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Research Article

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Determination of nonylphenol polyethoxylates in water samples of microbial degradation by second derivative ultraviolet spectrum

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ABSTRACT

Nonylphenol polyethoxylates (NPEOs) is an important kind of nonionic surfactant widely used in the manufacturing and life of human beings. A second derivative ultraviolet spectrum method was established for the determination of the total NPEOs (the average n was 10) in microbial degradation water samples, and the optimal experimental conditions were studied. Water was used as the solvent. The derivative peaks of 283 nm and 288 nm were characteristic peaks, and the vertical distance of their culminations was used as the quantitative basis. Under the optimal experimental conditions, the standard curve of NPEOs was linear within the range of 1.8~440 μg/mL. The linear correlation coefficient was 0.9995, and the detection limit was 0.5 μg/mL. Actual NPEOs degradation water samples were determined. The recoveries of NPEOs ranged from 98.1% to 104.4% and the relative standard deviation varied from 1.9% to 2.1%. The results showed that the second derivative ultraviolet spectrum method was simple and fast, and was suitable for the determination of the total NPEOs in microbial degradation water samples.

Key words: determination conditions; nonylphenol polyethoxylates; second derivative ultraviolet spectrometry; water samples

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INTRODUCTION

Nonylphenol Polyethoxylates (NPEOs) is the prime ingredient of nonionic surfactant, which is widely used in the manufacturing and life of human beings. The nonionic surfactant is a kind of substance that can reduce the surface tension of solvent (generally is water), change the interface status of system, and which can produce effects (or on the contrary) in moisture, emulsification, blistering and solubilization only with small doses [1,2]. It is widely used in many fields such as oil industry, mining and metal-processing [3].

NPEOs have low biodegradability compared with anionic surfactant and other nonionic surfactant. The degradation products of NPEOs both have estrogenic activity and mutagenic activity, which could be strengthened as the time increasing [4,5]. And they could seriously harm aquatic organism [6], mammal and human body [7].

The operations of ultraviolet (UV) spectroscopy were relatively simple [8-10], and were widely used in actual determination of the total amount of alkylphenol ethoxylates (APEOs) [11]. Qian *et al.* determined APEOs by UV spectroscopy [12]. Li *et al.* established second derivative UV spectrometry in determining the total amount of APEOs of DTY finish [13].

In this study the second derivative UV spectrometry was used to scan the UV absorption spectra of water samples directly in wavelength range of 260~310 nm, and the vertical distance (amplitude D) of the two vertexes of characteristic peaks 283nm(-) and 288nm(+) was regarded as the quantitative criteria by second differential and

derivative processing, and by which the total amount of NPEOs could be determined.

EXPERIMENTAL SECTION

Equipments

(1) TU-1900 Double beam UV-visible light spectrophotometer: Beijing Purkinje General Instrument Co., Ltd. Analysis;
(2) Quartz cuvette: 1cm, Shanghai Industrial Glass fourth plant;
(3) Electronic balance: accurate to 0.0001 g, German Sartorius Corporation;
(4) SZ-93Automatical double pure water distillatory: Haiya Rong Biochemical Instrument;
(5) Pipette: 100 μL and 1 mL, Waters Corporation USA.

Reagents and samples

(1) NPEOs: Reagent grade, the average value of n was 10, Tokyo Kasei Co., Ltd., Japan;
(2) Dichloromethane, Ethyl alcohol: Analytical pure, Tianjin Bodi Chemical Co., Ltd.;
(3) Chloroform: Analytical pure, Shenyang Xinhua Reagent Factory;
(4) NPEOs standard stock solution: Dilute 0.1074 g of NPEOs with deionized water to 50 mL, the concentration of the standard stock solution was 2148 μg/mL;
(5) Water samples of microbial flora degradation: From an activated sludge NPEOs treatment system of Northeastern University. The components of raw water were shown in Table 1.

