# Supporting information

## Non-thermal Optical Emission Spectrometry: Direct Atomization and Excitation of Cadmium for Highly Sensitive Determination

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**Overview:** This supporting information section presents reagents and sample pretreatment; microwave digestion procedures for certified reference materials; experimental parameters and analytical performances; calibration graphs for cadmium; effects of discharging voltage, discharging gap and helium flow rate.

## 1. Reagents

All the reagents used in this study were at least of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co. (China-SCRC) unless specified otherwise. Deionized water of 18 MΩ cm was used throughout the experiment. A stock solution of 1000 mg $L^{-1}$ cadmium was prepared by dissolving 0.5 g of spectropure cadmium powder in 15 mL of 50% (v/v) hot $HNO_3$ and diluted to 500 mL. After stepwise dilution of the stock solution, the final working standards of cadmium with the conductivity of ca. 1.1mS $cm^{-1}$ were prepared in 2% (v/v) ethanol and 0.6g $L^{-1}$ KCl. The purity of argon and helium as carrier gas was more than 99.99%.

## 2. Sample pretreatment

The validation of the present miniature optical emission spectrometric system for cadmium determination was performed by using certified reference materials (Community Bureau of Reference & China National Center for Standard Materials), including CRM176 (city waste incineration ash), GBW10023 (laver) and GBW08608 (water). The sample pretreatment procedure is given in the following:

0.4 g of laver and 0.1 g of city-waste incineration ash were immersed separately into 2 mL of $HNO_3$ with 1 mL $H_2O_2$ in a PTFE tank for microwave digestion (COOLPEX microwave digestion system, Yiyao Instrument Technology Development Co., LTD, Shanghai, China), and the full details for microwave digestion parameters are summarized in Table S1. After that, the residue of acid was heated gently to near dryness and diluted with deionized water to 3 mL. Considering the fact that 0.5 mol $L^{-1}$ $HNO_3$ in GBW08608 water would seriously interfere with cadmium determination by the present system, 8 mL of GBW08608 water sample was heated gently to near dryness and diluted with deionized water to 1 mL for the removal of $HNO_3$.

As the high content of nitrate (>20 mg $L^{-1}$) might interfere with cadmium determination by the present system, sample solution was required to pass through a 717 anion-exchange resin column for the removal of nitrate by exchanging with chloride ion.

All the effluent was collected and diluted to appropriate volume (5 mL for laver sample, 100 mL for city waste incineration ash sample and 2 mL for water sample) to ensure that the final solution contained 2% (v/v) ethanol and 0.6 g $L^{-1}$ KCl.

## 3. Microwave digestion procedures for certified reference materials

Table S1. The microwave digestion procedures of laver and city-waste incineration ash samples.

| Sample | Step | Temperature (°C) | Pressure (atm) | Time (min) |
|---|---|---|---|---|
| GBW10023 laver | 1 | 100 | 15 | 4 |
| | 2 | 150 | 15 | 3 |
| | 3 | 190 | 24 | 10 |
| CRM 176 City-waste incineration ash | 1 | 120 | 20 | 5 |
| | 2 | 180 | 30 | 3 |
| | 3 | 220 | 35 | 12 |

## 4. Experimental parameters and analytical performances

Table S2. The experimental parameters for the excitation and emission spectrometric determination of cadmium in the present DBD-OES system as well as the characteristic performance data of the analytical procedure.

| Parameter | Value |
|---|---|
| Detection wavelength | 228.8 nm |
| Discharging voltage | 2.9 kV |
| Discharging gap | 2 mm |
| Sampling flow rate | 3 μL $s^{-1}$ |
| Helium flow rate | 600 mL $min^{-1}$ |
| Ethanol concentration of sample solution | 2% (v/v) |
| KCl concentration of sample solution | 0.6 g $L^{-1}$ |
| Sampling volume | 80 μL |
| Sampling frequency | 60 $h^{-1}$ |
| Linear range | 5-1000 μg $L^{-1}$ |
| Regression equation | I=11.8C (μg $L^{-1}$)+17.9 |
| LOD(3σ, n=11) | 1.5 μg $L^{-1}$ |
| RSD(200 μg $L^{-1}$, n=9) | 3.6% |

