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Analysis Sulphur (S) Content of SP-36 Fertilizer PT Petrokimia Using In-House and Innovation Method

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Abstract. Fertilizer is an essential component in increasing food self-sufficiency in Indonesia. PT Petrokimia Gresik is one of the fourth-largest fertilizer producers in Indonesia and produces various kinds of fertilizers. One of the fertilizer is SP-36, contains sulphur and phosphate. This study investigated the sulphur (S) content in SP-36 fertilizer using the in-house and innovation method. The difference between the two methods is BaCl_2 ; the in house method used BaCl_2 powder, while the Innovation method used liquid BaCl_2 . Different used of BaCl_2 were based on their colloid formation. This study used a UV-Vis spectrophotometer instrument to calculate the sulphur content of SP-36 fertilizer. The results obtained from the research show that the two methods tested can be used to measure the sulphur content in SP-36 fertilizer. The most accurate result was In house method. The average value of sulphur content in SP-36 fertilizer using the in house method is 4,83%, while the average value of sulphur content in SP-36 fertilizer using the innovation method is 5,22%.

Keywords: In-house method, Innovation method, SP-36 fertilizer, Sulphur

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Introduction

Fertilizer is a compound containing nutrients and minerals to be given to plants in a specific amount and size. Generally, fertilizer consists of water-repellent substances, nutrients, consistency regulators, fillers, dirt, and others. Farmers had assumed that fertilizer was an essential element in agricultural farming. Fertilizer plays a vital role in plant growth and plant maintenance to produce agricultural products as expected. Plants need optimum factors in order to achieve production results as expected, including the soil availability of nutrients. If the soil did not contain sufficient nutrients for plants, it is important to apply fertilizer to meet this deficiency. In a broad sense, fertilizer is any substance added to the soil to provide the essential element that plants need [1].

Fertilizers based on their content, physical form, the release of nutrients, chemical reactions, compounds and manufacturing processes were classified into organic fertilizers and inorganic fertilizers. Organic fertilizers derived from weathering the remains of plants, animals and other natural materials. Organic fertilizers could be processed naturally or through human engineering [2], either solid or liquid. The fertilizers included inorganic fertilizers are manure, compost, humus and artificial organic fertilizers. Inorganic fertilizers, synthetic fertilizers or natural fertilizers made from chemicals, including nitrogen, phosphorus and potassium (NPK), ammonium sulfate (ZA), Urea, triple super phosphate (TSP) and others [3].

SP-36 fertilizer (Super Phosphate) was the best choice to meet the needs of soil and plants for phosphate nutrients because some of its advantages include having a high content of phosphate in the

form of P_2O_5 . The 36% of phosphate nutrients in SP-36 fertilizer almost entirely soluble in water, did not affect soil acidity because it is neutral, difficult to be absorbed by water, can be mixed with urea or ZA fertilizer in its use. The characteristics of SP-36 fertilizer were granular, grey, and non-hygroscopic. The nutrient content of P in SP-36 fertilizer can promote good root growth and root system, stimulate flower growth and ripeness of fruit or seeds, accelerate harvesting, increase the percentage of flowers formation into fruit or seeds, increase plant resistance to pests, diseases and drought. Superphosphate fertilizer ($Ca(H_2PO_4)_2$) can cause the soil to become acidic. Phosphoric acid completely formed H^+ ions into the soil when the pH starts from 3.0 to 7.0 [4].

The sulphur content in the SP-36 fertilizer is 5%. The methods used in determining sulphur contents were in-house methods and innovative methods. The in-house method was used by Petrokimia, referring to the Indonesian National Standard (SNI) and the American Society for Testing and Materials (ASTM) modified and validated. Current study modified in-house method to find out time and cost efficiency in the analysis process. The in-house method used $BaCl_2$ powder in 15 mL of the acidic salt as a suppressor, while the innovative method used 20 mL of 0.2 % $BaCl_2$ in 15 mL of the acidic salt. $BaCl_2$ powder took longer time to form colloids but usually clumps formed as a result of imperfect analysis using UV-Vis spectrophotometer. In contrast, solution of $BaCl_2$ formed colloids more quickly as well as detected sample using UV-Vis spectrophotometer. Water content of SP-36 fertilizer was analyzed through thermogravimetry analysis.

