

## **Nonthermal optical emission spectrometry for simultaneous and direct determination of zinc, cadmium and mercury in the spray**

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## Electronic Supplementary Information

## Sample pretreatment

8 mL of GBW 08608 water sample was heated gently to near dryness and diluted with deionized water to 1 mL for the removal of  $\text{HNO}_3$ . For GBW08608 (water), a simple calibration curve method was used for the determinations of Zn and Cd due to a simple sample matrix. All the standard solutions and GBW08608 water sample were prepared in 2% (v/v) ethanol and  $1.0 \text{ g L}^{-1}$  KCl at pH 5.

0.1 g of CRM 176 city-waste incineration ash sample was immersed into 1.5 mL of HCl with 0.5 mL of  $\text{H}_2\text{O}_2$  in a PTFE tank for microwave digestion, and the details for microwave digestion parameters are summarized in Table S3. After that, the residue of acid was neutralized by NaOH to pH 4-5, and diluted with deionized water to 50 mL. For CRM 176 (city-waste incineration ash), a standard addition method was used for the determinations of Zn, Cd and Hg due the complicated sample matrix. Various amounts of Zn, Cd and Hg and appropriate amounts of ethanol and KCl were added into CRM 176 sample solution. All the CRM 176 sample solutions were prepared in 2% (v/v) ethanol and  $1.0 \text{ g L}^{-1}$  KCl.

Table S1 Helium spectral lines used for the excitation temperature measurement

$\lambda$ (nm)	Transition	$g_k$	$A_{ki}$ ( $10^8$ s $^{-1}$ )	$E_k$ (eV)
388.9	$2s\ ^3S_1 - 3p\ ^3P^0_J$	9	0.095	23.01
501.6	$2s\ ^1S_0 - 3p\ ^1P^0_1$	3	0.134	23.09
587.6	$2p\ ^3P^0_J - 3d\ ^3D_J$	15	0.707	23.07
667.8	$2p\ ^1P^0_1 - 3d\ ^1D_2$	5	0.637	23.07
706.5	$2p\ ^3P^0_J - 3s\ ^3S_1$	3	0.278	22.72
728.1	$2p\ ^1P^0_1 - 3s\ ^1S_0$	1	0.183	22.92

Table S2 Spectral parameters for Zn, Cd and Hg

	$\lambda$ (nm)	$g_0$	$g_k$	$A_{ki}$ ( $10^8 \text{ s}^{-1}$ )	$E_k$ (eV)
Zn I	213.9	1	3	7.09	5.80
Cd I	228.8	1	3	5.3	5.42
Hg I	253.7	1	3	0.084	4.89

Table S3 The microwave digestion procedure for city-waste incineration ash (CRM 176)

Sample	Step	Temperature (°C)	Pressure (atm)	Time (min)
	1	120	25	2
CRM 176	2	150	30	1
	3	200	35	7

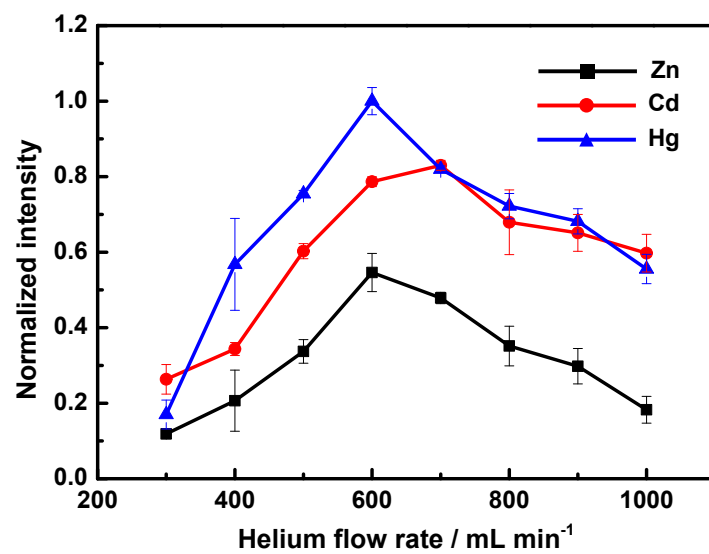


Fig. S1 The dependence of optical emission intensities of zinc, cadmium and mercury on helium flow rate. Details of the experimental parameters are given in Table 1.