Table 1 Composition and content of the raw water

Category	Name	Concentration (μg/mL)
Carbon source	$NP_{10}EO$	300
Nitrogen source	$(NH_4)_2SO_4$	165
Phosphorus source	K_2HPO_4	45
Buffer solution	$NaHCO_3$	120
Inorganic salt	$CaCl_2$	6
	$FeSO_4 \cdot 7H_2O$	0.55
	$MgSO_4 \cdot 7H_2O$	6
	$MnSO_4 \cdot H_2O$	6

Equipment Operation

(1) Turned on the voltage regulator, main power source, monitor, computer mainframe and UV and visible spectrophotometer in turn.
(2) Turned on the UV and visible spectrophotometer and preheat it for 15~20 minutes, then started the UVWin software to do self-testing.
(3) Set the UV scanning range from 260 to 310 nm, checked baseline by double-distilled water, transferred the water sample to 1 cm cuvette to scan the UV spectrum after diluting, processed the UV spectrum with second differential and derivative by UVWin software, and recorded the vertical distance (amplitude D) of the two vertexes of characteristic peaks 283 nm(-) and 288 nm(+).
(4) Data processing: brought the amplitude D into standard curve, and calculated the concentration of NPEOs in water sample.
(5) Turned off the UVWin software after determining, and then turned off the UV and visible spectrophotometer, computer mainframe, monitor, main power source and voltage regulator in turn.

RESULTS AND DISCUSSION

The inorganic salts were specifically added into the microbial raw water samples to insure the microbial degradation flora had enough nitrogen and phosphorus as the source of nutrition and the pH environment that more suitable for degradation. The presence of inorganic salts in water samples could affect the UV determination, if the normal UV spectrometry was carried out, the NPEOs was needed to be extracted organically from the water sample to get rid of the interference, by which the analysis process was complicated. Derivative UV spectrometry could eliminate the absorption of turbidity background and interference of coexisting impurities by differential and derivative processing. So in this study the derivative UV spectrometry was carried out to determine the water sample of microbial degradation to eliminate the interference by inorganic salts, because of which the analysis process could be simplified and the analytical cycle could be shorten.

Selection of differential order numbers

Observed the derivative UV spectrum of different orders of NPEOs, as shown in Fig. 1, and the derivative UV spectrum of different orders of NPEOs-negative solution was shown in Fig. 2. Derivative UV spectrum of first,

second and third derivatives of NPEOs all had characteristic peaks, but the value of first derivative was not zero, which could affect the determination, and the response value of third derivative was lower, so the derivative UV spectrum of second derivative was carried out in this study.

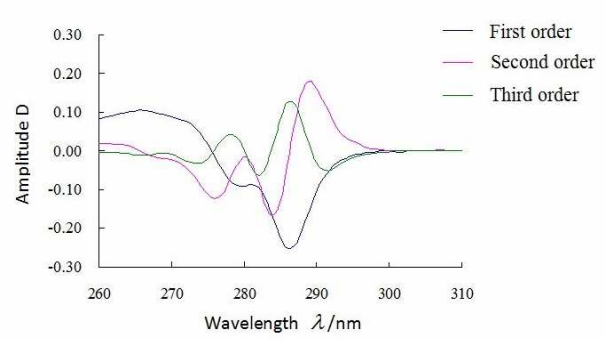

Fig. 1 Differential UV spectrum of different orders of NPEOs

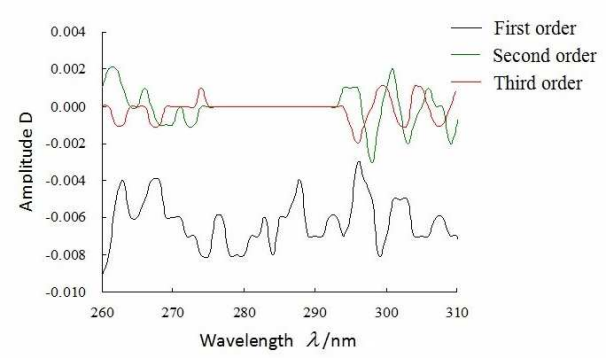

Fig. 2 Differential UV spectrum of different orders of NPEOs-negative solution

Selection of solvents

The effects of different solvents on second derivative UV spectrum of NPEOs were shown in Fig. 3. The second derivative UV spectrum of NPEOs in different solvents showed that the shapes of spectra in different solvents of water, ethyl alcohol, dichloromethane and trichloromethane presented less difference. And compared with other solvents, water has lower volatility, which couldn't cause the changes of concentration of solvents in the process of determination; besides, the sample solution to be determined was water, and the solvent that used was water as well, for which the process of extracting solute could be omitted, the analysis process could be simplified and accelerated, and the large amounts of organic reagents could also be saved. So water was chosen as the solvent in this study.

