Study on the traceability of equivalent water content of nitrogen tetroxide measured by nuclear magnetic method

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Abstract. This paper studies the traceability of the certified value of the reference material with the equivalent water content of nitrogen tetroxide (NTO) and green nitrogen tetroxide (MON), which lays the foundation for the certified value of the reference material. The purity of bibenzyl was measured by differential scanning calorimetry (DSC), the water content of deuterium acetonitrile (DAN) was measured by Karl Fischer method, the proton content and water content of deuterium acetonitrile (DAN) were measured by nuclear magnetic resonance spectroscopy (NMR), and the equivalent water content of deuterium acetonitrile (DAN) - nitrous oxide system was measured. All of these three methods can be directly traced to SI units, which are internationally recognized potential reference measurement methods. Therefore, the fixed value of equivalent water content reference material has metrological traceability.

1. Introduction

NTO and MON are commonly used propellants in the aerospace field [1]. In order to control the quality of NTO and MON, the state has issued national military standards, in which the equivalent water content is an important index [2,3]. Because considerable water content directly affects the corrosion rate of NTO storage tank and the physical state of corrosion products, thus affecting the storage and transportation of NTO, and even the success of space launch. Therefore, the equivalent water content of nitrogen tetroxide is strictly controlled at home and abroad, and the accuracy of the measurement of equivalent water content is directly related to the measurement method used.

In the seventies of last century, foreign countries have carried out the research on the determination of equivalent water content in NTO and MON by NMR [4,5]. In recent years, with the increasing popularity of superconducting high-resolution Fourier transform NMR, more and more measuring institutions use nuclear magnetic method to quantitatively analyze the content of a certain component in the mixture [6-9]. This provides a good foundation for the determination of the equivalent water content of nitrogen tetroxide by NMR.

Traceability refers to the characteristic that the measurement result or standard value can be connected with the specified reference standard, national measurement standard or international measurement standard through the continuous comparison chain with the...
specified uncertainty [10]. In measurement activities, all measurement results shall be traceable. It is of great significance to carry out the research on the traceability of the standard material with the equivalent water content of NTO by NMR.

In this paper, NMR method is considered to be a potential standard measurement method based on the study of the process of the certified value of the equivalent water standard substance of NTO.

2. Study on the technical traceability of the standard material with the equivalent water content of NTO

2.1. Measurement method of equivalent water content of NTO

The main methods to determine the equivalent water content in nitrogen tetroxide are gas chromatography, near infrared spectroscopy and microwave method.

Liu Zaihua et al. [11] of Xichang Satellite Launch Center systematically carried out theoretical and Experimental Research on gas chromatography, near-infrared spectroscopy and microwave method. It was pointed out that these three methods can be used for daily measurement of nitrogen tetroxide equivalent to water content, and there is no obvious systematic error between the three methods, of which the precision and accuracy of near-infrared spectroscopy is the best, followed by microwave method. Gas chromatography is the worst. The accuracy and precision of gas chromatography are poor because of its complicated operation steps, complex injection system, inconsistent state between drawing working curve and actual test.

Gas chromatography, near infrared spectroscopy and microwave are all relative measurement methods, and their sensitivity, precision and accuracy are not ideal, only suitable for the measurement of daily samples. These three methods are obviously not suitable for the reference materials with high accuracy.

2.2. The basis of nuclear magnetic quantitative analysis

In NMR hydrogen spectrum, the resonance peak area of a certain kind of proton is directly proportional to its content in the sample. When the internal standard with known mass and purity is added to the sample to be tested, the formula (1) [6-9] for quantitative analysis by NMR can be obtained.

\[
C_x = \frac{A_x}{A_s} \frac{m_x}{m_s} \frac{M_x}{M_s} \frac{N_x}{N_s} \cdot C_s
\]

In formula:

- \(A_x\) - absorption peak area of the component to be tested in the sample;
- \(A_s\) - absorption peak area of internal standard;
- \(m_x\) - quality of samples;
- \(m_s\) - quality of internal standard;
- \(M_x\) - the relative molecular mass of the component to be tested in the sample;
- \(M_s\) - relative molecular weight of internal standard;
- \(N_x\) - the specific number of protons contained in a molecule of the component to be tested in the sample;
- \(N_s\) - the specific number of protons contained in a molecule of the internal standard;
- \(C_s\) - content of components to be tested in the sample;
The internal standard must be used in the quantitative analysis of nuclear magnetic method. The internal standard must meet the following conditions: high purity; no water absorption and volatilization; low chemical reaction activity and toxicity; only a few nuclear magnetic signals; chemical displacement covering different areas; short longitudinal relaxation time; dissolving in a variety of deuterium reagents.

