

Supporting Information

Impact of the Gas-Liquid interface on Photochemical Vapor Generation

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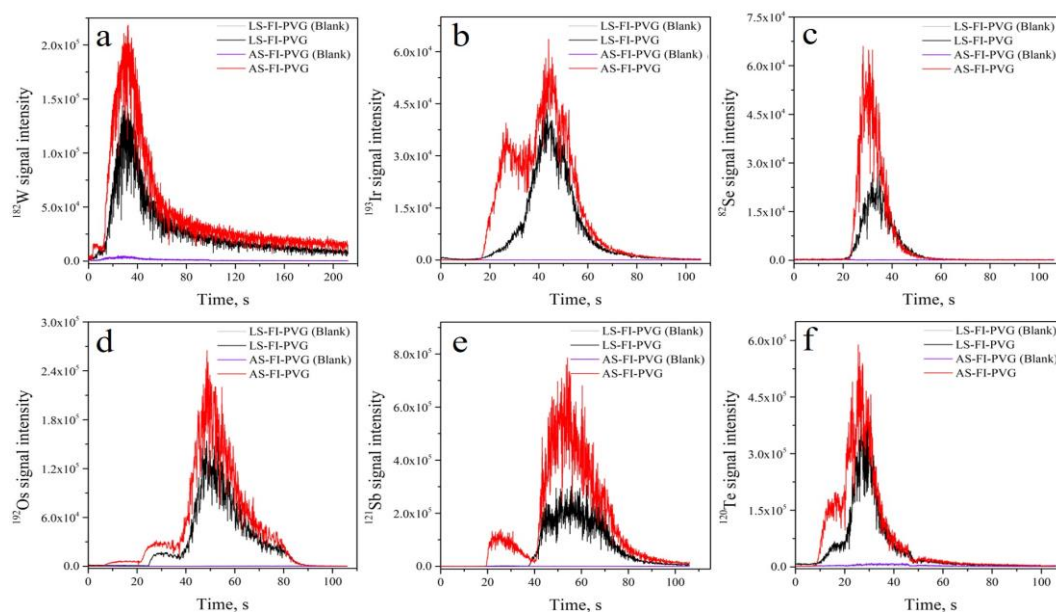


Figure S1. Time-resolved profiles of W, Ir, Se, Os, Sb, and Te in LS-FI-PVG, and AS-FI-PVG (air slug preceding the sample solution): a) 20 ng mL⁻¹ W, 40% (v/v) FA, 500 mg L⁻¹ Cd²⁺, 120 s UV irradiation time, and 2.24 mL of air slug; b) 2 ng mL⁻¹ Ir, 20% (v/v) FA; 25 mg L⁻¹ Cu²⁺, 45 s UV irradiation time, and 1.60 mL of air slug; c) 10 ng mL⁻¹ Se (IV), 15% (v/v) FA, 13 s UV irradiation time, and 2.88 mL of air slug; d) 5 ng mL⁻¹ Os, 5% (v/v) HNO₃, 150 s UV irradiation time, and 0.77 mL of air slug; e) 10 ng mL⁻¹ Sb, 5% (v/v) FA, 20% (v/v) AA, 60 s UV irradiation time, and 2.24 mL of air slug; f) 10 ng mL⁻¹ Te, 2% (v/v) FA, 20% (v/v) FA, 20 mg L⁻¹ Fe²⁺, 5 g L⁻¹ nano-TiO₂, 50 s UV irradiation time, and 1.28 mL of air slug.

