Supporting Information

Alternating-Current-Driven Microplasma for Multielement Excitation and Determination by Optical-Emission Spectrometry

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Table of contents

Reagents and Sample Pretreatment

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. Various single-element stock solutions of 1000 mg L^{-1} were purchased from National Center of Analysis for Nonferrous Metal and Electronic Material. After stepwise dilution of single-element stock solution, the final sample solutions were prepared in 5% (v/v) alcohol for solution nebulization, and in 1.5% (v/v) HCl for chemical vapor generation. Deionized water of 18 MΩ cm was used throughout the experiment. The purities of argon and helium as carrier gas were more than 99.99%.

Sample Pretreatment: 6 mL of GBW08608 or GBW(E)080039 water sample was heated gently to near dryness and diluted with deionized water to 2 mL for the removal of HNO_3. Then, a simple calibration curve method was used for the multielement determination due to a simple sample matrix. All the standard solutions and water samples were prepared in 5% (v/v) ethanol at pH 3 for solution nebulization.

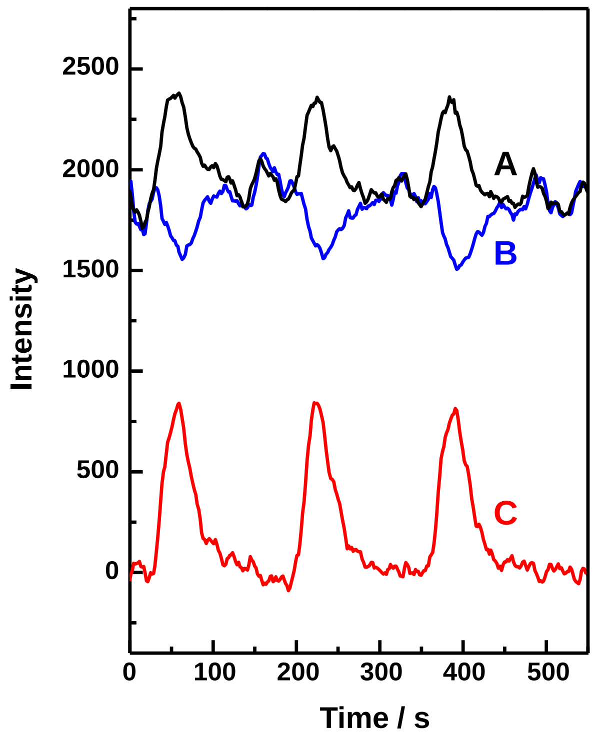

Figure S1. Blank correction for the emission spectra of Hg at 253.7 nm with the respect to the blank emission of microplasma obtained at 253.2 nm. (A) The raw spectra recorded at 253.7 nm for 30 μg L^{-1} Hg^{2+}; (B) The blank emission at 253.2 nm; (C) The net emission spectra after preforming blank correction.

