Simultaneous analysis of nitro compounds by Voltammetric method combined with the partial least squares (PLS) and the principal component regression (PCR)

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Abstract— *Nitro aromatic compounds exhibit a strong electrochemical behavior on hanging mercury drop electrodes (HMDE). The ability to simultaneously determine 6 nitro compounds including nitrobenzene (NB), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), 2,4- dinitrophenol (DNP) and trinitrophenol (TNT) in the same samples was investigated by differential pulse Voltammetry. The method is based on the electrochemical process at HMDE in acetate buffer of pH 4.6. It was found that peak potentials of voltammetric reduction waves of NB, 2-NP, 3-NP and 4-NP appeared at - 0.332, - 0.281, - 0.311 and - 0.387 V respectively. Under the same conditions there are three peak potentials at -0.131, - 0.227, - 0.332 V for TNT and two peaks at tại - 0.221, - 0.332V for DNT. The peaks of these compounds are very close together. Due to the serious overlapping of Voltammetric peaks of these compounds in the mixtures, so that by a conventional Voltammetry it not possible to individually determine each compound. In this study, linear multivariate regression methods such as partial least squares (PLS), principal component regression (PCR) was used to resolve the overlapped Voltammograms. The obtained relative standard errors of both methods are within ± 10%. The PLS (10.8% RSEt) results in data better than PCR (11.8% RSEt).*

Keywords— ***Nitrobenzene, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, Dinitrotoluene, Trinitrotoluene.***

I. INTRODUCTION

The simultaneous determination methods of the nitro - compound mixtures in the environmental samples have received considerable attention, because they are widely used to in industries to control the pollution of individual pollutants present in waste water. The high level toxicity of nitro- compounds and their propagation through environment are capable of polluting land, water, air and affecting on human, animal health, fish, aquatic organism and other life forms. There is a variety of analytical methods applied to determine these compounds including performance liquid chromatography (HPLC), UV-vis spectrophotometry and electrochemistry. These methods are often complex and time consuming and requiring sample pretreatments involving separation, extraction before analyzing [3-7]. For the Voltammetric methods, due to the serious overlapping of their reductive peak potentials caused by the general structural formula, the nitro-compounds cannot be quantitatively determined individually. Therefore these methods are usually limited to analyzing a single chemical composition or determining the sum of the nitro compounds in the mixtures [1,2,5-7].

In this study, linear multivariable regression methods such as partial least squares (PLS), principal component regression (PCR), (applying mathematical, statistical, graphics methods, etc) were applied for experimental planning, optimization of obtained experimental data used to resolve the overlapped Voltammograms of nitro-compounds [4]. Based on the PLS and PCR models, each nitro compound such as NB, 2-NP, 3-NP, 4-NP, DNT and TNT was simultaneously determined from Voltammograms of their mixtures.

II. EXPERIMENTAL PART

2.1 Chemicals and apparatus

- **Chemicals**

Chemicals such as TNT, DNT, 2-NP; 3-NP; 4-NP (in solid form) and NB (in liquid) with analytical purity imported from China. The stock solutions contained 100 mg /L of the nitro-compounds (TNT, DNT, 2-NP; 3-NP; 4-NP) were prepared by accurately weighing 0.100 g of each dissolved them into 1 liter volumetric flask with twice distilled water. NB solution was prepared by adding 83.40 mL NB into 1 liter volumetric flasks with twice distilled water.

The other chemical solutions : NH_4OH, CH_3COOH, CH_3COONH_4 with the analytical purity were available in the LAB.

- **Apparatus**
  - Metrohm 797 Computed Electron Analyzer using three-electrode cell, including an HMDE, an Ag–AgCl reference electrode and a platinum were auxiliary electrode.
  - pH measurements were made with pH INOLAB (Germany).

2.2 Experimental procedures

Add a suitable volume of solution each containing a nitro-compound, 0.1 mL of acetate buffer solution (pH 4.6) into an electrochemical cell and diluted to 10 mL with twice distilled water. The solution was purged with pure nitrogent for 120 s to remove soluble oxygent before analyzing. The electrochemical behaviors as well as optimal condition for the determination by Voltammetry of some nitro- compounds were studied in the previous work [1]. The DPV was applied with the parameters such as the potential range from 0,0 to - 0.6 V; scan rate of 12.5 mV/s; pulse amplitude of 50 mV; stirring rate of 2000 rpm, 4- mercury drop size;15 s rest. The analytical samples were prepared including 6 nitro compounds with the predetermined concentration. The concentration of each of nitro-compound denoted independent variables X, the analytical information of maximum peak current at different potential denoted Y parameters respectively. Basing on the obtained data, a relation function between Y and X was established used for analyzing each component in their mixtures [4]. The PCR is used to process with the signal matrix to find the principle component (PC) number, while PLS model is applied to process both data sets of X and Y independently, then the orthogonal matrix T of X and Y would be found and PC and by this way the regression coefficients of the model might be calculated. For each multivariate regression model, its correctness was established by the following expression.

