

Supplementary material

Green analytical approach for multielemental determination in oily matrices combining extraction induced by emulsion breaking (EIEB) with ICP OES

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Parameters of the ICP OES

Table 1S. Optimized parameters of the ICP OES.

Parameters	
Energy (kW)	1.10
Plasma gas flow (L min ⁻¹)	16.5
Auxiliary gas flow (L min ⁻¹)	0.75
Nebulizer pressure (kPa)	200
Delay (s)	0
Integration time (s)	5
Aspiration time (mL)	1
Oxygen flow (L min ⁻¹)	0.15 ^a
Emission lines (nm)	Cd II (214.439), Cr II (267.716), Cu I (327.396), Ni II (221.647), Ti II (336.122), and V II (292.402)

^afor samples containing 2-propanol or 1-butanol media

Calibration curves parameters

Table 2S. Calibration curve parameters in HNO₃ + Triton X-114, 1-butanol, and 2-propanol.

Metal	Linear coefficient	Angular coefficient	R²
3% (v/v) HNO₃ + 2% (w/v) Triton X-114			
Cd	-25.92	10.20	0.9978
Cr	-12.02	5.10	0.9976
Cu	-22.02	5.24	0.9975
Ni	-8.57	4.87	0.9982
Ti	12.62	14.72	0.9992
V	6.64	9.16	0.9992
1-butanol			
Cd	1.75	6.10	0.9999
Cr	-2.23	1.92	0.9996
Cu	1.60	0.94	0.9999
Ni	-5.09	0.81	0.9997
Ti	6.01	6.71	0.9995
V	8.02	4.19	0.9996
2-propanol			
Cd	20.1	3.79	0.9953
Cr	7.97	0.97	0.9957
Cu	0.77	0.55	0.9932
Ni	6.88	0.92	0.9920
Ti	23.2	3.43	0.9950
V	-66.55	4.09	0.9941

t-test statistics

Heating times

Table 3S. Calculated t values, critical t values, and p -values ($\alpha = 0.05$) for the t -test of the significance of the difference between the heating times of 15 and 60 min (difference considered significant when $t_{\text{calc}} > t_{\text{crit}}$).

Metal	t_{crit}	t_{calc}	p -value
Cd		0.20	0.854
Cr		1.77	0.151
Cu	2.78	1.92	0.128
Ni		4.17	0.014
Ti		0.08	0.941
V		1.41	0.232

Centrifugation times

Table 4S. Calculated t values, critical t values, and p -values ($\alpha = 0.05$) for the t -test of the significance of the difference between the centrifugation times of 15 and 60 min (difference considered significant when $t_{\text{calc}} > t_{\text{crit}}$).

Metal	t_{crit}	t_{calc}	p -value
Cd		1.98	0.12
Cr		3.20	0.049
Cu	2.78	2.80	0.049
Ni		5.73	0.029
Ti		6.22	0.003
V		4.13	0.015

Table 5S. Calculated t values, critical t values, and p -values ($\alpha = 0.05$) for the t -test assessing the significance of the difference between centrifugation times of 15 and 30 min (difference considered significant when $t_{\text{calc}} > t_{\text{crit}}$).

Metal	t_{crit}	t_{calc}	p -value
Cd		4.90	0.008
Cr		2.45	0.070
Cu	2.78	0.77	0.498
Ni		1.86	0.160
Ti		4.90	0.008
V		2.97	0.041

Table 6S. Calculated t values, critical t values, and p -values ($\alpha = 0.05$) for the t -test assessing the significance of the difference between centrifugation times of 45 and 60 min (difference considered significant when $t_{\text{calc}} > t_{\text{crit}}$).

Metal	t_{crit}	t_{calc}	p-value
Cd		0.71	0.517
Cr		6.86	0.006
Cu	2.78	0.39	0.715
Ni		0.54	0.629
Ti		1.58	0.189
V		2.32	0.081

Table 7S. Calculated t values, critical t values, and p -values ($\alpha = 0.05$) for the t -test assessing the significance of the difference between centrifugation times of 15 and 45 min (difference considered significant when $t_{\text{calc}} > t_{\text{crit}}$).

