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Quantitative extraction of linear alkylbenzenesulfonates using supercritical carbon dioxide and a simple device for adding modifiers

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ABSTRACT

Quantitative extraction of anionic surfactants, linear alkylbenzenesulfonates (LAS), from soil, sediment, and municipal wastewater treatment sludge was achieved using a simple apparatus for the preparation of high concentrations of organic modifiers in supercritical CO_2. The method allows several different modifiers to be tested without the necessity of mixing modifiers in the pump or purchasing pre-mixed fluids. Of the several modifiers tested, methanol yielded the best extraction efficiencies, and >90% recoveries of LAS were achieved using a 30-min extraction at 380 atm with *ca.* 40 mol % methanol in CO_2. Extraction efficiency *versus* time plots for ^{14}C-labeled and native LAS showed good agreement, indicating that the spiked LAS was representative of the native LAS.

INTRODUCTION

The use of supercritical fluids for analytical-scale extraction of organic chemicals from environmental samples has received increasing attention because of several potential advantages over conventional liquid solvent extractions including speed, superior recoveries, reduction in liquid solvent usage and solvent waste, and the ability to directly couple the extraction step with capillary gas chromatography (GC) and supercritical fluid chromatography (SFC) [1]. The majority of investigations involving environmental samples have used pure supercritical fluids (primarily CO_2 and, to a lesser extent, N_2O) to extract relatively non-polar analytes, *e.g.*, those that are amenable to GC analysis including fuel hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and non-polar pesticides [2–7]. When more polar and higher molecular weight analytes need to be extracted, conventional supercritical fluids such as CO_2 generally do not have sufficient polarity for efficient extractions. In such cases, the addition of organic modifiers is used to increase the polarity of the fluid, and thus increase the extraction efficiency [1,8–10].

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Modified supercritical fluids are generally introduced as mixtures of the modifier and CO_2 in the pump, or supplied by dual pumping systems. Both of these approaches involve exposing the pump to the organic modifier, which may cause contamination of the pump by the modifier, and makes the rapid evaluation of several different modifiers experimentally difficult. Small volumes of modifiers can also be added directly to the sample before performing supercritical fluid extraction (SFE) under static conditions [9], but this approach can not supply a continuous supply of modified CO_2 extraction fluid. A simple device to provide a constant high concentration of modified CO_2 for dynamic SFE that does not require exposing the pumping system to the organic modifier, and simplifies the testing of several different modifiers for optimizing extractions is described here. This device has been used to develop quantitative extraction conditions for widely-used anionic surfactants, linear alkylbenzenesulfonates (LAS) from environmental solids.

Commercial LAS is a mixture of homologues and isomers with the predominant formulation having *n*-alkyl chain lengths from C_{11} to C_{14} [11]. LAS is extensively used in domestic detergent formulations, and as an ionic compound, approximately 75% of LAS is disposed as part of domestic wastes in municipal wastewater treatment facilities [12], where it is largely removed from the water by biological degradation and adsorption to solids [13]. The sludges from the treatment facility are often disposed of by mixing into agricultural soils [11], providing a route for LAS to enter the environment. Because of the potential for finding LAS in environmental solids, the SFE methods were evaluated for the extraction of LAS from soil, river sediment, and sludge from a municipal wastewater treatment facility.

EXPERIMENTAL

Samples

Anaerobic digester sludge was collected from a municipal wastewater treatment facility in a non-industrialized rural town. Soil and river sediment samples (alluvial silty clays) were collected in the Ohio River valley. The soil was from an agricultural field which had been used for the disposal of wastewater treatment sludge approximately one year before sample collection, and is henceforth referred to as "sludge amended soil". Small rocks and sticks were removed from the soil and sediment samples, and all samples were air dried and crushed to <600 μm prior to use.

Portions of the three samples were spiked by suspending 7 g in 20 ml ethanol containing ^{14}C-labeled dodecylbenzenesulfonate (^{14}C-LAS), stirring for 3 h, then air drying for several days. Resulting concentrations of the ^{14}C-LAS were *ca.* 2 μg/g with an activity of *ca.* 100 000 dpm/g. All spiked samples were aged for a minimum of 3 months prior to use.

