# COMPARISON OF SOME SOIL TOTAL NITROGEN DETERMINATION METHODS
# DAŽU AUGSNES KOPĒJĀ SLĀPEKĻA NOTEIKŠANAS METOŽU SALĪDZINĀJUMS

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**Abstract:** The soil total nitrogen ($N_{tot}$) determination was made for 37 top-layer soil samples taken from agricultural land in Latvia. The soil tests were carried out simultaneously at the Latvia University of Agriculture (in cooperation with Dr. G.Mezals) and at the Swedish University of Agricultural Sciences (in cooperation with prof. J.Persson and Dr. E.Otabbong) making use of the standard Kjeldahl method and dry combustion procedure. Additional indirect $N_{tot}$ calculation was made based on soil pH and organic matter content. A new method for indirect $N_{tot}$ calculation is proposed in the form of equation of regression. The obtained data present high mutual correlation between the applied analytical methods as well as indirect calculations.
**Key words:** total nitrogen, analytical methods, soil.

## 1. Introduction

Crop requirements for nitrogen are very high and nitrogen comparatively can be regarded as one of the most deficient plant nutrients under natural conditions. There has been accumulated a considerable amount of nitrogen in the arable layer of soil arable layer (0-25 cm) consisting of 1500-10 000 kg $ha^{-1}$ N in mineral soils. Soil total nitrogen determination is not commonly used in soil tests. This is largely because 95-99 % of N in soil is present in complex organic compounds and slowly becomes available to plants through microbial decomposition. However, this information focuses on the potential soil nitrogen pool which can partly and continuously provide plants with this nutrient.

The classical and well known worldwide Kjeldahl procedure (which was first published in 1883) is still applied by soil researchers in Latvia. Dry combustion technique for the determination of total N (as well as for total C, S, H) which is now dominating in western countries, is not yet available for our specialists due to the lack of relevant modern equipment. The idea of the presented investigation

is to examine the compatibility of soil total nitrogen determination methods used in Latvia and Sweden. Additionally, an indirect $N_{tot}$ calculation method was tested which was proposed by soil scientists in late 1920s.

## 2. Material and methods

For the experiment 37 top-layer (0-20 cm) soil samples were taken from agricultural land in Latvia. Scope of samples represents 3 different locations with the following soil characteristics:

- Vidini, brown soil *(Luvisols)*, loam;
- Lapas, sod-gleysolic soil *(Mollic Gleysols)*, sand;
- Kronauce, brown soil *(Luvisols)*, loamy sand.

The soil samples were simultaneously tested at the Latvia University of Agriculture (in cooperation with Dr. G.Mežals) and at the Swedish University of Agricultural Sciences (in cooperation with Prof. J.Persson and Dr. E.Otabbong) making use of conventional methods as applied in Latvia and Sweden. The following methods were used for the determination of total nitrogen, organic matter and pH test:

Kjeldahl procedure. 10 g of air-dried (< 1 mm) soil was placed into 800 ml Kjeldahl flasks. High temperature (330-450$^{o}$ C) digestion in concentrated $H_2SO_4$ (20 ml) in the presence of catalyst (mixture of $CuSO_4$, $K_2SO_4$, Se) was completed. The ammonia distillation was performed in alkaline medium. Evaporated ammonia was captured in 0.1 M $H_2SO_4$ and titrated excess acid with 0.1 M NaOH solution making use of methyl red as an indicator. This procedure was performed in Latvia.

Dry combustion. Total nitrogen and carbon were simultaneously determined by a CHN 932 Elemental Analyzer, model 600-800-332. The method is based on dry combustion of the samples (approx. 2 mg of finely ground-soil (< 0.08 mm) placed in a tin microcapsule) in an oxygen-helium atmosphere, reduction over copper, and determination of the combustion products by thermal conductivity cell. Procedure was performed in Sweden.

Soil pH. Soil/salt solution suspension (1N KCl), soil/solution ratio - 1:5, extraction time - 5 minutes. pH measurement.

Organic matter - (Tyurin's method). Wet combustion by $K_2Cr_2O_7+H_2SO_4$, reduction over $FeSO_4.7H_2O+H_2SO_4$. Photometric determination.

As the soils' organic compounds contribute to the dominating part of the total nitrogen, researchers paid attention to the high correlation between the contents of $N_{tot}$ and organic matter (OM) in soil. This phenomena has been quite commonly used for indirect calculations of soil total nitrogen.

