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Hg atomization on a UV/nano-ZrO_2/HCOOH photocatalytic reduction unit for its determination and speciation using HPLC-AFS

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A novel UV/nano-ZrO_2/HCOOH system was developed and fabricated as an atomization unit and/or an online interface between HPLC and AFS for Hg determination and speciation for the first time. UV-generated electrons at the conduction band of nano-ZrO_2 reduce mercury species into mercury cold vapor, achieving mercury atomization for AFS determination. The LODs (3σ) of inorganic mercury (Hg^{2+}), methylmercury (MeHg) and ethylmercury (EtHg) tested in this study were respectively down to 10, 6, and 8 ng L^{-1} when using AFS under flow injection mode (FI). Moreover, Hg speciation could be also performed when coupled with HPLC, and the LODs (3σ) of Hg^{2+}, MeHg and EtHg were 24, 13, and 16 ng L^{-1}, respectively, under HPLC-(UV/nano-ZrO_2/HCOOH)-AFS system with the RSDs better than 4.6% (n = 6) at 20 μg L^{-1} each. FI-(UV/nano-ZrO_2/HCOOH)-AFS and HPLC-(UV/nano-ZrO_2/HCOOH)-AFS were validated through analyzing a certified reference material (GBW10029, tuna fish) and applied to mercury determination and speciation of the local seafood around Xiamen Island.

Introduction

As we have already known that mercury is one of the most toxic elements in this world. However, it has been irresistible to be used in industry, agriculture and medicine due to its unique physicochemical properties, leading to its anthropogenic sources in the environment and biota besides its natural sources.[1] In addition to various chemical forms of mercury directly from the anthropogenic sources, inorganic mercury ion (Hg^{2+}) is flexible to undergo chemo/bio-transformation into various Hg species including organomercury which are bioconcentrated because they are better retained by organisms at various levels in the food chain.[2-5] The resulting species demonstrated different behavior in mobility, bioavailability and toxicity, and thus were widely studied.[6, 7] During which the effective analytical methods for the determination of total Hg and its speciation were much desired and played crucial roles.[8] Among them, atomic optical and mass spectrometry were the most frequently and practically used tools; when coupled with gas chromatography (GC) and high performance liquid chromatography (HPLC) as well as capillary electrophoresis (CE), targeted mercury species could be analyzed.[9-11] Cold vapor generation of mercury using wet chemo-reductants, for example stannous chloride and tetrahydroborate (THB), as a sample introduction strategy was typically employed to improve the detection ability of atomic spectrometry. [12] In this way, except the advantage of great improvement of sensitivity, some disadvantages of instability of the reductant used and interferences of coexisting transition metals to vapor generation efficiency showed up. Latterly, novel photo-induced mercury cold vapor generation systems for mercury determination and speciation using atomic spectrometry were gradually developed,[13-24] in which reductive radicals such as $CO_2^{\cdot-}$ and R· generated in the presence of low molecular weight organics (LMWO) under UV irradiation and with microwave were utilized to reduce Hg species into Hg^0. Moreover, other approaches like solution cathode glow discharge[25,26] and electrolytic vapor generation from an L-cysteine modified graphite electrode[27] were also reported.

Nanomaterials like TiO_2 have semiconductor properties. When nano-TiO_2 is illuminated by a light, which has an energy higher than the energy gap (3.2 eV) between the conduction band (CB) and valence band (VB), electron (e^-) and hole (h^+) will be photogenerated separately on CB and VB. This feature was first used to split H_2O into O_2 and H_2.[28] We once proposed to use CB e^- of nano-TiO_2 under UV-irradiation and HCOOH as a VB h^+ scavenger (UV/nano-TiO_2/HCOOH) to reduce Se^{VI} to Se^{IV} for hydride vapor generation of Se^{VI} before further reduction by KBH_4 or on a carbon fiber cathode.[29,30] Direct vapor generation of inorganic Se species based on UV/nano-TiO_2/LMWO was subsequently developed.[31,32] These UV/nano-TiO_2/HCOOH (or LMWO) system were further applied for direct cold vapor generation of Hg species as a sample introduction unit for total Hg determination, and an interface between HPLC and atomic fluorescence spectrometry (AFS) or inductively coupled plasma mass spectrometry (ICP-MS) for Hg speciation.[33,34] In order to avoid the rapid recombination of e^-/h^+ pairs and thus improve the reduction efficiency of CB e^-, we deposited noble metals onto nano-TiO_2. The noble metals such as silver could effectively trap e^- to increase e^- density on CB, achieving direct hydride generation of inorganic Se species (Se^{IV} and Se^{VI}) and organic Se species ($(SeCys)_2$ and SeMet) as well.[35] On the other hand, a bigger band-energy gap of nanosemiconductor like ZrO_2 (5.0 eV) results in a more negative potential of CB e^- (-1.0 V versus normal hydrogen electrode (NHE), pH = 0).[36] Such a higher negative potential of the CB e^- facilitated the direct hydride generation of Se species, and the LODs of Se species were down to ng mL^{-1} and pg mL^{-1} level when using AFS and ICP-MS.[35]

