Quantitative accuracy comparison of component determination of unsymmetrical dimethylhydrazine through peak height and area

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Abstract. Standard water, dimethylamine and unsym hydrazine solutions were prepared and then measured using gas chromatography (GC) in five replicates for each solution. Peak height and area were compared in terms of repeatability. In addition, two kinds of standard curves were fitted separately according to the peak heights and areas measured above. At last, unknown samples were determined. The results showed that among the three kinds of component measured, the average relative errors of peak height and area of each one were no larger than 3.9% and 4.16% separately. Beyond that, both linear dependences of the standard curves plotted through peak heights and areas were higher than 99% and the intercepts were almost the same. It was also found that the absolute deviations of all three components in unknown samples determined through peak height and area were not greater than 0.004%. To conclude, either peak height or area is applicable to the determination of the components in unsymmetrical dimethylhydrazine (UMDH).

1. Preface
As one kind of the most frequently used storable high-energy liquid propellants, UMDH is mainly used as the bipropellant for satellites and spaceships [1]. Its purity has always been viewed as a key factor to the quality of UMDH because its component contents have a marked impact on its combustion performance [2-4].

Generally speaking, GC external standard method is adopted in the purity analysis of UMDH [5]. What we got in GC analysis were mostly tailing peaks for chromatographic columns used in the past were packed ones, which resulted in poor separation effect and quantitative accuracy. In order to solve this problem, Wang Ying et al. [6] developed a capillary column suitable for the analysis of hydrazine propellants and explored the optimum conditions for peaks separation. Based on the above-mentioned achievements, quantitative methods of peak height and area were compared in UMDH purity determination to find out which method is better.

2. Experimental

2.1. Instrument
Gas chromatograph: Agilent 7890B with TCD detector; automatic sampler: Agilent 7693A; capillary column: Licp ERC-311, self-made (The inner wall is deactivated through static-pressure cyclic deactivation method and polysiloxane containing phenyl and cyanopropyl is used as the stationary
liquid. The contents of phenyl and cyanopropyl are adjusted to achieve ideal polarity.); electronic scale: Mettler, made in Switzerland, model of AB204-S with a division value of 0.1mg.

Aqueous solution of dimethylamine: analytically pure and concentration of 33.03% (mass fraction); high-purity hydrogen: purity higher than 99.999%; unsym hydrazone: purity of 98.00% (mass fraction); UMDH sample: purity higher than 99.0%; distilled water: self-made.

2.2. Preparation of standard samples of each component
Preparation of standard samples of each component: Seven 4mL sample bottles were taken and weighed and value W1 was recorded separately. About 3.8mL of UMDH was injected into each bottle through a micro syringe and these bottles were weighed again and value W2 was recorded. According to the amounts worked out in advance, different quantities of distilled water were added into the seven bottles and these bottles were weighed again. So, the standard samples of distilled water were prepared and the concentrations of this series of standard samples ranged between 0~0.8%. Standard dimethylamine and unsym hydrazone samples were prepared this way as well but the concentrations ranged between 0~0.8% and 0~2.5% separately. Calculation formulas for the content (added) of each component are shown below:

\[ W = \frac{Q}{P+Q} \times C \times 100\% \]  

Where:
- \( W \) —— mass fraction of distilled water or dimethylamine or unsym hydrazone injected into bottles;
- \( P \) —— mass of UMDH, equal to W2 minus W1, g;
- \( Q \) —— mass of distilled water or dimethylamine or unsym hydrazone injected into bottles, g;
- \( C \) —— concentration of distilled water or dimethylamine or unsym hydrazone (mass fraction), %.

![Gas chromatogram of UMDH.](image)

3. Results and discussion

3.1. UMDH separation effects
The standard samples prepared above were tested with GC and separation effects are shown in figure 1.
As shown in the gas chromatogram of UMDH, the retention times of water, dimethylamine, UMDH and unsym hydrazone are 1.643min, 2.129min, 3.483min and 4.836min separately. It can also be seen from this figure that these peaks are complete and symmetrical. There is no tailing peak as well. To conclude, components in UMDH are well separated under the conditions above.

3.2. Quantitative repeatability of peak height and area

Take the average value of five measurement results as the true value and the relative error between measured values and true values of peak height or area can be defined as follow [7]:

$$R = \left| \frac{\overline{A} - A}{A} \right| \times 100\% \quad (2)$$

Where:
- relative error;
- average value of peak height or area;
- measured peak height or area.

Average relative error between measured values and true values of peak height or area can be defined as follow:

$$\varepsilon = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\overline{A} - A}{A} \right| \times 100\% \quad (3)$$

Where:
- average relative error;
- number of measurement.

