



Carbon & Sulfur Determination in Steel Plants and Foundries with ELTRA's ELEMENTRAC CS-i Analyzer

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Introduction

Steel plants observe the decreasing carbon content during the whole steel production process from raw iron with up to 4-5% carbon to a few ppm in stainless steel. The carbon content influences not only the texture, but also the material properties of iron, such as magnetism, hardness or elasticity. For example, cast iron (2-4% C) is brittle but castable; tool steel (0.4-1,7% C) is elastic and ductile, carbon steel (<0.4% C) is forgeable and useable for sheets, tubes and steel girders (1). The element carbon can be present in different forms in an iron matrix, bound to other elements as carbide, solved in the iron matrix or as elemental carbon (2). Due to their impact on the material properties, carbon and sulfur concentrations are listed in the cross-reference book Key to Steel.

Measurement of carbon and sulfur concentrations

That is why it is important to determine the content of carbon and sulfur quickly and efficiently.

Different methods are applied to measure C/S concentrations in steel, iron-based products, or in typical foundry products, such as ferro chromium. Among them are multi-element techniques like spectrometry or specialized carbon/sulfur analysis.

Multi-element techniques like spark OES or GDOES remove a small part of the surface and excite the removed atoms. This excitation causes element-specific optical emission which can be measured by an optical system (e. g. Rowland circle with CCD detection). The emitted wavelengths of the excited atoms depend on their chemical nature and are different for every element. Consequently, it is possible to simultaneously measure carbon and sulfur but also other element concentrations, like manganese or chromium. A successful and reliable measurement requires a flat, clean sample surface. Samples such as wires, granulates, powders or samples with elemental impurities of carbon and sulfur can either not be analyzed with these multi-element techniques or the process of carbon/sulfur analysis is considerably limited (3).

Other spectrometric methods like ICP OES are not restricted to a specific sample shape but require a dissolved sample. Particularly when the carbon and sulfur concentration to be analyzed is very low, like in stainless steel, the blank values of used acids and solvents have to be taken into account.

Carbon/Sulfur analyzers, which are also called combustion analyzers, use a different measurement principle. The sample is melted with the help of an induction furnace and a high flow of oxygen (e. g. 180l/h) is applied. The bound carbon and sulfur are combusted to carbon dioxide and sulfur dioxide which are measured with electronic detectors like infrared cells or thermal conductivity cell.

Before analyzers with electronic detectors for simultaneous carbon and sulfur measurement came up, time-consuming techniques, which took up to 90 minutes to determine one element, were the rule (2). Samples were combusted in a resistance furnace at 1200 °C for carbon and at 1400 °C for sulfur determination. The released gases were quantified via gravimetry, gas volume measurement, coulometry, conductometry or alkalic titration (2). These techniques were error-prone because of the various manual working steps involved and the comparably low temperatures in a resistance furnace

Modern Combustion Analyzers

In contrast to these outdated methods, modern combustion analyzers determine carbon and sulfur concentrations within a few seconds. An analyzer like ELTRA's ELEMENTRAC CS-*i* requires only a nominal analysis time of 40 seconds to measure both carbon and sulfur. For reliable, fast elemental analysis, the CS-*i* uses a power-controllable induction furnace with intelligent lance management, a heated dust trap, and an integrated catalyst. Up to four infrared cells provide a wide measuring range. This set-up allows measuring the carbon and sulfur content from several ppm up to the percentage range and complies with all relevant international standards (table 1) and literature (4). The determination of carbon and sulfur in this way is fast, easy, and can be carried out by academic and non-academic staff alike. The analytical process requires only a few working steps which include weighing the sample in a ceramic crucible, logging it into the software, adding an accelerator, and starting the measuring process. All further steps are controlled by the soft- and hardware of the analyzer without further intervention of the user. For a better understanding of the "black box combustion analyzer", the following paragraphs provide more details about the analysis process.

