

Determination of Different Carbon Species in Solids – Using the Real Chemistry to Obtain the Right Results

When considering carbon and its manifestations in the environment there are different species, which are fundamentally different in their chemical behavior. Neglecting the ubiquitous carbon dioxide and heavy digestible carbides, there are three basic carbon species which are covered in various technical standardizations and legal regulations. The total inorganic carbon (TIC) is typically defined as the carbon which is liberated as carbon dioxide by acid treatment of the sample (carbon in carbonates/hydrogen carbonates). The total organic carbon (TOC) represents all carbon which is bound in hydrocarbons and other organic compounds.

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The elemental carbon (EC) is the pure carbon found in compounds with only carbon-carbon bonds. This can be found in coal, especially in the more valuable types as anthracite coal or coke but also in soot or in its pure form in graphite, diamonds and fullerenes. These three species (TIC, TOC, EC) are called the sum parameters of carbon and are used for various evaluations and purposes, like e.g. for assessment of soil quality in agriculture, quality monitoring of raw materials and final products (e.g. for building materials), or the classification of waste for landfills. In landfills especially the amount of organic matter (TOC) is important, as this is the basis for waste classification. The parameter TOC can be determined according to different norms, e.g. EN 13137 or EN 15936. Various techniques are allowed to be used, but all are based on a treatment of the sample with an inorganic non oxidizing acid as one step of the complete procedure. The carbonates react with the acid and form CO₂, which is either quantitatively determined using the approach of the so-called indirect method (TOC = TC - TIC) or CO₂ is just eliminated from the sample with the aim to measure the TOC directly afterwards. According to the definition of many standard methods the parameter TOC contains the carbon species which are not affected by acid treatment. That's why the acid resistant elemental carbon is also part of the TOC as per definition.

From the environmental point of view, carbonates are not dangerous at all. They are ubiquitous and can be found in nearly all kind of soils and rock formations in different concentrations. Acidified they produce CO₂, but apart from that the influence on the environment or the public health is rather low. Elemental carbon behaves similarly. Under normal conditions it is inert. Various problems may be caused by the organic compounds. Either the substance itself is toxic, or it is subject to microbiological degradation processes. These may lead to a release of complex bound heavy metal ions or the formation of methane.

Thus especially waste or soils destined for a deposition have to

be analyzed for their EC and TOC contents. Classification of the waste and related costs for disposal are based on the TOC value. As stated above it is scientifically and economically reasonable to analyze the parameters TOC and EC in detail. In slags or ashes for instance the amount of EC is much higher than the amount of real organic substances. That is why a lot of regulations allow the subtraction of the EC from the TOC value which defines a new parameter, the biodegradable organic carbon (BOC). Now, it is the analytical challenge to distinguish between the different species and reliably determine the EC and the BOC.

Two mayor techniques are used for this purpose, the temperature gradient method or the separate pyrolysis of “real” organic matter in an inert atmosphere and the detection of the specific components. Using a temperature gradient (according to the draft method DIN 19539) the sample is heated up to discrete temperatures in an oxygen atmosphere and the CO₂ formation within certain temperature intervals is measured. Assuming that all organic substances are combusted to CO₂ between 150°C and 400°C, the results are valued as TOC (=BOC) parameter. Subsequent to that the temperature is increased to 600°C to determine the EC which derives from the CO₂ formation at this temperature. In a final step the temperature is increased to 900°C to decompose inorganic carbon compounds and detect them as TIC.

While this approach sounds simple in theory, measuring real samples is more complex. Organics and the elemental carbon will be oxidized at their discrete temperatures. But carbonates (inorganic carbon compounds) have very different decomposition temperatures. Figure 1 shows several decomposition and ignition temperatures of selected carbonates and other carbon containing compounds. Carbonates decompose and release CO₂ over a wide temperature range starting from 200°C up to 1400°C. Especially the alkaline carbonates of the transition metals as well as mixed carbonates, e.g. dolomite, form CO₂ at temperatures below 600°C already. Using the temperature gradient method these will be detected as BOC or EC and falsify the results.

