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Determination of Alkylbenzyldimethylammonium Chlorides in River Water and Sewage Effluent by Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry

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This study presents a modified method to analyze alkylbenzyldimethylammonium chlorides (ABDACs) in river water and sewage effluent. The method involves mixed samples with linear alkylbenzenesulfonates (LAS) as a counterion to enhance the extraction of ABDAC residues from an RP-18 solid-phase cartridge by formation of hydrophobic ion-pair complexes. The ABDACs were then eluted with methanol−ethyl acetate (1:1, v/v) and formed to their corresponding alkyldimethylamines by the Hofmann degradation with potassium *tert*-butoxide. The alkyldimethylamines were then identified and quantitated by gas chromatograph/mass spectrometry (GC/MS). The results indicate that, in the presence of LAS, debenzylation of ABDACs occurs selectively at a temperature higher than 90 °C to produce the corresponding nonionic alkyldimethylamines. The method proposed herein provides a high precision and sensitivity for ABDACs, to quantitation at ≤0.1 μg/L in 500 mL of the water samples. The average recovery of ABDAC spiked water samples was 95% with relative standard deviations (RSD, $n = 7$) of 9%. The RSDs of three replicate environmental sample analyses ranged from 5 to 11%. Direct HPLC method was applied to evaluate the GC/MS method, and compatible results were observed.

Alkylbenzyldimethylammonium chlorides (ABDACs) are widely used cationic surfactants, which are mixtures of unbranched alkyl homologues of dodecyl- (C_{12}-), tetradecyl- (C_{14}-), hexadecyl- (C_{16}-), and octadecyl- (C_{18}-)benzyldimethylammonium chlorides. In Taiwan, more than 8000 metric tons of cationic surfactants are produced and consumed annually.[1] Here, C_{12}-, C_{14}-, and C_{16}-ABDACs are applied as bactericides, disinfectants and sanitizers in sanitary products, and antistatic agents in textile-softener formulation. C_{18}-ABDAC is applied mostly as a main ingredient of hair conditioners, which imparts softness, manageability, and antistatic properties to hair. Their acute toxicity (effect/lethal concentration) to fish (*Rasbora heteromorpha*) is 2.0−3.5 mg/L (LC_{50})[2] and toxicity to invertebrates varies from 1 (LC_{100} for annelid, *Enchytrae albidus*) to 50 mg/L (EC_{50} for ostracods, *Cypridae*).[3] For toxicity to bacteria, an EC_{50} of 10 mg/L was reported.[4] However, because of Taiwan's deficient municipal and industrial wastewater treatments, large quantities of ABDACs in wastewaters are discharged directly into the rivers. Due to the toxicity and persistence, it is necessary to develop an accurate and sensitive analytical technique to study the occurrence and fate of trace level ABDAC residues in the aquatic environment.

Numerous analytical methods for cationic surfactants, quaternary ammonium compounds (QACs), have been developed for water quality investigation in water treatment industries. QACs are commonly treated with anionic dyes, resulting in complexes of QAC−dye, which can be measured colorimetrically.[5] However, this method is unsuitable for monitoring ABDACs in sewage or environmental samples in which anionic surfactants are also present, as the affinity of ABDACs for anionic surfactants is often greater than that for the dyes. High-performance liquid chromatography (HPLC)[6−8] and fast atom bombardment mass spectrometry (FAB-MS)[9,10] techniques have been applied to analyze relatively high concentrations of ABDACs in a variety of matrixes, particularly in pharmaceutical formulations and ophthalmic products. Although HPLC and FAB-MS identified the homologues of ABDACs, these methods are not sufficiently sensitive or specific for routine environmental analysis. Capillary electrophoresis (CE) is a relatively recent separation technique with the advantages of high resolution and efficiency, low consumption of solvent, and the possibility of rapid method development. Potentially applicable to most classes of surfactants, ionic surfactants in particular have been studied.[11−15] The concern of CE for trace analysis of

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environmental samples is its short optical path associated with on-column detection and complex matrixes. However, gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) is not only more readily available in many environmental laboratories but also provides a higher chromatographic resolution with a capillary column. GC has been used for qualitative determination of long-chain cationic surfactants by converting them to the corresponding tertiary amines by thermal decomposition in the injection port[16,17] or by severe reaction conditions to decompose them.[18,19] A promising debenzylation of $C_{12}-C_{16}$-ABDACs in commercial wet wipes with potassium *tert*-butoxide at room temperature has been reported.[20] However, quantitative recoveries at low $C_{12}-C_{18}$-ABDAC concentrations in complicated environmental samples with potassium *tert*-butoxide have yet to be achieved.