Metal	t_{crit}	t_{calc}	p-value
Cd		2.26	0.087
Cr		3.00	0.040
Cu	2.78	4.41	0.012
Ni		2.33	0.102
Ti		12.81	0.0002
V		2.07	0.107

Nitric acid concentrations

Table 8S. Calculated t values, critical t values, and p -values ($\alpha = 0.05$) for the t -test assessing the significance of the difference between nitric acid concentrations ranging from 3 to 15% (difference considered significant when $t_{\text{calc}} > t_{\text{crit}}$).

Metal	t_{crit}	t_{calc}	p-value
Cd		1.53	0.200
Cr		1.16	0.331
Cu	2.78	0.81	0.462
Ni		2.28	0.085
Ti		1.34	0.252
V		3.55	0.024

Table 9S. Linear and angular coefficients and determination coefficients of calibration curve in 3% HNO₃ medium.

Metals	Linear coefficient	Angular coefficient	R ²
Cd	5.90 ± 2.90	3.66 ± 0.23	0.9997
Cr	-0.68 ± 2.40	2.63 ± 0.07	0.9995
Cu	21.6 ± 12.6	3.67 ± 0.18	0.9979
Ni	4.20 ± 2.80	0.90 ± 0.01	0.9993
Ti	-21.6 ± 5.10	12.6 ± 0.5	0.9998
V	-20.5 ± 14.2	3.59 ± 0.16	0.9995

Table 10S. Linear and angular coefficients and determination coefficients of the standard addition curves for Conostan[®] mineral oil and the biodiesel reference material.

Metals	Linear coefficient	Angular coefficient	R ²
Biodiesel			
Cd	79.72 ± 21.3	7.75 ± 0.04	0.9989
Cr	22.77 ± 5.8	3.36 ± 0.10	0.9977
Cu	75.6 ± 2.0	3.71 ± 0.09	0.9999
Ni	14.2 ± 8.7	3.43 ± 0.08	0.9949
Ti	176.7 ± 37.3	10.61 ± 1.36	0.9983
V	29.3 ± 3.2	7.32 ± 0.22	0.9972
Conostan[®] mineral oil			
Cd	13.2 ± 20.3	8.47 ± 0.11	0.9999
Cr	36.9 ± 8.2	3.75 ± 0.12	0.9977
Cu	24.8 ± 11	4.08 ± 0.16	0.9979
Ni	11.4 ± 24.0	3.80 ± 0.19	0.9988
Ti	128.9 ± 41.7	11.51 ± 0.47	0.9959
V	49.5 ± 20.0	7.39 ± 0.29	0.9982

Table 11S. Linear and angular coefficients and determination coefficients of the standard addition curves for the edible oil samples.

Metals	Linear coefficient	Angular coefficient	R²
Canola			
Cd	15.00 ± 3.1	4.51 ± 0.24	0.9982
Cr	1.64 ± 5.86	1.28 ± 0.07	0.9971
Cu	22.1 ± 28.8	2.31 ± 0.16	0.9804
Ni	28.8 ± 1.7	1.89 ± 0.11	0.9967
Ti	35.8 ± 12.0	1.75 ± 0.05	0.9846
V	17.6 ± 9.6	4.54 ± 0.20	0.9981
Corn			
Cd	36.5 ± 15.9	5.61 ± 0.25	0.9960
Cr	15.5 ± 7.1	2.04 ± 0.06	0.9964
Cu	29.1 ± 12.4	2.73 ± 0.15	0.9841
Ni	35.8 ± 10.1	2.39 ± 0.13	0.9868
Ti	65.6 ± 5.4	6.79 ± 0.31	0.9938
V	29.9 ± 7.0	6.45 ± 0.15	0.9977
Cottonseed			
Cd	9.76 ± 11.23	6.41 ± 0.25	0.9980
Cr	9.81 ± 2.50	2.52 ± 0.04	0.9997
Cu	7.22 ± 0.63	3.13 ± 0.07	0.9993
Ni	17.9 ± 4.2	2.85 ± 0.06	0.9993
Ti	46.6 ± 15.0	7.80 ± 0.14	0.9992
V	16.2 ± 4.4	7.19 ± 0.08	0.9996
Olive			
Cd	22.1 ± 7.7	5.58 ± 0.24	0.9984
Cr	24.3 ± 1.7	2.09 ± 0.05	0.9927
Cu	20.4 ± 4.9	2.58 ± 0.06	0.9933
Ni	34.3 ± 8.6	2.38 ± 0.14	0.9952
Ti	130 ± 13	5.76 ± 0.17	0.9886
V	58.2 ± 8.7	5.06 ± 0.12	0.9879
Soybean			
Cd	18.7 ± 4.6	5.60 ± 0.01	0.9982
Cr	20.3 ± 7.0	2.00 ± 0.16	0.9925
Cu	16.1 ± 8.5	2.76 ± 0.19	0.9956
Ni	26.0 ± 5.3	2.32 ± 0.08	0.9949
Ti	119 ± 29	7.39 ± 0.54	0.9964
V	32.0 ± 3.9	5.18 ± 0.11	0.9958