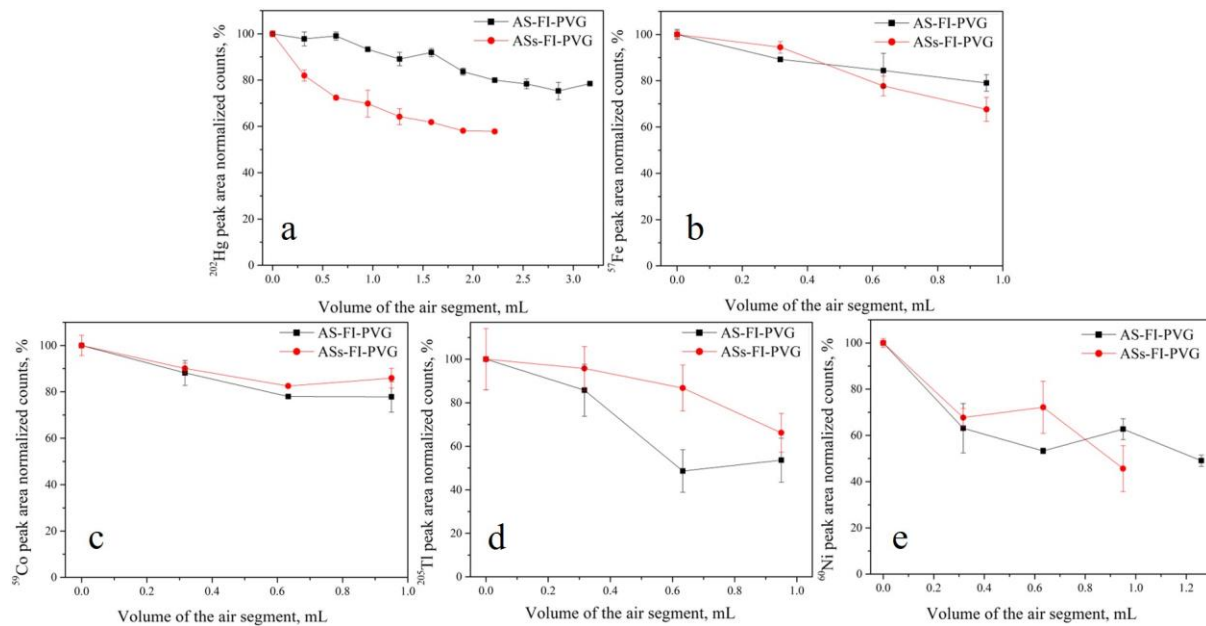


Figure S2. Effect of the volume of the air segment on ^{202}Hg , ^{57}Fe , ^{59}Co , ^{205}Tl and ^{60}Ni responses: a) $10\text{ ng mL}^{-1}\text{ Hg}$, 15% (v/v) FA, and 13 s UV irradiation time; b) $10\text{ ng mL}^{-1}\text{ Fe}$, 60% (v/v) FA, and 180 s UV irradiation time; c) $10\text{ ng mL}^{-1}\text{ Co}$, 50% (v/v) FA, and 180 s UV irradiation time; d) $20\text{ ng mL}^{-1}\text{ Tl}$, 20% (v/v) FA, $20\text{ mg L}^{-1}\text{ Co}^{2+}$ and 110 s UV irradiation time; e) $10\text{ ng mL}^{-1}\text{ Ni}$, 50% (v/v) FA, and 180 s UV irradiation time.