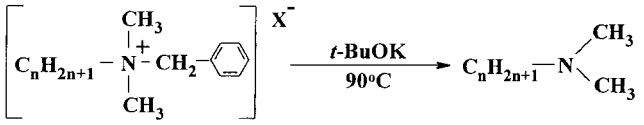
The objective of this study was to develop a method to routinely determine $C_{12}-C_{18}$-ABDACs in aqueous samples by applying RP-18 solid-phase extraction and GC/MS analysis of their corresponding alkyldimethylamines by debenzylation with potassium *tert*-butoxide. To validate the quantitative GC/MS method by employing Hofmann degradation conditions, the results were compared to those obtained with the direct HPLC method. Our results further demonstrate the effectiveness of the method in determining ABDACs at trace levels in environmental samples.

EXPERIMENTAL SECTION

Chemicals and Reagents. Unless stated otherwise, all high-purity chemicals and solvents were purchased from Aldrich (Milwaukee, WI), Tedia (Fairfield, OH), and Merck (Darmstadt, Germany) and were used without further purification. Dodecyl-, tetradecyl-, hexadecyl-, and octadecylbenzyldimethylammonium chloride (all above 98% purity), 4-octylbenzenesulfonic acid sodium salt (4-C_8-LAS, 97%, as ion-pair reagent), and undecyldimethylamine ($C_{11}H_{23}N(CH_3)_2$, as internal standard) were purchased from Aldrich. Standard mixture containing 100 μg/mL of each ABDAC compound in methanol was prepared. Reagent grade potassium *tert*-butoxide was purchased from Riedel-deHaen (Seelze, Gemany). Deionized water was further purified with a Minipore water purification device.

Sample Collection. Samples of river water were collected from the Lao-Jie River at two sampling sites. Sample A was sampled at the Chung-Jen bridge in downtown Chung-Li (Taiwan), with a specific conductance of 110 μS/cm and 130 μg/L total linear alkylbenzenesulfonates (LAS). Sample B was sampled at Nan-Tain bridge in a suburban agricultural area, 15 km south of Chung-Li, with a specific conductance of 370 μS/cm and 78 μg/L total LAS. Here, untreated municipal wastewaters are discharged directly into the rivers. Two industrial effluents, with specific conductances of 2180 (from Ruen-Tai Co.) and 1200 μS/cm (from Lien-I Co.), and 250 and 300 μg/L total LAS, respectively, were collected directly from industrial effluent outlets in Tai-Yuan Industrial Park, Tao-Yuan County (Taiwan). The total LAS concentrations in water samples were determined according to a procedure described elsewhere.[21] Duplicate 500-mL samples were collected and shipped to the laboratory in ice-packed containers. Upon arrival, the samples were immediately adjusted to pH 2−3 by adding concentrated HCl, and then stored at 4 °C until analysis.

Scheme 1



Sample Extraction and Preparation. Extraction of cationic surfactant residues from a water sample is very difficult owing to their ionic properties compared to extraction of nonionic organic compounds. To extract ABDAC residues from environmental samples quantitatively and qualitatively, our method involved mixed water samples with LAS, such as 4-C_8-LAS in this study. Herein, LAS served as a counterion to enhance the extraction of ABDAC residues from the RP-18 solid-phase cartridge (SPE) by forming hydrophobic ion-pair complexes.[22] The effects of LAS on Hofmann degradation and extraction recoveries were also investigated as relatively high concentrations of LAS residues have been found in Taiwan's rivers and effluents.[21,23] 4-C_8-LAS was added in excess of expected ABDAC concentration to a final concentration of 5 μg/mL in acidified river water and effluent samples. To eliminate contamination, all glassware was cleaned and rinsed subsequently with hot tap water, deionized water, methanol, and acetone before drying and then heated overnight at 250 °C.

