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SOIL CHEMISTRY

Methods for Measuring Organic Carbon Content in Carbonate-Containing Soils: A Review

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Abstract—In the world practice, the organic carbon content (C_{org}) in the soils containing carbonates is measured in different ways. We have analyzed the methods for solving this problem including the state-of-the-art approaches, such as thermogravimetry, differential scanning calorimetry, and spectroscopy. As is shown, the presence of $CaCO_3$ does not prevent the C_{org} measurement with dichromatometric method (Tyurin and Walkley–Black variants). The disadvantages of this method comprise the laborious analysis, constant presence of operator, incomplete oxidation of organic compounds, and environmental pollution. The measurement of soil weight loss-on-ignition (LOI) is economical and rapid but overestimates C_{org} content because of inadequacy of the conversion factor of 1.724, the presence of adsorbed and chemically bound water, as well as mineral components decomposing at $T = 105–550°C$. The most relevant solution for assaying the C_{org} content in carbonate soils is to use an analyzer and a calcimeter although the accuracy of C_{org} measurements in the presence of carbonates is significantly reduced because the errors of two methods are quadratically summed. A high cost of the device, maintenance, verification, and repair limit its widespread use in soil laboratories. The content of soil carbonates can be measured using both gravimetric (LOI) and volumetric (calcimeter) methods. The latter method is preferable for the soils with the prevalence of $CaCO_3$ in carbonates. The preliminary removal of carbonates from soil samples is labor-intensive and can cause a partial loss of C_{org} via acid extraction. A high cost of the instruments and the absence of the libraries of soil spectra hinder the development of Vis-NIR and MIR spectroscopy as an alternative to wet chemistry methods. Further comparative studies will give a deeper insight into the spatial patterns in the distribution of soil organic carbon.

Keywords: comparative analysis, soil organic and inorganic carbon

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INTRODUCTION

In soil, carbon is present in the organic matter and individual organic compounds (C_{org}), as well as in different species of carbonates, mainly those of calcium and magnesium (C_{inorg}). On a global scale, carbonate soils cover over 30% of the Earth's surface [27, 48, 79] and approximately one-third of the total carbon is represented by its inorganic species [13].

Carbon continuously circulates in the biosphere as a result of chemical, physical, and biological processes. Two forms of carbon are tightly interrelated [88, 96]. On the one hand, carbonates slow down the cycling of organic carbon via C_{org} stabilization by the physical protection (occlusion) against degradation [64]. On the other hand, the organic acids formed via functioning of biota [5] dissolve carbonates. Carbon as the carbon dioxide formed in the reaction is eliminated from the system [7, 8, 58, 60, 80, 109]. A tight correlation between the contents of C_{org} and C_{inorg} ($r = –0.983$, $p < 0.000$, $n = 9$ [6]), characteristic of the soils of the Polar Urals (Bolshoi Paipudynsky Ridge) confirms the course of these processes (Fig. 1).

The literature sources give controversial information about the correlation between different carbon species, reporting both positive and negative (less tight) correlations as well as its absence. This is determined by soil properties and genesis, origins of organic and inorganic compounds, climate, land use and management practices [51, 56, 107]. The example of the Bolshoi Paipudynsky Ridge is unique because the soils there have developed on the eluvial–colluvial derivates of calcareous rocks with a uniform composition and the content (ω) of $CaCO_3$ reaching 100% (correspondingly, $\omega(C_{inorg}) = 12\%$).

The organic and inorganic carbon cycle responds to climate change and contributes to its regulation. Carbonates are regarded as a reliable paleoecological indicator and are used in regional paleoclimatic studies [108, 112]. The system of soil C_{inorg} is a key sink of atmospheric CO_2 [24, 44, 59, 110, 111]. On the other hand, voluminous data set demonstrates a lateral removal of dissolved carbon of carbonates. Note that the scale of C_{inorg} aqueous export as H_2CO_3, HCO_3^-, and CO_3^{2-} can severalfold exceed the level of its stabilization [43, 66, 77].

Thus, the assessment of both soil carbon species within the total pool of this element becomes ever more relevant in the epoch of global changes [27, 98]. The analysis of the papers in this area demonstrates a disproportionally larger number of the studies on the methods for measuring C_{org} in carbonate-free soils. However, the comparison of the approaches to measure the C_{org} content in the presence of carbonates is rather ignored [34, 87]. Meantime, such these studies are necessary to integrate the global data aiming to monitor the current state of soil carbon and forecast its changes caused by natural and anthropogenic factors [72, 86]. The absence of the comparable data is one of the reasons underlying a poor accuracy of the global maps for the stock of soil organic carbon, including the carbonate-containing soils [40].

The efforts of the Global Soil Laboratory Network (GLOSOLAN) with the Global Soil Partnership of the Food and Agricultural Organization (FAO) are aimed at resolving the problems in standardization and unification of the methods for quantification soil properties. Over 5 years, the worldwide work of scientists brought about more than 20 protocols for harmonizing soil analytical data (https://www.fao.org/global-soil-partnership/glosolan/), and the work is continuing.

The goal of this work was to critically analyze the techniques for measuring the C_{org} content in carbonate soils including their advantages and disadvantages.

FACTORS THAT INFLUENCE THE MEASUREMENT ACCURACY OF CARBON CONTENT IN THE SOIL

In the world practice, the organic and inorganic carbon content in soils is measured with different methods. When choosing a particular method, the specific chemical features of assayed soil, the necessary measurement accuracy, the time necessary for analysis, its cost, ecological friendliness (safety for engineers and environment), and the possibility to measure other characteristics in the same sample (for example, N, S, O, and H) are taken into account.

All techniques for determination of C_{org} content are based on its oxidation to carbon oxide (IV). Some methods utilize the combustion of organic compounds (dry technique) based of measuring the amount of CO_2 and the C_{org} oxidation methods in solutions (wet techniques). The latter imply the assessment of the amount of oxidizing agent necessary to transform C_{org} into CO_2 or the amount of the reduced species of the used oxidizer formed in redox reaction [3].

