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Validation of calcium (Ca) analysis in dolomite fertilizer using atomic absorption spectrophotometer (AAS)

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ABSTRACT

The method of determining calcium (Ca) in dolomite fertilizer has been validated using atomic absorption spectrophotometer (AAS). Determining calcium (Ca) in dolomite fertilizer refers to the Indonesian National Standard (SNI) 02-2804-200. Based on the results of the calcium (Ca) test on dolomite fertilizer, the correlation coefficient (r) was 0.9949, and the % relative standard deviation (RSD) was 0.6472%, less than 2/3 CV Horwitz of 1.5963. The accuracy value is 100.30%, the precision value is 0.6471%, the detection limit for the LOD method is 0.2817, the LOQ is 0.9390, and the instrument detection limit is LOD 0.1159 and LOQ 0.3864. This study shows that the determination of calcium (Ca) in dolomite fertilizer using the SNI method using the Atomic Absorption Spectrophotometer (AAS) can be used with valid results.

Keywords:
Atomic absorption spectrophotometer (AAS), Calcium (Ca), Dolomite fertilizer, Validation

1. Introduction

Oil palm is one of the plantation commodities that is experiencing a rapid growth rate. However, the increase in area is mainly carried out on less fertile land because land with high suitability is used for food crop development.

The increase in production can be influenced by the effort made. This increase can be done with intensification. The intensification process is carried out starting from the plant in the nursery until the age of the plant is not productive. One factor that needs to be considered in this intensification is the aspect of fertilization. The continuous need for plant nutrients cannot be provided by the soil naturally, so additional nutrients are needed from the outside. According to [1] the benefits obtained from fertilization include supplementing the availability of nutrients in the soil and replacing nutrients lost due to leaching and being transported at harvest time so that soil conditions are suitable for oil palm growth and development.

Based on the number of nutrient needs in plants, it is distinguished into macro and micronutrients. Macro nutrients are the needs of nutrients needed in large quantities, if the needs of these nutrients are not fulfilled will affect the effectiveness of plant growth and production that will be reduced. Macro nutrients needed by plants include N, P, K, Ca, and Mg. Micronutrients are nutrients that are needed by plants in small quantities, in the fulfillment of these nutrients if too little amount will result in disruption of plants and if it exceeds the need to poison plants. The micronutrients needed by plants include B, Cu and Zn.

In the fulfillment of Ca elements, the community usually uses agricultural lime. The agricultural lime used comes from dolomite lime. The administration of dolomite

lime will improve the characteristics of the soil and can help in increasing the pH of the soil, increase in the availability of ca and mg nutrients that are the needs of plants, increase the availability of elements P and Mo, reduce the potential for poisoning of Fe, Al, and Mn, increase the efficiency of absorption of nutrients in the soil, improve soil porosity, aeration structure, beneficial for soil microbiology and chemistry [2].

The method of determining the level of Ca in fertilizer can be done using the spectrophotometry method. Research related to the determination of levels in fertilizers spectrophotometry has been widely done, but research on the validation of this method for the analysis of Ca on dolomite fertilizer is still limited. Validation needs to be done to assess the parameters - those parameters meet the operating standards' requirements. The study aims to validate the Ca analysis of dolomite fertilizers. Parameter validation includes linearity, precision, accuracy (%recovery), and detection limits.

2. Materials and Methods

The test was carried out by verifying the analysis method of the element Ca in Dolomite fertilizer according to SNI 02-2804-2005 using a spectrophotometer as close as atomic. Verification testing of this method aims to show how the method works to ensure Ca, especially in dolomite. Parameter analysis used in this test includes linearity, precision, accuracy (% recovery), and detection limit.

2.1. Materials

The materials used in this study are dolomite fertilizer as a reference sample, $CaCO_3$ HCL 37% pa, HCL Solution 2 N, Filter paper, distilled, lanthanum solution 2000 ppm and 20,000 ppm and standard Ca 3 ppm.

2.2. Preparation of Solutions and Reagents

2.2.1. Solution of HCL 2 N

Pipette 12.8 mL HCL 37% then diluted with distilled in the pumpkin measure 1 L to the limit mark.

