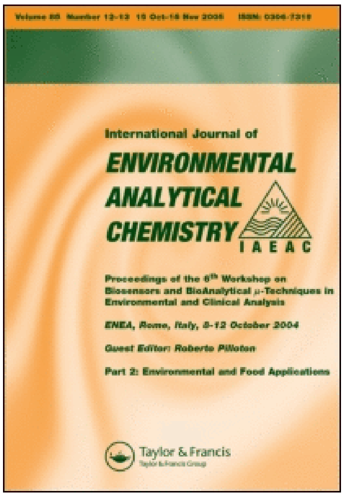

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Intercomparison Among SFE, ASE, Soxhlet and Sonication for the Trialkylamine Determination in Sediment and Sludge

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INTERCOMPARISON AMONG SFE, ASE, SOXHLET AND SONICATION FOR THE TRIALKYLAMINE DETERMINATION IN SEDIMENT AND SLUDGE

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Accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE) have been compared to Soxhlet and sonication extraction procedures for the determination of long-chain trialkylamines ($CH_3NR_1R_2$ where R_1 and $R_2 = C_{14}H_{29}$, $C_{16}H_{33}$ or $C_{18}H_{37}$) in sediment and sludge. An hybrid experimental design was applied for the first time to the optimization of temperature and modifier composition for the SFE of incurred trialkylamines from marine sediment and primary sewage sludge. SFE at 50 °C and 30 MPa with CO_2 modified dynamically with MeOH and statically with triethylamine yielded concentrations of incurred TAMs 10–77% higher than Soxhlet or sonication (3 extractions) with dichloromethane-methanol mixture (2:1). However, the ASE technique with the same extraction mixture at 150 °C and 17 MPa showed the highest extraction efficiency among the extraction methods evaluated. The precision improvement in SFE was attributed to the direct analysis of extracts by GC-NPD without any cleanup step whereas Soxhlet, sonication and ASE extracts required an alumina cleanup prior to their determination. Furthermore, analysis time in SFE and ASE techniques is reduced by a factor of 3 and 20 compared to sonication and Soxhlet extraction, respectively. Solvent usage in both ASE and SFE is reduced.

Keywords: Trialkylamines; supercritical fluid extraction; extraction optimization; accelerated solvent extraction; intercomparison extraction techniques

INTRODUCTION

Long-chain trialkylamines (TAMs) constitute a class of widespread persistent organic contaminants occurring in the aquatic environment which have been proposed as sewage addition markers into the ocean[1–4]. Their concurrent identification along the most widely used cationic surfactant dimethylditallowammonium

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chloride (DTDMAC) in sewage and coastal sediments has lead to postulate a common origin[5] which was confirmed by the identification of TAMs in several fabric softeners containing DTDMAC as active product[4]. Therefore, several European countries have already replaced it by the more environmental acceptable ester-quat based formulations but being still necessary fast and cost-effective analytical techniques for monitoring of both, quaternary and tertiary amines, in environmental samples.

Conventional sample extraction procedures for solid samples tend to be labor intensive and time consuming, and use large amounts of solvents. In the last few years several emerging extraction techniques have appeared to replace the conventional extraction techniques. In this work, SFE and ASE were evaluated as possible rapid, low solvent usage alternatives to Soxhlet and sonication extraction methods.

Supercritical fluid extraction (SFE) is considered one of the most interesting alternatives to conventional methods of sample preparation in environmental analysis since it reduces the solvent usage, extraction time and sample preparation steps[6–12]. Despite most of the reported SFE procedures have been developed for the extraction of low to medium polarity contaminants, the optimization of the type of comodifier is the foremost important variable for the extraction of polar or ionic incurred contaminants from solid environmental samples[13–15]. Very recently, SFE procedures have been developed for the extraction of the cationic surfactant DTDMAC from sludge and coastal sediment yielding from 30 to 40% higher extraction efficiency than solvent extraction techniques[16,17].

Accelerated solvent extraction (ASE) is another emerging extraction procedure that uses organic solvents at high pressures and temperatures above their boiling point. The application of this technique for quantitative extraction of other organic contaminants has been recently reported[18–21].

