Analytical Solutions for Powder Metallurgy and Additive Manufacturing Processes: Determination of Ar, O, N, H and C, S by Gas Fusion Analysis and Combustion Methods

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Introduction
According to ASTM F2792-10, additive manufacturing (AM) is defined as "the process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" [1] such as machining. In the recent years AM technologies developed rapidly and techniques like Electron Beam Melting (EBM), Selective Laser Melting (SLM), Selective Laser Sintering (SLS), Laser Metal Deposition, Powder Bed Fusion, just to mention some variants, prepared the ground for AM technologies being increasingly established in the metal part production industry, not only for prototyping. Generally AM is complementing other powder metallurgy (PM) technologies like Hot Isostatic Pressing (HIP) or Metal Injection Molding (MIM). HIP is used to produce massive, near net shape parts of several 100 kilograms (with fine and full isotropic microstructure) but also as a densification step for parts produced by AM technology. In contrast MIM, like other press & sintering technologies, is widely used to produce large series of small near net shape parts. Although the choice of a suitable PM process depends on the type and size of part to be produced and on the requirements and possibilities of the user, all techniques share one common element: the metal powder.

Metal Powders for Additive Manufacturing
Among the metal powders regularly used for AM are different steels, nickel and cobalt base superalloys, titanium- and aluminum alloys. Various other metals like copper alloys, precious metals and refractory metal alloys are under evaluation. The powders are produced by a process called "atomization".

In the gas atomization (GA) process, a stream of molten metal, pouring from a tundish through a nozzle is hit by a jet of inert gas such as nitrogen or argon. This inert gas jet nebulizes the molten metal into very small droplets which cool down and solidify while falling down inside the atomization tower. The particles are then collected as powder. This process is the most common applied process to produce spherical metal powders [1]. Since the liquid metal is not protected from ambient air, the GA process is suitable for less reactive metals like steels, certain aluminum alloys and precious metals.

For more reactive elements like titanium, high purity aluminum or in order to avoid particularly oxygen build up in superalloys a modification of the process is recommended [1], where the melting takes place under vacuum. The Vacuum Induction Melting (VIM) gas atomization process [2] is such a modification where the melting is done by induction heating under vacuum. The droplet formation is still driven by an inert gas jet. In case of titanium or aluminum, high purity argon shall be used as nebulizer gas since nitrogen would react with the molten metal and form stable nitrides of these elements.

Interim Conclusion

It got clear the liquid metal is exposed to process gases like argon or nitrogen during the atomization process. These process gases can be entrapped into the powder particles in form of micro pores which are sealed during the solidification process. Actually the initial argon content of available Inconel and Ti_6Al_4V powders exanimated varies vastly from < 100 ng/g (ppb) to over 1500 ng/g. Despite using optimized process parameters for the AM process, defects like pores and shrink holes cannot be completely avoided (e.g. the SLM process itself takes place under argon atmosphere). One key aim of the AM process is to build parts without porosity and thus the remaining porosity is one main quality feature of the parts. Especially argon filled pores would affect the quality and mechanical properties of the final part [3]. The HIP process is attracting more and more attention as post-processing technique for AM parts, since HIP can strongly reduce the internal porosity of AM produced parts, thus enhancing product quality [3]. Porosity filled with a process gas like argon, prevents a perfect post-densification by means of HIP. Another problem arises when the part is exposed to higher temperatures because entrapped gases would create internal stresses and may support cracking. Thus, an argon content over 400 ng/g is not permitted for HIPed parts [4] with safety limits down to 50 ng/g [5].

The remaining porosity can be measured by micro CT, but this technique cannot give information about whether or not porosity is filled by a process gas. Thus an argon analysis shall be conducted.

