Supplementary Information (SI) for Journal of Analytical Atomic Spectrometry.

Electronic Supplementary Information

Vortex-Assisted Reverse-Phase Dispersive Liquid-Liquid Microextraction for On-Site Determination of Ti, Cr, Mn, Ni, and Cu in Lubricating Oil Using Total Reflection X-ray Fluorescence Spectroscopy

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Table S1. Factors and levels of the Plackett-Burman design

Experimental factor	Low level (-1)	High level (1)
A:Sample volume (mL)	1	5
B: Extractant volume(μL)	50 μL	100 μL
C: Acidity(mol L^{-1})	0	0.1 mol L^{-1}
D:Vortex time(min)	1 min	3 min
E:Centrifugation conditions(min)	0	3 min

Table S2. Screening study matrix of the Plackett-Burman design

Experiment	A	B	C	D	E
1	5	100	0.1	1	3
2	1	100	0.1	3	0
3	5	50	0.1	3	3
4	1	100	0	3	3
5	1	50	0.1	1	3
6	5	50	0	3	0
7	1	50	0	1	0
8	5	100	0	1	0
9	5	50	0.1	1	0
10	1	100	0	1	3
11	5	100	0.1	3	0
12	1	50	0	3	3

Table S3. Experimental results of the Plackett-Burman design

Experiment	Ti		Cr		Mn		Ni		Cu	
	AR	EF	AR	EF	AR	EF	AR	EF	AR	EF
1	0.41	16.0	0.051	3.0	0.40	4.3	0.44	4.9	0.34	4.6
2	0.48	18.3	0.055	3.3	0.80	8.5	0.70	7.9	0.59	7.9
3	0.24	9.1	0.032	1.9	0.19	2.1	0.22	2.5	0.18	2.4
4	0.05	1.8	0.010	0.6	0.02	0.2	0.03	0.4	0.04	0.5
5	0.61	23.4	0.075	4.4	1.12	11.9	1.04	11.7	0.93	12.4
6	0.07	2.7	0.014	0.8	0.06	0.7	0.09	1.0	0.08	1.1
7	0.09	3.4	0.020	1.2	0.07	0.7	0.08	1.0	0.08	1.1
8	0.02	0.9	0.005	0.3	0.02	0.2	0.03	0.4	0.03	0.3
9	0.05	2.1	0.014	0.9	0.16	1.7	0.15	1.7	0.13	1.7
10	0.03	1.0	0.004	0.2	0.03	0.3	0.03	0.4	0.03	0.4
11	0.44	16.7	0.066	3.9	1.30	13.8	1.21	13.5	1.06	14.2
12	0.13	5.1	0.022	1.3	0.11	1.1	0.11	1.3	0.13	1.7

AR: Area ratio of the analyte element to the internal standard element

EF: Enrichment factor of the analyte element

Table S4. Factors and levels of the CCCD

Factors	Level			Star points (α=1,414)	
	Low (-1)	Central (0)	High (+1)	-α	+α
Sample volume (mL)	2	3	4	1.6	4.4
Extractant volume (μL)	58	75	93	50	100

Table S5. Optimization study matrix of the CCCD

Experiment	Sample volume (mL)	Extractant volume (μL)
1	2	58
2	4	58
3	2	93
4	4	93
5	1.6	75
6	4.4	75
7	3	50
8	3	100
9	3	75
10	3	75
11	3	75
12	3	75

Table S6. Experimental results of the CCCD

Experiment	Ti		Cr		Mn		Ni		Cu	
	AR	EF	AR	EF	AR	EF	AR	EF	AR	EF
1	0.08	3.1	0.015	0.9	0.30	7.9	0.27	7.5	0.24	7.9
2	0.05	1.9	0.013	0.8	0.20	5.4	0.20	5.5	0.17	5.7
3	0.11	4.1	0.012	0.7	0.46	12.2	0.36	10.0	0.36	12.1
4	0.06	2.1	0.008	0.5	0.22	5.9	0.20	5.7	0.19	6.3
5	0.07	2.5	0.014	0.8	0.34	9.1	0.29	8.1	0.30	9.9
6	0.03	1.2	0.010	0.6	0.12	3.3	0.10	2.9	0.15	5.1
7	0.11	4.2	0.022	1.3	0.47	12.5	0.43	12.0	0.36	11.9
8	0.17	6.5	0.037	2.2	0.61	16.1	0.54	15.2	0.47	15.8
9	0.20	7.8	0.038	2.2	0.79	21.1	0.68	19.1	0.64	21.4
10	0.20	7.5	0.034	2.0	0.80	21.2	0.69	19.4	0.63	21.1
11	0.16	6.3	0.029	1.7	0.67	17.8	0.58	16.3	0.54	17.9
12	0.17	6.4	0.031	1.8	0.64	17.1	0.55	15.3	0.51	17.1