Table 11S. Continuation.

Sunflower			
Cd	-0.32 ± 9.77	5.14 ± 0.33	0.9997
Cr	5.81 ± 8.80	1.87 ± 0.11	0.9988
Cu	4.54 ± 7.47	2.53 ± 0.10	0.9987
Ni	14.0 ± 5.1	2.23 ± 0.19	0.9994
Ti	47.5 ± 15.2	7.30 ± 0.37	0.9964
V	24.0 ± 6.2	5.77 ± 0.11	0.9970

Table 12S. Linear and angular coefficients and determination coefficients of the standard addition coefficients of the standard addition curves for the essential oil.

Metals	Linear coefficient	Angular coefficient	R ²
Lavender			
Cd	-8.26 ± 3.20	6.04 ± 0.05	0.9995
Cr	10.6 ± 2.4	3.03 ± 0.06	0.9995
Cu	0.21 ± 3.15	4.41 ± 0.10	0.9999
Ni	-1.72 ± 6.78	3.04 ± 0.09	0.9990
Ti	31.1 ± 6.6	12.1 ± 0.2	0.9996
V	-6.71 ± 5.34	7.32 ± 0.06	0.9998
Lemon			
Cd	6.73 ± 11.07	4.30 ± 0.11	0.9994
Cr	0.47 ± 8.66	2.62 ± 0.04	0.9968
Cu	5.13 ± 4.12	1.55 ± 2.49	0.9996
Ni	2.19 ± 4.96	2.12 ± 0.07	0.9990
Ti	71.3 ± 6.9	9.18 ± 0.18	0.9996
V	11.4 ± 8.5	5.19 ± 0.03	0.9997
Clove			
Cd	6.83 ± 7.7	5.58 ± 0.29	0.9995
Cr	0.04 ± 2.5	2.57 ± 0.02	0.9954
Cu	6.38 ± 0.71	2.83 ± 0.01	0.9923
Ni	7.6 ± 2.9	2.57 ± 0.14	0.9939
Ti	-15.5 ± 10	7.76 ± 0.20	0.9959
V	-3.66 ± 4	5.01 ± 0.02	0.9952

Table 13S. Precision (intra- and interday) n=3.

Metal Concentration $\mu\text{g kg}^{-1}$	Intraday (CV, %)	Interday (CV, %)
Cd		
60.0	4.42	4.15
120	0.740	4.29
240	0.808	6.50
Cr		
60.0	4.20	4.24
120	2.30	4.32
240	3.00	4.07
Cu		
60.0	4.63	4.13
120	2.42	3.99
240	3.48	3.43
Ti		
60.0	3.75	3.77
120	4.10	5.55
240	3.45	3.90
Ni		
60.0	4.61	5.78
120	3.72	3.54
240	2.97	2.85
V		
60.0	4.04	4.34
120	1.98	4.55
240	3.52	3.77

Criteria, scoring, and weight considered in the Agree

Criteria	Score	Weight
1. Direct analytical techniques should be applied to avoid sample treatment.	0.3	2
2. Minimal sample size and minimal number of samples are goals.	0.65	2
3. If possible, measurements should be performed in situ.	0.0	2
4. Integration of analytical processes and operations saves energy and reduces the use of reagents.	1.0	2
5. Automated and miniaturized methods should be selected.	0.75	2
6. Derivatization should be avoided.	1.0	2
7. Generation of a large volume of analytical waste should be avoided, and proper management of analytical waste should be provided.	0.69	2
8. Multi-analyte or multi-parameter methods are preferred versus methods using one analyte at a time.	1.0	2
9. The use of energy should be minimized.	1.0	2
10. Reagents obtained from renewable sources should be preferred.	0.0	2
11. Toxic reagents should be eliminated or replaced.	0.59	2
12. Operator's safety should be increased.	0.8	2

Fig. 1S Criteria, scoring, and weight considered in the Agree Software for the sample preparation steps.

