

Electronic Supplementary Information

Wear metals determination in lubricating oils by reversed-phase dispersive liquid-liquid microextraction and microwave induced plasma optical emission spectrometry

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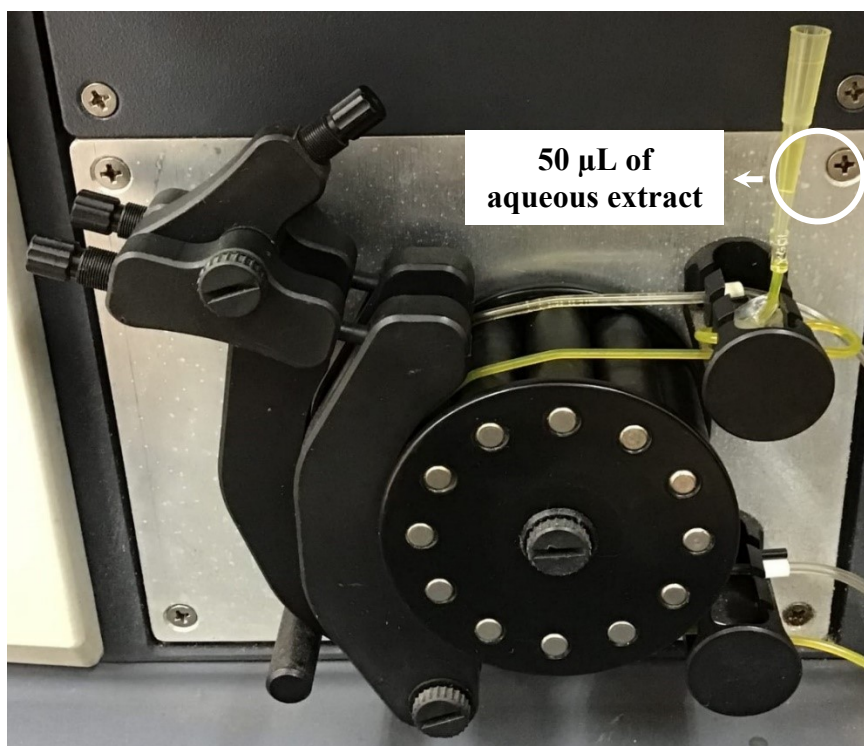


Figure S1. Photograph of part of the sample introduction system for the introduction of low volume of aqueous extract.

