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Supporting Information

Using Solid Phase Microextraction Coupled with Reactive Carbon Fiber Ionization Mass Spectrometry for the Detection of Aflatoxin B1 from Complex Samples

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Additional Experimental Section

Reagents and materials

AFB1 was purchased from Fermentek (Jerusalem, Israel). Acetic acid, AFG1, arginine, cytochrome c, and hexylamine were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ametryn and ethanol were purchased from Riedel de Haën (Seelze, Germany). Tris(hydroxymethyl)-aminomethane (Tris), Tris hydrochloride, and nitric acid were obtained from J. T. Baker (Phillipsburg, NJ, USA). Butylamine was purchased from Alfa Aesar (Ward Chester, PA, SA), whereas acetonitrile was acquired from Merck (Darmstadt, Germany). Acetone and methanol were purchased from Echo (Miaoli, Taiwan) and Macron Fine Chemicals (Center Valley, PA, USA), respectively. Synthetic peptides were obtained from GL Biochem (Shanghai, China). Ultrapure water (18.2 Ω) was obtained from a Merck Millipore water purification system (Billerica, MA, USA). Mechanical pencil leads (types: HB, B, and 2B) were obtained from Pilot (Tokyo, Japan). Sandpapers and peanuts were purchased from local stores.

Instrumentation

All the mass spectra were obtained using a Bruker Daltonics AmaZon SL mass spectrometer (Bremen, Germany). When operating in positive ion mode, the voltage applied to the orifice of the mass spectrometer was set to −4500 V. The nebulizer was switched off during MS analysis. The temperature of the ion transfer capillary was set at 200 °C. The number of collecting ions set at the ion charge control was 70,000, whereas the maximum acquisition time was set to 100 ms. The length of the metal extension tube (inner diameter: ~1.0 mm; outer diameter: ~1.5 mm) adapted to the orifice of the mass spectrometer was ~ 4 cm. The inner diameter of the ion transfer capillary was ~0.024 inch (= ~0.061 cm), while the outer diameter of the ion transfer capillary was ~0.256 inch (= ~0.657 cm). An assembled Raman spectroscope (Protrustech, Taipei, Taiwan) equipped with a spectrometer (Andor Technology Ltd., Belfast, UK) and a continuous-wave laser (λ = 532 nm) was used to obtain Raman spectra. The total exposure time for signal acquisition was 1 s, whereas each spectrum was obtained from 10 acquisitions. A camera (SG-210X) from Sage Vision (New Taipei City, Taiwan) was used to record and take images during MS analysis. Ultraviolet-visible absorption spectra were obtained using a Varian Cary 50 UV-Vis absorption spectroscope (CA, USA).

Additional Tables

Table S1. List of the existing methods for analysis of AFB1 and related mycotoxins.

Sample pretreatment	Analytes	Sample preparing time (h)	Detection tool	Analysis time (min)	Real samples or matrix	LOD (or LOQ) of AFB1	Ref.
ELISA	AFB1, AFB2, AFG1, and AFG2	~55	HPLC	15	Peanuts, Corn, Pistachio, and Soybeans	32.02 nM	23
LLE–LTP	AFB1, AFB2, AFG1, AFG2, AFM1 and OTA	>12	HPLC/FLD	60	Breast milk	LOQ= 0.016-0.10 nM	24
ECL sensor	AFB1	~73	ECL Aptasensor	-	Peanut, Maize, and Wheat	0.12 pM	25
Versatile ECL and EC "on–off" assays	AFB1 and MTase	~35	ECL Biosensor	2.75 hr	Peanuts	0.06 pM	26
QuEChERS	AFB1	~0.5	LC-MS/MS	4.5	Pu-erh tea	1.60 nM	27
SPE	BPA, AFB1, OTA, and patulin	~1	LC/MS/MS	20	Grape juice, Apple juice, Cereal, Cereal-based baby formula, and Peanut butter	LOQ=1.6 nM	28
LLE combined with SPE	AFB1, BP and 4-Nonylphenol	~1	UPLC-MS/MS	6	Peanut oils	LOQ= 0.64 nM	29
Miniaturized SPE	AFB1 and AFM1	~0.5	UHPLC–Q/TOF-MS	8	Milk and Jujube	0.07 nM	14
SPE	AFB1-Lys	~76	LC/MS/MS	14.8	Rat serum	0.80 nM	30
MGO affinity probe	AFB1	~20	SALDI-MS	<1	Wheat extract, peanut extract, spore lysate of *A. flavus* 30112	1 nM	31
SPME	mVOCs emitted by toxigenic and non-	~4	GC-MS	~55	-	-	32

	toxigenic strains of *A. flavus*						
HLLE	AFB1	~1	HPLC-FLD	20	Rice and grain	0.01 nM	33
UHPLC-FLD	AFB1and OTA	~26	UHPLC-FLD	15	Rat plasma, liver, and kidney	6.4 nM in plasma and 25.6 nM in liver and kidney.	34
MSPE	AFB1, AFB2, AFG1and AFG2	< 15 min	HPLC-FLD	20	Vegetable oils	0.06 nM	35
SPE	AFB1	~59	HPLC	15	Moldy corn and peanut	28.82 nM in corn and 73.65 nM in peanut	36

