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Review on the Leak Detection Technology of Unsymmetrical Dimethylhydrazine

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Abstract: Unsymmetrical dimethylhydrazine (UDMH) is a flammable, combustible, volatile and highly toxic hazardous chemical with strong corrosiveness. The leak detection technology of unsymmetrical dimethylhydrazine mainly includes sensor method, detection tube method and personal monitor method. This review covers the theories, characteristics and applications of several gas leakage detection methods for unsymmetrical dimethylhydrazine (UDMH), and its development prospect is also discussed.

1. Introduction

Unsymmetrical dimethylhydrazine features high specific impulse and energy, low freezing point, ease of use but it is inflammable, explosive, and severely corrosive. Its main physicochemical properties are as shown in table 1^[1]:

Table 1. The toxicity index of UDMH.

Items	Animal	Approach	UDMH (mg/kg)
LD ₅₀	Rat	Celiac	112
	Dog	Vein	60
	Mouse	Vein	250
	Rabbit	Skin	1063
LC ₅₀	Rat	Inhale for 4 h	673
	Mouse	Inhale for 4 h	459
LC	Rabbit	Inhale for 0.75 h	1800

LD₅₀: Median lethal dose

LC₅₀: Lethal concentration 50

LC: Lethal concentration

As the liquid propellant widely applied in the launching of various missiles, satellites and space launch vehicle, unsymmetrical dimethylhydrazine is a flammable, combustible, volatile and highly toxic hazardous chemical with strong corrosiveness. Leakage, seepage, flow and even large-area leakage accident may happen inevitably during its production, transportation, storage, conversion, filling and usage, causing poisoning and casualties, environmental pollution and even fire explosion. According to statistics, among the major accidents happened in the history of world space activities, over 60% were caused by propellant leakage, which is the main cause of damaged missile (rocket) and satellites, ground test failure and other accidents.

Meanwhile, during the storage, transportation, conversion and filling process of unsymmetrical dimethylhydrazine, its release, steam, leakage and seepage, especially in the case of large amount of liquid propellant leakage and breakage accident, its steam released into the air also may pose varying degrees of pollution and hazard to the operating personnel and the environment. If the concentration of



these substances in the air is too high, people will have dizziness, inattention, loss of memory and other phenomena, posing serious injury to their health. In the established hygienic standards of china, there is special regulation on unsymmetrical dimethylhydrazine: in the environment where working personnel have long-term operation, the allowable concentration of unsymmetrical dimethylhydrazine is 0.5mg/m^3 , and its daily mean concentration in the residential area shall not exceed 0.03mg/m^3 . If we adopt measures to detect the concentration of unsymmetrical dimethylhydrazine in the air in time, its hazard to people and the environment will be reduced or even avoided.

The leak detection methods of unsymmetrical dimethylhydrazine in the environment adopted in recent years are summarized in this article, mainly including sensor method, detection tube method and personal monitor method. Their advantages and disadvantages are analyzed respectively. and the development direction of this field is envisioned further.

2.The Leak Detection Technology of Unsymmetrical Dimethylhydrazine

2.1 Sensor Method

Sensor is a detection device that can transform information received to electric signal to realize information transmission, recording and control. With the rapid development of sensor technology, sensor not only can realize automatic detection and automatic control, but also have the advantages of high sensitivity, good selectivity and being convenient to carry. It has become one of the hot spots in the research in recent years to detect hydrazine compound in the environmental sample with sensor. The sensors reported in related literature mainly include electrochemical sensor, optical sensor, photoionization sensor and probe.

