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To cite this article: B Yang *et al* 2015 *IOP Conf. Ser.: Mater. Sci. Eng.* **103** 012027

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Infrared spectroscopy for a quantitative determination of $\text{CH}_{3-n}\text{Cl}_n\text{COCl}$ in TiCl_4

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Abstract. Infrared spectroscopy permits a determination of the concentration of CHCl_2COCl , CH_2ClCOCl and CCl_3COCl as the organic impurities in TiCl_4 . In this study, an infrared spectrometer with ZnSe window and the cell of PTFE was assembled, and used to determine the concentration of three organic impurities. The detection limits of CCl_3COCl , CHCl_2COCl , CH_2ClCOCl were determined as 3.16×10^{-3} $\mu\text{g/g}$, 1.92×10^{-3} $\mu\text{g/g}$ and 1.55×10^{-2} $\mu\text{g/g}$ respectively. The new method is applied to quality control of refined TiCl_4 from titanium sponge.

1. Introduction

Titanium is a transition metal with various excellent properties, such as low density and high corrosion resistance. Titanium sponge is important for titanium manufacture [1]. An enrichment correlation presented among the impurities in Titanium sponge and that in fine TiCl_4 . Therefore, the impurities of TiCl_4 are the key of titanium quality control [2]. The composition and content of impurities are analyzed quickly and quantitatively to removal of impurities $\text{CH}_{3-n}\text{Cl}_n\text{COCl}$ (CCl_3COCl , CHCl_2COCl , CH_2ClCOCl) during the production of Titanium sponge. The quality control standard of TiCl_4 is strict in Japan, America and Russia, organic compound was determined by infrared spectral analysis, besides the determination of inorganic compound like As, Sb, Si, Cl, Al, Cu, Fe, Pb, V, Ni and Sn [3-6]. At present, the general determination of impurities in domestic titanium industry just includes SiCl_4 , FeCl_3 , VOCl_3 , and chromaticity analysis [7]. The lack of effective determination method of organic impurities (CCl_3COCl , CHCl_2COCl , CH_2ClCOCl) reduces the products' hardness. However, CCl_3COCl in fine TiCl_4 was determined by infrared semi-quantitative method [8-9] and Fourier-transform infrared spectroscopy (FT-IR) [10].

SiCl_4 , FeCl_3 and VOCl_3 are the main impurities in fine TiCl_4 . It did not have any other interference to the determination of $\text{CH}_{3-n}\text{Cl}_n\text{COCl}$ due to they are inorganic compounds. FT-IR cannot detect the peak of Fe and Si since the different bond vibration compared to organic compound. Since TiCl_4 and $\text{CH}_{3-n}\text{Cl}_n\text{COCl}$ undergone rapid hydrolysis in the presence of moisture, an infrared liquid cell is damaged, and the results can be influenced. Therefore, a new liquid cell is designed with good tightness and adaptive thickness. Many other IR transparent inert solid window materials for liquid cells are known – some are cheaper and established. A superior waterproofness is the reason for the choice of ZnSe. It is safe, simple, easy removable, washable and reusable. Spiking method or standard addition [11] was done to determine the trace organic impurities due to the content of organic

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impurities are quite low in TiCl_4 .

FT-IR quantitative analysis was based on absorption strength and it was able to quantify the gas, solid and liquid sample. In the same time, the component of mixture was calculated through the characteristic peak. Therefore, it was able to determine the infrared spectrum of the mixtures by FT-IR without pre-processing. And this measurement method was convenient, visible and quickly with several calculation method. In the study, the component of fine TiCl_4 was determined by the Standard addition method.

2. Experimental procedure

2.1. Instrument and reagents

Reagents Titanium tetrachloride was purchased from Zunyi Titanium Company (Guizhou, China), Chloroacetyl chloride, Dichloroacetyl chloride and trichloro-acetic chloride were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Aladdin, dry calcium chloride, absolute ethyl alcohol are purchased from Shanghai Chemical Company.

A Thermo (IR 200) FT-IR was used in the experiment, and it connected with a spectrophotometer operated at a resolution of 4 cm^{-1} . Thirty-two scans were scanning to improve the signal-to-noise ratio.

2.2. IR liquid cell

Make sealed IR liquid cell for avoiding TiCl_4 reacts vigorously with moisture. It is made of a Teflon body, a window of ZnSe ($25\text{ mm} \times 2\text{ mm}$, $7800\sim 440\text{ cm}^{-1}$) and soft Teflon gaskets. Filling the TiCl_4 from these cells into the atmosphere was also found to be a troublesome process for routine analysis. Hence, this IR cell was fabricated. Structure and practicality chart of IR seal cell showed below (figure 1).

