

## Research Article

# Quantitative Analysis of Silicon Tetrachloride, Carbon Disulfide, and Dichloroethane Concentration by Raman Spectroscopy

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Quantitative analysis of silicon tetrachloride, carbon disulfide, and dichloroethane concentrations to obtain vapor-liquid equilibrium data of the  $\text{SiCl}_4\text{-CS}_2$  and  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary systems was established by Raman spectroscopy. The cheap glass sampling pipe was used as a carrier for Raman spectroscopy measurements. The Raman peak height of the internal standard was used to remove interference factors such as sampling pipe diameter, temperature, laser power, and other effects from the instrument. The peak height ratio between the Raman characteristic peak of the analyte and that of the internal standard was proportional to the analyte concentration. During the measuring process of vapor-liquid equilibrium data for the  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary system, the linear equation of  $y = 0.0068 + 0.75x$  with  $R^2$  of 0.9939 was used for the determination of  $\text{SiCl}_4$  concentration at the  $422\text{ cm}^{-1}$  band. The linear equation of  $y = 0.0019 + 0.2266x$  with  $R^2$  of 0.9966 was used for the determination of  $\text{C}_2\text{H}_4\text{Cl}_2$  concentration at the  $754\text{ cm}^{-1}$  band. For the  $\text{SiCl}_4\text{-CS}_2$  binary system, the linear equation of  $y = 0.0494 + 4.7535x$  with  $R^2$  of 0.9962 was used for the determination of  $\text{SiCl}_4$  concentration at the  $422\text{ cm}^{-1}$  band. The linear equation of  $y = 0.8139 + 8.7366x$  with  $R^2$  of 0.9973 was used for the determination of  $\text{CS}_2$  concentration at the  $654\text{ cm}^{-1}$  band. The concentration of standard samples calculated by these standard curves was compared with the actual value to verify the accuracy of this method. The reproducibility is good when determining silicon tetrachloride and dichloroethane concentrations for the  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary system, with RSEP values of 2.81% and 2.17%, respectively. Meanwhile, the RSEP values are 3.55% and 4.16%, respectively, when determining silicon tetrachloride and carbon disulfide concentrations for the  $\text{SiCl}_4\text{-CS}_2$  binary system.

## 1. Introduction

Titanium-containing liquid waste coming from the rectifying process is the major waste in the titanium metallurgy industry. Generally speaking, the concentration of  $\text{SiCl}_4$  and  $\text{TiCl}_4$  in the titanium-containing liquid waste is 15~20% and 60~70%, respectively [1]. The liquid waste containing  $\text{TiCl}_4$  and  $\text{SiCl}_4$  is a valuable resource, but it is hydrolyzed easily in a moist environment, producing a large amount of HCl, which is a toxic gas [2–4]. Therefore, improper disposal of titanium-containing liquid waste would lead to waste of resources and destruction of the eco-environment [5, 6]. Resource utilization of the titanium-containing liquid waste is always of great importance in China, and effort has been

made to extract  $\text{SiCl}_4$  from the liquid waste for a long time [7–9]. Besides  $\text{SiCl}_4$  and  $\text{TiCl}_4$ , there are also a small amount of impurities in the liquid waste such as  $\text{FeCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{CS}_2$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and so on. In order to extract purified  $\text{SiCl}_4$ , these impurities must be removed. The method to obtain high-grade  $\text{SiCl}_4$  includes adsorption, rectification, partial hydrolysis, and photochlorination [10–13]. Among all these methods, rectification may be the best way to extract purified  $\text{SiCl}_4$  from the liquid waste because no additional impurities are introduced. Unfortunately, due to the little difference in  $\text{SiCl}_4$  and  $\text{CS}_2$  or  $\text{C}_2\text{H}_4\text{Cl}_2$  in boiling point, the rectification process is energy-sucking. In order to reduce energy consumption, the accurate vapor-liquid equilibrium data for the  $\text{SiCl}_4\text{-CS}_2$  and  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary systems must be

measured to optimize the design of the rectifying column. During the measurement, the content of  $\text{SiCl}_4$ ,  $\text{CS}_2$ , and  $\text{C}_2\text{H}_4\text{Cl}_2$  in the sample must be analyzed to obtain accurate gas-liquid equilibrium data.

Generally, inorganic substances could be detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES) by dissolving in acid solution. Organic compounds could be analyzed by gas or liquid chromatography and infrared (IR) spectroscopy [14–17]. However, these methods could not be used for simultaneous analysis of inorganic and organic compounds. Recently, quantitative analysis of components in solution by Raman spectroscopy has been reported, and there are several advantages to using Raman spectra for quantitative analysis [18–22]. For example, it is a nondestructive technology that is usually applicable without any sample preparation process, which is convenient for online quantitative determination [23, 24]. This analytical method may also be applied to samples containing  $\text{SiCl}_4$ ,  $\text{CS}_2$ , and  $\text{C}_2\text{H}_4\text{Cl}_2$ . Creighton and Sinclair studied the Raman spectra of liquid  $\text{SiCl}_4$  and  $\text{CS}_2$  as early as 1973 [25], Gong studied the Raman scattering from liquid  $\text{CS}_2$  for different concentrations of benzene [26], and Steffen gave information about the 2D Raman response of liquid  $\text{CS}_2$  [27]. Meanwhile, the spectral information of  $\text{C}_2\text{H}_4\text{Cl}_2$  could also be found in literature [28–30], but there is nearly no study on the quantitative determination of  $\text{CS}_2$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{SiCl}_4$  in liquid samples by using Raman spectra.

Therefore, the purpose of the present study is to establish a rapid and accurate method to determine the concentration of  $\text{CS}_2$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{SiCl}_4$  simultaneously in liquid samples. During the analysis procedure, the standard solutions with internal standards were sealed in cheap glass capillaries for the Raman spectrometer. Then, the peak height ratio between the Raman characteristic peak of the analyte and that of the internal standard was calculated to establish the calibration curves of  $\text{CS}_2$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{SiCl}_4$ . After that, the Raman spectrometries of standard samples were measured, and the concentration of the analyte was calculated using the standard curves to confirm the availability of this method.