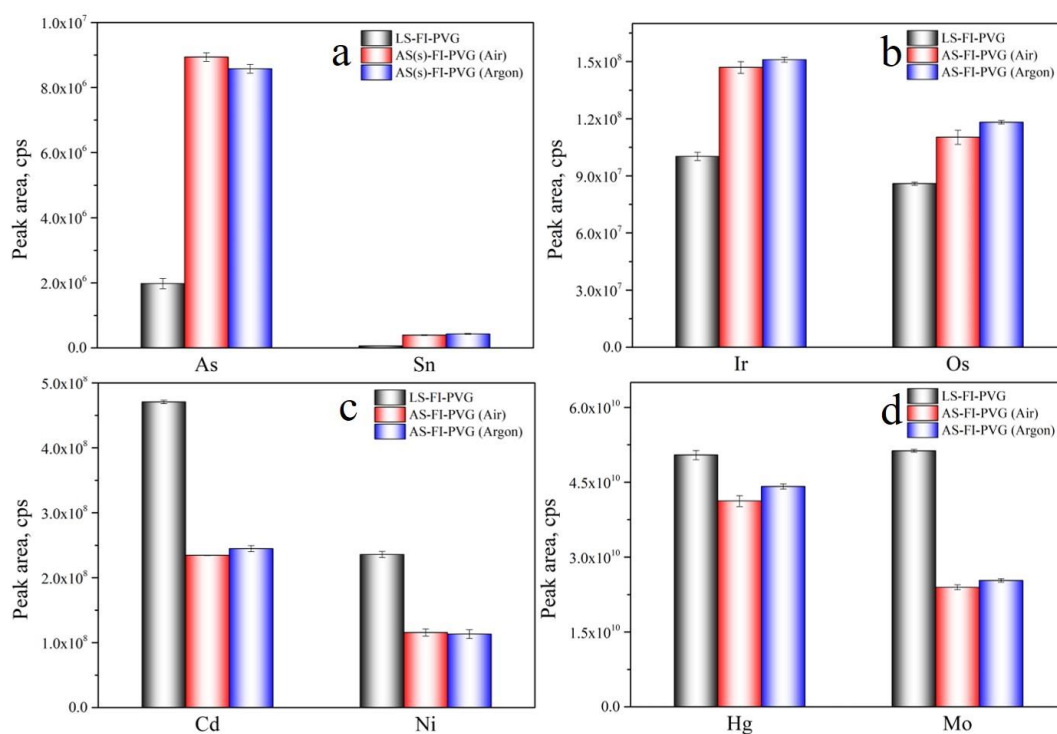


Figure S3. Effect of the air/Ar slugs on As, Sn, Ir, Os, Cd, Ni, Hg and Mo responses in AS(s)-FI-PVG system. a) As, 4% (v/v) FA, 20% (v/v) AA, 15 mg L⁻¹ Fe³⁺, 30 s irradiation, and 2.88 mL of air slug preceding the sample; Sn, 0.8% (v/v) AA, 0.01% (v/v) HCl, 32 s irradiation, and 1.60 mL of air slugs preceding and succeeding the sample; b) Ir, 20% (v/v) FA, 25 mg L⁻¹ Cu²⁺, 45 s UV irradiation time, and 1.60 mL of air slug preceding the sample; Os, 5% (v/v) HNO₃, 150 s UV irradiation time, and 0.77 mL of air slug preceding the sample; c) Cd, 40% (v/v) FA, 30 mg L⁻¹ Co²⁺, 80 s UV irradiation time, and 1.28 mL of air slug preceding the sample; Ni, 50% (v/v) FA, 180 s UV irradiation time, and 1.28 mL of air slug preceding the sample; d) Hg, 15% (v/v) FA, and 13 s UV irradiation time, and 3.20 mL of air slug preceding the sample; Mo, 20% (v/v) FA, 20 mg L⁻¹ Co²⁺, 2.5 mg L⁻¹ Cu²⁺, and 60 s UV irradiation time, and 1.28 mL of air slug preceding the sample.

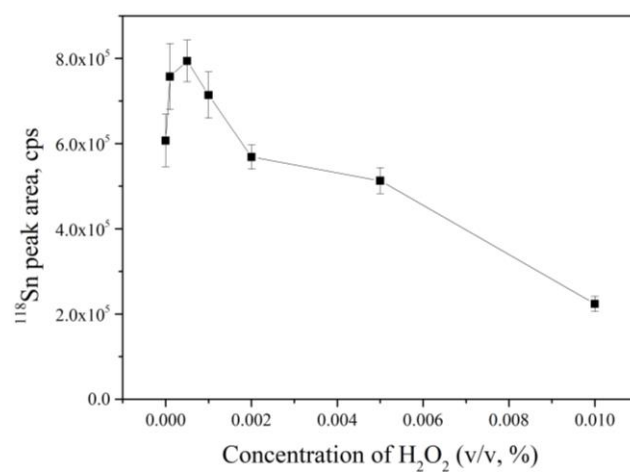


Figure S4. Effect of the concentration of H_2O_2 on ^{118}Sn response with 32 s UV irradiation in the absence of gas-liquid interface.