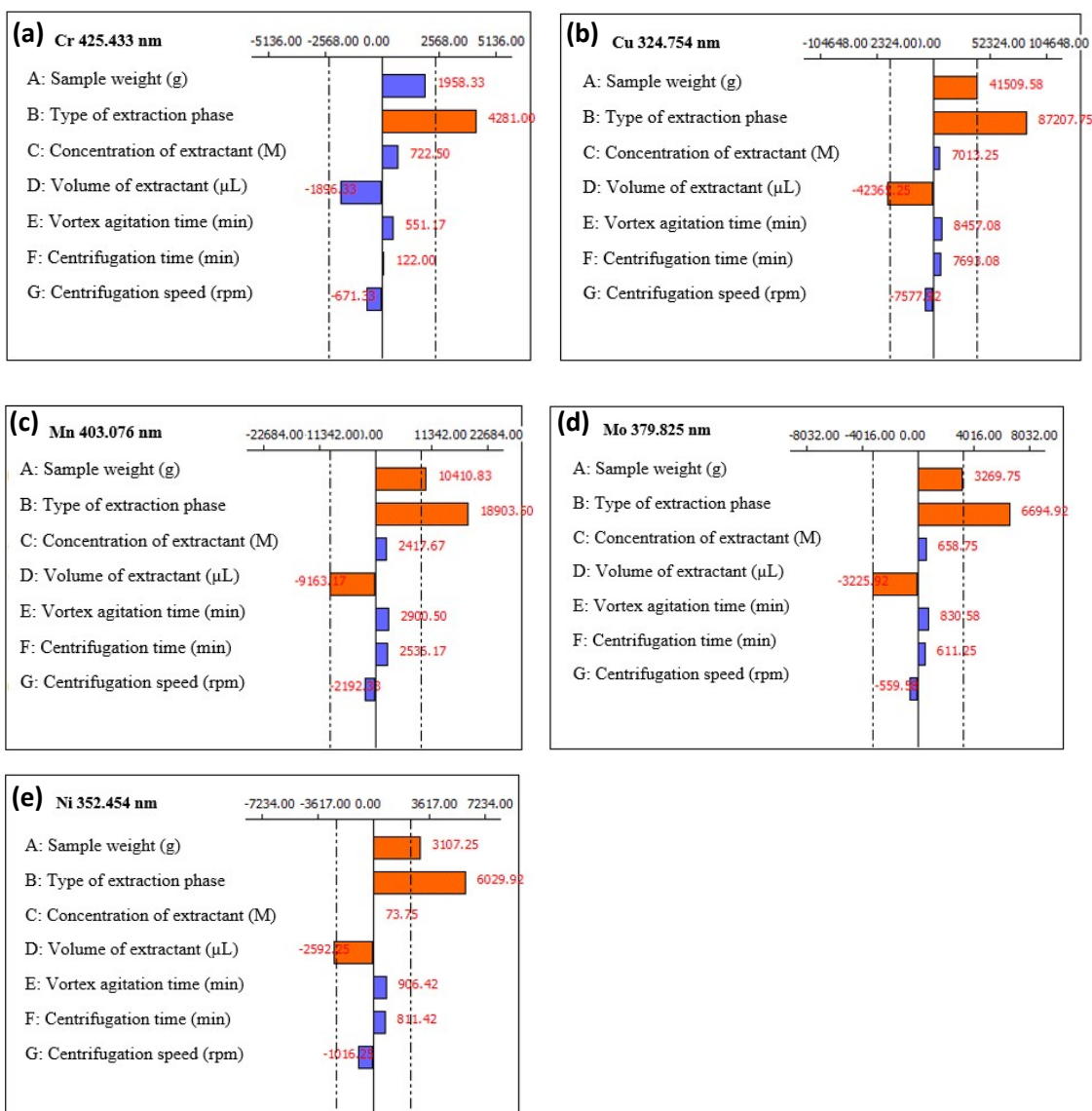


Figure S2. Pareto charts of the Plackett-Burman design obtained for: **(a)** Cr; **(b)** Cu; **(c)** Mn; **(d)** Mo and **(e)** Ni.