Experimental

Instruments and materials

The instrumentation used included a Shimadzu UV 1800 UV-Vis spectrophotometer, and other supporting tools, namely a spiral hotplate, a 4-decimal analytical balance, magnetic stirrer, Whatman filter paper number 41, plastic funnel, volume pipette, beaker glass, oven, measuring flask,

mortar pestle, spatula. The raw materials used were obtained from the Laboratory Factory II-B Petrokimia, Gresik including SP-36 fertilizer, HCl p.a (Honeywell), $BaCl_2$ p.a (Merck), salt acid suppressor (NaCl-HCl 0,02%), sulfuric standard solution (Merck).

Analysis Test of Sulphur (S) Content Using In-House and Innovation Method

The first step in both of methods was made a sample solution. The sample of the SP-36 product was mashed using a mortar and pestle. Refined samples then weighed of ± 0.5 g for in-house method and ± 0.8 g for innovation method. Sample was diluted in distilled water, then added 15 mL of HCl p.a. The sample solution was homogenized with a magnetic stirrer and filtered. For in-house method, 5 mL of sample was added by 15 mL salt acid suppressor, one spoon BaCl_2 , mixed with distilled water and homogenized, while for innovation method was took 10 mL, 15 mL of salt acid suppressor and 20 mL of BaCl_2 0,2%. Both of samples were analyzed UV-Vis Shimadzu UV 1800 spectrophotometer at a wavelength of 425 nm using 5 ppm of SO_4^{2-} standard for in-house method and 50 ppm of SO_4^{2-} standard for innovation method standard as blank solution. Sulphur content was calculated with following formula (Equation 1):

$$\% S (\text{ADBB}) = \frac{\frac{Mr S}{Mr \text{SO}_4^{2-}} \times \frac{\text{Abs Sample}}{\text{Abs Standard}} \times VLT \times FP \times C \text{ standard}}{\text{weight}} \times 100\% \quad (1)$$

The cup was cleaned then weighed with the lid (W_0). The SP-36 fertilizer sample of $\pm 2,0$ g (W_1). was put into a cup and was heated at 105 °C for 30 minutes, then weighed after cooling (W_2). H_2O content was calculated using the following formula:

$$\% \text{H}_2\text{O} = \frac{W_1 - W_2}{W_1 - W_0} \times 100\% \quad (2)$$

Then %S and % H_2O was used to calculate basis of dry weight (ADBK) using Equation 3.

$$\text{ADBK} = \frac{\% S}{100\% - \% \text{H}_2\text{O}} \times 100\% \quad (3)$$

Results and Discussion

The sulfur content test aimed to determine the sulfur content in the SP-36 fertilizer product. The experiment methods in this study were in-house method and innovative method, which were analyzed using UV-Vis spectrophotometer. Each data was taken as many as 30 data (see Table 1). The initial preparation carried out is to refine the sample because the sample was stilled in the form of a granule. It was necessary to expand the surface of the sample in powder form, to speed up the reaction and to homogenize the sample.

The process of collecting data on the sample using the in-house method and innovation method used HCl p.a. because technical HCl has a high sulfur content, so that it interfered with the final sulfur content in SP-36 fertilizer. The sulfate content of the sample was determined after adding HCl and BaCl_2 . The addition of HCl aimed to acidify the solution so that the minerals were dissolved. Meanwhile, the addition of BaCl_2 aimed to make the sulfate able to bind Ba^{2+} ions and to form a white precipitate in the form of BaSO_4 [1], see Equation 4.



The working principle of the UV-Vis spectrophotometer refers to the Lambert-Beer law [6]. The study used a UV-Vis Shimadzu 1800 spectrophotometer which had been modified with a capillary. The data obtained from the UV-Vis spectrophotometer was absorbance that used to calculatesulphur content based on wet weight (ADBB) in the sample. Based on calculations, the average value of sulphur content in SP-36 fertilizers using the in-house method is 4,83%. While the average value of sulphur content in the SP-36 fertilizer using the innovation method is 5,22%.

Furthermore, analysis of H_2O content in the SP-36 sample was carried out due to the effect of storage of the SP-36 sample influenced by temperature. For instance, when sample was stored in a very humid condition, affected its water content so that to maximize the sulfur content contained in the SP-36 sample. The data of H_2O content can be shown in the Table 2.

