



Analysis of Sulfate (SO₄) Concentration in Bittern as Raw Material for Magnesium Sulfate (MgSO₄)

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ABSTRACT

The investigation on traditional salt production had developed in the characterization of Bittern. Bittern is the dense residual liquor with specific gravity $\geq 1.28 \text{ gr/cm}^3$ obtained after precipitation and harvesting of NaCl salt from seawater. In this research, the measurement of sulfate in the bittern was carried out. Sulfate is one of the raw materials for MgSO₄. The determination of sulfate concentration is using a turbidimetric method according to SNI 6989 20:2009 using a spectrophotometer at a wavelength of 420 nm. In this process the Sulfate in an acidic environment reacts with barium chloride (BaCl₂) to form barium sulfate (BaSO₄) crystals. The light absorbed by the barium sulfate suspension is measured with a photometer and the sulfate content is calculated by comparing the readings with the calibration curve. The results of the analysis showed that at 31° Baume the sulfate content is 40.0 g/L, at 32° Baume the sulfate content is 42.6 g/L, at 33° Baume the sulfate content is 42.8 g/L. The sulfate concentration in the bittern showed a linear increase with increasing water concentration. The sulphate content of bittern with 31°Be levels has an average value of 40.028 g/L, at 32°Be levels the average sulphate content is 42.599 g/L and at 33°Be levels it is 42,825 g/L.

Keywords: Bittern, Sulfate, °Be

ABSTRAK

Investigasi produksi garam tradisional telah berkembang dalam karakterisasi Bittern. Bittern adalah cairan residu padat dengan berat jenis 1,28 gr/cm³ yang diperoleh setelah pengendapan dan pemanenan garam NaCl dari air laut. Pada penelitian ini dilakukan identifikasi konsentrasi sulfat pada bittern. Sulfat merupakan salah satu bahan baku MgSO₄. Perhitungan konsentrasi sulfat dilakukan dengan menggunakan metode turbidimetri menurut SNI 6989 20:2009, yakni menggunakan spektrofotometer pada panjang gelombang 420 nm. Pada proses ini Sulfat dalam suasana asam bereaksi dengan barium klorida (BaCl₂) membentuk kristal barium sulfat (BaSO₄). Cahaya yang diserap oleh suspensi barium sulfat diukur dengan fotometer dan kandungan sulfat dihitung dengan membandingkan pembacaan dengan kurva kalibrasi. Hasil analisis menunjukkan bahwa pada 31°Be kandungan sulfatnya 40,0 g/L, pada 32 °Be kandungan sulfatnya 42,6 g/L, pada 33 °Be kandungan sulfatnya 42,8 g/L. Konsentrasi sulfat dalam bittern menunjukkan peningkatan linier dengan meningkatnya konsentrasi air. Kadar sulfat pahit dengan kadar 31 °Be memiliki nilai rata-rata sebesar 40,028 g/L, pada kadar 32 °Be kadar sulfat rata-rata adalah 42,599 g/L dan pada kadar 33 °Be sebesar 42.825 g/L.

Kata kunci: Bittern, Sulfate, Kadar Be

1. Introduction

Bittern is a residual product from the production of salt, conventionally referred as old water. It has a form of a yellowish liquid, placed on the crystallization table and does not settle during the evaporation process. Bittern has a special parameter in the form of concentration

levels, which is called °Be. Generally, the °Be of seawater is 26 °Be - 29 °Be. Mustafa and Abdullah (2013) stated that Bittern is a solid residue liquid having a specific gravity of 1.28 gm/cm³. In addition, the bittern has a lot of mineral content that does not crystallize in the salt table which makes it a saturated solution

with the rich content of minerals and other minor elements (Nuzula et al., 2021). Several references state that Bittern contains various minerals such as magnesium (Mg²⁺), potassium (K⁺), sodium (Na⁺), chloride (Cl⁻) sulphate (SO₄²⁻) and other minor compounds (Pratiwi et al., 2021, Aral et al. al., 2004). Faizah, et.al., 2018, also identified that there are various compounds such as magnesium sulphate (MgSO₄), sodium chloride (NaCl), magnesium chloride (MgCl₂), potassium chloride (KCl), calcium chloride (CaCl₂).

