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*Full Paper*

# An economical ultrasonic-assisted extraction for the spectro-photometric determination of anionic surfactants

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**Abstract:** An economical ultrasonic-assisted extraction system was developed for the extraction / spectrophotometric determination of anionic surfactants based on methylene blue method. A low-cost ultrasonic cleaner was employed to enhance extraction efficiency and also to reduce chemical consumption, time and cost of analysis. Optimum conditions for extraction and detection were determined. Extraction time of 30 seconds and a volume ratio of aqueous sample to organic solvent of 8:1 were found to be optimum. Concentrations of methylene blue and $Na_2SO_4$ were selected at $10^{-5}$ and $10^{-2}$ M respectively. Simultaneous parallel extraction of 12 samples could be carried out. Standard solutions of sodium dodecyl sulphate (0.10 mg $L^{-1}$) were evaluated for reproducibility and the relative standard deviation was found to be 4.8%. The method was applied to the analysis of 7 real water samples. The concentrations of AS were found in the range of 0.054–0.123 mg $L^{-1}$. The results obtained were compared to those from the standard method and no significant difference was observed. Recovery was found to be 106–112%.

**Keywords:** ultrasonic-assisted extraction, methylene blue, anionic surfactants

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## INTRODUCTION

Anionic surfactants (AS) are widely used in household, cosmetic and industrial products as well as in research laboratories [1-3]. Because of their difficult biodegradation, the resulting contamination of water source can affect water quality and aquatic animals [4]. In order to determine the content of the surfactants accurately, an effective analytical method is needed. The official method for determination of AS in water is based on the formation of an ion-associated complex between an anionic surfactant and methylene blue (MB) cationic-dye molecules in the stoichiometric ratio of 1:1. The complex is extracted into chloroform and determined spectrophotometrically at 654 nm [5]. This method involves multiple steps and tedious extraction procedure which is time-consuming and consumes a large volume of organic solvent [2-3, 6].

Ultrasonic-assisted extraction (UAE) is expeditious and inexpensive compared to conventional extraction [e.g. 7-8]. When the ultrasonic wave passes through a liquid medium, the liquid is compressed and decompressed leading to the generation of bubbles. Numerous micro-bubbles form, grow, oscillate quickly and collapse violently, thus producing shock wave, a phenomenon called cavitation [9-13]. The phenomenon can be applied for various purpose, e.g. cleaning [9-10], stripping [11], accelerating liquid-liquid or solid-liquid extraction [12-13], digesting [14-15], emulsifying [16-17], homogenising [18], degassing [19], filtering [20] and crystallising [21].

UAE method can be achieved by various types of ultrasonic devices such as ultrasonic probe [17, 22-23], ultrasonic bath [24-25], sonoreactor [26] and cup horn [27]. Although an ultrasonic probe provides the highest intensity of sonication because it immerses directly into the solution [28-29], the extraction can only be done for individual samples and with a risk of contamination. While a sonoreactor, cup horn and ultrasonic bath give lower sonication intensities because the ultrasonic wave needs to cross the medium solution or the wall of the container, a simultaneous extraction without contamination is possible [11, 29].

The scientific ultrasonic instruments of various types as described above are of large size and expensive. In this work, a small ultrasonic cleaner that is generally used for cleaning small objects was applied as a UAE system. This instrument is simple, low-cost and small in size. The system was used for the extraction of anionic surfactants based on MB method employing dichloromethane as organic solvent. The main factors affecting the extraction efficiency were optimised with emphasis on extraction efficiency and reduction of organic solvent volume and time needed for extraction.

## MATERIALS AND METHODS

### Chemicals and Standard Solutions

Deionised water from a Milli Q & Elix 10 element system (Millipore, USA) were used throughout. Sodium dodecyl sulphate (SDS) (98.0%, Fluka) and dichloromethane (99.8%, Lab-scan) were used as standard anionic surfactant and organic solvent respectively. Methylene blue (MB, 95.0%) was purchased from Riedel-de Haën. Other chemicals used for preparing the working MB solution were sodium sulphate (99.5%, Fluka), potassium dihydrogen phosphate (99.5%, Merck) and sulfuric acid (98.0%, Lab-scan). Chemicals used for interference study were sodium chloride (99.0%, Lab-scan), potassium bromide (99.5%, Rankem), sodium nitrite (99.0%, Merck), sodium nitrate (99.5%, Merck), sodium thiocyanate (98.0%, Fluka), sodium sulphate (99.0%, Fluka) and sodium phosphate (98.0%, Rankem).

