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# Fractionated combustion analysis of carbon in forest soils – New possibilities for the analysis and characterization of different soils

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**Abstract.** The fractionated combustion analysis of carbon allows the sequential analysis of the total organic carbon (TOC), total inorganic carbon (TIC) and total carbon (TC) fractions in forest soils. Magnesium carbonate and calcium carbonate of the inorganic carbon fraction can also be detected separately. Soils from various forest stands cause different combustion characteristics of the organic carbon fraction, also depending on the soil profile depth. This automatic combustion technique is suitable to characterize the organic carbon fraction of different soil types.

## Introduction

For the general characterization of forest soils the total carbon (TC) content is determined by combustion analysis with pure oxygen at 1200 °C. At this high temperature all carbon compounds like the organic carbon (TOC) are cracked under the influence of temperature and oxidized under the influence of oxygen to carbon dioxide, whereas the inorganic carbon (TIC) can be detected after decomposition of the carbonates to carbon dioxide by this temperature resulting in the total carbon (TC) content of a soil. Unfortunately the TOC and the TIC cannot be measured separately with this method.

In another laboratory routine method the TOC is generally analyzed directly by "wet oxidation" using potassium dichromate and sulfuric acid as oxidizing agents releasing carbon dioxide from the organic carbon matter. The TOC is then determined by measuring the consumption of dichromate by photometric methods or by titration [1]. Furthermore the TOC can also be measured indirectly by determining the loss due to burning at 550 °C [2], assuming that all organic carbon fractions are oxidized under the influence of air oxygen at this temperature.

The TIC of calcareous soils is calculated indirectly by the difference between the TC and TOC content.

Often the carbonate content of calcareous soils has to be determined according to SCHEIBLER [3], also for a better reproducibility of the measurements. In this process carbon dioxide is released from inorganic carbonate by adding hydrochloric acid to determine the TIC-content of a soil without being able to differentiate between calcium- and magnesium carbonate.

These techniques are expensive and time-consuming and no method gives the TC-, TOC- and TIC-content within the same measurement. For this reason automatic and simultaneous methods for the analysis of different soil carbon fractions are preferred, especially when these methods are applicable to characterize the organic and inorganic soil matter in addition. Therefore investigations have been carried out on soil differentiation described as "dry combustion" and "temperature decomposition" of soils [4, 5].

For reasons of method development the RC-412 Carbon Analyzer of LECO INSTRUMENTS has been tested for its applicability to determine the carbon fractions of forest soils. The results and the possibilities for a routine soil carbon analysis with this instrument will be discussed by some examples.

## Methods

Soils differing in their organic and inorganic carbon characteristics from various forest stands are analyzed with the LECO RC-412 for TOC, TIC and TC by dry combustion and temperature ramping.

To determine the different carbon fractions of soils at one time, about 1 g of dried and homogenized ground soil (< 0.001 mm) is combusted by slowly increasing the temperature from 25 up to 1200 °C. At selected temperatures the increase of the furnace temperature is halted for about 2 min to determine the decomposition characteristics of the TOC- and TIC-fractions at a certain temperature interval. The TOC is detected up to 550 °C according to [2] and the TIC can be detected at temperatures higher than 550 °C when carbon dioxide is released by the decomposition of inorganic carbonate. The temperature increase of the oven from 25–1200 °C is therefore automatically controlled by a computer and can be plotted in dependence on the relative signal change of the IR-cell caused by the released carbon dioxide as shown in

