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Short communication

Determination of naphthalenesulfonic acid isomers by large-volume on-line derivatization and gas chromatography–mass spectrometry

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Abstract

This work presents a modified method to analyze polar and water-soluble naphthalene monosulfonic acid (NS) isomers in industrial effluents and river water samples. The method involves extraction of samples by a styrene–divinylbenzene copolymer solid-phase extraction cartridge, and on-line derivatization in the GC injection port using a large-volume (10 μl) sample injection with tetrabutylammonium salts. The analytes were then identified and quantitatively determined by GC–MS. The large-volume injection-port derivatization technique provides sensitivity, fast and reproducible results for NS isomers, to quantitation at 0.05 μg/l in 200 ml of water sample. Enhanced extracted mass chromatograms of molecular ion and $[M-56]^+$ ion of butylated NS isomers by electron impact ionization MS allows us to determine residues at trace levels in environmental samples. Recoveries of the NS isomers in spiked water samples ranged from 70 to 82% with RSDs around 10%. Naphthalene-2-sulfonic acid was found as a major pollutant and propagated in surface water and industrial effluents.

Keywords: Derivatization, GC; Water analysis; Environmental analysis; Naphthalenesulfonic acids; Organosulfur compounds; Surfactants; Alkyl benzenesulfonates, linear

1. Introduction

Polar naphthalenesulfonic acid isomers [NSs; naphthalene-1-sulfonic acid (N-1-S) and naphthalene-2-sulfonic acid (N-2-S)] are applied in an extensive variety of industrial, household and commercial applications, especially in the production of pharmaceuticals, azo dyes, and tanning agents. In contrast to linear alkylbenzenesulfonates (LASs), these NS isomers without long alkyl side chains are reported to be persistent [1–3]. They have been detected in wastewater effluents [4–7], surface waters [8–11], and landfill leachates [12–14]. Since Taiwan's deficient municipal and industry wastewater treatment leads to a higher concentration of LAS residues in rivers [15,16], and the considerable quantities of naphthalenesulfonic acids used in practice, the possible ubiquitous character of these compounds seems to propagate through the aquatic environment, and is worth investigating.

Various solid-phase extraction (SPE) methods combined with high-performance liquid chromatography (HPLC) [4,8,11,13,14], capillary electrophoresis (CE) [10,17–20], gas chromatography–mass spectrometry (GC–MS) [11,21,22] and liquid chromatography–mass spectrometry (LC–MS) [5–7,12–

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14] as identification and quantitation methods have been developed. An exhaustive review including references to work done up to 1995 has been reported by Reemtsma [23]. Among them, ion-pair HPLC and LC–MS techniques have been successfully applied to analyze aromatic sulfonate residues in a variety of matrices. However, GC–MS is a more readily available technique in many environmental laboratories, and provides a better chromatographic separation for isomers with a capillary column. In order to overcome the polar and ionic problems of its application to aromatic sulfonic acids, it is necessary to convert the sulfonic acid to a corresponding ester derivative. Methylation with diazomethane or tetramethylammonium cation, as well as derivatization by two-step thionyl chloride–trifluoroethanol were reported elsewhere [11,15,22,24]. However, these procedures are generally time-consuming and need highly reactive reagents. Currently, the procedure of injection-port derivatization with ion-pair reagents has been reported as a rapid and simple alternative to conventional derivatization methods for aliphatic, aromatic acids and sulfonic acids [25–28].

The large-volume sample introduction (LVI) is an attractive method of improving detection sensitivity, and of preventing discrimination inside the syringe needle and injector liner from injecting a small volume of sample. Mol et al. have evaluated and reviewed the technique of inserting glass wool in the large dimensions of injector liners, and referred to this sample introduction method as ''solvent-split injection'' [29]. Recently, Amirav and co-workers developed a direct sample introduction device that enables direct sampling of solid materials into a GC instrument [30,31]. This device has been commercially available as the ChromatoProbe from Varian. The device operates by placing a 20-μl microvial that contains the sample into the GC injection port. For liquid extracts, it is placed in the microvial and can be operated just as in LVI techniques. Furthermore, the microvial can be used as a small reactor for an on-line injection-port derivatization procedure which has been successfully developed in our laboratory and used to determine LASs and carboxylate surfactant metabolites [32–34], as well as chlorophenoxy acid herbicides [35] in water samples.

