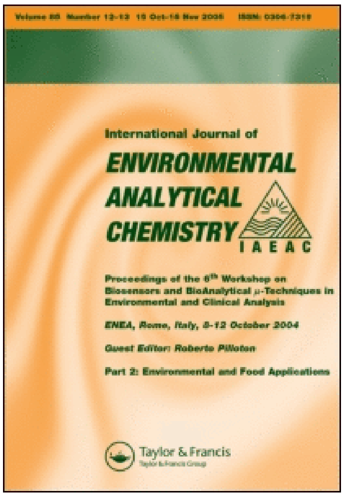

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Inaba, Kazuho(1987) 'Determination of Trace Levels of Polyoxyethylene-Type Nonionic Surfactants in Environmental Waters', International Journal of Environmental Analytical Chemistry, 31: 1, 63 — 73
To link to this Article: DOI: 10.1080/03067318708077130
URL: http://dx.doi.org/10.1080/03067318708077130

Intern. J. Environ. Anal. Chem., Vol. 31, pp. 63–73
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Printed in Great Britain

Determination of Trace Levels of Polyoxyethylene-Type Nonionic Surfactants in Environmental Waters

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(*Received 9 January 1987; in final form 10 May 1987*)

An analytical method for polyoxyethylene-type nonionic surfactants is proposed. It was found that the surfactants are preconcentrated by solvent extraction with toluene and many coexisting substances such as LAS or humic acid are washed out at the same time. Those in the toluene can extract cobalt(II) from aqueous thiocyanate solution. By determination of the metal with spectrophotometry as 4-(2-pyridylazo-)-resorcinolato complex, the concentration of the surfactants can be measured. Use of toluene as the solvent is useful not only for the purification of the surfactants from many interferences but also for the easier treatment of waste solvents in comparison to i.e. halogenated organic solvents.

KEY WORDS: Nonionic surfactants, spectrophotometry, purification, preconcentration.

INTRODUCTION

Polyoxyethylene-type nonionic surfactants (POE-NS) are widely used for industrial and domestic detergents[1] and thus increased water pollution by surfactants is feared. It has been reported that NS in environmental water is toxic toward fishes and microbials.[2] There is thus the pressing need to monitor NS in water.

For the determination of NS in water, the spectrophotometric method in which solvent extraction of tetrathiocyanatocobalt(II) dipottasium salt (CTAS method)[3] is carried out has been accepted as the official method by APHA, AWWA and WPCF. However, this method is rather complex and its sensitivity is low. Several other methods[3-7] have been recommended in place of the official one, but no definite decision has been made. Moreover, with growing interest in the pollution of groundwater[8] by halogenated organic solvents such as chloroform, use of these halogenated organic solvents such as chloroform, use of these solvents is at issue. These solvents are hardly degradable in the waste treatment, moreover, they have a heavy toxicity for humans. However, most methods previously reported use these solvents and thus development of a new technique not requiring the use of these solvents is necessary.

In the present work, improvement of the CTAS method was made to achieve greater sensitivity and simplicity. For this purpose, the amount of cobalt(II) which extracted into organic phase was determined by using 4-(2-pyridylazo)-resorcinol (PAR) as a spectrophotometric reagent. The molar absorptivity of the cobalt(II)-PAR complex is about 33 times larger than that of the thiocyanato complex (54000 ($M^{-1}cm^{-1}$) for the former[9] and 1700 ($M^{-1}cm^{-1}$) for the latter,[10] respectively).

EXPERIMENTAL

Reagents

All reagents were of analytical grade and used without purification. The pure sample of octaethyleneglycol mono-n-dodecylether ($C_{12}POE_8$; more than 99% GC) which was used for the standard POE-NS was obtained from Nikko Chemicals, Tokyo, Japan.

Preliminary tests

A 10 ml of an aqueous solution containing 1 to 8 M of ammonium thiocyanate, 0.01 to 0.25 M of cobalt(II) nitrate, and $C_{12}POE_8$ was placed in a glass tube and the same volume of toluene was added. The addition of a large amount of pottasium chloride salt caused saturation. The solution was shaken mechanically for 10 minutes.

