Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 18, No. 3, 2025

Application of Near-Infrared Spectroscopy in Stability Testing of Shipborne Weapon Propellants

Bohao Zhao, Yongtao Zhou *, Chen Xie, Jintao Wang, Xiannian Zhang, Youcai Wang

Rocket Force University of Engineering, Xi'an, Shaanxi, China

*** Corresponding author:** Yongtao Zhou

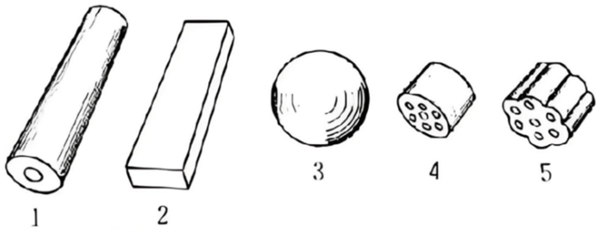
Abstract: Modern naval weapon propellants exhibit diverse compositions with varying components, particularly tri-base propellants representing the trend toward high energy and low vulnerability. Examples include tri-guanidine propellants, primarily composed of azidonitramine, nitroguanidine, nitrocellulose, nitroglycerin, dinitrotoluene, stabilizers, and performance additives. Compared to traditional single-base or double-base propellants, their composition is more complex. Interactions between components become more pronounced under harsh conditions, potentially accelerating the rate and severity of physicochemical changes induced by environmental factors. This heightens the urgency for rapid on-site detection and evaluation. This study investigates the application of near-infrared spectroscopy in detecting the stability of naval weapon propellants, aiming to promptly obtain fundamental performance data and enable real-time, accurate stability assessments. This research is crucial for ensuring the safety and reliability of naval weapons during maritime missions and safeguarding personnel lives.

Keywords: Near-infrared Spectroscopy Technology; Naval Weapons; Propellants; Stability.

1. Introduction to Propellants and Stabilizers

1.1. Types and Properties of Propellants

Propellants are energetic materials that generate large volumes of high-temperature, high-pressure gases through stable combustion within sealed or semi-sealed chambers, converting chemical energy into kinetic energy for projectiles. Chemically, propellants primarily consist of nitrate compounds such as nitrocellulose and nitroglycerin, supplemented with functional additives like stabilizers and retarders to form a composite system balancing energy density and combustion stability. Common propellant types are illustrated in Figure 1.



1-Tubular 2-Strip-shaped 3-Spherical 4-Seven-hole granular 5-Five-hole plum blossom-shaped

Figure 1. Common Propellant Shapes

(1) Single-Base Propellants

Monobase propellants, the most widely used category, rely solely on nitrocellulose (nitrate cellulose, NC) as their energy source, typically containing over 90% NC. During preparation, non-energy components such as solvents and stabilizers (e.g., diphenylamine) are specifically added based on different application scenarios and product specifications, supplemented with small amounts of plasticizers and processing aids for formulation. Its defining characteristics are simplicity of composition and mild combustion properties. Due to its stable energy output, single-base propellant is widely used in medium- and small-caliber weapon systems, meeting the demands for firing accuracy and sustained combat capability in such equipment. A typical monopropellant formulation is shown in Table 1.

Table 1. Typical Single-Base Propellant Formulation

Component Name	Mass Fraction (%)
Nitrocellulose	94~96
Diphenylamine	1.2~2.0
Desensitizer	1.1~2.2
Volatile matter	1.7~3.4

(2) Double-base Propellant

As a mixed nitrocellulose propellant, double-base propellant has become a globally representative propellant type due to its high energy output and excellent mechanical strength. The core energy carriers of double-base propellants are nitrocellulose and glycerol trinitrate (nitroglycerin, NG), which together typically account for over 75% of the composition, with nitrocellulose constituting no less than 50%. Currently, double-base propellants are primarily used in naval guns, mortars, tank guns, and the booster systems of certain missiles, providing stable propulsion for medium-to-long-range firepower delivery. A typical dual-base propellant formulation for artillery is shown in Table 2.