2.2.2. Lanthanum Solution 20,000 ppm

Weighing 23.5 grams of LaCl then added distilled up to 200 mL then added HCL 37% as much as 45 mL then sorted until homogeneous (a homogeneous solution of clear color), then diluted on pumpkin 1 L with distilled to the limit mark.

2.2.3. Lanthanum Solution 2000 ppm

Take 200 mL of Lanthanum solution 20,000 ppm then added with 1800 mL distilled.

2.2.4. Standard Solution Ca 3 ppm

Pipette parent solution Ca 100 ppm then diluted with a distilled in the measuring pumpkin 100 mL with a distilled to the limit mark.

2.3. Linearity Test

The linearity test is determined through the linear regression equation $Y = aX \pm b$. Prepared standard series solution 3 ppm Ca. For linearity testing analyzed five repetitions of the standard series. One standard series is read as a standard series of

tests and four standard series are read as samples. Correlation is expressed very strongly if the r value obtained is above 0.9 but less than 1.0 according to the criteria. [3].

2.4. Accuracy Test

The accuracy of a method should be determined using a minimum of 3 concentration ranges between 80–120% of the target concentration, i.e., at concentrations of 80%, 100%, and 120%. The range of errors presented in each analyte concentration in the matrix according to the AOAC can be seen in Table 1.

Table 1. Percentage of recovery received in accordance with the level concentration of analytes [4]

Concentration of Analyte on The Sample Matrix	Average Earned (%)
100%	98–101
10%	95–102
1%	92–105
0.1%	90–108
0.01%	85–110
10 $mg.g^{-1}$ (ppm)	80–115
1 $mg.g^{-1}$	75–120
10 $kg.kg^{-1}$ (ppb)	70–125

$$\%\ \mathrm{Re} - \mathrm{Acquisition} = \frac{(C_3 - C_2)}{C_1} \times 100 \quad (1)$$

Information:
C_3 = Calcium concentration in example + calcium standard ($mg.L^{-1}$)
C_2 = Calcium concentration in the example ($mg.L^{-1}$)
C_1 = Standard concentration of calcium added ($mg.L^{-1}$)
%Re = Percentage of recovery

2.5. Precision

Precision is the degree of conformity between the test results of multiple analytical results that have been taken measurements with the same procedure [15]. Precision correlates with the result of looping a homogeneous measurement method in a homogeneous sample under controlled conditions. The precision of a method can be tested by repeating the analysis, if the variation in the result is small, it is said that the accuracy of the measurement is high [16]. Precision is expressed as standard deviation (SD) or relative standard deviation (coefficient of variance, RSD). Precision can also be interpreted as the degree of reproducibility or repeatability of the analysis procedure. Precision criteria are given if the method provides a relative standard deviation or coefficient of variation of 2% or less [3].

$$SD = \sqrt{\frac{\sum (X_i - X)^2}{n-1}} \quad (2)$$

Information:
SD = Standard deviation
X_i = Calcium measurement concentration ($mg.L^{-1}$)
X = Average concentration of calcium ($mg.L^{-1}$)
n = Number of repetitions

Percent Relative Raw Deviation (%SDR)/(%RSD)

$$\%SDR = \frac{SB}{X} \times 100 \quad (3)$$

Information:
SDR = Relative standard deviation (%)
SD = Standard deviation
X = Average concentration of calcium ($mg.L^{-1}$)

$$\%CVHorwitz = 2^{(1-0.25\log C)} \quad (4)$$

Information:
%CVHorwitz = Coefficient variance Horwitz (%)
C = Concentration fraction

2.6. LOD and LOQ Test

In this test is done by measuring 7 pieces of standard solution with the lowest concentration. The measurement value is equal to the value b in the linear line equation y = a + Bx

$$LOD = X + 3\,SD \quad (5)$$

$$LOQ = X + 10\,SD \quad (6)$$

Information:
LOD = Limit of detection
LOQ = Limit of quantification
X = Average concentration of blank
SD = Standard deviation

2.7. MDL and IDL Test

MDL (Method Detection Limit) or method detection limit is a value that indicates the extent to which the smallest concentration of an analysis method can be measured, while IDL (Instrument Detection Limit) or instrument detection limit is a value that shows the extent of the instrument's ability to detect the smallest concentration of an analysis method. The determination of MDL and IDL of an analysis method varies depending on the method of analysis used.

