Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Methodology for elemental analysis of mineral fertilizer, some of its raw materials and limestone using microwave-induced plasma optical emission spectrometry (MIP OES)

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Table S1. Analytical parameters and data related with the spectral lines evaluated; those marked with asterisk were selected.

Element	Espectral Line, nm	Excitation Energy, eV	State	LOD, µg L^{-1}	LOQ, µg L^{-1}	Sample Flow Rate, mL min^{-1}	Integration Time, s	Calibration Curve Equation	R
Ag	328.068*	3.78	Atomic	0.4	1.3	1.54	3	Linear	0.9999
	338.289	3.66	Atomic	2	6.4	1.54	3	Linear	0.9999
	546.549	2.27	Atomic	-	-	2.31	10	Linear	< 0.9
Al	396.152	3.13	Atomic	0.5	1.3	1.54	5	Quadratic	0.9983
	394.401*	3.14	Atomic	0.4	1.1	1.54	3	Quadratic	0.9992
	309.271	4.01	Atomic	13	43	2.31	5	Quadratic	0.9999
B	249.772*	4.96	Atomic	13	43	2.31	10	Linear	0.9997
	249.677	4.96	Atomic	24	82	2.31	20	Linear	0.9998
	208.957	5.93	Atomic	42	139	0.79	20	Linear	0.9999
Ba	455.403	7.93	Ionic[a]	0.2	0.77	1.54	3	Linear	0.9995
	493.408	7.72	Ionic[a]	0.2	0.67	1.54	3	Linear	0.9997
	614.171*	7.23	Ionic[a]	0.2	0.57	1.54	3	Linear	0.9996
Be	234.861*	5.28	Atomic	1	3.5	1.54	3	Linear	0.9999
	313.042	13.28	Ionic[a]	-	-	1.54	3	Quadratic	< 0.9000
	313.107	13.28	Ionic[a]	107	357	1.54	3	Linear	0.9983
Ca	393.366*	9.26	Ionic[a]	0.06	0.19	0.79	3	Linear	0.9998
	396.847	9.23	Ionic[a]	0.1	0.40	2.31	3	Linear	0.9994

Tble S1 Continued

	422.673	2.93	Atomic	0.1	0.46	2.31	5	Linear	0.9995
Cd	228.802*	5.42	Atomic	10	34	1.54	5	Linear	0.9999
	226.502	14.46	Ionic[a]	-	-	1.54	5	Linear	0.9873
	214.439	14.77	Ionic[a]	17	31	2.31	10	Quadratic	0.9868
Co	340.512	3.64	Atomic	8	16	0.79	3	Quadratic	0.9843
	345.351*	3.59	Atomic	2	5.2	0.79	3	Linear	0.9999
	350.228	3.54	Atomic	6	16	2.31	10	Quadratic	0.9941
Cr	425.433*	2.91	Atomic	0.08	0.27	2.31	5	Linear	0.9997
	357.868	3.46	Atomic	0.5	1.1	1.54	3	Quadratic	0.9999
	427.480	2.90	Atomic	0.10	0.33	2.31	10	Linear	0.9999
Cu	324.754*	3.82	Atomic	2	8.2	0.79	3	Linear	0.9995
	327.395	3.78	Atomic	3	5.4	2.31	5	Quadratic	0.9985
	510.554	2.43	Atomic	4	12	1.54	3	Linear	0.9977
Fe	385.991*	3.21	Atomic	0.6	1.99	1.54	10	Linear	0.9998
	373.713	3.32	Atomic	8	26.93	2.31	3	Linear	0.9953
	358.119	3.46	Atomic	5	15.23	1.54	10	Linear	0.9999
K	766.491*	1.62	Atomic	0.1	0.47	0.79	3	Linear	0.9998
	769.897	1.61	Atomic	0.4	1.34	1.54	3	Linear	0.9996
	404.414	3.06	Atomic	-	-	2.31	5	Linear	< 0.9