2.3. The basic steps of quantitative equivalent water content by NMR

First, the purity of bibenzyl was measured by DSC. Secondly, using bibenzyl as internal standard, the proton content and water content of DAN were measured by NMR. Thirdly, the water content of DAN was measured by Karl Fischer method. At last, DAN was used as internal standard to measure the equivalent water content of NTO by NMR.

2.3.1. Determination of the purity of bibenzyl by DSC. Bibenzyl is a suitable internal standard for the determination of proton content and water content in acetonitrile deuterium. Bibenzyl is a white monoclinic prismatic, acicular or small flake crystal, melting point (50-53) °C, easy to dissolve in carbon disulfide, ether and chloroform.

The purity of bibenzyl was determined by DSC. DSC method is a classical test method for the purity of high-purity organic matter. It is based on the principle of freezing point drop, with reliable thermodynamic basis and clear mathematical expression. It is an internationally recognized benchmark measurement method and has been used as the standard method of American Society for testing and materials [12]. Compared with other purity determination methods, DSC is used to determine the total amount of impurities, which has nothing to do with the type of impurities. For the samples with purity over 98%, the results are accurate and reliable.

2.3.2. Measurement of proton content and water content of DAN by NMR. The NMR spectrum of the Dan solution of tribenzyl is shown in figure 1, and the assignment of the peaks is shown in table 1.

![NMR spectrum of bibenzyl in DAN solution](image-url)
Table 1. Spectral peak assignment of bibenzyl in DAN solution.

| Peak δ | Multiplicity | Assignment |
|--------|--------------|------------|
| 1.93   | Quintuple peak; $J_{\text{H-D}}=2.5$Hz | $^1\text{H}$ peak position of DAN |
| 2.15   | Single peak | $^1\text{H}$ peak position of water in Dan |
| 2.91   | Single peak | $^1\text{H}$ peak position of methylene |
| 7.25   | Multiple peaks | $^1\text{H}$ peak position of benzene |

The content of protons in acetonitrile deuterium can be calculated by formula (2):

$$P_{an} = \frac{4m_{bb}M_{an}A_{an}}{3m_{an}M_{bb}A_{bb}}$$  \hspace{1cm} (2)

In formula:
- $P_{an}$ - proton content in DAN;
- $m_{an}$ - mass of DAN;
- $m_{bb}$ - quality of tribenzyl;
- $M_{an}$ - relative molecular weight of acetonitrile (CH$_3$CN);
- $M_{bb}$ - relative molecular weight of bibenzyl;
- $A_{an}$ - proton resonance peak area in DAN;
- $A_{bb}$ - proton resonance peak area of methylene in bibenzyl.

The water content in acetonitrile deuterium can be calculated by formula (3):

$$C_{an} = \frac{3M_{w}A_{w}P_{an}}{2M_{an}A_{an}}$$  \hspace{1cm} (3)

In formula:
- $C_{an}$ - water content in acetonitrile deuterium;
- $A_{w}$ - proton resonance peak area of water in deuterated acetonitrile;
- $M_{w}$ - relative molecular mass of water.

