Research Progress on Detection Methods of Trace Dimethyl Hydrazine

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Abstract. UDMH is an important fuel for missiles, satellites and spacecraft launch tests and carrier rockets. It is still very difficult to detect trace UDMH in environmental samples. The research status of gas chromatography (GC), high performance liquid chromatography (HPLC), ion chromatography (IC) and other techniques applied to the analysis of trace UDMH is reviewed. The advantages and disadvantages of these methods are discussed.

1. Introduction

Unsymmetrical dimethylhydrazine (UDMH) is widely used in military and aerospace fields as an important engine fuel for missile, satellite and spacecraft launch tests and launch vehicles. With the development of science technology and the exploration of human outer space, the use of UDMH has gradually increased, but as a highly toxic compound, the strict requirements of the allowable concentrations in the environment is put forward around the world, for example, The interim standard of allowable mass concentration of UDMH in urban water sources is 0.06 μg/L [1-2] in Russia, and the maximum allowable emission concentration of GB/T 14376-93 and GJB 3485A-2011 is 0.5 mg/L in China. In addition, due to its strong chemical activity UDMH is easily oxidized into hydrazine, amines and other substances, it becomes more difficult to detect UDMH. At present, Because the impact of trace amounts of UDMH in water, atmosphere and soil on the surrounding environment and human life is concerned, the detection of UDMH is crucial.

2. UDMH detection method

2.1. Gas Chromatography (GC)

Gas chromatography (GC) is a color separation analysis method using gas as mobile phase. It has high sensitivity, high separation efficiency, high selectivity, rapid analysis and easy operation. It is suitable for qualitative and quantitative analysis of volatile organic compounds. For non-volatile liquids and solid substances, it can be analyzed by pyrolysis and gasification.

2.1.1. Detection of UDMH in soil and water. GC analysis of UDMH mainly uses three detectors: nitrogen phosphorus detector (NPD), mass spectrometer detector (MS) and flame ionization detector (FID). SASavchuk et al. [3] used GC to analyze UDMH in soil samples. UDMH was first derivatized with 4-nitrobenzaldehyde and then analyzed by GC. The detectors of NPD, FID and MS could be...
selected, and the results showed that, at the signal-to-noise ratio of 3:1, the detection limits of NPD, FID, and MS were 3 μg/kg, 10 μg/kg, and 8 μg/kg, respectively, and the error was minimal when using NPD. Sotnikov et al. [4] reacted UDMH with 4-nitrobenzaldehyde to form hydrazone, extracted with hexane at room temperature, and concentrated by evaporation in an argon atmosphere, after headspace analysis, temperature programmed, NPD was used for detection. The detection of UDMH in water was achieved, and the detection limit was 0.03 μg/L.

2.1.2. Detection of gaseous UDMH. In the quantitative analysis, it is often necessary to correct the signal output with a known pure sample. In addition to physical absorption, the solution absorption process is accompanied by chemical absorption (including derivatization). Because dimethyl hydrazine is very soluble in water, it is attempted that the aqueous solution containing the derivatizing reagent is used as the absorbing solution of sampling and the effect of different sampling flows on the sampling efficiency was investigated.

Cao et al. [10] proposed that a dynamic gas distribution device was used to generate a constant concentration of dimethyl hydrazine gas, and the gas volume was 0.05 mg·m⁻³, 9 mg·m⁻³, and 25 mg·m⁻³, respectively, and two bubble absorption tubes were connected in series, the sampling flow is 1 L·min⁻¹, 0.6 L·min⁻¹, and 0.2 L·min⁻¹, and the sampling time is 2~100 min, and the dimethyl hydrazine in each absorption bottle is determined according to the test method. The test shows that when the flow rate is 1 L·min⁻¹, 0.6 L·min⁻¹, and 0.2 L·min⁻¹, the sampling efficiency is 78%~89%, 85%~91%, and 95%~98%, respectively. The results show that a relatively high sampling efficiency can be obtained by selecting a lower sampling flow, and it is feasible that the aqueous solution containing the derivatization reagent is used as the absorption liquid, and the bubble absorption tube is used as the gas collector. Compared with the specified sampling method using solid adsorption, it avoids the sampling loss caused by the desorption process, the sampling process is simplified, and the high sampling efficiency is obtained. The recovery and precision results are shown in Table 1 [10].

| Add a scalar/μg | Recycled/μg | Recovery rate/% | RSD/% |
|----------------|-------------|-----------------|-------|
| 5              | 4.5         | 90.0            | 4.09  |
| 20             | 17.6        | 88.0            | 3.29  |
| 60             | 55.8        | 93.0            | 2.96  |

Although the GC method has many advantages, the direct qualitative analysis by the GC method must be compared with the corresponding chromatographic peaks using known data, or combined with other methods (such as mass spectrometry, spectroscopy).

