Agri - Food

Chemicals

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Energy

Application Note

TIC analysis in soil carbonates

Instrument: TIC DISCOVER

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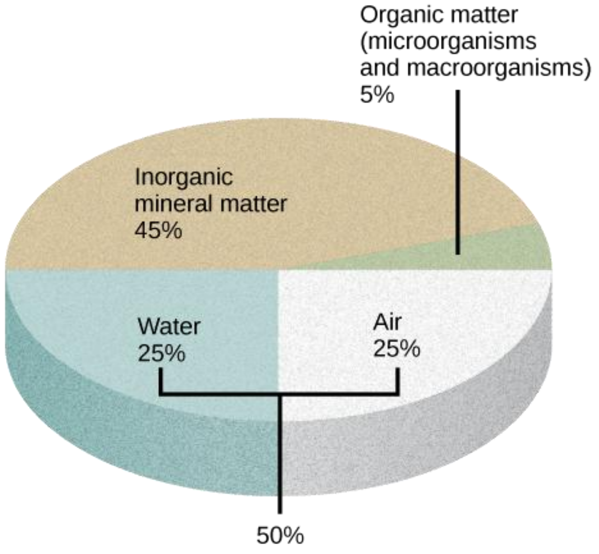
NC TECHNOLOGIES
Innovative Elemental Analysis

Soil composition

Soil develops very slowly over long periods of time, and its formation results from natural and environmental forces acting on mineral, rock, and organic compounds. Soils can be divided into two groups: organic soils are those that are formed from sedimentation and primarily composed of organic matter, while those that are formed from the weathering of rocks and are primarily composed of inorganic material are called mineral soils. Mineral soils are predominant in terrestrial ecosystems, where soils may be covered by water for part of the year or exposed to the atmosphere.

Soil consists of these major components:

- inorganic mineral matter, about 40 to 45 percent of the soil volume
- organic matter, about 5 percent of the soil volume
- water and air, about 50 percent of the soil volume



The amount of each of the four major components of soil depends on the amount of vegetation, soil compaction, and water present in the soil. A good healthy soil has sufficient air, water, minerals, and organic material to promote and sustain plant life.

The organic material of soil, called humus, is made up of microorganisms (dead and alive), and dead animals and plants in varying stages of decay. Humus improves soil structure and provides plants with water and minerals. The inorganic material of soil consists of rock, slowly broken down into smaller particles that vary in size.

The new trend of soil studies: the Inorganic Carbon

Soils are a major player in the global carbon (C) cycle and climate change by functioning as a sink or a source of atmospheric carbon dioxide (CO2). The largest terrestrial C reservoir in soils comprises two main pools: organic (SOC) and inorganic C (SIC), each having distinct fates and functions but with a large disparity in global research attention.

The Organic Carbon

Organic C is a vital component of healthy soils due to its crucial role in nutrient cycling, physical and chemical soil properties, as well as positive impact on microbial functions. This organic C is a major player in global climate change because of its dual roles as sink or source of atmospheric CO2 depending on soil management, plant biomass input, land use, and climatic conditions.