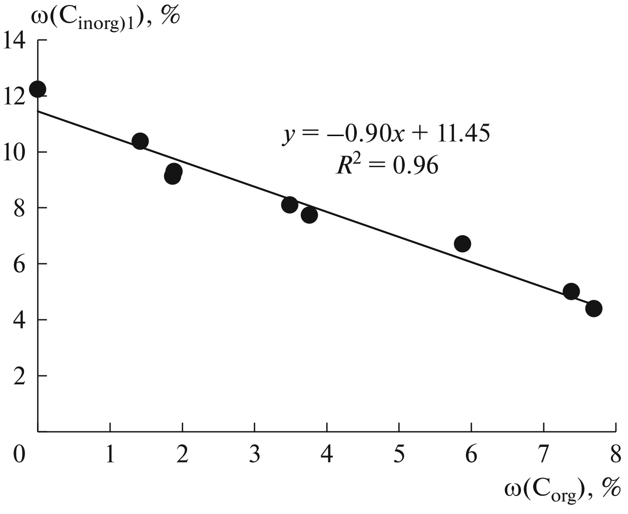

Fig. 1. Correlation between the organic and inorganic carbon contents, $\omega(C_{org})$ and $\omega(C_{inorg})$, in the mountain–tundra carbonate soils of the Polar Urals (according to [6]). Hereinafter, $\omega(C_{inorg})$ is measured volumetrically.

Different equipment levels of chemical laboratories limit the comparison of the C_{org} contents measured with alternative methods. The change and development of analytical methods also contribute to the problems in a long-term monitoring of individual areas [49, 50]. However, the use of different methods is not the only reason for the discrepancies of results [67].

Free rendering of analytical protocols resulting from the absence of comprehensive descriptions for all procedures causes serious difficulties in the interpretation of the time series of soil carbon dynamics. Other factors also contribute to the incompatibility of soil data, in particular,

(1) Changes in field sampling schemes [69] and natural heterogeneity of soil formation conditions [23, 74];

(2) Different sample preparation procedures, including the volume of undecomposed plant residues removed [35, 45, 106], choice of particle size (sieve mesh size), and insufficient sample uniformity [36, 40];

(3) Selection of the weight of the sample that determines the accuracy of measurement result (Horwitz's trumpet, that is, an increase in the measurement error with a decrease in the concentration of the assayed substance in the analyzed sample) [104];

(4) Change in operators in laboratory; and

(5) Duration and conditions of soil storage. This factor requires more attention in future studies [16]. The change in sample composition during storage can result from microbiological activity. According to Blake at al. [19], the repeated analysis of the soils stored for approximately 30 years in closed glass containers did not show any changes in the total carbon content. However, another research team [32, 103] reported a decrease in carbon content caused by continuous CO_2 emission.

METHODS FOR MEASURING CARBON CONTENT IN SOILS

Carbon high-temperature catalytic oxidation (HTCO) in analyzers. This method for measuring total carbon (C_{tot}) content in soil in a TOC analyzer (combustion of organic compounds and decomposition of carbonates at a temperature over 1000°C) is regarded as a gold standard [26, 31, 36].

This method has a number of advantages over other techniques for assaying soil carbon, in particular,

(1) It guarantees a complete oxidation of soil organic carbon and decomposition of inorganic carbon;

(2) It is selective since the intensity of analytical signal (area of CO_2 peak in a chromatographic pattern) is independent of the presence of other soil components;

(3) It is suitable for a wide range of carbon content (from 0.1 to 100%);

(4) Reference samples are available for calibration of analyzers (both individual organic compounds, state (**SRS**) and departmental (**DRS**) reference samples of soils, plant materials, and other solid objects are used);

(5) It is rapid and, thus, allows a batch of soil samples (up to 100 samples) placed in a sampler to be assayed in an automated mode; and

(6) It has a high measurement accuracy, which depends on the carbon content in soil. The relative errors (δ) of $\omega(C_{tot})$ amount to $\pm\delta = 23$, 15, 10, and 3.5% for the $\omega(C_{tot})$ ranges of 0.1–2, 2–5, 5–30, and >30%, respectively.[1]

Correspondingly, the method for assessing the total soil carbon content in an analyzer is frequently used as the reference technique when comparing the experimental data on the carbon content measured with different methods [86].

A disadvantage of this method is that the conditions for separate measurements of C_{org} and C_{inorg} are not worked out in detail for most of the analyzer types. That is why, an additional estimation of carbon in carbonate ions is necessary when assaying carbonate soils. In this case, the accuracy of $\omega(C_{org})$ measurements decreases because the errors of two methods are quadratically summed:

$$\omega(C_{org}) = \omega(C_{tot}) - \omega(C_{inorg}),$$

$$\delta(\omega(C_{org})) = \frac{100\sqrt{\Delta^2(\omega(C_{tot})) + \Delta^2(\omega(C_{inorg}))}}{\omega(C_{tot}) - \omega(C_{inorg})}, \quad (1)$$

where δ is the relative measurement error for C_{org} content and Δ, absolute measurement fraction error for C_{org} content.

Note that the relative error of the characteristic calculated according to the difference between two values is this case depends in a statistically significant manner on the ratio of minuend and subtrahend. Find below the two methods for solving this problem: preliminary removal of carbonates from soil samples and the measurement of the carbon in inorganic compounds by volumetric method (**VMM**) using a calcimeter.

Implementation of the target problem using carbon HTCO in an analyzer in the presence of carbonates implies three measuring devices: analyzer, calcimeter (or incinerator), and analytical balance. Together with the cost of expendables, maintenance, testing, and repair, carbon HTCO technique in analyzers may well be rather expensive and financially unavailable for many laboratories [61].

Applied soil science actively uses the analogs of analyzers. In particular, Dokuchaev Soil Science Institute tested AN-7529 rapid analyzer (Gomel) for assaying total carbon as early as in the beginning of the 1980s [2]. As compared with CNS analyzers, the soil assay with this device was considerably (at least tenfold) cheaper; however, it could not simultaneously determine the contents of other elements. In addition, the upper limit of $\omega(C_{org})$ determination was only 10%. In this approach, the problem of additional C_{inorg} determination was solved by measuring the CO_2 formed when treating the other soil weighed sample with $HClO_4$ (coulometric titration).