Selection of detective wavelength

The inorganic salts in water samples of degradation could affect the determination of derivative UV spectrum of second derivative of NPEOs. The Second derivative UV spectrums in NPEOs standard solution and in NPEOs-negative solution respectively were shown in Fig. 4 and Fig. 5. It showed that there exist derivative peaks near 226 nm(-), 236 nm(+), 283nm(-) and 288nm(+). But the derivative values of NPEOs-negative solution at 226nm and 236nm were not zero, and it presented zero baseline when the wavelength got higher than 260nm, so the peaks at 283 nm(-) and 288 nm(+) were chosen as the characteristic peaks, and the vertical distance (amplitude D) of the two vertexes of characteristic peaks was regarded as the quantitative criteria, as shown in Fig. 6. Followed both the second derivative value and amplitude D of NPEOs-negative solution were not zero, which couldn't affect the determination.

Selection of smooth points and magnification

The different smooth points in the processing of differential and derivative of UV absorption spectrum could be chosen, more points, better smoothness of spectral curve, but lower amplitude D. The second derivative UV spectra of NPEOs of different smooth points at 5、7、9、11 and 13 were shown in Fig. 7. The results showed that there appears maximum amplitude at the point of 5 and minimum at 13, and the spectra of different smooth points almost presented the same shapes, the changes of smoothness were also very small. So 5 was chosen as the smooth point by considering sensitivity.

The amplitude D could be increased by choosing the suitable magnification in differential and derivative, which could increase the sensitivity. But the over-high magnification might increase the baseline noise, and the derivative peak of component to be determined would be interfered. The second derivative UV spectrums of NPEOs-negative solution of different magnification (10, 20, 30, 40 and 50) were shown in Fig. 8. When the magnification got higher than 20, the derivative value of spectrum at 283 nm and 288 nm were no longer zero, which could interfere the determination, so 20 was chosen as the magnification.

