

Supporting Information

Sensitivity improvement of solution cathode glow discharge- atomic emission spectrometry by refrigerating anodes for optical determination of metal elements

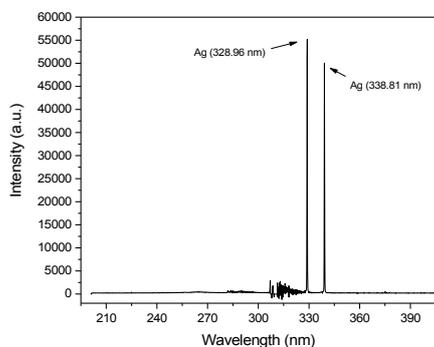
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and Chunhong Lai

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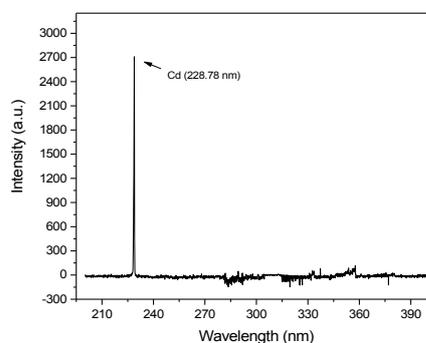
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1. Analytical spectral lines

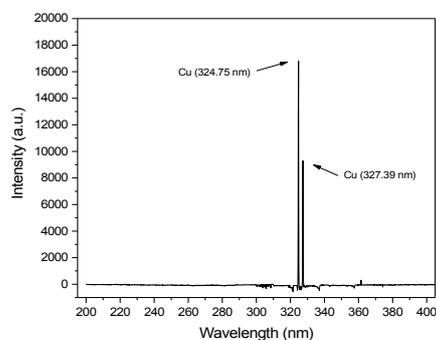
Heavy metal elements usually exhibit multiple emission spectral lines in the emission spectrum. Therefore, the selection of the appropriate spectral line is the primary key to detecting heavy metal elements. In this study, an optical fiber spectrometer was used to detect and compare the spectral signals of a blank solution and the analyze solutions to find the optimal spectral detection lines of heavy metal elements. As shown in Figure SI-1, Ag has apparent emission spectral lines at 328.96 and 338.81 nm. Comparing the performance of the two Ag spectral lines in Fig. SI-1 (a), the spectral intensity at 328.96 nm is 9.34% stronger than that at 338.81 nm. Therefore, we selected 328.96 nm as the Ag detection spectral line. Similarly, as shown in Fig. SI-1 (b-e), the spectral lines corresponding to Cd, Cu, Mn and Zn are at 228.78, 324.75, 279.48 and 214.03 nm, respectively. The concentration of solution selected in the subsequent experiments is: 5 mg/L Ag, 5 mg/L Cu, 10 mg/L Cd, 10 mg/L Mn and 10 mg/L Zn.