Removal of carbonates from the soil sample. To assay soil in an analyzer, excess hydrochloric acid is added in a dropwise manner to a weighed sample (1.5–20 mg depending on the C_{org} content) until the gas (CO_2) ceases emitting. The assay is conducted in silver containers. Two weighed samples are used when it is necessary to assess $\omega(C_{inorg})$ by measuring C_{tot} in the initial sample and C_{org} after the removal of carbonate anions.

A similar procedure of carbonate removal from soil sample is also used in other methods [11, 34, 63, 83]. Different acids (HCl, H_2SO_3, and H_3PO_4) are used to decompose carbonates [22]. However, the preliminary removal of carbonates is laborious and can result in a partial loss of C_{org} because of the acid extraction when removing the excess of acid by decantation [10, 84]. Centrifugation is recommended to minimize the losses in organomineral colloid particles [22]. Another acidification method is to fumigate the soil sample placed into a capsule with acid fumes [34, 52].

The technique of in situ acidification consists in the treatment of soil samples with acid solution followed by their drying to avoid the loss in acid-soluble components. The in situ acidification methods allow the losses in acid-soluble C_{org} to be prevented because

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[1] Vanchikova, E.V., Kondratenok, B.M., and Tumanova, E.A. Measurement protocol no. 88-17641-004-2016 (FR.1.31.2016.23502). Soils; grounds; bottom sediments; peat and its products; solid materials of plant, animal, natural, and industrial origins; and chemical compounds. Protocol for measurement of nitrogen, carbon, and organic matter in EA 1110 (CHNS-O) elemental analyzer. Institute of Biology, Komi Scientific Center, Ural Branch, Russian Academy of Sciences: Syktyvkar, 2016. 29 p.

they do not require the repeated weighing of the samples treated with the acid [95].

Acidimetry, utilizing the back-titration of residual acid after the reaction with assayed sample, is another possible approach [71].

Gravimetric measurements (weight loss-on-ignition, **LOI**) with CO_2 emission was also proposed as a more rapid, inexpensive, and accurate variant for determining the carbonate carbon [47, 78]. All acid-soluble compounds are removed after soil treatment with the acid solution when eliminating its excess and the carbonate anions are replaced by anions of the used acid when using its minimum amount; correspondingly, the nature of the compounds via LOI is vague.

Taking into account that all approaches are based on the interaction of soil carbonates with soil, the limitations include different duration of the reaction for different carbonate types, which depends on their reactivity. In addition, these methods are often insufficiently accurate at a low content of carbonates [71].

Volumetric methods for measuring soil inorganic carbon content with the help of calcimeter. In this approach, the carbonates present in soil are decomposed with hydrochloric acid solution. The pressure in the reaction container connected with burette increases with CO_2 emission and the water level in the burette rises. The change in water level is the measure of CO_2 amount. Calcimeter is calibrated using carbonate weighed samples. The calcimeter by Eijkelkamp (The Netherlands)[2] has shown a good performance; this device allows for simultaneous measurement of carbonates in five samples [6]. Calcimeter is rather simple in use. The results of measurements are related to $CaCO_3$ content; correspondingly, calcimeter is preferable when analyzing soils with the prevalence of $CaCO_3$ among carbonates. However, the problems associated with the soils containing $MgCO_3$ and Na_2CO_3 are solvable by expressing the measurement results as C_{inorg} content. Note that the compounds that interact with HCl solution with emission of gas products (SO_2, H_2S, and so on) can interfere with the measurements.

The relative error when measuring the content of calcium carbonate and, correspondingly, C_{inorg}, for $\omega(CaCO_3) = 0.5–5\%$ and $\omega(C_{inorg}) = 0.06–0.6\%$ amounts to $\delta = 20\%$; for $\omega(CaCO_3) = 5–15\%$ and $\omega(C_{inorg}) = 0.6–1.8\%$ amounts to $\delta = 15\%$; and for $\omega(CaCO_3) > 15\%$ and $\omega(C_{inorg}) > 1.8\%$, amounts to $\delta = 10\%$.

As is shown above (Eq. (1)), the estimation of $\omega(C_{org})$ according to the difference between C_{tot} and C_{inorg} contents gives an increased relative error of C_{org} content. As an example, Table 1 lists the theoretical (calculated according to the errors of the corresponding methods) values of the relative error in $\omega(C_{org})$ measurements in carbonate-rich soils [87]. The error depends on the share of C_{inorg} in the total carbon content $\left(\frac{\omega(C_{inorg})}{\omega(C_{tot})}\right)$. At $\frac{\omega(C_{inorg})}{\omega(C_{tot})} \le 40\%$, the error of C_{org} measurement does not exceed 20%. In turn, the error of 70–290% is characteristic of the soils with the prevalence of carbonates (samples 18–23, Table 1), where $\frac{\omega(C_{inorg})}{\omega(C_{tot})} = 80–90\%$).

Dichromatometric method (modifications of Tyurin and Walkley–Black techniques). The disadvantages here comprise laboriousness, constant presence of operator, and environmental pollution [98].

The limitations of this method are the presence of Cl^-, Mn^{2+}, and Fe^{2+} in soils, as well as of the components resistant to oxidation, such as charcoal, and uncertainty of the conventional zero degree of organic carbon oxidation in the reaction with potassium dichromate [38, 39].

However, the evident difficulties and limitations do not prevent an active applied use of dichromatometric method implemented in two variants the most widespread in world soil science—the Tyurin and Walkley–Black protocols. According to the reference document,[1] the organic carbon or organic matter (**OM**) is measured by the oxidation with dichromate anions in the range of $\omega(C_{org}) = 0.17–8.7\%$ ($\omega(OM) = 0.3–15\%$).

According to this reference protocol, the C_{org} nonoxidizable by potassium dichromate at a measurement accuracy of 20% is taken into account with the help of correction factors amounting to 1.15 and 1.3[1] (Tyurin and Walkley–Black methods, respectively). In our view, the discrepancy of correction factors for two variants of the wet method is associated with a higher dispersion of the soil solid phase and the heating duration of the system. These factors lead to more efficient oxidation of organic carbon in the Tyurin variant as compared with Walkley–Black one [4, 86].

