

# Determination of trace quaternary ammonium surfactants in water by combining solid-phase extraction with surface-assisted laser desorption/ionization mass spectrometry

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**This study demonstrates the feasibility of combining solid-phase extraction (SPE) with surface-assisted laser desorption/ionization (SALDI) mass spectrometry to determine trace quaternary ammonium surfactants in water. The trace surfactants in water were directly concentrated on the surface of activated carbon sorbent in SPE. The activated carbon sorbent was then mixed with the SALDI liquid for SALDI analysis. No SPE elution procedure was necessary. Experimental results indicate that the surfactants with longer chain alkyl groups exhibit higher sensitivities than those with shorter chain alkyl groups in SPE-SALDI analysis. The detection limit for hexadecyltrimethylammonium bromide is around 10 ppt in SPE-SALDI analysis by sampling 100 mL of aqueous solution, while that of tetradecyltrimethylammonium bromide is about 100 ppt. The detection limit for decyltrimethylammonium bromide and dodecyltrimethylammonium bromide is in the low-ppb range. Copyright © 2001 John Wiley & Sons, Ltd.**

Conventionally used as textile softeners, disinfectants, foam depressants, and antistatic agents,<sup>1</sup> quaternary ammonium surfactants are often discharged to surface waters through wastewater treatment plants. Gas chromatography (GC)<sup>2</sup> and liquid chromatography (LC)<sup>3–6</sup> are traditionally used to determine trace quaternary ammonium compounds from wastewater or sediments. These ammonium compounds with high polarities require chemical derivatization before using GC for analysis. HPLC has been used in the direct analysis of these surfactants.<sup>3–6</sup> Due to the lack of UV absorption by quaternary ammonium surfactants, electrical conductivity detection is usually used in HPLC, giving detection limits for these surfactants of around 2 to 30 ppb.<sup>4,6</sup> Electrospray mass spectrometry has also been used as a quantitation method for quaternary ammonium compounds.<sup>7</sup> These quaternary ammonium surfactants could be quantified over the range 50–300 ppb with linear correlations ( $r^2 > 0.995$ ).<sup>7</sup>

Solid-phase extraction (SPE) is an effective means of removing trace organics from aqueous solution and is often employed as a pretreatment method for extracting trace organics from a large volume sample solution. Graphitized carbons have been reported as useful SPE sorbents for extracting polar analytes.<sup>8</sup> Our previous studies developed an analytical method by combining SPE with surface-assisted laser desorption/ionization (SALDI) mass spectro-

metry in negative ion mode to determine trace nitrophenols in aqueous samples by using activated carbon as the SPE sorbent.<sup>9,10</sup> SALDI involves mixing a sample solution with a matrix consisting of a suspension of  $\mu\text{m}$ -sized carbon powder in a mixture of glycerol, sucrose and methanol, conveniently referred to as the SALDI liquid.<sup>9–12</sup> The  $\mu\text{m}$ -sized carbon powder is used as the energy absorbent, and the liquid plays a role as buffer medium.

In the present work the activated carbon was used as the adsorbent in SPE and was also a required component in the SALDI matrix system. The ability to use activated carbon in both methods enables their combination for organic analysis. An advantage of this approach is that, once the trace organics are adsorbed on the surface of activated carbon, it can be directly mixed with SALDI liquid for further SALDI analysis without elution as is usually required in conventional SPE.

The surface of activated carbon appears to interact strongly with cationic surfactants owing to the negative functional groups on its surface<sup>10</sup>. Activated carbon can thus effectively absorb the cationic surfactants in SPE, and it seemed likely that a high sensitivity could be possible when using SALDI as the ionization method. Furthermore, the SALDI matrix contributes only a few signals ( $m/z$  values) in the positive ion mode, whereas the positively charged ions from samples such as quaternary ammonium surfactants are easily observed in the SALDI mass spectra. The present work was undertaken to investigate the possibility of developing a fast, sensitive analytical method for quaternary ammonium surfactants using these principles.