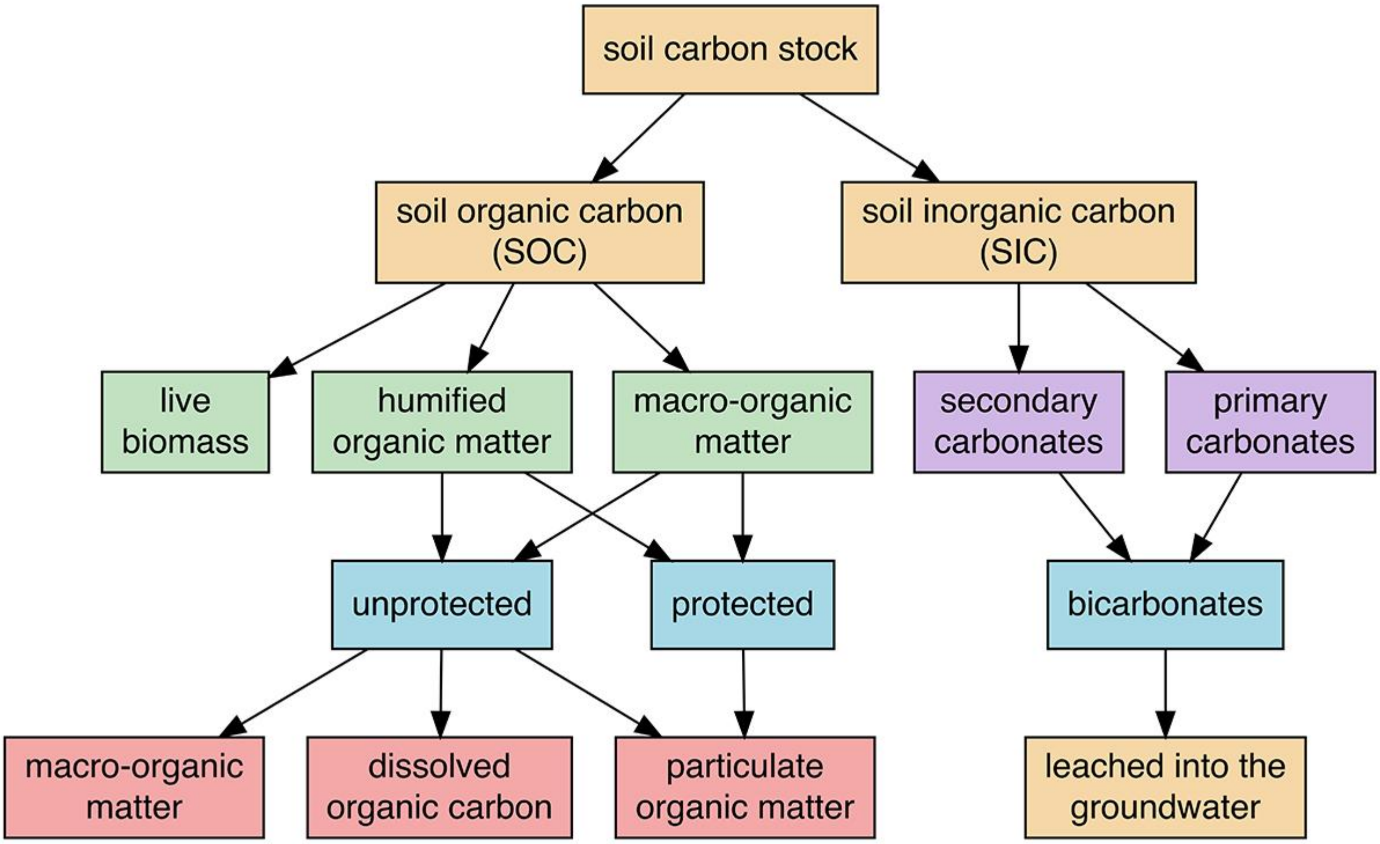
The Inorganic Carbon

The SIC pool is larger than the atmospheric CO2 pool or terrestrial plant biomass C. It is often assumed that SIC changes very slowly over geological time scales because its contribution to biological cycles is much lower than SOC.

Many recent studies, however, report that SIC is far from stable and can be vulnerable to land use changes and intensive crop production, soil acidification, and water flow and recharge – processes that can reduce and even deplete SIC stocks within a few decades.

Soil inorganic C is a major player in the global C cycle and climate change, whose contributions are mainly by releasing CO2 in the atmosphere, that must be understood to achieve mitigation goals related to global land use and climate change.

There is a considerable disparity in the level of global research attention dedicated to SOC and SIC. Although several studies have generally indicated that SIC is an overlooked C pool, but it remains unclear how much specifically SIC is understudied in global soil C research. The differences in the contributions of SOC and SIC pools in global soil C research remain to be quantified.



A vast majority of studies investigating carbon fluxes at the soil–atmosphere interface considered biogenic respiration as the main source of CO2. However, careful consideration is required while estimating the carbon budget of calcareous soils since a significant amount of CO2 emission might originate from abiotic sources.
Ignoring the impact of inorganic carbon in calcareous soil may result in an overestimation of soil respiration, particularly when assessing organic matter decomposition.

Subject to various management practices, soil carbonates could be a major source of C via dissolution and CO2 emission and, together with soil respiration, could have a significant impact on the global C balance.

How to analyse the Soil Inorganic Carbon

Soil inorganic carbon is analyzed by measuring the amount of carbon released after treating a soil sample with an acid, which converts carbonates into CO2 gas.

With our *TIC DISCOVER* all the process of analysis is automatic.

The instrument is equipped with an autosampler up to 68 positions which hosts 40 or 60 ml vials sealed with septum and screw cap.
After filled in the vials with the samples (up to 2 gr), the instrument starts adding automatically acid, through a probe, into each vial.
The acid reacts with the sample and release CO2 (that is the CO2 from the inorganic content).
The probe will collect an aliquot of the CO2 to inject into the basic unit, that detect the amount of carbon through an NDIR detector.

