ELTRA®
ELEMENTAL ANALYZERS

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METAL POWDER AND FEEDSTOCK ANALYSIS WITH THE ELTRA ELEMENTRAC SERIES

Introduction

All complex technical products like cars, airplanes or even bicycles are equipped with other, less complex technical parts, like engines and gears or bicycle frames, to ensure their functionality. These smaller technical components again are assembled from basic parts like housings, screws, gear wheels, wires and so on. In the end, all parts can be traced back to the raw materials, like pure metals or alloys like steel, copper, titanium, or to synthetic organic products which are also based on natural products like oil, gas or coal.

Beside the wide range of material composition of complex technical products, the applied fabrication technology is of interest. Classical technical production processes are e. g. founding, drilling, or welding and of course many more. Further description and definitions of production techniques are described in the German DIN 8580 standard. For the production of a challenging product like an airplane, of course not only a single manufacturing step is required, but a lot more.

A relatively new production method like additive manufacturing (AM) can overcome some disadvantages of classical production techniques like founding or welding, because complex structures can be created in one single step. The DIN EN ISO/ASTM 52900:2018 standard (Additive manufacturing- General principles) defines additive manufacturing as a general term of those technologies that, based on a geometrical representation, create physical objects by successive addition of material. Essential for this process is the usage of an AM machine which is capable to build the requested product. AM products meanwhile can be found in different industries like food, fashion, transportation, safety or healthy. (wikipedia.org).

Fig. 1: ELEMENTRAC CS-i analyzer

Although the additive manufacturing method is completely different in comparison to classical methods like founding or drilling, one important thing is common. Regardless of the use, size and geometry either of an AM or a traditionally manufactured product, always a raw material with defined specifications is used for its production. For classical production methods the raw material could be solid steel, cast iron etc. which is usually shaped as sheet, bar, tube or wire. Founding of course requires a liquid raw material which could be based on cast iron, aluminium or any other alloy.

AM raw material is usually solid powder and is called feedstock (chapter 3.6.6 of ASTM 52900). Feedstock can be based on aluminium, cobalt, iron, nickel, titanium, copper, precious metals or customized mixtures. The chemical composition of the raw material, independent of its shape, will influence the mechanical properties of the resulting product. Especially the content of non-metals like carbon, sulfur or gases like oxygen, nitrogen and hydrogen can influence the resulting hardness, ductility and brittleness. Whereas traditional production methods can refer to long established standards like the ASTM E 1019 for quality control of the raw material, quality control of feedstock is relatively new and due to the powder shape and the wide range of chemical compositions sometimes challenging.

The new DIN EN ISO /ASTM 52907 from 2020 (Additive manufacturing- Feedstock materials- Methods to characterize metal powders) lists the following technical parameters to characterize the quality of metal powder:

- Particle size distribution
- Chemical composition
- Characteristic densities
- Morphology
- Flowability
- Contamination
- (Packing, handling, storage)

This article focusses on the chemical analysis of metal powders, especially the measurement of the elements oxygen, nitrogen, hydrogen as well as carbon and sulfur, and describes the current status of elemental analysis.

Chemical composition

The general chemical characterization of metal powders comprises the determination of various metal elements like Mn, Fe, Cu, which can be present as major or minor part or in traces, and the determination of nonmetals and gases like carbon, sulfur, oxygen, nitrogen and hydrogen. For a safe and reliable measurements of metals, nonmetals and gases different analytical techniques are required.

The ASTM 52907 standard recommends for the first group spectrometric methods like AAS, X-Ray fluorescence analysis, and for the second group combustion and fusion techniques. Spectrometric techniques provide in general a reliable analysis of the metal parts, whereas combustion and fusion techniques allow a wide range determination of carbon, sulfur, oxygen, nitrogen and hydrogen. The ASTM 52907 standard refers to other established standards (table 1) for C/S and O/N/H analysis without further special recommendations for powder analysis.

Table 1: Recommend standards for C/S and O/N/H analysis (ASTM 52907)

Matrix	Carbon	Sulphur	Oxygen	Nitrogen	Hydrogen
Steel and Iron	ISO 9556, or ISO 15349-2 or ISO 15350 or ASTM E1019	ISO 13902 or ISO 15350 or ASTM E1019	ISO 17053 or ASTM E1019	ISO 10720 and ISO 15351 or ASTM E1019	NN
Titanium and titanium alloys	ASTM E1941	NN	ISO 22963 or ASTM E1409	ASTM E1409	ASTM E1447
Nickel and nikkel alloys	ISO 7524 or ASTM E1019	ISO 7526 or ASTM E1019	ASTM E1019	ASTM E1019	NN
Aluminium and aluminium alloys	NN	NN	NN	NN	ASTM E2792
Cobalt alloys	ISO 11873 or ASTM E1019	ISO 11873 or ASTM E1019	ASTM E1019	ASTM E1019	NN
Copper and copper alloys	NN	ISO 7266	ASTM E2575	NN	NN