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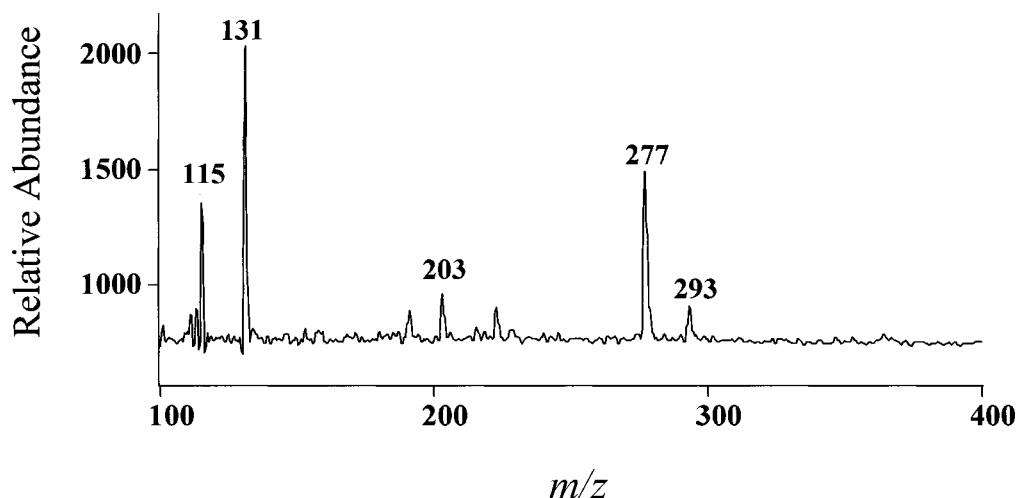


Figure 1. SPE-SALDI mass spectrum of water (pH <3).

## EXPERIMENTAL

### Reagents

Decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, glycerol, and acetic acid were obtained from Riedel-de Haën (Deisenhofen, Germany). Methanol was purchased from Mallinckrodt (Phillipsburg, NJ, USA) and sucrose from J. T. Baker (Phillipsburg, NJ, USA). Concentrated surfactant solutions were prepared in acidic water (pH <3). Acetic acid was used to adjust the pH values throughout this study. Sample solutions at various concentrations were prepared by dilution. SALDI liquid was prepared by mixing equal volumes of 15% sucrose/glycerol dissolved in methanol. The activated carbon powder (Darco G60) was purchased from Aldrich (Milwaukee, WI, USA). This mesoporous carbon exhibits a pore size distribution from 2 to 500 Å, with a mean pore radius of 33 Å, and a total surface area of 600 m<sup>2</sup>/g (dry basis)<sup>14</sup>. Microscopic examination revealed that the typical particle size was around 10 μm.

### SPE

The SPE setup used in this study has been described elsewhere<sup>8</sup>. An air pump was used rather than a syringe pump to regulate the flow rate in SPE. The setup consisted of three parts: an air pump for regulating the flow of sample solution through the SPE cartridge; a syringe for loading the sample solution; and an SPE cartridge containing the activated carbon sorbent. The cartridge was assembled using a 200-μL micropipette tip. A piece of cotton was first gently packed in the narrow end of the tip. Activated carbon powder (1mg) was then added. The cotton plugs prevented loss of activated carbon powder from the cartridge. The syringe was filled with a solution; the SPE cartridge was connected to the syringe tip; and the syringe was attached to an air pump. The SPE cartridge was first conditioned with 6 mL of methanol followed by 6 mL of acidic water (pH <3) before use. Following conditioning, SPE extraction was performed from a sample solution volume of 100 mL at a