Stock standard solution (1000 mg $L^{-1}$) of SDS was prepared by dissolving the anionic surfactant (0.1109 g) in water and diluting to 100 mL. Working standard solutions were prepared daily by diluting the stock standard solution with water to obtain desired concentrations.

A stock solution (1.0 ×$10^{-3}$ M) of MB was prepared by dissolving the dye (0.0333 g) in water (100 mL). A working MB solution (1.0 ×$10^{-5}$ M) was prepared by mixing the following together: MB stock solution (2.5 mL), $Na_2SO_4$ (0.3552 g), $KH_2PO_4$ (0.25 g) and $H_2SO_4$ (0.5 mL), and adjusting the volume to 250 mL with water [30]. This solution was then pre-extracted with dichloromethane (1/5 volume) to prevent a background level when partitioning MB into the organic phase. The organic solvent was also shaken with water (1/5 volume) before use to saturate the solvent with water.

## Apparatus and Operation Procedure

The extraction of anionic surfactants was carried out by mixing aqueous solutions of SDS and MB in a test tube (10 x 1.7 cm) followed by adding a small volume (1 mL) of dichloromethane. The volume ratio of the aqueous solution to organic solvent was kept at 8:1. The test tubes were placed on a rack that was immersed in the bath of a simple ultrasonic cleaner (dimension: 10.5 × 18 × 9 cm; DADI DA-968, Ling Tong Electronic Factory, China) for the extraction under a sonication frequency of 40 KHz (50 W). After extraction, the two phases were separated by centrifugation. The organic phase was subjected to measurement by a UV-VIS spectrophotometer (Shimadzu UV 1600, Japan) at 660 nm.

Because of the small volume of extracting solvent, the use of a general cuvette for measurement was not possible. A flow cell with an internal volume of 400 μL was then used by connecting to PTFE tubing (i.d. 0.030 inch) and a simple hypodermic syringe (Figure 1). The PTFE tubing was dipped into the organic phase and the solution was sucked into the flow cell by the syringe until it filled the flow cell. After the absorbance was read, the solution was pushed out of the flow cell. The absorbance obtained for the standard or sample solution was substracted by that of a blank solution before being used for plotting a calibration curve.

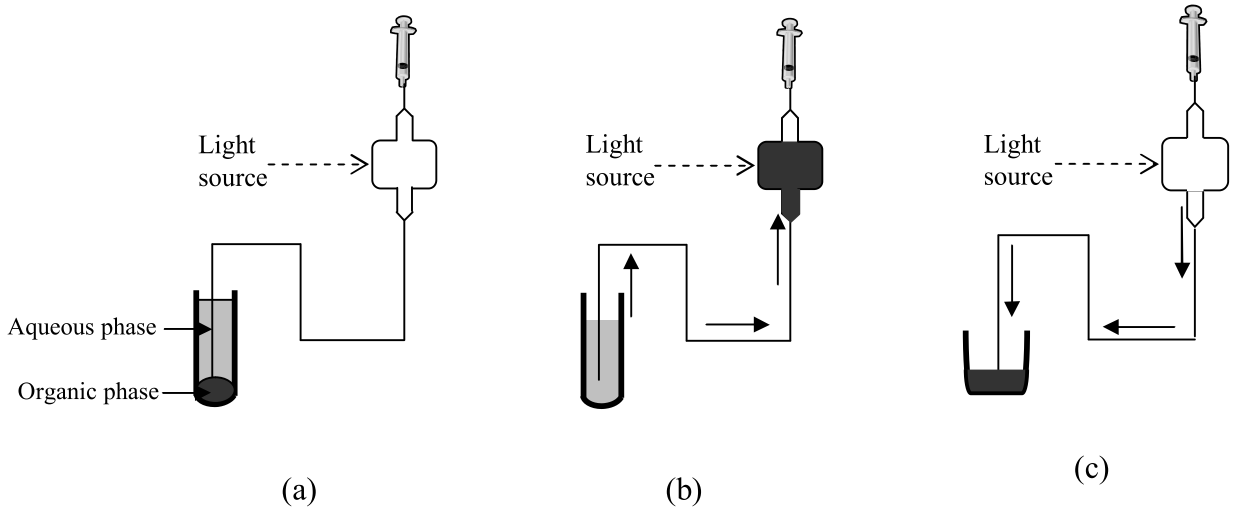

**Figure 1.** The flow cell and steps for use: (a) PTFE tube was dipped into organic phase; (b) solution was sucked up to fill flow cell for spectrophotometric measurement; (c) extract was pushed out of flow cell.