Tble S1 Continued

La	394.910	8.72	Ionic[a]	3	8.0	2.31	10	Quadratic	0.9930
	408.672	8.61	Ionic[a]	1	3.6	0.79	3	Linear	1.000
	433.374*	8.44	Ionic[a]	0.3	0.95	0.79	3	Linear	1.000
Li	670.784*	1.85	Atomic	0.03	0.08	2.31	5	Linear	0.9997
	610.365	2.03	Atomic	0.2	0.72	1.54	10	Linear	0.9999
	460.289	2.69	Atomic	7	21.78	0.79	3	Linear	0.9992
Mg	285.213	4.35	Atomic	1	4.25	1.54	3	Linear	0.9999
	280.271*	12.07	Ionic[a]	0.3	0.86	0.79	10	Linear	0.9996
	279.553	12.08	Ionic[a]	0.4	1.24	1.54	3	Linear	0.9999
Mn	403.076	3.08	Atomic	0.3	1.1	0.79	3	Linear	0.9992
	403.307*	3.07	Atomic	0.2	0.56	0.79	3	Linear	1.000
	257.610	12.24	Ionic[a]	16	55	0.79	5	Linear	0.9978
	352.454	3.52	Atomic	17	41	2.31	5	Quadratic	0.9998
Ni	352.454	3.52	Atomic	17	41	2.31	5	Quadratic	0.9997
	361.939*	3.42	Atomic	2	5.3	0.79	3	Quadratic	0.99988
	588.995*	2.10	Atomic	0.5	1.7	0.79	3	Linear	0.9997
Na	589.592	2.10	Atomic	-	-	1.54	3	Linear	< 0.9
	330.237	3.75	Atomic	-	-	1.54	3	Linear	< 0.9

Tble S1 Continued

Pb	405.781	3.05	Atomic	35	117	2.31	10	Linear	0.9959
	283.305	4.38	Atomic	99	329	2.31	10	Linear	0.9161
	363.957*	3.41	Atomic	3	10	0.79	10	Linear	0.9974
Sr	407.771*	8.73	Ionic[a]	0.01	0.033	0.79	3	Linear	1.0000
	421.552	8.63	Ionic[a]	0.1	0.24	1.54	3	Linear	0.9998
	460.733	2.69	Atomic	0.1	0.20	1.54	10	Linear	0.9998
Tl	535.046*	2.32	Atomic	1	3.9	0.79	3	Linear	0.9996
	377.572	3.28	Atomic	-	-	2.31	5	Linear	< 0.9
	351.924	3.52	Atomic	-	-	0.79	3	Linear	< 0.9
V	309.311	10.76	Ionic[a]	4	15	2.31	5	Quadratic	0.9905
	437.923*	2.83	Atomic	0.2	0.61	1.54	3	Linear	0.9999
	310.230	12.76	Ionic[a]	80	266	2.31	5	Linear	0.9862
Zn	213.857*	5.80	Atomic	15	50	2.31	10	Linear	0.9996
	481.053	2.58	Atomic	7	20	1.54	3	Quadratic	0.9967
	202.548	15.51	Ionic[a]	10	33	0.79	10	Quadratic	0.9633

[a]: total energy (ionization + excitation)

Table S2. Multi-nutrient (SRM 695) analysis results (mean ± standard deviation for 3 replicates); US: ultrasonic assisted extraction, MAD: microwave assisted digestion, MP: heating on metallic plate.

Element	Certified	Unit	Found			Average Recovery, %		
			US	MAD	MP	US	MAD	MP
Al	(0.61 ± 0.03)	%	0.61 ± 0.03	0.59 ± 0.06	0.49 ± 0.02	100	96	80
B	(0.111 ± 0.002)	%	-	0.117 ± 0.050	0.062 ± 0.002	-	105	56
Ca	2.26 ± 0.04	%	2.38 ± 0.04	2.20 ± 0.04	2.29 ± 0.04	106	97	101
Cd	16.9 ± 0.2	mg kg^{-1}	16.2 ± 0.4	17.5 ± 0.6	nd	96	103	-
Co	65.3 ± 2.4	mg kg^{-1}	68.4 ± 7.9	77.6 ± 10.6	57.1 ± 5.4	105	119	87
Cr	244 ± 6	mg kg^{-1}	240 ± 0.5	253 ± 12	248 ± 10	98	104	102
Cu	1225 ± 9	mg kg^{-1}	1265 ± 46	1231 ± 32	1239 ± 59	103	100	101
Fe	3.99 ± 0.08	%	3.63 ± 0.10	3.99 ± 0.08	3.95 ± 0.02	91	100	99
K	11.65 ± 0.13	%	9.19 ± 0.41	8.91 ± 0.18	10.35 ± 0.05	79	86	89
Mg	1.79 ± 0.05	%	1.88 ± 0.01	1.78 ± 0.03	1.79 ± 0.01	105	99	100
Mn	0.305 ± 0.005	%	0.318 ± 0.012	0.304 ± 0.006	0.304 ± 0.009	104	100	100
Na	0.405 ± 0.007	%	0.474 ± 0.004	0.446 ± 0.011	0.416 ± 0.015	117	110	103
Ni	135 ± 2	mg kg^{-1}	225 ± 2	218 ± 16	268 ± 5	167	161	199
Pb	273 ± 17	mg kg^{-1}	161	208 ± 23	273 ± 91	59	90	100
V	122 ± 3	mg kg^{-1}	167 ± 1	120 ± 1	125 ± 6	137	98	102
Zn	0.325 ± 0.005	%	0.323 ± 0.029	0.332 ± 0.003	0.325 ± 0.008	99	102	100