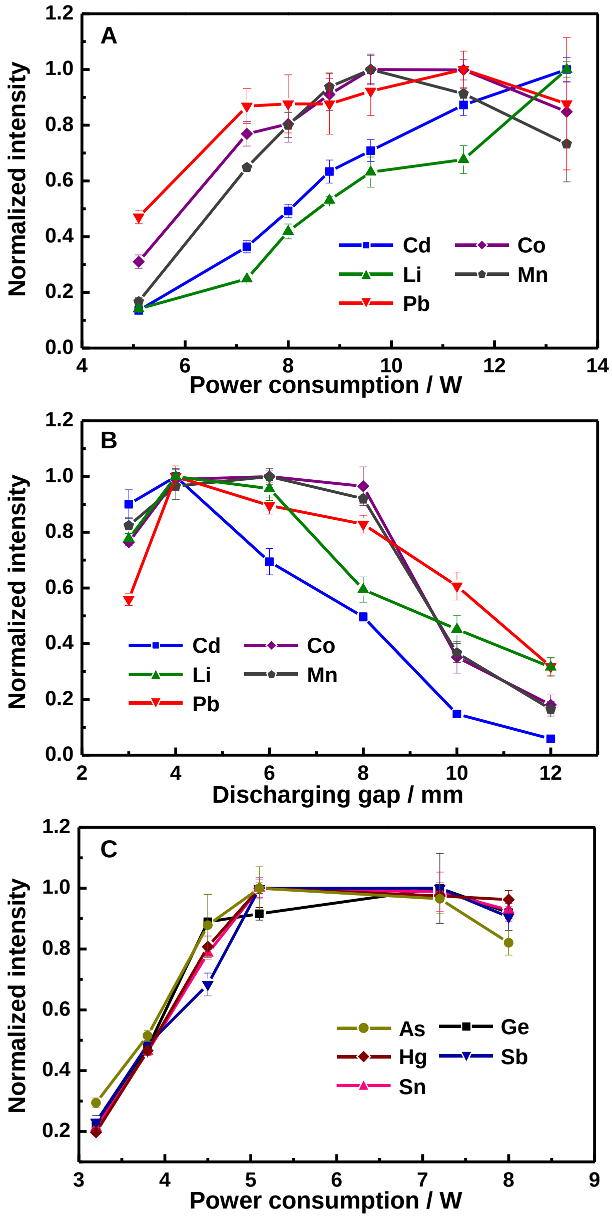

Figure S2. Dependence of optical emission intensities on (A) power consumption and (B) discharging gap with solution nebulization, and on (C) power consumption with chemical vapor generation. Sample solution containing 0.2 mg L^{-1} Cd^{2+}, 2 mg L^{-1} Co^{2+}, 1 mg L^{-1} Li^{+}, 1 mg L^{-1} Mn^{2+}, and 2 mg L^{-1} Pb^{2+} is employed for solution nebulization. Sample solution containing 5 mg L^{-1} As(III), 2 mg L^{-1} Ge^{4+}, 0.5 mg L^{-1} Hg^{2+}, 2 mg L^{-1} Sb^{3+}, and 1 mg L^{-1} Sn^{4+} is employed for chemical vapor generation. Other experimental parameters are given in Table S2 and Table S3.

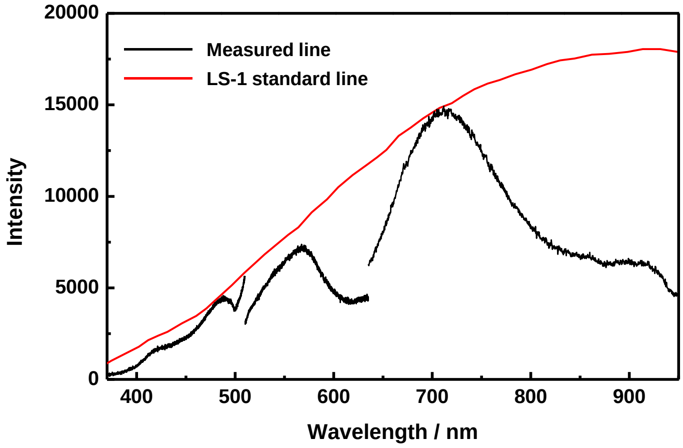

Figure S3. Responses of the CCD detector at different wavelengths. A halogen tungsten lamp with known spectral characteristicsis used to evaluate correction coefficients (R_λ) for the CCD detector response at different wavelengths.