Nowadays, bittern has begun to get a lot of attention to be identified as a cheaper source to produce minerals and reduce seawater pollution. Megawati et al. (2021) stated that the higher of °Be of the liquid being measured will make the density of the liquid is greater, which means the mineral content such as Mg, K and SO₄²⁻ will be higher. In this case, sulfate is one type of ion contained in bittern with the chemical formula SO₄²⁻ has an atomic mass of 96.06 atomic mass units. Sulphate is composed of a central Sulphur atom surrounded by four oxygen atoms in a tetrahedron arrangement, the sulphate ion is negatively charged (Erviana et al 2018). The sulphate contained in the bittern comes from sulphur. The formation of sulphur comes from volcanic activity in the form of gas originating from the active crater of Solfatara or it can also come from hot water that flows into the sea, then settles to form sediment (Indiyati, 2002).

The sulphate will be higher linear with the °Be of seawater (Nuzula et al 2021). In the industrial, sulphate is widely used as additional raw material in the manufacture of fertilizers multi nutrients. The usage of sulfuric acid as one of the components for fertilizers multi nutrients production serves to grow natural food (plankton) in fish ponds (Nadia et al. 2015).

Sulfuric acid is one of the supporting materials that is widely used in the production of phosphoric acid which is used for the manufacture of phosphate fertilizers, pharmaceuticals and is widely used in the manufacture of detergents and paper (Hakim et al 2018). In addition, the SO₄ can also be used as raw material for Magnesium Sulphate (MgSO₄) (Hapsari, 2006; Sani, 2010). This study aims to analyze the concentration of sulphate (SO₄) in bittern with different levels of °Be, there is 31 °Be, 32 °Be and 33 °Be.

2. Material and Method

This sulphate analysis was carried out based on SNI 6989 20:2009, namely the

method of turbidimetric sulphate (SO₄²⁻) testing on water and wastewater. Samples of Bitter were taken on October 9, 2021 at PT Garam located on Pamekasan with the initial °Be of bittern is 27 °Be. The materials used in this study include sulphate-based solution, magnesium chloride hexahydrate (MgCl₂·6H₂O), sodium acetate trihydrate (CH₃COONa·3H₂O), potassium nitrate (KNO₃), concentrated acetic acid (CH₃COOH 99%), barium chloride (BaCl) and Aqua Bidestilata, while the tools used in this research are Baume Meter, spectrophotometer, Erlenmeyer, beaker, volumetric flask, stirrer, volumetric pipette and analytical balance. The analysis of the Spectrophotometer taken on Advanced Laboratory of Trunojoyo Madura University with spectrophotometer model of UV-2700 240V EN, Cat. No. 27700-45, Serial No. A11674900027 S3, Made in Japan.

2.1 Increment of °Be bittern

Firstly, the main concern of this research was to increase the °Be bittern in the initial conditions, from 27 °Be into 31 °Be, 32 °Be and 33 °Be. The increasing process is done by transferring the bittern sample from the prototype into the UTM salt house. This process is presented in Figures 1 and 2.

2.2 Sulphate Level Test on Bittern

Analysis of the sulphate level test on bittern using the turbidimetric method. As per SNI 6989 20:2009, the first step is to make a working solution using a standard sulphate solution. The standard series of working



Figure 1. Salt House of University of Trunojoyo Madura (UTM)



Figure 2. Bittern Sample

solutions in the sulphate test used was 0 mL, 20 mL, 40 mL, 60 mL, 80 mL and 100 mL. The manufacture of the sulphate working solution is used to create a calibration curve, where the series of working solutions that have been made are inserted into a 250 mL Erlenmeyer, then added 20 mL of buffer solution, then stirred at a constant speed using a magnetic stirrer. During the stirring process, 0.25 grams of BaCl was added. Stirring was carried out for 1 minute from the addition of BaCl. The absorption of blanks was measured using a spectrophotometer at a wavelength of 420 nm. The purpose of making a calibration curve is to determine the equation of the regression line.

