

FERTILIZER ANALYSIS

In this group, analyzes are carried out at regular intervals for 24 hours in order to control fertilizer production in intermediate stages and analyzes in daily mixture for quality control purposes.

A. DETERMINATION OF HUMIDITY IN THE FERTILIZER:

A.1. Oven Method: It is based on the principle of drying the weighed sample at 105 °C and determining the amount of moisture from the weighing difference.

Required Material:

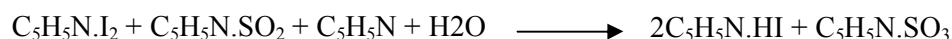
- Health, set to 105 °C.
- container
- Precision, analytical balance
- Desiccator

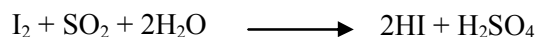
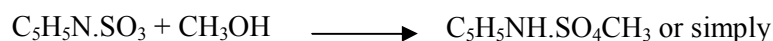
Preparation: (Vezin) container is kept in the oven for at least two hours and brought to constant weight. It is cooled in desiccator. The refrigerated counter is weighed precisely and the weight is recorded (G_1). 4-5gr. the fertilizer sample is put. Re-weigh the container with the fertilizer (G_2). (Vezin) container, the lid is opened half-open. 105 °C for 2.5 hours. At the end of the period, the tin container removed from the oven is cooled and weighed in the desiccator (G_3).

Result:

$$\% \text{H}_2\text{O} = \frac{G_2 - G_3}{G_2 - G_1} \times 100$$

A.2. Karl-Fischer Method: It is based on the principle that the fertilizer sample is dissolved in an inert liquid such as methanol or ethyleneglycolmonomethyl ether and titrated with the karlfischer reagent in a system isolated from air. Generally, 1ml RKF is equivalent to approximately 3.5 gr water. The color of the solution during titration remains in the canary yellow in untreated fertilizer. When all water is retained (turning point), the color turns brown due to unreacted iodine. Thus, the reagent acts as its indicator. Electrometric method is recommended for water determination in quantities less than 0.5 mg. In our laboratory this work is done amperometrically.





Required Material:

-Fischer reagent: KFI and KFII solutions are mixed in an equal volume of fume hood and kept in a brown sealed bottle for at least 24 hours. This reagent is mixed with iodine, pyridine, sulfur dioxide and methanol.

1 ml of RKF corresponds to about 3 mg of H₂O.

-Methanol (or ethylene glycol monomethyl ether): The amount of water should be less than 0.05%.

-Methanol standard water solution: 5 ml distilled water dissolved in 100 ml methanol. 5ml of this is taken up again in 100 ml of methanol. 5ml-12.5 mg of this solution corresponds to H₂O.

-Silica gel

-Amperometric Karl Fischer device (see figure 6)

- 5ml pipettes

-Safety pipette filler

Preparation: A sample of 5 g of fertilizer is taken up in a dry 50 ml flask and approximately 30 ml of methanol is added. Shake for 1 hour on the shaker. It is then finished with 50 ml of methanol and allowed to settle for a while to settle the insoluble part.

a. Preparation of the device: 40-50ml of dry and clean titration cell is taken up. It is titrated with RKF to the turning point by mixing with magnetic stirrer. The turning point is when the addition of the RKF by 1 is able to hold the yield intensity higher than 5 A for 20 seconds.

b. Determination of water value of RKF: After preparation of the instrument as described above, 5 ml of methanol is taken into the cell and titrated with RKF. At least three times, if necessary further processing is repeated and the consumption is averaged (S_1). Then, 5 ml of methanol standard water solution is put into the cell and titrated with RKF, which is carried out at least three times (S_2).

c. Study the sample: 5 ml (500 mg) of the sample is taken and transferred to titration cell, titrated with RKF. This is done at least three times. Coverages are averaged (S_3).

$$\text{Result: 1 mL} \longrightarrow \text{RKF} \quad \frac{12,5}{S_2 - S_1} = t \text{ mg H}_2\text{O is equal.}$$

$$\% \text{ H}_2\text{O} = \frac{(S_3 - S_1).t.100}{\text{amount in sample}(500\text{mg})}$$

Notes:

1. The RKF should be checked once a month and the consumption of RKF for 5 ml methanol before each analysis.
2. Platinum electrodes should be washed occasionally with dilute HF to prevent the detection of turning point in long-term work. (or with HCl)
3. Dried water may be present on the walls of dried containers at 1100C. This water can be removed by agitating the container with methanol.
4. At the end of each analysis, the excess solution accumulated in the titration cell must be transferred to the waste bottle by vacuum. However, not all of the solution is removed. The pipette should remain aligned with the tip of the pipette tip.
5. The silicagel on the device should be changed frequently and air tightness should be ensured at the connection points.
6. The device must be protected from moisture.