AFB1, AFB2, AFG1, AFG2 and AFM1: Aflatoxin B1, B2, G1, G2, M1; AFB1-Lys: Aflatoxin B1-lysine adduct; BPA: Bisphenol A; EC: Electrochemical; ECL: Electrochemiluminescence; ELISA: Enzyme-linked immunosorbent assay; GC-MS: Gas chromatography–mass spectrometry; HLLE: homogeneous liquid–liquid extraction; HPLC: High performance liquid chromatography; HPLC-FLD: High performance liquid chromatography with fluorescence detector; LC-MS/MS: Liquid chromatography-tandem mass spectrometry; LLE: Liquid-liquid extraction; LLE-LTP: Liquid–liquid extraction with low temperature purification; MGO: Magnetic graphene oxide; MSPE: Magnetic solid phase extraction; MTase: Dam methylase; mVOCs: Microbial-derived volatile organic compounds; OTA: Ochratoxin A; QuEChERS: Quick, easy, cheap, effective, rugged and safe; SALDI-MS: Surface-assisted laser desorption/ionization mass spectrometry; SPE: Solid-phase extraction; SPME: solid phase microextraction; UHPLC-FLD: Ultra high performance liquid chromatography with fluorescence detector; UHPLC–Q/TOF-MS: Ultra high-performance liquid chromatography and quadrupole time-of-flight tandem mass spectrometry; UPLC-MS/MS: Ultra performance liquid chromatography-tandem mass spectrometry

Table S2. List of the existing SPME approaches for the analysis of AFB1.

SPME adsorbents	Time for preparation the adsorbents (h)	Extraction time (min)	Elution Time (min)	Volume of elution solvent	Detection tools	Analysis time (min)	LOD (nM)	Ref.
Carbon nanotube reinforced sol–gel in-fiber	~7	60	15	2 mL	HPLC-DAD	10	0.24	64
Home-made PDMS/DVB 60 μm fiber	-	30	3.5	8 mL	HPLC-PD-FD	8	0.22	65
GC capillary column (Supel-Q PLOT)	-	Total 25 min		8 mL	LC-MS	12	7.69	66
Molecularly imprinted polymer	~102	15	15	5 mL	LC-MS/MS	15	0.66	67
Molecularly imprinted polymer	~52	10	15	5 mL	UHPLC-MS/MS	15	1.34	68
Functionalized zinc oxide nanorods	~48	1	2	1 mL	HPLC-FLD	-	0.22	69
C18	-	2	-	100 μL	UHPLC-Q/TOF-MS	8	0.07	14
Poly (MAA-co-DVB) monolithics	~38	13	6	360 μL	HPLC	7	6.5	70
2B pencil lead	~5	120	< 1	10 μL	CFI-MS	< 1	1.25	This work

ACN: acetonitrile; C18: silica particles functionalized with octadecyltrimethoxysilane; CFI-MS: carbon fiber ionization-mass spectrometry; EtOH: ethanol; HPLC: high performance liquid chromatography; HPLC-DAD: high performance liquid chromatography–diode array detection; HPLC-FLD: high performance liquid chromatography with fluorescence detector; HPLC-PD-FD: high performance liquid chromatography with post-column photochemical derivatization and fluorescence detection; LC-MS: liquid chromatography–mass spectrometry; LC-MS/MS: liquid chromatography-tandem mass spectrometry; MeOH: methanol; PDMS/DVBH: polydimethylsiloxane/divinylbenzene; Poly (MAA-co-DVB): poly (methacrylic acid-co-diethenyl-benzene); Supel-Q PLOT: porous polymer-type capillary column (divinylbenzen polymer, film thickness of 17 μm); UHPLC-MS/MS: ultrahigh-performance liquid chromatography-tandem mass spectrometry; UHPLC-Q/TOF-MS: ultra-high performance liquid chromatography and quadrupole time-of-flight tandem mass spectrometry

