Hand-Held XRF Analyzers Advance PMI Programs

New features and training combine to provide turnkey programs that reduce risk in the face of OSHA's National Emphasis Program

BY TOM ANDERSON AND JON SHEIN

The requirement for positive material identification (PMI) of alloy materials in refinery systems and petrochemical plant operations has grown dramatically over the past 20 years. The consequences of using the wrong material in a process plant are well documented. According to data compiled by the U.S. Occupational Safety and Health Administration (OSHA), since May 1992, 32 fatality/catastrophe incidents related to the release of highly hazardous chemicals have occurred in the petroleum refining industry. Many of these incidents occurred as a direct result of the use of incorrect alloy material in a critical process component. These incidents resulted in 52 employee deaths and 250 injuries. The new OSHA *CPL 03-00-004 — Petroleum Refinery Process Safety Management National Emphasis Program* is an example of the type of enforcement taking place worldwide as a result. New developments in technology and training are making it easier to perform PMI in more locations, with greater accuracy, and with better-trained operators than ever before.

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The Role of Hand-Held XRF in PMI

X-ray fluorescence (XRF) technology has been utilized in alloy analysis and identification for more than 40 years, but it is due to the technological advances of the past 10 years that it has become the primary method of choice for PMI. In contrast to the "portable" XRF systems of the mid 1990s, today's hand-held XRF systems are only a small fraction of the size and weight, and have more than 100 times the speed and precision of their ancestors — making 100% PMI of process systems truly feasible for petrochemical operations. Now instead of lugging a 15–20 lb piece of equipment on one's back, and testing for 15–20 s to achieve a grade identification, the PMI inspector can climb a scaffold carrying a small 3-lb XRF "gun" in a belt holster that will provide a laboratory-quality chemical analysis and positive grade identification in only 2–5 s.

The Science behind XRF Technology

Despite the complex physics involved, the basic premise behind XRF technology is really quite simple: When exposed to external X-rays of a sufficient energy, each of the individual elements present in a sample will produce a unique set of characteristic fluorescent X-rays that are essentially a "fingerprint" for that specific element — Fig. 1.

At the atomic level, an element produces a fluorescent X-ray when an external X-ray generated by either a miniature X-ray tube source or sealed radioisotope within the analyzer strikes an atom, thereby dislodging an electron from one of the atom's orbital shells causing it to enter a state of excitation. As the atom regains stability, it fills the electron vacancy with an electron from one of its higher energy orbital shells. This electron drops to the lower energy state by releasing a fluorescent X-ray, the energy of which is equivalent to the difference between the two quantum states of the electron. Figure 2 illustrates this principle using the classic Bohr model of an atom — Fig. 2.

These characteristic X-rays can then be categorized and counted when they contact an X-ray detector within the XRF instrument. The X-ray detector, a small semiconductor, receives the emitted X-ray, and passes it to the instrument processor as an electronic signal. By counting the individual emission events from each element over a period of time, this information can be modeled to produce a chemical composition of the sample being analyzed.

Advances in microprocessor technology, X-ray detectors, and the miniaturization of X-ray tubes over just the past few years have all contributed to the development of the hand-held, lab-quality XRF instruments that are available to us today. From a

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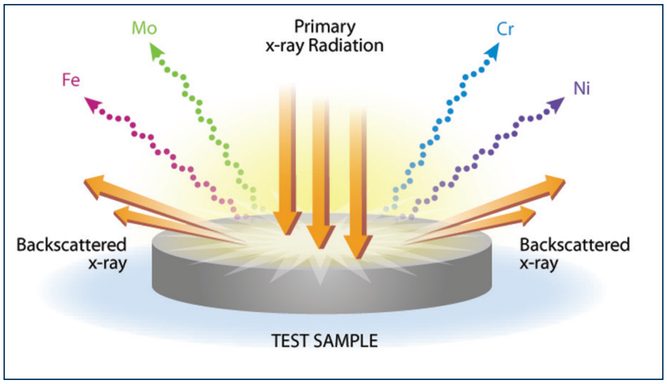


Fig. 1 — The basic premise behind XRF technology.

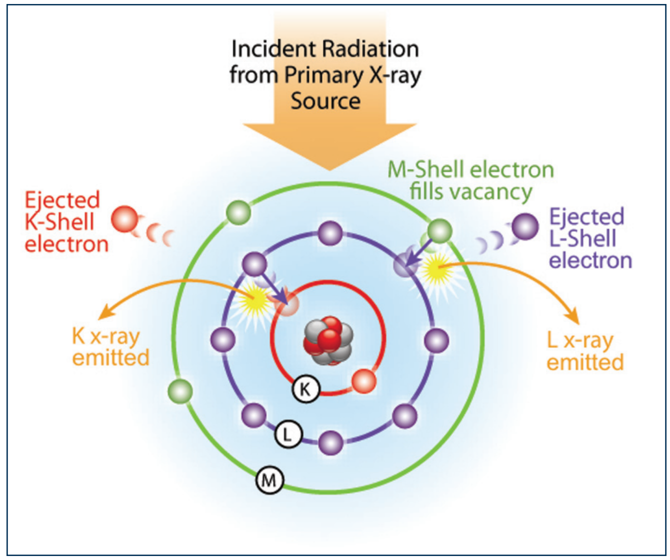


Fig. 2 — The Bohr model of an atom illustrates the principle behind XRF technology.

