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Development and evaluation of a dispersive liquid–liquid microextraction based test method for quantitation of total anionic surfactants: advantages against reference methods

Research Article

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Abstract: A small-scale, simple, and rapid dispersive liquid-liquid microextraction (DLLME) procedure in combination with fiber optic-linear array detection spectrophotometry (FO-LADS) with charge-coupled device (CCD) detector has been developed, with benefits from the use of a micro-cell. The official reference methods (ASTM D2330 – 02, ISO 7875-1), which require tedious procedures, were replaced with a modified method. The new method provides a major reduction in sample size, elimination of the use of expensive glassware, and a decrease in the quantity of chloroform used, as well as increased sensitivity. Our method requires only one twentieth of the sample (5.0 mL), and less than one three-hundredth of microextraction solvent (chloroform = 138 μL). It provides a faster analysis time than official analytical methods (less than one minute). The calibration curve was linear in the range of 6–80 μg g L^{-1} of sodium dodecyl sulfate (SDS) with a correlation coefficient (r) of better than 0.99 and the LOD was 2 μg L^{-1}. The repeatability of the proposed method (n=7) was found to be 4.5% and 3.6% for the concentrations of 0.03 and 0.07 mg L^{-1}, respectively. The enrichment factor was found to be 75 for SDS.

Keywords: *Dispersive liquid–liquid microextraction • Water analysis • Methylene blue active substance • Anionic surfactant • Fiber optic-linear array detection spectrophotometry*

1. Introduction

A growing public concern over protecting our environment obliges chemists, including analytical chemists, to change their activities so that they will be conducted in an environmentally friendly manner. Sampling, and especially sample preparation frequently involves generation of large amounts of pollutants. This is why sample preparation techniques have been developed to use a small amount of organic solvent or none at all [1-4].

Anionic surfactants (AS) are widely used in household cleaners, industrial detergents and cosmetic formulations. When released to natural water reservoirs as municipal and industrial wastes, these surfactants are well known to have adverse effects on aquatic organisms. The monitoring of surfactants in environmental samples is therefore of great importance [5,6].

For the measurement of the total surfactant concentration, titration methods have been extensively explored [7,8]. Several ion-selective electrodes sensitive to anionic surfactants have been reported so far [9-11].

Anionic surfactants are usually determined by spectrophotometric methods using methylene blue (MB). Such a standard method determines AS in surface and tap-water samples (ASTM D2330 – 02, ISO 7875-1) [12,13]. The method is based on the formation of a blue-coloured chloroform extractable ion-pair between the AS and the cationic MB. This requires three successive extractions of AS–MB content in 100 mL of sample with 15, 10, and 10 mL of chloroform. The ion-pair is determined by spectrophotometry, measuring the absorbance at 650 nm. However, these official methods are not only long and tedious, but also require great quantities of sample and chloroform, which has harmful effects on chemists and the environment. Besides, this method needs lot of laboratory glassware, which makes these procedures extremely expensive and uncomfortable for the operator. There is a need to search for new alternatives to this method, in order to increase laboratory productivity, operator safety and

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comfort, and to drastically reduce reagent consumption and waste production.

Koga *et al*. proposed a reduction in sample size employed for AS determination in water. This modification to the standard method involves the use of 50 mL of water and 5 mL chloroform, and provides a 6-fold increase in laboratory productivity [14]. Another simplified method that reduces the quantities of reagent by using a certain kind of adsorbent has been proposed [15]. However, this method also involves tedious procedures. Other researchers also studied the primary biodegradation of AS in aerobic screening tests, based on the formation of ion-pairs of AS and MB [16].

Flow Injection Analysis (FIA) is a widely accepted and rapidly evolving technique for the determination of AS. Despite significant advantages of FIA compared to batch assays, such as automation of sample preparation, increased sampling rate, easy to handle, low instrumentation costs etc, adoption of FI in an industrial environment for processing and analytical purposes has been hindered by several drawbacks:

1. In certain cases flow manifolds were complicated, involving multi-channeled setups that had to be re-configured in order to apply different “chemistries”.