TIC DISCOVER

The *TIC DISCOVER* is a fully PC controlled instrument, with its own software Windows based.
This allows a fully unattended highly reliable automation for overnight operation.

Examples

In this study, total inorganic carbon values were determined in various soil reference materials by using TIC DISCOVER.
TIC DISCOVER accurately quantifies total inorganic carbon in different types of solid samples. The analysis encompassed different types of carbonates such as calcite, aragonite, dolomite, siderite, and rhodochrosite, as well as the potential presence of soda in arid soil regions. The findings underscore the importance of precise inorganic carbon analysis in soil studies, providing valuable insights into soil composition and environmental conditions.

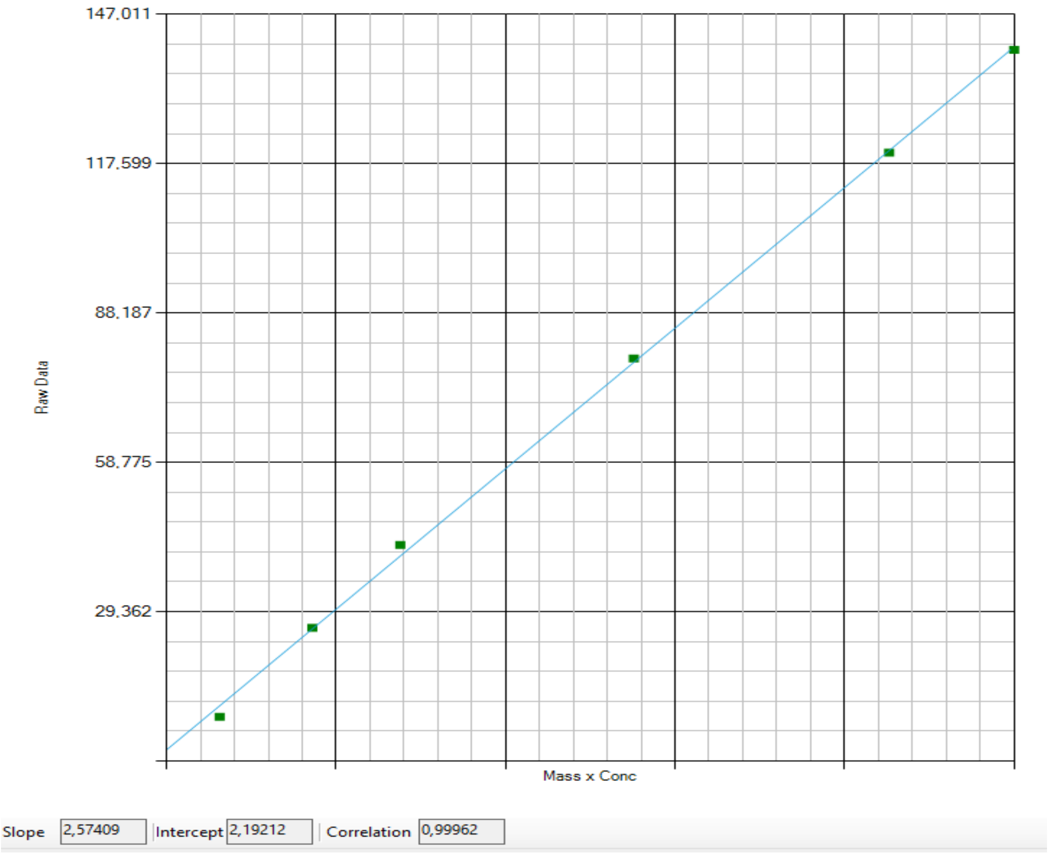
Materials and Methods

First, soil reference materials ranging from 10 to 200 mg were weighed into 60 ml glass vials. TIC DISCOVER purges the headspace, adds set amount of acid, 4 N phosphoric acid (H_3PO_4), stirs and evolved CO2 is swept through Non-Dispersive Infrared (NDIR) detector automatically. The CO2 signal is integrated by software.
Calibration was performed using different weights of CaCO3 – A2O3 solid mixture.CaCO3 – A2O3 are mixed 1:19 ratio to achieve 0.6 % TIC content.
High purity dry air was used as carrier gas and set as 200 ml/min by means of mass flow controller in TIC DISCOVER. Well-controlled flow ensures efficient transport of the evolved carbon dioxide (CO_2) through the system, facilitating accurate measurements by the Non-Dispersive Infrared (NDIR) detector and also long-term calibration stability.
The Total Inorganic Carbon content in soil reference materials was determined by analyzing the signal from the NDIR detector and referencing it to the calibration curve.

