Electronic supplementary information (ESI)

Microplasma-induced vapor generation for rapid screening of mercury in fruits and vegetables

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Author Contributions

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

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1. Effect of punctured position on the fruit surface.

The effect of the punctured position on the fruit surface was investigated. Three test positions located at the top, middle and bottom (a, b, and c) of a tomato were punctured, and then the juices collected from these positions were analyzed, as shown in Figure S1. The results show that the intensities of Hg obtained from different positions are slightly different. The reason needs to be further explored. Since the position of b was easy to be operated and offer highest intensity, thus, the sampling was performed at the position of b in subsequent experiments.

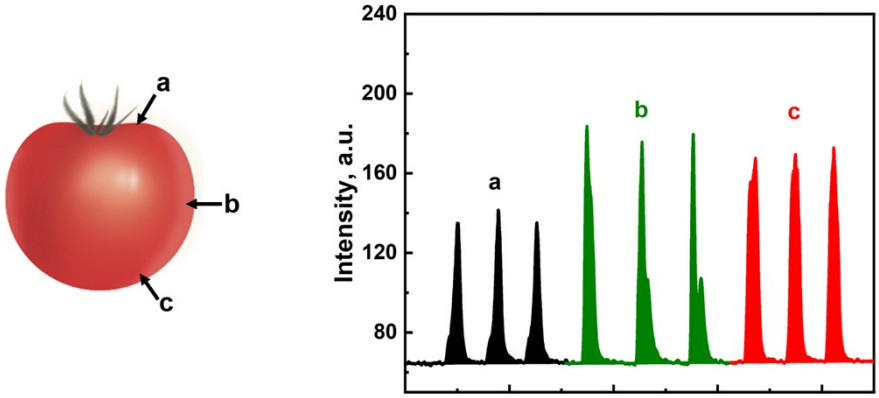

Figure S1. Optimization of the punctured position on the fruits surface.

2. Effect of capillary on the microplasma-induced vapor generation.

The change in temperature with increasing discharge time was monitored with an IR thermometer, as shown in Figure S2a. The change in temperature is not obvious and the temperature is increased from 20 to 28 °C even 30 min of discharge time used. Finally, the effect of temperature on the response of mercury was investigated by wrapping a resistant filament (nichrome wire) around the stainless-steel capillary. The results summarized in Figure S2b show that the change in the response of mercury is not evident as the temperature ranging from 20 to 40 °C. Therefore, the effect of temperature can be ignored in the proposed method because the change of temperature is not obvious during the analytical process.

The effects of capillary type and their inner diameter on the capillary liquid electrode discharge microplasma-induced vapor generation of mercury were investigated using silica capillary and stainless-steel capillary with inner diameter ranging from 200 to 700 μm. As shown in Figure S1a, the intensity of atomic fluorescence for mercury increased from 200 to 500 μm and reached a plateau at bigger inner diameters regardless of the type of capillary. Thus, an inner diameter about 500 μm was used in the subsequent experiments. Although both silica capillary and stainless-steel capillary with a diameter about 500 nm could provide the highest intensity of atomic fluorescence for mercury, the tip of silica capillary was destroyed as the operation time prolonged to tens minutes, thus resulting in the instability of microplasma and decreasing the vapor generation efficiency of mercury (please see Movie S1). In contrast to silica capillary, stainless-steel capillary not only have longer operation life but also remains the discharge microplasma stable over the operation time (please see Movie S2). Therefore, a stainless-steel capillary with 500 μm of inner diameter was chosen for the following experiments. The effect of the length of the stainless-steel capillary on the response of mercury was also investigated with analytical results summarized in Figure S1b. The analytical results show that the response significantly increased with increasing the length of stainless-steel capillary in the range of 1.5–2.5 cm, followed by an obvious decrease at longer length. The results show that the optimal capillary length is about 2.5 cm.

