Supporting Information

Rapid, clean quantitative analysis of Cu^{2+} in copper refining electrolyte via chemometrics driven Vis-SWNIR absorption spectroscopy

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17 Pages, 8 Tables, 7 Figures

Contents

Table S1

Table S1. Python packages employed in this work

Packages	Version
numpy	2.2.6
pandas	2.2.3
scipy	1.15.3
spectrochempy	0.8.1
scikit-learn	1.7.0
torch	2.7.1

Table S2

Table S2. Composition of samples simulating real copper refining electrolyte

(a) Cu^{2+} and Ni^{2+} concentration in the samples

Sample / No.	Cu^{2+} concentration (g/L)	Ni^{2+} concentration (g/L)
1	40.0	4.5
2	40.0	9.0
3	40.0	13.5
4	40.0	18.0
5	45.0	4.5
6	45.0	9.0
7	45.0	13.5
8	45.0	18.0
9	50.0	4.5
10	50.0	9.0
11	50.0	13.5
12	50.0	18.0
13	55.0	4.5
14	55.0	9.0
15	55.0	13.5
16	55.0	18.0

(b) Other species' concentration in the samples

Species	H_2SO_4	Cl	As	Sb	Bi	Pb	Fe	Zn	Ca
Conc. (g/L)	180	0.06	10	0.4	0.4	0.02	0.4	0.6	0.2

Table S3

Table S3. Detailed ICP-MS analysis results of the real copper refining electrolyte samples

Items	Raw intensities		Net intensities		Concentrations	
	Cu 63 (cps)	Ni 60 (cps)	Cu 63 (cps)	Ni 60 (cps)	Cu 63 (ppb)	Ni 60 (ppb)
Blank	8147.3	1037.0	□	□		
Standard 1	179090.3	69374.0	170943.0	68337.0	10.0	10.0
Standard 2	356642.8	139419.8	348495.5	138382.8	20.1	20.0
Standard 3	540192.9	212246.6	532045.6	211209.6	30.2	30.2
Standard 4	730631.8	284557.4	722484.5	283520.4	40.5	40.3
Standard 5	912178.1	357896.1	904030.8	356859.1	50.4	50.4
sample1	837746.0	75612.6	829598.7	74575.6	46.2	10.5
sample2	920772.3	80531.0	912624.9	79493.9	50.8	11.2
sample3	873913.3	78519.5	865765.9	77482.5	48.2	10.9
sample4	936176.3	79860.4	928029.0	78823.4	51.7	11.1
sample5	995791.7	87027.2	987644.4	85990.2	52.5	12.1

Table S4

Table S4. Detailed spectrophotometric analysis results of the real copper refining electrolyte samples

Items	Absorbance at 440 nm	Cu^{2+} concentration (g/L)
Standard 1	0.10201	10.00
Standard 2	0.19869	20.00
Standard 3	0.23711	30.00
Standard 4	0.31781	40.00
Standard 5	0.38710	50.00
Standard 6	0.47673	60.00
sample1	0.33063	41.06
sample2	0.34595	43.19
sample3	0.34040	42.42
sample4	0.35185	44.01
sample5	0.34636	43.25

Note: The test method refers to the Chinese national standard "***Water quality—Determination of copper—Spectrophotometric method***" (HJ 485-2009). Prior to testing, the samples had been diluted to the concentration range applicable to this method.

Table S5

Table S5. Detailed ICP-MS analysis results of the simulating copper refining electrolyte samples