B. DETERMINATION OF NITROGEN PERCENTAGE

B.1. Formal Method: It is based on the principle of neutralization of formaldehyde by ammonium ion and titration of HNO₃ with NaOH adjusted to ammonium nitrate.



Required Material:

- 1/4 HCl
- 10 N KOH
- 1 N H₂SO₄
- 0.1 N NaOH
- 1 N NaOH
- 15% formaldehyde solution: 430 ml of 35% formaldehyde (37% of 405 ml) is taken up to 1 liter of pure water and neutralized against phenolphthalein.
- methylorange indicator solution
- phenolphthalein

Preparation: 5g of fertilizer is weighed precisely and placed in a 250 ml container and moistened slightly. 15 ml of HCl is added. When the dissolution is complete, complete with distilled water to 250 ml. It is homogenized by mixing well. Pipette 50 ml of this solution into a wide-mouthed flask. Add 2-3 drops of methylorange, neutralize with 10 N NaOH, 1N H₂SO₄ and 0.1 N NaOH. 15ml formaldehyde solution is added after complete neutralization is complete. One drop of phenolphthalein is added dropwise and titrated with 1 N NaOH.

Result:

$$\% N = 2.8 \times S \quad (S = \text{NaOH consumption})$$

B.2. Dewarda Method: It is based on the principle of reducing the nitrate to ammonia by hydrogen released by the effect of NaOH on the dewarda alloy and keeping the ammonia in distilled H_2SO_4 and back titration of the excess acid with the adjusted NaOH.

Required Material:

- 1 N NaOH

- 0.1 N H_2SO_4

- 1 N H_2SO_4

- 10 N NaOH

- $\frac{1}{4}$ HCl

-methylred-methylene blue indicator (Tashiro indicator): 0.1 g methyl red 100 ml dissolved in 96% alcohol. If insoluble parts remain, they are filtered. (A)

1g of methylene blue is dissolved in 100 ml of water. 4ml is taken and dissolved in 96ml alcohol. (B)

A and B solutions are mixed in equal volume. This indicator has a pH of up to 4 colors violet, pH = 5.5-4 is dirty gray, pH > 5.5 is green. Gray as a turning point. Life is 1 month.

- Dewarda alloy consists of 50% copper by weight, 45% aluminum and 5% zinc.

- Distillation device

- Phosphoric acid: 25 ml of acid is completed in 1 liter with distilled water.

Preparation: 10g fertilizer sample is placed in 250 ml balloon. 30 ml $\frac{1}{4}$ HCl is placed on top of the solution. Then complete with distilled water to 250 ml. 10 ml is taken from the distillation flask. Add 10 ml of phosphoric acid and 250 ml of water to remove the harmful effect of calcium. 3-4 boiling stones are discarded. 15 ml of 1 N H_2SO_4 and 50 ml of distilled water and a few drops of Tashiro indicator are placed in the collection container.

Distillation balloon 6 g of Dewarda alloy and a 30 ml 10 N NaOH with a bladder ball is closed very quickly. Shake it for a while and wait for H_2 for 15 minutes without heating. Then wait for 20 minutes from the bottom very slowly heated. Distillation is continued by increasing the temperature gradually. After 200 ml distillation is achieved, the distillation is terminated. Wash water is collected in the collecting bottle by washing with back coolant. Distillate is titrated with 1 N NaOH up to dirty gray. Consumption is recorded. Distilled water should also be made with a witness.

Result:

$$\% N = 1.4x (S_0 - S_N - S_N)$$

S_0 : used 1 N NaOH Consumption in blank experiment.

