

A novel single-run dual temperature combustion (SRDTC) method for the determination of organic, in-organic and total carbon in soil samples

Isabella Bisutti, Ines Hilke, Jens Schumacher, Michael Raessler*

Max-Planck-Institut fuer Biogeochemie, Hans-Knoell-Strasse 10, D-07745 Jena, Germany

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Abstract

The quantification of organic (OC) and inorganic carbon (IC) in soils provides an essential tool for understanding biogeochemical processes. Examples of its potential application are the assessment of the humification degree of soil organic matter, the calculation of carbon fluxes and budgets in terrestrial systems on a regional and global scale and the investigation of the carbon storage potential of soils. The verification of changes in carbon stocks requires an extensive number of samples as well as precise and reliable analyses.

Due to the wide variation in the concentrations of the two forms of carbon in solid samples, the exact distinction is very difficult. We present the advantages of a single-run dual temperature combustion method (SRDTC) at 515 °C for OC and 925 °C for IC, which allows the determination of OC, IC and total carbon (TC) within one single analytical run. The three parameters are analyzed in less than 30 min. Additionally, the method is characterized by a significantly reduced variability and low operator bias, as there is no need of chemical sample pre-treatment. It is applicable to a broad range of varying OC and IC contents, which is demonstrated by the use of numerous synthetic soil mixtures that have been analyzed. Furthermore, SRDTC indicates the presence of thermally instable carbonates, like magnesite, in the sample. Use of silver boats as a catalytic agent results in an improved distinction between OC and IC in this case. To examine the accuracy and reliability of the SRDTC method, it was compared to other techniques frequently used for carbon determination in soil samples: total combustion by elemental analysis to determine TC and acidification of the sample prior to combustion to determine OC. We will show that the rugged SRDTC method offers a substantial progress for both the reliable and rapid OC and IC determination in soil samples where elemental carbon is negligible.

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1. Introduction

The exact determination and characterization of organic and inorganic carbon (OC and IC, respectively) in solid samples is one of the most extensively performed analyses in geological studies [1] and of growing importance in the environmental field [2,3]. Soils contain a large amount of carbon [4]. The world soil carbon pool is estimated to host 2157–2296 Pg (10^{15} g) of C in the first 100 cm, divided into about 2/3 OC and 1/3 IC [5]. In addition, soils contain almost three times more carbon than the aboveground biomass [6]. Therefore, it is important to quantify changes occurring in soil carbon storage in order

to evaluate the carbon cycle on regional and global scales [4], which establishes the demand for an extensive number of soil carbon measurements to be made [7].

An overview of current methods used for carbon determination in soil samples has recently been compiled by Bisutti et al. [8]. In general, combustion of the sample is used for the determination of total carbon (TC). An acid or an ashing pre-treatment removes IC or OC, respectively, allowing the determination of the remaining carbon fraction by combustion. The complementary part of carbon is afterwards calculated by difference [9]. Several procedures have been developed for the first [10,11] and the second method [12,13]. The major disadvantages of the acid pre-treatment technique are the non-quantitative removal of significant amounts of carbonate carbon resulting in a great variability of the OC results [14], the loss of acid-soluble [10] and/or volatile OC (VOC) [9]. The major problems concerning the ashing pre-treatment are the thermal instability of carbonates [13] and the uncertainty of total OC removal [1]. Furthermore, none

* Corresponding author at: Max-Planck-Institut fuer Biogeochemie, Hans-Knoell-Str. 10, P.O. Box 100164, D-07745 Jena, Germany.

Tel.: +49 3641 576500; fax: +49 3641 577500.

E-mail address: raessler@bgc-jena.mpg.de (M. Raessler).

