

# Electronic Supplementary Information

## Compact Electrothermal-flame Tandem Atomizer for Highly Sensitive Atomic Fluorescence Spectrometry

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## 1. Sample Preparation and Analytical Procedure

### 1.1 Sample Preparation

Approximately 250 mg of CRMs (GBW08510 and GBW08511) were weighed into 70 mL precleaned Teflon vessels, with adding 0.5 mL DIW for wetting the samples. 10 mL of HNO<sub>3</sub> and 2 mL of H<sub>2</sub>O<sub>2</sub> were then added. Three sample blanks were processed along with samples. The sealed vessels were heated in a Master 40 microwave oven (SINEO Corporation, Shanghai, China) operated under the conditions: 10 min at 130 °C and 1000 W, 10 min at 150 °C and 1000 W, 30 min at 180 °C and 1000 W. After cooling, the caps were removed and the digests were transferred to precleaned 100 mL Teflon crucibles and evaporated on an electric hot plate (Model EG20A, LabTech Corporation, Beijing, China) at 175 °C to near dry. The residues were diluted to 50 mL with 0.5% v/v HCl and then subjected to analysis after diluted to a suitable concentration in the linear range with 0.5% v/v HCl.

### 1.2 Analytical Procedure

**Table S-1. Heating program for the W-coil**

Step	Current (A)	Duration (s)	Description
1	2.7	45	Desolvation
2	2.8	15	Pyrolysis
3	0	5	Cooling*
4	4.5 for Cd and Pb; 5.0 for Au and Ag	10	Atomization/vaporization
5	9.0	4	Cleaning the residue off the W-coil
6	0	30	Cooling

\* The cooling step before the atomization/vaporization is generally used to cool the W-coil. In this case, the time needed for W-coil to reach the atomization/vaporization temperature is longer than that without and the signal profile would be broadened; and at the beginning of this step, the power supply would send a synchronization signal to the control software of AFS instrument to start data acquisition. Temperatures corresponding with current: 2.7 A, 300 °C ; 2.8 A, 310 °C; 4.5 A, 500 °C; 5.0 A, 650 °C; 9.0 A, 2200 °C.

## 2. Optimization of Tandem Atomizer for AFS Detection

### 2.1 Atomization/vaporization current

As shown in Figure S-1a and Figure S-2a, both responses from Cd and Pb increased significantly with increasing the current within 4.5 A, followed by obvious decrease at high current, so 4.5 A was selected for the subsequent experiments for Cd and Pb. Optimum sensitivities for Au and Ag were obtained in the range of 5 - 6 A and 4 - 5 A, respectively. A current of 5 A was selected for convenient simultaneous measurement.

### 2.2 Gas flow rate

#### 2.2.1 Carrier gas Ar

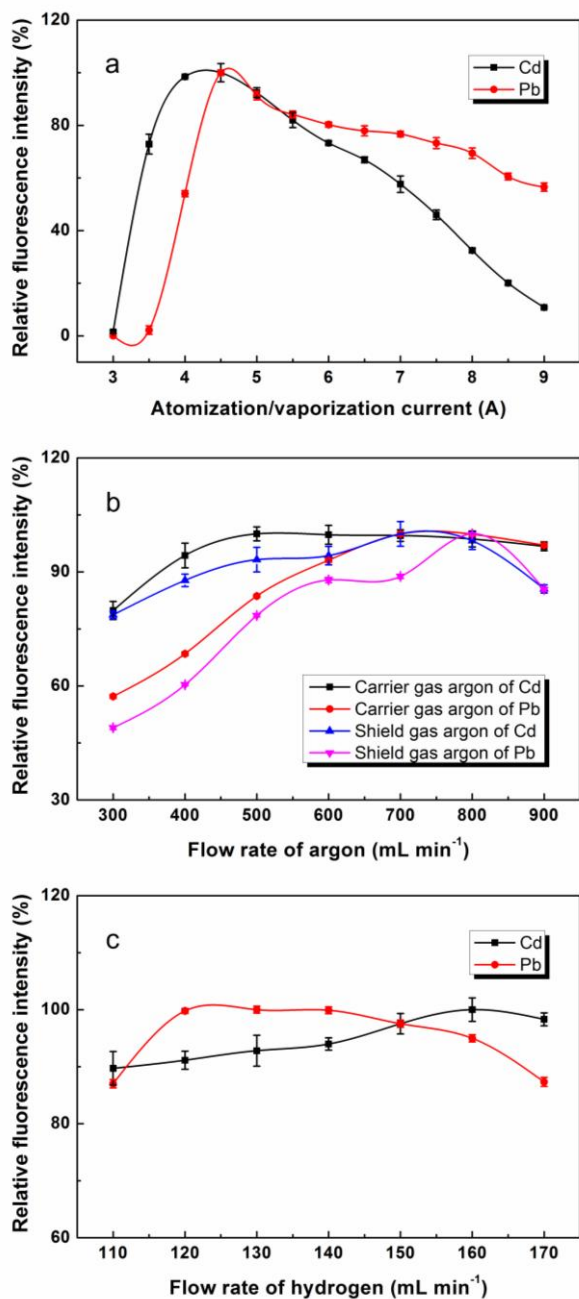
As shown in Figure S-1b and Figure S-2b, response plateaus for Cd and Pb were obtained in the range of 500 - 700 mL min<sup>-1</sup> and 700 - 800 mL min<sup>-1</sup>, followed a slight decrease at higher flow rate. Optimum sensitivities for Au and Ag are shown at 700 mL min<sup>-1</sup> and 600 mL min<sup>-1</sup> with intensity decreasing at both lower and higher flow rates, respectively. So a carrier flow rate of 700 mL min<sup>-1</sup> was selected for all the elements' further experiments.

