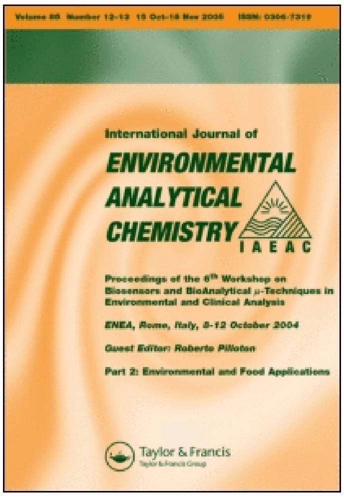

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Determination of Anionic Surfactants in Water

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The use of ternary complexes in the determination of anionic surfactants has been investigated and an analytical method using linear alkyl sulfonates as a test substance has been developed. The method involves the formation of the chloroform-extractable bisphenanthroline Cu(II)–linear alkyl sulfonate (LAS) complex and the subsequent equilibration of the extract with erythrosine to form the extractable bisphenanthroline Cu(II)–erythrosine complex. In the equilibration step erythrosine displaces LAS quantitatively, allowing the determination of the LAS originally present by measuring the absorbance of the extracted bisphenanthroline–Cu(II)–erythrosine complex. Results are reported of studies made to determine the optimum analytical conditions, the sensitivity, and the precision for the method described.

The commonly accepted method for the determination of anionic surfactants in water is based upon a colorimetric procedure involving the formation of a chloroform-extractable methylene-blue surfactant complex from slightly acidic solution.[1] This procedure is tedious, requiring no less than five extractions, and is lacking in precision and sensitivity. Large sample volumes are required, as much as 250 ml, and there are a number of positive interferences such as organic sulfates, chlorides, nitrates, and thiocyanates which form ion pairs with the methylene blue.

Perhaps the greatest drawback of the methylene-blue method is the tendency to form heavy emulsions during extraction, which may make separation of the two phases difficult.

Other methods for the determination of anionic surfactants include an adsorption method described by Maehler *et al.*[2] In this procedure the aqueous sample is passed through an activated carbon column, eluted, and then subjected to infrared analysis. The advantage of this method is that it is possible to differentiate between linear alkyl sulfonate (LAS) and alkyl benzene sulfonates (ABS). However, the procedure is nonquantitative and the preliminary work-up is even more tedious than the methylene-blue method.

Den Tonkelaar and Bergshoeff[3] have recently developed a colorimetric procedure involving the extraction into chloroform of the complex formed by the dyestuff Azure A with anionic surfactants in an acid medium. The method combines simplicity with sensitivity, but is restricted in the size of sample that can be used, since large sample volumes result in the incomplete extraction of the Azure A surfactant complex.

The method introduced is based upon the formation of a chloroform-extractable ternary complex, bisphenanthroline–copper(II)–surfactant, and the subsequent equilibration of this complex with the dye stuff erythrosine, tetraiodo-R-fluorescein (Figure 1), to form the bisphenanthroline–copper(II)–erythrosine complex.

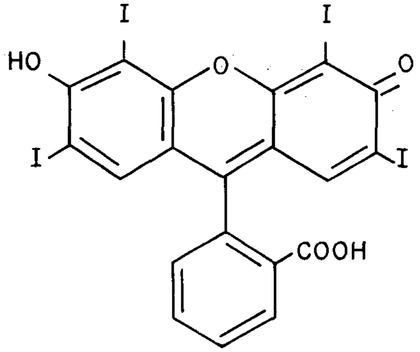

FIGURE 1 Erythrosine—Structural formula of tetraiodo-R-fluorescein.

The bisphenanthroline–copper(II)–erythrosine complex is formed via a three-step mechanism. Initially, cupric ions react with phenanthroline to form the bisphenanthroline–copper(II) complex which in turn reacts with the LAS to produce the ternary complex ($Cu(Phen)_2LAS$). After extraction from the aqueous solution into chloroform the ($Cu(Phen)_2LAS$) is reacted with erythrosine which displaces the LAS producing the bisphenanthroline–copper(II)–erythrosine complex.

Previous to this work, ternary complexes have been used in the spectrophotometric and spectrofluorometric determination of metals.[4–6] The use of ternary complexes in the determination of anionic surfactants was first described by Bailey in 1967.[4]

EXPERIMENTAL

Instrument

Beckman Model DU Spectrophotometer with 1-cm cuvettes

Reagents

10^{-3}M copper solution (prepared from copper sulfate)
10^{-2}M 1,10-phenanthroline (aqueous)
pH 8 phosphate buffer
LAS stock solution 10 mcg/ml
pH 6 phosphate buffer
10^{-3}M ethylenediamine tetraacetic acid, disodium salt
0.1% erythrosine
Chloroform

RESULTS AND DISCUSSION

Preliminary Investigation

The spectrum of the $(Cu(phen)_2eryth)$ complex shows an absorbance maximum at 545 nm (Figure 2). All subsequent measurements were made at this wavelength.