The second stage after making the calibration curve is testing the bittern sample at each different Baume scale level, by pipetting 0.1 mL of a bittern in each sample into a 10 mL volumetric flask, dissolving it with aqua bidestilata to the limit of *tera*, then transferring it to an Erlenmeyer 250 mL, and added 2 mL of the buffer solution stirred at a constant speed using a magnetic stirrer. During the stirring process, BaCl was added and stirred for 1 minute starting from the addition of BaCl. After stirring, the absorption rate was measured using a spectrophotometer with a wavelength of 420 nm. Calculation of sulphate levels based on SNI 6989 20:2009 as the following formula:

$$\text{Level of Sulphate (MgSO}_4^{2-}/\text{L)} = C \times f$$

Note: C = Sulphate content obtained from the calibration curve (mg/L); f = Dilution factor.

3. Result and Discussion

Bittern is a waste obtained from the salt production process. Bittern is formed at °Be more than 27 °Be, where one of the main components is sulphate (SO₄) (Wajima, 2015). The minerals contained in bittern is a content that no longer settles at °Be <25 °Be (Adi et al., 2006). In this research, the bittern used had a 27 °Be.

This sample was used as an initial sample and then the °Be level was increased to 31 °Be, 32 °Be and 33 °Be at Salt House of the University of Trunojoyo Madura. The results of the research showed that the duration to increase the °Be bittern to 31 °Be was 7 days, at 32 °Be took 10 days while for 33 °Be was took 15 days. The time needed to increase the °Be is various because it is strongly influenced by climatic conditions. In addition, wind speed, air humidity and temperature also affect the speed of the evaporation process (Adira and Setiawan, 2014). The characteristics of the Baume scale can be seen from the colour of the liquid, which is the yellower means the Baume scale is higher. it can be seen in Figure 3. Analysis of the sulphate content at the Baume scale of a bittern in line with SNI 6989 20:2009 using the turbidimetric method. Measurements for each concentration level were repeated five times respectively. The results of the analysis of the sulphate content in bittern with different °Be are presented in Figure 4. The results of the average sulphate content at different levels of °Be show that the highest sulphate content is in the bittern sample with the degree of Baume of 33 °Be with an average value is 42,800 g/L while the lowest sulphate content is in 31 °Be bittern samples having an average of 40.029 g/L.