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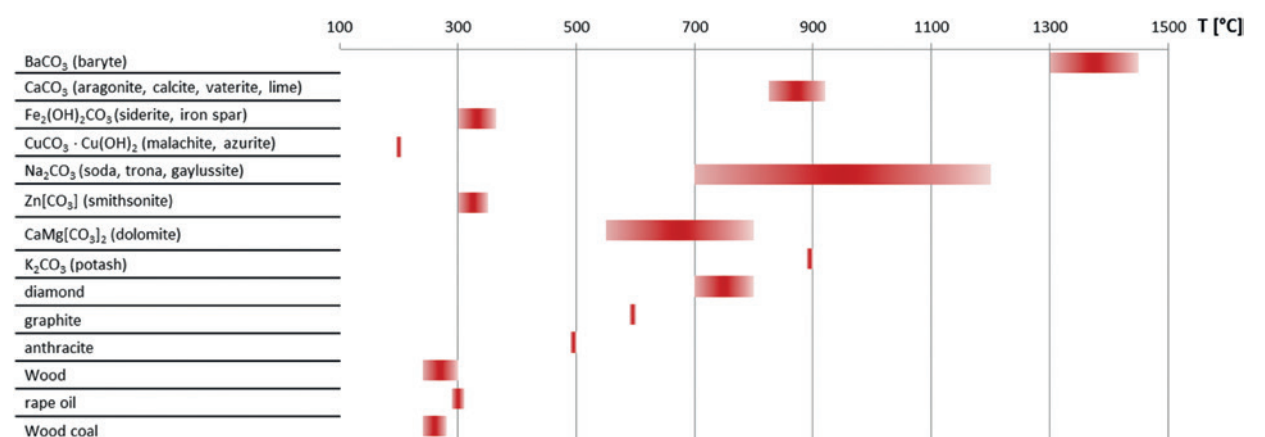


Figure 1: Overview of decomposition temperatures of several carbonates compared to the ignition temperatures of elemental and organic carbon. Ignition temperatures may be lower than the ideal combustion temperature.

Another technique to distinguish between the different carbon species uses their chemical properties. To obtain all relevant parameters three measurements are performed using the multi EA[®] 4000. The Total Carbon (TC) is determined at 1200°C in a pure oxygen atmosphere. All species (TOC, EC, TIC) are reliably decomposed or combusted. The TIC is measured by acidification of the sample and detection of the liberated CO₂. The elemental carbon is determined directly in a third measurement. The sample is heated in an argon atmosphere to a temperature of 850°C or above. Under these conditions, several carbonates decompose thermally and the organic compounds undergo a pyrolysis and form volatile compounds. These gases and the CO₂ formed by the carbonate are discharged from the furnace and will not be analyzed. After this pyrolysis step the system automatically switches back to the oxygen supply and the residual carbon in the sample is oxidized. Since the organics have been pyrolysed, only the elemental carbon, which is not affected by the pyrolysis conditions, is oxidized. Potentially stable carbonates will remain in the samples since the temperature is not changed. Therefore the EC is determined without other influences. The three parameters TC, TIC and EC are obtained by separate measurements based on different chemical approaches. The parameter TOC or BOC can be calculated: TOC/BOC = TC – TIC – EC

Experimental

For full automatic analysis the elemental analyzer multi EA[®] 4000 was configured with a TIC automatic module for automatic acidification of the samples and a solid sampler. Using this setup it was possible to obtain all parameters of interest automatically without any changes to the system. For the TC measurement the sample was weighed in to a ceramic boat and introduced in the furnace at a temperature of 1200°C, in a pure oxygen atmosphere. The measuring gas containing the CO₂ was filtered, dried and directed through a halogen trap. The detection was done using a non-dispersive infrared (NDIR) detector. For the determination of the TIC, an aliquot of the sample was automatically acidified on the sample boat. It was then placed at the inlet of the combustion tube at about 100°C to ensure the complete digestion and liberation of the CO₂ out of the sample. The gases were cleaned, dried and detected as described above. To determine the EC the furnace temperature was reduced to 850°C and the ceramic combustion tube was constantly flushed with argon. A third aliquot of the sample was introduced into this hot and inert atmosphere. The pyrolysis took place for 360 s. After this period the measuring gas was switched to oxygen and the residual elemental carbon was oxidized. Cleaning and drying of the gases were performed as for the TC measurement. The experimental setup is shown in Figure 2.



