Note

A sample preparation method for reducing variability in the chemical analysis of mineral fertilizers

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ABSTRACT: Analyses of fertilizer are essential to ensuring that fertilizer sold to final users presents chemical and physical qualities in the range determined by law. As regards the sampling of fertilizers, the official method currently used in Brazil for sampling preparation is to reduce the size of the sample (from ~ 3 kg to ~ 0.25 kg) by quartering, followed by grinding (so as to pass through a 0.85 sieve) and nutrient quantification. Herein, we propose an alternative method of sampling preparation by grinding the total sample (~ 3 kg) before quartering to improve accuracy and reduce segregation during quartering. Six formulations of fertilizers (basal samples) were weighed (0.01 kg precision) and sampled according to the two methods (official and alternative), followed by the quantification of nutrient concentration in duplicate. Results showed that both methods presented similar nutrient concentrations for most formulations compared to the basal samples. However, the alternative method presented higher precision (less variation between replicates) and accuracy (versus the basal samples) than the official method. Consequently, the alternative method can be used for sampling preparation fertilizers with high accuracy and precision in determining nutrient concentration.

Keywords: accuracy, chemical composition, fertilizer quality, nutrient, precision

In agriculture, mineral fertilizers are the primary source of nutrients in the crop system, directly impacting crop nutrient balances, nutrient use efficiency, and food security. Since the mid-twentieth century, crop production has been continually increasing due to its direct association with the application of fertilizers, particularly mineral fertilizers (FAOSTAT, 2022).

Fertilizer performance is influenced by the chemical and physical properties of those raw materials, which are characterized by a high tendency towards caking when stored, formation of dust during handling, and segregation in fertilizer blends (Loganathan et al., 1992). Generally, the raw materials used for bulk blends are solid granulates with different granulometry (Miserque and Pirard, 2004). Granulometry is an example of physical properties that influence fertilizer quality and the level of homogeneity between particles (Lillerand et al., 2021). Segregation is influenced by granulometry and defined by the separation and selective accommodation of the constituent particles motivated by their movement and vibration (Thaper et al., 2022).

The process of fertilizer sampling is fundamental to guaranteeing fertilizer quality in accordance with legal regulations. The official methodology for collecting and preparing fertilizer samples in Brazil is based on Normative Instruction, number 53, issued by the Ministério da Agricultura, Pecuária e Abastecimento (MAPA, 2013). According to this method, after collecting the sample of solid fertilizer, the entire sample (around 3 kg) is reduced in size (to approximately 0.25 kg) with a sequential quartering of the samples by hand or using Jones-type equipment. After quartering, all that remains of the resulting sample is ground and passed through a 0.85 mm sieve following chemical analysis. One potential error in this method is the segregation of fertilizer particles during quartering before analysis. This is especially true for formulations with different raw materials. To overcome this limitation, we propose herein an alternative method that differs from the official one by grinding the total sample (~ 3 kg) and passing it through a 0.85 mm sieve before quartering.

Based on the premise that fertilizer sample preparation influences the representativeness of the fertilizer submitted to chemical analysis, this study compared the official method of sample preparation with an alternative method to check its reliability for quality control of mineral fertilizers. In addition, the study compared the impact of nutrient sources on the accuracy of the analysis.

The experiment was developed from Mar to Oct 2021, and two sample preparation methods were tested. The first method was the official method according to Brazilian legislation (MAPA, 2017), and the second was a modified version of the official method, developed and described herein as an alternative method.

The experimental design included six blend fertilizers, two methods of sample preparation, and five repetitions. The fertilizers used in the study were prepared in the laboratory, weighing on a scale with a precision of 0.01 kg. Raw materials used to prepare the fertilizers were obtained from commercial fertilizer companies and dried in an oven with forced air circulation at 40 °C for 48 h.