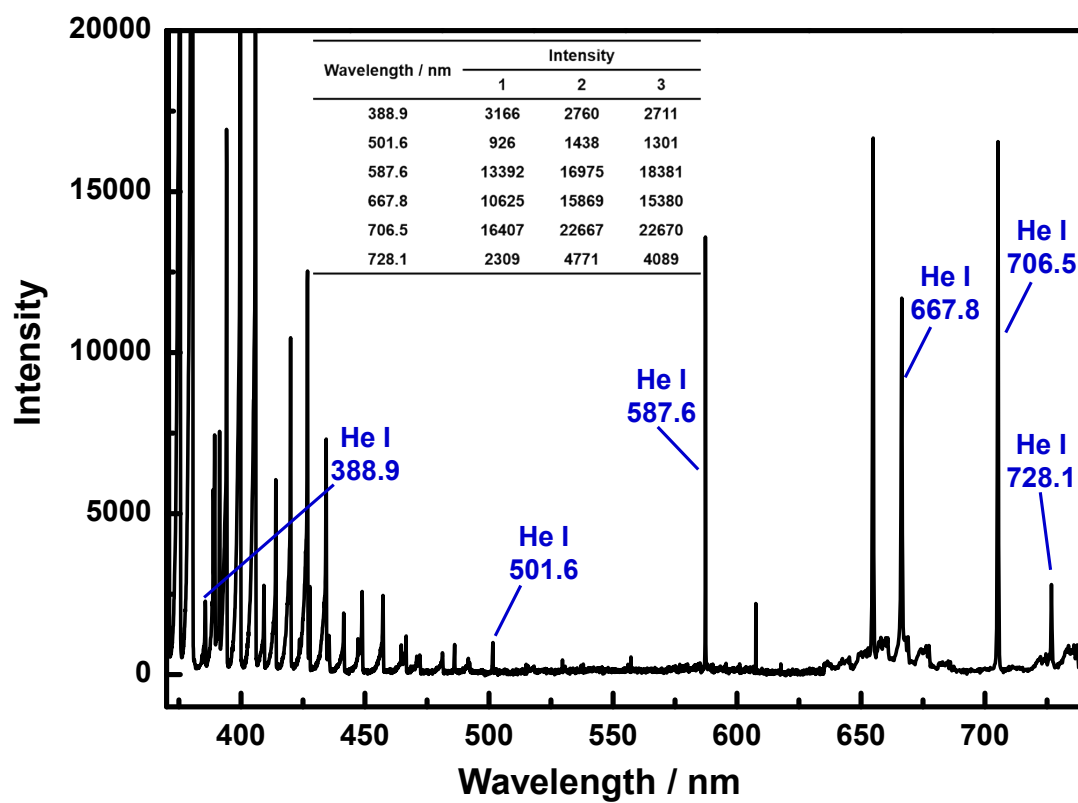


Fig. S2 The intensities of spectral lines for He I at 388.9, 501.6, 587.6, 667.8, 706.5 and 728.1 nm. The measurement was repeated 3 times.