The objective of this study was to develop a modified method for the rapid and unequivocal determination of N-1-S and N-2-S isomers in aqueous samples. These two isomers have been the most frequently detected in various wastewaters and with relatively higher concentrations than the other naphthalene disulfonic acids [4–13]. The results further demonstrated the effectiveness of the method in determining NS isomers at trace levels in environmental samples.

2. Experimental

2.1. Sample collection

River water samples were collected from two major river estuaries: Kao-Ping River and Dong-Kang River, in southern Taiwan. The yearly average of selected water quality parameters and the estimated percentages of three major wastewater contributions (from municipal, industrial and livestock farming) of the two rivers have been displayed elsewhere [36]. Two industrial effluents, with specific conductances 1580 μS/cm (from Li-Pong Co.) and 960 μS/cm (from Hsin-Yu Co.), were collected directly from industrial effluent outlets in Tai-Yuan Industrial Park, Tao-Yuan County (Taiwan). Details on sample collection and preservation can be found elsewhere [33,34].

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 tetrabutylammonium hydrogensulfate (TBA-HSO_4) was purchased from TCI (Tokyo Chemical Industry, Tokyo, Japan). Sodium salts of naphthalene-1-sulfonate, naphthalene-2-sulfonate, and the surrogate 4-octylbenzenesulfonate (C_8-LAS) were purchased from Aldrich. Stock solutions of these analytes (1000 μg/ml) were prepared in methanol. Working solutions at lower concentrations were also prepared in methanol by serial dilution.

2.3. Sample extraction

Since polystyrene–divinylbenzene (PS–DVB) SPE provides high extraction efficiency for polar and hydrophilic aromatic sulfonic acids as reported elsewhere [5,18], LiChrolut EN polymeric sorbent (from Merck) based on PS–DVB was chosen in this study for enrichment of NS isomers from environmental samples. Before extraction, each SPE cartridge was conditioned with 4 ml methanol–acetone (3:2, v/v) and 5 ml, pH 2 deionized water on an SPE manifold (VacMaster, IT Sorbent Technology, Cambridge, UK). Acidified 200-ml spiked samples were passed through the LiChrolut EN cartridge at a flow-rate 5–10 ml/min via a siphon tube with the aid of a vacuum. When the extraction was completed, the cartridge was dried under vacuum for 2 min. The NS isomers were then eluted from the cartridge with 4 ml of methanol–acetone (3:2, v/v) eluent. The extract was then completely evaporated to dryness by a stream of nitrogen. The residues were then re-dissolved in 100 μl of chloroform with internal standard containing 20 m*M* TBA-HSO_4, and made ready for GC–MS analysis.

2.4. GC–MS analysis

A Varian 3400CX gas chromatograph directly connected to a Saturn 2000 ion-trap mass spectrometer (Varian, Walnut Creek, CA, USA) were used in the analysis of the sample extracts. A Chromato-Probe and a temperature-programmed injector (Varian) was used to introduce a large-volume sample and on-line derivatization approach, as described elsewhere [32–35]. A DB-5MS capillary column (30 m×0.25 mm I.D., 0.25 μm film, from J&W, USA) connected to 2 m of deactivated fused-silica column (as retention gap), was used. The GC temperature program was as follows: 100°C for 3 min, followed by a 8.5°C/min ramp to 300°C, and hold for 7 min. The conditions of the ion-trap MS system can be found elsewhere [35].

The quantitation of NS isomers was calculated from the four-level calibration curve (or average response factor) covering the range 1 to 20 ng/μl, each divided by the fixed concentration of internal standard ([$^2H_{12}$]chrystene) [35]. The precision of the curve or linearity, as indicated by the relative standard deviation (RSD) of response factors, was 8.2 and 8.3% for butylated N-1-S and N-2-S, respectively. This on-line injection-port derivatization procedure was found effective for naphthalene and benzene monosulfonic acids (i.e., LASs, N-1-S, N-2-S, and *p*-toluenesulfonic acid), while their disulfonic acids, and amino derivatives were not detectable with this procedure (data not shown).

