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Determination of cationic surfactants in water samples by their enhanced resonance light scattering with azoviolet

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Abstract A simple assay of cationic surfactants in water samples was developed based on the measurements of enhanced resonance light scattering (RLS). At pH 6.09 and ionic strength 0.03 M, the interactions of azoviolet (AV) with cationic surfactants, including zephiramine (Zeph) and cetyl trimethyl ammonium bromide (CTMAB), result in enhanced RLS signals characterized by the peaks of 470.0, 485.0 and 495.0 nm. The enhanced RLS intensity is proportional to the concentration of cationic surfactant of Zeph in the range of $0.2\sim 6.0\times 10^{-6}$ M, and to that of CTMAB in the range of $0.4\sim 4.8\times 10^{-6}$ M. The limit of determination (3σ) is 2.1×10^{-8} M and 3.8×10^{-8} M for the two surfactants, respectively. Determinations of cationic surfactants in synthetic and tap water samples were successfully made with a recovery of 90.5~108.6%.

Keywords Resonance light scattering (RLS) · Cationic surfactants · Azoviolet (AV) · Zephiramine (Zeph) · Cetyl trimethyl ammonium bromide (CTMAB)

Introduction

The special structure and properties of surfactants make them play important roles in the fields of life, industry and agriculture. It is meaningful to propose novel assays of surfactants in environmental samples, and to study the diversion and the movement under certain environmental conditions and in physiological progress [1, 2]. Spectrophotometric methods are commonly used for their quantitative analysis and environmental assessment, since these methods are simple and reproducible [3, 4, 5], although they are not sensitive. Thus, it is necessary to propose more sensitive assays. Liu et al. [6] proposed a method for

the determination of cationic surfactants based on second-order scattering. Herein, we report a resonance light scattering (RLS) method based on the measurements of enhanced RLS signals by using a common spectrofluorometer. The RLS technique has proved to be very simple and sensitive and can be widely applied to the determination of trace amounts of metal ions [7, 8] and biomacromolecules [9, 10, 11].

Light scattering originates from the fluctuation of the refractive index of a solution [12, 13]. The refractive index can be divided into a real and imaginary part [14], which are related to the molecular absorption [15]. The refractive index is related to the Rayleigh ratio, which characterizes the intensity of the light scattering of the system [16]

$$R(90^\circ) = \frac{4000\pi^2 n^2 c}{\lambda_0^4 N_A} \left[\left(\frac{\partial n}{\partial c} \right)^2 + \left(\frac{\partial k}{\partial c} \right)^2 \right] C_v \quad (a)$$

in which $R(90^\circ)$ is the Rayleigh ratio for 90° detection, N_A is the Avogadro constant, n is the refractive index of medium, λ is the wavelength of incident light, c is the molarity of scattering particle, $\partial n/\partial c$ and $\partial k/\partial c$ are, respectively, the increments (per 1 M solution concentration) in the real part and the imaginary part of the refractive and C_v is the Cabannes factor which accounts for the enhancement of the intensity of the light-scattering. For molecular particles with a size 20-fold smaller than the wavelength of the incident beam in a transparent isotropic medium, the Rayleigh scattering law is obeyed, since the imaginary part of the refractive index originating from molecular absorption can be neglected [14]. However, if the wavelength of the incident beam is close to the absorption band of the molecular particles, the refractive index varies steeply and the contributions to the scattered light from both the real and imaginary parts should be considered. For a medium in which molecular aggregates exist, the contribution of the imaginary part of the index to light scattering is very significant, and enhanced RLS can be expected in absorption medium. The enhanced RLS signals in an aggregation medium can even be detected by using a common spectrofluorometer [6, 7, 8, 9, 10, 11, 12, 13].

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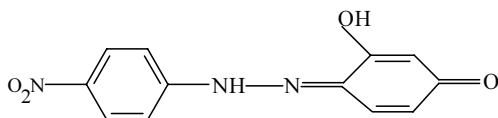


Fig. 1 The molecular structure of azoviolet (AV)

Azoviolet (AV), whose molecular structure is displayed in Fig. 1) is commonly used to determine magnesium. It has proved that cationic surfactants including zephiramine (Zeph) and cetyl trimethyl ammonium bromide (CTMAB) exist as single molecules and micelles when their concentrations are lower than the value of critical micelle concentration (cmc), and can interact with AV to form ion associates [5]. We found that the formed ion associates have strong RLS signals, and with these signals the two surfactants can be determined with the limits of determination of 10^{-8} M quantities.

