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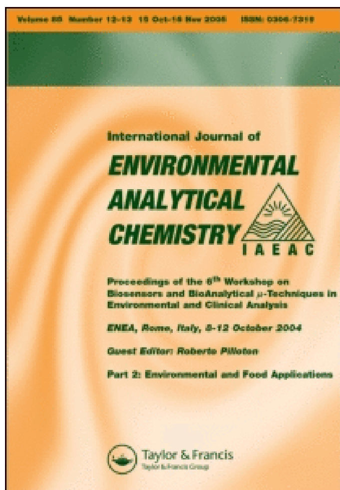

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Rapid Screening Method for Ditallowdimethylammonium Chloride at the Low PPB Level in Surface Water Using Solid Phase Extraction and Normal-Phase Liquid Chromatography With On-Line Post-Column Ion-Pair Extraction and Fluorescence Detection

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To cite this Article Gort, S. M. , Hogendoorn, E. A. , Baumann, R. A. and van Zoonen, P.(1993) 'Rapid Screening Method for Ditallowdimethylammonium Chloride at the Low PPB Level in Surface Water Using Solid Phase Extraction and Normal-Phase Liquid Chromatography With On-Line Post-Column Ion-Pair Extraction and Fluorescence Detection', International Journal of Environmental Analytical Chemistry, 53: 4, 289 — 296

To link to this Article: DOI: 10.1080/03067319308044433

URL: http://dx.doi.org/10.1080/03067319308044433

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Intern. J. Environ. Anal. Chem., Vol. 53, pp. 289-296
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RAPID SCREENING METHOD FOR DITALLOWDIMETHYLAMMONIUM CHLORIDE AT THE LOW PPB LEVEL IN SURFACE WATER USING SOLID PHASE EXTRACTION AND NORMAL-PHASE LIQUID CHROMATOGRAPHY WITH ON-LINE POST-COLUMN ION-PAIR EXTRACTION AND FLUORESCENCE DETECTION

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(Received, 30 November 1992; in final form, 4 February 1993)

A rapid high-performance liquid chromatographic screening method for ditallowdimethylammonium chloride (DTDMAC) in surface water is described. Sample preparation involves solid phase extraction of DTDMAC from 25 ml surface water. Analysis is carried out by normal-phase liquid chromatography coupled on-line with post-column ion-pair formation, with 9,10-dimethoxyanthracene-2-sulphonate (DAS) as the fluorescence extraction reagent. A reaction coil is used to extract the aqueous reagent from the organic/aqueous effluent. Two phase separators, connected in series, separate the aqueous and the organic phase. The organic phase is monitored using a fluorescence detector operated at excitation and emission wavelengths of 384 and 452 nm, respectively.

Using this procedure, the recovery of DTDMAC from samples spiked at the 4.9 ppb level was 21±3.4 %, and at the 9.8 ppb level 42±4% (n=5). DTDMAC can be monitored in surface water samples with a limit of determination of 5 ppb (μg/l).

KEY WORDS: Cationic surfactants, HPLC, water, ion-pair formation.

INTRODUCTION

Ditallowdimethylammonium chloride (DTDMAC) is a cationic surfactant, mainly used in products like detergents, in which it is applied as a fabric softener. Quaternary ammonium compounds are highly adsorptive for anionic surfactants, particles and sediments in water systems. Therefore, an extensive survey is carried out on the presence and ecotoxicological properties of cationic surfactants in the environment[1-9]. DTDMAC occurs in raw surface

water (max. 30 μg/l), bank infiltrate (max. 5 μg/l) and in drinking water (max. 4.3 μg/l).[2] Maximum permissible risk levels for DTDMAC in aquatic ecosystems range from 18 to 100 μg/l, depending on the calculation method and the confidence level chosen[3]. In the Netherlands, an agreement between the Dutch government and manufacturers was made to ban these compounds from soap products, starting in 1993.

