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Short communication

Determination of a non-ionic surfactant by solid-phase microextraction coupled with high-performance liquid chromatography and on-line derivatization

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Abstract

Solid-phase microextraction coupled with high-performance liquid chromatography (SPME–HPLC) and fluorescence detection was used to determine an alcohol ethoxylate (Brij 56) and 1-hexadecanol in water samples. Determinations were achieved by extraction with polydimethylsiloxane–divinylbenzene (PDMS–DVB) SPME fibers and pre-column derivatization with 1-naphthoyl chloride in the presence of 4-(dimethylamino)pyridine (DMAP) as catalyst. Variables such as time of reaction and concentration of surfactant in water were evaluated. The limit of detection of the method was found to be 0.1 mg/l of Brij 56.

Keywords: Derivatization, LC; Solid-phase microextraction; Surfactants; Alcohol ethoxylates

1. Introduction

Non-ionic surfactants are used worldwide as defoamers, emulsifiers and in some pesticide formulations. In 1994, the consumption of surfactants in United States, Western Europe and Japan was estimated to be five million metric tons. An estimated 500 000 tons per year of alkyl phenol ethoxylates (APEOs) are currently used worldwide [1]. However, due to their poor biodegradability their use will be phased out by the year 2000 [2]. As a result, alcohol ethoxylates (AEs) will be the most important surfactants used [3].

Analysis of non-ionic surfactants has been well documented [2,4,5]. Extraction of surfactants from aqueous solutions is achieved by solvent sublation, liquid–liquid extraction, solid-phase extraction, precipitation, dialysis or solid-phase microextraction (SPME) [6].

Non-ionic surfactants may be detected by refractive index detection [7], flame ionization detection or evaporated light scattering detection (ELSD); however poor sensitivity is obtained in all cases. The presence of the benzene ring in the APEO allows detection by UV absorbance and by fluorescence detection [8]. In contrast AEs require derivatization prior to detection by UV or fluorescence. Our aim is to determine non-ionic surfactants by SPME–high-performance liquid chromatography (HPLC) using fluorescence detection.

A review of derivatization procedures is given by Marcomini and Zanette [4]. Nozawa and Ohnuma [9]

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used 3,5-dinitrobenzoyl chloride on a large scale; no limit of detection was reported. A reasonable limit of detection (0.05 mg/l) was obtained by using a polyaromatic derivatizing compound such as 1-anthroylnitrile [10], which unfortunately is not commercially available. The limit of detection using 1-naphthoyl isocyanate (NIC) was 5 ng and with 1-naphthoyl chloride (1-NC) was 10 ng.

SPME–HPLC was first used to analyze polycyclic aromatic hydrocarbons [11] and alkyl ethoxylate surfactants [6]. A review is given by Eisert and Pawliszyn [12]. Derivatization–SPME–gas chromatography (GC) has been described for polar analytes such as carboxylic acids [13,14], haloacetic acids [15] and phenols [16]. So far, derivatization–SPME–HPLC has not been reported. The aim of this work was the determination of AEs (Brij 56) in water samples by means of derivatization–SPME–HPLC with fluorescence detection. For this purpose, in fiber on-line derivatization of the alcohols with 1-NC was performed.

2. Experimental

2.1. Instrumentation

The HPLC system consisted of a Varian 9050 autosampler, a Varian 9010 gradient pump and a Linear Instruments LC 304 fluorescence detector. The system was coupled to the SPME–HPLC interface (Valco valve, internal volume 60 μl, Supelco, Bellafonte, USA) by connecting the autosampler valve (valve 1) in series with the SPME–HPLC system (Fig. 1). In order to avoid overloading the detector with an excess of reagent, a three-port valve (valve 3) was placed between the column and the detector. This valve was opened at the beginning of the HPLC run to allow excess reagent to be discarded.