Table 2. Formulation of a Typical Dual-Base Propellant for Artillery

Component Name	Mass Fraction (%)
Nitrocellulose	65
Digested Glycerin	29.5
Fixing agent	2
Petroleum jelly	3.5

(3) Triple-Base Propellant

Triple-base propellant is a composite propellant with nitrocellulose, nitroglycerin, and nitroguanidine (NQ, a high-energy, insensitive explosive) as its core components. Developed by incorporating solid energetic materials into dual-base propellants, triple-base propellants combine high energy with low ablation characteristics. As a critical propellant source for artillery, it finds widespread application in high-performance weapon systems such as large-caliber naval guns and heavy howitzers, serving as a key propellant material for achieving beyond-visual-range precision strikes on modern information-based battlefields. A typical ternary propellant formulation is shown in Table 3.

Table 3. Typical Three-Base Propellant Formulations

Component Name	Mass Fraction (%)
Nitrocellulose	20~28
Nitroglycerin	19~22.5
Nitroguanidine	47~55
Dibutyl phthalate	0~4.5
Diphenylamine	0~1.5
No.2 Medium Setting Agent	0~6
Other additives	0~1.9

1.2. Function and Composition of Stabilizers

Stabilizers are chemical substances added to propellants, primarily functioning to inhibit the autocatalytic decomposition reactions of key propellant components such as nitrocellulose, nitroglycerin, and other nitrate compounds. During storage or use, nitrate compounds slowly decompose to produce nitrogen oxides like NO and NO_2. These byproducts accelerate self-decomposition, forming a catalytic cycle that may ultimately cause propellant spontaneous combustion, explosion, or performance degradation. Stabilizers block this cycle by binding with nitrogen oxides, thereby extending propellant shelf life, ensuring chemical stability, and reducing accidental reaction risks.

In propellant manufacturing, diphenylamine (DPA) and Stabilizer No.2 (dimethyl diphenylurea, C_2) are the two most widely used stabilizers. Diphenylamine features the molecular structure (C_6H_5)-NH-(C_6H_5), appearing as white crystals at room temperature with melting and boiling points of 52.9°C and 302°C, respectively. Its solubility characteristics include poor solubility in water but good solubility in organic solvents such as ethanol, diethyl ether, and benzene. It also exhibits weak alkalinity and reducing properties. These physicochemical attributes enable it to react efficiently with NO_2, thereby inhibiting the decomposition process of propellants.

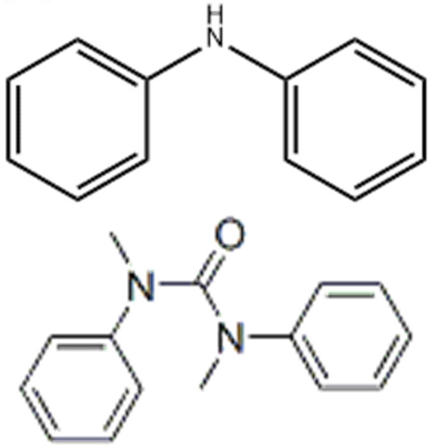


Figure 2. Molecular structural formulae of DPA and C_2

Another commonly used secondary stabilizer has the molecular formula $C_{15}H_{16}N_2O$. It appears as white crystalline flakes with melting and boiling points of 121°C and 350°C, respectively. Compared to diphenylamine, it exhibits higher solubility in water and ethanol. Functionally, Stabilizer No.2 primarily absorbs nitrogen oxides generated during propellant decomposition, thereby mitigating autocatalytic decomposition effects. Beyond propellants, this compound serves as a stabilizer in explosives, smokeless powders, and various nitrates, enhancing storage stability and safety for these energetic materials. Molecular structures of DPA and C2are shown in Figure 2.

