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Determination of non-ionic polyethoxylated surfactants in sewage sludge by coacervative extraction and ion trap liquid chromatography–mass spectrometry

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Abstract

Alkylphenol polyethoxylates (APE, nonyl and octyl) and alcohol ethoxylates (AE, C_{12}–C_{16}) were analysed in sewage sludge by extraction with sodium dodecane sulphonate (SDoS), that undergoes coacervation under acid conditions, followed by quantitation with liquid chromatography/atmospheric pressure chemical ionisation ion/trap mass spectrometry, in positive ion mode. Coacervative extraction was optimised using an aged, fortified dehydrated sludge. Recoveries ranged from 78 to nearly 100% irrespective of the sludge matrix analysed. The method provided good agreement between the ethoxamer distribution of surfactants after extraction from sludge and that in the original surfactant. Detection limits for polyethoxylated surfactants in the sludge were 0.09–0.38 mg/kg. The procedure was used to assess the concentrations of APE and AE in activated and dehydrated sludge from two sewage treatment plants. Polyethoxylates were found in all samples in the concentration ranges 11–151, 100–138 and 23–141 mg/kg for octylphenol, nonylphenol and individual AE homologues, respectively. The method did not require clean-up or preconcentration steps.

Keywords: Coacervative extraction; Surfactants; Alkylphenol polyethoxylates; Alcohol ethoxylates

1. Introduction

Alkylphenol ethoxylates (APE, C_nH_{2n+1}-C_6H_4-$(OCH_2CH_2)_xOH$; n = 8, 9; x = 1–23) and alkyl ethoxylates (AE, C_nH_{2n+1}-$(OCH_2CH_2)_xOH$; n = 12–18; x = 1–23) are the major non-ionic surfactants in the market [1]. APE have been in use for more than 45 years as detergents, emulsifiers, wetting agents, and dispersing agents in household, agricultural and industrial applications.

Because of the hormone-disruptive effects of nonylphenols (NPE_x) [2], recent environmental initiatives have led to demands for their removal from product formulations in favour of less harmful alternatives (e.g. AE). Both, APE and AE are relatively resistant to degradation under anaerobic digestion [3], which is the predominant treatment of sludge from primary settling tanks, and therefore surfactants can pass through a wastewater treatment plant relatively untreated. Application of sludge to agricultural land may provide a large source of AE and APE to the soil environment [4], so rapid and simple methods to control them in sewage sludge that is to be spread on land are necessary.

Current available methods for determining APE and AE in solid environmental matrices (i.e. sewage sludge, sediment, soil, etc.) include the following steps: (a) Soxhlet extraction with solvents such as basic methanol [5,6] or hexane isopropanol [7], or sonication-based repetitive extractions [7,8]; (b) concentration of extracts by evaporation; (c) clean-up with C_{18}-SPE, and (d) reversed-phase LC/MS [7,9–12]. Liquid chromatography separates AE and APE according to their alkane chain length and MS allows the identification of oligomers, that differ in the number of ethoxy units.

Limitations associated to these methods include the need for concentrating analytes after extraction, the large vol-

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umes of organic solvents used, and the long time required for sample treatment. The use of supercritical fluid extraction has been proposed to reduce these limitations, but this technique fails with aged spiked samples due to the strong matrix–analytes interaction [13]. On the other hand, it is important to ensure that the extraction method maintains the same oligomer distribution in extracted and original samples [14], since for many solvent extraction methods this does not occur or it has not been assessed.

