



FIRST Newsletter

January 2015, Issue 31

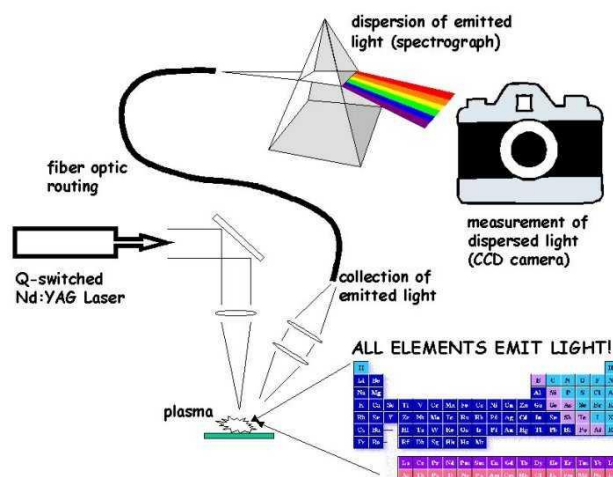
Compare and Contrast: HH-XRF and HH-LIBS for Alloy Analysis

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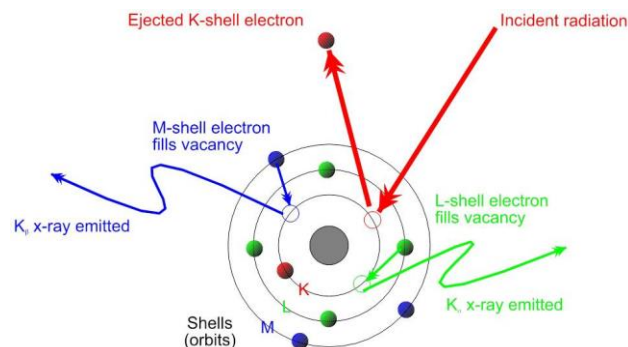
Handheld alloy analyzers: does LIBS exceed XRF?

Handheld X-ray fluorescence spectrometry (HH-XRF) has been established in the last 10 years as the gold standard among analytical methods for in-situ elemental determination in metals and alloys. 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 showing very promising capabilities for alloy analysis which can potentially exceed those of HH-XRF so that HH-LIBS could become the method of choice for in-situ elemental analysis in metals.

These methods are based on different principles: in [HH-XRF](#), radiation produced by a miniaturized 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 detected with a Si-detector.



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



Characteristic X-ray production in handheld XRF

LIBS is a method of optical emission spectrometry (OES) and 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

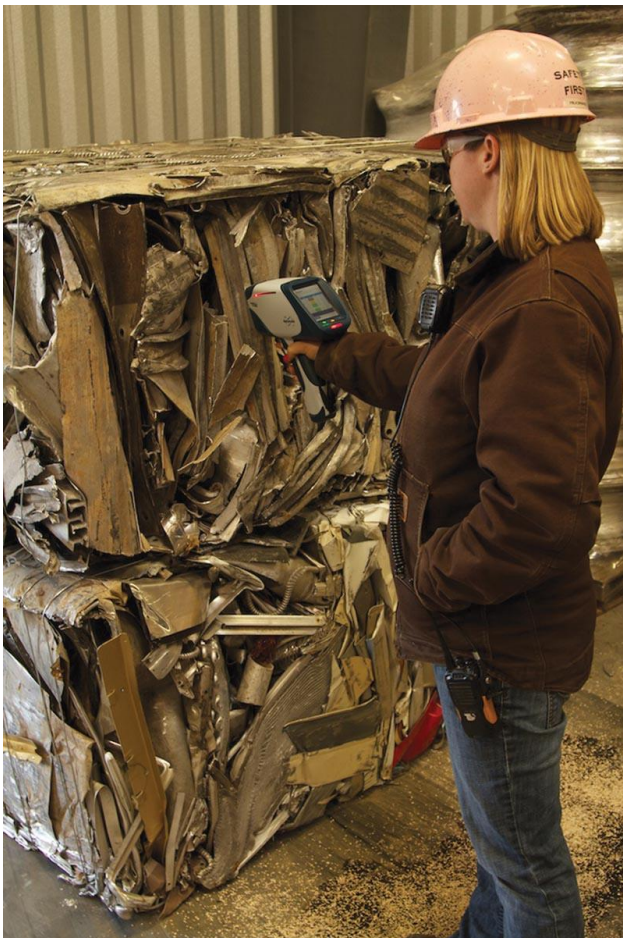
plasma, the matter constituting the samples is dissociated into atoms (atomization) and partially ionized. Those atoms and ions will be excited (transition of electrons from lower to higher energy levels of valence shell) and by returning to their ground state (transition from higher to lower level of 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.

