

Simultaneous analysis of nitro compounds by Voltammetric method combined with the principal component regression (PCR)

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Abstract— 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 on hanging mercury drop electrodes (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 - 0.297, - 0.251, - 0.267 and - 0.337 V respectively. Under the same conditions there are three peak potentials at -0.076, - 0.161, - 0.267 V for TNT and two peaks at *t_{ai}* - 0.176, - 0.282V 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, the linear multivariate regression method such as principal component regression (PCR) was used to resolve the overlapped Voltammograms. The obtained relative standard error (RSEt) of method is less 10%. The percent of recoveries were within $\pm 10\%$ of the target value. The developed method was then applied to the analysis of these nitro-substituted aromatic compounds in field samples with similar satisfactory results.

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

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 [7]. 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 [3,4,5]. 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 [6-8].

In this study, linear multivariable regression method which is 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 [3]. Based on the PCR model, each nitro compound such as NB, 2-NP, 3-NP, 4-NP, DNT and TNT was simultaneously determined from Voltammograms of their mixtures. In order to eliminate background effect, multivariable regression equation using the measured signal when carry out the experiment on the sample base instead of only using distilled water.

II. EXPERIMENTAL PART

2.1 Chemicals and apparatus

2.1.1 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 , $\text{CH}_3\text{COONH}_4$ with the analytical purity were available in the LAB.

2.1.2 Apparatus

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

2.2 Experimental procedures

Preparation of the sample base: Use some collected samples such as surface water, ground water and waste water, mixed together to obtain a mixed solution (A). Accurately determine the concentration of 6 study compounds including NB, 2-NP, 3-NP, -NP, DNT and TNT in the real sample by HPLC or LCMS / MS.

Add a suitable volume of solution each containing a nitro-compound, 0.5 mL of acetate buffer solution (pH 4.6) and 5 mL A into an electrochemical cell and diluted to 10 mL with twice distilled water. The solution was purged with pure nitrogen for 120 s to remove soluble oxygen 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; 10 s rest. The measured data were sampled by a computer at 120 potential points, in the range of 0 and -600mV with 5mV intervals. 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. For each multivariate regression model, its correctness was established by the following expression.

2.2.1 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, $\hat{C}_j$ 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, $\hat{C}_{ij}$ is the concentration calculated from the regression equation.

III. RESULTS

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)

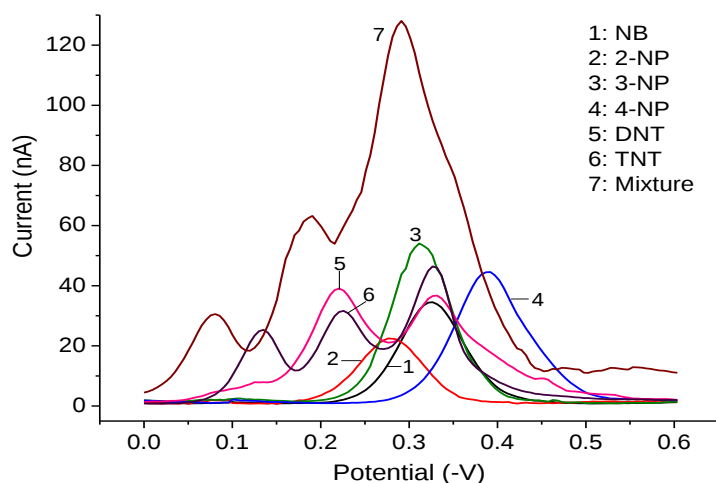


FIG 1: The Voltammograms of NB, 2-NP, 3-NP, 4-NP, DNT, TNT (1ppm) and their mixtures

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 - 0.297, - 0.251, - 0.267 and - 0.337 V, three TNT peaks at - 0.076 (TNT1), - 0.161 (TNT2), - 0.267 V (TNT3) and two DNT peaks at - 0.176 (DNT1), - 0.282 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 cannot 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	0.01-5.0	0.01-5.0	0.01-5.0	0.01-5.0	0.05-5.0	0.05-5.0	0.05-5.0	0.05-5.0	0.05-5.0
R ²	0.998	0.998	0.999	0.998	0.998	0.999	0.999	0.999	0.989
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 model. The concentration matrix (60 x 6) was established from the experimental data of 75 standard samples (including 60 standard samples and 15 standard samples for testing matrix) simultaneously containing 6 nitro- compounds such as NB, 2-NP, 3-NP, 4-NP, DNT and TNT with the concentration range of 0.5-2.5ppm respectively. Sample matrix concentration and standard sample size (60 x 6) and (15 x 6). 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 (60 x 120) and (15 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	2.50	2.00	1.50	1.00	1.06	1.52
2	2.50	2.50	2.00	1.50	1.56	2.02
3	2.00	1.80	1.50	2.00	1.06	1.52
4	1.50	1.50	1.00	1.50	1.06	1.52
5	1.50	1.50	1.50	1.00	0.56	1.02
6	1.00	2.00	1.50	1.50	0.56	1.52
7	1.50	2.00	1.50	2.00	2.06	2.02
8	2.00	1.50	1.00	1.50	1.06	2.02
9	1.60	1.20	1.20	1.20	1.20	1.20
10	2.00	1.60	0.80	0.80	0.80	0.40
11	1.00	1.50	2.00	0.50	1.00	0.50
12	1.60	1.30	1.00	1.00	1.50	1.50
13	1.60	1.90	1.00	1.50	1.50	1.00
14	2.00	1.90	1.50	1.00	2.00	1.50
15	1.20	1.20	1.20	0.80	1.20	0.80

