Establishment of a New Analysis Method for Trace Nitrogen Trifluoride in Helium detection by Gas Chromatography

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Abstract. In this experiment, a method for the determination of trace nitrogen trifluoride in helium (NF₃/He) by gas chromatography (GC) was established. First, a series of NF₃/He gas standard substance with accurate concentration was prepared by gravimetric method. And then, we had analyzed for the trace nitrogen and oxygen impurities in NF₃, and the specific property experiment was used to verify that the impurity did not affect the measured value of the component. However, the analytical calibration curve of NF₃ was nonlinear in the concentration range from 1 to 1000 μmol·mol⁻¹. Nonlinear curves were transformed into linear curves by a linear power method, and the formula for the uncertainty of the fitting curve was calculated. Moreover, the consistency and uncertainty of the blind test results were evaluated. The results show that the method has high precision; the nitrogen or oxygen impurity has no effect on the specificity of the method; consistency of blind sample test result is well. Furthermore, it may be an ideal method for the research on the trace NF₃ in helium.

1. Introduction

Nitrogen trifluoride (NF₃) is toxic, colorless, odorless, nonflammable, oxidizing compressed gas. It’s an excellent plasma etchant and cleaning agent, mainly used in the microelectronics industry; when NF₃ is used as a gas cleaner, it has high cleaning efficiency and without trace; NF₃ also has excellent etch rate and selectivity for silicon semiconductor materials[1]. In addition, NF₃ is used as a fluorine source in high-energy lasers; it is also used as an electrochemical fluorinating agent for the production of perfluoro organic and inorganic compounds[2], and used as a reagent for preparing tetrafluorohydrazine and producing fluorozirconate glass[3,4]; it is used as a special welding gas, because its characteristics of hot reacting with hydrogen; it also can be used for separation and purification of uranium and plutonium in the nuclear industry[5].

However, NF₃ has some toxicity, which combines with hemoglobin easily. Hemoglobinemia can be caused by a certain amount of inhalation by the human body[6]. Additionally, NF₃ is a gas with a strong green house effect, its ability to store heat is about 17 thousand times that of carbon dioxide, it cannot be removed by other atmospheric processes in the atmosphere (reacting with ozone, water, etc.), and its atmospheric life lasts for 740 years. In recent years, NF₃ emissions are still increasing, which means that NF₃ emissions become a serious environmental problem. But, in China, the technology of NF₃ detection is still in its infancy now. All in all, research on NF₃ is particularly important.

Gas chromatography is a powerful analytical method, and it is capable of qualitative and quantitative. Particularly, GC with pulsed helium discharge ionization detector (PDD) is a fast and efficient detection method. Based on this, a GC method for systematic analysis of trace amounts of...
NF₃ in helium is established. The calibration curve is prepared by using the pure component of the predicted component, and the uncertainty of the result is obtained.

2. Experimental

2.1 Materials
High-purity nitrogen trifluoride gas (99.99%) was purchased from Chengdu KEYUAN CO., LTD; high-purity helium gas (99.999%) was purchased from DALIAN SPESICAL GASES CO., LTD; high-purity oxygen gas (99.998%) and high purity nitrogen were purchased from Dongguan Shenguang Sanjun Industrial Gas.

2.2 Preparation of nitrogen trifluoride in helium standard gas
A series of NF₃/He standard gases with accurate concentrations from 100-1000 μmol·mol⁻¹ were prepared by gravimetric method. Fill the gas with a gas distribution device and weigh the gas and cylinder through the CCE40K3 electronic. In addition, preparing NF₃/He containing 10 μmol·mol⁻¹ nitrogen and oxygen impurities was used for the specific experiment. Before preparation, it is necessary to use a RC-Y5 cylinder vacuum drying device to treat the seamless aluminum alloy gas cylinder; after preparation, mixing the filling gas with a cylinder rolling device. Use the NF₃ in helium standard gases for the establishment of analytical methods and obtain calibration curves. As a parallel sample, two sets of NF₃/He standard gases were verified the consistency of the calibration curve. Additionally, the uncertainty of NF₃ in helium standard gas was calculated by previous formulas [11].

2.3 Chromatographic conditions
High purity helium gas (99.999%, 0.6 MPa) was used as a carrier gas and highly pure nitrogen was used as a drive gas in the analysis of NF₃/He, with the column CST and 5A temperature 50 ℃, column Q temperature 40 ℃, and the detector temperature (PPD) 150 ℃. The specification of the quantitative tube is 0.5 mL, and automatic injection with a ten-way valve. Figure 1 shows the gas path of GC in the standby state, the valve switching time is shown in Table 1.