Additional Figures

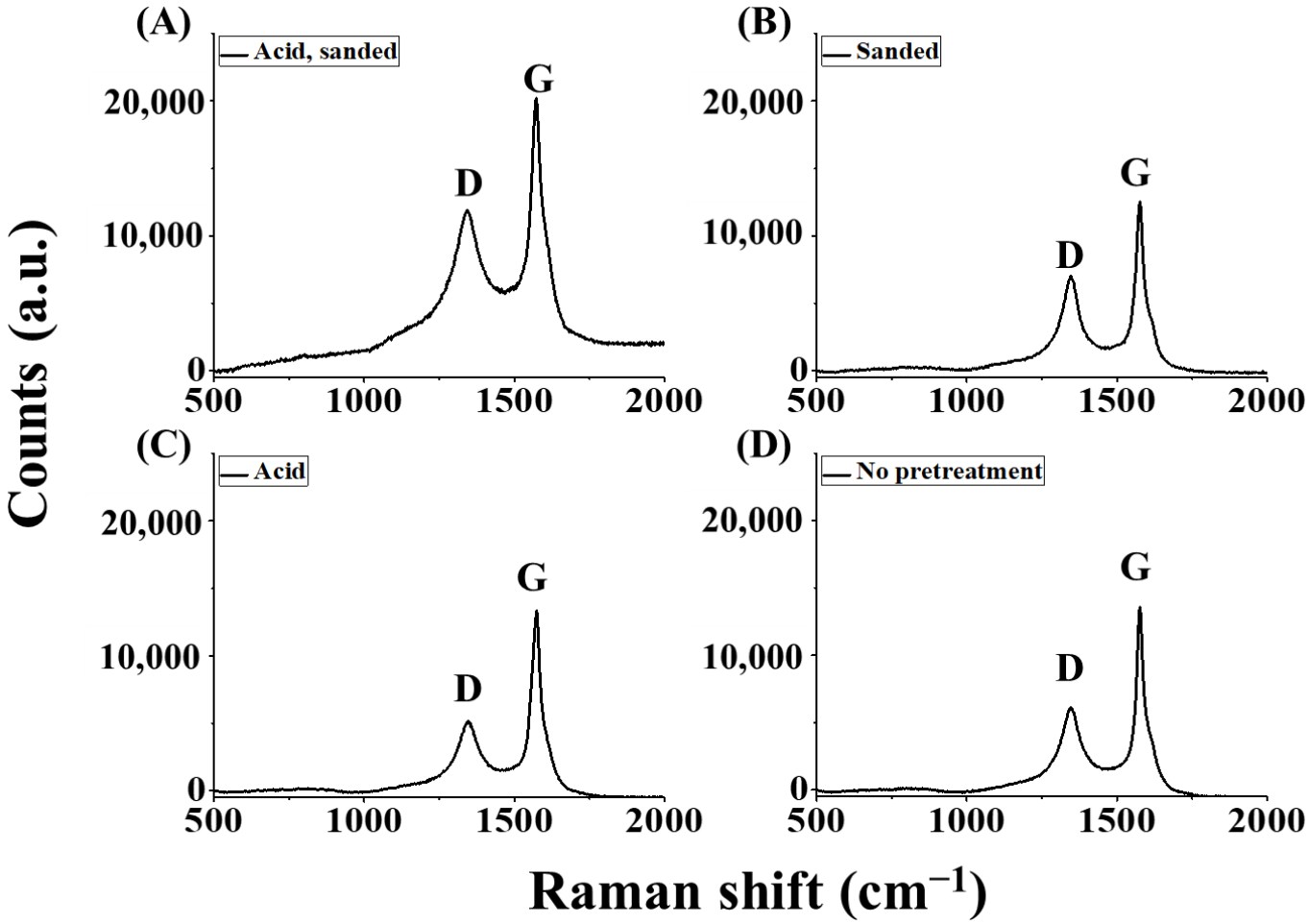

Figure S1. Raman spectra of 2B pencil leads obtained after treated by (A) sanding and subsequent acid treatment, (B) sanding treatment only, (C) soaking in acid treatment, (D) no treatment. The G band stands for the graphite structures, and the D band stands for the discorded graphite structure.

