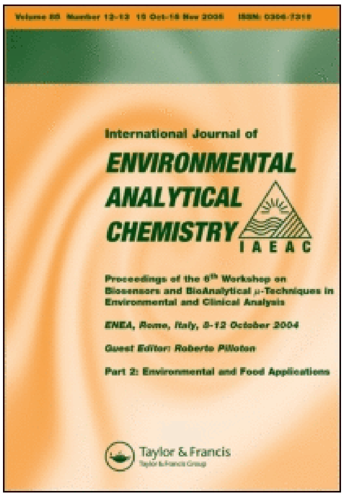

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A novel direct spectrophotometric determination of traces of polyoxyethylene non-ionic surfactant in environmental water using meso-tetra (3,5-dibromo-4-hydrooxylphenyl) porphyrin-Pb (II) complex

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A NOVEL DIRECT SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF POLYOXYETHYLENE NON-IONIC SURFACTANT IN ENVIRONMENTAL WATER USING MESO-TETRA (3,5-DIBROMO-4-HYDROOXYLPHENYL) PORPHYRIN–Pb (II) COMPLEX

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A novel direct spectrophotometric method is developed to determine traces of polyoxyethylene non-ionic surfactants (such as Triton X-100) in environmental water. It is based on the formation of a ternary complex, Meso-tetra (3,5-dibromo-4-hydrooxylphenyl) Porphyrin (T (DBHP) P)–Pb (II)–Triton X-100 in NaOH medium. Under the optimum reaction conditions, T (DBHP) P–Pb (II) complex reacts with Triton X-100 to form a yellow ternary complex immediately. The complex, which has a maximum absorption peak at 479 nm, is stable for at least 24 h. The mean molar absorption coefficient and the limit of detection for Triton X-100 is $1.1 \times 10^4\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ and $0.02\ \mu\mathrm{g\,mL^{-1}}$, respectively. Beer's law is obeyed in the concentration range of $0–0.5\ \mathrm{mg\,mL^{-1}}$ Triton X-100. It is found that all the studied coexisting substances, especially cationic and anionic surfactants, which always seriously interfere in some reported methods, can be tolerated in considerable amounts. The method is used for the direct determination of PE in environmental water and has a good precision and accuracy.

Keywords: Polyoxyethylene; Non-ionic surfactant; Ternary complex; Environmental water; Spectrophotometry

INTRODUCTION

Polyoxyethylene (PE) is a class of non-ionic surfactant (NS) widely used in detergents, emulsifiers, solubilizers, wetting and dispersing agents in household products and industrial chemicals. At present, NS concentrations in environmental waters are higher than those of anionic surfactants (AS) despite the fact that AS are manufactured in greater amounts than NS [1]. This is because the currently used AS, like alkylbenzene sulphonate (ABS), are better biodegraded than the currently used NS, like Triton X-100 [2]. This may result in long-term environmental and ecological affection. Therefore, it is

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necessary to establish a convenient and effective method to measure these in environmental waters for environmental evaluation and control.

In recent decades, much research has been conducted to develop new analytical techniques for the determination of NS. These are mainly chromatographic [3–5], titrimetric [2,6–8] and spectrophotometric methods [9–15]. Although chromatographic methods can give not only the concentration, but also the distribution of the EO numbers of PE, this detailed information is not always necessary. Because different EO numbers of PE have a similar ecological and toxicological behavior, it is convenient to measure NS as a whole for the purpose of environmental evaluation [16]. Titrimetric methods and spectrophotometric methods usually suffered from many interfering substances especially cationic and anionic surfactants, which usually coexist with NS in environmental water. Owing to the low amounts of NS in environmental samples, pre-treatment, such as extraction or concentration, is always a necessary step in those analytical methods, which require lengthy procedures and cause errors. Therefore, a simple direct method for the determination of non-ionic surfactants content is more convenient and precise.

Though non-ionic surfactants have been widely used as enhancers to increase the sensitivity of the determination of metal ions in a large number of color reactions [17], it is difficult to apply this property to direct analysis of their contents due to the poor water solubility of chromogenic reagents and metal complexes. Moreover, the degrees of enhancement caused by non-ionic surfactants were not always significant enough to establish the quantitative relations between the degree of enhancement and the concentration of non-ionic surfactants. However, in our previous research [18], we found that non-ionic surfactants such as Triton X-100 can increase the sensitivity of the spectrophotometric determination of lead remarkably. Both the chromogenic reagent, Meso tetra (3,5-dibromo-4-hydrooxylphenyl) Porphyrin, T (DBHP) P, and the ternary complex, T (DBHP)–Pb (II)–Triton X-100, dissolved in water easily. More importantly, the increase in absorbance was proportional to the concentration of Triton X-100 in a certain range. Therefore, it is quite possible to use this type of color reaction system to establish a simple direct method for spectrophotometric determination of non-ionic surfactants.