According to MAPA (2017), raw materials were analyzed in duplicate before the preparation of fertilizers. The six fertilizers evaluated in this study were prepared with different raw materials, containing only macronutrients or a mixture of macro- and micronutrients, to represent different formulations of fertilizers marketed in Brazil. Formulation 1 (F1 = 04 – 14 – 08 + 10 % Ca + 1 % S + 4.9 % Mg), Formulation 2 (F2 = 04 – 10 – 30 + 0.03 % B + 0.1 % Mn + 0.1 % Zn), Formulation 3 (F3 = 14 – 14 – 16), Formulation 4 (F4 = 18 – 00 – 18 + 2.8 % Ca + 1.4 % Mg) Formulation 5 (F5 = 20 – 00 – 20 + 10 % S), Formulation 6 (F6 = 20 – 04 – 18 + 2.2 % Mg + 0.2 % B + 0.3 % Zn). The numbers 04-14-08, 04-10-30, 14-14-16, 18-00-18, 20-00-20, and 20-04-18 in the formulations refer to concentrations of nitrogen (N), phosphorus (P), and potassium (K), respectively.

Formulation 1 was based on a mixture of monoammonium phosphate (270 kg t^{-1}), ammonium sulfate (50 kg t^{-1}), potassium chloride (134 kg t^{-1}), carbonate of calcium and magnesium (546 kg t^{-1}). Formulation 2 was based on a mixture of triple phosphate (186 kg t^{-1}), potassium chloride (500 kg t^{-1}), ammonium sulfate (179 kg t^{-1}), 03-17-00 (85 kg t^{-1}), and micronutrients (50 kg t^{-1}). Formulation 3 was based on a mixture of urea (53 kg t^{-1}), ammonium sulfate (410 kg t^{-1}), monoammonium phosphate (270 kg t^{-1}), and potassium chloride (267 kg t^{-1}). Formulation 4 was based on a mixture of nitrate ammonium and calcium (700 kg t^{-1}) and potassium chloride (300 kg t^{-1}). On the other hand, F5 was based on a mixture of urea prill (241 kg t^{-1}), ammonium sulfate (425 kg t^{-1}), and potassium chloride (334 kg t^{-1}), while F6 was based on a mixture of monoammonium phosphate (77 kg t^{-1}), potassium chloride (213 kg t^{-1}), urea (417 kg t^{-1}), K Mag (243 kg t^{-1}) and micronutrients (50 kg t^{-1}) (Table 1). The mixtures of fertilizers tested herein were based on the main formulations consumed in Brazilian agriculture.

The raw materials were separated and weighed for the preparation of each fertilizer, using five replications (3 kg of formulation per sample) for each method. After weighing, the samples were mixed in a homogenizing mixer (Y-type) for 3 min, fixed at a rotation of 28 ± 2 per min in an agitation amplitude of 360°, and were then stored in sealed plastic bags until analysis (Figure 1A-C).

Following the procedure prescribed by the official method each fertilizer formulation (3 kg each) was transferred to a "Jones type" splitter and subsequently quartered into two subsamples of ~ 0.25 kg each (MAPA, 2013). Each subsample was ground in a fertilizer until 100 % of the granules had been passed through a 0.85 mm sieve. Following the procedures prescribed by the alternative method, each fertilizer formulation (3 kg each) was entirely ground in a fertilizer until 100 % of the granules had passed through a 0.85 mm sieve. The ground fertilizer was in a room with air conditioning set to 18 °C to reduce humidity and allow for good grinding conditions. The ground subsample (3 kg) was deposited over a flat and clean surface, separated into four "parts",

Table 1 – Fertilizers in formulations.

Fertilizers in formulations	Rates
	kg Mg^{-1}
Formulation 1 (04-14-08 + 10 % Ca + 1 % S + 4.9 % Mg)	
Monoammonium phosphate	270
Bran ammonium sulfate	50
Granulated potassium chloride	134
Carbonate of calcium and magnesium	546
Formulation 2 (04-10-30 + 0.03 % B + 0.1 % Mn + 0.1 % Zn)	
Triple phosphate	186
Granulated potassium chloride	500
Ammonium sulfate	179
03-17-00	85
Micro	50
Formulation 3 (14-14-16)	
Urea	53
Ammonium sulfate	410
Monoammonium phosphate	270
Granulated potassium chloride	267
Formulation 4 (18-00-18 + 2.8 % Ca + 1.4 % Mg)	
Nitrate ammonium and calcium	700
Granulated potassium chloride	300
Formulation 5 (20-00-20 + 10 % S)	
Urea prill	241
Bran ammonium sulfate	425
Granulated potassium chloride	334
Formulation 6 (20-04-18 + 2.2 Mg + 0.2 B + 0.3 % Zn)	
Monoammonium phosphate	77
Granulated potassium chloride	213
Urea	417
Mag potassium	243
Micro	50