Considering the strong reduction ability of the CB e^- on nano-ZrO_2, further improvement of cold vapor generation of Hg species and thus the sensitivity were expected. In this study, we developed a more efficient conversion strategy for Hg species to atomic mercury on nano-ZrO_2 under UV irradiation (UV/nano-ZrO_2) in the presence of formic acid as a hole scavenger for subsequent Hg determination and speciation using HPLC-AFS. This proposed method was validated by analyzing SRM (GBW 10029), and applied to Hg speciation in the local seafood around Xiamen island.

Experimental

Reagents

All reagents used were at least of analytical grade. Ultrapure water (UPW, 18.2 MΩ cm) was prepared in a Milli-Q system (Millipore Filter Co., Bedford, USA) and used throughout this study. Tetrapropyl zirconate ($Zr(OC_3H_7)_4$), ammonium pyrrolidine dithio carbamate (APDC) and formic acid were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). KBH_4 was obtained from the Tianjin Huachen Chemical Reagent Co. Ltd. (Tianjin, China). The HPLC-grade acetonitrile (ACN) was obtained from Tedia (Fairfield, USA). Mercury chloride was also obtained from Sinopharm Chemical Reagent Co. Ltd., and methylmercury chloride (MeHgCl) and ethylmercury chloride (EtHgCl) were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany).

Instrumentation

The UV/nano-ZrO_2 photocatalytic reduction unit was fabricated according to our previous report with some modifications.[35] Nano-ZrO_2 was prepared by a conventional sol-gel procedure. Briefly, the sol solution was prepared by mixing $Zr(OC_3H_7)_4$ and acetylacetone in ethanol; and then a pre-cleaned glass fiber (200 mm in length × 0.3 mm O.D., washed with UPW, acetone, UPW, 5 % chromate in H_2SO_4, and UPW in sequence, and then dried) was dipped into the prepared sol solution for 30 s; after repeating this step three times, the glass fiber was dried at 80 ºC for 0.5 h in an electric stove and then calcined under a gradually increasing temperature (1.5 ºC min^{-1}) to 600 ºC (keeping for 1 hour) to obtain a nano-ZrO_2 film (particle size 10 nm, thickness 400 nm) coated glass fiber (Fig. 1a). It was finally inserted into the specially designed central channel (200 mm in length × 1 mm I.D. × 4 mm O.D.) of a 10 W low pressure mercury lamp (λ_1 = 254 nm, λ_2 = 185 nm, Heraeus Noble light Ltd., Shenyang, China) and fixed using a septum at each end. Such a UV/nano-ZrO_2 unit had a 157 µL dead-volume, and was used for the cold vapor generation of Hg species as a sample introduction unit and/or an interface between HPLC and AFS. The chromatographic separation of Hg species was carried out on a Shimadzu LC-2010A liquid chromatographic system (Kyoto, Japan). A Shim-pack VP-ODS column (250 mm in length × 4.6 mm I.D., particle size 5 µm) was used to separate Hg species with a mixture of acetonitrile and water (65 : 35) containing 1.5 mmol L^{-1} APDC (pH 5.5 buffered by 0.1 mol L^{-1} acetic acid-ammonium acetate) as the mobile phase. Hg determination was performed on a model AFS-610A non-dispersive atomic fluorescence spectrometer (Beijing Rayleigh Analytical Instrument Co., Ltd., Beijing, China) equipped with a high-intensity Hg hollow cathode lamp (253.7 nm, Beijing Institute of Vacuum Electronics Research, Beijing, China), and signal acquisition and processing were carried out using HWH software Version 1.0.[37] A master Compact/Low flow peristaltic pump (Cole-Parmer, USA) was used to introduce reagents in the experiments. Sample solution by flow injection (FI) and/or HPLC effluent could flow through the UV/nano-ZrO_2 unit for mercury cold vapor generation (Fig. 1b). After gas-liquid separation, the generated mercury cold vapor was carried by Argon into AFS. A schematic diagram was shown in Fig. 1c and optimum instrumental parameters were listed in Table 1.