In this work, a SFE procedure has been developed for the extraction of TAMs ($CH_3NR_1R_2$ where R_1 and R_2 are $C_{14}H_{29}$, $C_{16}H_{33}$ or $C_{18}H_{37}$) incurred in sediment and sludge by the application of an hybrid experimental design. Aiming to minimize the amount of CO_2 primary modifier (methanol), triethylamine was used as methanol cosolvent which has been found very effective for the extraction of pirimicarb from soil[13]. ASE has been applied to the determination of native TAMs from a coastal sediment and a domestic sewage sludge. Obtained results were compared in terms of precision, accuracy and analysis time with those obtained by sonication and Soxhlet extraction.

EXPERIMENTAL

Samples and reagents origin

A surficial sediment (0–2 cm) was box-cored in the Rhône estuary (western Mediterranean) at 23 m water column depth (4° 50.63'N, 43° 18'E) at June 1987. Sample was immediately frozen, freeze-dried and sieved through 250 μm. A domestic sewage sludge was collected in the Barcelona primary treatment plant, centrifuged and freeze-dried. SFC grade carbon dioxide was obtained from Praxair (Barcelona, Spain). Pesticide grade dichloromethane, methanol and analytical grade basic alumina (activity 90, 70–230 mesh) were supplied by Merck (Darmstadt, Germany). Basic alumina was Soxhlet extracted with dichloromethane-methanol for 6 h before using. Analytical grade tridecylamine, triphenylamine, triethylamine and methyldioctadecylamine were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA).

Extraction procedures

Sonication

Extraction was performed with 1.5 g (dry wt) of sediment and 0.2 g (dry wt) of sewage. The samples were placed in glass centrifuge tubes owing PTFE screw caps and treated in an ultrasonic bath (Selecta, Barcelona, Spain) at room temperature for 20 min. with 20 mL dichloromethane-methanol (2:1). Following the extraction, organic extracts were centrifuged at 4000 rpm for 5 min and transferred to a heart-shaped flask. Extraction was repeated for two more times with 20 mL of fresh extractant mixture, which was rotary vacuum evaporated at 30 °C to small volume. Cleanup was carried out with basic alumina as described elsewhere[3].

Soxhlet

Extraction was performed with 3 g (dry wt) of sediment and 0.2 g (dry wt) of sludge using dichloromethane-methanol (2:1) for 18 h. Obtained organic extracts were handled as described above for sonication.

Supercritical fluid extraction

SFE was performed in a Fisons 3000 instrument (Milan, Italy) equipped with two high-pressure syringe pumps interfaced to a PC computer for pressure and extraction mixture programming. Carbon dioxide was delivered as liquid by cooling the syringe pump at 3 °C. Extraction of freeze-dried sediment (2 g) and sludges (0.2 g dry wt) was performed with extraction cells of 3.5 mL (Suprex, Pittsburgh, PA, USA) within an air heated oven. Fused silica tubing of 20–30 cm length and 50 μm i.d. (MicroQuartz, Munich, Germany) heated at 150 °C was used as restrictor. Extracts were collected in 10 mL of ethyl acetate at 5 °C. Extraction was sequentially performed in the static (15 min) and dynamic modes (20 mL). Tridecylamine was added into the collection vial to evaluate the possible losses due to evaporation. Recovered extracts in ethylacetate were analyzed by GC-NPD following a concentration under a gentle stream of nitrogen without any cleanup step.

Accelerated Solvent Extraction

It was carried out by placing subsamples (1.5 g soil and 0.2 g sludge) into an extraction cell (11 ml) and spiking directly with tridecylamine as surrogate. An inert material (sand, previously washed using the same extraction conditions of the sample) was placed at the inflow of the extraction cell. The cell was then closed, finger-tightened, and placed into the sample carrousel (ASE™ 200 Dionex). Then, the system was filled with dichloromethane-methanol (2:1) as extraction solvent, using approximately 20 ml per sample. When the set point of the heated block was reached, the cell was placed in the block assembly. The cell was allowed to equilibrate for 7 min before proceeding with the static extraction for 7 min at a pressure of 17 MPa atm and 150 °C. The extracted analytes were then purged from the sample cell using a N_2 purge (1.2 MPa) for 1 min; fresh solvent was introduced to flush the lines and cell (60% of total solvent volume); and the extract was collected into a vial (40 ml). Two extraction cycles were carried out per sample. Obtained organic extracts were handled as described above for sonication and Soxhlet extraction.