Nonylphenol is one of the major PE in common use, so Triton X-100 was used as the reference standard for our method. In this paper, we have carried out a study of optimum reaction conditions for T (DBHP)–Pb (II) complex with Triton X-100. The reaction combining with standard addition spectrophotometry [19] was used for direct determination of PE in environmental water.

EXPERIMENTAL

Apparatus

The absorption spectra were recorded and measured on a Beckman DU-7HS (Beckman Instruments, CA, USA) spectrophotometer with a 1-cm cell.

Reagents

T (DBHP) P Solution

T (DBHP) P was synthesized in our laboratory [18], and 0.4 g L^{-1} T (DBHP) P solution was prepared by dissolving 0.04 g of T (DBHP) P in 100 mL of *N*,*N*-dimethylformamide (DMF).

Standard Lead Solution

The stock solution of lead was prepared according to reference [18], and 150 μg Pb(II) mL^{-1} was prepared by dilution of the stock solution with distilled water.

Solution A

30.0 mL of 1.0 mol L^{-1} NaOH, 20.0 mL of 0.4 g L^{-1} T (DBHP) P, 10 mL of 150 μg Pb (II) mL^{-1} and 50.0 mL of distilled water were successively added into a 250-mL beaker, boiled for 5 min and cooled down to room temperature. Then, 20.0 mL of 5% Na_2SO_3 was added, transferred into a 250-mL calibrated flask and diluted to the mark with distilled water. Solution A was stable for at least 2 months when refrigerated (~ 4°C).

Triton X-100

Triton X-100 was obtained from Sigma (St. Louis, MO, USA). Its aqueous solution with a concentration of 1 mg mL^{-1} in distilled water was prepared.

Other reagents used were of analytical grade, and their solutions were prepared with distilled water.

Analytical Procedure

2.5 mL of solution A and 2.0 mL of 1 mg mL^{-1} Triton X-100 were transferred into a 25-mL calibrated flask, and water samples (containing no more than 0.5 mg mL^{-1} PE) were then added and diluted to the mark with distilled water. The absorption spectra were recorded or the absorbance was measured at 479 nm against a reagent blank (2.5 mL of solution A and 2.0 mL of 1 mg mL^{-1} Triton X-100) in a 1-cm cell.

RESULTS AND DISCUSSION

Effect of Reaction Media

Our previous work [18] studied the influence of the pH and medium on the absorbance of the T (DBHP)–Pb (II). It was found that the complex absorbance remained almost constant and at a maximum in borax buffer solution ($Na_2B_4O_7$–NaOH, $pH > 9$) or in NaOH ($pH > 9$). In this work, Borax buffer solution and NaOH were also chosen as the reaction media. The results showed that under certain conditions, the complex absorbance was almost at a maximum and unchangeable in both media. However, anionic surfactants had a higher permissible tolerance in NaOH solution than that in borax buffer solution. As various surfactants always coexisted in wastewater, selectivity is very important in a real-samples analysis. Therefore, we carried out the color reaction in NaOH solution in the following work to keep the reaction reproducible, sensitive and selective.

Effect of Temperature

The effect of temperature on the velocity of formation of both T (DBHP) P–Pb (II) complex and the ternary complex, T (DBHP) P–Pb (II)–Triton X-100 was studied.

It was found that when the temperature was below 15°C, T (DBHP) P–Pb (II) complex formed slowly; when the temperature was over 15°C, the complex could be formed completely and immediately. For the convenience of the analytical procedure, we first synthesized T (DBHP) P–Pb (II) complex (solution A) in a boiling bath, then deposited it in an icebox. Experiments indicated that solution A was stable for at least 2 months when refrigerated to 4°C. Solution A and non-ionic surfactants can carry out the reaction at any temperature, and thus a yellow ternary complex was immediately formed, which remained stable for at least 24 h in room temperature. Thus, we can easily carry out the chromogenic reaction at normal temperature.

