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Ultrasensitive Speciation Analysis of Mercury in Rice by Headspace Solid Phase Microextraction Using Porous Carbons and Gas Chromatography-Dielectric Barrier Discharge Optical Emission Spectrometry

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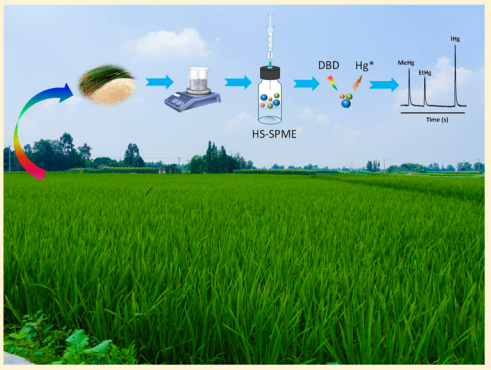
Supporting Information

ABSTRACT: Rice consumption is a primary pathway for human methylmercury (MeHg) exposure in inland mercury mining areas of Asia. In addition, the use of iodomethane, a common fumigant that significantly accelerates the methylation of mercury in soil under sunlight, could increase the MeHg exposure from rice. Conventional hyphenated techniques used for mercury speciation analysis are usually too costly for most developing countries. Consequently, there is an increased interest in the development of sensitive and inexpensive methods for the speciation of mercury in rice. In this work, gas chromatography (GC) coupled to dielectric barrier discharge optical emission spectrometry (DBD-OES) was developed for the speciation analysis of mercury in rice. Prior to GC-DBD-OES analysis, mercury species were derivatized to their volatile species with $NaBPh_4$ and preconcentrated by headspace solid phase microextraction using porous carbons. Limits of detection of 0.5 μg kg^{-1} (0.16 ng), 0.75 μg kg^{-1} (0.24 ng), and 1.0 μg kg^{-1} (0.34 ng) were obtained for Hg^{2+}, CH_3Hg^+, and $CH_3CH_2Hg^+$, respectively, with relative standard deviations (RSDs) better than 5.2% and 6.8% for one fiber or fiber-to-fiber mode, respectively. Recoveries of 90−105% were obtained for the rice samples, demonstrating the applicability of the proposed technique. Owing to the small size, low power, and low gas consumption of DBD-OES as well as efficient extraction of mercury species by porous carbons headspace solid phase micro-extraction, the proposed technique provides several advantages including compactness, cost-effectiveness, and potential to couple with miniature GC to accomplish the field speciation of mercury in rice compared to conventional hyphenated techniques.



INTRODUCTION

Mercury is one of the most hazardous and ubiquitous contaminants, and its emission to the environment has increased significantly as a result of anthropogenic activities such as mining and fossil fuel combustion.[1] Among the common mercury species, methylmercury (MeHg) is the most toxic because it is a strong neurotoxic agent with persistent and accumulative characteristics, thereby bioaccumulating to hundreds to thousands of times of its initial level in top level predators.[2−4] In general, consumption of fish and other contaminated marine products is considered as the main global pathway for human exposure to MeHg.[5−8] However, Feng et al. have recently found that the major pathway of MeHg exposure to inland people is due to the consumption of rice rather than seafood, especially for those living in Hg-contaminated areas.[9−14] Furthermore, the MeHg exposure from rice is found in many Asian countries because rice is their staple food with daily intake up to 0.5 kg (dry weight).[15−17] In addition, Yin et al. have recently found that iodomethane could significantly accelerate the methylation of mercury in soil under the sunlight.[18] Consequently, the potential threat of MeHg from rice is significantly increased when iodomethane is used as a common fumigant to control soil pests and weeds.[19] With the economic growth in developing countries, there is an urgent need to develop simple, inexpensive, accurate, and sensitive methods for the speciation of mercury in rice.

The most frequently used techniques for the speciation of mercury are hyphenated techniques, such as gas chromatography (GC) coupled to pyrolysis atomic fluorescence

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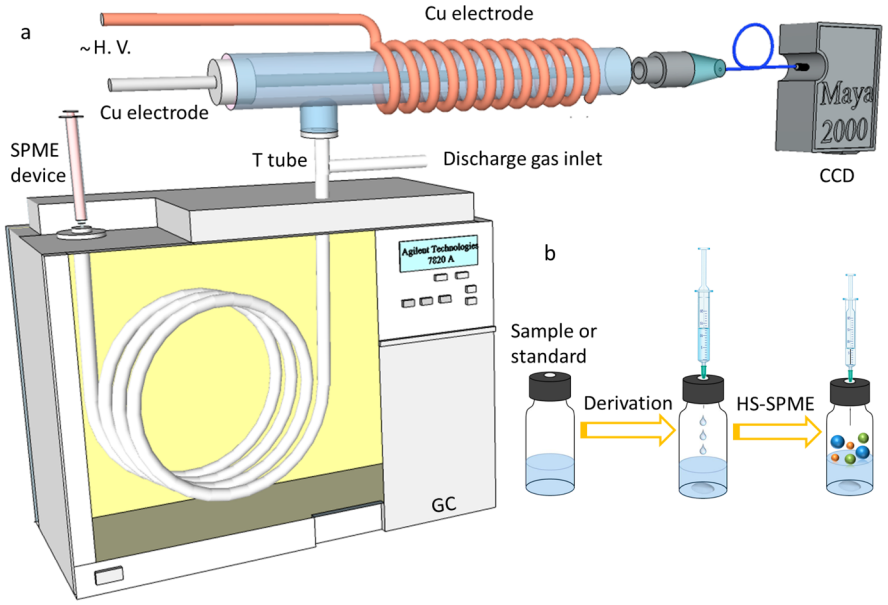

