

Product Spotlight: G4 ICARUS CS TF

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Introduction

The content of carbon and sulfur greatly influences the chemical and physical properties of organic and inorganic compounds. Material characteristics can be impacted by even trace amounts of these elements. For example, the carbon content in carbides must be precisely controlled because of its influence on the coating strength that is applied to tools and machinery. Further, carbon measurements are used to categorize and value shipments of coal because of its direct correlation with energy production and heat efficiency. Sulfur must also be closely monitored, but unlike carbon, because it is typically undesirable in most materials. Brittleness in steel-based alloys is typically attributed to the inherent sulfur concentration in the raw product. Likewise, emission regulations and policies force boiler plants to strictly monitor sulfur dioxide levels when burning fuels.

One can begin to see why plants and foundries place such emphasis on monitoring carbon and sulfur levels throughout the entire production process, from raw material to final product, and even in byproducts that may provide recycling opportunities. Fortunately, the **G4 ICARUS CS TF** from Bruker is available and becoming an essential tool in the marketplace for these and numerous other applications. Users are discovering that it can provide the reliable and rapid carbon and sulfur results required for their specific materials and applications.

Product Overview

The G4 ICARUS CS TF, often abridged to ICARUS TF by its users, is specifically designed for the direct determination of carbon and sulfur in a wide array

of solid materials. It can directly analyze both inorganic substances like ceramics, cement, limestone, lime, fly ash, and soils, as well as organics such as fuel oils. The ICARUS HF, as shown in Figure 1, incorporates a sleek design featuring two independent modules: a “furnace module” housing a resistance-based tube furnace (TF) for combusting the sample material and liberating the carbon and sulfur; and an “analyzer module” with infrared (IR) cells for detection and quantification of said carbon and sulfur.



Figure 1: G4 ICARUS CS TF with independent furnace (left) and analyzer (right) modules.

The procedure for analyzing sample material with the ICARUS TF is straightforward, requiring only minimal sample preparation followed by an analysis that is controlled by intuitive Windows-based software. Briefly, the sample is weighed directly into a ceramic sample holder using an analytical balance and the mass is electronically transferred to the software queue. The ceramic sample container, termed a ‘boat’ due to its shape, is typically annealed in a separate furnace prior to use to remove any carbon and sulfur impurities. Particularly difficult to combust samples, such as refractory materials, are commonly covered with an accelerant (or “flux”) like tungsten trioxide (WO_3), iron phosphate ($FePO_4$) or tin (Sn) granules to assist the combustion. The boat is subsequently inserted into the high-temperature furnace of the ICARUS, as illustrated in Figure 2, which is capable of

maintaining temperatures up to 1500°C. The combination of this high temperature and an excess of pure oxygen facilitates the requisite combustion.



Figure 2: Sample and ceramic boat being inserted into the furnace of the ICARUS TF.

Carbon and sulfur is subsequently oxidized, again due to the oxygen-rich environment, and liberated as carbon dioxide (CO₂) and sulfur dioxide (SO₂), respectively. The gas stream is purified and measured by solid-state non-dispersive infrared (ss-NDIR) detectors with no moving parts. Interpretation of the IR signal is handled by the software and the concentration of carbon and sulfur, automatically adjusted for its sample mass and the blank and calibration factors, is displayed on-screen. Report printing and sample archiving is easily done with the tools embedded in the instrument software.

Furnace Module

The tube furnace consists of a high-temperature ceramic combustion tube and four resistively heated silicon carbon rods, as modeled in Figure 3. The heating elements are connected in series and arranged around the combustion tube to provide even heating of the sample up to 1500°. The furnace temperature is regulated via a digital thermostat conveniently located on the front panel of the instrument, as shown in Figure 4. The design of the combustion tube has been optimized for efficiently and reproducibly combusting and oxidizing a wide-range of sample compositions and masses.