N_0 : NaOH normality

S : Consumption for sample

N : normality of NaOH

C. DETERMINATION OF CALCIUM NITRATE (= CaO dissolved in ethanol):

It is based on the principle of calcium nitrate dissolved in anhydrous ethanol and titration of calcium ions with regulated EDTA.

Required Material:

- 99.9% ethanol (= alcoholic alcohol)
- 50% triethanolamine solution
- NET indicator (see chapter V)
- Buffer K 10 (see section V)
- 0.1 N EDTA solution (see section V)
- Shaker
- White band filter paper (pleated, two pieces)

Preparation: Weigh 5 g of the fertilizer and place in a pre-dried 250 ml flask. Put about 200 ml of alcohol on the lid and close the lid and let it melt for 1.5-2 hours in the shaker. Mix well and filter through a double-layered braided tape. A 100 ml pipette is taken from the filtrate and transferred to the flask. 3 ml of triethanolamine solution, 10 ml of buffer K10, five six drop indicators are placed. Water is diluted. With 0.1 M EDTA, the violet color is titrated until it turns to sky blue.

Result:

$$\%CaO = S \times 0.28 \quad (S = 0.1 \text{ M EDTA Consumption})$$

D. DETERMINATION OF SULPHATE:

D.1. Turbidity Method: Photometric measurement of the turbidity of the sulfate ions in the solution by $BaCl_2$.

Required Material:

- Calibrated BaCl₂ crystal: The remaining portion in the range of 0.5 mm to 1.25 mm sieve is used. These sieves can be taken between 800□-315□.

Correction: When the rinsing process is completed, the abscess is completed with 250 ml.

- HCl concentrate

- 40g / l NH₄NO₃ solution

- Standard H₂SO₄ solution: prepared from 0.1 N H₂SO₄ (titrisol). This includes 1ml = 4,804mg SO₄

- Chronometer

- Spectrophotometer, 470 nm Wavelength and 1cm cuvette

Preparation: A quantity of the sample (5 g - 250 ml) is taken from the sample prepared for the determination of nitrogen percentage (section III-B) and filtered through common filter paper. This is taken from the filtrate into a beaker of 10, 15 or 20 ml in accordance with the sulfate concentration. Half of the difference from 50 ml (40, 35, 30 ml) is added in half of 40 g / L NH₄NO₃ solution and the other half in distilled water. The total volume (20,17,5, 15 ml of water and NH₄ NO₃) is 50 ml. In another beaker, 25 ml of distilled water and 25 ml of 40 g / L NH₄NO₃ are added. Add a scale of BaCl₂ and mix by hand for 1 minute, allow to rest for 15-20 minutes. The absorbance of the 470 nm wavelength spectrophotometer is measured to read the corresponding mg SO₄⁻² in the graph.

Preparation of the standard sulphate graph: to 1 liter volumetric flasks, 0-5-10-15-20 ml of 0.1 N H₂SO₄ are taken and completed with distilled water. These solutions contain 0-24, 02-48, 04-72, 06-96, 08-120, 10 mg sulfate. 25 ml each of these solutions in a pipette with a precision pipette. Threads. The sulphate amounts in each are 0-0, 6-1, 2-1, 8-2, 4-3mg.

Each well is put 25 ml of 40 ml / L NH₄NO₃ solution by pipette. One scale (approximately 250 mg) of calibrated BaCl₂ is added. The beakers are kept from the outside and rotated by hand and the BaCl₂ is melted. (Glass baguette or similar mixer should be used.) Mixing should be done for 1 minute each. Leave for 15-20 minutes. This time should never exceed 25 minutes. Absorbents of BaSO₄ impellents formed are read at 470 nm wavelength. A graph is drawn between absorbable read and mg SO₄⁻²

Result:

$$\% \text{SO}_4^{-2} = \frac{N \times V_1 \times 100}{V_2 \times E \times 1000}$$

M: chart value (mg)

V₁: first solution volume prepared with sample (250 ml)

V₂: taken volume for measurement (10, 15, 20 ml)

E: sample quantity (gr)

D.2. Determination of Sulfate by Simple Method: This method is based on the principle of comparing the turbidity of the sulphate with BaCl_2 to the standard sulphate solution in order to give the least information about the amount of sulphate in the ammonium nitrate sample taken during production.

Material:

- BaCl_2 solution: 20 g of BaCl_2 crystals are dissolved in 20 ml of HCl and filled with water.

