

# Flow Injection Double Solvent Extraction Determination of Anionic Surfactants

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## Abstract

A simple flow injection system for the determination of anionic surfactants in water using double solvent extraction is proposed. It is based on the Abbott's methylene blue method. A sample through-put of 30 injections  $\text{h}^{-1}$  with 1.5% RSD ( $0.40 \text{ mg SDS l}^{-1}$ ) and a detection limit of  $0.02 \text{ mg SDS l}^{-1}$  can be achieved. Other advantages are discussed. The procedure has been applied to determine anionic surfactants in real water samples.

**Keywords** Anionic surfactants, double solvent extraction, methylene blue

## 1. Introduction

Anionic surfactants are the most common agents in detergents for laundry dishwashing and general cleaning. The presence of anionic surfactants in environmental water has been of interest. Various analytical techniques have been applied for such the purposes. They include spectrophotometry [1-10], AAS [11], AES [11], voltammetry [12], potentiometric titration [13-15], HPLC [16-18], GC [19], and radiometry [20]. The common practice as a standard method involves spectrophotometry using methylene blue for Methylene Blue Active Substances (MBAS). The methylene blue cation forms an ion association compound with an ionic surfactant which is extracted into chloroform and measurement of the blue color in the chloroform is made spectrophotometrically at 652 nm [21]. The typical batch analysis using double solvent extraction proposed by Abbott [22] was modified from Longwell and Maniece to overcome interferences. The methylene blue-anionic

surfactant ion associate is partitioned into chloroform from an alkaline methylene blue solution to avoid the negative interference of proteinaceous material present in environmental samples. The chloroform phase is then back-extracted with an acidified methylene blue solution in order to remove the interference of those materials such as inorganic anions e.g. nitrate, chloride etc, that form methylene blue complexes of low chloroform extractability. There have been a number of reports on applying FIA to spectrophotometry [23-38], AAS [39], fluorimetry [34,40] and potentiometry [41,42]. We have attempted to apply a simple FIA procedure with double solvent extraction based on Abbott's method.

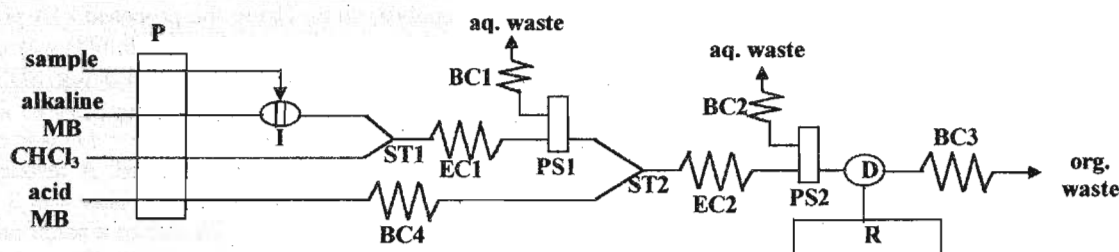
## 2. Experimental

### 2.1. FIA manifold

Fig.1 represents the FIA manifold for double solvent extraction for anionic surfactants as MBAS determination. A Lachat QuikChem 4200 system was used. Segmentor and phase separator are of those

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**Fig.1** FIA manifold for the determination of anionic surfactants using double solvent extraction  
P = peristaltic pump; I = injection valve; ST = segmentor; EC = extraction coils;  
PS = PTFE membrane phase separators; BC = back pressure coils; R = chart recorder  
D = spectrophotometer

previously reported [43]. A standard or sample is injected via an injection valve (I) into the stream of alkaline methylene blue solution. The stream is merged with a chloroform stream to create segments by a segmentor (ST1). The extraction takes place during the segments passing the extraction coil (EC1), until reaching a phase separator (PS1) where the organic phase is separated out and flowing further to merge with the stream of acid methylene blue at another segmentor (ST2). Extraction takes place again during the passage through the extraction coil (EC2). The phase separator (PS2) separates the organic phase out and the organic stream flows through the flow-cell to be monitored continuously at 650 nm. The FIA-grams are recorded by a chart recorder (Perkin-Elmer, Hitachi, Japan).

## 2.2. Reagents

Deionized water was used for all solution preparation.

Stock standard sodium dodecyl sulphate (SDS) 1000 mg l<sup>-1</sup> was prepared by dissolving 0.1087 g of SDS (Fluka) in water and diluting to 100 ml. Further appropriate dilutions were daily prepared.

Pre-equilibrated chloroform was obtained by equilibrating 700 ml of chloroform (MERCK) with three 140 ml portions of water. To prevent bubble formation, pre-equilibrated chloroform was degassed with air suction pump before use.

Alkaline borate solution was prepared by dissolving 4.77 g of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (MERCK) and 1.00 g of NaOH (BDH) in water and diluting to 500 ml.

Stock methylene blue (MB) 0.050% w/v solution was prepared by dissolving 0.125 g of MB in water and diluting to 250 ml. This stock MB solution was pre-extracted with three 25 ml aliquots of chloroform.

Alkaline methylene blue solution was prepared by adding 60 ml of the pre-extracted stock MB 0.050% w/v solution into 300 ml of alkaline borate solution and was diluted to 1000 ml with water.

Acid methylene blue solution was obtained by mixing 20 ml of pre-extracted stock MB 0.050% w/v solution and 5 ml of 0.50 M H<sub>2</sub>SO<sub>4</sub>. The mixture was added into 10 ml of alkaline borate solution and diluted to 500 ml with water.

