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Short communication

Analysis of linear alkylbenzenesulfonates in water samples by large-volume injection-port derivatization and gas chromatography–mass spectrometry

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Abstract

This work presents a modified method to analyze linear alkylbenzenesulfonates (LASs) in water samples. The method involves extraction of samples by a graphitized carbon black (GCB) cartridge, and direct derivatization in the GC injection port using a large-volume (10–20 μl) direct sample introduction (DSI) device with tetraalkylammonium (TAA) salts. The analytes were then identified and quantitated by ion-trap GC–MS. The large-volume DSI injection-port derivatization technique provides sensitivity, fast and reproducible results for LAS residues, to quantitation at 0.1 μg/l in 200 ml of water samples. The retention effect of TAA salts in the injection port was not detected. Enhanced selected mass chromatograms of $[M-55]^+$ ions of butylated C_{10}–C_{13} LASs by electron impact ionization MS allows one to determine LAS residues at trace levels in environmental samples. Recovery of total LASs in spiked variety water samples ranged from 89 to 112% while RSDs ranged from 2 to 13%.

Keywords: Water analysis; Environmental analysis; Derivatization, GC; Large-volume injection; Alkylbenzenesulfonates; Surfactants

1. Introduction

Linear alkylbenzenesulfonates (LASs) are the most commonly used anionic surfactants in diverse industrial, household and commercial applications. Taiwan's production exceeded $52 \cdot 10^6$ kg in 1996 [1]. However, municipal or industrial wastewater treatment plants treat less than 5% of all wastewater. Large quantities of the surfactant residues in wastewater are directly discharged into rivers. Taiwan's deficient municipal wastewater treatment leads to a higher concentration of LAS residues in Taiwanese rivers which is significantly higher than in other countries [2,3]. A convenient analytical technique must be developed to study the composition of LAS residues in untreated wastewater which are directly discharged into the aquatic environment.

Gas chromatography–mass spectrometry (GC–MS) is a widely used method for trace analysis of organic pollutants. However, GC–MS has not been recommended for analyzing ionic organic com-

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pounds owing to the low volatility and high interaction of such compounds in either the heated GC injector or column. Liquid chromatography (LC) [4–6] and LC–MS techniques with atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) interfaces [7–10] have been successfully applied to analyze such compounds in a variety of matrices. The LC–MS technique identifies the isomers, oligomers and homologues of surfactants, and determines the trace levels of their biodegradation products. However, as GC–MS is a more readily available technique in many environmental laboratories, and provides a higher chromatographic resolution with a capillary column, considerable efforts have been made to overcome the problems of volatility and polarity in its application to these compounds. One focus is to convert the analyzed compound to a corresponding ester which is suitable for GC analysis.

Previous analytical approaches to determine LAS residues in aqueous samples consisted of sequentially extracting nonionic and anionic surfactants from the water samples by graphitized carbon black (GCB) cartridges. The extract was then esterified by two-step thionyl chloride–trifluoroethanol derivatization procedures [2,3]. These procedures are generally time-consuming and need highly reactive reagents to convert sulfonic acids into their corresponding trifluoroethyl derivatives. The procedure of direct injection-port derivatization with ion-pair reagents, also known as the pyrolysis of tetraalkylammonium (TAA) salt derivatization method, is a rapid and simple alternative to conventional derivatization methods for aliphatic, aromatic acids and sulfonic acids [11–14]. The derivatization was initiated by reaction of the sulfonic acid group with TAA salts (i.e., tetrabutylammonium hydrogensulfate, TBA-HSO_4) to form LAS ion pairs [$RSO_3^-N(Bu)_4^+$] in solution. These ion pairs were then converted to butyl esters [RSO_3Bu] in the GC injection port.

This study presents a modified method to rapidly and quantitatively determine LAS residues in aqueous samples. The method involves extraction of LAS residues from water samples by GCB solid-phase extraction (SPE) and derivatization of LASs with TAA salts in the GC injection port by a large-volume direct sample introduction (DSI) device.

2. Experimental

2.1. Samples

Water samples containing high concentrations of primary industrial effluents (specific conductance 2180 μS/cm) were collected from a river which receives effluents from industrial wastewater treatment plants in the Tai-Yuan Industrial Park, Tao-Yuan County (Taiwan). The term ''industrial effluent'' is used herein for simplification. Samples of river water (specific conductance 740 μS/cm) polluted by surfactants were collected from Lao-Jie River at Chung-Li city (Taiwan). In this city, untreated municipal wastewater is discharged directly into the river. The samples were collected at a 0.5-m depth from mid-stream using pre-rinsed glass bottles. 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.