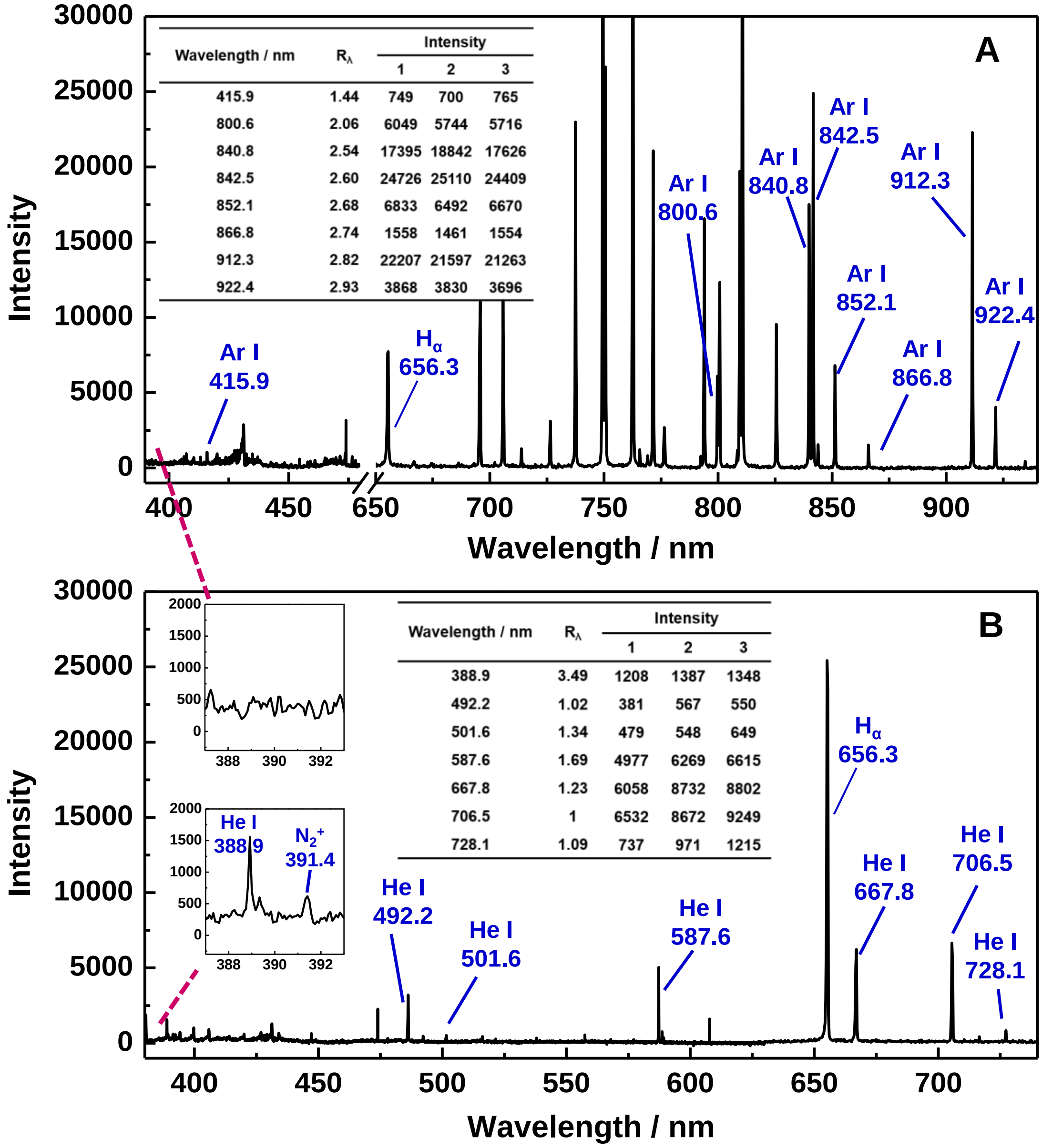

Figure S4. The intensities of spectral lines (A) for Ar I at 415.9, 800.6, 840.8, 842.5, 852.1, 866.8, 912.3, and 922.4 nm, and (B) for He I at 388.9, 492.2, 501.6, 587.6, 667.8, 706.5, 728.1 nm. The experiment is repeated for three times, and the data are displayed in the figure. The correction coefficients (R_λ) for the CCD detector at 388.9, 415.9, 492.2, 501.6, 587.6, 667.8, 706.5, 728.1, 800.6, 840.8, 842.5, 852.1, 866.8, 912.3, and 922.4 nm are also listed in the figure.

