COMPARISON OF SOIL ORGANIC MATTER DETERMINATION METHODS
AUGSNES ORGANISKĀS VIELAS NOTEIKŠANAS METOŽU SALĪDZINĀJUMS

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Abstract. In the field of soil science different methods of soil analysis are adopted in various countries. Therefore compatibility studies of soil test methods used in Latvia and other countries, especially those internationally accepted, are topical. For experiment 37 top layer soil samples were taken from agricultural land in Latvia: Brown lessive soil *(Stagnic Luvisol)*, silt loam, pH KCl 6.6 - 7.2, Pēterlauki; Sod-gleysolic soil *(Mollic Gleysol)*, fine sand, pH KCl 6.7 - 6.8, Lapukrogs; Brown soil *(Luvisol)*, loamy sand, pH KCl 4.7 - 6.6, Kroņauce. The soil tests were simultaneously done 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) using conventional methods and procedures for Latvia and Sweden. With some approximation it is possible to compare soil test data obtained by methods used in Latvia with those used in Sweden.
Key words: soil organic matter, analytical methods, compatibility of analytical methods.

1. Introduction

The integration of Latvia into activities of international research, environmental monitoring and natural resources inventory asks for dynamic and reliable information exchange. The problem exists as in the field of soil science different methods of soil analysis are adopted in various countries. Therefore compatibility studies of soil test methods used in Latvia and other countries are topical.

One of the basic parameters is the organic matter content in soil. It is a principal feature that differs soil from rock. The quantity and properties of organic soil matter help to determine the direction of soil formation processes as well as biochemical, chemical, physical and soil fertility properties. It affects the composition and mobility of adsorbed cations as well as soil color, heat balance, volume weight, consistency and specific gravity of the solid phase. Soil organic matter content is one of the principal criteria for soil diagnosis and classification.

All previously accumulated information about the soil organic matter content in Latvia is based on Tyurin's method, which is based on wet combustion by $K_2Cr_2O_7 + H_2SO_4$. This method has several disadvantages, like the necessity to work with high reactive solutions, environmental hazard risk from chromium waste and high labor consumption. Therefore there is an attempt to introduce more faster dry combustion technique which is widely used by soil researchers in other countries. Dry combustion analysis is rapid and clean. In the procedure no chemicals other than catalyst are involved. Samples do not require any pretreatment other than drying and grinding. By using this method the total carbon is determined in soil: organic which is mainly associated with the organic fraction and the inorganic C which generally occurs with carbonate minerals.

2. Materials and methods

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

- Pēterlauki, Brown lessive soil *(Stagnic Luvisol)*, silt loam, pH KCl 6.6 - 7.2 - 18 samples;
- Lapukrogs, Sod-gleysolic soil *(Mollic Gleysol)*, fine sand, pH KCl 6.7 - 6.8 - 8 samples;
- Kroņauce, Brown soil *(Luvisol)*, loamy sand, pH KCl 4.7 - 6.6 - 11 samples.

Additional characterization of samples used in the experiments can be found in the publications of A. Kārkliņš (Augsnes skābuma ..., 1996; Augsnes adsorbcijas ..., 1996).

The soil samples were tested simultaneously at the Latvia University of Agriculture (in cooperation with Dr. G. Mežals) and the Swedish University of Agricultural Sciences (cooperation with Prof. J. Persson and Dr. E. Otabbong).

Method used in Latvia

Wet combustion by $K_2Cr_2O_7$ + H_2SO_4, reduction over $FeSO_4.7H_2O$ + H_2SO_4. Photometric determination. Method known as Tyurin's method and used as standard for soil diagnosis and fertility tests in Latvia. Similar to method of Walkley - Black which is recommended by the FAO for use in soil diagnosis internationally.

Method used in Sweden

The total soil carbon was determined by a CHN-932 Elemental Analyzer, model 600-800-332. The method is based on dry combustion of soil in an oxygen-helium atmosphere, reduction over copper and determination of the combustion products (CO_2 gas) by thermal conductivity cell. Parallel determination of soil carbonates was done and soil organic carbon was obtained as a difference between soil total carbon and C in soil carbonates. By multiplying the content of organic carbon with factor 1.724 (van Bemmelen factor), the soil organic matter was computed.

3. Results and discussion

Soil samples used in the experiment represented a wide range of organic matter (OM) content in soil. Results obtained by using different methods produce OM values for the same soil sample with some diversity (Table 1). Explanation on that could be a well known fact that all dichromate methods (Tyurin's, Walkley - Black and their modifications, others) do not give complete oxidation of organic matter. Walkley and Black determined an average, recovery factor of 76 % (Soil Survey ..., 1995; 1995), accordingly to Tyurin - 85-90 % (Н. П. Бельчикова, 1965). Other studies have found recovery factors ranging from 60 to 86 % depending on soil, organic matter quantity and quality, modifications in the analytical procedure (L. E. Allison, 1960).