AR: Area ratio of the analyte element to the internal standard element

EF: Enrichment factor of the analyte element

Table S7. Optimal values for Cu, Ni, Mo, Mn and Cr

Analyte	Sample volume (mL)	Extractant volume(μL)
Ti	2.9	80
Cr	2.9	78
Mn	2.8	79
Ni	2.9	78
Cu	2.8	79

Table S8. ANOVA tables of the CCCD

Analyte	Analysis of Variance					
	Source	DF	Adj SS	Adj MS	F-Value	P-Value
Ti	Model	5	0.037875	0.007575	17.29	0.002
	Linear	2	0.003812	0.001906	4.35	0.068
	A	1	0.002119	0.002119	4.83	0.070
	B	1	0.001694	0.001694	3.87	0.097
	Square	2	0.033964	0.016982	38.75	0.000
	A*A	1	0.033053	0.033053	75.42	0.000
	B*B	1	0.004349	0.004349	9.92	0.020
	2-Way Interaction	1	0.000098	0.000098	0.22	0.653
	A*B	1	0.000098	0.000098	0.22	0.653
	Error	6	0.002629	0.000438		
	Lack-of-Fit	3	0.001369	0.000456	1.09	0.474
	Pure Error	3	0.001260	0.000420		
	Total	11	0.040504			
	Source	DF	Adj SS	Adj MS	F-Value	P-Value
Cr	Model	5	0.001083	0.000217	4.49	0.048
	Linear	2	0.000039	0.000020	0.41	0.682
	A	1	0.000021	0.000021	0.43	0.538
	B	1	0.000019	0.000019	0.39	0.555
	Square	2	0.001042	0.000521	10.80	0.010
	A*A	1	0.001029	0.001029	21.32	0.004
	B*B	1	0.000099	0.000099	2.06	0.202
	2-Way Interaction	1	0.000001	0.000001	0.03	0.878
	A*B	1	0.000001	0.000001	0.03	0.878
	Error	6	0.000290	0.000048		
	Lack-of-Fit	3	0.000250	0.000083	6.33	0.082
	Pure Error	3	0.000039	0.000013		
	Total	11	0.001372			
	Source	DF	Adj SS	Adj MS	F-Value	P-Value
Mn	Model	5	0.563596	0.112719	18.71	0.001
	Linear	2	0.069749	0.034875	5.79	0.040
	A	1	0.052055	0.052055	8.64	0.026
	B	1	0.017694	0.017694	2.94	0.137
	Square	2	0.488804	0.244402	40.57	0.000
	A*A	1	0.462840	0.462840	76.84	0.000
	B*B	1	0.086402	0.086402	14.34	0.009
	2-Way Interaction	1	0.005041	0.005041	0.84	0.396
	A*B	1	0.005041	0.005041	0.84	0.396
	Error	6	0.036142	0.006024		
	Lack-of-Fit	3	0.016375	0.005458	0.83	0.560
	Pure Error	3	0.019767	0.006589		
	Total	11	0.599737			

	Source	DF	Adj SS	Adj MS	F-Value	P-Value
Ni	Model	5	0.408585	0.081717	15.97	0.002
	Linear	2	0.038590	0.019295	3.77	0.087
	A	1	0.030142	0.030142	5.89	0.051
	B	1	0.008448	0.008448	1.65	0.246
	Square	2	0.368250	0.184125	35.98	0.000
	A*A	1	0.355288	0.355288	69.43	0.000
	B*B	1	0.053250	0.053250	10.41	0.018
	2-Way Interaction	1	0.001745	0.001745	0.34	0.581
	A*B	1	0.001745	0.001745	0.34	0.581
	Error	6	0.030703	0.005117		
	Lack-of-Fit	3	0.014915	0.004972	0.94	0.518
	Pure Error	3	0.015788	0.005263		
	Total	11	0.439288			
Cu	Source	DF	Adj SS	Adj MS	F-Value	P-Value
	Model	5	0.317721	0.063544	14.52	0.003
	Linear	2	0.036843	0.018422	4.21	0.072
	A	1	0.024682	0.024682	5.64	0.055
	B	1	0.012161	0.012161	2.78	0.147
	Square	2	0.278085	0.139043	31.78	0.001
	A*A	1	0.251004	0.251004	57.36	0.000
	B*B	1	0.068351	0.068351	15.62	0.008
	2-Way Interaction	1	0.002792	0.002792	0.64	0.455
	A*B	1	0.002792	0.002792	0.64	0.455
	Error	6	0.026254	0.004376		
	Lack-of-Fit	3	0.013251	0.004417	1.02	0.494
	Pure Error	3	0.013003	0.004334		
	Total	11	0.343974			