### 2.2.2 Carrier gas H<sub>2</sub>

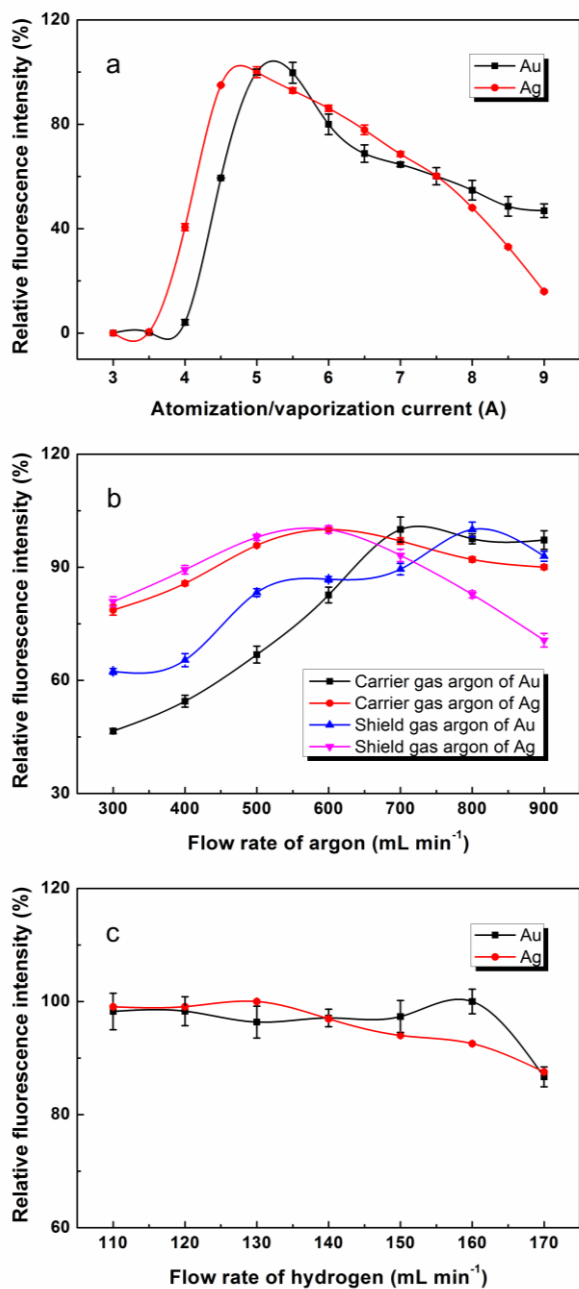
As shown in Figure S-1c and Figure S-2c, the optimum response was obtained for Pb at the range of 120 - 140 mL min<sup>-1</sup> whereas that for Cd continued to increase up to 160 mL min<sup>-1</sup>. Therefore, a flow rate of 150 mL min<sup>-1</sup> was selected for all subsequent measurements in order to simultaneously obtain better responses for Pb and Cd. Hydrogen flow rate had less effect on the responses from Au and Ag over the range of 110 - 150 mL min<sup>-1</sup>. A flow rate of 110 mL min<sup>-1</sup> was used for subsequent experiments for reduction of analytical cost.

