RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2002; **16**: 1243–1247
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/rcm.697

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Letter to the Editor

To the Editor-in-Chief
Sir,

Qualitative determination of trace quantities of nonyl phenyl polyethylene glycol ether in water based on solid-phase microextraction combined with surface-assisted laser desorption/ionization mass spectrometry

Solid-phase microextraction (SPME) is a technique used for solvent-free sample preparation, developed by Belardi and Pawliszyn in 1989.[1] It has been widely applied to the analysis of environmental, clinical, pharmaceutical, forensic, and food samples.[2] Chromatography[2–7] and mass spectrometry (MS)[8–12] are separation and detection methods that are commonly interfaced with SPME. Analytes of low polarity and high volatility, adsorbed on SPME fibers, are usually introduced into gas chromatography (GC)[2–4] or GC/MS[9,10] systems by employing thermal desorption. Also, more highly polar, less-volatile analytes, adsorbed on SPME fibers, are typically interfaced with liquid chromatography (LC)[5–9] or LC/MS systems.[12,13]

For the purpose of screening large numbers of samples, SPME can be directly combined with mass spectrometry without the need to interface with chromatographic separation. Electron impact (EI) and chemical ionization (CI) can be suitably interfaced with SPME to analyze highly thermally stable and low polarity analytes. However, many analytes are thermally labile and, therefore, they require the use of soft ionization mass spectrometric methods, such as electrospray (ESI) and matrix-assisted laser desorption/ionization (MALDI), for direct analysis without prior derivatization. A method, based on directly coupling SPME with ESI-MS, has been applied by several groups[14–16] for the rapid detection of trace organics in water.

To our knowledge, the direct interfacing of SPME with MALDI has not been reported. Moreover, the procedure for directly introducing extracted analytes from SPME fibers into solid MALDI matrices may be complicated, and interference from matrix background signals in the low mass range of MALDI spectra may limit applications of this procedure to large molecular weight analytes.

A properly designed laser irradiation technique might be ideal for desorbing analytes from the surfaces of SPME fibers. Previously, we described a new method for laser desorption, termed 'surface-assisted laser desorption/ionization' or SALDI, which can be coupled with conventional solid-phase extraction (SPE).[17,18] The matrix used in SALDI is composed of a μm-sized carbon powder and 15% sucrose/glycerol dissolved in methanol (SALDI liquid).[17,18] We proposed that the carbon powder serves as the medium to transfer the UV-laser energy into the liquid.[19] Since activated carbon was used as the sorbent in our previous SPE studies,[17] a natural extension would be to use the SPE and SALDI techniques in tandem as part of a new analytical procedure. In this method, analytes would be first adsorbed on the surface of activated carbon during SPE, and then the activated carbon powder would be mixed with the SALDI liquid. Finally, the analytes would be subjected to laser desorption and detected by mass spectrometry.

Such a protocol avoids the possibility of analyte loss during solvent evaporation. However, the drying process needed to eliminate water