3. Results and Discussion

3.1. Linearity

The correlation coefficient of a standard series becomes a determinant in the linearity of an analysis method because the correlation coefficient is a statistical measurement of covariation or association between two variables. In this case, the variables are absorbance and concentration. If the correlation coefficient is not equal to zero, then there is a relationship between the two variables. If the correlation coefficient is +1, it is called a perfect correlation relationship or a perfect linear relationship with a positive slope. Conversely, if the correlation coefficient is worth -1, then the relationship is called a perfect correlation relationship or a perfect linear relationship with a negative slope. When the relationship approaches 1, then the relationship gets stronger. Conversely, when the relationship approaches 0, then the relationship gets weaker. The correlation range ranges from 0 to 1 with positive and negative values.

Calcium linearity testing is done by measuring the standard sequence of calcium plants using the UV-Vis Cary 100 spectrophotometer at a wavelength of 430 nm. One standard series is read as a standard series for calibration curves and three standard series are read as samples with the measurement results attached. The measurements presented in Table 2 and 3, and Figure 1 and 2.

Table 2. Standard series calibration results

Concentration Standard (ppm)	Absorbance Standard
0.0	-0.008
0.75	0.0679
1.5	0.1255
2.25	0.1722
3.0	0.2237

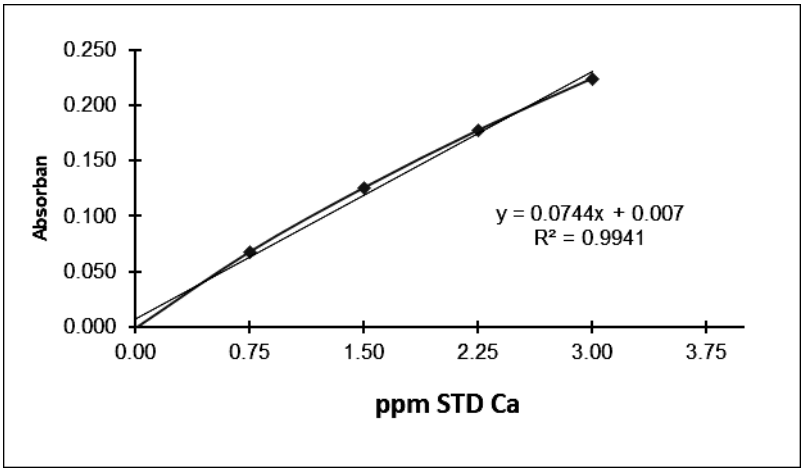

Figure 1. Calcium linearity curve

Table 3. Standard series reading results as samples

Standard mg.L^{-1}	Absorbance					Average	Regression
0	-0.0005	-0.0008	0	0.0001	0.0002	-0.0002	0.01597
0.75	0.0631	0.0679	0.065	0.0650	0.0651	0.06522	0.067354
1.5	0.1184	0.1255	0.115	0.1205	0.117	0.11928	0.118738
2.25	0.1776	0.1772	0.1705	0.1774	0.1745	0.17544	0.170122
3	0.224	0.2237	0.211	0.2185	0.2117	0.21778	0.221506

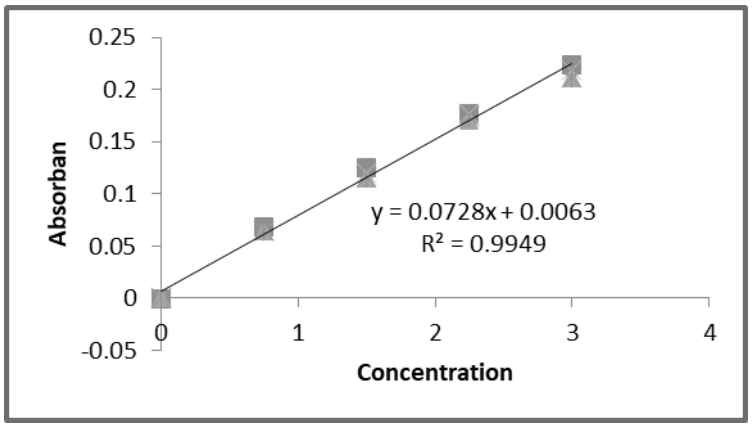

Figure 2. Standard series reading curve

From the results of these measurements can be known the slope of the standard series of 0.0728; intercept of 0.0063; and a correlation coefficient of 0.9949. Therefore, the analysis method is considered good because it has a correlation coefficient of > 0.9949 (SNI).

