

Solution Absorption/Spectrophotometry for Determination of Hydrazine in Air

Xu Yao^{1,2}, Guangyou Zhang², Xuanjun Wang¹, Li Wang², Chunhua Fan²

¹ High-Tech Institute of Xi'an, Xi'an 710025, China;

² Center for Propellants Determination and Protection, Space Systems Division, Beijing 100101, China.

Abstract: A solution absorption/spectrophotometry method was established for the determination of hydrazine in air. The collection efficiency of hydrazine in air under different sampling conditions was analyzed. The determination results were compared with those of the national standard method. We found that the collection efficiency of hydrazine gas was high with the solution absorption method; the relative standard deviation of determination results within this method was less than 5% and the relative error between the two methods was less than 2%. The proposed method had the characteristic of fast and relatively simple operation with high accuracy and reliability.

1. Introduction

As a kind of fuel, hydrazine (Hz) can be used for rocket launch and spacecraft attitude control[1]. Hydrazine is also a commonly used chemical raw material or intermediate, such as the production of herbicides, anti-corrosion boiler and ceramic production[2,3]. However, it is toxic and can cause poisoning through skin penetration, digestive tract absorption and respiration[4]. The production, transportation and storage of hydrazine and the process of rocket launch will produce waste gas which is easy to pollute the environment. The national standard in China rules that the maximum daily allowable average concentration of hydrazine is 0.02mg m^{-3} and the maximum allowable concentration of hydrazine is 0.05mg m^{-3} , providing the two standard detection methods, sorbent adsorption/spectrophotometry and sorbent adsorption/gas chromatography[5]; these two methods are complex, time-consuming and low efficiency because they need the preparation of adsorbents, the production of adsorption tubes and desorption process. Han et al.[6,7] studied the use of solution absorption/spectrophotometry to detect the unsymmetrical dimethylhydrazine in air; the results showed that the method is not only accurate and reliable, but also simple and fast. In order to further improve the detection efficiency of hydrazine in air, the determination of hydrazine in air was studied by solution absorption/spectrophotometry.

2. Experimental

2.1. Apparatus and reagents

2.1.1. Apparatus. Hydrazine gas was produced by the hydrazine fuel dynamic gas distributing device. UV-vis spectra were obtained on a Cary 50 UV-visible spectrophotometer, Gas collection was carried out using a QT-2A atmospheric sampler and the sampler was calibrated by a GL 102B soap film flow-meter.



2.1.2. Reagents. Hydrazine was self-purified ($\geq 99\%$); p-dimethylaminobenzaldehyde, sulfuric acid, methanol, ethanol and hydrazine sulfate were of analytical grade; water was secondary distilled water.

2.2. Procedure

2.2.1. Generation and collection of hydrazine gas. In this work, the hydrazine gas was generated by the self-developed hydrazine fuel dynamic gas distribution device[8], as shown in Figure 1. The device can produce different concentrations of hydrazine gas by adjusting the gas flow parameters and form the corresponding concentration of hydrazine gas atmosphere with a diffusion device; the bubble absorption tubes or sampling tubes, connecting to a atmospheric sampler, collected the hydrazine gas from the diffusion device. The bubble absorption tubes can be connected in series. The sampling velocity of the atmospheric sampler was corrected with a soap film flowmeter.

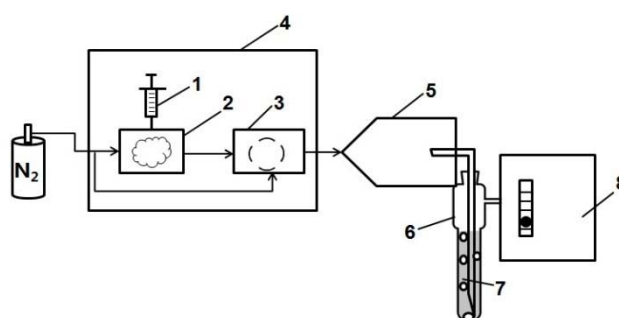


Fig. 1 Schematic diagram of gas generating and sampling system

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

2.2.2. Sorbent adsorption/spectrophotometry. Sorbent adsorption/spectrophotometry was implemented according to a China national standard *Hygienic Standard for Hydrazine in Air of Residential Area*[5].