Calibration

The calibration points and the corresponding raw data are provided in the table below

Standard ID	Weight (mg)	%TIC	Raw Data
$CaCO_3$-Al_2O_3	5,6	0,6	8,658
$CaCO_3$ in Al_2O_3	15,4	0,6	26,207
$CaCO_3$ in Al_2O_3	24,7	0,6	42,532
$CaCO_3$ in Al_2O_3	49,4	0,6	79,219
$CaCO_3$ in Al_2O_3	76,4	0,6	119,783
$CaCO_3$ in Al_2O_3	89,6	0,6	140,011



Results

Before proceeding with the measurement of soil reference materials, all should be ground and sieved through a 250 µm sieve (70 mesh). After sample preparation, the samples can be weighed directly. Depending on TIC content, sample weight should be between 10 to 200 mg. The weighing amounts for samples with lower TIC content can be increased. From here onwards, the samples can be directly analyzed using TIC DISCOVER.

During measurement, TIC DISCOVER uses 2 ml of acid. This amount of acid can vary depending on the matrix being analyzed and can be set via TIC DISCOVER sofware

Differences in carbonate types within different soil types result in variations in analysis time. TIC DISCOVER can analyze samples containing $CaCO_3$ in approximately 5 minutes. However, in soils with high dolomite content, this time can extend up to 20 minutes. The analysis cycle is completed automatically by TIC DISCOVER software when the baseline is achieved.

During measurement, the first peak is atmospheric carbon dioxide present in the 60 ml glass vial. After purging step, acid is added to the vial, the second peak is a result of CO_2 after reaction of acid with carbonates in sample.

The table below contains a list of soil reference materials used in this application note.

CRM ID & Certification Number	% TIC	Min %TIC	Max %TIC
TIC 0.6 % **	0.6	-	-
BCR – 032	1.39	1.37	1.41
UME RM 9908a	0.99	0.88	1.10
IRMM – 443 – 2 EUROSOIL 2 *	7.09	-	-
B2237 – 431970 *	0.10	-	-
B2182 – 376373 *	0.29	-	-
B2188 – 398157 *	0.83	-	-

*These data are uncertified but provided as additional information.
**Prepared in the laboratory.

The table in the next page provides reference materials, their reference values and the results.

Sample ID	Weight (mg)	%TIC	Mean	RSD (%)	Certified Value (%TIC)	Uncertainty ± (%TIC)	Analysis Cycle-Avg (min)
TIC 0.6 %	61.6	0.59	0.59	1.07	0.60**	NA	~5
TIC 0.6 %	61.1	0.61					
TIC 0.6 %	62.7	0.59					
TIC 0.6 %	58.8	0.59					
TIC 0.6 %	59.1	0.59					
BCR – 032	32.1	1.41	1.39	1.28	1.39	0.02	~6
BCR – 032	30.7	1.38					
BCR – 032	29.9	1.41					
BCR – 032	32.5	1.37					
BCR – 032	32.4	1.38					
UME RM 9908a	41.0	0.96	0.93	2.38	0.99	0.10	~5.30
UME RM 9908a	39.9	0.91					
UME RM 9908a	39.7	0.91					
UME RM 9908a	40.6	0.93					
UME RM 9908a	40.6	0.93					
EUROSOIL 2	10.5	6.83	6.93	1.55	7.09*	NA	~7
EUROSOIL 2	10.3	6.95					
EUROSOIL 2	10.2	7.13					
EUROSOIL 2	9.9	6.85					
EUROSOIL 2	10.3	6.88					
B2182	100.3	0.28	0.28	1.59	0.29*	NA	~7
B2182	101.8	0.28					
B2182	100.9	0.28					
B2182	103.2	0.28					
B2182	103.1	0.27					
B2188	31.5	0.82	0.79	4.44	0.83*	NA	~7.30
B2188	29.9	0.76					
B2188	30.6	0.83					
B2188	32.3	0.74					
B2188	31.2	0.78					
B2237	104.0	0.04	0.04	6.64	0.10*	NA	~5
B2237	99.4	0.04					
B2237	104.2	0.04					
B2237	98.6	0.03					
B2237	104.1	0.03					