Experimental

Apparatus and reagents

The RLS spectra and the intensities were recorded and measured with a Shimadzu RF-540 spectrofluorometer (Kyoto, Japan) by keeping the incident beam and the scattering light at 90° . Absorption spectra were obtained by using a Techcomp UV-8500 spectrophotometer (Hong Kong, China), and an MVS-1 vortex mixer (Beide Scientific Instrumental Ltd, Beijing, China) was used to blend the solutions in volumetric flasks.

The stock solution of azoviolet (AV) was prepared by dissolving the commercial crystal (The Third Chemical Reagent Plant of Shanghai, China) into 2–3 mL 0.2 M NaOH solution, and then diluted to 500 mL with doubly distilled water. The concentration of the reagents in the working solution was 1.0×10^{-4} M.

Both zephiramine (Zeph) and cetyl trimethyl ammonium bromide (CTMAB) were prepared by directly dissolving the crystal products (both purchased from Merck, Germany) in doubly distilled water. The concentration of working solution was 2.0×10^{-5} M.

Britton-Robinson (BR) buffer solution (pH 6.09, composed of 0.028 M H_3PO_4 , 0.028 M HAC, 0.028 M H_3BO_3 and 0.06 M NaOH) was prepared according to a literature method [17] and used to control the acidity. A 0.5 M NaCl solution was used to adjust the ionic strength of the aqueous solution. All reagents were of analytical grade and used without further purification. Water was doubly distilled.

Samples

The contents of Zeph and CTMAB in synthetic water samples and tap water samples were determined according to procedures described below. Thus, synthetic water samples were made according to the tolerance level of foreign materials. Tap water samples were determined directly.

General procedures

The appropriate working solution of cationic surfactant or sample solution of cationic surfactant, 0.4 mL NaCl solution and 1.0 mL AV solution were added to a 10 mL volumetric flask. This mixture was vortexed and 1.0 mL of buffer solution was added. The mixture was then diluted with doubly distilled water to 10 mL and thoroughly mixed. This mixture was used for absorption or RLS measurements.

The RLS spectra were scanned throughout by keeping the excitation and emission monochromators of the RF-540 spectrofluorometer with $\Delta\lambda=0$ nm. The RLS intensity was measured at 470.0 nm.

Results and discussion

Features of the RLS spectra

Lines 1 and 2 in Fig. 2 show the RLS spectral features of Zeph and AV, respectively. It can be seen that the RLS signals of AV are stronger than that of Zeph over the whole scanning region. However, both the RLS signals of Zeph and AV are weaker than that of their mixtures in the wavelength range 250–700 nm (lines 3–5). We found that the RLS signals of the mixture increase with increasing Zeph concentration. Namely, the RLS signals of AV can be enhanced by the presence of Zeph. We have proved that Zeph has rather weak RLS signals even if its concentration is higher than 4.0×10^{-5} M, so the enhanced RLS signals resulting from the mixture of Zeph and AV indicate that an interaction between Zeph and AV has occurred. By comparing the RLS spectra of AV itself with its mixture with Zeph, it can be seen that they have the same RLS spectra features, except for different RLS intensities (lines 2–5 in Fig. 2). All lines from 2 to 5 have three peaks at 470.0, 485.0 and 495.0 nm.

According to Pasternack et al. [12, 13], these enhanced RLS spectra are associated with the formed complex and the absorption features of the interacting system. Therefore, we should consider the absorption features of the interacting systems. As shown in Fig. 3, with increasing Zeph concentration, the characteristic absorption is reduced, displaying a hypochromic effect without wavelength shift. The hypochromic effect is good evidence to support an interaction between Zeph and AV. In our tested pH medium, AV is negatively charged, and the positive Zeph interacts with AV through electrostatic attractions producing AV-

