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A Green Analytical Tool for In-Process Determination of RDX Content of Propellant Using the NIR System

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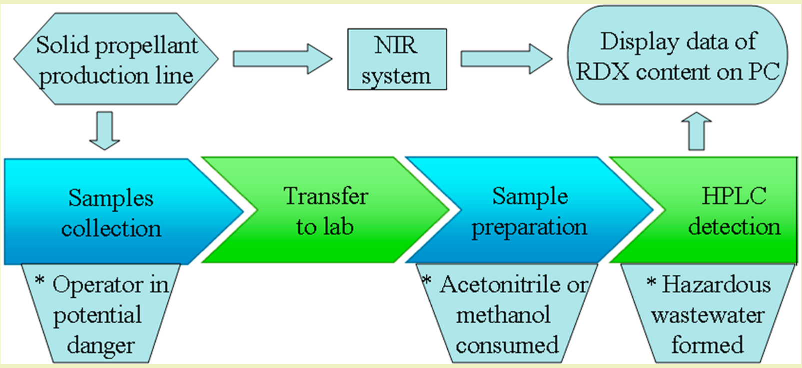

ABSTRACT: The conventional approach (high performance liquid chromatography, HPLC) used for determination of the hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) content of a solid propellant intermediate consumes toxic reagents, produces hazardous wastes, and cannot afford in-process monitoring at military plants. This work investigated the feasibility of using a near-infrared (NIR) system as a green alternative in lab scale. All raw materials were obtained from a propellant plant, and a fiber optic probe interfaced with a Fourier transform NIR (FT-NIR) spectrometer was directly inserted into samples that were continuously stirred to record in situ spectra. A quantitative chemometrics model based on the characteristic spectral regions of RDX was established using a partial least squares (PLS) regression algorithm. The developed model was assessed by external validation with the coefficient of determination (R^2 = 0.948) and root-mean-square error of prediction (RMSEP = 0.236). The proposed method was confirmed with samples covering the full concentration of a calibration set over a period of several months, and it exhibited good performance on reproducibility and repeatability. In addition, HPLC analysis was carried out to compare with the developed NIR method, and no significant difference between the NIR and HPLC values was obtained according to the result of a paired *t*-test. Using our proposed NIR method, there was no chemical reagent consumed and no waste formed during the overall prediction procedure. The results show that the NIR system is inherently rapid, clean, capable of preventing hazardous residuals originating from traditional analytical procedure, and has the potential for monitoring RDX content during solid propellant processing.

KEYWORDS: *NIR system, Green, RDX, Solid propellant, In-process*

■ INTRODUCTION

As one of the most extensively used highly energetic chemicals in the military field, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) plays a key role in solid propellant owing to improved combustion, energy output, and ballistic performance of the propellant.[1,2] In the production line of a propellant plant, intermediate samples are collected randomly by the operator, following which they are sent to a laboratory and analyzed with high performance liquid chromatography (HPLC) to determinate the RDX content for quality control of the final product. However, besides time and labor, hazardous wastewater including RDX, acetonitrile, methanol, etc. is formed after that analytical procedure.[3,4] RDX has been one of the main sources of soil and groundwater contamination near the regions of military factories due to its toxic nature, fate, and transport.[5] In addition, both acetonitrile and methanol are toxic chemical reagents that are harmful to one's health and the environment.[6,7] Toxic symptoms have been observed on animals and humans who are chronically exposed to RDX, such as headaches, severe nausea, vomiting, and muscular twitching.[8−10] Most attention was paid to solving the environmental problem through removing the chemical wastes from contaminated area, even though the extra treatments are complex, expensive, and accompanied with secondary pollution.[4,11,12] Considering environmental and economical benefits, the conventional analytical methodology requires further development to allow in-process monitoring and prevent hazardous waste prior to its formation.[13−15]

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Benefiting from the advantages of instrumental technology and chemometrics, a near-infrared (NIR) system is available to record spectra for complex mixtures with little or no pretreatment, rapid prediction of physical and chemical parameters from a single spectrum, and formation of no waste during the overall analytical procedure.[16,17] It has gained wide acceptance in the food, pharmacy, and petroleum industries as an efficient quality control implement.[18−20] Mottos et al. developed a NIR analysis as a rapid quality control tool for determining the content of mixtures of RDX and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) in a laboratory. The analytes were composed of RDX and HMX, prepared as transparent discs using powdered potassium bromide (KBr), and then analyzed in a NIR region ranging from 3891 to 5200 cm^{-1} under stationary conditions. The research showed that NIR analysis is accurate and precise for the energetic compounds and much faster and cleaner than the HPLC method.[21]

This work focuses on the feasibility of using a NIR system for in-process monitoring of the RDX content of solid propellant intermediates that consist of water, nitrocellulose (NC), nitroglycerine (NG), stabilizer, and RDX. A FT-NIR spectrometer in conjunction with a fiber optic probe was applied in situ to determine the RDX concentration of intermediates that were continosly stirred. The negative impact of water that causes spectra overlapping and continual stirring that leads to a low signal−noise ratio were conquered to some extent. A robust partial least squares (PLS) regression model was established based on the selected spectral regions that are the chemical interpretation of RDX. All of the above results reveal that a NIR system is an effective green analytical tool for improving the material efficiency, safety, and environmental protection during solid propellant processing.