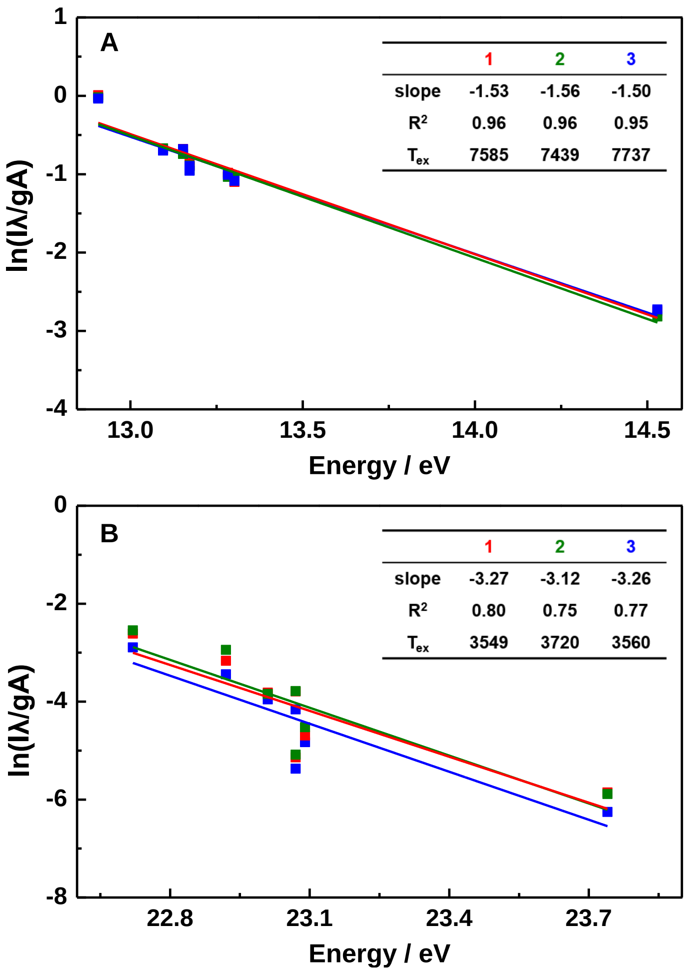

Figure S5. Boltzmann's plots of the selected (A) Ar I spectral lines and (B) He I spectral lines. The excitation temperatures of Ar microplasma obtained from Boltzmann's plot for three times are 7585, 7439, and 7737 K, respectively. The mean excitation temperature is 7587 ± 370 K (0.95 confidence, n=3). The excitation temperatures of He microplasma obtained from Boltzmann's plot for three times are 3549, 3720, and 3560 K, respectively. The mean excitation temperature is 3610 ± 238 K (0.95 confidence, n=3).