The line of the standard series calibration curve greatly affects the results of a test, especially the accuracy of the sample concentration readings. The reading of the concentration of a standard series solution as a sample of five repeats intends to test the accuracy produced by the standard series solution. One of the factors that can affect the approximately of the standard series calibration curve is the incorrect concentration of standard series solutions. The more linear the standard series calibration curve is produced, the closer the original concentration of the standard series solution is to its theoretical concentration.

If at certain points the concentration of the standard series solution reads more than or less than the proper concentration, then the standard series graph will become less linear. This will affect the results of reading the concentration of samples around these points. The concentration of the sample that is read will also become less accurate because the concentration of the standard series solution used as a comparison at the time of measurement is not precise. Therefore, the accuracy of the standard series calibration curve greatly affects the accuracy of the sample concentration reading results.

3.2. Precision

Precision is a measure that indicates the degree of conformity between individual test results measured through the spread of individual results from the average if

the procedure is applied repeatedly to samples taken from a homogeneous mixture. The experiment was conducted on at least six replica samples [5].

Precision is usually demonstrated using the standard deviation (SD) and the variance coefficient (CV) of the measurement series [6]. SD is used to describe the form of data distribution that has, while CV is used to describe the difference in results obtained each time a repeat of the examination is performed on the same sample. CVs can also be used to compare the performance of different methods, tools, and checks [7].

Precision can be known by comparing the %RSD test results with the %RSD contained in the reference method. If there is no %RSD, then %RSD test results compared to %RSD Horwitz and the result should be lower than 2/3% RSD Horwitz. The greater the difference between the %RSD test results with 2/3% of Horwitz RSD, the higher the precision.

Table 4. Results of precision tests of dolomite fertilizer reference samples

Sample Code	Sample Concentration (%)
Sample + Spike 1	30.4019
Sample + Spike 2	30.1640
Sample + Spike 3	30.5139
Sample + Spike 4	30.1050
Sample + Spike 5	30.3119
Sample + Spike 6	30.2688
Sample + Spike 7	29.9260
Average	**30.24**
Standard Deviation (SD)	0.1957
Variance	0.0383
Relative standard deviation (RSD)	0.0065
Variance coefficient (CV in %) or %RSD	**0.6472**
Concentration	30.24
C	0.3024
Log C	-0.5194
0.5*log C	-0.2597
1-0.5 Log C	1.25970
CV Horwitz Reproducibility (%)	2.3945
CV Horwitz Repeatability (%)-2/3 CV	**1.5963**

Precision testing of calcium dolomite fertilizer analysis by SNI 02-2804-2005 is done by measuring standard samples that have been standardized as many as 10 samples at the time of destruction of standard samples of dolomite fertilizer. As a blank sample, a standard solution is used zero. Then the extract is diluted with a dilution factor of 200X using a diluter tool. Next, measurements of the sample are carried out

using an atomic absorption spectrophotometer. From the results of these measurements then taken as much as at least seven data and, in this analysis, we took data as many as 7 times to be processed in the calculation of SD, RSD, and CV. The precision data obtained is presented in Table 4.

Based on the results of the standard sample precision test in the table above, the Relative Standard Deviation (%RSD) was obtained at 0.0065. The required Relative Standard Deviation Provision is %RSD < 2/3 CV Horwitz, following the calculation of 2/3 CV Horwitz which is 1.5693. Therefore, the testing of these methods provides precise results. Factors that can affect the results of precision testing include sample weighing, the use of hot plate heaters, and the consistency of analysts when preparing samples.

The standard sample used is dolomite fertilizer derived from a subsidiary of PT. Astra Agro Lestari is PT Badhhra Cemerlang. Standard samples of dolomite fertilizers were taken from several members of the fertilizer sample group who had traced theoretically appropriate calcium levels. Some samples of fertilizer are made into one in a container and then homogenized before being weighed so that in testing get precise results.