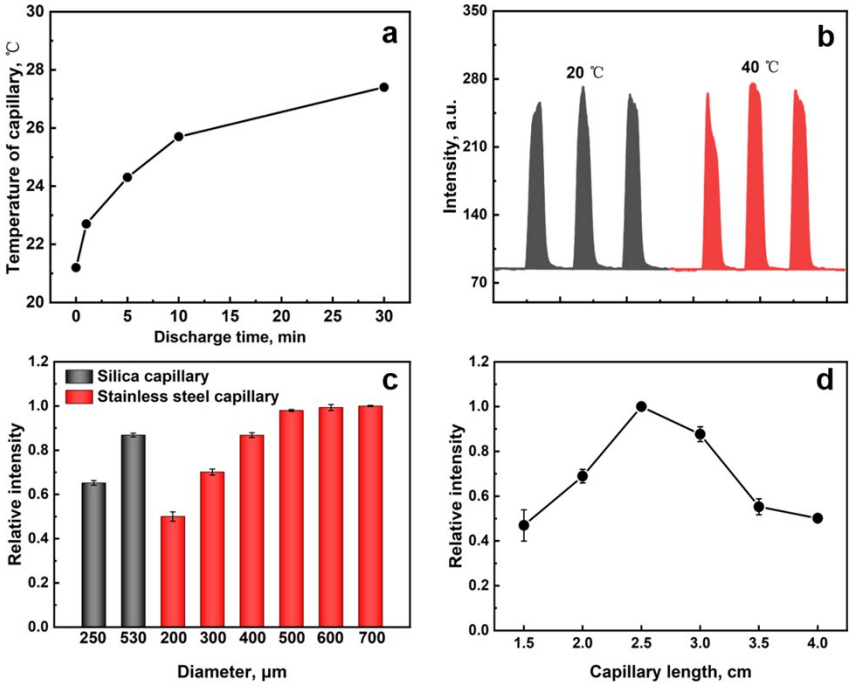

Figure S2. Effects of the capillary. (a) Sampling temperature of capillary; (b) the effect of temperature of capillary; (c) type and diameter of capillary; (d) length of capillary.

3. Optimization of operation parameters for CLED-μPIVG of mercury.

The effect of discharge voltage in the range of 1.64 to 2.36 kV was investigated. The results summarized in Figure S3a show that the intensity of atomic fluorescence for mercury increased with increasing the discharge voltage from 1.64 to 2.0 kV. The discharge failed to be sustained when the discharge voltage was lower than 1.64 kV. However, when the voltage was higher than 2.0 kV, large amounts of water vapor was generated and then influences the stability of discharge. Therefore, 2.0 kV of the discharge voltage was selected for the subsequent experiments.

As shown in Figure S3b, the obtained intensity increased with the discharge gap varying from 1 to 3 mm, following a decreasing intensity when the gap was higher than 3 mm. Thus, a discharge gap of 3 mm was used for the subsequent experiments.

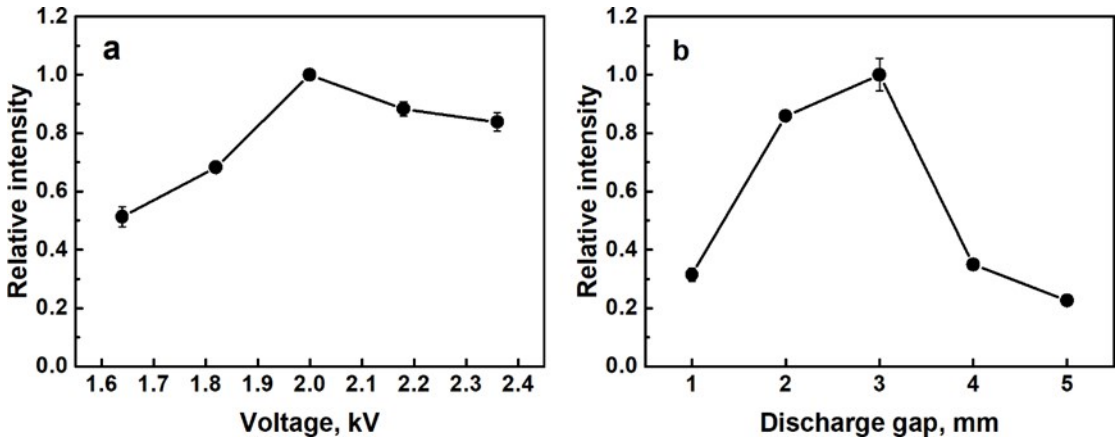

Figure S3. Effect of microplasma generation: (a) discharge voltage; (b) discharge gap.