The objective of this work was to overcome some of the above limitations by taking advantage of the ability of the acid-induced sodium dodecane sulphonate (SDoS) phase separation [15] (coacervative extraction) to extract amphiphiles from solid matrices [16] on the basis of the formation of extractant–analytes mixed aggregates. The final aim was to develop a rapid, simple and reliable method to the routine control of APE and AE in sewage sludge. The evaluation of the SDoS coacervative extraction for this purpose included investigation of the distribution of oligomers after extraction. Reversed-phase liquid chromatography/atmospheric pressure chemical ionization/ion trap mass spectrometry (LC/(APCI-IT)MS) was used for the separation and quantitation of non-ionic surfactants. The feasibility of the method was illustrated with the analysis of AE and APE in activated and dehydrated sludge from two wastewater treatment plants (WWTPs). This paper presents the first application of surfactant-mediated extractions for the analysis of non-ionic surfactants in environmental solid matrices.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were of the highest purity commercially available. Sodium dodecane sulphonate (SDoS) was obtained from Fluka (Madrid, Spain). Hydrochloric and acetic acids, and HPLC-grade acetonitrile and methanol were obtained from Panreac (Sevilla, Spain). All the individual polyethoxylated surfactants used as standards corresponded to pure homologues containing a mixture of oligomers with a determined average (x) of ethoxy units. Octylphenol ethoxylate (x = 9–10 Triton X-100) was obtained from Serva (Barcelona, Spain), nonylphenol ethoxylate (x = 6) from Masso y Carol (Barcelona, Spain), alcohol polyethoxylates C_{12} (x = 4) and C_{16} (x = 2) from Sigma (Madrid, Spain), and C_{10} (x = 3) and C_{14} (x = 4) from Fluka (Madrid, Spain). Stock solutions of analytes were prepared in methanol.

2.2. Sample collection and spiking

Activated and dehydrated sludge samples were collected from two WWTPs (Pozoblanco and Baena) in the south of Spain in December 2002 and March 2003, respectively. Pozoblanco WWTP receives domestic effluents and Baena WWTP receives about 30% of industrial effluents (mainly from laundries and olive oil industries) mixed with about 70% domestic wastewaters. Dehydrated sludge samples were freeze-dried in a Telstar Cryodos-50 freeze dryer (Terrassa, Spain), finely ground (<0.5 mm), and stored in glass amber bottles at 4 °C until analysis. Activated sludge samples were previously filtered, and then processed as dehydrated sludge.

Spiked samples were prepared from dehydrated sludge collected in the Pozoblanco WWTP (May 2002). Samples were freeze-dried and finely ground. Then 1 ml of 1 g/l methanolic solution and 10 ml of distilled water were added to 20 g (dry weight) of sludge. Samples were allowed to interact with the natural organic matter for 1 h under nitrogen to prevent aerobic degradation and under stirring. Then the sludge was freeze-dried, ground and stored in amber bottles at 4 °C. Extractions were carried out 6 months after spiking in order to check the ability of ACPE to extract APE and AE from aged samples.

2.3. Acid-induced cloud point extraction

The sludge sample (0.1 g) was mixed with 10 ml of 0.05 M HCl in a closed centrifuge tube and stirred at 700 rpm for 5 min. The acid solution containing alkaline and alkaline-earth metals was separated by centrifugation and discarded. Then, 10 ml of 2% SDoS in 4 M HCl was added to the solid residue and the samples stirred at 700 rpm for 1 h, in a water circulating thermostated (60 °C) beaker. Afterwards, it was centrifugated at 5000 rpm for 10 min. Three phases were observed in the centrifuge tube: the non-dissolved solid matrix at the bottom, a little volume of anionic surfactant-rich phase containing the non-ionic surfactants at the top and an aqueous phase in the middle. To make easier the separation of the surfactant-rich phase, the temperature was lowered to 0 °C, then this phase turned gelatinous, dense enough to be completely separated from the liquid phase using a simple tool (e.g a spatula). Under room temperature, the gelatinous phase rendered liquid (between 1.2 and 1.4 ml) and it was diluted to the mark with methanol in a 2 ml vial. Before injecting an aliquot in the chromatographic system, the sample was filtered through a 0.45 μm nylon membrane filter.