For covering the whole range of C/S and O/N/H analysis two different types of elemental analyzers are required which are described e. g. in the ASTM E 1019 or E 1447. Combustion analyzers differ in the integrated furnace type (induction or electrode), the applied carrier gas and the used sample carrier (crucible). The common principle is the melting of the sample in a gas stream and measurement of the released gases in infrared (IR) or thermal conductivity cells (TCD). Table 2 illustrates some basic features of a C/S and O/N/H combustion analyzer.

Table 2: Technical features of combustion analyzers

Elements	Technique	Carrier gas	Sample carrier	Sample weight (mg)	Suitable analyzer (ELTRA)
C/S	Combustion with induction furnace	Oxygen	Ceramic crucible	50-1000	ELEMENTARC CS-i (Fig.1)
O/N/H	Inert gas fusion via electrode (impulse) furnace	Helium / Nitrogen / (Argon)	Graphite crucible	50-3000	ELEMENTRAC ONH-p 2 (Fig. 2)

As mentioned above, the ASTM 52907 refers to the established standards for C/S and O/N/H measurement without giving recommendations or hints for the correct processing of feedstock samples. This can cause conflicts, because the established standards for elemental analysis (table 1) focus mainly on the analysis of solid samples or drillings. This conflict is usually not related to the technical specifications of the elemental analyzer but to the sample preparation process (see table 3).

Fig. 2: ELEMENTRAC ONH-p2 with optional autocleaner

Table 3: Requirements for sample preparation according to selected standards (March 2021)

Standard	Carbon & sulfur measurement	Oxygen measurement	Nitrogen measurement
ASTM E 1019-18	Particle size >=0.422 mm (40 mesh)	Use only solid specimens (Caution: surface oxidation!)	Refers to ASTM E 1806 (describes preparation of chips, drillings, slugs, solids) - No powders-
ISO 170 53	NN	Refers to ISO 14284 (preparation of pins for oxygen measurement)	NN
ISO 15350	Refers to ISO 14284 (various techniques for C/S analysis: Usually preparation of drillings)	NN	NN
ASTM E 1409	NN	Describes only solid pieces and required surface treatment	

Table 3 illustrates that correct C/S and O/N/H analysis of feedstock can be a challenge because the requirements of the different standards are inconsistent. For further clarification of the measuring process typical analyzers, settings and sample preparation steps are described in the following.

This article publishes analysis data of different powders measured with ELTRA's ELEMENTRAC ONH-p2 and CS-i analyzers, including the applied settings and sample preparation process. These data illustrate that the analysis not only of feedstock samples is safe, reliable and easy, provided some aspects are taken into consideration.

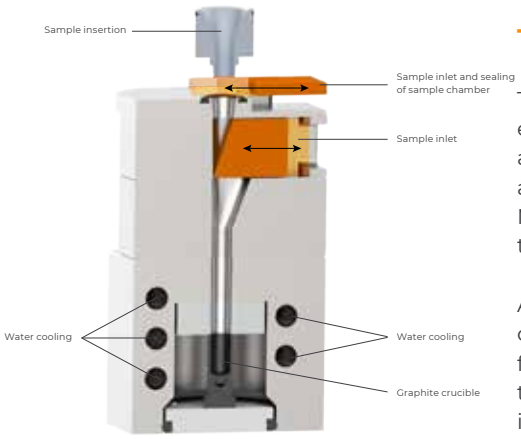


Fig. 3: Sample port and furnace of the ELEMENTRAC ONH-p2

The ELEMENTRAC ONH-p2 analyzer

The ELEMENTRAC ONH-p2 is a powerful inert gas fusion analyzer which utilizes a 8.5 kW electrode furnace, two infrared cells and a wide range thermal conductivity cell for a safe and reliable analysis of oxygen, nitrogen and hydrogen. Performing an analysis is safe, easy and convenient for trained and untrained users alike. The sample is logged in the ELEMENTS software with its weight, followed by the application to the sample port and starting the measurement in the software. All other steps are done automatically.

After analysis start in the software the sample port closes and the sample is flushed with carrier gas which prevents atmospheric gas (oxygen and nitrogen) from getting into the furnace. Meanwhile a graphite crucible is outgassed in the impulse furnace of the analyzer to remove possible contaminations After a short stabilization phase the sample is dropped into the crucible and melts. Due to the vertical sample transfer to the crucible (fig. 3) and the effective flushing, a sealing of capsules (which contain the powder) is not required. This simplifies the whole analysis process of feedstock and any other powdered samples.