Effect of Amounts of Triton X-100 on the Ternary Complex Formation

Though Triton X-100 is the best sensitizing agent to increase the absorption of the complex T (DBHP)–Pb (II) [18], the very low concentration of Triton X-100 (less than its CMC, 0.002 w/v% [20], e.g. 0.02 mg mL^{-1}) has no effect on the absorption. Experimental results show that only when the volume of Triton X-100 reaches 1 mL (about 0.04 mg mL^{-1} in a 25-mL calibrated flask) does the absorption of the complex begin to increase clearly. Moreover, with increasing concentration of Triton X-100, not only does the absorption of the ternary complex increase, but the wavelength of maximum absorption of the ternary complex also changes from 460 to 479 nm, as shown in Fig. 1.

Figure 1 shows that the concentration of Triton X-100 influences both the absorbance and the wavelength of maximum absorption of the ternary complex. This may be because of the complicated formation and the stability of the ternary complex. When the concentration of Triton X-100 is below its CMC, the ternary complex may be formed incompletely or be unstable. When the concentration of Triton X-100 is above its CMC, the stability of the ternary complex increases. According to the changes in the wavelength of maximum absorption of the ternary complex, we can see that the stability of the product increases along with the increase in the concentration of Triton X-100. Only when the volume of Triton X-100 reaches 1.5 mL (about 0.06 mg mL^{-1} in a 25-mL calibrated flask) does the wavelength of maximum absorption of the ternary

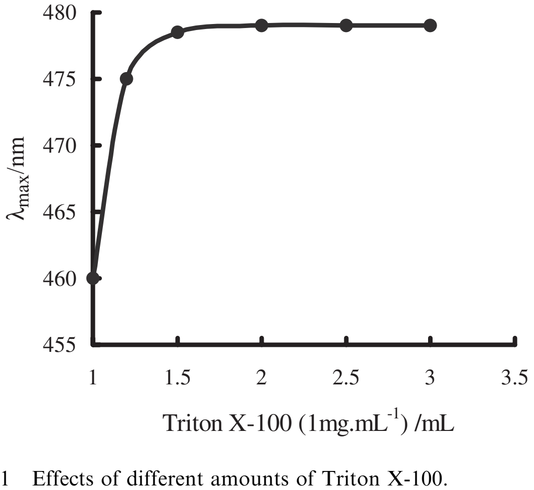

FIGURE 1 Effects of different amounts of Triton X-100.

complex remain unchangeable. Considering the analytical accuracy, repeatability and operation convenience, it is very important to keep the wavelength of maximum absorption of the ternary complex unchangeable. Therefore, it is necessary to transfer 2.0 mL of 1 mg mL^{-1} Triton X-100 into a 25-mL calibrated flask before the addition of environmental water sample.

Effect of Amounts of Solution A

Under the conditions employed, the volume of solution A is required to obtain a maximum and constant absorbance for the ternary complex. Studies have shown that the absorbance increases rapidly with the increase in volume of solution A up to 2.0 mL and remains almost constant at a maximum before dropping slowly when the volume of solution A exceeds 3.0 mL. Thus, the recommended volume of solution A is 2.5 mL.

Absorption Spectra

Figure 2 shows the absorption spectra of T (DBHP) P, T (DBHP)–Pb (II) and T (DBHP)–Pb (II)–Triton X-100. It can be seen that the maximum absorption of T (DBHP) P and T (DBHP)–Pb (II)–Triton X-100 is at 430 and 479 nm, respectively. The wavelength difference between T (DBHP) P and T (DBHP) P–Pb (II)–Triton X-100 is 49 nm. Figure 2 also shows clearly that the presence of Triton X-100 greatly increases the absorption of T (DBHP)–Pb (II) at 479 nm. This rapidly increasing absorbance at 479 nm is due to the formation of the ternary complex, T (DBHP) P–Pb (II)–Triton X-100. Therefore, the absorbance was measured at 479 nm in all the experiments.

Composition and Stability of the Complex

The composition of the ternary complex was evaluated with changing concentrations of individual components using the methods of continuous variations and molar ratios.