Please refer to Table 1 for the average peak heights (areas) as well as their average relative errors.

| Component     | Content (% dded) | Average peak height (μV) | Average relative error (%) | Average peak area (μV) | Average relative error (%) |
|---------------|------------------|-------------------------|----------------------------|------------------------|----------------------------|
| distilled water | 0.0000 | 5.82 | 2.47 | 10.62 | 3.24 |
|               | 0.0513 | 14.66 | 1.42 | 25.90 | 1.08 |
|               | 0.1054 | 26.08 | 3.90 | 45.96 | 4.16 |
|               | 0.2069 | 40.30 | 0.60 | 71.46 | 0.57 |
|               | 0.3074 | 57.66 | 0.19 | 102.28 | 0.30 |
|               | 0.4102 | 77.14 | 0.21 | 137.64 | 0.16 |
|               | 0.5055 | 94.14 | 0.12 | 166.60 | 0.07 |
|               | 0.0906 | 19.52 | 1.56 | 50.16 | 1.66 |
| dimethylamine | 0.0156 | 25 | 0.64 | 63.86 | 0.55 |
|               | 0.3146 | 52.94 | 0.54 | 135.20 | 0.50 |
|               | 0.3953 | 68.66 | 1.29 | 175.46 | 1.17 |
|               | 0.4918 | 78.88 | 2.34 | 202.78 | 1.33 |
|               | 0.0924 | 28 | 0.36 | 124.62 | 0.22 |
| unsym hydrazone | 0.4001 | 36.08 | 0.73 | 160.62 | 0.45 |
|               | 0.2851 | 50.68 | 1.01 | 225.7 | 1.06 |
|               | 1.3297 | 71.62 | 0.93 | 318.71 | 0.96 |
|               | 1.4934 | 95.6 | 0.33 | 424.38 | 0.59 |
|               | 2.388 | 109.6 | 0.88 | 487.9 | 0.45 |

We can see from Table 1 that the average relative errors of peak height and area were mainly about 1%, and the largest average relative errors were 3.9% and 4.16% respectively. The conclusion drawn from the data is that the quantitative repeatability of peak heights and areas of the components above was good. Besides, there was no obvious difference between average relative errors of peak height and area of one component at the same point.
3.3. Comparison of standard curves
Based on the data of peak heights and areas of each component, straight lines were drawn through linear fitting method [8]. Standard curves of the components are shown in the following figures. Standard curves of distilled water are shown in Figure 2.

**Figure 2.** Standard curves of water.

Standard curves of dimethylamine are shown in Figure 3.

**Figure 3.** Standard curves of dimethylamine.

Standard curves of unsym hydrazone are shown in Figure 4.

**Figure 4.** Standard curves of unsym hydrazone.
As shown in the three figures above, linear dependences of the standard curves of distilled water, dimethylamine and unsym hydrazone were all higher than 99%. Chromatographic peaks of water, dimethylamine, unsym hydrazone and UMDH were well separated so that there was no tailing or overlapping peak, thus improving the accuracy of peak height and area values. This contributed to good linearity. One thing notable is that the intercepts of these curves should be taken as the original contents of the corresponding components in UMDH solutions because standard solutions were prepared by adding various components into UMDH solution containing these components already. It was also found through comparing standard curves of peak heights and areas that for one component, the intercept of the standard curve drawn from peak heights was almost the same as that drawn from areas. All these gave us reasons to believe that no remarkable difference exists between the standard curves of peak heights and areas of each component.

### 3.4. Test of unknown samples

Three UMDH samples with unknown concentrations were determined through the standard curves drawn. Quantitative results calculated through peak heights and areas are shown in Table 2.

| Sample | Component     | Peak height (μV) | Content (%) | Peak area (μV·s) | Content (%) | Absolute deviation (%) |
|--------|---------------|------------------|-------------|------------------|-------------|------------------------|
| 1      | water         | 20.2             | 0.117       | 36.5             | 0.120       | 0.003                  |
|        | dimethylamine | 18.6             | 0.140       | 47.7             | 0.138       | 0.002                  |
|        | unsym hydrazone | 30.1           | 0.786       | 133.9            | 0.790       | 0.004                  |
| 2      | water         | 19.6             | 0.114       | 34.8             | 0.115       | 0.001                  |
|        | dimethylamine | 18.6             | 0.140       | 47.8             | 0.139       | 0.001                  |
|        | unsym hydrazone | 30.3           | 0.791       | 134.2            | 0.792       | 0.001                  |
| 3      | water         | 20.1             | 0.117       | 35.8             | 0.118       | 0.001                  |
|        | dimethylamine | 17.2             | 0.129       | 44                | 0.128       | 0.001                  |
|        | unsym hydrazone | 25              | 0.653       | 111.3            | 0.657       | 0.004                  |

As shown in Table 2, the contents of unknown samples determined through the standard curves of peak height and area were basically the same, with the absolute deviations of water, dimethylamine and unsym hydrazone being 0.003%, 0.002% and 0.004% respectively. A conclusion can be drawn that both quantitative methods are applicable to the purity determination of UMDH.

### 4. Conclusions

1. The average relative errors of peak heights and areas of water, dimethylamine and unsym hydrazone were about 1% and the maxima were 3.9% and 4.16% relatively. It indicates that both methods have high quantitative repeatability and there is no obvious difference between them.

2. Linear dependences of the standard curves drawn with peak heights and areas of the main components in UMDH were all higher than 99%. In addition, the difference between the two standard curves of any component was negligible.

3. After the unknown samples were determined through the standard curves of peak heights and areas, it was found that the absolute deviations of water, dimethylamine and unsym hydrazone were no higher than 0.003%, 0.002% and 0.004% respectively, which means the results were quite close to each other. Thus, both two kinds of standard curves apply to the purity determination of UMDH.

### References

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