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ARTICLE TYPE

Online solid sampling platform using multi-wall carbon nanotube assisted matrix solid phase dispersion for mercury speciation in fish by HPLC-ICP-MS

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The integrity of chemical species throughout the analytical procedure and sample throughput are usually two serious impediments in elemental speciation. In this work, a simple solid sampling platform using multi-wall carbon nanotubes (MWCNTs) assisted matrix solid phase dispersion (MSPD) was constructed for online coupling to high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) for the high accuracy and sample throughput mercury speciation in fish samples. Owing to the large surface area and excellent mechanical strength of MWCNTs which result in sufficient dispersion of sample matrix and diffusion of the eluent into the mixture of solid support and fish samples, a fast, efficient and online extraction of mercury species was achieved. Compared to the conventional MSPD and other sample pretreatment methods, the proposed method retains several advantages of integration of extraction, clean-up, separation and determination into one single step to achieve high sample throughput, eliminating the need of derivatization of Hg species and/or subsequent purification steps, reduced usage of solid support, minimized contamination and mild operation conditions. The limits of detection of 9.9 ng g^{-1} and 8.4 ng g^{-1} were obtained for Hg^{2+} and CH_3Hg^+, respectively, based on 1 mg of fish sample. The accuracy of the proposed method was validated by analyzing two Certified Reference Materials. The proposed method was applied for two fresh fish samples for Hg speciation.

Instruction

Speciation analysis facilitates more accurate evaluation of environmental and biological risks of element compared to its total concentration since mobility, bioavailability and toxicity of an element are significantly determined by its chemical forms.[1-4] Today's modern analytical instruments can offer adequate sensitivity for speciation analysis, but a number of serious impediments in elemental speciation analysis remains. One of them is the maintaining of the integrity of chemical species throughout the analytical procedure. In general, prior to analysis, analyte species are required to be extracted from complex sample matrix *via* various extraction methods.[5-8] However, a drawback of these methods is the possibility of altering analyte species during extraction. In addition, species degradation arising from the oxidation by dissolved oxygen is also inevitable during the storage step.[9] Moreover, these extraction methods are usually tedious and time-consuming, requiring toxic chemicals, and generating hazardous wastes.[10] Therefore, pretreatment methods possessing advantages of maintaining the integrity of chemical species, waste minimization and high sample throughput, have gain widespread interest in the field of elemental speciation analysis.

Matrix solid-phase dispersion (MSPD) has proven to be a simple and promising technique for the extraction of analytes from environmental and biological matrices, wherein it homogenously blends a sample with a solid matrix (e.g., silica, SiO_2, C18 or graphene) in a mortar to disrupt the sample architecture and weak bond between analyte and sample matrix, thereby achieving high extraction yields with good selectivity under mild conditions.[11-19] As a result, special equipment used for the complete decomposition of sample component and sophisticated operators are not required.[12] However, MSPD is mainly applied in the extraction of organic compounds (e.g. pesticides, drugs and persistent organic pollutants), and studies on the extraction of elemental species are quite limited. Moreda-Piñeiro[15] et al. pioneered the use of MSPD for the extraction of arsenic species from seafood products prior to off-line determination by high-performance liquid chromatography inductively coupled plasmamass spectrometry (HPLC-ICP-MS). Recently, CH_3Hg^+ and Hg^{2+} species from fish samples have been efficiently extracted by using a modified MSPD method prior to its derivatization with sodium tetraphenylborate (Na[B-$(C_6H_5)_4$])[16] and gas chromatography mass spectrometry (GC-MS) detection. Compared to the conventional extraction methods assisted by microwave or ultrasonic irradiation, integrity of the chemical species can be expected in the MSPD because of its milder extraction conditions. The drawback with GC-MS separation and detection is the need for the derivatization of analyte which can be time consuming and result in low sample

throughput, prior to its determination. Therefore, a method based on online coupling of MSPD to HPLC-ICP-MS would significantly accelerate analytical process, eliminate the derivatization step, alleviate manual handling, reduce the risk of species degradation and contamination, and minimize sample and chemicals consumption.

Therefore, the aim of the current work was to investigate the potential of MSPD coupled to HPLC-ICP-MS for online elemental speciation analysis. The speciation of mercury in fish samples was chosen to evaluate the feasibility of the proposed method because mercury is very toxic and it can be easily bio-accumulated in human body. To the best of our knowledge, this is the first report that successfully accomplished solid sampling and HPLC-ICP-MS for elemental speciation analysis based on the on-line MSPD. It is worth noting that sample throughput, automation and analytical process can be remarkably improved by use of an on-line solid sampling platform of sequential injection MSPD.

