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Impurity analysis of 1,4-dioxane in nonionic surfactants and cosmetics using headspace solid-phase microextraction coupled with gas chromatography and gas chromatography—mass spectrometry

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Abstract

1,4-Dioxane impurity in nonionic surfactants and cosmetics were analyzed using solid-phase microextraction (SPME) coupled with gas chromatography (GC) and gas chromatography—mass spectrometry (GC–MS). Experimental results show that there is no significant difference using SPME–GC and SPME–GC–MS for analysis of 1,4-dioxane in three types of nonionic surfactants at the 95% confidence level. The relative standard deviation (R.S.D.) values of each analytical method were smaller than 3%. The amount of 1,4-dioxane was found to vary from 11.6 ± 0.3 ppm to 73.5 ± 0.5 ppm in 30% of nonionic surfactants from manufacturers in Taiwan. These methods were linear over the studied range of 3–150 ppm with correlation coefficients higher than 0.995. The recoveries of 1,4-dioxane for these nonionic surfactants following SPME were all higher than $96 \pm 1\%$ (n = 3). The detection limits of 1,4-dioxane for these nonionic surfactants following SPME were from 0.06 ppm to 0.51 ppm. The experimentally determined level of 1,4-dioxane in cosmetics from manufacturers in Taiwan varied from 4.2 ± 0.1 ppm to 41.1 ± 0.6 ppm in 22% of daily used cosmetics following SPME coupled with GC and GC–MS. Conventional solvent extraction takes around 1 h for extraction and reconcentration but SPME takes only around 10 min. SPME provides better analyses of 1,4-dioxane in nonionic surfactants and cosmetics than conventional solvent extraction and head space pretreatments in term of simplicity, speed, precision, detection limit, and solvent consumption.

Keywords: Nonionic surfactants; Solid phase microextraction; 1,4-Dioxane

1. Introduction

Nonionic surfactants account for a very large percentage of worldwide surfactant use. They have been widely used in domestic and industrial detergents and related products [1–4]. Most nonionic surfactants are considered to be more effective in cleaning applications at low concentration and in removing oily soil from synthetic fabrics. Nonionic surfactants can be classified into three categories: polyethylene oxide, poly(ethylene/propylene) oxide, and polyhydric alcohol, based on their hydrophilic groups. Most of nonionic surfac-

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tant analyses were mainly focused on the active ingredients and related products [1,2]. Impurity in compounds can come from incomplete reaction of raw materials, side reactions of synthesis, or contaminations of process etc. The amount of impurities in nonionic surfactants might be low but they could have great side effects on the human and environment in applications. Therefore, impurity analysis is very important for quality control to minimize or eliminate the undesired impurities and their side effects on nonionic surfactants.

Ethylene oxide can be produced from most nonionic surfactants as an unreacted monomer for surfactants of polyethylene oxide and poly(ethylene/propylene) oxide or as one of side reaction products for surfactants of polyhydric alcohol. The combination and rearrangement of ethylene oxide could produce 1,4-dioxane. 1,4-Dioxane is a very concerned chem-

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ical in cosmetics and environment due to its potential carcinogen to human [5–7]. The analysis of 1,4-dioxane was performed using chromatography with solid-phase extraction GC and headspace GC–MS [8–12]. The 1,4-dioxane impurity in cosmetics was commonly found and deserved further attentions for consumers' health concerns [9]. The sample pretreatment time of 1,4-dioxane analysis is very long from 30 min to several hours for early methods on cosmetics. The precision of measurement and sample recovery were also low in these previous methods. Solid-phase microextraction (SPME) has become a very useful method for sample pretreatment in recent years [13–16]. SPME coupled with GC and GC–MS was used for 1,4-dioxane analysis of nonionic surfactants and cosmetics.