The weighing of the sample is done with caution and high thoroughness. In this case, weighing should be done consistently on the specified weighing number. Preparation between samples is done with the same treatment if you want high precision testing results.

After the destruction process is complete, the extract is diluted in a specified volume. It is diluted in a 500 mL measuring pumpkin. Dilution is done using pure water by way of volume transferred from the chemical glass into a measuring pumpkin of 500 ml.
Semi-automatic sampling with diluter has quite a lot of error points such as the condition of the piping equipment, and the presence of contamination from the equipment and reagents used. These errors can be overcome by using a calibrated diluter and in good condition; the implementation of the piping with good and correct techniques; the use of clean, dry, and the use of reagent that is always fresh.

3.3. Accuracy

Accuracy is the accuracy of the analysis method or proximity between measurable values and accepted values, either conversion values, actual values, or reference values. Accuracy is measured as the number of analytes recovered on a measurement by spiking a sample. Accuracy can be determined by comparison with other methods, the use of SRM (Standard Reference Material), or standard addition. Accuracy is expressed as percent of the added analyte recovery. Recovery is obtained from a comparison between the results obtained with the actual results.

Calcium accuracy testing on dolomite fertilizers is done by measuring standardized samples that have been constructed using HCl. Accuracy testing is done with the addition of a $CaCO_3$ solid solution for spiking. Performed 1 variation spike that spike as much as 100%, repetition as much as 10 times. In the addition of spikes that have been calculated, done with great caution. Measurements of the accuracy of calcium fertilizers are carried out using an atomic absorption spectrophotometer at

a wavelength of 422.7 nm. Calculation of the measurement results attached. The obtained %Recovery is presented in Table 5.

Table 5. Results of accuracy measurement with spiking process

Sample Code	Sample Weight (g)	Standard Spike (g)	Spike added (%)	Sample + Spike absorbance from the default curve	Sample + Spike concentration of the raw curve (%)	(%) Recovery
Sample + Spike 1	1.0000	0.5427	30.407	0.1892	60.172	98.43
Sample + Spike 2	1.0000	0.5430	30.423	0.1922	61.152	101.60
Sample + Spike 3	1.0002	0.5428	30.412	0.1910	60.748	100.31
Sample + Spike 4	1.0001	0.5428	30.412	0.1902	60.474	99.41
Sample + Spike 5	1.0001	0.5426	30.401	0.1911	60.782	100.46
Sample + Spike 6	1.0001	0.5425	30.395	0.2007	63.918	110.79
Sample + Spike 7	1.0000	0.5428	30.412	0.1922	61.152	101.64
Sample + Spike 8	1.0002	0.5430	30.423	0.1910	60.748	100.27
Sample + Spike 9	1.0002	0.5425	30.395	0.1982	63.099	108.10
Sample + Spike 10	1.0000	0.5430	30.423	0.2008	63.952	110.80
			Average			100.30

From the results of these tests can be known the average recovery of 100.30%. The value has met the requirements of good recovery, which ranges from 90-110% (AOAC). Therefore, the % recovery method is said to be good.

Calcium fertilizer accuracy testing in standard fertilizer samples is carried out by spiking method where the added spike concentration is around 100% of the standard sample concentration. If the added spike concentration is too low, it is most likely that the substance will bind to the sample so that the reading spike concentration is lower than it should be. However, if the added spike concentration is too high, it is likely that the concentration that reads is only the concentration of the spike.

3.4. Method Detection Limit (MDL) and Instrument Detection Limit (IDL)

LOD (Limit of Detection) is the lowest concentration of analyte in a sample that can still be detected, although it cannot always be quantified. LOD serves as a test limit

that specifically states whether the analyte is above or below a certain value. In general, there are two types of LOD, namely LOD method or MDL and LOD instrument or IDL.

MDL (Method Detection Limit) or method detection limit is a value that indicates the extent to which the smallest concentration of an analysis method can be measured, while IDL (Instrument Detection Limit) or instrument detection limit is a value that shows the extent of the instrument's ability to detect the smallest concentration of an analysis method. The determination of MDL and IDL of an analysis method varies depending on the method of analysis used.