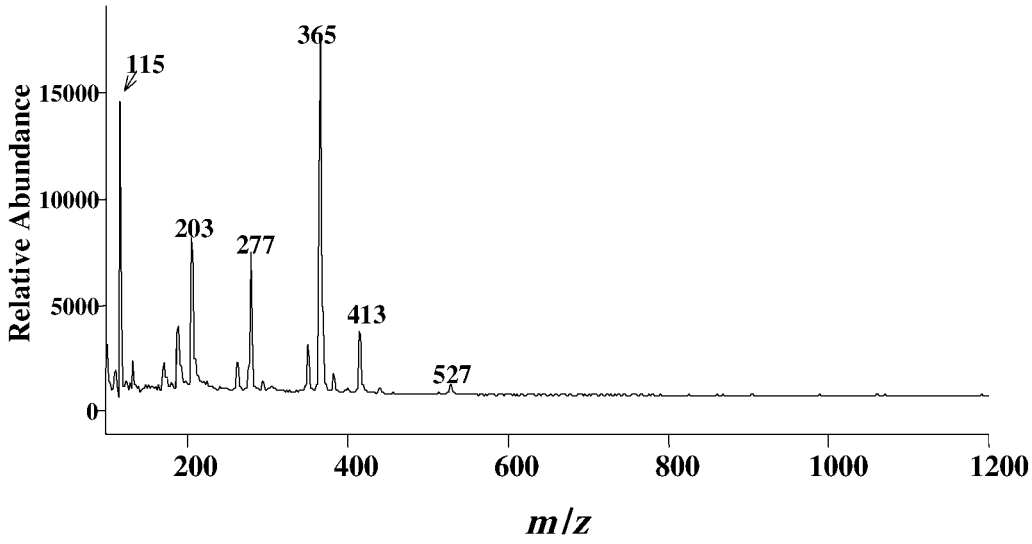

Figure 1. SPME-SALDI mass spectrum obtained in a control experiment in which a graphite fiber was immersed in a 10 mL of distilled water for 14 h.

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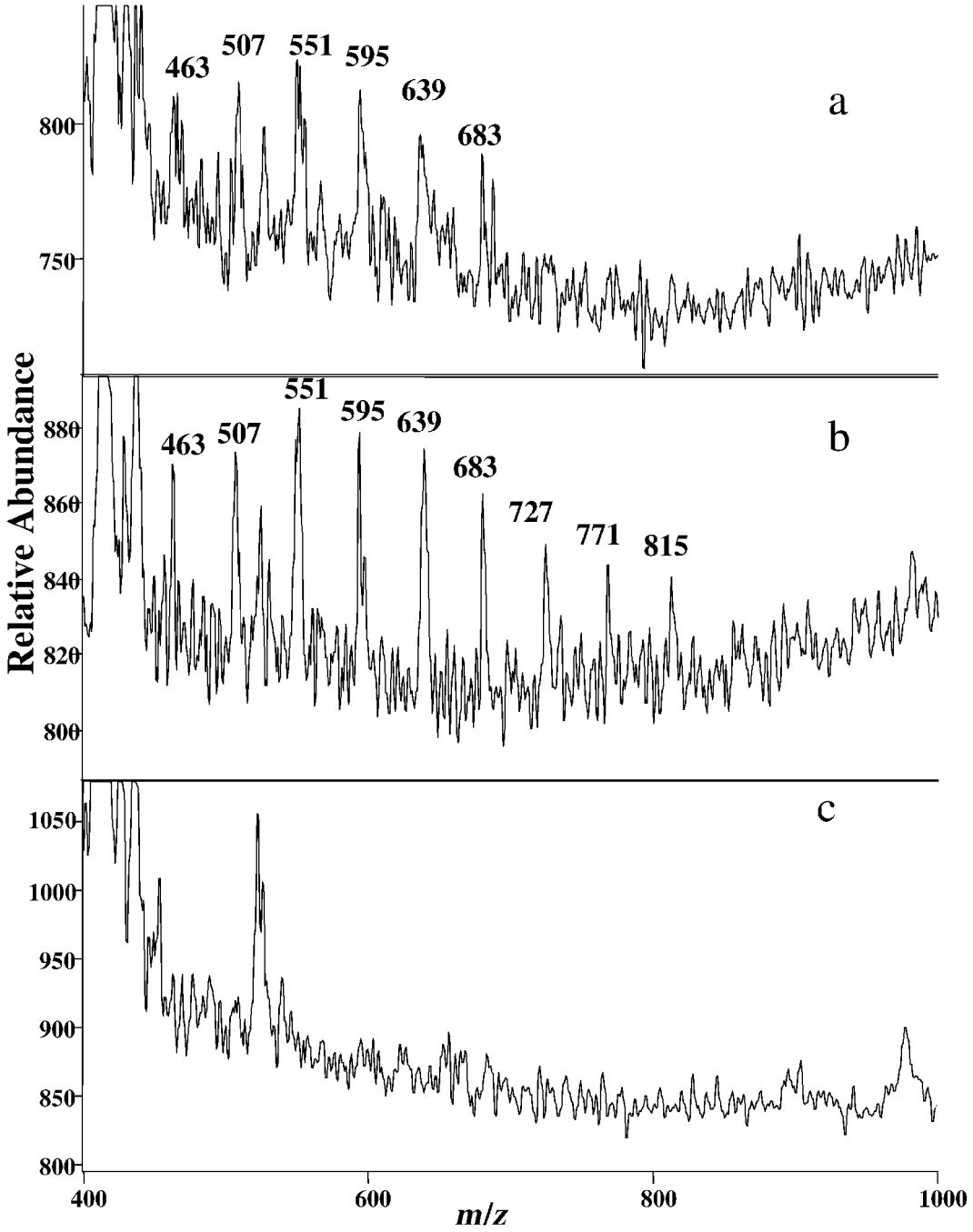