2. Experimental

2.1. Chemicals

The acetone, methanol, acetonitrile, 1,4-dioxane (99.94%), and tetrahydrofuran (THF) used were HPLC grade from Tedia (Fairfield, OH, USA). The sodium chloride was from Sigma (St. Louis, MO, USA). The nonionic surfactants were purchased from domestic and abroad. The nonionic surfactants of domestic part were purchased from manufacturers in Taiwan. The nonionic surfactants of imported part were from the USA and Europe. The cosmetic samples containing shampoos, liquid soaps, and dish washing detergents were obtained from local supermarkets in Taichung, Taiwan.

2.2. SPME fiber adsorption and desorption

Manual SPME holders were used with a 75 µm carboxen-poly(dimethylsiloxane) (PDMS-CAR), 85 µm poly(acrylate) (PA), and 100 µm poly(dimethylsiloxane) (PDMS) fiber assembly (Supelco, Bellefonte, PA, USA). The fibers were conditioned as recommended by the manufacturer before use. All fibers were cleaned and conditioned for 10 min at 250 °C before each new SPME experiment. A 5.0 ml sample was loaded into a 8.0 ml vial with a PTFE septum cap for sampling under room temperature at 23 ± 1 °C. Immediately after the SPME extraction, the SPME fiber was inserted into the 240 °C GC injection port and desorbed for 2 min in the splitless mode. The SPME fiber was put into vial above the sample solutions with stirring at 200 rpm during each extraction. The fiber absorption time was 2 min for most extractions and 10 min for cosmetics study. Standard addition methods were also used for 1,4-dioxane analysis in cosmetics. Standards of fixed concentrations of different volumes (0.3 ml, 0.6 ml, 0.9 ml, 1.2 ml, and 1.5 ml) were added into five flasks containing 2 ml of sample solutions in each flask, respectively. Each flask was filled with deionized water to the 10 ml mark and mixed after adding 5 ml of 20% NaCl solutions and 1 ml of 10 mg l⁻¹ THF internal standard. The 20% of NaCl

solutions were used as stock solutions to prepare various concentrations of NaCl in this study. The slopes and intercepts of the linear equations for these five flask measurements with peak area ratios of analyte standard to internal standard versus the added analyte standard concentrations were obtained for calculation of original analyte concentrations in the sample.

2.3. GC analyses

All GC analyses were carried out on a Hewlett-Packard (HP, Palo Alto, California, USA) 6890 GC system with flame ionization detection (FID) and a split/splitless injection port. An HP-1 (Agilent Technologies) column (30 m × 0.25 mm, 0.25 μ m) was used. The GC flow rates were: the column flow ($N_2 = 1$ mL/min), and the flows of the gases used with the FID system were $N_2 = 45$ ml/min, $H_2 = 45$ ml/min, air = 450 ml/min. A constant flow rate was used in the GC experiments. The split ratio was set at 1:30 after 2 min of splitless condition. The temperature programming used for nonionic surfactant samples was: initial = 40 °C (held 4 min) ramped at 10 °C/min to 100 °C (held 2 min), then ramped at 20 °C/min to 160 °C.

2.4. GC-MS analyses

All GC-MS analyses were performed on a Varian Saturn 3800 GC (Varian, Walnut Creek, CA, USA) coupled with a Varian 2000 ion trap mass spectrometer. The mass spectra library used was from the US National Institute of standards and Technology (NIST, Gaithersburg, Maryland, USA). The mass spectra were tuned with PFTBA standard before experiment. A VA-1 (Varian) column ($30 \text{ m} \times 0.25 \text{ mm}$, 0.25 µm) was used. The helium flow rate in GC-MS analysis was $1.0 \,\mathrm{ml}\,\mathrm{min}^{-1}$. The injection temperature was $240\,^{\circ}\mathrm{C}$. The column used for nonionic surfactant samples was programmed from 40 °C (held 4 min) ramped at 10 °C/min to 100 °C (held 2 min) then ramped at 20 °C/min to 160 °C for GC–MS analysis. The detector temperature was 270 °C. The full scan electron ionization mass spectra were obtained under the following conditions: mass-to-charge ratio scan range of 35-250 amu, scan time 1 s, solvent delay 2 min, manifold temperature 80 °C, emission current 10 µA, transfer line temperature 260 °C, and automatic gain control target 25 000. Characteristic ions of m/z 88 and m/z 71 were used, respectively for 1,4-dioxane and THF analysis in the mass detector. The choice of m/z 71 for THF was due to its high peak intensity. The base peak of each compound was monitored, and the specific ions were used as the confirmed ions. The quantitation of 1,4-dioxane was calculated from the sevenpoint calibration curve covering the range from $3.0 \,\mathrm{mg}\,\mathrm{l}^{-1}$ to $150 \,\mathrm{mg}\,\mathrm{l}^{-1}$, each divided by the fixed concentration of THF $(1 \text{ mg } l^{-1})$ as an internal standard. The response factors were calculated by comparing the peak area of characteristic ion chromatogram at m/z 88 to the peak area of THF. Detection limit was calculated at a signal-to-noise ratio 3:1. Calibration line of standard solutions was used for detection limit