In the following carbon monoxide is produced by the reaction of carbon in the graphite crucible and oxygen of the sample. Nitrogen and hydrogen are released in its elemental form. The carrier gas (helium) and sample gasses pass through a filter before entering a copper oxide catalyst which converts the CO to CO_2.
The CO_2 is measured by the infrared cells to determine the oxygen content. CO_2 and water are removed chemically, and the nitrogen content is measured in the thermal conductivity cell. In the case of hydrogen analysis, nitrogen carrier as well as sample gas pass through a Schuetze reagent instead of a copper oxide catalyst. As an option the less expensive Argon can be used to determinate the oxygen and nitrogen content during analysis.

THE ELEMENTRAC CS-i ANALYZER

Fig. 4: Applying accelerator to a weighed sample

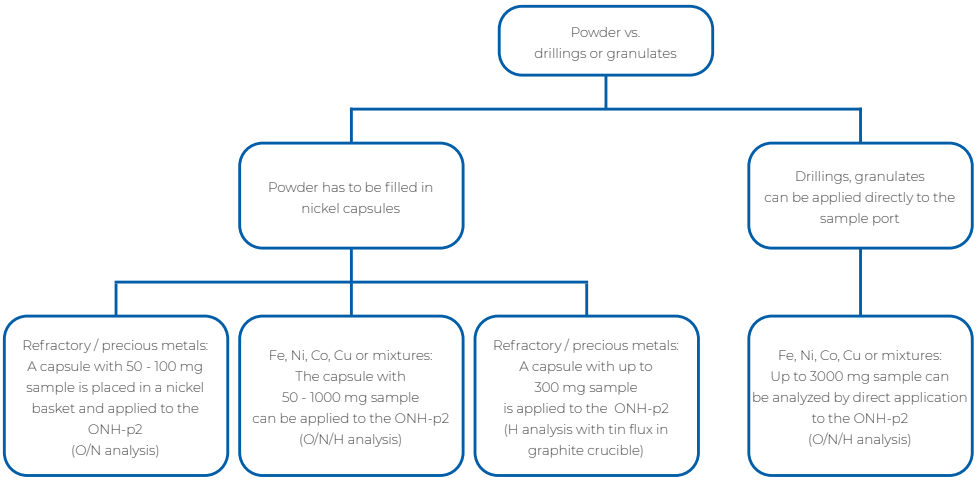
The elemental analyzer ELEMENTRAC CS-i measures the carbon and sulfur concentration in predominantly inorganic samples through combustion in an induction furnace and the subsequent analysis of the gaseous combustion products carbon dioxide and sulfur dioxide in up to 4 infrared cells.
The high temperature of more than 2000 °C ensures complete decomposition of the sample and thus reliable and accurate elemental analysis over a wide concentration range.

After weighing a feedstock sample in a ceramic crucible, logging in the sample the ELEMENTS software, an accelerator like tungsten (approx. 1.7 g) must be added (fig.4). After placing the sample on the pedestal (fig. 5) and starting the analysis all further steps are processed automatically. In the induction furnace of the elemental analyzer the sample and accelerator are melted in a pure oxygen atmosphere, causing sulfur to react to sulfur dioxide (SO_2) and carbon to a mixture of carbon monoxide (CO) and carbon dioxide (CO_2). The combustion gases pass through a dust filter and moisture absorber for purification. In the next step the sulfur dioxide is detected in infrared cells. In the CS-i infrared cells with different sensitivities (high/low) can be adapted according to the user's requirements. Oxidation of both, carbon monoxide to carbon dioxide and sulfur dioxide to sulfur trioxide follow the sulfur measurement. The SO_3 gas is subsequently removed with cellulose wool and the carbon content is detected by infrared cells.

Sample-related settings and preparation for ONH analysis

Fig. 5: Placing sample with accelerator on the pedestal of the ELEMENTRAC CS-i

For each metal powder, an individual application has to be developed first which takes into account the available sample amount, the chemical nature of the sample, as well as the particle size and shape. These specifications determine the suitable maximum amount of sample for a single analysis, the required sample preparation and of course the applied analysis power. The following diagram illustrates the general procedure:



The separation between powders and drillings is not defined clearly.

Fig. 6 above: Fine powder needs to be placed in a capsule before analysis in the ONH-p2.
Fig. 6 below: Granulate / drilling (iron-based) can be analyzed without capsule.

Usually, samples for additive manufacturing are fine powders (fig. 6). These samples always require a nickel capsule before they can be applied to an elemental analyzer. Without it they could cause blockages and the complete transfer to the graphite crucible would be unsafe.