Table (1): Standards for carbon and sulfur analysis with combustion analyzer

Standard	Released	Title
ASTM E 1941	2010; reapproved 2016	Standard Test Method for Determination of Carbon in Refractory and Reactive Metals and their Alloys by Combustion Analysis
ASTM E 1019	2011	Standard Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques

DIN 24935	1992	Determination of sulfur content of steel and iron by infrared absorption spectroscopy after combustion in an induction furnace
DIN EN ISO 9556	2002	Steel and iron - Determination of total carbon content - Infrared absorption method after combustion in an induction furnace
DIN EN ISO 15349-2	2003	Unalloyed steel - Determination of low carbon content - Part 2: Infrared absorption method after combustion in an induction furnace (with preheating)
DIN EN ISO 15350	2010	Steel and iron - Determination of total carbon and sulfur content - Infrared absorption method after combustion in an induction furnace (routine method)
ISO 13902	1997	Steel and iron - Determination of high sulfur content - Infrared absorption method after combustion in an induction furnace

Table 1: Standards for carbon and sulfur analysis

A) Sample preparation

Sample preparation for combustion analysis includes different processes such as preparing a sample from a liquid melt, reducing the size of a big sample (e.g. an iron bar), or cleaning a sample immediately before analysis (e.g. washing with acetone).

The sample preparation process from liquid iron or steel is described in DIN EN ISO 14284:2002 or the similar standard ASTM E1806. The sample preparation of a melt depends on the iron base to be analyzed (e.g. pig iron, cast iron, steel) and the preferred sampling tools. Common sampling procedures encompass the use of probes or sampling with spoons followed by cooling the sample in a mold. Some mold configurations create a sample for spectrometric analysis and some additional pins for elemental analysis (see figure 2 in the ASTM E 1806-09 standard). Such a mold only needs to be constructed once and can then be used several times. When pins are not available from the mold, a sample for C/S analysis may be obtained by drilling a bigger solid sample. The required speed of drilling and further details are listed in the aforementioned ASTM and ISO standard.

For iron samples, usually no sample preparation (e.g. cleaning) is required immediately before starting a carbon or sulfur analysis. It is important that samples taken during cast iron production or pig iron samples should not be treated with acetone or any other organic solvent, because this could alter the distribution of graphite and iron (ASTM E 1806) which would falsify the measured carbon content.

Other matrices, such as refractories, require a cleaning step before their carbon and sulfur concentrations are measured by a combustion analyzer. The ASTM E 1941 recommends acetone or another organic solvent to remove contaminations from the surface.

B) The combustion process

After preparing a sample of approx. 500 – 1000 mg, the material is transferred into a ceramic crucible and an appropriate accelerator is added. The induction furnace requires metallic accelerators like copper, tungsten, or a mixture of tungsten and tin, to ensure smooth combustion and complete release of the bound carbon and sulfur. The combustion process is started by moving the ceramic crucible with sample/accelerator mixture into the induction coil and starting the furnace. The induction coil creates an electrical field which interacts with the free electrons of the accelerator and in this way the mixture heats up to 2,100°C and melts. Because of the strong stream of oxygen (e.g. 180 l/h) in the combustion zone, the resulting temperature in the crucible is even higher than 2,100°C. The additional heat originates from the oxidizing process of the accelerator and the sample. The resulting temperature is even high enough to melt and oxidize refractories such as molybdenum (melting point 2,623°C).

The choice of the accelerator is important for the combustion process. Whereas tungsten or tungsten/tin mixtures can be used as accelerators for simultaneous carbon and sulfur measurements, copper can only be utilized for carbon determination because of the forming of copper sulphide during combustion which leads to measurement results with too low sulfur concentrations (5). International standards recommend different accelerators for different applications (table 2). Typical amounts of about 1.5 – 2.0 g are applied with a special accelerator spoon to avoid weighing.

Table (2): Overview of accelerators, calibration materials and sample weights

Standard	Measured elements	Recommendation
ASTM E 1941	Carbon	Calibration material: CRM Recommended sample weight: NN Accelerators: iron plus copper or other (tungsten / tin)
ASTM E 1019	Carbon, Sulfur	Calibration material: CRM for carbon; K ₂ SO ₄ for sulfur Recommended sample weight: 1000 mg Accelerator: copper (for carbon), tungsten (for sulfur)
DIN 24935	Sulfur	Calibration material: K ₂ SO ₄ Recommended sample weight 500 mg or 1000 mg Accelerator: tungsten
DIN EN ISO 9556	Carbon	Calibration material: BaCO ₃ ; Na ₂ CO ₃ ; sucrose Recommended sample weight: 500 mg or 1000 mg Accelerator: copper, tungsten, tungsten/tin
DIN EN ISO 15349-2	Carbon	Calibration material: sucrose, CaCO ₃ Recommend sample weight: 1000 mg Accelerator: copper; tungsten/tin
DIN EN ISO 15350	Carbon and Sulfur	Calibration material CRM Recommended sample weight: NN Accelerators: copper or tungsten or tungsten / tin
ISO 13902	Sulfur	Calibration material BaSO ₄ Recommended sample weight: 500 mg Accelerator: tungsten plus pure iron

