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

Salsa Fitrani*, Ika Nur Fitriani*

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

*Department of Chemistry, Faculty of Science and Technology, Islamic State University of Walisongo Semarang, Semarang 50185, Indonesia
Correspondence and requests for materials should be addressed to Salsa Fitrani (email: fitrani.salsa@gmail.com)
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, tripel 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 P₂O₅. The 36% of phosphate nutrients in SP-36 fertilizer almost entirely soluble in water, did not affect soil acidity because it is neutral, difficult 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 pets, diseases and drought. Superphosphate fertilizer (Ca(H₂PO₄)₂) can cause the soil 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 BaCl₂ powder in 15 mL of the acidic salt as a suppressor, while the innovation method used 20 mL of 0.2% BaCl₂ in 15 mL of the acidic salt. BaCl₂ 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 BaCl₂ 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), BaCl₂ 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 BaCl₂, mixed with distilled water and homogenized, while for innovation method was took 10 mL, 15 mL of salt acid suppressor and 20 mL of BaCl₂ 0.2%. Both of samples were analyzed UV Shimadzu UV 1800 spectrophotometer at a wavelength of 425 nm using 5 ppm of SO₄²⁻ standard for in-house method and 50 ppm of SO₄²⁻ standard for innovation method standard as blank solution. Sulphur content was calculated with following formula (Equation 1):

\[
\% S (ADBB) = \frac{\text{Mr } S}{\text{Mr } SO_4^{2-}} \times \frac{\text{Abs Sample}}{\text{Abs Standard}} \times \frac{\text{VLT} \times FP \times C \text{ standard}}{\text{weight}} \times 100\%
\]

(1)

The cup was cleaned then weighed with the lid (W₀). The SP-36 fertilizer sample of ±2,0 g (W₁). was put into a cup and was heated at 105 °C for 30 minutes, then weighed after cooling (W₂). H₂O content was calculated using the following formula:

\[
\% H_2O = \frac{W_1 - W_2}{W_1 - W_0} \times 100\%
\]

(2)

Then %S and %H₂O was used to calculate basis of dry weight (ADBK) using Equation 3.

\[
ADBK = \frac{\% S}{100\% - \% H_2O} \times 100\%
\]

(3)

SO₄²⁻(aq) + BaCl₂(aq) →↓BaSO₄(s) + 2Cl⁻(aq)

(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 H₂O 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 H₂O 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       | 6,086882                                     |                                               |
| 2                                            | 5,831651       | 5,848276                                     |                                               |

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 still 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 BaCl₂. The addition of HCl aimed to acidify the solution so that the minerals were dissolved. Meanwhile, the addition of BaCl₂ aimed to make the sulfate able to bind Ba²⁺ ions and to form a white precipitate in the form of BaSO₄[1], see Equation 4.
## Table 2. $H_2O$ content of in-house method and innovation method

| Data Replication | In-House Method Content of $H_2O$ % (w/w) | Innovation Method | Content of $H_2O$ % (w/w) |
|------------------|------------------------------------------|-------------------|--------------------------|
| 1-30             | 3.69                                     |                   |                          |
| 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’.

\[
N' = \left( \frac{K \sqrt{\frac{N \sum X^2 - (\sum X)^2}{\sum X^2}}}{S} \right)^2
\]

(5)

Information:
N’ = the number of observations that must be made
K = confidence interval in the observation (k = 2, 1-α = 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.

| 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+3α and Lower Control Line (LCL) = X-3α. The mathematical equation is as follows:

\[
\sigma = \sqrt{\frac{\sum(X - \bar{X})^2}{N - 1}}
\]

(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
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.

\[
\%RSD = \frac{\sigma}{X} \times 100\%
\]

(7)

\[
\%CV \text{\ Horwitz} = 2^{1-0.5\log c}
\]

(8)

While,

\[
S_{\text{combined}} = \sqrt{\frac{(N_1-1)\sigma_1^2+(N_2-1)\sigma_2^2}{N_1+N_2-2}} = 0.68
\]

(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 \( T_{\text{count}} < T_{\text{table}} \). However if \( T_{\text{count}} > T_{\text{table}} \), the experiment was not successful. To find out whether data was accepted or rejected (see Equation 11).