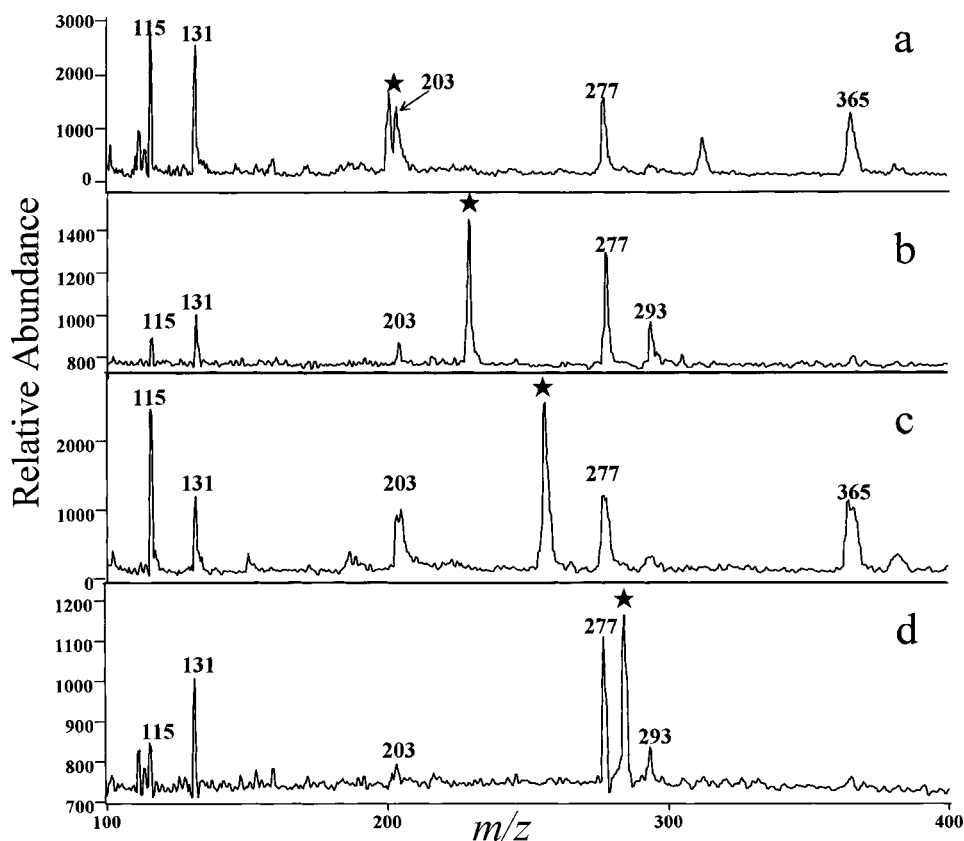
flow rate of approximately 5 mL/min. Using a lower flow rate did not improve the extraction efficiency. Acid treatment of the activated carbon was required to eliminate some chemical heterogeneity on the surface. Sample solutions were extracted under acidic conditions.

### SPE-SALDI sample preparation

The SPE cartridge was disconnected from the syringe and dried in room air following extraction. After overnight drying, the activated carbon powder was easily poured out of the cartridge. This process could be accelerated by placing the SPE cartridge in an oven at 60°C. Before placing the cartridge into the oven, a piece of cotton was cut off to eliminate most of the water adsorbed by the cotton. Eliminating the water in this way took about 2–3 h, and analytes were not lost during this treatment. However, this drying process is not recommended for analytes with high volatilities. The SALDI liquid was prepared by mixing equal volumes of 15% sucrose/glycerol dissolved in methanol. The carbon powder was mixed with the SALDI liquid at a ratio of 0.2 (w (mg)/v (μL)). About 0.3 μL of the resulting suspension was applied to the sample plate. The sample was air-dried for 5 min to allow most of the volatile methanol and water solvents to evaporate.

### Mass spectrometer

A Voyager linear time-of-flight mass spectrometer (PerSeptive, Framington, MA, USA) was employed in this work. The spectrometer was equipped with a continuous ion extraction source and a 1.2-m linear flight tube. A 3-ns pulsed 337-nm nitrogen laser was used for desorption. A horizontal sample holder could hold 100 samples simultaneously. The acceleration voltage was set at 20 kV. Since glycerol (significant volatility) was used as one of the components of the SALDI liquid, no more than three samples were loaded at once due to load on the vacuum system. Thus, the requirement to maintain high vacuum in the mass spectrometer is a limitation for application of this technique to high-throughput operation. The pressure in the ion source was <2 × 10<sup>-6</sup> Torr.