2.2. Chemicals and reagents

Unless stated otherwise, all high-purity chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA), Tedia (Fairfield, OH, USA) and Merck (Darmstadt, Germany), and were used without further purification. Reagent-grade TAA salts, TBA-HSO_4, tetramethylammonium hydrogensulfate (TMA-HSO_4) and tetramethylammonium hydroxide (TMA-OH) were purchased from TCI (Tokyo Chemical Industry, Tokyo, Japan). Commercial LASs were provided by Taiwan Surfactant (Taiwan) and used as a calibration standard. The surrogate 4-octylbenzenesulfonic acid (C_8-LAS) was purchased from Aldrich.

2.3. Sample extraction

The procedure using GCB cartridges (ENVI-Carb, Supelco, USA) to extract LAS residues from the water samples has been reported elsewhere [2–6]. Acidified 200-ml spiked samples were passed

through the GCB cartridge at a flow-rate of about 10–20 ml/min with the aid of a vacuum. The LAS residues were eluted from the cartridge with 3 ml of methylene chloride–methanol (9:1, v/v) eluent, modified with 2 m*M* TBA-HSO_4. After the elution process was completed, the volume of the extract of LASs was reduced to 100 μl, thus made ready for GC–MS analysis.

2.4. GC–MS analysis

Analyses were performed on a Varian 3400CX gas chromatograph directly connected to a Saturn 2000 ion-trap mass spectrometry (Varian, USA). A DSI device (or ChromatoProbe, Varian) and a temperature-programmed injector (Varian 1078 injection port) with a 3.4 mm I.D. liner, as described elsewhere [15,16], were used to introduce a large-volume sample. A 10 to 20 μl sample extract was introduced into a DSI micro sample vial. The vial was placed in the probe's vial holder and then heated in a heating module to evaporate the solvent at 70°C for 2 min before injection. When it was dry, the probe was pushed into the heated zone of the injection port. The temperature of the injector was held at 100°C for 1 min, then rapidly heated to 300°C, and held for another 40 min. The split ratio was 1:10. A DB-5MS capillary column (30 m×0.25 mm I.D., 0.25 μm film, J&W, USA) connected to 2–4 m of deactivated fused-silica per-column (as retention gap), was used. After the injector temperature had reached 300°C, the GC temperature program began as follows: 100°C for 3 min, followed by a 7°C/min ramp to 300°C, and hold for 7 min. At the end of the analysis, the sample vial was removed from the DSI vial holder, and disposed of. The transfer line was set at 280°C. Full scan electron impact ionization (EI) data were acquired under the following conditions: mass range m/z 50–550, scan time 1 s, manifold temperature 120°C, emission current 10 μA, automatic gain control (AGC) target 25 000 (represented as the target total ion current value). The precision of the injection-port derivatization and GC–MS analysis, determined from the relative standard deviation (RSD) of over 50 injections of C_8-LAS, ranged from 6 to 15%.

3. Results and discussion

3.1. Evaluation of tetraalkylammonium salts and injection port conditions

Owing to the availability of different TAA salts and the possible dependence of derivatization efficiency on the reagent selected, three TAA salts (TBA-HSO_4, TMA-HSO_4 and TMA-OH) were first evaluated for their reaction with the LAS mixture to form their corresponding alkyl esters. Among the three reagents tested, TBA-HSO_4 reagent was chosen because characteristic ions of butylated LASs (see Section 3.2) produced the highest average peak areas and quantitative results. The retention effect of TAA salts in the injection port was not detected since the DSI device with disposable micro vial was used and no glass wool was inserted into the inlet glass liner. Therefore, a routine check for sample carryover by subsequent injection of a different ion-pair reagent [such as (trifluoromethylphenyl)trimethylanilinium hydroxide] after a sample injection, as described by Field and co-workers [13,14], was not necessary in this method. The sharp and symmetric chromatographic peaks were still observed after a series of 50 sample injections.

The average peak areas did not significantly differ for butylated LASs obtained after the two solvent evaporation periods (2 min and 10 min). According to our results, the time required for this step is not critical, provided that 2 min is long enough for complete evaporation of the solvent. The effect of the injection temperature was evaluated. The average peak areas for the butylated LASs were not significantly different at 280, 300 or 320°C. A detailed study was not made of the decrease in yield at a lower temperature since 280 to 320°C represents a temperature range appropriate for most practical purposes. The injection temperature at 300°C was used in this study.

