Supplementary Information

Method Development and Total Uncertainty Estimation for Boron, Sulfur and Phosphorus Determination in Mineral Fertilizer Using ICP OES

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The following procedure was transcribed from the Official Methods of the Brazilian Ministry of Agriculture, Livestock and Supply (Ministério da Agricultura, Pecuária e Abastecimento (MAPA)).

Preparation of neutral ammonium citrate solution (NAC)

Dissolve 370 g of monohydrate citric acid ($C_6H_8O_7.H_2O$) in 1500 mL of water and add 345 mL of ammonium hydroxide (NH_4OH), containing 28 to 29% of NH_3. If the NH_3 concentration is lower than 28%, add more NH_4OH to compensate for the lower NH_3 concentration. Decrease the volume of water (the same volume of the additional aliquot of NH_4OH) in which citric acid is dissolved. Allow the solution to cool and then measure its pH. If necessary, adjust the pH to 7.0 ± 0.05 with NH_4OH solution (NH_4OH 8-fold diluted in water) or 10% (m/v) citric acid solution. Store the NAC solution in closed flask and check the pH weekly or when necessary.

Extraction of soluble Pusing NAC

(*i*) Weigh 1 g of sample with 0.1 mg of precision and transfer to filter paper with medium porosity, adapted in a funnel placed on a volumetric 500 mL flask.

(*ii*) Wash the sample with 180 mL of water by adding small portions.

(*iii*) Transfer the filter paper with the residue to a 250-300 mL Erlenmeyer flask and rinse the funnel with water, while transferring to the 500 mL volumetric flask.

(*iv*) Add 100 mL of NAC previously heated at 65 °C to the Erlenmeyer flask.

(*v*) Cap the flask and shake the mixture vigorously for a few minutes. Eventually, remove the cap for pressure release.

(*vi*) Place the flask tightly closed in oven or water bath with stirrer and stir for 1 hour, keeping the temperature at $65° \pm 5 ° C$;

(*vii*) After 1 h, remove the flask from the shaking system and leave the mixture to cool to room temperature. Subsequently, transfer the mixture to the flask containing the water-soluble phosphorus. Complete the volume of the flask and mix the solution.

(*viii*) Leave the mixture standing until a clear supernatant is observed. Then, filter the supernatant (medium porosity filter) or centrifuge it.

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Table S1. Maximum permissible errors for volumetric flasks, pipettes and volumetric micropipettes

Calibrated item	Maximum tolerated error[a]
Volumetric flask (50 mL)	0.12 mL
Volumetric flask (100 mL)	0.20 mL
Volumetric flask (200 and 250 mL)	0.30 mL
Volumetric flask (500 mL)	0.50 mL
Volumetric pipette (1 mL)	0.014 mL
Volumetric pipette (2 and 3 mL)	0.02 mL
Volumetric pipette (4 to 7 mL)	0.03 mL
Volumetric pipette (8 to 10 mL)	0.04 mL
Volumetric pipette (15 to 25 mL)	0.06 mL
Volumetric pipette (50 mL)	0.10 mL
Micropipette (50 µL)	0.50 µL
Micropipette (100 µL)	0.80 µL
Micropipette (200 µL)	1.6 µL
Micropipette (500 µL)	4.0 µL
Micropipette (1000 µL)	8.0 µL

[a]Quadratic sum of the expanded uncertainty and the measurement error.