Items	Raw intensities		Net intensities		Concentrations	
	Cu 63 (cps)	Ni 60 (cps)	Cu 63 (cps)	Ni 60 (cps)	Cu 63 (ppb)	Ni 60 (ppb)
Blank	16541.9	2055.1	-	-	-	-
Standard 1	677318.1	285552.1	660776.2	283496.9	10.0	10.0
Standard 2	1327543.2	573393.6	1311001.2	571338.5	20.0	20.0
Standard 3	1957932.1	863801.5	1941390.2	861746.3	29.8	30.1
Standard 4	2556655.0	1109768.6	2540113.0	1107713.4	39.0	38.9
Standard 5	3245265.0	1421925.7	3228723.1	1419870.5	49.7	49.9
Standard 6	3902114.3	1718252.6	3885572.4	1716197.5	60.2	60.4
sample1	2355355.3	125924.2	2338813.4	123869.1	36.2	4.4
sample2	2903538.6	263926.4	2886996.7	261871.2	44.7	9.2
sample3	2624390.4	391168.7	2607848.5	389113.5	40.4	13.7
sample4	2984374.1	634417.8	2967832.2	632362.6	46.0	22.3
sample5	3414174.2	165129.6	3397632.3	163074.4	52.7	5.7
sample6	3147702.8	298844.4	3131160.9	296789.3	48.5	10.5
sample7	3219741.9	469790.1	3203200.0	467735.0	49.6	16.5
sample8	3391312.0	644359.9	3374770.0	642304.8	52.3	22.6
sample9	3647296.8	171510.9	3630754.9	169455.7	56.3	6.0
sample10	3636018.8	328802.0	3619476.9	326746.9	56.1	11.5
sample11	3835693.1	534141.8	3819151.2	532086.7	59.2	18.7
sample12	3505782.4	629533.7	3489240.5	627478.6	54.1	22.1
sample13	3690723.8	151685.7	3674181.9	149630.6	56.9	5.3
sample14	3940461.1	309961.0	3923919.2	307905.8	60.8	10.8
sample15	4041278.9	481668.3	4024737.0	479613.2	62.4	16.9
sample16	4174905.4	647662.8	4158363.5	645607.6	64.4	22.7

Table S6

Table S6. Detailed spectrophotometric analysis results of the simulating copper refining electrolyte samples

Items	Absorbance at 440 nm	Cu^{2+} concentration (g/L)
Standard 1	0.08557	10.00
Standard 2	0.16407	20.00
Standard 3	0.2422	30.00
Standard 4	0.32673	40.00
Standard 5	0.41072	50.00
Standard 6	0.48771	60.00
sample1	0.34073	41.73
sample2	0.31509	38.57
sample3	0.35783	43.84
sample4	0.34641	42.43
sample5	0.38711	47.46
sample6	0.39968	49.01
sample7	0.40381	49.52
sample8	0.39646	48.61
sample9	0.44878	55.07
sample10	0.43654	53.56
sample11	0.42675	52.35
sample12	0.43051	52.82
sample13	0.50228	61.68
sample14	0.48337	59.34
sample15	0.47783	58.66
sample16	0.46745	57.38

Table S7

Table S7. Comparative measurement costs of different analytical methods (unit: USD $ per sample)

Methods	Chemical reagents required	Chemical reagents cost	Energy cost	Overall cost
This work	-	~0	~0[1]	~0
Directly Measured by spectro-photometer (DMS)	-	~0	0.2	0.2
Traditional Spectrophotometric Analysis (TSA)	$C_5H_{10}NNaS_2 \cdot 3H_2O$, C_2H_5OH, CCl_4, EDTA, $NH_3 \cdot H_2O$, $CHCl_3$	2-3	0.2	2.2-3.2
Analyzed by Inductively Coupled Plasma (ICP) approach	Ar, HNO_3	5-7	1	6-8
Zhou et al.[2]	Nitroso R salt, HAc, NaAc, EDTA	1-2	~0[1]	1-2
Liang et al.[3]	-	~0	0.2	0.2

[1] Due to the low power consumption and fast measurement time (seconds-level) of the micro/miniature spectrometer-based measurement system, its energy consumption can be considered negligible.

[2] Zhou, F., et al. (2020). "Development of a Miniature Spectrometer Based on Ultraviolet-Visible Spectroscopy for Quantitative Analysis of Copper and Cobalt." IEEE Access **8**: 131239-131247.

[3] Liang, Q., et al. (2024). "Determination of High Concentration Copper Ions Based on Ultraviolet—Visible Spectroscopy Combined with Partial Least Squares Regression Analysis." Processes **12**(7): 1408.