Before extraction, acidified water sample (500 mL) was adjusted to pH 7.0 with 1 N NaOH (see Results and Discussion). The ABDAC residues were then extracted by passing the sample through the RP-18 SPE cartridge (Bakerbond spe C_{18}, J. T. Baker, NJ) at a flow rate of ~3−5 mL/min, with the aid of a vacuum. After the extraction, the cartridge was dried completely by drawing air through it for 2 min. The ABDAC residues were then eluted with 10 mL of methanol−ethyl acetate (1:1, v/v) eluent. The moisture in the eluent was removed by passing it through a $MgSO_4$ column to increase the yield of debenzylation reaction.

After completing the elution process, the extract in the reaction vial was completely evaporated to dryness by a stream of nitrogen. The residue was then redissolved in 1 mL of benzene−DMSO (8:2, v/v) solution with 1 mg of potassium *tert*-butoxide. (*Caution:* Benzene is a known carcinogen and may pose a health hazard to workers; handle carefully). The solution was shaken vigorously and allowed to stand for 30 min at 90 °C (between 40 and 100 °C, above 90 °C being optimal; see Results and Discussion). According to Hofmann degradation, this procedure converts the ABDACs into corresponding nonionic alkyldimethylamines (Scheme 1). This debenzylation procedure keeps the characteristic long alkyl chain of homologous of ABDACs for easy identification. After cooling, 1 mL of chloroform was added followed by 2 mL of 10% sodium chloride solution, and the resultant mixture was then shaken vigorously with a vortex mixer. The chloroform layer was

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separated and dried by sodium sulfate. The extract was then evaporated to dryness, and the residue was redissolved in 100 μL of chloroform containing 20 ng/μL undecyldimethylamine ($C_{11}H_{23}N$-$(CH_3)_2$) as internal standard and made ready for GC/MS analysis.

GC/MS Analysis. Analyses were performed on a HP-5890 Series II gas chromatograph directly coupled to a HP-5973 mass-selective detector (Hewlett-Packard) operating in the electron impact (EI) mode. Samples (1 μL) were injected with the injection temperature at 280 °C in the splitless mode. A DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25-μm film, J&W, Folsom, CA) was used. The GC temperature program was as follows: 100 °C for 2 min, followed by a temperature ramp at 8 °C/min to 280 °C, and hold for 5 min. The transfer line was set at 280 °C. Full-scan EI data were acquired under the following conditions: mass range 50−400 m/z, scan time 1 s, solvent delay 5 min. The detector was tuned with perfluorotributylamine (PFTBA) by using the autotune program. The electron energy was 70 eV, and the electron multiplier was operating at 200−300 V above the autotune value with the high-energy dynode on. The peak areas of the extracted ion chromatograms (m/z 58) of the corresponding alkyldimethylamines were applied for quantitation and identification. The quantitation of ABDAC residues was calculated from the five-level calibration curve (or average response factor) covering the range 0.5−10 μg/mL, each divided by the fixed concentration of internal standard (undecyldimethylamine). The precision of the calibration curve, as indicated by the relative standard deviations (RSDs) of response factors, was 10, 9, 10, and 12% for corresponding dodecyl-, tetradecyl-, hexadecyl-, and octadecyldimethylamines, respectively. Fortified samples were quantitated by comparison with the corresponding derivatized standards containing the same amount of ABDACs as in the spiked samples.