■ MATERIALS AND METHODS

Sample Preparation. RDX, NG, NC, and stabilizer require homogeneous mixing during the blend procedure, during which water is essential for safety owing to the high sensitivity of RDX, nitroglycerine, and nitrocellulose. In this work, all raw materials were obtained from a solid propellant plant. NG, NC, and stabilizer first formed a solid compound in a production line and then were mixed with RDX in a laboratory. In a typical case, given that the total weight of one intermediate sample is 100 g, the nominal content of RDX and other solid components is 5 g, respectively. However, to cover the possible test concentration, the concentration ranges of RDX and other solid components were randomly distributed from 70% to 130% of the nominal ratio (50:50, wt %).[22] The required amounts of RDX were weighed on an analytical balance, and each sample was quantified to be 100 g finally through addition of water.[23,24] A total of 44 samples were prepared, among which 33 samples were used as the calibration set to construct a quantitative chemometrics model, and the remaining 11 samples were employed as a prediction set to evaluate the performance of the model (Table 1). In addition, a pure solid RDX sample was prepared to get a single NIR spectrum for the assistance of the characteristic spectral region selected.

Table 1. Statistics of RDX Contents of Calibration and Prediction Set[a]

data set	no.	min/g	max/g	mean/g	SD
calibration	33	3.5022	6.5032	4.9638	0.9784
prediction	11	3.6625	6.4947	5.0617	1.0373

[a] SD is standard deviation. The total weight is 100 g of each sample.

Spectral Measurement. NIR spectra were recorded using a Fourier transform NIR spectrometer (Nicolet Antaris-II, Thermo Fisher Scientific, Inc., U.S.A.) equipped with a quartz halogen lamp, an InGaAs detector, and a fiber-optic probe. Samples were stirred continually at 480 rpm by a magnetic stirrer (RET basic, IKA, Germany), and the fiber optic probe was directly inserted into samples for spectra collection with a transflectance mode. All in situ spectra were recorded in the 4000−10,000 cm^{-1} region with a resolution of 8 cm^{-1} and averaged over 32 scans. Each spectrum collection consumed approximate 20 s.

Chemometric Methods. Spectral preprocessing and multivariate regression methods were performed on TQ Analyst software (version 8.0, Thermo Fisher Scientific, Inc., U.S.A.). The first-derivative treatment in conjunction with a Norris derivative filter was utilized to preprocess all spectra in order to minimize the random noises and spurious contributions due to a baseline shift. Subsequently, a quantitative model was constructed for RDX over the selected wavenumber ranges using a PLS regression algorithm because it can extract the maximum useful information efficiently from signals.[25] The optimal number of PLS factors was obtained through leave-one-out cross-validation subjecting to the minimum statistic of root-mean-square error (RMSE)[24]

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (y_i^{\text{pred}} - y_i^{\text{ref}})^2}{n}}$$

where y_i^{pred} is the RDX content predicted by the NIR model, y_i^{ref} is that obtained by weighing, and n is the number of samples.

Quantitative Analysis by HPLC. The RDX contents of validated samples were confirmed by an Agilent HPLC module (1200 infinity, Agilent, U.S.A.) equipped with a quaternary pump and UV detector at 230 nm. [21] Acetonitrile was used as solvent for the intermediate, and the concentration of substances in the solution was 100 μg/mL. The sample solutions passed through a 0.45 μm filter for further instrumental analysis, and the total injection volume was 10 μL of each sample. Separation was carried out on a C_{18} 80 Å column (Eclipse XDB-C18, Agilent, U.S.A.), 5 μm, and 4.6 mm × 150 mm, using a binary mobile phase (acetonitrile/water, 90/10) at a flow rate of 1 mL/min. The quantitative analysis was performed on an Agilent ChemStation in conjunction with the standard curve of RDX.

■ RESULTS AND DISCUSSION

Spectral Analysis. The NIR range corresponds to molecular vibrations of stretching and bending overtones and combination bands; therefore, the coexistence of multiple chemical components causes spectra overlapping dramatically. This does not end up with a good performance model using the whole spectral region because many of the wavenumbers do not contain enough chemical information of analyte.