An ODS-Zorbax column (250 mm×4.6 mm, 5 μm particle size) and an ODS-Zorbax guard column (4.6 mm×1.25 cm) were used. The elution program was as follows; 60% A for 10 min, ramped to 95% A

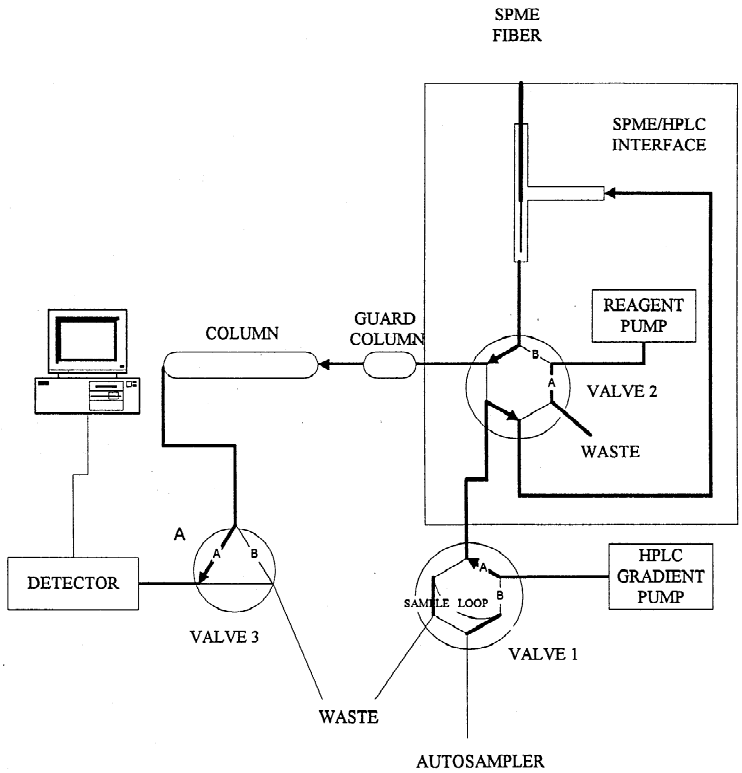

Fig. 1. SPME–HPLC with on-line derivatization system schematic.

at 10 min and 95% A thereafter. Phase A was methanol and phase B was water–acetonitrile (30:70). The flow-rate was 2.0 ml/min. Detection was at λ_{ex}=228 nm and λ_{em}=366 nm.

2.2. Materials

Brij 56 [$C_{16}H_{33}(OCH_2CH_2)_{10}OH$], 1-hexadecanol, 1-NC and DMAP were obtained from Aldrich (Milwaukee, WI, USA) and used as received. All solvents used were HPLC-grade or better. Deionized water was used in all aqueous samples. SPME fibers (60 μm film thickness polydimethylsiloxane–divinylbenzene; PDMS–DVB) were purchased from Supelco (Bellafonte, PA, USA) and conditioned by successively immersing them for 1 h in 4 ml of stirred acetonitrile, methanol and mobile phase B. Stock standards were prepared by weighing the appropriate standards (1-hexadecanol or Brij 56) and dissolving in pyridine, water or acetone.

2.3. Derivatization

2.3.1. Reaction in organic solvent

Derivatization reactions were first tested on a relatively large scale in organic solvents. Solutions of nominal concentrations of 68 g/l of Brij 56 or 24 g/l of 1-hexadecanol were placed in round bottom flasks and approximately 0.01 g of DMAP was added to each followed by the equivalent of a 4:1 molar ratio of 1-NC to active hydrogen. The solutions were stirred at 80°C for 24 h. Aliquots were taken at 1, 5, 15, 30, 60 min and 24 h and diluted with acetonitrile. The solutions were injected (20 μl) into the HPLC system. Derivatization was carried out in the presence of DMAP at 22, 36 and 80°C and for 1-hexadecanol in the absence of DMAP at 80°C as well. Product formation was confirmed by GC–mass spectrometry (MS).

For external calibration, aliquots of Brij 56 solution in acetone were made in the concentration range from 0.2–500 mg/l. Five hundred μl of a pyridine solution containing 2.5 mg 1-NC and 0.5 mg DMAP were added to each vial, and the reaction was allowed to take place at 80°C for 2 h. Five hundred μl of acetonitrile were added to each vial, the solutions were injected into the HPLC system.

