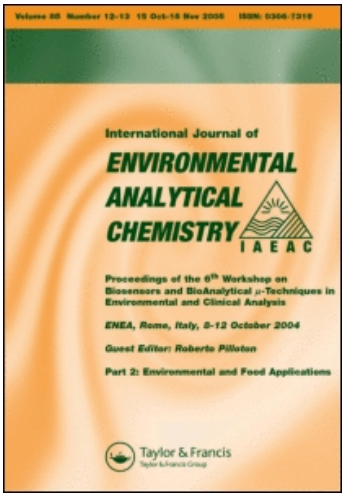

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MICELLAR EXTRACTION—A NEW STEP FOR ENRICHMENT IN THE ANALYSIS OF NAPROPAMIDE

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The determination of pesticides at trace levels demands an enrichment step due to the insufficient detection limits of most analytical techniques. Aim of this work is the application of the micellar extraction for the preconcentration of napropamide from ultrapure water and natural samples. This surfactant-mediated phase separation uses Genapol X 80 and Genapol X 150 as examples of nonionic surfactants. Combined with the fluorescent detection of the herbicide within the micellar phase, it was possible to achieve detection limits below 0.2 µg/l. The various effects like surfactant concentration and addition of salt on the enrichment has been studied. The results demonstrate the usefulness of the cloud point extraction system to extract and preconcentrate napropamide without use of any toxic and expensive organic solvent.

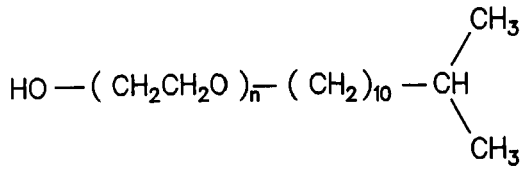
KEY WORDS: Micellar extraction, cloud point, napropamide, fluorescence detection.

INTRODUCTION

Pesticides are common contaminations of water resources. Regarding their low threshold limits outlined in the European Water Regulations even small concentrations in water samples have to be determined. The trace determination of pesticides demands very often a preconcentration step owing to the insufficient sensitivity of most detection techniques.

Popular enrichment methods are liquid-liquid extraction, the solid phase extraction and the extraction using supercritical CO_2 with and without modifier. In this work, the micellar extraction as a preconcentration step was exemplarily evaluated with the herbicide napropamide [N, N-diethyl-2-(1-naphthalenyloxy) propanamide].

The surfactant molecule consists of an unpolar as well as a polar moiety. The polar groups are in contact with the aqueous solution and the long alkyl chains are directed at the interior of the micelle. The proportion of the particular groups influences the solubility of the surfactant in water and the number of surfactant molecules forming the micelle. The micellar extraction and preconcentration is based upon two important characteristics of nonionic surfactants, the solubilization of organic compounds in a micelle and their phase separation behaviour.



n = 8: Genapol X 80

n = 15: Genapol X 150

Figure 1 Structure of the surfactants.

Highly concentrated aqueous solutions of surfactants like Genapol X 80 or 150 (Hoechst, Figure 1) are homogeneous and isotropic. Above a critical temperature (i.e. the cloud point) these solutions become turbid due to the diminished solubility of the surfactant in water. At higher temperatures the solutions separate into two transparent liquid phases, a surfactant-rich phase ("micellar phase") with the micelles and an aqueous solution with a diminished surfactant concentration.

Any analyte solubilized in the hydrophobic core of the micelles separates with the surfactant-rich phase and can be quantitatively determined by fluorescence measurements. The transfer of the fluorophore from the bulk aqueous phase into the micelle and the relatively high viscosity within this microenvironment diminish vibrational quenching from the hydrogen bond network of water and prevent the analyte from quenching by molecular oxygen by reduced diffusion rates[1-2]. The principle of micellar extraction is described in detail by Hinze[3-5]. A schematic representation is shown in Figure 2.

EXPERIMENTAL

Apparatus

The fluorescence spectrometer employed was constructed by Perkin Elmer (LS 50, Überlingen, FRG). Data acquisition and integration were performed with the Perkin Elmer fluorescence data manager software. All data was acquired at the excitation wavelength of 290 nm, excitation slitwidth of 2.5 nm and emission slitwidth of 5.0 nm with an ultra micro quartz cell (100 µl, Hellma, Müllheim, FRG). The evaluation was made by the base-line corrected peak areas (315–415 nm).

The volumetric flasks were placed in a water bath temperature-controlled by a thermostat (Haake D8, Karlsruhe, FRG). The refractometer was from Carl Zeiss (Abbe-Refraktometer Typ A, Oberkochen, FRG).

