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Key Factors for Rapid Detecting 1,1-dimethylhydrazine in Air by Solution Absorption/Spectrophotometry Method

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Abstract. In order to improve the detection efficiency of 1,1-dimethylhydrazine in air by solution absorption/spectrophotometry method, some key factors were analysed, such as the absorption velocity and the number of large bubble absorber tubes. The results of this method were compared with that of Chinese national standard method under different concentration of UDMH. The results showed that two bubble tubes in series could meet the collection efficiency and the best absorption velocity was 0.2 L min⁻¹. The standard deviation of the method was less than 5%, and the error of the method and the national standard method was less than 2%. The proposed method has the characteristics of simple operation, high precision and high reliability.

1. Introduction

1,1-dimethylhydrazine (Unsymmetrical dimethylhydrazine, UDMH) is widely used as a liquid propellant fuel for missile weapons and launch vehicles because of its high specific impulse characteristics[1-3]. UDMH can be absorbed through skin, respiration and digestive tract, causing damage to the nervous system and respiratory system[4,5]. The composition of decay products in the atmosphere is very complicated. There are quite a few studies that prove that UDMH and its decay-product is carcinogenic, mutagenic, and teratogenic to animals [6]. Appendix in Chinese standard GJB 2211-94 clearly stipulates that the maximum allowable concentration of UDMH in the workplace air is 0.5 mg m⁻³, and the maximum allowable concentration of UDMH in the residential area is 0.03 mg m⁻³. Therefore, the detection of UDMH in the air environment is of great significance for ensuring the health of workers, preventing accidents, controlling environmental pollution and ensuring the smooth completion of military tasks. In Chinese national standard GB 18059-2000, UDMH is detected by solid absorption/spectrophotometry method, which is complex and time consuming during the sampling process. Han et al. [7] developed a solution absorption/spectrophotometry which can simplify the sampling. In this study, the effect of several key factors of the method, such as the absorption velocity and the number of large bubble absorber tubes, were further studied.

2. Experimental

2.1. Apparatus and reagents

2.1.1. Apparatus. UV-vis spectra were obtained on a Cary 50 UV-visible spectrophotometer; UDMH gas was produced by the hydrazine fuel dynamic gas distributing device developed by ourselves [8]; a QT-2A atmospheric sampler was used for gas collection and calibrated by a GL 102B soap film flow-meter.



2.1.2. Reagents. UDMH was self-purified ($\geq 99\%$); Sodium nitroferricyanide, citric acid, disodium phosphate, ammonia, and sulfuric acid were of analytical grade; water was secondary distilled water.

2.2. Generation and collection of UDMH gas

The UDMH gas collection system in the experiment is shown in Figure 1. It mainly includes gas distributing device, gas diffusion device, bubble absorption tube and atmospheric sampler. The atmospheric sampler has a sampling rate ranging from 0.1 to 1.5 L min^{-1} , and is connected to a large bubble absorption tube or a sampling tube to collect UDMH gas from the diffusion device. The large bubble absorption tube can be connected in series. The sampling rate of the atmospheric sampler is corrected with a soap flow meter before each sampling.

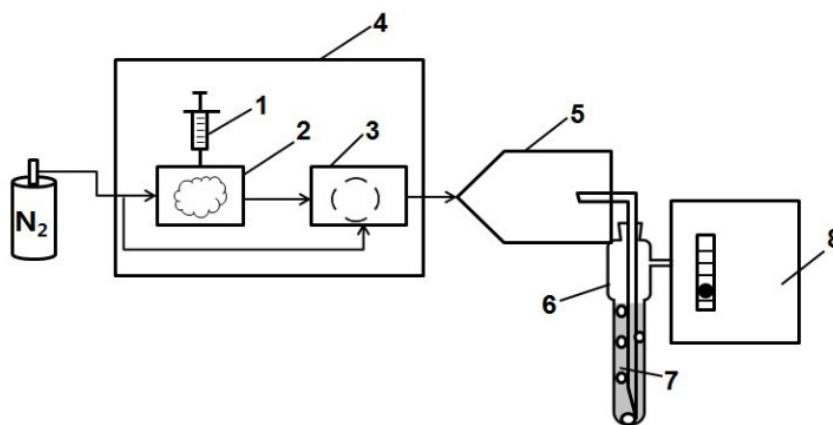


Figure 1. Schematic diagram of gas generating and sampling system

1-UDMH injector; 2-vaporization chamber; 3-mixing chamber; 4-gas distributing device;
5-gas diffusion device; 6-bubble absorption tube; 7-absorption solution; 8-atmospheric sampler