The numbers in the formulations, 04-14-08; 04-10-30; 14-14-16; 18-00-18; 20-00-20; and 20-04-18, refer to concentration of nitrogen, phosphorus and potassium, respectively. Boron = B; manganese = Mn; zinc = Zn; calcium = Ca; sulfur = S.

and only one part was collected. This step was repeated until two subsamples of 0.25 kg were obtained. This quartering procedure is an alternative to using the "Jones type" equipment following the official guidelines of MAPA (2013). The steps of sample preparation are shown in Figures 1D-E. Fertilizer samples obtained by both procedures were stored in sealed plastic bags, containing ~ 0.25 kg each, until analysis (Figures 1D-E).

During the development of the experiment, temperature and relative humidity were recorded inside the laboratory using a thermo-hygrometer, obtaining means of 25.0 ± 5.0 °C and 75 ± 5 % for temperature and relative humidity, respectively.

Each fertilizer sample was analyzed for micro- and macronutrient contents using the usual fertilizer methods following official methods of fertilizer analysis in Brazil (EMBRAPA, 2019). Briefly, the Kjeldahl method quantified the nitrogen content extracted by sulfuric digestion. Total phosphorus content was determined by the gravimetric method. Contents of magnesium (Mg), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), and
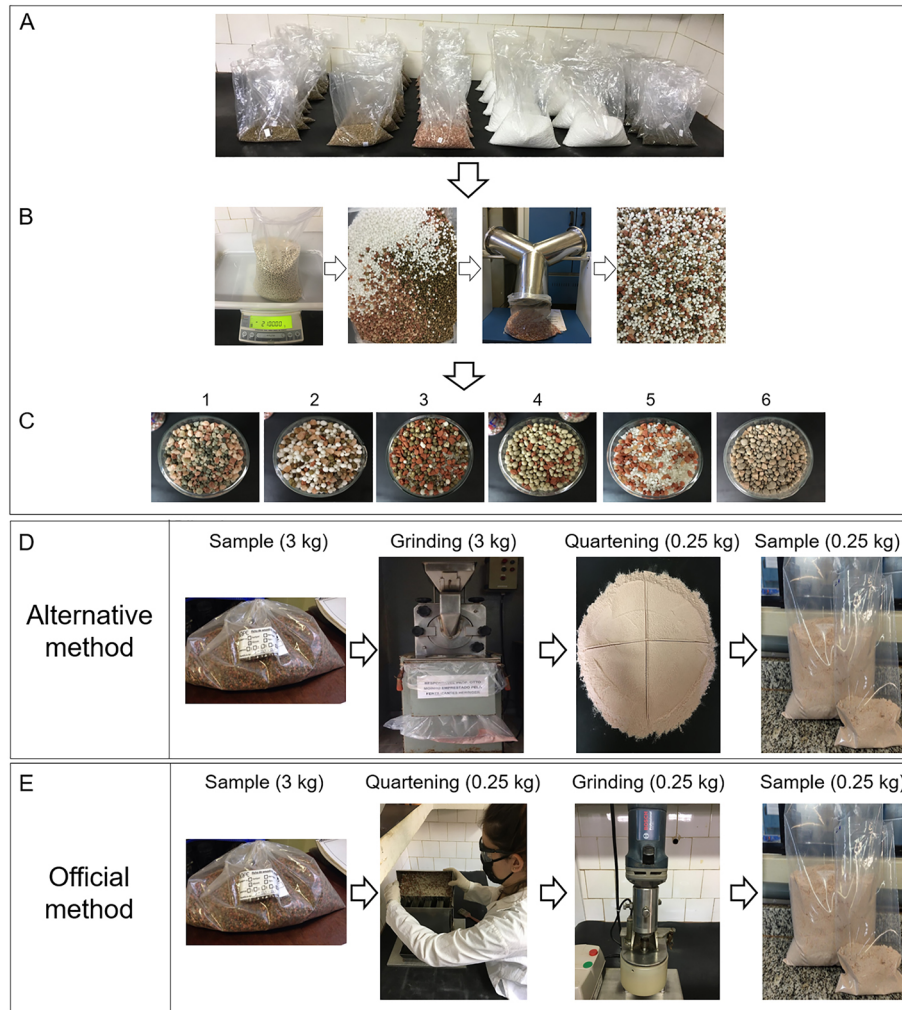
Figure 1 – A) Raw material; B and C) steps in the preparation of the six formulations; D) sample preparation of fertilizers according to the alternative; and E) official methods. Approximately 3 kg of each formulation was prepared.