Table 1. Analysis of sulfur content measurement using the in-house method and innovation method

Data No-	In-House Method		Innovation Method	
	% (w/w) ADBB	% (w/w) ADBK	% (w/w) ADBB	% (w/w) ADBK
1	5,616463	5,831651	5,848276	6,086882

2	5,513121	5,72435	4,636741	4,825916
3	5,737103	5,956913	4,574042	4,76066
4	5,513121	5,72435	4,704914	4,896872
5	5,013888	5,205989	4,546039	4,731514
6	5,395205	5,601916	4,534981	4,720005
7	4,185687	4,346056	3,859328	4,017204
9	5,054772	5,248439	4,220367	4,393012
10	4,736832	4,918318	4,304884	4,480987
11	4,621511	4,798578	3,561065	3,70674
12	4,492428	4,66455	3,549641	3,694849
13	3,886873	4,035793	5,184639	5,382165
14	4,524466	4,697816	5,365032	5,56943
15	4,07332	4,229384	5,35266	5,556587
16	4,693096	4,872906	5,247713	5,447642
17	3,903053	4,052594	5,206694	5,40506
18	3,906004	4,055658	5,105721	5,304645
19	4,157218	4,316497	5,256799	5,46161
20	4,78891	4,972391	5,207133	5,410008
21	4,351415	4,518134	5,331809	5,539542
22	4,506331	4,678986	5,405683	5,616294
23	3,950091	4,101434	5,86398	6,09498
24	3,82665	3,973264	5,923355	6,156694
25	4,192934	4,353581	5,97001	6,205186
26	3,942499	4,093551	5,900431	6,132866
27	4,591544	4,767463	5,689091	5,841555
28	6,025641	6,256506	5,557392	5,706328
29	5,018336	5,210608	5,499032	5,646403
30	4,886831	5,074064	5,506784	5,654363

Average of ADBK % (b/b): 4,8339967

Average of ADBK % (b/b): 5,222336

Table 2. H₂O content of in-house method and innovation method

In-House Method		Innovation Method	
Data Replication	Content of H ₂ O % (w/w)	Data Replication	Content of H ₂ O % (w/w)
1-30	3,69	1-6	3,92
		7-12	3,93
		13-17	3,67
		18-22	3,75
		23-26	3,69
		27-30	2,61

Data Adequacy Test

After obtaining the ADBK data, it was continued by calculating the data adequacy test, aiming to find out whether the sample data taken was sufficient. Observational data was considered sufficient if $N' < N$ [2].

The data adequacy test was used to determine the number of samples taken to meet the ideal data or to proceed to the next data processing process. **Equation 5** is the formula to calculate N' .

$$N' = \left(\frac{K \sqrt{N \Sigma X^2 - (\Sigma X)^2}}{S \Sigma X} \right)^2 \quad (5)$$

Information:

N' = the number of observations that must be made

K = confidence interval in the observation ($k = 2, 1-\alpha = 95\%$)

S = degree of accuracy of observation (5%)

N = amount of data obtained

X = observational data

Data adequacy test shown in **Table 3**, that data in the study were adequate, because both of methods were shown $N' < N$, it means that data were sufficient, so that it did not require retrieval of data again.

Table 3. Results of data adequacy test

Method	N'	N	Information	Conclusion
In House	27,297	30	$N' < N$	sufficient
Inovasi	29,615	30	$N' < N$	sufficient

Information: N' = The amount of data should be

N = The amount of data obtained

Data Accuracy Test

If data were sufficient, it was continued with the data uniformity test or accuracy test. The data accuracy test was used to determine how close the sample range to the desired value. With Upper Control Line (UCL) = $X + 3\sigma$ and Lower Control Line (LCL) = $X - 3\sigma$. The mathematical equation is as follows:

$$\sigma = \sqrt{\frac{\Sigma(X - \bar{X})^2}{N - 1}} \quad (6)$$

Data were considered accurate (adjacent) if all samples were in the upper limit (UCL) and lower limit (LCL) ranges [2]. Data of accuracy test from the Upper Control Limit (UCL) and Lower Control Limit (LCL) ranges shown in **Figure 1** for in-house method and **Figure 2** for innovation method. Based on the result were shown in the **Figure 1** and **Figure 2** then the accuracy range were 2.907 – 6.761 % w/w and 3.055 – 7.390 % w/w for in-house method and innovation method respectively. The blue line is dots repetition of data. Both results showed none of them out from the accuracy range, so that the data obtained had a good level of accuracy.