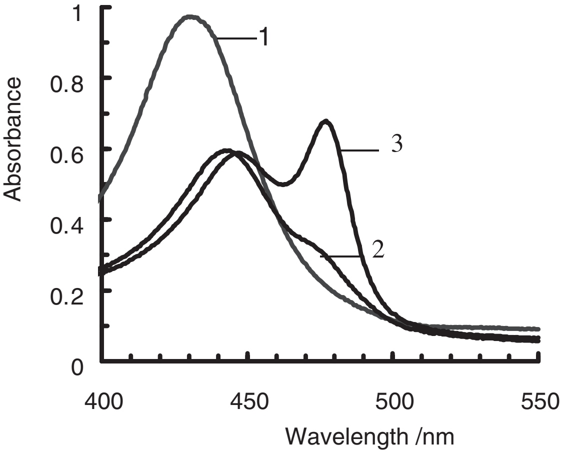

FIGURE 2 Absorption spectra of reagent and complexes against water: 1 – T (DBHP) P; 2 – T (DBHP) P–Pb; 3 – T (DBHP) P–Pb–Triton X-100.

Both showed that a molar ratio of the ternary complex in the solution with T (DBHP) P : Pb (II) : Triton X-100 equals 2 : 1 : 2.

Under the experimental conditions, the ternary complex formed immediately and remained stable for at least 24 h at room temperature.

Method Characterization

According to the analytical procedure, a calibration graph of the absorbance of the ternary complex against Triton X-100 was constructed by introducing various amounts of Triton X-100 into a 25-mL calibrated flask (Fig. 3). From Fig. 3, we found that the concentration of Triton X-100 was linear in the range of 0–0.5 mg mL^{-1}. The mean molar absorptivity of the ternary complex was calculated from the slope of the calibration graph to be 1.1×10^4 L mol^{-1} cm^{-1}. Ten-replication analyses of a test solution containing 0.1 mg mL^{-1} of Triton X-100 using the analytical procedure gave a mean of 0.101 mg mL^{-1} Triton X-100 with a relative standard deviation of 1.6%. Standard deviations calculated from multiple measurements were used to estimate the limit of detection (LOD), set equal to $3S_0$, where S_0 is the standard deviation of the analyte concentration at zero concentration [21]. The LOD for Triton X-100 was 0.02 μg mL^{-1}.

Further studies indicated that other polyoxyethylene NS (such as AEO_9), which have similar physical and chemical properties to Triton X-100, also increase the absorption of T (DBHP) P–Pb (II) complex. However, the sensitivity of AEO_9, with a mean molar absorptivity of 1.4×10^3 L mol^{-1} cm^{-1}, is much lower than that of Triton X-100.

Effect of Interfering Substances

Under the optimum conditions, the effects of various foreign substances on the determination of a solution containing 0.1 mg of Triton X-100 were examined separately, with a relative error of less than ±5%. The tolerance limits of various foreign substances are listed in Table I. It should be noted that commonly used cationic and anionic surfactants (SDS, SDBS, SS, CTAB and CPC), which have always been

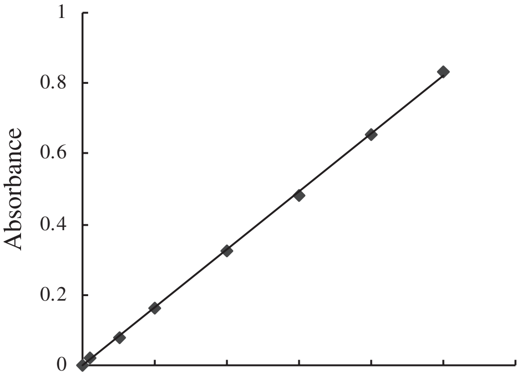

FIGURE 3 Calibration graph for Triton X-100.

TABLE I Effects of foreign substances

Foreign ion	*Tolerated limit* (mg)	*Foreign ion*	*Tolerated limit* (mg)
Cl^-	50	Fe^{3+}	15
I^-	40	Cu^{2+}	20
CO_3^{2-}	50	Zn^{2+}	20
SO_4^{2-}	50	SDS[a]	25
PO_4^{3-}	50	SDBS[b]	25
$C_2O_4^{2-}$	50	SS[c]	25
NH_4^+	100	CTAB[d]	15
Na^+	100	CPC[e]	15
K^+	100	Humic acid	30
Mg^{2+}	30	Acetic acid	30
Ca^{2+}	30	Alcohol	25
Al^{3+}	15	Glycerol	25

[a]SDS: sodium dodecylsulfate; [b]SDBS: sodium dodecylbenzenesulfonate; [c]SS: sodium stearate; [d]CTAB: cetyltrimetylammonium bromide; [e]CPC: cetylpyridinium chloride.