Supercritical fluid extractions

All extractions were performed at 380 atm using a syringe pump (ISCO Model 260D, Lincoln, NE, U.S.A.) filled with SFC-grade CO_2 or N_2O (Scott Specialty Gases, U.S.A.) and a 1-ml extraction cell (JASCO, Japan) for 1-g samples, or cells constructed as previously described from 1/16-in. "Parker" fittings for 50-mg samples [14]. A schematic of the device used for generating the modified CO_2 is shown in Fig. 1. The CO_2 is pumped to a 4-port valve which can be switched so that the flow goes

either directly to the extraction cell, or through the 9.5-ml stainless-steel modifier vessel. (*Caution*: Care must be taken to ensure that the modifier chamber and all related fittings have appropriate pressure ratings. Materials must also be chemically resistant to any modifiers used.) The modifier vessel's temperature was controlled at 60°C by placing it in a GC oven. The temperature of the extraction cell was controlled by a thermostatted tube heater which contained a 1/2 m coil of the stainless-steel transfer line to equilibrate the fluid's temperature before reaching the extraction cell. The loaded sample cells were placed in the tube heater for 5 min before extracting to ensure that the sample was preheated to the extraction temperature.

Extractions were performed by first pressurizing the sample cell with pure CO_2 for *ca.* 3 s, then rotating the valve so that the CO_2 flowed through the modifier vessel as shown by the arrows in Fig. 1. The CO_2 became saturated with the modifier (at the 60°C oven temperature) then flowed through the 4-port valve to the sample cell.

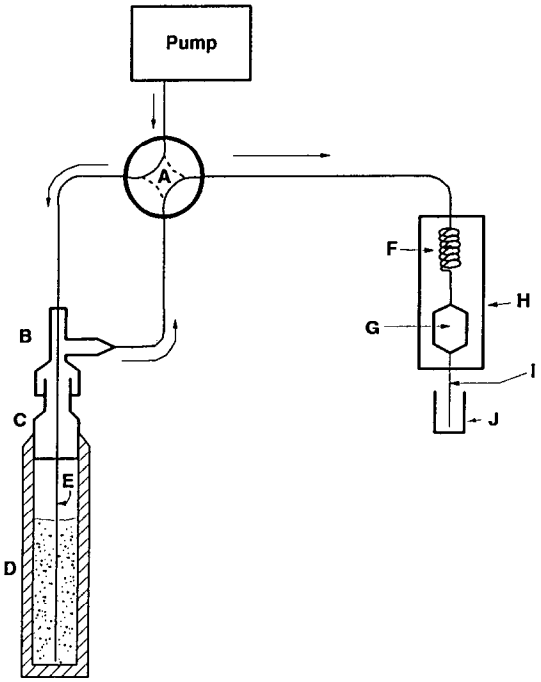

Fig. 1. Schematic diagram of the device used for the preparation of modified supercritical CO_2. Arrows show the flow directions during extraction with the modified supercritical fluid. Components: A = four-port valve; B = "Parker" or "Swagelok" brand 1/16 × 1/16 × 1/4 in. stainless-steel "tee" tubing fitting; C = 1/4-in. normal pipe thread × 1/4 in. tubing stub fitting which is threaded and welded into D; D = modifier chamber which was constructed by drilling a 1.1-cm diameter hole 10 cm long into an 11 cm long × 1.9 cm (3/4 in. diameter) stainless-steel rod. The modifier chamber (D) is placed into a GC oven for temperature control. The 1/16 in. O.D. stainless-steel tubing (E) is inserted through the tee fitting (B) and the tubing stub (C) so that the end of the tubing is at the bottom of the modifier reservoir (D). The CO_2 exits the tubing (E) and percolates through the modifier before exiting from the side arm of the tee fitting (B). The modified supercritical fluid is then preheated to the extraction temperature in the 1/2 m coil of 1/16-in. O.D. tubing (F), and finally enters the extraction cell (G) which is inside of the tube heater (H). The extracted analytes are then swept through the restrictor (I) and collected in the solvent vial (J). All pressurized components were chosen to have ratings of at least 600 atm.

Extracted analytes were then swept through the sample extraction cell outlet restrictor and collected in a scintillation vial which contained 5 ml of ethanol. Flow through the extraction cell (as liquid CO_2 measured at the pump) was maintained at 1.2 ± 0.1 ml/min or at 0.45 ± 0.1 ml/min, respectively, using 10-cm lengths of either 30 or 25 μm I.D,. fused-silica tubing as outlet restrictors. After the extraction was complete, the modifier chamber was refilled by detaching the tee at the tubing fitting at the top of the chamber, and pipetting in additional modifier. The chamber can easily be rinsed and/or baked out between modifiers without any detectable evidence of carryover.

