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PTFE capillary trap as a tool to monitor non-ionic surfactants in the aquatic environment

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Abstract

A method based on the separation of non-ionic surfactants (NS) in the PTFE capillary trap with final determination by the indirect adsorptive stripping tensammetry has been developed. The method is suitable for NS determination in river water, raw and treated sewage within the range of 2–10,000 μg l^{-1}. The sample volume varies between 0.1 and 50 ml depending on NS concentration, and the time necessary for a single determination is approximately 15 min. This is several orders of magnitude better than determination with the recommended BiAS method. In environmental samples, recoveries ranges from 81 to 95% and precision ranges from 3 to 10%.

Keywords: Non-ionic surfactant determination; Environmental samples; Indirect adsorptive stripping tensammetry; PTFE capillary trap

1. Introduction

Little attention is currently paid to the monitoring of non-ionic surfactants (NS) in the aquatic environment, despite the fact that NS are a major source of synthetic organic carbon discharged into surface water, mostly due to applications in the formulation of washing powders, liquids, tablets, etc. [1]. Generally, washing powders contain non-ionic surfactants and a mixture of anionic and non-ionic surfactants is common in washing powder formulation: 10–25% of surfactants are used. Liquid detergents contain more surfactants: 7–25% of anionic surfactants and 6–30% of non-ionic surfactants [2]. Surprisingly, non-ionic surfactants are not monitored or, at least, the results are unpublished. NS concentration in the River Rhine and its main tributaries was published until 1980. Therefore, the exception is the River Warta in Poznan where NS have been monitored since 1990 and the results are published [3]. These results (concerning the period 1991–2000), supplemented with the recent results, are shown in Fig. 1. The picture exhibits a very complex pattern with a declining tendency during recent years. However, the reasons for growth both over the period 1991–2001, as well as the decline during recent years are not known. It is necessary to stress that NS concentration reached 500 μl^{-1} in industrial regions along the River Warta. The conclusion is that NS should be strictly monitored.

The question arises as to why non-ionic surfactants remain unmonitored? This surprising fact seems to be caused by the relatively low toxicity and good biodegradability of NS, lack of visible symptoms of the presence (such as foam), as well as difficult, time-consuming and expensive NS analysis. Generally, the opinion concerning the easy biodegradability of NS is exaggerated; it is justified only when primary biodegradation is taken into account.

NS determination with the recommended methods (BiAS, CTAS) is expensive, mostly due to time-consuming procedures and high reagent costs [4]. The development of a fast

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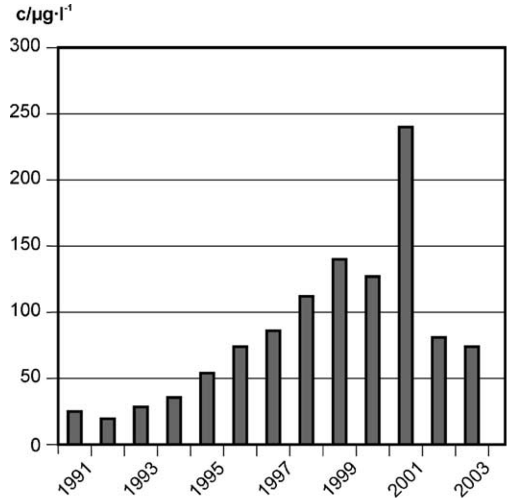

Fig. 1. Non-ionic surfactants in the River Warta, Poznan (Poland) (average values of spring–summer periods).

inexpensive method may well be a factor for reintroducing NS monitoring. An ideal solution would be the development of an automate for NS analysis.

