Effective Quality Control of Steel and Iron Products with Combustion Analysis

Introduction

The element concentration of carbon (C), sulfur (S), hydrogen (H), nitrogen (N), and oxygen (O) in iron products, such as steel, have a significant influence on material properties like ductility, brittleness, or hardness. Hence, reliable determination of the C, H, N, S, O contents is a routine quality control task in steel and iron production. This article explores the application fields and advantages of elemental analyzers, which are also known as combustion analyzers, in the steel industry.

Different analytical methods

A great variety of different analytical methods are used in steel and iron production[1]. Disregarding analyses of physical parameters, such as hardness or tensile strength, and focusing solely on chemical analyses, the different techniques can be categorized, for example, with regard to the measurement method applied (AAS, OES, photometry, mass spectrometry, etc.). A common differentiation is made between wet chemical techniques which require sample digestion, e.g. by ICP-OES, and direct analysis methods like spark spectrometry or combustion analysis. Another possible classification could be made for total element analysis as opposed to surface or layer analysis. The following article mainly focuses on the differences between spark spectrometry and combustion analysis as these are the most common and established techniques for measuring concentrations of C, H, N, S, O. Moreover, both methods are hardly mentioned in general textbooks about analytical chemistry[2], despite the fact that they are widely used in laboratories and production.

Spectrometric methods such as spark spectrometry are theoretically suitable for analysis of an unlimited number of elements of the periodical system. Combustion analyzers, however, are specialized in the quantification of carbon, hydrogen, nitrogen, sulfur and oxygen. The limitation to these elements has some advantages. It is possible to measure solid samples which, due to their geometry (powders, drillings, foils, pins), composition (coke, oils), or the

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[1] Handbuch für das Eisenhüttenlaboratorium, 2009, Band 1
[2] e. g. Cammann (Instrumentelle Analytik, 2001); Kellner, Mermet (Analytical Chemistry, 1997); Skoog (Instrumentelle Analytik, 2013

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element to be determined (e.g. hydrogen) are not suitable for analysis with a method like spark spectrometry.

However, there is no universal combustion analyzer available in the market which can measure all elements. A further differentiation with regard to the

Fig. 1: Carbon / Sulfur Analyzer CS-i

chemical nature of the sample is required. Thus, samples are divided into organic materials with high carbon content like coal or coke, and inorganic materials like steel, iron or copper. For organic samples a further differentiation is made between determination of C, S and C, H, N, O, S; respectively for inorganic materials between N, O, H and H analysis. These different requirements are covered by different analyzers. Table 1 gives an overview of analysis systems, reaction gases, temperatures and required additives. What all elemental analyzers have in common is a combination of sample disintegration by combustion and measurement of the released gases in infrared and thermal conductivity cells (e.g. in ELTRA's CS-i, Fig. 1).

Element	Sample	Furnace type, combustion temperature	Required additives
C,S	steel, iron	induction, > 2000 ° C	tungsten, iron
C,S	coal, coke	resistance furnace (ceramic), up to 1550 °C	none
N,O,H	steel, iron, ceramics	electrode furnace, > 3000 °C	nickel, tin
H	steel	resistance furnace (quartz), up to 1000°C	none

Table 1: Overview combustion analyzers

A specialty of combustion analyzers is the possibility of fractional analysis which is not - or only to a limited extent - available with spectrometric methods. Fractional analysis means determination of the elemental concentration according to the chemical and/or physical bonding in the material. TOC analysis (total organic carbon), fractional hydrogen analysis or determination of surface carbon have become an established part of routine analyses (see table 2). Measuring the surface carbon content with elemental analyzers is completely different from layer analysis with spectroscopic methods such as GD-OES. Combustion analyzers exclusively detect the surface carbon which originates

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from oil or process water, for example. Bound carbon, e.g. from carbonitriding, is not accessible with this technique. Technically possible is a differentiation between varieties of bound oxygen (e.g. from iron or lode stuff); however, due to a number of influencing factors it is hardly suitable for routine analysis.