Table 1/1. tabula

Soil OM value. Range of results, %
Augsnes organiskā viela, rezultātu intervāls, %

Parameters Rādītāji	Location of sampling Paraugu ņemšanas vieta		
	Pēterlauki	Lapukrogs	Kroņauce
In Latvia / Latvijā			
Min.	0.62	2.90	1.49
Max.	3.23	4.15	2.96
Average / Vidēji	2.58	3.45	2.22
In Sweden / Zviedrijā			
Min.	0.34	3.74	1.66
Max.	3.12	4.71	3.63
Average / Vidēji	2.21	4.12	2.15
Ratio Sweden/Latvia Attiecība Zviedrija/Latvija	0.86	1.19	0.97

There is a recommendation to use the average correction factor which yields erroneous values for many soils. Therefore dichromate methods are only an approximate or semiquantitative estimate of organic carbon. Analytical data by both dichromate methods (Tyurin's, Walkley-Black) are generally considered invalid if organic C in soil is more then 8 % (about 15 % OM) (Soil Survey ..., 1996; Практикум ..., 1987). Those methods also are not recommended by soil horizons with redoximorphic features (gleyic and stagnic properties) because the presence of significant amounts of ferrous ions as well as manganese dioxide result an error.

In average, dry combustion gives lower results for soils with a relatively low OM content (Pēterlauki, Kroņauce) and higher results for soil with high OM content (Lapukrogs). Ratio between the results produced by both methods shows difference in values for every soil and varies from 0.86 (Pēterlauki) up to 1.19 (Lapukrogs). Correlation and regression analysis were performed to study relationship between both OM determination methods for all 37 soil samples (Table 2).

Table 2/2. tabula

Correlation analysis
Korelācijas analīze

Parameters Rādītāji	Organic matter, % Organiskā viela, %		Ratio Attiecība
	WC[1]	DC[2]	DC/WC
Min.	0.62	0.34	0.34
Max.	4.15	4.71	1.48
Average / Vidēji	2.66	2.60	0.96
STDV			0.22
r	0.84		
r^2	0.71		
t	7.12		

1 - wet combustion
mitrā pārpelnošana
2 - dry combustion
sausā sadedzināšana

Probability test for correlation analysis:

Significance level	Probability distribution for correlation (*P*)	Theoretical *t* - distribution
$\alpha = 0.01$	0.09	2.576
$\alpha = 0.05$	0.07	1.960
$\alpha = 0.1$	0.06	1.645

Coefficient of correlation is relatively high $r = 0.84$ and significant up to level of $\alpha = 0.01$, and 71 % of distribution shows linear feature. Therefore the single factor linear regression was complete to evaluate statistical inferences of two OM determination methods and find the equation for their comparison. The obtained results are as follows:

$$M_T = a+b \cdot M_D$$

$$a = 0.978 \pm 0.194$$
$$b = 0.646 \pm 0.069$$

where M_T = OM (%) by Tyurin's method;
M_D = OM (%) by dry combustion technique.

This equation could be used to recompute analytical results obtained with one method accordingly to another. Mutual correlation of the used methods for OM determination, distribution of obtained results and regression line see in Fig. 1.

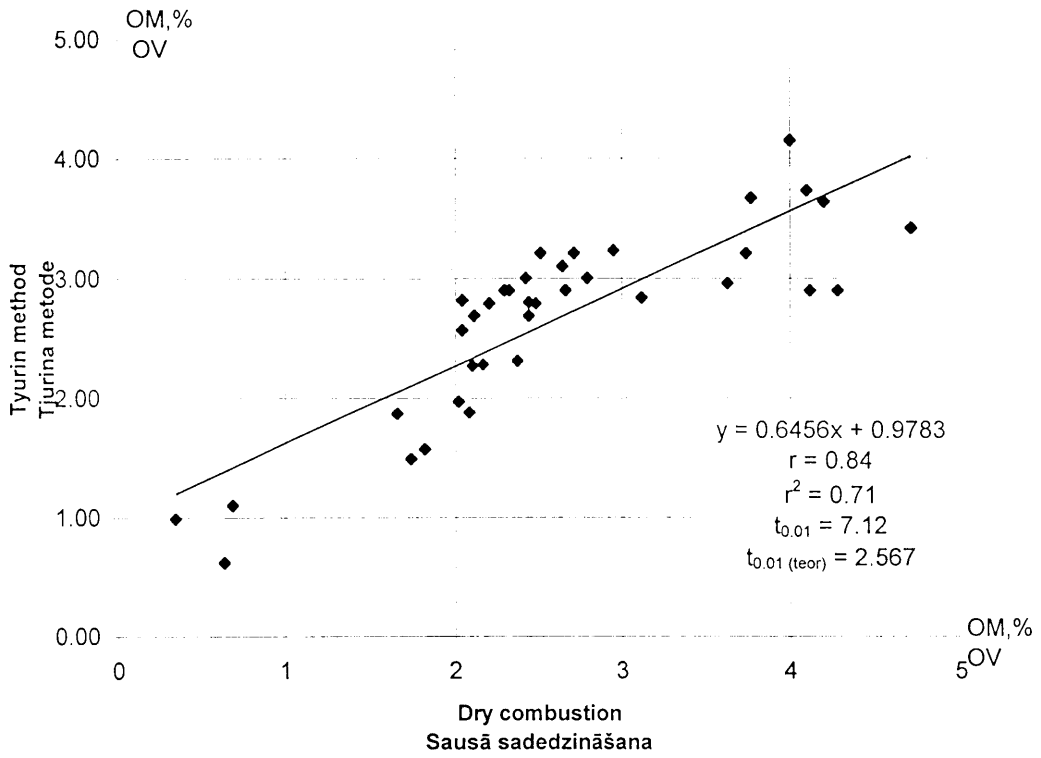

Fig. 1. Comparison of soil organic matter determination methods.
1. att. Augsnes organiskās vielas noteikšanas metožu salīdzinājums.