Although several authors recommend using a universal correction factor for the Walkley–Black method [49, 50, 61], a considerable number of their opponents deny the universality of this factor. Numerous published sources propose other values of correction factors from 1.2 to 1.85 [68, 75, 83, 86]. Many experts [25, 33, 49, 55, 61] believe that the value of correction factor depends on the soil type, C_{org} range, and particle size composition. A low level of carbon reduction can be associated with the local factors, such as a considerable amount of charred organic matter after fires [91]. In addition, some researchers believe that the value of correction factors in some samples depends on the climatic conditions of a particular year. Reithmaier et al. [77] believe that the search for correction factors for a particular plot and year is the best strategy for increas-

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[2] ISO 10693:1995. Soil quality—Determination of carbonate content—Volumetric method, 1995, p. 9.

Table 1. Quantified relative error (δ) of the measured organic carbon content (ω) in carbonate-containing soils (according to [87])

Soil sample no.	C_{tot}		C_{inorg}		C_{org}		$\delta(\omega(C_{org}))$	$\frac{\omega(C_{inorg})}{\omega(C_{tot})}$
	ω	±Δ	ω	±Δ	ω	±Δ		
	%							
$\frac{\omega(C_{inorg})}{\omega(C_{tot})} \le 0.4$								
1	13.6	1.4	0.8	0.1	12.8	1.4	11	0.06
2	6.3	0.6	0.6	0.1	5.7	0.6	11	0.1
3	6.7	0.7	1.1	0.2	5.6	0.7	12	0.16
4	4.4	0.7	0.9	0.1	3.5	0.7	19	0.2
5	2.7	0.4	0.6	0.1	2.1	0.4	20	0.22
6	6.3	0.6	1.6	0.2	4.7	0.7	14	0.25
7	6.1	0.6	1.6	0.2	4.5	0.7	15	0.26
8	5.7	0.6	1.6	0.2	4.1	0.6	15	0.28
9	23.6	2.4	7	0.7	16.6	2.5	15	0.3
10	12.1	1.2	4.4	0.4	7.7	1.3	17	0.36
11	12.4	1.2	5	0.5	7.4	1.3	18	0.4
$\frac{\omega(C_{inorg})}{\omega(C_{tot})} > 0.4$								
12	1.6	0.4	0.7	0.1	0.9	0.4	43	0.44
13	1.6	0.4	0.8	0.1	0.8	0.4	48	0.5
14	1.2	0.3	0.6	0.1	0.6	0.3	50	0.51
15	12.6	1.3	6.7	0.7	5.9	1.4	24	0.53
16	0.9	0.2	0.6	0.1	0.3	0.2	80	0.67
17	11.5	1.2	7.7	0.8	3.8	1.4	36	0.67
18	0.9	0.2	0.7	0.1	0.2	0.2	116	0.76
19	11.4	1.1	9.3	0.9	2.1	1.5	70	0.82
20	11	1.1	9.1	0.9	1.9	1.4	75	0.83
21	1.1	0.3	1	0.2	0.1	0.3	290	0.88
22	11.8	1.2	10.4	1.0	1.4	1.6	112	0.88
23	6.7	0.7	6.1	0.6	0.6	0.9	151	0.91

*$\omega(C_{org})$ was calculated as the difference between the $\omega(C_{tot})$ and $\omega(C_{inorg})_1$ measured with high-temperature catalytic oxidation and volumetric technique, respectively.

ing the data quality. However, this solution requires additional financial and human resources.

There are different expert opinions on the effect of carbonates on the results of $\omega(C_{org})$ dichromatometric assessment. Apesteguia et al. [10] regard the presence of carbonates as the limitation of this method. According to Vorob'eva [1], the carbonates of alkaline-earth metals react with the chromic mixture (neutralize the acid) and as a rule do not interfere with the measurement of organic carbon. The current state standard[3] has no information about the specificity of analyzing carbonate-containing soils. The Walkley–Black protocol implies the limitation on assays for soils containing considerable amounts of carbonized materials [37]; however, the threshold limit $CaCO_3$ content is not indicated.

A high variability of the measured organic carbon content is reported for the case when the inorganic carbon content is considerably higher than the organic carbon because carbonates are rather recalcitrant [68]. However, the experimental data demonstrate that carbonates do not influence the dichromatometric $\omega(C_{org})$ assessment [87]. This suggests that the measurement limits and the error characteristic of the Tyurin method modification and Walkley–Black method[1] are applicable to the carbonate soils as well.

The first evidence is the comparison of $\omega(C_{org})$ in carbonate-free reference soil samples (state reference

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[3] State standard GOST 26213-91 Soils. Methods for Determination of Organic Matter, Moscow: Izd. Standartov, 1992.

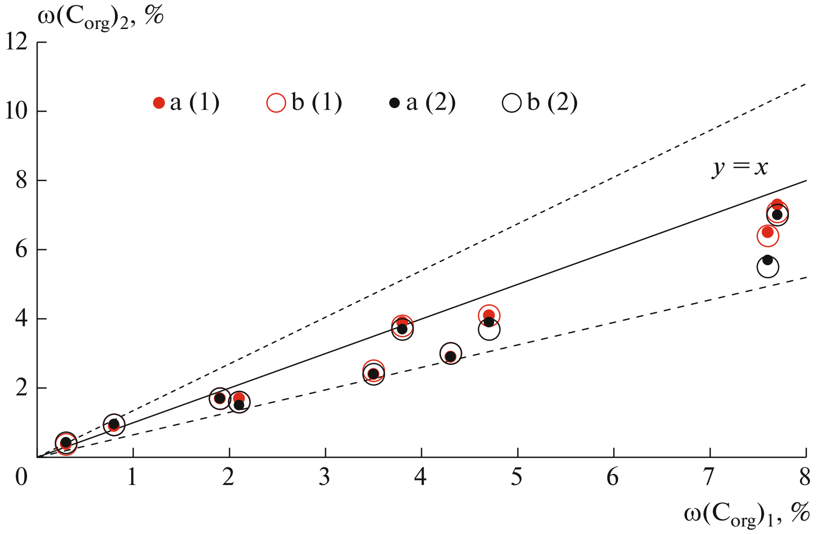

Fig. 2. Correlation of the organic carbon content $\omega(C_{org})_2$ measured by (*1*) Walkley–Black and (*2*) Tyurin methods with the reference value $\omega(C_{org})_1 = \omega(C_{tot}) - \omega(C_{inorg})_1$ in (a) initial soil samples and (b) the carbonate-free samples. Dashed lines show the boundaries of relative error $\delta = \pm 35\%$. Hereinafter, $\omega(C_{tot})$ is measured with high-temperature catalytic oxidation.

sample GSO 10413-2014 and departmental reference samples OSO 11201, OSO 21401, and OSO 29106, Russia) and their mixtures with $CaCO_3$. A threefold excess of carbon amount in carbonates over the organic carbon has no effect on the measured C_{org} content using the Tyurin and Walkley–Black methods [87]. Presumably, this fact is associated with the specific fabric of calcareous rocks.