## 5. Calibration graphs for cadmium

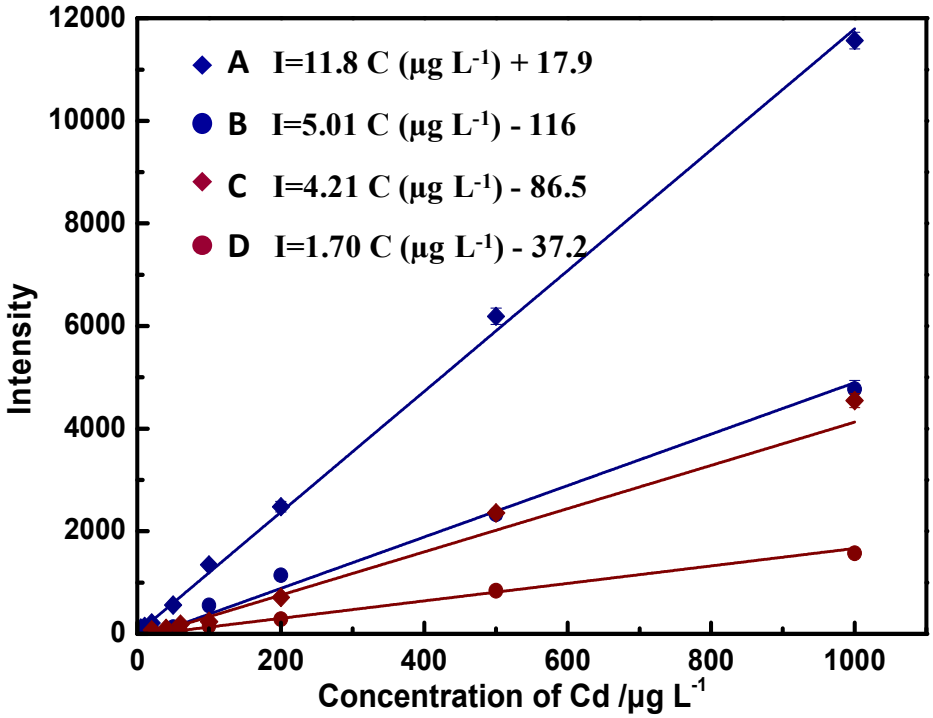


Figure S1. The calibration graphs for 5-1000 µg $L^{-1}$ $Cd^{2+}$ by the present DBD-OES system. A) Sample solution containing 2% (v/v) ethanol and 0.6 g $L^{-1}$ KCl excited by helium microplasma; B) Sample solution containing 2% (v/v) ethanol excited by helium microplasma; C) Sample solution containing 2% (v/v) ethanol and 0.6 g $L^{-1}$ KCl excited by argon microplasma; D) Sample solution without ethanol and KCl excited by helium microplasma.