In order to monitor the concentration of DTDMAC in surface water to evaluate the effect of the banning, a screening method for DTDMAC at the low μg/l level is necessary. Until now, only a few analytical methods for the determination of quaternary ammonium compounds have been published. De Ruiter *et al.*[10,11] described a procedure using a continuous post-column ion-pair extraction detector with a sandwich-type phase separator. The ion-pair is detected with either UV-vis absorbance or fluorescence. A method for the determination of trace levels of cationic surfactants in environmental matrices has been described by Simms *et al.*[12] using normal phase LC with fast atom bombardment mass spectrometry (FAB-MS) as detection technique. Tadao Sakai[13] developed a spectrophotometric determination of quaternary ammonium compounds in pharmaceuticals by a flow injection technique coupled with ion-pair extraction and thermochromism of the ion associates.

Based on the procedure of De Ruiter *et al.*[10], Bergers *et al.*[14] described a modified sample pretreatment resulting in a method for DTDMAC with a limit of determination of 1.1 μg/l in several types of water. However, this procedure possesses several drawbacks both in the laborious sample pretreatment as well as in the poor overall accuracy and reliability of the analytical procedure.

For the work described here, the detection principle of De Ruiter *et al.*[10] was chosen as starting-point for the development of a rapid screening method for DTDMAC with the aim to combine it with a simplified sample pretreatment step. This paper describes a method using solid phase extraction for the direct isolation of DTDMAC from surface water samples. The extract is analysed by normal-phase HPLC with on-line post-column ion-pair extraction and fluorescence detection.

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EXPERIMENTAL

Chemicals

Ditallowdimethylammonium chloride, activity 97%, was obtained from Procter & Gamble (Brussels, Belgium). 9,10-Dimethoxyanthracene-2-sulphonate (DAS), 98%, came from Fluka (Buchs, Switzerland). Ammonium acetate, copper(I) chloride, chloroform, 2-propanol and concentrated hydrochloric acid (37%) were obtained from Merck (Darmstadt, Germany). Methanol and acetone, both nanograde, were purchased from Promochem (Wesel, Germany). Rathburn (Walburn, United Kingdom) delivered HPLC-grade acetonitrile. A Milli-Q system from Millipore (Bedford, MA, U.S.A.) was used to obtain purified demineralized water for use in eluents. Disposable extraction columns (1 ml volume) packed with aromatic sulphonic acid (ArSO3H) bonded to silica gel (40 μm, 60 Å) were purchased from J. T. Baker (Deventer, The Netherlands).

Stock solutions of DTDMAC were prepared in acetone and dilutions were made in

acetone-chloroform (50:50, v/v). Surface water was spiked with an aliquot of a stock solution at the 4.9 and 9.8 ppb level.

The mobile phase for HPLC was chloroform-methanol-acetonitrile (92:4:4, v/v/v). To obtain the ion-pairing reagent solution, about 30 mg of DAS were dissolved in one litre of Milli-Q water; the solution was filtered over a 0.45 μm PTFE membrane before use.

The elution solvent mixture used in the sample pretreatment procedure was prepared by adding approx. 0.5 ml concentrated hydrochloric acid to 50 ml acetone, dissolving ca. 250 mg of copper(I) chloride in this solution, and finally diluting it with chloroform to 100 ml.

Equipment

A schematic representation of the HPLC equipment is shown in Figure 1. An LKB (Bromma, Sweden) Model 2150 HPLC pump {P-1} delivered the mobile phase at a flow rate of 1.0 ml/min to a 250 × 4.6 mm. I.D. Partisil PAC 10 μm analytical column {C}, from Hichrom (Reading, Berkshire, United Kingdom). Sample volumes (42 μl) were introduced by a Marathon autosampler {AS} (Spark Holland, Emmen, The Netherlands).