### 2.2.3 Shield gas Ar

As shown in Figure S-1b and Figure S-2b, the optimum sensitivity was obtained for Cd at a flow rate of 700 mL min<sup>-1</sup> with response decreasing at both lower and higher values whereas it was 800 mL min<sup>-1</sup> for Pb. A shield gas flow rate at 800 mL min<sup>-1</sup> was thus selected for the subsequent experiments in order to obtain the best response for Pb, considering its lower sensitivity than Cd. For Au and Ag, the optimum responses were at 800 and 600 mL min<sup>-1</sup>, respectively. In consideration of both elements with high sensitivity, a flow rate of 700 mL min<sup>-1</sup> was selected.



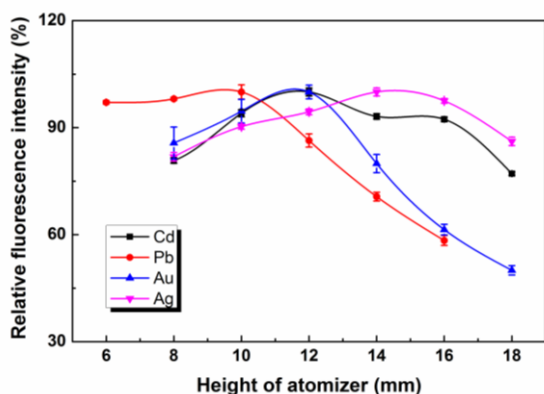
**Figure S-1.** Effect of atomization/vaporization current, Ar carrier flow rate, shield gas flow rate and hydrogen flow rate on response from 10  $\mu\text{L}$  0.5  $\mu\text{g L}^{-1}$  Cd and 10  $\mu\text{g L}^{-1}$  Pb solutions of (a) 500 mL  $\text{min}^{-1}$  Ar carrier flow rate, 700 mL  $\text{min}^{-1}$  shield gas flow rate and 130 mL  $\text{min}^{-1}$  hydrogen flow rate; (b) 4.5 A atomization/vaporization current, 700 mL  $\text{min}^{-1}$  shield gas flow rate and 130 mL  $\text{min}^{-1}$  hydrogen flow rate; 4.5 A atomization/vaporization current, 700 mL  $\text{min}^{-1}$  Ar carrier flow rate and 130 mL  $\text{min}^{-1}$  hydrogen flow rate; (c) 4.5 A atomization/vaporization current, 700 mL  $\text{min}^{-1}$  Ar carrier flow rate and 800 mL  $\text{min}^{-1}$  shield gas flow rate. The error bars represent “ $\pm$  one standard deviation of three trials”.



**Figure S-2.** Effect of atomization/vaporization current, Ar carrier flow rate, shield gas flow rate and hydrogen flow rate on response from 10  $\mu\text{L}$  25  $\mu\text{g L}^{-1}$  Au and 400  $\mu\text{g L}^{-1}$  Ag solutions of (a) 500  $\text{mL min}^{-1}$  Ar carrier flow rate, 700  $\text{mL min}^{-1}$  shield gas flow rate and 130  $\text{mL min}^{-1}$  hydrogen flow rate; (b) 5.0 A atomization/vaporization current, 700  $\text{mL min}^{-1}$  shield gas flow rate and 130  $\text{mL min}^{-1}$  hydrogen flow rate; 5.0 A atomization/vaporization current, 700  $\text{mL min}^{-1}$  Ar carrier flow rate and 130  $\text{mL min}^{-1}$  hydrogen flow rate; (c) 5.0 A atomization/vaporization current, 700  $\text{mL min}^{-1}$  Ar carrier flow rate and 700  $\text{mL min}^{-1}$  shield gas flow rate. The error bars represent “ $\pm$  one standard deviation of three trials”.

## 2.2.4 Height of atomizer

As shown in Figure S-3, the optimum sensitivity was obtained for Cd, Pb, Au and Ag at the height of 12, 10, 12 and 14 mm with fluorescence intensity decreasing at both lower and higher height. So a height of 12 mm was selected for all these elements.



**Figure S-3.** Effect of the height of atomizer on fluorescence intensity from 10  $\mu\text{L}$  0.5  $\mu\text{g L}^{-1}$  Cd, 10  $\mu\text{g L}^{-1}$  Pb, 25  $\mu\text{g L}^{-1}$  Au and 400  $\mu\text{g L}^{-1}$  Ag, respectively. The error bars represent “ $\pm$  one standard deviation of three trials”.