2.4. Liquid chromatography–mass spectrometry

Separation and quantification of APE and AE was performed by using a liquid chromatography/ion trap mass spectrometry system (1100 Series LC/MSD, Agilent Technologies, Waldbronn, Germany), which can be configured for APCI or ESI, and it is equipped with an automatic injector. The injection volume was set at 20 μl. The stationary phase column was a 15 cm Zorbax Eclipse XDB-C_8 column (5 μm particle diameter and 4.6 mm i.d.) supplied by Agilent (Waldbronn, Germany). The mobile phase was made up of acetonitrile-methanol (50:50, solvent A) and water (solvent B), both containing 1.5% ammonium acetate. The gradient

elution program was: isocratic conditions with 70%A:30%B for 5 min and then linear gradient from 30 to 5% B in 20 min. The flow-rate was set at 1 ml/min. The diver valve was programmed to send the mobile phase containing SDoS and the most polar matrix compounds to waste. So, only 7 min after the beginning of the elution gradient program, the eluted components were sent to the ionisation source.

Quantification was carried out in the "APCI(+)" mode. To optimise the APCI-MS parameters, a mixture of the target analytes (10 mg/l of each standard compound) in methanol was directly analysed using a KD Scientific, model 100, syringe pump (New Hope, Minnesota) at 800 μl/h. For selection of the best value for each parameter, criteria of sensitivity for each homologue were considered. The set of parameters used was: capillary voltage 3.5 kV; corona discharge current 4000 nA; source and vaporizer temperature 300 and 350 °C, respectively; drying gas flow 1 l/min; nebulizer gas 50 psi; capillary exit and skimmer voltage 180 and 25 V, respectively; trap drive 50; ion charge control 20,000 and mass scan range 200–1200 *m/z*.

Quantification was carried out under full-scan conditions by measuring the peak areas of the extracted molecular ion chromatogram for each homologue and the internal standard ($C_{10}E_x$, 200 ng absolute amount injected [17]), at the *m/z* values corresponding to the $[M + NH_4]^+$ ions obtained for the 20 oligomers (x = 1–20) that typically can make up AE and APE homologues. So, the mass spectra for homologues and the internal standard showed equidistant signals with mass differences of 44 corresponding to the different oligomers present. Smooth chromatograms were obtained by using the Gauss function (width = 3 points, cycles = 1). Correlation between peak areas and homologue concentrations (2–2000 ng absolute amount) were determined by linear regression and were in the range 0.998–0.9992.

3. Results and discussion

3.1. Mass spectrometry detection

LC/MS analysis of APE and AE has been carried out using both ESI [17] and APCI [15] interfaces in positive ion mode. Under preliminary experiments in which various combinations of water or acetonitrile/methanol (50%/50%) and acetic acid were used as mobile phases, APCI gave the highest signal for all AE and APE homologues investigated and therefore this ionisation source was selected. Another reason for selection was that APCI is generally less sensible to matrix interferences in environmental samples than ESI [18].

Mass spectra for homologues showed $[M + H]^+ \pm 44$ and $[M + NH_4]^+ \pm 44$ ions corresponding to the entire ethoxylate series, with the latter being usually the most abundant ions under all the conditions investigated, despite ammonium ions were not added to the mobile phase. The problem of the presence of ammonium adducts in the mass analysis of polyethoxylates due to impurities, composition of samples, etc., has been previously described [7]. Under addition of NH_4Ac (0–3%) the signal intensity for $[M + NH_4]^+$ corresponding to the entire ethoxylate series increased (30–60%) and it was practically constant from 1% NH_4Ac, therefore a percentage of 1% of this salt was selected as solvent modifier. Fig. 1a shows the total ion chromatogram obtained under the elution program recommended for analysis of AE and APE (see Section 2). Mass spectra for homologues showed $[M + NH_4]^+$ ions corresponding to the different oligomers (Fig. 1b–g) so, information on the oligomeric distribution of APE and AE can be easily obtained.