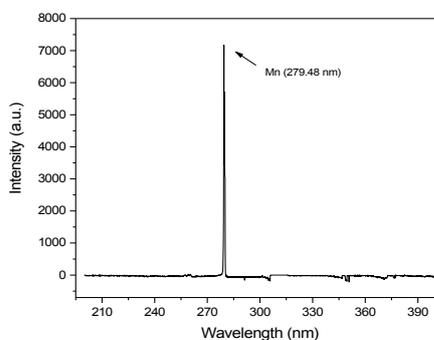
(a) Ag



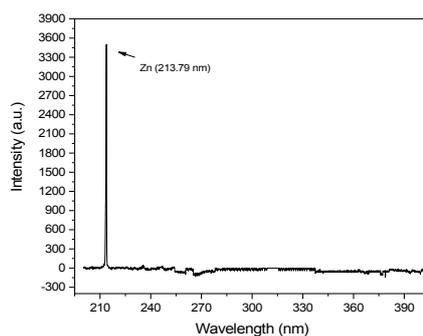
(b) Cd



(c) Cu



(d) Mn

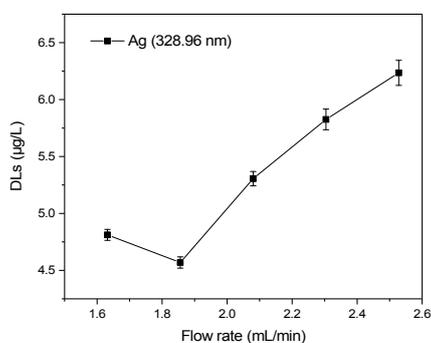


(e) Zn

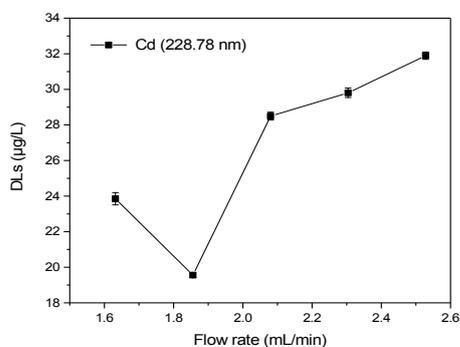
Appendix Fig. 1. Analytical spectral lines of metal elements. The spectral intensity of the solution and background analyze solution measured ten times and averaged. The corrected spectrogram is obtained by calculating the difference: (a) Ag, (b) Cd, (c) Cu, (d) Mn and (e) Zn.

2. Effect of the solution flow rate on DLs

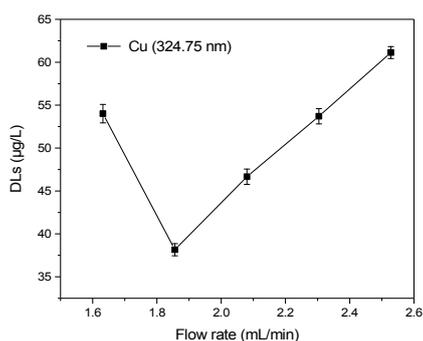
The stability of plasma generated in the solution cathode was directly affected by the solution flow rate. In this study, we evaluated the effects of flow rate from 1.60 to 2.60 mL/min on the DLs of metal elements, Fig. SI-2. When the flow rate is lower than 1.60 mL/min, the plasma exhibits fluctuations and quenching, whilst at the solution flow rate higher than 2.60 mL/min, the plasma stability decreases due to the fast flow rate. Within the detection range, as the flow rate increases, the DLs of the signal firstly decrease and then increase, reaching the lowest value at 1.86 mL/min. This phenomenon may be assigned to the maximum amount of analyze entering the discharge zone at optimal solution flow rate and the additional vapor evaporation in the higher solution flow rate. Therefore, the solution flow rate was set at 1.86 mL/min in subsequent experiments.



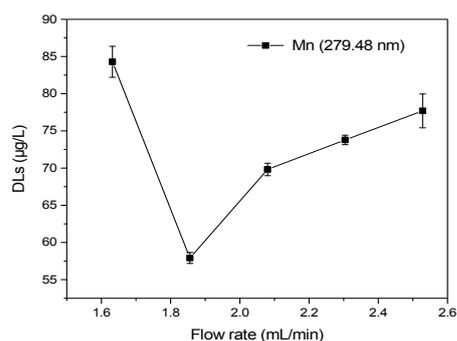
(a) Ag



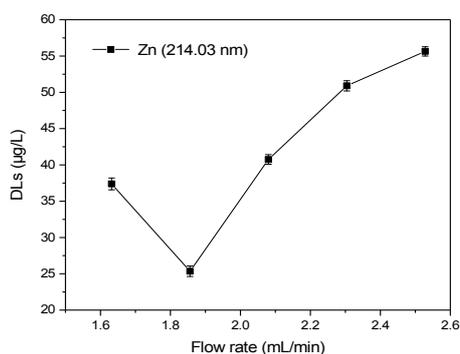
(b) Cd



(c) Cu



(d) Mn

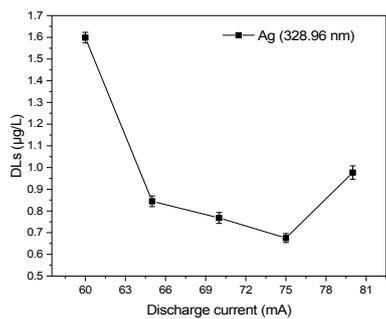


(e) Zn

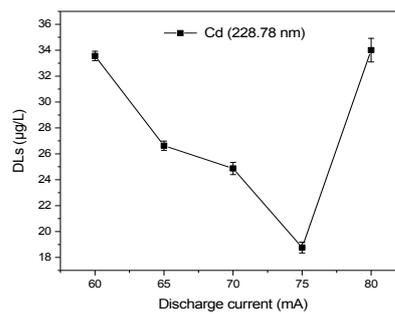
Appendix Fig. 2. Effect of the solution flow rate on DLs of metal elements: (a) Ag, (b) Cd, (c) Cu, (d) Mn and (e) Zn.