Analytical determination

Trialkylamines were determined by GC (Fisons 5300 series) equipped with a NPD (80-FL). Injection was performed with an AS 200 autosampler in the splitless mode at 280 °C in the injector port. Detector temperature was held at 310 °C. Column temperature was programmed from 70 to 150 °C at 20 °C min^{-1}, then to 210 °C at 6 °C min^{-1} and finally to 320 °C at 15 °C min^{-1}. Helium was used as carrier gas at 30 cm s^{-1}. Tridecylamine was used as a surrogate and was spiked at 500 ng g^{-1} 2 h before extraction. Calibration mixture containing triphenylamine (internal standard), tridecylamine (surrogate) and methyldioctadecylamine (calibration standard) were obtained from 10 pg to 50 ng ($r^2 = 0.999$).

Statistical treatment

Percentage of comodifier and the extraction temperature were optimized by using an hybrid experimental design. Table I shows the variable range used in the optimization. A parametric second order polynomial equation containing the linear, quadratic and the first order interaction terms was chosen:

$$R = aM + bT + cM^2 + dT^2 + eMT + f \qquad \text{(Eq 1)}$$

TABLE I Experimental conditions and response obtained in the SFE of incurred TAMs from a marine sediment

Experiment No	*temperature (°C)*	*% v/v TEA (comodifier)*	*Response (µg g^{-1})*
1	135	2	0.93
2	65	2	5.74
3	135	12	0.48
4	65	12	8.55
5	150	7	0.53
6	50	7	6.78
7	100	15	2.97
8	100	0	3.08
9	100	7	2.43
10	100	7	2.24
11	100	7	2.66
12	100	7	2.16

where R is the response (amount extracted), *a, b, c, d, e* are the adjustment coefficients and *f* the intercept. M and T are the comodifier percentage added into the extraction cell and temperature, respectively. Experiments were carried out in a randomized order for each mobile phase composition to minimize the bias effect. Multilinear least square regression was used to calculate the parametric coefficients *a, b, c, d* and *e*. Significance is determined by a *t*- test at a confidence level of 0.90 ($P<0.1$).

RESULTS AND DISCUSSION

SFE method development

The selected variables for the optimization of TAM extraction for sediment were temperature and percentage of comodifier added to methanol, since they are the most relevant whenever a strong interaction between the analyte and the matrix is expected[11–12]. Triethylamine (TEA) was selected as comodifier, added into the extraction cell as it was found very effective for the extraction of basic pesticides from soil[13] due to its high polarity. Pressure value has been set at 30 MPa because it compromises solubility, reasonable diffusion and miscibility of the MeOH-TEA mixture[22].

The extracted amounts of TAMs (response) in the selected experimental conditions is listed in Table I. Accordingly, the parametric coefficients of the first order polynomial equation 1 obtained by multiple regression are the following:

$$R = 0.277M - 2.75T + 0.476M^2 + 0.792T^2 - 0.815MT + 2.37 \qquad \text{(Eq 2)}$$

The simplified equation according to a confidence level of 90% in the *t*-student test ($p<0.1$) was as follows:

$$R = -2.72T + 0.698T^2 - 0.815TM + 2.75\,(r^2 = 92\%) \qquad \text{(Eq 3)}$$

Since this equation accounts for by the 92% of variance, it can be considered an useful descriptor for the extraction behavior of TAMs in the domain of variables optimized. The partial contribution of every single term to the total variance was 83.6T, 4.6T^2 and 3.8M, respectively. Consequently, temperature is by far the most important contributor to the extraction of TAMs. Its first order interaction with the comodifier percentage and the quadratic temperature term were less important but they are responsible for the non planar surface obtained in the temperature-cosolvent plot (Figure 1). Furthermore, the negative parametric coefficient value obtained for temperature is consistent with an increase in the extraction efficiency with density of fluid, whereas the effect of comodifier is weaker depending on the temperature (Eq 3). The lower the temperature, the higher was the response increase with the amount of cosolvent added into the extraction cell. At higher temperatures, a slight negative effect in the extraction of trialkylamines was found (Figure 1).