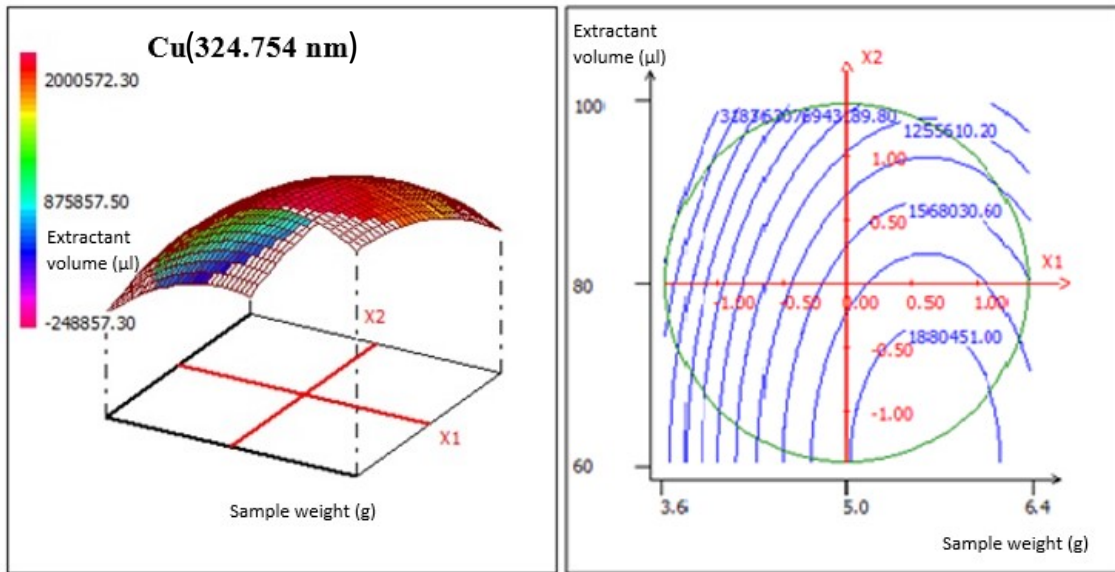


Figure S3. Response surface and contour plots from circumscribed central composite design for Cu.

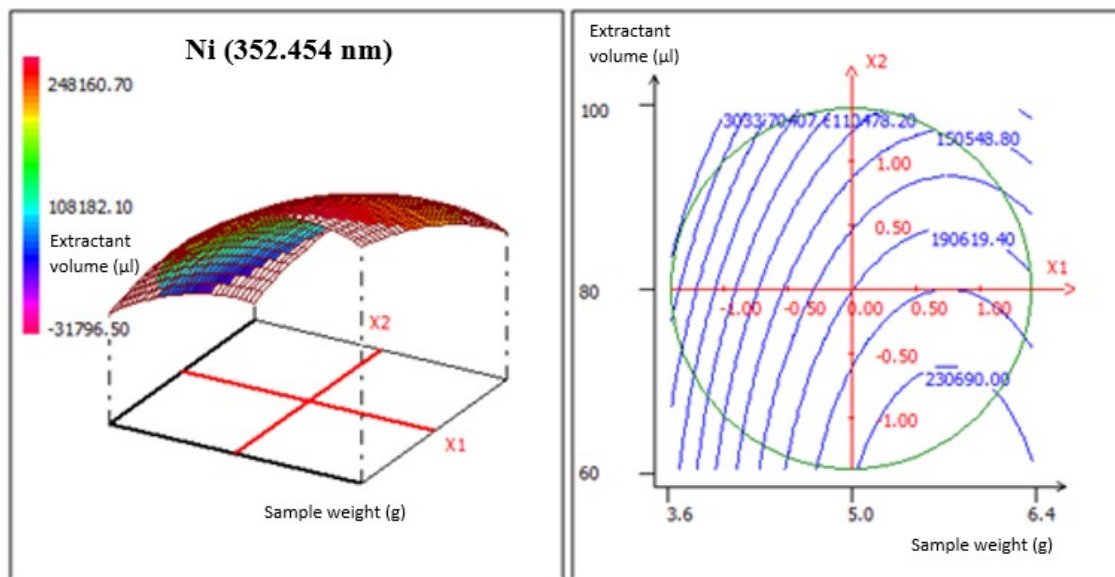


Figure S4. Response surface and contour plots from circumscribed central composite design for Ni.