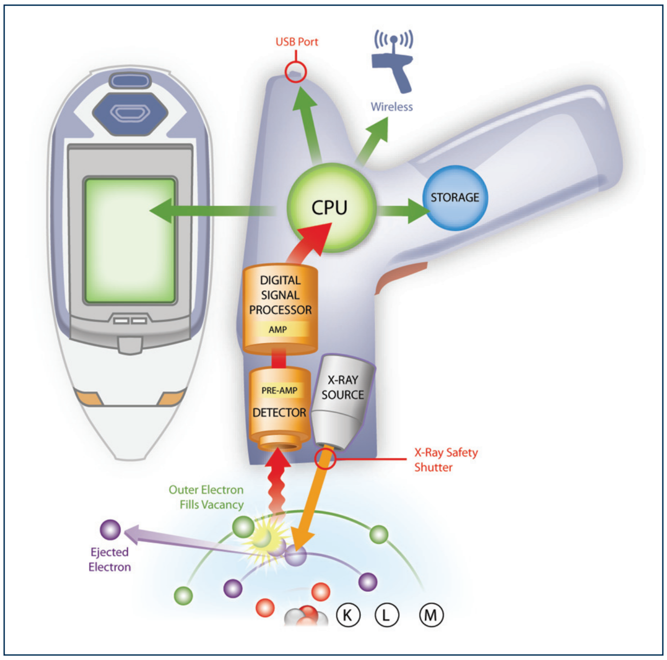


Fig. 3 — An illustration of what occurs between the analyzer and the sample during a measurement using an XRF instrument.

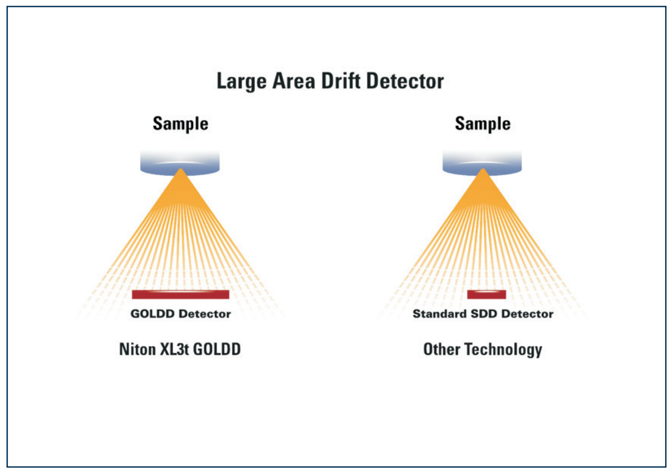


Fig. 4 — A comparison of the active area of the detector between GOLDD and standard technology.

user perspective, it is a simple point-and-shoot operation, but there is much happening behind the scenes during the analysis — Fig. 3:

1. Primary X-rays are released and directed at the sample
2. Primary X-rays cause elemental atoms in the sample to enter a state of excitation
3. The elements in the sample release characteristic X-rays that are captured by the X-ray detector
4. The detector converts the X-rays to electrical pulses, and sends them to a preamp
5. The signals from the preamp are sent to a digital signal processor for classification and counting
6. The digitized elemental intensity data are processed through advanced mathematical algorithms to convert to chemical composition data, which are then used to determine the alloy grade based on values from an internal grade library
7. The alloy composition values and grade identification are displayed on the instrument screen, and
8. The measurement data are stored for later recall or download to a PC.

New Detector Technology

Most recently, a new type of solid-state detector has been introduced that has once again revolutionized hand-held XRF analysis. The new geometrically optimized large area drift detector (GOLDD™) technology increases analyzer performance up to 10 times over the previous state-of-the-art Si PiN detector technology.

