Electronic Supplementary Information

Portable Photochemical Vapor Generation-Microwave Plasma Atomic Emission Spectrometer

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Table S1. Name, Specification and manufacturer/distributor of reagents.

Reagents	Specification	Manufacturer/distributor
Formic acid	analytical grade	Kelong Chemical Reagent Plant
acetic acid	analytical grade	Kelong Chemical Reagent Plant
HCl	analytical grade	Kelong Chemical Reagent Plant
HNO_3	analytical grade	Kelong Chemical Reagent Plant
$ZnCl_2$	analytical grade	Kelong Chemical Reagent Plant
$BaCl_2$	analytical grade	Kelong Chemical Reagent Plant
$CuCl_2$	analytical grade	Kelong Chemical Reagent Plant
$MnCl_2{\cdot}4H_2O$	analytical grade	Kelong Chemical Reagent Plant
$AlCl_3{\cdot}6H_2O$	analytical grade	Kelong Chemical Reagent Plant
$NiCl_2{\cdot}6H_2O$	analytical grade	Kelong Chemical Reagent Plant
Anhydrous $CaCl_2$	analytical grade	Aladdin Bio-Chem Technology Co., LTD.
$HgCl_2$	>99%	Aladdin Bio-Chem Technology Co., LTD.

Spectral characteristics

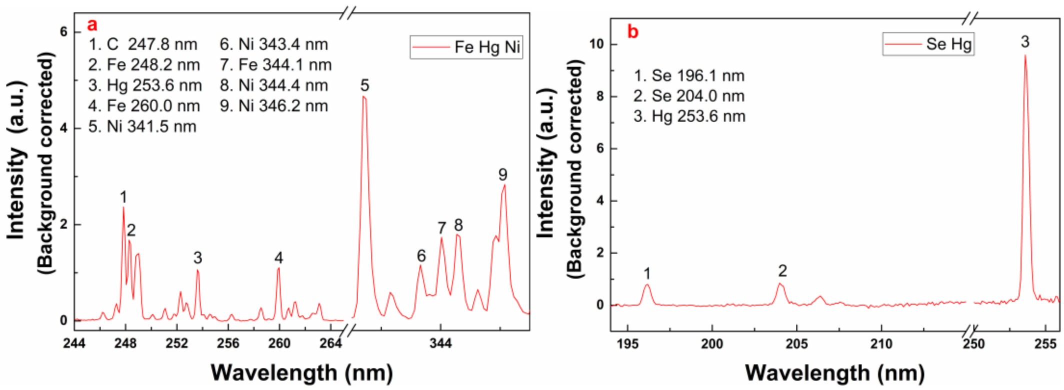

Fig. S1. Atomic emission spectra of simultaneous determination of : (a) 15 mg L^{-1} Ni(II), 500 μg L^{-1} Hg(II) and 10 mg L^{-1} Fe(III); (b) 500 μg L^{-1} Se(IV) and 4 mg L^{-1} Hg(II).

The simultaneous photochemical generation of Fe, Hg and Ni containing species with formic acid is practicable (as shown in Fig. S1). Their simultaneous determination was explored preliminarily and the limits of detection (LODs) were found to be 34 μg L^{-1}, 5 μg L^{-1} and 64 μg L^{-1} for Ni, Hg and Fe, respectively. The simultaneous photochemical vapor generation of Se and Hg with acetic acid is also workable and the LODs were found to be 52 μg L^{-1} and 63 μg L^{-1} for Hg and Se, respectively.

Optimization of experimental parameters

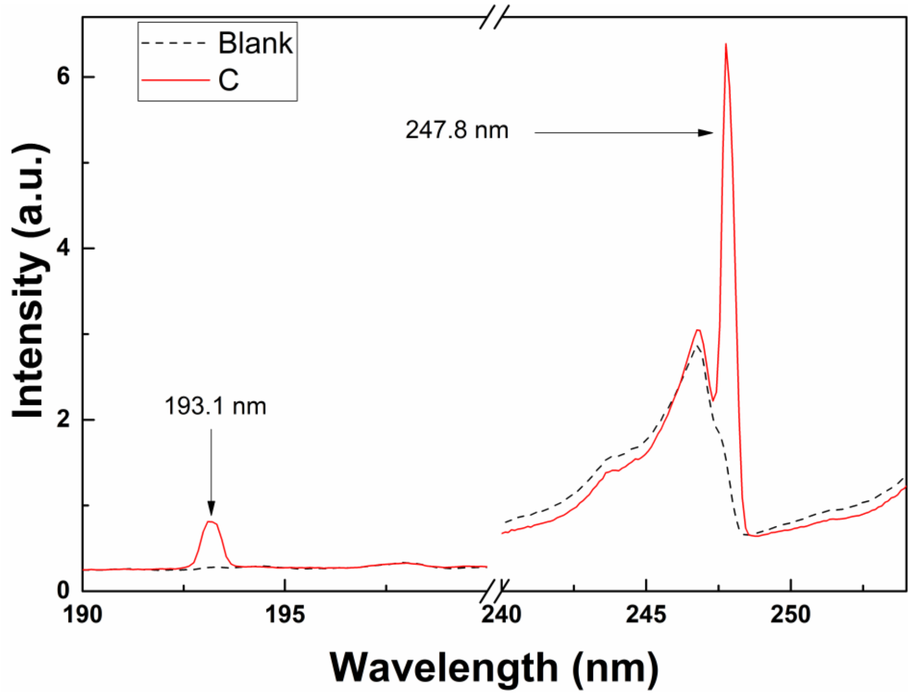

Fig. S2. Carbon atomic emission spectra.

