

# Determination of alkylphenols, alkylphenoethoxylates and linear alkylbenzenesulfonates in sediments by accelerated solvent extraction and supercritical fluid extraction<sup>1</sup>

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## Abstract

A method for the simultaneous extraction and determination of anionic surfactants in particular linear benzenesulfonates and non-ionic surfactants of the alkylphenoethoxylate-type and their degradation products, the alkylphenols, is presented. Extraction of anionic surfactants is achieved applying accelerated solvent extraction with pure methanol. For the complete extraction of the analytes the extraction pressure should be as low as possible (150 atm; 1 atm=101 325 Pa). Extraction of the alkylphenoethoxylates with recovery rates of 85% and 65% for nonylphenoethoxylate and octylphenoethoxylate, respectively, was accomplished by dynamic extraction using carbon dioxide modified with methanol. In this case, the extraction pressure should be as high as possible ( $\geq 450$  atm). The combined method was tested with spiked and aged samples showing its perfect applicability for anionic surfactants. For non-ionic surfactants the extractability of aged samples is substantially reduced. Nevertheless surfactant concentrations in real samples can be quite well determined. © 1997 Elsevier Science B.V.

**Keywords:** Sample handling; Extraction methods; Sediments; Environmental analysis; Accelerated solvent extraction; Alkylphenols; Alkylphenoethoxylates; Ethoxylates; Alkylbenzenesulfonates; Surfactants

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## 1. Introduction

Surfactants are widely used for washing purposes and for other applications, e.g. as formulating agents in pesticide formulations, in the treatment of textiles and fibres and for cosmetics, to name only a few.

Despite their high biodegradability, a certain amount of the unchanged compounds is released into the environment via waste water systems or in run-off waters. Here they may be adsorbed on surfaces especially on small particles like sediments. Thus, sediments can be regarded as indicators for the load of these analytes in an aquatic system reflecting the mean concentration and hence eliminating extreme concentration fluctuations.

Anionic surfactants namely linear alkylbenzenesulfonates (LASs) as well as non-ionic surfactants, which represent the second largest group of

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surfactants, have been of main interest in this study. Alkylphenoxyethoxylates (APEOs) and their biodegradation products, the corresponding alkylphenols (APs) were investigated, because the phenols are claimed to cause estrogenic effects in man and animals [1]. Thus, the determination of their concentration in environmental samples especially in aquatic systems is of great importance, to estimate the risk potential for aquatic organisms.

Soxhlet extraction with methanol is mainly applied for the extraction of anionic and non-ionic surfactants from solid matrices [2]. To reduce the amount of organic solvents needed and to perform rapid extractions, supercritical fluid extraction (SFE) has gained increasing importance. As shown by Hawthorne et al. [3] SFE with methanol modified carbon dioxide can be applied for the extraction of anionic surfactants (LASs). This was confirmed earlier [4] and it was shown that methanol is the most effective modifier for the extraction of anionic surfactants in comparison to pure carbon dioxide or other modifiers tested. Moreover, it was demonstrated, that derivatisation of anionic surfactants to form their methyl esters [5], chlorosulfonates [6] or ion-pairs [7] results in a better extraction efficiency. Only a few results have been published to date for the extraction of nonylphenol using SFE. Lee and Peart observed an enhanced extraction of nonylphenol after derivatisation to the acetic ester under supercritical conditions and subsequent extraction with pure carbon dioxide [8].

In this paper we present a simple method for the simultaneous extraction of anionic and non-ionic surfactants from one single sample, stressing in particular the influence of the most important extraction parameters affecting the extraction efficiency. In addition to the examination of spiked and aged samples, results from real sediment samples from the river Elbe will be discussed.

## 2. Experimental

### 2.1. Sediment samples

Sediment samples were collected in the river Elbe using a grab, homogenized by stirring and filled into LAS-free stainless steel containers. To prevent deg-

radation the samples were immediately frozen over liquid nitrogen and kept under these conditions until analysis. Before the analysis the samples were thawed at room temperature and the pore water was separated by centrifugation for 30 min at 10 000 r.p.m. The material to be used for the extraction studies was further dried at room temperature. For the analytical determination in real samples the sediments were directly used after centrifugation. Both materials were ground to a particle size <10  $\mu\text{m}$ ; their actual water content was determined by drying at 105°C for 12 h reaching constant mass. Before extraction the water content of the dried material was adjusted to 10% (w/w) by adding the appropriate amount of water to enable swelling. The material was used after one day of equilibration.