The effect of pH on the extraction of the copper–phenanthroline–LAS complex was determined using the following procedure: 25-ml samples containing 50 mcg LAS, 10^{-3}M $CuSO_4$, and 2×10^{-2}M 1,10-phenanthroline were adjusted to pH values in the range 2–11 and extracted with 25 ml chloroform. The chloroform extracts were then equilibrated with 10 ml of a 0.1% aqueous erythrosine solution buffered to pH 8. The absorbance of the resulting chloroform-soluble copper–phenanthroline–erythrosine complex was measured at 545 nm against a reagent blank. As can be seen in Figure 3, the copper–phenanthroline–LAS complex is extractable over the pH range 5–9. A pH of 8 was chosen for the second extraction since previous investigations have shown that the metal–phenanthroline–erythrosine ternaries are extractable only at a pH of 7 and above.[4]

The effect of copper–phenanthroline concentration on the extraction of the copper–phenanthroline–LAS complex was determined by treating 25-ml samples containing 50 mcg LAS with 2 ml of 10^{-2}M 1,10-phenanthroline and varying amounts of 10^{-4}M $CuSO_4$. The samples were

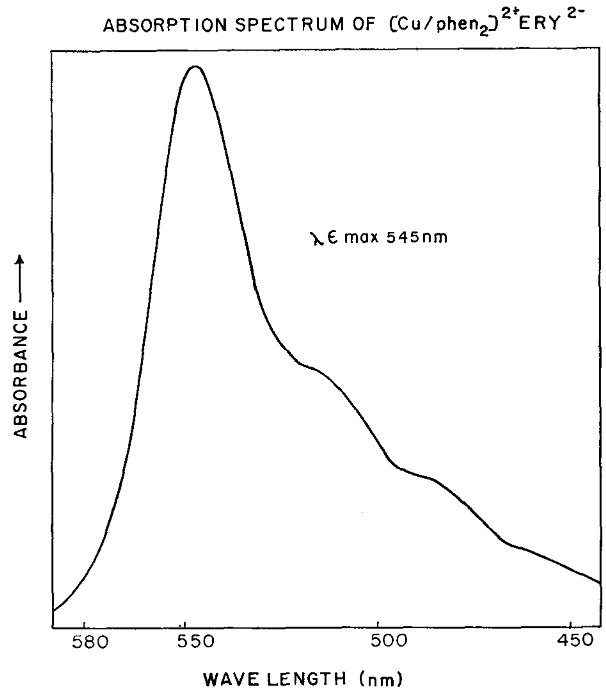

FIGURE 2 Absorption spectrum of complex run on Bausch and Lomb 505 Recording Spectrophotometer.

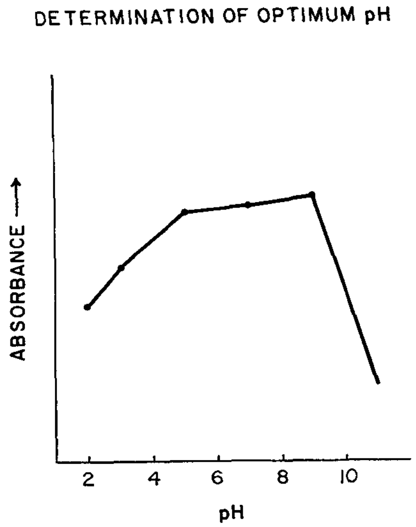

FIGURE 3 Determination of optimum pH for extraction of copper phenanthroline extract.

25 mcg LAS
5 ml 10^{-4} M copper
1 ml 10^{-2} M 1, 10 phenanthroline
Ammonia + acetic acid to get required pH's.

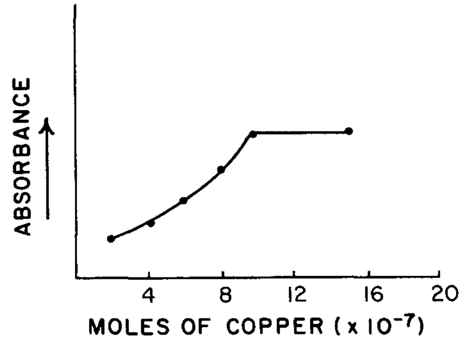

FIGURE 4 Determination of optimum copper–phenanthroline concentration for extraction of LAS complex

50 mcg LAS
2 ml 10^{-2} M 1, 10 phenanthroline (2×10^{-5} moles)
2 ml pH 8 phosphate buffer
2, 4, 6, 8, 10, and 15 ml 10^{-4} M copper sulfate.

