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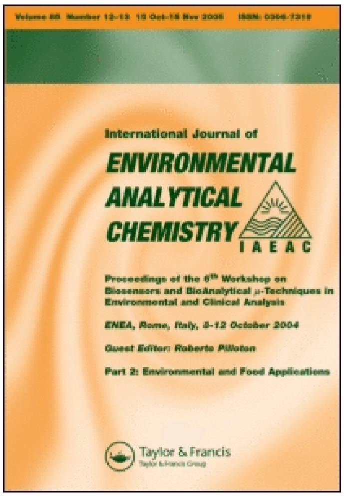

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# Determination of Nonionic Surfactants in Water by Atomic Absorption Spectrometry

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An analytical method for nonionic surfactants has been developed using sublation and ion-exchange for isolation of the surfactants and complex formation with potassium zinc tetrathiocyanate followed by atomic absorption spectrophotometric assay of zinc released from the complex through acid extraction. The detection limit for this method is 0.01 mg/l Triton X-100. Recoveries higher than 90% were obtained starting from samples spiked with 0.1 mg/l Triton X-100. The method has been applied to 70 surface water samples coming from a quality survey of the River Meuse in France, Belgium and The Netherlands organised by the RIWA—Cooperating Rhine and Meuse Water Supply Companies. The highest level (0.50 mg/l) was found below the outfall of a surfactant-producing firm. Downstream these discharge levels decreased rapidly.

KEY WORDS: Nonionic sufactants, atomic absorption spectrometry, potassium zinc tetrathionate complex formation, River Meuse quality survey.

## INTRODUCTION

Nonionic surfactants are increasingly used for industrial and household purposes. In 1984, 305,000 metric tons will be consumed within the E.E.C. Among these the alcohol polyethoxylates will be soon quantitatively as important as the alkylphenolpolyethoxylates.[1]

In spite of their increasing application few data are available concerning the presence and behaviour of these compounds in river waters. One of the reasons for this lack of knowledge seems to be the scarcity of methods allowing a reliable determination at levels encountered in environmental samples.

Several methods are based upon the ability of nonionic surfactants to form adducts with ammonium cobaltotetrathiocyanate, potassium zinctetrathiocyanate, and potassium picrate which can be extracted in an organic solvent. Quantitation takes place spectrophotometrically or by atomic absorption spectrophotometry.[2-5] Some of these methods are claimed to have detection limits below 0.1 mg/l. When applied directly to extracts of water samples most surfactants or foreign ions encountered in environmental samples interfere. Since the data available on the presence of nonionic surfactants in surface waters[6-9] indicate that levels below 0.2 mg/l have to be taken into account and the presence of ionic surfactants cannot be ruled out it seemed mandatory to include a concentration and purification step in order to obtain sufficient sensitivity and selectivity. The method described by Boyer *et al.*[6] seems to meet some of these requirements. The detection limit of this method is 0.1 mg/l. In order to reach a lower detection limit we decided to develop a method which combined the sublation-concentration step and ion exchange purification with potassium zinctetrathiocyanate adduct formation and atomic absorption spectrometric assay of zinc after acid back extraction. A method based on potassium zinctetrathiocyanate adduct formation[5] was preferred in spite of the poor reactivity of the reagent to surfactants containing less than five oxyethylene units because methods relying on gas chromatographic separations are limited to compounds containing up to 13 oxyethylene groups and the lack of pure reference substances renders the quantitation of individual compounds difficult.[7]

The method developed has been applied in a quality survey program of the River Meuse in France, Belgium and the Netherlands organised by the RIWA—Cooperating Rhine and Meuse Water Supply Companies. Seventy samples taken at 38 different sites were analysed.

## River system

The River Meuse (Dutch: Maas) is a 900 km long river, running from the village of Pouilly en Bassigny in the French department of the Vosges to the estuary of the Rhine in the Netherlands. The river

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basin covers about 30,000 km$^2$, and is situated in France, Belgium, Luxemburg, Germany and The Netherlands (Fig. 1). It is a typical rain river of the temperate zones, with low river flow during late summer, and maximum flow during winter and early springtime. The

