

# DIRECT GAS CHROMATOGRAPHIC DETERMINATION OF PROPIONYL CHLORIDE

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With the use of a carrier gas dried on phosphorus pentoxide, propionyl chloride was determined directly on two columns packed with Kel-F Wax 10/200 or "Aroclor 1232" and squalane partition liquids on polytrifluoroethylene support. The relative retention referred to acetone is given not only for propionyl chloride, but also for  $C_1$  and  $C_2$  hydrocarbons, chlorine, phosgene, propionaldehyde, etc.

## Introduction

Authors in general recommend indirect procedures for the gas chromatographic determination of the highly reactive acid chlorides. In the majority of these procedures the determination is based on the measurement of the free acid or of an ester. These methods could not be employed for the analysis of our systems, which contain besides propionyl chloride also hydrogen chloride, chlorine, ethyl chloride, etc.

Very few publications dealing with the direct determination of acid chlorides are to be found in the literature.

WASSECIAK and NADEAU [1] separated acetyl chloride from various esters on a "DC 550" silicone oil/Chromosorb-W column. However, this procedure was developed for the quantitative determination of ethers only.

SIMONAITIS and GUVERNATOR [2] reported their experimental findings in work aimed at the direct analysis of acid chlorides. A "Teflon 6" column covered with 10 wt.% Carbowax 20 M-Terephthalic acid was used. The quantitative determination of decanoyl chloride could not be achieved on this column: it was found that when the flow rate of the helium carrier gas was decreased from 100 to 60  $\text{cm}^3 \cdot \text{min}^{-1}$  the acid chloride peak was deformed to such an extent that its area increased by a factor of about 2.5 and in addition a pre-peak appeared. The phenomenon was

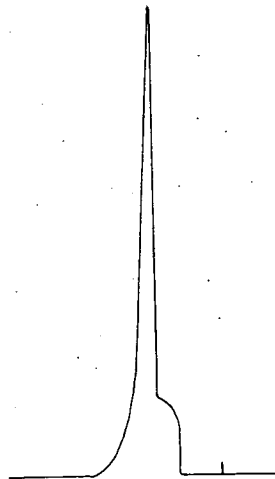


Fig. 1.

explained with the hydrolysis of the acid chloride by the water bound on the column.

Using nitrogen dried with silica gel as carrier gas, we obtained results similar to those of SIMONAITIS and GUVERNATOR in the analysis of propionyl chloride with 20 wt.%  $\beta$ ,  $\beta'$ -oxydipropionitrile or 20 wt.% Kel-F Wax 10/200 columns on Chromosorb W support dried in vacuum at 150°C (see Fig. 1). This disturbing effect disappeared when the silica gel used to dry the carrier gas was replaced by phosphorus pentoxide. When the carrier gas dried in this manner was employed, propionyl chloride showed up in the form of its customary peak in the chromatogram. This proved that the water content of the carrier gas was responsible for the hydrolysis of the acid chloride. Because of the strong adsorptivity of the support, columns packed with Chromosorb W were not suitable for the analysis of acid chlorides even after phosphorus pentoxide drying.

KROSCWITZ, BALLA and TAKÁCS [3] too determined various acid chlorides directly in argon carrier gas on a column packed with 1.2 wt.% SE 30 on sodium chloride support.

### Experimental

A gas chromatograph consisting of glass U-columns, Pye electric units and a Pye thermal conductivity detector was used with a 2 mV recorder.

The carrier gas was hydrogen dried with phosphorus pentoxide; its flow rate was varied between 25 and 90 cm<sup>3</sup>·min<sup>-1</sup>. The results in this publication refer to a column temperature of 56°. The temperature of the detector was 57°.

### Columns

Compounds used for gas chromatography were products of Carlo Erba.

#### a) "Kel-F" column

This was an 8.4 m long glass column with an internal diameter of 4 mm, charged with 3.3 wt.% Kel F-Wax 10/200 on polytrifluoroethylene support (because of its low wettability) having a particle size of 30–100 mesh.

#### b) "Aroclor" column

This was a column 6.8 m in length and 3 mm in internal diameter, charged with 2 wt.% "Aroclor 1232" and 0.1 wt.% of squalane on polytrifluoroethylene support.

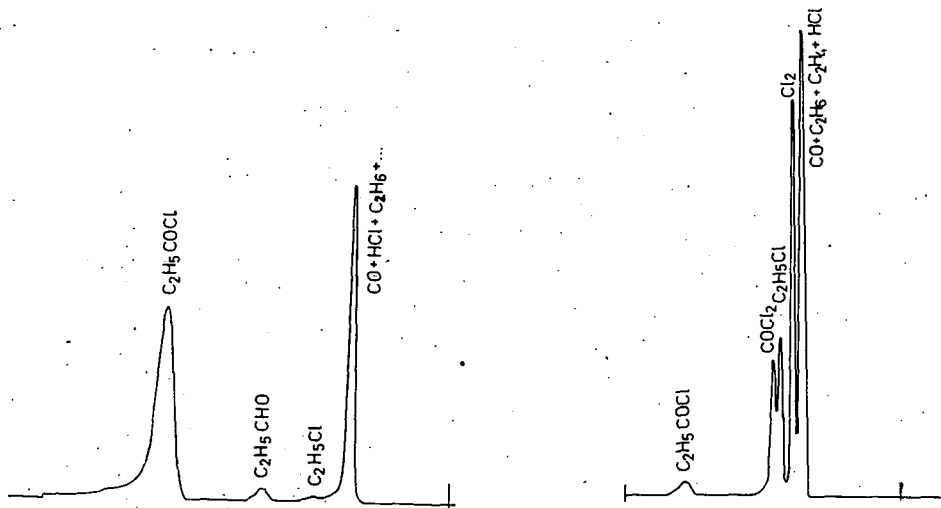
### Results

With a carrier gas dried with phosphorus pentoxide, the above columns can be used for the direct qualitative and quantitative determination of propionyl chloride. By measuring the height of the peak it was possible to determine propionyl chloride samples containing  $5 \times 10^{-6}$  to  $5 \times 10^{-7}$  mole with an error of 5%.