## RESULTS AND DISCUSSION

### Optimisation of Influencing Factors

Some factors that affected the extraction efficiency were studied, viz. extraction time, cationic dye (MB) concentration, volume ratio of aqueous solution to organic solvent, and salting-out effect. The effect of extraction time was first studied by using the initial condition: $10^{-5}$M MB, 0.05M $Na_2SO_4$, and 5:1 volume ratio of aqueous phase to organic phase. The extraction time was varied at 15, 30, 45, 60 and 75 seconds. A series of standard solutions of SDS (0.020-0.50 mg $L^{-1}$) was extracted in order to construct calibration graphs. Then the slope of the calibration graph versus extraction time was plotted as shown in Figure 2. Although it was found that the slopes (sensitivity) at different extraction times were not much different, an extraction time of 30 seconds which provided the highest sensitivity and lowest blank signal was chosen as optimum.

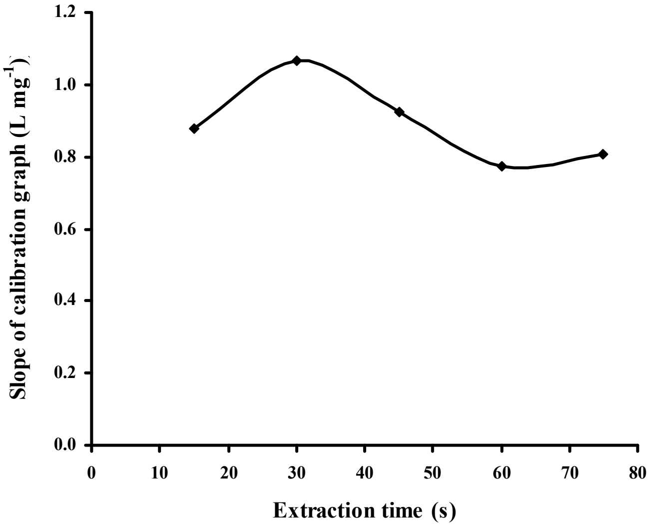

**Figure 2.** Effect of extraction time on slope of calibration graph

The influence of MB concentration was examined to observe the change in efficiency of extraction of the SDS-MB ion pair into the organic phase. The MB concentrations of $10^{-6}$, $10^{-5}$, $10^{-4}$ and $10^{-3}$M were used and a plot of concentration of MB as p-function (pMB) versus sensitivity (slope of the calibration graph) is illustrated in Figure 3. The result indicates that $10^{-5}$M MB gave the highest sensitivity.

Using conditions previously selected, the effect of volume ratio of aqueous to organic phase was investigated. The volume of dichloromethane was fixed at 1 mL while the aqueous volume was increased to obtain the aqueous:organic ratios of 1:1, 2:1, 5:1, 8:1 and 10:1. The obtained calibration graph (Figure 4) shows that the sensitivity increased with increasing aqueous volume. Although at the ratio of 10:1 gave the highest slope, the blank signal was also highest while the blank signals of the other ratios were much lower. Thus, the 8:1 ratio of was selected as optimum.