1.3. Influence of Stabilizers on Propellant Stability

In traditional single-base propellant formulations, the selection of stabilizers primarily relies on a single diphenylamine. Diphenylamine itself possesses weak alkalinity. During propellant production and processing, acidic products generated by nitrocellulose decomposition react chemically with diphenylamine, converting it into diphenylnitrosamine and significantly weakening its alkalinity. Therefore, under conventional usage conditions, diphenylamine does not cause saponification of nitrocellulose, preventing damage to the propellant's structure and performance due to saponification. In single-base propellants, optimal stabilization is achieved when diphenylamine content is controlled between 1% and 2%. This concentration effectively captures NO_2 produced by nitrocellulose decomposition, inhibits autocatalytic decomposition reactions, and prevents performance defects caused by excessive or insufficient components.

For double-base or triple-base propellants, Stabilizer No.2 is typically selected as the stabilizer. With advancements in propellant technology, some new propellants also adopt a stabilizer combination scheme featuring diphenylamine blended with Stabilizer No.2 (as the primary component).The amino and amide groups in the molecular structure of Stabilizer No.2 exhibit superior adsorption capacity for nitrogen oxides. It also demonstrates excellent compatibility with propellant matrices like nitrocellulose and nitroglycerin, without causing adverse reactions with other components. Its enhanced thermal stability prevents volatilization or decomposition under the moderate temperatures encountered during propellant processing.

In propellant stability assessment standards, a 50% reduction in the original stabilizer content is generally considered the stability threshold, which also marks the critical point for propellant stability lifespan. At this stage, the chemical stability of the propellant significantly decreases, potentially accelerating decomposition, increasing gas release, or even posing safety risks during storage. Prompt evaluation of its usability and implementation of corresponding protective measures are required.

1.4. Traditional Stabilizer Content Testing Methods and Their Limitations

Traditional methods for detecting propellant stabilizers primarily include chemical titration, litmus paper testing, and chromatographic analysis.

Chemical titration methods, such as bromination, require mechanically pulverizing aged powder samples to extract stabilizers. This process itself carries a high explosion risk due to the low stabilizer content and high sensitivity of aged samples. Additionally, this method employs low-boiling-point, flammable solvents like diethyl ether for reflux extraction lasting over 24 hours.

Test paper methods, such as the methyl violet test, offer relatively simple operation but rely heavily on the operator's subjective judgment. Assessing stability by visually observing test paper color changes caused by nitrogen oxides results in poor repeatability and significant error. This method is typically applicable only to single-base drugs.

Chromatographic methods, such as High-Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC), offer high precision and the ability to analyze multiple components simultaneously. However, they require expensive equipment with high maintenance costs and demand highly skilled operators. Due to lengthy single-analysis times—typically exceeding 30 minutes—these methods suffer from poor timeliness, making them unsuitable for rapid on-site or high-volume testing demands.

These methods share inherent hazards such as explosive powdering of samples and toxic solvent use. Traditional approaches suffer from cumbersome procedures, insufficient precision or lack of quantification capability, high equipment and maintenance costs, and environmental pollution, rendering them unsuitable for propellant testing in naval vessel environments. Therefore, recent research has shifted focus toward developing non-destructive rapid detection technologies. Near-infrared spectroscopy analysis requires no sample pulverization or hazardous solvents, completes testing within minutes, offers high precision, and adapts to complex propellant systems. It represents the future direction for achieving real-time, online, and safe assessment of propellant stability.

2. Near-Infrared Spectroscopy Technology

2.1. Fundamental Principles of Near-Infrared Spectroscopy

Near-infrared (NIR) light refers to electromagnetic waves with wavelengths between the visible and mid-infrared regions, typically spanning 780–2526 nm in wavelength and 3959–12820 cm^{-1} in wavenumber[1]. It is the earliest non-visible spectral region recognized by humans. Near-Infrared Spectroscopy (NIRS) is a non-destructive testing technology that rapidly analyzes the composition, structure, and physical properties of substances based on their absorption, reflection, or transmission characteristics of near-infrared light.