\[
T_{\text{count}} = \frac{\bar{X}_1 - \bar{X}_2}{S_{\text{combined}} \left( \frac{1}{N_1} + \frac{1}{N_2} \right)^{1/2}} = -1.5559
\]

(11)

Data were reject if \( T_{\text{count}} > T_{\text{table}} \) and if \( T_{\text{count}} \) had a negative value data were accepted, so that \( T_{\text{count}} < T_{\text{table}} \) [4], based on calculation of this experiment was -1.5559, while the \( T_{\text{table}} \) 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.

\[
c = \frac{\sigma}{100} = \text{content fraction}
\]

(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 BaCl\(_2\) powder which coagulates when dissolved, it took time to form colloids, while liquid BaCl\(_2\) formed colloids faster, but the detecting was not as soon as possible so that it formed a precipitate.

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 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%.
Acknowledgements

Thanks to Mr. Abizar Rahman Hadi as field Advisor Practical Work in Factory Laboratory II-B, Department of Energy Process an Management, PT Petrokimia Gresik who has helped the author by providing all the facilities until this research was complete.

References

[1] H. D. Foth, *Dasar-Dasar Ilmu Tanah*. Jakarta: Erlangga, 1994.

[2] F. G. Dewanto, J. J. M. R. Londok, R. A. V. Tuturoong, and W. B. Kaunang, “Pengaruh Pemupukan Anorganik Dan Organik Terhadap Produksi Tanaman Jagung Sebagai Sumber Pakan,” *Zootec*, vol. 32, no. 5, pp. 1–8, 2017, doi: 10.35792/zot.32.5.2013.982.

[3] E. S. Syarief, *Kesuburan dan Pemupukan Tanah Pertanian*. Bandung: Pustaka buana, 1986.

[4] Petrokimia, “Informasi Produk,” *Petrokimia*, 2020. [Online]. Available: https://petrokimia-gresik.com/product/pupuk-sp-36. [Accessed: 10-Feb-2020].

[5] R. Burhanudin, C. Z. Subarkah, and S. Sari, “Penerapan Model Pembelajaran Content Context Connection Researching Reasoning Reflecting (3C3R) Untuk Mengembangkan Keterampilan Generik Siswa Pada Konsep Koloid,” *JTK (Jurnal Tadris Kim.)*, vol. 3, no. 1, pp. 11–21, 2018, doi: 10.15575/jtk.v3i1.2595.

[6] Yanlinastuti and S. Fatimah, “Pengaruh Konsentrasi Pelarut untuk Menentukan Kadar Zirkonium dalam Paduan U-Zr dengan Mengguakan Metode Spektrofotometri UV-VIS,” *PIN Pengelolaan Instal. Nukl.*, vol. 1, no. 17, pp. 22–33, 2016.

[7] A. Daud, Suriati, and Nuzulyanti, “Kajian penerapan faktor yang mempengaruhi akurasi penentuan kadar air metode thermogravimetri,” *Lutjanus*, vol. 24, no. 2, pp. 11–16, 2019.

[8] A. Oktavia, Klara, Nurlina, Shofiyani, “Penurunan Kadara Ion Sulfat Dalam Air Menggunakan Komposit Kitosan/Zeolit/Pva,” *J. Kim. Khatulistiwa*, vol. 7, no. 4, pp. 66–74, 2018.

[9] C. Rahma, A. Ariska, and V. Afriasari, “Optimalisasi Pelayanan Unit BPJS RSUD Melalui Perhitungan Waktu Siklus Operator Pelayanan SEP,” *J. Optim.*, vol. 4, no. 1, pp. 11–20, 2018.

[10] Ambarwati, N. Ariyani, and M. F. Palupi, “Validasi Metode Spektrofotometri pada Uji Kadar Sediaan Injeksi Obat Hewan Enroflosasins,” *J. Sain Vet.*, vol. 31, no. 2, pp. 266–273, 2013.

[11] C. Montolalu and Y. Langi, “Pengaruh Pelatihan Dasar Komputer dan Teknologi Informasi bagi Guru-Guru dengan Uji-T Berpasangan (Paired Sample T-Test),” *d’CARTESIAN*, vol. 7, no. 1, p. 44, 2018, doi: 10.35799/dc.7.1.2018.20113.