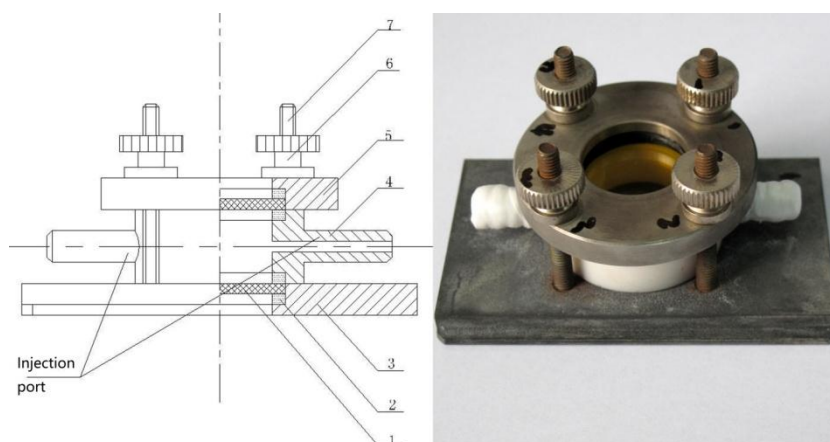


Figure 1. Structure and practicality chart of assembled infrared seal pool.

2.3. Sample preparation

Organic impurities mixture standard stock: Addition of $5\text{ }\mu\text{L}$ CCl_3COCl (98%), $9\text{ }\mu\text{L}$ CHCl_2COCl (98%), $45\text{ }\mu\text{L}$ CHClCOCl (98%) to a 20 mL flask, and dilute it to 20 mL .

Organic impurities mixture standard correction: addition of 150 , 180 , and $200\text{ }\mu\text{L}$ standard stock to a 20 mL flask respectively, and then diluted to 20 mL . The content of CH_2ClCOCl , CHCl_2COCl , and CCl_3COCl are $0.857 \times 10^{-3} \sim 2.143 \times 10^{-2}$, $1.714 \times 10^{-3} \sim 4.286 \times 10^{-3}$, $0.952 \times 10^{-4} \sim 2.381 \times 10^{-3}\text{ mg/g}$. These solutions were used as calibration.

Determination of organic impurities: The background was scanned while dry nitrogen flow through it at one end and seal the other end with PTFE; then the air tightness was checked by the soap bubble. Injection of 7 mL of organic impurities mixture standard correction and TiCl_4 to a vacuum IR liquid cell and the infrared spectrum was determined. The mass fraction of organic impurities in TiCl_4 was

calculated by standard addition or spiking method.

2.4. Air tightness test

One end of assembled infrared pool sealed with soft silicone rubber, and dry nitrogen was poured into the pool from the other end, then checked tightness with soap bubbles.

2.5. Overlapping peak resolve

The peak of $\text{CH}_3\text{-nCl}_n\text{COCl}$ was processed by OMNIC software. Set all the parameters and choose the peak position. Then the peaks were separated and it was convenient to quantify the three organic compounds.

3. Results and discussion

3.1. Stability test of IR liquid cell

An organic impurities standard calibration was added to IR liquid cell. And we recorded the absorbance of CCl_3COCl , CHCl_2COCl and CH_2ClCOCl in vacuum space every day for 7 days, and then calculate the content of each impurity. The determination result showed that no obvious difference on organic impurities content with the increase of storage period, and all RSD is less than 10%. It indicated this infrared liquid cell presented a superior inertia and seal.

3.2. Precision test

Table 1 indicated the content of CH_2ClCOCl , CHCl_2COCl and CCl_3COCl in TiCl_4 , and each sample was tested for five times. When RSD was less than 0.04%, it indicated a good precision of IR liquid cell which can meet the study requirement.

Table 1. The results of the same organic impurities mixed standard sample at five measuring times ($\mu\text{g}\cdot\text{g}^{-1}$).

Measure time	X (CH_2ClCOCl)	X (CHCl_2COCl)	X (CCl_3COCl)
1	1.7860×10^{-2}	2.1858×10^{-3}	3.629×10^{-3}
2	1.7858×10^{-2}	2.1857×10^{-3}	3.628×10^{-3}
3	1.7859×10^{-2}	2.1859×10^{-3}	3.626×10^{-3}
4	1.7859×10^{-2}	2.1859×10^{-3}	3.626×10^{-3}
5	1.7857×10^{-2}	2.1857×10^{-3}	3.627×10^{-3}
RSD (%)	0.0064	0.0045	0.0359

3.3. Detection limit by standard addition

Calculate detection limit by the lowest content of CHCl_2COCl in TiCl_4 (absorbance=0.003). The calculated detection limit of CCl_3COCl , CHCl_2COCl and CH_2ClCOCl were 3.159×10^{-3} , 1.917×10^{-3} and 1.554×10^{-2} mg/g, respectively. The measured value of CCl_3COCl , CHCl_2COCl and CH_2ClCOCl were lower than level standard of the compounds in fine TiCl_4 in Russia. So the precision can meet the quality control and analysis requirement of impurities in TiCl_4 production.