3.2. GC–MS of LASs

Fig. 1 depicts the full-scan EI mass spectra of the methylated (a) and butylated (b) 6-phenyl C_{12}-LAS by TMA-HSO_4 and TBA-HSO_4 reagents, respectively. The molecular ions of individual LAS homo-

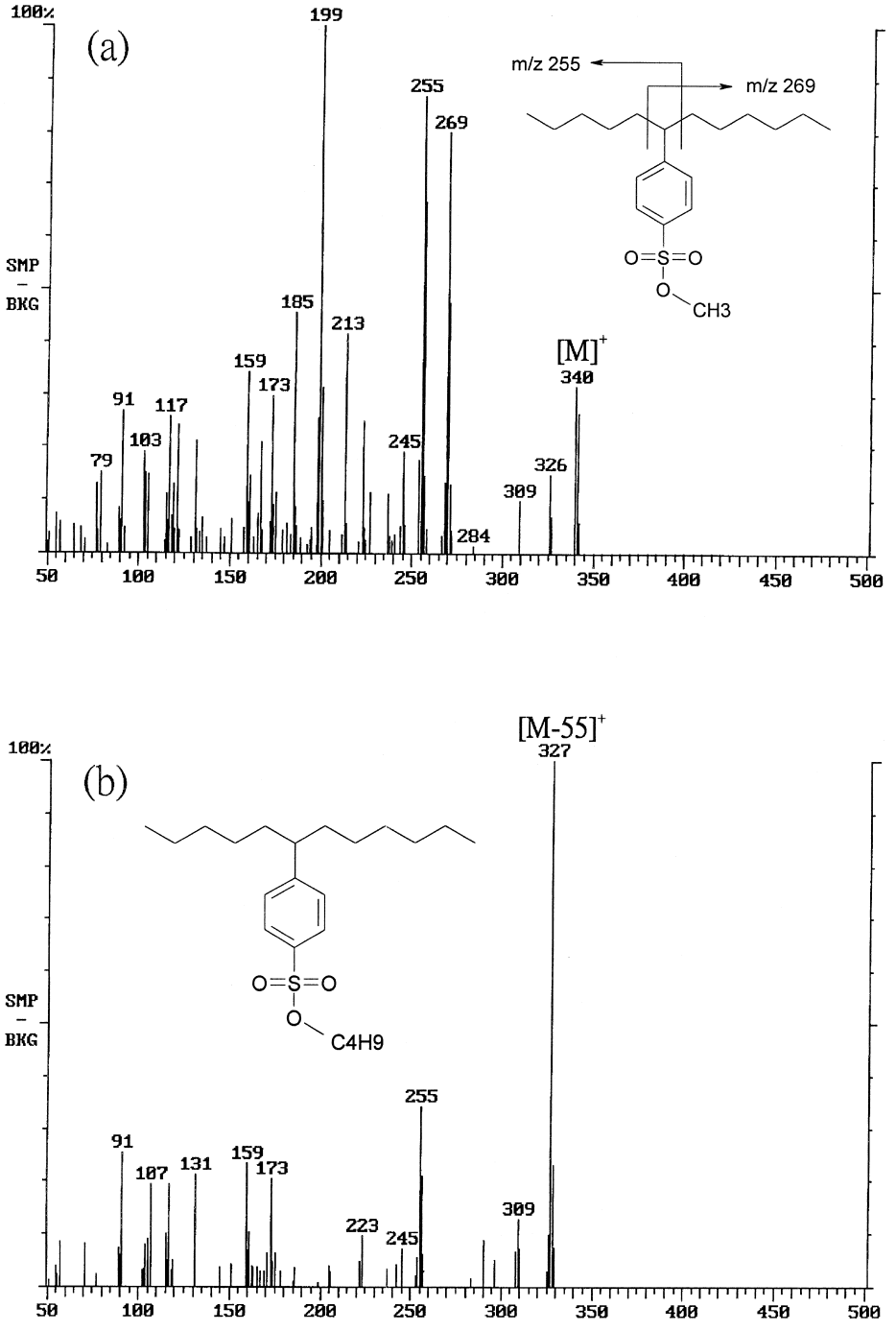

Fig. 1. Full-scan EI mass spectra of (a) methylated and (b) butylated 6-phenyl C_{12}-LAS residues detected in the sample of river water polluted by surfactants.