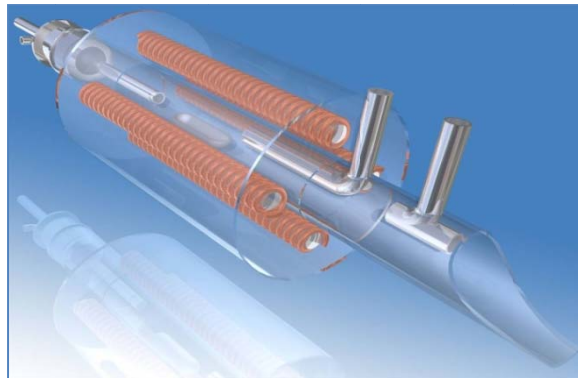


Figure 3. Model of the resistance-based tube furnace.

The gas system of the ICARUS TF is “open” in that the furnace is not sealed after sample insertion (see Figure 5). To prevent atmospheric air from penetrating into the furnace and subsequently altering the carbon results, oxygen is supplied to the furnace at a rate exceeding the amount displaced (i.e., “pulled”) and exhausted by a downstream diaphragm pump.



Figure 4: Front panel of the ICARUS TF furnace module.

Once purified by a magnesium perchlorate drying agent, described later, oxygen is supplied to the furnace at three locations, as represented in Figure 3. Two ports are located behind the sample-containing combustion boat and another is found near the furnace opening. The latter inlet near the tube opening assists in preventing ambient gases from penetrating the furnace. The smaller of the two inlets behind the boat, commonly termed the “lance”, is responsible for jetting oxygen across the sample. Another inlet located behind the boat (not shown in Figure 3) helps purge the system between

sample analyses and also ensures an efficient transport of the combusted products to the furnace exhaust.

A fourth port within the furnace, positioned in front of the sample boat, serves as an outlet for the post-combustion sample gases to pass through. The flow of this stream is assisted by a downstream pump for transporting the CO₂ and SO₂ products to the analyzer.



Figure 5: End-on view of the tube furnace and combustion boat.

To avoid the formation of sulfurous (H₂SO₃) and sulfuric (H₂SO₄) acid by reaction of the SO₂ with condensing water from the combustion, the sample gases pass through a reagent tube filled with a drying agent. The reagent, magnesium perchlorate (MgClO₄), is hygroscopic with a high affinity for any water vapor liberated from the sample. Fortunately this agent does not react with the species of interest, CO₂ and SO₂.

Upon removal of any moisture, the sample stream passes a paper filter to remove any dust particulates formed during the combustion process that could otherwise create restrictions in fittings, etc. Finally, the stream exits the furnace and enters the analyzer module (Figure 6) where the carbon and sulfur content can be accurately determined.

Analyzer Module

In addition to housing the aforementioned IR cells, the analyzer module of the ICARUS TF comprises a collection of reagents for removing gaseous interferences, flow meters for regulating the flow rate, and a diaphragm pump for actively transporting the gas stream. Many of these components are shown in Figure 6.

Lye, or sodium hydroxide (NaOH), fills one of the three reagent tubes. Its purpose is to react with any carbon dioxide (CO₂) impurities that may be present in the incoming oxygen. If not removed the CO₂ impurities would be detected by the CO₂-specific IR cell, thereby causing an artificially-inflated carbon result. A second reagent tube contains additional MgClO₄, while a sacrificial reagent, brass shavings, fills the third. The brass is necessary for sample applications (e.g., soils with high salt content) that release highly reactive vapors upon combusting due to the presence of halogens (e.g., fluorinated- and chlorinated-compounds). If not removed, these aggressive vapors could attack and compromise metallic components in the analyzer, such as brass fittings and the gold coating that lines the IR cell body.



Figure 6: Front panel of the ICARUS TF analyzer module.

Free-oxygen is consumed as the elemental carbon and sulfur oxidizes. Fortunately, the ICARUS TF is equipped with analytical technology that ensures the oxygen is sufficiently replenished. These

devices, like the oxygen-regulating flow meters located on the front panel, ensure an efficient combustion that is reproducible for each analysis.

