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Article

Simultaneous Determination of Nonylphenol and Nonylphenol Ethoxylates in Wastewater Samples from Biodegradation Process by High Performance Liquid Chromatography Method

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The degradation products of nonylphenol ethoxylates (NPnEO), nonylphenol (NP) and short-chain NPnEO are representative of environmental endocrine disruptors. They possess strong lipophilicity, toxicity, cumulative property and estrogenic effect. They can pollute the environment, cause body precocious, and induce the body's estrogen-sensitive cancer cell proliferation. A fast method using high performance liquid chromatography (HPLC) was developed to simultaneously quantify NP and 11 kinds of NPnEO in wastewater samples. The influence of mobile phase composition, mobile phase ratio, mobile phase flow rate, column temperature and sample injection volume on the separation effect was studied. Under the optimized conditions, NP and 11 kinds of NPnEO were separated successfully within 35 min. The method showed good linearity for NP and 11 kinds of NPnEO (n = 1-11). The linear correlation coefficients for the standard curves were 0.9720- 0.9999. The precision degree of the method was reliable and all the relative standard deviation (RSD) values (n = 0-11) obtained were less than 5.0%.

Keywords: chromatographic condition, high performance liquid chromatography (HPLC), nonylphenol (NP), nonylphenol ethoxylates (NPnEO), simultaneous determination

Introduction

In recent years, it was discovered that the endocrine disruptors in the environment could interact with the endocrine system in organism even with a small dosage. Endocrine disruptors perturb the synthesis, secretion, transport, metabolism, binding action, or elimination of endogenous hormones.[1] These endocrine disruptors not only pollute the environment but also cause a serious threat to people's health. The monitoring, analysis and inorganic treatment of these endocrine disruptors have attracted an increasing attention.[1-5]

Nonylphenol (NP) and nonylphenol ethoxylates (NPnEO) of short chain (n = 1, 2) are typical endocrine disruptors.[2,6] NP and short chain nonylphenol ethoxylates (SC-NPnEO) possess strong lipophilicity, toxicity, cumulative property and estrogenic effect.[2,6,7] They are the main degradation products of long chain NPnEO, which are the most commonly used nonionic surfactants.[2,7-9] Currently, the harmless treatment of NPnEO has become a hot topic in the environmental field. A lot of researches about the physicochemical or biological degradation of NP and NPnEO have been carried out.[5,8,10-12]

The anoxic-oxic activated sludge process (AOASP) is mainly combined with an anoxic unit, an oxic unit and a settlement unit.[11] The wastewater is introduced into the anoxic unit firstly. Some operations such as stirring are performed in anoxic unit to keep the activated sludge suspending. Then the wastewater flows into the oxic unit. Aeration is conducted in oxic unit to supply oxygen for the activated sludge bacteria. The circulation is carried out between the anoxic and the oxic unit to strengthen the treating effect such as NPnEO degradation. The settlement unit is used for the separation of treated water and activated

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sludge. A lab-scale AOASP was established to treat the synthetic long chain mixed NPnEO wastewater. In order to detect and quantify the composition of NP and NPnEO in wastewater samples from the AOASP, a method aimed at the simultaneous determination of NP and NPnEO (n = 1-11) was established in this study.

At present, gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC) are the main detection methods for determining NP and NPnEO.[3,9,13-16] However, GC-MS is much more expensive and suitable for the analysis of small molecules such as NP and NPnEO (n < 4).[14-16] In this study, according to the properties of target detection objects, the economical and practical HPLC method was chosen to determine NP and NPnEO (n = 1-11) in wastewater samples from biodegradation process. The influence of mobile phase composition, mobile phase ratio, mobile phase flow rate, column temperature and sample injection volume on the separation effect was investigated in detail. The linearity, linear correlation coefficient, relative standard deviation (RSD) and average recovery of this method were also studied. A simple, fast and reliable measuring method for NP and NPnEO (n = 1-11) was established and it is expected to offer helps for related researches.

Experimental

Experimental instruments and reagents

HPLC equipment used was Waters 2695 (Waters, USA), combined with 2487-UV detector and Hypersil APS-2 amino chromatographic column (250 × 4.6 mm, 5 μm, Thermo Electron, USA).

Isopropanol (C_3H_8O), *n*-hexane (C_6H_{14}) and dichloromethane (CH_2Cl_2) were chromatographically pure chemicals from Tianjin Concord, China. Standard reagents of NP and mixed NPnEO (average n ca. 2 and 5) were from Tokyo Chemical Industry Co. LTD, Japan. The standard stock was prepared using isopropanol with NP, mixed P2EO and mixed NP5EO concentrations of 1074, 2140 and 4920 μg mL^{-1}, respectively. During the optimization process, the used mixed standard solution was composed of: 10 times diluent of NP stock, 5 times diluent of NP2EO stock and 2.5 times diluent of NP5EO stock. Finally the NP, mixed NP2EO and mixed NP5EO concentrations were 107.4, 428.0 and 1968 μg mL^{-1}, respectively.