Quality Control

The quality of the initial metal powder used in AM plays an important role on the quality and properties of the final product but also for developing process parameters to ensure robust build-to-build consistency or reproducibility between different AM machines. An established parameter is the particle size, its distribution and the particle morphology (spherical vs. irregular shaped or porous particles). However, as explained above in case of entrapped argon, these more or less mechanical parameters are not sufficient for a full quality control process. Although AM methods become increasingly introduced in production processes, they are still new in terms of required process and quality control steps. For example there are currently no industry-wide standards settled describing or defining the necessary criteria.

The metal powders are usually analyzed for their initial elemental composition in regard to all major alloying elements (e.g. Ni, Cr, Mn, Al, Cu, etc.) by wavelength dispersive X-ray fluorescence like Bruker's S8 TIGER, which is perfectly equipped for this task. But while these alloying elements usually do not change during processing the powder and a one or two point control step along the production chain might be sufficient, the content and effect of various "foreign" elements does. These "foreign" elements (that usually do not belong into a metal) are also referred to as "gases in metals". The negative effect, especially that of hydrogen, is known since a long time and became so prominent that its effect was entitled "the hydrogen disease of certain metals" [6]. Elements like (O, N, H but also Ar) can easily vary during the production chain of AM manufactured parts. Likewise the carbon und sulfur concentration can be affected during the various melting (heat treatment) steps or due to contamination of the base powder material. Two other important points that underline the need for a close monitoring of mentioned elements, especially oxygen and hydrogen are:

- Storage conditions (like humidity, temperature, atmosphere, etc.) and aging of the metal powders. Packing shall be in air tight containers or better under argon atmosphere, especially for alloys containing reactive elements like titanium or aluminum.
- The reusability of the powder after subsequent additive manufacturing cycles. This is also referred to as "recycling" powder that was not used to build the part in the powder bed of the AM machine. Since a high purity powder with the right quality can be quite expensive, it is obvious unused powder is not thrown away but reused for the next production cycle. But since powder with a particle size between 5 μm and 150 μm has a high specific surface, the surface

oxygen content will increase with subsequent recycling steps.

Effect of Oxygen, Hydrogen and Nitrogen on Material Properties

Whereas the influence of carbon and sulfur on the properties of metals, especially steel is well known and summarized in Table 1. The influence of oxygen, nitrogen and hydrogen is less commonly known and worth to be briefly discussed.

Table 1. General influencing trends of carbon and sulfur on the physical properties of steels.

Physical Property	Carbon Influence	Sulfur Influence
Tensile Strength	Strongly increasing	Slightly reducing
Hardness	Strongly increasing	Slightly increasing
Strain	Slightly reducing	Strongly reducing
Stretching Limit	Strongly increasing	No effect
Notch Impact Strength	Slightly reducing	Strongly reducing
Long-term Strength	Strongly increasing	Strongly reducing
Thermal Conductivity	Slightly reducing	Strongly reducing
Electrical Conductivity	Slightly reducing	Strongly reducing
Wear Resistance	Strongly increasing	Slightly increasing
Cold Workability	Strongly increasing	Strongly reducing
Hot Formability	Slightly reducing	Strongly reducing
Cutting Quality	Strongly increasing	Slightly increasing
Corrosion Resistance	Slightly reducing	Slightly reducing

Oxygen

Oxygen is generally an unwanted, parasite element in all metals. In steel it causes ageing brittleness. In titanium even small amounts of oxygen do affect the mechanical properties like hardness considerably. Even small differences in the oxygen content may determine the difference between a top-quality (grade 1: 0.18% O) or low-quality (grade 3: 0.35% O) titanium alloy. One differentiates between bulk oxygen which can be present for example in form of oxidic inclusions and the oxygen layers on the surface (corrosion). Especially reactive elements like titanium and aluminum have a high oxygen affinity.