2.3. Sorbent adsorption/spectrophotometry

Sorbent adsorption/spectrophotometry was implemented according to Chinese national standard GB 18059-2000 *Hygienic Standard for Unsymmetric dimethylhydrazine in Air of Residential Area*.

2.4. Solution adsorption/spectrophotometry

2.4.1. The preparation of the solution. Trisodium-pentacyanoamino ferrate (TPF) was prepared referring to the Solution adsorption/spectrophotometry method. TPF solution: 0.1 g of TPF was dissolved in 100 mL of distilled water. Buffer solution: 21 g of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) was dissolved in 1000 mL of distilled water at a concentration of 0.1 mol L^{-1} ; 71.6 g of disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) was dissolved in 1000 mL of distilled water at a concentration of 0.2 mol L^{-1} . 505 mL of citric acid solution and 685 mL of disodium hydrogen phosphate solution were mixed into a buffer of pH 5.6. The pH of each preparation buffer was calibrated with a pH meter to make it equal 5.6. UDMH standard solution: 1.28 mL of UDMH was pipetted into a 100 mL volumetric flask, which was diluted with the above buffer solution to the scale and shaken, then 1 mL of the above solution was added to a 1000 mL volumetric flask, which was diluted with the buffer solution to the scale and shaken. The solubility of UDMH in this standard solution is $10 \mu\text{g mL}^{-1}$.

2.4.2. Detection procedure. First, a calibration curve between the UDMH content and solution absorption was established. As absorption solution, 10 mL buffer solution was added to a bubble tube for collecting UDMH gas. After sampling for a period of time, the absorption solution was transferred into a colorimetric tube containing 10 mL of the TPF solution, and the colorimetric tube was diluted to the scale with the buffer solution and shaken. The tube was then left at 25°C for 15 min . The

absorbance was determined according to the conditions and steps of making standard curve. The average absorbance was deducted from the blank absorbance. The content of UDMH in solution was obtained by comparing with the standard curve. The system should be balanced for at least 30 minutes before sampling.

2.4.3. Calculation. The concentration of UDMH in air was calculated according to equation 1.

$$c = \frac{w \times 1.013 \times 10^5 \times (273 + T)}{q \times t \times P_T \times 273} \quad (\text{Eq. 1})$$

Where c is the concentration (mg m^{-3}) of UDMH in air; w is the content (μg) of UDMH in the solution; T is the environmental temperature ($^{\circ}\text{C}$) when sampling; q is sampling velocity (L min^{-1}); P_T is the atmospheric pressure (Pa) when sampling; t is sampling duration (min).

3. Results and discussion

3.1. Calibration curves of this method

The standard curve of the absorbance A_{500} ordinate of the colorimetric tube at 500 nm is shown in Figure 2 with the UDMH content w in the colorimetric tube as the abscissa. Fitting analysis showed that the standard curve of w - A_{500} was $A_{500} = 0.02614w - 0.00649$, and the correlation coefficient $r=0.9999$, indicating that this method could be used for further gas concentration detection.