Pretreatment of wastewater samples

The used wastewater samples were the synthetic long chain mixed NPnEO influent and the effluent of the lab-scale AOASP. The wastewater samples were centrifuged for 5 min under 6000 rpm to remove the suspended solids. Then the supernatant was filtrated by a 0.45 μm organic membrane. 50 mL of diluted filtrate (influent for 12.5 times, effluent without dilution) was pipetted into 125 mL separating funnel, then 0.5 mL of 1 mol L^{-1} HCl and 2.5 g NaCl were added, and shaken well. After that, it was added 5 mL of dichloromethane, shaken for 2 min, stood for 20 min, and then the lower organic phase was collected, which was centrifuged at 5000 rpm for 10 min. Afterwards, the centrifuged upper water phase was moved back into the separating funnel, 5 mL of dichloromethane was added, and then the extraction and centrifugation processes were repeated. The centrifuged lower organic phase of two centrifugation processes was filtered to remove the floccules, then the filtrate was evaporated at 40 °C to dryness, the residue was dissolved with isopropanol, made to 2 mL, and filtered by 0.45 μm organic filtration membranes. The pretreated sample was finally achieved. The influent was concentrated for 2 times and the effluent was concentrated for 25 times.

In the Results and Discussion section (Wastewater sample determination sub-section), the recovery experiment is described. A certain concentration of standard solution was added into the influent. This solution was pretreated by the pretreatment method and then measured by the decided HPLC-UV method. The results proved the validation of the pretreatment method.

Chromatographic separation conditions

The mobile phase system, mobile phase ratio and gradient elution procedure, mobile phase flow rate, column temperature, injection volume were optimized in this study. The used HPLC-UV detection wavelength was 277 nm.

The tested mobile phase systems were *n*-hexane:isopropanol, *n*-hexane:dichloromethane and isopropanol (A):n-hexane (B):dichloromethane (C). The optimized process of mobile phase ratio and gradient elution procedure were operated step by step. The detailed process was shown in the Results and Discussion section (Selection of mobile phase ratio and gradient elution procedure sub-section). The tested flow rates were 0.8, 0.9, 1.0, 1.1 and 1.2 mL min^{-1}. The tested column temperatures were 23 (room temperature), 30, 32 and 34 °C. The tested injection volumes were 5, 10, 20 and 25 μL.

Results and Discussion

Selection of mobile phase system

The Hypersil APS-2 amino chromatographic column

used in this study was a normal-phase chemical bonding chromatographic column. In normal-phase chromatography, the elution capacity of mobile phase system increases with the solvent polarity. The appropriate selection of mobile phase system can significantly improve the selectivity of the measured components. In order to obtain suitable solvent strength, a binary or ternary solvent system is normally used as mobile phase. The used solvent can be divided into the based primer and the eluent. In normal-phase chromatography, low polarity solvents such as *n*-hexane, benzene, and chloroform are usually adopted as the based primer and polar solvents, such as ethers, esters, alcohols and ketones, are commonly selected as the eluent. Two binary mobile phase systems (*n*-hexane:isopropanol, *n*-hexane:dichloromethane) and one ternary mobile phase system (isopropanol:*n*-hexane:dichloromethane) were investigated in this study. The separation results of mixed standard solution were shown in Figure 1.

Figure 1a showed that the separation between NP and NP2EO was not clear and was difficult to improve with the changing of mobile phase ratio. NP and adjacent NPnEOs still have not been separated by the *n*-hexane:dichloromethane system in Figure 1b. The long chain NPnEOs mixed together and was difficult to separate. With the isopropanol:*n*-hexane:dichloromethane system, NP and adjacent NPnEOs have been fully

