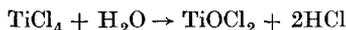


The application of infra-red spectroscopy to the analysis of titanium tetrachloride

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Abstract—A technique for determining a number of impurities in titanium tetrachloride by means of the infra-red absorption spectra has been developed. It has been established that the partial hydrolysis of titanium tetrachloride proceeds according to the scheme:



THE requirements imposed on the purity of titanium intended for production are very high, since its properties depend strongly on small quantities of impurities. The chemical and physicochemical methods of analysis used at the present time do not permit one to perform a complete examination of all the impurities in titanium tetrachloride which is an intermediate product of the manufacture of the metal. To analyse titanium tetrachloride for many impurities and to determine their molecular nature it is most convenient to use the method of infra-red absorption spectroscopy. In [1] the possibility of quantitative determination of some impurities in titanium tetrachloride from the infra-red absorption spectra is indicated and the spectrum of pure titanium tetrachloride in the 2–15 μ region is reproduced and its approximate interpretation is given. In [2] the possibility of spectrochemical, spectrophotocchemical and cryoscopic methods of analysis are also examined. The values of the natural vibration frequencies of the titanium tetrachloride molecule lie in the far infra-red region of the spectrum and therefore pure titanium tetrachloride possesses good transparency in a wide range of frequencies. This produces high sensitivity of analysis for many impurities and offers the possibility of building instruments for continuous inspection in a stream of liquid. The aim of the present work was to study the molecular composition of the various impurities in titanium tetrachloride and to develop methods of quantitatively determining them by means of infra-red absorption spectra.

The work was carried out on single-beam IKS-6, IKS-12 and Perkin-Elmer 12B spectrometers with lithium fluoride prisms in the range 1800–3600 cm^{-1} and sodium chloride prisms in the range 700–1850 cm^{-1} .

In the infra-red spectra of different samples of technical titanium tetrachloride, a large number of absorption bands belonging to organic and inorganic impurities were discovered. The most characteristic of these were HCl, TiOCl_2 , VOCl_3 , COCl_2 , C_6Cl_6 , CCl_3COCl , CHCl_2COCl , $\text{CH}_2\text{Cl.COCl}$, SiCl_4 . In some samples a number of bands in the vibration regions of the CH and OH groups belonging to compounds of unknown composition were observed.

[1] R. B. JOHANNESSEN, C. L. GORDON, J. E. STEWART and R. GILCHRIST, *J. Res. Nat. Bur. Standards* **53**, 197 (1954).

[2] W. S. CLABAUGH, R. T. LESLIE and R. GILCHRIST, *J. Res. Nat. Bur. Standard* **55**, 261 (1955).

In order to develop the techniques of analysing titanium tetrachloride quantitatively for the main impurities, the spectra of standard solutions of these substances in pure titanium tetrachloride were obtained. The calibration graph for all the cases has the form of a straight line and consequently the Lambert-Beer law is obeyed in the interval of concentrations studied. In Table 1, the absorption coefficients and analytical sensitivities for the impurities studied are quoted. Special attention was paid to the development of techniques for quantitatively determining the products of the hydrolysis of titanium tetrachloride, which in

Table 1

Impurity	Absorption band (cm^{-1})	Absorption coefficient (cm^{-1})	Sensitivity, (weight %)
HCl	2830	30.0	0.0002
TiOCl ₂	821	426.0	0.00001
	1184	4.3	0.0008
	1356	5.5	0.0006
	2061	1.15	0.004
VOCl ₃	2061	1.15	0.004
COCl ₂	1654	9.2	0.0015
	1812	110.0	0.0002
	1301	20.3	0.0005
C ₆ Cl ₆ CHCl ₂ COCl	1779	60.7	0.0001
	1809	61.0	0.0001
	1802	95.0	0.00006
CCl ₃ COCl CH ₂ ClCOCl	1785	23.3	0.0002
	1820	86.0	0.00005
	2338	164.0	0.00008
CO ₂	2338	164.0	0.00008

turn required the investigation of the mechanism of its partial hydrolysis. There are indications that the hydrolysis of titanium tetrachloride proceeds by two routes with the formation of oxychlorides and hydroxychlorides of titanium. In the spectra of solutions of small quantities of light and heavy water in titanium tetrachloride no bands due to OH and OD valency vibrations were found, which permits one to draw the conclusion that the hydrolysis process proceeds with the formation of oxychlorides of the Ti—O—Ti or Ti=O type and not of hydroxychlorides, in agreement with the results of the authors of reference [1]. In the spectra of these solutions bands were discovered at 821, 1184 and 1356 cm^{-1} , the frequencies being independent of the isotope composition and the intensity increasing with the quantity of water introduced into the titanium tetrachloride. Since the Ti—O—Ti group according to the results in reference [3] corresponds to two bands in the 750–850 cm^{-1} region there are no justifications for thinking that compounds of this type are formed in this case. An approximate estimate of the force constant of the Ti=O bond from GORDY'S [4] formula (for the parameter r_{TiO} , the TiO distance in rutile of 1.96 Å was taken) gives the value of 825 cm^{-1}

[3] V. A. ZEITLER and C. A. BROWN, *J. Phys. Chem.* **61**, 1174 (1957).