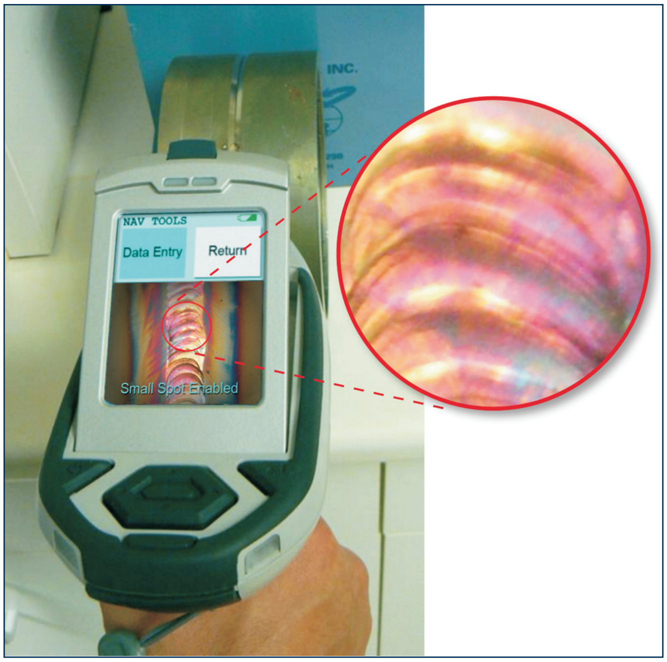
Of course, in order to take advantage of this high-capacity detector, the analyzer must have the ability to generate a sufficient number of fluorescent X-ray events from a sample, and position the detector to collect as many as possible. So there are more pieces to the puzzle than meet the eye.

The first piece is the silicon drift detector (SDD) itself — engineered to process more than 200,000 X-ray events per second.

The second piece is a 50-kV X-ray tube, which provides the excitation power necessary to take advantage of the detector capabilities.

Third is the larger active area of the detector, which allows fewer X-rays to slip past undetected — Fig. 4.

PMI of Welded Joints: A Technology Update



When analyzing welds, a software switch reduces the measurement area to 3 mm, and superimposes a "bull's-eye" on the display to ensure proper placement on the sample.

Similar to a chain, a process system is only as strong as its weakest link. The use of proper filler materials, and the ability to obtain proper weld dilution rates while joining two pieces of a process system together are as critical to the integrity of the pressure envelope as are the base materials (pipes, valves, etc.) themselves. Up to now, clip-on "weld masks" have been available for XRF analyzers that narrowed the instruments' field of view, permitting these measurements. While easy to use, they made it difficult to confirm that individual measurements completely isolated the filler material from the base metal.

Recent advances to certain hand-held XRF analyzers incorporate a WeldSpot™ and CamShot™ feature to better isolate and analyze welds. CamShot incorporates a CCD camera and sample imaging system that helps the user to properly position the instrument in the correct location for every measurement; at the completion of each measurement, it stores a digital picture of the sample along with the analytical results. WeldSpot goes one step further: It enables the user to easily select the spot size for each measurement, functioning similarly to an internal weld mask. While measuring base materials, the user selects the larger 8-mm measurement area; when analyzing welds, a simple software switch reduces the measurement area to 3 mm, and superimposes a "bull's-eye" on the CamShot display to ensure proper placement on the sample (see figure).

And last but not least, the geometrically optimized positioning of the detector, moving it closer to the sample so that the greatest number of X-ray events can be captured and processed.

As a result, these new GOLDD technology instruments have as much as a tenfold increase in performance over conventional Si-PiN based systems. In addition, they have the ability to provide analysis of certain light element content such as silicon, aluminum, sulfur, and phosphorus, without the need for helium or vacuum purging, something that was considered impossible as recently as a year ago — Fig. 5.

This greatly increases the ease of performing PMI on newer alloys such as ZeCor® found in high-sulfur processing environments, where the 6% silicon would otherwise require measurement with a helium-purged XRF analyzer or optical emission spectroscopy. It also introduces new PMI applications that require extreme sensitivity, such as the prevention of flow accelerated corrosion in HF alkylation units.

In short, technology continues to improve, and if we have learned anything, it is not to underestimate what the future might bring. Of course the real beauty of what these new generations of XRF instruments deliver is that the user need not have an understanding of the science behind them in order to benefit from their use. And that benefit can't be overstated. When employed in a refinery as part of a comprehensive positive material identification program, they reduce the many risks associated with the use of unknown metal alloys: OSHA fines and lost productive capacity, explosion and fire, injury and death.

API RP-578 Training

OSHA's National Emphasis Program places the burden of documentation and training squarely on the shoulders of refinery owners and operators. The American Petroleum Institute (API) has previously published inspection codes for piping (API-570), pressure vessels (API-510), and storage tanks (API-653). More recently, it has approved a recommended practice (API RP-578) to certify or recertify API 570 inspectors in proper guidelines and application procedures utilizing XRF and optical emission spectroscopy (OES) technologies for PMI. A two-day course provides attendees with a thorough understanding of the API RP-578 guidelines and procedures, as well as practical, hands-on experience with XRF and OES instruments; a third day of field testing is optional. More information on API RP-578 training is available at *www.api578.com*.❖

Fig. 5 — The newest XRF analyzers such as this Thermo Scientific Niton XL3t GOLDD can analyze light element content such as silicon, aluminum, sulfur, and phosphorus without the need for helium or vacuum purging.