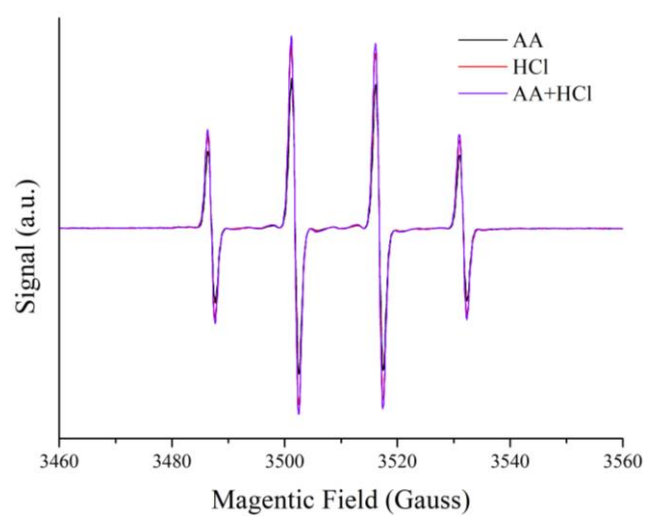


Figure S5. EPR results for PVG medium of Sn in LS-FI-PVG system: 0.01% (v/v) HCl, or/and 0.8% (v/v) AA.

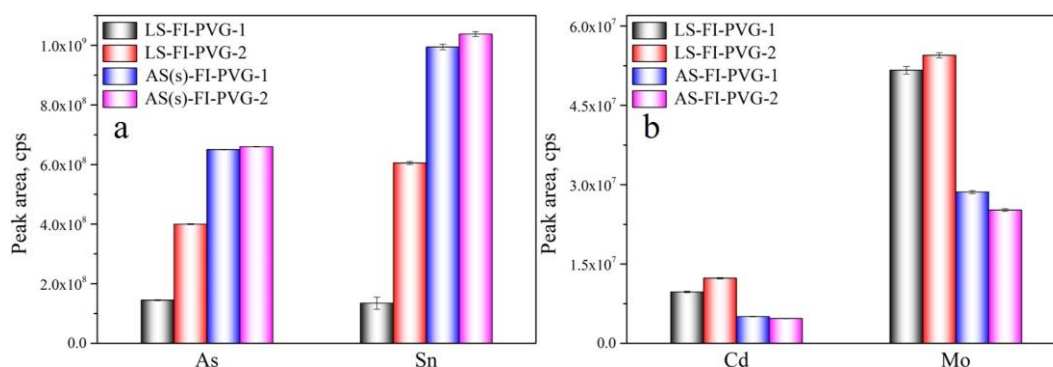


Figure S6. Effect of the internal temperature of PVG reactor on ^{118}Sn , ^{75}As , ^{111}Cd , and ^{98}Mo responses: a) 5 ng mL^{-1} As, 4% (v/v) FA, 20% (v/v) AA, $15 \text{ mg L}^{-1} \text{ Fe}^{3+}$, and 30 s irradiation; 50 ng mL^{-1} Sn, 0.8% (v/v) AA, 0.01% (v/v) HCl, and 32 s irradiation; b) 20 ng mL^{-1} Cd, 40% (v/v) FA, $30 \text{ mg L}^{-1} \text{ Co}^{2+}$, and 80 s irradiation; 10 ng mL^{-1} Mo, 20% (v/v) FA, $20 \text{ mg L}^{-1} \text{ Co}^{2+}$, $2.5 \text{ mg L}^{-1} \text{ Cu}^{2+}$, and 60 s UV irradiation time.

LS-FI-PVG-1: the blank solution was firstly introduced into the PVG reactor and followed by sample solution as described in the section of Analytical Procedure.