Derivatizing reagent {RE} is added post-column at a flow rate of 0.4 ml/min via a T-piece with an LKB Model 2150 HPLC pump {P-2}, equipped with a low-pressure pulse dampener {D}. This results in a segmented flow of plugs of (organic) mobile phase and (aqueous) reagent phase. Ion-pair formation and subsequent extraction to the organic phase took place in a 1000 × 0.25 mm. I.D. stainless steel tubing reaction coil {RC}. Separation of the organic and aqueous phases took place with two phase separators {PS-1 and PS-2} purchased from the Free University (Amsterdam, The Netherlands). The second phase separator was installed as a precaution to separate the organic and aqueous phases when occasional breakthrough of the aqueous phase occurred in the first phase separator. The flow rate of the organic phase through the detector was adjusted to 0.3 ml/min.

Detection was carried out by a Perkin Elmer (Norwalk, CT, U.S.A.) LS-4 fluorescence spectrophotometer {FD} operated at an excitation wavelength of 384 nm and an emission wavelength of 452 nm. Chromatograms were recorded on a Kipp en Zoonen recorder (Delft, The Netherlands). Quantification of peak-heights was done using a previous standard injection (0.49 μg/l) as calibration point.

A Model 6000 A Waters (Millipore) pump {P-3} was used to flush the system with 2-propanol {IPA}. For this purpose, a four-way high pressure valve {HV} was inserted between the analytical column and the T-piece.

Pretreatment of samples was performed employing a Baker-10 Solid Phase Extraction (SPE) system using 500 mbar pressure.

Sample pretreatment

About 750 mg ammonium acetate were added to 100 ml of sample. A pH of about 7 was established by the addition of diluted hydrochloric acid. Preconditioning of an SPE cartridge was done by washing with 4 ml of methanol followed by 4 ml of a solution in Milli-Q water containing an equivalent amount of ammonium acetate and diluted hydrochloric acid (pH≈7)

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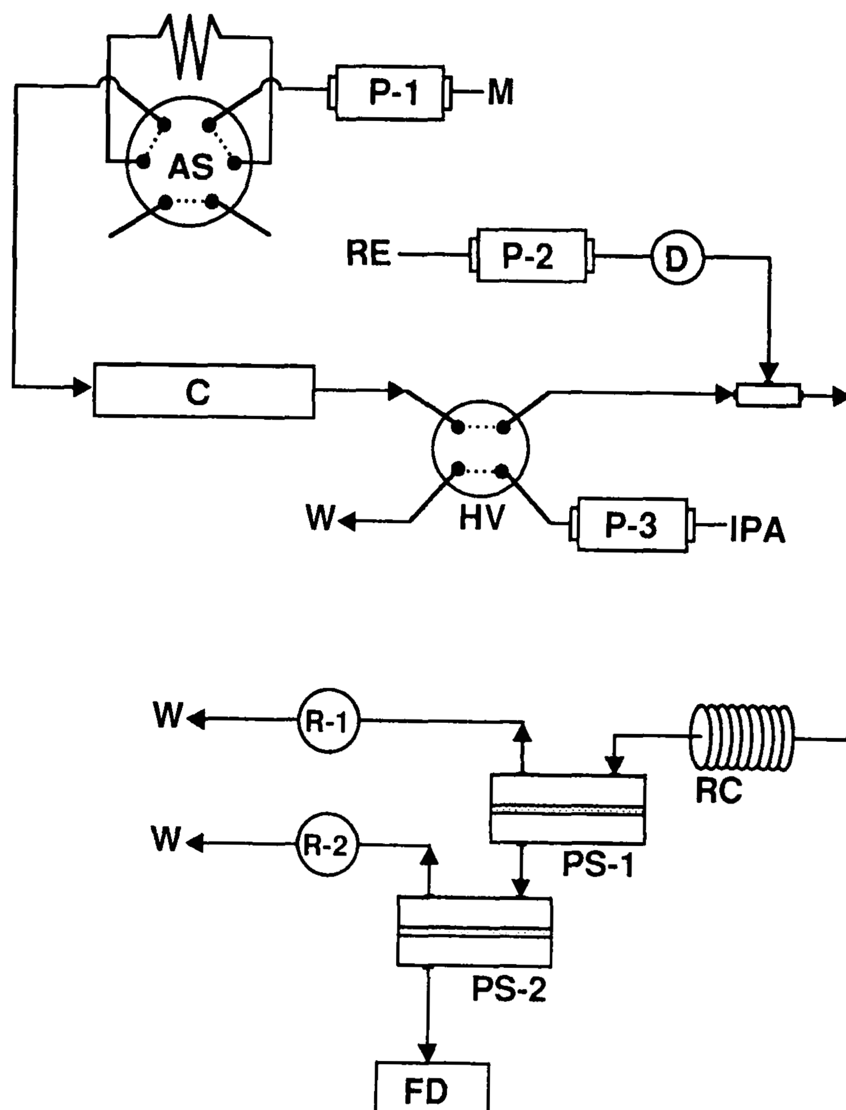