Depending on the chemical nature of the powder, further sample preparation steps are required for a reliable oxygen and nitrogen analysis. Refractories and precious metals like titanium, palladium and platinum have a high melting point. To assure a complete release of the embedded gases additional flux needs to be provided. The nickel capsule with the high-melting sample is placed in an additional nickel basket to reduce the melting point of the resulting alloy in the crucible. For reliable analysis, the sample amount is usually limited to 50-100 mg for oxygen and nitrogen measurement (fig. 7).

Since hydrogen is released much easier from the sample in case of hydrogen analysis, the sample amount can be increased, and a nickel basket is not required. ELTRA recommends applying tin flux to the graphite crucible to assure a smooth release of the embedded hydrogen.

Sample-related settings and preparation for CS analysis

In contrast to an ONH measurement for a CS measurement less parameter has to be taken into account for a reliable measurement. The particle size distribution in general is negligible, but due to the intensive combustion a possible sample lost due to swirling has to be considered. With common sample weights of 250-500 mg the sample is covered completely with accelerator and swirling is negligible. For higher sample weights the ELMENTRAC CS-i provides special solutions like induction power control and intelligent oxygen supply to assure a complete and smooth combustion without sample dust due to swirling or sputtering. Depending on the base of the feedstock different accelerators have to be added to guarantee a complete oxidation of the embedded carbon and sulfur The following table summarizes typical sample weights and recommended accelerators:

Feedstock base	Recommended sample weight for analysis (mg)	Recommended accelerator
Iron, nickel, cobalt	250-1000 mg	Tungsten (1.7g)
Copper !	1000 mg	Copper (2g) alternatively: Copper (1g)+ Iron (0.7g)
Refractories; precious metals	Up to 250 mg	Tungsten/tin (2g) ; alternatively tungsten (1.7g) /iron (0.7g)

Copper is printed in italic letters because the analysis of copper based or copper containing samples could be critical regarding precise and reliable sulfur analysis in general. Intensive combustion could cause minor sulfur determination induced by the forming of copper sulfide (ASTM E1941-10; Note 7).

A technical solution for this challenge is utilized in the ELEMENTRAC CS-i. A safe and reliable sulfur analysis in copper or even copper concentrates could be assured to the intelligent oxygen supply and ramping feature which always allows a smooth combustion without forming of copper sulfide. For further information ask for the ELTRA application notes 1037 and 1066

Fig. 7: Application of a nickel basket (flux for precious metals and refractories). Here without the nickel capsule and sample.

Fig. 8: Direct application of steel granulate

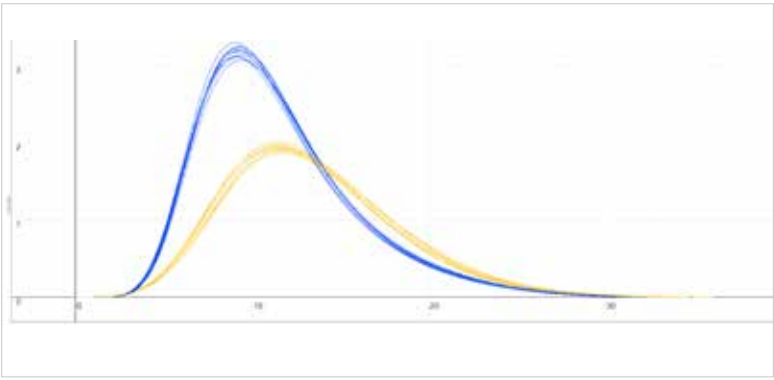
Application examples

In the following, typical analysis data for differently shaped samples with a different base are shown. The provided data are based on the analysis of customer samples as well as the analysis of certified reference materials.

a) Analysis of steel granulates (CRM)

Analysis	Oxygen and nitrogen with ELEMENTRAC ONH-p 2
Sample	EZRM 284-2
Sample preparation	None. Direct application to the furnace (see picture 8)
Settings	Standard steel analysis with 4500 W; 2,5 -3 min. cycle time per sample

Typical results		
Steel granulate ZRM 284-2*		
Weight (mg)	**Oxygen (ppm)**	**Nitrogen (ppm)**
1018	99.7	148.8
1057	96.5	152.6
1036	99.3	150.3
1027	99.1	150.6
1015	97.7	151.5
1021	102.0	150.1
1020	98.4	153.4
1035	99.2	150.0
1029	99.8	149.0
1011	98.1	153.4
Mean value		
	99.0	151.0
Deviation / Relative deviation (%)		
	1.5 (1.5)	1.7 (1.1)
* Certified value: O 99 +- 7 ppm; N 151 +- 2 ppm		