Experimental

Instrumentation

HPLC-ICP-MS analysis was performed with an Agilent 1200 LC system (Agilent Technologies, USA) equipped with a single pump and autosampler with a variable 100 µL injection loop. Mercury speciation was carried out with a reversed-phase chromatography column Agilent zorbax SB-C18 (4.6 mm i.d. × 250 mm, 5 µm). Online solid sampling platform consists two sequential injection valves (SIV, 1/16 × 75 mm, C25Z-3186, Valco Instruments Co. Inc., Houston, USA) and six stainless steel MSPD columns (4.6 mm i.d. × 50 mm length) withpolyethylene frits. The platform was connected to the HPLC system and the outlet of the HPLC was directly connected to a Babington-type nebulizer of Agilent 7700x ICP-MS (Agilent Technologies, USA) with PEEK (polyetheretherketone) capillary tubing (0.5 mm o.d.). The schematic of the whole instrumental system is shown in Fig. 1A. Scanning electron microscopy (SEM, JEOL, Japan) was used for characterization of the solid supports and their mixture with DORM-3 after blending.

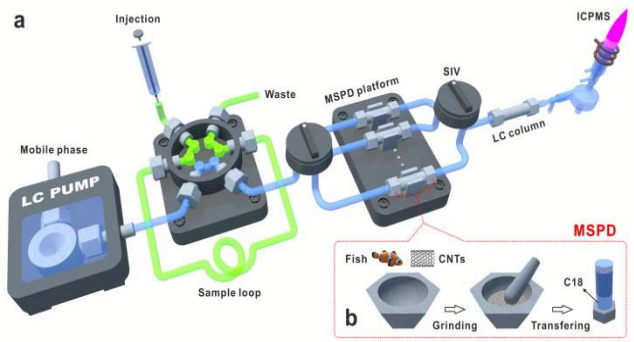

Fig. 1 Schematic of on-line MSPD platform coupled to HPLC-ICP-MS.

Reagents and solutions

High purity 18.2 MΩ cm^{-1} ultrapure water was obtained from a Milli-Q water purification device (Millipore, USA). Methanol (HPLC grade) was from Honeywell (B&J, USA). L-cysteine (≥ 98%), ammonium acetate, hydrochloric acid, nitric acid, hydroperoxide (guaranteed reagent grade) were from Sigma (Sigma-Aldrich, USA). A stock solution of inorganic mercury (Hg^{2+}, 1000 mg L^{-1} as Hg) containing 2% (v/v) HNO_3 and a 76 mg L^{-1} (as Hg) stock solution of methylmercury chloride (CH_3Hg^+) and ethylmercury chloride ($CH_3CH_2Hg^+$) dissolved in methanol were purchased from National Research Centre for Standard Materials (NRCSM, China). A 60 Å of Octadecyl-functionalized silica gel (DAISOGEL C18) was purchased from DASIO CO., LTD (Osaka, Japan). Multi-wall carbon nanotubes (MWCNTs) (Purity, >95wt%; 5-15 nm i.d.×≥50 nm o.d. ×10-20 µm length) and graphene plate (Purity, >99.5wt%; thickness, 4-20 nm; size, 5-10 µm; layers, ＜30) were obtained from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). Diatomaceous earth (DE) was from Kelong Chemical Factory (Chengdu, China).

Sample preparation

Two Certified Reference Materials (CRMs, DORM-2 and DORM-3) and two fresh fish samples were obtained from the National Research Council Canada and a local supermarket, respectively. The preparation of fresh fish samples was described here. Briefly, the scales, skin and bones of the fishes were removed. The residual soft tissues were homogenized by mechanical blending and freeze-dried using liquid nitrogen. The dried fish tissue samples were successively triturated, transferred to white polyethylene bottles and sealed with plastic seals. These samples were kept in a refrigerator at 4 °C prior to use.