-Standard sulphate solution: 860 g of ammonium nitrate, which does not contain sulphate, is dissolved with 54 ml of 1 N H_2SO_4 and completed with distilled water to liter. (The composition of this solution corresponds to the solution from the V202 tank.)

Preparation: The sample taken from the V200 tank is diluted 1/1 with water. 10 ml of BaCl_2 9 drops are placed in a test tube. Depending on the amount of sulphate present, a turbidity occurs. Similarly, 10 ml of BaCl_2 is placed in a second test tube and added dropwise from the standard sulfate solution until a turbidity is equivalent to that of the first tube.

Result:

$\text{SO}_4^{2-} = 0.1\%$, if 3 drops of standard solution

$\text{SO}_4^{2-} = 0.2\%$, if 6 drops of standard solution

$\text{SO}_4^{2-} = 0\%$, if 9 drops of standard solution is present

$\text{SO}_4^{2-} = 0.4\%$, if 12 drops of standard solution

If the solution to be analyzed gives too much turbidity, the number of drops is reduced. This time 10 ml of BaCl_2 and 3 drops of sample are put into the tube. To the second tube 10 ml of BaCl_2 and the standard solution are added dropwise until uniform turbidity is obtained.

Result:

$\text{SO}_4^{2-} = 0.3\%$ if 3 drops of standard solution

$\text{SO}_4^{2-} = 0.6\%$ if the standard solution is 6 drops

$\text{SO}_4^{2-} = 0.9\%$ if 9 drops of standard solution

$\text{SO}_4^{2-} = 1.2\%$ if 12 drops of standard solution

Note:

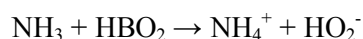
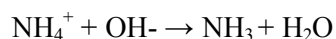
For both analyzes, the test tubes, cuvette and glass materials should be washed immediately with dilute HCl at the end of the experiment. Otherwise, BaSO₄ precipitates adhere to the walls and cause erroneous results in subsequent analyzes.

ANALYSIS OF NITROGEN FERTILIZERS - KJELDAHL METHOD

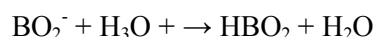
Nitrogen may be present as organic or inorganic compounds in their fertilizers. However, the determination of the total amount of nitrogen in fertilizers is requested. Quantitative determination of various compounds of nitrogen is required for specific purposes.

The Kjeldahl method can only be applied to samples containing organic nitrogen and ammonia. Nitrate nitrogen cannot be determined by this method. The method has widespread use. It does not require any special analysis and tests of large amounts of samples can be easily carried out by this method.

In this method, the nitrogen in the sample is converted to ammonium sulfate with hot concentrated sulfuric acid. If only sulfuric acid is used, the reaction is slow. Materials such as potassium sulfate, mercury-2-oxide and selenium are added to the medium to increase the temperature and increase the reaction rate. Once the cleavage is complete, ammonia is freed by adding sodium hydroxide to the medium and held with boric acid solution:



The resulting borate anion is titrated with hydrochloric acid solution and bromokrezol green or bromophenol blue indicator:



PRELIMINARY PREPARATIONS

Before the experiment, the students will perform the experiment;

They must come to the experiment with a thorough understanding of the information in the test sheet. They can also benefit from resources.

Before the test, they should check to see if there is a complete and sufficient quantity of materials and reagents to be used in the laboratory and if there is any deficiency they should inform the relevant laboratory staff.

