

Study on the Concentration Inversion of NO & NO₂ Gas from the Vehicle Exhaust Based on Weighted PLS

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Abstract

It becomes a key technology to measure the concentration of the vehicle exhaust components with the absorption spectra. But because of the overlap of gas absorption bands, how to separate the absorption information of each component gas from the mixed absorption spectra has become the key point to restrict the precision of the optical detection method. In this paper, the experimental platform for the absorption spectrum of vehicle exhaust components has been established. Based on the ultraviolet absorption spectra measured with the platform of exhaust gas NO & NO₂, the concentration regression model for the two components has been established with weighted partial least squares regression (WPLS). Finally the each spectral characteristic information of NO & NO₂ gas has been separated and the concentration of each corresponding component has been reversed successfully.

Keywords

Absorption Spectra, NO & NO₂ Gas, Weighted Partial Least Squares Regression, Concentration Inversion

1. Introduction

Nowadays the vehicle exhaust emissions have become one of the most important factors that affect the environmental air quality in our country. Therefore, it is urgent to strengthen the monitoring of vehicle exhaust emissions [1].

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exhaust components with the absorption spectra. But because of the overlap of gas absorption bands, how to separate the absorption information of each component gas from the mixed absorption spectra has become the key point to restrict the precision of the optical detection method [2] [3]. In this paper, based on the measured ultraviolet absorption spectra of exhaust gas NO & NO₂, the concentration regression models for the two components has been established with weighted partial least squares regression (WPLS). Finally the each spectral characteristic information of NO & NO₂ gas has been separated and the concentration of each corresponding component has been reversed successfully.

2. Weighted Partial Least Squares Regression: PLS

2.1. Partial Least Squares Regression

The partial least squares regression is multivariate statistical analysis method which is widely used. It focuses on multivariate regression modeling of multiple variables. The technology for synthesis and screening of information is used in PLS modeling process, combined with the functions of multivariate linear regression analysis, typical correlation analysis and principal component analysis [4] [5]. Then the modeling method of partial least squares regression using in the spectral analysis is introduced.

The spectral response matrix Y and its corresponding gas concentration matrix X are simultaneously decomposed into principal components, and new synthetic variables are obtained as follows:

$$X = TP^T + E \quad (1)$$

$$Y = UQ^T + F \quad (2)$$

where T & U are load matrixes of X & Y respectively, and P & Q are scoring matrixes of X & Y respectively. E & F are the errors introduced by using PLS method to fit X & Y respectively.

The regression model is built with PLS, which uses the characteristic spectral response matrix T and the characteristic concentration matrix U of which the vectors are orthogonal to each other.

$$U = T \times B \quad (3)$$

The regression coefficient matrix B is as follows, which is also called the correlation matrix.

$$B = (T^T T^{-1}) T^T U \quad (4)$$

Therefore, the main steps of PLS include the principal component decomposition for the variable matrix Y and the corresponding independent variable matrix X , and the calculation of the correlation matrix B .

2.2. Weighted Partial Least Squares (WPLS)

Although the PLS method has more advantages than the traditional multivariate

regression method, there is still low efficiency when analyzing the absorption spectra of multi-component gas, and the accuracy of the regression results is affected by the noise and sample distribution [6]. In order to improve the prediction accuracy, it is necessary to assign different weights to the samples in calibration sets. By analyzing the error and recovery rate of the calibration sets, the partial least squares (PLS) method can be further improved to into the error weighted partial least squares (EWPLS) and the variance weighted partial least squares (VWPLS) [7].

Assume that $Y_c \in \mathbb{R}^{M \times K}$ is the concentration matrix of the calibration set calculated by the PLS method, then the error of the recovery rate can be obtained as the following

$$E_c = \left| Y_c - \tilde{Y}_c \right| ./ Y_c \times 100\% \quad (5)$$

where“./”represents the division between the corresponding elements of matrices. $E_c \in \mathbb{R}^{M \times K}$ represents the recovery rate errors of K organic matters in M calibration samples. If $\{r_1, r_2, \dots, r_M\}$ is composed of the maximum error of the recovery rate of every row in E_c , the Gauss weight corresponding to the maximum error of the recovery rate is set as follows.