LS-FI-PVG-2: the blank solution was firstly introduced into the PVG reactor and undergone UV irradiation for a while (with the total UV irradiation time of 45 s for As, 25 s for Sn, and 20 s for Cd and Mo) and then sample solution was introduced into the reactor for PVG.

AS(s)-FI-PVG-1: the air slug was firstly injected into the PVG reactor and undergone UV irradiation for a while (with the total UV irradiation time of 45 s for As, 25 s for Sn, and 20 s for Cd and Mo) and then sample solution was introduced into the reactor for PVG.

AS(s)-FI-PVG-2: the air slug was injected continuously into PVG reactor (45 s for As, 25 s for Sn, and 20 s for Cd, Mo) and then sample solution was introduced into the reactor for PVG.

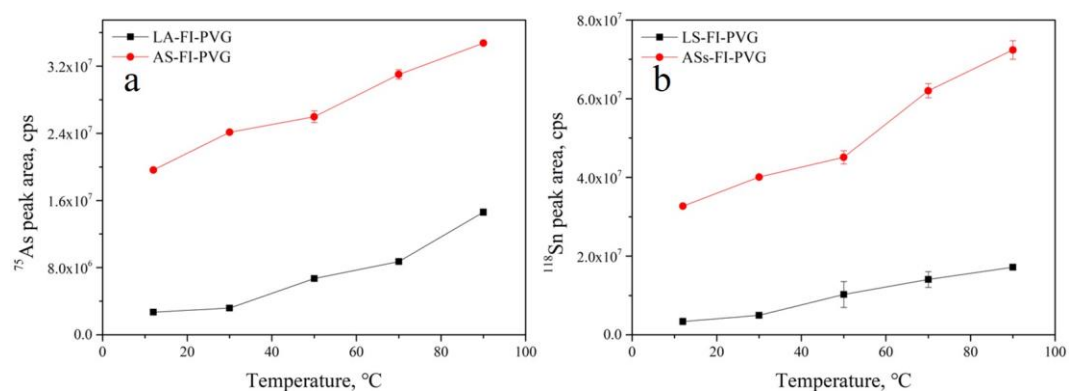
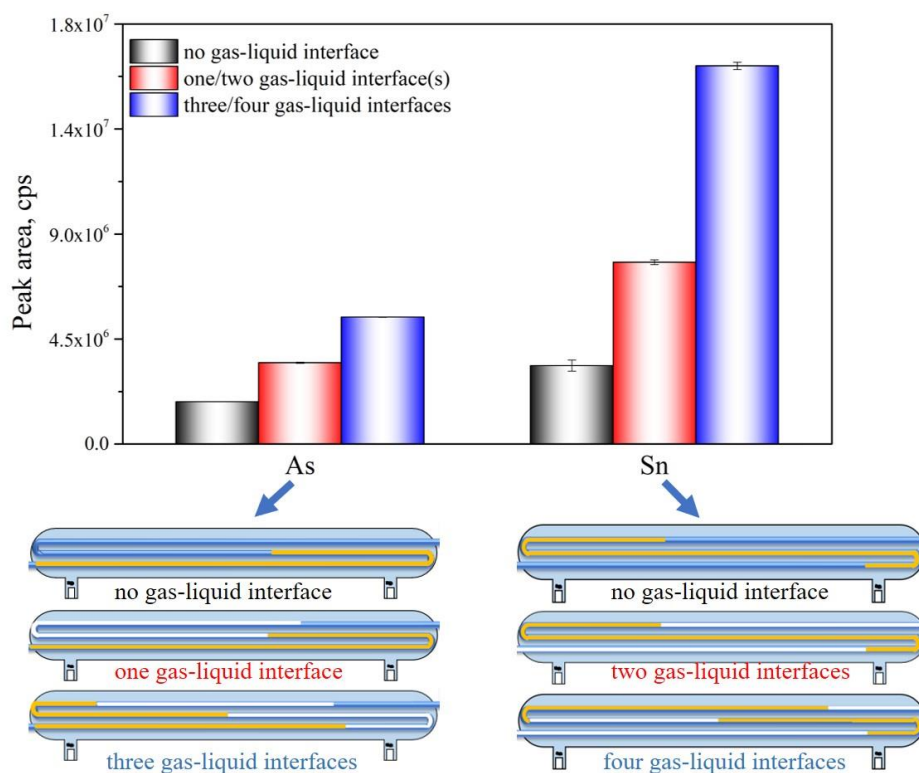