Table S8

Table S8. Instrument cost of the spectroscopic measurement system

Item	Manufactor	Detailed information	Price (USD)
Micro-spectrometer	Hangzhou Daohuozhe Technology Co., Ltd.	T34B2C10735FTAD, 350-1070 nm	~260
Tungsten-halogen Light Source	Bobei Optics	SMA905 interface	~180
Cuvette holder	-	Custom-made	~160
Optic Fiber	-	600 μm core diameter	~100
Overall			~700

Figure S1

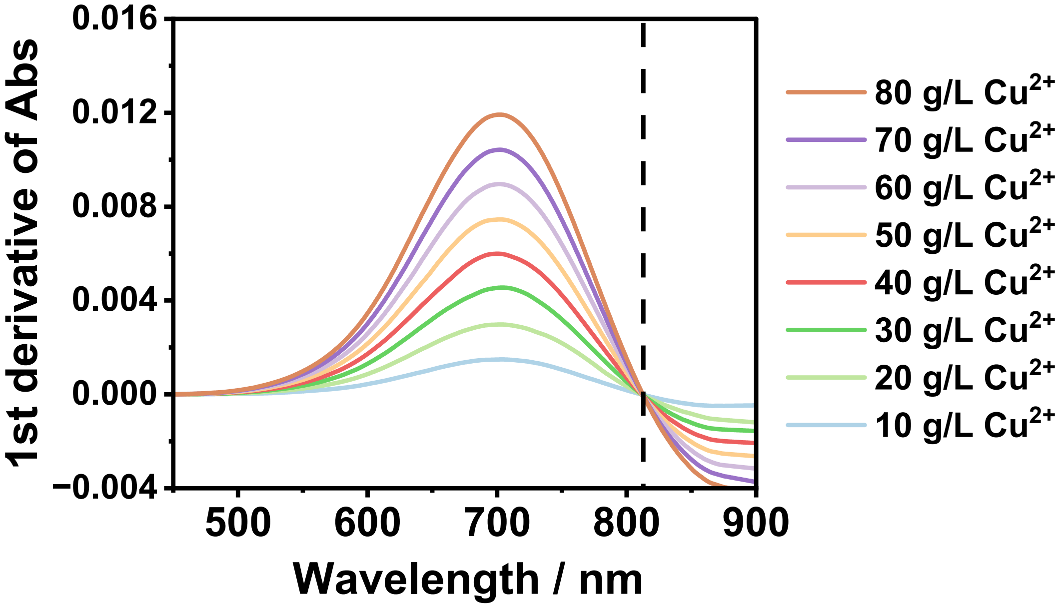

Figure S1. First derivative analysis of the Cu^{2+}'s Vis-SWNIR absorption spectra obtained in the Figure 2c

Figure S2

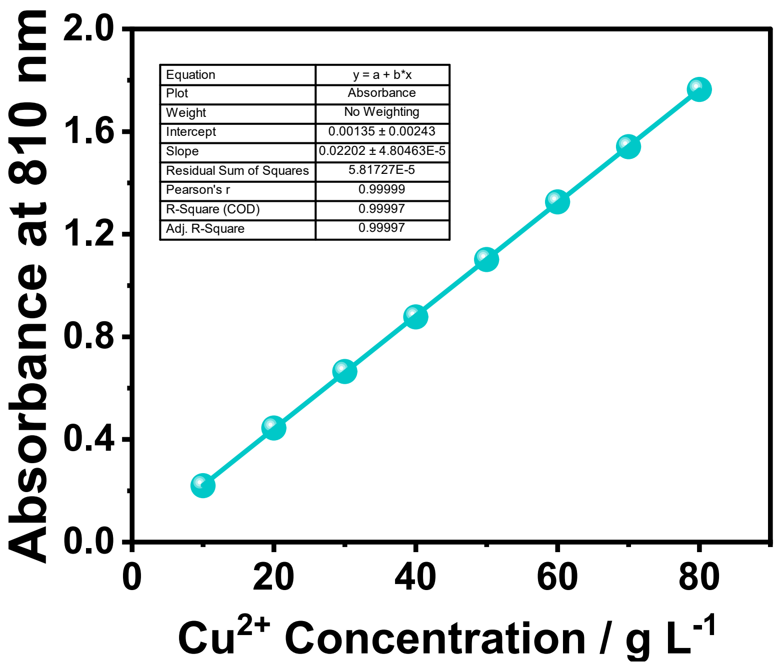

Figure S2. Relationship of Cu^{2+} concentration and absorbance at 810 nm in $CuSO_4$ solution.