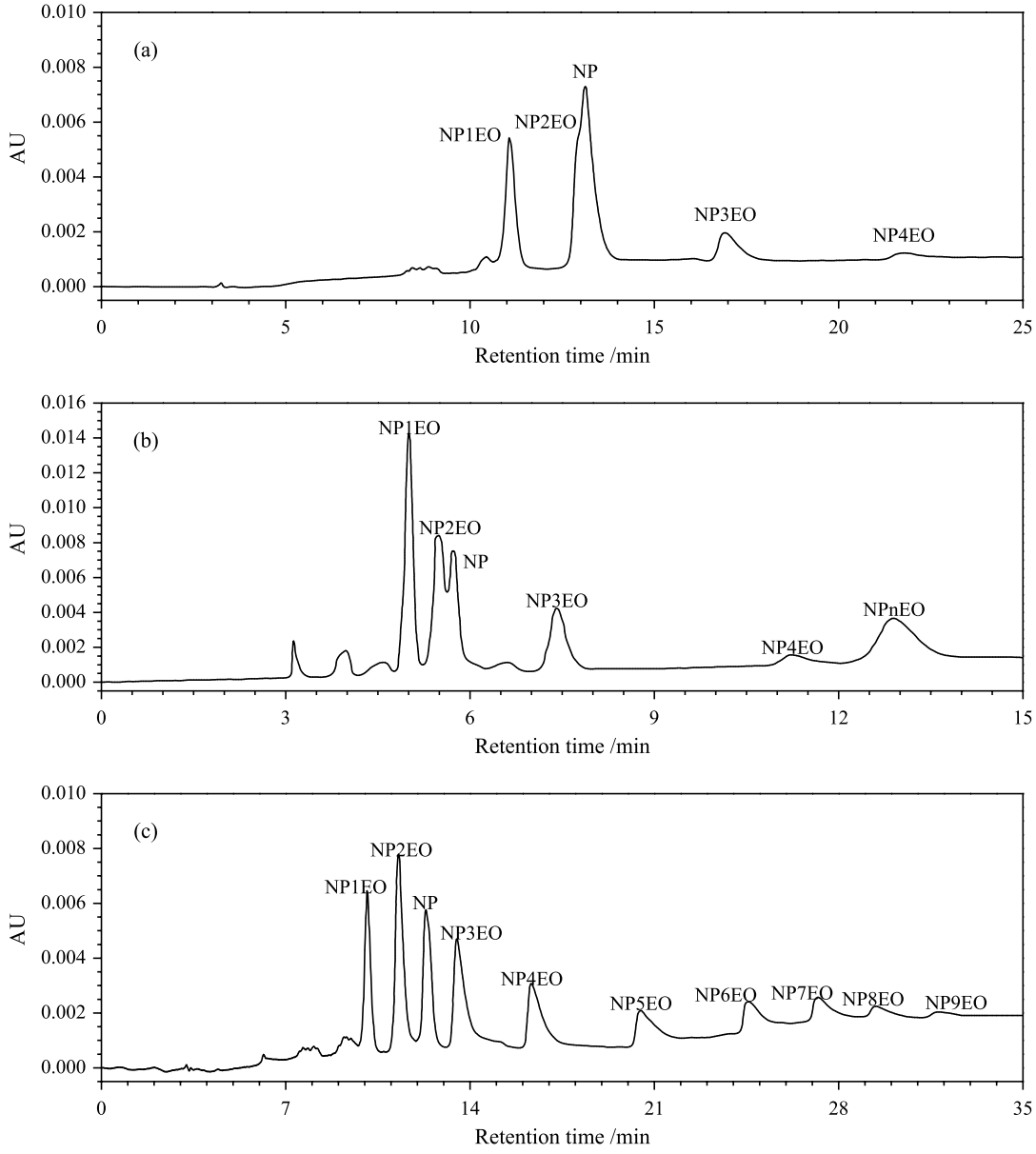

Figure 1. Chromatograms of mixed standard solution with three mobile phase systems: (a) *n*-hexane:isopropanol; (b) *n*-hexane:dichloromethane; (c) isopropanol:*n*-hexane:dichloromethane. The NP, mixed NP2EO and mixed NP5EO in mixed standard solution were 107.4, 428.0 and 1968 μg mL^{-1}, respectively.

separated. Long chain NPnEOs also presented a clear separation and shorter retention time. With the further optimization of chromatographic conditions, it was possible to separate NP and NPnEOs clearly and rapidly. Therefore, the isopropanol:*n*-hexane:dichloromethane ternary system was chosen as the mobile phase system in this study.

Selection of mobile phase ratio and gradient elution procedure

It was found that the small variation of dichloromethane ratio in the isopropanol (A):*n*-hexane (B):dichloromethane (C) system would affect the retention time and the separation degrees between NP and adjacent NPnEOs. Three gradient elution procedures with different dichloromethane ratios (A:B:C linear changed within 30 min: from 1:96:3 to 10:87:3, from 1:95:4 to 10:86:4, from 1:94:5 to 10:85:5) were performed to investigate the separation of NP1EO, NP2EO, NP and NP3EO. Under the dichloromethane ratio of 4% (Figure 2), NP1EO, NP2EO and NP achieved complete separation, while NP and NP3EO showed a little overlap, which could be improved by changing the isopropanol ratio in the gradient elution procedure. The optimal dichloromethane ratio was chosen as 4% and the initial A:B:C used was 1:95:4.

In gradient elution process, the changing rate of strong eluent ratio affects the separation degree of different components. A better separation degree will be achieved under bigger changing rate. Four gradient elution procedures with different isopropanol ratios (initial A:B:C = 1:95:4, linear changed within 14 min under different changing rates of isopropanol ratio: 0.20, 0.25, 0.30, 0.35% min^{-1}, then linear changed to 15:81:4 within 1 min and maintained for 10 min) were conducted. The results showed that all the separation degrees between NP1EO, NP2EO, NP and NP3EO achieved 1.4 under the isopropanol ratio changing rate of 0.25% min^{-1}. The corresponding chromatogram is shown in Figure 3.