2.2. High Performance Liquid Chromatography (HPLC)

The high performance liquid chromatography (HPLC) method is used for the analysis of organic compounds and various ions with high boiling point, large relative molecular mass and poor thermal stability. A UV detector is often used for HPLC analysis of UDMH. Han Ying et al. [11] studied HPLC method for UDMH concentrations detection in water sample, and the precision of the analytical method was examined. The theoretical value ρₘ, the average measured value ρₘ, and the standard deviation value ρₘ are shown in Table 2 [11], it can be seen that the relative standard deviation of the aqueous solution of UDMH with different mass concentrations is ≤ 1.69%. The reproducibility of the detection method is good, and the requirement of the relative standard deviation ≤ 5% in the trace detection can be satisfied. The recoveries of water samples are shown in Table 3 [11], which indicates that the established analytical methods are ideal and reliable.
Table 2. Precision of measurement results [11]

| \( \rho_{th} \) (UDMH)/ (\( \mu g \cdot L^{-1} \)) | \( \rho_m \) (UDMH)/ (\( \mu g \cdot L^{-1} \)) | \( \rho_d \) (UDMH)/ (\( \mu g \cdot L^{-1} \)) | Relative standard deviation/% |
|---------------------------------|---------------------------------|---------------------------------|-----------------------------|
| 5.0                            | 4.81                           | 0.063                           | 1.30                        |
| 20.0                           | 20.11                          | 0.340                           | 1.69                        |
| 50.0                           | 47.87                          | 0.579                           | 1.21                        |

Table 3 Determination of standard recovery [11]

| Add a scalar/ (\( \mu g \cdot L^{-1} \)) | Measured massconcentration/ (\( \mu g \cdot L^{-1} \)) | Recovery rate/% |
|---------------------------------|---------------------------------|------------------|
| 5.0                             | 4.81                           | 96.2             |
| 10.0                            | 10.21                          | 102.1            |
| 20.0                            | 20.11                          | 100.6            |
| 30.0                            | 29.69                          | 99.0             |
| 40.0                            | 41.07                          | 102.7            |
| 50.0                            | 47.87                          | 95.7             |

2.3. Ion chromatography (IC)

Ion Chromatography (IC) is a method of separating, characterizing, and quantifying a plurality of coexisting anions or cations by ion exchange. It has the characteristics of good selectivity, high sensitivity, low detection limit, convenient and quick.

The IC method is mainly detected by electrochemical detectors (including conductivity detection and amperometric detection) and optical detectors. Fiala [8] reported the separation of hydrazine, methyl hydrazine, 1, 1-dimethylhydrazine and 1, 2-dimethylhydrazine by the IC method. After electrochemical oxidation of +1.00 V (for Ag/AgCl), a cation exchange column filled with Aminex A-5 (porous anion exchange resin), a mobile phase with pH value of 8.9, and an amperometric detector were used for analysis. Based on high performance polymers of the cation exchanger Aminex A-5, the suitable retention times and separation selectivity are obtained by utilizing different degrees of protonation of the separated samples in the boric acid buffer solution.

Sun Sulli et al. [12] proposed a quantitative analysis method of dimethyl hydrazine by ion chromatography. Methanesulfonic acid solution with the concentration of 20 mmol\( \cdot \)L\(^{-1} \) was used as the eluent, and CS12A (250 mm\( \times \)4 mm) cation exchange column, a conductivity detector was selected, and an external standard method were used for quantification. The results of the precision measurement of dimethyl hydrazine are shown in Table 4[12]. The relative standard deviation (RSD) of dimethyl hydrazine was 1.10%, and the average content of dimethyl hydrazine in the sample was 49.5% [12].
Table 4 Precision measurement results of dimethyl hydrazine by ion chromatography [12]

| The serial number | The determination of value/% | The average/% | Mean standard deviation/% | RSD/% |
|-------------------|------------------------------|--------------|--------------------------|-------|
| 1                 | 49.6                         | 49.5         | 0.54                     | 1.10  |
| 2                 | 49.3                         |              |                          |       |
| 3                 | 49.5                         |              |                          |       |
| 4                 | 49.8                         |              |                          |       |
| 5                 | 49.9                         |              |                          |       |
| 6                 | 49.8                         |              |                          |       |
| 7                 | 50.5                         |              |                          |       |
| 8                 | 48.8                         |              |                          |       |

Although IC technology combines classical ion exchange methods, modern instrumental analysis techniques, and high-performance resins, the application prospects are broad; however, the main properties of IC filler materials (such as selectivity, retention time, chemical and mechanical stability, and non-specific interactions) are effected by the resin matrix, functional group characteristics, and ion exchange capacity, practical application and chromatographic performance are related to the test conditions. The possible way to optimize IC separation is to develop newer resins with better performance. It must be noted that the retention time of hydrazine is similar to that of a similarly structured amine on the cation exchange column [9].

2.4. Other testing methods
In addition to chromatographic detection of UDMH, there are spectrophotometric method and electrochemical method (EC). EC method not only has special selectivity, but also has high sensitivity; the glassy carbon electrode used in the electrochemical detector is electrochemically pretreated, and obtained very low oxidation potential [5]. Joseph Wang et al. [6] proposed chemically modify the glassy carbon electrode with RuCl₃/K₄Ru(CN)₆ solution when studying the hydrazine compound analysis method. The stability of the modified electrode was improved, the pH range was wider, and the electrochemical oxidation of hydrazine compounds could be realized in acidic and neutral media.

3. UDMH test considerations
The following points should be noted when actually measuring dimethyl hydrazine:
1. UDMH is highly toxic and cannot be tested on site. It needs to be pre-treated. In addition, in the course of testing, attention should be paid to prevent the degradation of UDMH and produce toxic nitrogen-containing compounds.
2. HPLC derivatization reaction and product stability are often interfered by matrix and excess reagents. The distribution coefficient of trace analysis is low, the organic solvent is toxic, and the pre-enrichment process is difficult to automate.
3. Temperature is the key factor of the derivatization reaction. The reaction rate is accelerated by the increase of the temperature, meanwhile, the decompose of UDMH could be accelerated, so the temperature of the derivatization reaction will affect the accuracy of the analysis results.

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