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Letter to the Editor

To the Editor-in-Chief
Sir,

Fiber introduction mass spectrometry: coupling solid-phase microextraction with sol-gel-assisted laser desorption/ionization time-of-flight mass spectrometry

Solid-phase microextraction (SPME) has been widely used in various fields and combined with different analytical methods owing to its ease of use for extraction. Chromatography and mass spectrometry are the common analysis techniques that have been combined with SPME.^{1–11} Previously, we demonstrated a method¹² for coupling SPME with laser desorption mass spectrometry, namely, surface-assisted laser desorption/ionization (SALDI) mass spectrometry, for qualitative analysis. The matrix used in SALDI comprises a μm -sized carbon powder and 15% sucrose/glycerol dissolved in methanol (SALDI liquid).^{13,14} We proposed that the carbon powder serves as the medium for transferring the UV-laser energy into the liquid.¹⁵ This previous study used a pencil lead as the SPME fiber. After the trace organics were absorbed on the surface of graphite fibers (pencil leads), the carbon powder scratched from the surface of the graphite fiber was mixed with SALDI liquid for SALDI analysis.

Because of the low matrix interference in the low mass range, SPME-SALDI is suitable for analyzing small organics. However, the fact that some liquid is required in the SALDI matrix may prove to be a limitation in applications of SPME-SALDI to high-throughput analysis. Additionally, care must be taken in the scratching procedure to ensure that the carbon powder obtained contains the trace analytes from the graphite fiber surface. Failure to take such care can result in non-optimal results.

Meurer *et al.*¹⁶ recently proposed a method called fiber introduction mass spectrometry (FIMS), which fully inserts an SPME fiber into an electron impact (EI) source for mass spectrometric analysis. Based on the concept of FIMS, the present study proposes a method of combing SPME with laser desorption mass spectrometry by directly introducing an SPME fiber into the mass spectrometer. The trace analytes adsorbed on the fiber are detected without concerns associated with scraping the carbon fiber when the SPME fiber is fully introduced into the mass spectrometer.

Recently, we also developed a new approach to laser desorption/ionization mass spectrometry, i.e. sol-gel-assisted laser desorption/ionization (SGALDI) mass spectrometry,¹⁷ which uses an organic/inorganic hybrid film as the sample substrate to generate mass spectra free of matrix-derived interferences. Analytes are directly desorbed from a sol-gel-derived film in the SGALDI method. The sol-gel-derived film was made by incorporating 2,5-dihydroxybenzoic acid (DHB) molecules into the sol-gel structure. The sol-gel-derived DHB film can assist the laser desorption/ionization of analytes. Sol-gel-derived products and polymer/sol-gel hybrid materials have been extensively used as fiber coatings in the SPME technique.^{18–26} The present study found that the sol-gel derivative used¹⁷ for the SGALDI analysis could be used as a coating material for the SPME fiber to extract analytes with similar polarity to the fiber coating.

It should be possible to combine SGALDI-MS with SPME. This study used an optical fiber coated with a thin sol-gel-derived DHB film as the SPME fiber. Owing to the nature of sol-gel chemistry, covalent bonds between the sol-gel and the surface of the optical fiber were formed after briefly immersing the optical fiber in a sol-gel solution. The optical fiber was then used to extract trace organics with a similar polarity to the fiber coating from aqueous solutions. Following extraction, the optical fiber was inserted into the mass spectrometer for SGALDI analysis without adding extra matrix. This approach was used

to design a straightforward method of coupling SPME with SGALDI-MS. Benzo[a]pyrene was used as the analyte to demonstrate the combination of SPME and SGALDI.

The experiments were performed using a Biflex III (Bruker, Germany) linear time-of-flight mass spectrometer. The mass spectrometer was equipped with a 337 nm nitrogen laser, a 1.25 m flight, and a sample target capable of loading 384 samples simultaneously. The accelerating voltage was set to 19 kV. The sol-gel derivative was prepared by reacting 0.059 g DHB (Sigma, MO, USA) in a starting sol solution, which comprised 4.5 mL of tetraethoxysilane (TEOS; Acros, NJ, USA), 1 mL of water and 0.4 mL of hydrochloric acid (0.01 N; Merck, Darmstadt, Germany). The mixture was stirred for approximately 24 h before use. SPME optical fibers (125 μm o.d.; Hua Eng Wire & Cable Co., Ltd, Kaoshiung, Taiwan) were immersed in a solution containing H_2SO_4 (Pharmaco, Brookfield, CT, USA)/ H_2O_2 (35% w/v; Janssen, Geel, Belgium) at a ratio of 7:3 (v/v) for 3 min, and subsequently washed with methanol to remove impurities. The optical fiber was then coated with a thin layer of sol-gel DHB derivative by dipping a 2 cm length of one end of the optical fiber (6 cm in length) into a sol-gel DHB solution for 1 min. Next, the optical fiber was taken out of the solution and left at room temperature for 24 h before use. The end of the treated optical fiber was immersed in the sample solution for a predetermined time at room temperature (around 22°C). Following extraction, the whole fiber was fixed on a Parafilm membrane (American National Can, WI, USA) using a transparent tape on both ends of the fiber. The Parafilm was previously attached to a sample target using a double-sided black carbon tape (Ted Pella, CA, USA). Subsequently, the sample target was directly inserted into the mass spectrometer for SGALDI-MS analysis. The analyte signal was obtained from the region around the treated end of the fiber. Figure 1 illustrates the experimental arrangement.