Figure 2. SPME-SALDI mass spectra of samples obtained by immersing graphite fibers in 10 mL solutions of NPPG (100 μg/L) for (a) 1 h and (b) 2 h. (c) SALDI mass spectrum of a 100 μg/L solution of NPPG obtained without preconcentration by SPME.

from activated carbon in conventional SPE-SALDI analysis is time-consuming.[17] In contrast, a practical solution to this problem is found in combining SPME with SALDI. The fact that graphite fibers are employed in SPME enables the technique to be used in direct combination with SALDI. In addition, SPME is experimentally simpler than SPE, since the latter method requires that a large volume of aqueous solution be passed through a SPE cartridge. Aranda *et al.* have used polycrystalline graphites (pencil lead) and glassy carbon as sorbents for SPME on non-ionic alkylphenol-ethoxylate surfactants, which were subsequently analyzed by coupling reverse-phase HPLC and fluorescence detection.[7] Wan *et al.* have also used pencil leads to extract pesticides.[20] These reports convincingly demonstrate that pencil leads can be employed as SPME sorbents to extract organic compounds from aqueous media.[7,20]

A new method using polycrystalline graphite as SPME fibers and SALDI-MS as the detection method is described below. Non-ionic alkylphenol-ethoxylate surfactants, such as nonyl phenyl polyethylene glycol, were used as analytes in this effort.