4. Optimization of operation parameters for atomic fluorescence spectrometer.

The operation parameters of atomic fluorescence spectrometer (AFS), including the flow rate of carrier gas, flow rate of shield gas, negative voltage, and height of atomizer, were optimized. The results are summarized in Figure S4. As shown in Figure S4a, the intensity of atomic fluorescence for mercury firstly increased as the flow rate of carrier gas increased from 150 to 250 mL min^{-1} and then decreased at higher flow rate. This is probably because that stable plasma and efficient separation and transport of the volatile species could not be accomplished when the Ar flow rate was lower than 250 $mLmin^{-1}$. However, higher flow rate of carrier gas significantly diluted the analytes and decreased the AFS responses of Hg. Therefore, the carrier gas flow rate of 250 mL min^{-1} was selected. For the optimization of other parameters of AFS, as shown in Figure S4b, c, and d, the optimum parameters for shielding gas flow rate, negative voltage, and the height of atomization were 1000 mL min^{-1}, 280 V, and 10 mm, respectively.

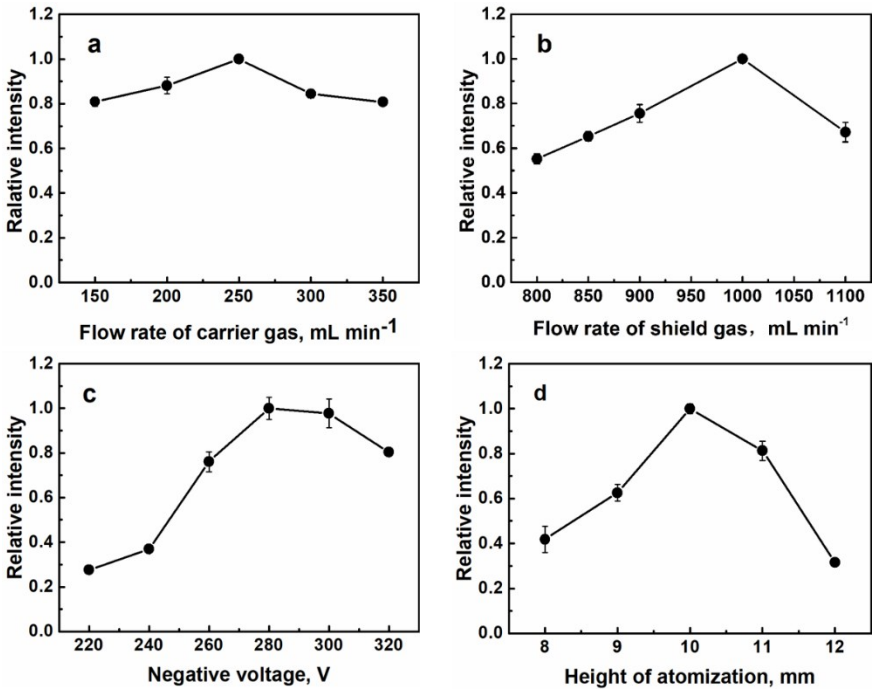

Figure S4. Effects of instrumental parameters. (a) Flow rate of carrier gas; (b) flow rate of shield gas; (c) negative voltage; (d) height of atomization.