TABLE II Analytical results of PE[a] in environmental water samples ($n = 3$)

Water samples	*Founded* ($mg\,L^{-1}$)			*Average* ($mg\,L^{-1}$)
	1	2	3	
Municipal sewage	4.16	4.50	4.24	4.30
River water	0.84	0.94	0.96	0.91
#1 Tai Lake water	0.34	0.29	0.38	0.34
#2 Tai Lake water	0.11	0.15	0.14	0.13

[a]PE: Triton X-100.

TABLE III Recovery of water samples

Water samples	*Background* (μg)	*Spiked* (μg)	*Found* (μg)	*Recovery* (%)
Municipal sewage	107.5	50	165.1	104.8
River water	22.8	50	73.5	101.0
#1 Tai Lake water	8.5	50	56.8	97.1
#2 Tai Lake water	3.3	50	53.6	100.6

found to interfere in other reported spectrophotometric methods, could be tolerated in considerable amounts in this proposed method. Therefore, it is much more convenient to directly determine the concentration of PE in real samples without any prior separations or extractions, and this will greatly increase the precision and the accuracy of the analysis results.

Application

The proposed method was used to determine the amount of PE in environmental water. All samples were preserved with 1% formalin and refrigerated when received [22]. Prior to analysis, the samples were filtered to remove small solid particles. Then, the analytical procedure was carried out to determine the concentration of PE. The analytical results of PE in environmental water samples and the recovery of water samples are listed in Tables II and III, respectively.

CONCLUSIONS

Table IV compares the proposed method and several spectrophotometric methods for the determination of non-ionic surfactants. From Table IV and the experiment results, we can see that the suggested method in this paper has several advantages over other reported spectrophotometric methods.

1. The proposed method is very simple and rapid. Unlike other reported spectrophotometric methods, it does not need any prior separation or extraction. Moreover, the method also has a much wider range of linear concentration than that of any other reported methods, so it is very convenient for directly determining the concentration of PE in environmental water.
2. The proposed method has a high degree of selectivity. All the studied foreign substances, especially cationic and anionic surfactants, which always interfere with the determination of PE in some reported methods, can be tolerated in considerable amounts in the proposed method. Thus, it is much better than other reported spectrophotometric methods.
3. The proposed method is sensitive. The analytical method that we developed combined the color reaction with standard addition spectrophotometry [19]. Thus, the method developed here not only precludes any effects of PE on the maximum absorption wavelength of the ternary complex but also ensures a high degree of accuracy. Moreover, it can determine the micro-quantities of PE in environmental waters sensitively and precisely. The molar absorption coefficient value is

TABLE IV Comparison of various spectrophotometric methods for the determination of non-ionic surfactants

Metal cation	*Extractant*	λ (nm)	*Beer's law range*	*Remarks*	*Ref.*
Sodium picrate	1,2-Dichloroethane	378	$0.1–1.0\,\mathrm{mg\,L^{-1}}$	Anionic surfactants interfere; cationic surfactants seriously interfere	[9]
Picric-K	1,2-Dichloroethane	378	$0.1–1.0\,\mathrm{mg\,L^{-1}}$	Anionic surfactants interfere; cationic surfactants seriously interfere	[10]
Picric-K	1,2-Dichloroethane	378	$0.01–1.0\,\mathrm{mg\,L^{-1}}$	Anionic surfactants interfere; cationic surfactants seriously interfere	[11]
Ammonium tetraisothiocyanato-cobaltate (II)	Chloroform	500	$0.3–2.0\,\mathrm{g\,L^{-1}}$	Not reported	[12]
Sodium picrate	1,2-Dichloroethane	378	$0–0.70\,\mathrm{mg\,L^{-1}}$	Quarternary ammonium surfactants and Fe (III) interfere	[13]
TBPE-K[a]	1,2-Dichloroethane	609	$2–60\,\mathrm{mg\,L^{-1}}$	Not reported	[14]
Not needed	Not needed	479	$0–0.5\,\mathrm{mg\,mL^{-1}}$	Anionic and cationic surfactants are tolerated in considerable amounts	This method

[a] TBPE-K: tetrabromophenolphthalein ethyl ester potassium.

$1.1 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ for PE (expressed as Triton X-100). Quantities of PE as little as $0.02\,\mu\mathrm{g\,mL^{-1}}$ can be detected.

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