Fresenius J Anal Chem (1992) 342:711–713

Fresenius' Journal of

Trace analysis of cationic surfactants in water using HPLC with conductometric detection

L. Nitschke, R. Müller, G. Metzner, and L. Huber

Bayerische Landesanstalt für Wasserforschung, Kaulbachstrasse 37, W-8000 München 22, Federal Republic of Germany

Received February 22, 1991

Summary. A simple and fast determination of trace amounts of commercially used cationic surfactants is described. After extraction from water cationic surfactants are separated by HPLC and detected by conductometry. The detection limit is 3 µg/l for distearyldimethylammonium chloride, 16 µg/l for ditallowimidazolinium methosulphate, and 6 µg/l for dodecylpyridinium chloride.

Introduction

Cationic surfactants are organic substances containing a positive charged heteroatom (e.g. N, P, or S) and at least one long-chain alkyl group. Only quaternary ammonium compounds are of commercial importance. They are used as fabric softeners, biocides, and phase transfer catalysts [1]. Today distearyldimethylammonium chloride (DSDMAC) is still the most important compound on the market with approximately 80% followed by alkylimidazolines (20%). Via sewer systems and waste water treatment these substances are discharged to surface water depending on the degree of their elimination. Hence, cationic surfactants can influence the ecological balance in aquatic systems [2]. A recent publication outlined the necessity to investigate more intensely the effect of cationic surfactants on higher aquatic organisms [3]. In this context the need for reliable analytical methods is obvious.

In Germany there is a standardized method to determine cationic surfactants in water [4]. After forming an ion pair of the cationic surfactants with disulphine blue a colorimetric detection is used. Beside problems with matrix effects and adsorption this determination is not specific for single compounds [5]. Hence, this method is not able to differentiate between various cationic species. This is not always satisfactory in the case of trace analysis. A separation technique is necessary if a special cationic surfactant is to be determined. HPLC could be an adequate technique to solve this problem.

Many quaternary ammonium compounds are non-UV absorbing substances, hence a direct photometric detection is not possible. With ion-pair HPLC this drawback can be avoided by using a light absorbing or fluorescent anion [6]. An alternative technique is to apply a conductometric detection due to ionic properties of the ionic surfactants. Small et al. [7] used the latter detection method for a qualitative and quantitative analysis of quaternary ammonium compounds after separation by ion-exchange chromatography for the first time. Wee and Kennedy [8] described a separation technique with conductometric detection for quaternary ammonium compounds. Their technique is characterized by eliminating the use of suppressor columns, separation without ion pairing, utilization of non-aqueous medium, and a detection limit of 0.2 µg/l quaternary ammonium compounds in environmental samples. A similar procedure was used by Klotz [9]. The technique developed by Wee and Kennedy was tested with the two commercially important cationic surfactants and one disinfectant (N-dodecylpyridinium chloride) and modified to adapt it to routine analysis in our laboratories to measure the concentration of test substances biodegradation.

Offprint requests to: L. Nitschke

Experimental

Chemicals

Commercially available products containing quaternary ammonium compounds with relatively high purity were used. Präpagen WK (74.8% distearyldimethylammonium chloride) was obtained from Hoechst, Frankfurt/M. Ditallowimidazolinium methosulphate was obtained from Rewo, Steinau an der Straße. N-dodecylpyridinium chloride (90%) was obtained from Merck-Schuchard, Hohenbrunn. The sodium dodecylbenzenesulphonate was of commercial grade (Fluka, Buchs) and the methylene chloride was of reagent grade (Merck). Methanol and chloroform (Merck) were of LiChrosolv quality.

Apparatus

Two HPLC pumps (Kontron 420) were used. The injection valve was fitted with a 100 µm loop. The conductometric detector (Sykam S 3110) was connected with an integrator (Hewlett Packard HP 3390A). Two 250 mm Partisil PAC columns (Latek; particle size 5 and 10 µm, respectively) were used for separation.

Procedure

A 100 ml up to 500 ml water sample is adjusted with hydrochloric acid to pH 1. A sodium dodecylbenzenesulphonate

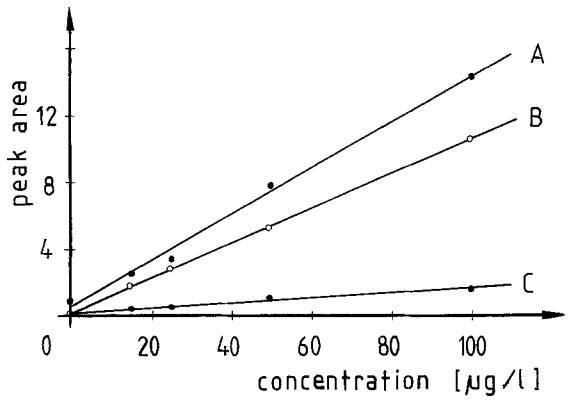

Fig. 1. Calibration plots for DPC (*A*), DSDMAC (*B*), and DTIM (*C*)