$$W_{r_i} = (e^{r_i})^\alpha \quad (6)$$

where α is the step adjustment parameter and $W_r = (w_{r_1}, w_{r_2}, \dots, w_{r_i})$ is the weight vector of the M calibration samples. The predictive results can be improved to some extent by adjusting the maximum error of the recovery rate. In addition, the weight vector of the PLS method can also be constructed by the variance of the recovery rate. If $(v_{r_1}, v_{r_2}, \dots, v_{r_i})$ represents the variance of the recovery rate in E_c , then the Gauss weight is as follows.

$$W_{v_i} = (e^{v_i})^\beta \quad (7)$$

where β is the step adjustment parameter and $W_v = (w_{v_1}, w_{v_2}, \dots, w_{v_i})$ is the variance weight vector of the recovery rate. Then the fluorescence intensity matrix and the concentration matrix can be updated by the weight vector.

$$\begin{cases} X_{cr} = \text{diag}(W_r)X \\ Y_{cr} = \text{diag}(W_r)Y \end{cases} \quad (8)$$

where $\text{diag}(W_r)$ is a diagonal matrix and the diagonal elements are $w_{r_1}, w_{r_2}, \dots, w_{r_i}$. And the new calibration sets X_{cr} and Y_{cr} are produced. Similarly, if the calibration sets are modified by the weight vector W_v , the new calibration sets X_{cv} and Y_{cv} can also be obtained. Next the EWPLS method is carried out as follows as an example.

1) Set initial vector u , calculate the weight w of X_{cr} , $w = X_{cr}^T u / u^T u$, calculate the score matrix t of X_{cr} , $t = X_{cr} w$.

2) calculate the weight c of Y_{cr} , $c = Y_{cr}^T t / t^T t$, calculate the score matrix u of Y_{cr} .

$$u = Y_{cr}c / c^T c .$$

3) If the convergence $\|t_{old} - t_{new}\| / \|t_{new}\| < \varepsilon$, has not reached, return to Steps 1 and 2, and otherwise continue with Step 4;

4) Remove the calculated components from X_{cr} , Y_{cr} , then

$$p = X_{cr}t / t^T t, X'_{cr} = X_{cr} - tp^T, Y'_{cr} = Y_{cr} - tc^T .$$

5) Return to Step 1, until all the components are extracted.

6) According to Equation (4), calculate the regression factor $B = (T^T T^{-1})T^T U$, then calculate $\tilde{Y}_{cr} = X_{cr}PBQ^T$.

7) If the convergence $\|Y_{cr} - \tilde{Y}_{cr}\| / \|Y_{cr}\| < \varepsilon$ has not reached, calculate W_p , X_{cr} ,

Y_{cr} , return to Step 1, Otherwise continue with Step 8.

8) calculate $\tilde{Y}_p = X_pPBQ^T$.

3. NO and NO₂ Feature Extraction and Concentration Inversion Experiments Based on WPLS

The UV absorption cross-sections of NO and NO₂ gas within the 180 nm - 400 nm band are shown in **Figure 1**. It shows a single peak absorption phenomenon of NO gas, which has a strong absorption peak at 205 nm, 215 nm and 225 nm. NO's absorption cross-section is at 10⁻¹⁹ magnitude orders. While it shows a continuous absorption phenomenon of NO₂ within 200 nm - 225 nm and 350 nm - 430 nm band, and the absorption cross-section magnitude is the same as NO. This will directly lead to the overlapping absorption of the two components and affect the concentration inversion of each single component seriously. So in this paper WPLS algorithm has been used to establish regression models to eliminate the interference and separate the independent components accurately.