3.4. Sample determination

The content of CCl_3COCl , CHCl_2COCl and CH_2ClCOCl in TiCl_4 were tested in IR liquid cell with a standard. Figure 2(a) showed peaks of CCl_3COCl , CHCl_2COCl and CH_2ClCOCl were highly overlapped, which is not able to quantify directly. Carbonyl group (C=O) presented at CCl_3COCl , CHCl_2COCl and CH_2ClCOCl with a sensitive peak at around 1800 cm^{-1} . Inductive effect and other synergistic effect to carbonyl group occurred and it varied from the number of chlorine atoms attached to methyl group. The effects made the difference of sensitive absorption peak, however, overlapping presented when the three organic was determined simultaneously. So the peaks were then separated by OMNIC software [13] for quantifying and the figure was showed in figure 2(b). The infrared

spectroscopy characteristic peak of CCl_3COCl , CHCl_2COCl and CH_2ClCOCl are 1801, 1809, and 1820 cm^{-1} respectively. The sample determination result was illustrated in table 2. These formulas are regression equation of the three impurity compound. The X illustrated the content of the impurity and the mean of Y was measure value of the compound by FT-IR. The correlation coefficient is 0.8995 for CH_2ClCOCl standard curve, which is the only one less than 0.996. The average level of CH_2ClCOCl , CHCl_2COCl and CCl_3COCl in TiCl_4 was 1.7859×10^{-2} , 2.1857×10^{-3} and $3.626 \times 10^{-3}\text{ }\mu\text{g/g}$ respectively. Furthermore, the correlation among the chloroacetic acids and their wavelengths of maximum absorbance was also tested. But no obvious correlation (linear or quadratics) can be found through the result.

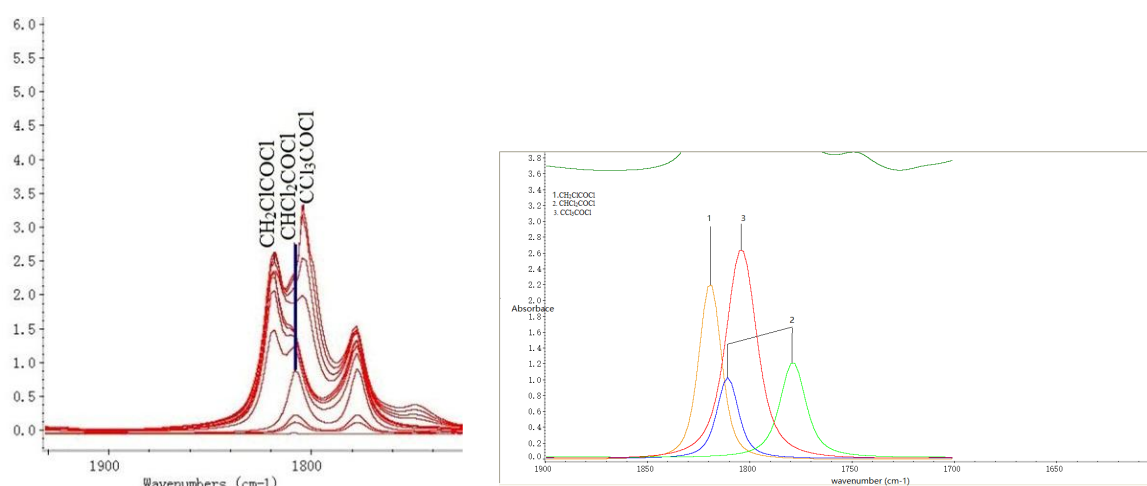


Figure 2. Infrared spectra of the organic impurities in TiCl_4 ((a) showed the original results by FT-IR, (b) showed the results processed by OMNIC software).

Table 2. The concentration of the three organic impurities in TiCl_4 .

Compound	Regression equation	Correlation coefficient(R^2)	Content($\mu\text{g} \cdot \text{g}^{-1}$)
CH_2ClCOCl	$y = -1.571x \times 10^{-5} + 1.00001785946$	0.8995	1.7859×10^{-2}
CHCl_2COCl	$y = -4.205x \times 10^{-4} + 1.00000223545$	0.9999	2.1857×10^{-3}
CCl_3COCl	$y = -1.273x \times 10^{-5} + 1.0000036264$	0.9962	3.626×10^{-3}

4. Conclusions

A new device with a window film of ZnSe and a body of PTFE can be used to determine the content of impurities in TiCl_4 . The regression equation of CH_2ClCOCl was $y = -1.571x \times 10^{-5} + 1.00001785946$, $R^2 = 0.8995$; the regression equation of CHCl_2COCl was $y = -4.205x \times 10^{-4} + 1.00000223545$, $R^2 = 0.9999$; and the regression equation of CCl_3COCl was $y = -1.273x \times 10^{-5} + 1.0000036264$, $R^2 = 0.9963$. The new infrared measuring device showed various advantages, including safe, simple, easily removable, washable and reusable. The process of peak by OMNIC software made the research convenient due to the measurement of different compound simultaneously. This new method prevented the influence of added solution on the matrix, which is applicable for multi-component analysis.

Acknowledgments

The research of this paper was financially supported by the Youth Fund in Academy of Guizhou Science. The test was done in Guizhou Academy of testing and analysis with FT-IR. In developing the ideas presented here, I have received helpful input from Tan H and He J L. I have to thank my co-author, Wang Y J.

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