Table 2: Overview of accelerators, calibration materials, sample weights

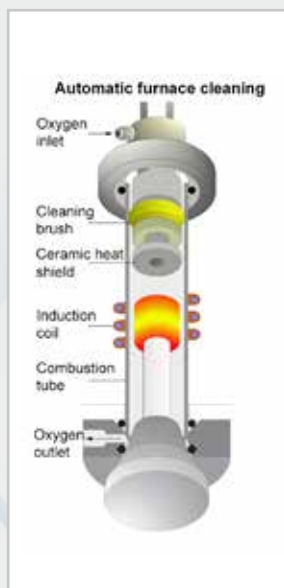


Figure 1: ELEMENTRAC CS-i Induction Furnace

In contrast to a resistance furnace, an induction furnace cannot be set to a constant temperature (e.g. 2,000 °C). The resulting temperature in the crucible is influenced by the chemical composition, the amount of accelerator and sample, as well as by the intensity of the oxidizing process. But it is possible to influence the combustion temperature by reducing the applied power of the induction furnace. For this purpose, the ELEMENTRAC CS-i uses a phase angle controller. In addition, low melting samples like copper or magnesia are analyzed more precisely at reduced temperatures. This improved precision is achieved primarily by reducing the sputtering inside the crucible. Sputtered samples usually condense in the combustion tube, making the bound carbon and sulfur inaccessible.

In addition to the correct choice of accelerator, a sufficient oxygen supply is needed to guarantee complete combustion in a carbon/sulfur analyzer. The intelligent lance management (ILM) of the ELEMENTRAC CS-i provides powerful control of the oxygen supply during the combustion process. For solid metallic samples such as steel, a high oxygen flow (180 l/h) is supported through a lance which focuses the oxygen stream directly on the sample and ensures complete combustion. Dusty samples like fine powdered ceramics or sands may be blown out of the crucible when the oxygen stream focuses directly on them. To avoid this, the oxygen is provided by a second supply which only flushes the chamber. Later in the combustion process (e. g. after 20 seconds), the intelligent lance management switches on the oxygen lance to ensure complete combustion.

C) Heated dust trap and dust management

The combustion of metallic samples generates fine dust which may affect the carbon and sulfur measurement in the infrared cells. To prevent deposits of dust inside the analyzer, the ELEMENTRAC CS-*i* uses a small meshed metallic filter which is located directly behind the induction furnace. This filter - arranged in a heated housing - avoids any condensation of water traces which might result in the measurement of too low sulfur concentrations. Traces of water vapor are found in the combustion gas because of the moisture of the sample and, to a lesser extent, of the oxidized hydrogen bound in the sample. Without a heated dust trap, the water vapor would condense in the metallic filter and absorb the gaseous sulfur dioxide and the formed sulfuric acid would no longer be available for determination in the infrared cells. The heated dust trap of the CS-*i* ensures the complete transfer of both water vapor and gaseous sulfur dioxide into an anhydron tube. This anhydron tube completely removes the water vapor without any negative effects on the sulfur dioxide and its measurement in the infrared cells.

D) Catalyst

During the combustion process carbon dioxide and sulfur dioxide are the primary reaction products formed. A very small amount of carbon monoxide is formed in every induction furnace. Carbon monoxide would not be detected in standard carbon dioxide infrared cells and without an additional oxidizing process, the determination of carbon would show lower results than expected. For converting carbon monoxide into carbon dioxide different chemicals, such as copper oxide or catalytic active substances like platinum are typically used. The ELEMENTRAC CS-*i* uses a platinum-based catalyst which is combined with silica as carrier material. This ensures not only safe and reliable oxidation but also reasonable purchasing prices. An increased catalyst length with temperature control in the CS-*i* guarantees maximum safety for carbon analysis.

