28. Determination of nitrogen in fertilizers by the Kjeldahl method

Nitrogen belongs to the most important fertilizing elements for plants, together with potassium and phosphorus. Its content in artificial fertilizers is then important in analysis. The fertilizers which contain nitrogen belong, among others, calcium nitrate (sold as a mixture of $Ca(OH)NO_3$ and NH_4NO_3 – *circa* 15.5% N), saltpeter (KNO_3, *ca*. 13% N) and nitro-chalk (NH_4NO_3 and $CaCO_3$ or $MgCO_3$ – *ca*. 20.5%). Note that in these substances nitrogen exists at the oxidation degree -3 or +5, or both.

The content of nitrogen can be determined acidimetrically after reduction by the Devarda's alloy (50% Cu, 45% Al, 5% Zn), which reduces nitrogen(V) to ammonia. Ammonia is then distilled in NaOH environment into a known amount of hydrochloric or sulphuric(VI) acid of known titer. The acid remaining after reaction with ammonia is after titrated using a solution of NaOH of known titer.

The above procedure is based on volatility of ammonia which is weak base. An excess of strong base added to ammonia salts and heating causes that ammonia is volatilizing according to the reaction:

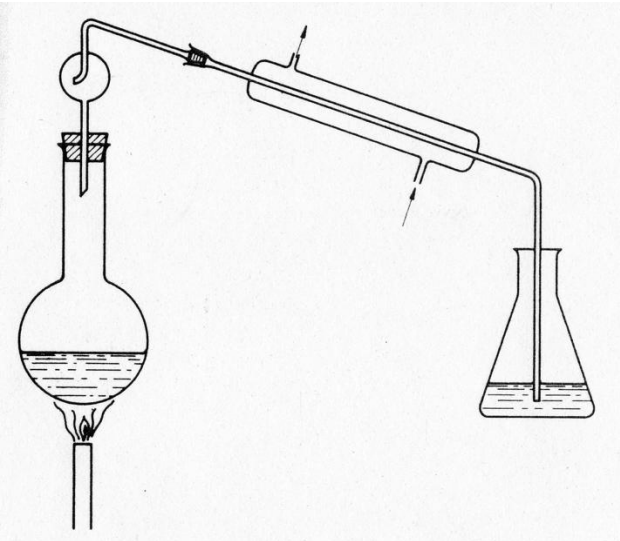
$NH_4Cl + NaOH \rightarrow NaCl + NH_3\uparrow + H_2O$

The evaporating ammonia is distilled to a distillation receiver containing an excess of HCl solution with known concentration and combines with the acid:

$NH_3 + HCl \rightarrow NH_4Cl$

The excess of non-reacted is titrated using NaOH titrant. The difference between number of moles of HCl in the initial solution and that of NaOH used in titration after absorption of ammonia corresponds to the number of ammonia in the sample.

Fertilizers can contain ammonia nitrogen (oxidation degree -3) and nitrate nitrogen (degree +3 and, mainly, +5). Thus, Kjeldahl analysis should be done twice: for the ammonia nitrogen directly and for the total nitrogen (a sum of ammonia and nitrate nitrogen) – after reduction using the Devarda's alloy.



The distillation set used in this analysis

Chemicals:

- 0.1 M HCl (prepared by the technicians or by students from fixanal).
- 0.1 M NaOH (prepared by the technicians or by students from fixanal).
- 0.1% methyl red in 60% ethanol.
- 20% NaOH solution.
- Devarda's alloy

Equipment:

- Distillation set: round flask 250 mL, catch-drop, condenser, receiver – conical flask 250 mL, two laboratory stands.
- Pieces of broken china.
- Goggles or face shield.

Determination of ammonia nitrogen

Procedure

1. Weigh, using an analytical balance, ca. 3 g of the fertilizer and transfer it to the beaker quantitatively. Dissolve it in ca. 100 mL of distilled water.
2. Filter the solution to the 200 mL volume flask. Complete the solution volume adding distilled water to the mark.
3. Measure 20 mL of the solution to round flask 250 mL in volume.
4. Measure exactly 50 mL of 0.1 M HCl to the receiver (conical flask 250 mL).
5. Add few pieces of broken china to the round flask, pour into it ca. 50 mL of 20% solution of NaOH. Immediately close the flask by the catch drop connected to condenser and receiver. The end of the condenser should touch the surface of acid in the receiver or it should be immersed in acid.
6. Heat the solution in round flask until boiling. Boiling should be moderate. When the volume of liquid will be reduced to 1/3 of the initial one, check pH with the universal paper. Neutral pH means than there is no ammonia in the distillate.
7. Cool down the content of the receiver. Add to it few drops of methyl orange indicator and titrate the remaining HCl by 0.1 M NaOH. The color should change from yellow to red..
8. Repeat points 3-7 two times minimum.

Determination of total nitrogen

Procedure

1. Measure 20 mL of the solution from points 1-2 of the former instruction to round flask 250 mL in volume.
2. Measure exactly 50 mL of 0.1 M HCl to the receiver (conical flask 250 mL).
3. Add few pieces of broken china to the round flask, pour into it ca. 50 mL of 20% solution of NaOH. Immediately close the flask by the catch drop connected to condenser and receiver. The end of the condenser should touch the surface of acid in the receiver or it should be immersed in acid.
4. Pull the closing with catch drop, pour to the round flask ca. 1 g of Devarda's alloy and close the flask immediately. Leave the set without heating for few minutes.
5. Continue according to points 5-7 of the previous procedure.

REPORT

Note all results obtained.
Calculate the mean number of moles of ammonia (in each analysis).
Calculate the mass of nitrogen and percent content of this element in the sample (total and ammonia form).
From the difference, calculate the percent of nitrate form of nitrogen in the sample.

Sources:
Internet: Wikipedia and http://www.zcha.us.edu.pl/
textbooks