Supporting Information (SI)

Flow Injection Photochemical Vapor Generation Coupled with Miniaturized Solution-Cathode Glow Discharge Atomic Emission Spectrometry for Determination and Speciation Analysis of Mercury

Jiamei Mo[&], Qing Li[&], Xiaohong Guo, Guoxia Zhang and Zheng Wang*

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China.

*Tel.: (+86) 021 52413503. Fax: (+86) 021 52413016. E-mail: wangzheng@mail.sic.ac.cn

[&]These authors contributed equally to this work and should be considered co-first authors.

Table of Contents

1. Background Correction Method

The background correction was used to improve the stability, by simultaneously recording the response of Hg at 253.7 nm and the background emission intensity (see Figure S1). The background and sample signals of Hg were obtained by deducting the responses at 254.0 nm from that at 253.7 nm for the blank and sample solution. The net emission intensity at 253.7 nm was derived by deducting the background signal from the sample signal.
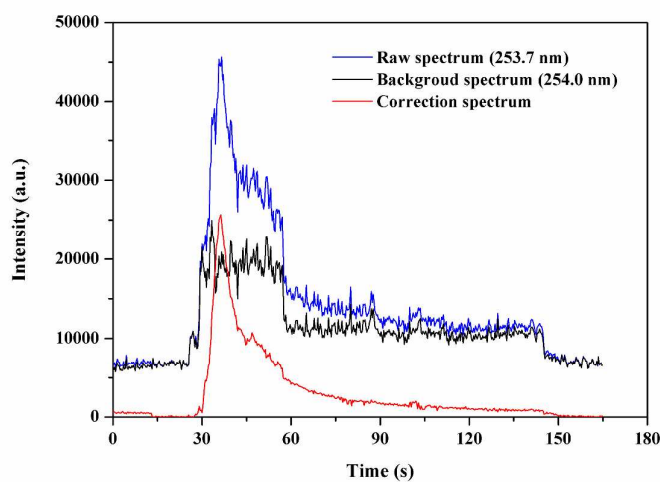

Figure S1. Signal processing and background correction.
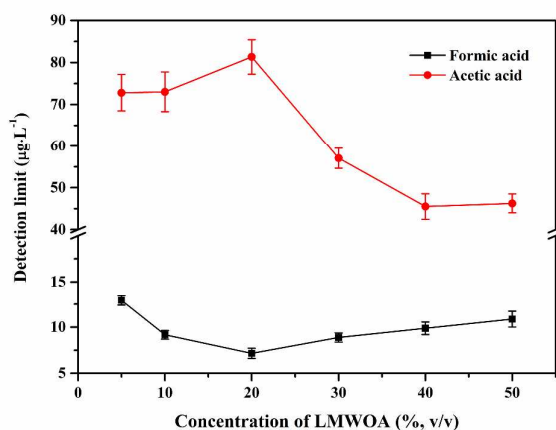
2. Type and Concentration of LMWOA

Figure S2. Effect of the concentrations of formic acid or acetic acid (irradiation time: 30 s, pump B revolution: 85 mL·min^{-1}, Ar flow rate: 80 mL·min^{-1}).

## 3. Optimization of SCGD Parameters

The effects of the SCGD parameters, including the electrolyte type and flow rate, the applied voltage, and the discharge gap were examined using the optimized PVG experimental conditions

described above. An inorganic acid at a given concentration was used as the electrolyte solution to ignite the SCGD device. Three acids, namely HNO_3, HCl, and H_2SO_4 at pH = 1.0 were passed into the SCGD system at the discharge cathode. It was observed that the DL using HNO_3 is comparable to that using HCl, and approximately 1/2 lower than that with H_2SO_4 (Figure S3a). However, Huang et al.[1] found that the anion affects the DL values for detecting Se, Ge, and Sn in the order of $HCl<HNO_3<H_2SO_4$. This result implied that the electrolyte solution had different effects on the metal ions, between the direct introduction of sample solution into SCGD[2,3] and gas sampling.[2] Finally, the pH = 1.0 HNO_3 was selected as the electrolyte solution.

When the flow rate was below 1.6 mL·min^{-1}, the plasma became unstable and intermittent quenching occurred, because there was not enough solution to sustain the plasma discharge. When the flow rate was above 2.4 mL·min^{-1}, on the other hand, the plasma became unstable and the hollow titanium tube turned red. Thus, the influence of the flow rate ranging from 1.6 to 2.4 mL·min^{-1} was investigated. Figure S3b indicates that the DLs were the lowest at 2.0 mL·min^{-1}, and therefore, this flow rate was chosen for subsequent experiments.

