Supporting information

Rapid Determination of Hg Isotopes in Low Concentration Water Samples by Flow Injection-Plasma Electrochemical Vapor Generation

Guan Wang[1], Xing Liu[1*], Shuyang Li[1], Junhang Dong[1], Xuan Wang[1], Yuzhe Wang[1], Dong He[1], Yuqing Huang[1], Yuanyuan Du[2], Hongtao Zheng[2], Shenghong Hu[1], and Zhenli Zhu[1,2*]

[1]State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430074, China

[2]Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan, 430074, China

Correspondence and requests for materials should be addressed to:
Dr. Zhenli Zhu, State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China, Email: zlzhu@cug.edu.cn
Dr. Xing Liu, State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China, Email: xliu_cug@163.com

Table of Contents

Section 1. Optimization of Experimental Conditions

Effect of formic acid concentration. Studies have shown that the addition of formic acid can greatly enhance the efficiency of mercury vapor generation. Therefore, the effect of formic acid concentration on signal intensity was investigated in the range of 0.1 to 4 % (v/v). As observed in Figure S1a, the signal of Hg reaches its maximum at a formic acid concentration of 0.4 %. Hence, a formic acid concentration of 0.4 % was selected for subsequent studies.

Effect of discharge current. The signal intensity of the analyte is highly dependent on the discharge current in PEVG. Therefore, the impact of discharge current was evaluated within the range of 10 - 30 mA. As depicted in Figure S1b, the signal of Hg reaches its maximum at 25 mA. Hence, a discharge current of 25 mA was chosen for subsequent studies.

Effect of sample flow rate. The sample flow rate affects the droplet size and the reaction between the sample and the plasma, playing a crucial role in the PEVG process. The influence of solution sample flow rate on the signal intensity was investigated within the range of 0.5 - 3.5 mL min^{-1}. From Figure S1c, it can be observed that ^{202}Hg signal of PEVG linearly increases as the flow rate varies from 0.5 to 1.5 mL min^{-1}. Beyond 1.5 mL min^{-1}, the signal growth slows with increasing flow rate. To avoid fractionation due to low vaporization efficiency, a sample introduction flow rate of 1.5 mL min^{-1} was chosen, resulting in a vaporization efficiency of 97.5%.

Effect of Ar flow rate. The signal intensity is significantly influenced by the flow rate of Ar (carrier gas of Hg) since it impacts plasma stability and analyte concentration in the carrier gas. We investigated the Ar gas flow rate ranging from 0.2 to 0.4 L min^{-1} (Figure S1d). The optimal signal was attained at an Ar flow rate of 0.3 L min^{-1}, which was employed for subsequent investigations

Section 2. Hg isotopic fractionation in PEVG

For additional performance assessment, the precision of PEVG in measuring Hg isotopes was examined. Several investigations have indicated that isotope fractionation may take place during plasma vapor generation, and it is crucial to understand the features of induced isotopic fractionation in this process for obtaining accurate isotope. The Hg isotope fractionation in the PEVG process is mass dependent fractionation, where ln($^{200}Hg/^{198}Hg$)-ln($^{199}Hg/^{198}Hg$) and ln($^{202}Hg/^{198}Hg$)-ln($^{199}Hg/^{198}Hg$) graph plotted linearly along the line with the slope of 1.9051 and 3.6831 (R^2=0.9928, 0.9899), and the corrected isotope ratios were calculated using linear regression slope method.

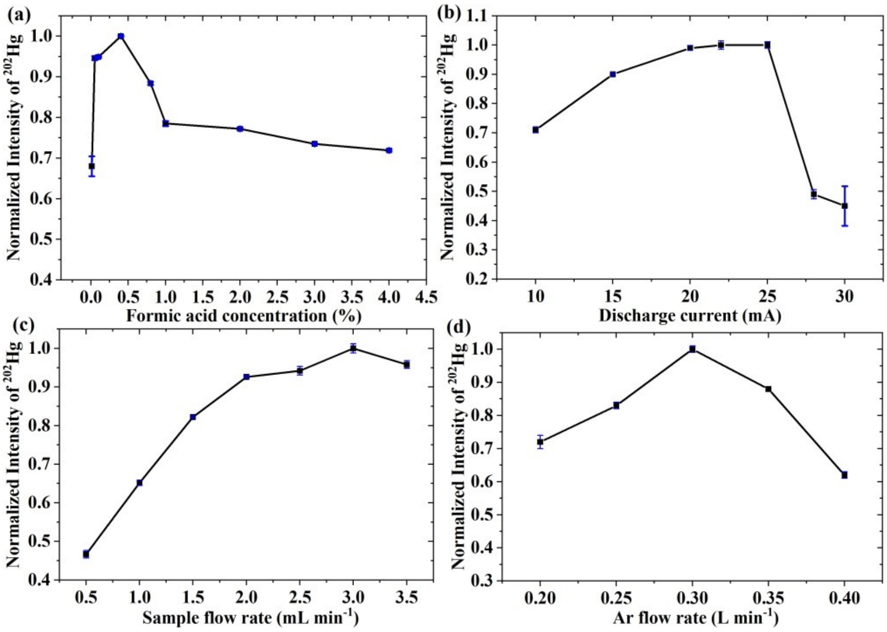

Figure S-1. Effect of the formic acid concentration (a), discharge current (b), sample flow rate (c), Ar flow rate on the ^{202}Hg signal intensity (d). Each point is the average from three measurements (n = 3). Error bars are defined as ±SD.

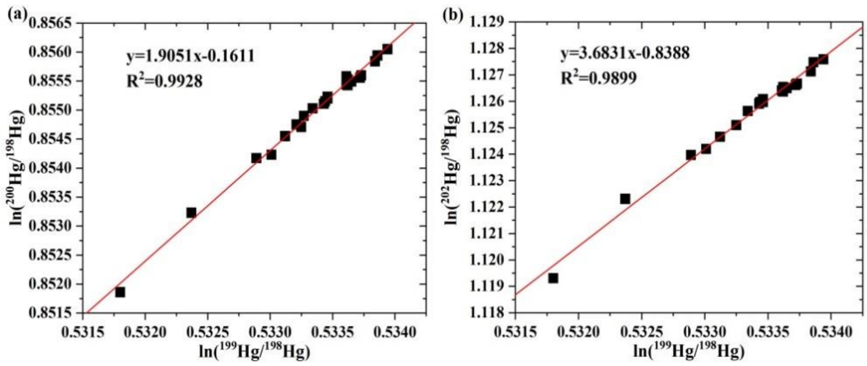

Figure S-2. Plot of ln(^{200}Hg/^{198}Hg)-ln(^{199}Hg/^{198}Hg) (a), ln(^{202}Hg/^{198}Hg)-ln(^{199}Hg/^{198}Hg) (b) data obtained with PEVG-MC-ICPMS for an standard solution of 10 μg L^{-1} Hg NIST 3133.