**Figure 2.** SPE-SALDI mass spectra of (a) decyltrimethylammonium bromide (1 ppb), (b) dodecyltrimethylammonium bromide (1 ppb), (c) tetradecyltrimethylammonium bromide (1 ppb), and (d) hexadecyltrimethylammonium bromide (100 ppt), sampled from 100 mL of water (pH <3). The quaternary ammonium peaks are marked by an asterisk in each mass spectrum.

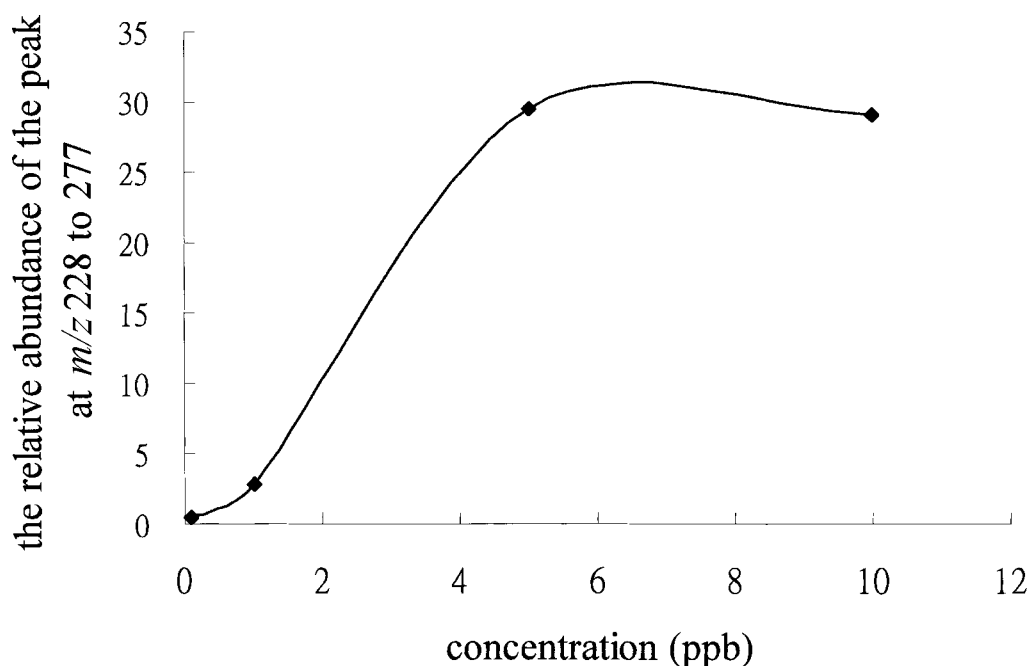
## RESULTS AND DISCUSSION

Figure 1 shows the SPE-SALDI mass spectrum of acidic water (100 mL) without any spiked analytes. The peaks at  $m/z$  115 and 131 correspond to the sodium and potassium adducts of glycerol. The peaks at  $m/z$  277 and 293 are associated with the sodium and potassium adducts of a sucrose fragment, while the peak at  $m/z$  365 is the sodium adduct of sucrose. Since glycerol and sucrose are two of the required components in this SALDI matrix system, the consistent appearance of these peaks in the SALDI mass spectra was not surprising. The other ions in Fig. 1 may arise from the surface of the activated carbon.

The background interference in the positive ion mode is much lower than that in the negative ion mode<sup>9</sup>. Accordingly, analytes with strong cationic characteristics can be observed in the positive SPE-SALDI mass spectra. Figure 2 shows the SPE-SALDI mass spectra of decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide, each spiked in 100 mL of water at levels of 1 ppb (100 ppt for the last-named compound) and extracted from 100 mL of solution. Each surfactant cation peak (i.e. no bromide) is marked by an asterisk in each mass spectrum. The other prominent ions at  $m/z$  115, 131, 203, 277 and 293 are from the matrix