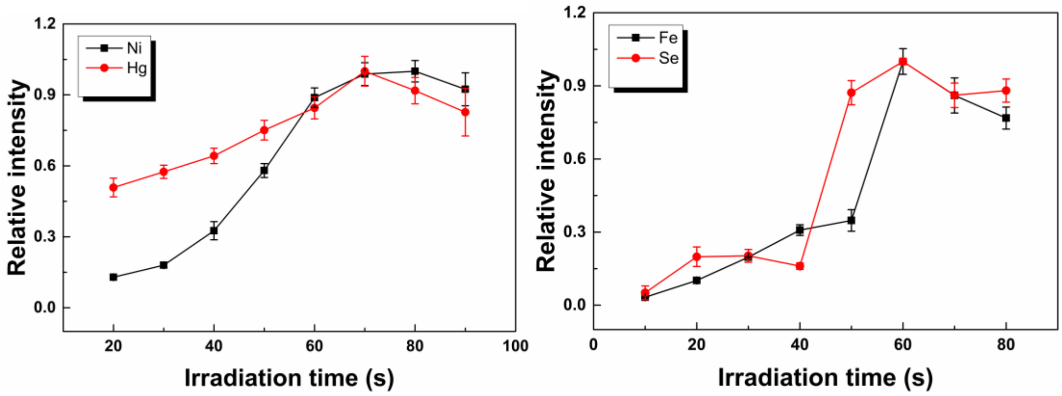

Fig. S3. Relative OES intensity obtained from different UV irradiation time. Experimental details: Ni(II), 1000 μg L^{-1}; Hg(II), 1000 μg L^{-1}; Fe(III), 1000 μg L^{-1}; and Se(IV), 1000 μg L^{-1}.

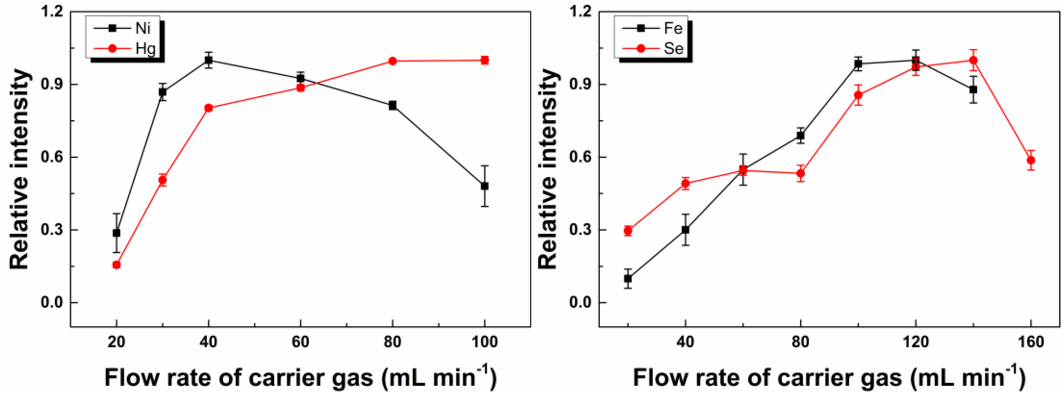

Fig. S4. Relative OES intensity obtained from different flow rate of carrier gas. Experimental details: Ni(II), 1000 μg L^{-1}; Hg(II), 1000 μg L^{-1}; Fe(III), 1000 μg L^{-1}; and Se(IV), 1000 μg L^{-1}.