Soil analysis performed at the Laboratory of Agricultural Chemistry, University of Latvia in 1920s showed the following average $N_{tot}$ contents in soil humus related to its pH:

- samples taken from fields with acid soil - 3-4.4 %;
- soil containing carbonates - 5.4 %;
- forest soils - 1.5-4.5 % N (Kulitans, Kruminsh & Bambergs, 1930).

Obviously, some decades later Skujans & Mezals (1960) relying on this information reported about the following relation between the soils' pH and $N_{tot}$ content in humus which was recommended for use (in rough estimations):

| | pH KCl | | | |
|---|---|---|---|---|
| | 4 - 5 | 5 - 6 | 6 - 7.5 | 7.5 - 8.5 |
| $N_{tot}$ in humus, % | 3.5 | 4.5 | 5.0 | 5.5 |
| $N_{tot}$ daudzums trūdvielās, % | | | | |

Accordingly to this distribution the scaling is very broad. Possibilities for errors arise due to the step by step increase of the values of $N_{tot}$ depending on the changes of pH interval as well as because of the non linear relationship. Therefore the pH/$N_{tot}$ relationship was transformed by the author of this article in the form of equation:

$$y_0 = 0.0762x^3 - 1.54x^2 + 10.7x - 20.3, \quad (1)$$

where $y_0$ - $N_{tot}$ in humus, %;
- soil pH Kcl.

Making some changes, the equation is ready for expression of $N_{tot}$ directly in soil:

$$y = (0.0762x^3 - 1.54x^2 + 10.7x - 20.3) \times 0.01\ OM \quad (2)$$

where

y - $N_{tot}$ in soil, %;
x - soil pH KCl;
OM - organic matter content in soil, %.

This equation was used for the calculation of indirect $N_{tot}$.

## 3. Results and discussion

Results obtained through the use of different methods for the determination of $N_{tot}$ are presented in Table 1. The Kjeldahl procedure was selected as a standard for this comparison as it is still in use in Latvia and is applied by researchers as well as commercial laboratories. Other methods - dry combustion (D.c.) and indirect calculations by using equation of regression (Eq) as proposed by the author and formula (F) proposed by Skujans & Mezals, 1960.

Table 1/1.Tabula

**Soil total nitrogen (comparison of determination methods)**
**Kopslāpekļa daudzums augsnē (metožu salīdzinājums)**

| Sample Paraugs | | | Total nitrogen N, % Kopslāpeklis N, % | | | | % from Kjeldahl % salīdzinājumā ar Kjeldāla metodi | | |
|---|---|---|---|---|---|---|---|---|---|
| No Nr. | OM OV | pH KCl | Kjeld. | D.C. sausā sadedzināšana | Eq. vienādojums | F formula | D.C. sausā sadedzināšana | Eq. vienādojums | F formula |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| VIDINI | | | | | | | | | |
| 1 | 3.23 | 7.0 | 0.188 | 0.191 | 0.170 | 0.162 | 101.6 | 90.7 | 86.2 |
| 1 | 0.62 | 6.6 | 0.051 | 0.064 | 0.032 | 0.031 | 125.5 | 62.5 | 60.8 |
| 3 | 2.84 | 7.1 | 0.176 | 0.191 | 0.151 | 0.142 | 108.5 | 85.7 | 80.7 |
| 3 | 1.10 | 6.7 | 0.055 | 0.079 | 0.057 | 0.055 | 143.6 | 103.6 | 100.0 |
| 4 | 2.90 | 7.2 | 0.143 | 0.162 | 0.155 | 0.145 | 113.3 | 108.5 | 101.4 |
| 4 | 0.99 | 6.6 | 0.052 | 0.059 | 0.051 | 0.050 | 113.5 | 98.0 | 96.2 |
| 5 | 3.10 | 6.5 | 0.148 | 0.165 | 0.158 | 0.155 | 111.5 | 107.1 | 104.7 |
| 6 | 2.90 | 6.4 | 0.168 | 0.170 | 0.147 | 0.145 | 101.2 | 87.6 | 86.3 |
| 7 | 2.79 | 6.5 | 0.153 | 0.164 | 0.143 | 0.140 | 107.2 | 93.2 | 91.5 |
| 8 | 2.80 | 6.5 | 0.119 | 0.157 | 0.143 | 0.140 | 131.9 | 120.3 | 117.7 |
| 12 | 3.21 | 6.5 | 0.148 | 0.166 | 0.164 | 0.161 | 112.2 | 110.9 | 108.8 |
| 13 | 2.69 | 6.7 | 0.119 | 0.158 | 0.139 | 0.135 | 132.8 | 117.0 | 113.5 |
| 14 | 2.28 | 6.6 | 0.158 | 0.159 | 0.117 | 0.114 | 100.6 | 74.2 | 72.2 |
| 16 | 2.90 | 6.6 | 0.143 | 0.152 | 0.149 | 0.145 | 106.3 | 104.3 | 101.4 |
| 27 | 2.79 | 6.7 | 0.138 | 0.131 | 0.144 | 0.134 | 94.9 | 104.7 | 97.1 |
| 32 | 3.00 | 6.7 | 0.163 | 0.152 | 0.155 | 0.150 | 93.3 | 95.3 | 92.0 |
| 48 | 3.21 | 6.4 | 0.143 | 0.174 | 0.163 | 0.161 | 121.7 | 114.0 | 112.6 |
| 54 | 3.00 | 6.6 | 0.153 | 0.168 | 0.154 | 0.150 | 109.8 | 100.9 | 98.0 |
| LAPAS | | | | | | | | | |
| 93 | 3.64 | 6.7 | 0.170 | 0.202 | 0.188 | 0.182 | 118.8 | 110.9 | 107.1 |
| 94 | 3.67 | 6.7 | 0.157 | 0.171 | 0.190 | 0.184 | 108.9 | 121.0 | 117.2 |

