

## Supplementary Information (SI)

### **Ultra-sensitive determination of inorganic arsenic valence by solution cathode glow discharge-atomic emission spectrometry coupled with hydride generation**

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## 1. Optimization of the SCGD parameters

### 1.1 Optimization of applied voltage

The influence of the applied voltage on the detection limit is shown in Fig. S1. Plasma was quickly generated upon application of voltage to the electrodes, and the SCGD plasma was stable in the 1030–1080 V voltage. As shown in Fig. S1, the As DL decreased continuously as the voltage was increased from 1030 to 1060 V, however, it began to increase over the 1060 to 1080 V voltage. A DL minimum was observed at an applied voltage of 1060 V, consequently, an applied voltage of 1060 V was employed in subsequent studies. It should be noted that the total SCGD input power was less than 100 W, hence, the SCGD source could be powered by a battery.

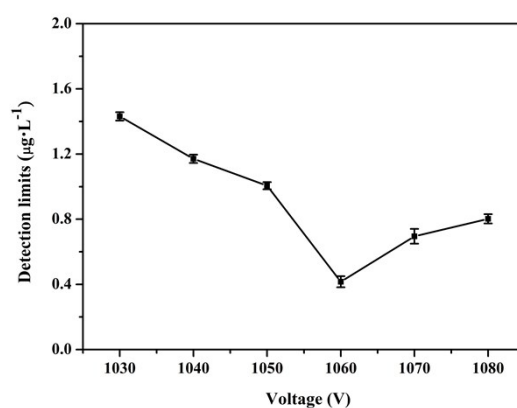


Fig. S1. Effect of applied voltage on the As DL

### 1.2 Optimization of the acid

In this work, three acids, namely HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub>, were adjusted to pH 1.0 and passed into the SCGD system at the discharge cathode. Among these acids, HCl provided the lowest DL, while H<sub>2</sub>SO<sub>4</sub> gave the highest (Fig. S2). The mobilities of the electrolyte ions (conductivity) decrease with increasing anion size, resulting in lower current since the current depends on the conductivity of the solution. Hence, lower intensity signals were observed when acids with larger anions were used. Consequently, HCl at pH 1.0 was selected as the electrolyte solution for the detection of arsenic.

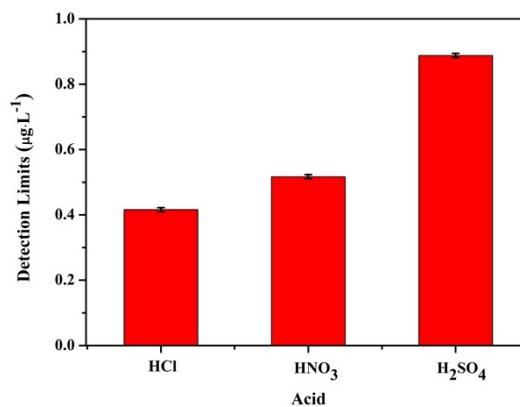


Fig. S2. Effect of acid on the DL of As

### 1.3 Optimization of electrolyte pH

It is well known that SCGD is influenced by solution pH. During the experiments, we found that the SCGD DL strongly depended on the pH of the electrolyte solution (adjusted with HCl). Fig. S3 shows the effect of pH on the As DL; the DL was observed to decrease with increasing pH from 0.6 to 1.0, and then increased between pH 1.0 and 1.4. The plasma is unstable below pH 0.6, while the signal intensities are weak above pH 1.4. Therefore, it was determined that stable plasma could be maintained between pH 0.6 and 1.4, with the lowest As DL observed at pH 1.0, which was the optimal pH employed for arsenic analyses.

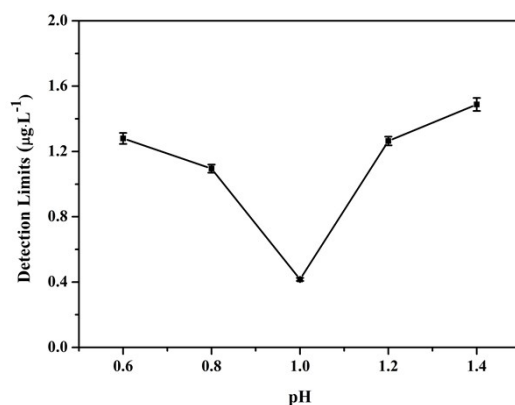


Fig. S3. Effect of pH on the DL of As

### 1.4 Optimization of solution flow rate

The influence of the solution flow rate on system performance was examined. As shown in Fig. S4, the DL was observed to decrease slightly with increasing flow rate over the 1.6 to 2.1  $\text{mL}\cdot\text{min}^{-1}$  range, but increased as the flow was increased from 2.1 to 2.3  $\text{mL}\cdot\text{min}^{-1}$ . The initial decrease in DL with increasing flow rate is attributed to the increasing working current. The slightly higher DLs at higher flow rates are a consequence of additional water vaporization, which reduces the energy or number of electrons available for atomic excitation. Therefore, the optimum flow rate of 2.1  $\text{mL}\cdot\text{min}^{-1}$  was employed in further experiments.

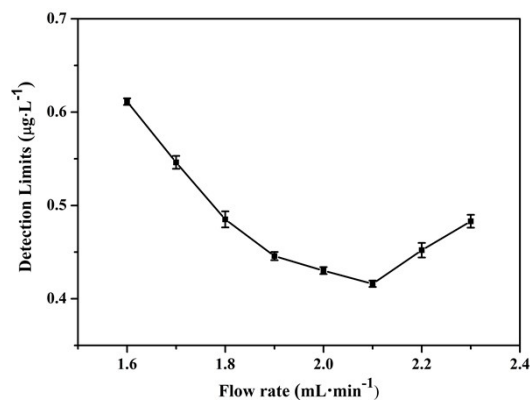


Fig. S4. Effect of flow rate on the DL of As