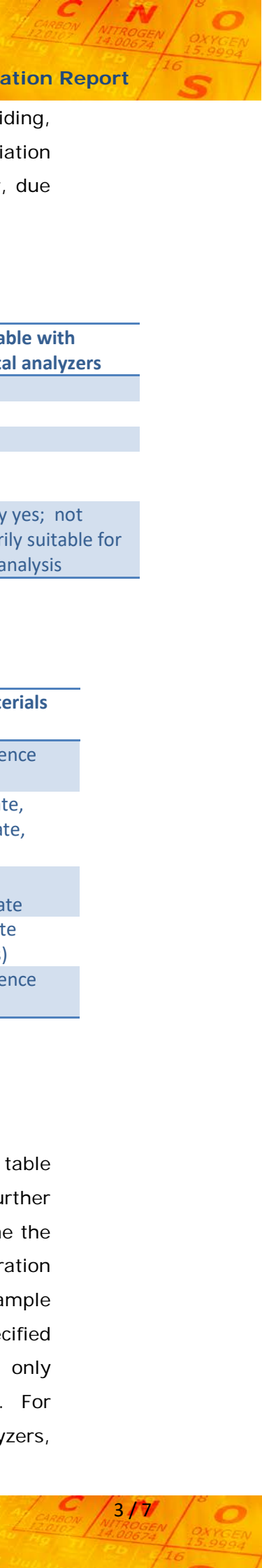| Element	Sample	Examples of fractions	Measurable with elemental analyzers
C	soil, waste, cement	organic (TOC), inorganic (TIC)	yes
C	steel	surface carbon	yes
H	steel	diffusible, residual	yes
N	steel , iron	surface nitrogen, e.g. after carbonitriding	no
O	steel, iron	different bondings of O in Fe_2O_3; O bound in lode or iron	generally yes; not necessarily suitable for routine analysis

Table 2: Examples of fractional analyses with combustion analyzers

Element	Standard	Matrix and scope	Calibration materials used
C,S	EN ISO 15350	C: 0.0005 % - 4.3 % S: 0.0005 % - 0.33 %	(certified) reference materials
C	EN ISO 9556	C: 0.0003 % - 4.5 %	barium carbonate, sodium carbonate, saccharose
C	EN ISO 15349-2: 2003	C : 0.0003 % - 0.010 %	saccharose, calcium carbonate
O	ISO 17053:2005 EN 10276-2:2003	O: 0.00075 % - 0.01 % O: 0.0005 % - 0.01 %	potassium nitrate (both standards)
N	EN ISO 15351: 2010	N: 0.002 % -0.6 %	(certified) reference materials

Table 3: Standards featuring combustion analysis

Specifications of combustion analyzers

The determination of C, H, N, S, O is stipulated in various standards (see table 3). Table 3 shows a representative excerpt; depending on the region, further ISO or ASTM standards (e.g. ASTM E1019) may apply. The standards define the allowed measuring range for a particular element, permissible calibration materials and their use and, where required, procedures of sampling and sample preparation. Technical requirements for analyzers, however, are hardly specified by the standards. For oxygen and nitrogen measurement, the standard only mentions general laboratory instruments without further specification. For carbon and sulfur analysis, however, standardized components of C/S analyzers,

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such as gas purification, dust trap or induction furnace are listed. Hence, all common C/S and O/N/H analyzers fulfill the requirements of the standard.

Despite the fact that spark spectrometers and combustion analyzers measure the same matrix and ascertain similar values, process steps such as sample preparation, calibration, measurement procedure and measuring range show significant differences which are described in the next paragraph.

Sample preparation for combustion analysis is quick and easy. All that is required is a representative analysis sample in a quantity which can be accommodated by the crucible used. Typical sample weights are between 250 mg and 1000 mg. Sample geometry (drillings, powders, wires, etc.) is not important for elemental analyzers. For O/N/H analysis it must be ensured that the sample is purged from surrounding atmosphere inside the sample drop mechanism. This is very easy for compact individual samples; powders or drillings, however, should either be analyzed in a special loading mechanism or by using air-tight tin or nickel capsules. Surface contaminations can be removed with the help of an organic solvent like acetone.