Figure 1. Schematics of the experimental setup (a) and PCs HS-SPME (b).

spectrometry (AFS), inductively coupled plasma mass spectrometry/optical emission spectrometry (ICP-MS/OES), or microwave-induced plasma optical emission spectrometry (MIP-OES).[20−25] Despite the wide use of these hyphenated techniques which exhibit advantages of ultrasensitivity and element-specific detection capability for mercury speciation, several disadvantages associated with instruments and sample pretreatment remain. In addition to its high instrument cost (usually more than $80,000 USD) and complex interface, other drawbacks associated with the current hyphenated techniques are the mercury species loss and serious memory effect/blank arising from the mercury species condensation on the intersurface of transport interface (mainly on transport tube) between GC and pyrolysis-AFS/MIP-OES/ICP-MS/OES. Although the analyte loss and blank could be mitigated by shortening the transport tube, the size of AFS/ICP-MS/OES remains an impediment to accommodate a very short transport tube. Furthermore, it is essential to derivatize non- or semivolatile mercury species into their volatile forms followed by a purge and trap preconcentration using a quartz tube packed with Tenax TA or headspace solid phase microextraction (HS-SPME) to achieve better sensitivity, low detection limits, and the alleviation of matrix and spectral interferences.[20,22,24] However, the Tenax trap cannot simultaneously treat several samples, resulting in low sample throughput. The SPME can partly solve the problems associated with Tenax trap, but the commercially available SPME fibers are expensive and cannot extract all mercury species simultaneously.

To overcome these problems, microplasma-OES/MS has been applied as an alternative to ICP/MIP-OES coupling to GC.[26] Among the microplasma detectors, dielectric barrier discharge (DBD) OES retains its unique advantages of simple setup, small size, low power consumption (5 W), low instrument cost (about $6,000 USD), high electron temperatures, and weak background radiation resulting from its low gas temperature. Recently, DBD-OES has been utilized for the determination of Hg, Cd, and Pb.[27−30] Compared to the conventional glow discharge, the depletion or erosion of the electrodes is reduced since at least one electrode of DBD is protected in dielectric medium, resulting in prolonged lifetime and better stability. Most recently, DBD-OES has been used as a simple and robust GC detector for analysis of halohydrocarbons and carbon containing compounds.[31,32] To date, GC-DBD-OES has never been utilized for elemental speciation analysis.

Recently, a simple and inexpensive method only using ethanol has been developed to prepare porous carbons (PCs) SPME fiber via DBD enhanced chemical vapor deposition (CVD).[33] The prepared PCs have hydrophilic and lipophilic groups, which is a preferable SPME fiber for absorbing analytes with a wide range of polarity. It is worth noting that the damage of the stationary phase of GC and DBD energy wasted on sample desolvation is significantly minimized due to the efficient separation of analytes from sample solution by HS-SPME, improving the sensitivity and the lifetime of GC-DBD-OES. Therefore, the analytical performance of GC-DBD-OES for mercury speciation should be significantly improved when porous carbons HS-SPME is used in the sample preparation protocol prior to the detection.

The purpose of this work was to integrate GC and DBD-OES to construct a simple, compact, robust, and inexpensive system with low power and low gas consumption for the speciation analysis of mercury in rice. Compared to the conventional hyphenated techniques,[15−18] the proposed method not only provides high sensitivities for determination of inorganic mercury (iHg), methylmercury (MeHg), and ethylmercury (EtHg) but also retains the benefits of a microplasma GC detector. Because of its small size, DBD-OES can be directly connected to the capillary of GC without using a transport tube, significantly reducing the analyte loss and the memory effect/blank. DBD-OES has the potential to be coupled with miniature GC to accomplish the field speciation analysis of mercury, attributed to its small size, low power, and low gas consumption. The proposed method was validated by analysis of several Certified Reference Materials (CRMs) and real rice samples obtained from a mercury mining region of Guizhou Province and Chengdu Plain of Sichuan Province in southwestern China, respectively.