a



b



c

Figure 3. Sampel bitter of (a) 31 °Be (b) 32 °Be (c) 33 °Be

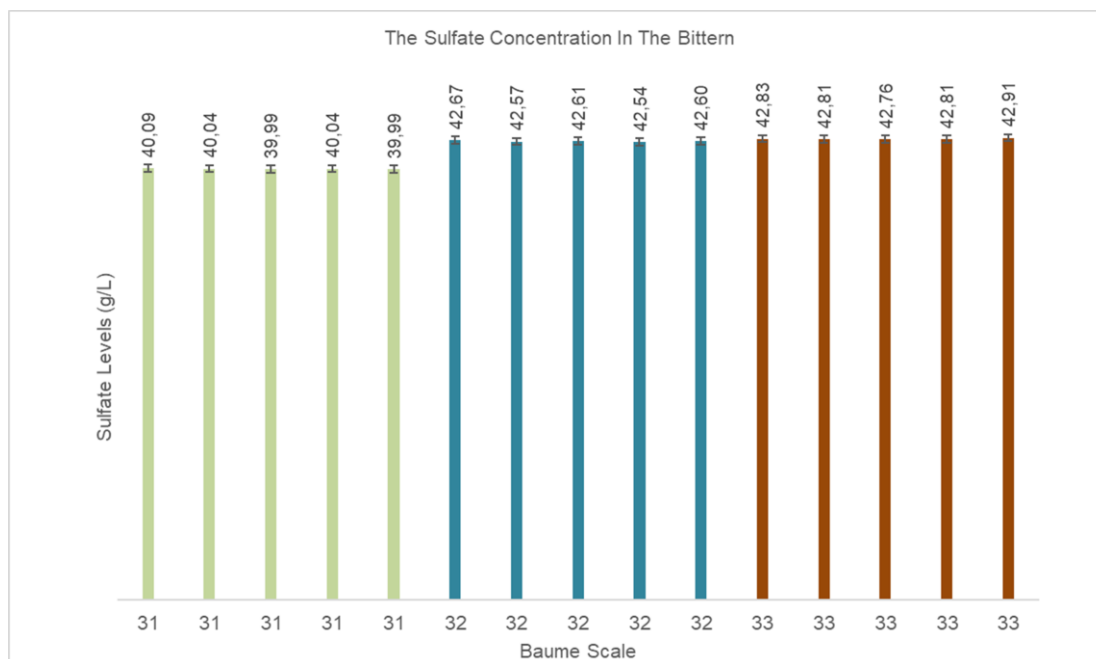


Figure 4. The Sulfate Concentration In The Bittern

The results of the analysis show that the higher concentration of bittern is linear with the higher sulphate content. This is also supported by the results of research by Abdel-Aal et al., 2017 which states that the concentration of sulphate content in bittern will increase if °Be had an increment too. Figure 4 shows that at 31°Be the sulphate content of the lowest value is 39.99g/L and the highest value is 40.09 g/L. While at 32°Be the lowest sulphate content was 42.54g/L and the highest value was 42.67g/L. Next, the bittern with 33°Be the lowest sulphate content is 42.76 and the highest value is 42.91g/L. Nuzula et.al., (2020) show a different result on the analysis of sulphate content (SO₄²⁻). The sulphate at 26°Be bittern is 41,257

g/L while the sulphate content at 29°Be measured at 44.7 g/L and 30°Be was 54.6 g/L. In contrast, the results of research by Sidik (2013) showed that the sulphate content (SO₄²⁻) in bittern 30°Be was 73.15 g/L but in Megawati et al., (2021) with the same concentration the sulphate content value produced was 60.2g./L.

This difference in sulphate content is identified due to the different sources of seawater raw materials used in the salt production process. This results in a different sulphate content in each bittern. Considering that the sulfuric content comes from organic waste produced, including livestock waste, industrial waste, agriculture and also urban

Table 1. Result of ANOVA

Table 1: Result of ANOVA

SUMMARY						
Groups	Count	Sum	Average	Variance		
Bittern 31 Be	5	200,144	40,0288	0,001835		
Bittern 32 Be	5	212,999	42,5998	0,002332		
Bittern 33 Be	5	214,128	42,8256	0,0032		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	24,13852813	2	12,06926	4915,063	3,28514E-18	3,885294
Within Groups	0,0294668	12	0,002456			
Total	24,16799493	14				

Table 2. Bittern 31 Be further test with 32 Be Bittern

	Bittern 32 Be	Bittern 33 Be
Mean	42,5998	42,8256
Variance	0,0023317	0,0032003
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	-6,78840671	
P(T<=t) one-tail	6,97317E-05	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,000139463	
t Critical two-tail	2,306004135	

areas. Hydrogen sulfide will be oxidized by photosynthetic bacteria to produce sulphate. The sulphate will be carried away by rainwater and groundwater to the mouth of the river and flows into the sea (Hadiarti, 2015).

3.1 Test Anova one-sample t-test

Analysis of variance (ANOVA) is a method to collect the statistical models and their associated hypotheses or other procedures used to analyze the differences among means. The Anova test hypothesis H_0 indicates that the data or groups are from the same population so that they have the same expected mean and variance, while H_1 indicates that the data has unequal or different variances (Marpaung 2020). The hypothetical determination of the ANOVA test is if the significance value is > 0.05 then accept H_0 and reject H_1 , but if the significance value is < 0.05 then accept H_1 and reject H_0 (Pratiwi 2021). The results of the ANOVA test for sulfate content in bittern samples with ^{31}Be , ^{32}Be and ^{33}Be showed a p-value < 0.05 as shown in Table 1.