Analysis of extracts

Extraction efficiencies of the ^{14}C-LAS were determined with standard scintillation counting techniques. The activities of both the extract and the extracted solid (CabO-Sil suspension) were determined for each extraction. Analysis of the native LAS extracted from the unspiked samples was performed using high-performance liquid chromatography (HPLC) with fluorescence detection as previously described [11].

RESULTS AND DISCUSSION

The modifier chamber allowed extractions of LAS using several different organic modifiers to be evaluated in a a relatively short time, since the apparatus was simple to clean, and reloading the chamber required only *ca.* 1 min. During the initial development of the SFE method for LAS, several different modifiers were tested using 50-mg samples, a relatively short extraction time (15 min) and a CO_2 flow-rate of *ca.* 1.2 ml/min. A 5-ml volume of the test modifier was added to the saturation chamber before each extraction. Approximate concentrations of the modifiers in the CO_2 saturated at 60°C (estimated by the volume of CO_2 required to empty the saturation vessel) were propylene carbonate (15 mol%), 2-methoxyethanol (20%), acetic acid (25%), 1-butanol (20%), and methanol (40%). The digester sludge was chosen for the modifier survey since it was expected to have the highest concentration of LAS, and therefore would be the most rigorous test of the ability of the modified supercritical fluids to dissolve the LAS.

Table I shows the effect of several different modifiers in CO_2 on the recovery of ^{14}C-LAS from the digester sludge at extraction temperatures of 65 and 125°C. While neither pure CO_2 nor N_2O yielded any detectable recovery of the LAS, the modifiers yielded recoveries ranging from *ca.* 50% for propylene carbonate to near quantitative recovery with the methanol modifier. In most cases the extraction at 125°C was more efficient than extraction at 65°C. The increased efficiency at 125°C may (or may not) be because extractions with some of the modifiers could possibly not have been supercritical at the lower temperatures. Unfortunately, phase diagrams are not available in the literature to allow determination of the critical parameters for most of the modifier mixtures tested. However, published results do show that the extractions with methanol modified CO_2 were supercritical at both temperatures [15].

The increased recoveries using methanol modifier for the LAS extraction was fortuitous since methanol is much more convenient to use than, for example, acetic acid. However, it is clear that different modifiers could be superior depending on the

TABLE I

RECOVERIES OF ^{14}C-LAS FROM DIGESTER SLUDGE USING 15-min EXTRACTIONS WITH DIFFERENT POLARITY MODIFIERS

Modifier	Recovery (%)[a]	
	65°C	125°C
Carbon dioxide (pure)	<1	<1
Nitrous oxide (pure)	<1	<1
Modifiers in carbon dioxide		
Propylene carbonate	47	54
2-Methoxyethanol	67	55
Acetic acid	55	64
1-Butanol	64	70
Methanol	85	98

[a] A 5-ml volume of each modifier was used for each 15-min extraction at 380 atm. Recoveries were based on the average of two extractions at each extraction temperature.

polarity of target analytes and, perhaps, the sample matrix. For example, the same extracts generated for Table I were also analyzed for the cation of the fabric softener DTDMAC, $(C_nH_{2n+1})_2N(CH_3)_2Cl$ where n = 16 or 18, using fast atom bombardment mass spectrometry [16]. The relative amounts of DTDMAC extracted from the digester sludge were estimated based on the ratio of characteristic ions (m/z = 550, 522, and 494 for the di-C_{18}-, mixed C_{18}-/C_{16}-, and di-C_{16}-DTDMAC, respectively) to those of the fast atom bombardment reagent (dithioerythritol/dithiothreitol "magic bullet" at m/z = 222). Based on these ratios, the relative extraction efficiencies achieved using the various modifiers was nearly opposite those for LAS. For DTDMAC, propylene carbonate was the most effective modifier followed, in order of decreasing efficiency, by methoxyethanol, butanol, acetic acid, and methanol.