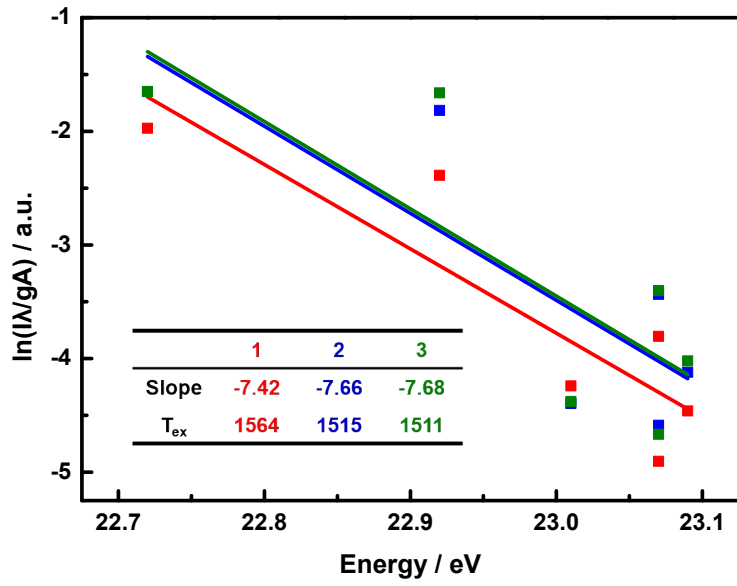


Fig. S3 Boltzmann's plot of the selected He I spectral lines. The excitation temperature values obtained from Boltzmann's plot are 1564, 1515 and 1511 K, respectively. The mean excitation temperature is  $1530 \pm 73$  K (confidence 0.95,  $n=3$ ).



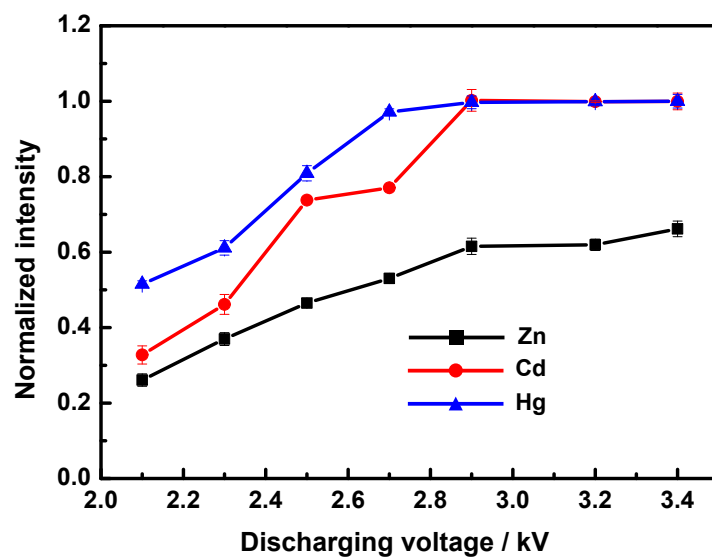


Fig. S4 The dependence of optical emission intensities of zinc, cadmium and mercury on the discharging voltage. Details of the experimental parameters are given in Table

1.

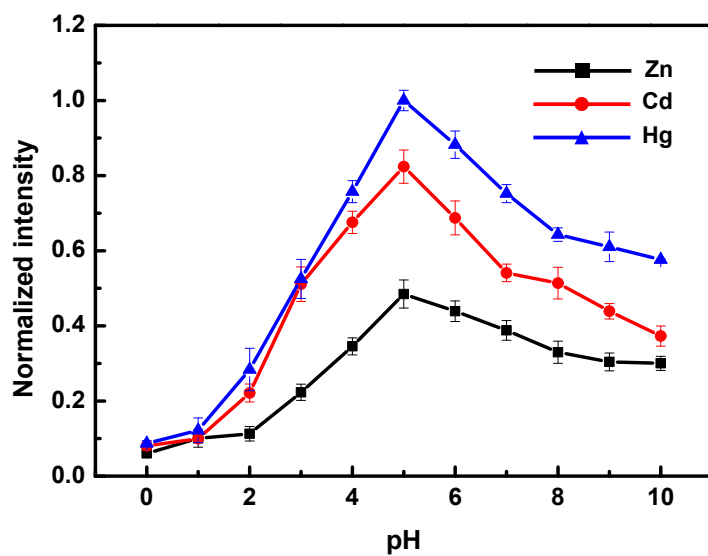


Fig. S5 The dependence of optical emission intensities of  $500 \mu\text{g L}^{-1}$  zinc,  $200 \mu\text{g L}^{-1}$  cadmium and  $500 \mu\text{g L}^{-1}$  mercury on solution pH value. Sample solutions were prepared in  $2 \text{ mol L}^{-1}$  KCl for investigation of the influence of pH value.