A local maxima in the variable domain was found at the lowest temperature (50 °C) and the highest concentration of comodifier (TEA) added into the extraction cell (15%) (Figure 1). Furthermore, the concentration of MeOH in the carbon dioxide and TEA in the extraction cell were also evaluated from 0 to 15%. Extraction temperature was set at its lower possible value (50 °C) to be in the one

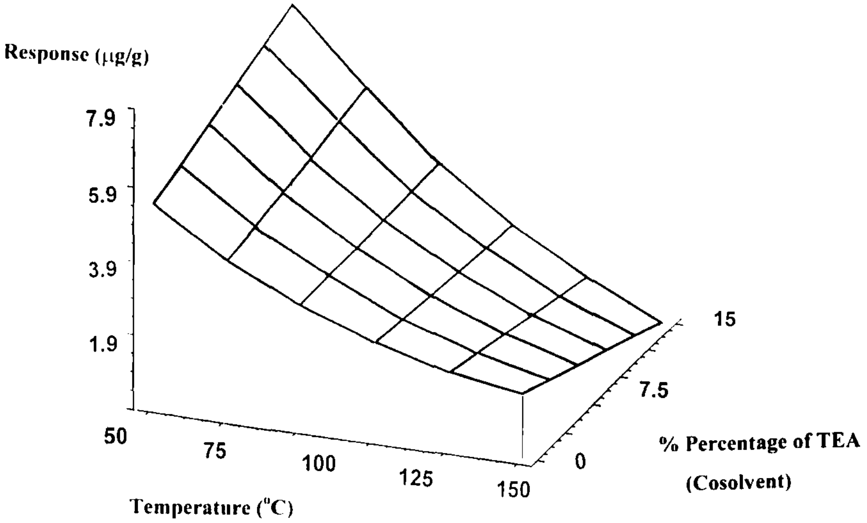

FIGURE 1 Response surface of the SFE of TAMs from sediment according to temperature and triethylamine (TEA) percentage added into the extraction cell. Extraction was performed at 30 MPa keeping constant 10 % MeOH in CO_2

phase region (32). Accordingly, the best extraction conditions were set at 15% MeOH, 10% of TEA in the extraction cell, performing the extraction at 50 °C and 30 MPa.

Selection of extraction conditions in Soxhlet, sonication and ASE

The main extraction variables such as solvent composition and extraction time used in Sohxlet and sonication were optimized before for a variety of contaminants in different environmental matrices[23,24]. Therefore, they have been applied to this intercomparison study. In case of ASE the same extraction mixture than Soxhlet and sonication was applied as suggested before[18]. Pressure is not considered as a variable in ASE and it was chosen high enough (17 MPa) to keep the extraction mixture in the liquid phase. Finally, the extraction temperature was selected at high values (150 °C) for this technique to enhance the TAM recovery[18–21]. In order to evaluate the TAM extraction efficiency in ASE, a sequential extraction was performed from a preextracted sewage sludge or sediment yielding only small amounts of TAMs in the second extraction (<5%) which allow to infer that TAMs are mostly extracted in the first extraction.

Intercomparison between extraction procedures

ASE provided for both sediments and sludges the highest extraction efficiency among the methods evaluated (Tables II and III). In case of sludge the values were one order of magnitude higher than those obtained from sonication and Soxhlet extraction and between four and five times higher than the SFE results. The enhanced extraction of TAMs from sludge with ASE could be attributable to the high temperature and pressure conditions that reduce solvent surface tension and viscosity favoring solvent penetration into the matrix and enhancing mass transfer of analytes from the matrix to the solvent. However ASE provided the poorest precision in the determination of TAMs. Precision was improved by SFE for both sediment and sludge compared to the other techniques which could be attributable to the direct determination of extracts without any cleanup step (Figure 1).

Sonication provided the poorest extraction efficiency and precision for both sediment and sludge, being from 50 to 80% lower than SFE. Probably, these results could be improved by increasing the number of sequential extractions and the solvent volume. However, it was not investigated further because more than 3 extractions with 20 mL of extracting agent was not considered acceptable in terms of solvent usage and disposal. The poorest precision obtained by sonication is also consistent with its lower extraction efficiency.

Analysis time in SFE and ASE is reduced by a factor of 3 and 20 compared to sonication and Soxhlet extraction, respectively. Solvent usage is reduced in SFE by a factor of 10 and in the case of ASE is comparable to sonication.