Table S9. Quantitative accuracy before and after matrix effect correction using the standard addition method

Analyte	True value	Before matrix correction		After matrix correction	
		Detection concentration /mg·L-1	Recovery Rate/%	Detection concentration /mg·L-1	Recovery Rate/%
Ti	2.5	0.8	33	2.1	84
Cr	2.5	0.9	37	2.1	84
Mn	2.5	2.1	85	2.4	96
Ni	2.5	2.2	90	2.6	104
Cu	2.5	1.3	54	2.2	88

Table S10. Calculation of Penalty points (PP) for assessing the greenness of propose method and traditional method

	This work		Ref. 25	
	Penalty Item	Penalty Points (PP)	Penalty Item	Penalty Points (PP)
Reagents	Nitric Acid	4	Hydrochloric Acid	4
	Petroleum ether for dilution	8	Petroleum ether for dilution	8
	Reference materials	1	Reference materials	1
Instruments	TXRF analysis	0	MIP OES analysis	1
	Waste	6	Waste	8
Analytical Eco-Scale Total Score	81		78	

Table S11. Comparison of properties of petroleum ether, water and Deep Eutectic Solvents (DES)

Solvent Type	Density (g/mL)	Polarity	Viscosity (cP)
Petroleum Ether	0.64 - 0.66	0.01 (Extremely Low, Non-polar)	~0.3 (Very Low)
Water	0.997 (at 25°C)	10.2 (High, Polar)	0.89 (at 25°C)
DESs (General Range)	Typically > 1.0	Tunable, Wide Range (Typically Moderate to Polar)	Very High (Typically ranges from 10 to > 50,000; significantly higher than water and petroleum ether)

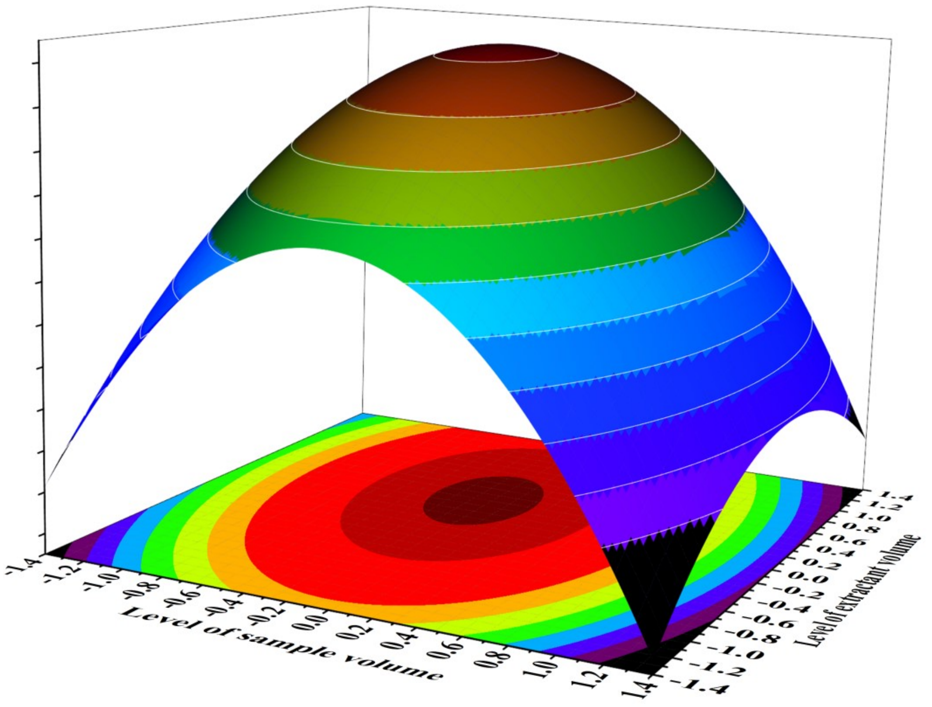

Figure S1. Response surface and contour plots from circumscribed central composite design for Ti