The other evidence is the comparison of $\omega(C_{org})$ in the soils initially containing carbonates and the samples, in which carbonates are removed with a sufficient amount of sulfuric acid. The Tyurin and Walkley–Black methods were used for measuring $\omega(C_{org})$ and the difference between the measured $\omega(C_{tot})$ by HTCO in analyzer and $\omega(C_{inorg})$ by VMM in calcimeter was taken as the reference $\omega(C_{org})$ value (Fig. 2). As is evident from Fig. 2, the $\omega(C_{org})$ values measured with the Tyurin and Walkley–Black methods in the initial soils and the samples with removed carbonates do not deviate from the reference values by more than 35%. The difference of the values for the initial sample and the sample after removal of carbonates by both the Tyurin and Walkley–Black methods does not exceed 7%.

In the current worldwide practice in soil science, the ever more attention is paid to the assurance of soil data quality, both external (interlaboratory comparisons or loopback tests) and internal (https://www.fao.org/global-soil-partnership/glosolan/). As is known, the latter is implemented using either an alternative (reference) method or reference samples. The range of the certified C_{org} values for reference samples is $\omega(C_{org}) = 0.2–9\%$. Any state and departmental reference samples for higher C_{org} values are absent. Correspondingly, another approach (HTCO together with VMM [87]) was used to assess the measurement quality of dichromatometric C_{org} assessment in the carbonate soils with a *wide* range of C_{org} content by elevating the upper limit of the C_{org} content from $\omega(C_{org}) = 8.7\%$ ($\omega(OM) = 15\%$)[1] to $\omega(C_{org}) = 46\%$ ($\omega(OM) = 79\%$). The overall data array for $\omega(C_{org})$ was divided into two subranges, namely, 0.17–10% (99 samples; of them, 18 ones containing carbonates) and 10–46% (54 samples; of them, four containing carbonates) (Fig. 3). The content of soil inorganic carbon falls into the range of 0.3–10%.

In the first subrange, the relative deviation of the C_{org} values measured with the Walkley–Black method from the difference between C_{tot} and C_{inorg} contents amounts to over 25% for the samples with $\omega(C_{org}) \leq 2\%$ (Fig. 4a). Thus, the error of the reference method exceeds the specified error for dichromatometric measurement, amounting to 20%,[1] which is unacceptable. In this case, the quality of the $\omega(C_{org})$ measurement in carbonate soils with the Walkley–Black method[1] using two devices (analyzer and calcimeter) is assessable only for $\omega(C_{org}) > 2\%$. This experimental conclusion confirms and refines the calculation of theoretical relative errors (taking into account the errors of all methods): the measurement quality can be controlled for the samples with the lower $\omega(C_{org})$ content of 2% and $\frac{\omega(C_{inorg})}{\omega(C_{tot})}$ not exceeding 30% (braced in Fig. 5). Consequently, the quality of dichromatometric data for the carbonate soils with $\omega(C_{org}) = 0.17–2\%$ should be controlled only using the reference samples certified according to this method. However, the state ref-

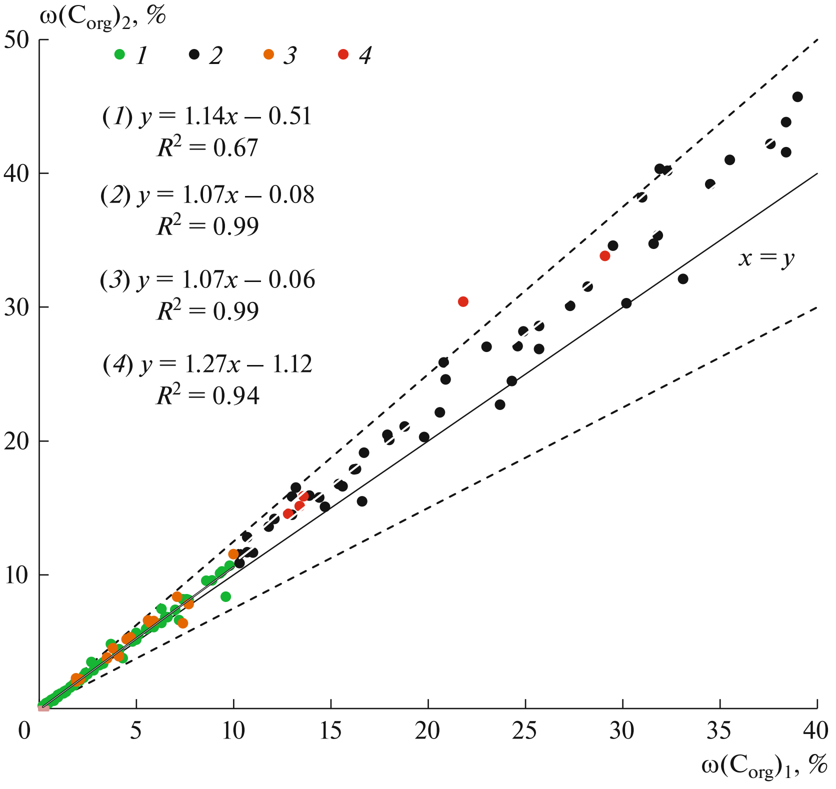

Fig. 3. Correlation between the organic carbon content $\omega(C_{org})_2$ measured with the Walkley–Black method and the reference value $\omega(C_{org})_1 = \omega(C_{tot}) - \omega(C_{inorg})_1$: (*1*) carbonate-free soils with $\omega(C_{org})_1$ of 0.17–10% and (*2*) 10–46% and carbonate soils with $\omega(C_{org})_1$ of (*3*) 2–10% and (*4*) 10–46%. Dashed lines show the boundaries of relative error $\delta = \pm 25\%$.