## 2. Materials and Methods

**2.1. Raman Spectrometer.** Raman spectrometry of all samples was detected by the LabRAM HR Evolution spectrometer, equipped with an Olympus BX41 microscope with a 10X objective lens ( $\text{NA} = 0.25$ ), which was used for focusing the laser beam on the sample. A 532 nm Ar ion laser (Spectra Physics 2017) was used for excitation with power of ~50 mW. The back scattering light was passed into a monochromator and detected with a charge coupled device (CCD) detector. The Raman spectrum between 100 and 3200  $\text{cm}^{-1}$  was collected with an exposure time of 30 s and 2 accumulations for each spectrum.

**2.2. Sample Preparation for Raman Analysis.** The sample containing  $\text{SiCl}_4$  is easily hydrolyzed to release HCl in the air, which is not convenient for Raman detecting. Therefore, the

sample containing  $\text{SiCl}_4$  will be sealed before it was submitted for Raman detecting according to our previous work [31]. The liquid sample stored in a sealed colorimetric tube was first moved into a drying oven. The colorimetric tube was then opened, and a little glass sampling pipe was inserted into the colorimetric tube. After the liquid sample entered the little glass sampling pipe by capillary action, the little glass sampling pipe was taken out and moved to the alcohol lamp. The both ends of the glass sampling pipe were heated and melted to allow the liquid sample to get sealed in it. The preparation process is convenient, and the material is inexpensive.

**2.3. Preparation of Standard Samples.**  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  were purchased from Coron Chemical Industry Co., Ltd. There is often little water remaining in the purchased  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{CS}_2$ , which may lead to the hydrolysis of  $\text{SiCl}_4$ . Hence, the purchased  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{CS}_2$  were dehydrated first. The dehydration process is also similar to our previous work [31], just with a different distillation temperature: firstly, anhydrous calcium chloride (stored in a vacuum drying oven at 105°C for 24 h before use) and  $\text{C}_2\text{H}_4\text{Cl}_2$  or  $\text{CS}_2$  were put into a desiccative conical flask with a stopper. Then, the mixture was magnetically stirred at room temperature for 12 h. Finally, the filtrate from the mixture was distilled at certain temperature (90°C for  $\text{C}_2\text{H}_4\text{Cl}_2$  and 50°C for  $\text{CS}_2$ ), and the distillate was collected for the preparation of standard samples. In the measurement of vapor-liquid equilibrium data for the  $\text{SiCl}_4$ - $\text{CS}_2$  and  $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  binary systems, the concentrations of  $\text{SiCl}_4$ ,  $\text{CS}_2$ , and  $\text{C}_2\text{H}_4\text{Cl}_2$  in liquid samples should be analyzed simultaneously. Thus,  $\text{CS}_2$  was used as an internal standard during the concentration determination of  $\text{SiCl}_4$  and  $\text{C}_2\text{H}_4\text{Cl}_2$  for the  $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  binary system, while  $\text{C}_2\text{H}_4\text{Cl}_2$  was used as an internal standard during the concentration determination of  $\text{SiCl}_4$  and  $\text{CS}_2$  for the  $\text{SiCl}_4$ - $\text{CS}_2$  binary system. Then, the working standard solutions at several concentration levels of  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  were prepared.

**2.4. Establishment of Calibration Curves.** Working standard solutions with different concentrations of  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  were prepared for Raman detecting. The baselines of the obtained Raman spectra were taken out by using Origin 8.5 to avoid noise and fluorescence effects. After that, the characteristic peak heights of  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  were extracted from the revised Raman spectra, respectively. The peak height ratio between the Raman characteristic peak of the analyte and the internal standard was subsequently calculated according to the following equation:

$$R = \frac{I_A}{I_S}, \quad (1)$$

where  $I_A$  is the Raman intensity of analyte and  $I_S$  is the Raman intensity of internal standard. The calibration curve was generated by plotting the characteristic peak height ratio against the concentration of analytes.

### 3. Results and Discussion

**3.1. Raman Spectra of the Mixed Solution Containing  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$ .** In order to obtain the characteristic peaks of  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  for quantitative analysis, the Raman spectra of a mixed solution containing  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  are detected, as shown in Figure 1. Figure 1(a) shows the full spectrum of the mixed solution from  $200\text{ cm}^{-1}$  to  $3200\text{ cm}^{-1}$ . The full spectrum is partly displayed in Figures 1(b) and 1(c) so that the characteristic peaks of  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$  can be clearly observed. Figure 1(b) shows the spectrum of the mixed solution from  $200\text{ cm}^{-1}$  to  $1000\text{ cm}^{-1}$  band, and Figure 1(c) shows the spectrum from  $1000\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$  band. In order to rapidly and conveniently find the Raman band of  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$ , the details of the Raman peaks in Figure 1 are shown in Table 1. The C-S vibrating mode of carbon disulfide [25] is found at the  $654\text{ cm}^{-1}$  band in Figure 1(b), and the intensity reaches up to 5368. Two obvious bands with the maximum intensity at  $422$  and  $480\text{ cm}^{-1}$  appeared, respectively, in Figure 1(b), which is attributed to the Si-Cl vibrating modes of silicon tetrachloride [32]. The vibrating mode of liquid dichloroethane is found in Figures 1(a)–1(c). The band at  $2968\text{ cm}^{-1}$  shown in Figure 1(a) belongs to the symmetrical stretching vibration of C-H<sub>2</sub>. The bands at  $300$  and  $754\text{ cm}^{-1}$  in Figure 1(b) are ascribed to deformation vibration of C-C-Cl and stretching vibration of C-Cl, respectively [33]. The peak at  $1053\text{ cm}^{-1}$  band in Figure 1(c) is assigned to stretching vibration of C-C, and the peaks at  $1204$ ,  $1301$ , and  $1431\text{ cm}^{-1}$  band are due to the twisting vibration, wagging vibration, and scissoring vibration of C-H<sub>2</sub>, respectively [33].