Since the device used in this study provides CO_2 that is saturated with the test modifier (at the 60°C oven temperature), there was initially some concern that the fluid could separate into two phases sometime during the extraction process. Preliminary experiments with CO_2–methanol demonstrated that phase separation did indeed occur if the extraction cell was not properly heated. Fortunately, phase separation was simple to determine by observing the pump flow-rate display. With a single phase system, the flow-rate of CO_2 was essentially unchanged whether the extraction was being performed with pure or modified CO_2, as would be expected since the viscosity of the modified CO_2 should not be greatly different from that of the pure CO_2 as long as the modified CO_2 remained a single-phase system. However, if phase separation occurred, the flow-rate of CO_2 dropped dramatically because the relatively high viscosity of the liquid phase greatly reduced the flow through the outlet restrictor. Since the solubilities of modifiers in CO_2 generally increase with temperature, extraction temperatures used in this study were higher than the modifier chamber temperature to ensure that a single phase system existed during the extractions. For example, the CO_2 flow (at the pump) with CO_2–methanol saturated at 60°C remained constant at 1.2 ml/min when the extraction temperature was held above 60°C, but dropped to <0.1 ml/min when the temperature of the extraction cell was lowered. However, the

flow returned to normal when the sample cell and the inlet end of the restrictor were heated to above the modifier chamber temperature. In all of the extractions reported here, the flow of CO_2 was monitored and care was taken that the extraction cell was completely heated to the desired temperature before beginning the extraction. With this precaution, no phase separation occurred as evidenced by a consistent flow-rate at the pump.

Based on the results of the modifier and temperature studies summarized in Table I, each subsequent extraction was performed at 125°C and the modifier chamber was completely filled with methanol (9.5 ml). Since, during an extraction, the CO_2 becomes saturated with the modifier, the flow-rate used for the extraction determines how long the modified supercritical fluid is supplied before the chamber is empty. With an extraction flow-rate of *ca.* 1.2 ml/min (as CO_2 at the pump), the 9.5 ml of methanol lasted *ca.* 10 min before it was exhausted. However, when the extraction flow was lowered to *ca.* 0.45 ml/min, the 9.5 ml of methanol lasted *ca.* 28 min. Both flow-rates resulted in a concentration of the methanol modifier of *ca.* 40 mol% (estimated based on the volume of CO_2 used to dissolve the 9.5 ml of methanol) but, since the lower flow-rate resulted in longer contact time between the modified supercritical fluid and the sample, it was suspected that the lower flow-rate might yield improved extraction efficiencies. The sludge amended soil was chosen for this comparison since initial extractions demonstrated that recoveries of LAS were poorer from the sludge amended soil than either the river sediment or digester sludge. Each extraction was carried our for 30 min, with the only difference being in the flow-rate of the supercritical fluid. As shown in Table II, the longer contact time with the methanol modifier afforded by the lower extraction flow-rate yielded significantly higher recoveries of the ^{14}C-LAS from the sludge amended soil. Table II also shows that the recoveries of the ^{14}C-LAS from the river sediment and the digester sludge were essentially quantitative using a 30-min extraction at the lower flow-rate.

TABLE II

RECOVERIES OF ^{14}C-LAS USING 30-min EXTRACTIONS AT 380 atm WITH METHANOL-MODIFIED CO_2

Trial	Recovery (%)			
	Sludge amended soil		Digester sludge, 0.45 ml/min	Sediment, 0.45 ml/min
	1.2 ml/min[a]	0.45 ml/min		
1	74.2	91.4	97.3	99.1
2	76.3	89.0	98.7	99.6
3	74.8	90.1	96.7	98.2
4	75.7	91.7	–	98.1
5	76.9	91.8	–	98.0
Mean ± S.D.	75.6 ± 1.1	90.8 ± 1.3	97.6 ± 1.0	98.6 ± 0.7

[a] Extraction flow-rates (measured as liquid CO_2 at the pump) were controlled at *ca.* 1.2 ml/min or 0.45 ml/min as described in the text. Each extraction was performed at 125°C with 9.5 ml methanol modifier.