Figure S3

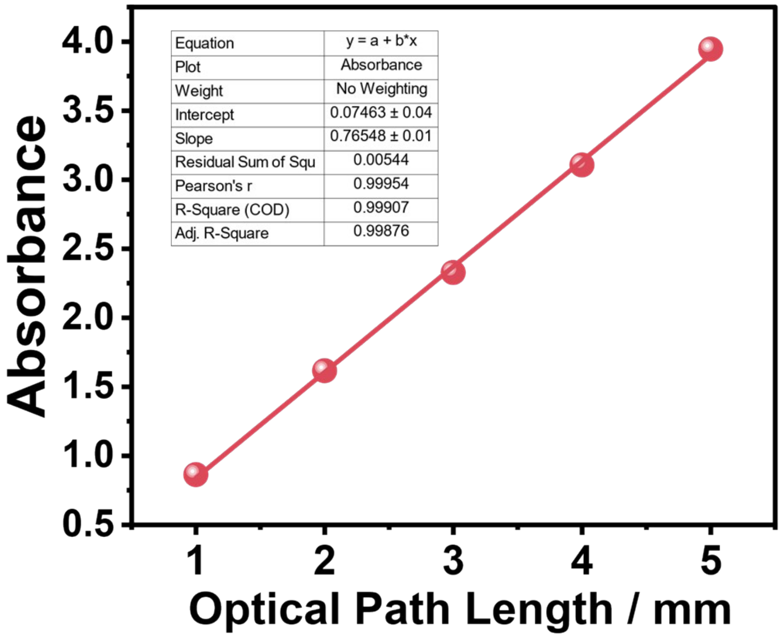

Figure S3. Relationship of optical path length and absorbance at 810 nm in $CuSO_4$ solution.

Figure S4

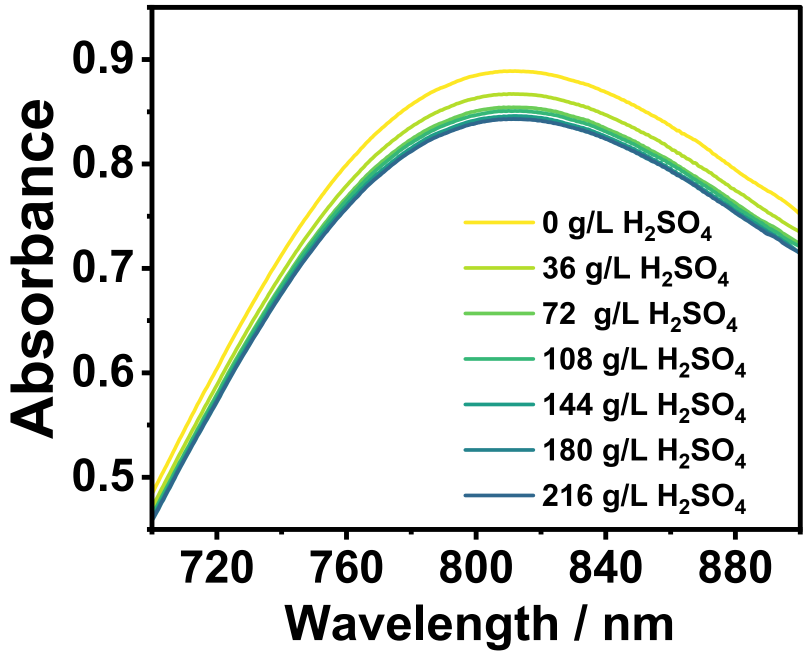

Figure S4. Influence of H_2SO_4 concentration on the Vis-SWNIR absorption spectra of Cu^{2+}