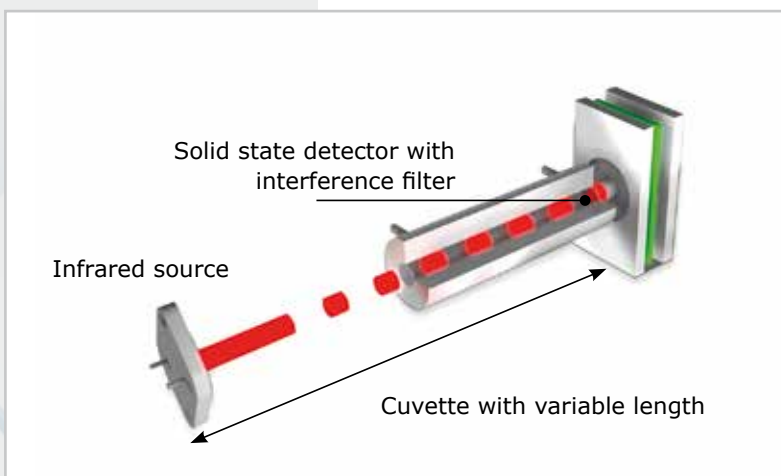
E) Detection

Modern electronic detectors for combustion analyzers are infrared or thermal conductivity cells. Whereas an analyzer with a thermal conductivity cell, as described in the ASTM E 1019-11, can only determine carbon, the ELEMENTRAC CS-*i* uses up to 4 infrared cells to ensure a safe simultaneous carbon and sulfur analysis over a wide concentration range. In contrast to a thermal conductivity cell, the IR cells are element selective which means that the determination of sulfur, for example, is not influenced by the presence of a high amount of carbon dioxide. Infrared cells use the specific wavelength absorption of the carbon dioxide and/or sulfur dioxide molecule. This means that the chemical bonding in the mentioned molecules starts to swing when IR radiation of the corresponding wavelength is applied. Before combustion gases pass the IR cell, the emitter and detector provide a constant electrical signal. With the entry of the combustion gas the detector receives only a reduced amount of light due to the interaction of emitted light with the carbon dioxide or sulfur dioxide molecules. The resulting changing of the electrical voltage of the detector is displayed as peak which can be used for mathematical integration. The measuring data of the CS-*i* in the

appendix show some typical peaks for different matrices. ELTRA provides IR cells with different sensitivities in the ELEMENTRAC CS-*i*, which can be adjusted to suit customer requirements. A short IR path length means a short reaction path of IR light and combustion gas and such a cell is well suited for high element concentration. Increasing the IR path length also increases the reaction path of light and gas molecule and the IR cell becomes more sensitive for low element concentrations.

Although infrared cells are generally a robust detection system, they may nevertheless be damaged by gaseous halogens like fluorine or chlorine. These halogens occur in samples like ores, salts or acidified matrices. To avoid damage of the IR cell, the use of a halogen trap is recommended, as is the usage of a golden IR path for more chemical resistance. The ELEMENTRAC CS-*i* can optionally be equipped with a halogen trap or golden IR cells for maximum safety.

Figure 2: Infrared cells with flexible measuring range



F) Calibration

In contrast to classic measuring techniques, like gravimetry or gas volume measurement, combustion analyzers like the ELEMENTRAC CS-*i* require a calibration process for measuring correct element concentrations. Like spectrometric methods, combustion analysis is a relative measuring method meaning that the peak area of a carbon or sulfur measurement must be correlated with an element concentration. Due to the inductive combustion of samples which guarantees a complete release of the bound carbon and sulfur, C/S analyzers can be calibrated with certified reference materials (CRM) or with primary substances like CaCO₃ or BaSO₄ (Table 2). Whereas the use of CRM is common daily practice, the usage of primary substances provides more safety for samples which are analyzed in a round robin test.

G) Conclusion

Measuring carbon and sulfur concentrations with the ELEMENTRAC CS-*i* is done quickly and easily: sample weighing, applying the accelerator and logging the sample in the software is all it takes. With these few working steps precise and robust carbon and sulfur measurements are possible for a variety of samples and matrices which is illustrated by the following measuring data.