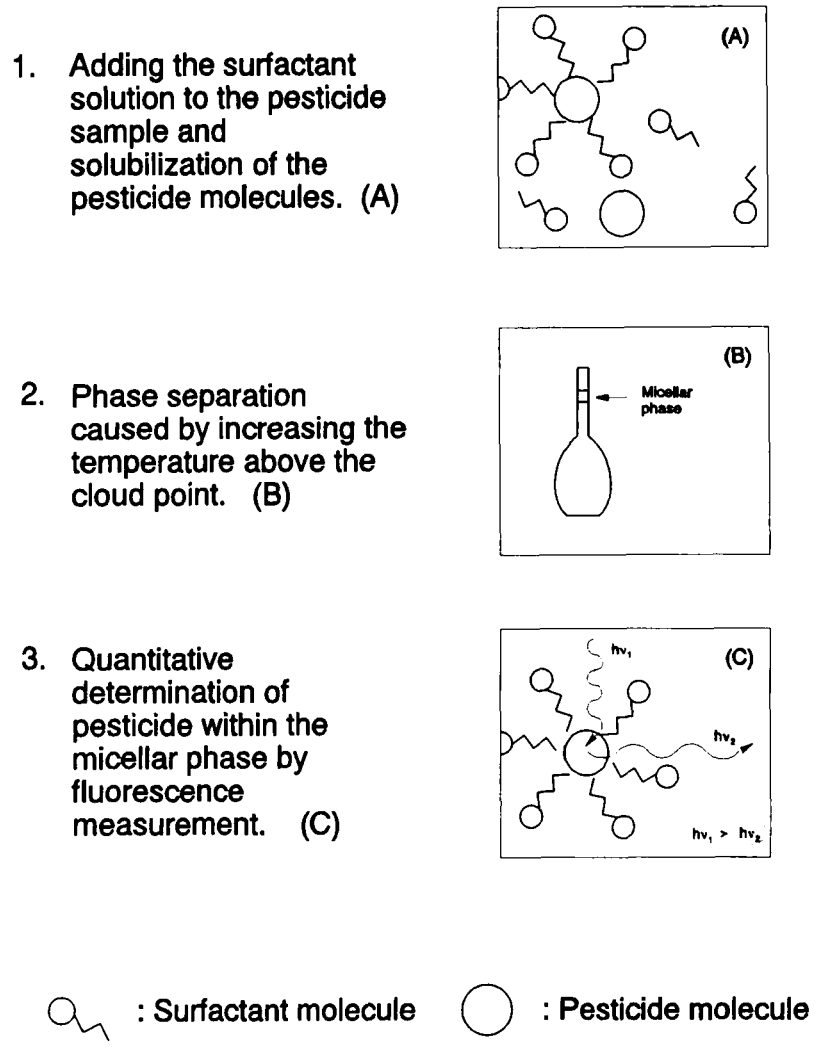


Figure 2 Principles of the micellar extraction.

Materials

The surfactants Genapol X 80 and Genapol X 150 were received from Fluka and Hoechst (Gendorf, FRG), respectively. Napropamide was purchased from Dr. Ehrenstorfer (Augsburg, FRG) and Na_2SO_4 from Merck (p.a., Darmstadt, FRG). All chemicals were used as received. The water employed for the preparation of pesticide solutions was double-distilled and UV-treated. Tap water of Munich and samples of a mineral spring (Kondrauer Mineralsprudel) were tested too.

Methods

Preparing the samples, an appropriate amount of Genapol X 80 or Genapol X 150, of Na_2SO_4 and of a stock solution of napropamide in methanol were dissolved in water which was degassed by an ultrasonic treatment before. The final concentrations were 2% salt, 4.5 µg/l pesticide and 0.25% (w/w) Genapol X 80 and 5% salt, 4.5 µg/l pesticide and 0.3% (w/w) Genapol X 150, respectively. All samples were shaken for approximately 10 min and placed in the water bath. After 1.5 h (Genapol X 80) and 24 h (Genapol X 150) the micellar phases were removed and transfered into the micro cell and analysed without applying any further clean-up steps.

The preconcentration factors P_{surf} and P_{naprop} are determined by the quotient of final and initial concentrations. The final concentration of napropamide in the micellar phase was calculated by fluorescence measurement using spiked micellar phases of the respective water in the calibration. The final concentration of the surfactant in the micellar phase was determined by refractometry. In the given range of concentration the value of refractive index shows an excellent linearity to the surfactant concentration. On the other hand, the axis intercept of the calibration graph is influenced by Na_2SO_4. The electrolyte was added in order to lower the cloud point temperature and to simplify the phase separation by increasing the density of the bulk aqueous phase. The amount of Na_2SO_4 in the micellar phase is generally lower than in the initial solution. Thus the salt concentration [Na_2SO_4] was gravimetrically determined (8 h, 400 °C) and had to be considered in the calculation of the final surfactant concentration $[surf]_{MP}$.