Finally, the concentration ratios between TAM homologues, normalized to methyldihexadecylamine, were calculated in order to evaluate the extraction selectivity among the different extraction techniques according to the TAM carbon number. Generally, a higher extraction selectivity was found for sediment and sludge being ASE and SEE the most efficient techniques for the higher molecular weight homologues (Tables II and III). Particularly, ASE presented the highest extraction efficiency for the methyldioctadecylamine while sonication led to the poorest for the longer alkyl chain TAMs.

In order to illustrate the different extraction selectivity among the different extraction techniques evaluated, typical GC-NPD chromatograms of sediment are shown (Figure 2). Despite of the application of a cleanup step prior to GC-NPD determination, after Soxhlet extraction and sonication the chromatograms exhibit interfering peaks in the TAMs and surrogate retention times which might difficult the final quantitative determination. The ASE extracts, injected after a cleanup with alumina, also presented a complex pattern in the surrogate retention time. Conversely, the GC-NPD chromatogram obtained by SFE showed the highest selectivity for TAMs despite its direct determination without any cleanup step.

TABLE II Intercomparison between extraction procedures for trialkylamine ($CH_3NR_1R_2$; R_1, R_2 = 14, 16, 18) determination in sediment

extraction technique	$^{*}R_1=C_{16}H_{33}$ $R_2=C_{16}H_{33}$	$R_1=C_{16}H_{33}$, $R_2=C_{18}H_{37}$	$R_1=C_{18}H_{37}$, $R_2=C_{18}H_{37}$	*total***	$C_{1:16:18}$	$C_{1:18:18}$***
SFE (n=5) (μg g^{-1} dry wt.)	1.40	4.87	3.84	10.11	3.5	2.7
SD	0.079	0.24	0.14	0.35		
%RSD	5.65	5.0	3.6	3.5		
ASE (n=5) (μg g^{-1} dry wt.)	1.46	4.38	4.69	11.5	3	3.3
SD	0. 32	0.93	1.02	1.94		
%RSD	21.99	21.20	21.88	16.9		
Soxhlet (n=5) (μg g^{-1} dry wt.)	1.41	3.84	3.88	9.12	2.7	2.8
SD	0.13	0.21	0.22	0.44		
%RSD	9.29	5.47	5.61	4.78		
Sonication (n=5) (μg g^{-1} dry wt.)	1.39	2.51	1.77	5.67	1.8	1.3
SD	0.32	0.55	0.30	1.12		
%RSD	23.2	21.8	16.9	19.8		

* Coelution with $R_1=C_{14}H_{37}$, $R_2=C_{18}H_{37}$.

** Sum of TAM concentrations.

*** Normalised concentration of TAM homologues to $C_{1:16:16}$.

TABLE III Intercomparison between extraction procedures for trialkylamine ($CH_3NR_1R_2$; R_1, R_2 = 14, 16, 18) determination in incurred domestic sludge

extraction technique	*$R_1=C_{16}H_{33}$ $R_2=C_{16}H_{33}$	$R_1=C_{16}H_{33}$, $R_2=C_{18}H_{37}$	$R_1=C_{18}H_{37}$, $R_2=C_{18}H_{37}$	*total***	$C_{1:16:18}$	$C_{1:18:18}$***
SFE (n=5) (µg g^{-1} dry wt.)	167	404	317	888	2.4	2.5
SD	39.5	68	49.8	129.9		
%RSD	23.7	16.8	15.7	14.6		
ASE (n=5) (µg g^{-1} dry wt.)	535	1430	1413	3380	2.7	2.7
SD	80.8	222	263	558		
%RSD	15.1	15.5	18.6	16.5		
Soxhlet (n=5) (µg g^{-1} dry wt.)	121	221	216	559	1.9	1.8
SD	17.1	14.1	19.9	45.7		
%RSD	14.1	6.36	9.23	8.17		
Sonication (n=5) (µg g^{-1} dry wt.)	43.6	93.3	63.9	201	2.2	1.4
SD	7.42	16.9	13.3	36.8		
%RSD	17.0	18.1	20.8	18.3		

[*] Coelution with $R_1=C_{14}H_{29}$, $R_2=C_{18}H_{37}$ in the analytical conditions.

[**] Sum of TAM concentrations.

[***] Normalised concentration of TAM homologues normalised to $C_{1:16:16}$.