Figure S7. Effect of the sample solution temperature on ^{75}As and ^{118}Sn response in LS-FI-PVG and AS(s)-FI-PVG systems: a) As, 4% (v/v) FA, 20% (v/v) AA, $15 \text{ mg L}^{-1} \text{ Fe}^{3+}$, and 30 s irradiation; b) Sn, 0.8% (v/v) AA, 0.01% (v/v) HCl, and 32 s irradiation.



Blue color: the PVG medium; yellow color: sample solution; white color: air slug.

Figure S8. Effect of the gas-liquid interfaces on As and Sn detection with 0.3 mL of sample consumption and 0.3 mL of total air-segmented: As, 4% (v/v) FA, 20% (v/v) AA, $15 \text{ mg L}^{-1} \text{ Fe}^{3+}$, and 30 s irradiation; Sn, 0.8% (v/v) AA, 0.01% (v/v) HCl, and 32 s irradiation.

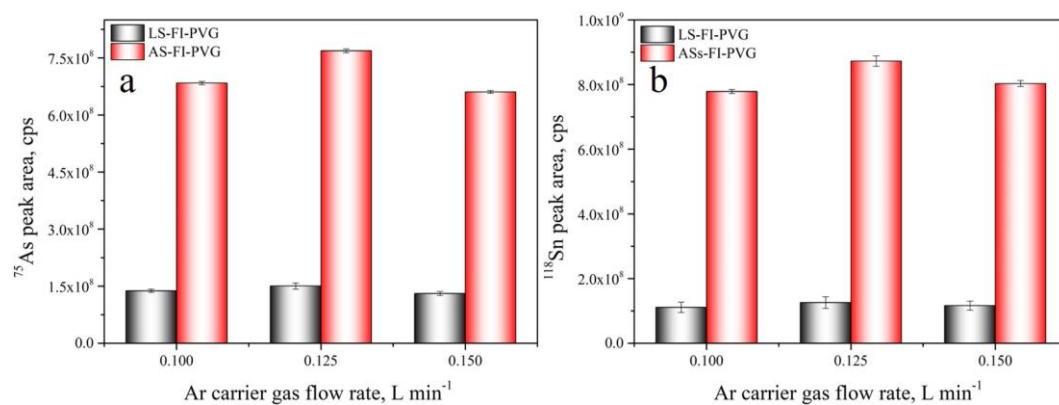


Figure S9. Effect of the Ar carrier gas flow rate on As and Sn responses in PVG. a) As, 4% (v/v) FA, 20% (v/v) AA, 15 mg L⁻¹ Fe³⁺, and 30 s irradiation; b) Sn, 0.8% (v/v) AA, 0.01% (v/v) HCl, and 32 s irradiation.

