Supporting information

Just dip it: online coupling of "Dip-it" polymer monolith microextraction with plasma assisted laser desorption ionization mass spectrometry

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EXPERIMENTAL SECTION

Materials and reagents

Methacrylic acid (MAA) and ethylene dimethacrylate (EDMA) were obtained from Alfa-Aesar (MA, USA). 3-(Trimethoxysilyl) propyl methacrylate, multi-walled carbon nanotubes (MWNT with 10-20 nm diameter and 5-15 µm length), HPLCgrade acetonitrile, methanol, acetone and ammonium formate were purchased from Sigma-Aldrich (MO, USA). Analytical grade toluene. dodecanol, N.Ndimethylformamide, azobisisobutyronitrile (AIBN) and sodium chloride (NaCl) were from Sinopharm Chemical Reagent Co. (Beijing, China). Seven analytes (simazine, gesatamine, desmetryn, prometon, ametryn, propazine and prometryne) were all supplied by AccuStandard (New Haven, USA). Individual stock solution of these triazines was prepared in methanol at the concentration of 1 µg/mL and stored at 4 °C in darkness. Atrazine-d5 was bought from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and used as the internal standard. Purified water was provided by Wahaha Group (Zhejiang, China).

Instrumentation

Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 scanning electron microscope (Hitachi, Tokyo, Japan). Brunauer-Emmett-Teller (BET) surface area and mesopore size distribution of the monolithic coating were measured by nitrogen sorption experiments with the ASAP2020 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics, Norcross, USA). The through-pore properties of the monolith were determined using an Autopore IV 9500 mercury porosimeter (Micromeritics, Norcross, USA).

A DART ion source (IonSense, Saugus, MA, USA), which worked as the plasma generator, was fitted to an Agilent MSD ToF MS (Agilent Technologies, Palo Alto, CA, USA) after removing the original Agilent electrospray ionization source. Nitrogen was used as the working gas at the temperature of 400 °C. The discharge needle voltage and grid voltage were set at 6000V and 80V, respectively. The pulsed Nd:YAG laser (Lai Yin Opto-Electronics Technology, Beijing, China) was operated at 355 nm with a pulse length of 10 ns at 10 Hz. For the introduction of samples, Multi "Dip-it" holder (IonSense, Saugus, MA, USA) was positioned between the DART ion source and ToF MS. The holder was fixed on the 1D-platform, and the movement of the platform was controlled by software, so every sampler would be ionized by the DART and detected by the MS simultaneously (Fig. S1).

The mass spectrometer was operated in the positive mode and the parameters were set as follows: gas temperature, 300 °C; capillary voltage, 3.5 kV; fragmentor, 175 V; and skimmer, 65 V. The m/z scan range was from 100 to 800 with the acquisition rate of 1.02 spectra/s and the protonated molecular ions of triazines were selected as target ions. The obtained data were analyzed by MassHunter Qualitative Analysis B.02.00 (Agilent Technologies, CA, USA).

Preparation of monolith coated "Dip-it" sampler

The glass capillary of "Dip-it" sampler was activated with 1M NaOH, water and 1M HCl in sequence. After rinsing with water, it was dried under N₂ flow. Thereafter, the glass capillary was immersed in the 3-(trimethoxysilyl) propyl methacrylate / N,N-dimethylformamide solution (1/1, v/v) at 70 °C for 20 h, then washed with methanol and dried before use.

Oxidative cutting of the MWNT was performed before polymerization reaction.^{1, 2} The oxidized MWNT were then dispersed into dodecanol through sonication to get a homogeneous black solution, which was used as one of the porogenic solvents in the preparation of monolith. The pre-polymerization mixture was prepared by mixing 3.3% (w/w_{total}) MAA, 29.1% (w/w_{total}) EDMA, 7.6% (w/w_{total}) toluene, 59.6% (w/w_{total}) dodecanol containing pretreated MWNT and 0.4% (w/w_{total}) AIBN. 50 µL of the pre-polymerization mixture was moved to an Agilent CE vial with 250 µL polypropylene insert, into which the glass capillary of "Dip-it" sampler was inserted and then sealed with parafilm (Fig. S2). The reaction was performed in an oven at 70 °C for 16 h. After polymerization, the "Dip-it" sampler with monolithic coating was taken out from the CE vial, and washed with methanol to remove the residual reagents. The monolith coated "Dip-it" sampler was kept in ammonium formate solution (10mM, pH 6.0) before use.

"Dip-it" PMME-PALDI-MS method

As shown in Fig. 1, "Dip-it" PMME was performed on a magnetic stirrer by extracting 25 mL sample solution at room temperature. After a given extraction period, the "Dip-it" sampler (with monolithic coating) was washed with water, and then applied on the PALDI-MS system for online desorption and detection. The sampler was placed to the Multi "Dip-it" holder and the movement of the holder was controlled by software. When the "Dip-it" sampler was moved to the outlet of the DART ion source, the laser beam was focused on the monolithic coating exactly and impinged the monolith surface with quasicircular focal spots of approximate 250 µm. So the analytes would be desorbed from monolith by the laser beam, ionized by the

DART and detected by the MS simultaneously. After the experiment, the monolithic coating was reconstituted by immersing in acetone and shaking at 150 r/min for 20 min, the extraction device can be reused for at least twenty times with no significant change in extraction efficiency. In order to get high sensitivity, a series of operating parameters were optimized systematically, including the temperature of DART working gas, the distance between DART outlet and MS inlet, and the laser energy.