According to the separation degree between NP2EO and NP, the long retention time of long chain NPnEOs in Figure 3 and the maximum of n, the following procedures of the three gradient elution were carried out: initial A:B:C = 1:95:4, linear changed to 4.5:91.5:4 within 14 min, in 14-15 min linear changed to 17:79:4, maintained for 7 min, in 22-36 min linear changed to 45:51:4, 59:37:4 or

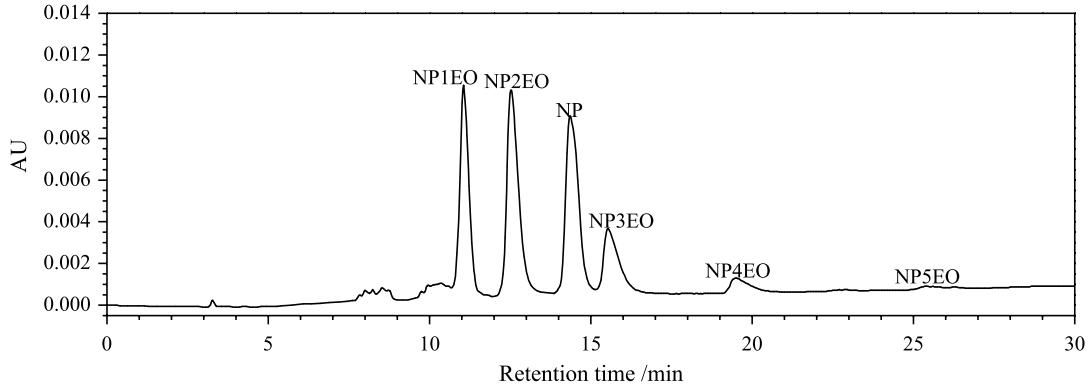

Figure 2. Chromatogram of gradient elution procedure with dichloromethane ratio of 4%. The NP, mixed NP2EO and mixed NP5EO in mixed standard solution were 107.4, 428.0 and 1968 μg mL^{-1}, respectively.

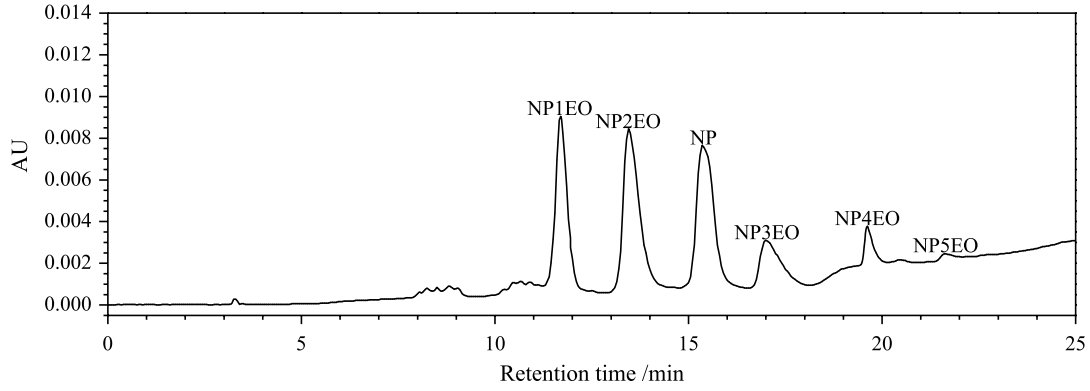

Figure 3. Chromatogram under the isopropanol ratio changing rate of 0.25% min^{-1}. The NP, mixed NP2EO and mixed NP5EO in mixed standard solution were 107.4, 428.0 and 1968 μg mL^{-1}, respectively.

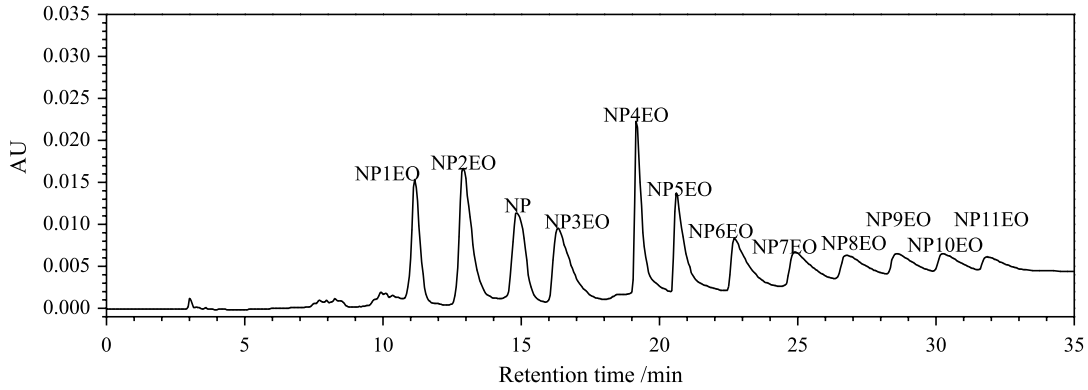

Figure 4. Chromatogram of final gradient elution procedure. The NP, mixed NP2EO and mixed NP5EO in mixed standard solution were 107.4, 428.0 and 1968 μg mL^{-1}, respectively.