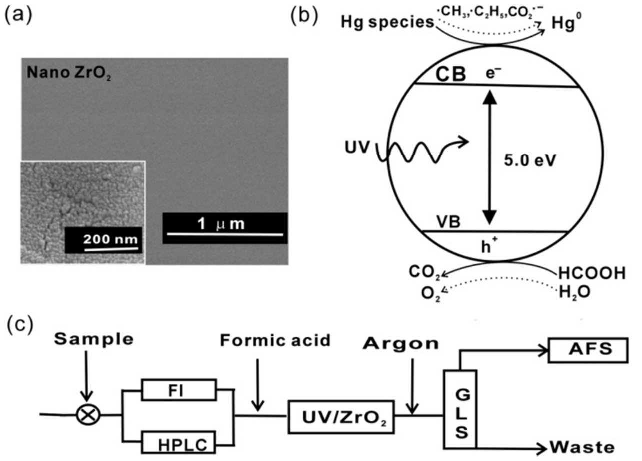

Fig. 1. (a) SEM image of Nano-ZrO_2 film; (b), atomization of Hg species on the UV/nano-ZrO_2/HCOOH; (c), FI/HPLC-(UV/nano-ZrO_2/HCOOH)-AFS system. GLS: gas liquid separator.

Sample preparation

Sample preparation procedures followed the protocol as described in our previous work.[19,33] A microwave-assisted digestion method[19] was used for total Hg determination. 0.1 g the certified reference material GBW10029 (tuna fish) purchased from National Research Center for Standard Materials (Beijing, China) and real seafood samples bought from the local market (Xiamen, China) after lyophilization were accurately weighed and put respectively into PTFE bombs, 5 mL of ultrapure HNO_3 was then added, and they were laid up overnight for pre-digestion at room temperature. The sealed bombs were then digested for 5 minutes using a MK-III optical fiber pressure controlled microwave decomposition system (Shinco, Shanghai, China) with a full power of 1,200 W. After cooling the sealed bombs, the resulting transparent solutions were diluted with UPW to 10 mL and filtered through a 0.45-µm filter, finally injected into FI-(UV/nano-ZrO_2/HCOOH)-AFS for total Hg determination. An acid extraction procedure was applied to extract both organomercury and Hg^{2+}.[33] Briefly, 3 mL 5 mol L^{-1} hydrochloric acid was respectively added to 0.2 g GBW10029 or 1.0 g the real seafood samples in a 50 mL centrifuge tube. Then the mixture was placed in an ultrasonic bath for about 10 min. After ultrasonic-assisted extraction, the suspension was centrifuged at 3,500 rpm for 10 min, and the supernatant was decanted into a 25 mL centrifuge tube. The residue was extracted again as described above. The two supernatant portions obtained were combined and neutralized to pH 5 with 10 mol L^{-1} NaOH, then diluted with ultrapure water to 25 mL, and filtered through a 0.45 μm membrane. Hg speciation analysis was finally performed on HPLC-(UV/nano-ZrO2/HCOOH)-AFS.

Table 1 Optimum parameters of HPLC-(UV/nano-ZrO_2/HCOOH)-AFS

HPLC	
Mobile phase	65% CH_3CN-35% H_2O containing 1.5 mmol L^{-1} APDC, pH 5.5
Flow rate	0.5 mL min^{-1}
Sample injection volume	100 μL
AFS	
PMT voltage	-310 V
HCL current	40 mA
Resonance wavelength	253.7 nm
Argon flow rate	300 mL min^{-1}
Photocatalytic Reduction	
UV lamp	Low-pressure10 W (λ_1, 254 nm; λ_2, 185 nm)
Photocatalyst	Nano-ZrO_2, particle size, 10 nm; thickness, 400
Formic acid concentration	10 % (V/V), pH 3
Formic acid flow rate	0.6 mL min^{-1}