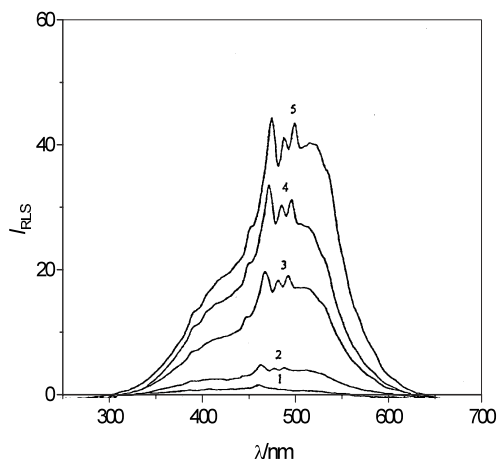


Fig. 2 RLS spectra of the interaction AV with Zeph. Line 1 Zeph, line 2 AV, lines 3–5 AV-Zeph. Concentrations: Zeph ($\times 10^{-6}$ M): 1 40.0, 2 0.0, 3 2.0, 4 4.0, 5 6.0. AV (except for line 1 in which no AV was added): 1.0×10^{-5} M. pH 6.09, ionic strength 0.03 M

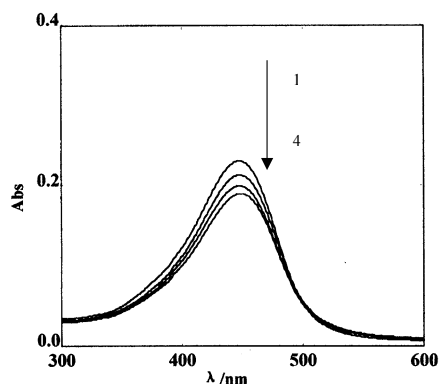


Fig. 3 Absorption spectra of the interaction of AV and Zeph. Line 1 AV, line 2 AV and Zeph. Concentrations: Zeph ($\times 10^{-6}$ M): 1 0.0, 2 2.0, 3 4.0, 4 6.0. AV: 1.0×10^{-5} M. pH 6.09, ionic strength 0.03 M

Zeph complexes that are large particles. Therefore, the hypochromic effect and enhanced RLS signals are clearly observed. Similar phenomenon are also found for the interaction of CTMAB with AV.

Optimal conditions for the interaction

We found that the RLS signals of AV and the RLS signals produced by the mixture of AV and Zeph are influenced by the pH value of the aqueous medium. As shown in Fig. 4, the RLS signals of AV are very strong in the acidic medium, but decrease with increasing pH of the medium. We can prove that the strong RLS signals of AV in acidic medium result from its aggregation. As shown in Fig. 5, with decreasing pH value of the medium, the absorption of AV decreases, displaying a wide absorption band. When the pH value is lower than 4.78, a significant bathochromic shift can be observed (Fig. 5). This wide absorption band can be assigned to the aggregation of AV in acidic medium [9]. AV is protonated in acidic medium (we found that

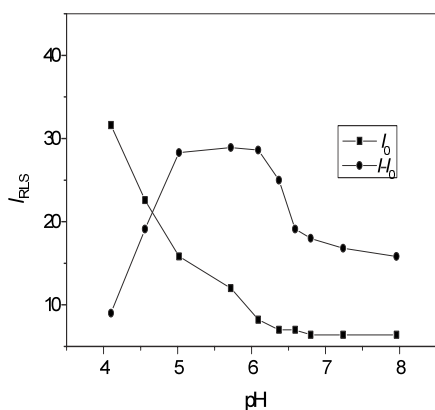


Fig. 4 Dependence of the RLS intensity on pH. Concentrations: AV: 1.0×10^{-5} M; Zeph: 4.0×10^{-6} M. Ionic strength was kept to 0.03 M by adding 0.5 M NaCl solution, $\lambda=470.0$ nm. A mixture of AV with a buffer was used as the blank solution

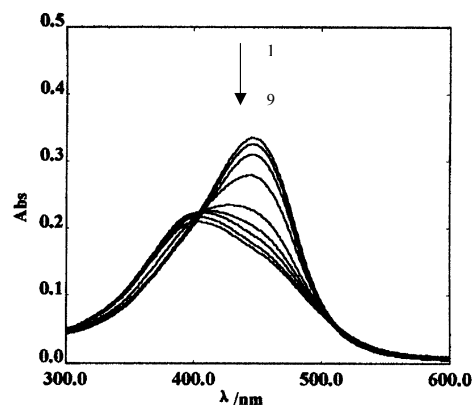


Fig. 5 Absorption spectra of AV in acid medium. pH: 1 7.24, 2 6.59, 3 6.09, 4 5.33, 5 4.78, 6 4.35, 7 3.78, 8 2.87, 9 2.36. Concentrations: AV: 1.0×10^{-5} M. Ionic strength was kept to 0.03 M by adding 0.5 M NaCl solution