logues were observed in methylated LAS derivatives (Fig. 1a). The characteristic fragment of the 6-phenyl isomer is the ion at m/z 269, representing the benzylic cleavage of the five-carbon alkyl chain $[M\text{-}C_5H_{11}]^+$ ($[M-71]^+$). The ion at m/z 255 represents the loss of the six-carbon alkyl chain on the other side of the phenyl group from the 6-phenyl isomer. The ion at m/z 199 is the base ion produced by the loss of the remaining five- or four-carbon alkyl group from the fragment of $[M\text{-}C_5H_{11}]^+$ or $[M\text{-}C_6H_{13}]^+$, respectively.

The intense peak of the $[M-55]^+$ ion of 6-phenyl C_{12}-LAS was observed in butylated LAS derivatives due to the loss of C_4H_7 (Fig. 1b) [14]. The characteristic fragment of the 6-phenyl isomer is the ion at m/z 255, representing the benzylic cleavage of the five-carbon alkyl chain from the $[M-55]^+$ ion ($[M-55\text{-}C_5H_{11}]^+$). Similar MS spectra of the $[M-55]^+$ ion were obtained for all LAS isomers and homologues. Fig. 2 displays the selected mass chromatograms of butylated LAS residues extracted from a river water polluted by surfactants. The individual LAS isomers and homologues are clearly depicted by the peaks representing the intense ions of the $[M-55]^+$ at m/z 299, 313, 327 and 341, which can be used to characterize of C_{10}-, C_{11}-, C_{12}- and C_{13}-LASs, respectively. The numbers above the peaks indicate the positions of benzenesulfonates. The results of the determination of the enhanced sensitivity of LAS residues by the abundance of $[M-55]^+$ ions are similar to those of our previous study which determined LAS residues from enhanced quasi-molecular ion chromatograms by chemical ionization (CI) MS [2]. Therefore, the procedures used herein indicate that direct derivatization by TMA-HSO_4 or TBA-HSO_4 reagent is an effective means of positively identifying and reliably determining LAS residues in complex aqueous samples.

3.3. Recovery study and application to environmental samples

The quantitation limits of butylated C_8-LAS by EI-MS was 1.0 ng/μl, defined at a signal-to-noise (S/N) ratio≥10. The method for 10 ng/μl to 200 ng/μl of the total butylated LASs was accurate to within 3% RSD. The recovery from GCB-SPE was evaluated by a known amount of spiked C_8-LAS (as surrogate standard) and a LAS mixture in deionized water. Three replicate 200-ml deionized water samples were each spiked to obtain final concentrations of 5 μg/l of C_8-LAS and 50 μg/l of LAS mixture. The degree of LAS recovery was indicated by the calibration curve (or average standard response factor) which was calculated from four levels of LAS mixture between 50 ng/μl to 200 ng/μl, each divided by the fixed concentration of C_8-LAS surrogate. The average recovery was 112% with 2% RSD.

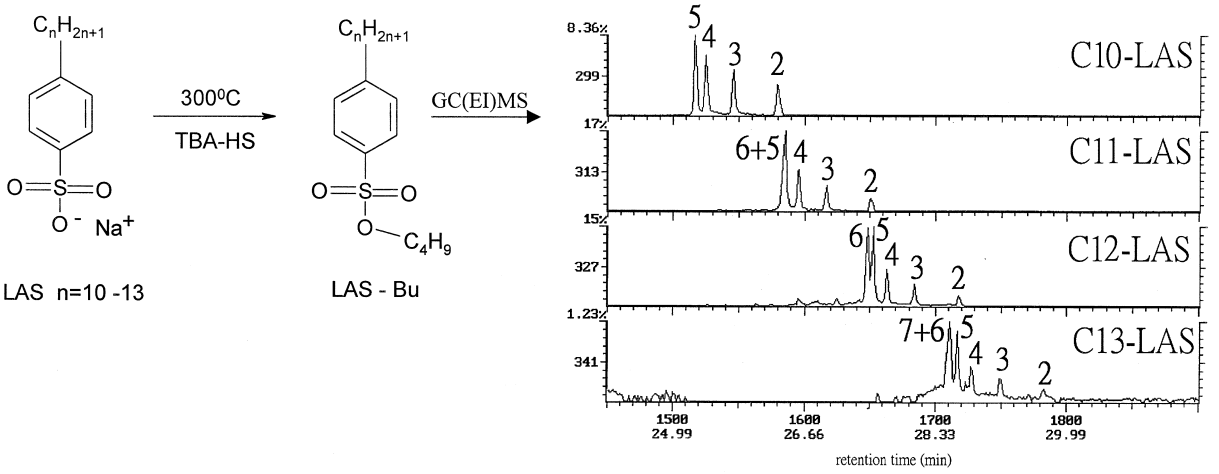

Fig. 2. Flow diagram of chemistry and the selected EI characteristic ion $[M-55]^+$ chromatograms of butylated LAS residues isolated from the sample of river water polluted by surfactants.