Online sequential injection solid-phase matrix dispersion platform

Initially, an off-line MSPD procedure summarized in Section 1 of the Supporting Information (SI) was used in our preliminary studies. The schematic of the online sequential injection MSPD platform is shown in Fig.1A. It has two sequential injection valves and six MSPD columns instead of single online MSPD column to improve sample throughputand simplify the operation procedure. Since the extracted species were directly separated on the reversed-phase chromatography column without dilution, only 1 mg of fish sample and 2 mg of MWCNTs were blended and transferred to the stainless steel column. It should be noted that 0.20 g of C18 was placed on the bottom of the column prior to transferring the mixture of fish sample and MWCNTs to prevent the sample matrices being flushed into the chromatography column, as shown in Fig.1B. The columns were pumped for 30 min to remove air in order to avoid preferential channels prior to use. It is worth to note that the adsorbent in the column was used one time and discarded after the extraction, thus the memory effect was eliminated.

On-line sequential injection MSPD coupled with HPLC-ICP-MS

An eluent containing HCl (2%, v/v) and L-cysteine (1.5%, m/v) was manually injected to a 100 µL loop through a six-port valve by a syringe. The six-port valve and the two sequential injection valves were activated to pass a mobile phase (containing 8% (v/v) CH_3OH, 0.12% (m/v) L-cysteine and 10 mM NH_4Ac at pH 7.5) at a flow rate of 1 mL min^{-1} to flush the eluent to the MSPD column for the extraction of mercury species. The extracted species were further directed to the reversed-phase

chromatography for separation and subsequent detection of mercury species by ICP-MS. The sequential injection valves were activated again to direct the eluent to other MSPD columns after the accomplishment of speciation analysis. Total inorganic mercury was directly measured by ICP-MS after microwave-assisted acid digestion of the fish samples, which was briefly described in Section 2 of the SI. Bismuth was used throughout as internal standards for the ICP-MS measurements.

Results and discussion

Optimization of Speciation Analysis of Mercury by HPLC-ICP-MS

Optimization of instrumental parameters of ICP-MS was quickly performed without HPLC by monitoring the intensity of 201Hg using a 1 μg L^{-1}standardsolution of Hg^{2+}. Typical values of parameters are summarized in Table 1. According to the previous study,[17] a series of mixtures containing various concentrations of methanol and L-cysteine were used as mobile phase and their effects on separation of mercury species were investigated using a standard solution containing 1 μg L^{-1} Hg^{2+} and 1.5 μg L^{-1} CH_3Hg^+. It was found that the mercury species could be completely baseline-resolved and their peaks appeared at 1.8 min (Hg^{2+}) and 2.8 min (CH_3Hg^+), respectively, by using the mixture containing 8% (v/v) CH_3OH and 0.12% (m/v) L-cysteine.

Table 1. Operation conditions of HPLC-ICP-MS instrument.

Parameters	Values
HPLC	
Column	Agilent zorbax SB-C18 (4.6 mmi.d. ×250 mm, 5 μm)
Mobile phase	8% (v/v) CH_3OH, 0.12% L-cysteine, 10 mM NH4Ac, pH 7.5
Flow rate of mobile phase	1 mL min^{-1}
Injection volume	100 μL
ICP-MS	
RF power (W)	1550
Nebulizer gas flow rate (L min^{-1})	2
Auxiliary gas flow rate (L min^{-1})	1
Plasma gas flow rate (L min^{-1})	15.0
Quantification	Peak area

On-line MSPD development and optimization

Although Durate et al[16]. developed a modified MSPD method and obtained satisfactory recoveries of Hg^{2+} and CH_3Hg^+ from fish tissues, this method could not be used online with HPLC-ICP-MS since that extraction procedure involved several subsequent off-line steps including stirring, centrifugation and derivatization with sodium tetraphenylboron. Previous works[11-16, 18-20] reported that the analyte recoveries obtained by MSPD were strongly dependent on solid support. Therefore, an improved MSPD retaining capability of online, rapid and efficient extraction of mercury species from fish tissues may be attainable when an appropriate solid support is used. MWCNTs were firstly used as solid support in this study: 4 mg of MWCNTs was blended with 10 mg of DORM-3 for 5 min. The mixture was transferred to the polypropylene column together with 0.20 g of co-sorbent C18. Then, 2 mL of solution containing L-cysteine or HCl was used to extract the mercury species. The extracted species were off-line analyzed by HPLC-ICP-MS, and the recoveries of Hg^{2+} and CH_3Hg^+ were found to be above 20% regardless of the use of 5% (v/v) HCl or 1% (m/v) L-cysteine as eluent, better than those reported in previous studies.[16] Therefore, MWCNTs-based MSPD was coupled to HPLC-ICP-MS for the further evaluation of its feasibility for on-line speciation of mercury. The on-line sequential injection MSPD platform consisting of six MSPD stainless steel columns was used to simplify the optimization of experimental conditions and to improve sample throughput.