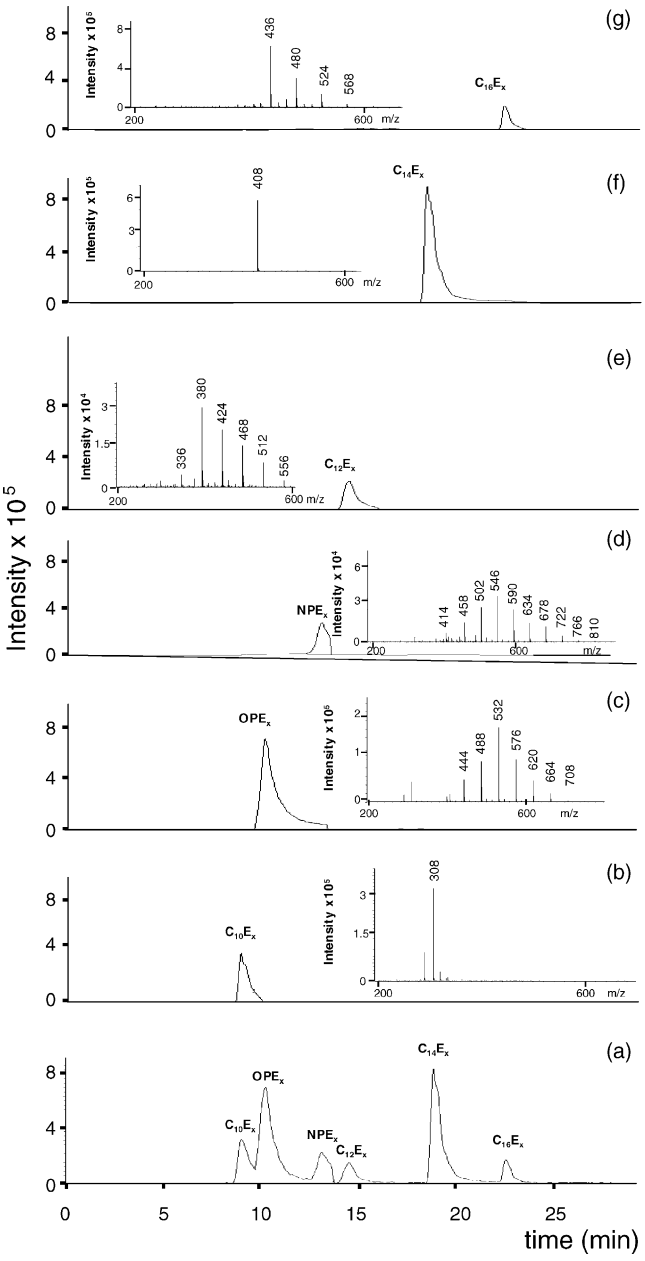

Fig. 1. Reconstructed ion chromatogram (a) and mass spectra (b–g) obtained for a standard solution containing 10 mg/l of the target compounds by using LC/(APCI-IT)MS.

3.2. Coacervative extraction of AE and APE

The ability of SDoS to extract AE and APE was assessed using dehydrated sludge samples spiked with standards of different alkyl chain length and number of ethoxy units (see Section 2 and Fig. 1), since no standard reference materials were available.

Acid conditions (2.5–5 M HCl) are necessary to separate SDoS aqueous solutions into two isotropic phases [15]. Because organics with ether groups can degrade under concentrated acid conditions (HI > HBr > HCl) and high temperatures, we investigated the stability of AE and APE in the ranges 2.5–5 M HCl, 20–60 °C and 5–60 min. The target compounds were found stable under all the experimental conditions tested.