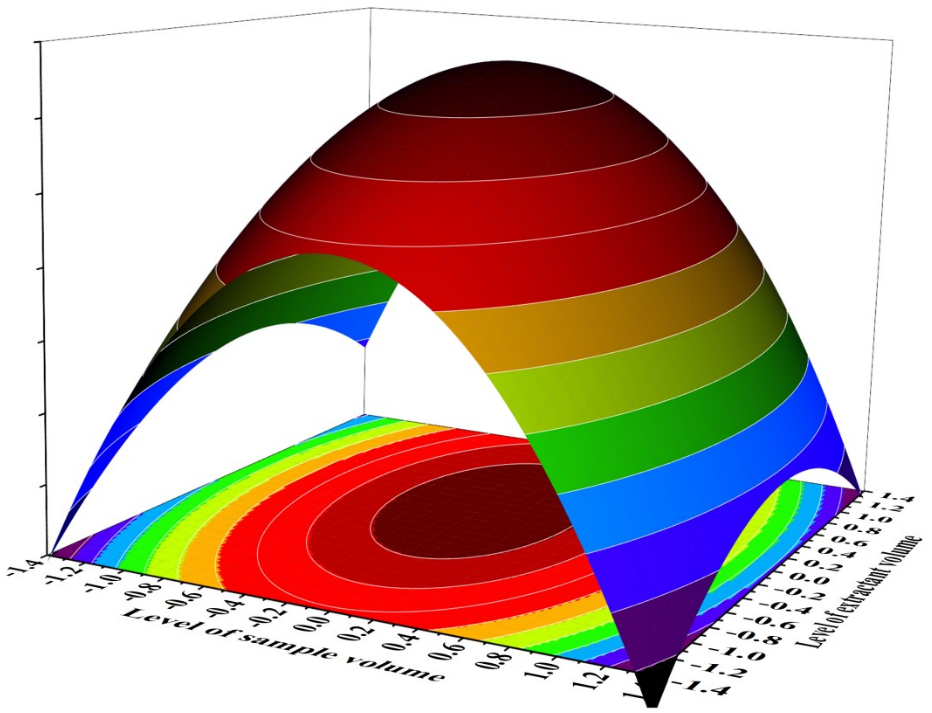

Figure S2. Response surface and contour plots from circumscribed central composite design for Cr

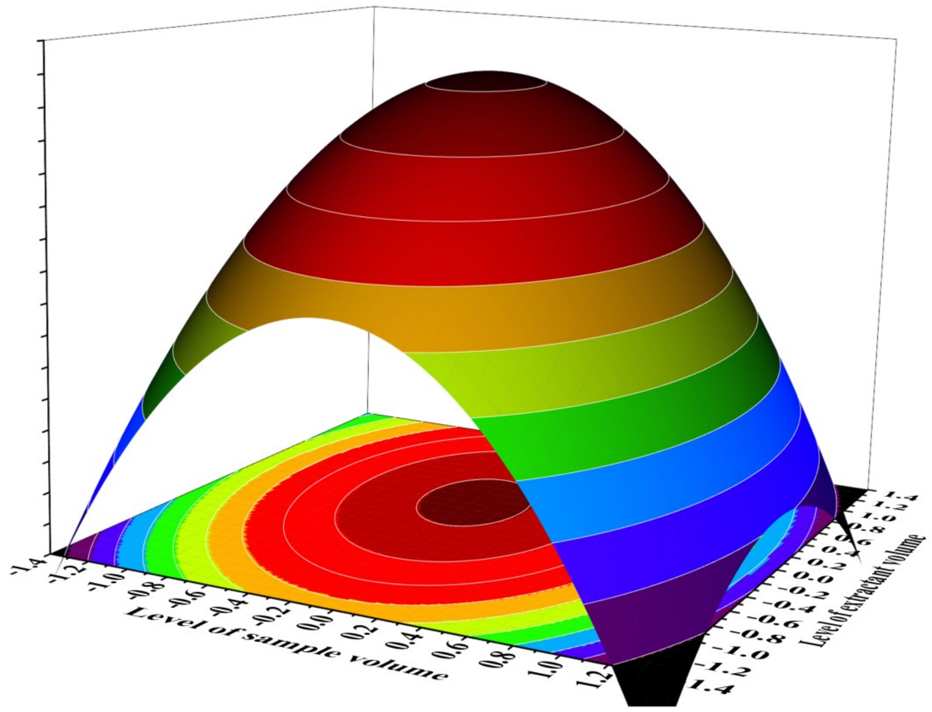

Figure S3. Response surface and contour plots from circumscribed central composite design for Mn

