HH-XRF and HH-LIBS for alloy analysis
Choosing the Right Tool for the Right Job

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Handheld X-ray fluorescence spectrometry (HH-XRF) has been established as the gold standard method for in-situ elemental determination in metals and alloys in the last 10 years. More than 5,000 analyzers are sold yearly worldwide for scrap metals sorting and positive material identification (PMI). PMI is a quality assurance tool consisting of the identification of alloy grades in various industries using metals in order to verify compliance to specification and to avoid mixing up of the materials. Handheld laser induced breakdown spectrometry (HH-LIBS) is an emerging method which show promising capabilities for alloy analysis and may be able to complement HH-XRF in alloy analysis, especially in alloys containing low atomic number elements like Be, Li, Mg, Al and Si (e.g. light elements).

These methods are based on different principles:

HH-XRF is a method of EDXRF in which the radiation produced by a miniature X-ray tube strikes the sample surface and causes ionizations of the inner shell of the atoms constituting the sample. The resulting vacancies in the inner shell of the atom are filled by electrons from higher shells and thereby photons specific to the element are emitted and

Figure 1: Characteristic X-ray production in handheld XRF

detected with a Si-detector. Since XRF involves transition within inner shells of atoms, the spectra obtained will contain a limited number of lines, typically 2 to 6 resolved lines per element in energy-dispersive XRF. For metal analysis, HH-XRF can work simultaneously for determining elements ranging from Ti to Pb within few seconds. When needed, a second beam condition is used to determine light elements resulting in longer measurements of typically 10 to 60 sec.
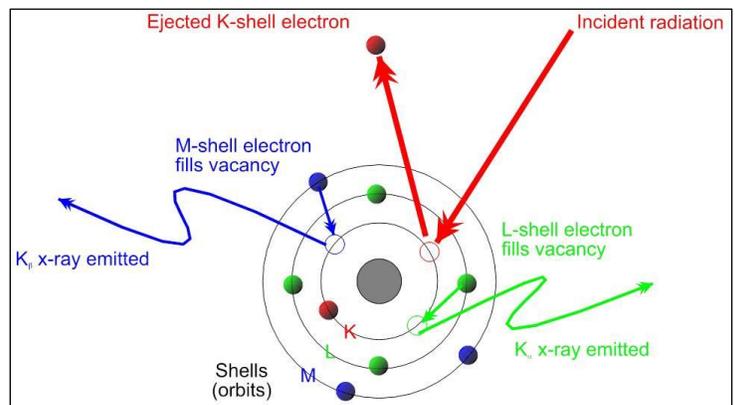
HH-LIBS is a method of optical emission spectrometry but unlike spark-OES, the emission is subsequent to the generation of a plasma induced by a laser. In HH-LIBS, a laser pulse strikes the surface of the sample and ablates an amount of material in the range of 1 ng and generates a plasma plume (partially ionized gas) in the temperature range of 5,000-20,000K. The energy of the laser is low, but is focused to a microscopic point on the sample to generate the plasma. In this plasma, the matter constituting the samples is dissociated into atoms (atomization) and partially ionized. Those atoms and ions will be excited (transition of electrons from lower to higher energy levels of valence shell) and by returning into their ground state (transition from higher to lower level of valence shell) they will emit characteristic lines for each element. The emitted light is transmitted through optical fibers and the polychromatic radiation is dispersed in one or more spectrometers by diffraction gratings and detected by CCD chips. The spectra of LIBS

Figure 2: Schematic of LIBS (laser-induced breakdown spectroscopy) by US Army Research Laboratory - Courtesy of US Army Research Laboratory

can contain hundreds or even thousands of lines for a single element. The sensitivity of those lines can differ by several orders of magnitude and result in extremely line rich spectra, especially when the sample contains high concentrations of transition metals as it is the case for alloys like stainless steel. In typical HH-LIBS systems, the dispersion power of the spectrometer is often limited by its size and some important analytical lines may not be fully resolved from lines emitted by the matrix. In order to cover the entire spectral range between 180 and 800 nm multiple spectrometers may be required. Moreover, wavelengths of less than 200 nm (like C 193.09 nm or S 180.73 m) are strongly absorbed by air and require an argon purge of the optical path to be detected. Almost any element generally contained in metals can be detected with HH-LIBS: the sensitivity for alkaline (Li, Na, etc.) and alkaline-earth metals (Be, Mg, etc.) is very high and the sensitivity for transition metals is good, except for refractory elements like Nb, Mo, W, or Ta which are difficult to determine [1,2]. The sensitivity for C, P and S is generally not sufficient to analyze those elements at relevant levels in alloys.
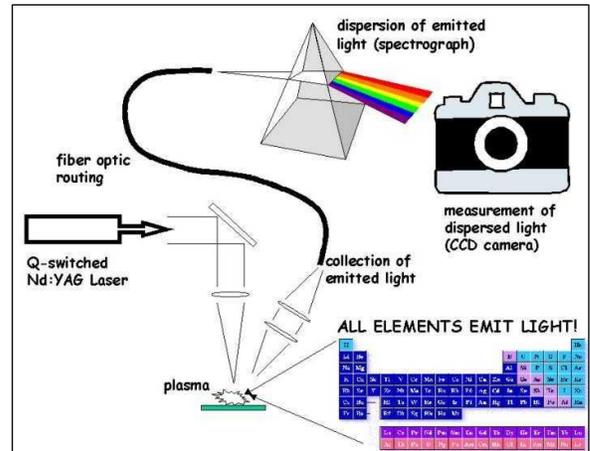

Typical spot diameter of HH-XRF is 3 to 8mm, whereas the crater generated by the laser in HH-LIBS has a diameter of typically 50 to100 μm. Only a fraction of 15 to 20 μm in diameter of this crater will actually be analyzed. Hence HH-LIBS may be more sensitive to local heterogeneities. The laser pulse can be moved

during the analysis to correct for effects caused by heterogeneities. On the other hand, much smaller spots and very narrow weld seams can be analyzed using HH-LIBS.