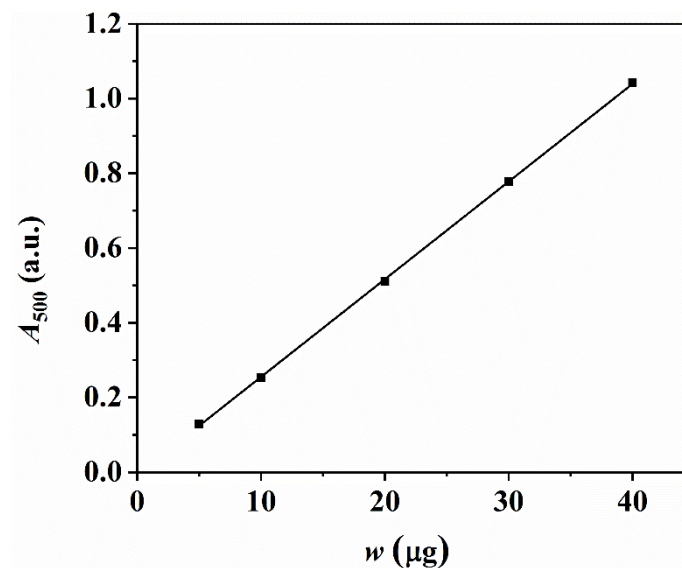


Figure 2. Calibration curves of solution absorption/spectrophotometry

3.2. Effect of sampling velocity

To investigate the effect of gas collection rate q on the efficiency of the sampling tube, the collection rate q of atmospheric sampler was set to 0.1 L min^{-1} , 0.2 L min^{-1} , 0.3 L min^{-1} and 0.4 L min^{-1} . Under the condition of fixed dynamic gas distribution parameters, the c - q relationship is shown in Figure 3

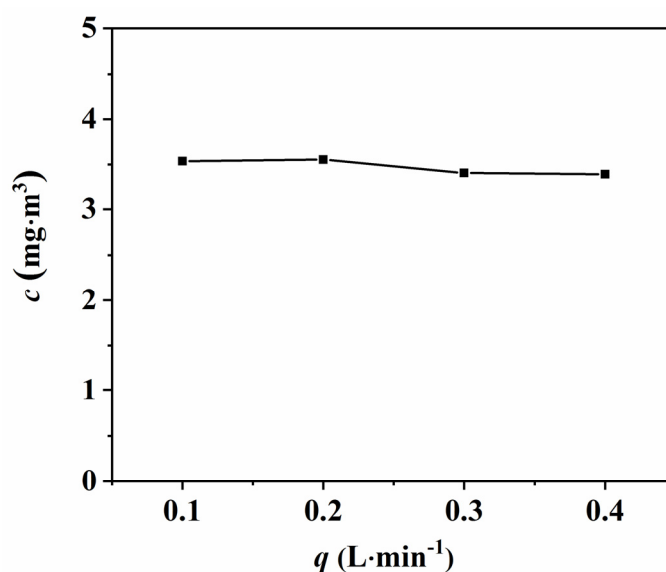


Figure 3. Effect of sampling rate on absorption efficiency of UDMH gas

As can be seen from Fig. 3, the concentrations of UDMH gas measured at different sampling rates were slightly different. As sampling velocity increased, the measured concentrations of UDMH gas decreased slightly. Consider the time factor, the sampling rate of the subsequent experiments was set at 0.2 L min⁻¹.

3.3. Effect of two tubes in series

Without other test methods for reference, it was hard to say whether one bubble tube could collect UDMH gas efficiently or not. Therefore, it is necessary to examine the absorption effect of the absorption tube by connecting a plurality of absorption tubes in series. The experiment used two absorption tubes in series to collect UDMH gas. According to the near and far order of the diffusion device, they were 1 (near) and 2 (far), and three sets of parallel experiments were performed, numbered 1-1, 1-2, 2-1, 2-2, 3-1 and 3-2, respectively. The UDMH content w in each of the absorption tubes were obtained as shown in Figure 4.