Table 1
Carbonate minerals in soil samples; impact of temperature and acid

Mineral	T _{DECOMP} (°C) (according to [23])	Impact of temperature	Impact of acid
Calcite (CaCO ₃)	675 ^a	500 °C/7 h no loss of carbonate; 600 °C/4 h loss of about 90% [13]; 780 °C/15 min completely converted [18]	5–25 s HCl 20% [25]; 1 h at 50 °C H ₃ PO ₄ [26]
Aragonite (CaCO ₃) Dolomite (CaMg(CO ₃) ₂)	645 450 ^b	500 °C/16 h loss up to 20% [1]; 800 °C/5 min completely decomposed [18]	Up to 24 h for total reaction [25,26]
Magnesite (MgCO ₃)	425 ^c	500 °C/4 h loss up to 80% [13]	Not dissolved with normal acid treatment [25]; 52 days at 50 °C H ₃ PO ₄ [26]
Siderite (FeCO ₃)	425	550 °C/15 min 93% is decomposed [18]	See dolomite [25]; 14 days at 50 °C H ₃ PO ₄ [26]

T_{DECOMP}: decomposition temperature.

^a Also cited in literature: 800 °C [10], 750 °C [15]; 550 °C [17,18].

^b Also cited in literature: 700–750 °C [24].

^c Also cited in literature: 450 °C [15], 400 °C [10].

of these methods can provide TC, OC, and IC content within one single analytical run [15].

The most promising way for reliable OC and IC determination is a dry combustion at two different temperatures. The method is based on the assumption that OC is combusted at lower temperatures and oxidized to CO₂ in an atmosphere of pure oxygen whereas substantially elevated temperatures are needed for the complete decomposition of IC. Chichester and Chaison [4] as well Rabenhorst [16] performed the OC combustion at 575 °C and the IC combustion at 1000 °C. In both cases, however, all samples had to be analyzed twice due to instrumental restrictions: after previous combustion at low temperature, the samples were run a second time at the higher level once the furnace temperature had equilibrated. Apart from substantially longer analysis times, a possible loss of VOC will not be detected by these methods. Another method for OC and IC determination in soil samples is fractionated combustion [15]. It is objected, however, that thermal dissociation of carbonate material during removal of OC by decomposition at low temperatures was possible [18]. Data from Table 1 indicate that accurate distinction between OC and IC by this method is severely hampered since combustion and decomposition temperatures of carbonates overlap [10]. To overcome this problem, it was suggested to apply lower combustion temperatures, to pyrolyze the sample in a nitrogen stream or to refer to the additional detection of the water signal appearing during combustion. However, at lower temperatures small amounts of OC remain unaffected [1]. Additionally, the assumption that only carbonates are decomposed during pyrolysis is not always true. Even in cases where the formation of water can be correlated with the combustion of OC, water will also be detected together with the CO₂ produced by easily decomposable IC [19].

Despite the problems listed above, combustion at two temperatures is the most straightforward method for OC and IC determination in soil samples if a dynamic heater combined with catalytic post-combustion is used. This fundamental improve-

ment, called single-run dual temperature combustion (SRDTC) allows the determination of OC, IC and TC from one sample in a single analytical run. Additionally, no loss of VOC is possible since all carbon is oxidized. Finally, presence of thermally instable carbonates, like magnesite, is indicated. In the latter case, use of silver boats as a catalytic agent results in an improved distinction between OC and IC. The method was successfully applied to numerous soil samples.

2. Experimental section

2.1. Instrumentation

SRDTC analysis was carried out using a liquiTOC analyzer (Elementar Analysensysteme, Hanau, Germany), in the solid sample version. This analyzer is equipped with two combustion units: a dynamic heater able to raise the temperature from ambient to 925 °C within 160 s, and an oven kept at a constant temperature of 800 °C, containing a Pt/TiO₂ catalyst to achieve complete oxidation of all combustion products released by the dynamic heater. Combustion took place in pure oxygen at a flow rate of 200 mL/min (Fig. 1). The formed CO₂ was detected by IR. To avoid interferences by ambient CO₂, the analyzer automatically pushed out the air that had entered while the sample was inserted. About 20 mg of sample were weighed in stainless steel crucibles that were heated prior to analysis to avoid contamination by C residues. The sample weight depended on the C content and could be extended up to 150 mg in case C contents were very small. Samples containing higher amounts of thermally instable carbonates, like magnesite, were weighed into silver boats prior to combustion. OC was detected at 515 °C and IC at 925 °C.

The analysis was stopped in case no further CO₂ was produced or the maximum integration time was exceeded. In the latter case, data were processed by a software programme developed in our laboratory. Both graphical and numerical data were obtained. The instrument was calibrated with CaCO₃ suprapur

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