In addition to controlling the combustion and oxidation processes, the oxygen stream also serves to transport the combusted constituents to the detector. Relying on a static diffusion of the sample stream would result in unnecessary long analysis times and broad peak shapes. Instead, a diaphragm pump is integrated downstream of the furnace that actively 'pulls' the stream through the analyzer, resulting in rapid analysis times of approximately 60 to 120 seconds depending on the sample material and mass.

The IR cell assembly consists of separate detectors specifically optimized for measuring carbon and sulfur. Each detector has an infrared radiation emitter, infrared transducer and a measuring cell (i.e., cuvette) placed in the light path between the emitter and transducer. The cuvette is a highly-reflective gold-coated tube that provides optimal transmission of the IR radiation from the source to the transducer. It is closed on both ends with optical windows and surrounded by optical bandpass filters that pass only the specific wavelength of each particular molecule (e.g., CO₂ or SO₂).

As the sample stream passes through the cuvette the CO₂ molecules absorb a portion of the IR light transmitted by the emitter, thereby attenuating the infrared radiation. The degree of attenuation, called absorption, corresponds to the concentration of CO₂. The same principle applies to the sulfur channel in which the optical filter is tuned to the absorption band of SO₂.

After amplification and rectification the output voltage from the IR detectors is interpreted by an analog-to-digital (A/D) converter and displayed as a more tangible value on the screen (i.e., concentration in % or ppm) at the end of the analysis. The software displays the raw temporal signal profile for both elements simultaneously in real-time, as shown in Figures 7 and 8.

Software

The analysis software of the ICARUS TF shares commonality with all other gas analyzer products offered by Bruker. The primary tasks are organized into four individual screens to maximize convenience and productivity:

Analysis. This is the primary view and where samples are queued and analyzed, allowing the sample peak profiles to be viewed in real-time during each analysis.

Parameters. Configurations that control the sample combustion are defined and saved in this pane.

Statistics. Provides the ability to statistically evaluate the analysis results and generate sample reports.

Calibration. Allows the instrument to be calibrated with results from pure substances or certified reference materials via single-point, two-point or multi-point calibrations.

Applications and Representative Data

The ICARUS TF can analyze a wide range of sample types including minerals, organics and inorganics, as summarized in Table 1.

Coal. The heating efficiency of coal is primarily dependent upon the content of carbon (desirable), and to a lesser extent, the amount of sulfur (undesirable). Accordingly, shipments of coal are analyzed and assigned a value based on the concentrations of each. The ICARUS TF can readily analyze coal for these purposes.

Because coal is primarily composed of carbon, a large amount of CO₂ is produced as it is burned. The ICARUS utilizes this product to its advantage to assess the carbon content via the CO₂-based IR detector. However, the combustion of coal for generating energy produces CO₂ on a much larger scale that is released into the atmosphere. The resulting concerns about global warming provide yet another well-suited application for the ICARUS TF.



Table 1: Concise summary of sample applications possible with the G4 ICARUS CS TF.

Material	CS
Minerals	
Ores	●
Rock	●
Slag	●
Ceramics	●
Glass	●
Cement	●
Lime	●
Gypsum	●
Inorganic compounds	
Salts	●
Carbides	●
Oxides	●
Nitrides	●
Ash	●
Soil, Manure	●
Sludge etc.	●
Refuse etc.	●
Organic compounds	
Coal, Coke	●
Plants, Peat	●
Rubber	●
Tobacco	●

Cement. The ICARUS can readily analyze the components comprising cement, such as limestone (i.e., calcium carbonate), clay, chalk, etc. For example, the calcination process whereby calcium carbonate (CaCO_3) is reduced and CO_2 is formed provides another environmental-based application for the ICARUS. Representative results of a typical cement analysis are shown in Figure 7 and Table 2.



Figure 7: Carbon (blue) and sulfur (green) temporal peak profiles from a single analysis of cement.

Table 2: Typical carbon and sulfur data from the analysis of five cement samples.