2. Peristaltic pumps did not provide stable flow on a 24 hr operational basis. The frequent maintenance they required increased the cost of analysis.

3. The continuous flow of reagents. even at low flow rates, produced a considerable amount of waste material in the case of 24 hr process control applications.

These disadvantages were more or less overcome by the introduction of Sequential Injection Analysis (SIA). However, SI suffers from other disadvantages such as:

1. A generally reduced sampling rate in comparision to analogous FI assays.

2. The difficulty in adapting certain FI sub-techniques such as solvent extraction.

3. The need for suitable software to run the SI system.

By early 2006 Assadi and his research group introduced an attractive, high performance and powerful liquid-phase microextraction (LPME) method and named their techniques “Dispersive liquid–liquid microextraction” (DLLME) [17-19]. Beyond the traits of simplicity of operation and rapidity, consumption of the microextraction solvent was reduced to micro-level volume, and samples prepared in this way were more compatible with analytical instruments. These are profitable and attractive features of DLLME as a sample pre-treatment method [20-25].

For highly sensitive, accurate, rapid, and inexpensive measurements with consumption of extraction solvents at micro-level volume, we propose a simplification of the spectrophotometric MB method that can be useful for determining anionic surfactants in aqueous samples. A successive DLLME in combination with fiber optic-linear array detection spectrophotometry (FO-LADS) using a charge-coupled device (CCD) detector allowed the advantageous use of a micro-cell for this purpose.

2. Experimental Procedure

2.1 Reagents and standards

The reagents used in the experiments were of analytical grade: MB (used as a cationic dye), sodium dodecyl sulfate (SDS, employed as a representative anionic surfactant), acetone (disperser solvents), chloroform (microextraction solvent), NaOH, HNO_3 (65%), HCl (37%), acetic acid, and sodium acetate (making buffer solution). All reagents were obtained from Merck (Darmstadt, Germany). Absolute ethanol (> 99.6%) was purchased from Bidestan company (Qazvin, Iran).

The required quantity of SDS was dissolved in pure water to make a standard solution of 1000 mg L^{-1}. The stock solutions of MB (3×10^{-3} mol L^{-1}) were prepared by dissolving appropriate amounts in double distilled water. All plastic and glassware was cleaned by soaking for 24 h in 10% v/v HNO_3. After cleaning, all containers were thoroughly rinsed three times with double distilled water and twice with acetone prior to use. Detergent was not used to clean glassware because it is difficult to remove from surfaces.

2.2. Apparatus and instrumentation setup

The fiber optic-linear array detection spectrophotometer was purchased from Avantes (Eerbeek, Netherlands). It has the advantages of a thermo-electric cooled fast trigger fiber optic spectrometer, 2048 pixel CCD detector, USB/RS232 interface, detector collection lens, 100 µm slit size, UA type gratings, 20 ms integration time and 30 average measurements. The light beam from the UV-Vis source (Deep UV long-life deuterium-halogen light source, 190-2000 nm, TTL shutte) was focused on the sample micro-cell (Starna Scientific, Essex, England, Cat. NO. 16.40F-Q-10/Z15). The micro-cell location is at the adjusted cuvette holder (10 mm path, 2 beams, 4x UV/VIS/NIR collimating lenses and cover). The spectrograph then accepts the light beam transmitted through the optical fiber (600 µm solarization resistance (SR) fiber with Sub Miniature version A terminations) and disperses it via a fixed grating across the 2048 element CCD-linear array detector. Data processing was carried out using Ava software program version 7.3. A Universal EBA 20 centrifuge equipped with an angle rotor (Angle rotor for 8×15 mL tubes, 6000 rpm, Cat. No. 2002) was obtained from Hettich (Kirchlengern, Germany). An

adjustable pipette (10–100 µL) was purchased from Brand (Wertheim, Germany), and all 0.1, 1.0 and 2.5 mL syringes from Hamilton (Reno, NV, USA).