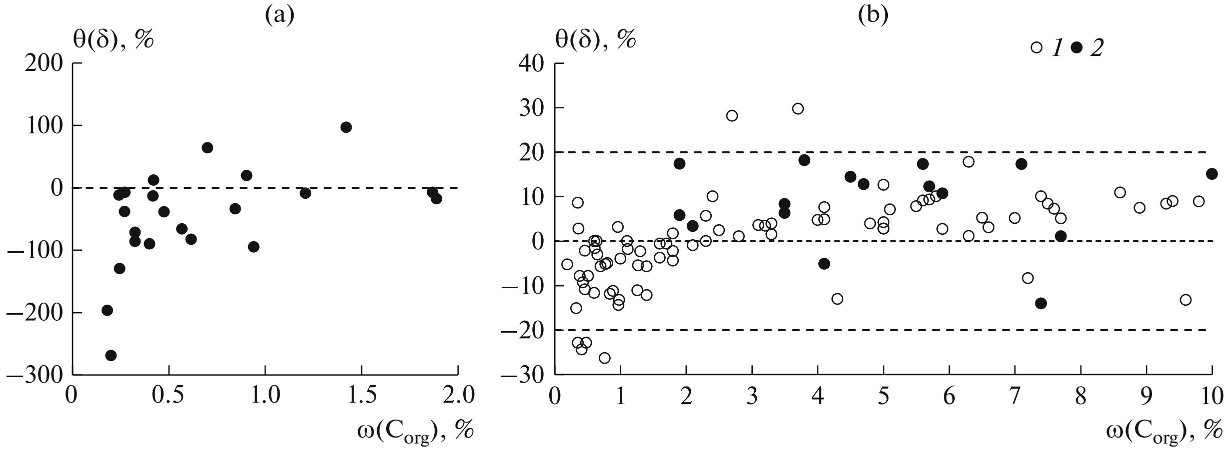

Fig. 4. Relative deviation θ(δ) of the $\omega(C_{org})$ content with the Walkley–Black method from the reference $\omega(C_{org}) = \omega(C_{tot}) - \omega(C_{inorg})_1$ in (a) the carbonate-containing soils with $\omega(C_{org}) < 2\%$, (*1*b) and > 2% and (*2*b) carbonate-free soils.

erence samples of this type have been never met during long-term work of the analytical laboratory.

As for the carbonate-free soils and the carbonate soils with $\omega(C_{org}) > 2\%$, including the soils of the second subrange with $\omega(C_{org}) > 10\%$, the deviation in most cases (93 of 99) does not exceed 20% (Fig. 4b). Moreover, the examined soils with $\omega(C_{org}) > 10\%$ displayed a high correlation of the measured characteristics ($r > 0.9$, $p < 0.000$, and $n = 54$) with the reference values (the difference between HTCO and VMM values). Consequently, an additional metrological study of soil organic horizons is promising to certify the Tyurin and Walkley–Black methods for assessing the C_{org} content in soil at $\omega(C_{org}) > 8.7\%$ ($\omega(OM) > 15\%$).

Note that the majority of the C_{org} values measured with Walkley–Black method at its content exceeding 2% are overestimated as compared with the reference value (Fig. 5b). The factors that take into account an incomplete oxidation of organic carbon by dichromate ions under the Walkley–Black conditions amount on the average to 1.24 rather than 1.3. Dichromate ions oxidize even higher part of organic compounds in the range of $\omega(C_{org}) = 10–46\%$ (Fig. 3, deviation from the $y = x$ line). In this case, the correction line decreases from 1.3 to 1.15. This additionally confirms the variability in the value of this correction factor, which depends on the nature of soil organic compounds and, consequently, on the soil type, conditions of OM formation, range of $\omega(C_{org})$ values in sample, and so on.

Note in addition that the absolute deviation for the results of $\omega(C_{org})_2$ obtained with the Walkley–Black method (Fig. 4) in carbonate-containing soils is determined by the errors of three methods: $\theta(\Delta) = \omega(C_{tot}) - \omega(C_{inorg}) - \omega(C_{org})_2$. That is why, the relative deviation $\theta(\delta)$ is that high at a low C_{org} content (Fig. 4a).

Gravimetric method (soil weight LOI) is regarded as an economical, ecologically friendly, rapid, simple, and relatively inexpensive technique for assessing the content of both carbon species [15, 100, 105, 108]. This method requires conventional equipment available in the majority of laboratories: analytical balance, drying cabinet, incinerator, and porcelain crucibles. This method is based on soil ignition at a high temperature for a certain time interval and is mainly used to measure the OM content in soils at its content over 15% (mats, litters, peat, and so on) [1], as well as to recalculate the data of elemental analysis per incinerated soil.

The adherence to temperature regime is the most important requirement especially when measuring $\omega(C_{org})$ in carbonate-containing soils. However, the relevant literature and reference protocols lack any uniform recommendations for heating conditions. As it is believed, the optimal temperature is determined, on the one hand, by the degree of OM removal (T = 500–600°C) and, on the other hand, by minimization of the loss in weight caused by the decomposition of carbonates (T = 750–850°C). Some guidelines recommend the temperature of 450°C [42] or 500°C [63]. However, a complete decomposition of soil organic compounds is reached at T= 550°C [54]. The presence of copper, iron, manganese, and magnesium carbonates as well as complex carbonates decomposing at T= 380–600°C interferes with the accuracy in measuring $\omega(C_{org})$ [53, 73, 101].

This method is used to directly measure the soil weight LOI (as is believed, all organic compounds incinerate at this temperature); correspondingly, the share of C_{org} in the removed compounds is necessary to calculate $\omega(C_{org})$ (Fig. 5). According to the review by Pribyl [75], the commonly recognized C_{org} share in the so-called OM of $\frac{\omega(C_{org})}{\omega(OM)} = 0.58$ (1/1.724) is not universal [63]. Its values according to different published sources can be pooled into the range of 0.4–0.71 [56, 75, 81, 87]. The variability of the measured $\frac{\omega(C_{org})}{\omega(OM)}$ ratio is associated with different natures of organic compounds in soils.