Since the extractions shown in Table II were all performed on 50- to 60-mg samples (to conserve the limited supply of ^{14}C-LAS), there was some concern that the recovery of LAS from larger samples would be lower, particularly for the highly concentrated digester sludge sample which was shown by HPLC analysis to contain 3.5 mg of native LAS/g. The extraction of samples larger than 50 mg would also be useful to ensure more representative sampling. Sufficient quantities of the spiked digester sludge and the sludge amended soil were available to allow single extraction of 1-g samples in order to determine whether the 30-min extraction was sufficient to yield good recoveries of the ^{14}C-LAS. A comparison of the extraction rates for a 57-mg and a 1-g sample of the spiked digester sludge is shown in Fig. 2. While the extraction of the 1-g sample did proceed at a slightly lower rate, recoveries were still essentially quantitative with 95% of the ^{14}C-LAS being recovered in 30 min (compared to 98% for the 57-mg sample), and 99% being recovered in 60 min. (For extractions longer than 30 min, the modifier chamber was refilled at 20-min intervals to ensure a constant supply of methanol.)

In contrast to the digester sludge extractions, the recoveries of the LAS from 1.1-g and 50-mg samples of the sludge amended soil proceeded at essentially identical rates, with 93% of the LAS recovered from the 1.1-g sample in 30 min (compared to 92% for the 50-mg sample), and 97% recovery after 60 min. It is also interesting to

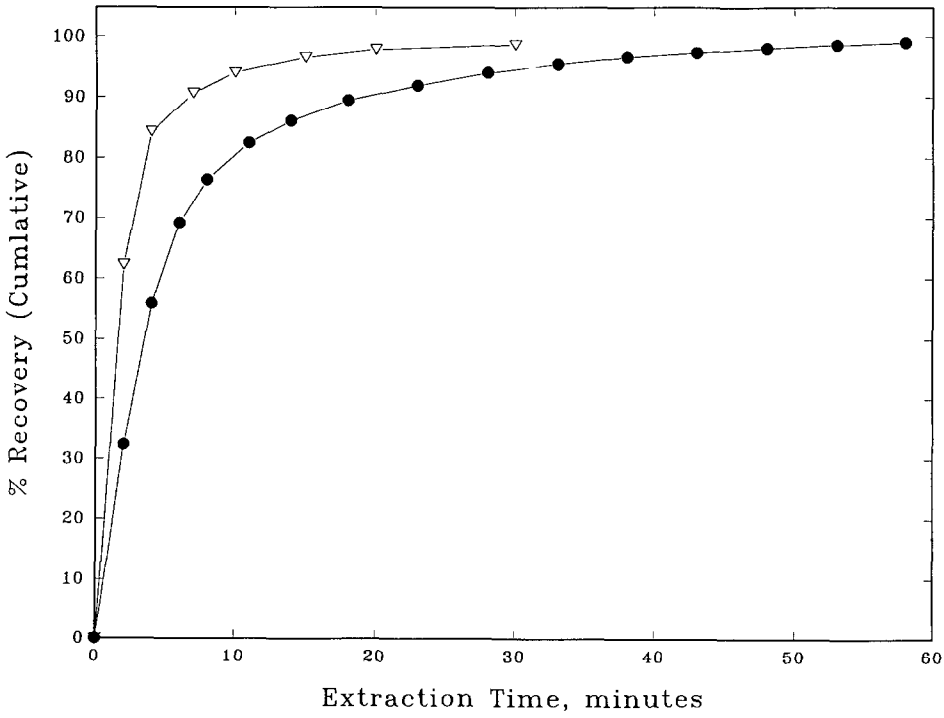

Fig. 2. Relative extraction rates of ^{14}C-LAS from 57-mg (▽) and 1-g (●) samples of digester sludge from a municipal wastewater treatment facility. Extractions were performed with 380 atm CO_2 at 125°C with methanol modifier as described in the text.

note that the 1-g samples of digester sludge and sludge amended soil showed nearly identical extraction efficiency curves despite having greatly different concentrations of native LAS (3.5 mg/g for the digester sludge versus 0.12 mg/g for the sludge amended soil). This similarity indicates that saturation of the supercritical fluid with LAS, which could reduce the extraction rate for the digester sludge, did not occur.

The extraction of the 1-g sample of digester sludge also provided enough LAS for HPLC analysis to allow the individual extraction curves for the major LAS species, C_{12}-, C_{13}- and C_{14}-LAS to be plotted (Fig. 3). While each of the species was >50% recovered after only two minutes of extraction, the extraction rates were slightly slower for the higher molecular weight LAS homologues, as might be expected since both the solubility and diffusivity of the C_{14}LAS should be lower in the supercritical extraction fluid than those of the lower molecular weight homologues.