Nitrogen

In steel the nitrogen content may be differentiated into a desired (e.g. nitriding as surface hardening treatment) and undesired fraction. There are special steel applications which allow high nitrogen content but in these cases its chemical form matters. In its elemental form nitrogen appears along the grain boundaries and influences the ductility significantly. Nitrogen chemically bounded to other elements is usually not considered to be important. This changes when the steel is alloyed with significant amounts of titanium or other elements that form stable, sometimes refractory nitrides. Titanium nitride with a melting point of ~2930°C is an excellent example for refractory inclusions that finally represent failures in the underlying metal structure and thus affect brittleness.

Hydrogen

Hydrogen-induced material damage is a widespread and dreaded phenomenon. It is manifested in a way that a component, even without visible indication of corrosion, fails or breaks unforeseeable under the influence of mechanical stress, which may lead to life- and environment-threatening damages. Particularly high-tensile and high-strength low-alloyed steels tend to this kind of hydrogen induced stress corrosion cracking which commonly is called hydrogen embrittlement. Hydrogen can be supplied during various manufacturing and processing steps, e.g. during melting (incl. AM), etching and annealing as well as through corrosion and during welding processes. Apart from the interstitial diffusion of atomic hydrogen (more precisely a proton) in the metal lattice, hydrogen can accumulate in areas of the metal which are exposed to tensile stress. Thus, hydrogen in metals can be present as:

- Diffusible hydrogen (DH): hydrogen atoms, located on interstitials, high mobility, solubility increases with temperature, released from a ferritic steel even at room temperature over a period of time.
- Residual hydrogen (RH): weakly to strongly trapped hydrogen atoms and molecules, with a differentiation between reversible and

irreversible traps according to the binding energy, not mobile, solubility decreases with temperature, released at elevated temperatures. Stable hydrides of e.g. Nb, V, Ta, Zr, Ti and Mg form the strongest bound form of residual hydrogen.

The special and individual microstructure of steel greatly influences its susceptibility for hydrogen induced embrittlement even on < 1 ppm levels in high strengths steels. Diffusible hydrogen has a less damaging effect in titanium or aluminum base materials. In titanium inclusions of stable titanium hydride degrade the mechanical properties whereas in aluminum, hydrogen is responsible for porosity created during the solidification process. Generally, hydrogen is likewise oxygen an unwanted element in metals but often with much higher harmful impact.

Analytical Methods
There are different methods to determine the elemental and impurity composition; most methods for impurity analysis require a destruction of the sample to ensure that all relevant compounds of the sample are released quantitatively. Combustion analysis for carbon and sulfur or inert gas fusion (IGF) for oxygen, nitrogen hydrogen and argon shows a number of advantages. Solid samples up to 1g in form of small pieces, powders, chips, and drillings can directly be used for analysis without further sample preparation. Although each measurement is fast not all elements can be measured in one single analysis. Oxygen, nitrogen, hydrogen as well as argon are analyzed by an inert gas fusion analyzer like the G8 GALILEO, carbon and sulfur by combustion analysis in the G4 ICARUS HF. This is because of different methods are applied.

Advancing Carbon and Sulfur Analysis with the G4 ICARUS HF
In combustion analysis a solid sample is weighed into a ceramic crucible together with a combustion accelerator (W, W/Sn, Fe) that will readily couple with the electromagnetic field produced by an RF-coil that surrounds the crucible (see Fig. 2). The accelerator is necessary to ensure a good coupling with the electromagnetic field and to provide additional energy to the combustion process so that a fluid melt is achieved. The sample and accelerator
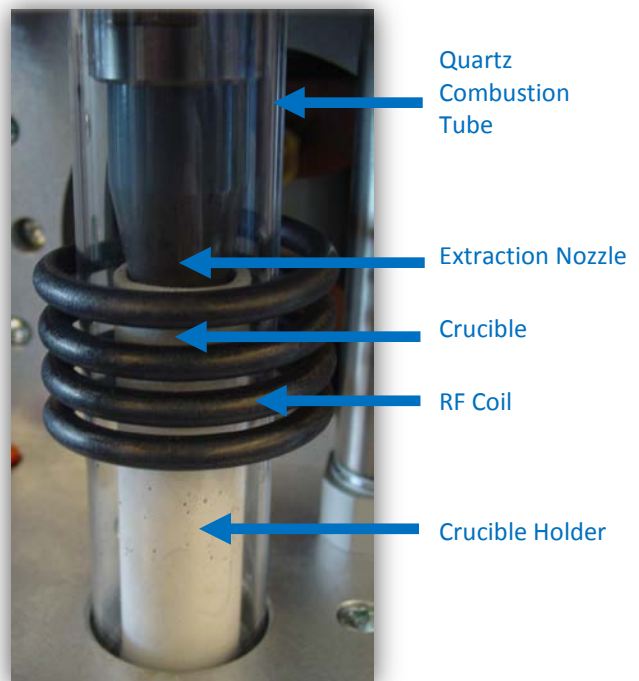