Figure 1(a) shows that the NIR spectrum is dominated with two major peaks located around 6890 and 5180 cm^{-1} due to the high molar absorptivity of the O−H group of water. The two absorption peaks as well as another weaker broad peak around 8500 cm^{-1} all correspond to the combination bands involving the symmetric, asymmetric, and bending modes of the water molecule.[26] The chemical features of RDX were weakened and overlapped under the broad water band, which results in a strong obstacle to development of an accurate model. Moreover, the physical factor of continuous stirring has a negative impact on the signal−noise ratio of the in situ spectra, which especially causes the region ranging from 4500 to 4000 cm^{-1} to not be acceptable for the requirement of a precise model, even though that region appears as a characteristic spectral interval both in RDX and the sample spectra.[27] Hence, the selection of the optimal spectral range was critical for achieving a reliable prediction model. Chemometrics software is available to provide a suggestion on choosing the

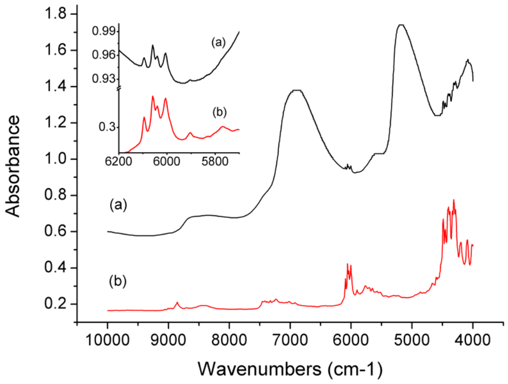

Figure 1. Raw NIR spectrum of sample (a) and pure solid RDX (b). The most characteristic spectral region of RDX is presented in detailed drawing.

appropriate spectral regions; however, that way is not always best for the calibration model because analysts become confused with the lack of convincing chemical definitions of suggested regions. Therefore, more informative and characteristic regions should be selected based on the chemical structure of RDX. Two optimum spectral intervals were utilized in this work, and the possible assignments of RDX are presented in detail (Table 2).[21,26,28] Additionally, the characteristic spectral regions of RDX were confirmed by the first-derivative spectra of samples (Figure 2).

Table 2. Spectral Regions Used for Model Construction[a]

spectral regions (cm^{-1})	possible assignments of RDX
6179−5720	ν CH_2 + ν N−NO_2 + ν ring/ν CH_2 +δ CH_2 + ν N−C−N
4703−4543	2ν CH_2 + ν ring/ν CH_2 + ν NO_2+ ν C−N−C

[a] ν: stretching vibration. δ: bending vibration. 2ν: first overtone of stretching vibration.

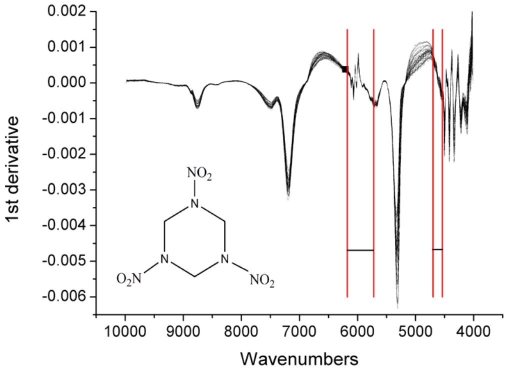

Figure 2. First-derivative spectra of calibration samples and chemical structure of RDX. The two areas defined with red vertical lines are used for model construction.

Model Construction. Leave-one-out cross-validation was used to determine the proper number of factors. In a typical procedure, one sample is removed from the calibration data set, and a calibration model is developed on the remaining unselected samples. The root-mean-square of cross-validation (RMSECV) is calculated every time with a new model constructed. That process is repeated until every calibration sample has been left out once, and the optimal number of factors that corresponds to the minimum RMSECV is used for model construction. Here, four factors were selected to develop the quantitative model (Figure 3).

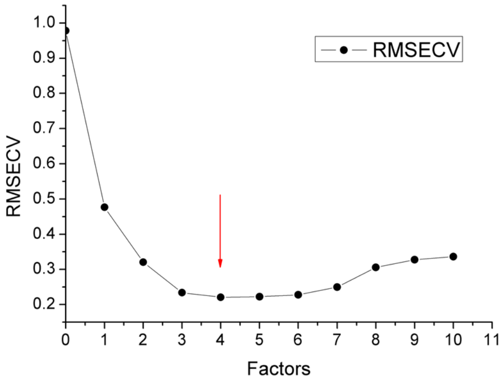

Figure 3. Different number of factors vs RMSECV of cross-validation. The optimal number of factors is marked by a red arrow.

The residual predictive deviation (RPD) statistic that is defined as the standard deviation (SD) of the reference values divided by RMSECV was obtained in cross-validation step. RPD is an important index for evaluating the predictive ability of the NIR calibration model. It is considered that a model is acceptable for analytical purpose with a RPD > 3.[20]

Model Performance. The external validation procedure was applied to evaluate the performance of the calibration model and avoid overfitting that causes accurate prediction for calibration samples only and bad prediction for unknown samples. A total of 11 independent samples excluding calibration set were scanned in situ by a fiber optic probe under all the same conditions with the spectra collection of calibration samples. The quality of prediction was assessed in terms of root-mean-square error (RMSE) and coefficient of determination (R^2).[25] As shown in Figure 4 and Table 3, the results of the calibration model in predicting the RDX contents are well accepted.

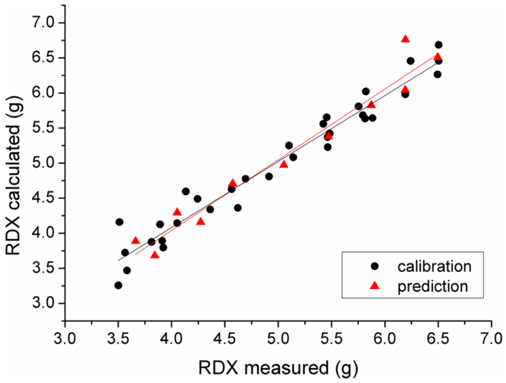

Figure 4. Measured values are plotted vs calculated values for the RDX content of calibration and prediction samples.

Furthermore, six intermediate mixtures covering the full calibration concentrations were prepared and analyzed again over a period of several months using the NIR system. Three in situ spectra of each sample were collected in the same parameters as the calibration process and quantified with the developed model. The analytical results are summarized in

Table 3. Calibration, Cross-Validation, and Prediction Results in PLS Model for RDX

calibration			cross-validation				prediction		
no.	R^2_{c}	RMSEC	R^2_{cv}	RMSECV	RPD	factors	no.	R^2_{p}	RMSEP
33	0.972	0.158	0.942	0.226	4.329	4	11	0.948	0.236

Table 4, and it is observed that the NIR system showed good reproducibility after several months and exhibited good repeatability during replicate testing given the low standard deviations values. In addition, the HPLC analysis was carried out to validate the performance of the NIR system using a paired *t*-test.[24]

Table 4. Repeatability of Developed NIR Method and Comparison of NIR and HPLC Values[a]

sample code no.	actual conc. of RDX (%)	average triplicate NIR value (%)	SD of triplicate (%)	error of NIR (%)	average triplicate HPLC value (%)	error of HPLC (%)
45	35.42	37.58	0.11	2.16	35.10	−0.32
46	41.43	39.04	0.08	−2.39	41.01	−0.42
47	47.91	44.97	0.13	−2.94	48.52	0.61
48	52.88	51.12	0.09	−1.76	52.21	−0.67
49	57.59	59.60	0.16	2.01	58.03	0.44
50	64.26	62.17	0.11	−2.09	64.87	0.61

[a] $t_{calc} = 0.8922$; $t_{crit} = 2.5706$, $\alpha = 0.05$, $n = 6$.

Comparison of NIR and HPLC Procedures. As shown in Table 4, the analytical results obtained from the NIR system were precise and acceptable in the tolerable range but less accurate than HPLC. However, no significant difference between the NIR and HPLC values was observed according to the paired *t*-test ($t_{calc} < t_{crit}$). Hence, it could be declared that the NIR system is much more suitable for in-process monitoring of RDX content in large scale samples to maximize materials efficiency and economic benefit, while few or temporary propellant samples, excluding those from the concentration ranges of the calibration set, are suggested to be analyzed by HPLC or other conventional methods in a laboratory.

Although solid propellant intermediate is a complex mixture that consists of solid and liquid components, the RDX content is available to be analyzed in situ by a NIR system with no prior manipulation, no chemical reagent consumed, and no waste formed when the optimal calibration model was established. Moreover, the combined application of a fiber optic probe allows analysis and the NIR instrument be far from the aggressive atmosphere of propellant industrial plants, which especially has a positive effect on the safety and health of operators who work in the propellant production line.[29]

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Notes

WARNING: RDX is highly energetic chemical as well as being harmful to your health and the environment. Please pay special attention on its explosive tendencies and toxicity.
The authors declare no competing financial interest.

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