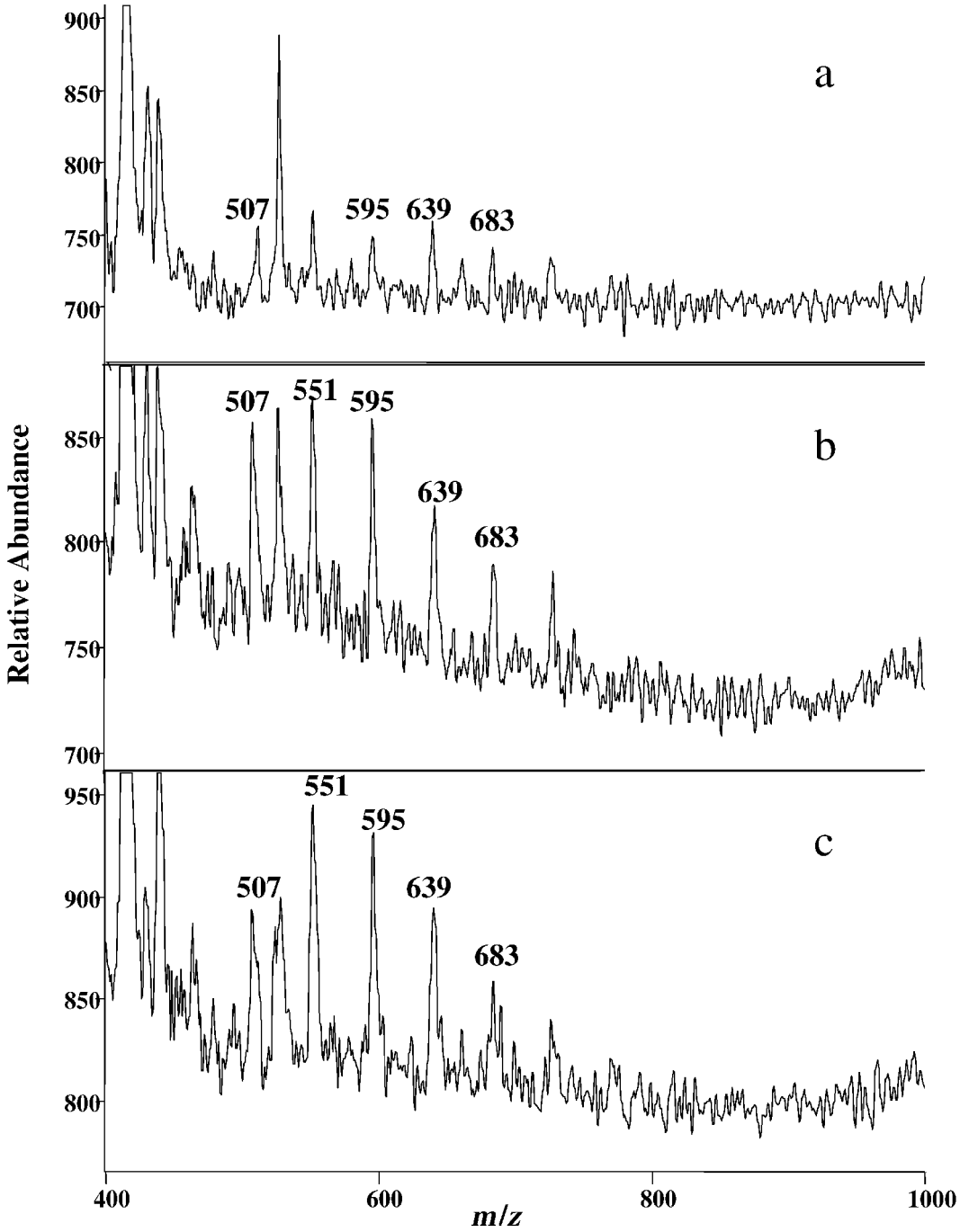

Figure 3. SPME-SALDI mass spectra obtained by immersing graphite fibers in 10 mL solutions of NPPG (10 ng/L) for (a) 1 h, (b) 2 h, and (c) 5 h.

These non-ionic surfactants are of environmental concern since their decomposition products may have estrogenic properties.[21–23] In brief, the procedure we have developed involves immersing a carbon fiber in a sample solution, removing the adsorbed analyte by scraping carbon powder from the graphite surface, mixing the powder with the SALDI liquid, and subjecting the sample to laser desorption mass spectrometric analysis.

Sucrose was purchased from J. T. Baker (Philipsburg, NJ, USA). Nonyl phenyl polyethylene glycol ether (NPPG, $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$) was purchased from Fluka (Milwaukee, WI, USA). Pencil leads (0.3×60 mm; B grade) were purchased from Pentel (Tokyo, Japan). Methanol was purchased from Mallinckrodt (Philipsburg, NJ, USA). Glycerol and acetic acid were purchased from Riedel-de Häen (Deisenhofen, Germany). Concentrated surfactant solutions (1 mg/mL) were prepared in methanol and serial dilution was used to prepare aqueous solutions of precisely and accurately known concentrations.