### 2.2. Sample pretreatment and spiking

For the extraction, 1.00 g of sediment was mixed thoroughly with 0.75 g of copper powder (particle-size <63  $\mu\text{m}$ , Merck, Darmstadt, Germany) according to [9] to prevent an extraction of elementary sulfur, which can obstruct the whole extraction system. The material was filled into a 5-ml extraction chamber (Suprex, Pittsburgh, PA, USA) and condensed applying a glass bar.

The recovery experiments were performed using recently spiked samples. Internal standards and known amounts of the target analytes, dissolved in 200  $\mu\text{l}$  of methanol (Merck) were carefully distributed on top of the condensed sediment/copper mixture and then gently soaked through the extraction chamber for an ageing period of 15 min. As internal standards 5  $\mu\text{g}$  linear 1-nonylbenzenesulfonate (LAS-9, Hüls, Marl, Germany) for anionic surfactants, 4  $\mu\text{g}$  heptylphenol (HP, Lancaster, Morecambe, UK) for alkylphenols, and 2.5  $\mu\text{g}$  decylphenolmonoethoxylate (DPEO, synthesised in our laboratory) for alkylphenoxyethoxylates were used. As anionic surfactants linear decyl- up to tridecylbenzene-sulfonate (LAS-10 to LAS-13, 5  $\mu\text{g}$  each, Hüls) and as non-ionic surfactants 10  $\mu\text{g}$  technical octylphenoxyethoxylate with 9,5 ethoxylate groups (OPEO, Triton X-100, Fluka, Buchs, Switzerland), 5  $\mu\text{g}$  technical nonylphenoxyethoxylate, with 13 ethoxylate groups (NPEO, Fluka) and 10  $\mu\text{g}$  4-nonylphenol (NP, Fluka) were applied. For reference

experiments the sediment samples were spiked with 200  $\mu\text{l}$  pure methanol and extracted after 15 min of ageing under the same experimental conditions.

### 2.3. Aged samples

A 100-g portion of the dry sediment was slurried in 70 ml methanol, and internal standards as well as target analytes were added at the same concentration level as outlined above. The mixture was treated with ultrasonication for 10 min and the methanol was then allowed to evaporate at room temperature over four days. The dried material was stored in a tightly closed brown glass bottle at room temperature for four months in the dark. Prior to the extraction, the water content was adjusted to 10% (w/w) and the material was allowed to swell for one day. A blank sample was prepared in the same way using pure methanol as spiking agent.

All recovery rates given are calculated from the concentration difference of three spiked and three unspiked samples relative to the spiked amount.

### 2.4. Extraction procedure

After 15-min ageing the volume of the extraction chamber was filled up with glass beads (3 mm I.D.) and the remaining space of 2 ml was made up with pure methanol (analytical-reagent grade, Merck). The extraction chamber was closed and mounted into the SFE apparatus (PrepMaster with AccuTrap and modifier pump, all Suprex) as described elsewhere [4,10]. As extraction fluid SFE-grade carbon dioxide (Air products, Hattingen, Germany) was applied, which for some extractions was modified with 27.5% (v/v) methanol via a modifier pump. The lowest extraction pressure which could be realised with this system was 130 atm (1 atm=101 325 Pa) because of the initial pressure in the flask. After a static step (accelerated solvent extraction, ASE) of 10 min at 150 atm and 100°C a subsequent dynamic extraction (SFE flow-rate 1.0 ml min<sup>-1</sup>) of 5 min at the same pressure and temperature was performed for the detailed study of the static extraction. For the study of extraction parameters influencing the dynamic extraction the initial extraction at 150 atm was carried out as described before, followed by dynamic

steps at 200, 300 and 450 atm, respectively (flow-rate 1.0 ml min<sup>-1</sup>). For the examination of the influence of pressure on the recovery rates carbon dioxide modified with 27.5% (v/v) of methanol was applied as extraction fluid. Investigating the contribution of methanol on the extraction a pressure of 450 atm was used for the dynamic extraction.