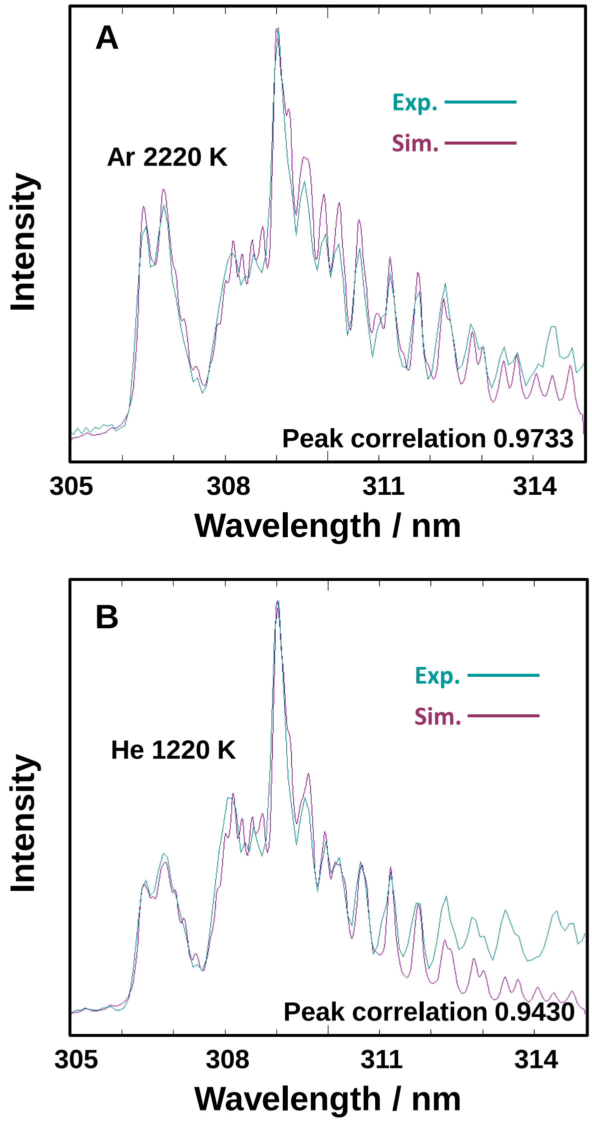

Figure S6. Illustrations for the simulated spectrum (Sim.) of OH(0, 0) band and its experimental spectrum (Exp.) at a power consumption of 9.6 W. (A) Argon microplasma; (B) Helium microplasma.

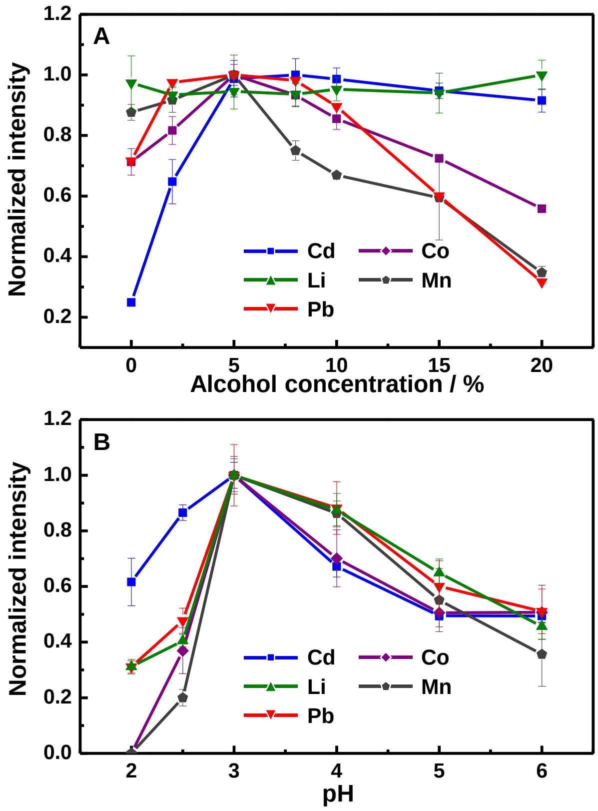

Figure S7. Dependence of optical emission intensities on (A) alcohol concentration of solution matrix and (B) pH value. Sample solution containing 0.2 mg L^{-1} Cd^{2+}, 2 mg L^{-1} Co^{2+}, 1 mg L^{-1} Li^{+}, 1 mg L^{-1} Mn^{2+}, and 2 mg L^{-1} Pb^{2+} is employed for solution nebulization. Other experimental parameters are given in Table S2.