Figure 1. Example of different SLM produced test specimens (cubes) and the initial powder metal used.

Quartz Combustion Tube

Extraction Nozzle

Crucible

RF Coil

Crucible Holder

*Figure 2. Furnace of the **G4 ICARUS HF** analyzer featuring a patented extraction design.*
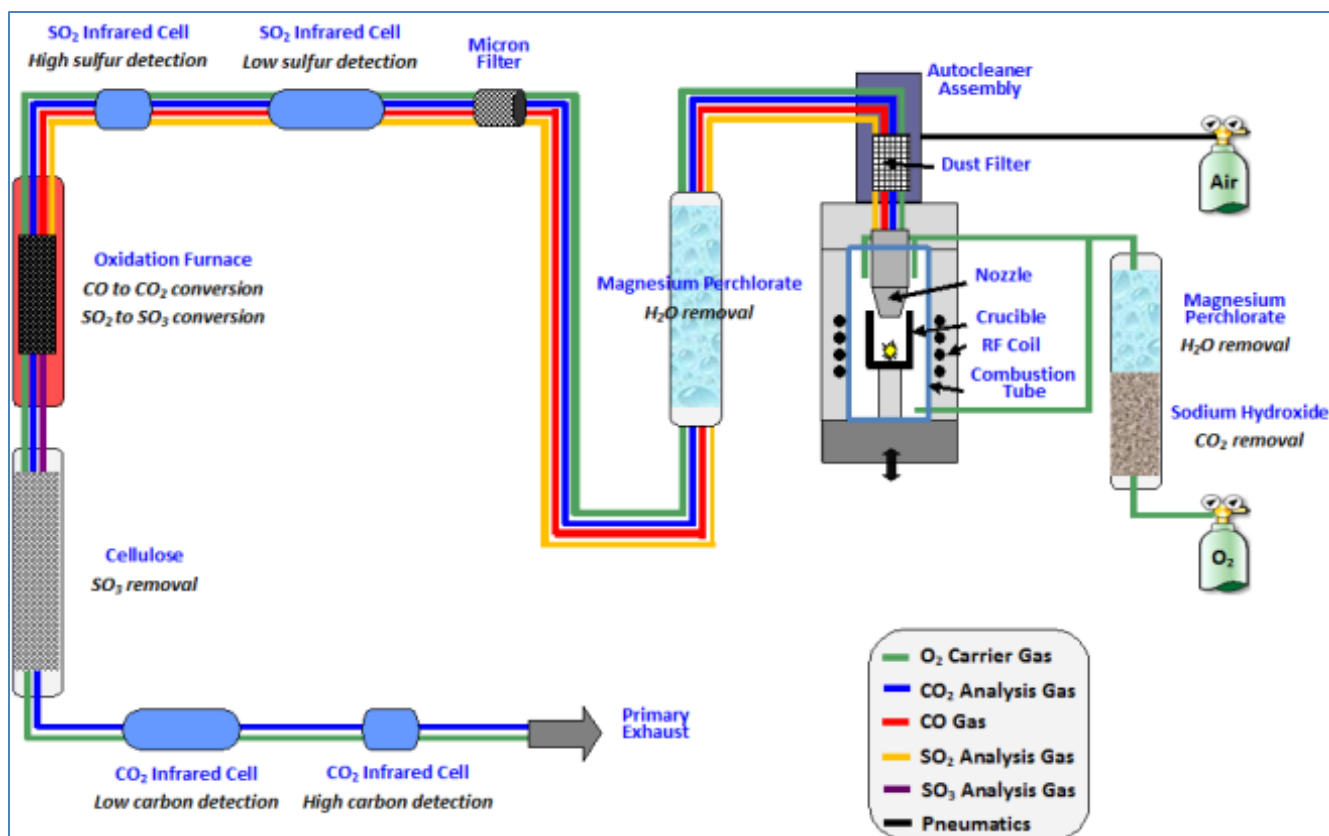
*Figure 3. Block diagram representation of the **G4 ICARUS CS HF** showing primary components and the analytical flow path.*