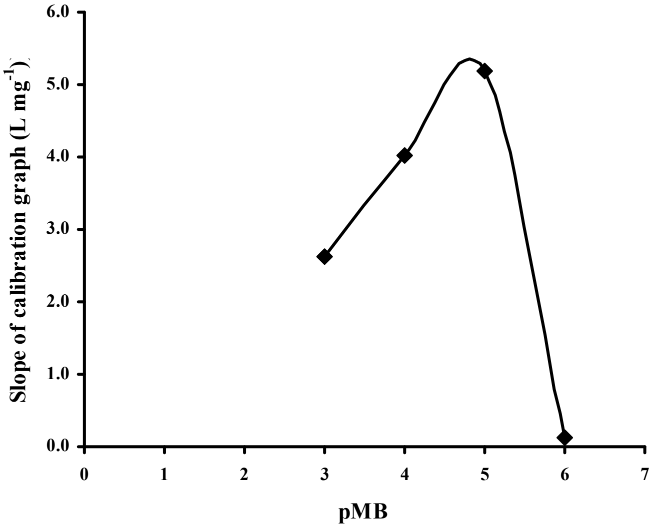

**Figure 3.** Effect of MB concentration on slope of calibration graph

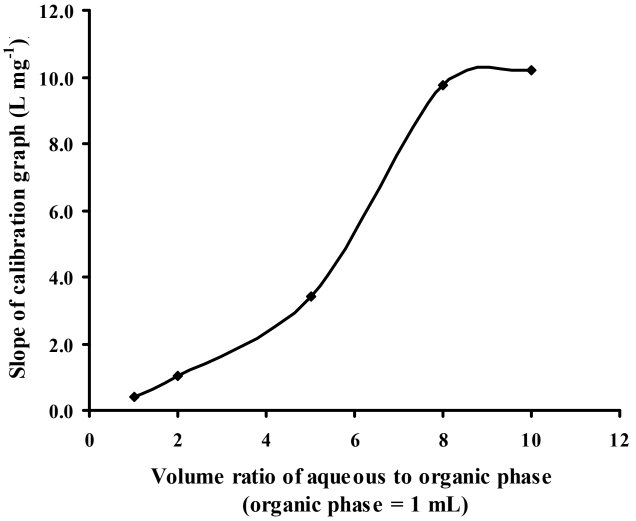

**Figure 4.** Effect of volume ratio of aqueous to organic phase on slope of calibration graph

A higher ionic strength was reported to greatly enhance the extraction efficiency of organic compounds from aqueous solutions to the organic phase and thus improve the sensitivity and precision of the determination, i.e. the so-called salting-out effect [31-32]. Various salts can be employed while $Na_2SO_4$ was used in this work because it gives a high ionic strength and is readily available. Different concentrations of $Na_2SO_4$ (5.0, 10.0, 50.0, 100.0 and 200.0 mM) were added to the working standard solution of SDS. The result in Figure 5 shows that a sharp increase in sensitivity occurred between 5.0-10.0 mM $Na_2SO_4$. The sensitivity enhancement then slightly decreased between 10-100 mM and steadily decreased after that. The solutions were also observed to be turbid due to the high concentration of salt. Thus, $Na_2SO_4$ at 10 mM was selected as optimum.

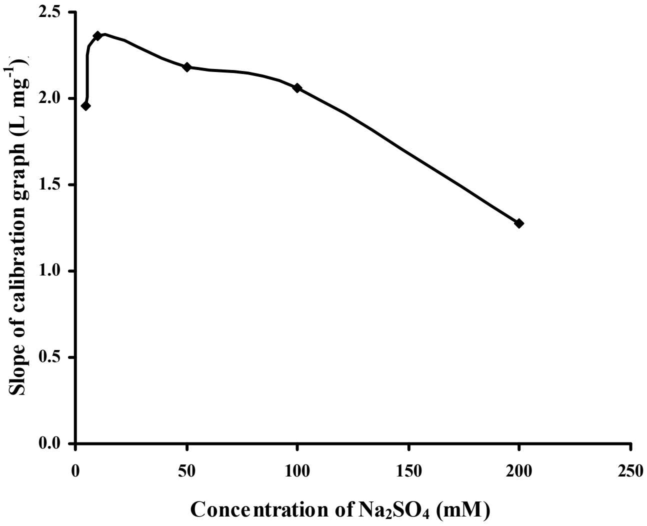

**Figure 5.** Salting-out effect of $Na_2SO_4$

## Analytical Characteristics

Under the selected set of conditions, i.e. extraction time of 30 seconds, ratio of aqueous to organic solutions of 8:1, and concentrations of MB and $Na_2SO_4$ of $10^{-5}$ M and 10 mM respectively, a series of standard solutions of SDS after treatment with MB solution were extracted as described above. The organic phase was separated and analysed spectrophotometrically. The calibration graph was then constructed by plotting absorbance versus concentration of SDS (0.0, 0.020, 0.10, 0.20 and 0.50 mg L$^{-1}$). A linear calibration graph ($y = 1.5151x + 0.1218$, $R^2 = 0.9920$) was obtained. The limit of detection (LOD) calculated from 3 × standard deviation of blank / slope of the calibration graph [33] was found to be 0.010 mg L$^{-1}$.