$$[surf]_{MP} = \frac{n_{20} - m_2[Na_2SO_4] - n_{20,w}}{m_1}$$

n_{20}: Measured refractory index
$n_{20,w}$: Refractory index of pure water
m_1: Slope (n_{20} vs. $[surf]_{MP}$)
m_2: Slope (n_{20} vs. [Na_2SO_4])

The fluorescence enhancement factor FE is determined by:

$$FE = 1/n \sum_{i=1}^{n} \frac{a_{i,MP} - a_{blank,MP}}{a_{o,water} - a_{blank,water}}$$

$a_{i,MP}$: Areas of spiked micellar phases
$a_{i,water}$: Areas of spiked water
$a_{blank,MP}$: Integral of the pure micellar phase
$a_{blank,water}$: Integral of pure water

The detection limit is calculated from calibration graphs (blank + 3 s) considering the achieved preconcentration.

The determination of the preconcentration factor from the volume ratio of the initial and

the micellar solution is not recommendable. Incomplete separation and variations in temperature will lead to serious errors. Much more better is the calculation of the enrichment parameters considering the concentration of the surfactant in the micellar phase.

The preconcentration factor of the surfactant P_{surf} represents the upper limit for the enrichment of the pesticide P_{naprop}. Therefore the recovery rate R [%] of napropamide is given in reference to the enrichment of the surfactant.

$$R = \frac{P_{naprop}}{P_{surf}} * 100$$

RESULTS AND DISCUSSION

Enrichment factor depending on salt and surfactant concentration

The extent of phase separation and enrichment significantly depends on the employed surfactant concentration, the amount of electrolyte and on the polarity of the surfactant itself. Figure 3 illustrates the effect of added Na_2SO_4 on the enrichment factor of Genapol X 80. The more salt is added, the higher are the surfactant concentrations in the micellar phase.

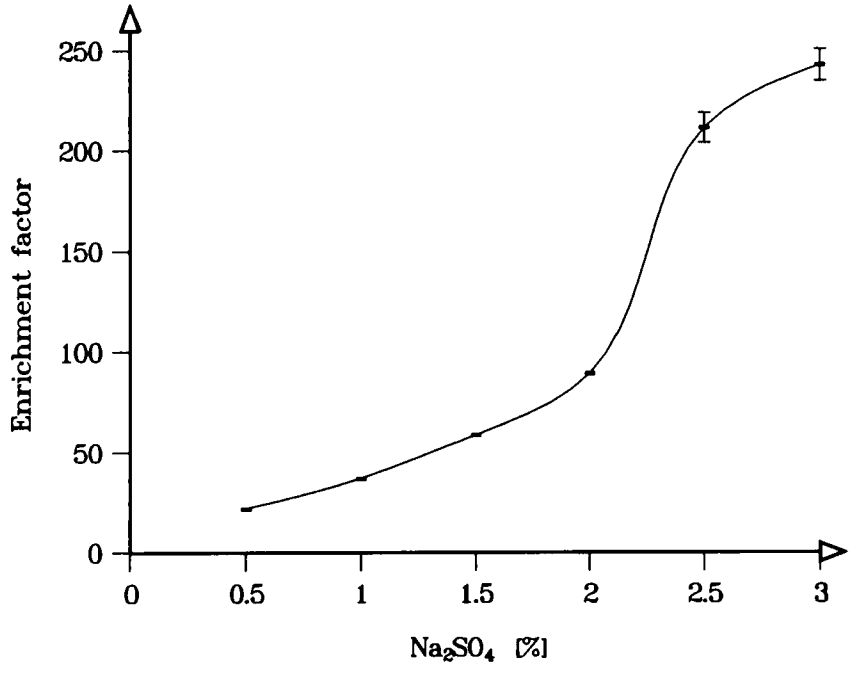


Figure 3 Influence of added salt on the enrichment factor. The initial concentration of Genapol X 80 was 0.25 % (w/w) (n = 3; 1 s).