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MATERIALS AND METHODS

Instrumentation. The GC-DBD-OES system was constructed according to our previous works,[31,32] as shown in Figure 1a. The system consists of a 7820A gas chromatography (GC, Agilent Technologies, Inc.) equipped with an HP-5 capillary column (30 m length × 0.32 mm i.d. × 0.25 μm film thickness), a miniaturized cylindrical DBD, and a commercial hand-held charge coupled device (CCD) spectrometer (Maya 2000 Pro, Ocean Optics Inc., Dunedin, FL, USA), providing 0.4 nm of spectral resolution and a detectable spectral range from 200 to 600 nm. The DBD device was made using a quartz tube (60 mm × 3 mm i.d. × 5 mm o.d.) and two copper wires (1.2 mm in diameter) as electrodes. One of the electrodes was tightly wrapped around the outer side of the quartz tube evenly, and the other was inserted into the tube. The GC capillary column was connected to the DBD device through a T quartz tube (20 mm length × 2.0 mm i.d. × 2.5 mm o.d.), conveniently introducing Ar discharge gas. It is worth noting that the DBD device can connect to GC oven in close proximity because of its small size and compactness, avoiding condensation of the analytes on the inner surfaces of the transport tube and the T tube. The DBD microplasma was generated when high voltage from a compact ac ozone generation power supply (YG. BP105P, Electronic Equipment Factory of Guangzhou Salvage, Guangzhou, China; 6 cm long × 4 cm wide × 3 cm high, with a rated output of 4 kV, 20 kHz, and 12 W at 220 V, 50 Hz input) was provided between the electrodes. In order to conveniently adjust the discharge power, a transformer (TPGC2J-1, Shanghai Pafe Electronic Equipment Ltd. Co., Shanghai, China) was used to control the ozone generation power supply. Subsequently, the characteristic atomic emission line of mercury at 253.7 nm was collected through focusing the plasma optical radiation onto the entrance slit of the CCD spectrometer, which was set about 3 mm to the observation window for alleviating the interferences from oxygen filled in the optical path.

Reagents and Materials. 1000 mg L^{-1} stock solutions of Hg^{2+} and MeHg were prepared from dissolution of mercury chloride ($HgCl_2$, 99%, Aladdin, Shanghai, China) and methylmercury chloride (CH_3HgCl, 99%, Aladdin) with methanol (HPLC grade, Aladdin), respectively. The quality control of these prepared stock solutions was verified using Hg^{2+} (GBW08617) and MeHg (GBW08675) from the National Research Center for Certified Reference Materials (Beijing, China). 76.4 mg L^{-1} stock solution of ethylmercury chloride was obtained from Putian Technology Company (Beijing, China). These stock solutions were stored in a refrigerator at 4 °C prior to use. Calibration solutions were prepared daily by diluting the stock solutions with 18.2 MΩ cm deionized water (DIW) produced by a water purification system (Chengdu Ultrapure Technology Co., Ltd., China). 1% (m/v) sodium tetraphenylborate ($NaBPh_4$, Aladdin) solution was prepared in DIW and was used to derivatize the mercury species. Ethanol and other reagents were of analytical reagent grade and were purchased from Kelong Reagent Company (Chengdu, China). A buffer solution (pH = 5) was prepared by mixing appropriate amounts of 0.2 M acetic acid and 0.2 M sodium acetate. Argon (99.99%, Qiaoyuan Gas Company, Chengdu, China) was used as both discharge gas and carrier gas in the current work. Commercial SPME fibers of 75 μm Carboxen/PDMS, 100 μm PDMS, and 65 μm PDMS/DVB were obtained from Supelco (Bellefonte, PA, USA). Stainless steel fiber used to prepare PCs-SPME fiber was obtained from the Boruike Company (Chengdu China). The preparation of PCs SPME fiber was undertaken according to the previous work[33] and described in Section 1 of the Supporting Information (SI). All the SPME fibers were conditioned in the injection port of GC at 270 °C for 1 h prior to HS-SPME.

Sample Collection and Preparation. One serious problem associated with the conventional technique for the determination of mercury is the high blank arising from the chemicals and the residual mercury on the intersurface of the transport tube and the cold vapor generator. In order to minimize the blank, 50 mL Teflon centrifuge tubes used for sample preparation and 25 mL brown glass vials used for HS-PCs-SPME were treated according to the reported method.[34] Briefly, the tubes and vials were soaked overnight in 20% (v/v) HNO_3 solution and then successively triple-rinsed with DIW and methanol. The vials and the tubes were then dried in an oven at 75 °C and double-bagged prior to use.

Certified Reference Materials (CRMs) obtained from the National Research Council Canada (NRCC) and the National Institute of Standards and Technology (NIST) were used to validate the accuracy of the proposed method, including TORT-3, DORM-4, and SRM1568b. Rice samples ($^{\#}1$–$^{\#}6$) and ($^{\#}6$–$^{\#}12$) were collected from an unpolluted district of Chengdu Plain, Sichuan Province of China and an abandoned Hg mining district of Guizhou Province of China, respectively, and were used to evaluate applicability of the developed method. All rice samples were ground to less than 150 mesh, sealed in polyethylene bags, and stored in refrigerator at 4 °C. The most used method[34,35] was followed for the sample preparation of these CRMs and rice samples. In brief, 10.0 mL of 25% (w/v) potassium hydroxide (KOH)-methanol was added to ∼1 g of CRMs or rice samples which were heated at 65 °C for 4 h in a water bath. After heating, the digest was diluted to 25 mL with methanol and stored in a refrigerator at 4 °C prior to HS-SPME. The sample blanks were processed along with the samples.