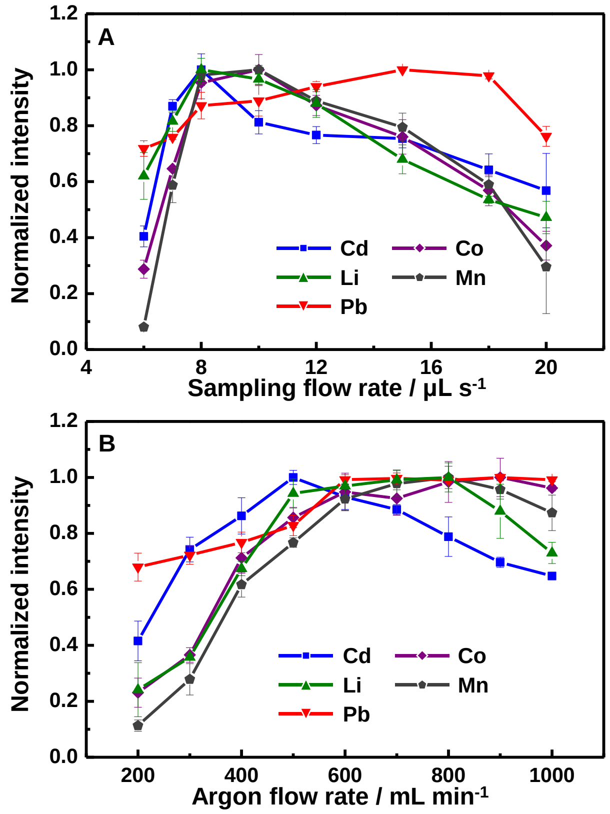

Figure S8. Dependence of optical emission intensities on (A) sampling flow rate and (B) argon flow rate. Sample solution containing 0.2 mg L^{-1} Cd^{2+}, 2 mg L^{-1} Co^{2+}, 1 mg L^{-1} Li^{+}, 1 mg L^{-1} Mn^{2+}, and 2 mg L^{-1} Pb^{2+} is employed for solution nebulization. Other experimental parameters are given in Table S2.

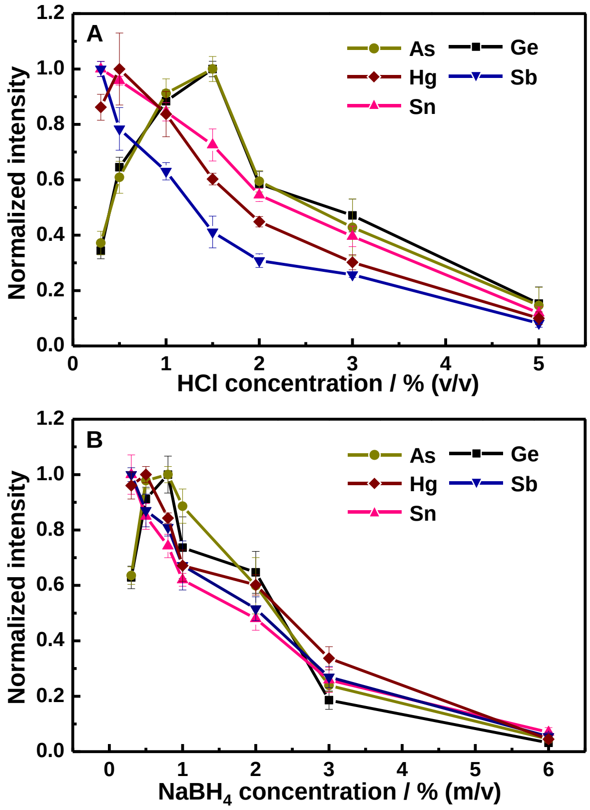

Figure S9. Dependence of optical emission intensities on (A) HCl concentration and (B) $NaBH_4$ concentration. Sample solution containing 100 μg L^{-1} As(III), 100 μg L^{-1} Ge^{4+}, 30 μg L^{-1} Hg^{2+}, 100 μg L^{-1} Sb^{3+}, and 100 μg L^{-1} Sn^{4+} is employed for chemical vapor generation. Other experimental parameters are given in Table S3.