The optical emission induced by the laser is a transient phenomenon, whereas the X-ray beam is constant and well controlled. Hence, it is expected that HH-XRF delivers more stable, repeatable and reproducible results than HH-LIBS. The quantitative analysis is considered as Achilles' heel of LIBS - first because of the complex laser-sample interaction process which depends upon both laser characteristics and material properties, and second, due to the plasma–particle interaction process which are time and space dependent [2].

When compared to HH-XRF, HH-LIBS offers new possibilities in terms of applications: Li can be detected in aluminum alloys used in aerospace, Be can be detected in Be-bronze and C can be detected in carbon steel and cast iron. Moreover, the sensitivity of Mg and Al is much higher in HH-LIBS than HH-XRF so that sorting of Aluminum and Titanium alloys is significantly faster (few seconds vs. 30-60s with HH-XRF). In contrast, HH-LIBS may not be able to detect low concentrations of S and P which can be quantified by HH-XRF in stainless steel (SS 303, SS 416) and in phosphorous bronzes. Generally, for scrap metal sorting, HH-LIBS is expected to be faster for aluminum alloys and more or less equivalent to HH-XRF for stainless steel. HH-LIBS may be able to sort most of the Ti-alloys faster than HH-XRF, with few exceptions like Ti Grade 11 containing around 0.15% Pd, which can be identified using HH-XRF. Sorting of stainless steel can be done within few seconds using both HH-XRF and HH-LIBS. For heavier alloys like super alloys, copper alloys (except aluminum and beryllium bronze), solders, lead alloys or precious metal alloys, HH-XRF delivers better sensitivity and accuracy for the analysis than HH-LIBS. In addition, the measurement of Tramp elements in scrap may be difficult for HH-LIBS, for example, the detection of Pb and Sn in stainless steel alloys at 100-500 ppm will be difficult using HH-LIBS.

Figure 3: Metal sorting by means of handheld XRF

For fast sorting of aluminum alloys based upon light elements, HH-LIBS is clearly the best alternative as well as for separating many magnesium and titanium grades. When precision and accuracy matter more as in PMI analysis and quality control or when price figures are required in scrap trading (Ni, Mo, etc.), then HH-XRF is the still the method of choice. From a regulatory point, the use of HH-XRF requires, paperwork,

licensing and in some countries, long radiation safety training. In contrast, the utilization of lasers (class 1 or 3b) does not require any of these.

Thus, if your main application is measuring magnesium, aluminum or titanium alloys or red metals containing significant amounts of Be, Al or Si, the instrument of choice will be HH-LIBS. If your application is measuring stainless steel, high temp alloys or other heavy metal alloys, the instrument of choice will be HH-XRF. In both cases, the instrument of choice can be used to measure most alloy classes, however, there are compromises in speed, accuracy and precision which must be understood. Make sure that you evaluate the various choices on your unique set of samples and select the tool which meets your needs the best.

Pros & Cons of HH XRF and HH LIBS

HH XRF	HH LIBS
Pros • Speed of analysis for element Ti-U (2-5s) • Established technique • Robust and reliable method • Large analyzed surface (7 to 50 mm^2) • Excellent sensitivity and accuracy for metals with atomic number >22 • Good for analysis of Tramp elements • Completely non-destructive method	**Pros** • Speed of analysis (2 s) including light element • Lower LODs for light elements with low excitation potential / low ionization potential (alkaline and alkaline-earth elements) • No x-ray safety requirement • Ideal to analyze small areas like weldings • Potential to measure Li, Be, B, C
Cons • Needs compliance with local radiation safety regulation • Long measurement time when light elements required (10 s and more) • No detection of Li, Be, B, C, Na	**Cons** • Not a mature method • Not accepted by important organizations such as API • Not yet suitable for trace analysis – e.g. cannot analyze most Tramp elements • Can't quantify C at 200-300 ppm • High LODs for S, P. • Poorer accuracy due to transient nature of plasma • Small analyzed area sensitive to heterogeneities • Resolution of compact spectrometers/need of multiple spectrometers + optical fibers resulting in bulky and heavier instruments • Destructive method (small crater or pattern left on the analyzed item)

References:

[1] R.C. Wiens, S. Maurice, The Chem The ChemCam Instrument Suite on the Mars Science Laboratory Rover Curiosity: Remote Sensing by Laser-Induced Plasmas, Geochemical News 145 (June 2011).

[2] D.W. Hahn, N. Omnetto, Laser Induced breakdown spectrometry, Part 1: Diagnostics and plasma-particle interactions: still-challenging issues within the analytical plasma community, Applied Spectroscopy 12 (2010), 335A-360A.