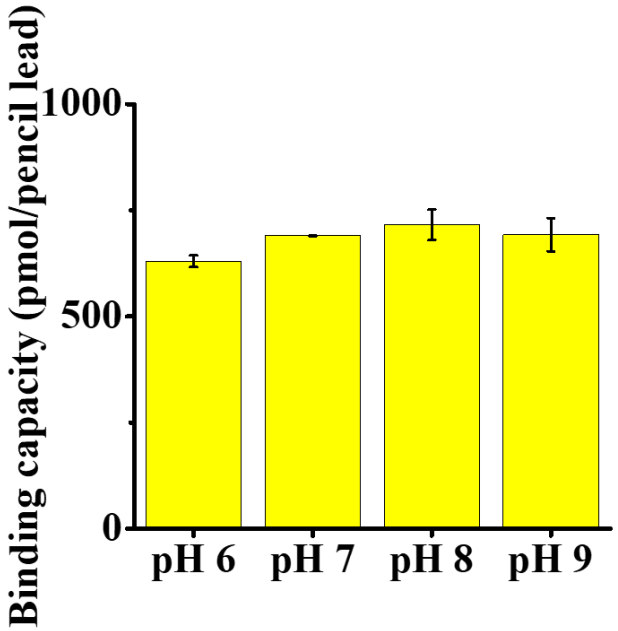

Figure S2. Examination of pH effects. Three piece of pencil leads (length: 1cm) were used to trap AFB1 from the sample (0.3 mL) containing AFB1 (10^{-5} M) at different pH conditions under vortex-mixing for 2 h. The optical density at the wavelength of 365 nm of the supernatants obtained before and after enrichment was used to determine the binding capacity. .

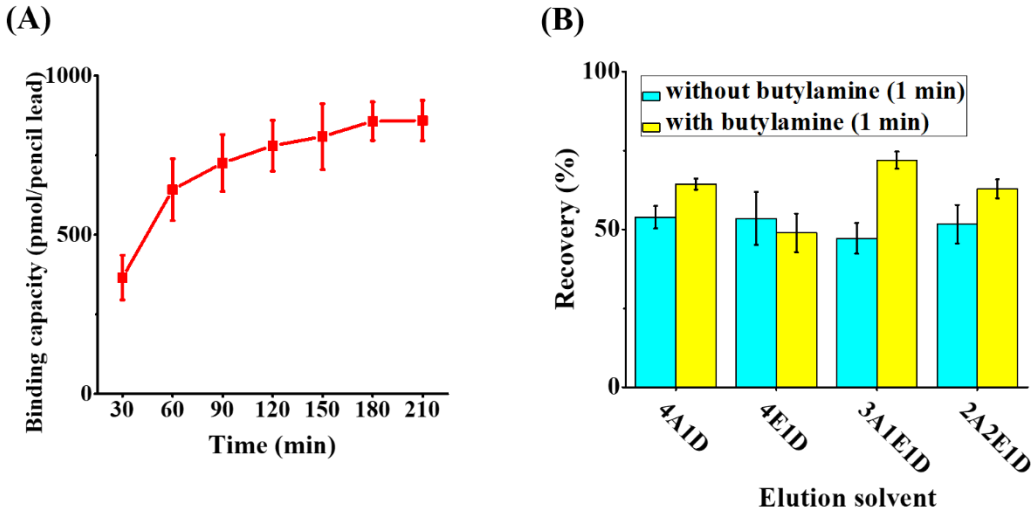

Figure S3. Examination of (A) the optimal enrichment time and (B) the recovery with different elution solvents by vortex-mixing the pencil lead adsorbed with AFB1 for 1 min. The experiments were conducted by putting three pieces of pencil leads (length: 1cm) in the sample solution (0.3 mL) containing AFB1 (10^{-5} M) under vortex-mixing for 2 h. The binding capacity was determined by examination of the optical density at 365 nm of the supernatants obtained before and after enrichment. A, D, and E stand for acetonitrile, deionized water, and ethanol, respectively. .

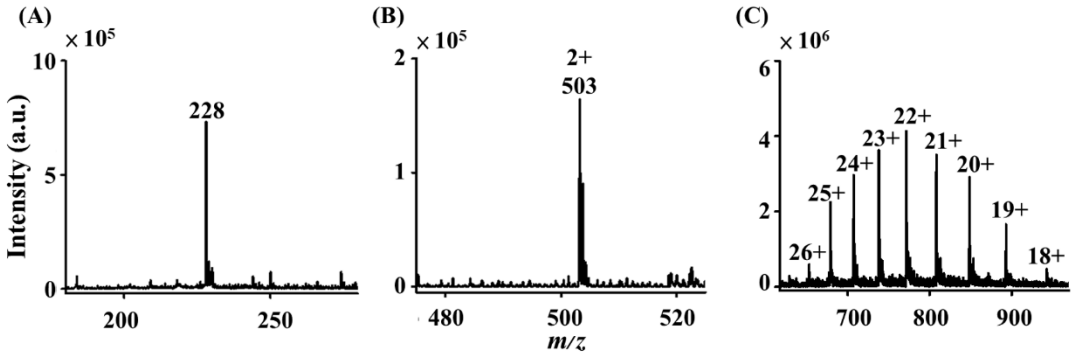

Figure S4. Analysis of standard samples using our ionization setup. Mass spectra of (A) ametryn (0.1 μM), (B) DK-10 (1 μM), and (C) myoglobin (1 μM) obtained using our setup. 10 μL of each sample were introduced to the tip of the pipette. All analytes were prepared in solvent containing deionized water and acetonitrile (1:4, v/v). 0.1% acetic acid was added to the sample containing myoglobin.