Before extraction of AE and APE from the sludge, it was necessary to remove alkaline-earth metals from the matrix since these metals yield very insoluble salts with anionic surfactants bearing sulphonate groups [19]. The sample was stirred with 10 ml of HCl (0.01–0.1 M) or AEDT (0.1 M) for 5 min. Alkaline-earth metals present in sludge as carbonates were only efficiently removed for HCl concentrations equal or above to 0.05 M. No AE, that consist of short ethoxy units (Fig. 1), were observed in the discarded acid phase. However, the dissolved fraction in this phase of NPE_x and OPE_x, that were made up of longer ethoxy units and therefore were less hydrophobic that AE, increased as the acid concentration increased. Thus, the percentage of NPE_x and OPE_x dissolved was about 0, 9 and 14% for HCl concentrations of 0.01, 0.05 and 0.1 M, respectively; 0.05 M HCl was selected as a compromise.

Table 1 shows the recoveries of AE and APE from aged spiked sludge as a function of the SDoS concentration. The recoveries calculated for total non-ionic surfactants are also included. The extraction efficiency for all target compounds was maximal around 2% SDoS and this was the concentration selected. The use of percentages of SDoS above 2.5% were not advisable because the greater difficulty in handling the surfactant rich phase.

Lower recoveries were obtained for APE compared to AE (Table 1), probably due to their different ethoxamers composition. Losses of APE during removal of alkaline-earth metals (see above) undoubtedly contributed to these results. We investigated if additional losses of APE occurred by their partition between the aqueous and the surfactant-rich phase after sludge extraction: in a cloud point extraction of solid matrices three phases are always obtained; the non-dissolved solid matrix, a small volume of surfactant-rich phase containing the analytes and other matrix components, and an aqueous phase in between. So, the partition of analytes between the aqueous phase and the surfactant rich phase should always be considered. To estimate this partition, extraction of AE and APE by SDoS (2%) from an acid solution (4 M HCl) was carried out. The recoveries found were greater that 99% for AE and about 94% for APE, and therefore we assumed that this factor also contributed to the loss of APE in the extraction process from sludge. Since degradation of AE and APE in environmental samples causes losses of ethoxy units and therefore short ethoxamers should predominate, this slight decrease in the extraction efficiency with the number of ethoxy units from aqueous solutions should not produce an important skewing of the apparent distribution of AE and APE in sludge.

The influence of the temperature on the efficiency of the coacervative extraction of AE and APE was studied in the range 20–80 °C (data not shown). This parameter considerably increased the recoveries of the less hydrophobic compounds up to 60 °C: recoveries for OPE_x, NPE_x and $C_{12}E_x$ increased about 40, 25 and 27%. On the other hand, high recoveries were obtained for the more hydrophobic target compounds, $C_{14}E_x$ and $C_{16}E_x$, in the temperature range studied (the recoveries were 90–100% in the 20–80 °C interval) indicating that hydrophobic interactions were essential for SDoS coacervative extraction.

Table 2 shows results on the influence of the HCl concentration on the recoveries of the target compounds. Maximal recoveries were obtained from 3.5 M HCl. Since the phase volume ratio (volume of surfactant-rich phase/volume of aqueous solution, after the extraction step) decreases with HCl concentration, a value of 4 M is recommended as a compromise between recovery and preconcentration.

The influence of the extraction time on the ability of SDoS to extract AE and APE was investigated for 30–120 min. Recoveries increased 10–20% when the extraction time increased from 30 to 60 min, and then became essentially constant. About 1 h is recommended as optimum value.

Table 1
Mean percent recoveries[a] obtained for the extraction of AE and APE from sewage sludge as a function of SDoS concentration

SDoS (%)	OPE_x	NPE_x	$C_{12}E_x$	$C_{14}E_x$	$C_{16}E_x$	Recovery[b] (%)
0.75	45	43	38	30	39	39
1.5	60	65	70	77	83	71
2	78	81	89	99	101	90
2.5	65	76	81	89	93	81
3	58	63	72	76	90	72

[a] Based on three replicates; range of R.S.D. values 1–4%.
[b] Average recoveries of AE and APE. Experimental conditions: 60 °C, 4 M HCl and 1 h.