References

- (1) Hollemann Wiberg, Inorganic Chemistry, 33rd edition, 1993, p 1133ff
- (2) Handbuch für das Eisenhüttenlaboratorium; 2nd edition, 2013; Part (1) classic method ; Volume (2): Analysis of metals
- (3) ASTM E 1806-09; page 13
- (4) Handbuch für das Eisenhüttenlaboratorium; 2nd edition, 1998; Part (2) new method ; Volume (2): Analysis of metals
- (5) ASTM E 1941-10; page 2, Note 7

Measuring Data of the ELEMENTRAC CS-i

(1) Steel samples

Steel samples can be analyzed with a sample weight of 500 or 1000 mg and with 1.5 g tungsten as accelerator:

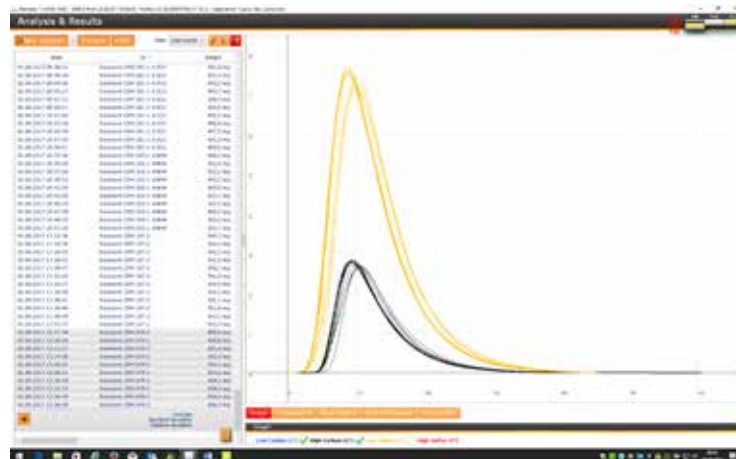
Reference material: ECISS EURONORM - ZRM 079-2 Machining Steel(*)

(*) certified value:

C: 0.596 % ± 0.006

S: 0.192 % ± 0.006

Weight [mg]	Carbon [%]	Sulfur [%]
498.9	0.5981	0.1855
498.8	0.5997	0.1928
501.0	0.5930	0.1913
503.0	0.5974	0.1932
506.7	0.5922	0.1930
503.2	0.5984	0.1946
504.5	0.6002	0.1960
504.4	0.5991	0.1949
504.3	0.5902	0.1893
506.5	0.5955	0.1925
Mean value	0.5964	0.1923
Deviation / relative deviation	±0.0035 (0.6%)	±0.0030 (1.6%)



Reference material: Alpha Resources AR 875 (LOT 1216F) Steel rings (*)

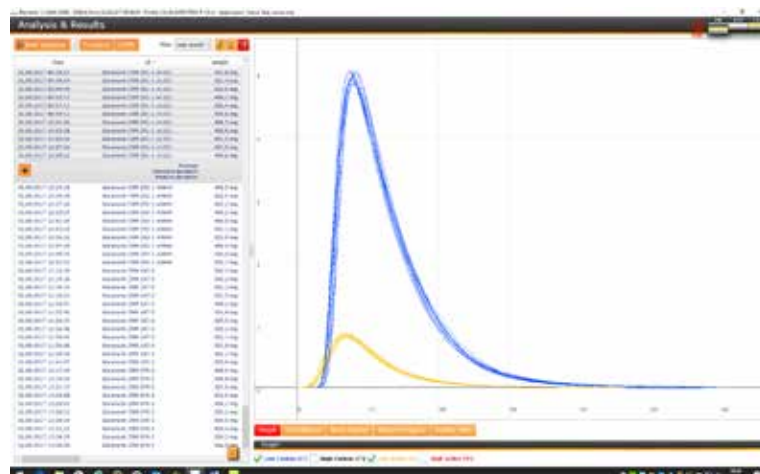
(*) certified value:
C: 0.799 % ±0.017
S: 0.0125 % ±0.0034

Weight [mg]	Carbon [%]	Sulfur [%]
1003.4	0.8005	0.0128
1001.9	0.8003	0.0125
1002.6	0.8012	0.0126
1003.2	0.8007	0.0126
1001.8	0.7971	0.0125
1004.2	0.7952	0.0125
1003.6	0.7962	0.0124
1003.1	0.7976	0.0123
1003.2	0.8020	0.0124
1002.9	0.8024	0.0123
Mean value	0.7993	0.0125
Deviation / relative deviation	±0.0026 / 0.32 %	±0.0002 / 1.21 %