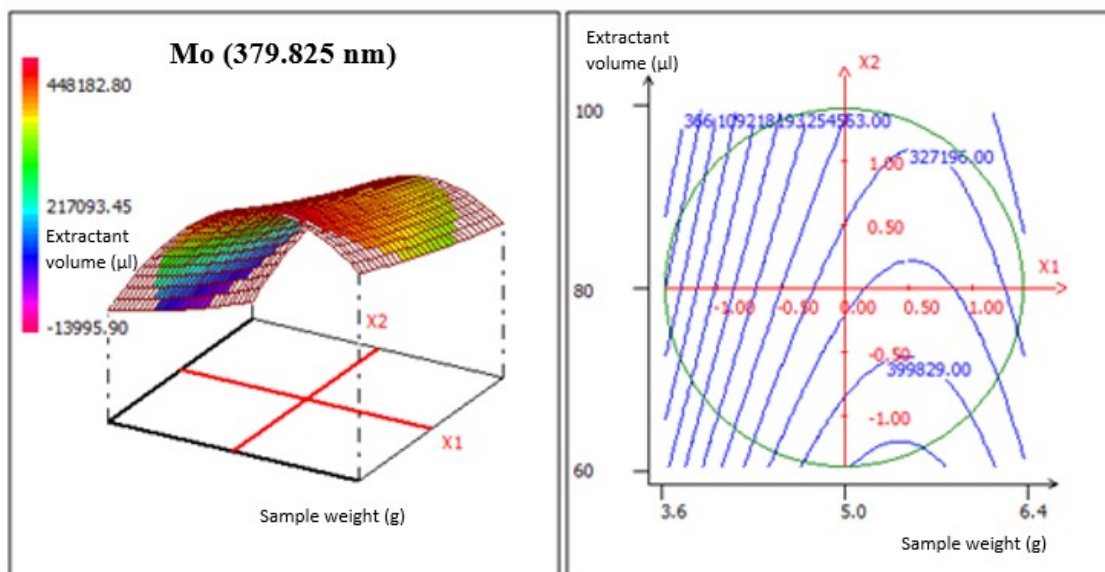


Figure S5. Response surface and contour plots from circumscribed central composite design for Mo.

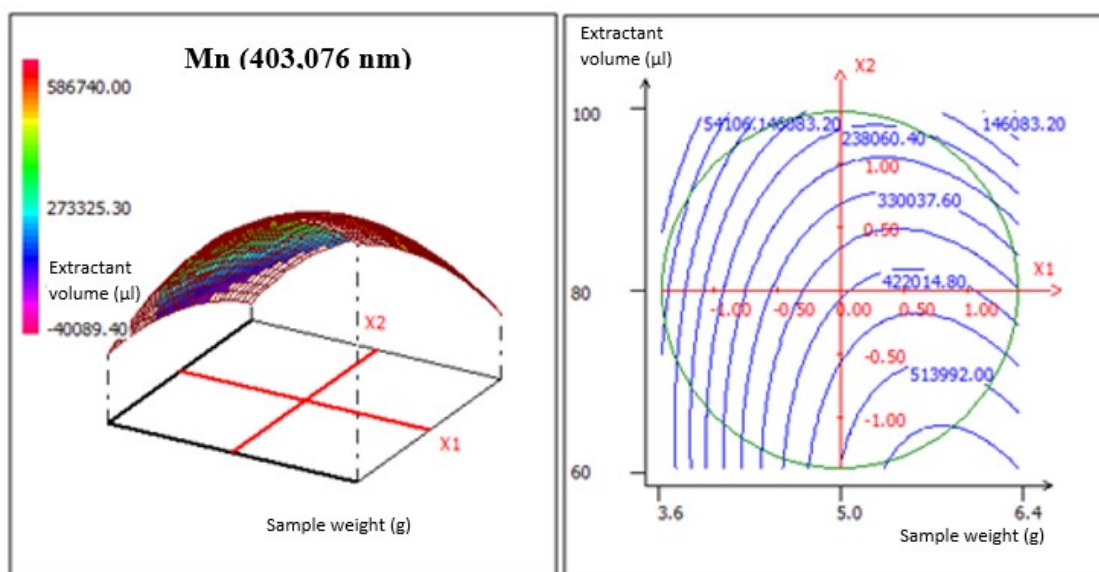


Figure S6. Response surface and contour plots from circumscribed central composite design for Mn.