2.1.1 Electrochemical Sensor. Electrochemical sensor is the sensor used most for hydrazine detection.is simple in structure and cost-effective, so it Electrode is the core component of electrochemical sensor, so related research on this is mainly about electrode material improvement or modification, for example, using graphene nanosheet composite film decorated with bismuth nanoparticle to modify electrode, greatly improving the selectivity, stability and reproducibility of amperometric sensor^[2]; the nanocomposite composed of conducting polymer, 4,5-dihydro-1,3-thiazol-2-ylsulfanyl-3-methyl-1,2-benzenediol and gold nanoparticles can be used to modify MWCNTs/GC electrode, and if it is applied in electrochemical sensor, the detection limit for hydrazine can reach $0.6\mu\text{mol/L}$, with good linearity within the scope of $2.0\text{-}350.0\mu\text{mol/L}$ ^[3]. The modification process for electrode material is tedious, and modifier attenuates easily in the surface modification process. Wang et al.^[4] used copper rod as the substrate to design a porous copper oxide nanoribbon combination electrode, which has ultra-high sensitivity to hydrazine detection, a detection limit up to 10^{-7}mol/L , and no need for tedious modification process. China also has research report on such aspect, as early as 1997, Yang Dequan et al.^[5] prepared an organic complex LB film with Langmuir-Blotgett technology and applied it in resistance sensor, showing a detection limit of anhydrous hydrazine in the air superior to $0.5\mu\text{g/mL}$, and a response time and recovery time both less than 10s. The major defect of electrochemical sensor is easy loss, especially the electrode part, so it needs to be properly maintained during application.

2.1.2 Optical Sensor.Optical sensor utilizes the optical properties and chemical properties^[6] of the materials to make the object detected and sensitive element material have chemical reaction to generate products that can cause the change of sensitive elements' optical properties or have fluorescent effect, thus realizing the detection of target object through changing optical signals. For example, Nandi et al.^[7] developed sensor made from liquid crystal material mixed with 4-dodecyloxybenzaldehyde, and its principles are making 4-dodecyloxybenzaldehyde and hydrazine react to generate diimine compound, thus interfering the homogeneity of 5CB molecular orientation, and causing change in optical properties. This method applies to hydrazine detection in gas phase, with high selectivity, and the result can be directly observed with naked eyes without other devices. Sun et

al.^[8] constructed an ICT mechanism-based new fluorescent colorimetric sensor with high selectivity and sensitivity, rapid detection and obvious color change, which has been successfully applied in hydrazine detection in biological system. Optical fiber sensor is a kind of optical sensor which is often used for gas detection, and its basic operation principles are sending the light from the light source to modulator via optical fiber, causing changes in optical properties after the interaction between the gas to be detected and the light of the modulation area, and making the light become the signal source of modulation. Then the light will be sent to optical detector via optical fiber, and relevant parameters of the gas to be detected can be obtained after modulation^[9]. Alfred et al.^[10] made a reversible optical fiber crack sensor with commercial silica fiber, while organic mixture containing pentacene diquinone was used as the sensitive material. This sensor can detect the presence of trace hydrazine and its concentration. Compared with electrochemical sensor, optical sensor has higher sensitivity and more rapid response speed and relatively higher cost.

2.1.3 Photoionization Sensor. The principles of photoionization sensor is using UV-irradiation to make the gas molecules of analyte ionize to generate positively charged ions or electrons, which will form detectable current under the action of electric field, thus reaching the detection aims. Based on the principles above, Fan et al.^[11] designed a photoionization sensor for hydrazine detection that has the advantages of fast response, high precision, being convenient to carry and continuous testing, and can realize online monitoring of hydrazine vapor concentration in the site environment of aerospace engineering. Because of fewer studies on hydrazine detection with photoionization sensor, it is difficult to be promoted and applied, and more complicated and more in-depth studies need to be conducted.

2.1.4 Probe Sensor. The several types of sensors above are often used for hydrazine detection in gas phase, while hydrazine in liquid phase is often detected with detector, also known as probe. Probe is also one type of sensor, which is generally irreversible, with high sensitivity and selectivity. There are many literature reports on using fluorescent probe to detect hydrazine in the aqueous phase. Zheng et al.^[12] designed and synthesized an imidazoline fluorescent probe which has very high selectivity to hydrazine in aqueous phase with a pH value of 5.0-9.0. Its detection limit can reach $6.16 \times 10^{-6} \text{ mol/L}$. Tan et al.^[13] synthesized an intramolecular charge transfer effect-based fluorescent colorimetric probe with very high sensitivity to hydrazine in aqueous phase, with a detection limit as low as 0.11 ng/mL , as well as a large range of detection concentration and significant color change. The principle of gold nanoparticle colorimetric probe is making AuCl_3^- and hydrazine compound react to generate gold nanoparticles, and using the localized surface plasma resonance absorption caused by this reaction in the aqueous phase, which can be used to determine the concentration of hydrazine compound, with a detection limit of $1.1 \times 10^{-6} \text{ mol/L}$ ^[14]. Besides, there are also three-output optical probe^[15] and coumarin chemical dosing probe that can be used for hydrazine detection. Drawing upon its advantages of small volume, simple synthesis and fast response, probe has become one of the important means of trace material detection, but the shortcomings of irreversibility and difficult to realize automatic detection need to be overcome for its practical application in hydrazine detection.