Even though the spiked samples were all aged for several months prior to extraction, there was some concern that the ^{14}C-LAS spike was not truly representative of the native LAS found on the samples, and thus the ^{14}C-LAS may be more easily extracted than the native LAS. In order to investigate the extraction characteristics of the spiked and native LAS, unspiked samples of digester sludge and sludge amended soil were extracted under identical conditions to those used for the spiked 1g samples just discussed, except that the extraction of each sample was continued for

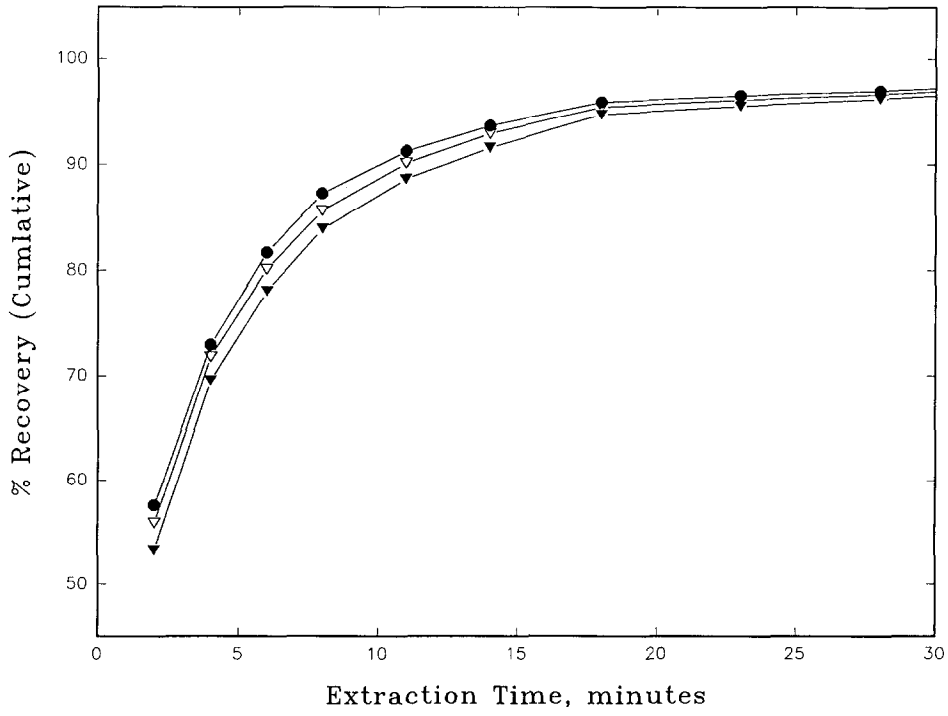

Fig. 3. Relative extraction rates of dodecyl (●), tridecyl (▽) and tetradecyl (▼) homologues of LAS from a 1-g sample of municipal wastewater treatment digester sludge. Extraction conditions are the same as for Fig. 2.

100 min, *i.e.*, until no more detectable LAS was recovered. Each fraction was then analyzed by HPLC for LAS as described above, and the extraction efficiency curves were compared with those of the spiked ^{14}C-LAS extractions. Fig. 4 shows a comparison of the extraction curves for the spiked and native LAS from the sludge amended soil samples. The good agreement between the extraction curves shows that the extraction behavior of the spiked ^{14}C-LAS and the native LAS was essentially identical, indicating that the use of the spiked ^{14}C-LAS was valid for these studies. The extraction rates for the spiked LAS (Fig. 2) and native LAS (Fig. 3) from the digester sludge sample were also very similar, further indicating that the spiked LAS was representative of the native LAS.

CONCLUSIONS

A simple and inexpensive saturation chamber can be used to provide organically modified supercritical CO_2 for supercritical fluid extractions of polar analytes from solid samples. Using this device, reproducible and quantitative recoveries (>90%) of anionic linear alkylbenzenesulfonates can be achieved from soil, sediment, and municipal wastewater sludge in 30 min with methanol modified CO_2.

