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The determination methods for non-ionic surfactants

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ABSTRACT

A large number of non-ionic surfactants are discharged into water, which cause deterioration of water quality. Non-ionic surfactants have become an indicator of water quality monitoring. This article provides an overview of the classification of non-ionic surfactants, introduces the nature and hazards of fatty alcohol ethoxylates and alkyl phenol ethoxylates, and analyzes determination of non-ionic surfactants. Gas chromatography - mass spectrometry and liquid chromatography - mass spectrometry method are the focuses of the rapid development.

Keywords: Non-ionic surfactants; Fatty alcohol-polyoxyethylene ether (AEOs); Alkylphenol polyethoxylate (APnEO); Nonylphenol polyoxyethylene ether (NPE); Determination

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INTRODUCTION

Nonionic surfactants produce no ions in an aqueous solution. The lipophilic nonionic is substantially the same with ion surfactants, and the hydrophilic group is constituted by a number of oxygen groups (such as hydroxyl group and a polyoxyethylene chain). Nearly 20 years, nonionic surfactants develop rapidly, more and more widely. The number of nonionic surfactants is next to that of anionic surfactants. Nonionic surfactant is an important variety of demanding use. With the development of oil industry and the cost of ethylene oxide reducing, the production of nonionic surfactants will continue to grow. Nonionic surfactant is divided into two types of polyoxyethylene and polyhydric alcohols according to the hydrophilic groups. Polyoxyethylene is the addition reaction product of ethylene oxide and active hydrogen. Polyoxyethylene type is divided into seven categories such as fatty alcohol-polyoxyethylene ether and alkylphenol polyoxyethylene.

THE PROPERTIES AND HARM OF AEO$_S$

Fatty alcohol-polyoxyethylene ether (AEOs, $C_nH_{2n+1}O(OCH_2CH_2)_mH$) are the fastest growing and largest species in nonionic surfactants [1]. In recent years, AEOs develop very rapidly and have partially replaced benzene sulfonate. Foreign researchers predicted that AEOs consumption will continue to grow, and will become the leading household detergents [2-4]. In use, containing AEOs waste water inevitably are discharged into the water, soil and other environments, so that environmental pollution problems have become increasingly serious. When the concentration of AEOs reach 1 mg/L, the water may occur persistent foam, and a lot of persistent foam in water form isolation layer, which weaken the gas exchange of water and the atmosphere, and cause the water stink [5]. The emissions of containing a large number of AEOs wastewater are harmful to the aquatic environment, not only directly kill microorganisms in the environment, and inhibit the degradation of other toxic substances, but also lead to the reduction of dissolved oxygen in water [6-8]. AEOs pollute the water environment, harm aquatic organisms, affect the marine economy and endanger human health. Therefore, it is important to establish the analytical detection method of AEOs.

THE PROPERTIES AND HARM OF APNEO

Alkylphenol polyethoxylate (APnEO) (also known as polyoxyethylene alkyl phenol ether), is one species of non-ionic surfactants in early development, and the world's second-largest commercial non-ionic surfactants. Nonylphenol polyoxyethylene ether (NPE) is the second largest category of non-ionic surfactants, following by the

fatty alcohol ethoxylates. [7]

Nonylphenol is one of 27 priority control persistent toxic pollutants identified by the United Nations Environmental Protection Agency. U.S. Environmental Protection Agency in 1997 rated NP as 70 kinds of environmental endocrine disruptors.

Most substances have no environmental endocrine disruptors itself, but after intermediate environmental degradation or biological treatment by sewage treatment plants, it may produce environmental endocrine disrupting effects. The biodegradation products of NPnEO have both estrogenic activity and mutagenic activity. They increase with the degradation time, the degradation products of estrogenic activity and mutagenic growth [9].