SPME graphite fibers (pencil leads) were conditioned in methanol for

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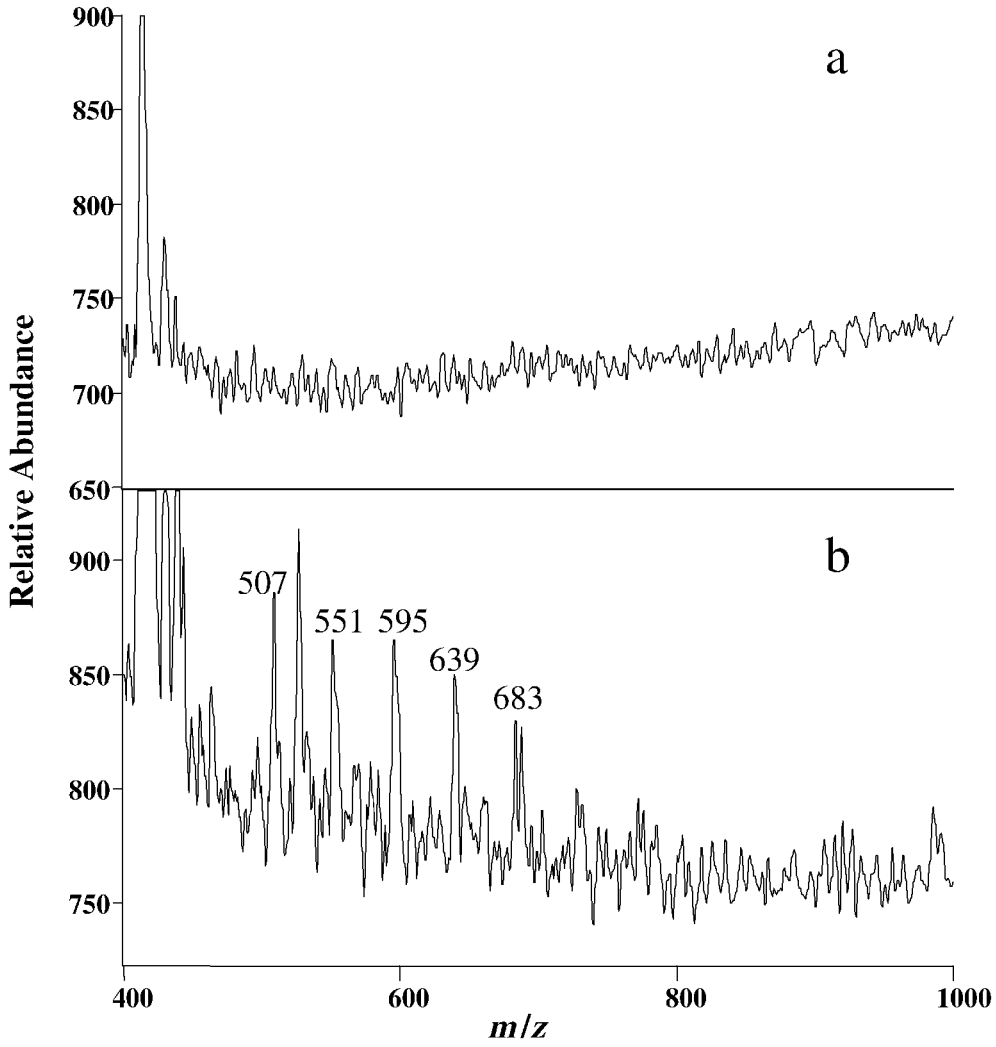

Figure 4. SPME-SALDI mass spectra obtained by immersing graphite fibers in 10 mL solutions of NPPG (100 pg/L) for (a) 5 h and (b) 14 h.

1 min and then in water (pH < 3) for 1 min before use. Sampling was performed by immersing one end of the graphite fiber (1-cm length) into a stirred solution of the analyte for a fixed time period. The graphite fiber was removed from the solution and air-dried at room temperature for 10 min. A knife was then used to scrape off only the surface of the graphite fiber. The carbon powder (~0.05 mg, based on the average value from weighing 10 samples) obtained in this manner was mixed with ca. 0.5 μL of the SALDI liquid, composed of 15% sucrose/glycerol in an equal volume of methanol. The sample was air-dried for 5 min at room temperature.

Mass spectra of the graphite powders were obtained by using a Voyager linear time-of-flight (TOF) mass spectrometer (PerSeptive Biosystems, Framingham, MA, USA). The continuous ion extraction instrument has a 1.2-m linear flight tube, and a 3-ns pulsed 337 nm nitrogen laser is used for desorption. The laser energy used in these analyses was ca. 10% higher than that typically used in performing MALDI analysis. The acceleration voltage was set to 20 kV.

Figure 1 shows the SPME-SALDI mass spectrum obtained for a control sample, in which the SPME fiber was immersed in 10 mL of distilled water for ca. 14 h. The matrix background ions, derived from sucrose and glycerol, appear in the spectrum below *m/z* 400. The peak at *m/z* 115 corresponds to the sodiated ion of glycerol, those at *m/z* 203 and 277 to the sodiated ions of sucrose fragments, and that at *m/z* 365 to the sodium adduct of sucrose. The rest of the peaks observed in this spectrum (e.g., *m/z* 413 and 527) are attributed to the graphite fiber. Nevertheless, an almost clear window exists in this spectrum between *m/z* 400 and 1000 and, as a result, analytes with molecular weights in this mass range are easily observed.

