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## Note

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### Determination of impurities in thionyl chloride by gas chromatography

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The purity of thionyl chloride has been evaluated by such methods as argentometry, alkalimetry and iodimetry [1–3], but the results characterize only approximately the content of the main component. More complex chemical reactions have been used for the determination of impurities in thionyl chloride [4]. However, these procedures are time consuming and difficult to implement as routine methods.

Quality requirements for analytical-reagent grade thionyl chloride [5] include limits on impurities such as sulphur dioxide and sulphur monochloride, determined by gas chromatography (GC), but no details of the procedure are available.

In quality requirements for technical thionyl chloride [6] the following impurities appear:  $\text{SO}_2$ ,  $\text{SO}_2\text{Cl}_2$ ,  $\text{S}_2\text{Cl}_2$  or  $\text{SCl}_2$  and  $\text{CCl}_4$ ; as an analytical method GC [7] has been mentioned and the separation of thionyl chloride from sulphuryl chloride has been presented [7]. It was achieved by using a hot-wire detector and a column packed with DC-200 silicone on Chromosorb W AW, but sulphuryl chloride underwent some decomposition. Such decomposition was negligible if fluorine-containing stationary phases, such as Kel F No. 3, were used; no analysis of impurities in thionyl chloride was described.

A glass column containing the nitrile-silicone rubber XE 60 on Khezasorb AW-HMDS at 70°C and a hot-wire detector have been used for the determination of  $\text{Cl}_2$ ,  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_3$ ,  $\text{SOCl}_2$ ,  $\text{POCl}_3$  and  $\text{S}_2\text{Cl}_2$  as impurities [8] in  $\text{AsCl}_3$ . Determination of impurities in thionyl chloride by gas GC has been mentioned in connection with the performance of lithium batteries [9]. Volatile halide compounds, including hydrogen chloride and thionyl chloride, were separated on an SP-2100 column and detected in the effluents by using a chloride-sensitive electrode [10].

In this paper, the determination of impurities in thionyl chloride by GC is described. The method allows hydrogen chloride, chlorine, sulphur dioxide, sulphur dichloride, sulphuryl chloride and sulphur monochloride to be separated from thionyl chloride. The method was used in the analytical control of the purification of thionyl chloride. Samples containing up to 99.5% of thionyl chloride were analysed.

## EXPERIMENTAL

A Chromatron GCHF 18.3 gas chromatograph with a hot-wire detector was used. The inside of the detector cell and the filaments were gold plated by wetting with a benzene solution of an organic gold complex (Gold Paint ZS-10B, Poland) and heating at 450°C for 3 h.

Two columns (2 m × 3 mm I.D.) were used. The glass column was packed with Chromosorb W HP (100–120 mesh) coated with 10% trifluoropropylsilicone OV-210 (Applied Science Labs.). The PTFE column had the same Chromosorb support but was coated with 9% benzyldiphenyl (for GC, May and Baker).

Hydrogen was used as the carrier gas at a flow-rate of 30 ml/min. Before entering the column the hydrogen was dried by passing it through silica gel and molecular sieve 4A filters. The OV-210 column was conditioned at 200°C and the benzyldiphenyl column at 100°C. To improve their efficiency, small volumes of thionyl chloride were injected five times onto the columns followed each time by complete elution at the conditioning temperature. The bridge current was 200 mA and the chart speed 0.33 cm/min.

Volumes of 2–5  $\mu$ l of the thionyl chloride samples were injected using a syringe with a 7-cm long needle, thus making on-column injection possible. For small amounts of impurities peaks were recorded at the lowest signal attenuation; for the thionyl chloride peak the attenuation was suitably increased to permit calculation by internal normalization.

Larger amounts of HCl or SO<sub>2</sub> could be determined by using the external standard method. Suitable standard solutions were prepared by bubbling pure HCl or SO<sub>2</sub> (Merck) through benzene and by subsequent dilution, if necessary, to concentrations of 0.1–0.3 wt.% determined by alkalimetric titration.