Apart from official BiAS and CTAS procedures, the GC hydrogen bromide cleavage method developed by Wee [6], is used. Each ethoxylene subunit of NS is transformed into dibromoethane. However, gas-stripping into ethyl acetate or liquid–liquid extraction into chloroform, followed by evaporation of the organic solvent is necessary prior to GC determination. The HPLC determination of NS in surface water is difficult because of the large number of individual compounds of the NS mixture. Additionally, derivatisation is necessary. The indirect tensammetric method (ITM) is developed for NS determination in environmental samples [7]. Together with the more sensitive indirect adsorptive stripping tensammetry (I-AdST) [8], ITM is very useful in NS determination in surface water, raw and treated sewage, as well as in testing NS biodegradation [9,10]. Only 200 ml of river water is required, though liquid–liquid extraction into ethyl acetate is needed. The bottleneck in all reported methods is the time-consuming NS separation from the water matrix, although AdS-ITM seems to be the most promising candidate for the potential development of an automate for NS analysis.

The PTFE capillary trap provides a new opportunity to separate NS from the water sample [11]. The water sample is pneumatically pushed through the PTFE capillary. Adsorbed NS are eluted with organic solvent and determined by the I-AdST [11]. The aim of this work is to characterize NS determination with this method. Triton X-100 was used as a model NS. An advantage of the PTFE application as a sorbent material is the generally weak adsorptive ability. Therefore, only the strongest surfactants, e.g. NS, are adsorbed on the surface of the PTFE trap. Anionic surfactants can be also adsorbed in the trap, however, the I-AdST tolerates these surfactants.

2. Experimental

2.1. Apparatus and reagents

All measurements were performed with the non-ionic surfactants analyser (see Fig. 2) consisting of the PTFE trap [11], electroanalytical cell and electrochemical analyser. The PTFE trap is a pneumatically driven facility with a PTFE capillary. An ECO Chemie General Purpose Electroanalytical System µAUTOLAB working in sinusoidal ac voltammetry mode was used. A standard mode of measurement (without phase sensitivity), a frequency of 60 Hz, a superimposed alternating voltage amplitude of 2 mV and a scan voltage rate of 400 mV min^{-1} were applied.

A computer controlled growth mercury drop electrode was used, together with a fused silica cell, saturated calomel reference elect rode and a platinum wire auxiliary electrode. All potentials cited are against the saturated calomel electrode. The beaker of the measuring cell was replaced by a quartz beaker, to prevent adsorptive loss on the glass surface [12]. The ceramic frit on the end of the salt bridge was protected by the fitting of a polyethylene tube. This ceramic frit indicates a very large adsorptive ability [12] and the protection it gives very effectively reduces the adsorptive loss of surfactants. The measuring cell was carefully cleaned with methanol between measurements.

The following surfactants were used without additional purification: Triton X-100 (Rohm and Haas), sodium dodecyl sulphonate (BDH). Ethyl acetate (POCh, Poland) of gas chromatographic grade was used. Other reagents were of p.a. grade. Purified sodium sulphate was used for the preparation of the aqueous 0.5 M base electrolyte. All solutions were prepared in water triply distilled from quartz. Only freshly distilled water was used.

2.2. Typical experiment (procedure, measurement and evaluation)

Water sample of 0.1–50 ml containing 0.2–1.2 µg of non-ionic surfactants is introduced into the sample vessel. The sample is pneumatically pushed through the PTFE trap and directed to waste. About 0.75 ml of ethyl acetate was introduced into a sample vessel and pneumatically pushed through the trap to the measuring cell containing 0.5 M aqueous sodium sulphate solution. Subsequently 1 ml methanol was also pushed through the trap into the measuring cell.

The ethyl acetate emulsion was stirred for 10 min to achieve clarity of the solution due to evaporation of the excessive ethyl acetate. This excessive ethyl acetate extracts surfactants, therefore it must be removed and this is evidenced by the disappearance of turbidity. After a quiescent period (30 s), the tensammetric curve of ethyl acetate was recorded in the cathodic direction starting from −1.20 V (versus SCE) using a new mercury drop. The difference between the height of the peak of ethyl acetate (recorded in a separate measurement) and the peak height of ethyl acetate in the presence of