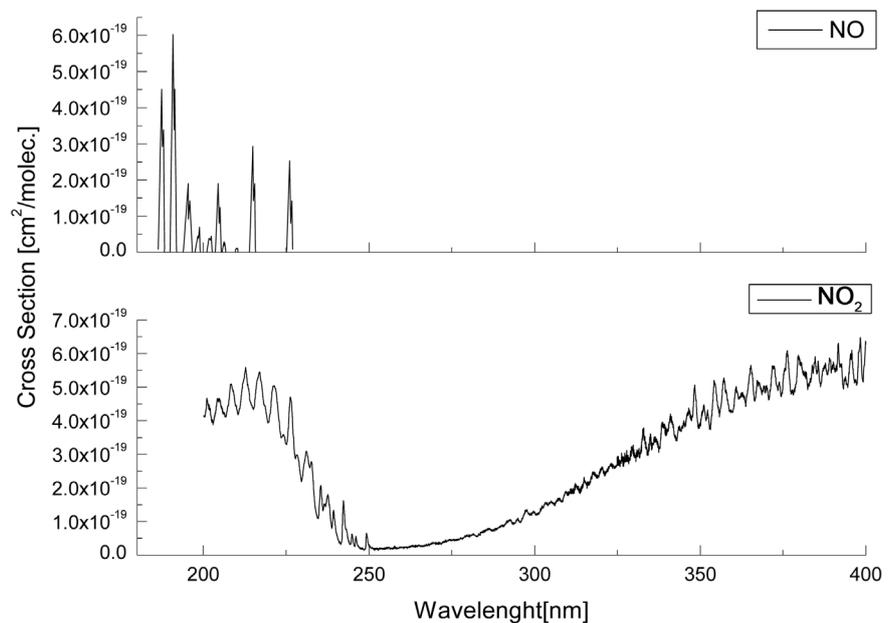


Figure 1. Absorption cross-sections of NO & NO₂ in the near UV band.

3.1. Acquisition of NO & NO₂ Absorption Spectra from the Vehicle Exhaust

As shown in **Figure 2**, the experimental platform for absorption spectra acquisition of NO_x from the vehicle exhaust has been built. It's composed of a gas distribution unit and a measuring unit. The gas distribution unit can mix two gases of different concentrations with a precision of 1%. And the measuring unit consists of a flashing xenon lamp, an ultraviolet spectrometer, a sample gas chamber and a data processing terminal and so on, which can measure the ultraviolet spectrum data of the sample gas effectively at a certain temperature and pressure.

In order to avoid multicollinearity, the orthogonal principle is followed in the sample concentration design for NO & NO₂. Samples of different concentration are designed as shown in **Table 1**.

Then a series of designed NO or NO₂ UV absorption spectra (200 nm - 440 nm) of different concentrations have been obtained with the platform, also with their mixture absorption spectra. The NO absorption spectra of different concentrations are shown in **Figure 3(a)**, meanwhile the NO₂ absorption spectra of different concentrations are shown in **Figure 3(b)** and **Figure 3(c)** also with a series of their mixture absorption spectra in **Figure 3(d)**.

Table 1. Designed concentration of NO and NO₂ sample gas.

Single NO ₂	Single NO	Single NO	Mixed NO & NO ₂	
608	308	2549	1022	0
547.2	277.2	2294.1	919.8	254.9
516.8	261.8	2166.65	868.7	382.35
486.4	246.4	2039.2	817.6	509.8
456	231	1911.75	766.5	637.25
425.6	215.6	1784.3	715.4	764.7
395.2	200.2	1656.85	664.3	892.15
364.8	184.8	1529.4	613.2	1019.6
334.4	169.4	1401.95	562.1	1147.05
304	154	1274.5	511	1274.5
273.6	138.6	1147.05	459.9	1401.95
243.2	123.2	1019.6	408.8	1529.4
212.8	107.8	892.15	357.7	1656.85
182.4	92.4	764.7	306.6	1784.3
152	77	637.25	255.5	1911.75
121.6	61.6	509.8	204.4	2039.2
91.2	46.2	382.35	153.3	2166.65
60.8	30.8	254.9	102.2	2294.1

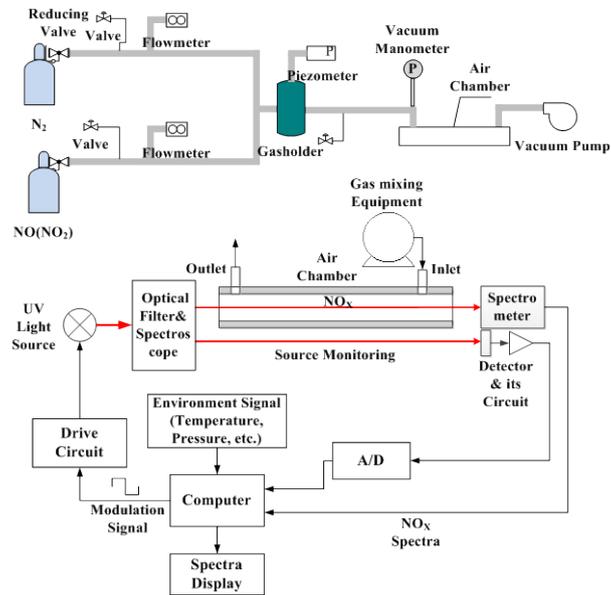


Figure 2. Schematic diagram of the experimental platform for NO_x spectra acquisition.