Tyurin's method is similar to the internationally recommended Walkley-Black method as both are based on oxidation of organic carbon by mixture of $K_2Cr_2O_7$ + H_2SO_4. But there are also some differences in procedures which could affect the analytical values.

Wet combustion according to Tyurin's method* is done by using of 0.4 *N* $K_2Cr_2O_7$ and H_2SO_4 (1.84 g cm^{-1}) at the volume ratio 1:1. The sample treated with oxidation solution is heated for 1 h at 100° C. Reaction is stopped by rapid cooling and adding distilled deionized water. Using the method of Walkley-Black a sample is oxidized with 1 *N* $K_2Cr_2O_7$ and concentrated sulfuric acid (H_2SO_4) in 1:2 volume ratio. The sample is shaken for 1 min. in reciprocating shaker and left to stay for 30 min., afterwards reaction is halted by dilution with water. The excess dichromate is back-titrated by both methods using $FeSO_4 \cdot 7H_20$, or $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\ H_2O$. (for Tyurin's method).

Organic matter is usually calculated by using van Bemmelen factor. This factor is based on the assumption that organic matter contains 58 % organic carbon. The proportion of organic carbon in soil organic matter for a range of soils is highly variable (Soil Survey ..., 1995; P. J. Howard, 1965). Studies also show that subsoils have a higher factor that surface soils (F. E. Broadbent, 1953). The factors usually vary from 1.8 to 2.0 for surface soils and about 2.5 for subsurface soils. Therefore many authors give a preference to report organic carbon rather than to convert organic C to organic matter through use of an approximate correction factor.

4. Conclusions

The used OM determination methods produced different values for the same soil sample. Therefore it is impossible to make a direct comparison of results if analytical methods differ. Compatibility studies should be performed for mutual comparison of information obtained by using different methods, as well as before introducing the new analytical technology.

* The indicated details are given accordingly to the standart GOST 26213-84. Many modifications could be recomended and applied for this method.

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ANOTĀCIJA

Darbs tika veikts sadarbībā ar Zviedrijas Lauksaimniecības universitāti. Tā mērķis bija savstarpēji salīdzināt tradicionālo augsnes organiskās vielas noteikšanas metodi (Tjurina metode), kura Latvijā tiek pielietota gan augsnes zinātnes pētījumos, augsnes diagnostikā, gan arī augsnes auglības novērtēšanā ar tā saukto "sausās sadedzināšanas" metodi, kas guvusi plašu pielietojumu ārzemēs. Pēdējā ir ievērojami ātrāka un ērtāka, jo nav nepieciešams lietot kodīgus un ekoloģiskā ziņā nevēlamus reaģentus, tādus kā koncentrēta sērskābe un kālija bihromāts. Taču tās veikšanai ir nepieciešama moderna aparatūra.

Pētījumiem tika izmantoti 37 augsnes aramkārtas paraugi: Lesivētā brūnaugsne *(Stagnic Luvisol)*, vidējs putekļains smilšmāls, pH KCl 6.6 - 7.2, Pēterlauki; Velēnglejotā augsne *(Mollic Gleysol)*, saistīga smilts, pH KCl 6.7 - 6.8, Lapukrogs; Brūnaugsne *(Luvisol)*, mālsmilts, pH KCl 4.7 - 6.6, Kroņauce. Augsnes paraugu ievākšana un sagatavošana analīzei tika veikta atbilstoši Latvijā pieņemtajai metodikai.

Iegūtie rezultāti rāda, ka pastāv atšķirības starp augsnes organiskās vielas noteikšanas metodēm, pie kam tās dažādām augsnēm ir dažādas. Abu analītisko metožu korelācija ir samērā augsta, $r = 0.84$, $r^2 = 0.71$ pie $\alpha = 0.01$. Tādējādi analītisko rezultātu savstarpējai salīdzināšanai, kuri iegūti lietojot dažādas metodes, tiek rekomendēts izmantot sekojošu vienfaktoru lineārās regresijas vienādojumu:

$$M_T = a+b \cdot M_D$$

$$a = 0.978 \pm 0.194$$
$$b = 0.646 \pm 0.069$$

kur M_T = OM (%) pēc Tjurina metodes,
M_D = OM (%) pēc "sausās sadedzināšanas" metodes.

Papildus dots arī Tjurina un starptautiski rekomendētās Walkley-Black metodes apraksta salīdzinājums.