ANALYSIS OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATES STATUS

There is little international research on analysis and detection of NPnEO and AEOs. The main methods for the determination of NP and AEOS are gas chromatography - mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC) [10-12]. In the current literature, GC-MS method accounts for a large proportion. In recent years, HPLC in the separation and determination of NPnEO and AEOs gain rapid development. In addition, UV, IR, NMR spectroscopy and other methods are also used to analyze NPnEO.

Gas Chromatography

Gas chromatography (GC) is generally that hydroiodic acid derives and potassium iodide etherifies and esterifies AEOs samples pretreatment [13-14], and then the products are analyzed by GC. GC is only to analyze polyoxyethylene ethers whose boiling point is less than 350 ^{o}C and EO addition is less than 10. Deng Qigang [15] used capillary GC to separate only octanol ethoxylates (EO addition number 1-9), with some limitations on the number of material separation.

Gas Chromatography - Mass Spectrometry

Gas chromatography - mass spectrometry (GC-MS) method for the determination is the major method which detects environmental interfering-substance in environmental and biological samples. GC has high separation efficiency, and mass spectrometry can provide a wealth of structural information. High sensitivity and selectivity can adapt to a wide variety of environmental endocrine disruptors and the different needs of applications. Most detection of NP is this method, but due to poor NP volatile, generally it requires sample pretreatment, thus extending the analysis time. NPnEO (n>4) is difficult to volatilize, therefore GC-MS analysis is only suitable for of NPnEO (n<3)[16,17]. For high adduct number NPnEO, we usually select trimethylsilyl and trifluoroacetamide as silylation reagents to derive NPO samples, and then they are pretreated by solid phase extraction. Finally, we use GC-MS to detect samples.

Hao Ruixia et al [18] use solid phase extraction GC-MS and DB-XLB capillary column to detect quantitatively total NP isomers in water samples. In spectrum of NP isomers, m/z=107,121,135,149,163 five kinds of ions abundance are high and have strong specificity. These five kinds of ion chromatogram areas are as the quantitative measurement of the integral basis, they accurately reflect the composition of various isomers, but also exclude the interference of background ions. The linear correlation coefficient of calibration curve R is 0.9976~0.9986; relative standard deviation of the sample is 2.5%~11.5%; recovery rate is 92.2%~98.6%. It quantitatively analyses the actual NP content of 0.125~200 g/L in the effluent sample.

Zhou Yiqi et al [19] derive samples by trimethylsilyl trifluoroacetamide to determinate NP in sewage. Three-factor orthogonal experiment is to optimize the sample preparation method; samples are derived after solid phase extraction. Comparison of two methods of deriving and no deriving, the recognition of derivative method can completely separate 11 common NP isomers, the detection limit is 0.55ng/L; the average recovery is 81.1%; and RSD is 1.0%.

Liquid Chromatography - Mass Spectrometry

Liquid Chromatography - Mass Spectrometry (LC-MS) matured increasingly in recent years. The analytes are separated and detected by liquid chromatography, and then confirmed by mass spectrometry, obtaining accurate and reliable test results. There is little literature about AEOS using LC-MS method, while there are much literature about NP and NPEO using LC-MS detection.

Yuan Chunli et al [20] use liquid chromatography - tandem mass quadrupole (LC-MS/MS) technique to separate and detect polyoxyethylene lauryl ether, polyoxyethylene cetyl alcohol ether and eighteen polyoxyethylene ethers substances. Mass resolution and fragmentation patterns are studied under ESI^+ source. Neutral loss, precursor ion scanning and scanning ion mass spectrometry are to verify the mass spectrometry analytical results, and to infer the standard contained 41 kinds of fatty alcohol ethoxylates components. For the first time, it establishes a simple, rapid

separation and identification of mixed alcohols polyoxyethylene ethers of different carbon chains and different addition numbers, providing test basis for environmental water detection. This experiment does not require derivative pre-treatment, and the operation method is simple. The experiment solves the difficulty of separation of high-carbon addition number of fatty alcohol polyoxyethylene ethers substances, and breaks limitations of traditional methods of detecting low carbon addition number.