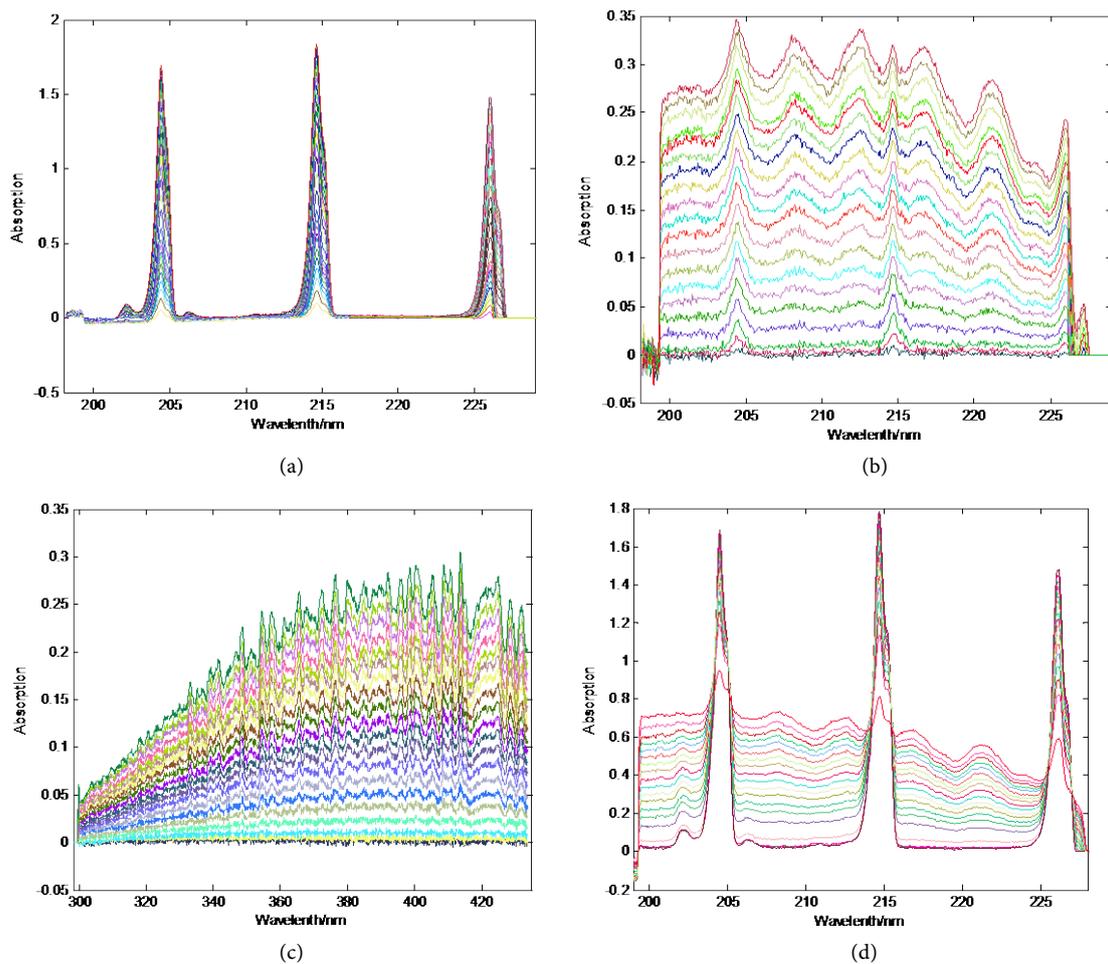


Figure 3. Absorption spectra of NO & NO_2 at different concentrations. (a) NO absorption spectra (29 samples); (b) NO_2 absorption spectra (20 samples, 198 - 229 nm); (c) NO_2 absorption spectra (20 samples, 299 - 439 nm); (d) mixed absorption spectra.