are heated via induction from the RF-coil to temperatures up to 2000°C in a pure oxygen atmosphere. Under these conditions carbon and sulfur components in the sample react quantitatively with the oxygen to carbon dioxide and sulfur dioxide which are detected and quantified downstream by infrared detectors (see Fig. 3).

Separating itself from other commercially-available combustion analyzers, the G4 ICARUS HF provides many unique and beneficial features like a patented gas extraction design, a unique vacuum-free automatic furnace auto-cleaner for dust removal, high precision electronic mass flow controllers and improved detectors for highest linear dynamic range and single ppm detection capabilities.

Oxygen, Nitrogen, Hydrogen Determination with the G8 GALILEO
The determination of the oxygen and nitrogen resp. hydrogen content in solids with the G8 GALILEO is

performed using the inert gas fusion (IGF) principle. The sample is fused inside a graphite crucible under a flow of inert gas. The freely programmable temperature of the electrode furnace is monitored and controlled by a contact-free optical sensor. Temperatures up to 3000°C, sufficient to decompose even refractories with highest melting points, can be reached by this method. At the applied high temperatures and with carbon present in excess, oxygen in the sample (which in general is present in form of oxides) reacts to carbon monoxide (CO) quantitatively by a redox reaction. Furthermore, existent nitrogen compounds are decomposed evolving N_2 gas. Hydrogen is set free in form of H_2 just by melting the sample. The evolved measuring gases are swept by the carrier gas through the high-stable, sensitive detection system, consisting of one or optional two selective NDIR-detectors for CO and a thermal conductivity cell (TCD) for the detection of N_2 or H_2. The removal of interfering gases is made by means of a specific set of reagents. The switching-over from nitrogen to
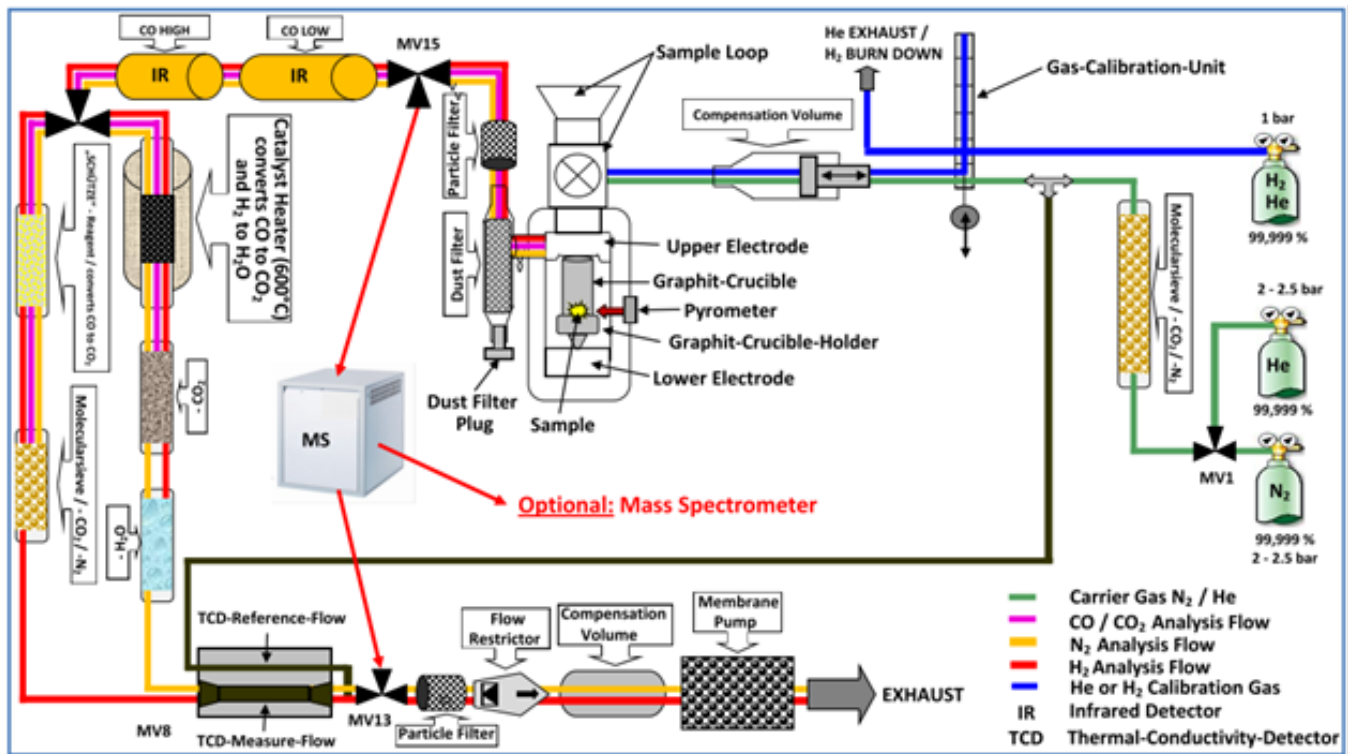
*Figure 4. Block diagram representation of the **G8 GALILEO** showing primary components and the analytical flow path.*