Analytical Procedure. The fiber coated PCs was mounted into a 1 mL syringe to build the homemade SPME device and subsequently conditioned in the GC injector under nitrogen at 260 °C for 3 min before HS-SPME. The analytical procedure is presented in Figure 1b. A Teflon-coated magnetic stir bar was placed in a 25 mL brown glass vial wherein a portion of 8.0 mL sample or standard solutions containing iHg, MeHg, and EtHg and 1 mL of the acetate buffer (pH = 5.0) were added. The vial was sealed with a polytetrafluoroethylene-coated silicon rubber septum. Then, 1 mL of 1% (w/v) aqueous $NaBPh_4$ solution was immediately injected through the septum. The mixture was stirred at 1500 rpm for 5 min at room temperature, and the vial was then placed in a water bath at 60 °C. The needle of the syringe was inserted into the head space through the septum to expose the PCs on the SPME fiber to the volatile mercury species for 20 min, while the mixture was stirred continuously. After extraction, the fiber was removed from the vial and immediately inserted into the GC injection port for thermal desorption at 260 °C during 2 min before GC-DBD-OES analysis.

For comparison purposes, the digests of CRMs and samples were filtered through a 0.22 μm membrane filter and diluted 1:1 with the mobile phase prior to their analysis by high performance liquid chromatography (HPLC) ICP-MS. The information about HPLC-ICP-MS and its typical operation parameters are summarized in Table S1 in Section 2 of the SI.

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RESULTS AND DISCUSSION

Feasibility of PCs HS-SPME-GC-DBD-OES for Mercury Speciation and Its Optimization. An initial experiment was performed to evaluate the feasibility of PCs HS-SPME-DBD-OES for the speciation analysis of mercury. A blank and a standard solution containing 15 μg L^{-1} of iHg, MeHg, and EtHg were tested using the constructed system. Comparison of the GC responses of mercury atomic emission at 253.7 nm from the blank and the standard solution is shown in Figure 2. The result shows that these mercury species can be completely baseline-resolved with adequate signals, confirming its feasibility for the speciation of mercury.

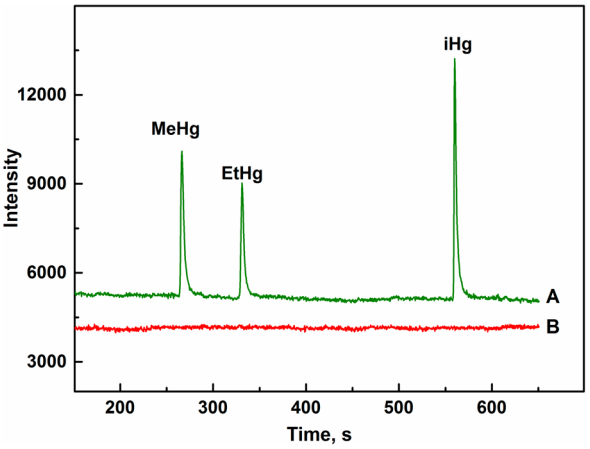

Figure 2. Typical chromatograms of PCs HS-SPME-GC-DBD-OES for a mercury standard solution containing 15 μg L^{-1} iHg, MeHg, and EtHg (a) and a blank solution (b).

To obtain the optimum analytical performance, the parameters affecting the sensitivity of the DBD-OES including the type and flow rate of discharge gas and the discharge voltage were initially optimized. According to our previous works,[30−32] argon was chosen as discharge gas due to the fact that helium is expensive and N_2 usually generates many strong emission bands around the atomic emission of mercury at 253.7 nm, resulting in serious spectral interferences on mercury measurements. In addition, the stability of analyte atomic emission excited by microplasma is usually not satisfactory and is influenced by plasma background even by use of Ar as discharge gas. Therefore, a background correction method was used to improve the stability by recording the background emission intensity at 254.0 nm simultaneously. Net emission intensity at 253.7 is derived by subtracting the background signal from the total raw intensity.

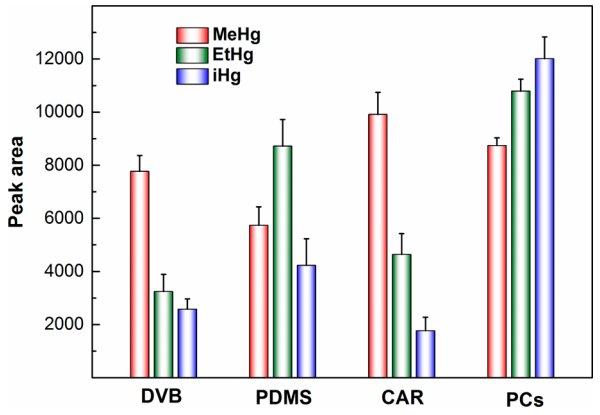

Figure 4. Comparison of extraction efficiencies of iHg, MeHg, and EtHg obtained by PCs SPME fiber and commercial SPME fiber.

