

Supplementary Information

Simultaneously determination of noble metals (Rh, Pd, Ir, Pt, and Au) in environmental sample by nebulized film dielectric barrier discharge vapor generation coupled with inductively coupled plasma mass spectrometry

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Fig. S3 Effect of different organic acid species (formic acid, acetic acid and propionic acid) with the same concentration of 7% mixed with nitric acid (2%) on the integrated response of Rh, Pd, Ir, Pt, and Au ($5 \text{ }\mu\text{g L}^{-1}$) by FI-NFDBD sampling system. Each point is the average from three measurements ($n = 3$). Error bars are defined as $\pm\text{SD}$.

Fig. S4 Comparison of the integrated response for Rh, Pd, Ir, Pt, and Au ($5 \text{ }\mu\text{g L}^{-1}$) in 2% nitric acid with and without formic acid (7%) by FI-NFDBD sampling system with DBD plasma off. Each point is the average from three measurements ($n = 3$). Error bars are defined as $\pm\text{SD}$.

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The pretreatment process of sediment sample

The sediment sample needed some digestion steps before analysis. The digestion steps were as follows: 1) 80 mg sediment sample was dissolved with a mix acid of 5 mL HF, 2 mL HNO₃ and 1 mL HClO₄ in a PTFE digester at 60°C, 90°C, 120°C and 150°C step by step on a hot plate for 2 h; 2) subsequently, 5 mL HF and 2 mL HNO₃ were added to the PTFE digester again under the heat process same to step 1) and further at 180°C for continuous digestion for 24 h; 3) next, the sample solution was cooled to room temperature and dried at 120°C; 4) then, the above steps 1) -3) were repeated once; 5) next, 3 mL HClO₄ was added to the digester three times (1 mL per time) to remove HF at 130°C; 6) finally, the sample residue was completely dissolved in 30 mL 2% nitric acid and filtered with 0.45 μm polyethersulfone membrane before analysis.