![Figure 1. Gas path diagram of gas chromatography](image)

Table 1. Analytic procedure of nitrogen trifluoride in helium

| stage number | V1  | V2  | V3  | V4  |
|--------------|-----|-----|-----|-----|
| 1            | 0.00| 0.00| 4.09| 0.00|


Table 1: Analytic procedure of nitrogen trifluoride in helium
During the injection analysis, the column CST and the column Q can rapidly separate H₂, O₂, Ar, N₂ etc., but the separation speed of the gas such as NF₃ is slower. Therefore, the valve 1 is quickly switched to separate the N₂ and O₂ impurities and discharge the NF₃; due to the close peak time of O₂ and N₂, further separation of O₂ and N₂ by column 5A; switch valve 3 at a later time, discharge N₂ and O₂ impurities flowing out of column Q and analyze the NF₃ peak at around 6 min.

3. Results and discussion

3.1 Qualitative analysis

The NF₃ raw material gas was qualitatively analyzed by Tensor 27 Fourier transform infrared spectroscopy (FTIR) and Solarix XR Fourier transform mass spectrometry (FTMS) respectively. The experimental spectra are compared with the standard spectrum SDBS. Before the FTIR detection, the gas tank should be evacuated, and then the gas to be tested is introduced into the quartz gas tank with the infrared light-transmitting KBr window at both ends. Figure 2 shows the FTIR spectra of NF₃ raw material gas. The absorption bands at 1000 cm⁻¹ is attributed to the N-F stretching vibration. Figure 3 shows the FTMS spectra of NF₃ raw material gas. The molecular ion peak of m/z=71 can be found, and matching with high resolution mass spectrometry is 99.5 %. The results showed that it is the NF₃ raw material gas.

![Figure 2. FTIR spectra of nitrogen trifluoride](image1)

![Figure 3. Mass spectrogram of nitrogen trifluoride](image2)

3.2 Calibration curve establishment and uncertainty analysis

The concentration of the standard gas configured by the gravimetric method is shown in Table 2, and the uncertainty is analyzed by the previous formula[11]. Then, the NF₃/He concentration was determined by the analysis method of 2.3, and the peak height was used as the response value. Table 3 shows the preparation concentration and instrument response value of the sample to be tested, and the reproducibility of each group of data was calculated.

| Number | Concentration (μmol·mol⁻¹) | u₁ (%) | u₂ (%) | u₃ (%) | u (%) | u_{rel}(%) |
|--------|--------------------------|--------|--------|--------|-------|-----------|
| 1      | 103                      | 0.01   | 0.001  | 0.2292 | 0.2294| 0.4588    |
| 2      | 201                      | 0.01   | 0.001  | 0.0730 | 0.0737| 0.1474    |
| 3      | 297                      | 0.01   | 0.001  | 0.0563 | 0.0572| 0.1144    |
| 4      | 488                      | 0.01   | 0.001  | 0.0224 | 0.0246| 0.0492    |
By chemical analysis of the calibration fit curve, the process is to measure the signal values of multiple sets of samples of known concentration under the same conditions, and then, taking the signal value as a function of the sample concentration value, and the concentration as an independent variable and the signal value as the dependent variable. Finally, using the fitted curve to establish a regression equation \( y = f(x) \) for concentration and signal values. Substituting the measured signal value into the regression equation to calculate the concentration value \( x = f^{-1}(y) \) of the sample to be tested. In practical applications, the regression equation is often expressed as a function of the concentration value and signal value, the signal value is treated as an independent variable, and the concentration value is regarded as a dependent variable, which makes the calculation more convenient.

In gas chromatography, when the concentration of sample is high, the corresponding signal of the instrument will not be linear with the nominal concentration. The data in Table 3 was analyzed by linear regression analysis. It can be seen a significant bending tendency from the fitted graph and the residual graph (Figure 4.), and the data should be fitted with higher order regression equations. For higher-order regression equations, the correlation coefficient of the higher-order curve is greater than that of the lower-order curve and the accuracy of the high-order fitting result is higher than that of the low-order fitting. For analytical testing, a cubic curve can generally be given\(^\text{[12]}\). In this paper, a unary cubic polynomial fitting is selected, and there is no trend between the residual and the horizontal graph, and the fitting result is better. The polynomial fitting formula is as follows:

\[
y = ax^3 + bx^2 + cx + g = 1.42223e^{-16}x^3 + 1.61057e^{-9}x^2 + 0.00146x + 0.60935
\]

\( R^2 = 0.99971 \)

For the linear fitting curve, the dependent variable and the independent variable have their own uncertainty formula\(^\text{[13]}\). The uncertainty formulas of the dependent variable uncertainty are as follows:

\[
SR = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n-2}}
\]

\[
u(\bar{y}_0) = SR \times \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(\bar{x}_0 - \bar{x})^2}{\sum_{i=1}^{n} (x_i - \bar{x})^2}}
\]
Where $SR$ is the residual standard deviation of the calibration curve; $y_i$ is the concentration value in the data of the calibration curve; $x_i$ is the instrument signal value in the data of the calibration curve; $\hat{y}_i$ is the concentration value obtained from the calibration curve; $n$ is the number of sampling points of the calibration curve; $\bar{y}_0$ is the average concentration of the parallel samples; $x_{0}$ is the average of the signals of the parallel samples; $P$ is the average number of measurements of the sample point.