DORM-3 was used to sequentially optimize the effects of experimental conditions on the extraction efficiencies of mercury species. The extraction efficiency was evaluated from a comparison of the obtained and certified values of mercury species in DORM-3. In order to facilitate online separation and detection by HPLC-ICP-MS, and to avoid any extra dilution or splitting flow of the extracted solution, 100 μL eluent was used. Owing to no dilution of the extracted species and high sensitivity of ICP-MS, only 1 mg DORM-3 was needed in all optimizations.

The effect of eluent containing various concentrations of L-cysteine and HCl was firstly investigated, as shown in Fig. 2A and B. The results show that the recoveries of Hg^{2+} and CH_3Hg^+ increased to 94% and 106%, respectively, with increasing HCl concentration from 0 to 2% (v/v), in the presence of 1% (m/v) L-cysteine. Fig. 2B shows very little effect of L-cysteine concentration on the extraction efficiency of CH_3Hg^+. However, the extraction efficiency of Hg^{2+} was significantly increased over the range 0.5-1.5% (m/v) and maintained quantitative extraction at higher concentrations. This is probably due to Hg^{2+} needs more L-cysteine to form stable complex to be extracted from fish tissues compared to that of CH_3Hg^+. Therefore, an eluent containing 2% (v/v) HCl and 1.5% (m/v) L-cysteine was selected for all subsequent experiments.

A typical chromatogram obtained for mercury speciation by on-line MSPD-HPLC-ICP-MS using the optimized eluent is shown in Fig. 3A. In order to confirm the most outstanding advantage of the MSPD that combines the extraction and cleanup steps into one single step, another 100 μL eluent was injected to the extraction MSPD column again and online analyzed by HPLC-ICP-MS. As shown in Fig. 3B the concentrations of Hg^{2+} and CH_3Hg^+ from the second extracted solution were negligible compared to those obtained in the first extraction, indicating that mercury species can be completely extracted with one single extraction.

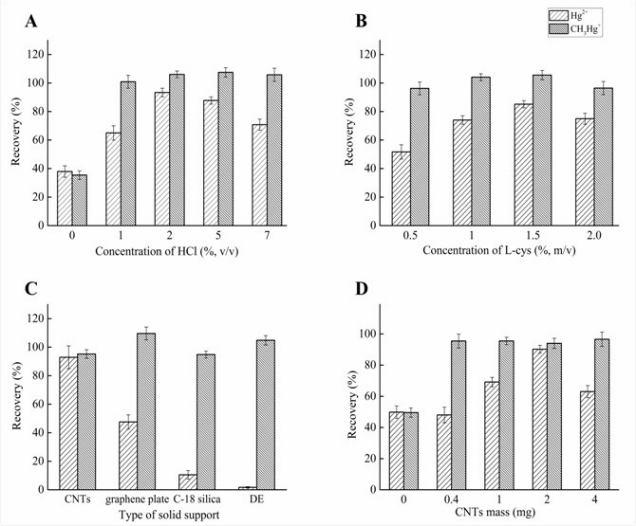

Fig. 2 Optimization of MSPD. (A) Effect of HCl concentration on the recoveries of Hg^{2+} and CH_3Hg^+ using 1% (m/v) L-cysteine; (B) effect of L-cysteine concentration on the recoveries of Hg^{2+} and CH_3Hg^+ using 2% (v/v) HCl ; (C) comparison of MWCNTs with other solid supports (graphene plate, C-18 silica and DE) for extraction of Hg^{2+} and CH_3Hg^+ from fish tissues; (D) effect of MWCNTs mass on the recoveries of Hg^{2+} and CH_3Hg^+. The extraction efficiencies were evaluated by mean recoveries of Hg^{2+} and CH_3Hg^+ (n=3).

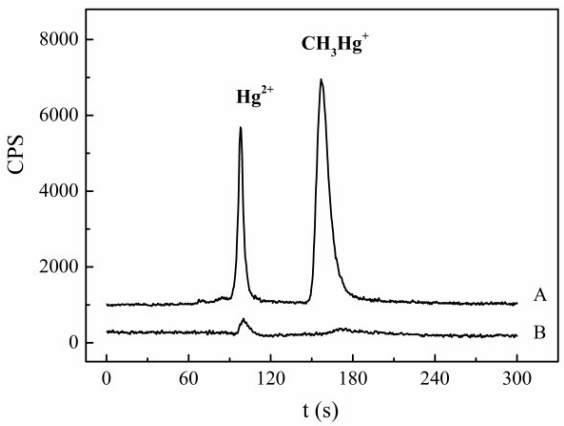

Fig. 3 Typical chromatogram of HPLC-ICP-MS for Hg^{2+} and CH_3Hg^+ from fish tissues with on-line MSPD procedure (A), and second injection into the last used column (B).