The effect of applied voltage on the response is shown in Figure S3c. The DLs decreased as the applied voltage increased from 1020 to 1060 V, because the discharge obtained more energy for exciting the atoms under a higher applied voltage. However, when the applied voltage was over 1060 V, the hollow titanium tube turned red, and stray light could be produced, which impacted the detection accuracy. The minimal DL values were obtained at an applied voltage of 1060 V, which was thus used in the subsequent experiments. The stable plasma could not be obtained when the gap was less than 3 mm or bigger than 4.5 mm. Finally, 3.5 mm was selected as the gap in consideration of both efficient excitation of the atoms and stability of the plasma discharge (Figure S3d).
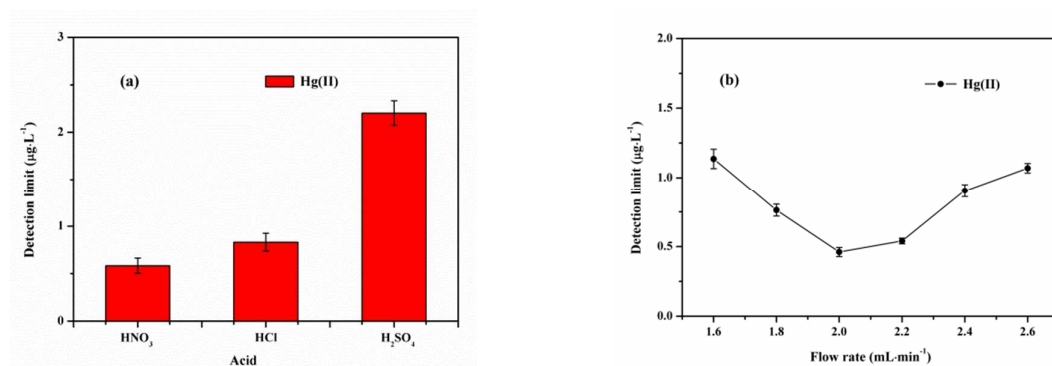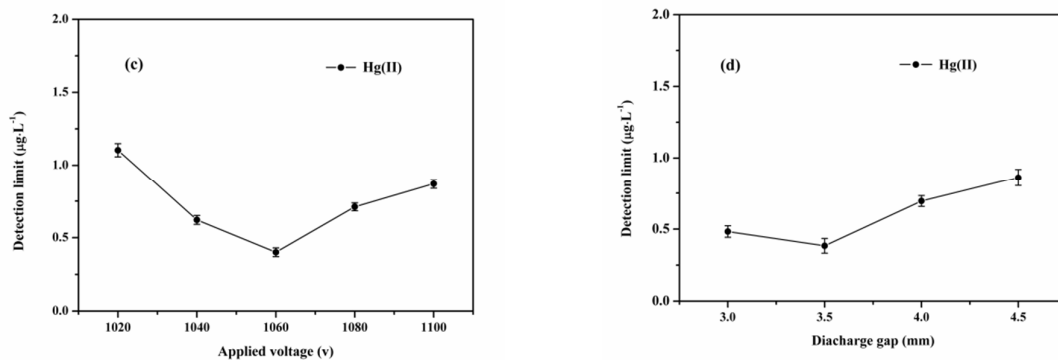
Figure S3. Effect of instrumental parameters on the SCGD microplasma: (a) electrolyte type, (b) electrolyte flow rate, (c) applied voltage, and (d) discharge gap.

4. Influence of Ni(II) on PVG Efficiency
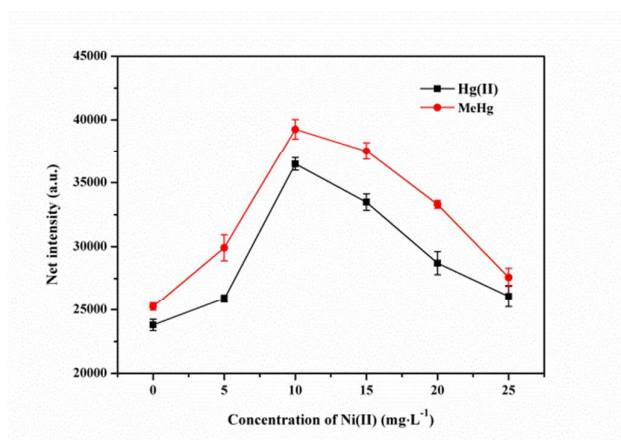
Figure S4. Effect of the Ni (II) concentration on the net intensity of Hg(II) or MeHg emission.