In order to reduce the background noise interference, a characteristic peak with high intensity should be used for quantitative analysis. Thus, the characteristic peak of dichloroethane at  $300$ ,  $1053$ ,  $1204$ ,  $1301$ , and  $1431\text{ cm}^{-1}$  with weak intensity could be excluded during the analysis while the characteristic bands of dichloroethane at  $754$  and  $2968\text{ cm}^{-1}$  with high intensity could be used for quantitative analysis. Meanwhile, C-S vibrating mode of carbon disulfide at  $654\text{ cm}^{-1}$  band and Si-Cl vibrating modes of silicon tetrachloride at  $422$  and  $480\text{ cm}^{-1}$  band are clearly observed with high intensity. Therefore, these characteristic bands may be used for quantitative determination.

#### 3.2. Standard Curves for the $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$ Binary System

**3.2.1. Raman Spectra of the Standard Solutions for the  $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  Binary System.** In order to obtain the standard curves for the  $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  binary system, the Raman spectrums of the standard solutions with different  $\text{SiCl}_4$  and  $\text{C}_2\text{H}_4\text{Cl}_2$  concentrations were detected when carbon disulfide was added as an internal standard, and the results are shown in Figure 2. The Raman spectrum around the characteristic peak of carbon disulfide at  $654\text{ cm}^{-1}$  in the standard solutions is shown in Figure 2(a), which could be used to calculate the peak height ratio for the standard curve.

It can be seen from Figure 2(a) that the intensity of carbon disulfide at  $654\text{ cm}^{-1}$  is not changed with the variation of silicon tetrachloride and dichloroethane concentration. The slight increase or decrease in intensity may be due to the change in laser power.

The Raman spectra of standard solutions on the characteristic peak of silicon tetrachloride at  $422$  and  $480\text{ cm}^{-1}$  are presented in Figure 2(b). The Raman spectra of standard solutions around the characteristic peak of dichloroethane at  $754$  and  $2968\text{ cm}^{-1}$  are shown in Figures 2(c) and 2(d), respectively.

It can be seen from Figure 2(b) that the Raman intensity of silicon tetrachloride at  $422\text{ cm}^{-1}$  increases with the rising  $\text{SiCl}_4$  concentration in standard solutions, while the Raman intensity of silicon tetrachloride at  $480\text{ cm}^{-1}$  is irregular with the  $\text{SiCl}_4$  concentration. Thus, the characteristic peak of silicon tetrachloride at  $480\text{ cm}^{-1}$  is not suitable for quantitative analysis. In addition, although the Raman intensity of silicon tetrachloride at  $422\text{ cm}^{-1}$  increases with the increase in  $\text{SiCl}_4$  concentration, the linear relationship between Raman intensity and  $\text{SiCl}_4$  concentration is not good. It can be verified from Figure 3 that the equation is  $y = 32.74 + 23883.45x$  with  $R^2$  of 0.9719, where  $y$  and  $x$  denote the Raman intensity and the mole fraction of silicon tetrachloride, respectively. This indicates a bad linear relationship. Therefore, Raman absolute intensity cannot be used to calculate the  $\text{SiCl}_4$  concentration accurately.

#### 3.2.2. Standard Curves for the $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$ Binary System.

Generally, the Raman intensity of  $\text{SiCl}_4$  at characteristic peak ( $422\text{ cm}^{-1}$ ) indicated as  $I_A$  can be given by the following equation [34]:

$$I_A = K_A V C_A P_L, \quad (2)$$

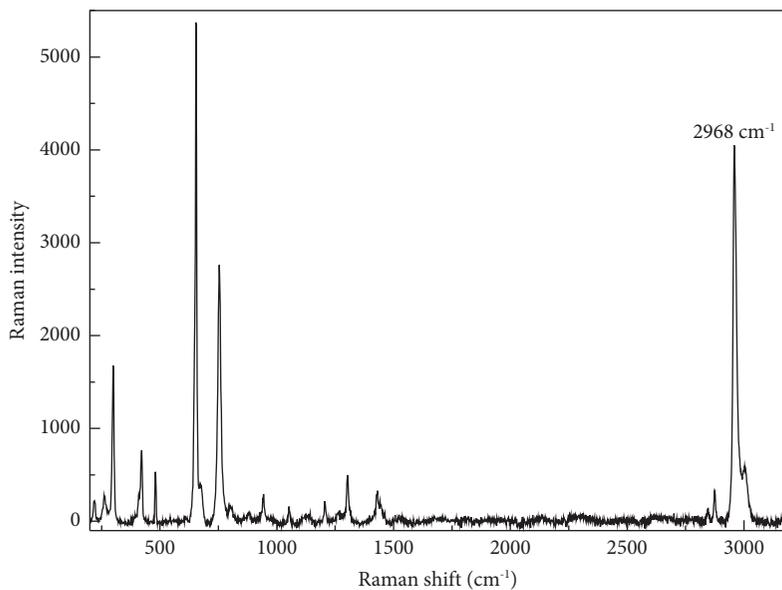
where  $C_A$  is the  $\text{SiCl}_4$  concentration,  $P_L$  is the density of laser power, and  $K_A$  is the Raman signal constant of  $\text{SiCl}_4$  at  $422\text{ cm}^{-1}$ , which can be affected by instrumental throughput and the apparent Raman-scattering efficiency.  $V$  is the volume of sample illuminated by the laser and viewed by the spectrometer. According to equation (2), the Raman intensity of  $\text{SiCl}_4$  ( $I_A$ ) will change with the variation of  $K_A$  and  $P_L$ . There is often inevitable fluctuation of laser power, test temperature, and instrument during the measurement of the Raman spectrum. Thus, it is easy to understand the bad linearity between the Raman intensity and the mole fraction of  $\text{SiCl}_4$ . In order to remove the effect of laser power, test temperature, and instrument, the characteristic peak height ratio was introduced:

$$R_A = \frac{K_A V C_A P_L}{K_{IS} V C_{IS} P_L} = \frac{K_A C_A}{K_{IS} C_{IS}} = k C_A, \quad (3)$$