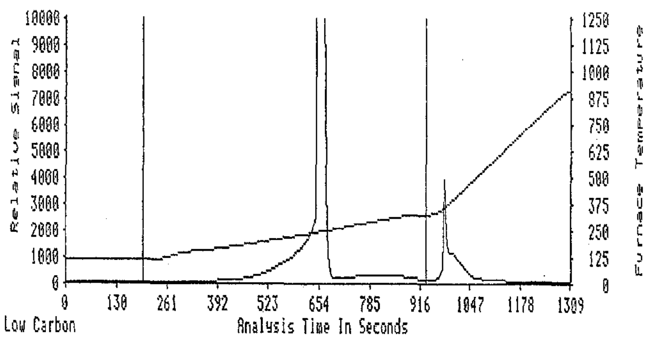


**Fig. 1.** Fractionated combustion analysis of an organic forest soil humus layer. Temperature range 125–900 °C. TC: 29.0%; TOC at 240 °C: 27.0%; TOC at 352 °C: 2.01%

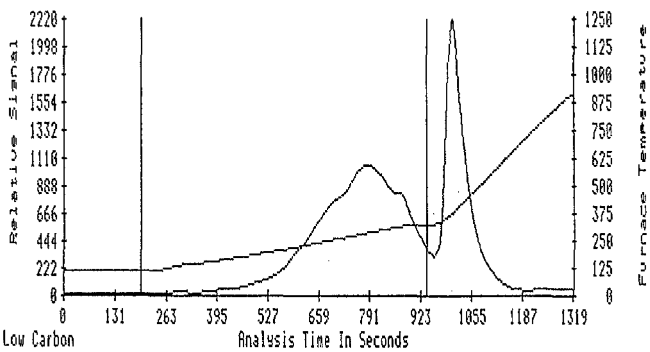


**Fig. 2.** Fractionated combustion analysis of a forest soil (profile depth 0–10 cm). Temperature range 120–900 °C. TC: 5.05%; TOC at 282 °C: 3.24%; TOC at 369 °C: 1.80%

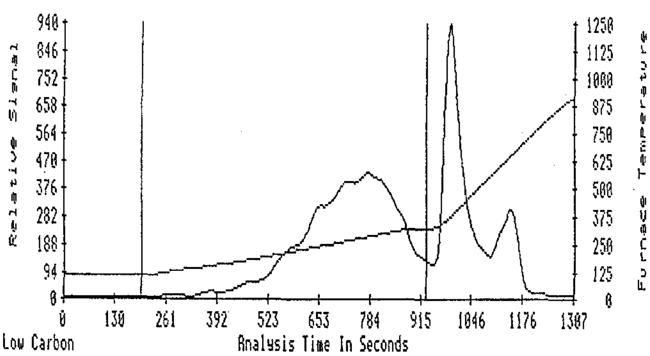


**Fig. 3.** Fractionated combustion analysis of a forest soil (profile depth 10–30 cm; same profile as in Fig. 2). Temperature range 120–900 °C. TC: 2.65%; TOC at 282 °C: 1.58%; TOC at 368 °C: 1.06%

Figs. 1–5. The TC is calculated by adding the individual results of the TOC and the TIC by computer.

The oxygen flow is about 3 l/min using 99.5% pure oxygen at a pressure of 2.8–3.0 bar allowing the detection of 0.02% carbon from 250 mg soil sample. Very low carbon contents of soils will be detected much more easily by using larger soil samples up to about 1 g.

The carbon dioxide emerging under the influence of oxygen by dry combustion is detected by an infrared cell against a reference gas flow. This allows the quantitative determination of the different carbon fractions by integrating the relative signals of the emerging carbon dioxide from the IR-detector at the selected furnace temperature halts. The ramping and the furnace halting time at a selected temperature can be varied depending on the combustion characteristics of the soil.