To clean out the micro-cell sufficiently to avoid memory effects, and to improve the repeatability of procedure, it was washed three times with about 2 mL of acetone between each analysis, and dried with a stream of cold air by use of a hair dryer.

2.3. Reference procedure

100 mL of sample was placed into a 250 mL separating funnel and 10 mL of a 1×10^{-3} mol L^{-1} MB solution and 15 mL chloroform were added. After shaking the mixture vigorously for 1 min, the two phases were left to separate and the chloroform layer was taken for analysis. Each sample was extracted additionally two times using 10 mL portions of chloroform. Absorbance measurements were made at 650 nm, followed by an external calibration prepared from SDS. Solutions in the range between 0.1 and 0.5 mg L^{-1} were extracted in the same way as samples.

2.4 Recommended analytical procedure

SDS solutions of a range of concentrations (5.0 mL) were pipetted into a series of screw cap glass test tubes with conical bases. Then 25 µL of 3×10^{-3} mol L^{-1} MB standard solution was added. Then 2.00 mL ethanol (disperser solvent) containing 138 µL chloroform (microextraction solvent) was injected rapidly into the sample solution using a 2.50 mL syringe. This injection produced a cloudy solution, caused by fine droplets of chloroform in the aqueous sample. The phase separation was accelerated by centrifuging at 5500 rpm for 3 min. After this step the dispersed fine droplets of chloroform had settled at the bottom of the aqueous solution in the conical test tube. Subsequent to this procedure, the upper aqueous solution was removed using a long needle connected to a 10 mL injection syringe, which was immersed into the test tube and drawn to leave only 200-300 µL of aqueous phase at the top of the organic layer. The volume of the settled organic phase, determined using a 100 µL microsyringe at 25ºC, was 65±2 µL. 60 µL of this settled phase was removed by micropipette and introduced into the micro-cell. The ordinary absorbance of AS-MB ion-pair in chloroform was measured at wavelength 650.0 nm by means of FO-LADS.

3. Results and Discussion

In order to obtain a high sensitivity, several parameters affecting DLLME were optimized, including the type of microextraction and the disperser solvents as well as their volume, concentration of MB, pH, and the microextraction time.

The enrichment factor (EF) was defined as the ratio of analyte concentration in the settled phase to the initial analyte concentration in the aqueous sample. The analyte concentration in the settled phase was calculated from the calibration graph obtained by the conventional liquid-liquid extraction (LLE)/FO-LADS (extraction conditions: 2.0 mL standard water sample in the concentration range of 4.5×10^{-4} - 1.5×10^{-3} mol L^{-1} of MB and 1.5 - 5.0 mg L^{-1} SDS was extracted with 2.0 mL chloroform).

3.1. Reaction of SDS and MB

The equilibrium between SDS, MB and the distribution of SDS–MB ion-pairs in water and chloroform has been qualitatively reported in the literature [14]. The AS dissolved in water are slightly soluble in chloroform. On the other hand, MB dissolves well in both chloroform and water, providing a blue colored solution in all cases. When pure water is mixed with a chloroform solution of MB the blue color is rapidly transferred to the aqueous phase.

3.2. Effect of ion-pair formation condition parameters

The main factor affecting ion-pair formation of SDS and MB is the concentration of each, but pH and time may also be important. Our attempts were primarily centered on optimizing these parameters under microextraction conditions (DLLME).

In this study, the time required for ion-pair formation was tested between 0 sec - 10 min. The results for ion-pair formation using different reaction times indicated that the reaction time has no effect on ion-pair formation efficiency, and longer time periods did not improve the reaction. To determine the optimal pH for ion-pair formation, several sample pH values ranging from 2.5 – 7.5 were used to test ion-pair formation of AS and MB in 5.0 mL water samples containing 0.04 mg L^{-1} SDS and excess amounts of MB. The highest microextraction efficiency was achieved in the pH range studied. It was found that in alkaline solution MB itself would extract into chloroform, in the absence of any MBAS. In the optimization procedures no buffer solution was used, because the added reagents themselves produced slightly acidic solutions in the desired pH range.