Figure S5

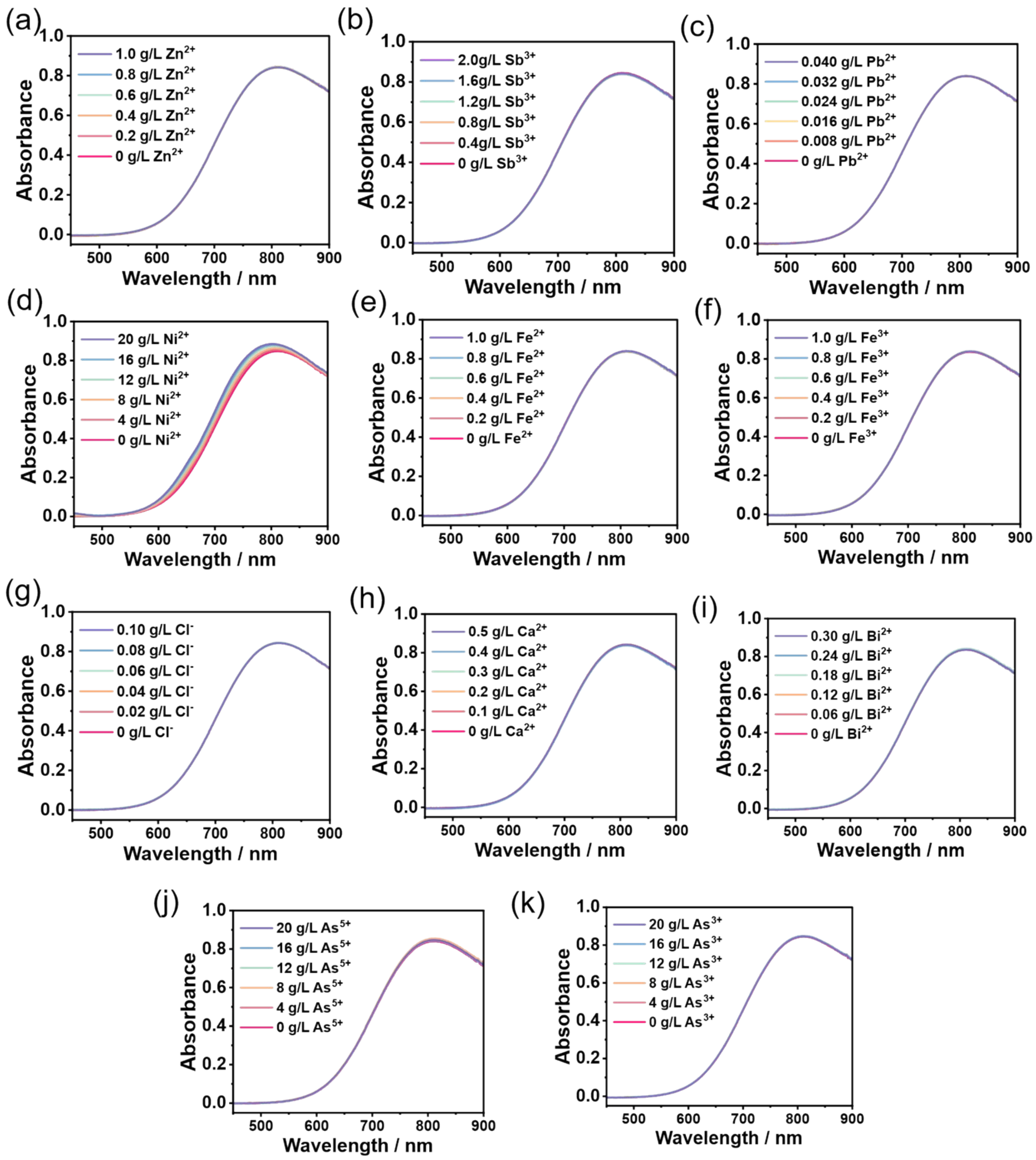

Figure S5. Influence of species presented in real copper refining electrolyte on the Vis-SWNIR absorption spectra of Cu^{2+}: (a) Zn^{2+} (b) Sb^{3+} (c) Pb^{2+} (d) Ni^{2+} (e) Fe^{2+} (f) Fe^{3+} (g) Cl^{-} (h) Ca^{2+} (i) Bi^{2+} (j) As^{5+} (k) As^{3+} , all samples were prepared in 180 g/L H_2SO_4 and 40 g/L Cu^{2+}