[4] W. GORDY, *J. Chem. Phys.* **14**, 305 (1946).

for the vibration frequency of the Ti=O group, which almost coincides with the experimental value of 821 cm^{-1} . The high intensity of the 821 cm^{-1} band also supports this interpretation. From the results of chemical analysis the ratio of the quantities of Ti and Cl in the product of the hydrolysis of titanium tetrachloride is equal to 1:2, while ebullioscopic measurements of its molecular weight give a value close to 135 [5]. On these grounds one may draw the conclusion that in excess of titanium tetrachloride its hydrolysis proceeds according to the scheme:



To develop the technique of analysing TiCl_4 for HCl, the preparation of standard solutions was carried out by introducing known quantities of water into pure TiCl_4 breaking ampoules containing water situated in a sealed flask containing TiCl_4 . The concentration of hydrogen chloride was calculated by starting from the quantity of water introduced in accordance with equation (1). To estimate small quantities of titanium oxychloride in titanium tetrachloride up to 0.05 per cent the 821 cm^{-1} band is more convenient since it is approximately a hundred times more intense than the two other bands. At concentrations of 0.05–0.5 per cent the 1356 cm^{-1} band is more convenient than the 1184 cm^{-1} band since the latter masks the bands of other impurities. However, in the case of the presence of hexachlorobenzene, which has a band at 1351 cm^{-1} , the 1184 cm^{-1} band has to be used for analysis.

In the spectra of technical samples of titanium tetrachloride were observed two absorption bands characteristic of VOCl_3 , one at 1035 cm^{-1} belonging to the fundamental valency vibration of the VO group and the other at 2061 cm^{-1} corresponding to the first overtone of this vibration [1, 6]. The overtone band was chosen for analytical purposes since a strong titanium tetrachloride band superimposes on the 1035 cm^{-1} band. The analytical sensitivity with this band is not high but it is sufficient for practical purposes.

Two analytical bands were chosen for the determination of phosgene, viz. the valency vibration of the carbonyl group at 1812 cm^{-1} and a band at 1654 cm^{-1} belonging to the first overtone of the antisymmetric valency vibration of the CCl_2 group. The authors of reference [1] recommend the 1812 cm^{-1} band for analysis but it is convenient to use it in those cases where chlorine-substituted acetyl chlorides, the carbonyl bands of which superimpose on the 1812 cm^{-1} phosgene band, are not present in the TiCl_4 . Of other organic impurities in titanium tetrachloride, hexachlorobenzene was found; in the spectrum of this, two intense absorption bands at 1301 and 1351 cm^{-1} are observed. The 1301 cm^{-1} band was chosen for analysis since the band at 1351 cm^{-1} is almost always masked by the titanium oxychloride band at 1356 cm^{-1} . In the spectrum of the solution of carbonic acid gas in titanium tetrachloride one maximum with a frequency of 2338 cm^{-1} , which was used for quantitative analysis, is observed.

In reference [1] the impossibility of simultaneously determining mono-, di- and tri-chloroacetyl chloride in titanium tetrachloride from the valency vibration band

[5] T. A. ZAVARITSKAIA and S. S. PUSTOVALOVA, *Tsvetnye metal* **10**, 50 (1958).

[6] F. A. MILLER and L. R. COUSINS, *J. Chem. Phys.* **26**, 329 (1957).

of the carbonyl group is pointed out, since this has the same frequency of 1802 cm^{-1} for all three molecules. The investigations of the spectra of solutions of chloracetyl chlorides in titanium tetrachloride carried out by us showed that only in the case of trichloroacetylchloride does the position of the maximum of the band of the carbonyl group coincide with the values given, while in the case of both mono- and di-chloroacetylchloride the bands have two maxima, viz. at 1785 and 1820 cm^{-1} , 1779 and 1809 cm^{-1} , respectively. Depending on the conditions of analysis it is possible to use any of the bands indicated for the simultaneous determination of chloroacetyl chlorides in titanium tetrachloride (see also [7]).

The analysis error in the determination of the impurities in titanium tetrachloride enumerated does not exceed 8–10 per cent.

The use of infra-red spectroscopy for the analysis of titanium tetrachloride permitted one to check the purification process and also to decide a number of questions concerning the preparation of titanium. In addition, it proved possible to determine the solubility of certain gases (HCl , CO_2 , COCl_2) at various temperatures by means of this method.

[7] L. J. BELLAMY and R. L. WILLIAMS, *J. Chem. Soc.* 3465 (1958).