Doehlert matrix

A Doehlert matrix with three variables can be represented as a cube-octahedron.[1] The exact composition of the experimental array, with the definition of values used for each experiment, may change with the cube-octahedron spin.[1,2] Figure S1 illustrates a possible visualization of the composition for the present study, whereas the numeric values of the coordinates are given in Table S2. The values of the coordinates were converted into real values. A dimension of the spatial model was assigned to a studied factor; the zero coordinate in the space corresponded to the average value of the experimental range for the factor. Then, the distance from the average to the maximum value of this range was determined. This distance is equivalent to the radius of the sphere containing the cube-octahedron. Thus, the average value plus the value of the radius of the sphere was the highest in the range considered. Coordinate +1 was attributed to this value, whereas the minimum value of the range was assigned to coordinate –1.
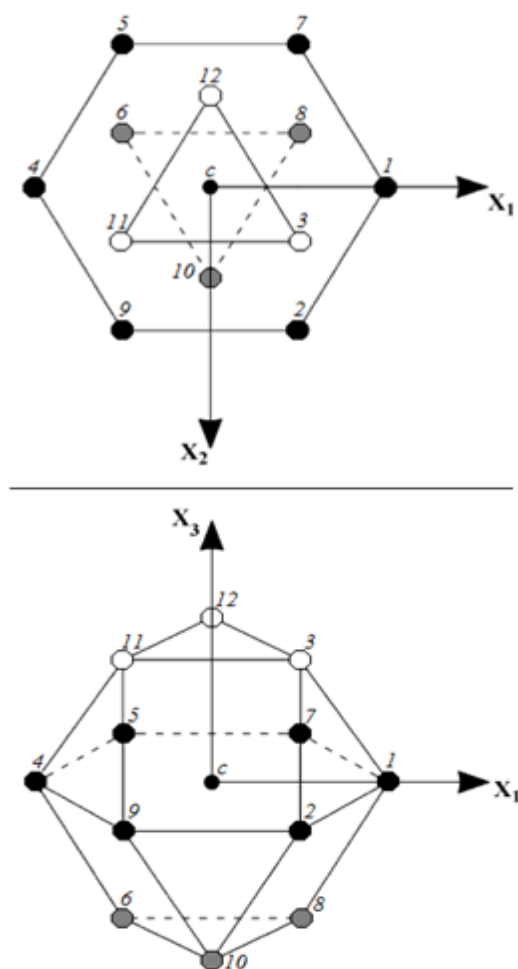
Figure S1. Experimental Doehlert design. (Top) Model in perpendicular view to the axis X_3. (Bottom) Scheme of a three dimensional view. The geometric representation of numbered points corresponds to each test number in Table S2. C_1 to C_n are the repetitions of the central point. X_1, X_2 and X_3 represent the first, the second and third experimental variable, respectively.[3]

Table S2. Experimental Doehlert matrix

Assay	X_1	X_2	X_3
1	1	0	0
2	0.5	0.866	0
3	0.5	0.289	0.817
4	−1	0	0
5	−0.5	−0.866	0
6	−0.5	−0.289	−0.817
7	−0.5	−0.866	0
8	0.5	−0.289	−0.817
9	0.5	0.866	0
10	−0.5	0.577	−0.817
11	0	0.289	0.817
12	0	−0.577	0.817
c_1	0	0	0
c_2	0	0	0
...	0	0	0
c_n	0	0	0

X_1, X_2 and X_3 represent the first, the second and third experimental variable, respectively.

Table S3. Factors and levels evaluated in optimizing the instrumental conditions and results obtained

Assay	Levels and factors			Intensity			Plasma robustness
	Power / kW	Peristaltic pump speed / rpm	Nebulizer gas pressure / kPa	S	P	B	Mg(II)/Mg(I)
1	1.45	15.00	200.00	805	2124	5192	5.88
2	1.30	24.00	200.00	744	1806	4879	5.17
3	1.30	18.00	220.00	692	1610	4788	4.81
4	0.75	15.00	200.00	208	358	1379	2.34
5	0.90	6.00	200.00	312	536	1839	3.22
6	0.90	12.00	180.00	402	742	2394	3.41
7	1.30	6.00	200.00	566	1453	3763	5.27
8	1.30	12.00	180.00	735	1907	4575	5.49
9	0.90	24.00	200.00	374	669	2402	3.09
10	1.10	21.00	180.00	638	1355	3788	4.42
11	0.90	18.00	220.00	325	577	2217	2.73
12	1.10	9.00	220.00	447	909	3022	3.86
13	1.10	15.00	200.00	570	1144	3527	4.15
14	1.10	15.00	200.00	583	1156	3526	4.16
15	1.10	15.00	200.00	577	1149	3518	4.16
16	1.10	15.00	200.00	567	1154	3561	4.14
17	1.10	15.00	200.00	572	1145	3516	4.17
18	1.10	15.00	200.00	576	1144	3524	4.16
R^2	–	–	–	0.9956	0.9913	0.9915	0.9939

R^2: coefficient of determination.