Zhang Jing et al [21] adopt liquid chromatography - electrospray ionization mass spectrometry to analyse NPnEO and its metabolites in water. The chromatographic column is Waters reversed-phase column, methanol and ammonium acetate solution are as the mobile phase gradient elution. ESI^+ is to analyze NPnEO and ESI^- is to analyze NPEC and NP. M/z scan range is 200~1200 u; the scan cycle is 1 s; ion source temperature is 120 ^oC. This method achieves quantitative detection of each monomer of NPnEO and NPnEC; the detection limit is 1~50 pg; recycling rate is from 75% to 98%; RSD is less than 12%. The results show good separation, and can be completed simultaneously NPnEO metabolite analysis.

Jin Fen et al [22] use GCB solid phase extraction as a purification method, LC-ESI-MS method detects different addition of polymerization NPnEO ($n \geq 3$) in fish. Comparing with conventional alumina method, GCB as solid phase extraction for purifying has a high recovery rate. The recoveries of different addition of polymerization NPnEO are from 70.4% to 120.0% and the method detection limit is 1 ng/g, basically meeting trace analysis. The results of detecting NPnEO in fish body in Beijing and Tianjin rivers show the total concentration of NPnEO is 40 ~ 680 ng/g.

The reliability results of LC-MS are high. However, the price is expensive, and most university laboratories and enterprises do not have the instrument conditions so that the method is limited in practical applications.

High Performance Liquid Chromatography

The principle of liquid chromatography is that light source gives out wavelength range spectrum, passes into the detection cell, and finally reaches to photodiode detector which generates electrical signals by ultraviolet light absorbing groups.

AEOs have no UV absorption above 220 nm, so they are generally difficult to use HPLC-UV detection. For simpler components of AEOs samples, Wang Xiaochun et al [23] use phenyl isocyanate and sulfobenzoic anhydride (SBA) to derive AEOs and make the components of AEOs produce UV absorption at 254 nm.

The volatility of NP and NPnEO are poor. Therefore it is more suitable to use HPLC determination. The reverse phase chromatography generally use C18 or C8 column with a mobile phase of methanol - water or acetonitrile - water. However, due to the same retention behavior of NP, NPnEO, it is difficult to separate completely, and can only measure the total amount of NPnEO. Normal phase chromatography adopts aminosilane column and gradient elution, and separates NPnEO according to ethoxy chain length.

Liu Xin [24] establishes a normal phase chromatographic separation method to detect biodegradable NP and short-chain NPnEO in water samples. We investigate different proportions of ethyl acetate - ethanol as the mobile phase separation of the components. We ultimately determine that the proportion is 5% ethanol, and the flow rate is 1.0 mL/min. The linear correlation coefficient of NP and NPnEO ($n=1\sim3$) are 0.9974~0.9991, relative standard deviation is less than 3.0%, the detection limits of NP and NPnEO are 0.1 mg/L and 0.5 mg/L.

Shao Bing [25] establishes the NPnEO determination of pseudo-reverse phase chromatography using Capcell Pak C18 column and Waters Spherisorb SW3, improving the reproducibility of the experiment and the separation effect. Mobile phase A and B are respectively ultrapure water and acetonitrile in gradient elution. Fluorescence excitation wavelength is 230 nm, and emission wavelength is 305 nm. Combined with graphitized carbon black solid phase extraction techniques, the method can measure simultaneously NPnEO (EO values up to 28) in 30 min, recoveries are over 90%, the detection limits of standard NPnEO samples ($n=1\sim6$) are 10 g/L (S/N=10). The Jialing and Yangtze water samples are measured NPnEO with this method, and the total concentration NPnEO is between 1.99 g/L and 37.28 g/L.

UV - visible spectrophotometry

UV-visible spectrophotometry instrument has the advantage of simplicity, and practical applications are more in the determination. However, this method is vulnerable to be interfered. The pretreatment method is relatively complex, and it can only detect the total concentration, which limits its application.