A study was made of the separation of propionyl chloride, its decomposition products and other substances on the two columns. The retention data for the individual compounds were determined by applying the pure components individually and in mixtures. The data obtained are presented briefly below in order to illustrate the separation of different components on the two columns, and the chromatograms of some mixtures of different compositions are also given.

a) *Kel-F Wax—polytrifluoroethylene column*

Under the experimental conditions employed the  $C_1$  and  $C_2$  hydrocarbons (methane, ethane, ethylene) were not separated on the column; indeed, they appeared in a common peak together with carbon monoxide and hydrogen chloride. The



Figs. 2a, 2b

separation of chlorine from this peak was comparatively good. The peaks of phosgene and ethyl chloride were strongly superimposed. The column barely distinguished between propionaldehyde and acetone. Methyl ethyl ketone, diethyl ketone and propionic acid appeared as separate peaks after the propionyl chloride peak in the chromatogram. These results are illustrated in Figs. 2a and 2b.

The relative retentions referred to acetone and calculated from the net retention volumes are given in Table I.

At the temperature employed propionic acid exhibited a very long retention time and is therefore not included in the Table. In these experiments the flow rate of the carrier gas was  $90 \text{ cm}^3 \cdot \text{min}^{-1}$ .

b) *Aroclor 1232—polytrifluoroethylene column*

On this column the common peak of the  $C_1$  and  $C_2$  hydrocarbons and carbon monoxide is slightly separated from that of hydrogen chloride, but butane can not be distinguished from chlorine. In contrast with the previous column, propionaldehyde

Table I

Relative retentions on "KEL-F" column

Substance	Relative retention
Methane	0.01
Ethane	0.01
Ethylene	0.01
Hydrogen chloride	0.01
Chlorine	0.17
Ethyl chloride	0.32
Phosgene	0.44
Propionaldehyde	0.91
Acetone	1.00
Propionyl chloride	-1.70
Methyl ethyl ketone	2.35
Diethyl ketone	5.34

appeared separately from acetone, but phosgene and ethyl chloride yielded a common peak. The relative retentions referred to acetone and measured at a carrier gas flow rate of  $25 \text{ cm}^3 \cdot \text{min}^{-1}$  are given in Table II.

Table II  
Relative retentions on  
„Aroclor” column

Substance	Relative retention
Carbon monoxide	0.00
Methane	0.00
Ethane	0.00
Ethylene	0.01
Hydrogen chloride	0.05
Butane	0.12
Chlorine	0.13
Vinyl chloride	0.15
Phosgene	0.29
Ethyl chloride	0.30
Propionaldehyde	0.63
Acetone	1.00
1,1-Dichloroethane	1.17
Propionyl chloride	2.13
1,2-Dichloroethane	2.73

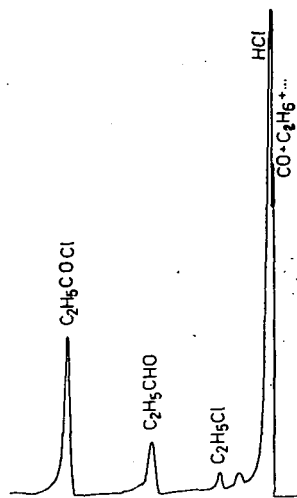


Fig. 3

Peak 3 was not identified in the chromatogram of Fig. 3, which illustrates the above findings.

The two columns described here are also suitable for the determination of other organic acid chlorides, provided that special care is devoted to the drying of the carrier gas.

#### References

- [1] Wasseciak, P., H. G. Nadeau: *Anal. Chem.* **36**, 764 (1964).
- [2] Simonaitis, R. A., G. C. Guvernator: *J. Gas Chromatog.* **5**, 527 (1967).
- [3] Kroschwitz, H., J. Balla, J. Takács: Lecture at Second Chromatographic Congress, Szeged, 11—14 September, 1972.

#### НЕПОСРЕДСТВЕННОЕ ГАЗО-ХРОМАТОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПРОПИОНИЛ-ХЛОРИДА

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Непосредственное определение хлорангидрида пропионовой кислоты проводили на двух колоннах с политрифторэтиленовым носителем и с „Kel-F Wax 10/200” и „Aroclor 1232 + squalan” неподвижными фазами соответственно, с применением газа-носителя, высушенного над фосфорным ангидридом. Кроме определения хлорангидрида пропионовой кислоты даны относительные времена элюции по ацетону для ряда других веществ:  $\text{C}_1$ ,  $\text{C}_2$  углеводородов, хлора, соляной кислоты, этилхлорида, фосгена, пропионового альдегида и. т. д.