The two phases were then allowed to separate by centrifugation (10 min at 2500 rpm) and 5 ml portion of the organic phase was transferred into another glass tube. The separated organic solution was agitated with an aqueous 0.01% PAR solution whose pH was adjusted to 8 by phosphate buffer. The cobalt(II) extracted into the toluene phase was back-extracted as the PAR complex species whose absorbance in the aqueous phase was then measured.

RESULTS AND DISCUSSION

The absorption spectra of the tetrathiocyanatocobalt(II) complex in toluene and of the PAR complex in aqueous phase were found to have maxima at 625 and 510 nm and were thus chosen for measurement.

Extraction of $[Co(SCN)_4]^{2-}$ with $C_{12}POE_8$

In the present method, the amount of POE-NS in a water sample was determined by the amount of cobalt(II) extracted into toluene by the surfactant. Hence, experiments for examining the extraction behavior of $[Co(SCN)_4]^{2-}$ are necessary to achieve a more sensitive determination.

Experiments were carried out in the absence and presence of saturated amounts of KCl salt, by which the absorbance of the organic phase was previously found to increase. It was found that absorbance increased with increase of the concentration of SCN^- and/or Co(II) when the aqueous phase contained no KCl salt. When the aqueous phase was saturated by KCl salt, the change in absorbance with change in SCN^- and/or Co(II) concentration was found to be slight. It was thus concluded that extraction conducted in the presence of a saturated amount of KCl salt is favorable. The absorbance of the metal complex species in toluene was not affected by standing for a few hours.

Back-extraction of cobalt(II) with PAR

Back-extraction of the cobalt(II) extracted into toluene as a thiocyanato complex was examined by PAR in the range of 0.001 to

0.2 % of the reagent. The absorbance of the cobalt(II)-PAR complex in the aqueous phase was not affected by change in reagent concentration in the present experiment. However, the PAR solution had absorbance at 510 nm and absorbance of the blank solution was greater when the concentration of the reagent was higher. Thus, the reagent blank was concluded to be necessary. Absorbance of the PAR complex in the aqueous solution was stable and did not change even when the solution was left standing for a few hours.

Calibration curves for $C_{12}POE_8$

A set of calibration curves for $C_{12}POE_8$ was drawn using the absorption of tetrathiocyanato or PAR complex. Figure 1 gives the results. The curve for the PAR complex slightly deviated from a straight line when the concentration of POE-NS was lower than 3×10^{-6} M. The molar absorptivity for $C_{12}POE_8$ was about 900 ($M^{-1} cm^{-1}$) for the thiocyanato complex at 625 nm and about 23 000 ($M^{-1} cm^{-1}$) for the PAR complex at 510 nm.

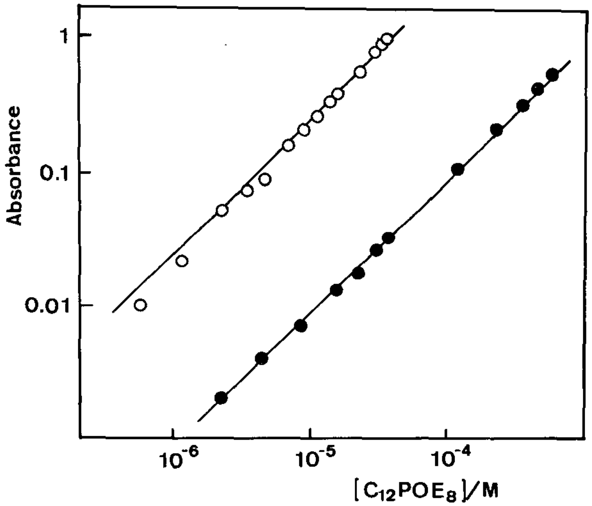

Figure 1 Calibration curves of $C_{12}POE_8$ by determination with the absorption of tetrathiocyanatocobalt(II) at 625 nm (●) and the PAR complex at 510 nm (○). The slope of the straight line in the figure is +1.