Near-infrared light possesses relatively low energy levels. When interacting with molecules, it can only induce changes in the molecular vibrational energy levels (accompanied by rotational energy levels). The spectrum formed by molecules absorbing near-infrared light energy falls under the category of vibrational spectroscopy. Due to the quantized nature of vibrational energy level transitions, the spectrum manifests as spectral bands. Molecular vibrations can be described through fundamental vibrations, harmonic vibrations, and composite vibrations. The infrared spectral characteristics of different molecular vibration types are compared in Table 4.

Table 4. Comparison of Infrared Spectral Characteristics for Different Molecular Vibration Types

Vibration Type	Frequency Behavior	Absorption Band	Absorption Intensity	Role in Spectroscopic Techniques
Fundamental Frequency Vibration	Molecular Natural Vibration (Ground State)	Mid-infrared (2500–25000 nm)	Strong	Core basis of traditional infrared spectroscopy
Harmonic Vibrations	Integer multiples of the fundamental frequency	Near-infrared (780–2500 nm)	Weak	Primary absorption sources in near-infrared spectroscopy
Combined frequency vibration	Combination or difference of multiple fundamental frequencies	Near-infrared (780–2500 nm)	Weaker	Auxiliary absorption sources in near-infrared spectroscopy

When molecular vibrational energy levels transition from the ground state to higher energy levels, it triggers near-infrared light absorption effects. The key signals captured by near-infrared spectroscopy are primarily manifested as harmonic absorption and sum-frequency absorption formed during the vibration of hydrogen-containing functional groups (such as C-H, O-H, N-H, etc.).Since different functional groups or the same functional group in different chemical environments exhibit significant variations in the wavelength and intensity of near-infrared absorption, this characteristic endows near-infrared spectroscopy with rich structural features and compositional information about substances[2].

2.2. Detection Process of Near-Infrared Spectroscopy Technology

The detection and analysis process of near-infrared spectroscopy technology is a systematic procedure designed to address challenges in spectral measurement and achieve precise analysis. Its core components include establishing and optimizing quantitative models, as well as predicting the composition and content of unknown samples.

For quantitative model establishment and optimization: Step 1 involves preparing standard samples. The sample quantity must be sufficient to cover varying component concentrations and physical states, preventing model randomness due to sample homogeneity. Step 2 entails sample set division, categorizing samples into calibration and validation sets. The calibration set is used for model construction and optimization, while the validation set assesses predictive capability. The third step involves acquiring near-infrared spectra by placing the sample set into a near-infrared spectrometer for measurement, yielding raw spectral data. The fourth step entails spectral preprocessing: preliminary screening of spectra to eliminate outliers with significant deviations, removing noise, background interference, and light scattering to highlight effective feature signals.Step 5 involves wavelength selection. From the full spectral range, effective wavelength intervals highly correlated with the target components are identified to reduce redundant information, further enhancing model accuracy and efficiency.Step 6 involves establishing quantitative models by selecting appropriate modeling methods and performing preliminary model construction based on the calibration set. Step 7 entails model validation and optimization, testing the model's repeatability, accuracy, and stability using the validation set to ensure applicability under varying conditions and obtain a stable, reliable model.

Predicting the component content of unknown samples follows the same standard procedure as the modeling phase: collect the spectrum of the test sample and input its spectral data into the optimized quantitative model. The model then rapidly outputs the content of relevant components in the test sample via algorithmic processing, achieving efficient conversion from spectral information to component information.

