Challenge

Is it possible to determine the TOC in flue ash, slag and filter dust by the direct method?

Solution

The direct determination of TOC in flue ash, slag and filter dust can be performed fast, reliably and cost-efficient with the multi N/C duo systems.

Determination of TOC in Ash, Slag and Filter Dust

Introduction

Fly ash or flue ash is typically a coal combustion product that is composed of fine particles that are driven out of the boilers of power plants together with the flue gases. Ash that falls to the bottom of the boiler's combustion chamber is called bottom ash. In modern coal-fired power plants, fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys. Depending upon the source and composition of the coal being burned, the components of fly ash vary considerably, but always includes substantial amounts of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and calcium oxide (CaO) from the main mineral compounds in mined coal. Minor constituents are various heavy metals and soot or unburnt carbon.

In the case of waste incineration, e.g. in a waste-to-energy facility, the ash may contain higher levels of contaminants than coal ash. In that case the ash produced is often classified as hazardous waste.

The fly ash collected by emission control equipment is either dumped in landfills or recycled, e.g. used as a pozzolan to produce hydraulic cement or plaster or as a partial replacement for Portland cement in concrete production.

Clinker/ slag are terms used for residues and waste from industrial processes like incineration of fossil fuels for power and energy production or metal smelting processes. Clinker is often of a glassy look because of the formation of molten silica compounds in the processes. It is often used as cheap construction material for foodpaths or as an additive in concrete in combination with Portland cement.

The parameter total organic carbon (TOC) is one of the important factors in clarifying the issue of recycling or disposal of fly ash or slag. The basics for the

determination of the parameter TOC in solids are described in the DIN EN 15936 (also: EN 13137). Various techniques can 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 CO_2, which is either quantitatively determined using the approach of the so-called indirect method (TOC = TC - TIC) or the CO_2 is just eliminated from the sample with the aim to measure the TOC directly afterwards.

Materials and Methods

The samples were directly weighted into ceramic boats and subsequently acidified by adding 500 µl of 10% HCl in two steps to each boat for destroying and removing all carbonates and hydrogen carbonates (= TIC) present in the samples. The completeness of TIC removal was tested by careful addition of 100 µl of 25% HCl until no more gas (CO_2) was formed. Afterwards the sample boats were placed on a heating plate and dried overnight at 40 °C. The TOC determination was then done by direct and catalyst-free combustion of the treated samples 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. The direct measurement of TOC was the preferred method for the power plant samples due to its analysis speed (only one measurement) and short sample preparation time. This method is in accordance with the procedure described in several standard methods, e.g., EN 15936, EN 13137.

Samples and Reagents

Sample Preparation

The grey and yellowish samples were directly weighted into ceramic sample boats. Further pretreatment/ homogenization was not necessary because all samples were fine powders. A set of 3 boats for each sample and an additional set for the control standard (mixture A acc. to EN 15936) was prepared.

Calibration

The solid TOC analyzer was calibrated by a single standard ("diluted" $CaCO_3$) applied in different amounts. A diluted standard was chosen due to the expected low carbon concentrations of the samples. Preparation of the diluted standard was made by milling pure $CaCO_3$ (containing 12% C) together with pure Al_2O_3 in a ratio 1:10. The resulting concentration of the standard was 1.2% C, different quantities of this standard were weighted 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 [%]	Calibrated Range [mg $C_{absolute}$]
TC	$CaCO_3$ diluted with Al_2O_3	1.2	17 – 176	0.2 – 2.1

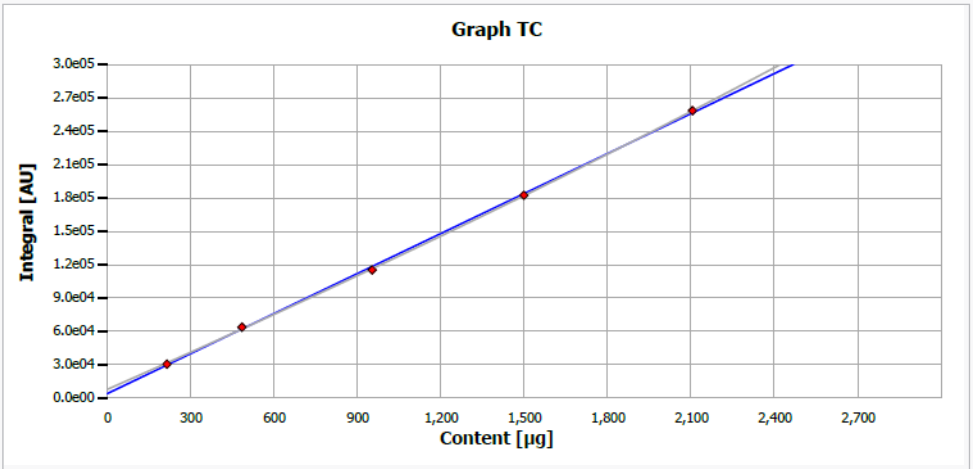

Figure 1: Calibration curve and method characteristics

Instrumentation

Instrument Settings

Measurements were performed with multi N/C 3100 duo consisting of the main instrument multi N/C 3100 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 2100 duo (multi N/C 2100 + AS 60 + HT1300 + 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 2100S + HT 1300 multi N/C 3100 + 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 of 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 flue ash, slag and filter dust samples. An addition of oxidation or retarding agents was not necessary.
The parameter settings for the combustion and sample introduction are summarized in Table 3.