For identification of peaks, chromatograms of commercial thionyl chloride samples were recorded and the retention times were measured. Small amounts (*ca.* 0.2–1.0%) of substances known to be possible impurities were added successively to samples and the chromatograms were recorded again. An increase in the peak height indicated its identity. The presence of phosphorus oxychloride was confirmed by determination of PO<sub>4</sub><sup>3-</sup> after oxidation with nitric acid.

TABLE I

RETENTION TIMES RELATIVE TO THIONYL CHLORIDE ON OV-210 AND BENZYL-DIPHENYL COLUMNS

No.	Compound	OV-210 column	Benzyldiphenyl column
1	"Air"	0.18	0.06
2	Hydrogen chloride	0.18	0.09
3	Chlorine	0.18	0.09
4	Sulphur dioxide	0.22	0.13
5	Sulphur dichloride	0.50	0.49
6	Sulphuryl chloride	0.51	0.58
7	Thionyl chloride	1.00	1.00
8	Phosphorus oxychloride	2.90	1.42
9	Sulphur monochloride	1.82	5.53

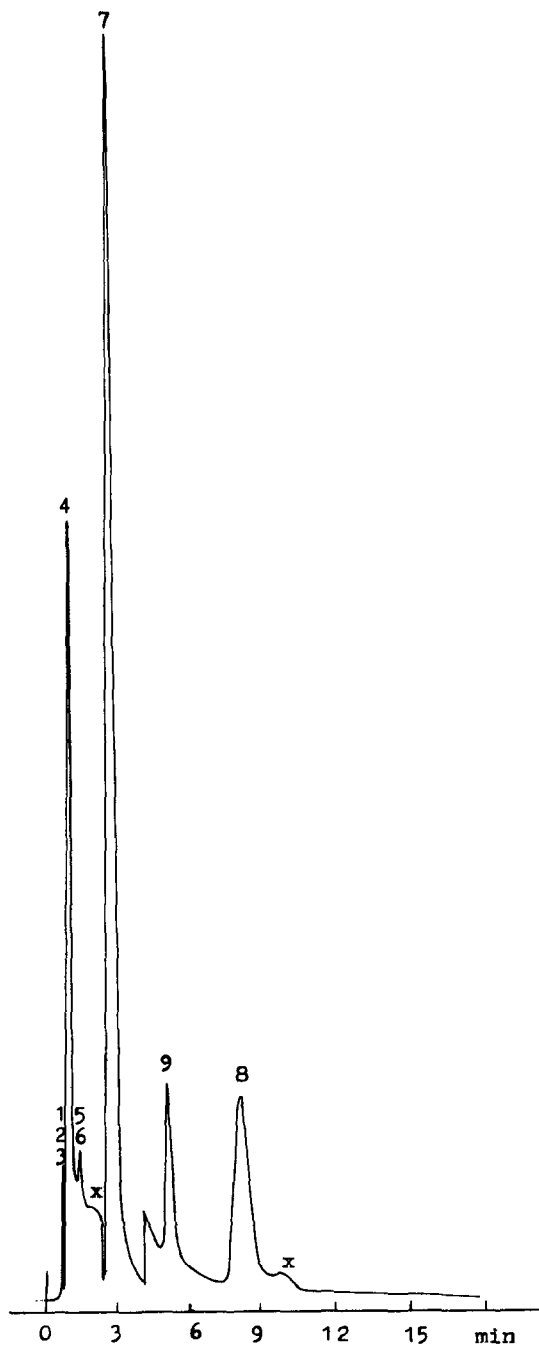


Fig. 1. Gas chromatogram of a technical thionyl chloride sample with *ca.* 0.6% sulphur monochloride added, OV-210 column. Sample: 3  $\mu$ l. Attenuation 1 for impurities and 16 for thionyl chloride. Peaks numbered according to Table I; x = unknown.