Direct HPLC Analysis. The procedure used for HPLC analysis was carried out similar to Prince et al.[24] The dry residue from the RP-18 extraction was redissolved in a fixed volume of mobile phase. Analyses were performed on a HP-1100 high-performance liquid chromatograph system connected to a UV/visible detector (Hewlett-Packard) operating at 254 nm. A Hypersil-CPS column (25 cm × 0.46 cm i.d., 0.5 μm packing, ThermoQuest, Runcorn, U.K.) was used at a flow rate of 2 mL/min, and the injection volume was 20 μL. Isocratic elution was performed with a mixture of 60% acetonitrile and 0.1 M sodium acetate adjusted to pH 5.0 with acetic acid. The quantitation of ABDAC residues was carried out using commercial ABDACs as external standards to construct a five-level calibration curve (or average calibration factor, CF = peak area/amount) covering the range 10−250 μg/mL. The precision of the curve, as indicated by the RSD of calibration factors, was 2.8, 3.0, 2.8, and 1.5% for corresponding C_{12}-, C_{14}-, C_{16}-, and C_{18}-ABDACs. The calibration curves were linear with coefficients of determination $r^2 \geq 0.998$.

RESULTS AND DISCUSSION

Method Optimization. *Hofmann Degradation.* First, the effect of temperature on the alkyldimethylamine formation was investigated. Figure 1 indicates that, in the presence of LAS, the optimum conditions for debenzylation of ABDACs with potassium *tert*-butoxide occurs at a temperature exceeding 90 °C to produce the corresponding alkyldimethylamines. The result suggested that, in the presence of LAS, an increase in the reaction temperature increases the reaction efficiencies by overcoming the energy of debenzylation of ABDACs and steric interference. Our result contrasted with the debenzylation observed by Suzuki et al.,[20] which converted ABDACs to corresponding alkyldimethylamines at a temperature lower than 40 °C when no LAS or other anionic substances were present.

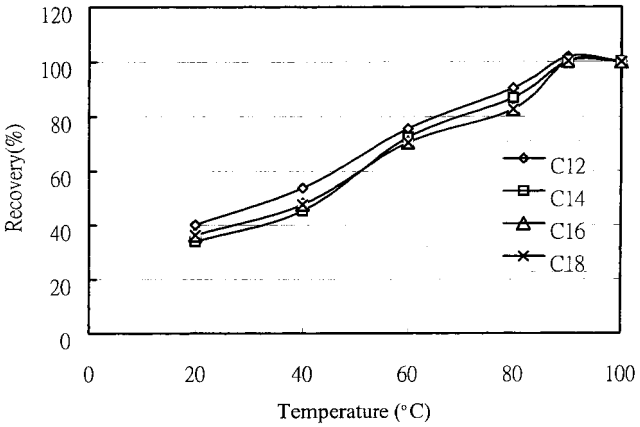

Figure 1. Effects of reaction temperature on the formation of alkyldimethylamines for four ABDACs.

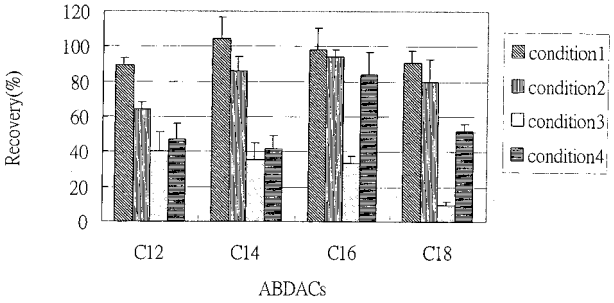

Figure 2. Extraction recoveries of ABDACs in various conditions as described in text. Extractions were performed on three replicates; standard deviation is reported as an error bar.

Sample Extraction. To determine the optimum sample extraction procedures, various extraction conditions were investigated under a debenzylation temperature of 90 °C. Figure 2 reveals that by adjusting the sample to pH 7.0, and eluting analytes with 10 mL of methanol−ethyl acetate (1:1, v/v) (the moisture was removed from the eluent by passing it through a $MgSO_4$ column), maximum recoveries (89−104%) were achieved (in condition A). Addition of 1% calcium chloride in the eluent (in condition B) has been applied to increase the recoveries of ABDACs as described by Kummerer et al.[8] However, relatively lower recoveries were observed in our results (61−93%), owing to the salts of calcium chloride that formed on the surface of the vial after the extract was evaporated to dryness by a stream of nitrogen. When calcium chloride was omitted in the eluent, or the eluent was not pretreated with $MgSO_4$, a significantly lower recovery of C_{18}-ABDAC was obtained (in condition C). Removing the moisture from the eluent was necessary to conduct the complete Hofmann degradation because potassium *tert*-butoxide is water sensitive. The effect of pH was also investigated by extracting acidified samples with an RP-18 SPE cartridge when LAS was added (in condition D).