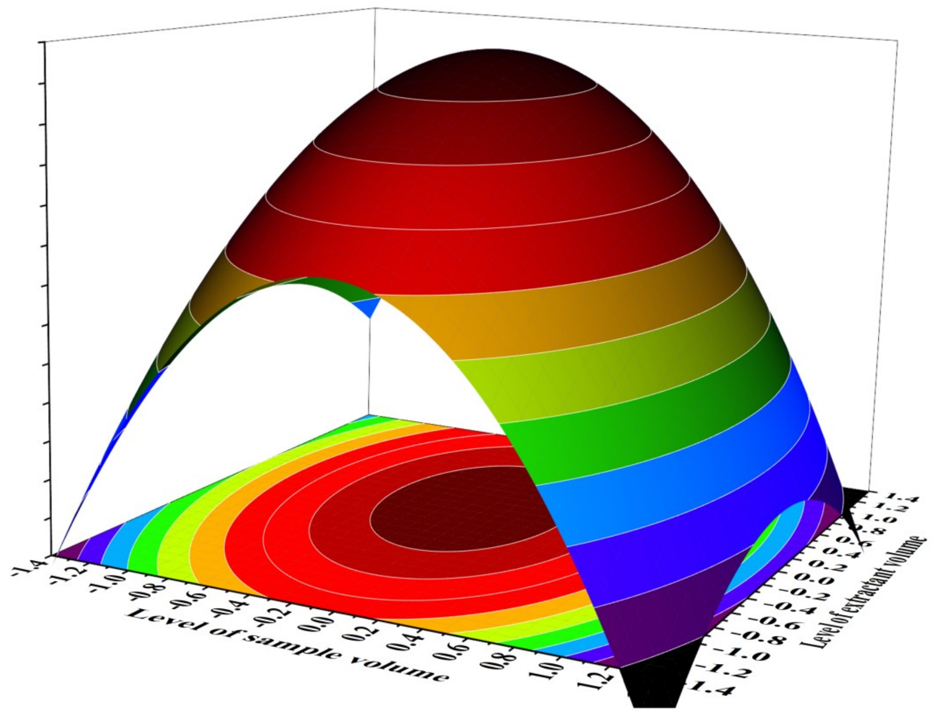

Figure S4. Response surface and contour plots from circumscribed central composite design for Ni

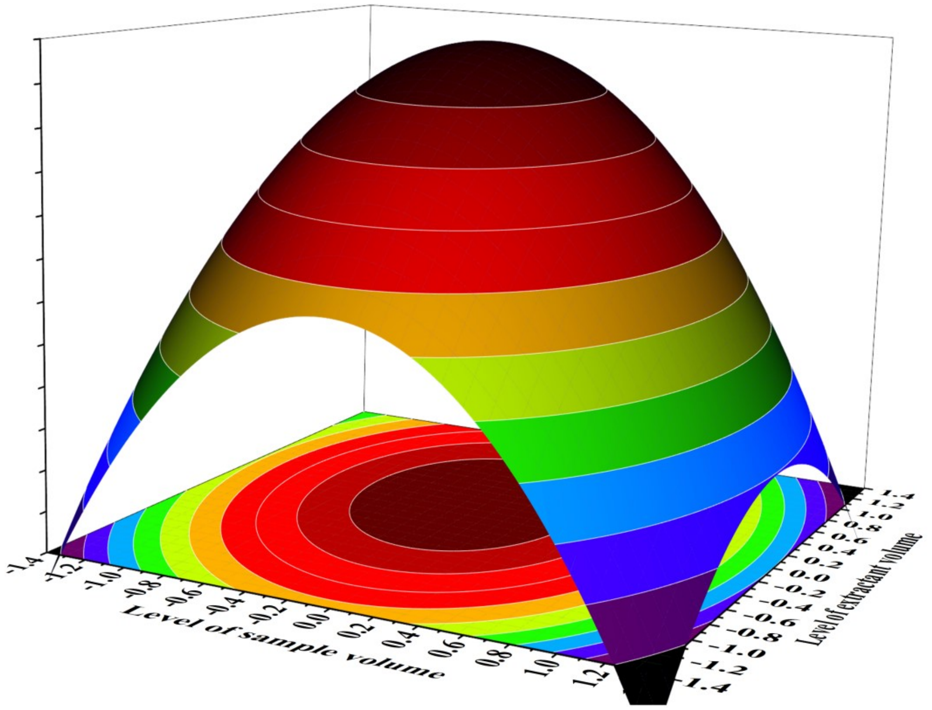

Figure S5. Response surface and contour plots from circumscribed central composite design for Cu