background. Hexadecyltrimethylammonium bromide has the highest response among these four surfactants in SPE-SALDI analysis. The detection limit for hexadecyltrimethylammonium bromide was determined to be about 10 ppt, and around 100 ppt for tetradecyltrimethylammonium bromide and dodecyltrimethylammonium bromide, based on the definition of a signal-to-noise ratio greater than 3. However, the detection limits for decyltrimethylammonium bromide are about 1 ppb. These results are consistent with those of our previous study, which demonstrated that surfactants with longer chain alkyl groups show higher response in SALDI analysis.<sup>13</sup> Due to these low detection limits, the present hyphenated method is suitable for applications in trace analysis for screening purposes. In some cases, such as hexadecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and dodecyltrimethylammonium bromide, the detection limits were appreciably lower than those demonstrated previously.<sup>4,6</sup>

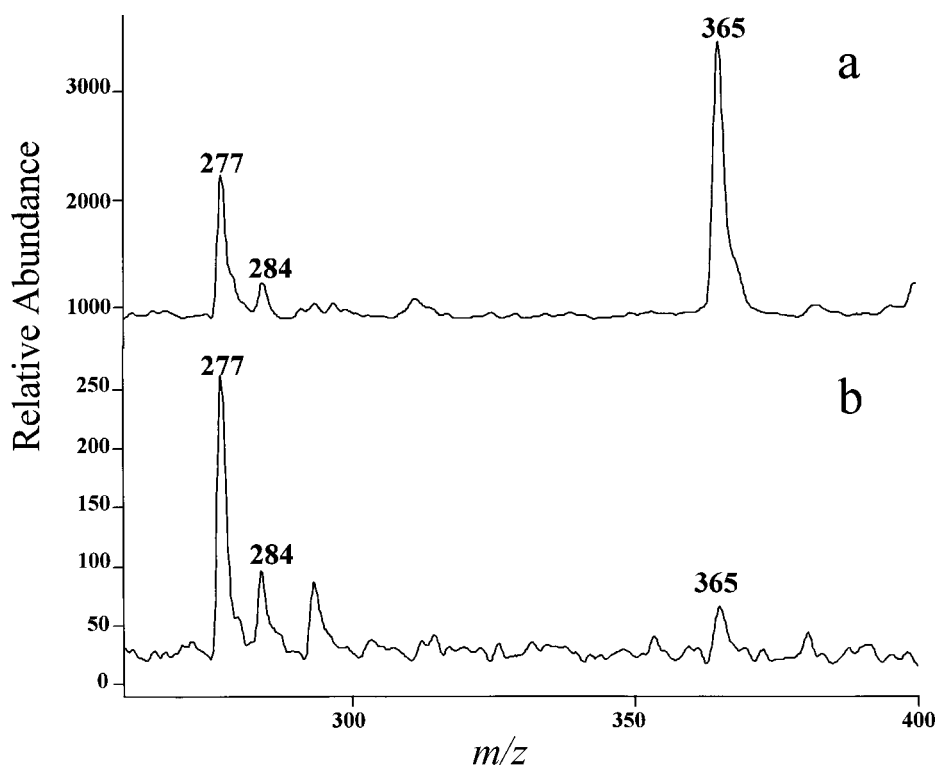
In SALDI, the intensities of analyte ion signals are roughly proportional to the concentrations of the analytes in the SALDI liquid. The analyte signals obtained in SPE-SALDI analysis possess a similar property. Figure 3 shows the intensity of the dodecyltrimethylammonium ion peak ( $m/z$  228) relative to that of the peak at  $m/z$  277 (sodiated sucrose fragment) versus the concentration of dodecyltrimethylammonium bromide in the 100 mL of aqueous solution



**Figure 3.** Ratio of the intensity of the dodecyltrimethylammonium peak at  $m/z$  228 to that of the peak at  $m/z$  277 in the SPE-SALDI mass spectra versus the concentrations of dodecyltrimethylammonium bromide in 100 mL of aqueous solution. The points correspond to averages resulting from two independent experiments, each of which sampled five different irradiated spots on the sample surface.

extracted in the SPE step. The ion corresponding to sodiated sucrose was not chosen for internal control (reference peak) because the ion was not consistently observed in each SPE-