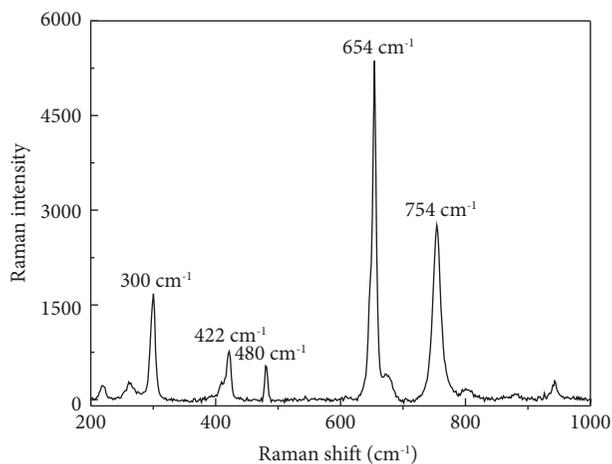
where  $R_A$  is the peak height ratio between  $\text{SiCl}_4$  and the internal standard  $\text{CS}_2$ ,  $C_{IS}$  is the concentration of  $\text{CS}_2$ , which is considered as invariable in all standard solutions, and  $K_{IS}$  is the Raman signal constant of  $\text{CS}_2$  at  $654\text{ cm}^{-1}$ . Thus, the characteristic peak height ratio is proportional to the concentration of  $\text{SiCl}_4$ , which is verified in Figure 3. The result in Figure 3 indicates that the linearity between the mole fraction of  $\text{SiCl}_4$  and the Raman peak height ratio at

TABLE 1: Details of Raman peaks in Figure 1.

Raman peak in Figure 1 ( $\text{cm}^{-1}$ )	Attribution	Substance
654	Vibrating mode of C-S	$\text{CS}_2$
422 and 480	Vibrating modes of Si-Cl	$\text{SiCl}_4$
300	Deformation vibration of C-C-Cl	
754	Stretching vibration of C-Cl	
1204	Twisting vibration of C-H <sub>2</sub>	$\text{C}_2\text{H}_4\text{Cl}_2$
1301	Wagging vibration of C-H <sub>2</sub>	
1431	Scissoring vibration of C-H <sub>2</sub>	
2968	Symmetrical stretching vibration of C-H <sub>2</sub>	

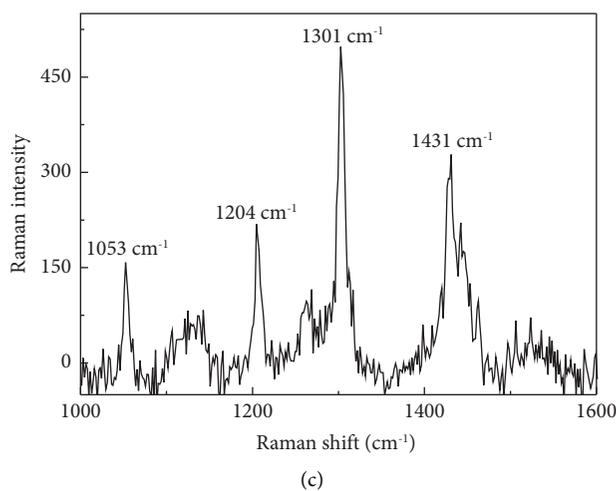
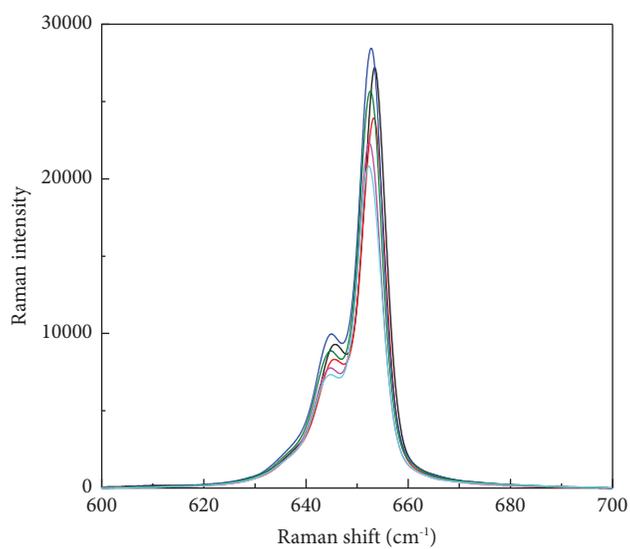


(a)

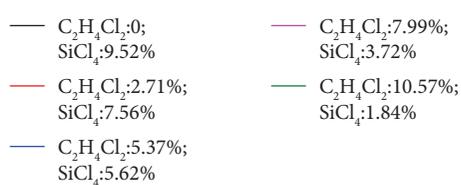
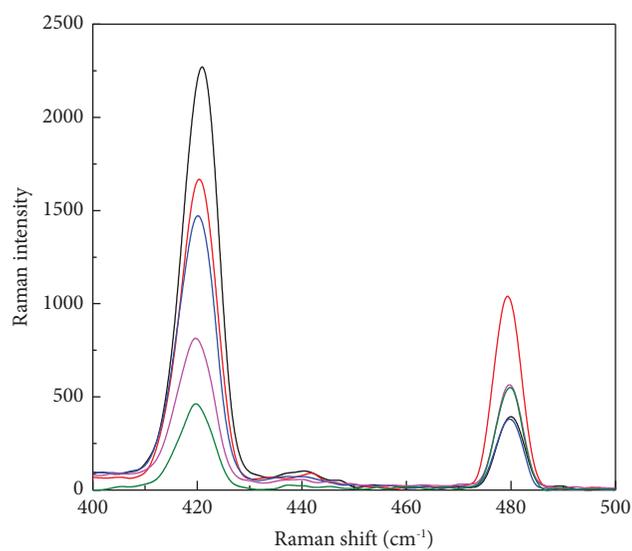


(b)

FIGURE 1: Continued.

FIGURE 1: Raman spectra of the mixed solution containing  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , and  $\text{CS}_2$ .

(a)



(b)

FIGURE 2: Continued.