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Table 1. Background Concentrations and the Recovery Results of ABDACs Spiked into Various Water Samples

	ABDACs			
sample	C_{12}	C_{14}	C_{16}	C_{18}
deionized water ($n = 7$)				
spiked recovery (%)	89[a] (4.4)[b]	104 (12)	98 (12)	90(7.0)
river water sample A ($n = 3$)				
background concn (μg/L)	2.5 (10)	0.6 (11)	3.3 (9.2)	18 (5.0)
river water sample B ($n = 3$)				
background concn (μg/L)	1.8 (8.3%	0.3 (8.2)	3.2 (10)	17 (9.1)
spiked recovery (%)	88 (16)	81 (10)	92 (12)	90 (11)

[a] The spike recovery. [b] The relative standard deviations (%) are given in parentheses.

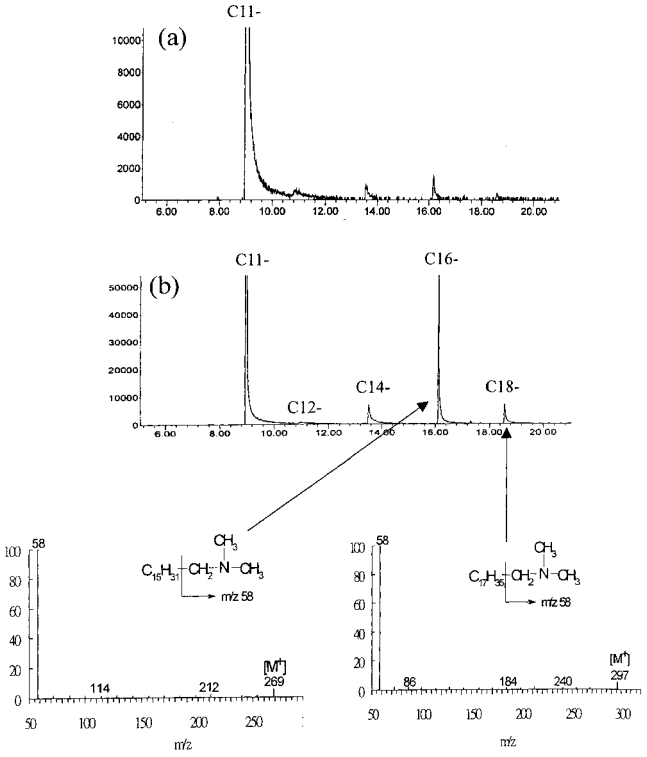

Figure 3. Extracted ion chromatograms (*m*/*z* 58) of ABDACs as their corresponding alkyldimethylamines and the internal standard (undecyldimethylamine) (a) prior to debenzylation and (b) after Hofmann degradation with potassium *tert*-butoxide at 90 °C; and their corresponding electron impact ionization mass spectra detected in the water sample from Kao-Ping river.

Adding acid and LAS to the sample to facilitate the extraction of the cationic surfactants by liquid−liquid extraction has been demonstrated.[22] However, when the sample was acidified to pH 2.0, lower recoveries from RP-18 SPE were observed (52−79%). This finding indicates that an acidified sample with a low pH may affect the recovery efficiency from SPE extraction.