Table 2
Mean percent recoveries[a] obtained for the extraction of AE and APE from sewage sludge as a function of HCl concentration

HCl (M)	OPE_x	NPE_x	$C_{12}E_x$	$C_{14}E_x$	$C_{16}E_x$	Recovery[b] (%)
2.5	54	51	73	80	86	69
3	56	59	76	80	90	72
3.5	78	80	83	100	99	88
4	78	81	89	99	101	90
4.5	77	78	83	90	98	85

[a] Based on three replicates; range of R.S.D. values 2–7%.
[b] Average recoveries of AE and APE. Experimental conditions: 60 °C, 2% SDoS and 1 h.

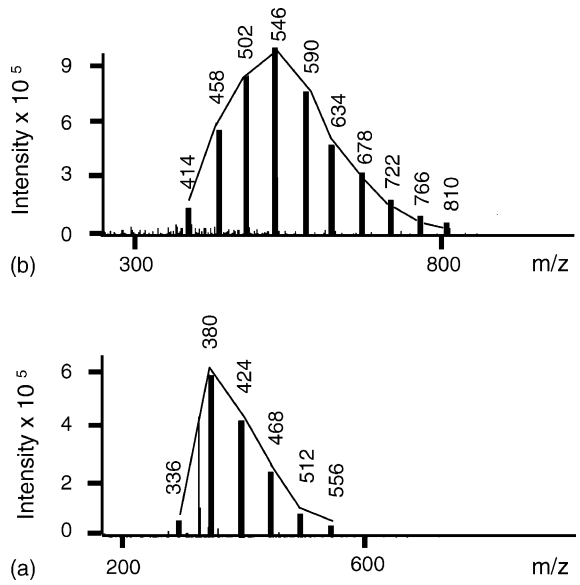

Fig. 2. Comparison of ethoxamer distribution between direct LC/(APCI-IT)MS analysis of a 50 mg/l standard solution containing $C_{12}E_x$ (a) and NPE_x (b) and SDoS coacervative extraction/LC/(APCI-IT)MS analysis of both surfactants in a fortified sludge sample (results for standards are indicated by the solid line above the graph).

An important consideration in the analysis of non-ionic surfactants is the integrity of the ethoxamer distribution found after extraction. In some liquid–liquid extraction methods, smaller ethoxamers are better extracted than larger ones, producing a skewing of the apparent distribution in the extracted sample [17]. For this reason, we compared the distribution of ethoxamers in spiked sludge extracts (using the proposed coacervative extraction) with that found for direct injection of a standard solution. Fig. 2 shows the signals obtained for the ethoxamers of NPE_x and $C_{12}E_x$ from a fortified sludge sample. The ethoxamer distribution obtained by injecting a standard solution is indicated by the solid line above the graph. Good agreement was obtained for all ethoxamers making up the homologues; therefore we can assume that no skewing was produced by SDoS coacervative extraction for the ethoxamers investigated (i.e. number of ethoxy units lower than 15). However, these results cannot be extrapolated to homologues with higher number of ethoxy units (e.g. greater than 20–25) because of the lower extractability of the more hydrophilic ethoxamers.