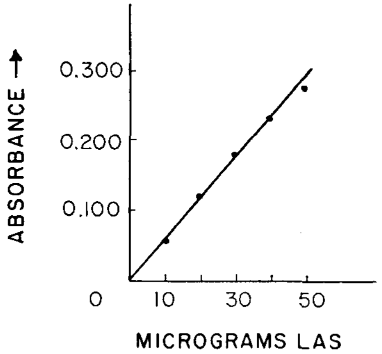

FIGURE 5 Beer's law plot.

buffered to a pH of 8 and extracted with 25 ml of chloroform. The chloroform extract was then equilibrated with erythrosine at a pH of 8 and the absorbance of the resulting copper–phenanthroline–erythrosine complex was measured at 545 nm against a reagent blank. As shown in Figure 4, complete extraction of 50 mcg LAS requires at least 10^{-6}M copper(II).

The curve in Figure 5 shows a strict adherence to the Beer–Lambert law over the range of 0.5–50 mcg LAS.

Reproducibility and Sensitivity

In a reproducibility study of the procedure six 25-ml aliquots containing a 1.2 ppm LAS solution were found to have a standard deviation of ±0.84 mcg or 2.8%. A similar study conducted by the Analytical Reference Service on the methylene-blue procedure showed a standard deviation of ±1.04 mg or 12.5% on a solution containing 8.18 ppm LAS.[1]

A sensitivity comparison between the ternary complex and methylene-blue procedure showed that the ternary complex method is more than twice as sensitive. Twenty mcg of LAS in 200 ml of solution was analyzed by both procedures. The erythrosine method produced an absorbance of 0.117, which is a sensitivity of 0.17 mcg. The sample run by the methylene-blue procedure had an absorbance of 0.047, for a sensitivity of 0.43 mcg.

TABLE I
Sensitivity comparison

	Erythrosine	Methylene blue
Concentration LAS	20 mcg/200 ml	20 mcg/200 ml
Absorbance	0.117	0.047
Sensitivity[a]	0.17 mcg	0.43 mcg
Extinction coeff.	3.7×10^5 litre/cm mole	1.5×10^5 litre/cm mole

[a] Sensitivity is defined as amount of LAS required to give a differential absorbance of 0.001.

Interferences

Several anions and cations were tested as possible interferences. It was found that nitrate, bromide, chloride, sulfate, persulfate, fluoride, and carbonate in 1000-fold excess cause no interference. Thiocyanate and perchlorate will not interfere up to 100-fold excess. Picric acid causes a slight positive interference, but is not generally encountered in water samples.

The only cationic interference was found to be iron, which gave a large negative interference, due to the formation of the trisphenanthroline–iron–LAS complex. This interference was removed by masking the iron with ethylenediamine tetraacetic acid and lowering the pH of the first extraction to 6, where EDTA is more selective to iron than copper. This technique was found to completely mask the iron and in no way affected the extraction of the bisphenanthroline–copper–LAS complex.

Analytical Procedure

1) Transfer by pipette a sample containing 10–50 mcg LAS into a separatory funnel previously washed with acid and rinsed with acetone.

2) Add sufficient distilled water to blank, standards, and samples to bring solutions to a uniform volume.

3) Add 2 ml phosphate buffer (pH 6), 2 ml 10^{-3} M copper sulfate, 2 ml 10^{-2} M 1,10-phenanthroline, and 2 ml 10^{-3} M EDTA.

4) Add 25 ml of chloroform and extract by shaking vigorously for one min.

5) Allow phases to settle and transfer the chloroform layer to a second separatory funnel that has been washed with acid and rinsed with acetone.

6) To the extracted phase add 10 ml 0.1 % w/v erythrosine, 2 ml phosphate buffer (pH 8) and 10 ml distilled water.

7) Extract by shaking vigorously for one min. Allow phases to settle and wait five min, swirling intermittently.

8) Transfer the chloroform layer to a 1-cm cuvette and measure the absorbance at 545 nm against a reagent blank.

CONCLUSION

This method was found to be simple, sensitive, and not subject to interferences. Extraction was found to be quantitative, using sample volumes ranging from 25–250 ml. Thus, the method is felt to be generally applicable to the determination of anionic surfactants in potable water, ground water, and industrial wastes.

It appears that the determination of anionic surfactants by means of formation of the bisphenanthroline–copper(II)–LAS complex and subsequent equilibration with erythrosine is more sensitive and more reproducible, and it is subject to fewer interferences than the widely used methylene-blue method. Also, it is not nearly so time-consuming or tedious.

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