Reference material: EURONORM - CRM 281-1 Highly Alloyed Steel(*)

(*) certified value:
C: 0.048 % ±0.002
S: 0.016 % ±0.001

Weight [mg]	Carbon [%]	Sulfur [%]
501.8	0.0482	0.0163
501.4	0.0479	0.0162
503.0	0.0479	0.0161
506.4	0.0481	0.0161
505.6	0.0481	0.0160
498.5	0.0482	0.0160
498.8	0.0477	0.0158
497.5	0.0479	0.0158
501.5	0.0479	0.0158
499.6	0.0479	0.0161
Mean value	0.0480	0.0160
Deviation / relative deviation	±0.0002/0.4%	±0.0002/1.1%



(2) Cast iron

Steel samples can be analyzed with a sample weight of 500 mg and with 1.5 g tungsten and 0.7g high purity iron as accelerator:

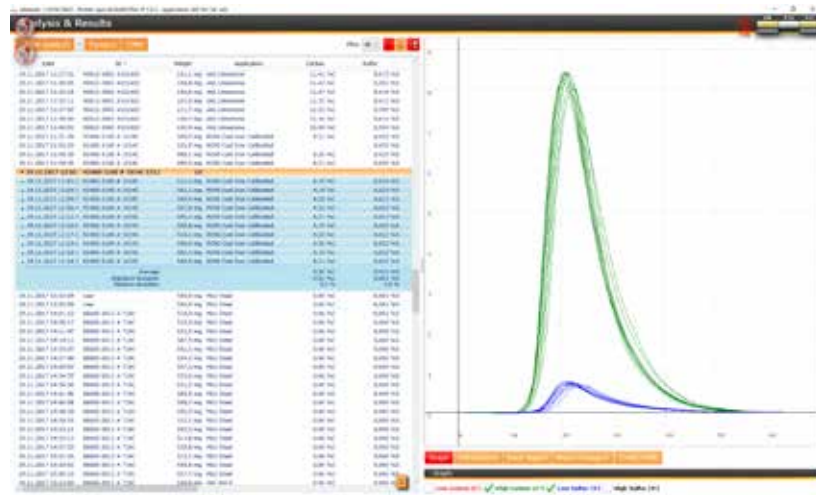
Reference material: ELTRA cast iron 92400-3100 (LOT1014C) (*)

(*) certified value:

C: 4.20% ± 0.06 (1.42%)

S: 0.023% ± 0.002 (8.69%)

Weight [mg]	Carbon [%]	Sulfur [ppm]
512.2	4.19	0.024
501.1	4.19	0.024
509.5	4.20	0.022
507.0	4.21	0.023
505.1	4.21	0.023
500.8	4.19	0.022
518.1	4.20	0.022
500.0	4.20	0.022
502.2	4.19	0.022
500.5	4.21	0.022
Mean value	4.20	0.023
Deviation / relative deviation	±0.01 / 0.2%	±0.001 / 3.54%



(3) Pure Iron

Pure iron samples can be analyzed with a sample weight of 500 or 1000 mg and with 1.5 g tungsten as accelerator. For best precision the usage of a carrier gas purification furnace is recommended.

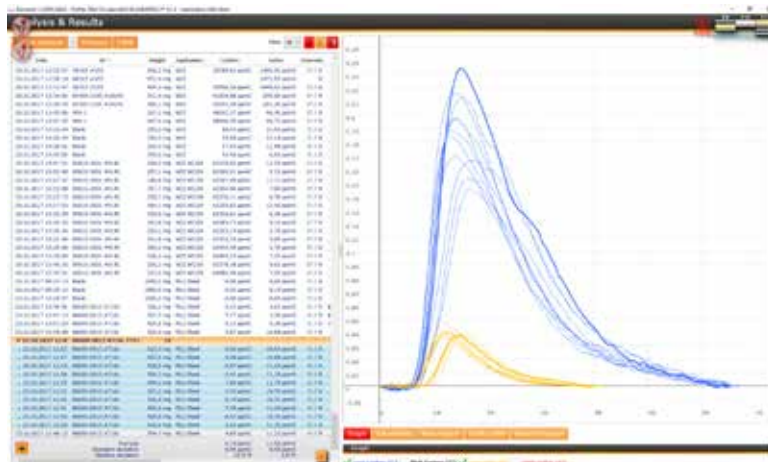
Reference material: ELTRA 88600-0013 (LOT 716C) (*)