The dynamic extraction process was divided into three 5-min, one 10-min and one 30-min periods. The analytes were trapped during the extraction in an AccuTrap at -5°C on silanised glass beads and were eluted afterwards using methanol at 40°C. Each extract was collected in a separate vial (5, 10, 15, 20, 30, 60 min total extraction time) and the concentration of the analytes was determined in each extract. The concentration for each analyte is summed up in case of the dynamic extraction, the recovery of the static extraction is shown directly in the graphs.

### 2.5. Determination

The extracts were evaporated to dryness under a gentle stream of argon. The residue was dissolved in 1.0 ml methanol and the standard substances for the HPLC determination were dissolved in 50  $\mu\text{l}$  methanol added [anionic surfactants: 5  $\mu\text{g}$  sodium *n*-hexadecyl sulfate (C<sub>16</sub>SO<sub>4</sub>Na) (Lancaster); non-ionic surfactants: 10  $\mu\text{g}$  2,4,6-trimethylphenol (Aldrich, Steinheim, Germany)]. After sonication and filtration the samples were directly used for HPLC determination.

The final analysis was performed by HPLC (Merck) applying a RP-18 column (Inertsil-ODS 80 A 5  $\mu\text{m}$ , GL Science Japan, 12.5-cm length) for the non-ionic surfactants with direct fluorescence detection at 230 nm excitation and 305 nm emission. The limit of detection for this determination was 10 ng with a reproducibility of  $\pm 7\%$ . For the anionic surfactants a C<sub>1</sub> column (Spherisorb C<sub>1</sub> 5  $\mu\text{m}$ , Phase Sep, UK, 5-cm length) was chosen with subsequent post-column derivatization to a fluorescence dye complex as described earlier [4,11,12]. For this determination the limit of detection was 10 ng with a reproducibility of  $\pm 13\%$ . All other details for the HPLC determination have been described in the literature [4,11,12].

### 3. Results and discussion

#### 3.1. Influence of the extraction pressure

To examine the influence of the extraction pressure on the recovery of the surfactants, experiments were carried out at different pressures ranging from 150–450 atm. An increasing extraction efficiency with increasing extraction pressure is generally found because of the higher density of the extraction fluid and its improved solvation power. However, the experiments clearly show, that the recovery rates of the anionic surfactants are substantially reduced with increasing pressure (Fig. 1). Only at an extraction pressure of 150 atm is a quantitative extraction of the LAS surfactants achieved. An increase to 200 atm reduces the recovery by about 50%, at higher pressures the recovery is even further reduced. This effect might be the result of the following three reasons: (a) the analytes are lost because of forming aerosols, (b) the solubility of the substances is decreased with increasing pressure or finally (c) the pressure induces a change of the matrix surface resulting in a reduced extraction of the analytes.

The first explanation, discussing the loss of the analytes due to the formation of aerosols has already

been published [13]. However, this explanation may not be the reason for the observed low recovery rates in our experiments: No aerosols were observed during the dynamic extraction and the duration of the extraction with only 5 min was too short to yield such large losses. Moreover, trapping devices like plugs of glass wool sealing the orifice of the sample vial did not result in better extraction efficiencies.

As regards explanation (b) further extraction experiments with silanised glass wool as inert matrix showed that the extraction pressure had no influence on the solubility of the surfactants. The recovery rates varied only within the range of the R.S.D. values.

Thus for anionic surfactants the low recovery rates may only be attributed to changes in the matrix induced by pressure. Fahmy et al. [14] reported an irregular swelling of inorganic and organic matrices depending on pressure and a correlation of extraction efficiency with the extent of matrix swelling. Consequently, a correlation between extraction pressure and swelling may be possible. The problem can be illustrated as follows: if the analytes are adsorbed on the active sites located inside a pore, the orifice may be closed by the deformation of the particles due to increasing pressure. Thus, the extractabilities of the