Since XRF involves transition within inner shells of atoms, the obtained spectra will contain a limited number of lines, typically 2 to 6 resolved lines per element in energy-dispersive XRF, whereas the spectra of LIBS 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 is the case for alloys like stainless steel. In typical HH-LIBS systems, the power of dispersion of the spectrometer is often limited by its size and some important analytical lines are not resolved from lines emitted by the matrix. The coverage of the entire spectral range between 180 and 800 nm requires the use of multiple spectrometers, in order not to degrade the resolution too much resulting in size and weight increase. Moreover, wavelengths of less than 200 nm (like C 193.09 nm or S 180.73 nm) are strongly absorbed by air and require an argon purge of the spectrometer to be detected.

For metal analysis, HH-XRF can work simultaneously for determining elements ranging from Ti to Pb within a few seconds. When needed, a second beam condition is used to determine elements from Mg to Ca resulting in longer measurements of typically 10 to 60 sec. 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 8 mm, whereas the crater generated by the laser in HH-LIBS has a diameter of typically 50 to 100 μm . Only a fraction of the 15- to 20- μm diameter of this crater will be actually analyzed. Hence HH-LIBS will 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 an Achilles' heel of LIBS first because of the complex laser-sample interaction process which depends upon both laser characteristics and material properties, and second,



Metal sorting by means of handheld XRF

Pros & Cons of HH-XRF and HH-LIBS

| HH-XRF | HH-LIBS |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Pros <ul style="list-style-type: none"> • Speed of analysis for element Ti-U (2-5s) • Established method • Robust and reliable method • Large analyzed surface (7 to 50 mm²) • Excellent sensitivity and accuracy for metals with atomic number >22 • Can use fundamental parameter approach correct for matrix effects • Non-destructive method | Pros <ul style="list-style-type: none"> • Speed of analysis (2 s) including light element • Lower LODs for elements with low excitation potential / low ionization potential (alkaline and alkaline-earth elements) • No hassle with radiation safety • Ideal to analyze small areas like welds • Can measure Li, Be, B, C |
| Cons <ul style="list-style-type: none"> • 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 <ul style="list-style-type: none"> • Not yet a mature method • Not yet suitable for trace analysis • Can't quantify yet 300 ppm C • High LODs for S, P • Accuracy due to transient nature of plasma • Small analyzed area sensitive to heterogeneities • Needs a lot of standards for empirical calibration • 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) |

due to the plasma–particle interaction process which is 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 to Mg and Al is much higher in HH-LIBS than HH-XRF so that sorting of aluminum and

titanium alloys is significantly faster (a few seconds vs. 10-30s). In contrast, HH-LIBS might 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 a 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, it is expected that HH-XRF delivers better sensitivity and accuracy for the analysis of those materials than HH-LIBS. For in-situ analysis of low alloy steel, HH-XRF and HH-LIBS are complementary but generally still less suitable than mobile spark-OES analysis.

For fast sorting of aluminum alloys sorting based on Li or Mg, 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 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.

References:

[1] R.C. Wiens, S. Maurice, The Chem Cam 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.