Figure 2(a) shows the SPME-SALDI mass spectrum obtained by sampling a 10 mL aqueous solution of NPPG (100 μg/L) for 1 h. The series of peaks separated by 44 mass units at *m/z* 463, 507, 551, 595, 639, and 683 correspond to the sodiated ions of NPPG. The mass spectrum (Fig. 2(b)) of NPPG (100 μg/L) obtained by sampling 10 mL of aqueous solution for 2 h also

contains this series of peaks along with ions at *m/z* 727, 771, 815, and 859 which all correspond to sodiated ions of NPPG oligomers. Importantly, no signals for NPPG are observed in the SALDI mass spectrum (Fig. 2(c)) of NPPG (100 μg/L) obtained without SPME pretreatment. These results demonstrate that the technique, which uses graphite fibers as sorbents in SPME and of SALDI for analysis, can be employed to detect trace quantities of NPPG in aqueous solutions.

However, for this technique to be useful for rapidly screening a large number of samples, its detection limit must be low. Figures 3(a), 3(b) and 3(c) display mass spectra for samples obtained by immersing graphite fibers in solutions (10 mL of 10 ng/L) of NPPG for 1, 2, and 5 h, respectively. These spectra show that exposing the graphite fiber to the solution for >2 h leads to sufficiently strong mass spectrometric signals for NPPG. After immersing the graphite fiber for 5 h, the absolute intensities of the NPPG signals remained essentially unchanged, indicating that equilibrium between dissolved and absorbed analyte has been achieved. Of course, longer extraction times are required for lower concentrations of analytes. For example, no NPPG signals are observed in the SPME-SALDI mass spectrum (Fig. 4(a)) of a sample obtained by immersing a graphite fiber in 10 mL of a NPPG (100 pg/L) solution for 5 h. However, when an immersion time of ca. 14 h was used, NPPG signals could be detected in the mass spectrum of the sample (Fig. 4(b)). Finally, no NPPG signals are observed in the SPME-SALDI mass spectrum when lower concentrations of NPPG solution (e.g., 10 pg/L) are used even if immersion of the graphite fiber is carried out for long time periods (e.g., 14 h). Thus, we conclude that the detection limit of the new SPME-SALDI method for alkylphenoyl-ethoxylate surfactants is comparable to that (500 ng/L) obtained by using previously developed techniques, such as interfacing SPME with HPLC for the analysis of alkylphenoyl-ethoxylate surfactants.[7,9]

It is worth noting that the scraping procedure used in this method plays a significant role in determining the detection limit for an analyte. Since only trace quantities of analyte molecules are adsorbed, on only the surface of the graphite fiber, scraping below the surface results in dilution of the analyte in the powder and thus in weaker mass spectrometric signals.

In summary, a new, simple and cost-effective technique, based on the combined use of SPME and SALDI, has been developed for analysis of alkylphenoyl-ethoxylate surfactants in water. A low nanogram per liter detection limit has been demonstrated for analysis of nonyl phenyl polyethylene glycol ether by using this method. In addition, this study has shown that two preexisting analytical methods, SPME and SALDI, can be combined to generate a procedure for rapid analysis of analytes without the need for additional instrumentation design.

However, a standardized procedure for scraping the surface of the graphite fiber is required in order to apply this technique to high-throughput uses. Finally, the new method has potential versatility since pencil leads show high affinities toward non-ionic surfactants in general. We are currently searching for proper procedures to modify the surface of pencil leads in order to improve and tailor the extraction efficiencies for analytes that have variable polarities. Additional investigations, aimed at developing further applications of the SPME-SALDI method, are currently underway.

Acknowledgements

The authors would like to thank the National Science Council of Taiwan for their financial support of this work.

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Received 13 February 2002
Revised 16 April 2002
Accepted 17 April 2002