Figure 2: multi EA[®] 4000 with TIC automatic module and solid sampler FPG48 for the automated determination of different carbon species in solid and selected liquid samples

Table 1: Results of the different carbon species in various sample matrices.

Sample	TC [%]	SD	TIC [%]	SD	EC [%]	SD	BOC [%]	SD
drilling 1	13.9	±0.62	0.04	±0.03	13.6	±0.3	0.64	±0.24
drilling 2	3.04	±0.024	0.08	±0.01	2.93	±0.02	0.02	±0.02
drilling 3	26.99	±0.12	0.33	±0.02	25.79	±0.32	0.79	±0.23
mining waste 1	11.86	±0.15	0.18	±0.01	10.0	±0.09	1.68	±0.1
mining waste 2	14.36	±0.31	0.18	±0.006	13.77	±0.14	0.41	±0.2
ash	10.1	±0.12	0.3	±0.01	9.50	±0.11	0.3	±0.09

Table 2: Results of the automated TC, TIC and TOC in different matrices with the multi EA[®] 4000

Sample	TIC [%]	SD	TC [%]	SD	TOC [%]	SD
wood soil	7.83	±0.06	8.43	±0.03	0.6	±0.08
wood soil	12.33	±0.09	15.73	±0.15	3.4	±0.09
wood soil	1.92	±0.13	30.36	±0.13	28.45	±0.05
agricultural soil	2.64	±0.07	6.96	±0.13	4.32	±0.15
agricultural soil	2.32	±0.07	4.8	±0.08	2.48	±0.1
clay	0.014	± 0.0002	0.033	± 0.0011	0.02	± 0.0008
clay	0.027	± 0.0005	0.05	± 0.0002	0.023	± 0.0007
land fill material	1.21	±0.05	4.77	±0.08	3.57	±0.06
land fill material	0.11	±0.03	10.41	±0.37	10.3	±0.33
marine sediment	0.16	±0.02	4.92	±0.04	4.76	±0.02
marine sediment	1.62	±0.11	2.75	±0.00	1.31	±0.07
dried filter cake	2.1	±0.04	2.87	±0.05	0.77	±0.04
waste treatment sediment	2.54	±0.01	2.89	±0.05	0.35	±0.04
waste treatment sediment	8.84	±0.22	13.06	±0.04	4.22	±0.26
paper sludge	4.58	±0.18	29.39	±0.33	24.81	±0.28

The system calibration was done using different standards. For the TC and TIC calibration CaCO₃ (12% C) or solid dilutions of CaCO₃ in an inert substance (e. g. Al₂O₃) were applied. For the EC calibration pure classy carbon in Al₂O₃ was used.

Complete determination of TC, TIC, EC, BOC

The determination of diverse carbon species is of particular importance for landfills as the organic content defines the waste classification. But also in mining or drilling operation it is of interest to distinguish between EC and BOC. Table 1 shows the results of the carbon species determination in different matrices.

TC, TIC and TOC determination

Depending on the application a full determination of all possible parameters is not always necessary. For instance no EC is expected in agricultural soils or waste material with oil pollution. The flexible method settings of the multi EA[®] 4000 allow the operator to skip additional measurements according to the application. The parameters TC, TIC and TOC can be determined easily and fast using a differential (indirect) method. The TOC is calculated: TOC = TC – TIC. In Table 2 some application examples and their results are shown.

Conclusion

The multi EA[®] 4000 is perfectly suited for the automatic determination of different carbon species without any changes in the system setup. Unlike the temperature gradient approach, which may generate falsified results when carbonates are present, the different carbon species were determined by utilization of their different chemical properties. Carbonates were decomposed by acidification and the produced was CO₂ detected. For the EC determination the sample is treated with a pyrolysis step to dispel possible organic and inorganic compounds. Therefore the EC is measured error-free. The TC is determined at 1200°C. With these parameters the BOC can be calculated. Falsified results from carbonates are not possible. Activating and deactivation of single parameters can be done at any time. The adjustment of procedures to individual application needs is done easily due to the diverse application options of the multi EA[®] 4000.

Furthermore the system can be upgraded modularly for the determination of sulphur and chlorine (halogens) in solids and nonvolatile liquids.

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