The influence of the MB concentration on ion-pair formation/microextraction efficiency was studied in the range 0 – 2.1×10^{-5} mol L^{-1} with a fixed concentration of SDS at 0.04 mg L^{-1}. While this concentration was varied, the other experimental variables were kept constant. The results showed the microextraction efficiency increasing

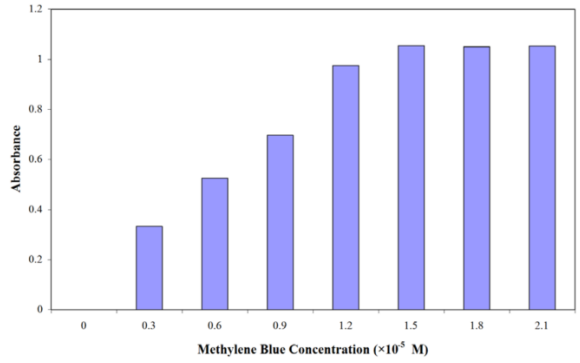

Figure 1. Effect of MB concentration on the absorbance of AS-MB ion-pairs obtained from DLLME. Extraction conditions: volume of water sample, 5.0 mL; volume of disperser solvent (ethanol), 2.00 mL; volume of microextraction solvent (chloroform), 138 µL; SDS amount, 0.04 mg L^{-1}.

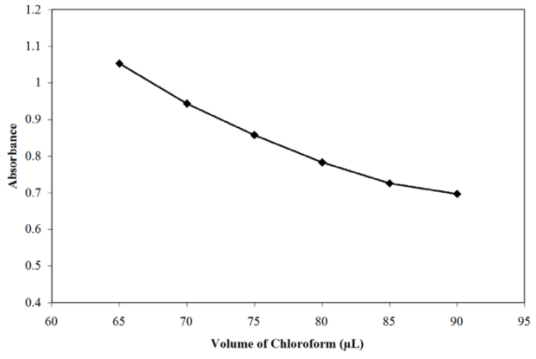

Figure 2. Effect of the volume of chloroform (microextraction solvent) on the absorbance of AS-MB ion-pairs obtained from DLLME. Extraction conditions, as with Fig. 1; concentration of MB, 5.0×10^{-5} mol L^{-1}.

with MB concentration up to 1.5×10^{-5} mol L^{-1} , and then no further variation was observed (as depicted in Fig. 1). Considering the fact that the proposed method is linear up to 0.08 mg L^{-1}, a concentration of 5×10^{-5} mol L^{-1} MB was considered and selected as an appropriate excess amount.

3.3. Influence of microextraction solvent type and volume

It is vitally important to select an appropriate microextraction solvent to achieve high sensitivity in DLLME, so several types and volumes of solvent were studied for optimization. The special characteristics required of a microextraction solvent in DLLME are very low solubility in water, efficient extraction of compounds of interest, and it should be much denser than water. Chloroform and carbon tetrachloride are the most commonly used microextraction solvents in DLLME. During our preliminary studies we found that carbon tetrachloride is not capable of extracting the ion-pair of SDS-MB at all. Moreover, the recommended solvent in standard methods is chloroform; therefore, it was our primary choice.

To investigate the effect of microextraction solvent volume, experiments were performed by using 2.00 mL ethanol containing different volumes of chloroform (138, 143, 148, 153, 158 and 163 µL). With the increase in volume of chloroform from 138 to 163 µL, the volume of the settled phase increases approximately from 65 to 90 µL. The results (Fig. 2) show that absorbance decreases with increasing volume of chloroform; it is clear that by increasing the volume of chloroform the volume of the settled phase increases. Consequently, at low volumes of microextraction solvent, high absorbance and enrichment factor were obtained.

3.4. Influence of the disperser solvent kind and volume

In DLLME selecting an appropriate disperser solvent is important since the disperser solvent should be miscible with both microextraction solvent and the aqueous sample. Two rather safe and convenient disperser solvents, acetone and ethanol, were studied to see which was more suitable. A series of sample solutions was studied using 2.00 mL of each disperser solvent containing 138 µL of chloroform and the enrichment factors were determined. The results showed that ethanol had a much better efficiency than acetone (enrichment factor of 75 and 17, respectively). Lower toxicity and higher microextraction efficiency of ethanol made it the better choice.