The effect of discharge voltage on responses of three Hg species is shown in Figure 3a. The results indicate that the maximum response can be achieved using 225 V of discharge voltage. Lower discharge voltage cannot generate and maintain stable plasma, whereas the electrodes can be etched much faster and the responses decreased at higher voltage. Thus, discharge voltage of 225 V was selected for all subsequent experiments.

The effect of the flow rate of Ar is summarized in Figure 3b. It is evident that responses from the tested mercury species increased significantly with the flow rate of discharge gas increased from 100 to 200 mL min^{-1} and then decreased at higher flow rates. Lower Ar flow rates resulted in inefficient generation of DBD plasma and lower efficiency of analyte transport to the DBD detector; higher flow rate resulted in significant dilution of analyte in the carrier gas. A flow rate of Ar at 200 mL min^{-1} was selected for all subsequent experiments in order to achieve optimum sensitivities.

Extraction Performance of PCs HS-SPME. In order to improve the extraction efficiency of PCs HS-SPME, the extraction time, extraction temperature, and pH of sample solution as well as concentration of derivatization reagent were studied, as described in detail in Figure S1 in Section 3 of the SI. As a result, optimum conditions of 60 °C of extraction temperature, 20 min of extraction time, pH = 5 HAc-NaAc

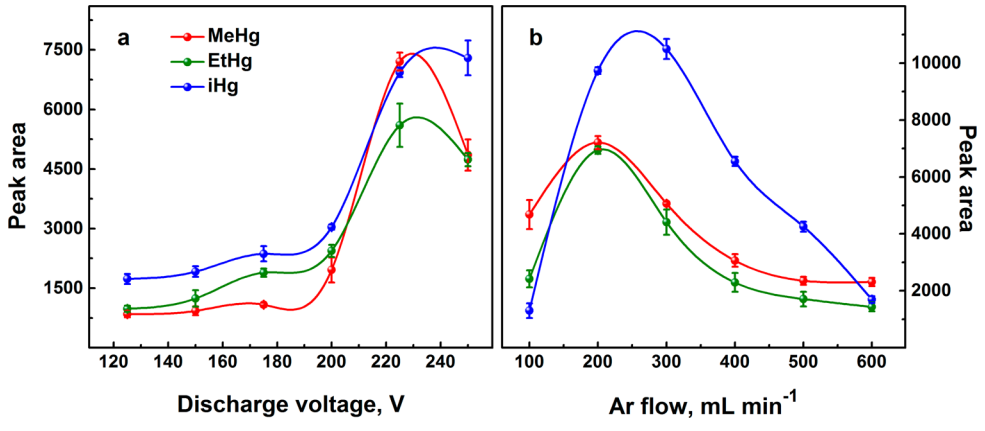

Figure 3. Optimization of GC-DBD-OES. (a) Effect of discharge voltage and (b) effect of the flow rate of discharge gas.

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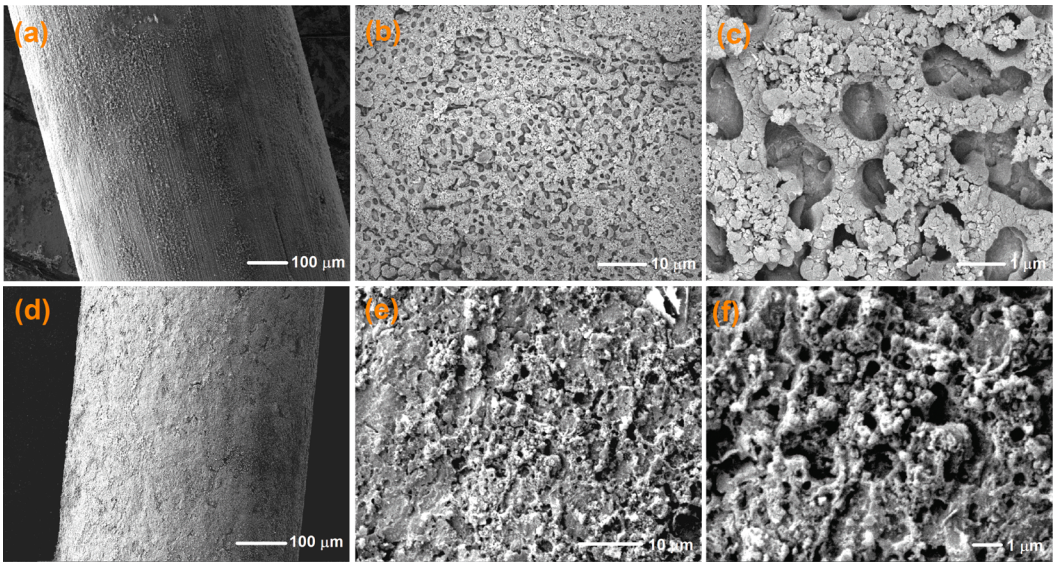

Figure 5. SEM image of the surface of the PCs SPME fiber. (a-c) before extraction and (d-f) after 200 replicate extraction cycles.