3.2. Experiments and Result Analysis

Here, the concentration inversion of NO and NO₂ components from the vehicle exhaust with ultraviolet absorption spectrum based on WPLS is actually a partial least squares regression problem with three independent variables and two dependent variables, as shown in **Table 2**. The regression equation of $Y_1 - Y_2$ for $X_1 - X_3$ should be established to determine the relationship between the concentration of the two components gas, Y and their absorbance, X.

According to Steps 1-8 in 2.2, a data processing program has been compiled with MATLAB, and then the regression models have been established with the obtained spectral sample data from which one spectral data has been selected and taken out, then the concentration have been inversed by put the selected spectral data into the model. That's the same with every concentration. Finally the experimental results are shown in **Figures 4-9**.

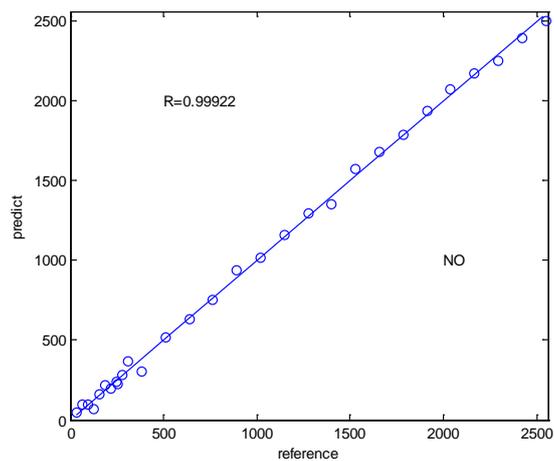


Figure 4. Experimental results of pure NO spectra (28 samples for modeling and 1 sample for prediction).

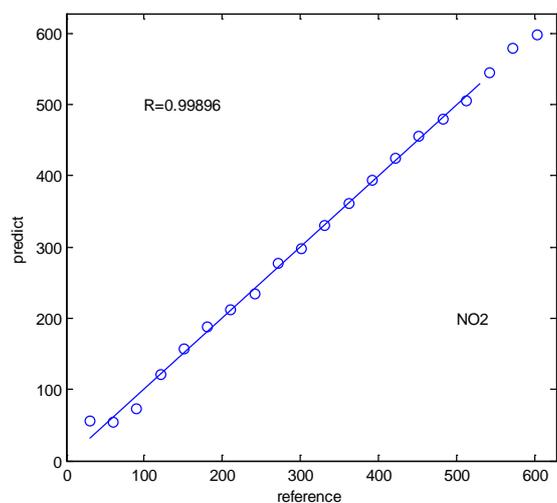


Figure 5. Experimental results of pure NO₂ spectra (19 samples for modeling and 1 sample for prediction).

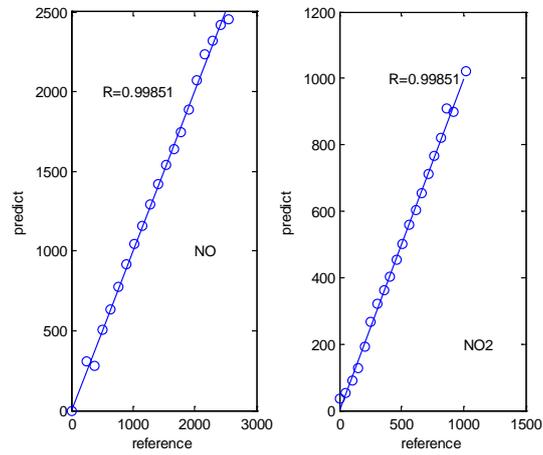


Figure 6. Experimental results of NO & NO₂ mixed spectra (19 samples for modeling and 1 sample for prediction).

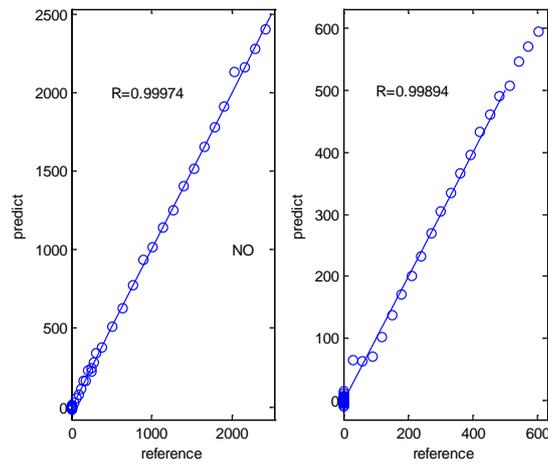


Figure 7. Experimental results of pure NO and mixed spectra (48 samples for modeling and 1 sample for prediction).

