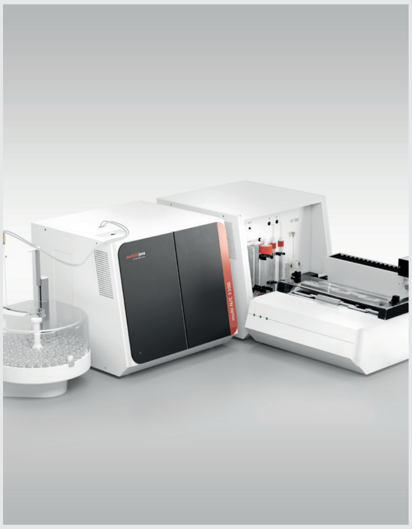
Application Note · TOC Solid Analyzer

Determination of TOC in Oil Shale



Challenge

Can high concentrations of TOC in oil shale samples be determined by the direct method?

Solution

TOC analyzers, like the multi N/C duo systems are capable for an automated, fast and direct determination of TOC in oil shale samples and related matrices.

Introduction

Oil shale is fine-grain sedimentary rock containing significant amounts of organic material in the form of kerogen and/or bitumen that can be used to produce the liquid and gaseous hydrocarbons. Oil shale is defined by its properties characterized by the low solubility of its organic content in low-boiling organic solvents and the generation of liquid (shale oil) or gaseous (oil shale gas) organic products by destructive distillation (retorting). Oil shale needs to be differentiated from bitumen-impregnated rocks (oil sands and petroleum reservoir rocks), humic coals and carbonaceous shale. While oil sands do originate from the biodegradation of oil, heat and pressure have not transformed the kerogen in oil shale into petroleum yet.

In addition to oil production, oil shale can also directly be burned in furnaces as a low-grade fuel for power generation and district heating. However, oil shale mining and combustion leads to significantly higher CO_2 emissions compared to other fossil energies.

In order to determine the geological source rock quality for oil and gas production purposes, the total organic carbon (TOC) concentration is a critical parameter. Oil shale is typically constituted of at least 67% clay minerals, carbonate minerals and less than ⅓ of organic matter. A TOC value of 0.5% by weight is considered the minimum for a suitable source rock, whereas concentrations above 2% are already classified as good quality for oil production usage.

According to DIN EN 15936 (DIN EN 13137 or ISO 10694 provide identical method definitions) two methods of TOC determination can be applied, the difference and the direct procedure. For the difference method two independent measurements are to be performed, once a combustion of the untreated sample for the determination of TC (Total Carbon) and in a second step the determination of the CO_2 which is released by acid treatment of the sample, representing the TIC (Total Inorganic Carbon). The TOC content is then calculated by subtraction: TC – TIC = TOC. The direct TOC method requires only one measurement step plus a sample pretreatment step (acidification) for TIC removal.

Materials and Methods

The direct measurement of TOC was the preferred method for the oil shale samples due to its analysis speed (only one measurement) and short sample preparation time. The samples were directly weighed into ceramic boats and subsequently acidified by adding 500 µL of 10% HCl in two steps to each boat with the goal to destroy and remove all carbonates and hydrogen carbonates present in the samples. The completeness of reaction was tested by careful addition of 100 µL of 25% HCl until no more gas was produced. Afterwards the sample boats were placed on a heating plate at 40 °C and dried overnight (min. 12 h). The TOC determination was then done by direct and catalyst-free combustion of the treated sample at 1200 °C in a ceramic combustion tube in a pure oxygen atmosphere. The formed combustion gases were filtered and dried, the formed CO_2 was detected by an NDIR (non-dispersive infrared) detector.

Sample Preparation

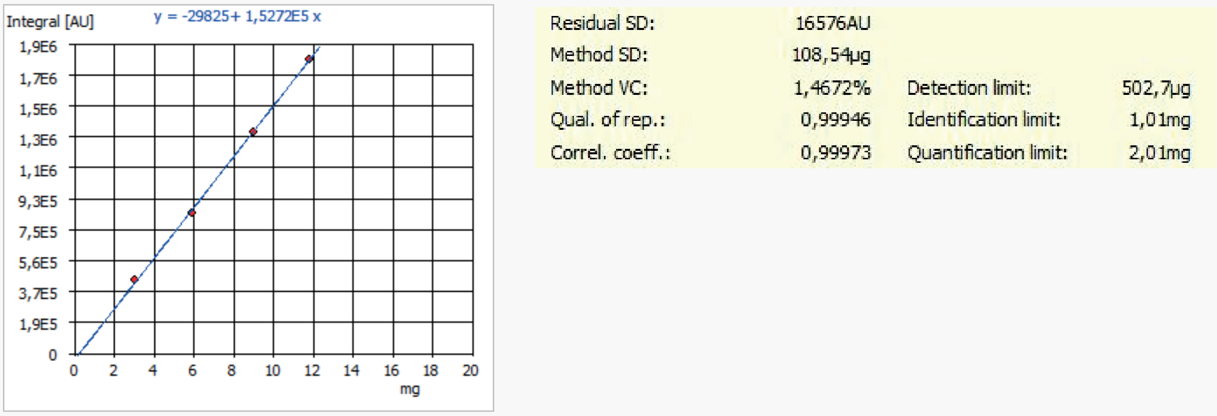
All samples were already ground sufficiently to a small grain size. The fine and dark grey powders were weighed into ceramic sample boats without further homogenization. A set of three boats for each sample and an additional certified reference material was prepared.