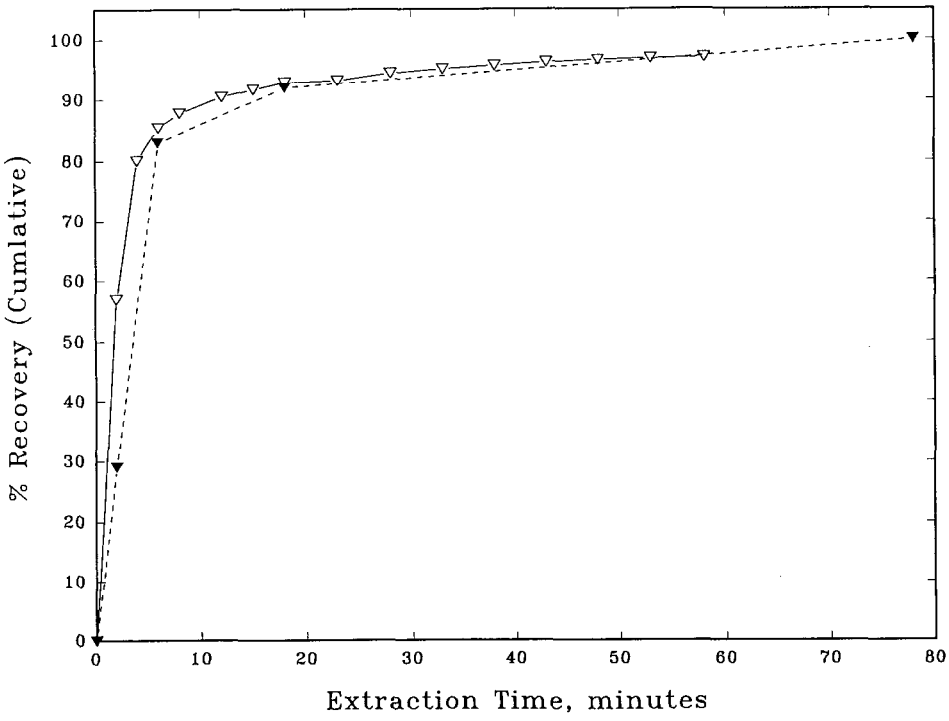

Fig. 4. Relative extraction rates of spiked ^{14}C-LAS (▽) and native LAS (▼) from agricultural soil which had been used for the disposal of digester sludge one year before sample collection.

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REFERENCES

1 S. B. Hawthorne, *Anal. Chem.*, 62 (1990), 633A.
2 B. W. Wright, C. W. Wright and J. S. Fruchter, *Energy Fuels*, 3 (1989) 474.
3 V. Janda, G. Steenbeke and P. Sandra, *J. Chromatogr.*, 479 (1989) 200.
4 J. M. Levy, R. A. Cavalier, T. N. Bosch, A. M. Rynaski and W. E. Huhak, *J. Chromatogr. Sci.*, 27 (1989) 341.
5 S. B. Hawthorne, D. J. Miller and J. J. Langenfeld, *J. Chromatogr. Sci.*, 28 (1990) 2.
6 M. W. Raynor, I. L. Davies, K. D. Bartle, A. A. Clifford, A. Williams, J. M. Chalmers and B. W. Cook, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 766.
7 S. B. Hawthorne and D. J. Miller, *Anal. Chem.*, 59 (1987) 1705.
8 N. Alexandrou and J. Pawliszyn, *Anal. Chem.*, 61 (1989) 2770.
9 J. R. Wheeler and M. E. McNally, *J. Chromatogr. Sci.*, 27 (1989) 534.
10 F. I. Onuska and K. A. Terry, *J. High Resolut. Chromatogr.*, 12 (1989) 357.
11 M. A. Castles, B. L. Moore and S. R. Ward, *Anal. Chem.*, 61 (1989) 2534.
12 R. A. Rapaport and W. S. Eckhoff, *Environ. Toxicol. and Chem.*, 9 (1990) 1245.
13 R. A. Rapaport, *Environ. Toxicol Chem.*, 7 (1988) 107.
14 S. B. Hawthorne and D. J. Miller, *J. Chromatogr.*, 403 (1987) 63.
15 E. Brunner, W. Hultenschmidt and G. Schlichtharle, *J. Chem. Thermodynamics*, 19 (1987) 273.
16 J. R. Simms, T. Keough, S. R. Ward, B. L. Moore and M. M. Bandurraga, *Anal. Chem.*, 60 (1988) 2613.