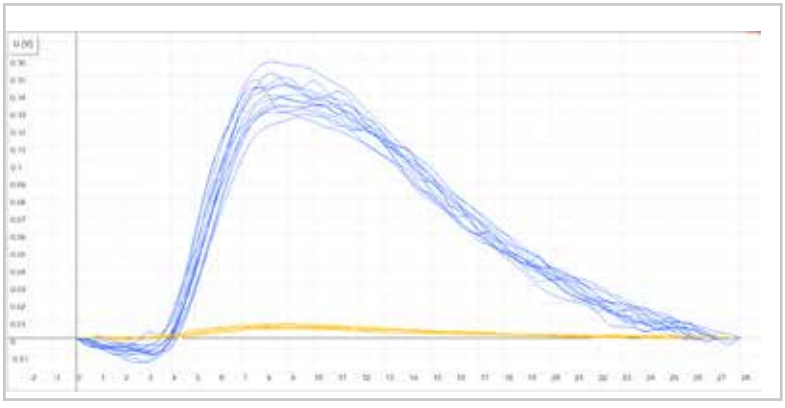


Measuring graph
blue peak: oxygen signal
x-axis: time (sec)
yellow peak: nitrogen signal
y-axis: intensity (voltage)

Analysis	Carbon and sulfur with ELEMENTRAC CS-i
Sample	JSS003-8
Sample preparation	None
Settings	Accelerator 1.7 g tungsten Cycle time: 90 seconds/ analysis

The analysis data may not represent a typical feedstock sample, but it illustrates that even very low carbon and sulfur concentrations could be measured precise and reliable.

Typical results		
JSS 003-8 *1		
Weight (mg)	**Carbon (ppm)**	**Sulfur (ppm)**
1093	3.9	1.5
1069	4.4	1.8
1026	4.0	1.8
1002	4.3	1.7
1095	3.5	1.5
1034	4.0	1.4
1082	4.2	1.5
1007	4.2	1.5
1093	3.9	1.6
1044	4.0	1.5
Average values		
	4.1	1.6
Deviation / Relative deviation (%)		
	0.26 (6.3%)	0.1 (9.4%)



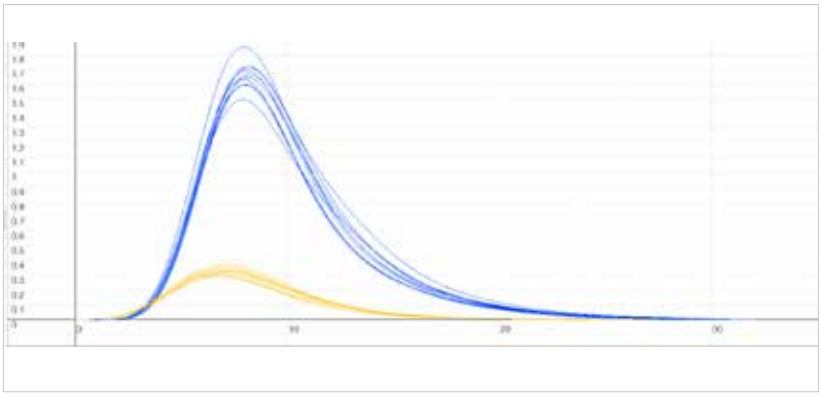
Measuring graph
blue peak: carbon signal
yellow peak: sulfur signal
x-axis: time (sec)
y-axis: intensity (voltage)

Fig. 9: Application of open capsule with powder

b) Analysis of nickel feedstock

Analysis	Oxygen and nitrogen with ELEMENTRAC ONH-p 2
Sample	Nickel powder from ASTM Cycle AMPM 2010
Sample preparation	Sample filled in nickel capsule (see picture 9)
Settings	Standard steel analysis with 4500 W; 2,5 -3 min. cycle time per sample

Typical results		
Nickel powder ASTM AMPM 2010		
Weight (mg)	**Oxygen (ppm)**	**Nitrogen (ppm)**
260	198	108
250	199	111
225	202	105
243	199	108
227	203	108
287	202	106
233	203	107
291	203	105
270	202	109
255	199	108
Mean value		
	201	107
Deviation / Relative deviation (%)		
	2.0 (1.0)	1.7 (1.6)
* Certified value: not available		



Measuring graph
blue peak: oxygen signal — yellow peak: nitrogen signal
x-axis: time (sec) — y-axis: intensity (voltage)

The measured oxygen content is informative and was not part of the ASTM cycle. Due to the fine particle size of the powder a surface is oxidized during storage time could be possible.
For a first evaluation of a possible oxidation effect the measurement was repeated after 12 weeks. For O/N analysis another aliquot was used which was stored for 12 weeks in a 150 ml brown glass bottle.

