method which uses two columns in series, two thermal conductivity detectors and a condensation trap. The first column is connected to one of the detectors and is used to separate the low-boiling impurities and the greater part of the vinyl chloride; the high-boiling impurities are collected in the cooled trap and then separated in the second column and detected with the second detector. LAZARIS[2] studied the composition of the impurities in commercial vinyl chloride obtained from the hydrochlorination of acetylene produced from calcium carbide.

We have developed a direct one-step method for the analysis of the low- and high-boiling impurities in commercial vinyl chloride, obtained both by hydrochlorination of acetylene (produced by cracking of methane) and cracking of 1,2-dichloroethane. We used tricresyl phosphate as liquid phase and a flame ionization detector, obtaining a detection sensitivity of 0.2 p.p.m. for the impurities eluted before and of some p.p.m. for those eluted after the vinyl chloride.

Experimental

The impurities listed in Table I can be found in the raw vinyl chloride produced

by the two above-mentioned processes; many of them can also be found in the corresponding commercial product, their presence depending on the effectiveness of the purification.

In the case of the impurities, the presence of which was already known, we went on to the addition of pure products and to gas chromatographic analyses on stationary phases with different polarities. In the case of other impurities, we undertook their preliminary enrichment by distillation of raw vinyl chloride, their separation from the enriched fractions by preparative gas chromatography, and their identification both by the retention times on stationary phases of different polarity and by infrared and mass spectrometry.

In order to achieve a complete separation of all the low- and high-boiling impurities in a single operation, chromatographic analyses with variable amounts of different partition liquids (dinonyl phthalate, Carbowax, triallyl citrate, Ucon, Tween 80, Epikote 828, tricresyl phosphate) on different supports were carried out using columns of different lengths and diameters.

The best results were achieved with a 10 m long column packed with tricresyl phosphate on Chromosorb P, which accomplishes the best separation between vinyl chloride, vinylacetylene and ethyl chloride. The column efficiency measured from the

TABLE I

RELATIVE RETENTION TIMES OF IMPURITIES IN VINYL CHLORIDE ON TRICRESYL PHOSPHATE

Peak No.	Component	Temperature	
		50°	35°
1	Ethane, ethylene	0.06	0.05
2	Acetylene	0.17	0.15
3	Propane	0.20	0.17
4	Propene	0.25	0.22
5	Isobutane	0.38	0.34
6	Propadiene	0.52	0.48
7	n-Butane	0.57	0.53
8	Butene-1, isobutene	0.65	0.64
9	Propyne	0.70	0.68
10	Butene-2, trans	0.85	0.77
11	Methyl chloride	1.00	0.96
12	Butadiene-1,3	1.00	1.00
13	Vinyl chloride	—	—
14	Vinylacetylene	1.94	2.05
15	Ethyl chloride	2.39	2.48
16	2-Chloropropene-1	2.79	2.91
17	Vinyl bromide	3.14	3.28
18	2-Chloropropane	3.89	4.17
19	1-Chloropropene-1, cis	4.08	4.37
20	1,1-Dichloroethylene	4.45	4.78
21	1-Chloropropene-1, trans	5.07	5.52
22	1-Chloropropane	6.23	6.88
23	Diacetylene	6.88	7.66
24	3-Chloropropene-1	6.88	8.14
25	1,2-Dichloroethylene, trans	8.48	9.60
26	Dichloromethane	9.68	11.02
27	2-Chlorobutane	10.50	12.05
28	2-Chloro-butadiene-1,3	11.18	12.85
29	1,1-Dichloroethane	12.25	14.22

1,1-dichloroethylene peak is about 6,500 theoretical plates. Working at a temperature of 50° the methyl chloride–butadiene-1,3 and diacetylene-3–chloropropene-1 pairs, which appears as a single elution peak, remain unresolved (see Fig. 1). However, even these components can be resolved and determined on performing the analysis at a temperature of 35° without varying any other parameter (see Fig. 2). As a result of the lower temperature, the separation of vinylacetylene from vinyl chloride is improved; the sensitivity of detection is almost unaffected for the components until 1,1-dichloroethylene, and becomes slightly lower for the higher boiling components.