2.2 Detection Tube Method

As a detection method, detection tube method has the advantages of being speedy, direct-reading, easy to use, cost-effective and easy to carry. For the detection of unsymmetrical dimethylhydrazine, bromophenol blue is used as the indicator while silicon dioxide as the carrier. Quantitative determination can be conducted according to the bluish violet color column length (length comparison method) generated from unsymmetrical dimethylhydrazine and bromophenol blue.

China once developed unsymmetrical dimethylhydrazine detection tube in the late 1980s, but the detection tube developed then was only limited to low-concentration unsymmetrical dimethylhydrazine detection (0.5-50 ppm). Then Zhang Guangyou et al.^[16] developed the unsymmetrical dimethylhydrazine detection tube with a detection concentration range of 50-7000 ppm.

The detection tube has an applicable temperature range of 0-40°C and humidity range of 30-85%, and a quantitative error under 20%. It features fast measurement, intuitional reading, light weight and being easy to use, and can meet the needs of fast detection of high-concentration unsymmetrical dimethylhydrazine in rocket propellant waste gas treatment and unexpected accident scene in the satellite launch site. However, this method has a big determination error, and alkali gas will pose certain interference to the determination.

2.3 Personal Monitor

The development effort of hydrazine propellant personal monitor was started in United States Naval Research Laboratory in 1950s. The United States once conducted a preliminary study on unsymmetrical dimethylhydrazine active or passive badge personal monitor in 1990s, but because the color developing agent selected had the disadvantages of difficulties in synthesis, short storage time and high price, it was not put into practical application. The unsymmetrical dimethylhydrazine personal monitor successfully developed by China can measure the dosage of unsymmetrical dimethylhydrazine that can be accepted by the operating personnel. In this experiment, 2, 4 -nitrobenzaldehyde is selected as the color developing agent of unsymmetrical dimethylhydrazine personal monitor, and visual colorimetry is adopted to determine the dosage of unsymmetrical dimethylhydrazine according to the colors of varying shades generated in different time and their comparison with standard colors. Its calculation formula is as follows:

$$c = \frac{d}{t}$$

Where c is the *concentration* (ppm) of UDMHr; d is the result of personal monitor(ppm•h); t is sampling duration (min);

This monitor can determine the dosage of unsymmetrical dimethylhydrazine that can be accepted by individual in 0.5 hour to 8 hours, with determination sensitivity of 0.2ppmh and determination range of 0.2-1.2ppm•h. It can be continuously used for 8 hours, with the advantages of being easy to operate, convenient to use, easy to observe and cost-effective. However, its determination result has big error, and high-concentration hydrazine and methylhydrazine may interfere with the determination, so it is applicable to specific place using unsymmetrical dimethylhydrazine.

3. Conclusion

The sensor method is widely used in the detection of unsymmetrical dimethylhydrazine leakage. On the basis of automatic detection and automatic control, it also has the advantages of high sensitivity, good selectivity and convenient carrying. There are advantages and disadvantages depending on the type of sensor. Electrochemical sensors have the advantages of low detection limit and short response time. In the meantime, the disadvantage is that it is easy to wear down, especially the electrode part, which needs frequent maintaining. The optical sensor has the advantage of the highest response time. However, the high cost is inhibiting its development. With fast response time, the probe sensor is small and simple to synthesize. But it is irreversible and difficult to achieve automatic detection. The detection tube method and the personal dosimeter method have low cost and simple operation, but the error is great, and they are easily affected by other reducing properties. In the future, the aerospace industry will develop rapidly. The amount of various propellants used, including dimethyl hydrazine, will inevitably become larger and larger. The risk of environmental pollution will increase. The technical requirements for the detection of unsymmetrical dimethylhydrazine leakage will be higher and higher. The future development trend will miniaturize and integrate the equipment, improve the detection sensitivity, lower the detection limit and shorten the detection time. However, for all current detection methods, they can only detect dimethyl hydrazine or other hydrazine leakage in the air or water, and the leakage site cannot be determined. With the rapid development of nanotechnology, the synthesis of new detection materials, the development of portable detectors, the establishment of fast visual positioning detection methods will be the key research directions for unsymmetrical dimethylhydrazine leakage detection.