In order to check the extraction efficiency of SDoS, we investigated for any residual APE or AE under the proposed extraction conditions, by performing three consecutive extractions of both fortified (n = 3) and non-fortified (n = 3) sludge samples. Recoveries did not increase compared to those obtained by performing a single extraction. Thus, the amount of AE and APE extracted from non-fortified sludge was similar and the recoveries and relative standard deviations obtained from fortified sludge were 83% (±2%), 84% (±2%), 92% (±5%), 100% (±4%) and 99% (±3%) for OPE_x, NPE_x, $C_{12}E_x$, $C_{14}E_x$ and $C_{16}E_x$, respectively (compare these data with those shown in Table 2). The same sludge samples were extracted by using a widely accepted method based on three extractions with methanol in an ultrasonic bath [8,10,11]. The recoveries from fortified samples (n = 3) were 85% (±7%), 87% (±7%), 87% (±7%), 78% (± 6%) and 76% (±5%) for OPE_x; NPE_x, $C_{12}E_x$, $C_{14}E_x$ and $C_{16}E_x$, respectively. These results indicate that extraction efficiencies for the more polar non-ionic surfactants are similar using coacervative and ultrasonic bath extractions and that SDoS surpasses methanol in the extraction of the more apolar surfactants. The use of coacervative extraction causes significant time and solvent saving compared with ultrasonication and Soxhlet [5–7] extraction. Thus, the extraction of sludge samples takes about 1 h, 1–2 h, and 4–24 h, using coacervation, ultrasonication and Soxhlet, respectively. Solvent consumption in coacervative extractions is less than 1 ml of methanol, but 60–150 and 100–250 ml for ultrasonication and Soxhlet, respectively.

3.3. Analytical performance

Quantification was carried out using external calibration. Instrumental detection limits were calculated by using a signal-to-noise of 3 (the ratio between the peak area for each non-ionic surfactant and internal standard and peak area of noise). Detection limits were 0.07, 0.24, 0.32, 0.30 and 0.38 ng for OPE_x, NPE_x, $C_{12}E_x$, $C_{14}E_x$ and $C_{16}E_x$, respectively. From these values and taking into account the amount of sample extracted, the volume of extract injected and the recovery obtained from spiked samples, the detection limits of non-ionic surfactants in sludge were 0.09–0.38 mg/kg. The intra-day precision was estimated by extracting eleven independent sludge samples. The relative standard deviation ranged from 1.5 to 3.2%.

The influence of matrix components that could coelute with AE and APE causing ion suppression and/or space-charge effects was assessed by comparison of calibration curves obtained from standards and fortified sludge samples. No differences were obtained in the analytical features of both types of calibration curves and therefore matrix components

Table 3
Mean concentration (mg/kg sludge) ± S.D.[a] of AE and APE found in sludges collected from two WWTPs, analysed by coacervative extraction/LC/(APCI-IT)MS

Sample location	OPE_x	NPE_x	$C_{12}E_x$	$C_{14}E_x$	$C_{16}E_x$
Activated sludge, Pozoblanco	11.6 ± 0.4	100 ± 3	80 ± 1	23 ± 2	38 ± 4
Dehydrated sludge, Pozoblanco	26 ± 1	138 ± 2	71 ± 1	40 ± 3	56 ± 1
Activated sludge, Baena	89 ± 2	134 ± 2	122 ± 1	56 ± 1	141 ± 5
Dehydrated sludge, Baena	151 ± 4	124 ± 3	99 ± 1	58 ± 1	123 ± 1

[a] Based on four replicates.