Spark spectrometry requires samples with a planar surface, a certain thickness to prevent the spark from penetrating the sample, and electric conductivity. Contaminations of the surface can be prevented by „presparking". A suitable spectrometric method for analyzing nonconductive samples is, for example, high frequency glow discharge.

Measurement procedure and calibration

With spark spectrometry all elements are detected simultaneously. The sample is fed to the spectrometer, "presparked" if required, and finally the spark is used to measure the intensity of the emitted radiation. A necessary prerequisite for spectroscopic measurement of oxygen and nitrogen is the use of a spectrometer with a suitable wave length (e.g. 130-780 nm)[3]. Calibration is usually carried out by the manufacturer; the user only needs to make a drift correction using certified reference material which contains the desired concentration of the elements to be determined. The calibration usually matches a narrow concentration range with each matrix (e.g. pig iron, different steel alloys, pure iron, etc.) requiring an individual measuring method and calibration. The drawback of this procedure is its dependence on the required reference materials.

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[3] Data obtained from manufacturers such as OBLF, Thermo Scientific

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Fig. 2: CS-2000 for simultaneous analysis of carbon and sulfur in organic and inorganic samples.

The measurement of C, H, N, S, O concentrations with combustion analyzers is separated into C/S analysis and N/O/H analysis. Pure chemical substances or pure gases are suitable calibration materials for both methods. For calibration with gas a defined volume of, for example, CO_2 is introduced and directly guided to the measurement unit without entering the furnace. Both methods allow for a daily calibration update, or the existing calibration can be updated with a daily factor. In contrast to spark spectrometry there is no strict matrix dependency. The user can easily exchange the used standards against others. For C/S analysis the sample is mixed with additives such as tungsten or iron, introduced into the induction furnace, combusted in an oxygen stream, and finally the resulting reaction gases CO_2 and SO_2 are detected in the infrared cells. ELTRA's CS-2000 offers a combination of inductive combustion with a resistance furnace (fig. 2).

For O/N/H analysis in an electrode furnace the sample is placed in a sample drop mechanism where it is purged from ambient atmosphere and dropped into a hot graphite crucible. The sample melts, elemental hydrogen and nitrogen are released and the oxygen contained in the sample reacts with the graphite crucible. The method for quantification of the released gases depends on the instrument manufacturer. The standards don't mention any limitations regarding the method. A typical C/S analysis takes approximately 45 seconds, O/N analysis about 2 to 3 minutes. This is due to the integrated outgassing of the graphite crucible to reduce possible contaminations. Whereas a spark spectrometer processes a signal which is constant over time, combustion analysis produces transient signals (see fig. 3) which are integrated through the software. This does not have a negative influence on the precision and correctness of the measured values.
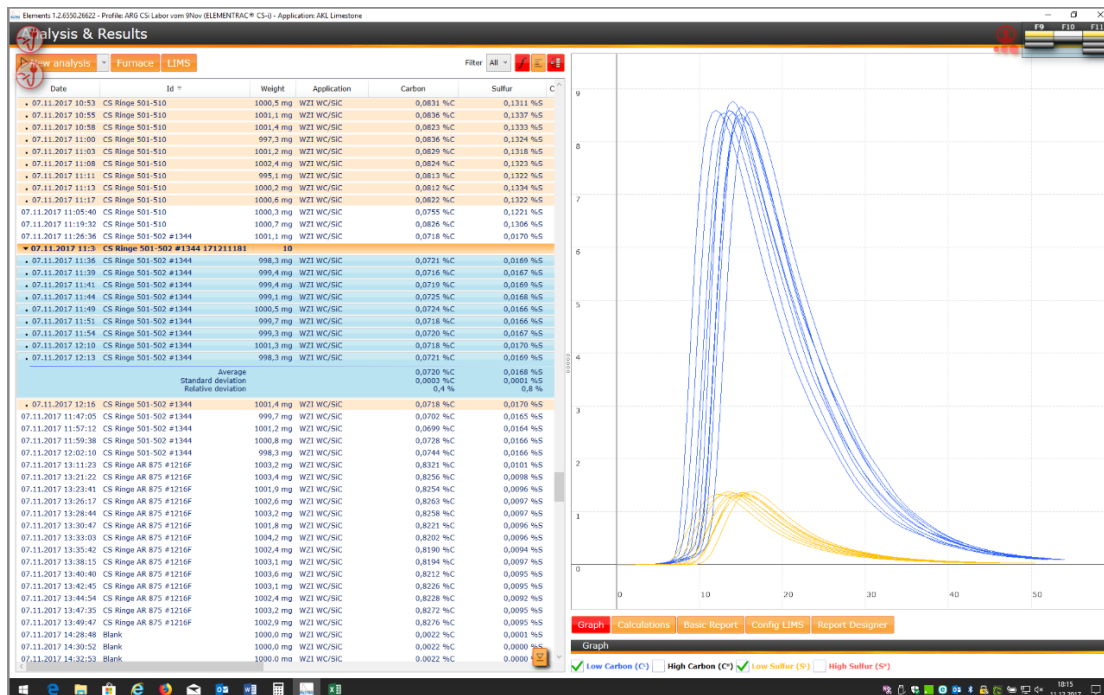
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Fig. 3: Transient signal of C/S analysis