2.3.3. Measurement of water content of acetonitrile deuterium by Karl Fischer method. The water content of d-acetonitrile has a great influence on the equivalent water content of NTO. For this reason, two different methods are used to measure the water content of acetonitrile deuterium. Karl Fischer method is to use water and Karl Fischer reagent to produce quantitative reaction to measure the content of water. This method is a benchmark measurement method with high precision and accuracy, which has been determined as a standard measurement method by many countries and professional technical institutions [13,14]. Karl Fischer method is divided into capacity method and Coulomb method. The capacity method is suitable for the analysis of constant moisture and the coulometric method for the analysis of micro moisture. The measuring principle of coulometry is to measure the quantity of electricity in electrolytic reaction or the content of water by measuring the electrolytic current and time. After being treated with 3A molecular sieve for a few days, the moisture content of d-acetonitrile will be very low, which can be as low as 0.0043% [5] according to foreign research, and it is suitable for coulometric measurement.
2.3.4. **Determination of equivalent water content of NTO by NMR.** The ratio of the number of protons in the equivalent water of nitrogen tetroxide to the number of protons in the equivalent water of acetonitrile deuterium is equal to the ratio of the area of the proton resonance peak of the equivalent water of NTO to the area of the proton resonance peak of acetonitrile deuterium. The equivalent water content of NTO can be obtained by measuring the area of the two proton resonance peaks.

Acetonitrile is a kind of colorless liquid with a boiling point of (80-82) °C, soluble in water. After the hydrogen atom (H) in acetonitrile (CH$_3$CN) is replaced by deuterium atom (D), three kinds of compounds are formed: CH$_2$DCN, CHD$_2$CN and CD$_3$CN. Among them, CD$_3$CN content $\geq$ 99.8%, CHD$_2$CN trace, CH$_2$DCN and CHD$_2$CN content almost zero.

The total content of water measured by nuclear magnetic method must be subtracted from the water content of acetonitrile deuterium to obtain the equivalent water content of NTO, as shown in formula (4):

$$C_w = \frac{(m_w - m_{an} C_{an})/m_{n\text{ito}}}{2A_{an} M_{an} - m_{an} C_{an}}$$  \hspace{1cm} (4)

In formula:
- $C_w$ - equivalent water content of NTO;
- $A_w$ - the proton resonance peak area of NTO equivalent to that of water;
- $A_{an}$ - proton resonance peak area of acetonitrile deuterium;
- $M_w$ - relative molecular mass of water;
- $M_{an}$ - relative molecular weight of acetonitrile (CH$_3$CN);
- $m_{an}$ - mass of acetonitrile deuterium;
- $m_{n\text{ito}}$ - quality of NTO;
- $P_{an}$ - proton content of DAN;
- $C_{an}$ - water content of DAN.

The NMR spectrum of DAN-NTO solution is shown in Figure 2, and the assignment of each peak is shown in table 2.

![NMR spectrum of DAN-NTO](image)
Table 2. Peak assignment of DAN-NTO.

| Peak δ | Multiplicity | Assignment                                      |
|--------|--------------|------------------------------------------------|
| 1.93   | Quintuple    | 1H resonance peak of DAN                       |
| 13.78  | Single       | 1H resonance peak of water in Dan and NTO      |

2.4. Traceability analysis of equivalent water content by NMR

It can be seen from formula (1) that the content of the components to be tested in the sample mainly involves the purity of the internal standard, the mass of the sample and the internal standard, the relative molecular mass of the components to be tested and the internal standard, and the absorption peak area of the components to be tested and the internal standard in the sample. The area of absorption peak is the main source of the uncertainty of measurement results. According to the definition of reference measurement method [14], it can be judged that the nuclear magnetic quantitative analysis method belongs to the reference measurement method. Foreign scholars also believe that nuclear magnetic quantitative analysis belongs to the benchmark measurement method [6-9].

DSC method and Karl Fischer method are also used in the determination of the equivalent water content of NTO, and these two methods have been generally recognized as benchmark measurement methods by the international metrology community. Therefore, the determination method of the equivalent water content of nitrogen tetroxide belongs to the benchmark measurement method, which has metrological traceability.

3. Conclusions

DSC, Karl Fischer and NMR methods were used to determine the equivalent water content of NTO. Through the analysis and research of nuclear magnetic method, it is known that nuclear magnetic method is a benchmark measurement method, while DSC method and Karl Fischer method have been generally recognized as benchmark measurement methods by the international metrology community. Therefore, the determination method of the equivalent water content of NTO belongs to the benchmark measurement method, which has metrological traceability.

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