Benzo[a]pyrene was dissolved in methanol (1 mg/mL), and serial

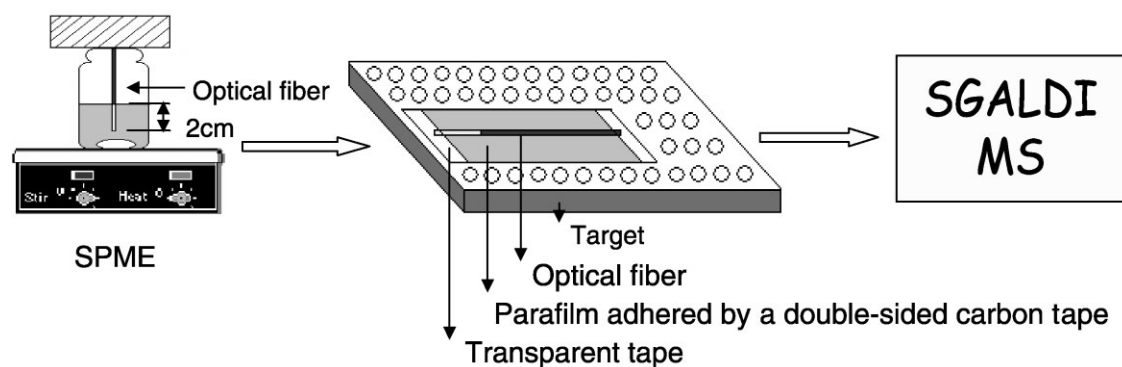


Figure 1. Schematic of the SPME-SGALDI method.

dilution was used to prepare aqueous solutions for extraction. No analyte signal was found in the SGALDI mass spectra when 0.1 μL of a sample solution containing 10 ppb benzo[*a*]pyrene (Sigma) was directly deposited on the optical fiber coating with sol-gel DHB derivative for SGALDI analysis. However, after immersing the optical fiber in 15 mL of sample solution containing 10 ppb of benzo[*a*]pyrene solution, the molecular ion of benzo[*a*]pyrene at m/z 252 appeared in the SGALDI mass spectrum (see Fig. 2(a)). The ion at m/z 39 is potassium, which is the only ion found in the background. The potassium ion is observed in the SGALDI mass spectra from time to time. In most

cases, the mass spectra contain only the molecular ions of the analyte. When the extraction time for the benzo[*a*]pyrene solution (10 ppb, 15 mL) was increased to 1 h, a more intense signal at m/z 252 was observed in the mass spectrum (see Fig. 2(b)). These results indicate the usefulness of using the sol-gel DHB derivative as both the coating on SPME fibers for extracting benzo[*a*]pyrene and as sample substrate (matrix) for SGALDI analysis.

Figure 3(a) shows the SPME-SGALDI mass spectrum of benzo[*a*]pyrene (1 ppb) extracted from 15 mL of aqueous solution for 1 h. The benzo[*a*]pyrene molecular ion remains the only ion observed in the mass spectrum. The

lowest concentration extracted from 15 mL of aqueous benzo[*a*]pyrene solution by using this approach is approximately 500 ppt (see Fig. 3(b)). Notably, in order to obtain the mass spectrum of benzo[*a*]pyrene shown in Fig. 3(b), a higher laser power than that used in Fig. 2 was required. When laser power was increased, observation of a few background ions in the low mass range became unavoidable.

This study has demonstrated the usefulness of using the sol-gel DHB derivative as both the SPME coating and the SGALDI matrix material for analyzing benzo[*a*]pyrene. Since sol-gel-derived products and polymer/sol-gel hybrid materials have been