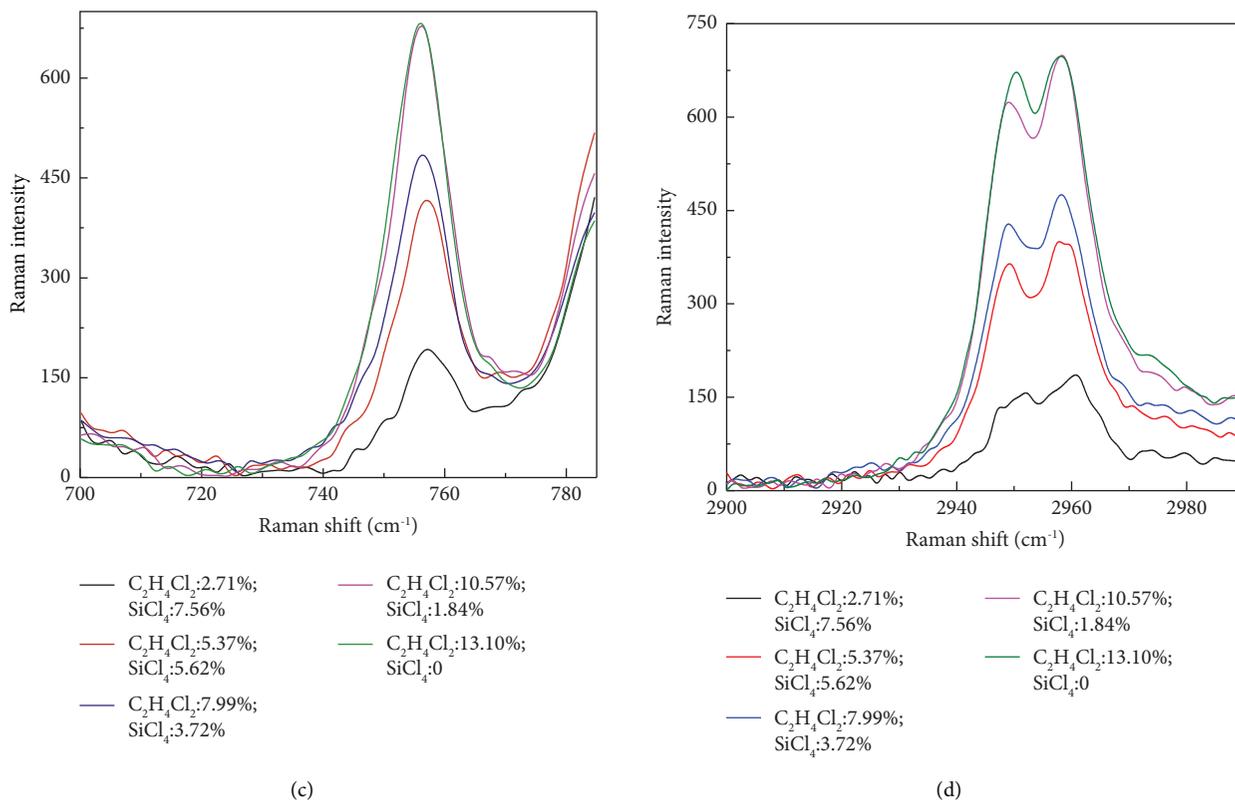


FIGURE 2: Raman spectra of the standard solutions for the  $SiCl_4$ - $C_2H_4Cl_2$  binary system: (a) the characteristic peak of carbon disulfide at  $654\text{ cm}^{-1}$ , (b) the characteristic peak of silicon tetrachloride at  $422$  and  $480\text{ cm}^{-1}$ , (c) the characteristic peak of dichloroethane at  $754\text{ cm}^{-1}$ , and (d) the characteristic peak of dichloroethane at  $2968\text{ cm}^{-1}$ .

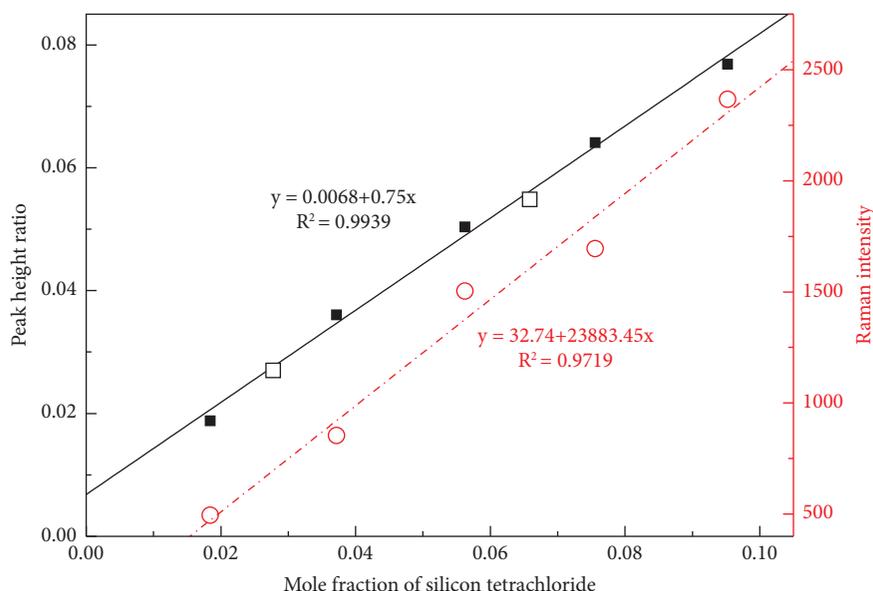


FIGURE 3: Calibration curve for the determination of silicon tetrachloride for the  $SiCl_4$ - $C_2H_4Cl_2$  binary system at  $422\text{ cm}^{-1}$  (■: standard solution used to establish calibration curve; □: standard solution used to verify the accuracy of the calibration curve).

$422\text{ cm}^{-1}$  is good, and the equation is  $y = 0.0068 + 0.75x$  with  $R^2$  of 0.9939, where  $y$  and  $x$  denote the Raman peak height ratio and the mole fraction of  $SiCl_4$ , respectively. Therefore, the characteristic peak height ratio will be used for the following standard curves.