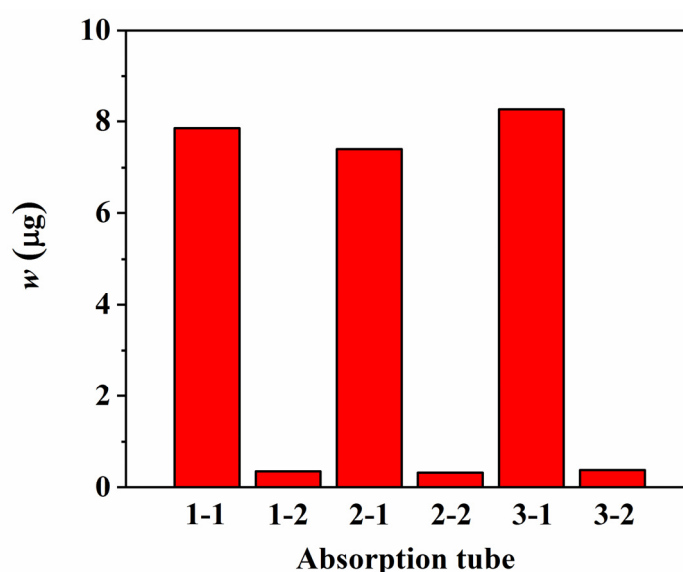


Figure 4. UDMH content in different absorption tubes

As can be seen from Fig. 4, the results of the three sets of experiments didn't have much difference. The content of UDMH collected in No. 1 tube was 7.852 μg , 7.4 μg , and 8.258 μg , respectively, while the content of UDMH collected in No. 2 tube was 0.363 μg , 0.333 μg , and 0.393 μg , respectively. In the three sets of experiments, the UDMH content of No. 2 tube accounted for about 4.62%, 4.50%, and 4.72% of the No. 1 tube, respectively, indicating that the UDMH gas was not sufficiently absorbed by the No. 1 tube, and that the unabsorbed UDMH gas was absorbed by the No. 2 tube. At the same time, the amount of UDMH entering the No. 2 tube was very low, accounting for about 4.6% of the No. 1 tube averagely. Therefore, the use of two absorption tubes can meet the sampling requirements.

3.4. Determination results under different concentrations of UDMH gas

To examine the accuracy of solution absorption/spectrophotometry for the detection of UDMH in air, the solid adsorption/spectrophotometry method in the China national standard was used as a standard reference method, and the concentration of UDMH gas was measured under different gas distribution parameters. The experimental results are shown in Figure 5.

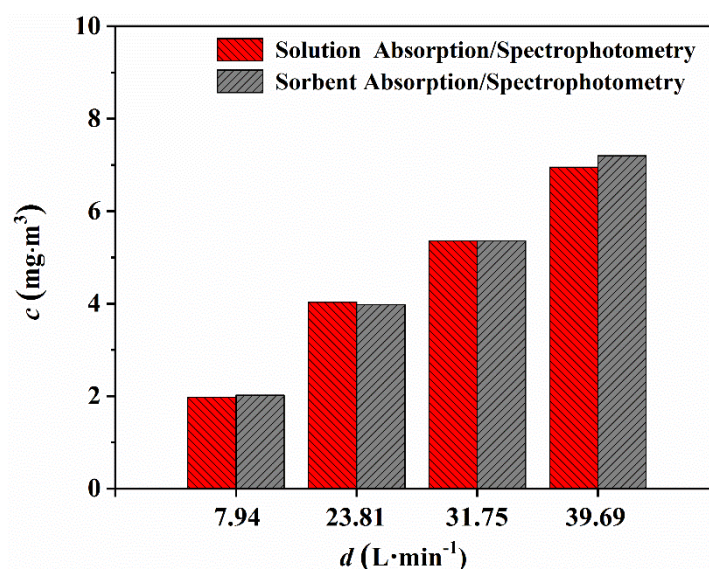


Figure 5. Comparison of the results of two detection methods under different gas distribution parameters

It can be seen from Fig. 5 that under different gas distribution parameters, the relative deviations of the two methods were all less than 5%, and the detection results are close. It was calculated that the results errors between the two methods was less than 2%, indicating that the solution absorption/spectrophotometry method can be used for detecting the UDMH concentration in air instead of the stand method.

4. Conclusion

In this paper, the concentration of UDMH gas was measured by solution absorption/spectrophotometry. The effects of different absorption rates, number of absorption tubes and gas concentration conditions on the method were studied. The main conclusions are as follows: The sampling rate of the atmosphere can affect the absorption efficiency of the absorbing solution for UDMH gas. The higher the rate, the lower the absorption efficiency. This experiment selected a sampling rate of 0.2 L min^{-1} . The absorption of the UDMH gas is not efficient enough with one bubble tube, and two absorption tubes in series need to be connected for gas sampling to ensure accurate results. The results of solution absorption/spectrophotometry were close to that of solid adsorption spectrophotometry under the four concentrations of UDMH gas in the experiment, and the errors were

all less than 2%. Moreover, the relative standard deviation was less than 5%. This method can replace the national standard method for rapid detection of UDMH gas concentrations in air.

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