Calibration

The solid TOC analyzer has been calibrated using a single standard ($CaCO_3$) applied in different quantities. The resulting calibration curve covers a wide concentration range. Pure calcium carbonate (TC = 12%) was weighed in different portions directly into ceramic sample boats. These boats were introduced into the furnace of the solid TOC analyzer and combusted. The calibration curve is shown in Figure 1.

Table 1: Calibration

Parameter	Calibration Standard	Carbon Content [%]	Weight [mg]	Calibrated Range [mg $C_{absolute}$]
TC	$CaCO_3$	12	25 – 100	3 – 12



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Residual SD:        16576AU
Method SD:          108,54µg
Method VC:          1,4672%     Detection limit:          502,7µg
Qual. of rep.:      0,99946     Identification limit:     1,01mg
Correl. coeff.:     0,99973     Quantification limit:     2,01mg
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Figure 1: Calibration curve and method characteristics

Instrument Settings

Measurements were performed with multi N/C 3300 duo consisting of the main instrument multi N/C 3300 with AS vario ER combined with a high temperature furnace HT 1300 and a solid sampler FPG 48. The following instrument configurations may alternatively be used for the determination of TOC in oil shale or similar matrices by direct or differential method:

Table 2: Further Instrument configurations

Instrument configuration	Operation mode	Additional parameters /benefits
multi N/C 2300 duo (multi N/C 2300 + AS 60 + HT 1300 + FPG 48)	Automated determination of TOC, direct method	NPOC/TOC/TIC/TC determination in water samples, upgradable with TN_b option (CLD, ChD) for water samples
multi N/C 2300 + HT 1300 multi N/C 3300 + HT 1300	Manual determination of TOC, direct method	NPOC/TOC/TIC/TC determination in water samples, upgradable with TN_b option (CLD, ChD) for water samples
multi EA 4000 + FPG 48	Automated determination of TOC, direct method	Upgradable for TS (Total Sulfur) and TCl (Total Chlorine) determination in solid samples
multi EA 4000 + FPG 48 + TIC auto	Automated determination of TOC and/or TIC, difference or direct method, automatic acidification	Upgradable for TS (Total Sulfur) and TCl (Total Chlorine) determination in solid samples

All instruments listed above are equipped with a robust ceramic combustion tube which is not affected by high amounts alkali or earth alkali metals or acid vapors. Combustion temperatures of up to 1300 °C (multi N/C duo systems) resp. 1500 °C (multi EA 4000 configurations) ensure a quantitative digestion of all carbon compounds.

Method Parameters

Standard method settings for non-reactive samples were chosen for the analysis of the oil shale samples. Addition of oxidation additives was not necessary.
The parameter settings for the combustion and sample introduction are summarized in Table 3.

Table 3: Method settings multi N/C 3300 duo

Parameter	Combustion temperature [°C]	Sample introduction speed [mm/min]	Holding position autosampler [mm]	Waiting period at holding position [s]
TC	1200	300	-	0

Results and Discussion

Analysis results of all oil shale samples are shown in Table 4. Measurements were performed as triplicates, the achieved standards deviations (SD) were very low. Typical measuring curves are shown in the Figures 2 on the next page.