2.3.2. SPME–derivatization in the interface (on-line derivatization)

Solid-phase microextractions were performed by exposing the fiber to stirred solutions of Brij 56 (6.0 ml) for 1 h. The fiber was then air-dried in the headspace for 5 min and transferred to the SPME–HPLC interface previously filled with a pyridine solution containing 500 mg/l of each DMAP and 1-NC; this solution was delivered by means of an HPLC pump connected to valve 2 in position B. After reaction, valve 2 was switched to position A for 2 min to inject the sample and valve 3 to position B for the first 5 min to reject excess derivatizing reagent. Experiments to determine the effect of reaction time were performed by analyzing 10 mg/l solutions of Brij 56 in deionized water.

In order to study product formation as a function of concentration, aqueous solutions containing 0–10 mg/l of Brij 56 were extracted for 60 min and derivatized for 30 min.

The dependence of adsorption and derivatization processes of Brij 56 on the concentration of 1-hexadecanol was evaluated. Aliquots of 100 mg/l of 1-hexadecanol in acetone were transferred to 7-ml vials to give a final concentrations of 0–100 mg/l; the acetone was evaporated by blowing nitrogen. 6.0 ml of 10 mg/l Brij 56 was added to each vial, and the solutions were mixed for 5 min. Extractions and on-line derivatization were performed as described above.

3. Results

3.1. Derivatization

3.1.1. Derivatization reaction in organic solvents

The presence of DMAP improved the yield of the reaction of 1-hexadecanol by four-fold at 80°C. Moreover, the yield of derivative obtained at 80°C without DMAP was similar to those obtained at 36°C and 22°C with DMAP (Fig. 2). Significant product was obtained after 1 min and did not increase after 5 min (22 and 36°C). The same trend was observed for Brij 56. In spite of the greater yield obtained at 80°C with DMAP, reactions in the SPME–HPLC interface were performed at room temperature so that no heating device was required.

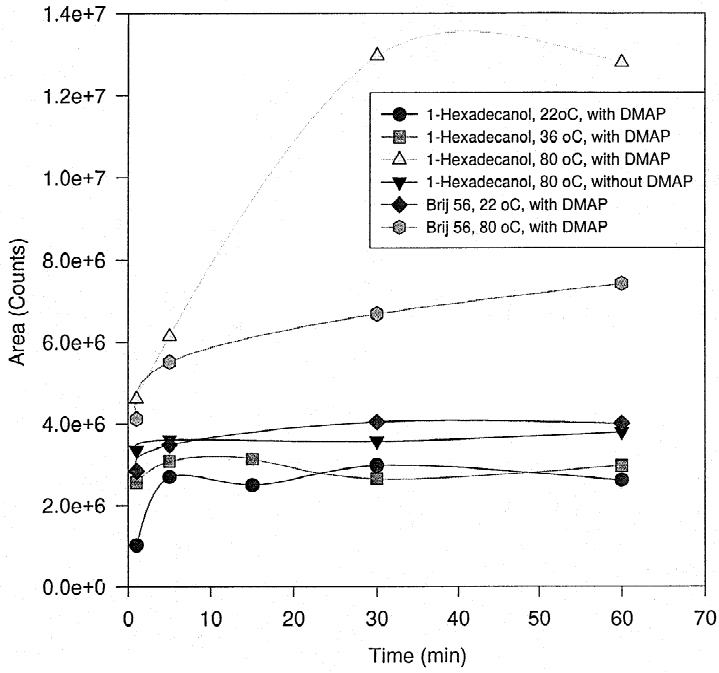

Fig. 2. Derivatization of 1-hexadecanol and Brij 56 with 1-NC as functions of time and temperature.

3.1.2. SPME–HPLC derivatization

Derivatization after extraction was chosen in this work for various reasons. The poor resistance of the fiber towards 1-NC prevents simultaneous derivatization and extraction. Due to the low vapour pressure of alcohol ethoxylates or their esters, headspace extraction is difficult to perform. However, the desorption chamber in the SPME–HPLC interface allows a static desorption and pre-column derivatization. The chosen scheme was therefore extraction of the analytes from water using the SPME fiber, followed by derivatization and desorption of the derivative in the SPME–HPLC chamber.