3. Effect of the discharge current on DLs

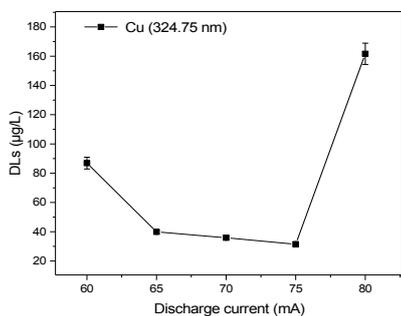
The discharge current significantly influences the plasma excitation state in the process of plasma generation. Fig. SI-3 illustrates the influence of the discharge current on the DLs of metal elements in the range from 60 to 80 mA. The spectral intensity of several metal elements increases with the increase of discharge current because atoms and ions in the plasma were more easily excited at high current conditions, resulting in an increase in light intensity. However, the enhancement of the excited state undermines the plasma stability, and a higher current degrades the quartz capillary, making the discharge unstable. The DLs of Ag, Cd, Cu, Mn and Zn at 75 mA are the lowest, Fig. SI-3. Hence, 75 mA is set as the subsequent experimental parameter.



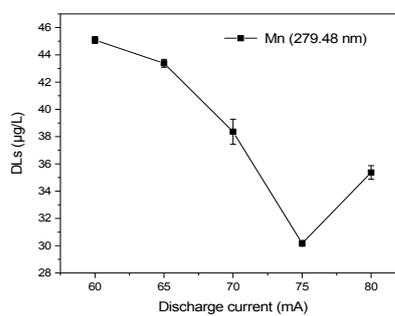
(a) Ag



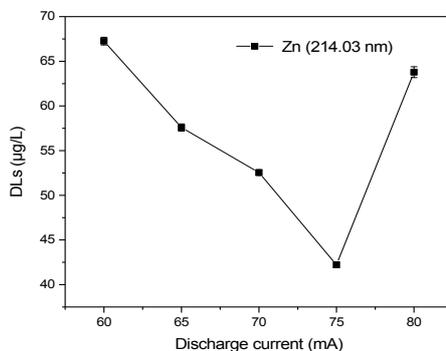
(b) Cd



(c) Cu



(d) Mn



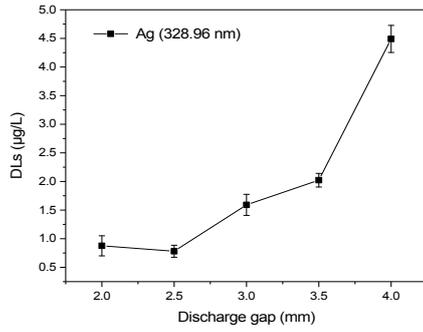
(e) Zn

Appendix Fig. 3. Effect of the discharge current on DLs of metal elements: (a) Ag, (b) Cd, (c) Cu, (d) Mn and (e) Zn.

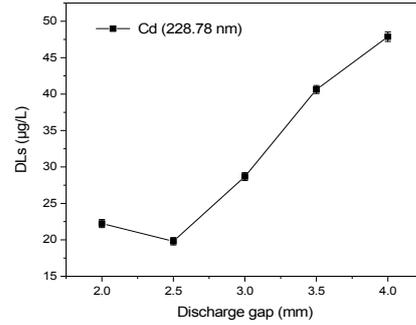
4. Effect of the discharge gap on DLs

The effect of the discharge gap on the DLs is shown in Fig. SI-4. When the pole spacing is too small, the plasma state cannot be fully excited, and the metal anode quickly turns red, causing a more significant material loss of the metal anode. When the magnetic pole spacing is too large, the normal discharge cannot be maintained under a certain voltage, plausibly because of the small molecules, such as NO and N₂, in the

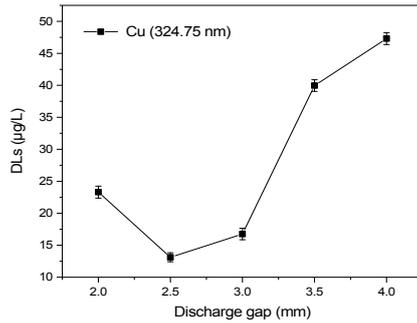
air entering the discharge gap area. Therefore, according to the optimal parameters of discharge current, we chose a 2 - 4 mm pole spacing to study the influence of the discharge gap of DLs. Fig. SI-4 shows that the DLs of the investigated metal elements increase with the discharge spacing. The smallest DL is obtained when the electrode pitch is 2.5 mm, so the distance of 2.5 mm was chosen as an experimental parameter.