2.2.3. Solution adsorption/spectrophotometry

2.2.3.1. The preparation of the solution. Sulfuric acid solution (0.05 mol L^{-1}): 2.8mL of concentrated sulfuric acid was slowly added to 1000mL of distilled water with a pipette suction; Chromogenic agent solution: 10.0g of p-dimethylaminobenzaldehyde was dissolved in 500 mL of ethanol, followed by drop-wise addition of 20mL of concentrated sulfuric acid; Hydrazine standard solution ($1 \mu\text{g mL}^{-1}$): 0.4066g of hydrazine sulfate was added to a 1000 mL volumetric flask, which was diluted with sulfuric acid solution to the scale and shaken. 5.0 mL of the above solution was added to a 500 mL volumetric flask, which was diluted with sulfuric acid solution to the scale and shaken.

2.2.3.2. Detection procedure. Firstly, the calibration curve was established by adding different content of hydrazine standard solution with chromogenic agent solution. 10mL of sulfuric acid solution, as absorption solution, was added to a bubble absorption tube, which was used to collect hydrazine gas. After a certain time of sampling, the absorption solution was transferred to a colorimetric tube containing 10mL of chromogenic agent solution, and the colorimetric tube was diluted with sulfuric acid solution to the scale and shaken. Then, put the tube aside for 30min. The absorbance was measured according to the conditions and steps of making the calibration curve, and the average absorbance was obtained. The calibration curve was used to get the hydrazine content (μg) of the solution.

2.2.3.3. Calculation. The concentration of hydrazine in air was calculated according to formula (1).

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

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

3. Results and discussion

3.1. Calibration curves of two methods

Using the least squares method, the calibration curves of the two methods were established as shown in Figure 2. It can be seen from Figure 2 the coefficient of determination (R^2) of the two methods were all more than 0.999, indicating that the experimental operation was reliable and the calibration curve was so qualified for gas concentration detection.

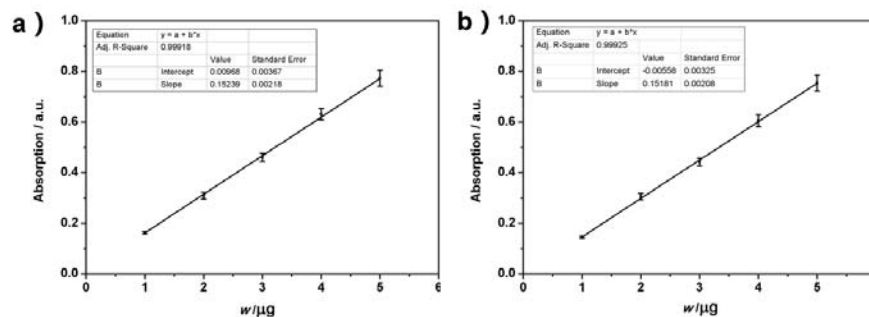


Fig. 2 Calibration curves of two detection methods (a) solution absorption/spectrophotometry, b)sorbent absorption/spectrophotometry)

3.2. Effect of sampling velocity

Figure 3 shows the effect of sampling velocity (q) on the absorption efficiency of hydrazine gas, which is represented by the atmospheric concentration of hydrazine (c). In view of the outgassing velocity ($\sim 0.5 \text{ L min}^{-1}$) of the dynamic gas distribution device, the experimental gas sampling velocity was set less than 0.5 L min^{-1} to avoid breaking the gas balance in the diffusion device. As can be seen from Figure 3, the concentrations of hydrazine measured at different sampling velocity were slightly different. As the sampling velocity increased, the measured concentration of hydrazine gas was slightly reduced.

