

Supporting Information

Dielectric Barrier Discharge for High Efficiency Plasma-Chemical Vapor Generation of Cadmium

Zhenli Zhu^{†*}, Qingju, Wu[§], Zhifu Liu^{†,‡}, Lu Liu[§], Hongtao Zheng[§], Shenghong Hu^{†,‡}

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

[‡]Faculty of Earth Sciences, China University of Geosciences (Wuhan), China, 430074

[§] Faculty of Material Science and Chemistry, China University of Geosciences (Wuhan), China, 430074

* To whom correspondence should be addressed.

Phone: +86-27-6788-3455. Fax: +86-27-6788-3456.

E-mail: zhuzl03@gmail.com, zlzhu@cug.edu.cn

1. Optimization of Thin-film DBD Plasma-CVG

a) **Effect of Discharge Gas Identity and Gas Flow Rate.** In addition to cold vapor AFS mode, the effect of discharge gas on the Cd fluorescence signal with QTA on was also investigated. It was also observed that Cd signal intensity in He-DBD was much higher than that from Ar-DBD, which was similar with results measured in cold vapor mode. As shown in Figure S1, when the QTA was on, the maximum signal was obtained at a flow rate of 700 mL min⁻¹ in He-DBD, while the optimal Ar flow rate was found to be at 600 mL min⁻¹. The signal decreased at higher flow rates, probably due to the dilution of the analyte by the plasma gas. Therefore, gas flow rates of 700 mL min⁻¹ and 600 mL min⁻¹ was chosen for the He-DBD and Ar-DBD, respectively, in the flowing study with QTA on.

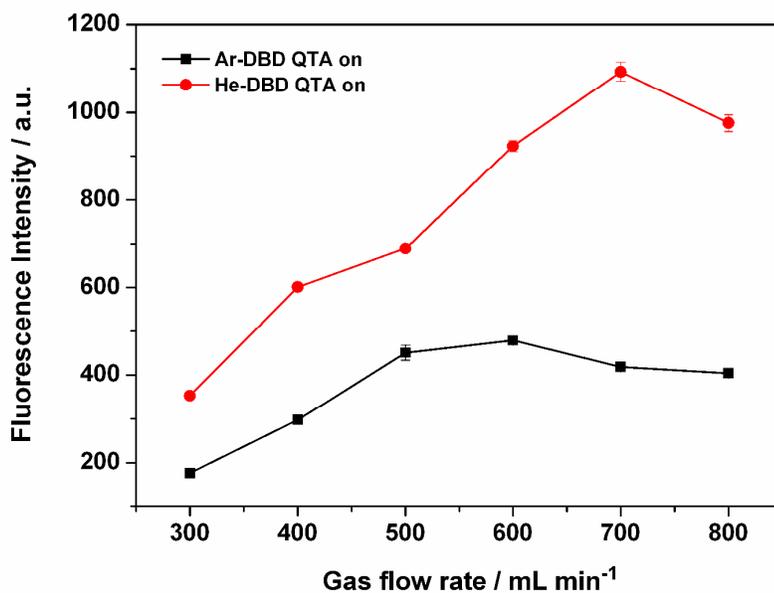


Figure S1. Optimization of carrier gas flow rate with heating applied to the QTA. (Cd concentration, 5 $\mu\text{g L}^{-1}$; Sample flow rate, 4.5 mL min⁻¹; Hydrogen flow rate, 125 mL min⁻¹ in Ar-DBD, 100 mL min⁻¹ in He-DBD; Power, 18 W.) Error bars in the figure represent standard deviations of the results (n=3).

b) Effect of Hydrogen flow rate. The effect of hydrogen gas flow rate on the plasma-CVG process was also investigated with heated QTA. It was observed that the Cd signal increased with increasing flow rate of hydrogen from 25 to 100 mL min⁻¹ in He-DBD. At higher hydrogen flow rate, the signal decreased, which may be caused by the cooling effect of hydrogen on the DBD plasma. In the Ar-DBD, similar trend was observed with the maximum response found at a hydrogen flow rate of 125 mL min⁻¹. Based on these results, hydrogen gas flow rates of 100 mL min⁻¹ and 125 mL min⁻¹ were selected for the He-DBD and Ar-DBD, respectively, in the flowing study with heated QTA.

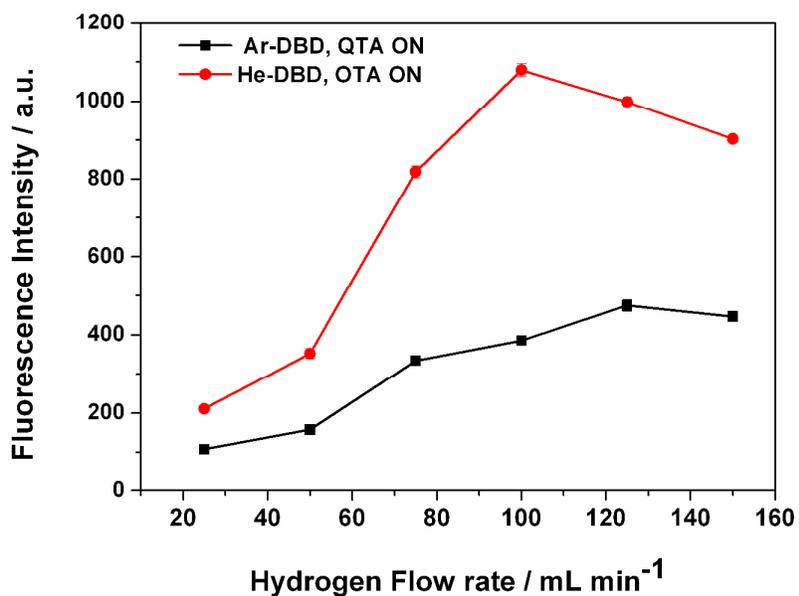


Figure S2. Influence of hydrogen gas flow on the fluorescence signal of cadmium with heated QTA. (Cd concentration, 5 $\mu\text{g L}^{-1}$, Sample flow rate, 4.5 mL min⁻¹; Gas flow rate, 600 mL min⁻¹ in Ar-DBD; 700 mL min⁻¹ in He-DBD; Power, 18 W.) Error bars in the figure represent standard deviations of the results (n=3).

c) Influence of sample flow rate

The influence of the flow rate of sample (the carrier solution) on the Cd fluorescence signal with QTA on was also evaluated by changing the rotation speed of the peristaltic pump from 2.0 to 6.0 mL min⁻¹. Similar with that in cold vapor mode, the peak area of the Cd signal was almost identical (at higher flow rates, it decreased but not significantly), which indicated that the similar vapor generation efficiency of Cd. From Figure S3 we found that, with the increase of the flow rates, the peak height signal intensity increased significantly at first and then decreased as the flow rate higher than 4.5 mL min⁻¹. The decrease of intensity at higher flow rate may be ascribed to the reduced the residence time (i.e reaction time) of the analyte in the plasma field. Therefore, a sample flow rate of 4.5 mL min⁻¹ was chosen in subsequent studies.

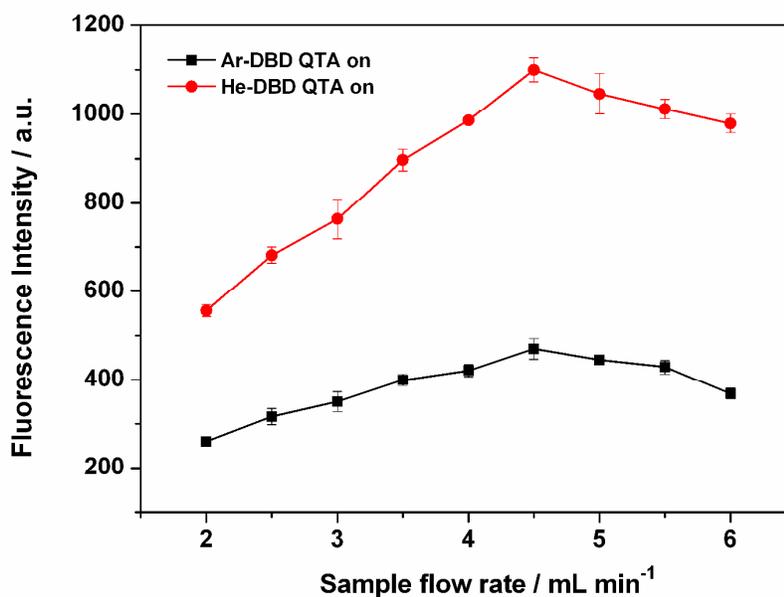


Figure S3. Effect of sample flow rate on the fluorescence signal (peak height) with heating applied to the QTA. (Cd concentration, 5 $\mu\text{g L}^{-1}$; Ar flow rate, 600 mL min⁻¹; He flow rate, 700 mL min⁻¹; Hydrogen flow rate, 125 mL min⁻¹ in Ar-DBD, 100 mL min⁻¹ in He-DBD; Power, 18 W.) Error bars in the figure represent standard deviations of the results (n=3).

d) Effect of discharge power

The effect of the discharge power on the vapor generation of Cd was also evaluated ranging from 5 to 30W. As shown in Figure S4, the maximum signal of $5 \mu\text{g L}^{-1}$ of cadmium was found at 18 W. It is not surprising that the higher discharge power enhances the vapor generation of Cd since the dissociation or excitation of H_2 may also be increased at higher power. However, the Cd signal decreased at power of 30 W, which may be explained by that stronger discharge may cause the dissociation of the generated Cd vapor. Therefore, a discharge power supply of 18 W was employed in the remaining parts of the study.

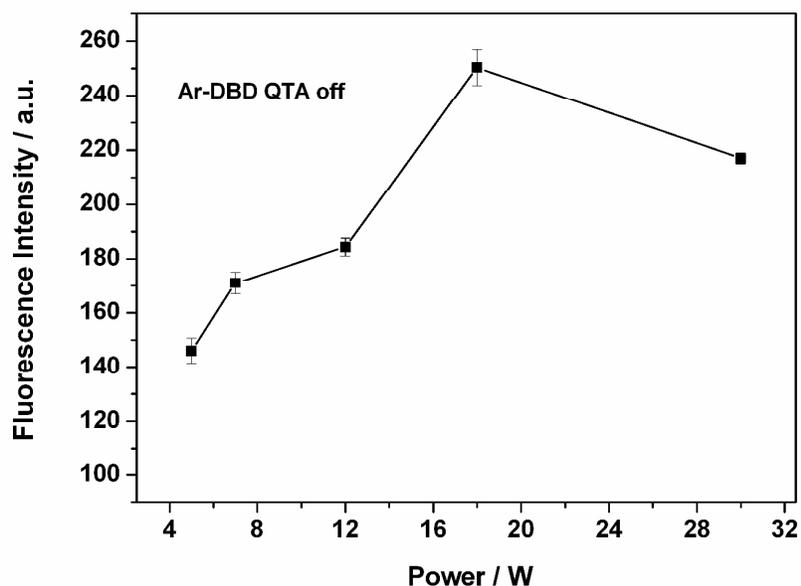


Figure S4. Influence of discharge power on the Cd fluorescence signal measured at room temperature. (Cd concentration, $5 \mu\text{g L}^{-1}$; Ar flow rate, 500 mL min^{-1} ; Hydrogen flow rate, 50 mL min^{-1} ; Power, 18 W.) Error bars in the figure represent standard deviations of the results ($n=3$).

2. Comparison of Cd Vapor Generation Efficiencies.

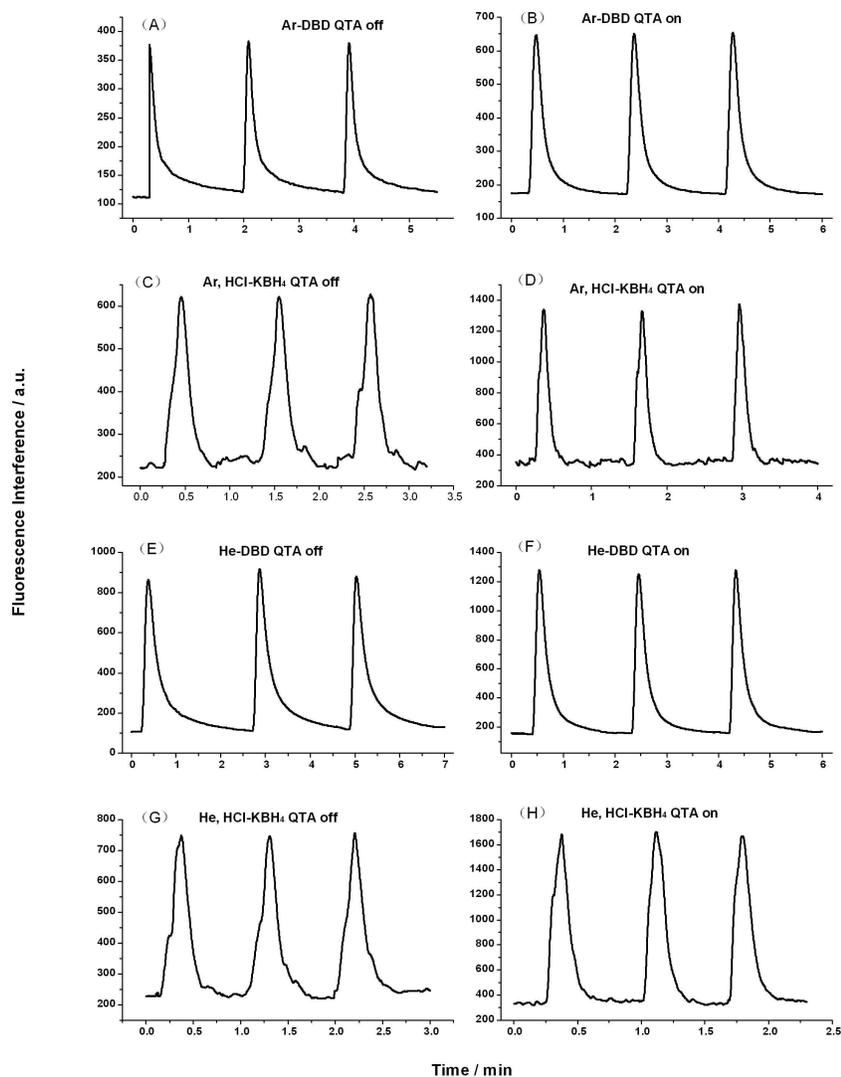


Figure S5. Comparison of the generation efficiencies (Cd signal) arising from eight modes. (Cd concentration, $5 \mu\text{g L}^{-1}$; conventional CVG: the reducing solution, 3.5% (m/v) NaBH_4 , 1.6% (m/v) thiourea, 0.7 mg L^{-1} cobalt in 0.2% (m/v) NaOH ; carrier solution, 2.5% HCl ; DBD plasma-CVG: carrier solution, water). A-D: carrier gas, Ar; E-H: carrier gas, He. A: Ar-DBD plasma-CVG with the QTA off; B: Ar-DBD plasma-CVG with the QTA on; C: conventional CVG with the QTA off; D: conventional CVG with the QTA on; E: He-DBD plasma-CVG with the QTA off; F: He-DBD plasma-CVG with the QTA on; G: conventional CVG with the QTA off; H: conventional CVG with the QTA on.

3. The repeatability of He-DBD plasma-CVG

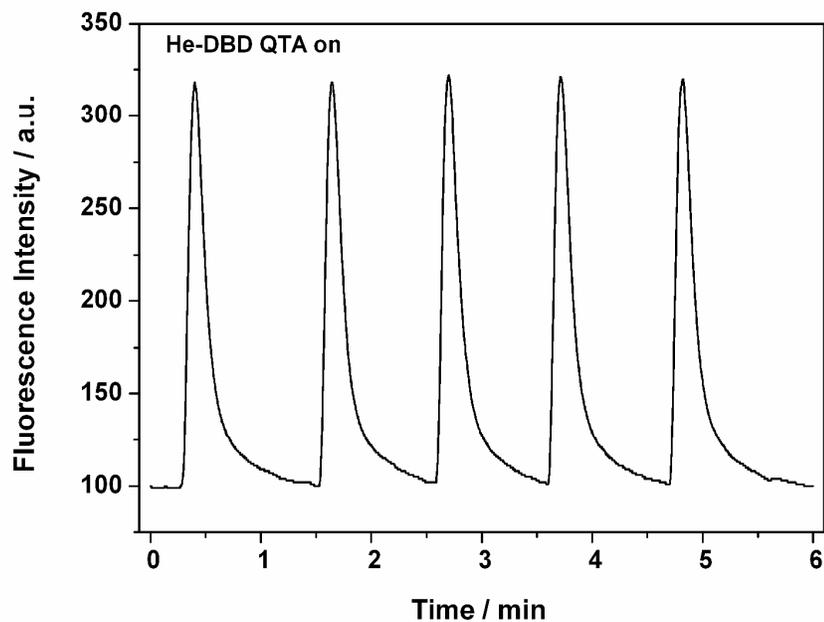


Figure S6. Stability of the thin-film He-DBD plasma-CVG-AFS technique with heating applied to the QTA, illustrated with 5 repetitive injections of a $1 \mu\text{g L}^{-1}$ Cd solution. (Sample flow rate, 4.5 mL min^{-1} ; He flow rate, 700 mL min^{-1} ; Hydrogen flow rate, 100 mL min^{-1} ; Power, 18 W.)