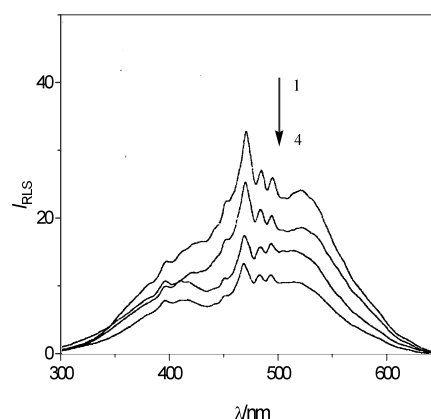


Fig. 6 RLS spectra of the AV in acidic medium. pH: 1 1.98, 2 2.21, 3 4.10, 4 5.72. Concentrations: AV: 1.0×10^{-5} M. Ionic strength was kept at 0.03 M by adding 0.5 M NaCl solution

$pK_a=5.19$ at 25°C with an ionic strength 0.03 M) and can form aggregate species of large particles [18]. As shown in Fig. 6, these aggregate species have strong RLS signals, which are identical to other reports concerning the aggregate species of dyes that have strong RLS signals [12, 13]. According to Fig. 4, the aggregate species of AV exist in the acidic medium, but disassociate in high pH medium.

Figure 6 shows that the RLS signals of AV in acidic medium have the same shape as that of the Zeph-AV interaction (Fig. 2); thus, the interaction of Zeph-AV is very similar to the aggregation of AV. In the same way, the similarity of hypochromic phenomenon of the absorption spectra in Fig. 3 and Fig. 5 supports the interaction mechanism of AV with Zeph. That is to say, the ion associate of Zeph-AV has strong RLS signals. Figure 4 shows that the enhanced RLS signals ($\Delta I_{\text{RLS}}=I-I_0$) are constant in the pH range of 5.02~6.09. Considering that the RLS value of the AV-buffer blank is weakest when the pH is 6.09, we controlled the pH value of the aqueous medium to be 6.09 with 1.0 mL BR buffer in this study.

Since the AV-Zeph ion association forms through electrostatic attractions, it is undoubtedly that the ionic strength

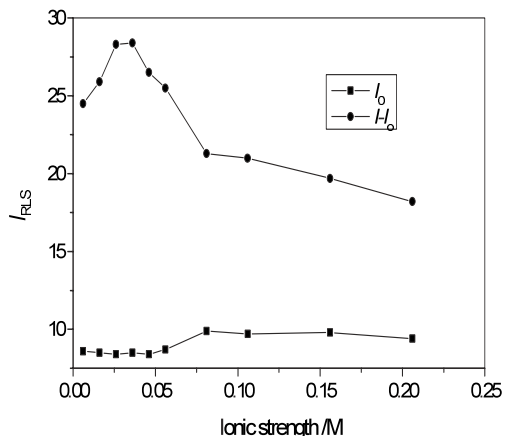


Fig. 7 Dependence of the RLS intensity on the ionic strength. Concentrations: AV: 1.0×10^{-5} M; Zeph: 4.0×10^{-6} M. $\lambda=470.0$ nm, pH 6.09. The blank solution was made of a mixture of AV with a buffer

of the aqueous medium has significant effects on the interaction of AV with Zeph. As shown in Fig. 7, for an ionic strength of 0.026–0.036 M, the enhanced RLS intensity (ΔI_{RLS}) is the strongest. For an ionic strength lower than 0.026 M, the ΔI_{RLS} increases with increasing ionic strength. For an ionic strength over 0.036, the ΔI_{RLS} decreases with increasing ionic strength. This is due to the shielding effect of the charges that make the electrostatic interaction between AV and Zeph decrease, and the opportunity to form ionic associate decrease accordingly. In our experiment, additional 0.5 M NaCl solution should be added to keep the ionic strength of the whole interaction system at 0.03 M.