Owing to the difficulty of handling the sample and finding a suitable internal standard, a method of direct calibration was adopted for the quantitative determination; an accurately measured and constant quantity of sample (1.5 ml) is always injected and the calibration curves of concentration (p.p.m.) vs. area are plotted by means of calibrated mixtures of the various impurities in vinyl chloride; they are linear over a wide range of concentrations.
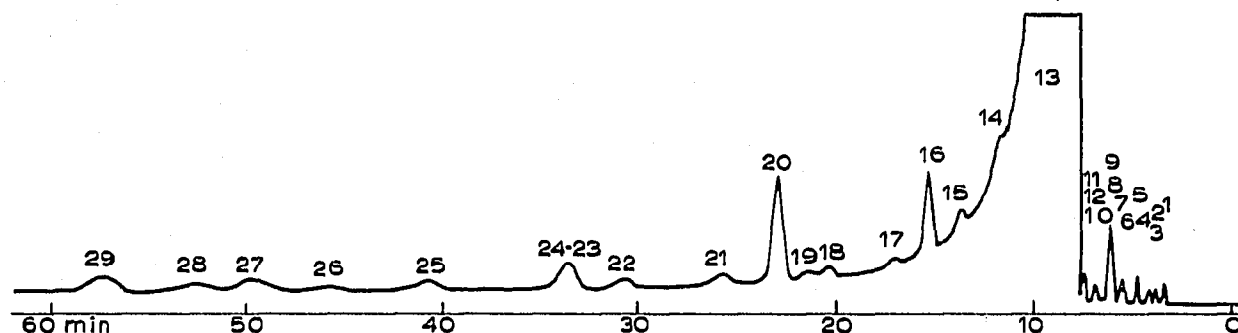

Fig. 1. Gas chromatogram of a synthetic mixture of impurities of vinyl chloride on tricresyl phosphate at 50°. The peak numbers correspond to the components reported in Table I.
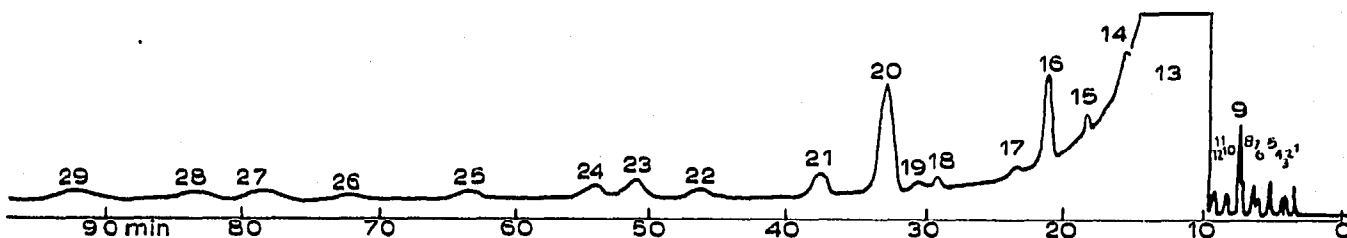

Fig. 2. Gas chromatogram of the same mixture as in Fig. 1, but at 35°.

In the impurity determination by this procedure the error is ± 10 %, which depends almost exclusively on the inaccuracy of the amount of sample injected. Table I reports the detected impurities and their relative retention times with respect to butadiene-1,3 (T_R = 1.00) at the temperature of 50° and 35°.

Fig. 3 shows the gas chromatogram of a commercial vinyl chloride obtained at 35°.

Instrumentation and operating parameters. A C. Erba Fractovap model C (type AID/f) gas chromatograph, equipped with a flame ionization detector, was used in our experiments. The recorder was a Leeds & Northrup Speedomax model G, 2.5 mV f.s., 1 sec f.s. and a chart speed of 12.7 mm/min. The gas sample (size 1.5 ml) was
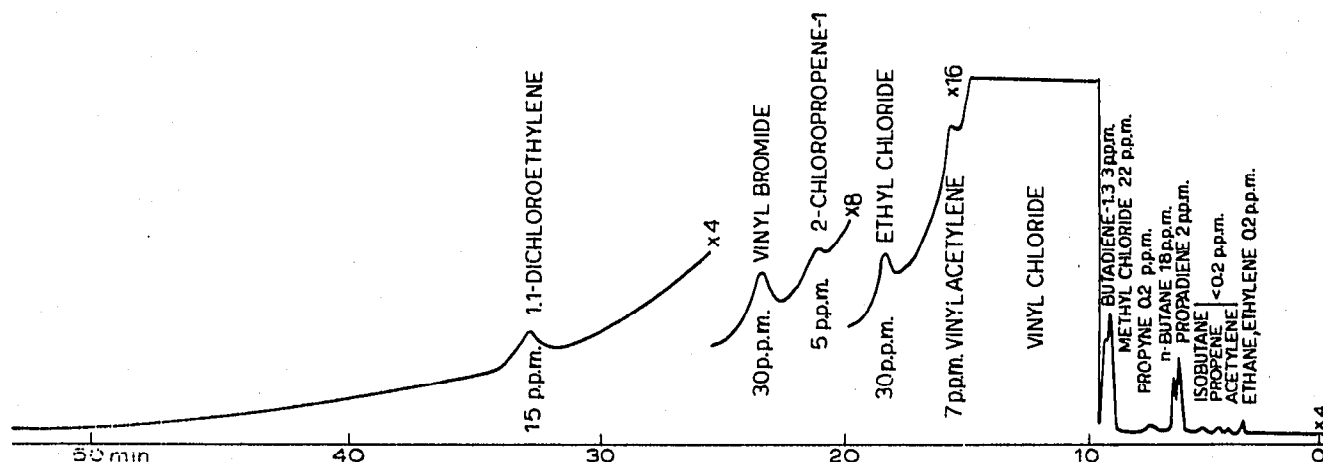
Fig. 3. Gas chromatogram of a commercial vinyl chloride, obtained at 35°.