Figure 1 Schematic of HPLC set-up used for screening DTDMAC in surface water. P1, 2 and 3, HPLC pumps; AS, AutoSampler; C, analytical Column; M, Mobile phase; HV, High pressure Valve; RE, Reagent; IPA, 2-Propanol; RC, Reaction Coil; PS-1.2, Phase Separators; R-1,.2, Restrictors; W, waste; FD, Fluorescence Detector.

as a sample. After a sample volume of 25 ml had been passed through the cartridge, flushing with air for 4 min resulted in almost complete dryness of the packing material. Elution took place manually by pushing 500 μl of an acidic acetone-chloroform (50:50, v/v) solution, containing 25 mMol copper(I) chloride, through the cartridge. The eluted fraction was collected in a vial, and an aliquot was injected in the HPLC system.

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RESULTS AND DISCUSSION

Equipment

The complex chromatographic system described in refs 10 and 14 proved difficult to operate over longer periods, contrary to what is reported in the quoted literature. The main cause of this malfunctioning is the instability of both the detection system and the separation system. Instability of the detection system resulted in baseline instability of the detector signal, while instability of the separation system resulted in instability of the retention time of DTDMAC. Getting a stable baseline within half a day, and maintaining this stability for several hours, was impossible because of occasional breakthrough of the aqueous part of the effluent into the detector cell. Even when decreasing the extraction efficiency of the phase separator, breakthrough appeared to be unavoidable. To prevent breakthrough effectively, two phase separators[9] were connected in series after the reaction coil. This modification of the equipment resulted in a constant system performance without solvent breakthrough for several weeks. Moreover, in one year of working experience, no interferences at longer retention times were observed despite isocratic elution of DTDMAC.

Economizing on the derivatizing reagent by reducing the flow rate from 0.8 to 0.4 ml/min had no negative effect on the sensitivity of the analysis.

The retention of DTDMAC in the HPLC system decreased with time. The retention time of a 0.49 μg/ml (ppm) standard solution in acetone-chloroform (50:50, v/v) decreased from 7.4 min to 6.3 min when the injection was repeated several days later. Nevertheless, despite this decrease, column efficiency remained constant. In the concentration range of 0.05–0.50 ppm DTDMAC in chloroform, the detector response was linear ($n=7$, $r=0.993$). Effects of acetone and acid upon this linearity were not investigated.

The retention of DTDMAC turned out to be concentration dependent in the present chromatographic system. Although several authors use comparable chromatographic systems[10,14], this phenomenon has not been described earlier. This often undesirable effect is illustrated in Figure 2. In our hands and using at least four Partisil PAC columns over a prolonged time period, the shift of retention time with concentration occurred with each single column.