In addition, we found that the enhanced RLS signals were greatly influenced by the addition order of reagents. If Zeph was mixed at first with AV, the enhanced RLS signals are the strongest. These data are available at room temperature after the final dilution and can be stable more than 2 h.

Tolerance of foreign substances on the determination of Zeph

Premixing Zeph with the interference substances tested the effects of foreign substances, including metal ions and surfactants on the determination methods. Table 1 shows that the commonly observed metal ions in waters such as K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ can be tolerated at high concentration levels (above 1.0×10^{-4} M), whereas ions such as Al^{3+} and Hg^{2+} are tolerated only at very low concentration levels. Generally, the tolerance level of the last two ions is much higher than the concentrations of the two ions in tap water. Therefore, the present method is practical for monitoring the contents of cationic surfactants in tap water. As for some special environmental water samples, some prior separation procedures may be necessary. Owing to the electrostatic interaction with Zeph, anionic surfactants are tolerated with low concentration levels. However, non-

Table 1 Tolerance of substance on the determination of Zeph

No	Foreign substances	Tolerance concentration ($\times 10^{-6}$ M)	Change of ΔI_{RLS} (%) ^a
1	$\text{Ca}^{2+}(\text{Cl}^-)$	5000	+7.9
2	$\text{Co}^{2+}(\text{Cl}^-)$	0.1	-9.9
3	$\text{Fe}^{3+}(\text{SO}_4^{2-})$	0.5	-10.2
4	$\text{Hg}^{2+}(\text{Cl}^-)$	0.025	+6.1
5	$\text{K}^+(\text{Cl}^-)$	5000	-2.6
6	$\text{Mn}^{2+}(\text{Cl}^-)$	3.0	+10.2
7	$\text{NH}_4^+(\text{Cl}^-)$	200	+2.0
8	$\text{PO}_4^{3-}(\text{Na}^+)$	50	-2.7
9	$\text{Al}^{3+}(\text{SO}_4^{2-})$	0.04	-2.8
10	$\text{Cd}^{2+}(\text{Cl}^-)$	0.1	-5.8
11	$\text{Cr}^{3+}(\text{Cl}^-)$	2.0	+4.4
12	$\text{Mg}^{2+}(\text{Cl}^-)$	1000	+3.7
13	$\text{Pb}^{2+}(\text{Cl}^-)$	20	+4.4
14	$\text{Cu}^{2+}(\text{SO}_4^{2-})$	0.5	-9.1
15	Triton X-100	5.0	+9.8
16	SDS ^b	2.5	-8.0
17	SLS ^c	2.5	-8.4
18	β -CD ^d	2.0	-3.8

^aChange of ΔI_{RLS} (%) can be expressed $\frac{\Delta I_{\text{RLS}}}{I_0} 100\%$, in which $\Delta I_{\text{RLS}} = I - I_0$, I_0 is the intensity of RLS when the concentration of Zeph is 4.0×10^{-6} M, and the I is the intensity of RLS after adding a foreign substance. Concentration: AV: 1.0×10^{-5} M; Zeph: 4.0×10^{-6} M. Ionic strength 0.03 M, pH 6.09, $\lambda=470.0$ nm. ^bSDS sodium dodecyl sulfonate. ^cSLS sodium lauryl sulfate. ^d β -CD β -cyclodextrin.

ionic surfactants, such as Triton X-100 can be tolerated at high levels.

Calibration curves

Under optimal conditions, we can construct calibration curves for Zeph and CTMAB by using different concentrations of AV. As shown in Table 2, the response of RLS signals varies with the cationic surfactant. Possible reasons are that different cationic surfactants have different molecular weight and stereostructures, and the sizes of the ion associates of the AV with cationic surfactants are different. In addition, the linear range and the sensitivity are dependent on the concentration of AV. With increasing AV concentration, the linear range is extended and the sensitivity (slope of the linear regression equation) increases. However, if the concentration of AV is excessively increased, the sensitivity is reduced. Nevertheless, the limit of detection is about 10^{-8} M. Thus, we can choose the proper concentration of AV according to practical necessity. In this assay, 1.0×10^{-5} M AV was used for the determinations of synthetic and tap water samples. As shown in Fig. 7, ionic strength has a strong effect. Considering that some samples may contain high contents of salt and display high ionic strength, we also list the analytical parameters in a medium of 0.11 M ionic strength in Table 2. As shown, the sensitivities in this medium are lower than that in the medium of 0.03 M ionic strength, but this method can also detect Zeph sensitively.