The Raman intensity of  $C_2H_4Cl_2$  at  $754$  and  $2968\text{ cm}^{-1}$  also increases with the increase in  $C_2H_4Cl_2$  concentration in standard solutions, which could be clearly observed in Figures 2(c) and 2(d). It can be seen from Figure 2(d) that the characteristic peak of dichloroethane at  $2968\text{ cm}^{-1}$  divides

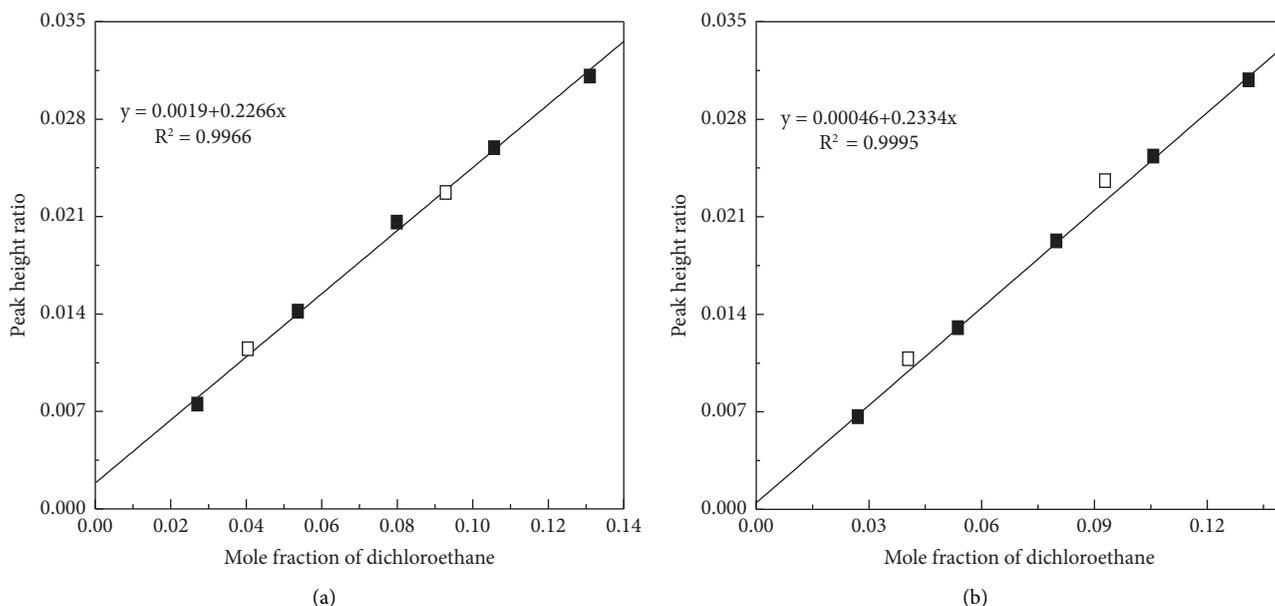


FIGURE 4: Calibration curve for the determination of dichloroethane for the  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary system at (a)  $754\text{ cm}^{-1}$  and (b)  $2968\text{ cm}^{-1}$  (■: standard solution used to establish calibration curve; □: standard solution used to verify the accuracy of the calibration curve).

into two peaks, so the mean Raman intensity of the two peaks was used for quantitative determination of dichloroethane. Similarly, the characteristic peak height ratio at  $754$  and  $2968\text{ cm}^{-1}$  was used to establish a standard curve for the determination of  $\text{C}_2\text{H}_4\text{Cl}_2$  concentration, and the result is presented in Figure 4. It can be seen from Figure 4(a) that the linearity between the mole fraction of dichloroethane and the Raman peak height ratio at  $754\text{ cm}^{-1}$  is good, and the equation is  $y = 0.0019 + 0.2266x$  with  $R^2$  of  $0.9966$ , where  $y$  and  $x$  denote the Raman peak height ratio and the mole fraction of dichloroethane, respectively. The result in Figure 4(b) indicates that the characteristic peak height ratio at  $2968\text{ cm}^{-1}$  is also proportional to the concentration of dichloroethane, and the equation is  $y = 0.00046 + 0.2334x$  with  $R^2$  of  $0.9995$ .

**3.2.3. The Veracity of the Standard Curves.** To verify the accuracy of these standard curves, the Raman spectra of standard samples with known concentrations of silicon tetrachloride and dichloroethane were measured. The peak height ratios calculated from the spectra were obtained and are shown by hollow squares in Figures 3 and 4. These hollow squares lie on the standard curve, though the measurement condition and target concentration are different from the standard curve. These results suggest that the characteristic peak height ratio method is credible for the determination of silicon tetrachloride and dichloroethane.

To compare the different characteristic peaks applied, the relative standard error of prediction, RSEP, is calculated according to the following equation:

$$\text{RSEP}(\%) = \sqrt{\frac{\sum_{i=1}^n (C_i - C_i^A)^2}{\sum_{i=1}^n (C_i^A)^2}} \times 100, \quad (4)$$

where  $C^A$  is the actual concentration of silicon tetrachloride or dichloroethane,  $C$  is the concentration calculated from the Raman spectrum, and  $n$  is the number of samples. The result in Table 2 shows that the RSEP value for the concentration of  $\text{SiCl}_4$  is  $2.81\%$  when the  $422\text{ cm}^{-1}$  band is used. The RSEP value for the concentration of  $\text{C}_2\text{H}_4\text{Cl}_2$  is  $2.17\%$  at  $754\text{ cm}^{-1}$  band and  $7.32\%$  at  $2968\text{ cm}^{-1}$  band. This means the band of dichloroethane at  $754\text{ cm}^{-1}$  may be the better choice for quantitative analysis.

**3.3. Standard Curves for the  $\text{SiCl}_4\text{-CS}_2$  Binary System.** Similarly,  $\text{C}_2\text{H}_4\text{Cl}_2$  was used as an internal standard during the quantitative determination of  $\text{SiCl}_4$  and  $\text{CS}_2$  for the  $\text{SiCl}_4\text{-CS}_2$  binary system. The Raman spectrum of the standard solutions around the characteristic peak of  $\text{C}_2\text{H}_4\text{Cl}_2$  ( $754\text{ cm}^{-1}$ ) is shown in Figure 5, which could be used to calculate peak height ratio. The Raman spectra of standard solutions around the characteristic peak of silicon tetrachloride and carbon disulfide ( $422\text{ cm}^{-1}$  and  $654\text{ cm}^{-1}$ , respectively) are presented in Figures 6 and 7. First, the characteristic peak heights of silicon tetrachloride, carbon disulfide, and dichloroethane were taken from these Raman spectrums, which are shown in Figures 5–7. Then, the peak height ratio was calculated according to the peak height of the solute and the internal standard. Finally, the peak height ratio was plotted against the mole fraction of silicon tetrachloride and carbon disulfide, which is also shown in Figures 6 and 7.