calcium (Ca) were determined by atomic absorption spectrophotometer. Sulfur was extracted gravimetrically as sulfate, and boron was determined by azomethine-H spectrophotometry.

Drawing on the nutrient content data in each fertilizer, we monitored the homogeneity of variance and normality of residuals using the Bartlett test (p = 0.05) and the Shapiro-Wilk test (p = 0.05), respectively. Transformation to normalized data was not required.

Under each method, nutrient concentrations in fertilizer (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, boron, zinc, and manganese) were treated as a population and compared by the t-test (Student's t-test; $p < 0.05$) using the average between groups with paired samples.

The precisions of the methods were based on the sample variance using the standard deviation information between the five replicates. They were used to explain error tolerance for each method, where low standard deviation values represented higher precision of one method over the other. Standard deviation was tested and compared by the Folded F test (Equal variance; $p < 0.0001$) based on variances in the data set.

The concentrations of nutrients obtained for each method were compared to the initial nutrient concentration of the basal samples (before sample preparation), allowing for the calculation of the level of accuracy according to Eq. (1). Accuracy levels close to 100 % show high assertiveness of the method, while values higher than 100 % demonstrate the overestimation of nutrient contents.

$$Accuracy_{(\%)} = \left[\frac{\left(NC_B \times 100\right)}{CN_A}\right] \tag{1}$$

where NC_B is the nutrient concentrations in the basal samples (before sampling), and NC_A the nutrient concentrations in fertilizer after sample preparation and analysis following the official and alternative methods.

Statistical analyses were performed in R (version 4.0.0, R Foundation for Statistical Computing), and the results were graphed in SigmaPlot (version 11.0; SYSTAT Software, Inc.).

Results demonstrated that the performance of methods varied according to the nutrient concentrations and formulations. In F1, the alternative method presented a superior concentration of N (up to 7.9 %), P (up to 2.2 %), and S (up to 7.1 %). In comparison, the official method presented higher concentrations of K (up to 9.7 %). The methods did not affect concentrations of Ca and Mg in the F1 with a respective average of 9.1 % and 4.3 % (Table 2).

The difference in concentration of P and K was observed in only F1, which had been expected due to low hygroscopicity and the segregation of sources. In all formulations, the source of K was granulated potassium chloride, which is classified as the main source of this

nutrient with high concentration (60 % K_2O guarantee). In contrast, sources of P were monoammonium phosphate (F1, F3, and F6) and triple phosphate (F2) used in the formulations.

The methods also influenced the N concentrations in F2 and F5, but higher N concentrations were associated with the official method in F2 (up to 2.4 %) and F5 (up to 1.9 %). In the other formulations, the N concentrations were not influenced by the methods in F3 (average = 14.0 %), F4 (average = 18.4 %), and F6 (average = 19.9 or 20.0 %). The N base was different in these forms with ammonium and calcium nitrate (F4), urea prill with bran ammonium sulfate (F5), and conventional isolated urea (F6). An exception to F3 is that as a source of nitrogen the ammonium sulfate associated with conventional urea was also there (Table 2).

In F1, the S concentrations were also influenced by the higher concentration under the alternative method,

Table 2 – Average and standard deviation (precision) of nutrient concentration in the studied formulation according to two sample preparation methods.