The partition coefficients of both Brij 56 and its derivatives from the pyridine to the fiber are small; therefore the reaction is more likely to occur in the pyridine and not on the fiber. This necessitated an excess of 1-NC in the pyridine, which would overload the detector. The addition of valve 3 partially solved the problem by allowing diversion of the early-eluting 1-NC to waste.

Reaction in organic solvent showed that the esterification reaction proceeds at room temperature, and that the product could be obtained even after 1 min. However, extractions of 10 mg/l of Brij 56 from water followed by reaction in the SPME–HPLC desorption chamber failed to produce detectable product after 1 min. Better results were obtained by increasing the time of reaction up to 30 min (Fig. 3). Therefore, experiments were performed as follows; time of extraction 60 min (with stirring), time of reaction 30 min.

The linearity of the method was determined by extracting Brij 56 from water over the range of 0.1 to 10 mg/l. The correlation coefficient was 0.991. The excess of 1-NC was added to the baseline (Fig. 4) having a negative effect on the limit of detection (0.1 mg/l) and linear dynamic range (two orders of magnitude). Moreover this may also be responsible for the somewhat broad peaks observed, due to modification of the HPLC stationary phase. The sensitivity of this method depends on several equilibria such as partitioning of the analyte onto the fiber, desorption of the analyte into pyridine and finally reaction of the analyte with 1-NC in the presence of DMAP. Our results indicate that the latter is the limiting factor in this method. 15–20% of the Brij 56 present in water is extracted by the PDMS–DVB

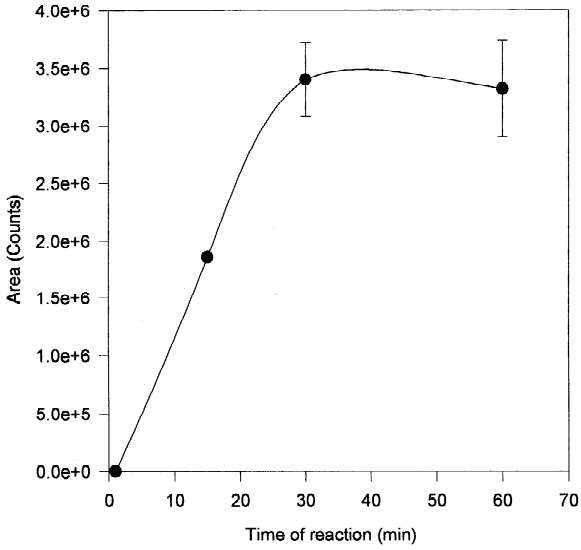

Fig. 3. Effect of derivatization reaction time on detector signal.

fiber (as shown by SPME–HPLC of Triton X-100 without derivatization) but only about 1% was converted to the derivative in these experiments. Better results could be obtained by heating the desorption chamber although deterioration of the fiber could be expected. The precision obtained from three replicates was 15%.

3.1.3. Effect of alcohol concentration on on-line derivatization

Enhancement of the solubility of non-polar compounds in water by surfactants has been documented [17,18]. Thus, we might expect that non-polar compounds may have an effect on the adsorption properties of surfactants, and so the amount of surfactant extracted could vary as the concentration of 1-hexadecanol varies. Indeed, the presence of 1-hexadecanol decreased the amount of Brij 56 extracted and derivatized (Fig. 5). This may occur as a result of increased solubility of the Brij 56 in water containing 1-hexadecanol, or decreased solubility in the PDMS–DVB fiber containing 1-hexadecanol. In either case, it is important to note the dependence of the results on the presence of surfactants in the water sample.

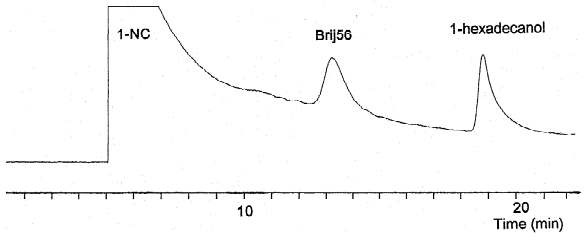

Fig. 4. Chromatogram of the 1-NC derivatives obtained by on-line derivatization of Brij 56 and 1-hexadecanol (10 mg/l each).