TABLE 2: RSEP of  $\text{SiCl}_4$  and  $\text{C}_2\text{H}_4\text{Cl}_2$  concentration for the  $\text{SiCl}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  binary system by quantitative analysis at different characteristic peaks.

	$\text{SiCl}_4$ ( $422\text{ cm}^{-1}$ )		$\text{C}_2\text{H}_4\text{Cl}_2$ ( $754\text{ cm}^{-1}$ )		$\text{C}_2\text{H}_4\text{Cl}_2$ ( $2968\text{ cm}^{-1}$ )	
Actual concentration (%)	2.78	6.59	9.28	4.04	9.28	4.04
Estimated concentration (%)	2.69	6.41	9.19	4.24	9.91	4.43
RSEP (%)	2.81		2.17		7.32	

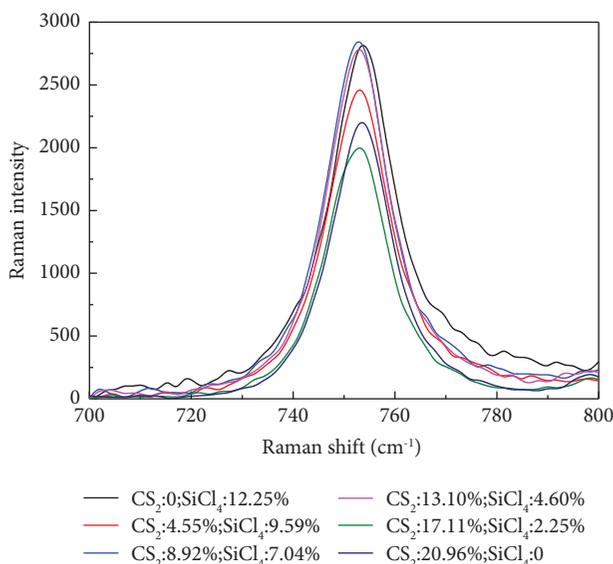


FIGURE 5: Raman spectra of the standard solutions for the  $\text{SiCl}_4$ - $\text{CS}_2$  binary system at the characteristic peak of dichloroethane ( $754\text{ cm}^{-1}$ ).

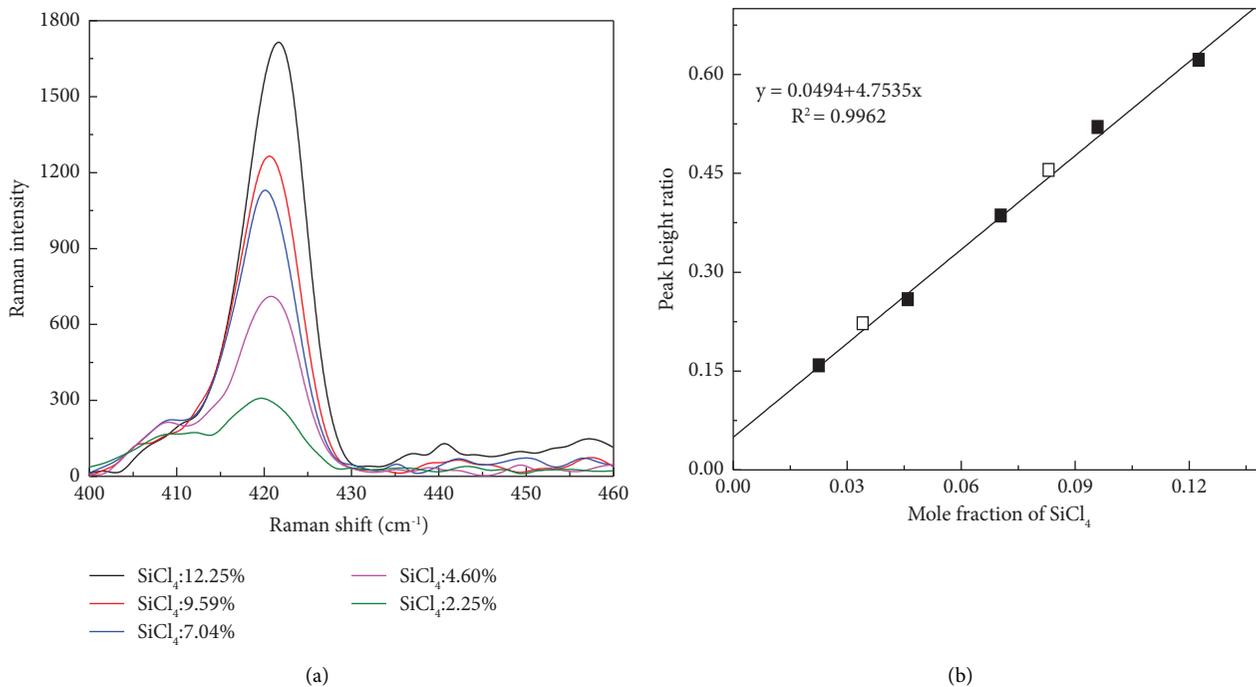


FIGURE 6: Raman spectra of standard solutions at the characteristic peak of silicon tetrachloride ( $422\text{ cm}^{-1}$ ) and the standard curve for determination of silicon tetrachloride for the  $\text{SiCl}_4$ - $\text{CS}_2$  binary system. (a) Raman spectrum and (b) calibration curve (■: standard solution used to establish calibration curve; ○: standard solution used to verify the accuracy of the calibration curve).