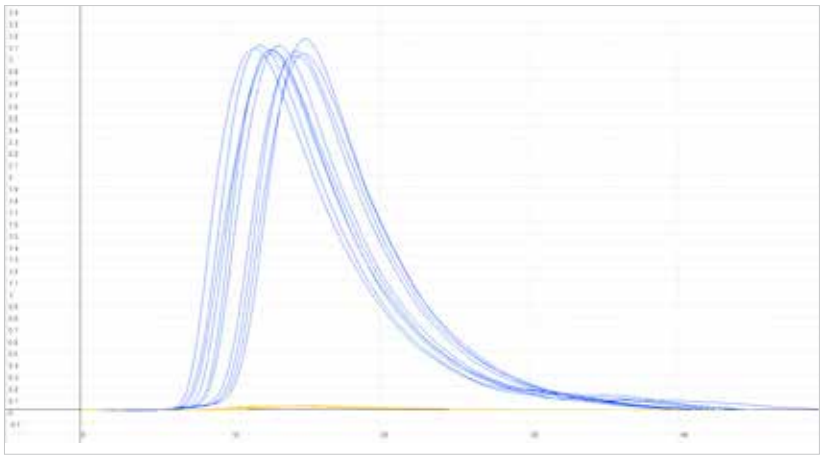
Nickel powder ASTM AMPM 20210: measurement after 12 weeks storage in a sealed, brown glass bottle (150 ml)	
Oxygen (N=4)	199 +- 1,2 ppm
Nitrogen (N=4)	109 +- 2 ppm

For this sample and lot surface oxidation seems to be negligible. This result may not be representative for other sample compositions, storage times and particle sizes

Analysis	Oxygen and nitrogen with ELEMENTRAC ONH-p 2
Sample	Nickel powder from ASTM Cycle AMPM 2010
Sample preparation	None
Settings	Accelerator 1.7 g tungsten Cycle time: 90 seconds/ analysis

Typical results

Nickel powder ASTM AMPM 2010		
Weight (mg)	**Carbon (ppm)**	**Sulfur (ppm)**
499.4	250.1	11.2
499.8	250.9	10.4
499.5	248.8	9.1
500.1	250.9	12.5
500.6	248.3	11.8
500.8	242.9	9.9
500.8	248.5	9.9
500.5	246.9	9.0
499.4	250.8	11.8
500.9	250.3	11.1
Mean value		
	248.8	10.7
Deviation / Relative deviation (%)		
	2.5 (1.0)	1.2 (11.2)
* Certified value: not available		

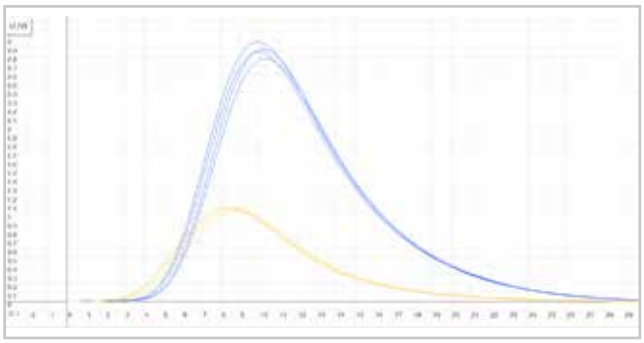


Measuring graph
blue peak: carbon signal
yellow peak: sulfur signal
x-axis: time (sec)
y-axis: intensity (voltage)

c) Analysis of iron/nickel feedstock

Analysis	Oxygen, nitrogen and hydrogen with ELEMENTRAC ONH-p 2
Sample	Customer sample: iron/nickel powder
Sample preparation	Sample filled in nickel capsule
Settings	Standard steel analysis with 4500 W (ON) Standard steel analysis with 3600 W (H)

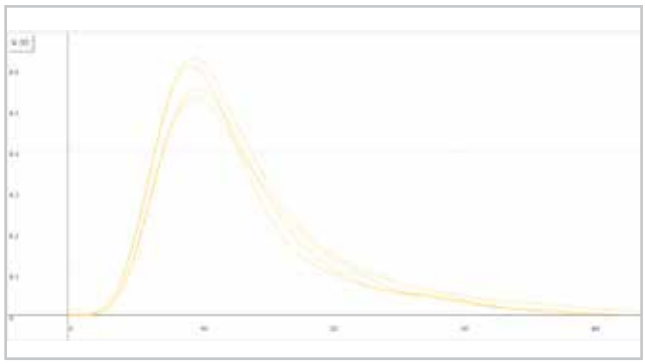
Typical results		
Customer sample Fe/Ni powder		
Weight (mg)	**Oxygen (ppm)**	**Nitrogen (ppm)**
158	479	327
154	473	328
152	455	330
157	457	330
Mean value		
	466	329
Deviation / Relative deviation (%)		
	11.8 (2.5%)	1.47 (0.4%)