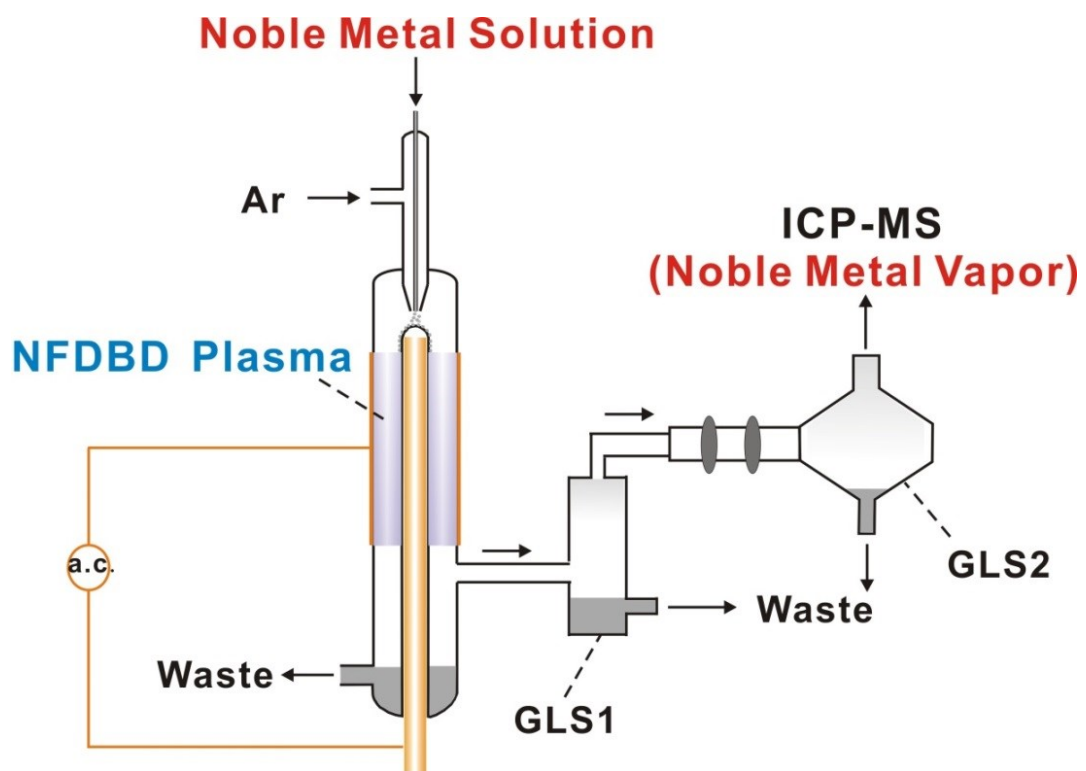


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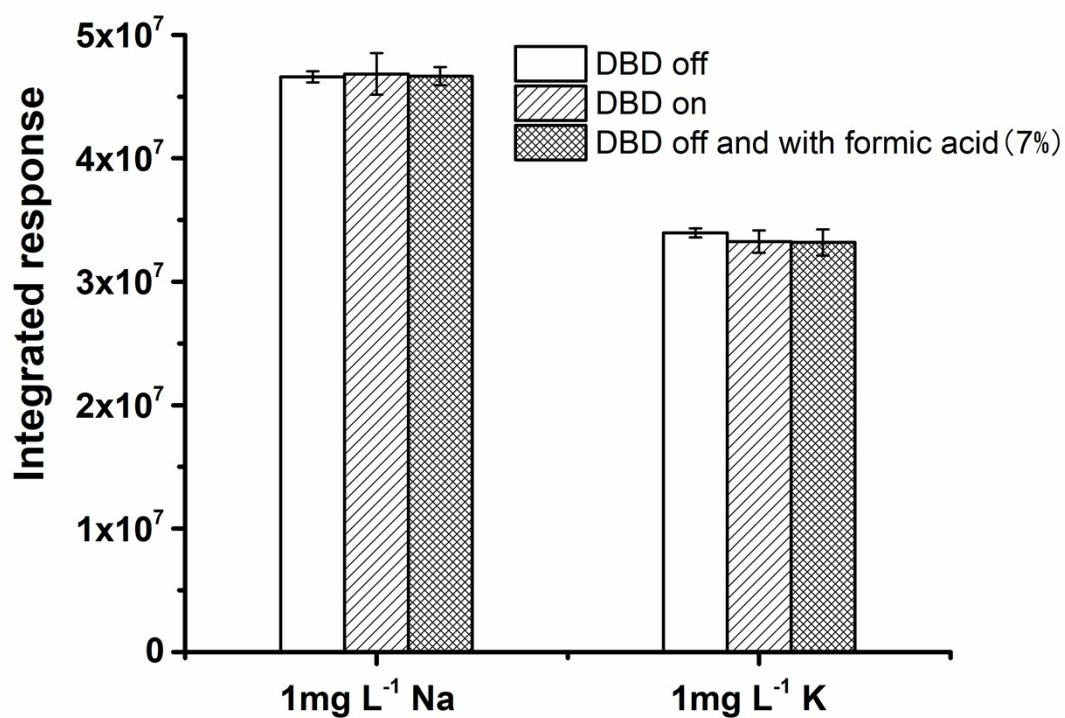


Fig. S2 Comparison of the integrated response of 1 mg L⁻¹ Na and K in 2% nitric acid by FI-NFDBD sampling system between DBD plasma off and on and adding with formic acid (7%) when DBD plasma was off. Each point is the average from three measurements (n = 3). Error bars are defined as ±SD.