Apart from MWCNTs and C18, DE and graphene plate were also used as solid support to investigate their effects on extraction efficiencies of mercury species. The results are summarized in Fig. 2C. It is clear that good extraction efficiencies between 90-110% were obtained for CH_3Hg^+ regardless of the solid support materials used. However, only MWCNTs-based MSPD provided satisfactory extraction efficiency for Hg^{2+}. The excellent mechanical strength, high surface area, flexibility, dramatically hydrophobic surface and unique structure with internal tube cavity of MWCNTs may attribute to this good extraction efficiency.[20,21] To support this hypothesis, these solid supports and their mixture with DORM-3 after blending were characterized by SEM. Fig. 4A, B, C and D show the SEM images of these solid supports of C18, DE, graphene plate and MWCNTs, respectively. The SEM images of the mixtures by using C18 (Fig. 4E), DE (Fig. 4F) and graphene plate (Fig. 4G) show these solid materials were completely blended into powder and densely enveloped the fish tissues, and immediately aggregated together when the eluent was flowed through the MSPD column, resulting in insufficient penetration of eluent into fish tissues for the efficient extraction of Hg^{2+}. Meanwhile, the backpressure was remarkably increased in these cases. On the contrary, MWCNTs were not blended into powder but generated numerous of carbon nanofibers, which benefit the dispersing the fish tissues and preventing the aggregation of the mixture, as shown in Fig. 4H. Therefore, the eluent can easily diffuse into the mixture and efficiently extract the mercury species from the fish tissues. MWCNTs was thus chosen as a perfect solid support for all subsequent experiments. The effect of amounts of MWCNTs on the extraction efficiency was also studied. The results are summarized in Fig. 2D and show that the extraction efficiency of CH_3Hg^+ reached 50% with direct transferring of 1 mg DORM-3 into MSPD column without use of any solid support, and increased to 95% with use of 0.4 mg MWCNTs. Quantitative extraction was obtained with use of 0.4 mg or higher amounts of MWCNTs. The extraction efficiency of Hg^{2+} was found to be strongly dependent on the mass of MWCNTs. It increased significantly in the range 0-2 mg and followed by a slight decrease at the higher mass of MWCNTs. Lower MWCNTs mass resulted in inefficient dispersion of the fish tissues and low extraction efficiency of Hg^{2+}; higher MWCNTs mass resulted in inadequate interaction between the tissues and eluent due to only 100 μL eluent was used. A MWCNTs mass of 2 mg was selected for all subsequent experiments.

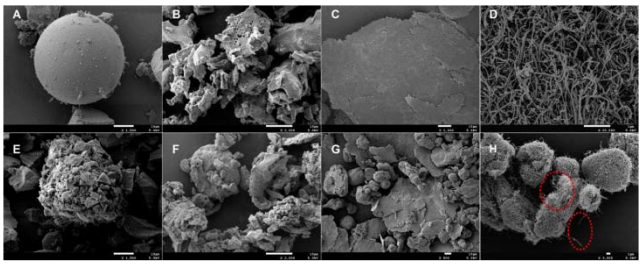

Fig. 4 SEM images of C18 (A), DE (B), graphene plate (C) and MWCNTs (D) and their mixture grounded with fish sample (C18, E; DE, F; graphene plate, G; and MWCNTs, H).

Analytical performance

Under the chosen experimental conditions, analytical figures of merit obtained using on-line MWCNTs assisted MSPD-HPLC-ICP-MS were evaluated. Typical calibration curves obtained for Hg^{2+} and CH_3Hg^+ using standard addition method can be characterized by the following calibration functions: y=868.3x+15656 and y=69.4x-1469 for Hg^{2+} and CH_3Hg^+, respectively. Linear coefficients of the calibration curves for determination of these mercury species were better than 0.99. The limits of detection (LODs) and the limits of quantification (LOQs) were calculated based on the 3σ and 10σ criterion (σ, according to signal to noise ratio). The LODs were 9.9 ng g^{-1} for Hg^{2+} and 8.4 ng g^{-1} for CH_3Hg^+, whereas the LOQs were 21.5 ng g^{-1} for Hg^{2+} and 18.3 ng g^{-1} for CH_3Hg^+, respectively, by use of 1 mg of tested sample. Precision of replicate measurements, expressed as a relative standard deviations (RSDs, n=5), were evaluated by direct replicate analysis of the CRMs and fish samples and ranged from 4.0 to 10.0% and 6.2 to 12.5% for Hg^{2+} and CH_3Hg^+, respectively, as shown in Fig.S1 (see Section 3 of the SI).