Relative standard error (RSE):

$$RSE(\%) = 100\sqrt{\frac{(\sum_{j=1}^{N} C_j - \hat{C}_j)^2}{\sum_{j=1}^{N} (C_j)^2}}$$

Here N is the number of samples, C_j is the concentration of the j^{th} compound in the mixture, C_j is the concentration calculated from the regression equation

The sum of the relative standard error (RSEt) of N samples is given as following expression.

$$RSE_t = 100\sqrt{\frac{\sum_{i=1}^{M}\sum_{j=1}^{N} (C_{ij} - \hat{C}_{ij})^2}{\sum_{i=1}^{M}\sum_{j=1}^{N} (C_{ij})^2}}$$

C_{ij} is the concentration of the component i in the sample, $C^{\wedge}{}_{ij}$ is the concentration calculated from the regression equation.

III. RESULTS CONCLUSION

3.1 Electrochemical characteristics of the reduction process of nitro - compounds

3.1.1 Electrochemical characteristics

The Voltammograms of the nitro-compounds were measured resulting in (Fig,1)

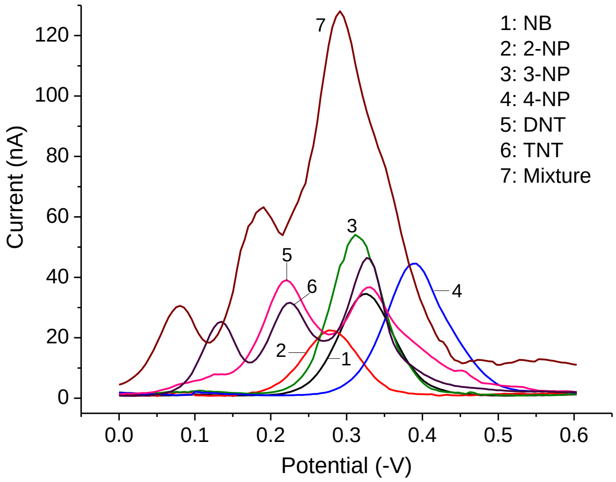

FIG 1: THE VOLTAMMOGRAMS OF NB, 2-NP, 3-NP, 4-NP, DNT, TNT (1PPM) AND THEIR MIXTURES

The Fig.1 showed that electrochemical behaviors of the studied nitro - compounds under the concrete conditions appeared the maximum peak currents such as NB, 2-NP, 3-NP, 4-NP at *0.332, - 0.281, - 0.311 and* - 0.387 V, three TNT peaks at - 0.131 (TNT1), - 0.227 (TNT2), - 0.332 V (TNT3) and two DNT peaks at - 0.221 (DNT1), - 0.332 V (DNT2), respectively.

It can be seen that peak potentials of these components are very close together and there is serious overlapping between the Voltammogram lines so each component can not be individually identified in the same mixture unless combined with the use of linear multivariate regression to simultaneously determine them.

3.1.2 Determination of the linear concentration range of nitro - compounds

Basing on the linear calibration of peak maximum height versus concentration of single nitro – components (not given here), and using the 6.0 Origin software the analytical characteristics of 6 nitro - compounds are presented in Table 1.

TABLE 1
THE LINEAR CONCENTRATION RANGE OF EACH NITRO – COMPOUND

Nitro-compounds	NB	2-NP	3-NP	4-NP	DNT (2peaks)		TNT (3peaks)		
					DNT1	DNT2	TNT1	TNT2	TNT3
Linear range, ppm	0.02-3.0	0.02-3.0	0.02-3.0	0.02-3.0	0.05-1.5	0.05-2.0	0.20-3.0	0.10-3.0	0.10-2.0
R^2	0.998	0.998	0.999	0.998	0.998	0.999	0.997	0.997	0.998
LOD, ppm	0.0045	0.0061	0.0033	0.0021	0.0062	0.004	0.0136	0.0053	0.0064
LOQ, ppm	0.0149	0.0202	0.0111	0.0071	0.0208	0.0132	0.0454	0.0176	0.0215

3.2 Multivariate regression equation

The multivariate regression equation was established based on PCR, PLS models. The concentration matrix (20 x 6) was established from the experimental data of 20 standard samples simultaneously containing 6 nitro- compounds such as NB, 2-NP, 3-NP, 4-NP, DNT and TNT with the concentration range of 0.3-1.2 ; 0.3-1.2 ; 0.9-1.8 ; 0.6-1.5 ; 0.6-1.5 ; 0.9-1.8 ppm respectively. The Voltammetric currents corresponding analyzed concentration were measured at a given potential from 0 to -0.6 V, then basing on the measured signal matrix (PCR, 20 x 120) PLS, 20 X 120) and using MATLAB software the electrolyte concentration in the mixtures would be calculated.