73:23:4 and kept for 6 min, in 42-43 min linear changed to 1:95:4, and balanced for 7 min.

The results showed that all the separation degrees of last two procedures were larger than 1.0 and achieved the minimum separation requirement. But the changing rate (to 59:37:4) in 22-36 min presented shorter total retention time. The final gradient elution procedure was obtained successfully. The corresponding chromatogram is shown in Figure 4 and all 12 components were separated within 35 min.

Selection of mobile phase flow rate

Based on the rate theory, the plate height is proportional to the mobile phase flow rate. Low mobile phase flow rate in HPLC can reduce the plate height and thus improve the column efficiency. However, the flow rate should not be too slow due to the broadening of chromatography peak and the increasing of retention time. Five mobile phase flow rates, 0.8, 0.9, 1.0, 1.1 and 1.2 mL min^{-1}, were used to investigate the influence on retention time and theoretical plate number. The results showed that the retention time of these components correspondingly reduced with the increasing of flow rate, but the separation degrees presented no significant differences. The influence of flow rate on theoretical plate number is shown in Figure 5. Most components under flow rate of 0.8-1.0 mL min^{-1} presented high column efficiency. Considering the column efficiency and retention time (analytical speed) together, the optimal mobile phase flow rate was selected as 1.0 mL min^{-1}.

Selection of column temperature

Column temperature has a significant impact on the column performance, mobile phase viscosity and solvent solubility. With the increase in temperature, the mobile phase viscosity will be reduced, therefore, the mass

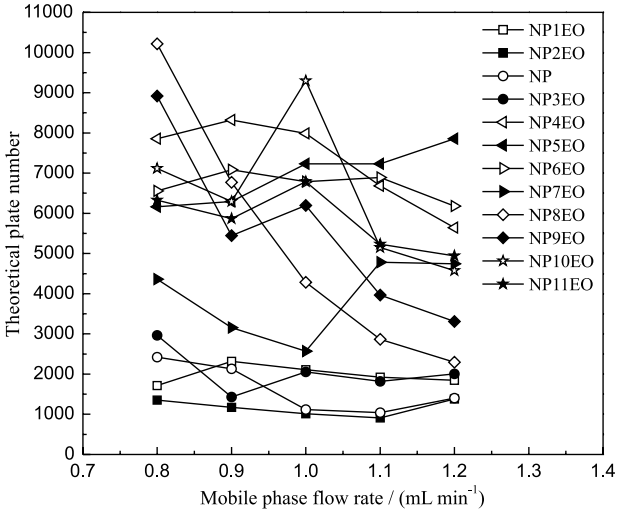

Figure 5. Influence of flow rate on theoretical plate number.

transfer will be improved and the column pressure will be lowered. But high temperature will affect the separation degree between the components and easily produce bubbles in mobile phase. Considering the boiling point of dichloromethane (39.8 °C), four column temperatures at 23 (room temperature), 30, 32 and 34 °C were investigated.

With the increasing of column temperature, the retention time of all components showed a downward trend. And the bigger the n value was, the more obvious the downward trend presented. The influence of column temperature on separation degree was calculated and drawn as in Figure 6. It was found that the separation degrees between 12 components could reach 1.0 or more only under the column temperature of 30 °C. So the optimal column temperature was selected as 30 °C.

Selection of injection volume

The increasing of injection volume can improve sensitivity. But the excessive injection can cause wide

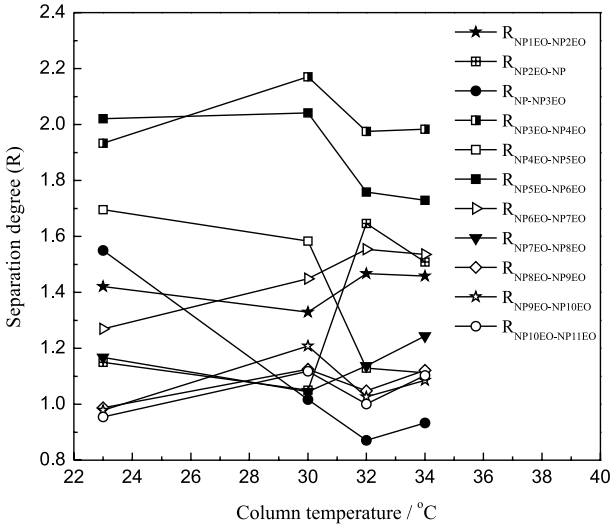

Figure 6. Influence of column temperature on separation degree (R).

peak, tailed peak, even exceeding of column capacity and reduction of column life. Five injection volumes as 5, 10, 15, 20 and 25 μL were investigated in this study. The results showed that the peak area increased linearly with injection volume. But the separation degree of some components decreased below 1.0 with the injection volumes of 20 and 25 μL. Therefore, injection volume of 10 μL was decided by considering the sensitivity and the separation degree.