## 2.3. Procedure

Using the conditions in Table 1, a series of standard solutions (SDS), 0.02-1.0 mg l<sup>-1</sup>, is injected into the FIA system. The peak heights are plotted *versus* the concentrations. Concentration of a sample can be obtained from the calibration via the peak height of the sample injected.

## 2.4. Sample storage

Addition of 1% v/v of a 40% formaldehyde solution to a water sample is required for storage [22].

## 2.5. Application

The proposed procedure was applied to natural waters, i.e. river, pond, sewage.

**Table 1** Conditions for FIA system with double solvent extraction

Parameter	Condition
Alkaline MB solution	0.0030% w/v MB, 0.0075 M Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> and 0.015 M NaOH
Acid MB solution	0.0020% w/v MB, 5.0x10 <sup>-4</sup> M Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , 1.0x10 <sup>-3</sup> M NaOH and 5.0x10 <sup>-3</sup> M H <sub>2</sub> SO <sub>4</sub>
EC1 dimension	0.5 mm i.d. x 50 cm length
EC2 dimension	0.5 mm i.d. x 50 cm length
BC1 dimension	0.5 mm i.d. x 150 cm length
BC2 dimension	0.8 mm i.d. x 50 cm length
BC3 dimension	0.8 mm i.d. x 50 cm length
BC4 dimension	0.5 mm i.d. x 100 cm length
Sample volume	150 µl
Flow-rate of alkaline MB solution	2.4 ml min <sup>-1</sup>
Flow-rate of chloroform	2.0 ml min <sup>-1</sup>
Flow-rate of acid MB solution	1.4 ml min <sup>-1</sup>
Wavelength	650 nm
Sensitivity of recorder	0.2 v
Chart speed of recorder	5 mm min <sup>-1</sup>

## 3. Results and Discussion

It was found that the water equilibrated chloroform resulted a smooth base-line and higher peak comparing to the results obtained when using the chloroform without water-pre-equilibration. Although a higher injection volume (20-200 µl) yielded better sensitivity (higher peak) but peak broadening was observed and resulting in longer analysis time. Using the proposed FIA procedure, a calibration,  $y = 238x - 2.32$  ( $r^2 = 0.998$ ) was obtained. A linear range was up to at least 1.5 mg SDS l<sup>-1</sup>. A detection limit ( $3\sigma$ ) [44] was 0.02 mg SDS l<sup>-1</sup>. Precision of 1.5% RSD (for 0.40 mg SDS l<sup>-1</sup>,  $n = 11$ ) was obtained. Fig. 2 represents FIA-grams obtained. A through-put of 30 injection h<sup>-1</sup> could be achieved. This was 2 min per analysis when comparing to 24 min of a batch procedure. This minimizes reagent consumption, especially chloroform which is toxic waste. The waste could also be recycled for re-use by distillation.

For the interference study, it was found that the following species: urea, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, S<sub>2</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> do

not interfere in the determination of SDS ( $0.10 \text{ mg l}^{-1}$ ) when the concentrations do not exceed 1000, 100, 100, 100, 1000 and  $500 \text{ mg l}^{-1}$  respectively.

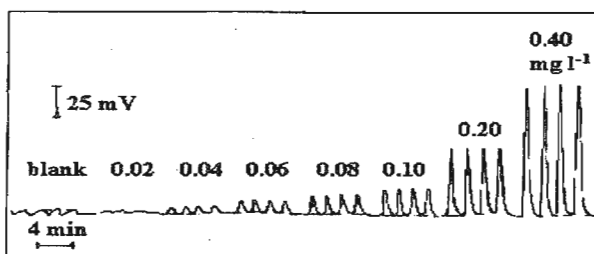


Fig.2 FIA-grams of standard SDS solutions

Table 2 demonstrates the application of the proposed procedure to different types of water. The results obtained by the FIA method agree with the batch ones. The recoveries were found to be  $100 \pm 10\%$  and  $100 \pm 20\%$  for the FIA and batch procedures respectively.

Sample pretreatment of three different methods using filter paper, PTFE membrane and centrifugation was also investigated. The results (Table 3) indicate that centrifugation which resulted good reproducibility should be used. The water sample is centrifuged before the clear upper portion in the centrifuge tube is suctioned into the sample loop of the injection valve.

Table 2 Application to real samples

Water sample	Conc. of anionic surfactants (as $\text{mg SDS l}^{-1}$ )	
	FIA	Batch (Abbott's method)
River	0.32	0.36
Pond	0.27	0.37
Sewage 1	0.76	0.60
Sewage 2	2.32	2.40
Sewage 3	0.45	0.45

Table 3 Effect of sample pretreatment method

Sample pretreatment method	Repeat No.	Conc. of anionic surfactants (as $\text{mg SDS l}^{-1}$ ) in water		
		Pond	Sewage A	Sewage B
Filtrated through filter paper	1	0.27	0.76	0.45
	2	0.55	1.10	0.56
	3	0.18	0.39	0.26
Filtrated through PTFE membrane	1	0.70	0.79	0.75
	2	0.22	0.55	0.33
Centrifugation	1	0.20	0.85	0.35
	2	0.21	0.85	0.30
	3	0.21	0.83	0.31
	4	0.21	0.85	0.28
	5	0.23	0.89	0.37

#### 4. Conclusion

The FIA procedure with on-line double solvent extraction for the determination of anionic surfactants is fast, economics, reproducible and accurate and can be applied to various types of natural water.

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