Methods	Nutrients								
	Nitrogen	Phosphorus	Potassium	Calcium	Magnesium	Sulfur	Boron	Zinc	Manganese
	-- % --								
Formulation 1 (04-14-08 + 10 % Ca + 1 % S + 4.9 % Mg)									
Alternative	3.9 ± 0.11 A	13.6 ± 0.26 A	8.5 ± 0.27 B	9.1 ± 0.77	4.3 ± 0.13	1.4 ± 0.10 A	-	-	-
Official	3.6 ± 0.20 B	13.3 ± 0.69 B	9.4 ± 0.59 A	9.1 ± 0.99	4.3 ± 0.15	1.3 ± 0.11 B	-	-	-
t test[1]	< 0.05	< 0.05	< 0.05	0.92	0.79	< 0.05	-	-	-
p-value (Folded F)[2]	< 0.05	< 0.05	< 0.05	0.31	0.43	0.49	-	-	-
Formulation 2 (04-10-30 + 0.03 % B + 0.1 % Mn + 0.1 % Zn)									
Alternative	4.0 ± 0.15 B	10.0 ± 0.15	30.0 ± 0.15	-	-	-	0.03 ± 0.01	0.10 ± 0.01	0.09 ± 0.007 A
Official	4.1 ± 0.21 A	10.0 ± 0.38	29.9 ± 0.38	-	-	-	0.03 ± 0.01	0.09 ± 0.01	0.08 ± 0.013 B
t test[1]	< 0.05	0.23	0.96	-	-	-	0.23	0.11	< 0.05
p-value (Folded F)[2]	< 0.05	< 0.05	< 0.05	-	-	-	0.57	0.43	< 0.05
Formulation 3 (14-14-16)									
Alternative	14.0 ± 0.26	14.4 ± 0.25	15.6 ± 0.28	-	-	-	-	-	-
Official	14.0 ± 0.27	14.5 ± 0.39	15.5 ± 0.38	-	-	-	-	-	-
t test[1]	0.22	0.54	0.51	-	-	-	-	-	-
p-value (Folded F)[2]	0.83	< 0.05	< 0.05	-	-	-	-	-	-
Formulation 4 (18-00-18 + 2.8 % Ca + 1.4 % Mg)									
Alternative	18.4 ± 0.48	-	17.3 ± 0.26	2.9 ± 0.13	1.6 ± 0.05	-	-	-	-
Official	18.4 ± 0.64	-	17.4 ± 0.76	2.8 ± 0.13	1.6 ± 0.05	-	-	-	-
t test[1]	0.77	-	0.91	0.60	0.64	-	-	-	-
p-value (Folded F)[2]	< 0.05	-	< 0.05	0.98	0.50	-	-	-	-
Formulation 5 (20-00-20 + 10 % S)									
Alternative	20.1 ± 0.39 B	-	19.8 ± 0.46	-	-	10.6 ± 0.23	-	-	-
Official	20.5 ± 0.99 A	-	19.5 ± 0.95	-	-	10.5 ± 0.49	-	-	-
t test[1]	< 0.05	-	0.11	-	-	0.35	-	-	-
p-value (Folded F)[2]	< 0.05	-	< 0.05	-	-	< 0.05	-	-	-
Formulation 6 (20-04-18 + 2.2 % Mg + 0.2 % B + 0.3 % Zn)									
Alternative	20.0 ± 0.46	4.2 ± 0.14	17.7 ± 0.38	-	2.6 ± 0.09	-	0.22 ± 0.05	0.28 ± 0.01	-
Official	19.9 ± 0.74	4.1 ± 0.25	17.7 ± 0.71	-	2.5 ± 0.18	-	0.21 ± 0.06	0.29 ± 0.03	-
t test[1]	0.49	0.09	0.94	-	0.21	-	0.51	0.92	-
p-value (Folded F)[2]	< 0.05	< 0.05	< 0.05	-	< 0.05	-	0.09	< 0.05	-

[1]Averages were compared by the t test (p < 0.05), and differences (between the sample preparation methods) were represented by distinct uppercase letters.
[2]Folded F test p-value < 0.05 indicates differences in the standard deviation of nutrient concentration between the methods. The numbers in the formulations, 04-14-08; 04-10-30; 14-14-16; 18-00-18; 20-00-20; and 20-04-18, refer to concentration of nitrogen, phosphorus and potassium, respectively. Boron = B; manganese = Mn; zinc = Zn; calcium = Ca; sulfur = S.

which was 7.1 % higher than the official method. In F2, the Mn concentrations were also higher under the alternative method, 11.1 % higher than under the official method (Table 2).