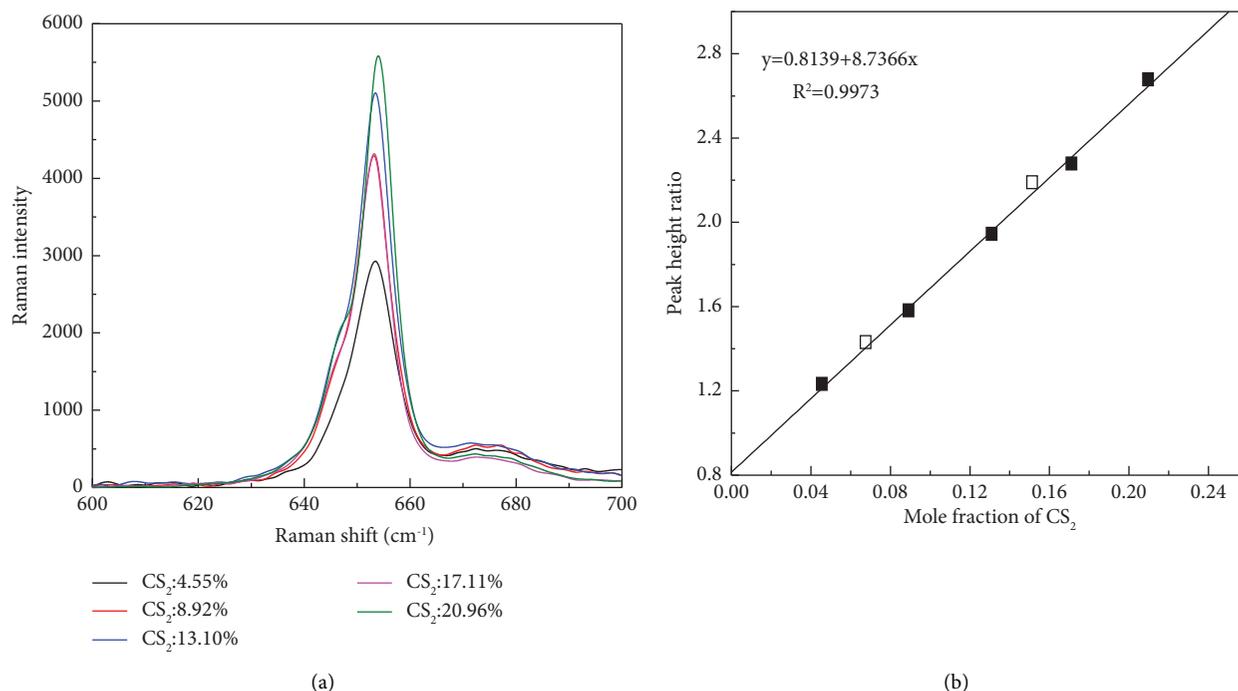


FIGURE 7: Raman spectrum of standard solutions at the characteristic peak of carbon disulfide ( $654\text{ cm}^{-1}$ ) and the standard curve for determination of carbon disulfide for the  $\text{SiCl}_4\text{-CS}_2$  binary system. (a) Raman spectrum and (b) calibration curve (■: standard solution used to establish calibration curve; □: standard solution used to verify the accuracy of the calibration curve).

The results in Figure 6 show that the linearity between the mole fraction of silicon tetrachloride and the Raman peak height ratio at  $422\text{ cm}^{-1}$  is good, and the equation is  $y = 0.0494 + 4.7535x$  with  $R^2$  of 0.9962, where  $y$  and  $x$  denote the Raman peak height ratio and the mole fraction of silicon tetrachloride, respectively. Similarly, there is also a good linearity between the mole fraction of carbon disulfide and the Raman peak height ratio at  $654\text{ cm}^{-1}$ . The equation is  $y = 0.8139 + 8.7366x$  with  $R^2$  of 0.9973, which is shown in Figure 7. In order to verify the accuracy of these standard curves, the Raman spectra of standard samples with known concentrations of silicon tetrachloride and carbon disulfide were also measured. The peak height ratios calculated from these spectra are shown by hollow squares in Figures 6 and 7. These hollow squares lie on the standard curve, which also confirms that the characteristic peak height ratio method is credible for the determination of silicon tetrachloride and carbon disulfide concentrations for the  $\text{SiCl}_4\text{-CS}_2$  binary system.

The relative standard error of prediction (RSEP) of the standard curve for the  $\text{SiCl}_4\text{-CS}_2$  binary system is also calculated according to equation (4), and the results are shown in Table 3. The result in Table 3 shows that the RSEP value of the  $\text{SiCl}_4$  concentration for the  $\text{SiCl}_4\text{-CS}_2$  binary system is 3.55% when the peak height ratio at the  $422\text{ cm}^{-1}$  band is used. The RSEP value of the  $\text{CS}_2$  concentration for the  $\text{SiCl}_4\text{-CS}_2$  binary system is 4.16% at the  $654\text{ cm}^{-1}$  band. These results also indicate that these standard curves are reliable during the determination of  $\text{SiCl}_4$  and  $\text{CS}_2$  concentrations for the  $\text{SiCl}_4\text{-CS}_2$  binary system.

TABLE 3: RSEP of  $\text{SiCl}_4$  and  $\text{CS}_2$  concentration for the  $\text{SiCl}_4\text{-CS}_2$  binary system by quantitative analysis at different characteristic peaks.

	$\text{SiCl}_4$ ( $422\text{ cm}^{-1}$ )		$\text{CS}_2$ ( $654\text{ cm}^{-1}$ )	
Actual concentration (%)	3.41	8.30	15.12	6.76
Estimated concentration (%)	3.63	8.53	15.74	7.06
RSEP (%)	3.55		4.16	

#### 4. Conclusion

Raman spectroscopy was applied to quantitatively determine the concentration of silicon tetrachloride, carbon disulfide, and dichloroethane during the resource utilization of the titanium-containing liquid waste. The liquid sample was sealed in a glass sampling pipe with an internal standard, and the whole preparation process is convenient and inexpensive. The peak height ratio between the Raman intensities of the target substance and those of the internal standard is proportional to the concentration of the target substance with a good linear relationship. This method shows good accuracy when the standard samples are detected and the calculated concentration is compared with the actual concentration. The relative standard error of prediction (RSEP) is 2.81% and 2.17%, respectively, when determining silicon tetrachloride and dichloroethane concentrations for the  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary system. The RSEP values are 3.55% and 4.16%, respectively, when determining silicon tetrachloride and carbon disulfide concentrations for the  $\text{SiCl}_4\text{-CS}_2$  binary system. These results

indicate that Raman spectroscopy can quantitatively determine the concentration of silicon tetrachloride, carbon disulfide, and dichloroethane when measuring vapor-liquid equilibrium data for the  $\text{SiCl}_4\text{-CS}_2$  and  $\text{SiCl}_4\text{-C}_2\text{H}_4\text{Cl}_2$  binary systems.

## Data Availability

All the data are included in the manuscript.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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