The results of the hypothesis test accept H_1 reject H_0 , where H_0 is the ^{32}Be level bittern does not affect the sulphate content value, while H_1 is the ^{32}Be level that affects the sulphate content value. The results of the ANOVA test showed that at the 95% confidence level the significance value was $3,28514 \times 10^{-18}$, so it can be concluded that accepting H_1 rejects H_0 which indicates the ^{32}Be has an effect on sulphate levels in bittern. The results of the study are in line with the statement of Pratama et al., (2016) which states that the concentration of bittern water has a significant influence on the mineral content in bittern, where the higher the concentration level, the higher the concentration of minerals contained in bittern, one of which is sulphate.

3.2 A further test of ANOVA

A further test is carried out in case of a significant difference in the results of the

Table 3. Bittern 31 Be further test with bittern 33 Be

	Bittern 31 Be	Bittern 33 Be
Mean	40,0288	42,8256
Variance	0,0018347	0,0032003
Observations	5	5
Hypothesized Mean Difference	0	
df	7	
t Stat	-88,13464827	
P(T<=t) one-tail	3,18788E-12	
t Critical one-tail	1,894578605	
P(T<=t) two-tail	6,37575E-12	

ANOVA test to find out the significant impact of sulphate concentration. The results of ANOVA shown in Table 2. Bittern 31 Be further test with 32 Be below. The P-value (2.818×10^{-13}) $< (0.05)$, then H_0 is rejected and H_1 is accepted, which means that there is a difference in the average sulfate content at the concentration level of bittern 31 Be water with bittern 32 Be concentration levels.

Next, the further analysis is in the Bittern 31 Be and 33 Be shown in Table 3. Bittern 31 Be further test with bittern 33 Be below. The P-value (6.375×10^{-12}) $< (0.05)$, then H_0 is rejected and H_1 is accepted, which means that there is a difference in the average sulfate content at the concentration level of bittern 31 Be water and bittern 33 Be.

The last is analysis from Bittern 32 Be and 33 Be as per Table 4. Bittern 32 Be further test with bittern 33 Be below. The P-value (6.973×10^{-05}) $< (0.05)$, then H_0 is rejected and H_1 is accepted, which means that there is a difference in the average sulfate content of the 32 Be bittern water concentration with the 33 Be bittern concentration level.

4. Conclusion

This study concludes that the sulphate content of bittern with ^{31}Be levels has an average value of 40.028 g/L, at ^{32}Be levels

Table 4. Bittern 32 Be further test with bittern 33 Be

	Bittern 32 Be	Bittern 33 Be
Mean	42,5998	42,8256
Variance	0,0023317	0,0032003
Observations	5	5
Hypothesized Mean Difference	0	
df	8	
t Stat	-6,78840671	
P(T<=t) one-tail	6,97317E-05	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,000139463	
t Critical two-tail	2,306004135	

the average sulphate content is 42.599 g/L and at 33°Be levels it is 42,825 g/L. The results of the ANOVA test obtained a p-value that the higher the °Be, the higher the sulphate content too.