Chromatogram under optimal conditions and linear regression equations

Under the decided optimal chromatographic conditions (ternary mobile phase of isopropanol:*n*-hexane:dichloro methane with a gradient elution procedure; mobile phase flow rate of 1.0 mL min^{-1}; column temperature of 30 °C; sample injection volume of 10.0 μL; HPLC-UV detection wavelength of 277 nm), the NP and 11 kinds of NPnEO were separated successfully within 35 min as shown in Figure 7. The separation of pure NP, mixed NP2EO and mixed NP5EO were also carried out to confirm the retention time of each component. According to the information (all components of the mixture are NPnEO with continuous n value) from Tokyo Chemical Industry Co. LTD and the principle (the bigger is the n value, the longer is the retention time of NPnEO), the relationship between retention time and the n value in Figure 7 was obtained. The concentration of each component in mixed standard solution was also decided by the area normalization method.

The used mixed standard solution was progressively diluted to 6 kinds of standard solutions (1, 2, 4, 8, 20 and 40 times) with different concentrations. After the chromatographic analysis of these diluted standard solutions, the standard curve of each component was obtained (see Figure 8). The linear regression equations, linear correlation coefficients and linear ranges are shown in Table 1. Except for NP11EO (97.2%), all other linear correlation coefficients achieved 99.9%. The limit of quantification (LOQ) values of the method were coincident with the smallest curve values in Table 1.

The precision experiments were repeated 11 times by measuring a certain concentration standard solution. The results are shown in Tables 2 and 3. Both retention time and peak areas were reproducible and all the RSD values (n = 0-11) obtained were satisfactory (< 5.0%). The stability of the standard solution was also investigated and the results showed that the standard solution could be stable for one week.

Wastewater sample determination

With the decided chromatographic method, the influent and effluent of the AOASP were analyzed. The results in Figure 9 indicated that the NP and NPnEOs in the wastewater samples were separated clearly and proved the effectiveness of this HPLC method. The concentrations

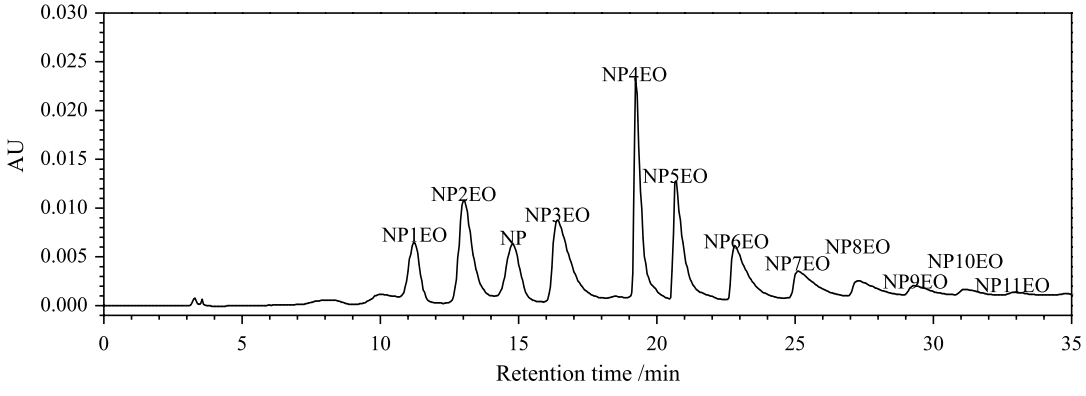

Figure 7. Chromatogram of mixed standard solution under the optimal conditions. The NP, mixed NP2EO and mixed NP5EO in mixed standard solution were 107.4, 428.0 and 1968 μg mL^{-1}, respectively.