Table 1 /continued/
1.Tabula /nobeigums/

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| LAPAS | | | | | | | | | |
| 95 | 4.15 | 6.8 | 0.201 | 0.183 | 0.216 | 0.208 | 91.4 | 107.6 | 103.5 |
| 96 | 2.90 | 6.8 | 0.147 | 0.187 | 0.151 | 0.145 | 127.2 | 102.8 | 98.6 |
| 97 | 3.21 | 6.7 | 0.152 | 0.171 | 0.166 | 0.161 | 112.5 | 109.3 | 105.9 |
| 98 | 2.90 | 6.7 | 0.142 | 0.203 | 0.150 | 0.145 | 143.0 | 105.7 | 102.1 |
| 99 | 3.73 | 6.7 | 0.152 | 0.176 | 0.193 | 0.187 | 115.8 | 127.1 | 123.0 |
| 100 | 3.42 | 6.8 | 0.196 | 0.220 | 0.178 | 0.171 | 112.2 | 90.9 | 87.2 |
| KRONAUCE | | | | | | | | | |
| 86 | 1.97 | 6.1 | 0.073 | 0.097 | 0.098 | 0.099 | 132.9 | 133.9 | 135.6 |
| 88 | 2.57 | 6.4 | 0.124 | 0.116 | 0.130 | 0.129 | 92.7 | 105.2 | 104.0 |
| 89 | 2.96 | 6.2 | 0.183 | 0.178 | 0.148 | 0.148 | 97.3 | 80.9 | 80.9 |
| 90 | 1.49 | 5.0 | 0.094 | 0.088 | 0.063 | 0.067 | 93.6 | 67.0 | 71.3 |
| 91 | 2.31 | 5.8 | 0.112 | 0.129 | 0.111 | 0.104 | 115.2 | 99.4 | 92.9 |
| 92 | 1.57 | 5.9 | 0.079 | 0.095 | 0.076 | 0.071 | 120.2 | 96.8 | 89.9 |
| 93 | 2.69 | 6.6 | 0.118 | 0.120 | 0.138 | 0.135 | 101.7 | 117.3 | 114.4 |
| 94 | 2.82 | 6.5 | 0.112 | 0.107 | 0.144 | 0.141 | 95.5 | 128.7 | 125.9 |
| 95 | 2.27 | 6.4 | 0.097 | 0.086 | 0.115 | 0.114 | 88.7 | 118.8 | 117.5 |
| 96 | 1.88 | 4.7 | 0.094 | 0.102 | 0.073 | 0.066 | 108.5 | 77.6 | 70.2 |
| 98 | 1.87 | 6.6 | 0.085 | 0.088 | 0.096 | 0.094 | 103.5 | 113.2 | 110.6 |
| | | | | | | | | | |
| | | Average | | | | | 111.1 | 102.5 | 99.4 |
| | | STDV | | | | | 14.2 | 16.6 | 16.6 |
| | | Confidence limit $_{0.05}$ | | | | | 4.6 | 5.3 | 5.3 |
| | | Confidence limit $_{0.01}$ | | | | | 6.0 | 7.0 | 7.0 |

On the average, dry combustion technique produces slightly higher results as compared to the Kjeldahl procedure. The analytical values in average are 111.5 % from those obtained by Kjeldahl. The mean relative values obtained by indirect calculations are more similar to the standard ones. However, standard deviation calculated from relative values of three checked methods shows a slightly lower distribution for dry combustion method (14.2 %) but higher - for indirect determination (16.6 %). Confidence limits returnig the average values of the tested samples to the average relative values for the entire population are as follows:

- for 0.05 level of significance - from ±4.59 to ±5.34 %;
- for 0.01 level of significance - from ±6.03 to ±7.01 %.