Figure S6

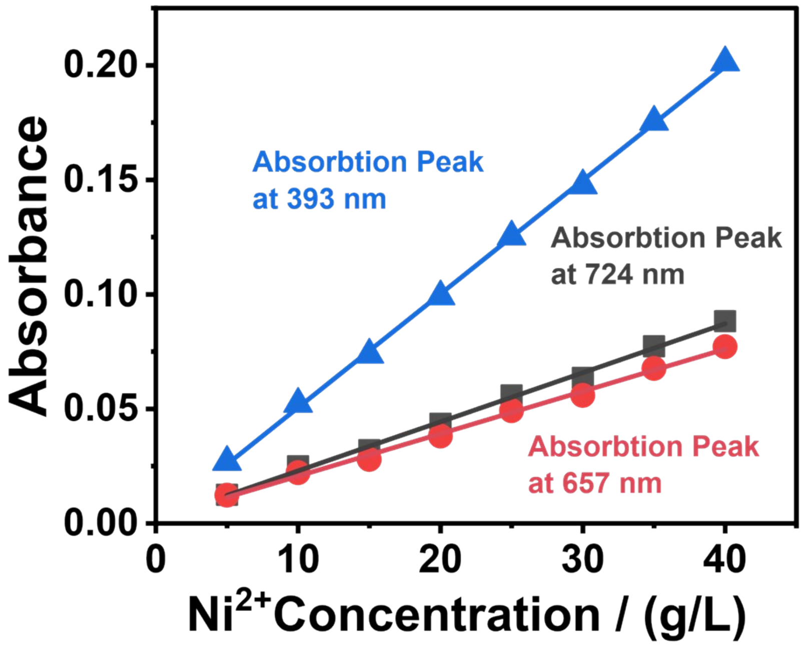

Figure S6. Relationship of Ni^{2+} concentration and absorbance at 393, 657, 724 nm in $NiSO_4$ solution.

Figure S7

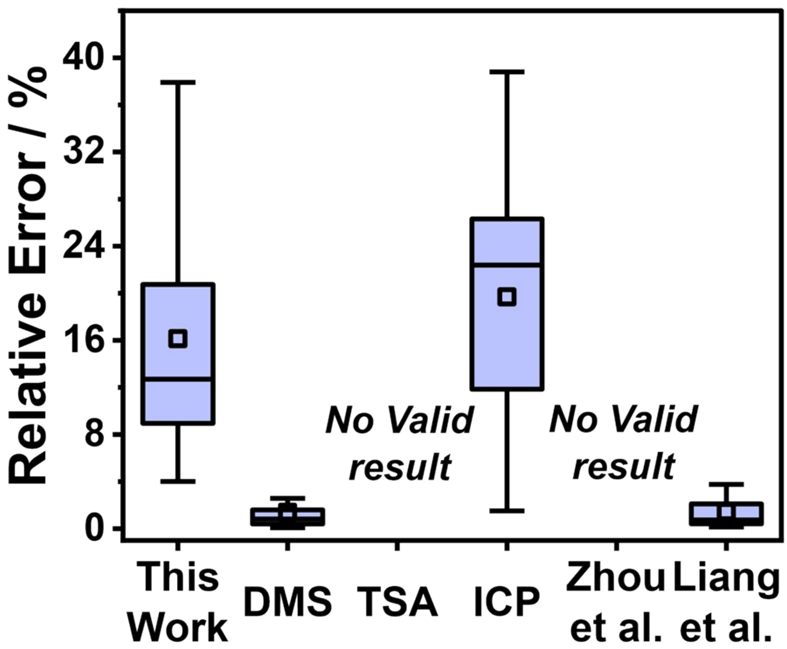

Figure S7. Performance assessment of various analytical methods for $c(Ni^{2+})$ analysis in simulated copper refining electrolytes.