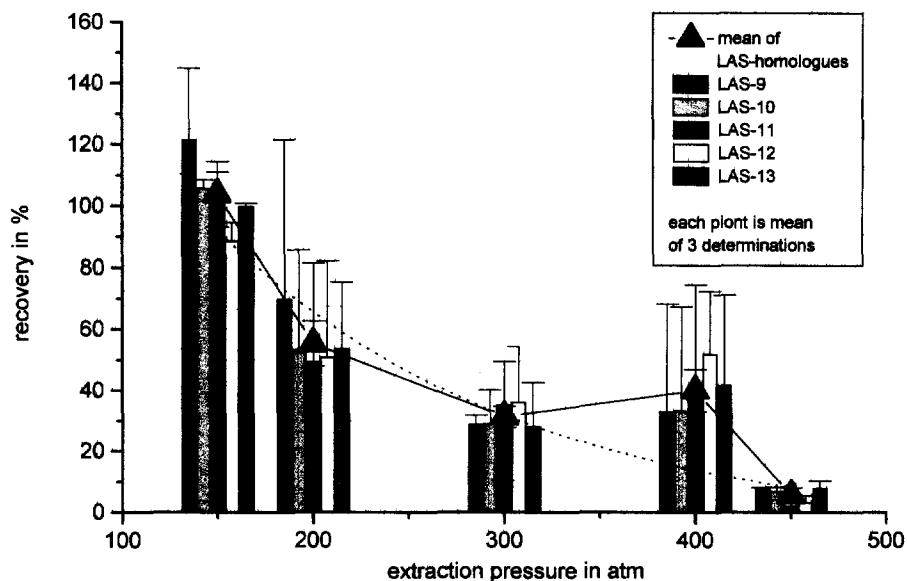


Fig. 1. Extractability of anionic surfactants from sediments, effect of extraction pressure, 10 min static extraction with methanol at 100°C.

analytes will be reduced. Further examinations applying a view-cell are required to prove this assumption.

In contrast to the anionic surfactants the removal of non-ionic substances is independent of pressure as can be seen from Fig. 2. The alkylphenols as well as DPEO can be extracted nearly quantitatively whereas the recovery rates of NPEO and OPEO are found only in a range between 15 and 40%. Although the HPLC determination of the DPEO is affected by matrix substances, the trend can be estimated.

### 3.2. Modifier volume

Methanol has been found to be the most effective modifier for the extraction of anionic surfactants [4]. To investigate the influence of the modifier volume, the extraction was performed with different amounts of modifier added directly to the spiked sediment samples in the extraction chamber. The results are presented in Fig. 3.

A positive linear correlation between the extractability of the LAS surfactants and the modifier volume was observed. When applying pure carbon dioxide, no anionic surfactants were extracted; by raising the amount of methanol up to nearly 100%,

the recovery was increased to the same extent in the same range. This might be a result of their high solubilities in methanol due to the increasing polarity and hydrogen-binding in contrast to their insolubility in pure carbon dioxide [15].

### 3.3. Alkylphenols and -ethoxylates: temperature and duration of static extraction

To achieve a complete extraction of the higher alkylphenoethoxylates further investigations with regard to temperature and duration of the static extraction were performed. Neither an elevation of the temperature from 100°C to 150°C nor an extension of the static extraction time from 10 to 30 min resulted in a higher extraction efficiency for all of the analytes investigated. Comparable results were obtained when lowering the extraction temperature to 30°C and omitting the static step. These findings confirm the assumption that the recovery rates of all non-ionic surfactants investigated are independent of the two parameters examined. Thus, the quantitative extraction of the alkylphenoethoxylates applying only a static extraction step seems to be impossible. Therefore systematic investigations with respect to the possibilities of a dynamic extraction procedure

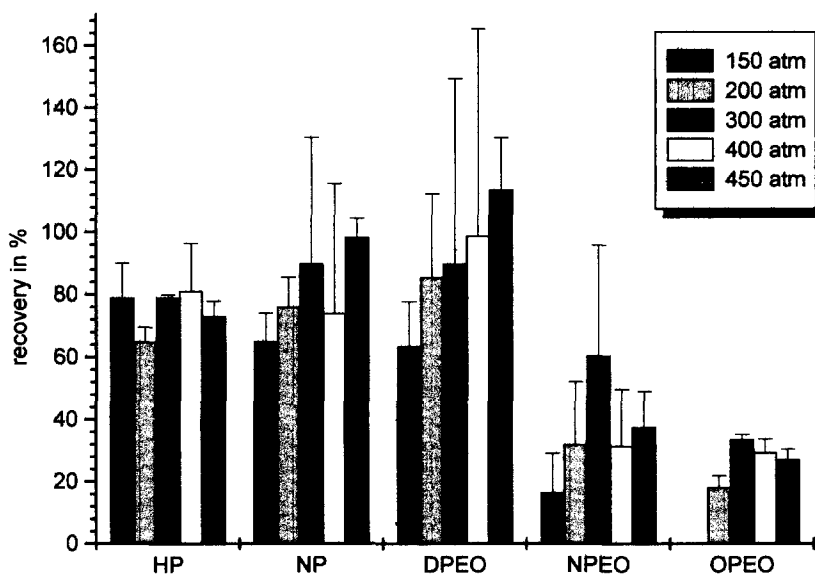


Fig. 2. Extractability of non-ionic surfactants from sediment, effect of extraction pressure, 10 min static extraction with methanol at 100°C.