5. Digestion of fruit and vegetable samples using microwave assisted digestion method.

The fruit samples were digested as follows: the tested fruit and vegetable samples were squeezed into a homogenate with a juicer. Aliquots of samples of 0.5 g of the homogenate were weighed into precleaned Teflon vessels and 5 mL of HNO_3 and 2 mL H_2O_2 were then added. The vessels were sealed and heated in a microwave oven (Master 40, Shanghai Sineo Microwave Chemistry Technology Co., China) operated under the following conditions: 10 min at 130 °C and 700 W; 20 min at 150 °C and 1400 W; 20 min at 180 °C and 1400 W. The caps were removed after cooling. Finally, the sample was diluted to 10 mL with DIW and stored at 4 °C prior to analysis

6. Potential application of CLED-μPIVG as sampling technique for miniature microplasma optical emission spectrometry.

According to previous works,[1,2] various chemical vapor generation (CVG) approaches are ideal sample introduction means for miniature microplasma optical emission spectrometry due to their advantages of high sample introduction efficiencies and efficient separation of analytes from the condense liquid phase. Therefore, the feasibility of the application of the CLED-μPIVG to coupling with miniature point discharge optical emission spectrometry (μPD-OES) for the field analyses of fruits and vegetables was investigated. A juice sample with an undetectable concentration of mercury was analyzed by CLED-μPD-OES before and after spiking with 1 mg L^{-1} Hg^{2+}. The analytical results are summarized in Figure S5, the specific mercury atomic emission signal (Hg 253.6 nm) from the sample spiked with 1 mg L^{-1} Hg^{2+} can be obviously detected by the proposed system. These analytical results support the feasibility of application of the CLED-μPIVG to couple with the μPD-OES for the determination of mercury. Compare to other CVG techniques such as hydride generation and photochemical vapor generation, the CLED-μPIVG not only retains the advantages of the conventional CVG techniques but also provides several unique advantages of simple experiment setup, simple reaction, and low power consumption, thus retaining the promising potential to couple with microplasma OES for the field analyses of fruits and vegetables.

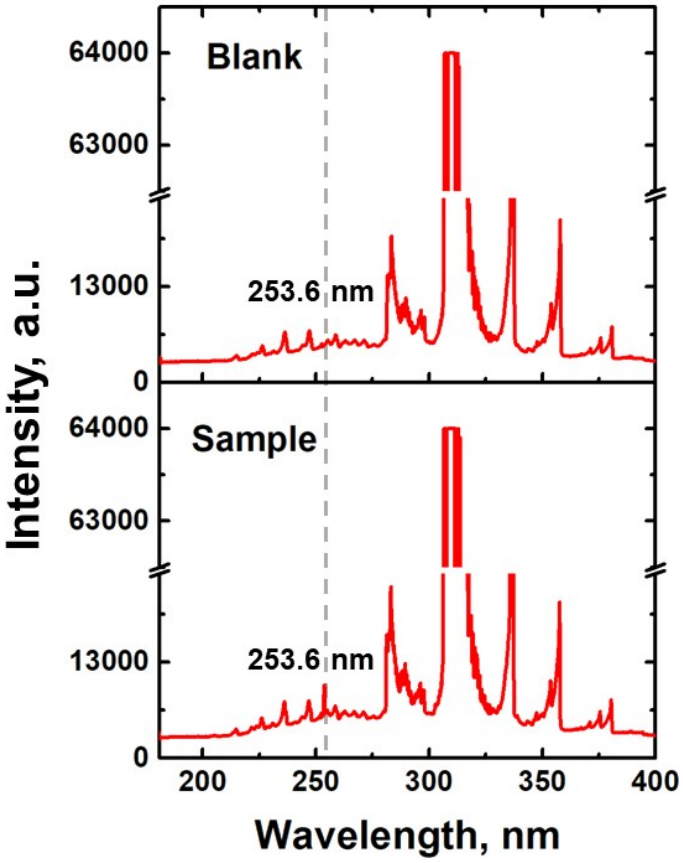

Figure S5. Optical emission spectra were obtained by analyzing juice sample by CLED-μPD-OES before and after spiking with 1 mg L^{-1} Hg^{2+}.

7. References.

1. A. Leng, Y. Lin, Y. Tian, L. Wu, X. Jiang, X. Hou and C. Zheng, *Anal. Chem.*, 2017, **89**, 703-710.

2. S. Xia, A. Leng, Y. Lin, L. Wu, Y. Tian, X. Hou and C. Zheng, *Anal. Chem.*, 2019, **91**, 2701-2709.