## 6. Effects of discharging voltage and discharging gap

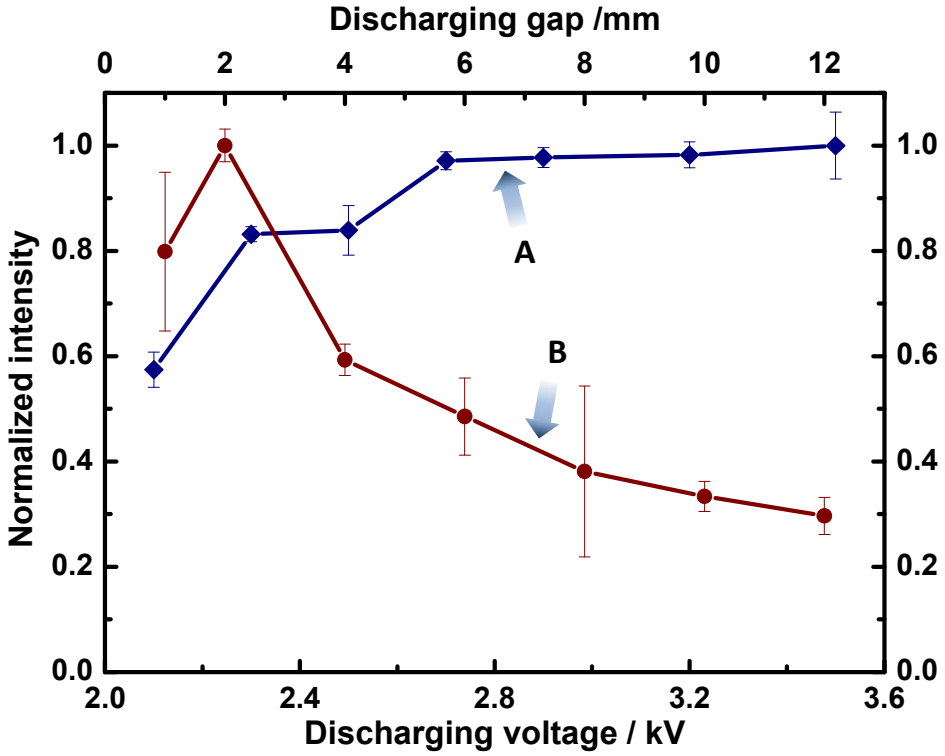


Figure S2. The dependence of optical emission intensity of cadmium on discharging voltage (A) and discharging gap (B). 80 μL of 200 μg $L^{-1}$ $Cd^{2+}$ in 2% (v/v) ethanol and 0.6 g $L^{-1}$ KCl is used.

## 7. Effect of helium flow rate

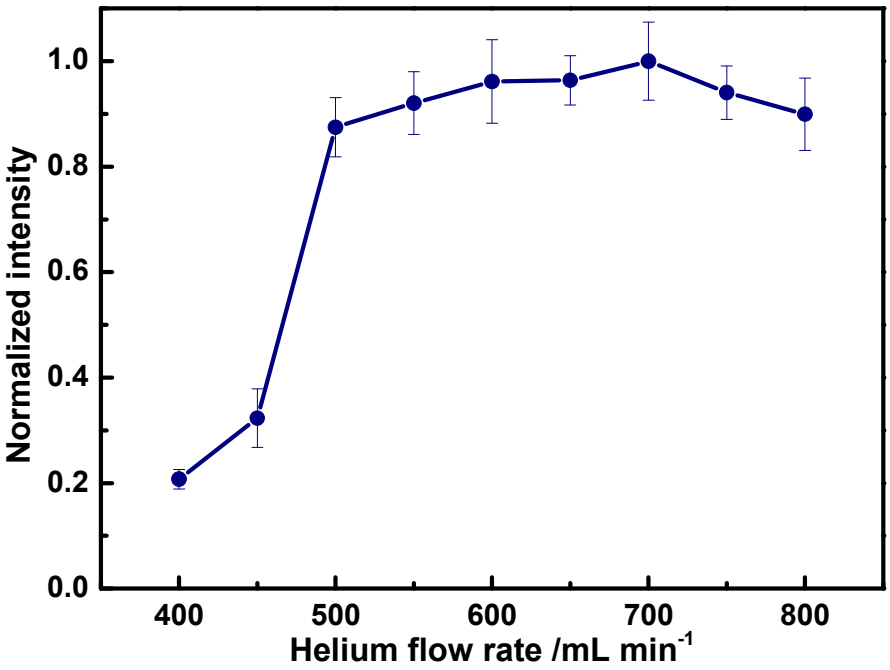


Figure S3. The dependence of optical emission intensity of cadmium on helium flow rate. 80 μL of 200 μg $L^{-1}$ $Cd^{2+}$ in 2% (v/v) ethanol and 0.6 g $L^{-1}$ KCl is used.