Preconcentration of POE-NS by partition of the toluene-H_2O system

The liquid–liquid partition of $C_{12}POE_8$ between water and toluene was in favour of the latter solvent. When the volumes of the two phases were similar, more than 99% of the surfactant was transferred into toluene. This is because POE-NS has neither a negative nor positive charge and therefore its solubility into an organic eluent is rather high. By this "organophilic" character, it should be possible to concentrate very low levels of POE-NS in environmental samples. Figure 2 shows the effect of the volume ratio of toluene and water on the percentage extractability of the surfactant into toluene. As can be seen from Figure 2, the extraction of the surfactant exceeds 90% for volume ratios of the aqueous to the organic phase of up to 100. On the other hand, it was found that the volume of the organic phase somewhat decreased with increasing concentration ratio due to the dissolution of toluene into water. However, this effect was not too large and up to 100 times concentration factors of 100 was concluded to be possible.

Effects of coexisting substances on the partition of POE-NS in the toluene-H_2O system

The effects of coexisting substances on the extraction recovery (preconcentration) of $C_{12}POE_8$ with toluene were also examined. An

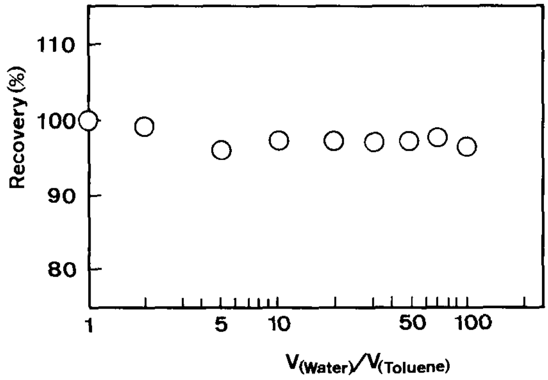

Figure 2 Recovery of $C_{12}POE_8$ by toluene extraction from water as a function of the water/toluene volume ratio.

aqueous solution containing a certain amount of $C_{12}POE_8$ and a substance was agitated with toluene. The surfactant extracted into the toluene phase was then determined by the present spectrometric method.

The coexistence of linear alkylbenzene sulfonates (LAS) lowered the recovery for $C_{12}POE_8$, but it still remained higher than 80%. Thus, the error resulting from interference with LAS may be concluded to be rather small. When the extraction of cobalt(II) was carried out without preconcentration of POE-NS by toluene, the absorbance of the organic phase was considerably affected by the presence of LAS. For example, an aqueous solution of 10 ppm LAS containing no POE-NS was determined with and without this pretreatment. The organic phase treated by the extraction procedure at first had no absorption while without pretreatment it had an absorption corresponding to an aqueous solution containing about 1 ppm $C_{12}POE_8$.

The determination of $C_{12}POE_8$ was slightly affected by polyethylene glycol (PEG-300:MW = 300), which was regarded as an intermediate of the biodegradation of POE-NS both with and without pretreatment, hence the amount of polyethylene glycol in environmental samples should not exceed that of POE-NS.[11]

Other substances such as humic acid and NaCl did not affect the extraction and determination of $C_{12}POE_8$ in the present study. The results are summarized in Table 1.

Complex effect of coexisting substances

The complex effect of interfering substances on the extraction and determination of the surfactant was studied. These coexisting substances, 10 ppm of LAS and 3 ppm of humic acid, were added to an aqueous solution containing 0.09 or 0.03 ppm of $C_{12}POE_8$ followed by extraction of the surfactant into toluene. The results are also listed in Table 1. When the aqueous solution contained 0.6 M NaCl, the concentration of $C_{12}POE_8$ determined by the present method exceeded that of the surfactant added, while in the absence of NaCl, the concentration was similar as that expected theoretically. This could be explained by the fact that when the salt concentration is high, coexisting substances such as LAS may be extracted into toluene as ion-pairs or by a setting out effect which interferes with