There was no difference between the methods for any nutrient concentrations in F3 (N, P, and K), F4 (N, K, Ca, and Mg), and F6 (N, P, K, Mg, B, and Zn) (Table 2).

In all formulations, the alternative method presented greater precision when monitoring the N concentrations considered higher in F1 (up to 45.0 %), F2 (up to 28.5 %), F4 (up to 25 %), F5 (up to 60.6 %), and F6 (up to 37.8 %) compared with the official method, except in F3, where there was no difference in values in standard deviation between the official (0.27 %) and the alternative methods (0.26 %) (Table 2). These results clearly demonstrate that when fertilizer samples were ground before the separation of fertilizers (alternative method), there was less variation in nutrient determination compared with the official method (ground after the separation) (Table 2).

Additionally, the alternative method also presented high precision when monitoring Mn in F2 (up to 46.1 %) and Zn in F6 (up to 66.6 %). In both formulations, 50 kg t^{-1} of micro was added as a source of Mn and Zn (Table 2).

In our study, we used the amount of fertilizers in plastic bags (3 kg of formulation per sample), as recommended by the MAPA methods for the preparation of each fertilizer. Based on the results and samples, the sample using 3 kg of the formulation was classified as adequate with consolidated results.

Both method's accuracy was higher than 90 % in most formulations, showing an adequate performance in reproducing reliable results from the chemical composition of fertilizers. The accuracy of the alternative method achieved values closer to 100 % with low segregation and randomized values. On the other hand, the official method presented systematic accuracy values that indicated a tendency and the formation of two clusters (Cluster 1 and 2) (Figure 2A-B).

The official method resulted in more samples in discordance with legislation compared with the alternative method. Specifically, the official method presented a potential of 12 nutrients outside the tolerance limits, representing 42 % of all observations, while the alternative method presented a potential of only five disparities, representing 18 % of all observations (Figure 3A-F).

The performance of methods varied according to the nutrient concentrations and formulations. The high variations in N concentration are explained by the sources which present ammonium sulfate (F1 and F2) or ammonium sulfate associated with conventional urea (F5). The ammonium sulfate is classified as an inorganic salt containing nitrogen (21 %) and sulfur (24 %) (Wu et al., 2019).

Ammonium sulfate is hygroscopic and can uptake water depending on the relative humidity of the surrounding medium (Tobon et al., 2021). In our study, there was no effect of hygroscopicity due to the adequate and controlled temperature conditions (25.0 ± 5.0 °C) and relative humidity (75 ± 5 %). Typically, ammonium sulfate is produced by combining anhydrous ammonia and sulfuric acid. However, there are other production routes, such as a by-product of caprolactam production (James and Speight, 2017), and the size of the resulting crystals determines the reaction conditions (IPNI, 2019). The small size of the ammonium sulfate (which was tested as a small crystal size) contributed to the segregation of fertilizer, which explainss the variation in performance with better performance of the alternative method in F1 and the official method in F2 and F5.