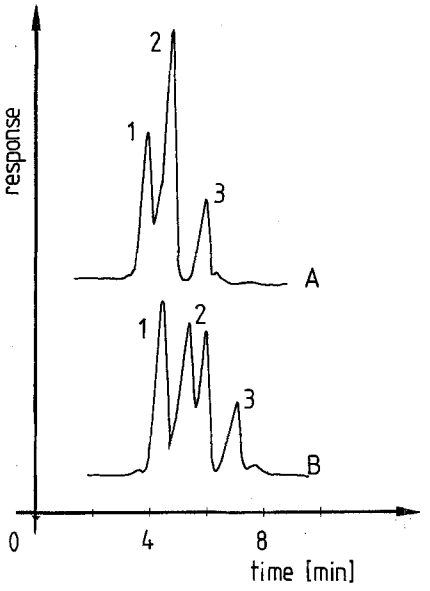

Fig. 2. Chromatograms of an extracted water sample with an original content of 0.25 mg/l of DSDMAC (*1*), 1.5 mg/l DTIM (*2*), and 0.1 mg/l DPC (*3*) after separation with a 10 µm particle size column (*A*), and a 5 µm particle size column (*B*). Eluent: chloroform:methanol (80:20). Flow rate: 0.5 ml/min

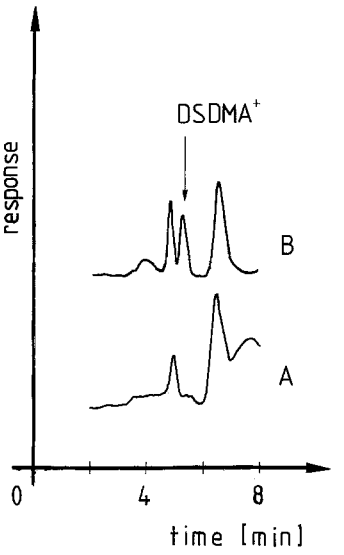

Fig. 3. Chromatogram of a 200 ml surface water sample (*A*) and after adding 50 µg/l DSDMAC (*B*). Eluent: chloroform:methanol (80:20). Flow rate: 0.5 ml/min

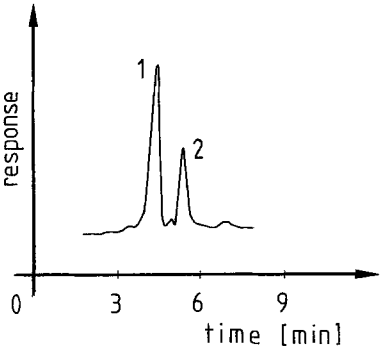

Fig. 4. Chromatogram of DSDMAC (*1*) and naphthyl-1-amine (*2*), each 1 mg/l in water. Eluent: chloroform:methanol (80:20). Flow rate: 0.5 ml/min, 5 µm particle size column

solution is added to a final concentration of 2 mg/l. The conditioned sample is extracted with three 50 ml portions of methylene chloride. After each extraction the methylene chloride extract is evaporated to dryness to minimize the size of evaporation equipment. Then the residue is redissolved in chloroform:methanol (80:20) to a final volume of 10 ml. HPLC separation is carried out with the same mixture of chloroform:methanol (80:20).

Results and discussion

Calibration plots are given in Fig. 1 for small amounts of N-dodecylpyridinium chloride (DPC), distearyldimethylammonium chloride (DSDMAC), and ditallowimidazolinium methosulphate (DTIM) in water. Extraction from 200 ml water and determination were conducted as described. The calibration plots are linear up to the mg/l-range. The resulting 3σ detection limits are: 6 µg/l for DPC, 3 µg/l for DSDMAC, and 16 µg/l for DTIM.

The reproducibility of the analytical results was tested by accomplishing extractions of three 200 ml water samples each containing 20 µg N-dodecylpyridinium chloride. Four determinations were conducted in parallel with every sample. A standard deviation of 4.5% was obtained. This indicates a reasonable reproducibility.

The efficiency of the extraction procedure was tested. A 200 ml water sample containing 100 µg/l DSDMAC was extracted three times with 50 ml methylene chloride as described. The residue was redissolved in 10 ml chloroform:methanol (80:20). The obtained area of the signal peak was 98.1% in comparison with the peak of a 2 mg/l solution of DSDMAC in the same chloroform:methanol solvent.