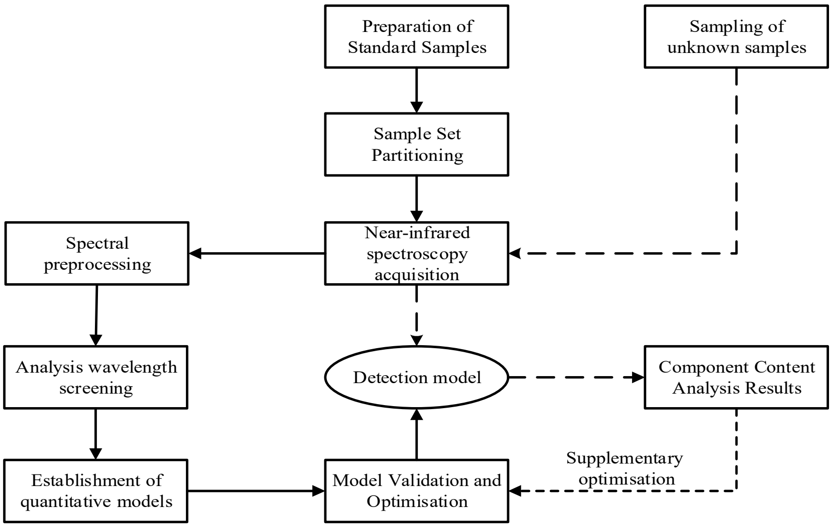


Figure 3. Flowchart of Detection and Analysis Process for Near-Infrared Spectroscopy Technology

3. Current Research Status of Near-Infrared Spectroscopy in Propellant Detection

NIR spectroscopy offers advantages including no sample pretreatment, safety, simplicity, speed, non-destructive analysis, environmental friendliness, and simultaneous multi-component/multi-channel measurement. It is widely applied in food, pharmaceuticals, agricultural products, and chemical industries. Significant progress has also been made in propellant component analysis and rapid on-site detection, substantially reducing testing time compared to traditional methods.

3.1. Current Research Status in Propellant Component Detection

Entering the 1990s, driven by industrial demand and technological breakthroughs, near-infrared spectroscopy equipment entered a golden age of rapid development, with significant acceleration in performance optimization and product diversification. Additionally, María López-López et al. employed Fourier Transform Infrared Spectroscopy (FTIR) to compare the spectral characteristics of single-base, double-base, and triple-base smokeless powders. Based on direct spectral comparisons, they demonstrated rapid identification of nitrocellulose-containing powders and triple-base powders, proposing this technique as an effective forensic tool for powder classification and unknown powder sample identification. Ma. Ángeles Fernández de la Ossa et al. employed near-infrared hyperspectral imaging (NIR-HSI) combined with chemometricsestablished a spectral library using polyethylene sheets via partial least squares discriminant analysis (PLS-DA) models. This enabled 100% sensitive and specific detection of explosive residues and ammonium nitrate residues at the pixel level. Fingerprint tests confirmed the potential of near-infrared spectroscopy for rapid identification of explosive residues and detection of explosive contact behavior. In recent years, advancements in instrument miniaturization, wireless data transmission, cloud storage, and multivariate data analysis have propelled the development of near-infrared spectroscopy. Portable near-infrared spectrometers equipped with these analytical capabilities are now deployed across security domains to enable rapid identification of intact energetic materials and mixtures.

3.2. Current Research Status in On-Site

In the field of rapid on-site detection, near-infrared spectroscopy technology has also developed rapidly in China in recent years. Innovations in instrument technology have significantly enhanced the performance of portable near-infrared spectrometers, endowing them with compact and intelligent features. The emergence of various NIR instruments has provided a robust hardware platform and technical foundation for advancing NIR technology in the field of explosives detection, enabling its gradual application in this domain. Zhang Xiangnan et al. designed a near-infrared moisture detection method for explosives. By comparing three standard sampling methods, they established oven-drying protocols. Combining near-infrared moisture detection principles, they analyzed key factors affecting detection accuracy and developed calibration correction methods, addressing challenges such as difficulty in obtaining standard samples and low detection precision in explosive moisture testing.Liang Jinhua et al. noted that excess residual solvent (RS) in triegyldiglycol dinitrate (TEGDN) dual-base propellants significantly degrades combustion performance. They employed reflectance mode near-infrared spectroscopy (NIR) to establish a rapid and accurate detection model for RS content in this propellant, providing an efficient method for RS testing and qualification assessment.Li Wenzhao et al. conducted corrosion tests on substitute materials for munitions components—including D60 steel, No. 8 copper detonator casings, and propellants—by simulating high-temperature, high-humidity, and high-salt-fog environments typical of island regions. They analyzed corrosion products using infrared spectroscopy and proposed relevant corrosion mechanisms.