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Sample pretreatment

In ref.[14], the first step in the sample pretreatment is the addition of 1 ml of a solution of linear alkylbenzenesulphonate (LAS) to 100 ml of a water sample. LAS forms an insoluble complex with DTDMAC. After the addition of LAS, the procedure consists of a series of laborious and time-consuming evaporation and concentration steps. Moreover, the described multiple redissolution of the residue with small volumes of organic solvent introduces an undesirable source of variation.

With the addition of LAS to a sample as starting-point, several experiments were done in order to find a more convenient way to isolate DTDMAC from surface water. Direct isolation of the DTDMAC-LAS complex using SPE cartridges, filled with various quantities

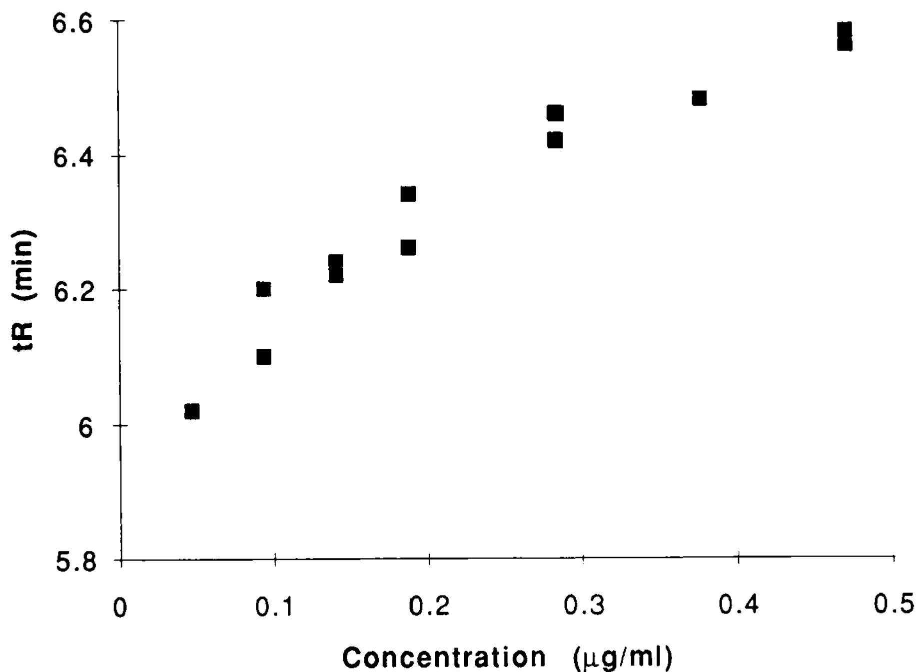

Figure 2 Retention time, t_R, as function of DTDMAC concentration in chloroform.

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of C_8, C_{18} and C_{18} LD (Low Displacement) bonded silica, resulted in low recoveries of 0–18% of the analyte at the 10 μg/l level. Pretreatment of the added volumes of water following the procedure described in the experimental section, showed that there was a retention and/or complexation problem with the cartridges. Therefore, a different approach had to be introduced.

Under suitable pH conditions, positively charged compounds such as DTDMAC can be isolated from aqueous solutions with SPE on cation exchange cartridge.[15] Packing material containing an aromatic sulphonic acid moiety was used to isolate DTDMAC directly from water without the addition of LAS. SPE conditions comparable to those used for the isolation of catecholamines from aqueous solutions appeared to be suitable.[15] A solution of 0.1 M ammonium acetate was used to isolate DTDMAC from surface water onto the packing material of the cartridge. A solution of low ionic strength of copper(I) chloride, at low pH, was sufficient to elute DTDMAC in a volume of 500 μl. The corresponding chromatograms are shown in Figure 3. Analysis of surface water samples spiked with the same amounts of DTDMAC gave constant recoveries with fully acceptable repeatability. These recoveries were 21±3.4 and 42±3.8% (n=5) at the 5 and 10 ppb level, respectively. Low recoveries were also found by Simms *et al.*[12] In their case, river water samples spiked with 5 and 10 ppb of DTDMAC showed recoveries of 16 and 42%, respectively. In other words, the recovery is dependent on the DTDMAC concentration. This aspect was not studied any further. Obviously, for a reliable quantitation of the concentration of DTDMAC in surface