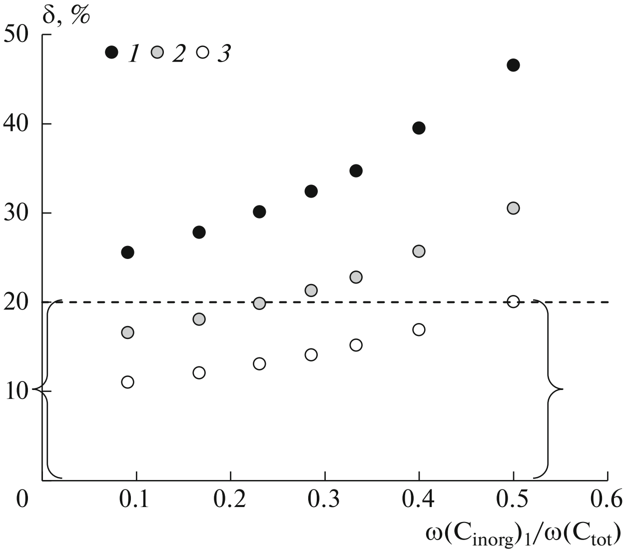

Fig. 5. Calculated relative error (δ) of the measured $\omega(C_{org})$ contents of (*1*) 1%, (*2*) 2%, and (*3*) 5% in carbonate-containing soils using two methods depending on $\frac{\omega(C_{inorg})_1}{\omega(C_{tot})}$.

Shamrikova et al. [87] analyzed 153 soil samples using gravimetric technique. The contents of organic compounds measured by this method in the $\omega(C_{org})$ range of 0.2–5% are overestimated by 85 to 18%, respectively. Consequently, the lower limit of $\omega(C_{org})$ measurement is 5% (further, the samples with $\omega(C_{org}) \leq 5\%$ were omitted). A comparison of the $\omega(C_{org})$ measured by different methods and the OM amount determined according to soil weight lost-in-ignition (72 soil samples were carbonate-free and 16 contained carbonates; Fig. 6-I) allowed for the assessment of $\omega(C_{org})$ in the organic compounds removed from the soil heated to T= 550°C, which amounted to 0.43–0.48 (reference value $\omega(C_{org}) = \omega(C_{tot}) - \omega(C_{inorg})$; reference method, Walkley–Black technique).

In addition to the decomposition of organic compounds, other processes take place during soil heating. This factor to a greater degree depends on soil mineralogical composition and the content of clay and col-

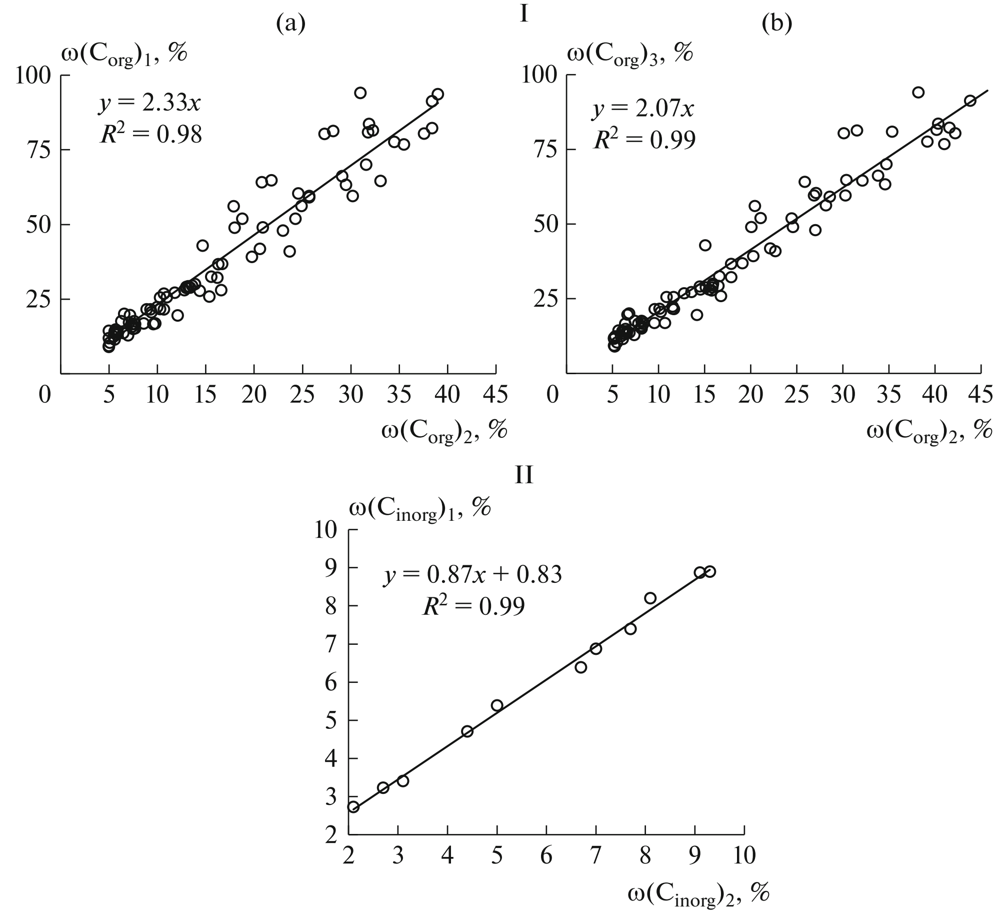

Fig. 6. Correlations of (Ia and Ib) the organic and (II) inorganic carbon contents measured by different methods: calculation according to high-temperature catalytic oxidation in combination with volumetric technique, $\omega(C_{org})_1 = \omega(C_{tot}) - \omega(C_{inorg})_1$; Walkley–Black method, $\omega(C_{org})_3$; gravimetric method, $\omega(C_{org})_2$ and $\omega(C_{inorg})_2$; and volumetric method, $\omega(C_{inorg})_1$.

loid fractions, for example, removal of chemically bound water. Crystalline hydrates lose water when heated (T = 105–550°C) [100]. The carbonates with higher volatility decompose in the same temperature range [20]; in particular, azurite, malachite, siderite, and rhodochrosite (T = 380–500°C); sodium hydrocarbonate (T = 60–200°C) [20, 53, 101]; and magnesite and dolomite (T = 600–800°C). Magnesium carbonate commences decomposing at T = 500°C. Gypsum and sulfide minerals can emit gas products at high temperatures [21, 82, 100]. Thus, the presence of copper, iron, manganese, magnesium, and sodium carbonates in soils, as well as complex carbonates can distort the results of $\omega(C_{org})$ measurements.