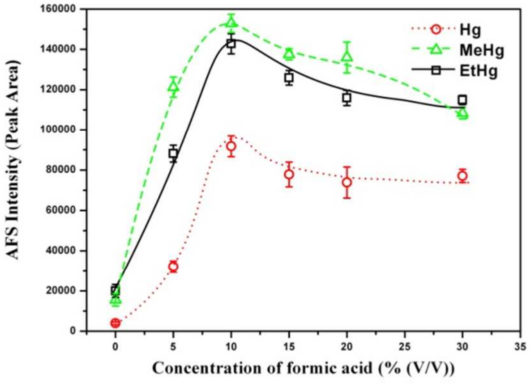

Fig. 2 HCOOH concentration dependent AFS intensity of Hg species (50 μg L^{-1} each). Other experiment conditions are listed in Table 1. The uncertainties shown as error bars were obtained with three replicates.

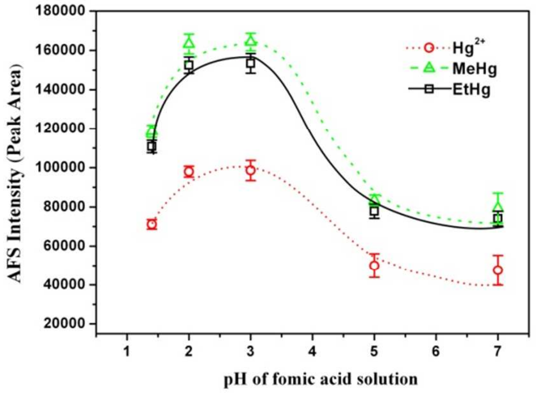

Fig. 3 pH-dependent AFS intensity of Hg species (50 μg L^{-1} each). Other experiment conditions are listed in Table 1. The uncertainties shown as error bars were obtained with three replicates.

Results and discussion

Atomization of Hg species. Atomization efficiency of Hg species on the UV/nano-ZrO_2 unit significantly depends on the reduction ability of the e^- on CB. As we already known that the UV-generated CB e^- and VB h^+ tend to recombination, leading to the decrease in CB e^- number and thus lower Hg atomization efficacy. Effective VB h^+ scavengers should be introduced into this system to interdict the spontaneous recombination process. The smallest organic acid, HCOOH ($E^{\circ}_{CO_2/HCOOH} = -0.2\,V$; $E^{\circ}_{CO_3^{2-}/HCOO^-} = -0.95\,V$), was thus employed for this purpose in addition to preventing from the formation of O_2 due to the possible oxidation of H_2O ($E^0_{O_2/H_2O} = 1.23\,V$), which can "eating" the CB e^- (-1.2 V, pH 3) (Fig.1 b). The obtained results indicated that AFS intensity of Hg species (Hg^{2+}, MeHg and EtHg tested) increased along with the increase in HCOOH concentration until 10 % V/V, and then slightly decreased with the increase to 30 % V/V (Fig. 2). The pH value was also a key element controlling not only the existing percentage of HCOOH and $HCOO^-$ ($pK_a = 3.75$) but also surface the charge of nano-ZrO_2 (pI = 7)[38]. The results in Fig. 3 indicated that AFS intensity increased from pH 1.5 to 3.0, and then decreased as pH increased to 7. The surface of nano-ZrO_2 should be positively charged in the experimental pH ranging 1.5 to 7, while the ratio of HCOOH/$HCOO^-$ decreased, resulting in more $HCOO^-$ competing the concentration gradient driving approach of Hg species to the surface of nano- ZrO_2. It is should be noted that positively surface of nano-ZrO_2 theoretically repels the approaching of Hg^{2+}, however, the resulted pH-dependent atomization efficiency of Hg^{2+} ($E^0_{Hg^{2+}/Hg^0} = 0.85\,V$) suggested that the conversion of Hg^{2+} to Hg^0 by the CB e^- was fast due to the enough negative redox potential of CB e^- of ZrO_2 under acidic conditions (for example, -1.0 V at pH 0, -1.2V pH 3 and -1.4V pH 7). This process was controlled primarily by the CB e^- reduction driving force rather than the affinity and the extent of adsorption of Hg^{2+} on the nano-ZrO_2 surface like in the case of TiO_2.[39] On the other hand, the possible oxidation of Hg^0 into HgO, which was reported to be favored in higher pH,[40] should be considered to contribute to the decrease of Hg AFS intensity from pH 3 to 7. Flow rate of HCOOH decides the residence time of Hg species and the amount of available HCOOH in the UV/nano-ZrO_2/HCOOH system. As we expected, the optimum flow rate of HCOOH was at the middle (0.6 mL min^{-1}) of 0.3 to 1.0 mL min^{-1} (Fig. 4). Moreover, the predominant emission lights (λ_1, 254 nm corresponding to 4.9 eV or 471 kJ mol^{-1}; λ_2, 185 nm 6.7 eV or 647 kJ mol^{-1}) from the low pressure Hg-lamp are powerful enough for cleaving the C-Hg bond (the bond energy of ClHg-CH_3 is 280.0 ± 12.6 kJ mol^{-1} and that of ClHg-C_2H_5 264.8 ± 12.6 kJ mol^{-1}),[41] resulting in the formation of Hg^{2+} and possible reductive radical $\cdot CH_3$ and $\cdot CH_2CH_3$ favorable for reducing Hg