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References

- Abdel-Aal, H., Khaled, Z. Maha, A. 2017. Seawater Bittern a Precursor for Magnesium Chloride Separation: Discussion and Assessment of Case Studies. *International Journal of Waste Resources*. Vol. 7 No. 1, p. 1-6.
- Adi, T.R., Agus, S. Budi S. Bangun M. S. Husni A. Tri H. P. Sudarto. Eddy, S. Agustin. R. 2006. *Buku Panduan Pengembangan Usaha Terpadu Garam dan Artemia*. Pusat Riset Wilayah Laut dan Sumberdaya Nonhayati Badan Riset Kelautan dan Perikanan Departemen Kelautan dan Perikanan. Jakarta.
- Adiraga, Y dan Achma, H. S. 2014. Analisis Dampak Perubahan Curah Hujan, Luas Tambak Garam dan Jumlah Petani Garam terhadap Produksi Usaha Garam Rakyat di Kecamatan Juwana Kabupaten Pati Periode 2003-2012. *Diponegoro Journal of Economics* Vol.33 No. 1, p. 1-13.
- Aral, H., Hill, B.D. and Sparrow, G.J. 2004. Production of Salts from Brine and Bittern, Proof of Concept, Appendix 2. *CSIRO Minerals*, report DMR-2378B.
- Faizah, N., Indriyani, L. Juwari, J. & Handogo, R. (2018). Pra Desain Pabrik Pupuk MgSO₄.7H₂O dari Bittern. *Jurnal Teknik ITS* Vol. 7 No.1 p.141–144.
- Hadiarti, D. 2015. Penentuan Kadar Sulfat Air Mineral Kemasan Gelas yang Beredar di Pontianak dengan Metode SM. Ed. 21 Th. 2005. *Prosiding SEMIRATA 2015 bidang MIPA BKS-PTN Barat*. Pontianak. 57-63.
- Hapsari & Nur. 2012. Proses Pemisahan Ion Natrium (Na) Dan Magnesium Dalam Bittern (Buangan) *Industri Garam Jurnal Teknik Kimia* Vol. 3 No. 1, p. 192–198.
- Indiyati, E. P. 2013. Aplikasi Isotop Sulfur-34 dan Oksigen-18 dalam Sulfat untuk Studi Panas Bumi dan Air Tanah. *Jurnal Ilmiah Aplikasi Isotop dan Radiasi* Vol. 6 No. 1, p. 65-92.
- Megawati, E., Bardi, S. & Setyabudi, I. 2021. Potential Combination of Bittern Water with Vitamin B Complex for Mineral Deficiency Therapy in Cattle: A Literature Study. *Jurnal Medik Veteriner* Vol. 4 No. 1, p. 137-154
- Kh Mustafa, A. M & Abdullah, W. R. 2013. Preparation Of High Puritty Oxide From Sea Bitten Residual Form NaCl Production On Al - Basrah Saltern, South Iraq Preparation of High Purity Magnesium Oxide from Sea Bittern Residual from Nacl. In *Iraqi Bulletin of Geology and Mining* Vol. 9, Issue 3.
- Nuzula, N. I., Pratiwi, W. S. W. Indriyawati, N. & Efendy, M. 2020. ANALISA KOMPOSISI KIMIA PADA BITTERN. *Seminar Nasional Kahuripan*, 173–176.
- Nuzula, N. I., Pratiwi, W. S. W. Indriyawati, N. & Efendy, M. 2021. Studi Penggunaan Senyawa CaCl₂ Dalam Menurunkan Kadar Sulfat Pada Limbah Produksi Garam. *Jurnal Kimia Riset* Vol. 6 No. 1, p. 20-25.
- Pratiwi, W. S. W., Nuzula, N. I. Suci, D. S. Kartika, A. G. D. & Effendy, M. 2021. Produksi MgCl₂ dari Bittern melalui Optimalisasi Pemisahan Ion Sulfat Menggunakan Reagen Kalsium Klorida Dihidrat. *Journal of Marine Research* Vol. 10 No. 2 , p. 243-251
- Sani. 2010. Proses Pembuatan Magnesium Sulfat dari Bittern dan Asam Sulfat. (Skripsi). UPN, Jawa Timur. 78 pp.
- Sidik, R. F. 2013. Variasi Produk Pupuk Majemuk Dari Limbah Garam (Bittern) Dengan Pengatur Basa Berbeda. *Jurnal Kelautan* Vol. 6 No. 2, p. 1907-
- Wajima, T. (2015). Synthesis of Hydrotalcite from Bittern, and Its Removal Abilities of Phosphate and Nitrate. *International Journal of Chemical Engineering and Applications* Vol. 6 No. 4, p. 228-231