Sample Mass (g)	Measured Carbon (%)	Measured Sulfur (%)
0.1066	1.0278	0.9181
0.0970	1.0627	0.9286
0.1240	1.0280	0.8981
0.1044	1.0665	0.8824
0.1001	1.0574	0.8967
<i>Average:</i>	<i>1.0485</i>	<i>0.9048</i>
<i>Std. Deviation:</i>	<i>±0.0191</i>	<i>±0.0184</i>

Fly ash. Fly ash, a byproduct of combustion processes, is typically found in the flue gases of industrial plants and provides multiple applications for the ICARUS TF. Analyzing the fly ash for carbon content can indicate the efficiency of the boiler processes. Further, the fly ash can be recycled and used elsewhere, such as a replacement for cement in concrete. Representative results from the analysis of fly ash can be found in Figure 8 and Table 3.

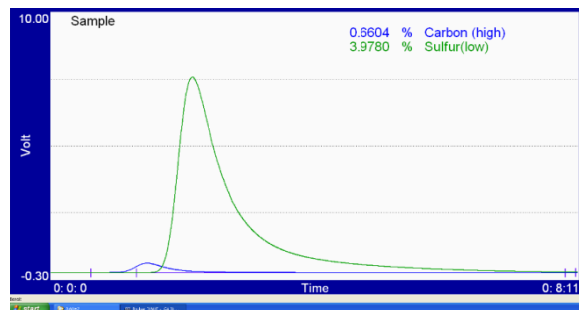


Figure 8: Carbon (blue) and sulfur (green) temporal peak profiles from a single analysis of fly ash.

Table 3: Typical carbon and sulfur data from the analysis of five fly-ash samples.

Sample Mass (g)	Measured Carbon (%)	Measured Sulfur (%)
0.0429	0.6935	4.0496
0.0417	0.6580	3.9661
0.0429	0.6546	4.0399
0.0367	0.6793	4.0032
0.0411	0.6602	3.9996
Average:	0.6691	4.0117
Std. Deviation:	±0.0167	±0.0337

Fractionated Carbon Determination. Organic-bound carbon is a critical parameter that is commonly monitored in water supplies because of its environmental and human health impact. Unfortunately the determination of total organic carbon (TOC) cannot be measured directly because inorganic-based carbon (TIC) also exists in these samples. The two forms of carbon, which together form the total carbon (TC) content in a sample, cannot be distinguished directly by combustion methods. The ICARUS TF, however, provides versatility by offering two techniques for assessing TOC: a “differential” method and a “direct” method.

The differential method relies on combusting a portion of the sample with the ICARUS TF to collect the TC content in the sample. TIC is then determined using another portion of the sample through acidification and decomposition techniques, followed by subsequent measurement of the released CO₂. The TOC content inherent in the sample is then calculated by difference (i.e., $TOC = TC - TIC$).

The direct method of measuring TOC with the ICARUS TF involves removing the TIC from the sample prior to measurement. By acidifying the sample with a strong acid (e.g., hydrochloric acid) and then purging the acidified contents with nitrogen the TIC can be removed. The remaining TOC, also called non-purgeable organic carbon (NPOC), can then be analyzed directly with the ICARUS TF to provide the amount of organic-bound carbon in the sample.

Instrument Specifications

Table 4: Instrument specifications of the G4 ICARUS CS TF.

Measuring Ranges	
Carbon	10ppm – 100%
Sulfur	5ppm – 100%
Furnace Temperature	
Maximum:	1500°C
Maximum permanent:	1450°C
Analysis Time	
	60s nominal*
	*sample mass and concentration dependent
Resolution	0.1ppm
Reproducibility	Better than half the std deviation of CRM
Carrier Gas	O ₂ , 99.995%, ~30psi
Dimensions (w x d x h)	
Furnace	25 x 30 x 19in
Analyzer	25 x 25 x 19in
Electrical Supply	
Furnace	230V, 2.3kW
Analyzer	230V, 500W