

A Study on the Determination of Total Nitrogen in Soils by Automatic Kjeldahl Nitrogen Analyzer

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Abstract

In order to enhance the accuracy of total nitrogen detection in soils, this paper optimizes the pretreatment process of the automatic Kjeldahl nitrogen analyzer method for determining total nitrogen by adjusting conditions such as digestion temperature, digestion time, distillation, and reagent selection. The optimal digestion temperature, digestion time, and distillation conditions are determined. Using this optimal method for soil total nitrogen detection significantly improves the accuracy and precision of the results.

Keywords

Soil; Total Nitrogen; Pretreatment; Digestion; Distillation.

1. Introduction

Total nitrogen in soils is a crucial indicator for evaluating soil fertility and an essential basis for scientific fertilization. Currently, the determination of total nitrogen in soils generally follows the standard "NY/T 1121.24—2012 Soil Testing Part 24: Determination of Total Nitrogen in Soils by Automatic Kjeldahl Nitrogen Analyzer." This standard provides only general guidance on the operation of this method, without detailed discussion of key details and influencing factors. This paper specifically verifies and discusses key steps such as soil particle size, sample weight, accelerator selection, and the digestion process. It identifies factors affecting accuracy in various detection stages and studies appropriate quality control measures to develop a simpler, faster, and more accurate method for total nitrogen determination.

2. Principle of the Method

After oxidizing nitrite nitrogen in the sample to nitrate nitrogen with potassium permanganate, all nitrate nitrogen is reduced using ferrous powder. With the participation of an accelerator, concentrated sulfuric acid is used for digestion. After high-temperature decomposition, various nitrogen-containing compounds are converted into ammonium nitrogen. After alkalization, the ammonia distilled is absorbed by a boric acid solution and titrated with a standard sulfuric acid (or hydrochloric acid) solution to determine the total nitrogen content in soils.

3. Brief Introduction to the Experimental Process

3.1. Digestion Excluding Nitrate and Nitrite Nitrogen

Weigh approximately 1 g (accurate to 0.0001 g, containing about 1 mg of nitrogen) of air-dried soil sample passing through a 0.25 mm sieve. Place the sample in the bottom of a dry digestion tube (avoid adhering the sample to the tube wall), moisten the sample with a small amount of deionized water (about 0.5–1 mL), and add 2 g of accelerator and 5 mL of concentrated sulfuric acid. Gently shake to mix, add a reflux device or place a bent-neck glass funnel at the tube opening, and place in a digestion furnace for low-temperature heating. When the reaction in the tube becomes mild (after about 10–15 minutes), raise the furnace temperature to 360–380°C (the furnace temperature should be measured with a thermometer placed inside the digestion furnace). Maintain this temperature until the sulfuric acid vapor condenses in the upper third of the neck. Continue digestion until the digestion solution and soil particles turn grayish-white with a slight greenish hue, then continue digestion for another 1 hour. After digestion, cool the sample and refer to the automatic Kjeldahl nitrogen analyzer instruction manual to place the digestion tube in the analyzer. Set the parameters to add 10–30 mL of water, 25 mL of sodium hydroxide solution, and 20–30 mL of boric acid absorption solution, and perform distillation followed by titration with a standard sulfuric acid (or hydrochloric acid) solution.

3.2. Digestion Including Nitrate and Nitrite Nitrogen

Weigh approximately 1 g (accurate to 0.0001 g, containing about 1 mg of nitrogen) of air-dried soil sample passing through a 0.25 mm sieve. Place the sample in the bottom of a dry digestion tube (avoid adhering the sample to the tube wall), add 1 mL of potassium permanganate solution, shake the digestion tube, slowly add 2 mL of sulfuric acid solution, and continuously rotate the digestion tube. Then, let it stand for 5 minutes and add 1 drop of octanol. Use a long-necked funnel to add 0.5 g (± 0.01 g) of ferrous powder to the bottom of the digestion tube. Place a reflux device or a bent-neck glass funnel at the tube opening, rotate the digestion tube to allow the iron powder to contact the acid, and after the vigorous reaction stops (after about 5 minutes), place the digestion tube on the digestion furnace and heat slowly for 45 minutes (the soil solution in the bottle should maintain a gentle boil to avoid excessive water loss). After heating, allow the digestion tube to cool, then use a long-necked funnel to add 2 g of accelerator and 5 mL of concentrated sulfuric acid, and shake well. Follow the digestion steps outlined in this paper until the soil solution turns yellowish-green, then continue digestion for another 1 hour. After digestion, cool the sample and refer to the automatic Kjeldahl nitrogen analyzer instruction manual to place the digestion tube in the analyzer. Set the parameters to add 10–30 mL of water, 25 mL of sodium hydroxide solution, and 20–30 mL of boric acid absorption solution, and perform distillation followed by titration with a standard sulfuric acid (or hydrochloric acid) solution.