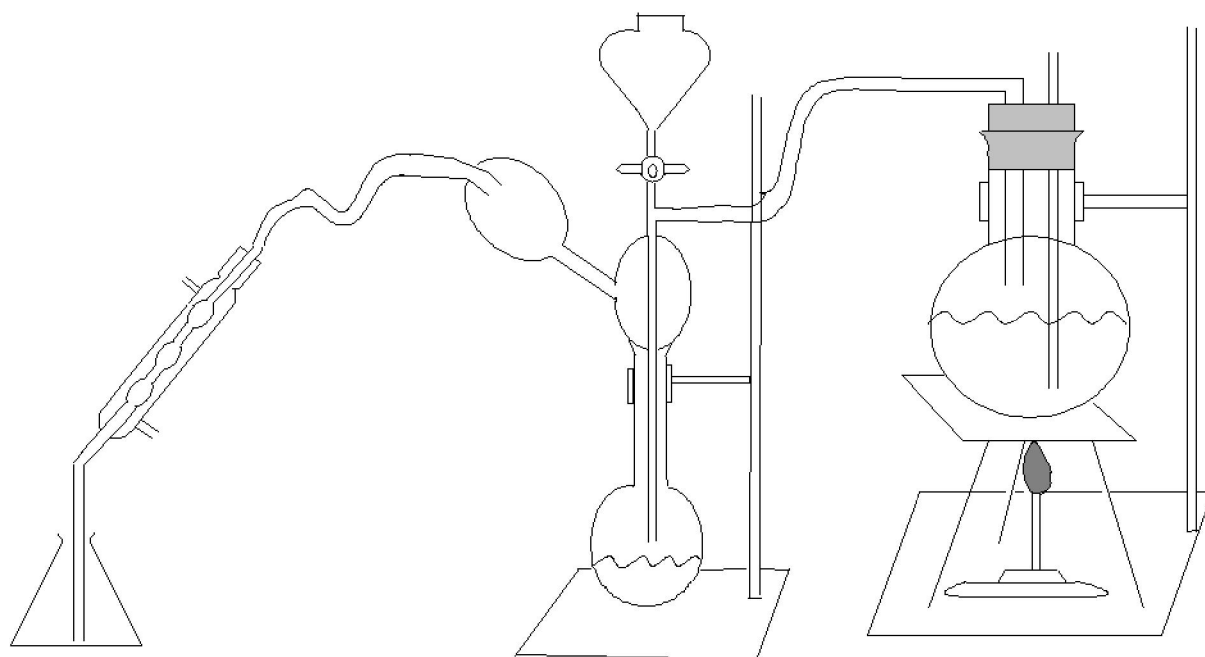
They must know how to remove the experimental connection they will use at the end of the experiment before they come to the experiment.

EXPERIMENTAL METHOD

a) Materials and Reagents Used:

1. Balloon
2. Flask
3. Refrigerant
4. Kjeldahl Balloon
5. Flask
6. burette
7. Phenolphthalein indicator
8. NaOH
9. Bromokrezol green or bromophenol blue indicator
10. 4% boric acid solution
11. 0.1 N hydrochloric acid solution

b) Experiment Assembly:



c) Experiment Preparation:

1. Weigh 0.1-0.2 g of the fertilizer sample into the Kjeldahl flask. Add 20 ml of distilled water and 3 drops of phenolphthalein indicator solution.
2. The balloon is placed in the system as shown in the figure and steam is sent to the system. A large amount of steam is passed through the system to allow air to drain.
3. 50 ml of 4% boric acid solution and 1-2 drops of bromokrezol green or bromophenol blue indicator is placed in the flask. During the installation, the end of the cooler is close to the bottom of the flask.
4. Open the tap of the drip funnel and allow 20% sodium hydroxide in the drop to flow. When the color of the solution turns pink, neutralization is complete. At this time the funnel is closed.
5. Steam is sent to the system and the released ammonia is dragged into the cooler. This process is continued until the gas is exhausted from the solution in the vessel. After the gas outlet is completed, steam is continued for 5 minutes to prevent ammonia remaining in the system.
6. The flask system removed and adjusted the amount of HCl spent by titrating the boric acid with the adjusted 0.1 N hydrochloric acid solution. (V_1).
7. 50 ml of 4% boric acid solution and 1-2 drops of the previously used indicator are placed to flask and titrated with 0.1 N HCl. The amount of acid spent is ml. (V_2).

RESULTS AND CALCULATIONS:

a) Results:

V_1 : At the end of the experiment, the consumption of the solution of boric acid in the titration with 0.1 N hydrochloric acid (ml).

V_2 : Consumption in the titration with 0.1 N hydrochloric acid by boric acid (ml).

b) Calculations:

At the end of the experiment with the fertilizer sample containing only organic nitrogen and ammonia, the percentage of nitrogen is calculated using the following data:

$$\% \text{ Nitrogen (m / m)} = (V_1 - V_2) \times N_{\text{HCl}} \times 1.4 / (\text{gr sample quantity})$$

RESOURCES: