



Quantitative determination on binary-component polymer bonded explosives: A joint study of ultraviolet spectrophotometry and multivariate calibration methods



Tao Lu^a, Zhining Wen^a, Lu Wang^a, Xuan He^b, Yuan Yuan^c, Minqi Wang^a, Yihuan Zhao^a, Menglong Li^a, Xuemei Pu^{a,*}, Tao Xu^{b,**}

^a College of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China

^b Institute of Chemical Materials, Chinese Academy of Engineering Physics, Mianyang 621900, People's Republic of China

^c College of Management, Southwest University for Nationalities, Chengdu 610041, People's Republic of China

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ABSTRACT

Explosive determination is of great importance in national defense and security fields. Simple, quick and reliable analytical techniques have been highly demanded in the field. In this work, we proposed a novel method for simultaneous determination of pentaerythritol tetranitrate (PETN), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and 2,4,6-trinitrotoluene (TNT) in binary-component polymer bonded explosive (PBX) samples by means of a combination of ultraviolet (UV) spectrophotometry with multivariable calibration methods. An orthogonal array design (DAD) was employed to construct the calibration set, which contains 27 reference samples. The calibration models were constructed using Partial Least Square regression (PLS-1) and Multiple Linear Regression (MLR). The variables were selected by the Successive Projection Algorithm (SPA) in MLR model. The predictive ability of the optimized models was validated by a test set including 18 samples. Finally, the two optimized models were successfully applied to simultaneously determine the content of PETN, RDX and TNT in five real binary-component PBX samples. Satisfactory results were obtained for the two models, in which the recovery yields were close to 100% for all the analytes. The computed elliptical joint confidence region (EJCR) further shows that the two models have no proportional and constant errors in the predicted concentrations. In addition, the statistical analysis indicates that MLR model with reasonable variable selection (SPA-MLR) could exhibit a slight superiority toward PLS-1 in the system. In a word, UV-spectroscopy in combination with multivariable calibration techniques has high potential to be a simple, quick and accurate analysis method for explosive determination in practice.

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1. Introduction

Pentaerythritol tetranitrate (PETN), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) are three of the most widely used secondary explosive ingredients in ammunition formulation and plastic explosives [1–4]. Also, they are organic explosives that contain multi-nitro functional groups ($-\text{NO}_2$). The binary-component polymer bonded explosives (PBXs), which contain RDX-TNT, TNT-PETN or PETN-RDX, respectively, have been commonly used in military and many explosive-based terrorist attacks in recently years [5,6]. Thus, it is very important to develop analytical methods to determine their contents rapidly and accurately in various explosive samples.

Up to now, many analytical methods have been proposed for detecting trace explosives in the field. Common analytical methods for the determination of explosive include mass spectrometry (MS) [7,8], ion mobility spectrometry (IMS) [9–11], gas chromatography (GC) [12,13], high performance liquid chromatography (HPLC) [14,15] along with gas chromatography-mass spectrometry (GC-MS) [16], and liquid chromatography-mass spectrometry (LC-MS) [17]. In spite of these instrumental techniques provide good sensitivity and excellent selectivity, they require expensive and large equipment and also involve time-consuming procedures [1]. Therefore, it is necessary to develop novel methods or improve the existing analytical techniques to enable faster, more sensitive, inexpensive and simpler determinations to facilitate the determination of explosives.

As is well-known, ultraviolet (UV) spectrophotometry is a simple, rapid, inexpensive and accurate analytical technique [18], which has been used for the quantitative analysis of a specific compound with a high degree of accuracy. However, UV spectrophotometry has poor

* Corresponding author. Tel./fax: +86 028 85412290.

** Corresponding author.

E-mail address: xmpuscu@scu.edu.cn (X. Pu).

selectivity for some samples, which exhibit strongly overlapped absorption bands resulted from their multicomponent. Consequently, it cannot be directly applied for the simultaneous analysis of multicomponent in complicated samples.

Nowadays, multivariate calibration methods have been developed and used for multicomponent systems in the quantitative spectrometry. Multiple linear regression (MLR), partial least squares (PLS) and principal component regression (PCR) [19–21] have been commonly used to assist experiments in order to directly determine the chemical components of interest in a complicated mixture. For the purpose of constructing well-fitted models, these methods in general require the selection of spectral variables [22], which could improve their predictive ability [23–25]. Compared to PLS and PCR regression models, which lack of a physical meaning for latent variables, MLR modes are simpler and more amenable to chemical interpretation model since it is based on real variables. However, MLR usually requires the selection of a suitable spectral variables for ensuring proper numerical conditioning and minimizing the propagation of random errors [26]. As a result, to resolve this problem, Araújo et al. proposed a novel variable selection strategy for selecting a subset of variables with a minimum multi-collinearity and suitable prediction power for MLR calibration, that is, the “successive projection algorithm” (SPA) [27,28]. In many applications, SPA-MLR models are comparable to full-spectrum PLS or PCR ones in terms of prediction ability, such as UV–Vis spectrometry [20], NIR spectrometry [29], spectrofluorimetry [30] and electrochemical method [31]. Moreover, SPA has also been compared with the genetic algorithm [27,28], which is a popular tool for variable selection in the multivariate calibration [32,33].