Table S4. Uncertainty contribution factors and sensitivity coefficients

Uncertainty component		Sensitivity coefficient
Analyte concentration (S)	L_1 (curve calibration regression)	$\dfrac{FD}{10000 \times m}$
	L_2 (standard total error)	$\dfrac{\frac{FD}{PC}}{10000 \times m}$
	L_3 (standard dilutions)	$\dfrac{-\frac{CP}{PC^2} \times FD}{10000 \times m}$
Dilution factor (DF)	DF (maximum tolerated error (including volumetric expansion of glassware))	$\dfrac{L}{10000 \times m}$
Sample mass (m)	m_1 (balance total error) m_2 (balance resolution) m_3 (eccentricity)	$-\dfrac{L \times FD}{10000m^2}$
R&R (intralaboratory reproducibility)		1
$\overline{REC}$ (average recovery)		1

PC: dilution of the solution with the highest concentration in the calibration curve; CP: concentration of the analyte in calibration solution.

Table S5. Contributions of each component to the uncertainty in the determination of B, S, and P in mineral fertilizer using ICP OES and analytes recovery

Uncertainty components		B	S	P	Degrees of freedom
Sample Concentration / % (m/m)		0.232	5.87	7.11	–
Analyte concentration (S)	L_1(curve regression)	0.0061	0.2667	0.6077	16
	L_2 (standard total error)	0.00111	0.2494	0.1386	∞
	L_3 (standard dilutions)	31.5352	0.2090	0.2014	∞
Dilution factor (DF)	DF (maximum tolerated error)	204.3333	3.1749	17.3181	∞
Sample mass (m)	m_1 (balance total error)		0.0003		∞
	m_2 (balance resolution)		0.00005		∞
	m_3 (eccentricity)		0.0002		7
Intralaboratory reproducibility / %		0.0279	0.017	0.0184	25
Accuracy / %		102.35	100	103.58	29

Table S6. Data obtained in the experiments of the laboratory reproducibility evaluation

Analyte	Sample	Repetition	Measurement	
			1	2
Boron (249.772 nm)	1542F/14	A	0.0724	0.0703
		B	0.0736	0.0690
		C	0.0711	0.0689
	1606F/14	A	10.77	10.64
		B	10.51	10.72
		C	10.64	10.53
	1731F/14	A	0.0415	0.0424
		B	0.0418	0.0406
		C	0.0407	0.0436
	F118/13	A	1.027	1.131
		B	1.030	1.051
		C	1.019	1.038
	1364F/14	A	0.2319	0.2445
		B	0.2357	0.2448
		C	0.2427	0.2361
Sulfur (181.972 nm)	162	A	13.70	13.31
		B	13.66	13.26
		C	14.13	13.48
	1605F/14	A	10.86	11.08
		B	10.84	11.05
		C	10.99	10.98
	0205F/15	A	2.057	2.127
		B	2.128	2.165
		C	2.083	2.125
	F0289/13	A	6.85	7.02
		B	7.08	6.94
		C	7.13	7.06
	1722F/14	A	5.747	5.872
		B	5.925	5.891
		C	5.894	6.003

Table S6. Data obtained in the experiments of the laboratory reproducibility evaluation (cont.)

Analyte	Sample	Repetition	Measurement	
			1	2
Phosphorus (213.547 nm)	0162F/15	A	10.69	11.02
		B	11.03	11.31
		C	10.96	11.26
	0172F/15	A	13.40	13.58
		B	13.70	13.71
		C	13.45	13.79
	1197F/14	A	5.63	5.56
		B	5.53	5.60
		C	5.35	5.59
	0186F/15	A	7.11	7.28
		B	7.26	7.52
		C	7.37	7.54
	0213F/15	A	6.49	6.68
		B	6.61	6.52
		C	6.72	6.57

The normalized error informed in Table 9 was calculated according to the following equation:

$$E_n = \left| \frac{\left(x_{lab} - X_{reference} \right)}{\sqrt{\left(U_{lab}^2 + U_{reference}^2 \right)}} \right| \qquad (1)$$

U = expanded uncertainty

E_n = normalized error

E_n < 1 to pass

References

1. Teófilo, R. F.; Ferreira, M. M.; *Quim. Nova* **2006**, *2*, 338.

2. Cataldi, T. R. I.; Orlando, D.; Nardiello, D.; Rubino, A.; Bianco, G.; Abate, S.; Ciriello, R.; Guerrieri, A.; *Anal. Chim. Acta* **2007**, *597*, 129.

3. Joint Committee for Guides in Metrology (JCGM); *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*, JCGM 100:2008, JCGM: Sèvres, 2008.