Figure 2 presents chromatograms of the three surfactants after their extraction from bidistilled water. When working with a 10 µm particle size column, the peaks of DSDMAC and DTIM are poorly resolved. A better resolution can be obtained by increasing the quantity of chloroform in the

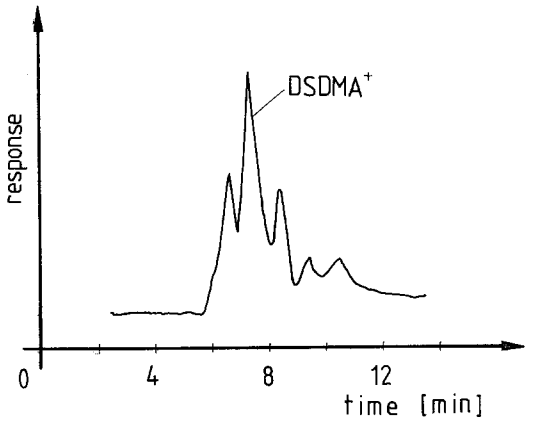

Fig. 5. Chromatogram of raw municipal waste water. Eluent: chloroform:methanol (80:20). Flow rate: 0.3 ml/min, 5 µm particle size column

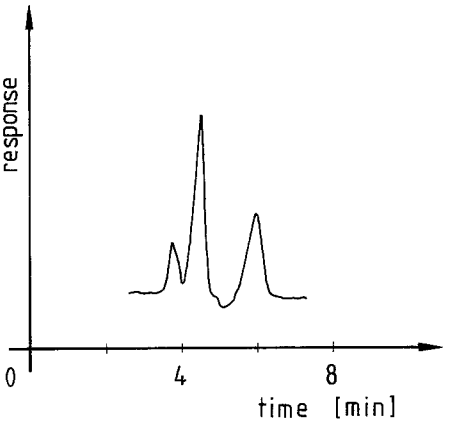

Fig. 6. Chromatogram of 10 mg/l ditallowesterammonium methosulphate (without extraction). Eluent: chloroform:methanol (80:20). Flow rate: 0.5 ml/min, 10 µm particle size column

chloroform/methanol eluent. Wee and Kennedy used a 92:8 ratio of chloroform and methanol [8]. In our experiments sensitivity decreased rapidly when the methanol content was below 20% in the eluent. A possibility to obtain a better resolution could be the use of a 5 µm particle size column. When applying a 5 µm column the single peak of ditallowimidazolinium methosulphate was split into two peaks. The long-chain alkyl groups of DTIM have various chain lengths due to the application of tallow in the production of DTIM. Tallow alkyl chain groups consist mainly of C_{16} and C_{18} species. This could explain the existence of two peaks when a 5 µm columns is used.

Figure 3 presents chromatograms of a clean surface water sample and an identical sample after adding DSDMAC (final concentration 50 µg/l). The content of DSDMAC in the original sample is below the detection limit, but other peaks are visible. Due to ion pair formation in acid solution, various organic substances (e.g. amides) are extracted. They might change the conductivity in the eluent after separation. In Fig. 4 an example of this phenomenon is shown. Besides the signal of DSDMAC a peak of naphthyl-1-amine was observed. Especially waste water samples contain high quantities of various substances being able to interfere with conductometric signals of cationic surfactants. Hence, the analysis of cationic surfactants in waste water can be difficult. Four unidentified peaks were occurring beside the peak of DSDMAC in a chromatogram of untreated municipal waste water (Fig. 5). In this example the signal of DSDMAC is satisfactorily resolved from interfering substances.

Additional investigations were conducted with "Esterquats". These substances replace DSDMAC in the future. Esterquats are quaternary ammonium compounds containing long-chain ester groups. The analysis of these substances seems to be more difficult. For example, by HPLC separation as described and conductometric detection of ditallowesterammonium methosulphate three peaks are obtained (Fig. 6). The reason for this phenomenon could be the different number of ester groups in the molecules.

Conclusions

A simple and rapid procedure for the determination of commercially used cationic surfactants is described. Time for extraction and conductometric detection after HPLC separation takes less than one hour.

In cases of waste water analysis where poorly resolved signals are obtained, the parameters of analysis have to be changed. A 5 µm particle size column must be used and the flow rate should be decreased. The chloroform:methanol ratio could be changed to a higher chloroform content with the disadvantage of a decreasing sensitivity and an increasing time of analysis.

The main advantage versus the disulphine blue method is that single cationic surfactant species can be determined at very low concentrations.

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