It is evident that standard Kjeldahl procedure also has analytical disadvantages which might cause some inaccuracy in the obtained results. For example, using the above mentioned concentrations for ammonia capturing in the process of distillation and excess acid titration, inaccuracy in titration by 0.1 ml generates an error equal to 0.05 % of N in the soil. Some other types of errors might be possible everywhere else in the digestion - distillation process.

Both of the indirect methods - the use of the equation of regression and simple calculation based on soil pH interval, generated similar results with a slightly lower distribution of relative values for data obtained by equation. Obviously, the selected soils were quite unfavourable for comparing both of the calculation methods as the dominating pH mostly falls in one interval - pH KCl 6 - 7.5 and, with few exceptions, was stable in the middle of the interval. Therefore it is not possible to make a definite conclusion before an additional experimental work is carried out with soils, representing wide range of pH.

Mutual correlation among $N_{tot}$ determination methods is high and coefficient of correlation falls in an interval from 0.8800 to 0.9979 (Table 2).

Table 2/2.Tabula

Mutual correlation among methods (r values)
Noteikšanas metožu kopsakarība (r vērtības)

| Method<br>Metode | Kjeldahl<br>Kjeldāla | Dry combustion<br>Sausā sadedzināšana | Equation of regression<br>Regresijas vienādojums | Formula<br>Formula |
|---|---|---|---|---|
| Kjeldahl | 1.00 | | | |
| Dry combustion | 0.9522 | 1.00 | | |
| Equation of regression | 0.8850 | 0.8647 | 1.00 | |
| Formula | 0.8800 | 0.8577 | 0.9979 | 1.00 |

## 4. Conclusions

Dry combustion technique for $N_{tot}$ determination shows a tendency to produce slightly higher results as compared with the standard Kjeldahl procedure. Indirect $N_{tot}$ calculation methods present good agreement with analytical results.

## References

1. Kulitans P.(ed), Krūmiņš K. and Bambergs K.(1930). Lauksaimniecibas analize. I. Augsna. Rīga, 320.

2. Skujāns R. and Mežals G.(1960). Augšņu pētīšana dabā un laboratorijā. Rīga, 245.

# ANOTĀCIJA

Darbs tika veikts sadarbībā ar Zviedrijas Lauksaimniecības Universitāti. Tā mērķis bija savstarpēji salīdzināt tradicionālo Kjeldāla metodi kopējā augsnes slāpekļa noteikšanā, kura Latvijā joprojām tiek pielietota gan augsnes zinātnes pētījumos, gan arī masveida augsnes analīzēs ar tā saukto "sausās sadedzināšanas" metodi, ko izmanto ārzemēs. Pēdējā ir ievērojami ātrāka un ērtāka, taču tās lietošanai nepieciešama moderna aparatūra, kādas mūsu rīcībā patreiz vēl nav. Papildus salīdzināta netiešās noteikšanas metode, kas pamatojas uz $N_{kop}$ kopsakarību ar augsnes trūdvielu saturu, par ko jau 1920-ajos gados rakstīja P. Kulitāns, K. Krūmiņš un K. Bambergs. Rakstā ieteikts šo kopsakarību izmantot pielietošanai ērtākā veidā - regresijas vienādojuma formā.

Pieņemot Kjeldāla metodi par standartu un ar tās palīdzību iegūtos rezultātus apzīmējot ar 100 %, pārējās metodes vidēji ir devušas sekojošus rezultātus:

- "sausās sadedzināšanas " metode - 111.1 %;
- pielietojot raksta autora ieteikto regresijas vienādojumu - 102.5 %;
- P. Kulitāna, K. Krūmiņa, K. Bamberga aprakstītā kopsakarība, ko vēlāk vispārinājuši R. Skujāns un G. Mežals - 99.4 %.

Vienlaicīgi konstatēta augsta savstarpējā korelācija starp visām pielietotām metodēm. Aprēķināts doto sakarību būtiskuma intervāls pie 0.05 un 0.01 ticamības līmeņa.