hydrogen analysis and vice versa is performed in a shortest time by a corresponding command in the software with which the suitable carrier gas and set of reagents are automatically activated by solenoid valves (see Fig. 4). The detectors are equipped with automatic level control and base line compensation; the optimal range for the evaluation is selected automatically. The concentrations are calculated from the time integral of the particular signals taking into account the calibration and the sample weight.

Typically the analyzer is calibrated by means of certified reference material. When appropriate reference material is not available, the calibration can be done by gas dose calibration. All required process, temperature and time parameters are set for a specified application on the parameter page in the software. The G8 GALILEO is available with an integrated cleaning system for the impulse furnace with dust removal, an automatic crucible loader as well as an autoloader for up to 40 samples.

Ar Determination Mass Spectrometer Coupling

The fusion of a sample in a high purity graphite crucible with subsequent transport of the released gaseous species by an inert carrier gas is referred to as carrier gas hot extraction (CGHE), gas fusion analysis (GFA) or inert gas fusion (IGF). For applications that require improved detection limits (e.g. sub-ppm determination of hydrogen in high strength steels or high purity aluminum) or selective and sensitive determination of other trace elements (e.g. Ar in HIP processed parts, Ar-atomized powders, AM processed parts) or isotopes, Bruker offers the possibility to couple an external mass spectrometer (MS) to its G8 GALILEO analyzer. By a special interface, a constant fraction of the carrier gas is swept into the ion source of the MS, which is operated under high vacuum and continuously being pumped by a turbo molecular pump. The mass spectrometer provides an m/z range from 1 to 100 amu. The unit compromises a gas tight electron impact ion source, a quadrupole mass analyzer and a channeltron detector for improved

sensitivity and higher sample rates. For measurement of argon (one main isotope: [40]Ar with 99.6% abundancy), the ion source was operated in positive ion mode to generate Ar^{+} ions and the mass analyzer tuned to m/z 40 with a test mixture of Ar in He. Due to the fact that nitrogen reacts with titanium at elevated temperatures, helium was chosen as carrier gas.