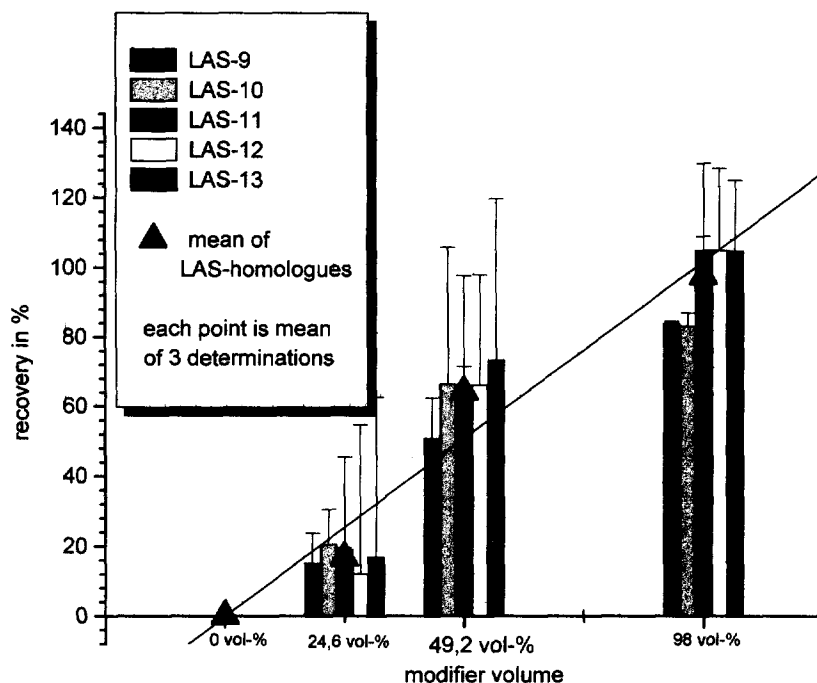


Fig. 3. Extractability of anionic surfactants from sediments, effect of modifier volume, 10 min static extraction with methanol at 100°C.

were carried out, to obtain a satisfactory extraction of these substances.

#### 3.4. Dynamic extraction: influence of extraction pressure

For the examination of the extraction kinetics as a function of time and pressure the extractability of alkylphenolethoxylates was measured stepwise over a total range of 60 min with intervals of 5, 10, 20 and 30 min, respectively (see Section 2). The respective recovery rates were determined at each time interval and are shown in Fig. 4 as summed-up values. As can be seen from the graph, the extractability of the alkylphenols at a constant pressure of 200 atm displays a linear relationship with time. At higher pressures, such as 300 atm and 450 atm the kinetics show a different shape. After a steep increase within the first 10 min the extraction curves level off so that an extraction time exceeding 20–30 min does not yield higher efficiencies. This pattern is characteristic for the removal of substances weakly adsorbed at the matrix.

It may be deduced from Fig. 4 that the extract-

ability of the alkylphenolethoxylates increases with increasing pressure. Therefore the highest yields were found at 450 atm. For NPEO as well as OPEO a linear correlation between extractability and extraction pressure was found for the pressure range investigated. Beyond the highest pressure chosen the curve must level off or recoveries exceeding 100% would occur. To prove this assumption extractions at higher pressures should have been carried out which was unfortunately impossible with the apparatus used.

Thus, for the extraction of alkylphenolethoxylates from solid samples like sediments dynamic extraction at 450 atm for 30 min seems to be sufficient to remove these substances with extraction yields of >85% for NPEO and >65% for OPEO, respectively.