4. Discussion on Experimental Conditions

4.1. Impact of Sample Weight

NY/T 1121.24-2012 specifies that approximately 1 g of air-dried soil sample passing through a 0.25 mm sieve should be weighed, accurate to 0.0001 g, with a nitrogen content of about 1 mg. The key control point is not the sample weight itself, but ensuring that the nitrogen content in the sample is controlled at approximately 1 mg. To ensure the accuracy of total nitrogen determination in soils, a preliminary measurement of the soil's total nitrogen content should be conducted to determine the weighing range. Generally, if the soil nitrogen content is below 1 g/kg, the sample weight should be around 1 g; if the nitrogen content is in the range of 1.0–

2.0 g/kg, the sample weight should be around 1–0.5 g; if the nitrogen content is in the range of 2.0–4.0 g/kg, the sample weight should be around 0.5–0.25 g.

4.2. Role of the Accelerator

As specified in NY/T 1121.24-2012, the accelerator is prepared by mixing 100 g of potassium sulfate, 10 g of copper sulfate pentahydrate, and 1 g of selenium powder in a mortar and grinding thoroughly. Currently, the standard has been updated to use titanium dioxide instead of selenium, with the accelerator composition being $K_2SO_4 : CuSO_4 \cdot 5H_2O : TiO_2 = 100 : 10 : 3$. We have verified the digestion effect of these two different accelerators on different batches of quality control samples, and both have yielded good results in total nitrogen detection. Therefore, from an environmental perspective, it is recommended to use titanium dioxide instead of selenium and adopt the new accelerator formula.

4.3. Control of Digestion Temperature

When the temperature is within the range of 360–410°C, the detection data falls within the error range of the standard value of the quality control sample. When the temperature is below 360°C or above 410°C, the detection results are significantly lower. The reason is that when the temperature is below 360°C, digestion is incomplete, especially for heterocyclic nitrogen compounds, leading to lower results. When the temperature exceeds 410°C, nitrogen loss can occur. Therefore, to ensure the accuracy of the results, it is recommended to control the digestion temperature for total nitrogen in soils within the range of 370–380°C.

4.4. Impact of Sample Fineness on Digestion

In the Kjeldahl method for total nitrogen determination, soil samples must be finely ground. The standard requires that soil samples for total nitrogen detection should have a particle size smaller than 0.25 mm. However, organic matter in 0.25 mm particle size soil samples is not easily oxidized and decomposed. To ensure effective oxidation and decomposition, a small amount of deionized water (about 0.5–1 mL) should be added to moisten the soil sample before digestion, and the sample should be ground with a glass rod with a rubber head to form a fine paste. This allows the particles and organic matter in clay soil samples to disperse effectively and improves the decomposition effect. To further verify this, parallel determinations were conducted on two different batches of soil samples using both 0.25 mm and 0.149 mm particle sizes.

For the same sample, using a soil particle size of 0.149 mm for total nitrogen detection yielded results slightly lower than those obtained with a 0.25 mm particle size. The reason is that the 0.25 mm sample is prepared by grinding and sieving a 2 mm particle size soil sample in an agate mortar, while the 0.149 mm sample is prepared by high-speed grinding in a soil grinder and then sieving through a 0.149 mm sieve. During the grinding process, the high-speed friction of the equipment can cause the soil sample temperature to rise, leading to the volatilization loss of inorganic nitrogen in the form of NH_3 , N_2 , NO , NO_2 , etc., especially when the pH is above 7.5 or when the soil has a high $CaCO_3$ content. This results in a total nitrogen content that does not objectively reflect the actual total nitrogen content in the soil. Therefore, soil samples for total nitrogen detection should have a particle size that passes through a 0.25 mm sieve.

4.5. Control of the Digestion Process

During the digestion process, to ensure effective digestion, the temperature should be gradually increased, starting with low-temperature pre-digestion. The low-temperature pre-digestion temperature is generally controlled around 100°C. Observe the digestion phenomenon, and when the reaction in the digestion tube becomes mild, raise the digestion temperature to the range of 370–380°C and continue digestion. Based on experience, low-temperature pre-digestion usually takes about 30 minutes. When the digestion temperature reaches 370–380°C,

the organic matter in the soil gradually decomposes. After the carbon is oxidized, the digestion solution turns bluish-green. At this point, it should be noted that the clarity of the digestion solution does not necessarily indicate that all nitrogen has been converted to ammonium. The soil particles in the digestion tube should all turn grayish-white with a slight greenish hue, and then continue digestion for another hour. This process is called post-digestion. Before completion, carefully observe whether there are any black carbon particles remaining in the digestion solution or on the tube wall. If so, extend the digestion time until all carbon particles disappear.

