

Supporting Information

Photochemical vapor generation coupled with solution cathode glow discharge optical emission spectrometry for the highly sensitive determination of Co, Fe, and Ni

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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1. Background correction

According to literature reports, the stability of the method can be improved through background correction¹. Specifically, emission signals for Co at 240.7 nm, Fe at 248.3 nm, and Ni at 232.0 nm from the sample solution were recorded, and the signals at 239.8 nm, 248.5 nm, and 232.5 nm were subsequently subtracted to obtain the emission intensities for each element. The background solution was similarly treated to determine the blank background emission intensities for each element. Finally, the processed emission intensities for each element were adjusted by subtracting the corresponding blank background emission intensities to yield the net signal intensities. A detailed processing method is illustrated in Fig. S1, using Ni (1 mg L⁻¹) as an example.

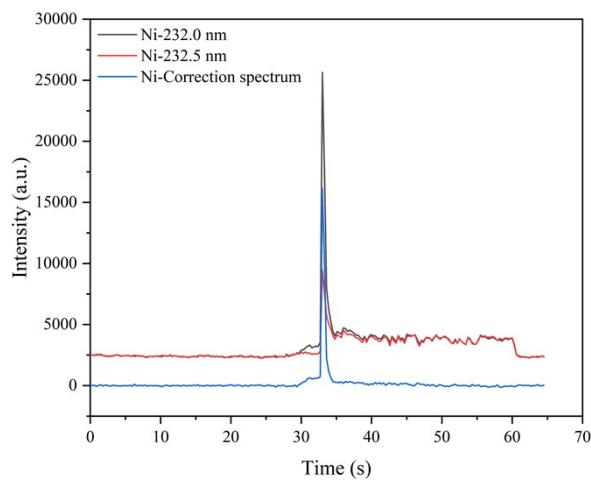


Fig. S1 Background correction (Using Ni as an example)

2. Optimal parameters for the PVG-SCGD-OES system

Table S1 Optimal parameters for the PVG-SCGD-OES system

System	Operation parameter	Co	Fe	Ni
PVG	Concentration of HCOOH (wt%, v/v)	10	40	20
	UV irradiation time (s)	30	60	40
	Ar flow rate of flow meter A (mL min ⁻¹)		90	
	Ar flow rate of flow meter B (mL min ⁻¹)		70	
SCGD	Concentration of ammonia (wt%, v/v)	/	20	/
	Electrolyte		HNO ₃ , pH=0.9	
	Discharge current (mA)		52	
	Electrolyte flow rate (mL min ⁻¹)	2.2	2.4	2.6
Discharge gap (mm)			3	

3. Evaluation of sensitization

Previous studies have reported that transition metals can enhance the PVG efficiency of certain elements²⁻³. Therefore, this experiment investigated the synergistic effect among Fe, Co, and Ni, revealing that 10 mg L⁻¹ of Fe(III) has a weak enhancing effect on both Co and Ni. Furthermore, the concentration of Fe (III) was optimized to further confirm whether an increase in Fe concentration can significantly enhance the PVG efficiency of Co and Ni. As shown in **Fig. S2**, after a certain increase in Fe(III), the PVG efficiencies of both Co and Ni decreased, leading to weaker net signals. The likely reason is that excessively high concentrations of Fe(III) can compete with radicals (CO[·]), leading to radical decomposition and recombination, which consumed the radicals required for Co or Ni⁴. The optimal enhancing effects for Co and Ni were observed at Fe(III) concentrations of 20 mg L⁻¹ and 50 mg L⁻¹, respectively, where the signal intensities of Co and Ni increased by 1.6 times and 1.8 times compared to the signals without Fe(III) addition. According to reports⁵, the possible sensitization mechanism of Fe³⁺ is that formic acid transforms the oxidative environment driven by ·OH into a reducing environment driven by ·CO₂[·]. In this way, better PVG efficiency was achieved through the synergistic effect of Fe³⁺ activated photo-Fenton effect and the reaction of generating reductive ·CO₂[·] between formic acid and ·OH. Of course, the specific mechanism research is beyond our current research scope, and due to the unsatisfactory sensitization effect, Fe³⁺ was not used as a sensitizer for performance analysis in subsequent experiments.

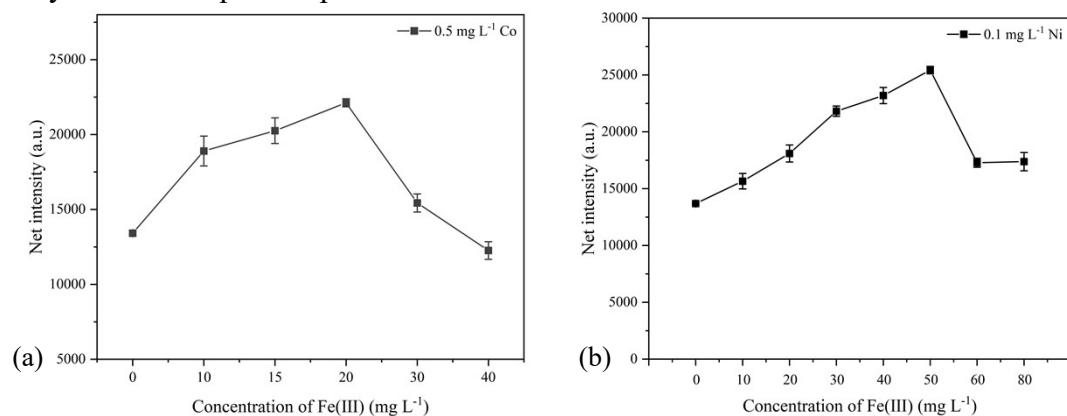


Fig.S2 The effect of the Fe (III) concentration in the medium

- [1] Mo, J. M.; Li, Q.; Guo, X. H., et al., Flow injection photochemical vapor generation coupled with miniaturized solution-cathode glow discharge atomic emission spectrometry for determination and speciation analysis of mercury. *Anal. Chem.* **2017**, *89* (19), 10353-10360.
- [2] Zeng, W.; Hu, Z. H.; Luo, J., et al., Highly sensitive determination of trace antimony in water samples by cobalt ion enhanced photochemical vapor generation coupled with atomic fluorescence spectrometry or ICP-MS. *Anal. Chim. Acta* **2022**, *1191*.
- [3] Zhang, Y.; Hu, J.; Li, C. H., et al., Iron and copper ions-synergistically enhanced cobalt photochemical vapor generation for its sensitive detection by inductively coupled plasma mass spectrometry. *Microchem. J.* **2025**, *218*.
- [4] Zeng, W.; Hu, J.; Chen, H. J., et al., Cobalt ion-enhanced photochemical vapor generation in a mixed acid medium for sensitive detection of tellurium(iv) by atomic fluorescence spectrometry. *J. Anal. At. Spectrom.* **2020**, *35* (7), 1405-1411.
- [5] He, Y. J.; Hu, J.; Zou, W., et al., Chemical vapor generation of tungsten for atomic spectrometric determination: Homogeneous sensitizer and mechanism study. *Anal. Chim. Acta* **2023**, *1278*.