Measuring graph
blue peak: oxygen signal
yellow peak: nitrogen signal
x-axis: time (sec)
y-axis: intensity (voltage)

For a reliable hydrogen measurement the ELEMENTRAC ONH-p 2 utilizes a TC cell and the less cost-intensive carrier gas nitrogen. Hydrogen in general leaves the sample in elemental form and requires a reduced analysis power for a repeatable measurement:

Typical results	
Customer sample Fe/Ni powder	
Weight (mg)	**Hydrogen (ppm)**
399	11.8
400	11.9
402	13.5
399	11.78
Mean value	12.28
Deviation	0.83
Relative deviation (%)	6.8



Measuring graph
yellow peak: hydrogen signal
x-axis: time (sec) y-axis: intensity (voltage)

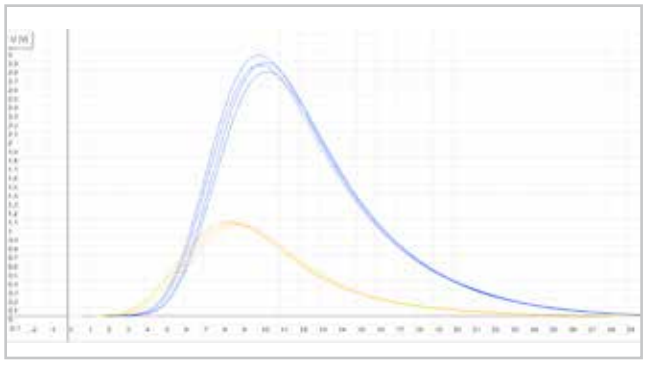
For further evaluation of the stability of the oxygen results the measurement was repeated after two weeks. The customer sample was stored in a sealed transparent plastic bag.

Fe/Ni feedstock: New measurement after 2 weeks of storage in a plastic bag	
Oxygen (N=4)	469 +- 10.9 ppm
Nitrogen (N=4)	333 +- 3.6 ppm

Like for the ASTM sample no significant increase of the measured oxygen or nitrogen content could be measured.

Analysis	Carbon and sulfur with ELEMENTRAC CS-i
Sample	Iron/Nickel feedstock (customer sample)
Sample preparation	None
Settings	Accelerator 1.7 g tungsten Cycle time: 90 seconds/ analysis

Typical results		
Customer sample Iron/Nickel Feedstock		
Weight (mg)	**Carbon (ppm)**	**Sulfur (ppm)**
500.4	176.3	153.5
500.3	186.6	166.1
500.4	183.7	166.2
Mean value		
	182.2	161.9
Deviation / Relative deviation (%)		
	5.3 (2.9)	7.3 (4.5)



Measuring graph
blue peak: carbon signal yellow peak: sulfur signal
x-axis: time (sec) y-axis: intensity (voltage)

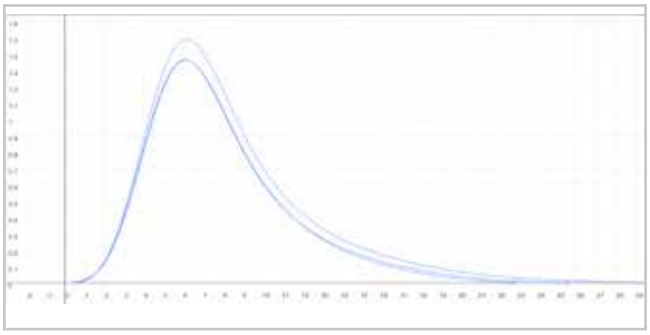
d) Oxygen and hydrogen analysis in precious metals

Analysis	Oxygen and hydrogen with the ELEMENTRAC ONH-p 2
Sample	Customer sample: PD sponge
Sample preparation	Sample filled in nickel capsule for H analysis Sample filled in nickel capsule and basket for ON analysis
Settings	Standard titanium analysis with 5600 W (ON) Standard titanium analysis with 3600 W (H)

Because of the high price, precious metals like gold, platinum or palladium are not widely used as feedstocks for additive manufacturing. Due their high melting point, the analysis of oxygen, nitrogen and hydrogen is very similar to the analysis of titanium.
In contrast to steel- or titanium-based feedstock, the carbon, sulfur and nitrogen content is usually less important and was not measured in this example.