In F1, the S concentrations were also influenced by the methods with a higher concentration in the alternative method, which was 7.1 % higher than the official method. However, there was S in F5, with no difference between the methods (Figure 3A). In both forms, ammonium sulfate is a source of S with 24 % (w/w) sulfur in its composition (Wu et al., 2019; IPNI, 2019).
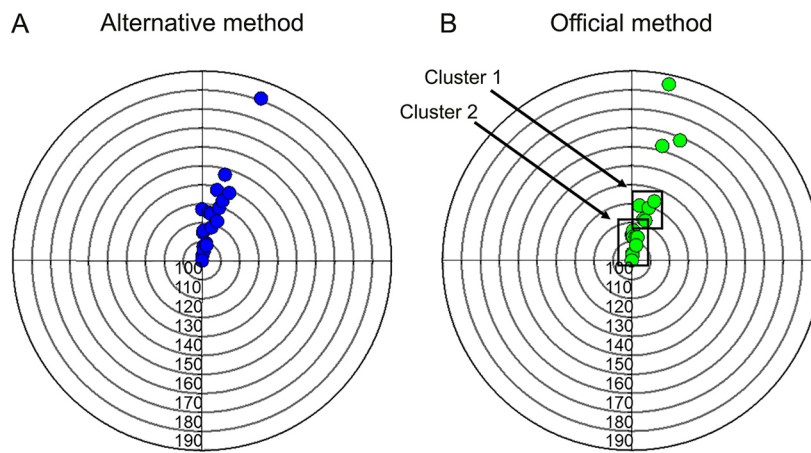

Figure 2 – A) Accuracy of nutrient concentrations in the alternative and B) official methods. Systematic accuracy in official methods with two clusters.
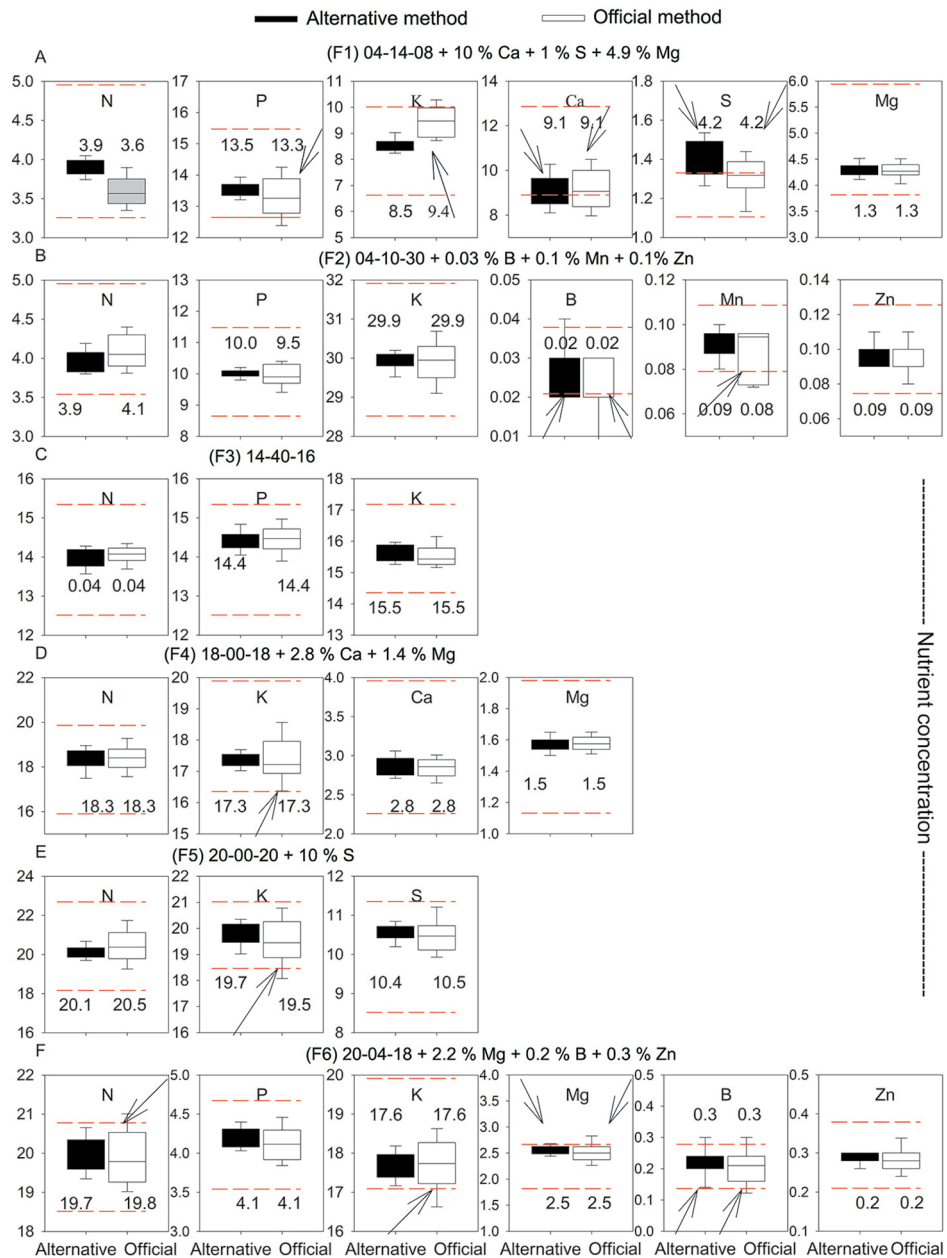
Figure 3 – Limit of tolerance allowed by current legislation in the studied formulations according to the sample preparation methods. Dashed lines represent the minimum and maximum tolerance of the nutrient concentration according to the legislation. The black arrows indicate the cases in which the limit was exceeded. The numbers in the formulations, A) 04-14-08; B) 04-10-30; C) 14-14-16; D) 18-00-18; E) 20-00-20; and F) 20-04-18, refer to concentration of nitrogen, phosphorus and potassium, respectively. Boron = B; manganese = Mn; zinc = Zn; calcium = Ca; sulfur = S.