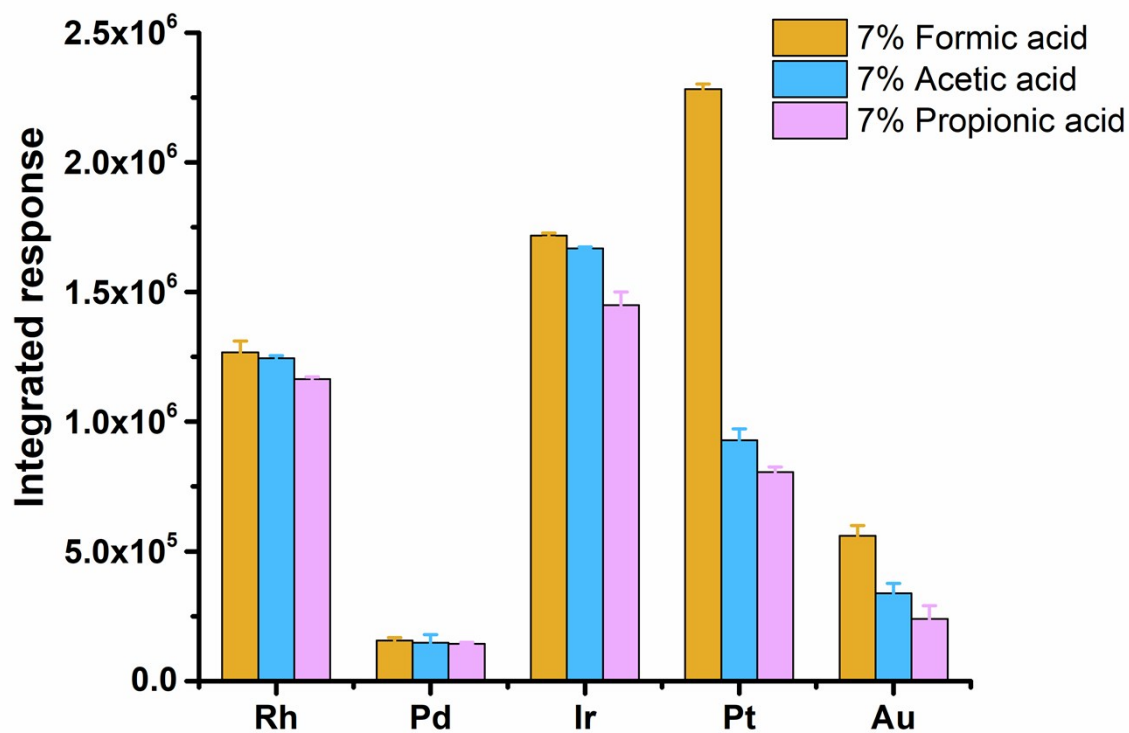


Fig. S3 Effect of different organic acid species (formic acid, acetic acid and propionic acid) with the same concentration of 7% mixed with nitric acid (2%) on the integrated response of Rh, Pd, Ir, Pt, and Au ($5 \mu\text{g L}^{-1}$) by FI-NFDBD sampling system. Each point is the average from three measurements ($n = 3$). Error bars are defined as $\pm\text{SD}$.