The reproducibility of the ultrasonic-assisted extraction was examined by performing 11 simultaneous extractions of 0.10 mg L$^{-1}$ SDS solutions under the optimum conditions. The average signal of absorbance was obtained and the relative standard deviation was 4.8%. The result showed good precision even though the extraction vessels were placed at different positions in the ultrasonic bath. The procedure consumed only 1 mL of organic solvent for each extraction and several extractions (up to 12 samples) could be performed simultaneously.

## Interference Study

Interference from foreign ions usually found in water samples was investigated. Various ions, namely $Cl^-$, $Br^-$, $NO_2^-$, $NO_3^-$, $SCN^-$, $SO_4^{2-}$ and $PO_4^{3-}$, of known concentrations were separately added to a solution containing a fixed concentration of SDS (0.20 mg L$^{-1}$ or $6.93\times10^{-7}$ M, the mean concentration of the calibration range). The tolerance limit, defined as the maximum concentration of a foreign ion per a fixed concentration of SDS that causes a deviation of absorbance not higher than ± 5% of the mean value of the absorbance due to the SDS solution without foreign ion, is summarised in Table 1.

**Table 1.** Maximum tolerance concentration ratio of various ions in AS determination

| Species | Tolerance limit ($C_{ion}$ / $C_{AS}$) |
|---|---|
| $Cl^-$, $Br^-$, $NO_2^-$, $SCN^-$, $SO_4^{2-}$ | 140 |
| $NO_3^-$, $PO_4^{3-}$ | 1400 |

It was found that ions normally found in water samples did not interfere in the extraction of AS under the proposed conditions. The concentration ratios of these ions to surfactant in water samples are usually lower than the tolerance limit. Moreover, these ions which are of smaller size than the surfactant may not form a strong ion association with MB and the small ion-pair compounds are unlikely to be effectively extracted into the organic layer.

## Analysis of Water Samples

Water samples (500 mL) were collected from various sources around Chiang Mai city (defined area of about 40 $km^2$), the sampling sites being about 5 km apart. All samples were filtered through a 0.45-µm membrane filter and analysed within 24 h without any preservation. Table 2 summarises the results on the AS content obtained by UAE under the determined optimum conditions compared to those obtained by the standard method carried out by batch extraction [5].

**Table 2.** Results of AS determination by UAE and standard methods

| Sample number | Source | Amount of AS (± SD) (mg $L^{-1}$) | |
|---|---|---|---|
| | | UAE method* | Standard method* |
| 1 | Canal | 0.082 ± 0.004 | 0.0520 ± 0.0002 |
| 2 | Canal | 0.069 ± 0.007 | 0.0580 ± 0.0002 |
| 3 | Drain | 0.123 ± 0.005 | 0.1160 ± 0.0002 |
| 4 | Drain | 0.072 ± 0.006 | 0.0510 ± 0.0009 |
| 5 | River | 0.058 ± 0.015 | 0.0420 ± 0.0004 |
| 6 | River | 0.054 ± 0.002 | 0.0350 ± 0.0000 |
| 7 | River | 0.065 ± 0.017 | 0.0380 ± 0.0004 |

* Mean of triplicate determinations

The values of AS content found by UAE method (x) agreed well with those found by the standard method (y), as indicated by the fact that the slope, intercept and coefficient of determination ($R^2$) of the correlation graph between the two methods were close to 1, 0 and 1 respectively ($y = 1.1508x + 0.0300$, $R^2 = 0.9279$). According to the paired t-test at 95% confidence level [33], there was no significant difference between the results from the two methods.

## Recovery Study

Three water samples in Table 2 were randomly taken for recovery study by addition of SDS standard solution (0.10 mg $L^{-1}$). This concentration was used because it was close to those found in most of the samples. Recoveries were found to be 106-112% with a relative standard deviation of 2.8%.

## CONCLUSIONS

The UAE technique using a simple ultrasonic cleaner for determination of AS based on MB method was found to be effective. Up to 12 samples can be simultaneously determined with low consumption of chemicals and time. Application to real samples gave results which were comparable to those obtained conventionally.

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