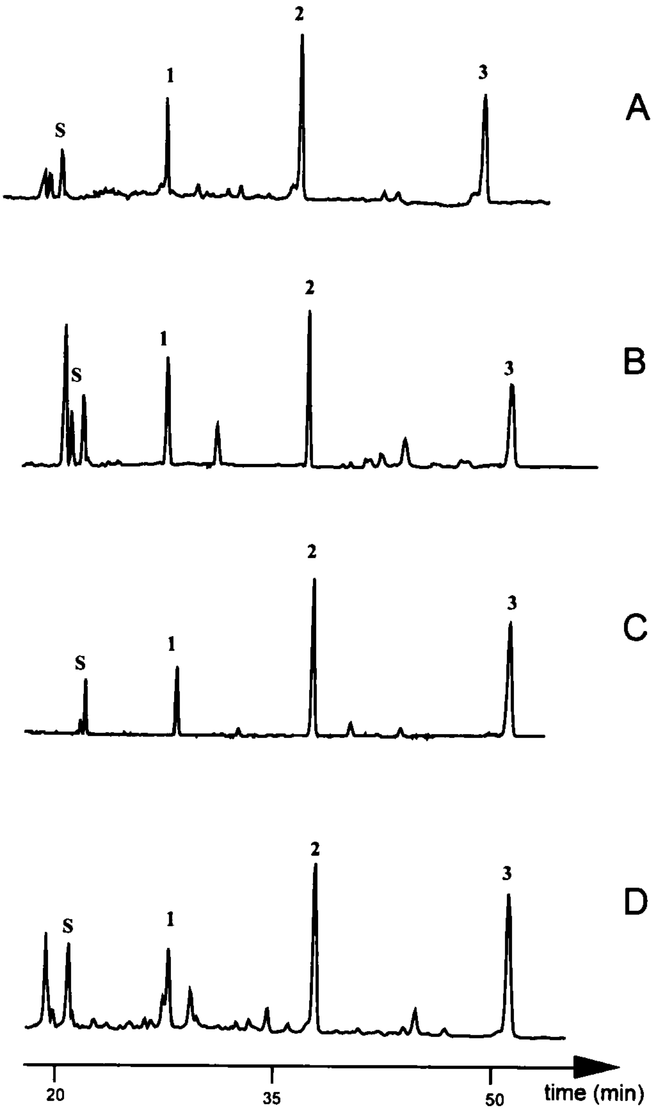

FIGURE 2 GC-NPD of TAMs obtained from marine sediment by A) Soxhlet (MeOH:CH_2Cl_2, 1:2, 18 h), B) sonication (MeOH:CH_2Cl_2, 1:2), C) SFE (50°, 30 MPa, CO_2 15%TEA in MeOH), D) ASE (150 °C, 17 MPa, MeOH:CH_2Cl_2, 1:2). Compounds identification: S: tridecylamine; 1, methyltetradecyloctadecamine + methyldihexadecylamine; 2, methylhexadecyloctadecamine and 3, methyldioctadecylamine

CONCLUSIONS

A SFE method for the determination of TAMs from sediment and sludge has been developed and intercompared with Soxhlet, sonication, SFE and ASE extraction techniques.

In SFE the usage of a comodifier (TEA) reduces the amount of primary modifier (MeOH). Temperature (reversed effect) was by far more effective than the comodifier (TEA) content in the SFE of TAMs from marine sediment which demonstrate that their extraction is primarily controlled by the solubility of fluid rather than the matrix effects. Probably, the weakness of the interaction between analyte with the matrix is associated to the steric hindrance of the long-alkyl chains to the basic nitrogen of trialkylamines. These results are contrasting with the strong interaction found in the SFE of polar pesticides from soil. Thus higher concentrations of acid or basic modifiers to yield quantitative extraction of polar pesticides were needed[13–14].

SFE and ASE are competitive in terms of precision, solvent usage and analysis time in comparison to conventional solvent extraction techniques (i.e. Soxhlet and sonication). However, ASE showed the highest extraction efficiency among the methods evaluated.

In case of sludge, concentration was found to be one order of magnitude higher than those obtained by using the conventional methods and between four and five times the SFE values.

Concerning the selectivity between TAM homologues, SFE and ASE provided higher extraction efficiency for the higher molecular weight homologues being ASE the most efficient for the methyldioctadecylamine while sonication presented poor recoveries for the higher molecular weight TAMs. Moreover, one striking advantage of ASE is that the optimization step is straightforward since few variables are needed to be optimized.

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