Table 1. Analytical Performance of the Proposed Method Using PCs Fiber

		linear range ($\mu g\ L^{-1}$)			limit of detection (ng)				
methods	derivation reagent	iHg	MeHg	EtHg	iHg	MeHg	EtHg	fiber/extraction time	ref
this method	$NaBPh_4$	0.5−30	0.5−50	1−100	0.16	0.24	0.34	porous carbon/20 min	
SPME-GC-ICP-MS	$NaBPr_4$				0.63×10^{-3}	0.31×10^{-3}		100 μm PDMS/5 min	36
SPME-GC-MS	$NaBEt_4$	0.025−2.5	0.025−2.5		0.07	0.15		100 μm PDMS/5 min	37
SPME-GC-AFS	$NaBEt_4$	0.1−20	0.1−100		8	5		100 μm PDMS/10 min	38
SPME-GC-AAS[a]	KBH_4		0−20[b]	0−16[b]		16	12	fused silica/1.5−2 h	39
SPME-GC-MIP-OES	$NaBPh_4$	0.1−8.0	0.2−3.0		1.71	0.24		100 μm PDMS/5−45 min	40

[a]AAS, Atomic absorption spectrometry. [b]$\mu g\ kg^{-1}$.

buffer solution, and 1.0% (w/v) of $NaBPh_4$ were selected for all subsequent experiments. To demonstrate the excellent extraction performance provided by the PCs SPME fiber, comparison of extraction efficiencies of the tested mercury species obtained by the PCs SPME fiber and commercial SPME fibers (100 μm PDMS, 65 μm PDMS-DVB and 75 μm Carboxen-PDMS fiber) were carried out, as shown in Figure 4. The results show the extraction efficiencies (peak area) of the tested mercury obtained by PDMS-DVB and Carboxen-PDMS fibers decrease in the order of MeHg > EtHg > iHg, while the PDMS fiber provides extraction efficiencies for mercury species in the order of EtHg > MeHg > iHg. These observations are probably due to the fact that the commercial PDMS-DVB and Carbonxen-PDMS fibers prefer adsorbing polar analytes. By contrast, PDMS favors the less- or no-polar analytes. Therefore, it is impossible to use one commercial SPME fiber to effectively extract all mercury species. It is noteworthy that the prepared PCs SPME fiber not only accomplishes simultaneously extraction of all three mercury species but also offers excellent extraction efficiencies for three mercury species.

To gain insight into the simultaneous and efficient adsorption of mercury by the PCs fiber, characterization of the fiber by various techniques was necessary. In previous work,[28] energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy, and Fourier Transform infrared spectroscopy were employed. Based on the results from these techniques, it was found that PCs on the surface of the fiber retained C−C and C−O groups. These residual hydrophilic and lipophilic groups on PCs not only enhance the adsorption of polar analytes on the fiber but also favor the adsorption of nonpolar analytes. Therefore, the prepared PCs fiber is a preferable SPME fiber for analyzing analytes with a wide range of polarity.

The stability and lifetime of the PCs fiber were also evaluated. Most interestingly, it was found that the PCs SPME fiber still maintained its extraction efficiency even after 200 replicate extraction cycles, which is longer than the commercial SPME fiber (about 100 times). To better understand this excellent capability of PCs on SPME, the surface morphology and chemical composition of the fiber before and after 200 replicate extraction cycles were characterized by SEM, as shown in Figure 5. The SEM images in Figure 5a, b, and c show that the synthesized PCs before extraction had a hollow morphology with an irregular structure, and the pore size distribution was in the 100 nm range. Thus, the PCs SPME fiber provides a high specific surface area and high pore volume, which result in excellent adsorption properties for mercury species. Figure 5d, e, and f shows that large amounts of PCs still remained on the surface of the fiber which result in a stable extraction capability, despite that the morphology of PCs become folded and random after 200 extraction. The fiber before and after extraction was further characterized by EDX spectrum to estimate the PCs loss after 200 replicate extraction cycles, as presented in Figure S2 in Section 4 of the SI. The

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Table 2. Analytical Results for iHg, MeHg, and EtHg Species in CRMs by GC-DBD-OES and HPLC-ICP-MS

sample	detected by this method (mg kg^{-1})			detected by HPLC-ICP-MS (mg kg^{-1})			certified (mg kg^{-1})		
	iHg	MeHg	total mercury	iHg	MeHg	total mercury	iHg	MeHg	total mercury
TORT-3	0.137 ± 0.013[a]	0.139 ± 0.011	0.276 ± 0.024	0.142 ± 0.010	0.141 ± 0.013	0.283 ± 0.023		0.137 ± 0.012	0.292 ± 0.04
DORM-4	0.069 ± 0.007	0.341 ± 0.032	0.410 ± 0.039	0.065 ± 0.005	0.348 ± 0.038	0.413 ± 0.043		0.354 ± 0.031	0.410 ± 0.12
Rice 1568b	5.53 ± 0.58[b]	n.d.	5.53 ± 0.58[b]	5.96 ± 0.67	n.d.	5.96 ± 0.67	5.91 ± 0.36[b]		5.9 ± 0.36[b]