3. Results and discussion

3.1. Evaluation of ion-pair reagents and injector-port conditions

According to our previous experience with ion-pair reagents, TBA-HSO_4 was the best reagent for on-line derivatization because characteristic ions of butylated NS isomers (see Section 3.2) produced the highest average peak areas and quantitative results. No retention effect either for TBA salt or sample was detected since the disposable microvial was used for sample introduction and no glass wool was inserted into the inlet glass liner. Among the four TBA concentrations (10, 15, 20 and 30 m*M*), 20 m*M* was selected because it produced the highest average peak areas of the butylated NS isomers. Details on how to evaluate the conditions of the injection-port can be found elsewhere [33,34]. This work employed an injection temperature of 300°C following the injector-temperature program as described in the Experimental section.

3.2. GC–MS of butylated NS isomers

Fig. 1 depicts the full-scan electron impact ionization (EI) mass spectrum of the butylated N-2-S isomer from an industrial effluent by TBA-HSO_4. The relative abundance of characteristic $[M-56]^+$ ion was determined due to the loss of a butene from the butyl ester side. The intense abundance of molecular ion of m/z 264 was also observed. NS isomers in the complex environmental samples can easily be confirmed by the ions of $[M-56]^+$ and $[M]^+$. Same mass spectrum of $[M]^+$ and $[M-56]^+$ ions was obtained for butylated N-1-S. Fig. 2 displays the extracted mass chromatograms of butylated NS isomers extracted from industrial ef-

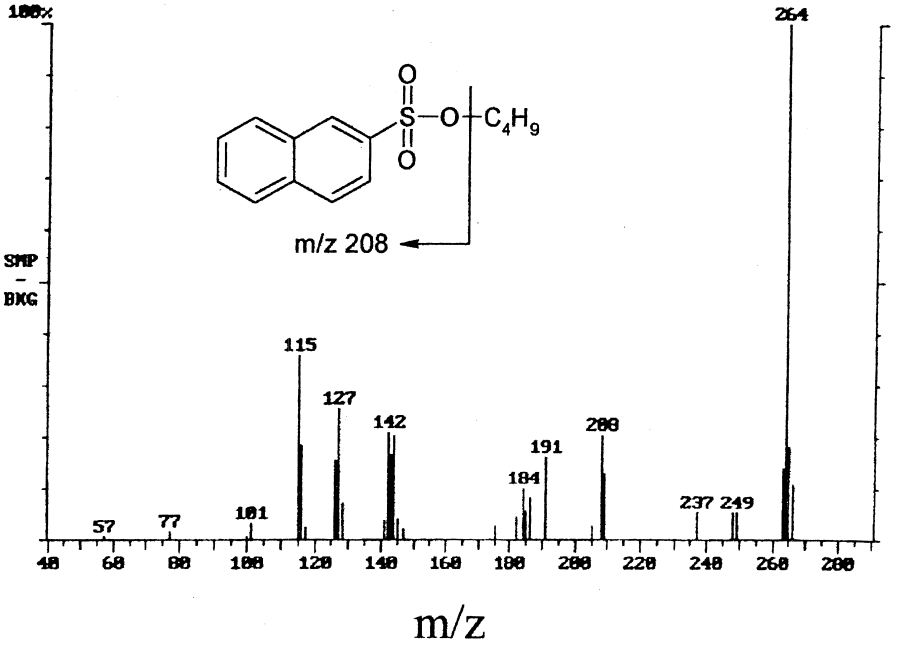

Fig. 1. Full-scan EI mass spectra of butylated N-2-S detected from an industrial effluent sample (Li-Pong).

fluent and river water samples. The NS isomers are clearly depicted by the peaks representing the intense ions at m/z 208 and 264. The procedures used herein indicate that on-line derivatization by TBA-HSO_4 reagent is an effective and robust technique of positively identifying and reliably determining NS isomers in aqueous samples.

3.3. Method validation and application to environmental samples

The detection limit of butylated NS isomers was 0.02 ng/μl, defined at a signal-to-noise ratio (S/N) ≥3. The quantitation limit (S/N≥10) was 0.05 ng/μl. The precision of the method was evaluated by determining their recoveries from the spiked samples (Table 1). Seven replicate 200-ml deionized water samples were each spiked to obtain final concentrations of 2.5 μg/l of NS isomers and C_8-LAS (surrogate). The method's reproducibility was indicated by the RSD of replicate sample preparation. Recoveries of butylated N-1-S and N-2-S in spiked deionized water samples were 93% (RSD=8%) and 89% (RSD=7%), respectively. The recovery of butylated surrogate C_8-LAS was 88% with RSD= 5%. The results were consistent with those reported in the literatures using PS–DVB as a sorbent for aromatic sulfonate extractions [5,18]. Recovery of spiked NS isomers in environmental samples was from 70 to 82% with RSD ranging from 8 to 11%. The relatively high concentrations of N-2-S were found in industrial effluents and river water samples.