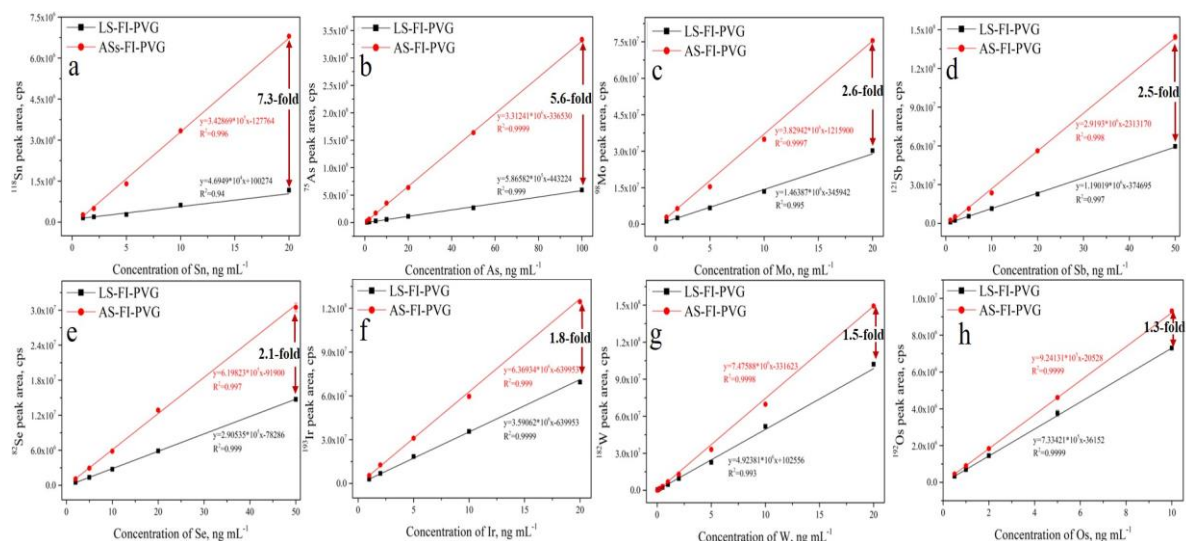


Figure S10. Calibration curves established using LS-FI-PVG and AS(s)-FI-PVG methods for elements: a) Sn, 0.8% (v/v) AA, 0.01% (v/v) HCl, 32 s UV irradiation time in the presence or absence of 1.60 mL air slugs; b) As, 4% (v/v) FA, 20% (v/v) AA, 15 mg L⁻¹ Fe³⁺, and 30 s irradiation in the presence or absence of 2.88 mL air slug; c) Mo, 30% (v/v) FA, 38 s UV irradiation time in the presence or absence of 1.09 mL air slug; d) Sb, 5% (v/v) FA, 15% (v/v) AA, 60 s UV irradiation time in the presence or absence of 2.24 mL air slug; e) Se (IV), 15% (v/v) FA, 13 s UV irradiation time in the presence or absence of 2.88 mL air slug; f) Ir, 20% (v/v) FA, 25 mg L⁻¹ Cu²⁺, 45 s UV irradiation time in the presence or absence of 1.60 mL air slug; g) W, 40% (v/v) FA, 500 mg L⁻¹ Cd²⁺, 120 s UV irradiation time in the presence or absence of 2.24 mL air slug; h) Os, 5% (v/v) HNO₃, 150 s UV irradiation time in the presence or absence of 0.77 mL air slug.

Table S1. Precision (n=7) obtained using peak area by LS-FI-PVG and AS(s)-FI-PVG methods.

Analytes	RSD %	
	LS-FI-PVG	AS(s)-FI-PVG
Sn	8.6	3.0
As	2.9	1.6
Bi	2.3	1.5
Se	3.2	1.1
Sb	2.6	2.4
W	3.6	3.0
Os	2.8	3.3
Mo	3.7	3.1
Ir	3.8	2.8

Table S2. Interferences from coexisting ions obtained in AS(s)-FI-PVG system.

Element	Interfering ions	Concentration (mg L ⁻¹)	[Interferent]/ Analytes	Recovery/%	
				LS-FI-PVG	AS(s)-FI-PVG
As	Co ²⁺	0.2	400	127±1	129±2
	Cu ²⁺	0.4	800	83±2	76±1
	Ni ²⁺	1	2000	106±1	111±1
Bi	Co ²⁺	0.02	40	109±1	110±1
Mo	NO ₂ ⁻	0.05	100	76±1	73±1
	NO ₃ ⁻	0.02	40	82±1	91±1
Sn	Fe ³⁺	0.05	100	112±3	103±1
	Co ²⁺	0.02	40	106±2	105±1
	Ni ²⁺	0.02	40	104±1	106±1
	Cu ²⁺	0.02	40	27±2	46±1