Table 1 Effects of coexisting substances on pretreatment of $C_{12}POE_8$

Coexisting substances	*Conc. (ppm)*	$[C_{12}POE_8]^a$ *(ppm)*	R^c	$[C_{12}POE_8]^b$ *(ppm)*	*Recovery (%)*	*Note*
C_{12}-LAS	10	0	1	0	—	
	5	3.12	1	3.01	97	
	10	3.12	1	3.04	97	
	20	3.12	1	2.96	95	
	30	3.12	1	2.83	91	
	5	0.62	1	0.53	86	
	10	0.62	1	0.46	75	
	15	0.62	1	0.58	93	
	20	0.62	1	0.62	100	
	25	0.62	1	0.51	82	
	30	0.62	1	0.42	68	
	20	0.062	30	0.055	88	
PEG-300	10	0	1	0.19	—	
	10	3.12	1	3.39	109	
Humic acid	20	3.12	1	3.25	104	pH 8
	40	3.12	1	2.97	95	pH 8
	40	3.12	1	3.02	97	pH 2
	40	3.12	1	2.83	91	pH 6
	40	3.12	1	3.29	105	pH 11
NaCl	0.6 (M)	3.12	1	3.04	97	
$C_{12}POE_8$ Humic acid NaCl	10 3 0.6(M)	0.10	30	0.18	180	
$C_{12}POE_8$ Humic acid	10 3	0.10	30	0.092	92	
$C_{12}POE_8$ Humic acid	10 3	0.031	100	0.026	84	

[a] Initially presented.
[b] Observed.
[c] Volume ratio of the toluene and water phases.

the determination. Thus, pretreatment such as ion-exchange should be proposed when using the present procedure for determination of the surfactant in sea water.

Recommended procedure

When the salinity of a sample is high as in the case of sea water and/or the concentration of interfering substances is very high as in waste water, an ion-exchange treatment has to preceed.

In a separatory funnel, take a certain volume of sample and 15 ml of fresh toluene and then agitate for 10 min. When the emulsion is formed, transfer the solution into a stoppered glass tube and the two phases are separated in a supersonic wave bath. Centrifuge the solutions (10 min at 2500 rpm) and then take 10 ml of the organic phase in a stoppered glass tube and add an equal volume of aqueous solution containing 0.08 M of $Co(NO_3)_2$ of 3 M of NH_4SCN; saturate the solution with KCl (about 3.5 g for 10 ml of solution is needed). Shake the tube for 10 min and then centrifuge it (10 min at 2500 rpm). If the content of POE-NS in the sample is rather high, the toluene phase is colored blue by the extracted cobalt(II) and the absorbance is measured at 625 nm. If the concentration of POE-NS is low, place 8 ml of the organic phase in another tube and add 4 ml of aqueous 0.01% PAR solution. Agitate the tube for 10 min and then centrifuge off (10 min at 2500 rpm). Measure the absorbance of the aqueous phase at 510 nm against the reagent blank.

Application to environmental waters

By the present method, the concentration of POE-NS in environmental water near this institute was determined. The locations of the sampling points and institute are illustrated in Figure 3. The results obtained are listed in Table 2. Marsh Tega, the worst polluted lakes and marshes in Japan,[1] contained 10 ppb levels of POE-NS, while other water bodies were polluted by a few ppb of the surfactant. The concentration of anionic surfactant in these samples was also determined by the MBAS method. The addition test was carried out on the samples and $C_{12}POE_8$ recovery was nearly 100% in all the experiments.

The reproducibility of the present method was also checked. The results obtained are listed in Table 3. As seen from Table 3, it was found that the reproducibility of the present method is high.

CONCLUSION

In the present method, the value of molar absorptivity for $C_{12}POE_8$ was 900 ($M^{-1} cm^{-1}$) with the tetrathiocyanato cobalt(II) complex