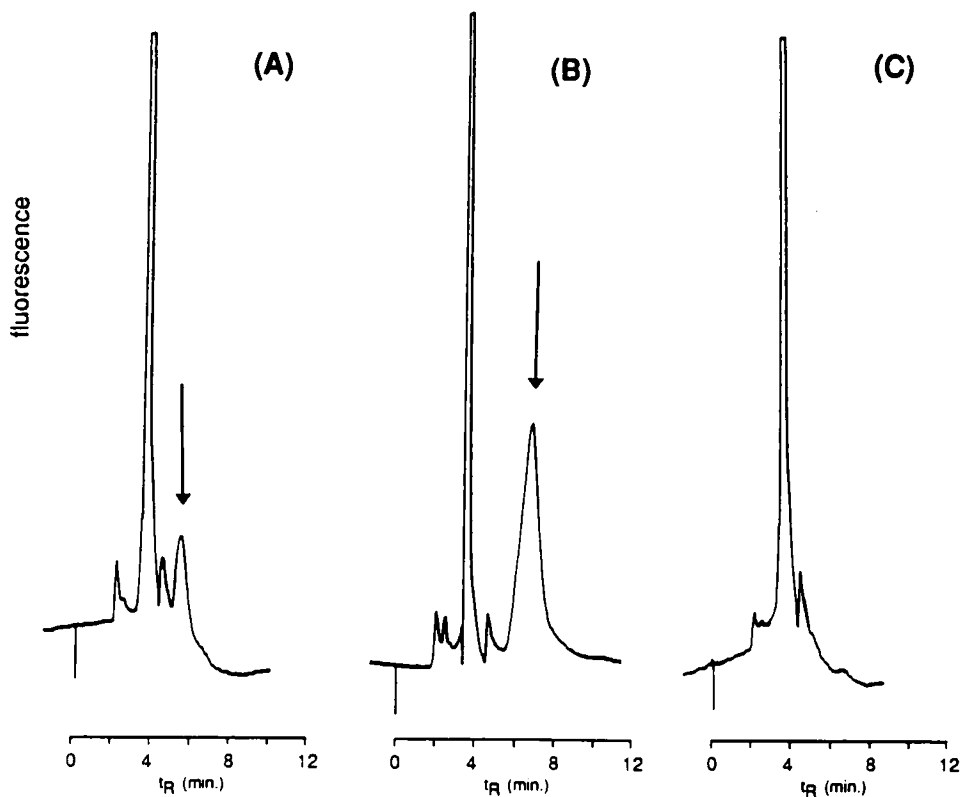

Figure 3 HPLC Chromatograms of surface water samples spiked with DTDMAC at the 4.9 µg/l level (A) and at the 9.8 µg/l level (B). (C) is the chromatogram of a blank surface water sample.

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water, a spiked sample with a concentration level comparable to that of the sample has to be analysed in the same series.

CONCLUSIONS

Using the present procedure, a fast screening of surface water can be carried out for DTDMAC at the low µg/l level with acceptable reproducibility. The advantages of SPE compared to evaporation procedures are higher speed and better reproducibility. Moreover, when using ion-exchangers as packing materials, the addition of LAS can be avoided. The collected elution solvent can be injected directly into the LC system.

Improving the extraction recovery is not really necessary, because the detection limit is sufficiently low to allow the monitoring of relevant DTDMAC levels in surface water. The introduction of a second phase separator in the analytical system results in a more reliable system performance. On the basis of results obtained in the analysis of several series of

samples, it is estimated that about 40 samples can be analysed per day. The present procedure can be automated quite easily, which will allow even higher sample throughputs.

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