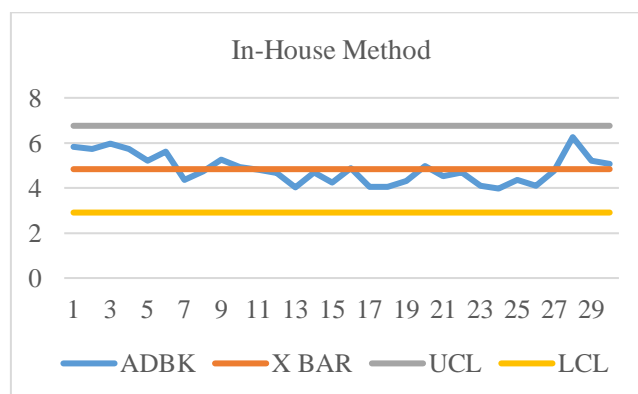


Figure 1. Results of data accuracy test using in-house method

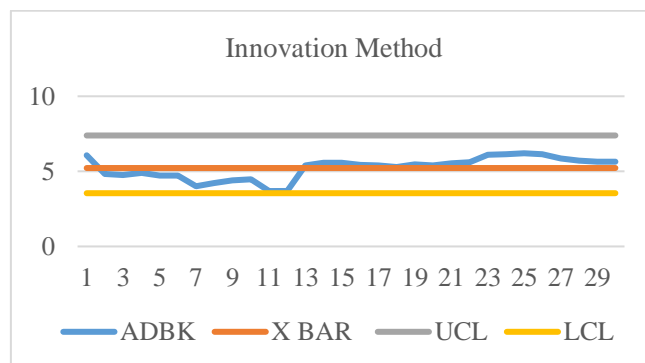


Figure 2. Results of data accuracy test using innovation method

Data Precision Test

Then proceed with the precision test to determine data precision and data accuracy, that calculated using Equation 7, while data accuracy was measured as the %CV Horwitz, see Equation 8.

$$\%RSD = \frac{\sigma}{\bar{X}} \times 100\%$$

$$\%CV \text{ Horwitz} = 2^{1-0,5 \log c} \quad (7)$$

(8)

While,

Data Analysis

Analyze data was done to calculate the $S_{combined}$ using formula at Equation 10.

$$S_{combined} = \sqrt{\frac{(N_1-1)\sigma_1^2 + (N_2-1)\sigma_2^2}{N_1 + N_2 - 2}} = 0.68 \quad (10)$$

The smaller standard deviation value, the better data that has been taken. Based on the calculations, the combined standard deviation of the two methods was 0,68. Furthermore, the T-test calculation was carried out. This experiment quiz to be accept or successful. It be proven by the T-test, if $T_{count} < T_{table}$. However if $T_{count} > T_{table}$, the experiment was not successful. To find out whether

Conclusion or Closing Remarks

The sulphur content test was used to determine the level or sulphur content in the factory SP-36 fertilizer. This test can be done through two methods, including in-house method and innovation method. The innovation method can be used as a substitute for the in-house method. The in-house

$$c = \frac{\sigma}{100} = \text{content fraction} \quad (9)$$

Precision test showed both methods were less precision because of %RSD > 2/3%CV Horwitz. Best accuracy obtained when %RSD value < 2/3%CV Horwitz [3]. This can be due to several factors, including did not use appropriate measurement tools during the in-house method, characteristic of BaCl₂ powder which coagulates when dissolved, it took time to form colloids, while liquid BaCl₂ formed colloids faster, but the detecting was not as soon as possible so that it formed a precipitate.

data was accepted or rejected (see Equation 11).

$$T_{count} = \frac{\bar{X}_1 - \bar{X}_2}{S_{combined} \left(\sqrt{\frac{1}{N_1}} + \sqrt{\frac{1}{N_2}} \right)} = -1.5559 \quad (11)$$

Data were reject if $T_{count} > T_{table}$ and if T_{count} had a negative value data were accepted, so that $T_{count} < T_{table}$ [4], based on calculation of this experiment was -1.5559, while the T_{table} value was 2.045. This data showed that the two methods were not much different or be used as a substitute for the in-house method.

method of sulphur content testing was more accurate than the innovation method, based on the calculation. The average value of sulphur content in SP-36 fertilizers based on the in-house method was 4,83%, while the average value of sulphur content in SP-36 fertilizers using the innovation method was 5,22%.

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