injected with a 2.5 ml gas-tight syringe (Hamilton mod. 1002 N). The operating parameters were:

Column: 15 % (w/w) tricresyl phosphate on Chromosorb P 40–50 mesh, 10 m × 3.6 mm I.D. nylon tube (Nyloflow pressure tubing, type H, of Polypenco Inc.).

Column temperature: 50° or 35°.

Detector temperature: 120°.

Injection port temperature: 50°.

Carrier gas: nitrogen at a flow rate of 50 ml/min measured at 35°.

Hydrogen flow rate: 60 ml/min.

Air flow rate: 340 ml/min.

Sampling. The vinyl chloride is injected in gas form. The gasification of the liquid sample (at 2.5 atm at 25°) is carried out in a 500 ml glass gas-sampling tube with two tension clip stopcocks, one of which is connected to a PVC tubing closed by a Hoffman clamp. The sampling tube and the PVC tubing are evacuated by a vacuum pump, the free stopcock is cooled with dry ice and filled with liquid sample. By turning the stopcock, about 2 ml of liquid sample are allowed to enter the gas-sampling tube and thus gasify. Then the needle of the syringe is introduced into the PVC tubing, the syringe is carefully washed and afterwards 1.5 ml of sample is drawn out and injected into the gas chromatograph.

Discussion

When the gas chromatographic method suggested above is used, a practically complete separation and determination of the impurities, which can be present in a commercial vinyl chloride, is achieved in one step. This method is applicable to monomers produced both by hydrochlorination of acetylene and by cracking of 1,2-dichloroethane, thus obtaining a complete picture of the purity.

The analysis at 35° is carried out as a control of the end product, while the one at 50° could be conducted to control the various purification stages. A limitation of this method, which, however, cannot be overcome, concerns the determination of acetaldehyde and methanol. These components can be separated and determined using other stationary phases supported on Chromosorb W; but at the same time a

great number of pairs are not separated. When Chromosorb W is used as a support for tricresyl phosphate, the acetaldehyde is eluted together with vinyl bromide as a single peak and in addition the low-boiling components are not clearly separated. When Chromosorb P is used, it is eluted as an asymmetric peak between vinyl bromide and 2-chloropropane and its retention time is dependent on its concentration; furthermore, because of the effect of the adsorption on the support, the small quantities of acetaldehyde present in commercial monomers are not detectable. The same thing occurs in the case of methanol which, when Chromosorb W is used as a support and the analysis in performed at a temperature of 50°, is eluted after diacetylene as an asymmetric peak; also, because it has a smaller response to the flame ionisation detector than acetaldehyde, it can only be detected if it is present in an even greater quantity.

The sample was injected with a gas-tight syringe and not with a gas-sampling valve (which would have given a better reproduction of the quantity injected) because the latter has the greater dead spaces which cause a larger band spreading of the sample so that the separation efficiency results decreased. On the other hand, when the sample is injected with the syringe the reproducibility of the quantity injected is lower. The greatest error obtained, which is ± 10 % and can be almost exclusively attributed to the operator and to the type of syringe used, is acceptable due to the low contents to be determined.

In order to reduce the troubles at the detector which are due to the corrosion caused by HCl (produced by the combustion of the vinyl chloride) the detector was constructed in Hastelloy C and Teflon; but even normally constructed commercial detectors can be used since corrosion can be reduced to a negligible level by means of thorough and periodic cleaning.

An analysis time of 36 min at 50° and of 52 min at 35° (which corresponds to the elution time of diacetylene) is sufficient for the analysis of a commercial monomer of medium purity.

The reproducibility of the retention times is excellent; even after a year of continuous use of the column no appreciable variation was noticed.

At present the method offers the following main advantages: simplicity and facility of analysis (even by not particularly experienced personnel), high speed performance, and good separation of practically all the impurities present in vinyl chloride.

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1 L. Mikkelsen and S. Spencer, in H. A. Szymansky (Editor), *Lectures on Gas Chromatography—1962*, Plenum Press, New York, 1963.
2 A. Ya. Lazaris, *Neftekhimija*, 5, No. 1, (1965) 166.