Gravimetric method makes it possible to assess $\omega(C_{inorg})$ too by sequentially heating a soil weighed sample at T = 550°C and then at $T \geq 800$°C assuming that only gas decomposition product of carbonates, CO_2, is removed at $T \geq 800$°C. However, on the one hand, halides decompose at $T \geq 800$°C as well and, on the other hand, sodium carbonate completely decompose only at T = 1000°C [57, 75, 92]. Correspondingly, T = 925°C, which was proposed to assess the content of carbonates [18], looks debatable.

A comparison of volumetric and gravimetric methods for assessing the inorganic carbon content in 23 soil samples for the $\omega(C_{inorg})$ range of 0.3 to 2% demonstrated that the latter method overestimated its value by 160 to 17%, respectively. In the $\omega(C_{inorg})$ range of 2 to 4%, the overestimation considerably decreased (by 28 and 8%, respectively). As for the higher contents, the discrepancy between the values obtained by these two methods did not exceed 4% (Fig. 6-II).

At an insignificant difference between the costs of a calcimeter and an incinerator, a smaller number of factors (except for random) affects the data obtained using calcimeter and decreases the accuracy of $\omega(C_{inorg})$ quantification as compared with gravimetric method [87].

Instrumental methods for thermal decomposition of carbon-containing compounds. Recently, soil research practice adopts alternative methods for quantification of different carbon species making it possible to resolve the problems with incomplete oxidation and removal of carbonates and exclude the use of harmful reagents. These are examples of the methods utilizing the thermolability of organic and inorganic compounds [10, 48, 102]. The combination of various methods for thermal analysis (thermogravimetry, differential scanning calorimetry, and gas emission analysis) in a single approach makes them a useful tool for soil research [85].

Vuong et al. [99] tested the capabilities of thermal imaging in quantifying both carbon species in soils and artificial samples and inferred that this method could be more reliable as compared with the traditional techniques. Thermal analysis was implemented for soil studies [10] using a Netzsch STA 409 PC Luxx synchronous thermal analyzer. The C_{org} content was assessed according to CO_2 emission in the range of $T = 120–550°C$ and C_{inorg}, $T = 550–850°C$. The authors believe that the additional advantages of this method are rapid assay, relatively low cost, and simplicity. The point of its inexpensiveness is rather dubious because not any chemical laboratory can afford a derivatograph.

Pillot et al. [73] demonstrated the feasibility of carbonate quantification in soils using Rock-Eval pyrolysis. The Rock-Eval 6 pyrolyzer measures the content of CO_2 emitted by decomposed carbonates of different metals based on the temperature gradient and identifies the nature of metal carbonate according to decomposition temperature.

Thus, the thermal analysis of soils retain the limitations mentioned when characterizing gravimetric method.

Spectroscopy. New methods for quantification of both soil carbon species—reflectance spectroscopy in the visible—infrared (Vis-NIR, 400–2500 nm) and mid-infrared (MIRS, 4000–400 cm^{-1}) with measuring diffuse reflectance coefficient [14, 30, 46, 93] are actively developed in the last 30 years.

A number of advantages of soil spectroscopic analysis are undeniable as compared with the traditional wet chemistry methods [12, 48]. The data recording in both ranges is very rapid (one scanning takes several seconds); sample preparation is mainly reduced to soil drying and grinding; any destruction of analyzed material is unnecessary; and soil is not spent during scanning. In addition, the spectrum of a single scanning allows several soil parameters (pH, total nitrogen, particle size composition, cation exchange capacity, and so on) to be simultaneously assessed. Correspondingly, spectroscopy makes it possible to avoid the potential variation in the soil characteristics associated with sampling [90].

Development of the technology of infrared spectroscopy set the stage for the accumulation of soil spectral libraries covering the territories of different spatial scales [17, 30, 62, 70]. Some calibration databases accumulate the information about soils on a national (France [46] and China [89]), continental (Europe [94]), and global [97] levels.

Spectrometers are rather expensive. In particular, an ASD Labspec spectral radiometer for Vis-NIR soil assay reaches $65 000. However, the cost efficiency is very high because tens of thousands of soil samples are analyzed, which gives a considerable payoff as compared with the initial investment [9, 29]. In total, these advantages provide a higher performance and lower cost of soil quantitative analysis as compared with the routine laboratory techniques [41].

This forms the background for an optimistic assertion [48] on the expected displacement of traditional physicochemical methods in soil analysis by spectroscopic approaches the availability of comprehensive spectral databases provided. The experts worldwide unite their efforts to reach this goal. The Global Soil Laboratory Network is a major contributor to the development of all kinds of spectroscopy for soil analysis.

CONCLUSIONS

In the epoch of global changes in environment, the monitoring of organic carbon is most relevant, including its content in soils. The demand for an adequate assessment of soil organic matter content as a key characteristic of soil fertility is ever increasing in terms of the problems in food safety as well. The integration of the data obtained by different methods frequently requires the use of correction factors. Correspondingly, the comparison of the methods for quantification of soil characteristics becomes most important for the integrated databases, inventory of soil resources, mapping, and prediction changes in the soil cover.

Our comparative analysis of the advantages and disadvantages of the corresponding methods can enhance the informed choice of the approaches to quantification of organic carbon in carbonate-rich soils. The need to further compare the data for soils in different geographic zones remains evidently relevant. In terms of the search for correction coefficients, it is important to use reference methods. The external (assurance of the qualification of soil laboratories via interlaboratory comparisons and loopback tests) and internal controls, as well as prevention of changes in the methodical standards will improve the measurement quality. Elaboration of standardized and comprehensive protocols comprising the sampling strategy (design, depth, and time), storage conditions, and analytical techniques, as well as harmonization of the collected data remains in demand.

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ETHICS APPROVAL AND CONSENT TO PARTICIPATE

This work does not contain any studies involving human and animal subjects.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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