For the nonlinear calibration fitting curve, if the uncertainty formula directly citing from the linear fitting curve, it will cause a large error, and the power linearization method can be used to calculate the uncertainty of the standard curve [14]. For the concave fitting curve we get, we need to increase the power exponent. That is to find an optimal power exponent $k$, then, $x_i$ will be exponentiation, fit the curve with $x_i^k$ as the abscissa and $y_i$ as the ordinate. After repeated trials, we find $k = 1.349$ with the largest judgment coefficient $R^2$, and the linearized curve is shown in Figure 5. At last, the uncertainty calculation formula of the nonlinear fitting curve is obtained:

$$
\frac{1}{SR} \times \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{x_{i}^{1.349} - \bar{x}_{i}^{1.349}}{\bar{y}_{0}^{1.349} - \bar{x}_{i}^{1.349}} \right)^2}
$$

(3)

3.3 Analysis of a blind sample

The blind sample assessment is an important part of the CMA/CNAS certification review. Analysis of a blind sample can reflect the actual level of the laboratory equipment and technical quality directly [15]. The NF3/He in the two linear intervals was used as a blind sample to test the consistency of the measurement results. Calibrate with the standard gas on the concentration of 1025 $\mu$mol·mol$^{-1}$. The test results are shown in Table 4. The calculation formula is as follows:

$$
a_{c} = \frac{x_{c}}{x_{i}} \times \bar{a}
$$

(4)

Where $a_c$ is the concentration value obtained by parallel peak height from mutual calibration substituting the calibration curve; $\bar{a}$ is the average value of parallel results; $\bar{x}_{c}$ is the average value of the standard results; $\bar{x}_{i}$ is the average results of the standard samples in the calibration curve. The data is substituted into the table 4, and the response values are 399028、231307, respectively.

| Concentration ($\mu$mol·mol$^{-1}$) | peak height ($\mu$V) | RSD (%) |
|-------------------------------------|----------------------|---------|
| 1                                   | 2                    | 3       | AVG  |

Table 4   The experimental data of nitrogen trifluoride in helium
According to 《general and statistical principles for characterization of reference materials》 (JJF 1343-2012) [16], it is clearly stated that the total uncertainty of the analytical method consists of three parts, the first part is the uncertainty caused by gravimetric distribution of gas, the second part is the uncertainty of the value stability, and the third part is the uncertainty of the calibration curve. Introducing the uncertainty \( u_{CRM} \) of the gravimetric distribution standard gas and uncertainty \( u_s \) of the value stability, the formula for calculating the synthetic uncertainty of the calibration curve is as follows:

\[
u_h(\overline{y}_0) = \sqrt{u^2(\overline{y}_0) + u^2_{CRM} + u^2_s}
\]  

(5)

In the formula, \( u_{CRM} \) and \( u_s \) take the maximum value of each concentration.

The results of the consistency and uncertainty results of two blind samples are shown in Table 5. The consistency results of the parallel samples are smaller than the uncertainty of the fitting results. Therefore, the consistency of the parallel sample is considered to be better.

| concentration (μmol·mol\(^{-1}\)) | average measurement value (μmol·mol\(^{-1}\)) | Consistency (%) | uncertainty of fitting results (%) |
|----------------------------------|---------------------------------|-----------------|-----------------------------------|
| 837                             | 855                             | 2.15            | 7.86                              |
| 415                             | 431                             | 3.86            | 7.67                              |

3.4 Specific experiment

The specificity experiment is a measure of mutual interference in the analysis of complex samples. In the case where other components may exist, the method used can determine the characteristics of the measured object accurately, and it can reflect the accurate measurement ability of the test substances in the presence of the coexisting object[17]. In the actual preparation process, a very small amount of impurities such as nitrogen and oxygen will be introduced. Therefore, a certain amount of impurities will be added to the sample to prove whether the presence of a small amount of impurities has an effect on the detection of NF\(_3\). The measurement results are shown in Table 6.

| concentration (μmol·mol\(^{-1}\)) | impurities | concentration of impurities (μmol·mol\(^{-1}\)) | average measurement value (μmol·mol\(^{-1}\)) | Consistency (%) |
|----------------------------------|------------|---------------------------------|---------------------------------|-----------------|
| 301 N\(_2\)                       | 10         | 307                             | 1.99                            |
| 403 O\(_2\)                       | 10         | 410                             | 1.74                            |

The results show that the existence of trace nitrogen and oxygen impurities can hardly affect the detection of NF\(_3\).

4. Conclusions

In this experiment, a method for analyzing trace amounts of NF\(_3/\)He by GC with PPD detector was established, and a calibration curve in the concentration of 100-1000 μmol·mol\(^{-1}\) was established. Furthermore, special experiment and blind sample tests are completed. The results show that the method can be used to quantitatively analyze the trace amount of NF\(_3\); the nitrogen and oxygen impurities have no effect on the specificity; and the consistency of blind sample test results are better. In general, the method has advantages of simple operation, high sensitivity and strong practicability. It is an ideal method for detecting trace NF\(_3\) in helium.

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