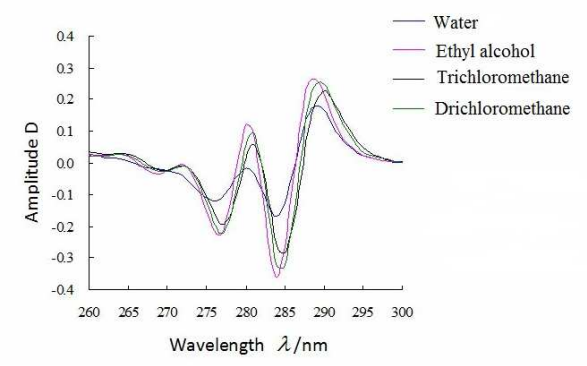

Fig. 3 Second derivative differential UV spectrum of NPEOs in different solvents

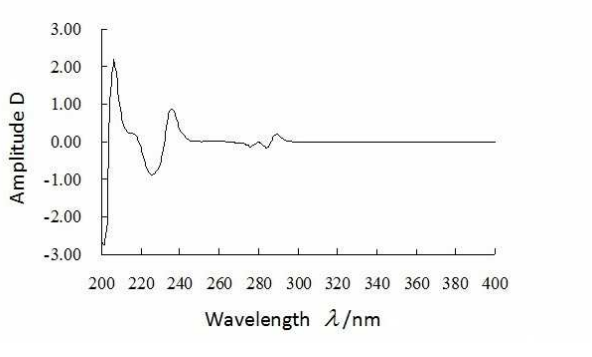

Fig. 4 Second derivative differential UV spectrum of NPEOs standard solution

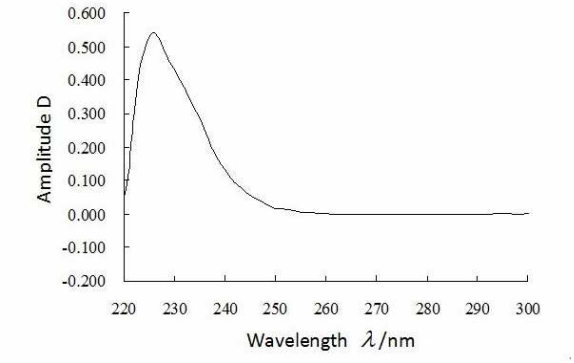

Fig. 5 Second derivative differential UV spectrum of NPEOs-negative solution

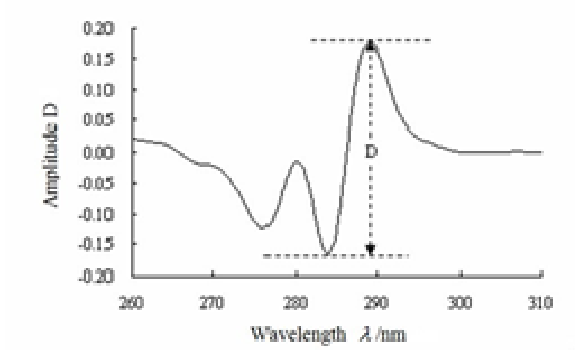

Fig. 6 Quantitative criteria for second derivative differential UV spectrum of NPEOs

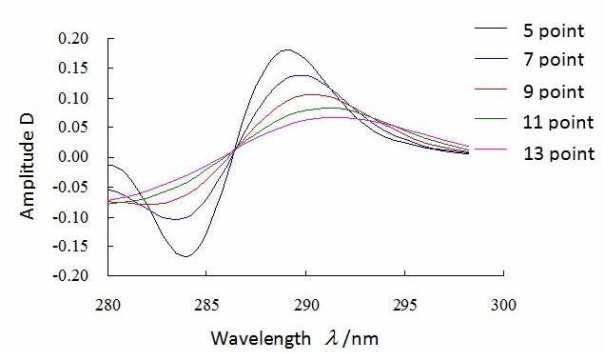

Fig. 7 Second derivative differential UV spectrum of different smooth points

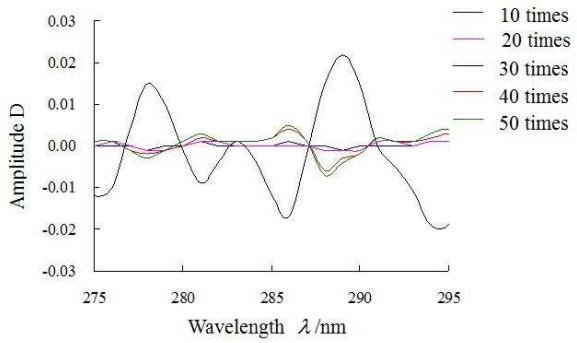

Fig. 8 Second derivative differential UV spectrum of different magnification

Standard curve

Separately transferred 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50 mL of the standard stock solution (2148 μg/mL) to 5 ml graduated test tubes, diluted with double-distilled water to 5 mL and mixed. The concentrations of all series of standard solution were 21.48, 42.96, 85.92, 128.88, 171.84 and 214.80 μg/mL, determined the second derivative UV spectrum, calculated the amplitude D and drew the standard curve, which was shown in Fig. 9. The equation of linear regression of the standard curve was y=0.0031x-0.0193, and the linearly dependent coefficient was R^2=0.9995.

Determination of water samples

Scanned the UV spectra of water samples and processed it by second differential and derivative after diluting, calculated the concentration of NPEOs of sample according to amplitude D. The NPEOs concentration of raw water was 265.42±1.55 μg/mL, and that of effluent water was 20.19±0.22 μg/mL.

Precision experiments

The standard solution of 21.48 μg/mL NPEOs were determined for 11 times. The determined corresponding

amplitude D were 0.055, 0.055, 0.054, 0.055, 0.056, 0.055, 0.055, 0.054, 0.055, 0.055 and 0.055. The average amplitude D was 0.055. The standard deviation was 0.001 and the relative standard deviation was 1.0%. The results proved that this method had good repeatability.

Recovery experiments

The raw water was diluted to 5 times (53.65 μg/mL of NPEOs) and the effluent water was diluted to 3 times (10.21 μg/mL of NPEOs). Then 42.96 and 10.74 μg/mL of NPEOs standard solutions were added into the diluted raw water and the diluted effluent water separately. The recovery results (shown in Table 2 and Table 3) showed that the recovery of NPEOs was 98.1%～104.4%, and the relative standard deviation of recovery results was less than 5 %, which indicated that the analysis results were precise and reliable, and it could meet the requirement of analysis and determination.