Based on the considerations above, we, herein, established a novel, simple, quick and accurate method to simultaneously determine PETN, RDX and TNT in polymer bonded explosive samples by UV spectrophotometry coupled to SPA-MLR and PLS-1 methods. Satisfactory results were obtained.

2. Chemometric methods

2.1. Partial least square regression (PLS)

Partial least squares (PLS) is a multivariable calibration method originally developed by Word [34,35] and has been successfully applied in spectrophotometric analysis of multicomponent mixtures so far [36–40]. PLS involves a calibration step in which the relation between the spectra and the component concentrations is estimated from a series of standard samples, followed by a prediction step where the component concentrations of the unknown samples are estimated by using the calibration results [41]. The PLS-1 version is optimized for the determination of a single component of interest at a time. During the model training step, The PLS-1 performs the decomposition for the calibration data by an iterative algorithm, which correlates the data with the calibration concentrations employing a so-called ‘inverse’ model [42]. This offers a series of regression coefficients to be applied to a new sample.

However, the crucial step in PLS-1 algorithm is to accurately select the optimum number of factors, which determinate the predictive ability of the calibration model. If the number of factors used in the model is small, it will cause under fitting. While the number of selected factors is too large, it will lead to over-fitting [43]. Therefore, a full cross-validation called leave-one-out cross-validation (LOO-CV) was utilized to solve the problem [42]. The main principle of LOO-CV was to leave out one sample from the calibration set in each iteration and perform the PLS-1 calibration with the remaining samples. The obtained PLS-1 model was used to predict the concentration of the hold-out sample. This procedure was iteratively repeated until each sample in the calibration set had been left out once. Finally, the known concentrations of the analytes in each reference sample were compared with the prediction concentrations of the analytes in each sample and the root

mean square error of cross-validation (RMSECV) was calculated in terms of Eq. (1):

$$\text{RMSECV} = \left[\frac{1}{m-1} \sum_{i=1}^m (C_{\text{act},i} - C_{\text{pred},i})^2 \right]^{1/2} \quad (1)$$

where $C_{\text{pred},i}$ is the predicted concentration of the interested component in i th mixture through the model, $C_{\text{act},i}$ is the real concentration, and m is the number of samples in the calibration set.

In principle, the optimum number of factors should yield minimum RMSECV. However, sometimes the number of factors with minimum RMSECV would lead to some over-fitting. Thus, a better select criterion is that the RMSECV value of the model with the optimum number of factors is not significantly greater than the minimal RMSECV. The F-statistic was used to make the significance determination by means of a comparison of the calculated F-value ($F = 1.31$) with the cutoff value ($\alpha = 0.25$), which was proposed to be a good criterion by Haaland and Thomas [42].

2.2. Successive projection algorithm-multiple linear regression (SPA-MLR)

SPA-MLR can be divided into three phases: in the first phase, the spectral data of the calibration samples are arranged in a matrix \mathbf{X}_{cal} of dimensions ($N_{\text{cal}} \times I$) such that the i th variable x_i is associated to the i th column vector $\mathbf{x}_i \in \mathfrak{R}^{N_{\text{cal}}}$. Then, these column vectors are subjected to a series of projection operations that generate I chains of M variables, where $M = \min(N_{\text{cal}} - 1, I)$ is the maximum number of variables that can be included in a MLR model. A new variable is selected in each chain according to the selected variable must have the maximum projection value on the orthogonal subspace of the previous ones from among all the remaining variables. The second phase consists of assessing the candidate subsets of variables which were extracted from the chains created in the first phase. For every one of those variable subsets, a MLR model is calibrated and the root mean square error of prediction (RMSEP) in the test set is also computed. The best subset of variables is selected on the basis of the smallest RMSEP for the validation samples. The third phase consists of a backward elimination step in order to discard uninformative variables, so that the parsimony of the model could be improved. A detailed explanation of SPA-MLR is given elsewhere [28,44–47]. It should be emphasized that the maximum number of selected variables must be less than the number of calibration samples in the process of SPA calculated.

2.3. Statistical parameters

Several statistical parameters were selected to evaluate the performances of the PLS-1 and SPA-MLR models for the simultaneous determination of PETN, RDX and TNT in mixed explosive mixtures. These parameters are the root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP), relative error of calibration (REC%), relative error of prediction (REP%) and the correlation coefficient of determination (R^2). These parameters are calculated for both the calibration and test sets in terms of Eqs. (2)–(4):

$$\text{RMSE(Cor P)} = \left[\frac{1}{m-1} \sum_{i=1}^m (C_{\text{pred},i} - C_{\text{act},i})^2 \right]^{1/2} \quad (2)$$

$$\text{RE(Cor P)} = \frac{100}{\bar{C}} \left[\frac{1}{m-1} \sum_{i=1}^m (C_{\text{act},i} - C_{\text{pred},i})^2 \right]^{1/2} \quad (3)$$

$$R^2 = 1 - \frac{\sum_{i=1}^m (C_{\text{act},i} - C_{\text{pred},i})^2}{\sum_{i=1}^m (C_{\text{act},i} - \bar{C})^2} \quad (4)$$

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