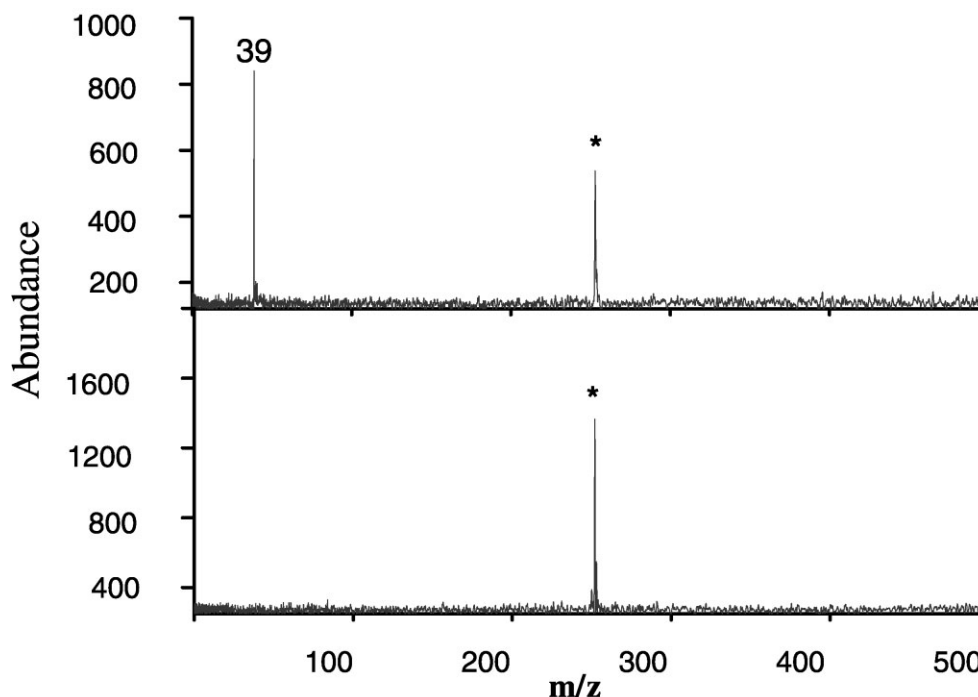


Figure 2. SPME-SGALDI mass spectra of benzo[*a*]pyrene obtained by extracting 15 mL of aqueous solution (10 ppb, 15 mL) for (a) 30 min and (b) 1 h. The molecular ion of benzo[*a*]pyrene is marked by an asterisk.

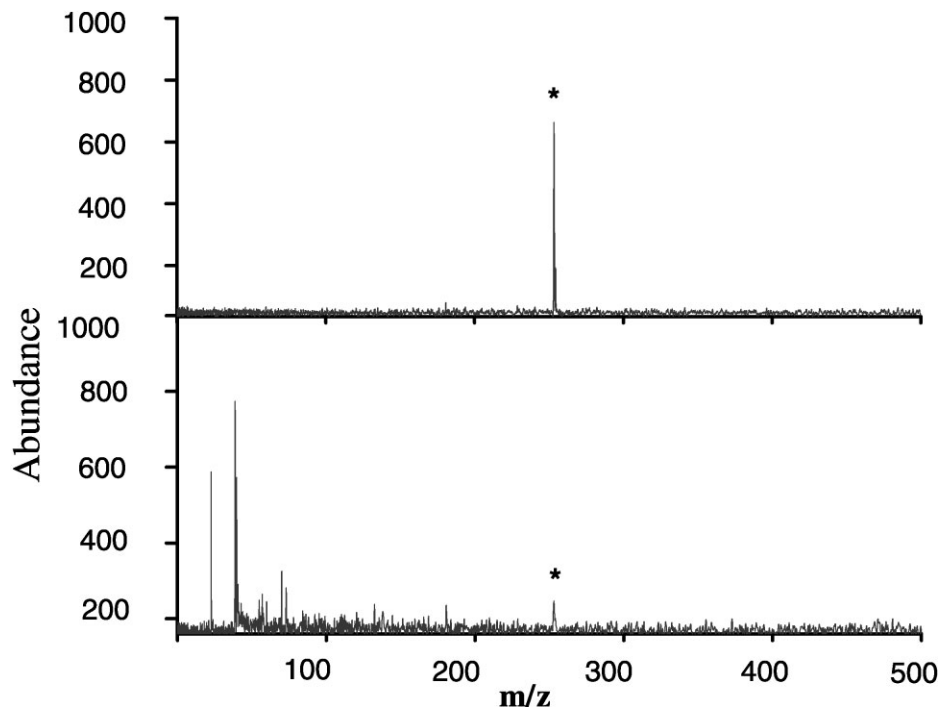


Figure 3. SPME-SGALDI mass spectra of benzo[a]pyrene obtained by extracting 15 mL of aqueous solutions of concentration (a) 1 ppb and (b) 500 ppt for 1 h. The molecular ion of benzo[a]pyrene is marked by an asterisk.

extensively used as the fiber coating in the SPME technique, it should be possible to extend the applications of SPME-SGALDI to various types of analytes by applying other suitable sol-gel materials to this combination. Consequently, further development of this combination involves designing and synthesizing more appropriate sol-gel derivatives for both the coating materials for SPME fibers and sample substrates for SGALDI analysis. Quantitation can be achieved by spiking the sample solution with an appropriate internal standard.

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