Table S1. Analytical wavelengths and LODs of 19 elements obtained by ICP-OES instrument with solution nebulization

Element	Wavelength (nm)	LOD ($\mu g\ L^{-1}$)	Element	Wavelength (nm)	LOD ($\mu g\ L^{-1}$)
As	I 189.0	3.4;[1] 12.31;[5]	Hg	I 185.0	1;[6]
	I 193.8	10.67;[5] 20;[2] 30;[6]		I 253.6	23;[4]
	I 197.3	5.9;[1]	K	I 766.5	30;[6] 200;[2]
	I 228.8	30;[6]	Li	I 670.8	0.3;[6]
Ca	II 317.9	1.05;[5]	Mg	II 279.1	1.84;[5]
	II 393.4	0.17;[5] 2;[6]		II 279.6	0.01;[6] 1;[2]
	II 396.8	20;[2]		II 280.3	0.04;[5]
	I 422.7	3;[6]		I 285.2	0.23;[5]
Cd	II 214.4	0.8;[3]	Mn	II 257.6	0.07;[5] 0.2;[1,4] 2;[2]
	II 226.5	0.4;[6]		II 259.4	0.09;[5] 0.2;[1]
	I 228.8	0.3;[6] 4;[2]	Na	I 589.0	0.1;[6]
Co	II 228.6	0.3;[1] 1.00;[5] 4;[2]	Ni	II 221.6	0.9;[1]
	II 238.9	0.4;[6] 0.9;[1] 0.91;[5]		II 231.6	1.3;[1] 2.6;[3] 10;[2]
Cr	II 205.6	1.8;[1]	Pb	II 220.4	15;[6] 30;[2]
	II 267.7	0.5;[6] 1.1;[1] 9;[2]		I 283.3	10;[6]
Cu	I 324.8	0.9;[4] 1.1;[3] 2;[2] 10;[6]		I 405.8	8;[6]
	I 327.4	0.3;[6] 10;[6]	Sb	I 206.8	10;[1] 11.84;[5]
Fe	II 238.2	0.4;[1] 0.7;[4]		I 217.6	13;[1] 15;[6] 17.8;[5] 20;[2]
	II 259.9	0.2;[6] 0.4;[1] 4;[2]		I 259.8	200;[6]
	II 261.2	7;[6]		I 287.7	5000;[6]
Ge	II 164.9	2.5;[1]	Sn	II 190.0	1.4;[1] 28.2;[3] 100;[2]
	I 199.8	200;[2]		I 242.9	27;[1]
	I 206.9	20.26;[5]		I 284.0	10;[6]
	I 209.4	21.47;[5]		I 303.4	20;[6]
	I 265.1	2;[6] 8.9;[1]	Zn	I 213.9	0.3;[6] 1.4;[3] 7;[2]

I: atomic line; II: ionic line.

REFERENCES

(1) Wiltsche, H.; Brenner, I. B.; Prattes, K.; Knapp, G. *J. Anal. At. Spectrom.* **2008**, *23*, 1253-1262.

(2) Wolnik, K. A.; Fricke, F. L.; Hahn, M. H.; Caruso, J. A. *Anal. Chem.* **1981**, *53*, 1030-1035.

(3) Fuentes-Cid, A.; Villanueva-Alonso, J.; Pena-Vazquez, E.; Bermejo-Barrera, P. *Anal. Chim. Acta* **2012**, *749*, 36-43.

(4) Giersz, J.; Bartosiak, M.; Jankowski, K. *Talanta* **2017**, *167*, 279-285.

(5) McLaughlin, R. L. J.; Brindle, I. D. *J. Anal. At. Spectrom.* **2002**, *17*, 1540-1548.

(6) Barnes, R. M.; Boumans, P. W. J. M. *Crit. Rev. Anal. Chem.* **2008**, *7*, 203-296.