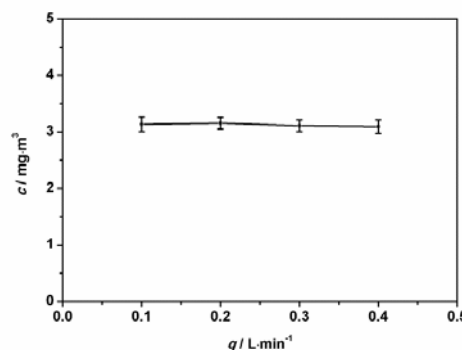


Fig. 3 Effect of sampling rate on absorption efficiency of hydrazine gas

3.3. Effect of two tubes in series

In the absence of other detection methods for reference, it was hard to say whether one bubble absorption tube could absorb hydrazine gas efficiently or not. Therefore, it was necessary to examine the absorption effect of several tubes in series. Three groups of parallel experiments were carried out using two absorption tubes in series to collect hydrazine gas, and the tubes were numbered as 1-1, 1-2, 2-1, 2-2, 3-1, 3-2. The hydrazine content in the absorption tubes is shown in Figure 4. As can be seen from Figure 4, the results of the three groups of experiments were not much different. The content of hydrazine collected in the No. 1- tubes was 6.515 μg , 6.558 μg and 6.500 μg , respectively, and that of the No. 2- tubes was 0.025 μg , 0.023 μg and 0.029 μg respectively, indicated that the hydrazine gas had been absorbed efficiently through the front tubes and the hydrazine content absorbed through the back tubes was very low. Therefore, only one bubble absorption tube can meet the requirements for collecting hydrazine gas.

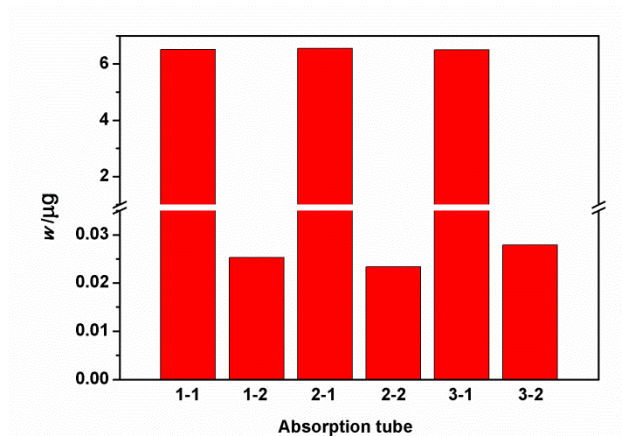


Fig. 4 Hydrazine content in different absorption tubes

3.4. Determination results under different concentrations of hydrazine gas

In order to investigate the accuracy of solution absorption/spectrophotometry for the determination of hydrazine in air, the solid adsorption/spectrophotometry in national standard was used as reference and the tests were carried out under different gas distribution parameters. The results are shown in Figure 5.

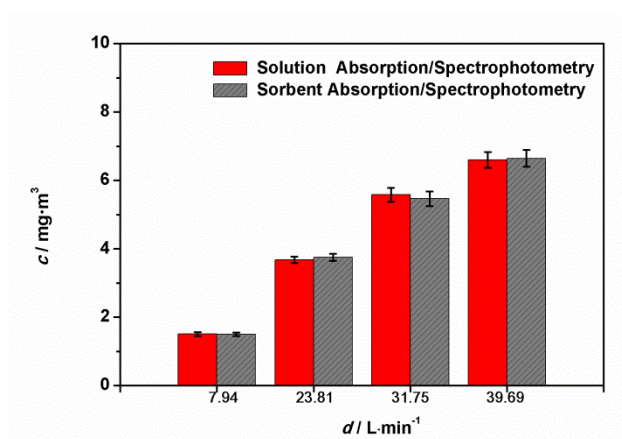


Fig. 5 Comparison of the results of two detection methods under different gas distribution parameters

It can be seen from Figure 5, under different gas distribution parameters, the results of the two methods were close to each other and the relative deviations were all less than 5%. The relative error of the two methods was less than 2%. The results show that the solution absorption/spectrophotometry can be used to detect the concentration of hydrazine in the air instead of the sorbent

adsorption/spectrophotometry. In the case of the two methods, errors are easily introduced in the process of sampling and sample transferring. The errors of the sorbent absorption/spectrophotometry are as follows: a) the content of adsorbent in different absorption tubes is difficult to be the same; b) the detection result will decrease due to the adsorption of hydrazine on the absorption tube when the sorbent is transferred from the absorption tube to the colorimetric tube.

The error of the solution absorption/spectrophotometry is mainly that the absorption solution is difficult to be transferred from the bulb absorption tube to the colorimetric tube.

4. Conclusion

In this work, the solution absorption/spectrophotometry for determination of hydrazine in air was established with a fast and simple operation. The relative standard deviation of this method was less than 5%. Compared to the sorbent adsorption/spectrophotometry, the relative error was less than 2%. Within 10 mL absorption solution, only one bubble absorption tube could absorb the hydrazine gas efficiently. The detection error of this method is concentrated in the process of absorption solution transferring.

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