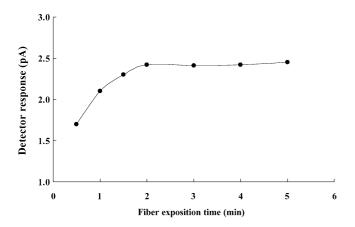


Fig. 1. Plot of fiber exposition time vs. detector response on solid-phase microextraction of 1,4-dioxane using GC with flame ionization detection.

determination. All the GC analysis was carried out using HP Chemstation software, and all the GC–MS analysis was carried out using Varian Saturn software.

3. Results and discussion

3.1. Optimization of SPME experimental conditions

Three different SPME fibers coated with 85 µm PA, 75 µm (PDMS-CAR), and 100 µm PDMS were tested with spiked 1,4-dioxane standards. The recoveries of 10 ppm and 100 ppm standards from the 100 µm PDMS fibers were at least 20% higher than the other two coated fibers; thus, they were used for all the remaining experiments. The desorption and extraction of SPME fiber need to be completed and studied before its speed consideration. Desorption time was studied from 0.5 min to 4.5 min with 0.5 min increments. The optimal fiber desorption time was determined to be 2 min based on the equilibrum approach of GC peak responses using residual test of fiber with saturated 1,4-dioxane standards. The optimal fiber extraction time was determined to be 2 min based on GC peak response areas for stirring solution of standards at 200 rpm, as shown in Fig. 1. The GC peak responses reached equilibrium as the fiber extraction time was 2 min. The optimal fiber extraction time was 2.2 min for no stirring solution. Fiber extraction with stirring solution at 200 rpm for 2 min was used for most experiments, with the exception of the cosmetics study. The salt concentration effect on SPME of 1,4-dioxane using GC is shown in Fig. 2. The amount of 1,4-dioxane extracted from SPME fibers increased linearly up to 15% of sodium chloride concentration. The salt out effect was useful to enhance 1,4-dioxane extraction on SPME fibers. However, high salt concentration would decrease the lifetime of SPME fiber coating. Therefore, sodium chloride salts with 10% (w/v) of concentration were added into the sample for 1,4-dioxane determination using SPME as a tradeoff between extraction efficiency and fiber coating life.

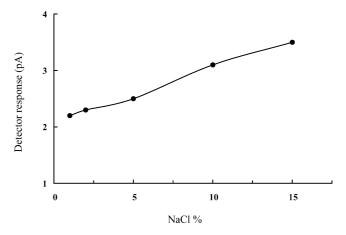


Fig. 2. Salt concentration effect on solid-phase microextraction of 1,4-dioxane using GC with flame ionization detection.