In conclusion, the analytical procedure developed herein demonstrates that PS–DVB SPE and injection-port derivatization using a large-volume sample introduction device with TBA salts, is a rapid and quantitative method for the trace determination and unequivocal confirmation of NS isomers in aqueous samples. The method significantly reduces the solvent waste and simplifies the sample preparation requirements, typically associated with NS extraction and derivatization. The application of internal calibration and surrogate recovery provide high precision and quality control. The survey is currently being studied across Taiwan in order to understand the fate and influence of NS isomers in untreated wastewater directly discharged into the aquatic environment.

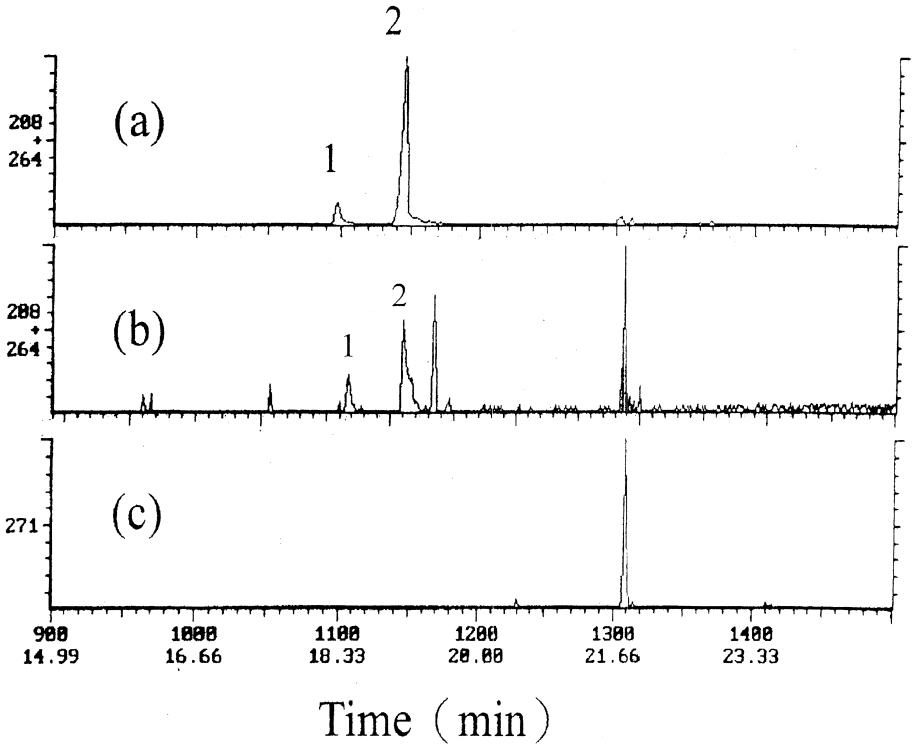

Fig. 2. The selected mass chromatograms of the butylated NS isomers isolated from (a) an industrial effluent (Li-Pong), (b) a river water sample (Dong-Kang River), and (c) the surrogate of the butylated C_8-LAS from a river water sample. Peaks: 1=N-1-S and 2=N-2-S.

Table 1
Recovery results and concentrations (μg/l) of NS isomers detected in various water samples

Sample	N-1-S	N-2-S	C_8-LAS (surr. recovery, %)
Deionized water (n=7)			
Spiked recovery (%)	93 (8%)	89 (7%)	88 (5%)
River water			
Kao-Ping River			
Background concentration	0.08	0.29	76%
Spiked recovery (%, n=3)	79 (10%)	72 (8%)	80 (9%)
Dong-Kang River			
Background concentration	0.20	0.40	99%
Spiked recovery (%, n=3)	76 (11%)	70 (9%)	82 (10%)
Industrial effluent			
Li-Pong Co.	21.1	173	70%
Hsin-Yu Co.	0.8	5.6	95%

The relative standard deviation (RSD) is given in parentheses.

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