#### 3.5. Dynamic extraction: influence of modifier

To get an insight into the influence of methanol on the dynamic extraction of alkylphenolethoxylates, dynamic extractions at 450 atm. were performed using (a) pure carbon dioxide and (b) carbon dioxide

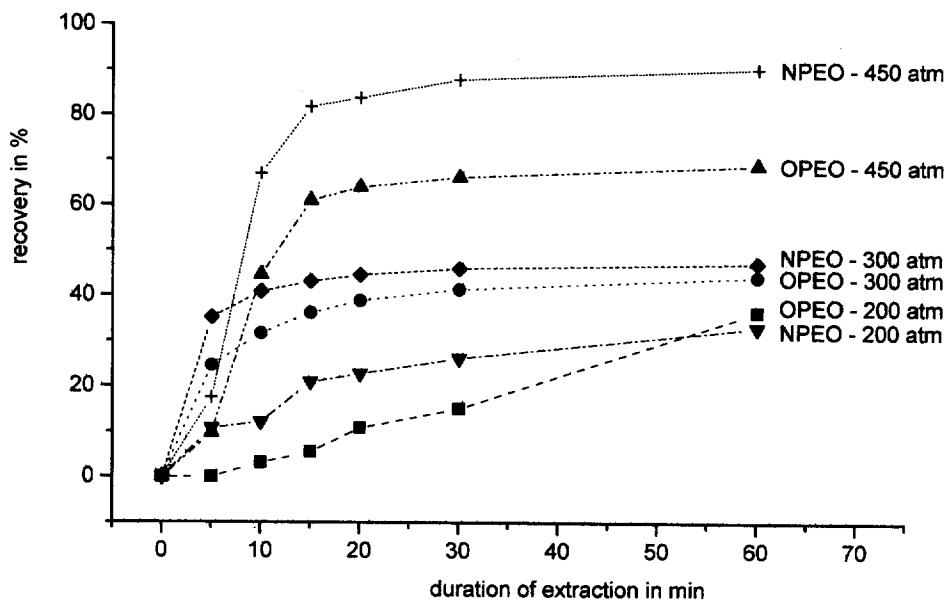


Fig. 4. Dynamic extraction of alkylphenoethoxylates from sediment as a function of pressure and time at 100°C.

modified with 27.5% (v/v) methanol, after the initial ASE-extraction with pure methanol.

As can be seen from Fig. 5, the resulting profiles are independent of the presence of methanol. However, the absolute recovery rates attained are significantly increased using methanol modified carbon

dioxide. This effect may be explained by the enhanced solubility of alkylphenoethoxylates in the methanol modified extraction fluid. In addition, the replacement of the adsorbed analytes by methanol molecules delivered continuously by the extraction fluid may contribute to a certain extent. However, it

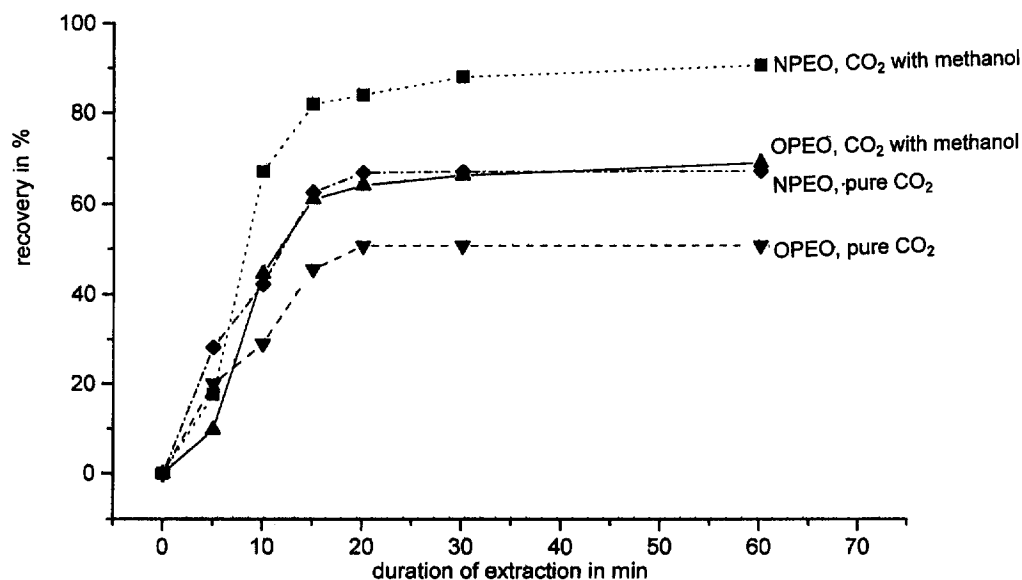


Fig. 5. Effect of methanol on the dynamic extraction of alkylphenoethoxylates at 450 atm and 100°C.

seems to be more or less impossible to raise the obtained recovery rates (65% for OPEO and 85% for NPEO) close to the 100% level under the experimental conditions used, due to differing binding states or different binding sites of the target molecules to be extracted. In particular, those molecules bound inside the matrix are strongly adsorbed, thus making extraction extremely difficult.