Adding organic solvent could have certain effects on SPME efficiency as shown in the SPME study. Organic solvent effect on SPME of 1,4-dioxane using GC is shown in Fig. 3. Organic solvents studied were methanol, acetonitrile, and acetone. The preconcentrated 1,4-dioxane obtained from SPME decreased around 30–40% after adding 1%, 5%, and 10% (w/v) of methanol and acetonitrile. The preconcentrated 1,4-dioxane from SPME increased slightly after adding 10% of acetone and decreased slightly after adding 5% and 10% of acetone. No organic solvent was added in the SPME study since most studied organic solvents showed a decrease GC response of 1,4-dioxane.

3.2. Determination of 1,4-dioxane from nonionic surfactants

Nonionic surfactants manufactured from domestic and abroad were studied with the 1,4-dioxane using SPME–GC and SPME–GC–MS. Nonionic surfactants studied were polyethylene oxide, poly(ethylene/propylene) oxide, and polyhydric alcohol. 1,4-Dioxane was not detected in all three types of nonionic surfactants from abroad (USA and Europe) for six samples. However, various amounts of 1,4-dioxane were detected from 30% of nonionic surfactants manufac-

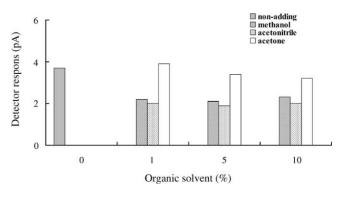


Fig. 3. Organic solvent effect on solid-phase microextraction of 1,4-dioxane using GC with flame ionization detection.

Table 1

Determined 1,4-dioxane from three types of nonionic surfactants from manufacturers in Taiwan using SPME coupled with GC and GC-MS

Type of nonionic surfactants	Extraction time (min)	1,4-Dioxane (ppm), mean \pm S.D., R.S.D. (%)	Detection limit (ppm)	Recovery (%)
Polyethylene oxide	2			
GC		$73.5 \pm 0.5 (0.6\%)$	0.51	98.8 ± 0.4
GC-MS		$72 \pm 1 (2\%)$	0.12	97.5 ± 0.8
Poly(ethylene/propylene) oxide	2			
GC		$12.3 \pm 0.1 (0.9\%)$	0.31	97.9 ± 0.6
GC-MS		$11.6 \pm 0.3 (3\%)$	0.06	96 ± 1
Polyhydric alcohol	2			
GC		$64 \pm 1 (0.6\%)$	0.49	98.8 ± 0.6
GC-MS		$65 \pm 2 (3\%)$	0.09	98 ± 1

n=3.

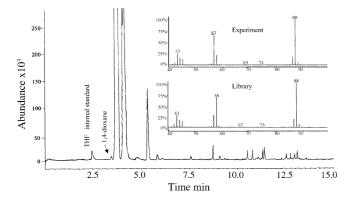


Fig. 4. Typical SPME–GC–MS chromatogram of poly(ethylene oxide) nonionic surfactant. The helium flowrate was $1.0\,\mathrm{ml\,min^{-1}}$. The temperature programming was initial = $40\,^{\circ}\mathrm{C}$ (held 4 min) ramped at $10\,^{\circ}\mathrm{C\,min^{-1}}$ to $100\,^{\circ}\mathrm{C}$ (held 2 min) then ramped at $20\,^{\circ}\mathrm{C\,min^{-1}}$ to $160\,^{\circ}\mathrm{C}$.

tured from Taiwan, as shown in Table 1. The SPME-GC and SPME-GC-MS analyses were consistent within each type of nonionic surfactants at 3% variation ranges. The correlation coefficients of calibration from SPME were all larger than or equal to 0.996. Surfactants of polyethylene oxide were detected with around 73 ppm of 1,4-dioxane, which might be from combination and rearrangement of unreacted polyethylene oxide monomers. Surfactants of polyhydric alcohol were also detected with about 64 ppm of 1,4-dioxane, which could be from polymerization of their side reaction products. Surfactants of poly(ethylene/propylene) oxide were detected with about 12 ppm of 1,4-dioxane. The recoveries of 1,4dioxane in all nonionic surfactants were all higher than 96%. A typical GC-MS chromatogram of nonionic surfactants is shown in Fig. 4. The mass spectrum of detected 1,4-dioxane was confirmed with the mass spectrum of library. The match of 1,4-dioxane mass spectra from experiment and library was reasonably good. In addition, the t_R values were also confirmed from standard addition experiments. Therefore, it is very reasonable to confirm the 1,4-dioxane identity. It is important to eliminate or minimize 1,4-dioxane impurities during or after formation of nonionic surfactants to avoid their side effects in applications for the human safety concerns.