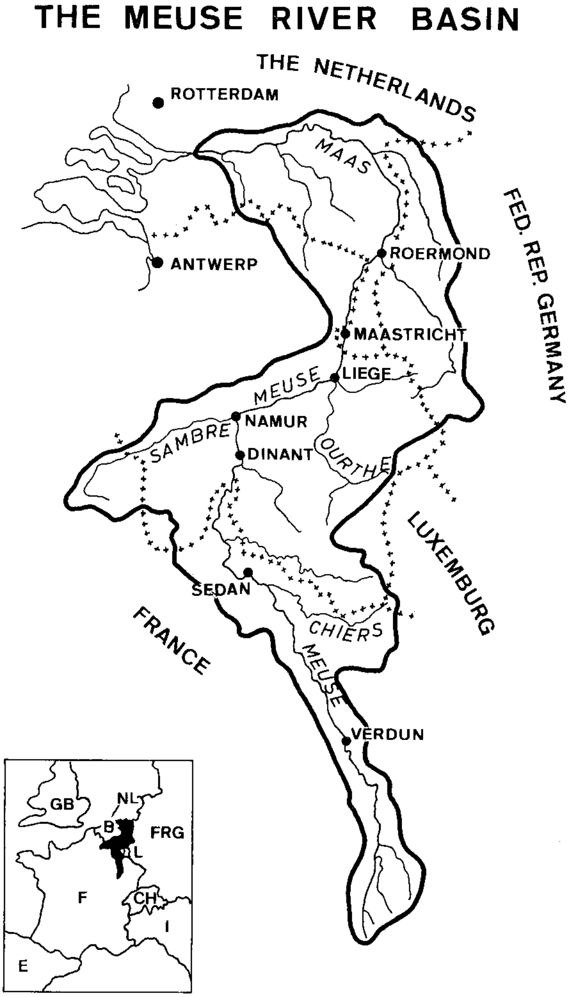

FIGURE 1 The Meuse river basin with indication of major cities (●), tributaries and borders (+ + +).

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mean river flow is about 325 $m^3/s$ at Lith (Netherlands), but the extreme values may differ a factor 10 from it.

The water quality of this river is fairly good as compared to some other European rivers, e.g. the Rhine, which makes it suitable as a raw water source for drinking water production. Some 5 million people in France, Belgium, and The Netherlands are now being supplied with treated Meuse water.

Nevertheless, this river too is subjected to severe pollution by industrial and domestic waste water, which concentrate in the central part of the water course: from the confluence with the tributary Sambre at Namur, to the city of Roermond in The Netherlands. This area is characterised by an important industrial activity, associated with iron and steel works, coke ovens, non-ferrous metals factories and electroplating industry. It has also the most dense population of the whole river basin.[10]

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## EXPERIMENTAL

### Reagents

Bio-Rad AG1-X2 anion exchange resin, hydroxide form, 50–100 mesh (converted from chloride to hydroxide by eluting with 1 N NaOH, followed by a methanol wash until the water has been displaced) and Bio-Rad 50 W-X8 cation exchange resin, acid form, 50–100 mesh were used for ion exchange purification.

Analytical reagent grade 1,2-dichlorobenzene (Merck) was purified by passing through a 20 cm column of activated alumina (Woelm B-Super I).

Triton X-100 (polyethyleneglycol-mono[p-(1,1,3,3-tetramethylbutyl)phenyl]ether) was obtained from Merck (gas chromatography grade). A stock reference solution containing 50 mg/l was prepared in 1,2-dichlorobenzene. Potassium zinc-tetrathiocyanate reagent was prepared by dissolving 116 g zinc sulphate heptahydrate, 312 g potassium thiocyanate and 40 g potassium acetate in hot distilled water and dilution to 2 l. The reagent was extracted three times with 50 ml of 1,2-dichlorobenzene and filtered over a Whatman No. 1 filter before use.

All other reagents were of analytical reagent grade quality. Anhydrous sodium sulphate was baked overnight at 600°C before use.

## Apparatus

The sublator has been described by Boyer *et al.*[6] A Perkin-Elmer 372 atomic absorption spectrophotometer was used for flame AAS determinations.

## Sampling

The sampling of Meuse river water was carried out as part of a comprehensive quality survey, organised 19–30 September 1982, by the "RIWA Cooperating Rhine and Meuse Water Supply Companies"; RIWA, grouping 10 Dutch and Belgian water supply companies, aims at the prevention and improvement of the quality of their water resources, the rivers Rhine and Meuse.

The River Meuse water was sampled from a ship at 38 sites situated between source and mouth. At each site, two or three samples were taken along the cross section, i.e., one near each bank, and in some cases, one in the middle. At the sites where the river was not navigable, only one sample was taken from a bridge. Downstream of Sedan, the distance between two successive sampling sites was 20 km, but in areas where an important influence from industrial discharges or tributaries was expected, this distance was reduced to 10 km.[11]

Water samples were taken with a 10 l water sampler, and collected in a 60 l glass container, equipped with a stirrer. Next, the water was divided over smaller containers of various types and capacities, in function of the quality parameter to be determined.