### 3.6. Combined extraction procedure

As a consequence of the various extraction conditions investigated the following combined procedure is recommended for the simultaneous extraction of anionic and non-ionic surfactants from sediment samples:

First step: void volume of the extractor to be filled up with methanol

Second step: static extraction: at 100°C, 150 atm, for 10 min

Third step: dynamic extraction: at 100°C, 150 atm, for 5 min, at a flow-rate of 1.0 ml min<sup>-1</sup>

Fourth step: dynamic extraction: at 100°C, 450 atm, for 30 min, at a flow-rate of 1.0 ml min<sup>-1</sup>.

With this procedure anionic and non-ionic surfactants can be simultaneously and satisfactorily ex-

tracted from recently spiked sediment samples. To investigate its applicability towards real specimen, spiked samples which had been aged for four months, were analyzed.

### 3.7. Aged samples

The different extraction behavior of spiked and native material has been discussed previously in the literature [16,17]. Accordingly the recovery rates decrease from recently spiked samples to aged samples and further on to native materials due to the growing influence of analyte–matrix interactions and diffusion into matrix particles.

The comparison of the two analyzed series performed (recently spiked and aged samples) is shown in Fig. 6, illustrating that the extraction of the anionic surfactants is not effected by aging. The slightly reduced extraction yields of the aged samples are in the range 5–23% and thus more or less coincident with the R.S.D. These results clearly demonstrate that in spite of the long contact time the weak interactions of the LAS surfactants with the matrix are not significantly intensified, as has been reported by Bartle [18]. Thus, it may be expected that the analyzed data obtained for LAS surfactants

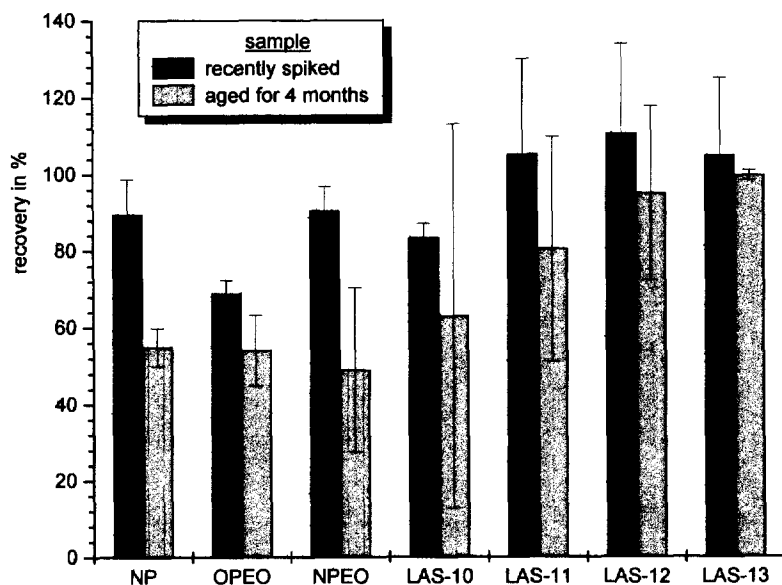


Fig. 6. Recovery of anionic and non-ionic surfactants from recently spiked and aged sediment samples.



in real environmental samples may be regarded as accurate concentration with an R.S.D. value of  $\pm 15\%$ .

Contrary to these findings, the extraction of alkylphenols and -ethoxylates from aged samples is more seriously reduced. For NPEO and the alkylphenol NP the recovery is reduced by approximately 40% while for OPEO only a 22% loss was observed. These results might be due to the fact, that during the ageing process the number of analyte–matrix interactions like hydrogen-bonding and dipole–dipole interactions is substantially increased, rendering the extraction more difficult. However, the combined extraction procedure can still be used for the reliable estimation of non-ionic surfactants in environmental samples. To eliminate the lower extraction efficiencies as a result of ageing, the surfactant concentrations can be calculated from the determined concentrations corrected with the reduced recovery rates determined using aged samples by correcting the measured concentrations with the reduced recovery yields obtained in aged samples.