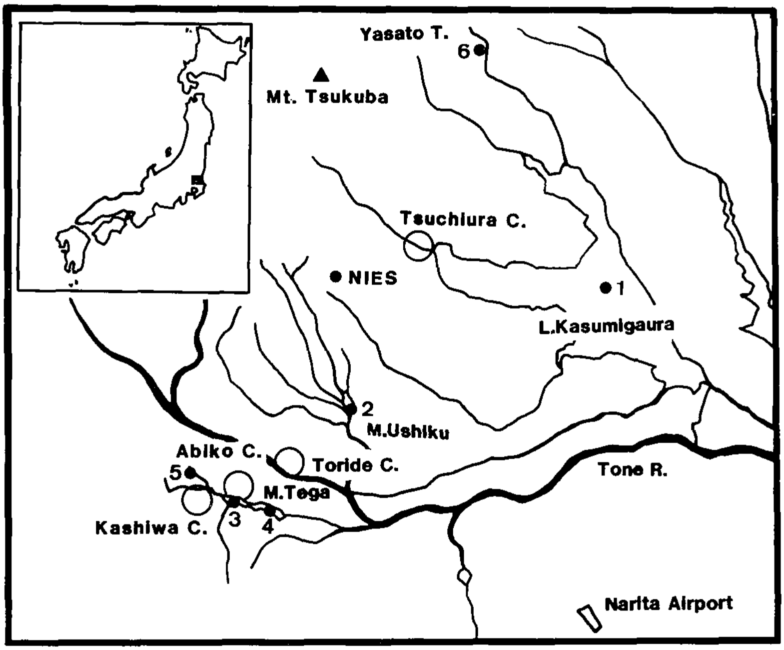

Figure 3 Illustration of the sampling points. 1. Lake Kasumigaura, 2. Marsh Ushiku, 3. Marsh Tega (inflow), 4. Marsh Tega (outflow), 5. Kashiwa City, 6. Yasato Town, NIES. Author's Institute.

and 23000($M^{-1}cm^{-1}$) with the PAR complex. This indicates that about 0.05 to 500mg/l of NS can be determined without preconcentration of the samples. The sensitivity of the present method is much higher than that in which absorption of tetrathiocyanato cobalt(II), picrate, or tetrathiocyanato iron(III) is carried out but somewhat lower than the method using tetrabromophenolphthalein ethyl ester previously reported.[3-6] However, these procedures involve solvent-extraction using a halogenated solvent. From the view point of the treatment of waste solvents, the present method compares favorably to that previously reported. The analytical methods are compounded with the problem that extractability of the cobalt(II) complex changes with the lengths of both alkyl and oxyethylene groups in the molecule. Such change affects the results

Table 2 Summary of determination of POE-NS

Sampling point	*No.*[a]	*Date*	*POE-NS*[b] *(ppb)*	*POE-NS*[c] *(ppb)*	*MBAS (ppb)*
L. Kasumigaura	1	Aug. 6 1986	ca 1	—	7
M. Ushiku	2	Aug. 18 1986	ca 2	—	—
			ca 3	—	111
			21	18	—
M. Tega	3	Jun. 19 1986	34	—	318
	4	Jun. 19 1986	11	—	62
	4	Aug. 14 1986	8	—	42
	4	Apr. 6 1987	26	—	—
			74	45	—
Domestic waste water					
Kashiwa C.	5	Aug. 8 1986	176	—	1510
			303	120	—
Yasato T.	6	Sep. 2 1986	25	—	—
			44	19	—

[a] Illustrated in Figure 3.
[b] As $C_{12}POE_8$.
[c] $C_{12}POE_8$ added.

Table 3 Summary of reproducibility test

Sample	*POE-NS/ppb added*[a]	*Number of test*	*POE-NS/ppb measured*[b]
M. Tega, Apr. 6 1987	0	8	26 ± 2
	45	3	74 ± 3
Distilled water	45	6	42 ± 1

[a] $C_{12}POE_8$ added.
[b] As $C_{12}POE_8$.

obtained by the present method. However, the length of both oxyethylene and alkyl chains should not vary widely, (for example, the number of the carbon in alkyl group was about 11 to 18 and that of oxyethylene group was about 7 to 10) in commercial products used in Japan.[12] Hence our method may be used to monitor surfactants in environmental water.

Acknowledgements

The author is grateful to Dr. Ryuichi Sudo of the National Institute for Environmental Studies, for encouragement of this work. Thanks are also due to Prof. Tatsuya Sekine of the Science University of Tokyo for his valuable comments on the present work.

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