GC/MS Analysis. To confirm that the corresponding alkyldimethylamines were not present in the environmental samples prior to the debenzylation of ABDACs, the entire extraction and GC/MS analysis procedures were conducted as described above. Figure 3a reveals that, prior to debenzylation, the extracted ion chromatogram did not display any significant alkyldimethylamines peaks. Figure 3b depicts the extracted ion chromatograms (*m*/*z* 58) of alkyldimethylamines, and their corresponding electron impact ionization mass spectra as detected in a river water sample. The corresponding alkyldimethylamines have the same mass spectra as C_{12}−C_{18}-alkyldimethylamines reported in the database of the NIST/EPA Mass Spectra Library. In general, the molecular ion $[M]^+$ exhibited a low abundance (<5%), which is consistent with the long alkyl chain of the alkyldimethylamines. The base peak, ion at *m*/*z* 58, of the mass spectra corresponds to the carbon−carbon bond α-cleavage with respect to nitrogen, which is stabilized by an imminium ion ($[CH_2{=}N(CH_3)_2]^+$), as reported previously for aliphatic amines of shorter alkyl chain.[25]

Recovery Study and Reproducibility. This technique provides high precision and sensitivity for ABDACs, to quantitation at ≤0.1 μg/L in 500 mL of water samples. The recovery from SPE was evaluated by a known amount of spiked C_{12}-, C_{14}-, C_{16}-, and C_{18}-ABDAC mixture in deionized water. Seven replicate 500-mL deionized water samples were each spiked to obtain final concentrations of 2 μg/L of ABDAC mixture. The average recovery of C_{12}-, C_{14}-, C_{16}-, and C_{18}-ABDAC spiked water samples were 89, 104, 98, and 90% with RSDs of 4.4, 12, 12, and 7.0%, respectively. The RP-18 SPE yielded a high recovery of ABDACs from aqueous samples, which was firmly retained on the RP-18 cartridge by strong hydrophobic and electrostatic interactions. The ABDACs can be then eluted selectively by the methanol−ethyl acetate solution, as found in a previous study.[7] No interference with other QACs, such as alkyltrimethyl- or dialkyldimethylammonium chlorides, was detected in the extract. Table 1 summarizes the average percentage recovery of ABDACs in the samples from two water samples, as well as their estimated background concentrations owing to optimized Hofmann degradation and GC/MS procedures. Recovery of total ABDACs ranged from 81 to 92% with the RSDs ranging from 10 to 16%. The RSDs of three replicate environmental samples ranged from 5 to 11%.

Application to Environmental Samples. The versatility of this method is demonstrated in Table 2, which lists the concentrations of ABDAC residues detected in rivers and industrial effluent samples. The extracted ion chromatograms of the samples had few interfering peaks and were essentially similar to those displayed in Figure 3b. In rivers, the concentrations of total measured ABDAC residues ranged from 2.5 to 65 μg/L. The most abundant compound was C_{18}-ABDAC (2.1−55 μg/L), followed by C_{16}-ABDAC (0.4−5.3 μg/L). Detection of a significantly high concentration of C_{18}-ABDAC is reasonable, as it is present in shampoo and hair conditioner. The data clearly indicate that a great amount of C_{18}-ABDAC is present in household wastewaters and is directly discharged into the rivers. To our knowledge, no data have been reported for the C_{18}-ABDAC concentrations

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Table 2. Concentrations (μg/L) of ABDACs Determined by a GC/MS Method in Selected Taiwanese Rivers and Industrial Effluents

sample	ABDACs C_{12}	C_{14}	C_{16}	C_{18}	total LAS (μg/L)	specific conductance μ·S/cm
rivers						
Tam-Sui	2.1	0.8	3.0	16	78	370
Tour-Chyan	nd[b]	nd	2.9	31	79	470
Pu-Tzu	nd	0.2	1.2	15	120	550
Kao-Ping					100	600
(Hofmann + GC/MS)	0.15 (6.1)[a]	0.49 (12)	2.4 (6.7)	2.6 (3.4)		
(direct HPLC)	0.17 (10)	0.51 (7.7)	2.8 (8.7)	2.6 (11)		
Dong-Kang	4.2	0.8	5.3	55	130	110
industrial effluents						
Ruen-Tai Co.	4.7	0.5	2.9	22	250	2180
Lien-1 Co.	2.6	1.1	9.1	100	300	1200
limit of detection (μg/mL)						
Hofmann + GC/MS	0.01	0.01	0.01	0.1		
HPLC	0.1	0.1	0.1	1.0		

[a] The relative standard deviations (%) are given in parentheses ($n = 3$). [b] nd, not detected at method quantitation limit.