Table 2 Recovery results of raw water

Number	Standard amount (μg/mL)	Recovery amount (μg/mL)	Recovery rate (%)
1	42.96	43.54	101.4
2	42.96	43.22	100.6
3	42.96	43.87	102.1
4	42.96	42.58	99.1
5	42.96	44.51	103.6
6	42.96	44.83	104.4
7	42.96	42.90	99.9
8	42.96	43.22	100.6
9	42.96	42.25	98.4
10	42.96	43.87	102.1
11	42.96	44.51	103.6
AVE	42.96	43.57	101.4
RSD/%	—	1.9	1.9

Table 3 Recovery results of effluent water

Number	Standard amount (μg/mL)	Recovery amount (μg/mL)	Recovery rate (%)
1	10.74	10.85	101.1
2	10.74	10.53	98.1
3	10.74	10.85	101.1
4	10.74	10.85	101.1
5	10.74	11.18	104.1
6	10.74	10.53	98.1
7	10.74	10.85	101.1
8	10.74	10.85	101.1
9	10.74	11.18	104.1
10	10.74	10.85	101.1
11	10.74	10.53	98.1
AVE	10.74	10.83	100.8
RSD/%	—	2.1	2.1

Stability experiment

The UV absorption spectra of standard solution of concentration of 42.96 μg/mL were scanned at different times to observe the stability of the solution, processed them by second differential and derivative and calculated amplitude D, which was shown in Fig. 10. The results showed that the amplitude D doesn't have much change in 7 days, which meant it could remain stable in a week.

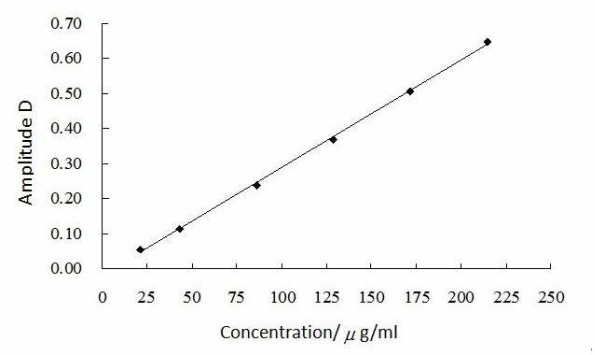

Fig. 9 Standard curve of NPEOs

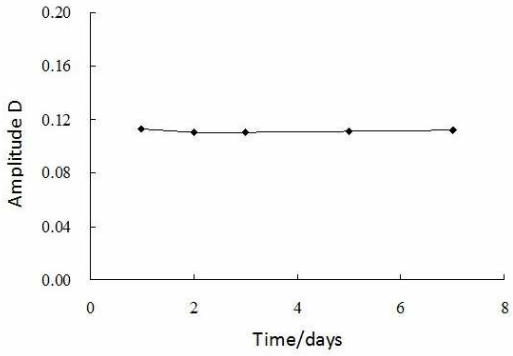

Fig. 10 Stability experiment

CONCLUSION

(1) The conditions of derivative spectrometry were settled down by condition experiments: second differential and derivative was carried out as the processing method, water was chosen as the solvent, 5 was set as the smooth point and 20 as the magnification, the derivative peaks at 283 nm(-) and 288 nm(+) were chosen as the characteristic peaks, the vertical distance (amplitude D) of the two vertexes of characteristic peaks was regarded as the quantitative criteria.

(2) Drew the standard curve of second derivative UV spectrum of NPEOs at the optimal experimental conditions. And the standard curve presented good linearity at the concentration range of 1.8~440 μg/mL, and the linearly dependent coefficient r was 0.9995, the detection limit was 0.5 μg/mL.

(3) In this study the real water samples of microbial degradation was determined, and the analytical results of this method were studied, which showed that when the recovery of NPEOs was 98.1~104.4%, and the relative standard deviation was 1.9~2.1%, it could meet the requirement of routine analyses.

(4) The instrument of second derivative UV spectrometry had low degree of automation, so the manual injection was needed. But the sample pretreatment and instrument operations were relatively simple, and the analysis was fast. The second derivative UV spectrometry established in this study was sensitive and accurate, which was suitable for the determination of the total amount of NPEOs in water samples of microbial degradation.

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