Table 3: Method settings multi N/C 3100S duo

Matrix	Combustion temperature [°C]	Sample introduction speed [mm/min]	Holding position autosampler [mm]	Waiting period at holding position [s]
TC	1200	500	-	0

Results and Discussion

Analysis results of all power plant samples are summarized in Table 4.
Measurements were performed as triplicates. The achieved measurement reproducibility was in the expected range. Typical measuring curves are shown in the Figures on the next page below.

Table 4: Method settings multi N/C 3100S duo

Sample ID	Sample weight [mg]	Result: TOC ± SD [%]	RSD [%]
Slag/clinker	approx. 500	< 0.04	-
Flue Ash	approx. 100	0.79 ± 0.02	2.5
Filter Dust	approx. 100	1.96 ± 0.06	3.1
Control Standard A acc. to EN 15936 (Na_2CO_3, Na_4-EDTA, Al_2O_3, 5% TOC)	approx. 40	4.92 ± 0.04	0.8

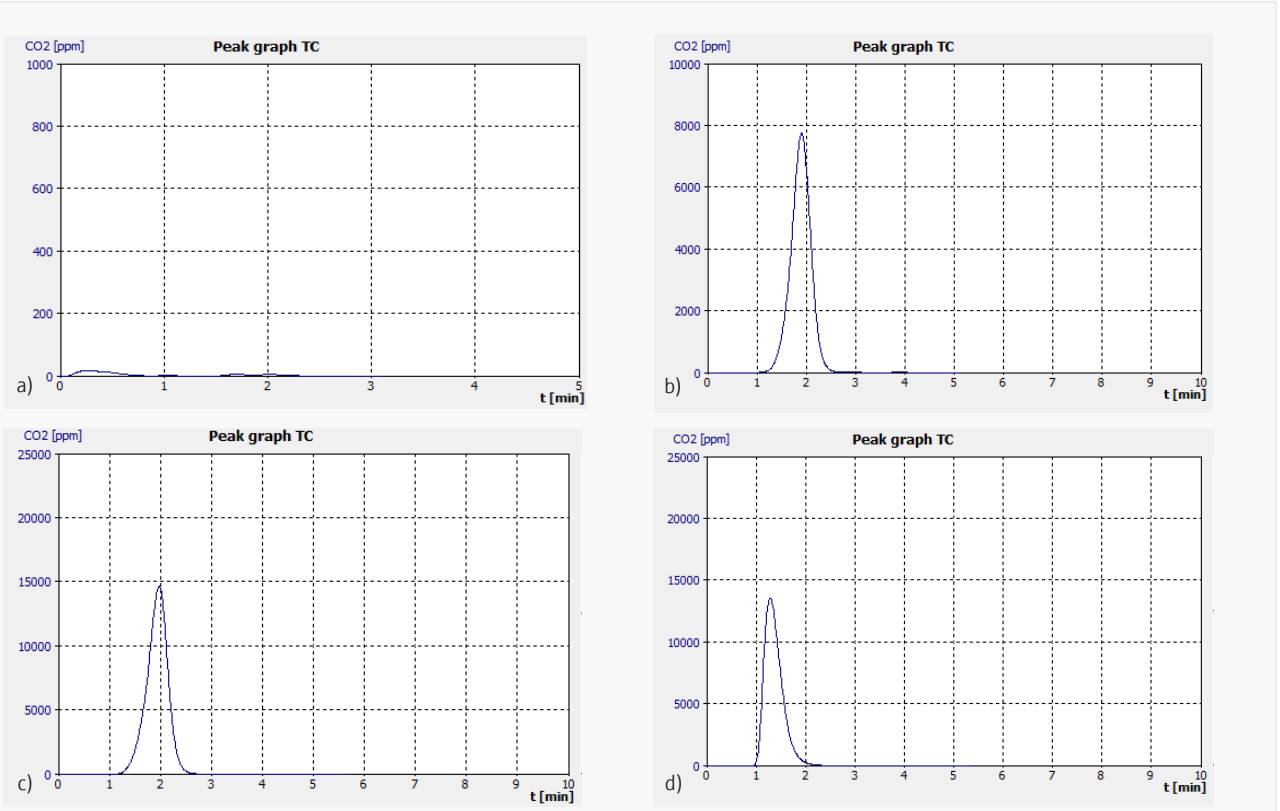

Figure 2: Typical measurement curves for the investigated samples: a) slag/clinker, b) flue ash, c) filter dust, d) control mixture A acc. to EN 15936

Conclusion

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 ceramic boats, acidification is done within a few minutes for a smaller batch of samples, drying overnight does not require additional effort. The fully automated measurement of the treated samples is fast and reliable. The obtained results underline the capability of the multi N/C duo systems to determine the TOC in typical power plant samples like flue ash, slag and filter dust.

The applied procedure was in full compliance with 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:
EN 13137 Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments
EN 15936: Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion

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