Criteria, scoring, and weight considered in the Agreeprep.

#	Criterion		Score	Weight
1.	Sample preparation placement:	Ex situ	0.00	1
2.	Hazardous materials:	0 [g or mL]	1.00	5
3.	Sustainability, renewability, and reusability of materials:	< 25% of reagents and materials are sustainable or renewable, but can only be used ONCE	0.00	2
4.	Waste:	1 [g or mL]	0.63	4
5.	Size economy of the sample	Mass or volume of the sample: 1 [g or mL]	0.67	2
6.	Sample throughput:	36 [samples/h]	0.84	3
7.	Integration and automation	Sample prep. steps: 3 steps, Semi-automated systems	0.38	2
8.	Energy consumption:	11.5 [W]	0.96	4
9.	Post-sample preparation configuration for analysis:	Advanced MS with high energy and/or noble gas consumption: ICP-OES, ICP-MS, etc.	0.00	2
10.	Operator's safety:	1 hazard	0.75	3

Fig. 2S Criteria, scoring, and weight considered in the Agreeprep Software for the sample preparation steps.

Table 14S. Comparison of the EIEB proposed method with other for metals determination in oily samples.

Samples	EIEB procedure	Analyte	LOD	References
Olive oil, sunflower, fish oil, soybean, canola, and corn	Sample quantity: 1g. 2% TX-114 and 3% HNO ₃ . Vortex 30s. Heating (90 °C) – 60 min	Sn	GF AAS 1.1 µg L ⁻¹ and ICP-MS 0.009 µg L ⁻¹	22
Crude palm oil	Sample quantity: 5 mL. 4% TX-114 and 2.0 mol L ⁻¹ HNO ₃ . Sonication time 18 min. Heating (90 °C) – 30 min	Cd and Pb	GF AAS 0.052 µg kg ⁻¹ (Cd) and 0.040 µg kg ⁻¹ (Pb)	25
Olive oil, avocado, babassu, primrose, coconut, piquí or souari nut, licuri, and grape seed oil	Sample quantity: 1 mL. 30% TX-100 and 30% HNO ₃ . Vortex 20s. Heating (90 °C) – 20 min	Al, Ba, Cu, Cr, P, Ni, Ti and Zn	MIP OES 0.4-3.7 µg kg ⁻¹ 3.7 (Al), 0.6 (Ba and Cu), 0.7 (Cr), 0.9 (P), 1.0 (Ni), 2.0 (Ti), and 0.4 (Zn)	43
Soybean oil, canola, corn, sunflower, coconut, olive oil and cottonseed	Sample quantity: 5.5 mL. 1.0% TX-114 and 3.0 mol L ⁻¹ HNO ₃ . Sonication time 12 min. Heating (90 °C)	Ca, Fe, Mg and Zn	HR-CS AAS 4.32-11.0 µg L ⁻¹ 4.32 (Ca), 7.53 (Fe), 11.0 (Mg), and 7.89 (Zn)	42
Essential oils (clove, lavender and lemon), biodiesel, cottonseed, canola, sunflower, soybean, corn and olive oil	Sample quantity: 1g. 2% TX-114 and 3% HNO ₃ . Vortex 60s. Heating (90 °C) – 15 min	Cd, Cr, Cu, Ni, V and Ti	ICP OES 0.20 – 0.80 µg kg ⁻¹ 0.20 (Cd), 0.60 (Cr), 0.70 (Cu), 0.50 (Ni), 0.60 (Ti) and 0.80 (V)	This work

GF AAS: graphite furnace atomic absorption spectrometry; MIP OES: microwave-induced plasma optical emission spectrometry; HR-CS FAAS: high-resolution continuum source flame atomic absorption spectrometry