SALDI mass spectrum. The absolute signal intensities did vary from spot to spot irradiated by the laser. The points in Fig. 3 are averaged over three sets of experiments in which



**Figure 4.** (a) SALDI mass spectrum of hexadecyltrimethylammonium bromide (0.25  $\mu$ L, 100 ppb) and (b) SPE-SALDI mass spectrum of hexadecyltrimethylammonium bromide (10 ppt, 100 mL).

identical concentrations were used. Each set of experimental values was obtained by averaging the relative ratios from five different sample spots in each experiment. The result shows that the linear range is around 100 ppt to 5 ppb ( $r^2 > 0.989$ ) since a saturation point was achieved when the concentration was over 5 ppb. Using more activated carbon powder as the SPE adsorbent may extend the linear range since the relative intensity of  $m/z$  228 to 277 did not change much when a higher concentration (10 ppb) of sample solution was used. This result indicates that the surface of 1 mg of activated carbon powder was saturated by dodecyltrimethylammonium bromide at 5 ppb in 100 mL of solution.

To estimate the efficiency of 1 mg of activated carbon in extracting trace concentrations of hexadecyltrimethylammonium bromide (10 ppt) from a large volume of aqueous solution (100 mL), the following experiments were performed: 25 mg of activated carbon powder has a volume of about 0.1 mL, estimated by measuring in a graduated Eppendorff polypropylene microcentrifuge tube (1.5 mL). Therefore, 0.3  $\mu$ L of SALDI suspension was estimated to contain 0.1  $\mu$ L (or 0.025 mg) of activated carbon. A SALDI mass spectrum was recorded by mixing 0.25  $\mu$ L of hexadecyltrimethylammonium bromide (100 ppb) with 0.3  $\mu$ L of SALDI matrix (Fig. 4(a)). The capture efficiency of the activated carbon for hexadecyltrimethylammonium bromide should be essentially 100% in this case since the surfactant was directly mixed with the activated carbon and is well below the saturation level. Thus, the hexadecyltrimethylammonium bromide adsorbed on the surface of activated carbon is equal to [100 ppb  $\times$  0.25  $\mu$ L] of hexadecyltrimethylammonium bromide on 0.025 mg of activated carbon, i.e. equivalent to [1000 ppb  $\times$  1  $\mu$ L/mg] of C powder. This provided the reference sample, assuming 100% extraction efficiency under these conditions. In the SPE-SALDI experiments themselves, however, 100 mL of hexadecyltrimethylammonium bromide solution (10 ppt) were extracted by 1 mg of activated carbon powder (Fig. 4(b)). In this case [10 ppt  $\times$  100 mL] hexadecyltrimethylammonium bromide/1 mg activated carbon is equivalent to [1000 ppb  $\times$  1  $\mu$ L] hexadecyltrimethylammonium bromide/mg activated carbon, i.e. the same as that for the reference experiment. In fact the relative intensities of  $m/z$  277 to 284 in Figs 4(a) and 4(b) are indeed similar, which implies that the extraction efficiency of 1 mg of activated carbon was quite good even for trace levels (10 ppt) in a large aqueous solution (100 mL). However, when such a low concentration (ppt) level was

used, equal quality of analyte signals was not obtained from every spot on the SALDI sample since, under this condition, the analyte distribution on the surface of the activated carbon was inhomogeneous.

## CONCLUSIONS

The combination of SPE and SALDI is suitable for analyzing analytes with strong signals in the positive ion mode because of the low matrix interference in positive SPE-SALDI mass spectra. Activated carbon was employed as the SPE adsorbent since it is also part of the SALDI matrix. The application of this approach to analytes such as quaternary ammonium surfactants was demonstrated. However, activated carbon powder is not a universal adsorbent for all analytes. One possible approach is to change the polarity of activated carbon powder by modifying its surface. Another approach involves using other known adsorbents for specific analytes and combining activated carbon powder with these adsorbents following extraction. However, the feasibility of this approach requires further investigation to determine a means of effectively combining non-carbon SPE adsorbents with activated carbon powder as the laser energy absorber.

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