After choosing ethanol as the disperser solvent it was necessary to optimize the volume to be used. The influence of the disperser solvent (ethanol) volume on the microextraction efficiency was tested over the range of 0.50 – 2.00 mL, but the variation of the ethanol volume (disperser solvent) caused changes in the settled phase volume. Hence, it was impossible to consider independently the influence of the ethanol volume on microextraction efficiency in DLLME. To avoid this problem and in order to attain a constant volume of the settled phase, the ethanol and chloroform volumes were changed simultaneously. The experimental conditions were fixed and included the use of different ethanol volumes: 0.50, 1.00, 1.50, and 2.00 mL, containing 97, 102, 121, and 138 µL of chloroform, respectively. Under these conditions the settled phase volume remained constant (65 ± 2 µL). Fig. 3 shows the curves for absorbance of SDS-MB ion-pair versus the volume of ethanol. The absorbance increased when the ethanol volume increased from 0.50 to 2.00 mL as the disperser solvent. As these results suggest, 2.00 mL ethanol was chosen as the

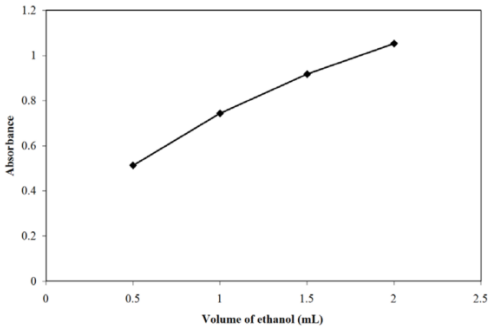

Figure 3. Effect of the volume of ethanol (disperser solvent) on the absorbance of AS-MB ion-pairs obtained from DLLME. Extraction conditions, as with Fig. 1; concentration of MB, 5.0×10^{-5} mol L^{-1}.

optimum disperser solvent volume.

3.5. Influence of microextraction time

Microextraction time (time interval from injection of a mixture of disperser solvent and microextraction solvent before starting to centrifuge) is an important factor that may affect microextraction efficiency of analytes from aqueous phase to organic phase. The variation for microextraction efficiency of SDS-MB as a function of microextraction time was studied in the range of 5 sec - 10 min. The results indicate that microextraction time has no significant effect on microextraction efficiency for the target compound. After formation of the cloudy solution the contact area between the microextraction solvent and the aqueous phase was extremely large, allowing the extraction equilibrium to be established very fast. In this method the most time-consuming procedure was centrifugation of the sample solution in the microextraction procedure, which took about 3 min. Considering the fact this period of time (3 min) is for eight test tube samples (microextraction vessels), the time required per sample is less than 25 seconds.

3.6. Analytical characteristics of the method

To evaluate the practical applicability of the proposed DLLME/FO-LADS technique for determination of MBAS in water samples, several analytical performance characteristics such as enrichment factor, linearity, limit of detection (LOD) and repeatability were determined using the optimized conditions. The calibration curve was linear in the range of 0.06×10^{-1} – 0.8×10^{-1} mg L^{-1} of SDS with a correlation coefficient (r) of better than 0.99.

The LOD, defined as $C_L = 3\ S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 2 μg L^{-1}. The repeatability of the proposed method expressed as relative standard deviations (RSDs, n=7) was found to be 4.5 and 3.6% for the concentration of 0.03 and 0.07 mg L^{-1}, respectively. The enrichment factor was found to be 75 for SDS.

3.7. Effect of diverse ions and application to practical samples

Any organic or inorganic compound that will form a chloroform extractible ion-pair with MB will interfere, producing high results. These positive interferences include; organic sulfonates, carboxylates, phosphates, and phenols, as well as inorganic cyanates, chlorides, nitrates, and thiocyanates. On the other hand, any compound effectively competing with MB to form an AS ion-pair will give low results. These negative interferences caused by some amines have analytical significance in the case of quaternary ammonium compounds. For pre-treatment of MBAS in all waters and waste waters that contain interfering substances, the following procedure is recommended in the ASTM reference method.