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 the mixtures.

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

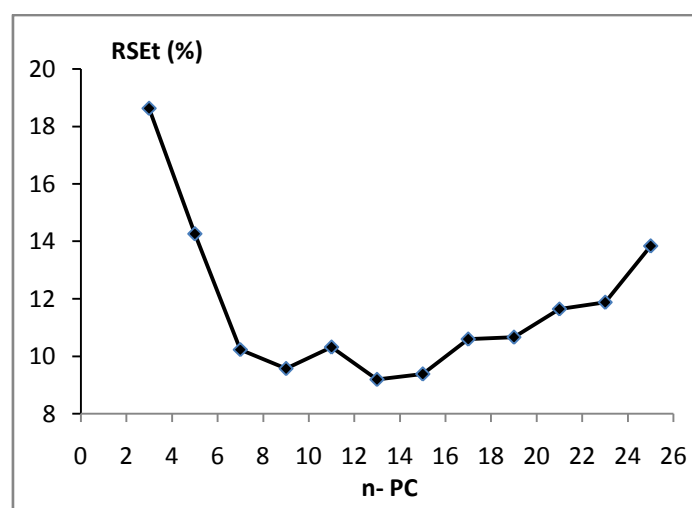


FIG. 2. Dependence of RSEt on PC wint PCR

The Fig.2 showed that RSEt (%) values of PCR model lower sharp from PC 6 to 15. The lowest RSEt can be obtained when $n = 13$ that was selected for further experiments.

3.3.2 Evaluation of the validity of the multivariate regression model

Using PC = 13 PCR model the relative error was calculated resulting in Table 3.

TABLE 3
THE OBTAINED RELATIVE ERRORS CORRESPONDING PC=13

Sample	Concentration (Co-ppm)						
		NB	2-NP	3-NP	4-NP	DNT	TNT
	RSE (%)	9.3	8.1	7.7	3.4	8.7	8.2
	Re(%)	100.6	101.2	101.6	99.6	94.9	102.4
	RSEt (%)	8.0					

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

The experimental data in Table 3 exhibited that multivariate regression method using PCR model showed good results. When PC = 13 was selected, the RSE(%) relative error of PCR components ranged from 3.4 to 9.3% and RSEt is 8.0%.

3.4 Application to environmental water and industrial waste-water samples

Analysis results of some samples collected by Von-Ampe method combined with multivariate regression using the PCR model are shown in Table 4.

TABLE 4
FIELD WATER SAMPLES PREDICTION BY PCR

		Found (ppm)	Added (ppm)	Found after added (ppm)	R (%)
Sample 1	NB	0.13	1	1.29	116
	2-NP	ND	1	0.96	96
	3-NP	ND	1	0.84	84
	4-NP	0.10	1	1.08	98
	DNT	0.01	1	0.87	86
	TNT	0.04	1	0.92	88
Sample 2	NB	0.51	1	1.48	97
	2-NP	0.70	1	1.61	91
	3-NP	ND	1	0.96	96
	4-NP	0.05	1	0.99	94
	DNT	0.24	1	1.16	92
	TNT	1.09	1	2.05	96

In general, most recoveries are in the range of 90-100%, the poorer recoveries (ca. <95 or >105%) tend to coincide with the 'not detected' or very low estimates of the amount of analyte present in the actual sample or indeed in the standard added.

IV. CONCLUSION

The multivariate regression using principle component regression (PCR) was successfully applied to simultaneously determine all 6 compounds: TNT, DNT, 2-NP, 3-NP, 4-NP and NB by Voltammetric using hanging mercury drop electrodes. Good validation results were obtained: RSE less 10%; recoveries (%) within 10%). As such, PCR method can be used to simultaneously analyze TNT, DNT, 2-NP, 3-NP, 4-NP and NB in the same mixture without separating them. The developed method was then applied to the analysis of the nitro-substituted aromatic compounds in field samples with similar satisfactory results.

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