[a]Mean ± SD, n = 3. [b]μg kg^{-1}; n.d., not detected.

results show that the PCs contents were only slightly decreased from 57.98% to 54.93%, indicating its excellent thermal stability, inconsistent with experimental results of TGA reported in the previous work,[33] which showed that the PCs were stable below 280 °C. Evidently, no significantly loss of PCs occurred at the 260 °C desorption temperature, and the extraction capability is maintained even after 200 replicate extraction cycles.

Analytical Figures of Merit. Under the optimized experimental conditions for PCs HS-SPME and operation parameters of GC-DBD-OES, the analytical figures of merit obtained using PCs HS-SPME-GC-DBD-OES were evaluated. Typical chromatograms of various concentrations of mercury species are summarized in Figure S3 in Section 5 of the SI, good linear calibration curves for iHg, MeHg, and EtHg with linear coefficients better than 0.99 were achieved. The limits of detection (LODs) and the limits of quantification (LOQs) were calculated based on the 3σ and 10σ criterion (σ, according to the signal-to-noise ratio), respectively. The LODs were 0.5 μg kg^{-1} (0.16 ng) for iHg, 0.75 μg kg^{-1} (0.24 ng) for MeHg, and 1.0 μg kg^{-1} (0.34 ng) for EtHg, whereas the LOQs were 1.6 μg kg^{-1} for iHg, 2.5 μg kg^{-1} for MeHg, and 3.5 μg kg^{-1} for EtHg, respectively. The precisions of replicate measurements expressed as a relative standard deviations (RSDs, n = 5), evaluated by replicate analysis of aqueous samples containing 15 μg L^{-1} each of the tested mercury species, varied between 3.7% and 5.2%. The fiber-to-fiber reproducibility evaluated using three PCs SPME fibers prepared using the same procedure was found to be in the range 4.2−6.8%. Table 1 summarizes figures of merit characterizing this method and comparison performance with other similar methods. The LODs obtained for the Hg species using the proposed method are inferior to those reported using SPME-GC-ICP-MS but are much better than those from inexpensive but large SPME-GC-MS/AAS/AFS/MIP-AES instruments. Most importantly, the proposed method is simple and cost-effective and has better potential for instrumental miniaturization compared to the conventional techniques.

Sample Analysis. The accuracy of the proposed method was validated by analyzing CRMs (Fish Protein, DORM-4; Lobster Hepatopancreas, TORT-3; and Rice Flour SRM 1568b), with results summarized in Table 2. The t test results confirmed that the obtained analytical results agree well with the certified values and the results obtained from HPLC-ICP-MS at the confidence level of 95%.

Since the objective of this work was to develop a simple and inexpensive method to meet the requirement from developing countries or regions for monitoring mercury species in rice. Therefore, the applicability of the proposed technique was further demonstrated by the speciation analysis of mercury in 12 rice samples. In order to evaluate the accuracy of the proposed method, mercury species and total mercury (THg) in the CRMs and the tested rice samples were measured by HPLC-ICP-MS and ICP-MS after microwave-assisted acid digestion, respectively. The microwave assisted acid digestion was briefly described in Section 6 of the SI.

The results in Table 3 and Figure 6 show both iHg and MeHg can be detected in the six samples obtained from the abandoned Hg mining district, in a range of 2.31−15.32 and 1.43−73.49 μg kg^{-1} for MeHg and iHg, respectively. On the other hand, only low concentration of iHg was found in two samples collected from the Chengdu Plain. More importantly, the obtained iHg and MeHg values agree well with those

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Table 3. Analytical Results of Mercury Species in Rice Samples Determined by PCs HS-SPME-GC-DBD-OES and HPLC-ICP-MS as well as Total Mercury Determined by ICP-MS After Microwave Digestion