In F2, the Mn concentrations were also higher under the alternative method. which was 11.1 % higher than the official method, F2 was the only manganese source with 50 kg t^{-1} of micronutrients (Figure 3B). The additions of micronutrients in forms are important to improving nutrient diversity in fertilizers, which increases the application efficiency. Mn plays an important role in crop production and is supplied with carbonate and oxides mainly by foliar applications (Migliavacca et al., 2022).

In accordance with the alternative method, 100 % of the fertilizer sample was ground into 0.85 mm, thereby reducing the segregation of fertilizer, which is defined as the separation and selective accommodation of the constituent particles motivated by their movement and vibration (Thaper et al., 2022). Fragment size distribution has a significant influence on segregation, which leads to chemical heterogeneity (Jain et al., 2013) and is denoted by an accumulation of fine particles in the center of the

heap, while the largest particles are concentrated in the periphery (Miserque and Pirard, 2004). In this study, the nutrient sources presented different sizes since particles were higher as granulated potassium chloride (between < 0.5 and 1-2 mm; Loganathan et al., 1992) and lower as ammonium sulfate (small crystals; IPNI, 2019), which explained the high variability and low precision in the official method.

In general, the accuracy of the alternative method achieved values closer to 100 % with low segregation and randomized values. On the other hand, the official method presented systematic accuracy values indicating a tendency and formation of two clusters (Cluster 1 and 2). Furthermore, the official method resulted in a potentially higher number of samples in discordance with legislation than the alternative method. Systematic accuracy of the data varies in predictable ways in the same direction and amount.

Additionally, the MAPA method starts by lowering the amount of sample which is practical, while the alternative method recommends grinding and sieving relatively higher amounts of the material to increase the precision and accuracy of the method.

In conclusion, this study compared two sample preparation methods for quality control of mineral fertilizers. Under the official method, the fertilizer sample (~ 3 kg) is quartered before grinding to obtain an aliquot for analysis. In contrast, the alternative method requires grinding the entire sample (~ 3 kg), followed by quartering until a representative sample for analysis is obtained. Both methods presented reliable results with slight differences in nutrient concentration between most formulations tested. However, the alternative method, despite being more time-consuming, presented less variation between the replicates (more precision) and higher levels of accuracy when compared to the official method. Based on this, the finding of this study is that the alternative method can be used for sample preparation of inorganic fertilizer in a program of quality control of fertilizers.

Authors' Contributions

Conceptualization: Otto R, Luz PHC. **Data curation:** Bet JA, Quaglio SR. **Formal analysis:** Ferraz-Almeida R, Lima CG, Bet JA. **Supervision:** Otto R, Luz PHC. **Writing-review & editing:** Ferraz-Almeida R, Otto R.

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