4.6. Control of the Distillation Process

4.6.1 Checking the Sealing of the Distillation Apparatus: A simple method to locate leaks is to open the rear cover of the instrument box, wrap the connections of the distillation pipeline with paper towels soaked in phenolphthalein indicator, and then add a certain amount of ammonium solution to the digestion tube and perform distillation as usual. If the paper towel turns from colorless to red, it indicates a leak at that connection. Depending on the actual situation, replace the sealing ring, connecting pipeline, or connector. If the problem is severe, contact the manufacturer for repair.

4.6.2 Checking the Distillation Water and Reagents: During the distillation process, distilled water, sodium hydroxide solution, and boric acid solution are used. To ensure the accuracy of the results and avoid systematic errors, the distilled water and reagents should be checked to ensure they do not contain target nitrogen. The check can be performed using the Nessler's reagent spectrophotometric method, and the results should be below the detection limit of the method to be considered qualified.

4.6.3 Checking the Cleanliness of the Distillation System: First, add 10 mL of distilled water to a clean digestion tube and perform distillation according to the procedure. The standard requires that the blank value should not exceed 0.04 mg of nitrogen. If the blank value is too high, it indicates that the distillation system is contaminated and needs to be cleaned. Clean the system with a 10% methanol solution and repeat the blank test until the blank value meets the standard.

4.6.4 Condensate Water: Before starting the distillation, turn on the condensate water first. The condensation temperature should be appropriate, generally controlling the temperature of the distilled water below 30°C. If the cooling water temperature is too high, ammonia in the condenser may not be fully condensed, leading to incomplete distillation. Moreover, after distillation, ammonia may slowly condense and adhere to the tube walls, causing the next distillation result to be high. Therefore, when the tap water temperature is high in summer, a low-temperature cooling circulator should be used for distillation cooling.

4.7. Control of Reagent Usage

4.7.1 Sodium Hydroxide Usage: The amount of sodium hydroxide solution added should be sufficient. Generally, the amount of 10 g/L sodium hydroxide solution should not be less than 25 mL. When sodium hydroxide solution is added to the digest, the solution becomes alkaline, and brownish CuO precipitate or blue Cu(OH)₂ precipitate may form, indicating that the digest has been alkalinized. If not, additional sodium hydroxide solution should be added.

4.7.2 Concentration and Usage of Boric Acid Acceptance Solution: The concentration and usage of boric acid acceptance solution should be sufficient to completely absorb NH₃. Generally, 1 mL of 10 g/L H₂BO₃ solution can absorb 0.46 mg of nitrogen (N). Typically, 30 mL of boric acid absorption solution (10 g/L) should be added, but this can be adjusted based on the estimated nitrogen content in the digest to ensure complete absorption.

4.8. Judgment of Complete Distillation

To determine whether distillation is complete, when the distillate in the receiving flask reaches about 55 mL, first rinse the condenser outlet with distilled water. Then, use a glass rod to dip a small amount of distillate from the condenser outlet and test it on pH indicator paper to check for alkalinity. If there is no alkaline reaction, it indicates that ammonia distillation is complete; otherwise, continue distillation. Do not rush to test with indicator paper to avoid removing high-concentration ammonia solution. After distillation is complete, rinse the end of the distillation tube with a small amount of distilled water to clean any residual ammonia solution and ensure the accuracy of the results.

4.9. Quality Control for Soil Total Nitrogen Determination

4.9.1 Blank Test: For each batch of sample analysis, two parallel blank tests should be conducted. It is recommended that each batch does not exceed 50 samples. The results of the two parallel blank tests should be relatively stable. If the deviation is large, the cause should be identified, and appropriate corrective and preventive measures should be taken, and the batch of samples should be retested. Stable and qualified blank values should be deducted from the sample test results during calculation.

4.9.2 Precision Control: In each batch of sample analysis, no less than 10% of the samples should be randomly selected for duplicate analysis. The absolute difference between duplicate analyses should be less than or equal to 0.04 g/kg. If the duplicates are unqualified, the cause of the unqualified result should be identified, appropriate corrective and preventive measures should be taken, and the samples associated with the duplicates should be retested.

4.9.3 Accuracy Control: When a certified reference material (or reference material) similar to the soil sample being tested is available, it should be inserted uniformly in each batch of sample analysis as a quality control sample. Each batch should include at least two groups of quality control samples with high and low total nitrogen content levels. The results of the quality control samples should meet the requirements. If unqualified results occur, the cause should be identified, appropriate corrective and preventive measures should be taken, and the standard material samples and all associated samples should be retested.

5. Conclusion

There are various methods for soil total nitrogen analysis, and the automatic Kjeldahl nitrogen analyzer method is now widely used. To ensure the accuracy of the results, it is necessary to standardize and control each step of the pretreatment, including digestion, distillation, and titration. The distilled water and reagents should be accepted, and their usage should be controlled. Effective quality control measures should also be implemented to avoid systematic and random errors. The project sponsorship is gratefully acknowledged (Project Number: DJNY2024-21 /2024WHZ0230).

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