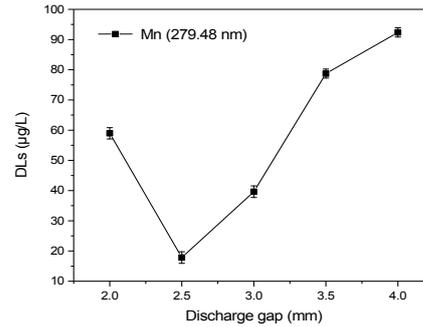
(a) Ag



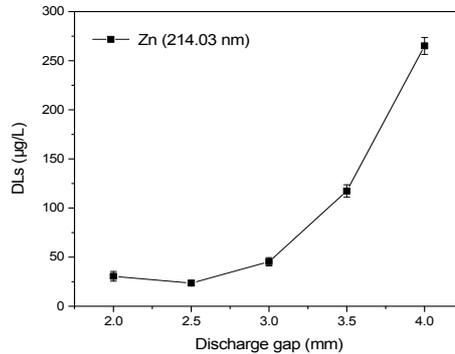
(b) Cd



(c) Cu



(d) Mn

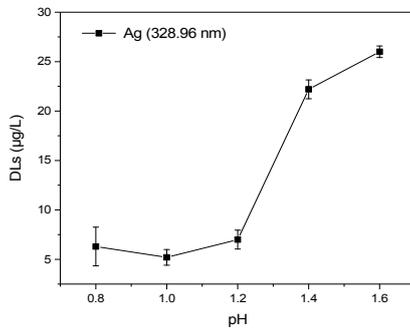


(e) Zn

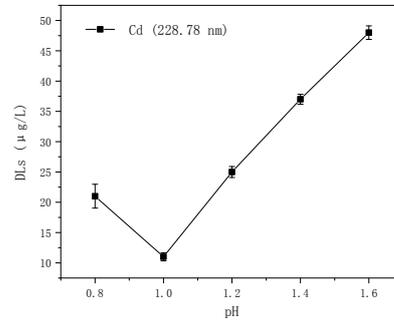
Appendix Fig. 4. Effect of the discharge gap on DLs of metal elements: (a) Ag, (b) Cd, (c) Cu, (d) Mn and (e) Zn.

5. Effect of the solution pH on DLs

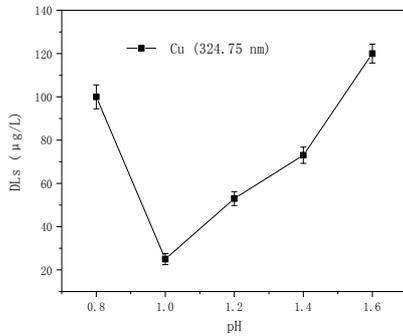
The pH of the sample solution affects the sensitivity and conductivity of the plasma during discharge. In this experiment, the influence of the pH in the range from 0.8 to 1.6 on the DLs of metal elements was studied, as shown in Fig. SI-5. When the solution pH is higher than 1.7, the investigated metal elements are hardly excited. When the solution pH is less than 0.8, the discharge is unstable. However, within the solution pH range from 0.8 to 1.6, the DLs of the investigated metal elements initially decrease and then increase, and the DL is the lowest at pH 1.0. Therefore, the solution pH of 1.0 was selected as the subsequent experimental condition.



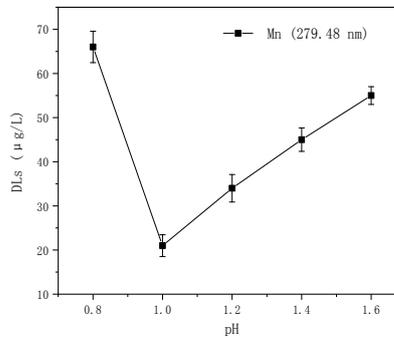
(a) Ag



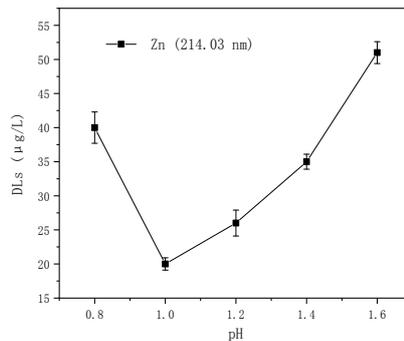
(b) Cd



(c) Cu



(d) Mn



(e) Zn

Appendix Fig. 5. Effect of pH on DLs of metal elements: (a) Ag, (b) Cd, (c) Cu, (d) Mn and (e) Zn.