Qian Jiangang [26] adopts UV spectrophotometric to detect alkylphenol ethoxylates in oil, 275 nm as wavelength of measuring OP-10 can effectively reduce the interference of sodium phosphate and sodium carbonate to oil. The

linear range is 0.1~0.7 g/L. The method is simple, stable, accurate, and suitable for the quantitative analysis of alkylphenol ether nonionic surfactants in oil.

Li Hongzan [27] establishes a direct determination of alkylphenol ethoxylates content in DTY oil by second derivative UV spectroscopy. In test conditions, the slit width is 2 nm, response time is 0.2 s, scan speed is 480 nm/min, and the amplification factor of the horizontal axis is 20 nm/cm. This study selects 282(-) nm and 284(+) nm for the characteristic peaks. Experimental results show that the relationship between difference D and concentration C has well linear in the 25~700 mg/L range; the linear regression equation D=0.027C+0.053; the correlation coefficient R is 0.9997; the relative standard deviation of the sample is less than 1.0% and the recovery is 99.9%~101.7%. The method uses the second derivative spectra to eliminate the influence of coexistent things, and simplify the analysis process.

Other analytical methods

In addition to the above methods, analytical methods of NP and NPEO are Infrared spectroscopy (IR), Nuclear magnetic resonance (NMR), Thin layer chromatography (TLC), polarography, capillary electrophoresis and Enzyme-linked immunosorbent assay (ELISA).

Infrared spectroscopy (IR) is the common identification of compounds and determination of the molecular structure of substances, with simple, rapid method, low sample consumption and informative features. IR spectra of nonylphenol ethoxylates (NP10EO) except for polyoxyethylene characteristic peak, there are the benzene ring vibration of 1609,1580, 1512 cm^{-1} and the counterpoint substitution peaks of 832 cm^{-1}, the strong absorption peaks of 1249 cm^{-1} aryl ethers of C─O─C peak, and 1116 cm^{-1} for EO of C─O─C. It can be used to quantitatively calculate the numbers of EO [28].

Nuclear magnetic resonance (NMR) spectroscopy is widely used in analyzing molecular structure, tracking the chemical reaction mechanism, and detecting qualitatively and quantitatively. NMR is suitable for the determination of nonylphenol ethoxylates HLB value and average molecular weight, with fast simple and reproducible characteristics [29].

Thin Layer Chromatography (TLC) is a fast, trace, easy-separation technology. With the improvement of TLC plates, the method has wide applications in the fields of food, medicine, pesticides, biological and environment, it can be used to analyze the lipophilic groups of alkyl phenol ethoxylates in the non-ionic surfactants, and detect molecular weight distribution of NPnEO homologues and EO number [30].

Polarography is one of electrochemical analysis methods, with high sensitivity, small relative error, fast speed and small amount of sample consumption characteristics. The effect of surfactants to polarographic currents is as the basis of quantitative determination of surfactants.

Capillary electrophoresis uses capillary as separation channel, according to the concentration of each component and the difference of samples distribution on the behavior, with analytical speed, high sensitivity, small sample size, low cost and easy automation features.

Enzyme-linked immunosorbent assay (ELISA) is a quick and easy method for biological detection with high specificity, high sensitivity and analysis speed advantages. ELISA bases on the responses of antigen-specific to determine the body of environmental endocrine disruptors, combining with antigen and the corresponding antibody. When the ratio of antigen and antibody is appropriate, antigen-antibody produces precipitation reaction. ELISA assay has been used for analysis and detection of NP [31].

CONCLUSION

The determination of nonionic surfactants in water has become an important task for water monitoring. UV-visible spectrophotometry method is simple, rapid, but it is complicated to operate, does not apply to large quantities.

Chromatographic determination requires small dosage of samples, can separate complex mixture. However, the operation is troublesome, and analysis time is long. It is necessary to establish a simple, fast, high accuracy, and practical method to detect the nonionic surfactants in the environment.

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