Typical results

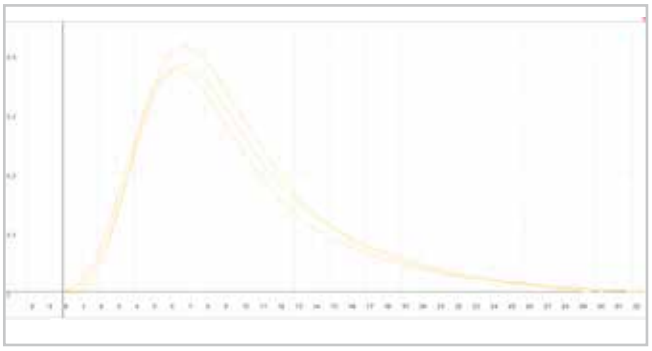
Customer sample Pd sponge	
Weight (mg)	**Oxygen (ppm)**
69	361
76	330
81	360
Mean value (ppm)	350
Deviation	17
Relative deviation (%)	4



Measuring graph
blue peak: oxygen signal
x-axis: time (sec) y-axis: intensity (voltage)

Typical results

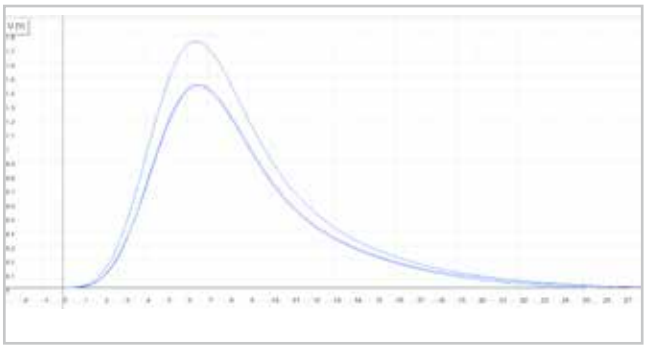
Customer sample Pd sponge	
Weight (mg)	**Hydrogen (ppm)**
69	30
56	36
56	34
Mean value (ppm)	33
Deviation	3
Relative deviation (%)	9.5



Measuring graph
yellow peak: hydrogen signal
x-axis: time (sec) y-axis: intensity (voltage)

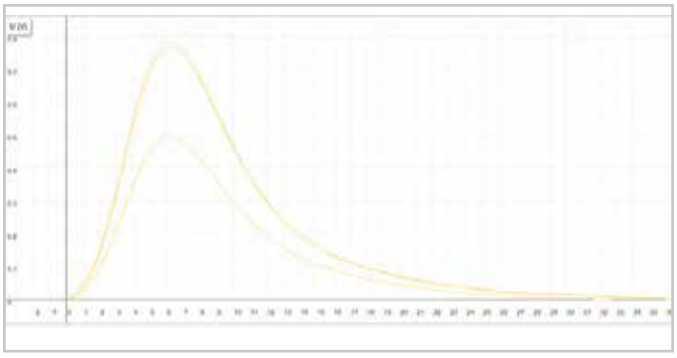
Analysis	Oxygen and hydrogen
Sample	Customer sample: Pt sponge
Sample preparation	Sample filled in nickel capsule for H analysis Sample filled in nickel capsule and basket for ON analysis (fig. 7)
Settings	Standard titanium analysis with 5600 W (ON) Standard titanium analysis with 3600 W (H)

Typical results	
Customer sample Pt sponge	
Weight (mg)	**Oxygen (ppm)**
93	301
86	321
109	327
Mean value (ppm)	316
Deviation	13
Relative deviation (%)	4



Measuring graph
blue peak: oxygen signal
x-axis: time (sec) y-axis: intensity (voltage)

Typical results	
Customer sample Pt sponge	
Weight (mg)	**Hydrogen (ppm)**
74	31
124	26
117	27
Mean value (ppm)	28
Deviation	2.5
Relative deviation (%)	8.9



Measuring graph
yellow peak: hydrogen signal
x-axis: time (sec) y-axis: intensity (voltage)

CONCLUSION

The analysis of feedstock, granulates and other powders is easy, safe and reliable with the ELTRA ELEMENTRAC series. The ELEMENTRAC CS-i and ONH-p2 ensure precise measurements of different materials like iron, nickel, or even platinum and palladium, over a wide concentration range.
The release of the DIN EN ISO/ASTM 52907 is a good starting point for the quality control process of feedstock but more detailed information could be useful to guarantee reliable measurement results. Especially process steps like sampling, preparation and storage of feedstocks should be further evaluated in the future to assure valid C/S and O/N/H measurements over a wide sample range and period of time.

Find out more at
www.eltra.com