Whereas different methods of C, N, S, O analysis produce very similar results, this is not the case with hydrogen analysis. The highest values are usually obtained by fusion in an electrode furnace. The applied temperatures of 3,000 °C melt the sample and the contained hydrogen is completely released. ELTRA offers analyzers like the ONH-p for this application or the H-500 analyzer for hot extraction at max. 1,000°C. Analyzing residual hydrogen at ambient temperature is also possible with ELTRA instruments.

Measuring range and accuracy of results

The measuring range of a spark spectrometer depends on the sample material (iron, steel, and aluminum), calibration standards and spectrometric parameters like optics, performance, etc., and is therefore difficult to define in general. Combustion analyzers, however, provide the same measuring range for a great variety of sample materials. An induction furnace determines, for example, a carbon concentration of 7% regardless whether the material is iron, titan, marble, or ceramic. The measuring range is usually defined for a nominal sample weight of 1,000 mg. By adjusting the weight it is possible to measure significantly higher concentrations. The lower detection limit is defined by the signal-to-noise ratio - comparable to spectrometric methods - but can be optimized by increasing the sample weight, pre-cleaning the crucibles and additives, or catalytic carrier gas purification. A general comparison of detection

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limits and accuracy of the two techniques is difficult as factors like sample homogeneity and equipment configuration need to be taken into account. Table 4 shows a basic comparison. The repeatability defined in standard ISO 15350 is hardly comparable with the standard deviation generally ascribed to spectrometers but it reflects a tendency. Spectrometers indeed seem to measure homogeneous samples more accurately whereas combustion analysis provides excellent repeatability even for different analyzers and users.

Parameter	Value
Detection limit spark OES (1)	0.0002 %
Standard deviation spark OES at 0.01 % C (1)	0.0003 %
Detection limit Eltra CS-i (2)	0.0001 %
Carbon content of standards NIST SRM2165 (3); measured with combustion analysis	0.0059 %
Repeatability of combustion analysis of NIST SRM 2165 (3)	0.00055 %

Table 4: Detection limits and accuracy of carbon analysis

Conclusion

When selecting a suitable method for elemental analysis, economic as well as analytic aspects need to be considered. From an economic point of view spark spectrometers, for example, are ideally suited for rapid analysis in the steel and iron production process. Thanks to the reliable determination of the classic elements C, N, S and O they offer possible cost savings for routine operations in the lab. However, this advantage needs to be weighed against the high investment costs, particularly for automated operations.

From an analytical point of view, combustion analyzers are high-performance instruments which offer additional benefits to the user. They allow for reliable measurement of samples with carbon inclusions, provide results over a wide measuring range as well as the possibility for fractional analysis. Combustion analysis is extremely reliable due to the fact that the results can be traced back to primary substances such as chemicals or pure gas. The instruments require low investment costs and have a long operating life which makes them attractive also from an economic point of view.

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