Samples for nonionic detergent analyses were stored in glass stoppered, 1 l brown glass bottles. 1 ml formaldehyde solution was added for conservation. All samples arrived at the laboratory at the latest 30 hours after sampling, and were cooled until analysis started.

## Procedure

500 ml river water samples to which 100 g NaCl and 5 g $NaHCO_3$ had been added are transferred to the sublator and are diluted with distilled water until the level reaches the drain cock. Nitrogen is passed through the solution in order to obtain efficient mixing between the sample and the distilled water. After stopping the nitrogen flow 100 ml of ethyl acetate are added and the sample is

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sublated by passing through nitrogen during 10 min at the fastest rate possible without mixing at the phase interface. The ethyl acetate layer is collected in a separatory funnel and the sublation is repeated twice. The ethyl acetate layer is separated from water in the separatory funnel and is further dried over anhydrous sodium sulphate and evaporated on a rotary evaporator. The residue is taken up in 10 ml methanol and added to anion–cation exchange column (10 ml Bio-Rad 50 W-X8 on top of 10 ml Bio-Rad AG 1-X2 separated by a glass wool plug). The nonionic surfactants are eluted with 125 ml methanol. The methanol is evaporated to dryness in a rotary evaporator and the residue is taken up in 20.0 ml 1,2-dichlorobenzene. 50 ml of the potassium zinctetrathiocyanate reagent are added. The two phases are vigorously mixed for 5 min on a mechanical shaker. Approx. 13 ml of the organic phase are brought into a 15 ml centrifuge tube and centrifuged at 2500 r.p.m. for 30 min. A 10.0 ml aliquot of the centrifuged sample is pipetted into a 25 ml volumetric flask and 10.0 ml 0.1 N HCl are added. The flask is stoppered and shaken vigorously for 2 min. The phases are allowed to separate and the aqueous layer is aspirated directly into the atomic absorption spectrophotometer. Working conditions are as follows: air–acetylene flame, 214 nm wavelength and 0.7 nm spectral band pass. Blank determinations are carried out with 500 ml distilled water. Nonionic surfactants concentrations are calculated by comparison with Triton X-100 standards run simultaneously without sublation.

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## RESULTS AND DISCUSSION

The approach used for the development of this method, adduct formation of nonionic surfactants with potassium zinctetrathiocyanate, does not allow the establishment of the identity of the species measured and will not detect some biodegradation products of nonionic surfactants. It was chosen because it allows the assay of a wide range of alkylphenol- and alcoholpolyethoxylates whereas gas chromatographic techniques are more limited in scope in this respect. Adduct formation with potassium zinctetrathiocyanate was preferred over reaction with ammoniumcobaltotetrathiocyanate since zinc can be more sensitively assayed than cobalt by atomic absorption spectrophotometry.

Blank absorbances are low ($\leq 0.010$). The method developed allows the detection of 10 μg/l nonionic surfactants, expressed as Triton X-100 starting from a 500 ml sample. This figure compares favourably with the detection limits mentioned by Crisp *et al.*[5] and Boyer *et al.*[6]

The recovery of Triton X-100 from distilled water was tested at different concentrations between 0.1 and 2.0 mg/l. The results are presented in Table I and are reported as means of five experiments at each concentration with standard deviations. All experiments were carried out with three sublations. Additionally, surface water samples spiked with 0.5 mg/l Triton X-1000 were analysed to detect matrix effects. In the concentration range of 0.1–0.5 mg/l Triton X-100 recoveries were higher than 90% starting from distilled water. A 90.0% recovery of Triton X-100 was obtained from surface water. In contrast to the procedure described by Boyer *et al.*[6] nitrogen was passed through the sample before ethyl acetate was added to the sublator causing an efficient mixing of the sample and the dilution water and preventing the dissolution of significant quantities of ethyl acetate in the aqueous phase.

In September 1982, the presence of nonionic detergents in the River Meuse was checked. The results of this survey are presented in the form of a longitudinal profile, which is shown in Fig. 2. At several locations downstream of the confluence of the River Sambre, samples were taken at the right and left bank of the river. When present, differences between those samples are depicted as shaded areas between the full lines. Results were not corrected for incomplete recovery.