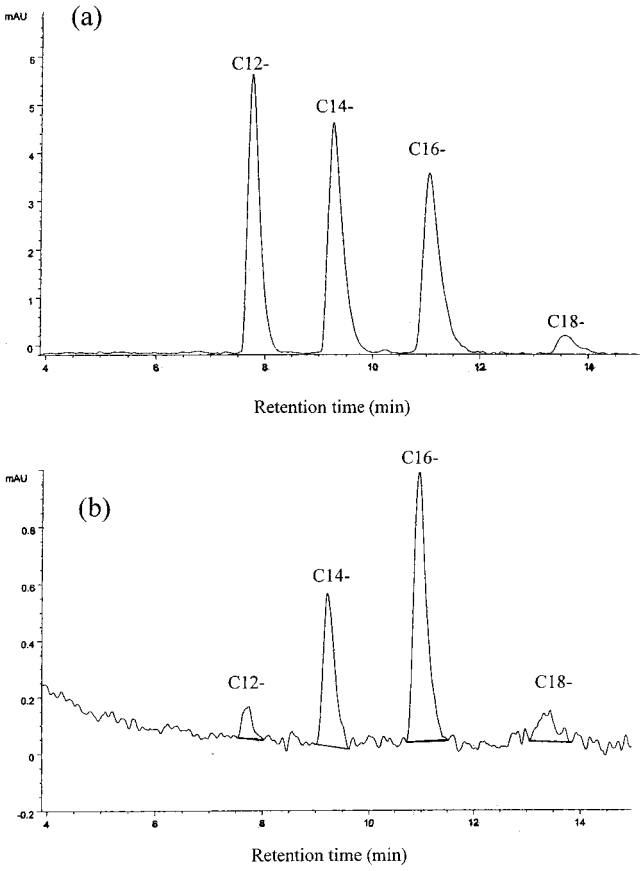

Figure 4. HPLC chromatograms for (a) standards containing C_{12}–C_{18}-ABDACs and (b) an RP-18 SPE extract of the water sample from Kao-Ping river. The corresponding concentrations are given in Table 2.

detected in environmental samples. Furthermore, as expected, relatively higher ABDAC residues were detected in industrial effluents.

Figure 4 indicates that the HPLC method for analysis of ABDAC mixtures produced adequate resolution of the four major peaks corresponding to C_{12}-, C_{14}-, C_{16}-, and C_{18}-ABDACs. The HPLC method produced an analysis time of 15 min for all four ABDACs, whereas the GC/MS method required more than 20 min. The sensitivities of the detection were ~0.1 (C_{18}-) to 0.01 μg/mL (C_{12}–C_{16}-) for GC/MS, and 1.0–0.1 μg/mL for HPLC, respectively. Owing to a low UV absorbance for ABDACs, the HPLC method was less sensitive. The quantitative results obtained from the GC/MS method using Hofmann degradation and the direct HPLC method are listed and compared in Table 2. The relative difference of the two methods for the test compounds was less than 14%. The precision of these two methods is compatible by comparison with their RSDs. Due to the lack of a standard reference method, it is recommended to always use two independent methods in order to compare and confirm the results.

CONCLUSION

The analytical procedure developed herein demonstrates that the RP-18 SPE and GC/MS methods with the Hofmann degradation reaction are reliable and sensitive and offer a convenient analytical technique for trace determination of ABDAC residues in complex environmental samples. As expected, GC/MS analysis leads to better peak shapes and higher efficiency and sensitivity, whereas direct HPLC analysis is superior in shorter sample preparation and analysis time. As far as accuracy and precision are concerned, both the methods gave satisfactory results. The RP-18 SPE worked well owing to the interaction between RP-18 solid phase and the hydrophobic ion-pair complexes of ABDACs plus LAS and the selective elution of the complex by methanol–ethyl acetate. Furthermore, our method reveals that ABDAC residues are widespread in Taiwan's rivers. The survey is currently being studied across Taiwan in order to understand the fate and influence of ABDAC residues in untreated wastewater directly discharged into the aquatic environment.

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