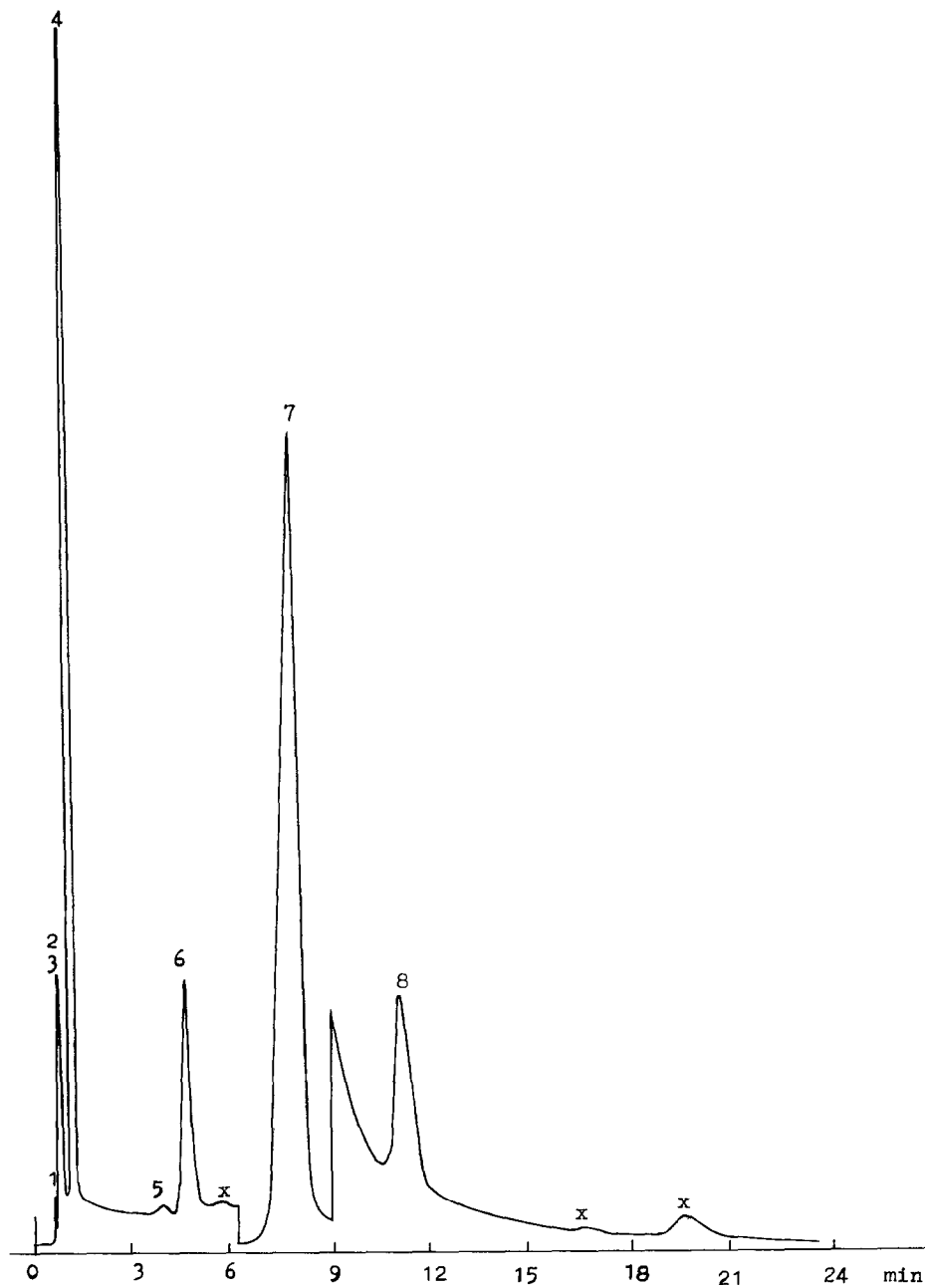


Fig. 2. Gas chromatogram of a technical thionyl chloride sample before purification. Purity determined: 96.4%. Benzylidiphenyl column. Sample: 2.5  $\mu$ l. Attenuation 1 for impurities and 16 for thionyl chloride. Peaks numbered according to Table I; x = unknown.

## RESULTS AND DISCUSSION

Both technical thionyl chlorides (products made in G.D.R.) and the products after purification (made in another department of this institute) were analysed. The GC apparatus and conditions, especially the use of a gold-plated detector and a PTFE column and the temperatures (as indicated under Experimental), provided minimal thionyl chloride decomposition, which may occur to some extent near its boiling point [6,11].