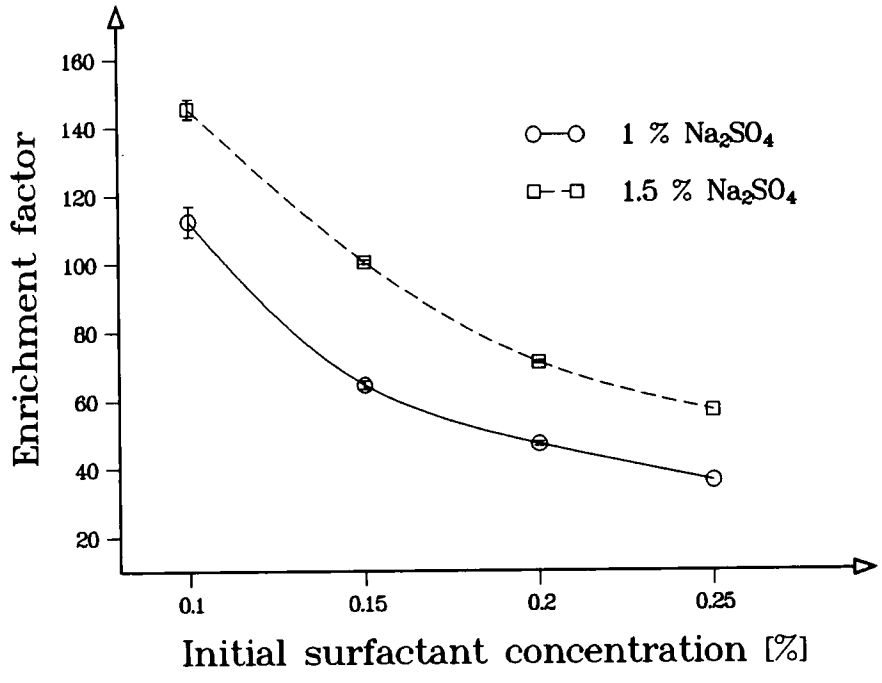


Figure 4 Surfactant concentration vs. enrichment factor. (n = 3; 1 s)

The influence of the initial surfactant concentration is shown in Figure 4. Using a small surfactant concentration increases the enrichment factor. The final surfactant concentration of Genapol X 80 in micellar phase is mainly determined by the added salt.

Extraction of napropamide

Under the chosen experimental conditions for the extraction of napropamide, the concentration of Genapol X 80 and Genapol X 150 within the micellar phase is increased by a factor of 74.6 ± 1.0 and 110.5 ± 1.6 (n = 3; 1 s). Table 1 summarizes the enrichment factors, the obtained recovery rates, the fluorescence enhancement factors and the detection limits

Table 1 Results of the extraction and preconcentration of napropamide from pure water (4.5 µg/l napropamide in 250 ml, n = 3; 1 s).

	Genapol X 80	*Genapol X 150*
Enrichment factor	56.6 ± 1.3	85.6 ± 6.4
Recovery rate [%]	75.8 ± 0.5	77.5 ± 5.8
Fluorescence enhancement	1.80 ± 0.07	2.04 ± 0.11
Detection limit [ng/l]	101	160

Table 2 Results of the extraction and preconcentration of napropamide from spiked natural water using Genapol X 80 (4.5 µg/l napropamide in 250 ml, n = 3; 1 s).

	Tap water	*Mineral water*
Enrichment factor	71.6 ± 1.8	67.8 ± 0.9
Recovery rate [%]	79.9 ± 0.5	75.7 ± 0.7

obtained by the micellar extraction of napropamide with Genapol X 80 and Genapol X 150 using ultrapure water.

Comparable results are obtained applying the method to spiked tap water of Munich or spiked samples of a mineral water. The better enrichment is caused by a higher concentration of electrolyte. Table 2 shows the enrichment factors and the recovery rates of napropamide using environmental samples and Genapol X 80.

The cloud point of nonionic surfactants is a characteristic of the molecular structure and is influenced by the surfactant concentration as well as by added salt. Nonionic surfactants with a larger unpolar part are less soluble in water than polar surfactants. Thus lower temperatures are necessary to achieve a turbid solution. Adding Na_2SO_4 to solutions of polar surfactant molecules decreases the degree of their hydration and consequently the cloud point. Genapol X 150 is much more polar than Genapol X 80. Therefore, more Na_2SO_4 have to be added.

At higher temperatures the density of the micellar phase decreases and one yields an easier phase separation. Therefore, increasing the temperature significantly above the cloud point results in a fast and complete separation.

CONCLUSION

Unlike extractions with toxic and inflammable organic solvents the use of aqueous surfactant solutions turned out to be a simple, safe, inexpensive and non-polluting method for extracting and enriching napropamide from water samples in one step. The potential hazards of the popular preconcentration techniques are avoided and the disposal of waste is simplified.

In contrast to other enrichment methods, no expensive or complex equipment is necessary. Moreover, the fluorescence enhancement increases the sensitivity due to the diminished quenching.

The extent of preconcentration is influenced by experimental parameters like surfactant and salt concentration. The lower the initial surfactant concentration and the more electrolyte is used, the higher the enrichment factor can be obtained.

Comparing Genapol X 80 and X 150, both surfactants can be used for the extraction and enrichment of napropamide. Nevertheless, Genapol X 80 should be prefered due to a shorter extraction time.

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