The selected sample is hydrolysed by boiling under partial reflux with hydrochloric acid. The residual products are neutralized to a controlled pH value and reacted with 1-methylheptylamine. Resulting ion-pairs are extracted into a chloroform phase and evaporated to dryness on a steam bath. The amine component of the ion-pair is removed by boiling it in an aqueous alkaline medium and the isolated MBAS are then determined under the described reference procedure.

Other researchers have also examined the effects of a wide variety of ions on the determination of AS by a similar method [14,6].

In order to establish the validity and applicability of the proposed method, it was applied to the determination of AS in several real water samples (mineral, tap, and well) by the proposed method. For this purpose 5.0 mL of each sample was pre-concentrated using the previously described DLLME technique (pH was adjusted with acetic acid/sodium acetate buffer if necessary). In order to assess matrix effect the standard addition method was applied for the determination of AS (at spiking levels of 0.02 and 0.05 mg L^{-1}) in spiked real samples, whose relative recoveries of analytes are included in Table 1. The results obtained were compared with those obtained from spiked distilled water. In all cases the spike recoveries confirm the reliability of the proposed method. The results obtained for relative recovery indicate that the matrix does not influence the microextraction efficiency in these samples (no serious interferences), There was, therefore, no need to remove interferences. As seen in Table 2 the proposed method shows distinct

Table 1. Determination of AS in mineral, tap, and well water samples, and relative recovery of spiked AS in these samples

Sample	Added AS / mg L^{-1}	Found AS Mean ± SD [a] / mg L^{-1}	Relative recovery / %
Mineral water [b]	0	n.d [e]	-
	0.03	0.028 ± 0.002	93
	0.07	0.068 ± 0.005	97
Tap water [c]	0	n.d [e]	-
	0.03	0.028 ± 0.003	93
	0.07	0.067 ± 0.004	96
Well water [d]	0	n.d [e]	-
	0.03	0.028 ± 0.003	93
	0.07	0.067 ± 0.005	96

[a] standard deviation (n = 3).
[b] bottled natural mineral water
c From drinking water system of Tehran, Iran
[d] From campus
[e] Not detected.

Table 2. Comparison of DLLME/FO-LADS with other extraction methods coupled to spectrophotometry for determination of AS in water

Method	Sample Consumption / mL	Extraction solvent volume / mL	[a] RSD / %	[b] LOD / mg L^{-1}	Linear dynamic range / mg L^{-1}	Reference
LLE	50	5	<7.5	<0.02	0.02-0.5	[14]
LLE	5	4	-	<0.22	0.22-2.5	[16]
Official method	100	35	<7.2 [ref. 14]	<0.03	0.03-1.5	[12]
DLLME/FO-LADS	5	0.138	<4.5	0.002	0.006-0.08	[As optimized in this study]

[a] RSD, relative standard deviation.
[b] LOD, limit of detection.

performance advantages over other methods, with reference to sample volume, extraction solvent volume, RSDs, LODs and linear dynamic ranges.

4. Conclusion

This study demonstrates that the DLLME procedure offers a reference method with attractive and robust characteristics for assay of AS. It uses very small amounts of microextraction solvent and it is also low in cost. Moreover, the new DLLME procedure in combination with FO-LADS equipped with charge-coupled device (CCD) detector and using a micro-cell demonstrated that LPME (DLLME) in combination with a spectrophotometer system could be used for micro-level sample volumes, without any dilution or decrease in sensitivity. Analysis of several real samples for AS content illustrated the accuracy, reliability, simplicity, reliability and cheapness of the method. It appears to be a time-saving technique, useful for laboratories needing to analyse a large number of samples with a rapid reporting time. Also we suggest that this method could be applied to monitoring the biodegradation of AS.

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