	detected by this method[a] (μg kg^{-1})			detected by HPLC-ICP-MS[a] (μg kg^{-1})			detected by ICP-MS after microwave digestion[a] (μg kg^{-1})
sample	iHg	MeHg	total mercury	iHg	MeHg	total mercury	total mercury
1	n.d.	n.d.		n.d.	n.d.		n.d.
2	n.d.	n.d.		n.d.	n.d.		n.d.
3	n.d.	n.d.		n.d.	n.d.		n.d.
4	n.d.	n.d.					
5	1.43 ± 0.11	n.d.	1.43 ± 0.11	1.26 ± 0.28	n.d.	1.26 ± 0.28	1.47 ± 0.18
6	8.06 ± 0.45	n.d.	8.06 ± 0.45	8.24 ± 0.78	n.d.	8.24 ± 0.78	9.07 ± 1.31
7	58.6 ± 3.75	2.31 ± 0.28	61.0 ± 4.03	60.9 ± 3.23	1.18 ± 0.12	62.1 ± 3.35	64.19 ± 1.37
8	60.7 ± 4.68	2.24 ± 0.31	63.0 ± 4.99	63.9 ± 4.56	1.91 ± 0.22	65.8 ± 4.78	70.30 ± 0.91
9	39.3 ± 3.26	5.47 ± 0.56	44.8 ± 3.82	42.5 ± 2.45	4.19 ± 0.38	46.7 ± 2.83	42.02 ± 2.93
10	51.0 ± 5.46	8.35 ± 1.07	58.3 ± 6.53	49.1 ± 2.29	8.67 ± 0.79	57.8 ± 3.08	56.44 ± 0.44
11	72.3 ± 6.87	9.36 ± 0.74	81.7 ± 7.61	69.4 ± 5.29	10.2 ± 0.68	79.6 ± 5.97	84.68 ± 9.88
12	73.5 ± 5.43	15.3 ± 1.46	88.8 ± 6.89	75.7 ± 8.18	16.4 ± 1.86	92.0 ± 10.04	90.9 ± 5.57

[a]Mean ± SD, n = 3; n.d., not detected; 1−6, rice samples collected from Chengdu plain, Sichuan, China; 7−12, rice samples obtained from the abandoned Hg mining district of Guizhou, China.

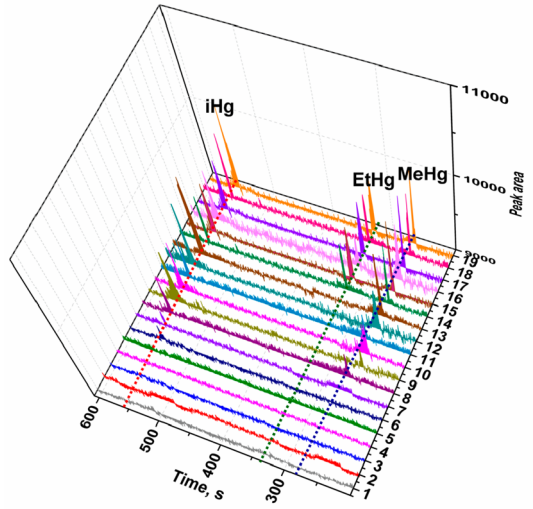

Figure 6. Chromatograms of PCs HS-SPME-GC-DBD-OES for rice samples. 1, blank; 2−7, rice samples collected from Chengdu plain, Sichuan, China; 8−13, rice samples obtained from the abandoned Hg mining district of Guizhou, China.; 14−19, spiked MeHg, EtHg, and iHg in rice samples.

obtained by HPLC-ICP-MS. The sum of the detected concentrations of mercury species is also consistent with the THg concentration obtained by ICP-MS after microwave-assisted acid digestion, validating the accuracy of the proposed method. Moreover, the accuracy of the proposed method was further confirmed by spike recovery test in rice. As summarized in Table 4, good recoveries (90−105%) of spiked mercury species were obtained, demonstrating the accuracy of the proposed method which offers a great potential for the simple, rapid, and inexpensive speciation analysis of mercury in rice. Owing to its small size, low power (5 W), and Ar gas consumption, the possibility of using DBD-OES as a miniature, inexpensive, and robust detector for miniature GC to realize filed speciation analysis and in situ monitoring of mercury in rice remains to be explored. Moreover, speciation analysis of other elements including Pb, As, and Sn can also be accomplished by this technique.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04328.

Synthesis of porous carbons SPMR fiber, operation conditions of the HPLC-ICP-MS, optimization of the PCs HS-SPME conditions, EDX spectrums of PCs fiber before and after 200 replicate HS-SPME cycles, chromatograms for various concentrations of mercury species for constructing calibration curves, and microwave assisted digestion of rice samples (PDF)

Table 4. Recoveries of Spiked 6.25 μg kg^{-1} Mercury Species in Rice Samples[a]

	found (μg kg^{-1})			recovery (%)		
sample	iHg	MeHg	EtHg	iHg	MeHg	EtHg
3	5.78 ± 0.39	5.93 ± 0.23	6.07 ± 0.46	92	95	97
4	5.93 ± 0.11	5.69 ± 0.27	6.19 ± 0.33	95	91	99
5	5.63 ± 0.09	5.79 ± 0.36	5.64 ± 0.67	90	93	90
6	6.05 ± 0.45	5.72 ± 0.27	5.92 ± 0.71	97	92	95
10	5.67 ± 3.45	6.35 ± 0.48	6.05 ± 0.73	91	102	97
11	6.01 ± 4.56	6.53 ± 0.36	6.21 ± 0.79	96	105	99

[a]3−6, rice samples collected from Chengdu plain, Sichuan, China; 10 and 11, rice samples obtained from the abandoned Hg mining district of Guizhou, China.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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