Table 2 Analytical parameters for the determination

Surfactant	Concentration of AV ($\times 10^{-5}$ M)	Linear range ($\times 10^{-6}$ M)	Linear regression equation ($c, 10^{-6}$ M)	LOD ^a ($3\sigma, \times 10^{-8}$ M)	LOQ ^c ($\times 10^{-8}$ M)	r^b
Zeph	0.5	0.2~4.5	$\Delta f = 0.15 + 6.69c$	2.2	7.3	0.9989
	1.0	0.2~6.0	$\Delta f = -0.4 + 7.12c$	2.1	7.0	0.9988
	1.0 ^d	0.9~7.0	$\Delta f = -0.57 + 3.88c$	8.9	29.6	0.9959
	1.5	0.2~7.0	$\Delta f = -3.68 + 7.11c$	2.0	6.7	0.9972
	2.0	0.2~7.5	$\Delta f = -3.88 + 6.93c$	2.2	7.3	0.9994
CTMAB	1.0	0.4~4.8	$\Delta f = -1.69 + 4.79c$	3.8	12.7	0.9944
	1.0 ^d	3.1~4.8	$\Delta f = -0.3 + 1.1c$	31.4	103.3	0.9951
	1.5	0.4~6.4	$\Delta f = -2.8 + 4.36c$	4.1	13.7	0.9936
	2.0	0.4~7.2	$\Delta f = -3.2 + 4.33c$	4.2	14.0	0.9954

^aLOD limit of determination (calculated as three times the signal-to-noise ratio), ^b r : correlation coefficient. ^cLOQ limit of quantification (calculated as ten times the signal-to-noise ratio). ^dIonic strength 0.11 M, otherwise, ionic strength 0.03 M, pH 6.09, $\lambda = 470.0$ nm.

Table 3 Determination results of cationic surfactants in synthetic water samples^a

Samples ($\times 10^{-6}$ M)	Co-existing components ($\times 10^{-6}$ M)	Found ($\times 10^{-6}$ M, $n=5$)	Recovery (% , $n=5$)	
Zeph	2.0	Al ³⁺ , 0.004; Cr ³⁺ , 0.02; Mn ²⁺ , 0.3	1.95	97.5 \pm 1.8
	2.0	Cd ²⁺ , 0.01; Pb ²⁺ , 0.02; SDS, 0.1	1.85	92.5 \pm 1.9
	2.0	Mg ²⁺ , 1000; Fe ³⁺ , 0.05; β -CD, 0.2	2.04	101.9 \pm 3.5
	2.0	NH ⁴⁺ , 20; Co ²⁺ , 0.01; Triton X-100, 0.5	1.89	94.3 \pm 2.3
CTMAB	2.0	Ca ²⁺ , 1000; Co ²⁺ , 0.01; Mn ²⁺ , 0.3	2.01	100.9 \pm 3.5
	2.0	Hg ²⁺ , 0.001; Mg ²⁺ , 1000; β -CD, 0.1	1.85	92.5 \pm 2.1

^aConcentration: AV: 1.0×10^{-5} M; ionic strength 0.03 M, pH 6.09, $\lambda = 470.0$ nm.

Table 4 Determination results of Zeph in tap water samples

Tap water samples	The concentration of Zeph added ($\times 10^{-6}$ M)	Obtained ($\times 10^{-6}$ M)	Recovery (%)
1	1.0	0.92	92.0 \pm 1.4
2	2.0	1.86	93.0 \pm 2.2
3	3.0	3.14	104.6 \pm 3.6

Concentration: AV: 1.0×10^{-5} M; ionic strength 0.03 M, pH 6.09, $\lambda = 470.0$ nm.

Sample determination

Four synthetic water samples containing a series of added foreign substances were determined according to the linear relationship given in Table 2. As shown in Table 3, the results are satisfactory. The recoveries were 90.5–105.0%. To test the practicality of this method, we tested the content of Zeph in tap water samples. The recoveries were 90.0–108.2% (Table 4). Therefore, this method is practical and dependable.

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