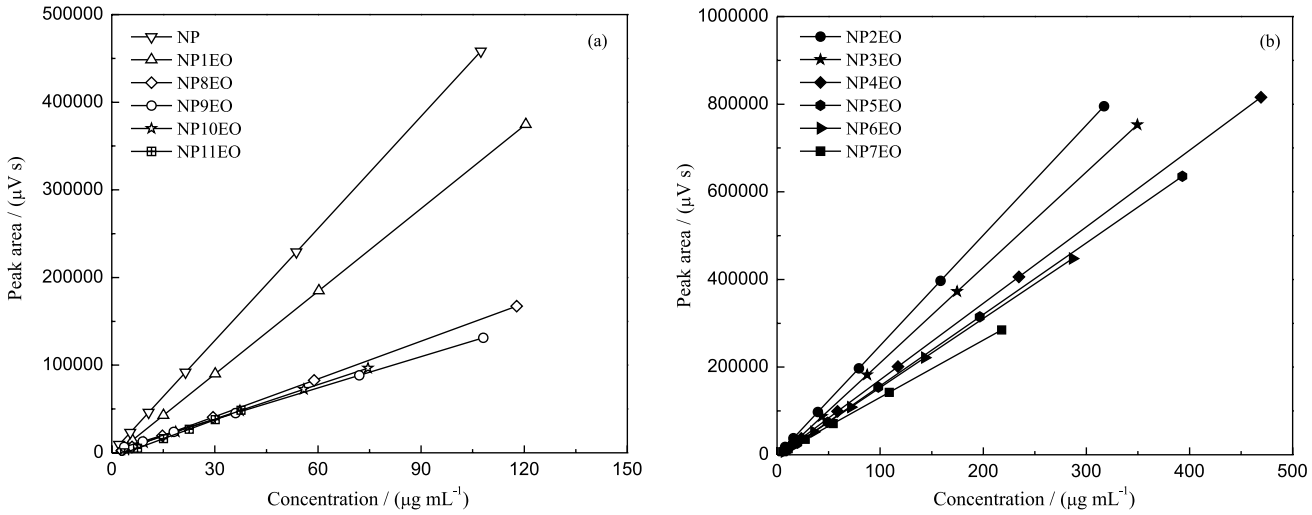

Figure 8. Standard curve of each component: (a) NP, NP1EO, NP8EO, NP9EO, NP10EO and NP11EO; (b) NP2EO, NP3EO, NP4EO, NP5EO, NP6EO and NP7EO.

Table 1. Linear regression equations, linear correlation coefficients and linear ranges

Component	Linear equation	Linear correlation coefficient	Linear range[a] / (μg mL^{-1})
NP1EO	y = 3150x − 4610	0.9995	3-120
NP2EO	y = 2510x − 1970	0.9996	8-320
NP	y = 4260x + 240	0.9998	2-110
NP3EO	y = 2180x − 7760	0.9997	9-350
NP4EO	y = 1750x − 3440	0.9998	12-470
NP5EO	y = 1630x − 5730	0.9998	10-390
NP6EO	y = 1580x − 4460	0.9998	7-290
NP7EO	y = 1310x − 130	0.9999	5-220
NP8EO	y = 1440x − 1820	0.9999	3-120
NP9EO	y = 1190x + 2300	0.9998	4-110
NP10EO	y = 1300x − 290	0.9991	5-70
NP11EO	y = 1440x − 5480	0.9720	4-40

[a]Limit of quantification (LOQ) values of the method were coincident with the smallest curve values of linear range.

Table 2. Results of precision experiments (NP and NP1EO-NP5EO)

No.	Peak area / (μV s)					
	NP1EO	NP2EO	NP	NP3EO	NP4EO	NP5EO
1	18478	83145	10836	15466	41937	46590
2	18383	83218	10607	15224	40555	45158
3	18327	83818	10120	15087	40125	45594
4	18833	82458	11583	15180	40744	45117
5	18558	83407	10743	16068	40519	45269
6	18231	83561	11943	16102	40956	44396
7	18814	84347	11443	15383	41300	45244
8	18903	83742	11368	15787	40375	44863
9	18792	83636	10909	16909	39788	44906
10	18791	82371	11140	16331	40896	45228
11	18722	83682	11294	16281	41120	46546
Average	18621	83399	11090	15802	40756	45356
RSD[a] / %	1.3	0.7	4.6	3.7	1.4	1.5

[a]Relative standard deviation.

Table 3. Results of precision experiments (NP6EO-NP11EO)

No.	Peak area / (μV s)					
	NP6EO	NP7EO	NP8EO	NP9EO	NP10EO	NP11EO
1	105174	73342	43285	25455	11595	3202
2	104254	73775	42640	24874	11761	3325
3	105185	73305	41848	25034	11773	3435
4	103157	73736	41627	24432	11320	3468
5	105798	73352	41921	24647	10924	3514
6	105067	73720	41931	25285	11610	3356
7	105954	73662	40786	24290	11226	3200
8	105151	73586	40703	24929	11595	3537
9	105548	74016	40870	24662	10875	3467
10	106023	74000	41368	25153	10617	3591
11	105783	74223	41547	24359	10469	3734
Average	105190	73701	41684	24829	11251	3439
RSD[a] / %	0.8	0.4	1.9	1.6	4.1	4.7

[a]Relative standard deviation.