Since certified reference material (CRM) does not exist for all matrixes and analytes (e.g. diffusible hydrogen or argon in metals) the calibration was performed by the optional gas dose calibration unit (see Fig. 5); a procedure that is also ideal for a rapid, independent verification of any reference material based calibration.

Calibration for Argon
Since there are no reference materials with defined Ar content available, the calibration has to be performed by dosing known amounts of Ar into the detection system. The optional gas calibration device of the G8 GALILEO enables computer controlled dosing of ten different, exactly determined volumes.
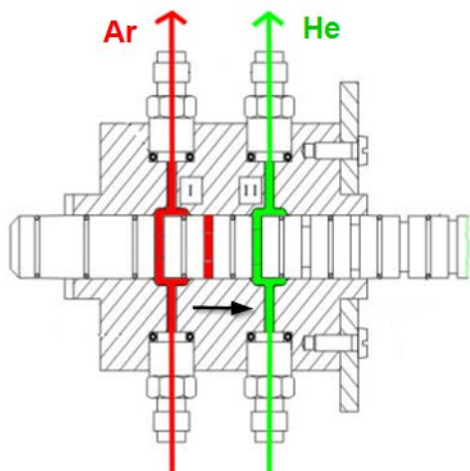
Figure 5. Schematic/cross section of the integrated gas dose device of the G8 GALILEO: 10 different volumes corresponding to 10 different grooves in a motorized brass rod. The volumes are separated by O-rings. By a linear movement of the rod, the volume purged and filled with the calibration gas (red) is first isolated and then released into the carrier gas stream (green). The size of each volume is exactly determined at the factory. Simultaneously, the pressure and temperature of the calibration gas is measured by sensors (not shown).

The absolute pressure and temperature of the calibration gas is internally measured, recorded and used for calculation of the absolute amount of Ar dosed into the carrier gas stream. The calculation of the absolute mass of an element X (here X = Ar) is done according to equation (1) by the ideal gas law:

$$m(X) = \frac{p\,V\,M(X)}{R\,T}\,c \qquad (1)$$

With:
$m(X)$ = mass of species X in µg (10^{-6} g)
p = (absolute) pressure of the calibration gas inside the volume in hPa
V = volume of the gas dosed in ml
$M(X)$ = molar mass of species X in g/mol; M(Ar) = 39.948 g/mol
R = molar gas constant; R = 83144.1 hPa ml / (mol K); [7]
T = absolute temperature of the gas in K
c = concentration of species X in the calibration gas in weight ppm (e.g. 980 ppm Ar)

The same test gas mixture used to calibrate m/z-axis of the quadrupole was used as calibration gas. The mixture was ordered from a gas supplier with a certified analytical lab. A mixture of ~1000 ppm of Ar and H_2 (each purity 5.0 = 99.9990%) in helium (purity 4.6 = 99.996%) was used. The certificate of analysis shows the resulting mixture has the following concentrations:

Hydrogen:	996.0 ppm (+/- 2% rel.)
Argon:	980.0 ppm (+/- 2% rel.)
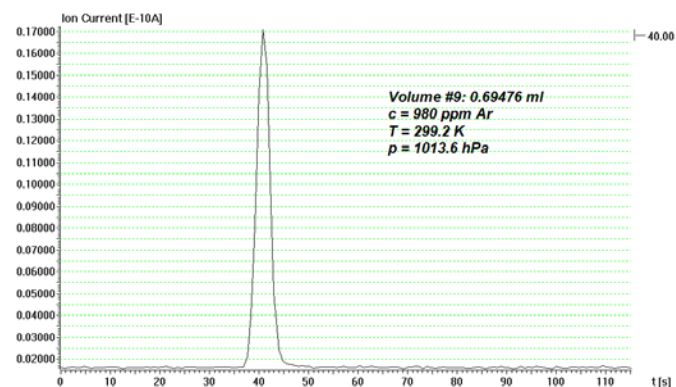
Figure 6. Typical MS signal of m/z 40 during gas dose calibration. In this example volume #9 was dosed. Due to equation (1) the peak corresponds to a mass of 1.1082 µg Ar (1108.2 ng Ar). The integrated peak area, 5.50232E-9 [A], in relation to the absolute mass of Ar is the slope of the linear calibration function: 4.9651E-9 [A/µg$_{Ar}$].

When combined with the mass spectrometer the G8 GALILEO provides selective detection capabilities on a low two digit ppb level for argon and sub-ppm level for hydrogen. Without the MS it does not provide argon detection capabilities but due to its advanced, high sensitive and stable TCD detector, a free selection of carrier gases and robust <1 ppm detection capabilities for hydrogen and nitrogen. Oxygen is quantified by one or more IR detectors in its initial form (CO) without any prior requirement to convert it into CO_2.

Figure 7. The G8 GALILEO applied in a laboratory.

Conclusion

Non-metallic elements like carbon, sulfur, hydrogen, oxygen, nitrogen and argon influence the properties of metallic materials. These elements are present either already in the powdered raw materials used for AM processes or may be introduced during the additive manufacturing process. Therefore, a thorough quality control should always comprise the analysis of the used powder feed stock, recycling cycles as well as the final product. Combustion/IGF analysis offers a convenient, fast and reliable way to establish and verify the necessary control limits. With its unique argon detection capabilities and its wavelengths dispersive XRF products, Bruker is currently the only vendor that can offer the full elemental analysis capabilities required to run a high quality AM production.

Please find out more at: www.bruker.com and do not hesitate to discuss your analytical needs with our experts.

References

[1] "Introduction to Additive Manufacturing Technology, a guide for designers and engineers", European Powder Metallurgy Association, 1st edition; free publication downloadable from the EPMA website: www.epma.com/epma-free-publications

[2] ERASTEEL Powder metallurgy information, http://www.erasteel.com/content/powder-metallurgy-0

[3] Schaak C., Tillmann W., Schaper M., Aydinöz M.E. (2016). Process Gas Infiltration in Inconel 718 Samples during SLM Processing. RTeJournal - Fachforum für Rapid Technologie, Vol. 2016 and references therein http://www.rtejournal.de/ausgabe-13-2016/4403

[4] Hofer B., Bigolin F., Hamentgen M., Stremming H., Zühlke C., "Measuring the gas content in HIP components and impurities in the argon- and chemical reacted gas used to compacting near net shape parts and castings. Presentation of the measurement technique.", session 215, HIP 2014 conference

[5] Mellin P., Östlund M., Fredriksson W., Strondl A. "Detecting Argon Trapped in Reference Samples Made by Hot Isostatic Pressing", World PM2016 proceedings https://www.researchgate.net/publication/308969503_Detecting_Argon_Trapped_in_Reference_Samples_Made_by_Hot_Isostatic_Pressing

[6] Baukloh W., Stromburg W. in "Über die Wasserstoffkrankheit einiger Metalle", Z. Metallkunde 29 (1937), S. 427-430

[7] P. J. Mohr, B. N. Taylor, D. B. Newell; "CODATA recommended values of the fundamental physical constants - 2010"; National Institute of Standards and Technology, USA http://physics.nist.gov/constants

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