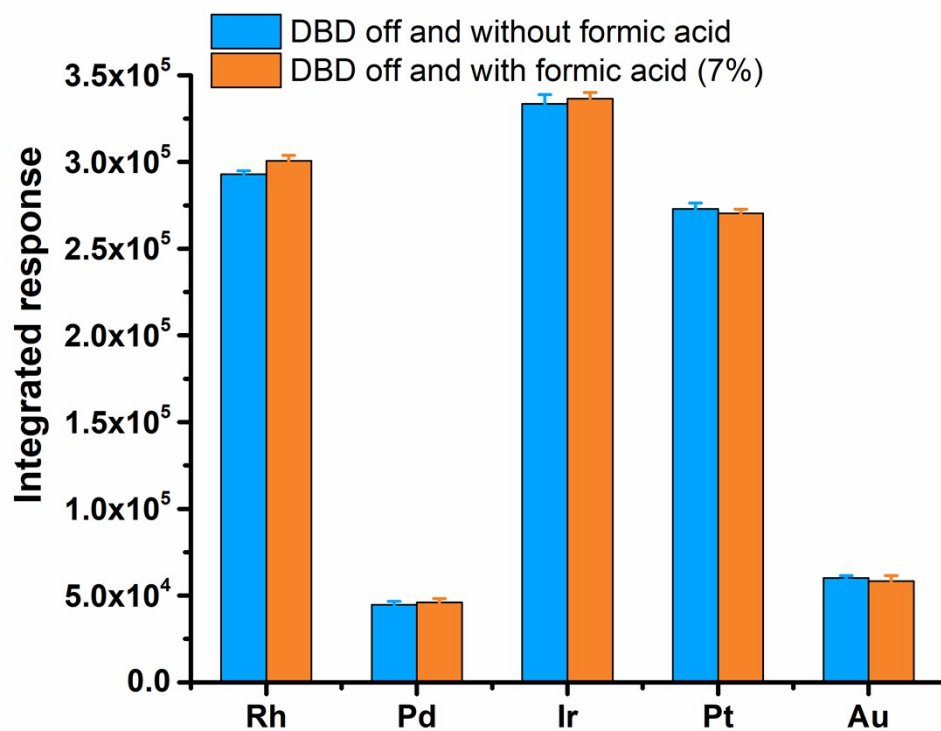


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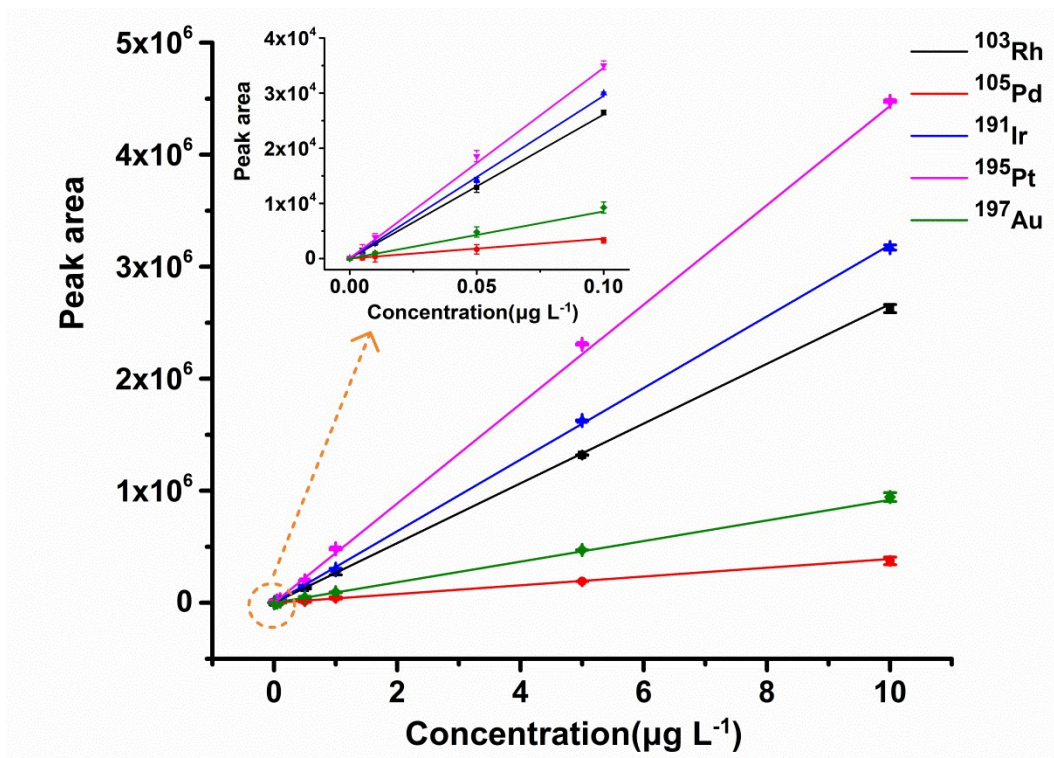


Fig. S5 Calibration curve of Rh, Pd, Ir, Pt, and Au in FI-NFDBD-ICP-MS system with the concentrations between 0.005 to 10 $\mu\text{g L}^{-1}$. The inset shows the calibration curve with the concentrations between 0.005 to 0.1 $\mu\text{g L}^{-1}$. Each point is the average from three measurements ($n = 3$). Error bars are defined as $\pm\text{SD}$.