Preparation of soil sample

Soil was obtained from the garden at Peking University and was air-dried at room temperature. 2 g of powdered soil was mixed with 25 mL of ammonium formate (10 mM, pH 6) and extracted for 1 h. After centrifugation, the supernatant was collected for further analysis.

Reference

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- J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert and R. E. Smalley, *Science*, 1998, **280**, 1253-1256.

Supporting Figures



Fig. S1 Experimental setup and configuration of the online "Dip-it" PMME-PALDI-MS, illustrating that the device is composed of four parts: (i) DART ion source; (ii) ToF mass spectrometry; (iii) laser system; (iv) Multi "Dip-it" holder. (A) Full view of the device. (B) Side view.



Fig. S2 Preparation of the extraction device-"Dip-it" sampler with monolithic coating.



Fig. S3 The through-pore size distribution of poly(MAA-EDMA-MWNT) monolith.



Fig. S4 The thermogravimetric Analysis curve of poly(MAA-EDMA-MWNT) monolith.



Fig. S5 The MS signals of seven triazines obtained after poly(MAA-EDMA-MWNT) monolith microextraction (Peak A), and obtained by direct DART-MS without extraction (Peak B).



Fig. S6 The MS signals of seven triazines obtained by online "Dip-it" PMME-PALDI-MS method: (A) the distance between the DART outlet and MS inlet was 1.0 cm; (B) the distance between the DART outlet and MS inlet was 0.6 cm.



Fig. S7 The MS signals of triazines obtained by the online "Dip-it" PMME-PALDI-MS method using poly(MAA-EDMA) monolith (curve A), and poly(MAA-EDMA-MWNT) monolith (curve B). The analytes were spiked in the solution at 1 ng/mL.

Method validation and application

| Analyte | Linear range (ng/mL) | R ² | LOD (ng/mL) | LOQ (ng/mL) | Precision | |
|------------|----------------------------|----------------|----------------|----------------|---------------------------|---------------------------|
| | | | | | Intra-day RSD (%, n=4) | Inter-day RSD (%, n=4) |
| Simazine | 0.05-20 | 0.9969 | 0.015 | 0.050 | 8.34 | 10.13 |
| Gesatamine | 0.05-20 | 0.9968 | 0.013 | 0.042 | 7.79 | 12.90 |
| Desmetryn | 0.01-10 | 0.9972 | 0.002 | 0.008 | 6.88 | 6.77 |
| Prometon | 0.05-20 | 0.9957 | 0.014 | 0.046 | 5.75 | 9.58 |
| Ametryn | 0.10-20 | 0.9980 | 0.016 | 0.054 | 4.04 | 5.42 |
| Propazine | 0.10-20 | 0.9981 | 0.029 | 0.097 | 6.79 | 7.13 |
| Prometryne | 0.02-20 | 0.9997 | 0.006 | 0.020 | 4.77 | 10.76 |

 Table S1 Validation of the developed online "Dip-it" PMME-PALDI-MS method.

| | Sniked | Solid sample (n=4) | | | | |
|------------|---------|--------------------|--------------|---------|--|--|
| Triazines | (ng/mL) | Measured (ng/mL) | Recovery (%) | RSD (%) | | |
| Simazine | 0 | N.D. ^a | - | - | | |
| | 1 | 1.02 | 102 | 7.01 | | |
| | 10 | 9.88 | 98 | 12.7 | | |
| Gesatamine | 0 | N.D. ^a | - | - | | |
| | 1 | 1.04 | 104 | 7.60 | | |
| | 10 | 10.1 | 101 | 9.55 | | |
| Desmetryn | 0 | 1.30 | - | - | | |
| | 1 | 2.41 | 111 | 5.01 | | |
| | 10 | 10.43 | 91.3 | 10.7 | | |
| Prometon | 0 | N.D. ^a | - | - | | |
| | 1 | 0.887 | 88.7 | 7.35 | | |
| | 10 | 9.14 | 91.4 | 8.62 | | |
| Ametryn | 0 | N.D.ª | - | - | | |
| | 1 | 0.921 | 92.1 | 12.4 | | |
| | 10 | 8.62 | 86.2 | 9.16 | | |
| Propazine | 0 | N.D. ^a | - | - | | |
| | 1 | 1.07 | 107 | 7.09 | | |
| | 10 | 9.44 | 94.4 | 10.5 | | |
| Prometryne | 0 | 0.02 | - | - | | |
| | 1 | 1.10 | 108 | 7.99 | | |
| | 10 | 10.30 | 103 | 9.38 | | |

 Table S2 Determination of seven triazines in soil sample by the proposed method.

^a N.D. = not detected.