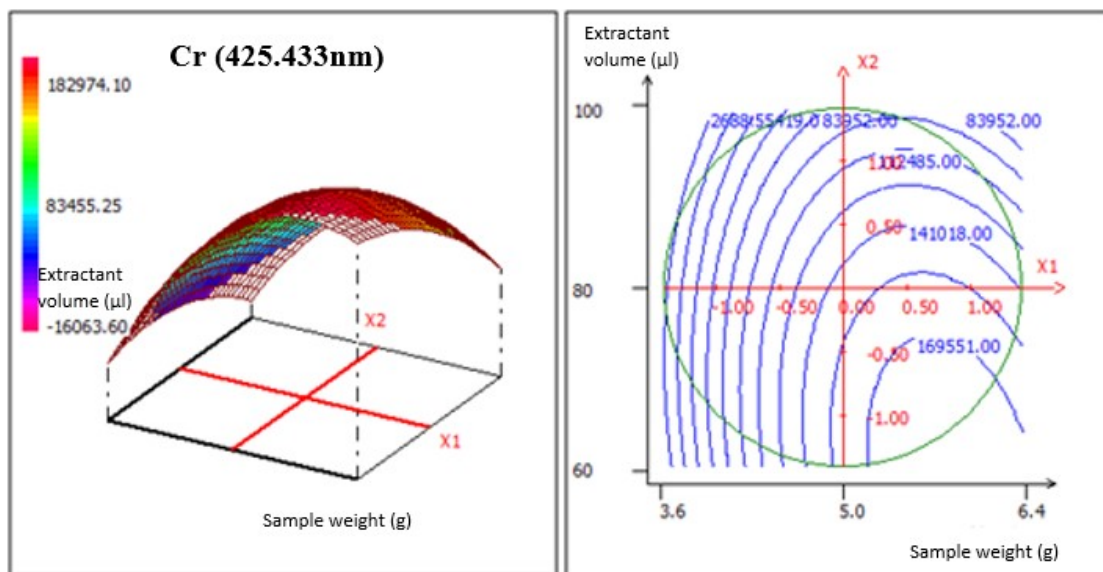


Figure S7. Response surface and contour plots from circumscribed central composite design for Cr.

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

Experimental factor	Low level (-1)	High level (+1)
A: Sample weight (g)	3	7
B: Type of extraction phase	HNO ₃	HCl
C: Concentration of extractant (M)	0	3
D: Volume of extractant (μL)	60	100
E: Vortex agitation time (min)	1	3
F: Centrifugation time (min)	1	3
G: Centrifugation speed (rpm)	2000	3000

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

Experiment	A	B	C	D	E	F	G
1	7	HCl	0	100	3	3	2000
2	3	HCl	3	60	3	3	3000
3	7	HNO ₃	3	100	1	3	3000
4	3	HCl	0	100	3	1	3000
5	3	HNO ₃	3	60	3	3	2000
6	3	HNO ₃	0	100	1	3	3000
7	7	HNO ₃	0	60	3	1	3000
8	7	HCl	0	60	1	3	2000
9	7	HCl	3	60	1	1	3000
10	3	HCl	3	100	1	1	2000
11	7	HNO ₃	3	100	3	1	2000
12	3	HNO ₃	0	60	1	1	2000

Table S3. Factors and levels of the CCCD.

Factors	Level			Star points ($\alpha=1,414$)	
	Low (-1)	Central (0)	High (+1)	- α	+ α
Sample weight (g)	4,0	5,0	6,0	3,6	6,4
Extractant volume (μl)	66	80	94	60	100

Table S4. Optimization study matrix of the CCD.

Experiment	Sample weight (g)	Extractant volume (μL)
1	4.0	66
2	6.0	66
3	4.0	94
4	6.0	94
5	3.6	80
6	6.4	80
7	5.0	60
8	5.0	100
9	5.0	80
10	5.0	80
11	5.0	80
12	5.0	80

Table S5. Optimal values for Cu, Ni, Mo, Mn and Cr.

Analyte	Sample weight (g)	Extractant volume (μL)
Cr	5,8	60
Cu	5,6	60
Mn	6,2	60
Mo	5,8	60
Ni	5,7	60

Table S6. Penalty points (PP) calculated to assess the greenness of the proposed method for Cr, Cu, Mn, Mo, and Ni determination in lubricating oils.

	Penalty Points (PP)
	Amount PP x Hazard PP
Reagents (Chemical Hazard)	
Hydrochloric Acid (37%)	4
Petroleum ether as solvent:	8
Conostan S-21:	1
Instruments (energy consumed by equipment)	
Vortex stirring (3min)	0
Centrifugation (3 min)	0
MIP OES analysis	1
Waste	8
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Analytical Eco-Scale Total Score	
100- 22 = 78	
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