Table 1
Background concentrations and the recovery results of LASs spiked into different water samples[a]

Sample	LAS				Total LASs
	C_{10}	C_{11}	C_{12}	C_{13}	
Deionized water					
Spiked recovery (%)	116 (4%)	120 (6%)	104 (4%)	88 (19%)	112 (2%)
Surfactant polluted river water					
Average background concentration (μg/l)	221 (11%)	300 (15%)	258 (9%)	19 (14%)	798 (13%)
Spiked recovery (%)	89 (2%)	92 (11%)	98 (4%)	62 (12%)	102 (2%)
"Industrial effluent" river water					
Average background concentration (μg/l)	5 (3%)	13 (5%)	28 (16%)	4 (9%)	50 (5%)
Spiked recovery (%)	89 (14%)	121 (9%)	117 (5%)	62 (19%)	89 (6%)

[a] The relative standard deviation (RSD) is given in parentheses, $n=3$.

Table 1 summarizes the average percentage recovery of C_{10}–C_{13} LASs in two environmental samples with different specific conductances, as well as their estimated average background concentrations in the samples. Recovery of total LASs ranged from 89 to 102% with RSDs ranging from 2 to 6%. The RSDs of three replicate environmental sample analyses ranged from 5 to 13%. The results indicated that the extraction efficiency of GCB was effected by neither the high ionic contents nor the variable compositions of environmental samples. The direct injection-port derivatization with ion-pair reagent procedure simplified the preparation of the calibration standard and quantification of the sample.

In conclusion, this work demonstrates that GCB-SPE and injection-port derivatization using a large-volume DSI device with TAA salts, is a rapid and quantitative method for determining trace levels of LAS residues in aqueous samples. The method significantly reduces the solvent waste and simplifies the sample preparation requirements, typically associated with LAS extraction and derivatization. Furthermore, it can be used as a rapid screening tool, and to obtain detailed information about the sources, behavior and fate of the LAS residues in both surface water and groundwater.

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References

[1] C.R. Shih, Chem. Technol. 5 (1997) 112.
[2] W.-H. Ding, J.H. Lo, S.H. Tzing, J. Chromatogr. A 818 (1998) 270.
[3] W.-H. Ding, S.H. Tzing, J.H. Lo, Chemosphere 38 (1999) 2597.
[4] A. Marcomini, W. Giger, Anal. Chem. 59 (1987) 1709.
[5] A. Di Corcia, M. Marchetti, R. Samperi, A. Marcomini, Anal. Chem. 63 (1991) 1179.
[6] A. Di Corcia, A. Marcomini, R. Samperi, Environ. Sci. Technol. 28 (1994) 850.
[7] E. Gonzalez-Mazo, M. Honing, D. Barcelo, A. Gomez-Parra, Environ. Sci. Technol. 31 (1997) 504.
[8] S.D. Scullion, M.R. Clench, M. Cooke, A.E. Ashcroft, J. Chromatogr. A 733 (1996) 207.
[9] J.J. Conboy, J.D. Henion, M.W. Martin, J.A. Zweigenbaum, Anal. Chem. 62 (1990) 800.
[10] A. Di Corcia, J. Chromatogr. A 794 (1998) 165.
[11] J.J. Bailey, Anal. Chem. 39 (1967) 1485.
[12] J.W. Schwarze, M.N. Gilmour, Anal. Chem. 41 (1969) 1686.
[13] J.A. Field, D.T. Miller, T.M. Field, S.B. Hawthorne, W. Giger, Anal. Chem. 64 (1992) 3161.
[14] J.A. Field, T.M. Field, T. Poiger, T.W. Giger, Environ. Sci. Technol. 28 (1994) 497.
[15] H. Jing, A. Amirav, Anal. Chem. 69 (1997) 1426.
[16] W.-H. Ding, S.H. Tzing, J. Chromatogr. A 824 (1998) 79.