3.3. Determination of 1,4-dioxane from cosmetics

The detection of 1,4-dioxane from cosmetics is very important for consumers' health concerns since cosmetics generally contain nonionic surfactant, and cosmetics are widely used in daily life. Cosmetics used for study were shampoo, liquid soap, and dish washing detergent. An SPME fiber extraction time of 10 min was used to insure more complete fiber absorption for cosmetics study. Nine samples of daily cosmetics and dish washing detergent were examined for 1,4dioxane using SPME-GC-MS, as shown in Table 2. Three out of nine shampoo samples were detected with 1,4-dioxane from 11.5 ppm to 44.1 ppm. Liquid soap and dish washing detergents were found at levels of 7.8 ppm and 6.5 ppm, respectively in one out of nine tested samples. These 1,4-dioxanes could be mainly come from the impurities of nonionic surfactants during synthesis. All these cosmetics deserve further attentions, since they are widely used in daily life. Table 3 shows the comparison of experimentally determined 1,4dioxane of cosmetics from manufacturers in Taiwan with those of literature. The recoveries of SPME versus those of literature using conventional pretreatments were improved from 3% to 19%. The advantages of SPME for 1,4-dioxane analysis versus SPE and head space techniques are as follows: SPME has at least three times shorter sample pretreatment time, two times better detection limit, and three times better precision. The percentages of cosmetics detected with 1,4-dioxane have gradually decreased since it was reported 10 years ago. According to the European Economic Commu-

Table 2
Experimentally determined 1,4-dioxane of daily cosmetics and dish washing detergent from manufacturers in Taiwan using SPME-GC-MS

	Shampoo	Liquid soap	Dish washing detergent
Sample number	9	9	9
Number of 1,4-dioxane detected	3	1	1
Concentration range (ppm)	11.5 ± 0.2 to 41.1 ± 0.6	7.8 ± 0.1	6.5 ± 0.1

Table 3
Comparison of experimentally determined 1,4-dioxane of cosmetics from manufacturers in Taiwan with literature

Method	Sample ^a pretreatment time (min)	1,4-dioxane (ppm)	R.S.D. (%)	Recovery (%)	Detection limit (ppm)
Experiment					_
SPME-GC	10	$0-40.1 \pm 0.6^{b}$	1.4 (n=3)	98.6 ± 0.4	0.3
SPME-GC-MS	10	$0-41 \pm 1^{b}$	3.2 (n=3)	96 ± 1	0.06
Literature					
SPE-GC [10]	30	>10	19.9	70æ80	0.5
Headspace GC-MS [9]	960	0.3æ96	9.1	92æ94	0.3

^a Conventional solvent extraction takes around 1 h for extraction and reconcentration.

nity directive on cosmetics, 1,4-dioxane must not be used in their formulations. However, 1,4-dioxane was still found in cosmetics of daily products in Taiwan. Monitoring and minimizing the quantity of 1,4-dioxane in cosmetics deserves further attentions to meet higher requirements of regulations for consumers' health concerns.

4. Conclusions

The SPME–GC and SPME–GC–MS methods both showed great promise for simple and fast 1,4-dioxane analysis in nonionic surfactants and cosmetics in comparisons of quantitative analysis factors such as recovery, precision, and detection limit. SPME reduces organic solvent consumption and environmental pollution. SPME provides better analyses of 1,4-dioxane in nonionic surfactants and cosmetics than conventional solvent extraction and head space pretreatments in term of simplicity, speed, precision, detection limit, and solvent consumption.

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^b Five out of 27 samples detected.