### 3.8. Environmental samples

The combined extraction method was applied to the determination of surfactant concentrations in sediments from the river Elbe, sampled from 1990 to 1994 in the area of the former German Democratic Republic. Because of the different sample composition due to sedimentation, the concentrations have been normalized to the fine corn fraction (particle size  $<20 \mu\text{m}$ ) for comparison. This fraction is assumed to enrich most of the organic and inorganic compounds due to its large surface [19].

Fig. 7 shows the concentration profiles of the LAS surfactants as an example of the results obtained applying this method. As can be seen from the graph, the concentration in all samples collected in 1990 were much higher at nearly all sampling sites than in the following years, where only the samples from Dessau (1992) and Magdeburg (1994) exhibited higher concentrations compared with the other samples of the respective year. The drastic decrease in concentration from 1990 to 1994 might

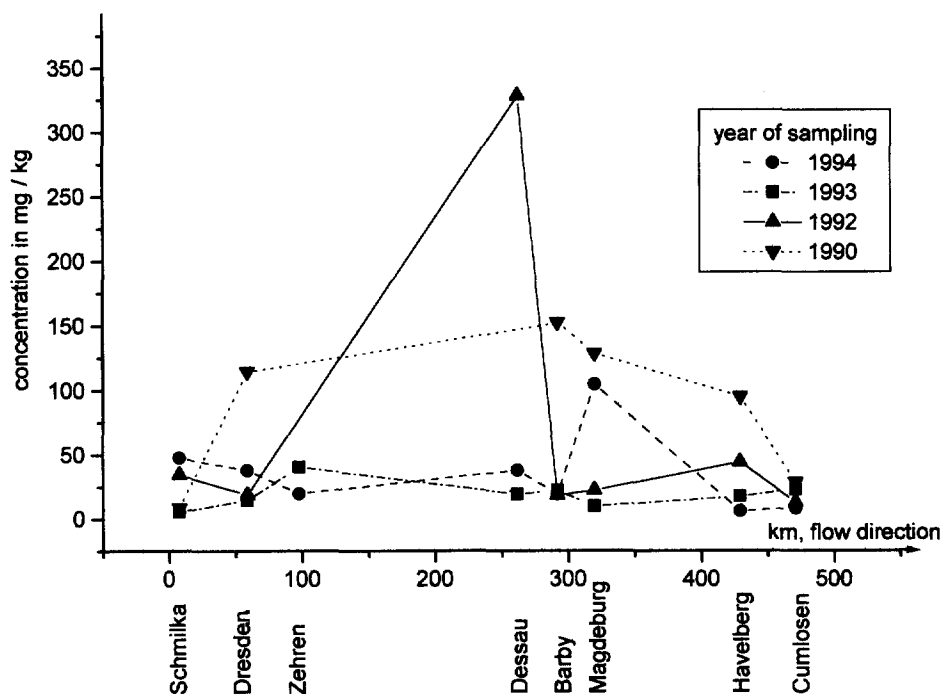


Fig. 7. Concentration of anionic surfactants in sediments of the river Elbe, (particle size  $<20 \mu\text{m}$ ) sampled from 1990 to 1994.

be the result of the construction of new sewage plants, where anionic surfactants are eliminated with the sludge to a great extent, and the closure of production facilities.

#### 4. Conclusion

By the combined ASE/SFE method the simultaneous extraction of anionic and non-ionic surfactants from sediments may be performed in less than 1 h. For the extraction of anionic surfactants of the LAS type the amount of methanol as modifier and the extraction pressure are the main parameters determining the extraction efficiency. Optimal yields may be obtained by pure methanol and a pressure as low as possible (e.g. 150 atm). While alkylphenols are easily extractable under the same experimental conditions, non-ionic surfactants like NPEO and OPEO require an additional extraction at 450 atm and 30 min with methanol modified carbon dioxide.

With the combined method recently spiked surfactants may be removed quantitatively from sediment samples. For aged samples slightly reduced recovery rates were measured in the case of anionic surfactants, while the extractability of non-ionic surfactants recovery was reduced by 22–40%. However, this method is a powerful tool for the simultaneous determination of surfactant concentrations in environmental samples and was successfully applied for the determination of these compounds in native sediments from the river Elbe.

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