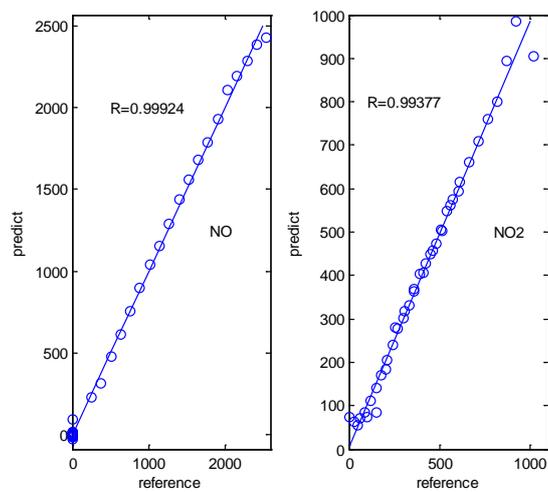


Figure 8. Experimental results of pure NO₂ and mixed spectra (39 samples for modeling and 1 sample for prediction).

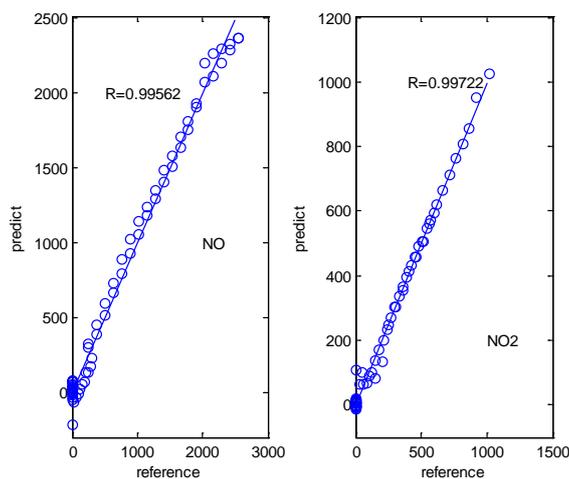


Figure 9. Experimental results of pure NO, pure NO₂ and their mixed spectra (68 samples for modeling and 1 sample for prediction).

Table 2. WPLS independent and dependent variables.

WPLS independent variable	X ₁ -NO ₂ absorbance	X ₂ -NO absorbance	X ₃ -NO, NO ₂ Mixed absorbance
WPLS dependent variable	Y ₁ -NO concentration	Y ₂ -NO ₂ concentration	

As seen from the above experimental results, using either the spectra of the individual components of NO or NO₂ or mixed spectra of the two components or even all the individual and mixed spectra for the regression modeling and concentration inversion based on WPLS, the experimental results are all excellent.

The approximation between the inversion results and real sample concentration are all above 99.4%, of which the highest can reach 99.97%. So it can be concluded that with WPLS algorithm the components' characteristics of the mixed spectral in which there're overlapped absorption with NO & NO₂ can be separated, and then each concentration of the samples can be inverted accurately.

In this experiment, it's not considered that the modeling optimization [6], the inversion band and spectral data denoising [8]. The spectral data used here in WPLS are the direct output of the spectrometer, of which the band is the whole detecting range of the spectrometer (its wavelength range: 198 - 438 nm, a total of 3648 sampling points). Meanwhile in the whole mixed spectra, there're not overlapped absorption at all sampling points, and there are also many places with zero absorbance, which will affect the accuracy of WPLS modeling.

4. Conclusion

Be aimed at the interference caused by spectral overlap absorption in the vehicle exhaust gas concentration detection with spectra method, the experimental

platform for absorption spectrum detection of exhaust gas has been built. On the basis of measuring the ultraviolet absorption spectra of exhaust components NO and NO₂, the weighted partial least squares regression (WPLS) algorithm has been used and then regression models of the components' concentration have been established, finally each NO or NO₂ concentration of the mixed gas samples has been inverted successfully. From the experimental results, under the condition without the original spectral denoising and WPLS modeling band optimization, the approximation of the concentration inversion results and the real samples can reach more than 99.4%.

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