5. Interference Study

The major drawbacks of hydride generation are the interferences caused by the transition elements, especially Fe(III), Co(II), Ni(II), and Cu(II); because they form the metallic state and colloidal forms in KBH_4 solution. The impact of adding various transition metal ions to 100 $\mu g \cdot L^{-1}$ Hg(II) and MeHg was also investigated. The results are presented in Table S1. No significant interference was observed, even at concentrations as high as 1000 $\mu g \cdot L^{-1}$ for Ni(II) and Fe(III); 5000 $\mu g \cdot L^{-1}$ for Al(III), Zn(II), and Cu(II); or 10000 $\mu g \cdot L^{-1}$ for Co(II), Mg(II), Na(I), and Mn(II). The analytical recoveries were reasonable (87–111%). It indicates that the proposed method could be used to determine trace Hg(II) or MeHg without interference from the complex matrix.

In the processing of real samples, inorganic acids (HCl, HNO_3, and H_2SO_4) are frequently used for sample pretreatment or digestion. Therefore, the effects of inorganic acids on mercury determination were also investigated. The responses of Hg(II) and MeHg from PVG both decreased significantly, when the concentrations of HCl and H_2SO_4 were higher than 2% (v/v) and 5% (v/v), respectively. HNO_3 is a strong oxidizing acid, and it can consume the reductants,

reducing the efficiency of mercury vapor generation. Hence, the responses for Hg(II) or MeHg from PVG were sharply reduced when the HNO_3 concentration was greater than 0.5% (v/v). With 2% (v/v) HNO_3, the signals of Hg(II) and MeHg were almost completely suppressed. Therefore, the samples should be first diluted to an appropriate concentration before measurement.

Table S1 Influence of coexisting ions on the determination of 100 μg·L^{-1} Hg(II) or MeHg.

Coexisting ion	Concentration (μg·L^{-1})	Recovery[a] of Hg(II) (%)	Recovery of MeHg (%)	Coexisting ion	Concentration (μg·L^{-1})	Recovery of Hg(II) (%)	Recovery of MeHg (%)
Ni(II)	1000	103.17	105.49	Na(I)	10000	100.11	95.60
Fe(III)	1000	89.21	90.27	Mg(II)	10000	96.27	108.71
Al(III)	5000	89.57	92.52	Mn(II)	10000	98.57	95.76
Cu(II)	5000	97.99	93.37	Cl$^-$	2[b]	90.91	89.83
Zn(II)	5000	94.64	91.87	NO_3^-	0.5[b]	87.89	88.35
Co(II)	10000	105.42	103.28	SO_4^{2-}	5[b]	109.94	111.04

[a] Recovery in the range of 85–115% is a reasonable error range.

[b] Concentration, % (v/v)

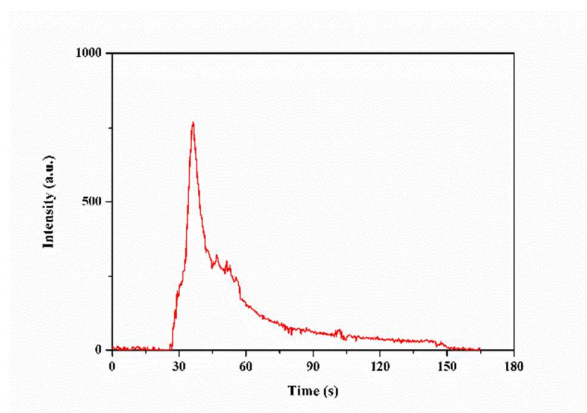## 6. The spectrum of 5 μg·L^{-1} Hg(II)

Figure S5. The spectrum of 5 μg·L^{-1} Hg(II).

REFERENCES

1   Huang, C.C.; Li, Q.; Mo, J.M.; Wang, Z. *Anal. Chem.* 2016, **88**, 11559-11567.

2   Wang, Z.; Gai, R.Y.; Zhou, L.; Zhang, Z. *J. Anal. At. Spectrom.* 2014, **29**, 2042-2049.

3   Yang, C.; Wang, L.; Zhu, Z.L.; Jin, L.L.; Zheng, H.T.; Belshaw, N. S.; Hu, S.H. *Talanta* 2016, **155**, 314-320.