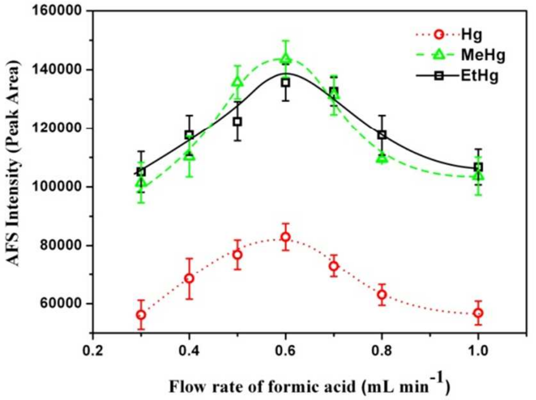

Fig. 4 Effect of the flow rate of HCOOH on AFS intensity of Hg species (50 μg L^{-1} each). Other experiment conditions are listed in Table 1. The uncertainties shown as error bars were obtained with three replicates.

species to Hg^0 as evidenced by the higher AFS intensity obtained in the case of MeHg and/or EtHg than that of Hg^{2+} (Fig. 2, 3 and 4). It should also be noted that $HCOOH/HCOO^-$ could be UV-oxidized to a very strong reductive radical $CO_2^{\cdot-}$ ($E^0_{CO_2/CO2^{\cdot-}} = -1.84\,V$ vs. NHE).[42] This was the reason of UV/HCOOH (or other LMWO) could be used to reduce Hg species. In the UV/nano-ZrO_2/HCOOH system, CB e^- and those reductive radicals synergistically worked for the atomization of Hg species, resulting in higher atomization efficiency than that obtained in the UV/HCOOH alone.

Analytical performance. Under the optimum conditions of 10 % V/V HCOOH, pH 3.0 and flow rate 0.6 mL min^{-1}, the cold vapor generation efficiencies of Hg species on UV/nano-ZrO_2/HCOOH were evaluated using FI-(UV/nano-ZrO_2/HCOOH)-AFS. They were remarkably improved, for example, 2.5-fold, 10-fold, and 8-fold for Hg^{2+}, MeHg and EtHg, respectively, when compared with those obtained in the conventional 2 % (w/V) KBH_4/0.5 % (w/V) NaOH-5 % (V/V) HCl system. The linearity ranged up to 100 μg L^{-1} (higher concentration was not tested) with the correlation coefficient more than 0.998. The LODs (3σ) of Hg^{2+}, MeHg and EtHg were down to 10, 6, and 8 ng L^{-1}. These LODs obtained without any preconcentration procedures were lower than those obtained when UV/LWMO alone was used with AFS detection;[17-20] and more sensitive than those obtained in (UV/nano-TiO_2/HCOOH)-AFS[33] due to the more negative CB e^- potential of -1.2V (pH 3) than -0.05 V of the CB e^- of nano-TiO_2. As we know that transition metal ions, especially Cu^{2+}, Co^{2+} and Ni^{2+}, could seriously affect the cold vapor generation efficiency of mercury in traditional THB/NaOH-acid system, in this study, the effects of these metal ions on the cold vapor generation efficiency of Hg species were investigated. Even as high as 10 mg L^{-1} for Co^{2+} and Ni^{2+}, and 1 mg L^{-1} for Cu^{2+} existing in a 20 μg L^{-1} Hg^{2+} solution, the recovery of Hg^{2+} was more than 92 % when compared with that without these metal ions, suggesting that no significant interferences from Co^{2+}, Ni^{2+}, and Cu^{2+} on the conversion of Hg^{2+} to Hg^0 in UV/nano-ZrO_2/HCOOH system.