Table 4: Results

Sample ID	Sample weight [mg]	TOC Average ± SD [%]	RSD [%]
1	approx. 100	11.5 ± 0.08	0.7
2	approx. 80	15.2 ± 0.22	1.4
3	approx. 80	13.5 ± 0.05	0.4
CRM (soil) 1.8% TOC NCS DC 73319	approx. 300	1.76 ± 0.03	1.7

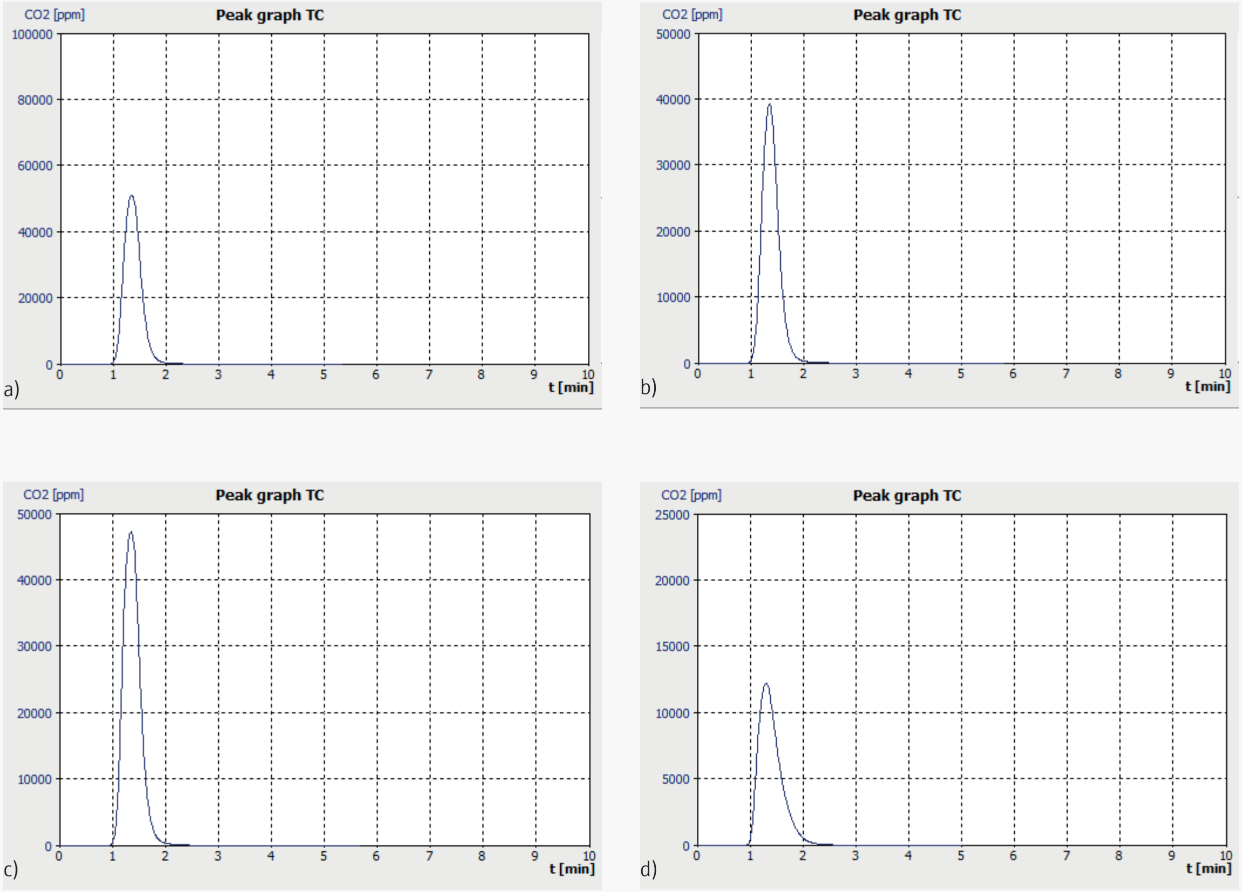

Figure 2: Typical TOC measurement curves for sample 1 – 3 (graph a - c) and certified reference material (soil – NCS DC 73319) (graph d)

Conclusion

The obtained results impressively underline the capability of the multi N/C duo systems to determine the TOC in oil shale samples and related matrices accurately and with high precision. The direct method of determination offers a few advantages for this sample type. A very simple sample preparation procedure can be applied directly in the sample trays (ceramic boats), acidification is done within a few minutes for a smaller batch of samples, drying overnight does not require additional manpower. Fully automated measurement of the treated samples is fast and reliable. The included very robust Focus Radiation NDIR detector allows the calibration of a very wide dynamic measuring range of up to 500 mg carbon absolute. Thus, samples with high amounts of TOC can be analyzed utilizing representative sample amounts, sample weights must not be reduced to a few milligrams only. The applied procedure was in full compliance with DIN EN 15936.
Furthermore, the multi N/C duo systems are suitable for the automated analysis of TOC (TIC, TC), NPOC, POC and TN_b in water samples without any laborious hardware modifications of the instrument. Changing the configuration setup in the software and loading the desired method are simply done by a few mouse clicks the solid TOC analyzer is convert into a fully automated liquid analyzer or vice versa.

References

DIN EN 15936: Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion
DIN EN 13137 Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments
ISO 10694 Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis)

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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