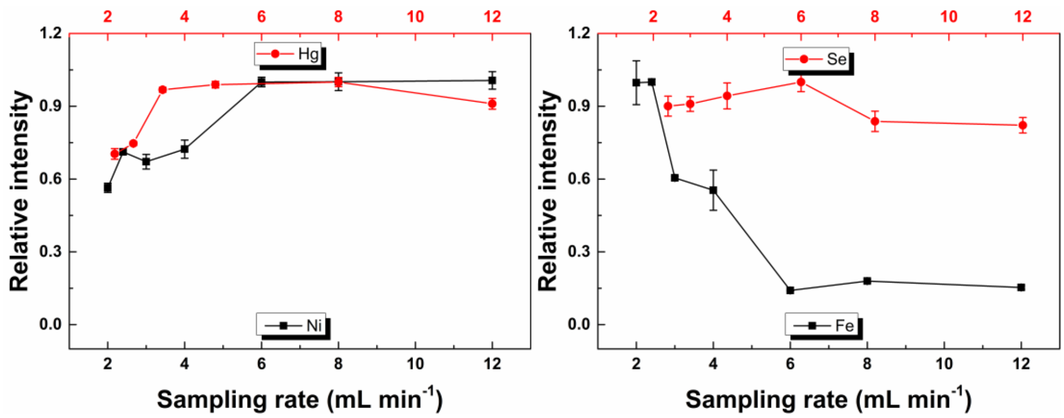

Fig. S5. Relative OES intensity obtained from different sampling rate. Experimental details: Ni(II), 1000 μg L^{-1}; Hg(II), 1000 μg L^{-1}; Fe(III), 1000 μg L^{-1}; Se(IV), 1000 μg L^{-1}.

Investigation of interference

The interference of some coexisting metal ions was studied, including alkaline earth metals, transition metals, etc. In addition, it has been reported that NO_3^- ions have an inhibitory effect on the PVG[1], so nitrate and nitric acid were also included. As shown in Table S2-S5, most metal cations and nitrate ions were found to have no significant effect on the measurement of these metals. Recovery of Ni in all cases were between 92-107%. Hg and Ni slightly inhibited each other's atomic emission signals; and in the measurement of Fe, NO_3^- and Cu^{2+} significantly depressed the signals. Fortunately, the interferences could be eliminated by heating treatment for removing acid and adding complexing agents for copper ion. Otherwise, Cu^{2+} has an influence on the photochemical vapor generation of Se, as reported in the literature.[2] In addition, high concentration of Hg also interfered with the determination of Se.

Table S2. Interference of common ions with determination of Ni.

Coexisting ion	[M] (mg L^{-1})	[M]/[Ni(II)] [a]	Recovery (%)
Ca^{2+}	50	250	107
Ba^{2+}	50	250	95
Al^{3+}	50	250	107
Cu^{2+}	50	250	93
Zn^{2+}	50	250	99
Hg^{2+}	50	250	92
Mn^{2+}	50	250	100
NO_3^-	30-330	150-1650	92-107

[a] 200 µg L^{-1} Ni solution

Table S3. Interference of common ions with determination of Hg.

Coexisting ion	[M] (mg L^{-1})	[M]/[Hg(II)] [a]	Recovery (%)
Ca^{2+}	50	500	104
Ba^{2+}	50	500	100
Al^{3+}	50	500	103
Cu^{2+}	50	500	89
Zn^{2+}	50	500	99
Ni^{2+}	50	500	81
Mn^{2+}	50	500	100
NO_3^-	92-330	463-1650	81-104

[a] 100 µg L^{-1} Hg solution

Table S4. Interference of common ions with determination of Fe.

Coexisting ion	[M] (mg L^{-1})	[M]/[Fe(II)] [a]	Recovery (%)
Ca^{2+}	50	100	109
Ba^{2+}	50	100	107
Al^{3+}	50	100	103
Cu^{2+}	50	100	-
Zn^{2+}	50	100	93
Ni^{2+}	50	100	112
Hg^{2+}	50	100	98
Mn^{2+}	50	100	106
NO_3^-	50	100	-

[a] 500 µg L^{-1} Fe solution

Table S5. Interference of common ions with determination of Se.

Coexisting ion	[M] (mg L^{-1})	[M]/[Se(IV)][1]	Recovery (%)
Ca^{2+}	50	100	99
Ba^{2+}	50	100	93
Al^{3+}	50	100	90
Cu^{2+}	50	100	53
Zn^{2+}	50	100	98
Ni^{2+}	50	100	96
Mn^{2+}	50	100	97
Hg^{2+}	50	100	69
NO_3^-	50	100	91

[a] 500 µg L^{-1} Se solution

Table S6. Comparison with other non-portable MWP spectrometric techniques [a]

Element	Introduction method	Desolvation method	LOD (μg L^{-1})	RSD (%)	Reference
Ni	USN	H + C + S	48	-	3
	PN		4	0.55	4
	PVG		0.3	4.8	5
	PVG[b]	-	7	5.0	-
Hg	USN	H + C + S	1.3	1.1	3
	ETV	H + C	0.03	-	3
	HG+USN	H	3.0	8	6
	PVG+USN	C	15	4	7
	PVG[b]	-	1	2.1	-
Fe	USN	H + C + S	37.5	2.8	3
	PN	-	150	0.49	4
	PVG[b]		20	6.0	-
Se	HG	H + C + P	45	2.3	3
	HG+USN	H	3.3	11	6
	PVG+USN	C	19	3	7
	PVG	-	40	3.5	This work

[a] *Abbreviations:* PVG, photochemical vapor generation; USN, ultrasonic nebulization; PN, pneumatic nebulization; ETV, electrothermal vaporization; HG, hydride generation; H, heating; C, condensation; S, absorption by concentrated sulfuric acid; and P, absorption by concentrated phosphorous acid.

References

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