Table 2. Analytical results for the determination of Hg^{2+} and CH_3Hg^+ species in CRMs and fish tissues by HPLC-ICP-MS after MSPD extraction and total mercury determination by ICP-MS after microwave-assisted digestion (μg g^{-1})

Sample	Hg^{2+}/found	CH_3Hg^+/found	Sum of species	Hg^{2+} / certified[a]	CH_3Hg^+/certified	Total[b]
DORM-2	0.11 ± 0.05	4.55 ± 0.26	4.66 ± 0.31	0.17 ± 0.04	4.47 ± 0.32	4.35 ± 0.17
DORM-3	0.020± 0.020	0.379 ± 0.012	0.399 ± 0.032	0.027 ± 0.004	0.355 ± 0.056	0.405 ± 0.040
grouper	0.047 ± 0.005	0.277 ± 0.020	0.324 ± 0.025			0.375 ± 0.026
puffer fish	0.016 ± 0.009	0.193 ± 0.016	0.209 ± 0.025			0.255 ± 0.036

[a]Values calculated by the difference between totalmercury and CH_3Hg^+ content. [b]Total mercury contents determined by ICP-MS after the microwave-assisted digestion procedure.

Sample analysis

The accuracy of the proposed method was evaluated by analysis of two CRMs (DORM-2 and DORM-3) and two fresh fish samples (grouper and puffer) were also used for its preliminary application analysis. The concentrations for Hg^{2+} and CH_3Hg^+ are summarized in Table 2. The results of t-test show that the analytical results obtained for the CRMs by the proposed method are not significantly different from those of certified values at the confidence level of 95%. In addition, the obtained sum of the detected concentrations of Hg^{2+} and CH_3Hg^+ agrees well with the total mercury concentration obtained by ICP-MS after microwave-assisted acid digestion.

$CH_3CH_2Hg^+$ was chosen as a model analyte to evaluate the feasibility of using this method for analysis of other mercury species. It was necessary to spike all the tested samples with 300 ng g^{-1} $CH_3CH_2Hg^+$ (as Hg) because the endogenous concentrations were not detectable by the proposed method. The chromatograms of tested samples and their spiked samples with $CH_3CH_2Hg^+$ are summarized in Fig.5. The recoveries for $CH_3CH_2Hg^+$ were in a range of 81 to 106%.

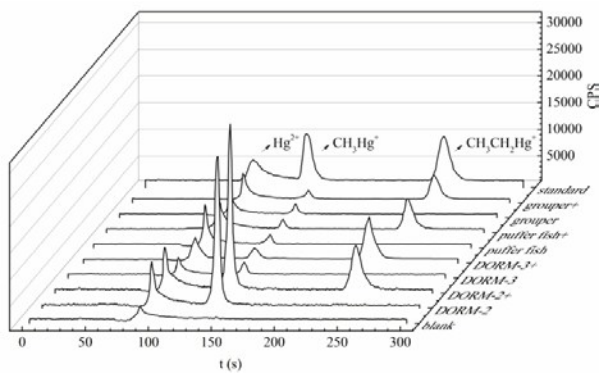

Fig. 5 Typical chromatograms of HPLC-ICP-MS obtained for unspiked and spiked of $CH_3CH_2Hg^+$ in fish tissues with on-line MSPD procedure (+: means spiked with $CH_3CH_2Hg^+$)

Conclusions

A simple solid sampling platform based on sequential injection MWCNTs assisted MSPD was developed and online coupled to HPLC-ICP-MS for sensitive and fast mercury speciation analysis of fish samples. Compared to previous MSPD, this method demonstrated several advantages, such as the elimination of further purification/ derivatization of the extracted elemental species, low consumption of sample and chemicals, minimized consumption of solid support, high sample throughput, less contamination and mild operation conditions. The method may have potential for mercury speciation analysis of other sample matrices or can be expanded to speciation analysis of other elements with high sensitivity and sample throughput by choosing an appropriate solid support.

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