UV/nano-ZrO_2/HCOOH unit was also used as an interface between HPLC and AFS for speciation analysis of targeted Hg species. A typical chromatogram of Hg^{2+}, MeHg and EtHg was shown in Fig. 5. The LODs (3σ) of Hg^{2+}, MeHg and EtHg determined by HPLC-(UV/nano-ZrO_2/HCOOH)-AFS reached 24, 13, and 16 ng L-1 with the RSDs of 4.6%, 3.1% and 4.2% at 20 μg L-1 each (n = 6).

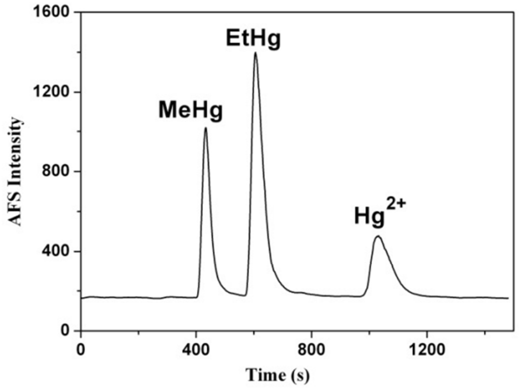

Fig. 5 A typical chromatogram of Hg^{2+}, MeHg and EtHg, 20 μg L^{-1} each. Experiment conditions can be found in Table 1.

Table 2 Method validation and sample analysis (n = 3)

Sample	Certified value (ng g^{-1})		Seafood (ng g^{-1})		
	total Hg	MeHg	MeHg	EtHg	Hg^{2+}
GBW 10029	850 ± 30	840 ± 30	834 ± 24	nd	nd
Ostrea			463 ± 9	nd	86 ± 14
Venerupis variegate			286 ± 7	nd	101 ± 15

nd, not detected.

Method validation and application. In addition to the total Hg determined (844 ± 20 ng g^{-1}) of the standard reference material GBW10029 (tuna fish) using FI-(UV/nano-ZrO_2/HCOOH)-AFS, which was well in agreement with the certificated value (850 ± 30 ng g^{-1}) (Table 2), UV/nano-ZrO_2/HCOOH was used as an on-line interface between HPLC and AFS for speciation analysis of targeted Hg species. The concentration of MeHg (834 ± 24 ng g^{-1}) measured in GBW10029 by HPLC-(UV/nano-ZrO_2/HCOOH)-AFS was well in accordance with the certified value (840 ± 30 ng g^{-1}), suggesting that the developed method was accurate. It was then applied to Hg speciation of the seafood, *ostrea* and *venerupis variegate*, bought from a local market on Xiamen Island. As can be seen from the results listed in Table 2, Hg^{2+} was also determined in addition to MeHg, suggesting that Hg^{2+} pollution in the seawater around Xiamen Island. There was not enough time to convert the Hg^{2+} into MeHg by the bacteria at the bottom of food chain, and might be directly taken in the shellfish analyzed. Anyway, the amount of MeHg determined is lower than the threshold (0.5 mg kg^{-1} MeHg)[43] of the national standard of China, suggesting safe of the local seafood.

Conclusions

UV/nano-ZrO_2/HCOOH may prove to be a superior alternative to the conventional and newly developed wet chemical and photo-induced as well as photocatalytic nano-TiO_2 based cold vapor generation techniques for Hg determination and speciation. It can be expected that, not limited to Hg species demonstrated here, UV/nano-ZrO_2/HCOOH with suitable modifications can be used as an atomization unit and/or an interface between a continuing separation technique and an atomic optical/mass spectrometer for the determination and speciation of other toxic elements in the near future.

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Notes and references

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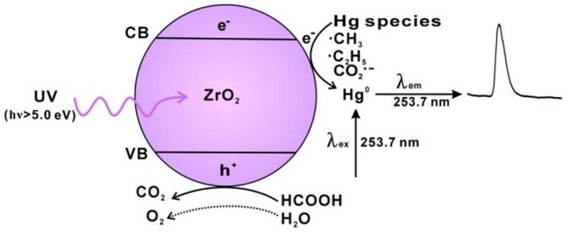

A novel UV/nano-ZrO$_2$/HCOOH atomization system was developed as a sample introduction unit and/or an online interface between HPLC and AFS for Hg determination and speciation for the first time.