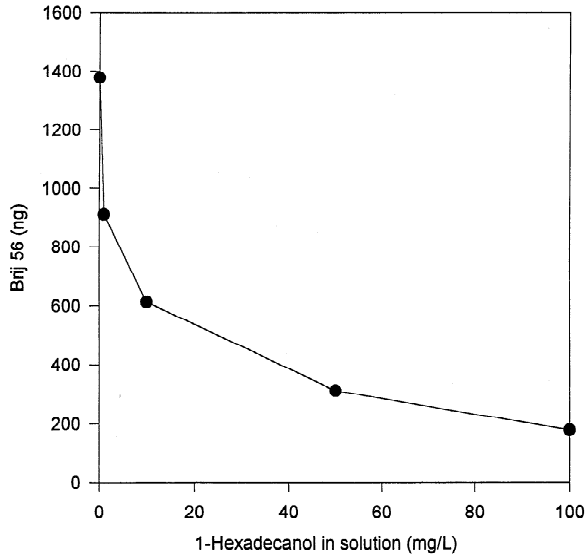

Fig. 5. Extraction of Brij 56 as a function of 1-hexadecanol concentration. Extraction with PDMS–DVB fiber for 60 min. On-line derivatization, reaction took place for 30 min. Desorption 2 min.

4. Conclusions

Analysis of Brij 56 was achieved by SPME followed by on-line derivatization–fluorescence detection. The high limit of detection (0.1 mg/l) and narrow linear dynamic range (two-orders of magnitude) are caused by a low esterification reaction yield and chromatographic problems due to the excess of derivatizing reagent. However it is evident that SPME–HPLC with on-line derivatization can be done.

This is a promising method that opens possibilities in the analysis of primary alcohols and other compounds requiring derivatization for detection. The main problem at present is deterioration of the fibers. Detection limits could be improved by the use of

fibers which are resistant to attack by the 1-NC. We are currently developing such fibers in our laboratory which should allow optimization with respect to temperature and choice of derivatizing agent.

The extraction–derivatization of Brij 56 is inversely proportional to the amount of 1-hexadecanol present in the sample. This is important to consider when environmental samples are analyzed, since it indicates the adsorption of the analyte onto the fiber is influenced by the presence of other compounds.

Acknowledgements

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References

[1] R. Renner, Environ. Sci. Technol. 31 (1997) 316A–320A.
[2] A.T. Kiwiet, P. de Voogt, J. Chromatogr. A 733 (1996) 185–192.
[3] E. Matthijs, E.C. Hennes, Tenside Surf. De. 28 (1991) 22–27.
[4] A. Marcomini, M. Zanette, J. Chromatogr. A 733 (1996) 193–206.
[5] W. Miszkiewicz, J. Szymanowski, Crit. Rev. Anal. Chem. 24 (1996) 203–246.
[6] A. Boyd-Boland, J.B. Pawliszyn, Anal. Chem. 68 (1996) 1521–1529.
[7] P.L. Desbène, F.I. Portet, G.J. Goussot, J. Chromatogr. A 730 (1996) 209–218.
[8] M.S. Holt, E.H. McKerrell, J. Perry, R.J. Watkinson, J. Chromatogr. 362 (1986) 419–424.
[9] A. Nozawa, T. Ohnuma, J. Chromatogr. 187 (1980) 261–263.
[10] M. Kudoh, H. Ozawa, S. Fudano, K. Tsuji, J. Chromatogr. 287 (1984) 337–344.
[11] J. Chen, J.B. Pawliszyn, Anal. Chem., 67 (1995) 2530–2533.
[12] R. Eisert, J. Pawliszyn, Crit. Rev. Anal. Chem. 27 (1997) 103–135.
[13] L. Pan, M. Adams, J. Pawliszyn, Anal. Chem. 67 (1995) 4396–4403.
[14] L. Pan, J. Pawliszyn, Anal. Chem. 69 (1997) 196–205.
[15] B. Aikawa, R.C. Burk, Int. J. Environ. Anal. Chem. 66 (1997) 215–224.
[16] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160–167.
[17] D.E. Kile, C.T. Chiou, Environ. Sci. Technol. 23 (1989) 832–838.
[18] C.T. Jafvert, P.L. Van Hoof, J.K. Heath, Water Res. 28 (1994) 1009–1017.