The retention times of the identified impurities relative to thionyl chloride are given in Table I. The total retention time of thionyl chloride on the benzyldiphenyl column was 15 min and the relative retention time of benzene on that column was 0.57. Table I shows that the resolution of peaks on the benzyldiphenyl column was better than that on the column with OV-210, which is similar to the FS 1265 phase reported [7] for sulphur oxyhalogens separation. By using the benzyldiphenyl column it was

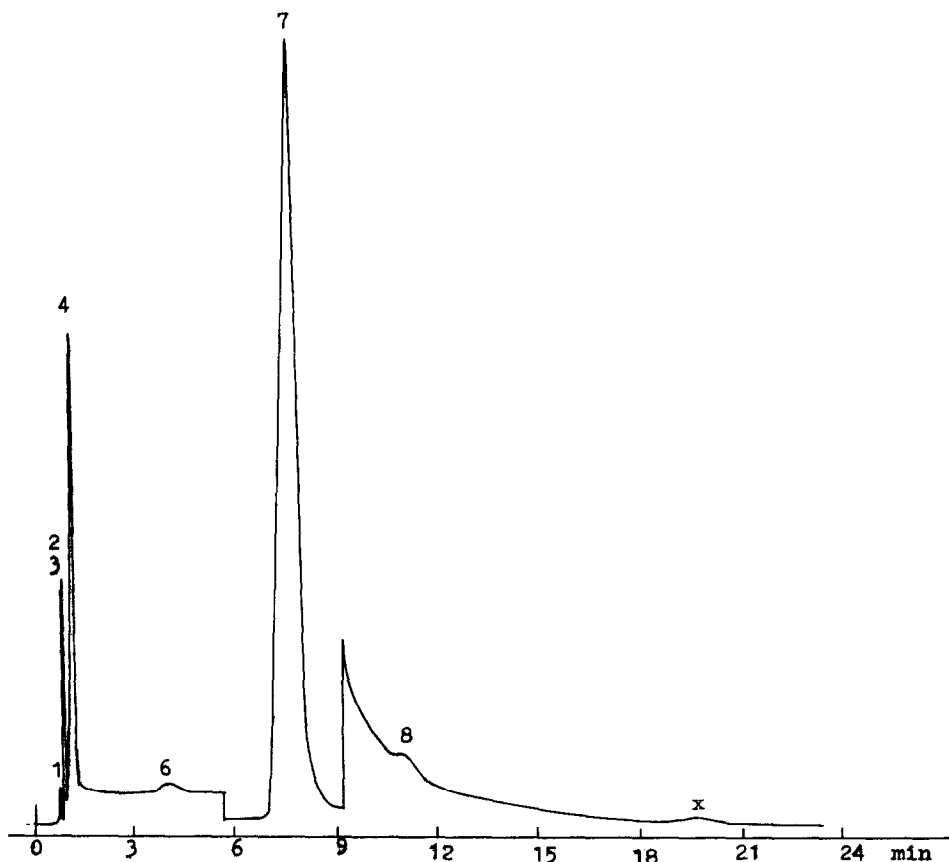


Fig. 3. Gas chromatogram of a technical thionyl chloride sample after purification. Purity determined: 99.2%. Benzyldiphenyl column. Sample: 2.5  $\mu$ l. Attenuation 1 for impurities and 16 for thionyl chloride. Peaks numbered according to Table I; x = unknown.

possible to separate hydrogen chloride from air and sulphur dichloride. The retention time of sulphur monochloride is relatively long but its presence can be detected from a chromatogram on the OV-210 column. A chromatogram of a technical thionyl chloride sample with added sulphur monochloride is shown in Fig. 1.

Chromatograms recorded for two thionyl chloride samples (before and after purification) are shown in Figs. 2 and 3. Phosphorus oxychloride was probably a by-product from the synthesis of thionyl chloride. Sulphur monochloride was not detected in the samples analysed.

In practice, taking into account the kind of chromatograph used, the detection limit of the gaseous impurities was about 0.005% and that of the heavier liquid impurities was about 0.01%. The relative standard deviation of the thionyl chloride determination ( $n = 5$ ) was 0.15% for samples of purity *ca.* 99%.

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