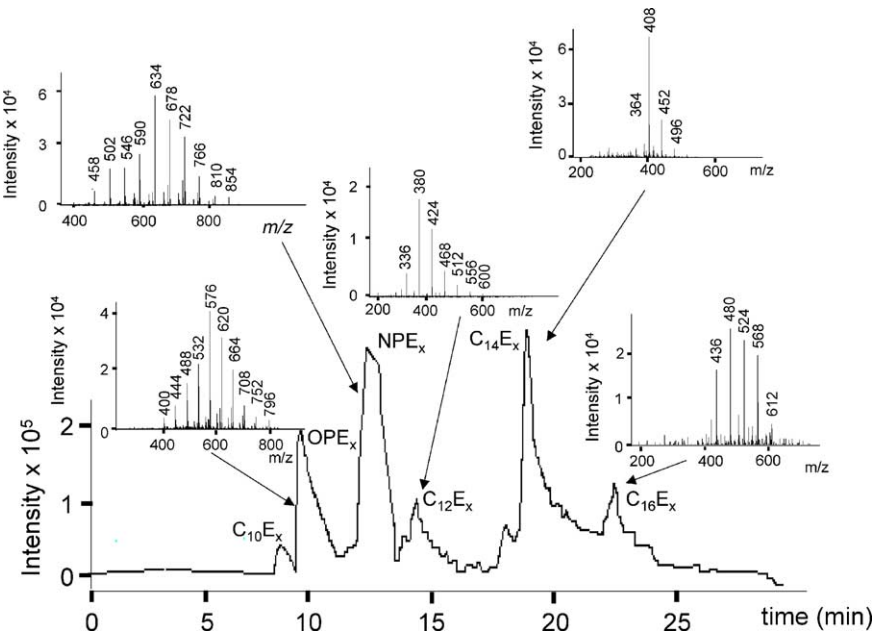

Fig. 3. Reconstructed ion chromatogram and mass spectra obtained for the target compounds from SDoS coacervative extraction/LC/(APCI-IT)MS analysis of an activated sludge sample collected in Baena's WWTP.

did not interfere. So, external calibration is recommended for the analysis of AE and APE, although it is advisable to check the influence of matrix for sludge samples arising from WWTP receiving an important load of specific industries no considered in this research.

3.4. Analysis of sewage sludge samples

Table 3 shows the results, expressed as the mean value (n = 4) and the corresponding standard deviation, for the analysis of sludge samples from two WWTPs. Total method recoveries were assessed by spiking sludge samples with 10 mg/kg of each target compound. The recovery values obtained were similar to those found for the spiked, aged dehydrated sludge used for optimisation purposes (i.e. between 78 and 100%).

Table 4
Influence of the number of masses considered for quantitation on the concentration of OPE_x found in the activated sludge collected in the Baena's WWTP

m/z	Slope of calibration[a]	Concentration of OPE_x (mg/kg)
268, 312, 356, 400, 444, 488, 532, 576, 620, 664, 708, 752, 796, 840, 884, 928, 972, 1016, 1060, 1104	0.0228	89
444, 488, 532, 576, 620, 664, 708	0.0198	97
532, 576, 620, 664	0.0100	123
532	0.0038	229
576	0.0023	234

[a] Using $C_{10}E_x$ as internal standard.

Fig. 3 shows the reconstructed ion chromatogram (RIC) and mass spectra obtained for an activated sludge sample collected in the Baena's WWTP. Both the number of ethoxamers and their relative intensities were different in standards and sludge (compare Figs. 1 and 3). This behaviour was observed for all the sludge samples analysed. This fact emphasize the necessity of using the masses corresponding to all ethoxamers (x = 1–20) for calibration. Table 4 shows as an example the values obtained for the slope of calibration curves and concentration of OPE_x (Baena's activated sludge sample, Table 3) as a function of the number of masses considered for calibration. An overestimation of the concentration of OPE_x occurred as the number of masses used for calibration decreased, as a result of the different distribution of ethoxamers in samples and standards. Also for the same number of masses considered (i.e. 532 and 576) the concentration found for OPE_x depended on the relative distribution of ethoxamers in standards and sludge (compare mass spectra for OPE_x in Figs. 1 and 3).

4. Conclusions

The approach based on SDoS coacervative extraction/LC/(APCI-IT)MS presented here is an useful tool for the routine analysis of APE and AE in sewage sludge. Several operational parameters associated to this separation technique make it specially valuable for this application. Thus, it uses water as extractant; it permits to perform simultaneous treatments with no special extraction equipment (we have routinely carried out the extraction of eight sludge samples in about one hour); no changes in the ethoxamer distribution

after extraction have been observed; recoveries higher that 75%, as recommended for EPA, have been obtained; no matrix effects have been detected, which permits to use external calibration; and no clean steps are necessary, which reduces the risk of laboratory contamination and analysis time. These advantages confirm the potential of surfactant-based phase separations for the extraction of amphiphilic compounds from solid environmental matrices on the basis of the formation of analyte–extractant mixed aggregates, which facilitates the breakdown of matrix–amphiphiles interactions.

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