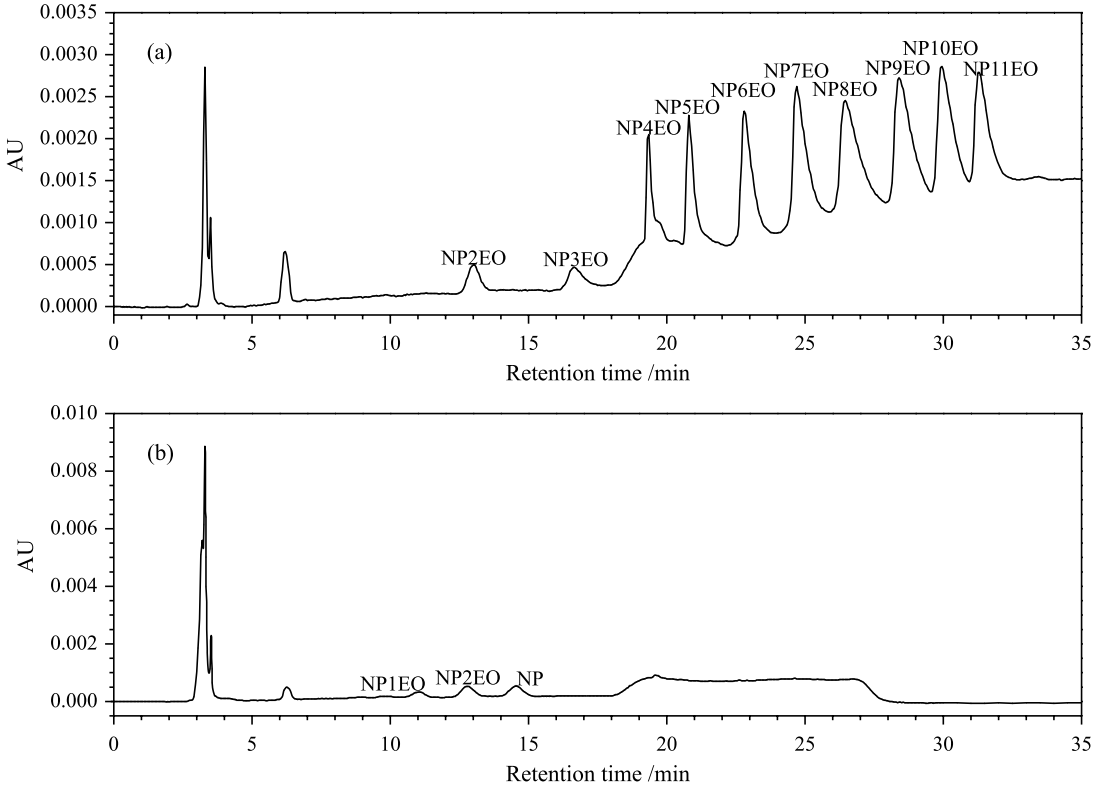

Figure 9. Chromatogram of wastewater samples from AOASP, (a) influent; (b) effluent.

of NP and NPnEO in wastewater samples are shown in Table 4. It also proved the feasibility of AOASP in degrading NPnEOs.

A certain concentration of standard solution was added into the diluted influent to confirm the recovery rates. The detailed recovery rates information is shown in Table 5. The results showed that the average recovery rates of NP and NPnEO (n = 1-11) were 84.4-121.4%, meeting the needs of scientific analysis. It also proved the validation of the pretreatment method for the wastewater samples.

Conclusions

HPLC was selected for simultaneous determination of NP and NPnEO (n = 1-11) in wastewater samples from AOASP. The mobile phase parameters, column temperature

Table 4. Concentrations of NP and NPnEO in wastewater samples

Component	Influent / (μg mL^{-1})	Effluent / (μg mL^{-1})
NP1EO	–	0.192
NP2EO	2.59	0.245
NP	–	0.129
NP3EO	3.62	–
NP4EO	5.14	–
NP5EO	9.86	–
NP6EO	15.40	–
NP7EO	17.02	–
NP8EO	20.85	–
NP9EO	18.46	–
NP10EO	16.50	–
NP11EO	10.78	–

Table 5. Recovery rates of influent

Component	Sample values before adding standard / (μg mL^{-1})	Adding standard / (μg $m^{-1}L$)	Measured values after adding standard / (μg mL^{-1})	Recovery rates / %
NP1EO	–	0.205	0.224	109.1
NP2EO	0.044	2.036	1.761	84.4
NP	–	0.086	0.085	99.8
NP3EO	0.068	3.823	3.644	93.6
NP4EO	0.099	6.092	5.971	96.4
NP5EO	0.192	5.332	5.397	97.6
NP6EO	0.290	3.931	3.989	94.1
NP7EO	0.366	2.988	3.579	107.5
NP8EO	0.389	1.616	1.899	93.4
NP9EO	0.440	0.988	1.618	119.2
NP10EO	0.401	0.511	1.021	121.4
NP11EO	0.337	0.206	0.576	116.0

and sample injection volume were optimized step by step. Under the optimized chromatographic conditions, the NP and 11 kinds of NPnEO were separated and determined successfully within 35 min. The linear correlation coefficients for the standard curves were from 0.9720 to 0.9999 and all the RSD values for precision degree were less than 5.0%. The average recoveries of NP and NPnEO (n = 1-11) for wastewater samples were 84.4-121.4% and achieved the scientific analysis requirement. The fast HPLC analytical method was proven successful and reliable, and could be used for relative NP and NPnEO determination.

Acknowledgments

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