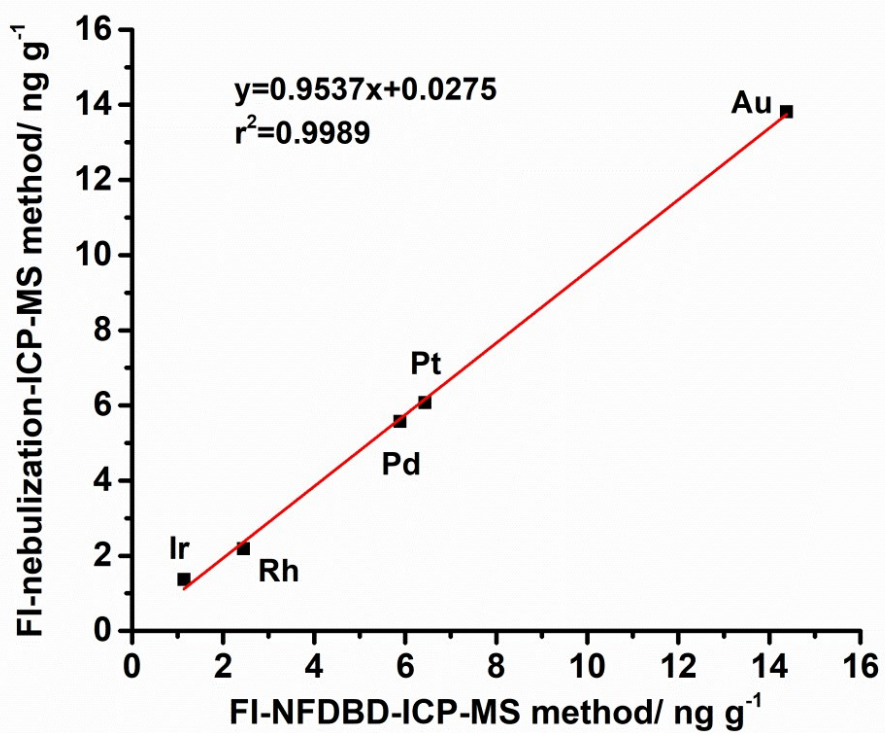


Fig. S6 Correlation of FI-NFDBD-ICP-MS method and FI-conventional nebulization-ICP-MS method for analysis of Rh, Pd, Ir, Pt, and Au in the same sediment sample.

Table S1 The recoveries of Rh, Pd, Ir, Pt, and Au ($5 \mu\text{g L}^{-1}$) with different matrix by FI-NFDBD sampling system.

Matrix	Concentration (mg L^{-1})	Recovery (%)				
		Rh	Pd	Ir	Pt	Au
NaCl	100	102.1±0.4	92.9±2.5	97.7±4.3	97.8±0.4	100.0±0.4
KCl	100	107.0±1.5	91.1±3.2	98.1±3.0	96.8±0.3	99.8±1.9
CaCl ₂	100	102.2±2.8	98.5±0.8	98.1±2.9	91.6±3.7	92.6±0.1
MgCl ₂	100	102.5±2.7	97.9±2.6	101.3±0.7	92.9±0.2	93.7±0.2
Cu(NO ₃) ₂	100	101.3±1.3	97.9±0.3	91.2±1.1	90.8±0.3	100.2±0.4
NiCl ₂	10	103.5±4.5	90.4±2.1	102.1±3.9	91.9±0.2	99.6±0.3
Co(NO ₃) ₂	10	102.4±4.5	93.5±2.3	100.1±3.5	96.3±0.3	100.3±0.4
Zn(NO ₃) ₂	10	100.4±2.3	91.7±1.2	92.0±1.9	102.3±0.3	96.7±0.2
Fe ₂ (SO ₄) ₃	10	108.4±3.2	92.3±3.3	106.1±1.7	95.5±0.2	96.8±0.4
CdCl ₂	10	100.5±0.7	99.7±0.9	101.3±3.4	102.5±1.7	99.5±2.8
Pb(NO ₃) ₂	10	100.3±4.6	100.8±0.3	100.2±1.2	94.5±1.9	98.5±0.5
AgNO ₃	10	100.2±0.2	99.8±2.1	100.2±2.4	102.2±1.9	98.5±3.1
ZrCl ₄	10	102.3±1.1	98.3±2.1	98.1±0.3	100.2±2.4	99.3±0.7
SrCl ₂	10	104.4±2.9	99.6±0.1	97.8±3.2	97.1±2.7	102.5±2.1
YCl ₃	10	97.3±0.8	99.9±3.4	100.2±2.3	98.5±0.2	96.5±0.7
HfCl ₄	0.01	102.3±1.2	99.8±0.3	100.2±1.7	97.6±2.8	101.4±0.7
LuCl ₃	0.01	104.4±2.5	93.5±0.3	97.7±3.3	102.4±0.3	99.5±0.4

Table S2 The LODs of noble metals determination by different vapor generation methods.

Vapor generation method	Detection method	LOD (ng L ⁻¹)					Ref
		Rh	Pd	Ir	Pt	Au	
NaBH ₄ in acid solution	AAS	—	—	—	—	766000	1
NaBH ₄ in acid solution with DDTC	AAS	—	—	—	—	24000	2
KBH ₄ in acid solution with RTIL	AFS	—	—	—	—	6300	3
NaBH ₄ in acid solution	MIP-OES with ultrasonic nebulizers	1800	1100	—	2900	1200	4
NaBH ₄ in acid solution	ICP-OES with solid phase extraction	—	3670	—	20	—	5
NaBH ₄ in acid solution	ICP-OES with solid phase extraction	100000	1500	570	30	620	6
Photochemical vapor generation with formic acid	ICP-MS	20	100	20	80	70	7
NFDBD vapor generation with formic acid	ICP-MS	0.34	0.65	0.26	0.11	0.50	This work

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