(*) certified value:

C: 6 ppm ±4 ppm

S: 11 ppm ±4 ppm

Weight [mg]	Carbon [ppm]	Sulfur [ppm]
504.6	5.48	11.27
499.6	5.86	11.18
504.7	6.39	11.84
497.9	5.86	11.42
498.6	5.87	10.49
503.9	6.95	11.92
503.3	6.46	11.17
498.3	5.84	10.68
507.2	6.41	11.75
498.6	5.64	11.29
Mean value	6.08	11.30
Deviation / relative deviation	±0.45 / 7.48%	±0.47 / 4.14%



(4) Ferro Chromium

Ferro Chromium samples can be analyzed with a sample weight of approx. 150 mg and with 1.5 g tungsten and 0.7 g of high purity iron as accelerator

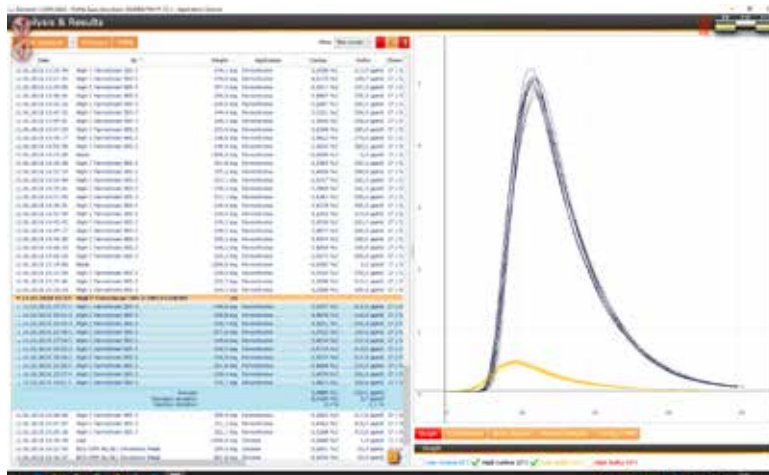
Reference material: Euronorm 585-2 (*)

(*) certified value:

C: 5.488 % ± 0.02 (0.4%)

S: 0.032 % ± 0.0012 (3.75%)

Weight [mg]	Carbon [%]	Sulfur [%]
149.8	5.506	0.032
150.8	5.468	0.032
150.7	5.502	0.033
157.6	5.502	0.033
149.8	5.461	0.032
150.3	5.472	0.031
154	5.504	0.032
151.8	5.487	0.032
150.4	5.497	0.033
155.7	5.482	0.031
Mean value	5.488	0.032
Deviation / relative deviation	±0.017 / 0.30 %	±0.001 / 2.09 %



Technical Data

ELEMENTRAC CS-i	
Measuring range*	For nominal sample weight of 1000 mg
2-cell configuration	Carbon: 2 ppm – 7% / Sulfur: 2 ppm – 0.42%
4-cell configuration	Carbon: 0.6 ppm – 3.5% / Sulfur: 0.6 ppm- 2.3%
Analysis time	40 seconds (nominal)
Cycle time	80 seconds
Measuring method	Combustion via induction furnace followed by Infrared detection for carbon dioxide (C) and sulfur dioxide (S)
Chemical reagent	Magnesium perchlorate Sodium hydroxide Platinized silica Cellulose
Gas requirements	Oxygen 99.5%; 2-4 bar (30-60 psi) Compressed air: 4-6 bar (60 – 90 psi)
Gas consumption	180 L/h (oxygen, during analysis)
Furnace	Induction 2.2 kVA (power adjustable 0-100%)
Operation conditions	15-35°; 20-80% rel. humidity (not condensing)
Electrical power requirement	230 VAC +-10%; 50/60 Hz; 16 A fuse
Weight	approx. 150 kg
Dimensions (W x H x D)	520 x 840 x 750 mm
Required accessories	PC, TFT, Balance
Options	Carrier gas purification furnace Autoloader (36 postions)

* depending on configuration; can be adapted to other working ranges; limit of detection measured with gas dose analysis and blank measurement; different values according to chosen application are possible

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