TABLE I

Recovery of Triton X-100 from distilled water and surface water.

| Triton X-100 added (mg/l) | Triton X-100 found (mg/l) | s (mg/l) | Recovery (%) |
|---|---|---|---|
| 0.10 | 0.09 | 0.01 | 92.2 |
| 0.50 | 0.50 | 0.07 | 100.0 |
| 1.00 | 0.77 | 0.12 | 77.0 |
| 2.00 | 1.62 | 0.28 | 81.0 |
| 0.50[a] | 0.45 | 0.07 | 90.0 |

[a] Surface water sample.

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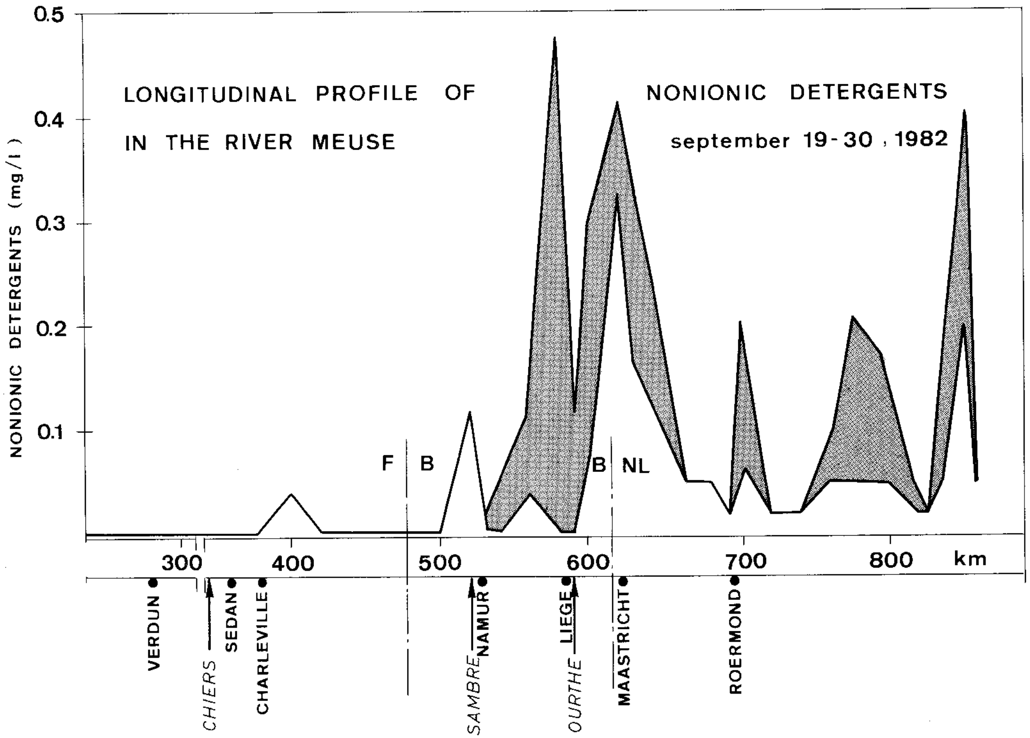

FIGURE 2 Longitudinal profile of nonionic detergents in the River Meuse. The grey area between the two lines indicates the differences in concentration between samples taken at the right and left bank.

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The maximum concentration, i.e. 0.5 mg/l, was found near Liège, immediately downstream of the waste water discharge of a detergent factory. This discharge is easily recognised by foam formation at the water surface.

The dissymetrical distribution of the nonionic detergents concentration at the site where the highest concentration was found, reflects the proximity of the discharge, which is situated on the right river bank. These results prove the importance of sampling at more than one point at each site, especially in wide rivers, where mixing phenomena play an important role in the distribution of pollutants along the transversal axis.

Upstream of the nonionic detergents peak concentration, two zones can be distinguished:

—a first zone, between the river source and the city of Dinant in Belgium, where the concentration remains below the detection limit, 0.01 mg/l, except for one site where 0.04 mg/l was measured.

—a second zone from Dinant to Liège where concentrations vary between $<0.01$ and 0.12 mg/l.

The quick decrease in the concentration of nonionic detergents suggests good biodegradability of these compounds, which has previously been reported by different authors.[1,7] After the maximum near Liège, a value of 0.05 mg/l is found 80 km downstream. Further downstream, peak values of 0.2 mg/l or more are recorded, especially towards the end of the river basin, where some tributaries discharge partially treated waste waters. The background concentration in this area is 0.05 mg/l.

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