4. Summary

Near-infrared spectroscopy, as a rapid, efficient, and non-destructive detection method, demonstrates exceptional application value in assessing the stability of propellants for shipborne weapons. This technology preserves the inherent structure of propellants while swiftly capturing critical stability evaluation indicators. This capability holds significant promise for addressing detection gaps in specialized environments like shipboard settings, providing crucial technical support for real-time monitoring of propellant safety status and mitigating usage risks. Compared to traditional detection methods, its advantages are primarily reflected in the following aspects[3].

(1) Rapid testing speed. Without complex sample pretreatment, a single test typically takes only seconds to minutes, offering a significant speed advantage over traditional methods that may require hours or even days.

(2) Non-destructive testing. Most traditional methods are destructive, consuming or altering sample properties during analysis. Near-infrared spectroscopy causes no damage or consumption to samples, preserving their original physical and chemical properties. Tested samples remain usable or storable.

(3) Multi-component analysis. NIR spectroscopy captures rich molecular vibration information. Through chemometric methods, it enables quantitative analysis of multiple components simultaneously. This eliminates the need for multiple separate tests required by traditional methods, which typically detect only one or a few components at a time.

(4) Excellent repeatability. Unlike traditional methods susceptible to environmental factors and operator variability, NIR spectroscopy employs internal instrument preprocessing to eliminate external interference. Automated data acquisition minimizes subjective human error, significantly enhancing the repeatability of model predictions and improving experimental data reliability.

(5) Environmentally friendly and cost-effective. The detection process requires no chemical reagents, generates no waste liquids or gases, minimizes environmental impact, and reduces reagent and disposal costs.

(6) User-friendly operation. The instrument is simple to operate, allowing personnel without specialized chemical analysis backgrounds to master it quickly. When using NIR spectroscopy to detect the content of propellant stabilizers, one only needs to place the sample into the instrument and use specific software for spectral acquisition and data analysis.

(7) Versatile application scenarios. Unlike traditional methods constrained by instrument size and operational conditions—limited to offline laboratory analysis—NIR spectroscopy adapts to diverse testing environments. It enables offline laboratory analysis, online production line monitoring, and field testing in various scenarios.

Although near-infrared spectroscopy offers numerous advantages over traditional detection methods, the technology still has certain limitations, primarily in the following two aspects:

(1) Indirect analysis. Near-infrared spectroscopy is an indirect analytical technique incapable of directly measuring component concentrations. It acquires spectral information from samples, converts this data into quantitative information using chemometric methods and software algorithms, and then indirectly derives sample composition based on pre-established models. Consequently, it lacks the ability to directly analyze the physicochemical characteristics of samples.

(2) Low sensitivity. The absorption signals in near-infrared spectroscopy primarily originate from the second-harmonic vibrations and sum-frequency vibrations of hydrogen-containing groups in molecules, which exhibit low energy and weak absorption intensity. This technique typically can only analyze components with concentrations above 0.1%. When detecting components with extremely low concentrations in a sample, this method is generally not employed.

References

[1] Li W, Zhao L ,Guo J , et al.Near-infrared spectral quantitative analysis with reduced moisture interference using a spectral decomposition optimization algorithm: A case study on Amadori compounds in tobacco leaves[J].Journal of Agriculture and Food Research, 2025,23,102261-102261.

[2] Prior F A, Rochat A ,Chevalley J, et al.Improving first responder forensic ca-pabilities: On-site detection and quantification of explosive precursors using po-rtable near-infrared spectroscopy and machine learning[J].Forensic science inter-national, 2025,368112378.

[3] Cozzolino D. Conventional Near-Infrared Spectroscopy and Hyperspectral Imag-ing: Similarities, Differences, Advantages, and Limitations[J].Molecules,2025,30(12):2479-2479.