LOQ (Limit of Quantification) is defined as the lowest concentration of analyte in a sample that can be determined with acceptable precision and accuracy under the operational conditions of the method used. Like LOD, LOQ is also expressed as a concentration with precision and accuracy that is also reported. LOQ is a quantitative test parameter for low-level compounds in the sample matrix [6].

Plant calcium MDL testing is done by measuring precision samples that have been diluted with a 2000 ppm lantana solution as much as 10 times repeat, while plant calcium IDL testing is done by measuring a standard solution of 0 ppm fertilizer as much as 10x repeat. MDL and IDL Plant calcium are expressed in ppm units. The measurements were made with an atomic absorption spectrophotometer at a wavelength of 422.7 nm.

From the results of these measurements are then taken as much as at least seven data for SD calculations to find out the LOD (Limit of Detection) and LOQ (Limit of Quantification) of the analysis method. The measurements are presented in Table 6 and 7.

Table 6. MDL calcium fertilizer

No.	Sample Blanco Concentration (ppm)	Sample Blanco Absorbance (Y)	Y_{count}	$(Y_{count} - Y_i)^2$
1	0.02	0.0219	0.0046	3.01E-04
2	0.02	0.0221	0.0048	3.00E-04
3	0.02	0.0219	0.0046	3.01E-04
4	0.02	0.0221	0.0048	3.00E-04
5	0.02	0.0219	0.0046	3.01E-04
6	0.02	0.0221	0.0048	3.00E-04
7	0.02	0.0221	0.0046	3.07E-04
Number of $(Y_{count} - Y_i)^2$				2.11E-03
Number of $(Y_{count} - Y_i)^2/(n - 2)$				4.22E-04
$s(y/x)^2$				0.0205
sy/x				0.0939
LOD 3 × SD (MDL)				0.2817
LOQ 10 × SD (MDL)				0.9390

Table 7. IDL calcium fertilizer

No.	Std. Zero concentration of the raw curve (ppm)	Absorbance Std. Zero from the raw curve (Y)	Y_{count}	$(Y_{count} - Y_i)^2$
1	-0.02	0.0019	-0.0044	3.96E-05
2	-0.02	0.0021	-0.0044	4.22E-05
3	-0.03	0.0018	-0.0055	5.31E-05
4	-0.02	0.0019	-0.0053	5.14E-05
5	-0.03	0.0012	-0.0059	5.02E-05
6	-0.03	0.0015	-0.0061	5.84E-05
7	-0.03	0.0013	-0.0066	6.21E-05
Number of $(Y_{count} - Y_i)^2$				3.57E-04
Number of $(Y_{count} - Y_i)^2/(n - 2)$				7.14E-05
$s(y/x)^2$				0.0084
sy/x				0.0386
LOD 3 × SD (IDL)				0.1159
LOQ 10 × SD (IDL)				0.3864

From the measurement of MDL and Plant Calcium IDL, it can be known that the MDL value of plant calcium is 0.2817, and the IDL value of plant calcium is 0.1159. IDL values smaller than MDL values indicate that the instrument used in the analysis method has a higher level of accuracy than the analysis method used, and vice versa. In fact, in the validation of analytical methods, there is no acceptable requirement for MDL and IDL testing. However, IDL values are generally required to be smaller than MDL values so that there is no bias due to the lack of sensitivity of the instruments used in detecting sample concentrations in an analysis method.

4. Conclusion

Calcium element analysis method in dolomite fertilizer refers to SNI 02-2804-2005 dilution of 500 mL using applied atomic absorption spectrophotometry has been valid because it qualifies the acceptance of an analysis method reviewed from linearity, precision (filtered extract), MDL (Method Detection Limit), and IDL (Instrument Detection Limit). The value obtained from the linearity parameter of 0.9945 (correspondence), accuracy 100.30 % (appropriate), precision 0.6471 < 1.5596 (corresponding), LOD method detection limit 0.2817 (appropriate) and LQD 0.9390 (appropriate), and LOD instrument detection limit 0.1159 (appropriate) and LOQ 0.3864 (accordance).

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