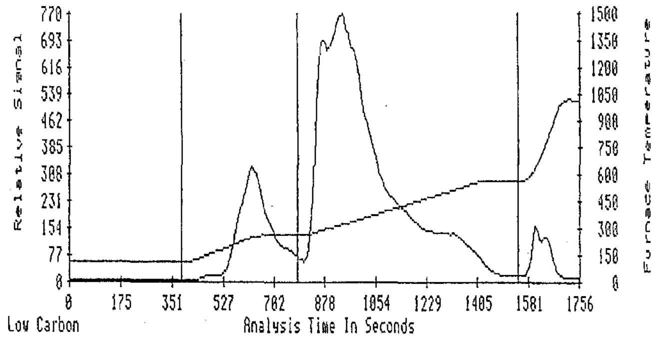


**Fig. 4.** Fractionated combustion analysis of a calcareous forest soil. Temperature range: 130–1040 °C. TC: 1.14%; TOC at 240 °C: 0.19%; TOC at 315 °C: 0.89%: TIC at 627 °C: 0.05%

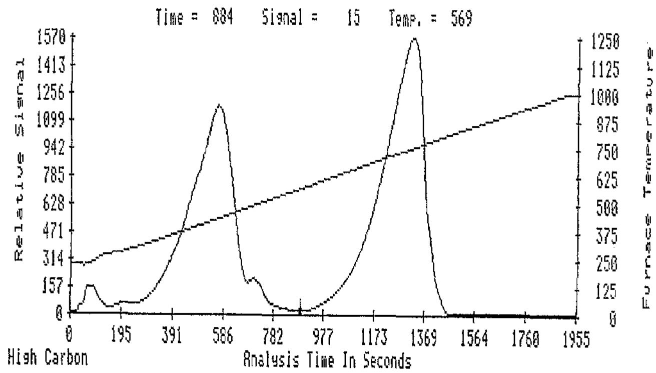


**Fig. 5.** Fractionated combustion analysis of a calcium carbonate / magnesium carbonate mixture. Temperature range: 240–1000 °C

The instrument is calibrated for the carbon determination with calcium carbonate or EDTA since these compounds show very good combustion characteristics. Nevertheless, any other carbon compound with suitable combustion characteristics can be used as well.

## Results

Figures 1–4 show the combustion characteristics of different forest soils at distinct ramping conditions. The relative signal gives the total carbon content at the chosen temperature interval. In addition, the combustion characteristics of a magnesium- and calcium carbonate mixture are shown in Fig. 5.

Naturally, the organic humus layer has the highest organic carbon content which appears in Fig. 1 at 240 °C and 352 °C. In this case no inorganic carbon could be detected at temperatures higher than 550 °C.

It is evident that soils from different forest stands vary in their combustion characteristics, especially within the TOC-fraction (Figs. 2, 4).

The combustion characteristics of the organic soil fractions from the same profile but a differing profile depth are similar (Figs. 2, 3), whereas the TC differs depending on the soil profile depth due to the organic carbon intake into the mineral soil horizon by the humus layer and the lime content of the mineral soil.

The identification of complex bound carbon compounds in soils can cause wide peaks of the relative signal over a wide temperature range as shown in Figs. 2 and 3. In contrast to Fig. 1 they do not clearly show small divided peaks at a small temperature interval. The thermal decomposition of the organic carbon fraction in this case is specific for the forest stand and the soil profile depending on the decomposition status of the organic carbon fraction.

Furthermore, magnesium carbonate and calcium carbonate show peaks of released carbon dioxide, which can be identified at 450° and 750 °C (Fig. 5). These two distinct peak maxima of inorganic carbon dioxide can also be detected in calcareous forest soils (Fig. 4).

## Discussion

The fractionated combustion analysis is applicable to determine the soil combustion characteristics of TOC and TIC. Therefore additional information about the soil carbon composition can be obtained concerning various forest stands and soil profiles. The soil can be characterized with regard to chemical and scientific questions concerning the composition and decomposition of the organic carbon fraction due to the combustion characteristics of the organic soil matter. In addition, this method allows the determination of TOC, TIC and TC of a soil sample within one single measurement, thus saving time, money and manpower without the need of chemical sample pretreatment. Magnesium and calcium carbonate can also be differentiated in calcareous soils by thermal decomposition at temperatures $> 550$ °C. In the future it would be interesting to determine the combustion characteristics of more well known soils from different forest stands, geological substrates and soil horizons, which will surely show the possibilities of this versatile chemical method.

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