References

- [1] Yang R, Liu J H, Li S H. (2005). Toxicology of Unsymmetrical Dimethyl Hydrazine and Protection for Exposed Staff. *Journal of Environmental & Occupational Medicine*, 22(6), 556-558.
- [2] Devasenathipathy, R., Mani, V., Chen, S. M. (2014). Highly selective amperometric sensor for the trace level detection of hydrazine at bismuth nanoparticles decorated graphene nanosheets modified electrode. *Talanta*, 124, 43-51.
- [3] Fakhari, A. R., Ahmar, H., Hosseini, H., Kazemi Movahed, S. (2015). Fabrication of novel redox-active poly (4,5-dihydro-1,3-thiazol-2-ylsulfanyl-3-methyl-1,2-benzenediol)-gold nanoparticles film on mwcnts modified electrode: application as the electrochemical sensor for the determination of hydrazine. *Sensors and Actuators B: Chemical*, 213, 82-91.
- [4] Wang, S. Xu, X., Zhang, X. (2015). Effective hydrazine electrochemical sensors based on porous cuo nanobelts supported on cu substrate. *Chemistry Letters*, 44(5), 642-644.
- [5] Yang D Q, Wang R F, Xie S P, Guo Y, et al. (1997). A High Sensitive Gas Sensor For N₂H₄ Gas Detected. *Chinese Space Science and Technology*, V17 (1), 41-45.
- [6] Gojon, C., Bernard Duréault, Hovnanian, N., Guizard, C. (1999). Optical chemical hydrazine sensor from hybrid organic-inorganic materials. *Journal of Sol-Gel Science and Technology*, 14(2), 163-173.
- [7] Nandi, R., Singh, S. K., Singh, H. K., Singh, B., & Singh, R. K. (2014). Fabrication of liquid crystal based sensor for detection of hydrazine vapours. *Chemical Physics Letters*, 614(614), 62-66.
- [8] Sun, M., Guo, J., Yang, Q., Xiao, N., Li, Y. (2014). A new fluorescent and colorimetric sensor for hydrazine and its application in biological systems. *Journal of Materials Chemistry B*, 2(13), 1846-1851.
- [9] Zhong Q, Mao Y N, Li J, Zhang X J. (2017). Progress in Environmental Detection Techniques of Hydrazines Propellant. *Chemical Reagents*. 39(3):221-226.
- [10] Andrawis, A. (2011). Hydrazine concentration fiber optic reversible sensor. *Proc Spie*, 7753(4), 125-130.
- [11] Fan Q S, Xue C Y, Liang T, Sun R X, Tan Q L, Zhang W D. (2009). Design of Sensor For Hydrazine Gas Based Photoionization Principle. *Transducer and Microsystem Technologies*, 28(7), 62-64.
- [12] Zheng, X. X. , Wang, S. Q. , Wang, H. Y. , Zhang, R. R. , Liu, J. T. , Zhao, B. X. (2015). Novel pyrazoline-based selective fluorescent probe for the detection of hydrazine. *Spectrochim Acta A Mol Biomol Spectrosc*, 138, 247-251.
- [13] Tan, Y., Yu, J., Gao, J., Cui, Y., Yang, Y., Qian, G. (2013). A new fluorescent and colorimetric probe for trace hydrazine with a wide detection range in aqueous solution. *Dyes and Pigments*, 99(3), 966-971.
- [14] Zargar, B., & Hatamie, A. (2013). A simple and fast colorimetric method for detection of hydrazine in water samples based on formation of gold nanoparticles as a colorimetric probe. *Sensors & Actuators B Chemical*, 182, 706-710.
- [15] Cui, L., Ji, C., Peng, Z., Zhong, L., Zhou, C., Yan, L., et al. (2014). Unique tri-output optical probe for specific and ultrasensitive detection of hydrazine. *Analytical Chemistry*, 86(9), 4611-4617.
- [16] Zhang G Y, Ge J Z. (1997). Development of Rapid Quantitative Detection Tube for High Concentration of Nitrogen Dioxide and Unsymmetrical Dimethylhydrazine. China Aerospace Society Ground Equipment and Launch Engineering Committee. Jiu Jiang. 1-5.