3.3 Evaluation of the validity of the multivariate regression model

3.3.1 Selection of the principle components (PC) of multivariate regression

The selection of PC (n-Factor) was based on building a test matrix containing standard tests with nitro – compounds as following.

A test matrix was constructed to check the validity of the multivariate regression model. The standard tests of 15 samples containing all inclusive NB, 2-NP, 3-NP, 4-NP, DNT and TNT with their known concentrations corresponding the multivariate calibration, Table 2.

TABLE 2
CALIBRATION CONCENTRATION OF NITRO-COMPOUNDS

Samples	Concentrations (Co-ppm)					
	NB	2-NP	3-NP	4-NP	DNT	TNT
1	1.5	1.5	0.9	1.2	0.9	0.6
2	1.8	1.8	1.5	1.5	1.2	0.6
3	1.5	1.2	0.9	0.9	0.6	0.6
4	0.9	1.8	0.6	1.5	1.2	0.9
5	1.5	1.2	1.2	0.6	0.9	0.9
6	1.2	1.5	0.9	1.2	0.6	0.9
7	1.2	1.8	1.2	1.2	0.9	1.2
8	0.9	1.5	1.5	1.5	0.3	1.2
9	1.8	1.8	0.9	1.2	1.2	0.9
10	1.5	1.2	0.6	0.6	0.9	0.3
11	1.2	1.5	0.9	1.0	0.9	0.6
12	1.5	1.2	0.9	1.2	1.0	0.9
13	1.6	1.2	1.0	1.0	0.9	0.9
14	1.0	1.0	0.9	0.9	0.9	1.0
15	1.0	1.2	0.9	1.2	0.9	0.6

The experimental data represented in the signal matrixes PCR (15 x 120) and PLS (15 x 120) and with the Matlab software were used to calculate the concentration of each nitro - compound in their mixtures.

The selection of the principle components was based on the dependence of RSEt (%) versus n factors (Fig.2).

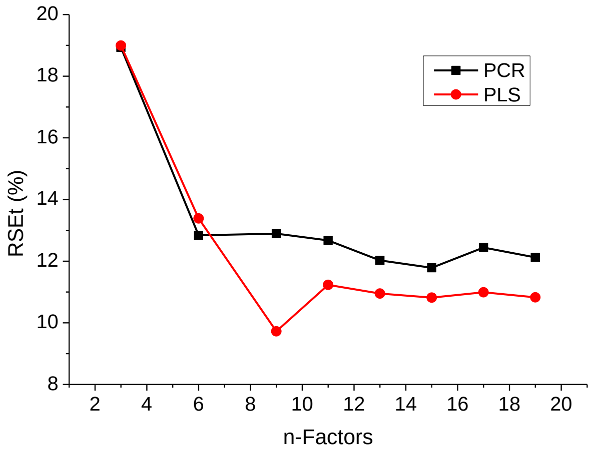

FIG. 2. DEPENDENCE OF RSET ON PC WINT PCR AND PLS

The Fig.2 showed that RSEt (%) values of both models (PCR & PLS) lower sharp from n = 6, when RSEt > 80% and RSEt > 90% from n = 8. The lowest RSEt can be obtained when n = 15 that was selected for further experiments.

3.3.2 Evaluation of the validity of the multivariate regression model

Using PC = 15 for both models PCR and PLS the relative error was calculated resulting in Table 3.

TABLE 3
THE OBTAINED RELATIVE ERRORS CORRESPONDING PC=15

Sample		Concentration (Co-ppm)					
		NB	2-NP	3-NP	4-NP	DNT	TNT
PCR	RSE (%)	11.3	12.8	12.6	12.8	8.0	10.4
	R (%)	104.1	90.4	100.7	90.5	95.9	93.5
	RSEt	**11.78**					
PLS	RSE (%)	10.4	12.1	11.8	9.9	9.7	9.3
	R (%)	105.1	107.4	99.7	94.8	92.4	93.9
	RSEt	**10.82**					

$$R : \text{Recoveries } (\%) = 100 \times \sum_{i=0}^{n} (\text{C found}/\text{Co})/n$$

The experimental data in Table 2. exhibited that multivariate regression method using PCR and PLS models showed good results. When PC = 15 was selected, the RSE(%) relative error of PCR components ranged from 10.4 to 12.8% and PLS was 9.3 to 12.1% respectively, TNT and DNT gave the lowest error results. The results from PLS method were better than PCR.

IV. RESULTS

The multivariate regression using partial least squared (PLS) and principle component regression (PCR) were successfully applied to simultaneously determine all 6 TNT, DNT, 2-NP compounds , 3-NP, 4-NP and NB by Voltammetric using hanging mercury drop electrodes. The relative standard errors for both methods are within ± 10%. The PLS (10.8% RSEt) has given better results than the PCR (RSEt = 11.8%). As such, PLS and PCR methods can be used to simultaneously analyze TNT, DNT, 2-NP, 3-NP, 4-NP and NB in the same mixture without separating them.

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