nd: not detected

Table S3. Dolomitic limestone (SRM 88b) analysis results (mean ± standard deviation for 3 replicates); US: ultrasonic assisted extraction, MAD: microwave assisted digestion, MP: heating on metallic plate.

Element	Certified	Unit	Found			Average Recovery, %		
			US	MW	MP	US	MW	MP
Al	0.178 ± 0.007	%	0.151 ± 0.003	0.174 ± 0.002	0.047 ± 0.002	85	98	27
Co	(1) [a]	mg kg^{-1}	< LOQ	< LOQ	< LOQ	-	-	-
Ca	21.40 ± 0.04	%	19.50 ± 0.08	21.90 ± 0.06	18.90 ± 0.10	91	102	88
Cr	(2.3) [a]	mg kg^{-1}	2.5 ± 0.2	2.2 ± 0.1	2.7 ± 0.5	108	97	116
Fe	0.194 ± 0.001	%	0.167 ± 0.001	0.196 ± 0.001	0.198 ± 0.003	86	101	102
K	0.0855 ± 0.0020	%	0.0908 ± 0.0038	0.0835 ± 0.0214	n.d.	106	98	-
Mg	12.68 ± 0.04	%	12.34 ± 0.31	11.87 ± 0.24	12.78 ± 0.28	97	94	101
Mn	0.0124 ± 0.0009	%	0.0125 ± 0.0003	0.0127 ± 0.0002	0.0125 ± 0.0001	101	102	101
Na	0.0215 ± 0.0005	%	0.0232 ± 0.0051	0.0270 ± 0.0108	0.0259 ± 0.0051	108	116	121
Sr	0.0064 ± 0.0002	%	0.0064 ± 0.0002	0.0062 ± 0.0001	0.0065 ± 0.00002	100	98	101

a: informed value: LOQ: limit of quantification (see Table 3)

Table S4. Phosphate rock (SRM 694) analysis results (mean ± standard deviation for 3 replicates); US: ultrasonic assisted extraction, MW: microwave assisted digestion, MAD: heating on metallic plate.

Analtye	Certified	Unit	Found			Average Recovery, %		
			US	MW	MP	US	MW	MP
Al	0.95 ± 0.05	%	0.77 ± 0.004	0.93 ± 0.008	0.88 ± 0.03	81	98	93
Cd	0.0131 ± 0.0026	%	0.0135 ± 0.0006	0.0128 ± 0.0004	0.0128 ± 0.0001	103	98	98
Ca	31.14 ± 0.29	%	29.58 ± 0.70	30.83 ± 0.50	27.71 ± 1.12	95	99	89
Cr	(0.068) [a]	%	0.086 ± 0.002	0.087 ± 0.003	0.077 ± 0.002	127	127	114
Fe	0.552 ± 0.042	%	0.492 ± 0.008	0.545 ± 0.022	0.550 ± 0.002	89	99	100
K	0.423 ±0.017	%	0.492 ± 0.034	0.434 ± 0.017	0.345 ± 0.003	116	102	82
Mg	0.199 ± 0.012	%	0.200 ± 0.003	0.198 ± 0.002	0.202 ± 0.001	101	99	102
Mn	0.0090 ± 0.0009	%	0.0091 ± 0.0005	0.0089 ± 0.0002	0.0087 ± 0.0006	101	99	97
Na	0.64 ± 0.03	%	0.63 ± 0.02	0.67 ± 0.01	0.65 ± 0.005	98	105	102
V	0.164 ± 0.039	%	0.168 ± 0.006	0.167 ± 0.004	0.160 ± 0.001	102	102	97
Zn	0.153[a]	%	0.148 ± 0.004	0.155 ± 0.007	0.157 ± 0.001	97	102	102

a: informed value