Table S2. The optimal experimental conditions for AC driven microplasma OES with solution nebulization

Parameter	Value
Power consumption	9.6 W
Discharging voltage	4.6 kV
Discharging gap	4 mm
Sampling flow rate	8 μL s^{-1}
Argon flow rate	600 mL min^{-1}
Sample volume	120 μL
Alcohol concentration	5% (v/v)
Sampling frequency	60 h^{-1}

Table S3. The optimal experimental conditions for AC driven microplasma OES with chemical vapor generation

Parameter	Value
Power consumption	5.1 W
Discharging voltage	3.5 kV
Discharging gap	4 mm
Sampling flow rate	40 μL s^{-1}
Argon flow rate	200 mL min^{-1}
Sample volume	500 μL
HCl concentration	1.5% (v/v)
$NaBH_4$ concentration	0.8% (m/v)
Sampling frequency	24 h^{-1}

Table S4. Argon spectral lines used for the excitation temperature measurement

λ (nm)	Transition	g_k	A_{ki} (10^7 s^{-1})	E_k (eV)
415.9	$3s^23p^5(^2P^0{}_{3/2})4s$ - $3s^23p^5(^2P^0{}_{3/2})5p$	5	0.14	14.529
800.6	$3s^23p^5(^2P^0{}_{3/2})4s$ - $3s^23p^5(^2P^0{}_{3/2})4p$	5	0.49	13.172
840.8	$3s^23p^5(^2P^0{}_{1/2})4s$ - $3s^23p^5(^2P^0{}_{1/2})4p$	5	2.23	13.302
842.5	$3s^23p^5(^2P^0{}_{3/2})4s$ - $3s^23p^5(^2P^0{}_{3/2})4p$	5	2.15	13.095
852.1	$3s^23p^5(^2P^0{}_{1/2})4s$ - $3s^23p^5(^2P^0{}_{1/2})4p$	3	1.39	13.283
866.8	$3s^23p^5(^2P^0{}_{1/2})4s$ - $3s^23p^5(^2P^0{}_{3/2})4p$	3	0.243	13.153
912.3	$3s^23p^5(^2P^0{}_{3/2})4s$ - $3s^23p^5(^2P^0{}_{3/2})4p$	3	1.89	12.907
922.4	$3s^23p^5(^2P^0{}_{1/2})4s$ - $3s^23p^5(^2P^0{}_{3/2})4p$	5	0.503	13.172

Table S5. Helium spectral lines used for the excitation temperature measurement

λ (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
492.2	2p $^1P^0_1$ - 4d $^1D_2$	5	0.199	23.74
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 S6. Comparison of analytical performances of the present microplasma OES system with those of other microplasma OES systems for simultaneous determination of multielements

Method	Element	Sampling flow rate (μL s^{-1})	LOD (μg L^{-1})	RSD (%)	Ref.
SCGD	Hg, Pb, Cu, Cd, Ag, Mg, Na, Li	42	0.06-22	0.9-2.9	1
SCGD	Ag, Cd, Cu, Fe, Hg, Mg, Ni, Pb, Se	30	1.1-3000	0.6-7	2
ac-EALD	Na, Cd	1.7-13	40, 90	1.6, 1.2	3
LE-DBD	Ag, Cu, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Hg, In, K, Li, Mg, Mn, Ni, Pb, Pd, Sr, Tl, Zn	0.3	1.6-41000	-	4
AC-driven	As, Ca, Cd, Co, Cr, Cu, Fe, Ge, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Zn	8	0.9-880	1.5-4.7	This work

REFERENCES

(1) Webb, M. R.; Andrade, F. J.; Hieftje, G. M. *Anal. Chem.* **2007**, *79*, 7899-7905.

(2) Doroski, T. A.; King, A. M.; Fritz, M. P.; Webb, M. R. *J. Anal. At. Spectrom.* **2013**, *28*, 1090-1095.

(3) Huang, R.; Zhu, Z.; Zheng, H.; Liu, Z.; Zhang, S.; Hu, S. *J. Anal. At. Spectrom.* **2011**, *26*, 1178-1182.

(4) Kraehling, T.; Michels, A.; Geisler, S.; Florek, S.; Franzke, J. *Anal. Chem.* **2014**, *86*, 5822-5828.