Recent Advances in Handheld X-Ray Fluorescence Based Alloy PMI/Material Testing

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Abstract. Recent improvements related to accuracy, ease of use, speed and durability of handheld X-ray fluorescence (HHXRF) are explained in practical terms. Intended for those responsible for plant piping system maintenance and safety, this paper reinforces the practical usage and value of non-destructive HHXRF analysis in positive material identification (PMI) of alloys. This most recent set of improvements positions HHXRF into a range approaching aspects of laboratory grade XRF analysis while maintaining portability. A brief overview of HHXRF technology, its traditional alloy analysis uses, and specific application studies relevant to metallurgical & maintenance engineers further illustrate the significance of recent innovations.

Background

Handheld X-ray fluorescence (HHXRF) is an essential field inspection tool for positive material identification (PMI) in refinery and processing plant operational alloy maintenance activities. The portable technology aids in the evaluation of in situ part composition and yields local, accurate, and timely results. The precise results can guide the user in all aspects of the maintenance process from verifying incoming materials prior to fabrication, to installation, to in-service inspection. HHXRF is commonly used for process equipment alloy verification on items such as piping, pumps, valves, and flanges. Even the welding wire used to join and fabricate these complex assemblies can be checked with HHXRF for compositional compliance to specification prior to use. By having an accurate chemical composition of the part of interest, the user is able to provide distinct traceability of the part itself, providing strength to corresponding quality records. Any breach in a quality system can result in catastrophic failure. With a user effectively utilizing HHXRF in maintenance activities, these breaches can be minimized.

X-ray fluorescence occurs when a sample is excited by high-energy X-rays generated from an X-ray tube. When the X-rays strike the sample, the distinct composition of the sample produces representative X-rays that fluoresce and then strike a detector that is an integral part of the HHXRF analyzer. Since a specific element has distinct fluoresced X-ray energy characteristics, the number of X-rays reaching the detector is proportional to the amount of the element in the sample. This basic premise is the foundation of determining element composition using X-ray fluorescence. The detector is connected to a pulse processing interface which generates a spectrum of the sample. This spectrum and its representative X-ray energy peaks is fed into a complex mathematical algorithm utilizing the Fundamental Parameters method of spectral calculation. After the data are run through this
algorithm, the accurate compositional result of the sample is displayed on the instrument’s user interface.

Recently, advances in the core technologies of HHXRF have opened possibilities that enable the analyzers to produce fast results that are even more accurate. Increased light element detection (Mg–Ca) has enabled inspectors to adhere to stringent regulations during routine use of the handheld instruments. Additionally, recent signal processing advancements have improved the limits of detection (LODs) of HHXRF. Improvements to LODs have facilitated robust and accurate detection of minute levels of elements of interest in alloy fabrications below previously observed amounts.

Equipment Used

Two Olympus handheld X-ray fluorescence analyzers were used to collect the data used in this paper: the Olympus DELTA Professional and the Olympus Vanta C-Series. The DELTA analyzer represents the historical baseline of HHXRF performance while the Vanta instrument highlights the improvements to the technology. The instruments were utilized with commercially available PMI methods, including the common alloy detection mode, as well as the heat-tolerant “Hot Test” mode for the DELTA.

Results

1.1 Detector Resolution and Count Rates

X-ray fluorescence results are commonly displayed on the user interface of the device with a compositional percentage coupled with a precision amount for the reading. Figures 1 and 2 show the output interface for both the DELTA and Vanta instruments for a low alloy steel and stainless steel. The precision value (+/−) is calculated by taking the square root of the number of counts defined in a specified energy region and dividing that number by the same number of counts in that region. Since the representative elemental fluoresced X-rays have known energies, these energy regions must be defined in order to provide the calculation of the composition. There are two pathways to accuracy in this consideration: the resolution (in electron volts, eV) of the X-ray detector and the width of the energy region assigned to a specific element.

Figure 1. User Interface Display of the Olympus DELTA (a.) and Vanta (b.), with Grade Match and precision results for Grade 91 Steel (UNS K90901).
Historically, the resolution of an X-ray-specific, silicon-based drift detector (SDD) has seen a range of 150–180 eV. The Olympus DELTA instrument typically performs at the lower end of this range. The theoretical limit of resolution of a silicon drift detector is in the range of 110–120 eV. Clearly, the need to reduce the resolution of the detector is paramount in precisely determining the energy level of the X-rays striking the detector. The more precise the detector resolves, the more accurate the energy level used to generate spectra. Assigned elemental energy regions have commonly been two to three times the detector resolution as a minimum and, in some cases, where energy regions are not in close proximity on the spectrum, they are even wider. The wide range needed for elemental energy ranges becomes problematic to the analyzer when the sample contains multiple transition metals as alloying elements (i.e. titanium through zinc) or lighter elements (i.e. magnesium through calcium) as the representative energies of these elements are very close, or worse, overlap.

Improvements in silicon drift detector technology and pulse processing enable the Vanta analyzer to reduce the detector resolution by nearly 40% towards the theoretical silicon drift detector resolution limit. This large improvement in performance has enabled any applicable elemental energy region where spectral interference or overlap with other elemental energy ranges to be reduced in size and, correspondingly, see gains in quantification accuracy. By reducing the size of the elemental energy regions, only very specific counts attributable to the analyte element are considered, improving overall compositional output. In addition, by reducing the size of the elemental energy regions via resolving peak energies more effectively, any inter-elemental effects that are accommodated by the Fundamental Parameters calculation process are more robust.

Once X-ray energies are able to be characterized effectively via resolution improvements, the pulses that they generate by striking the detector must also be efficiently processed to make the best use of the information being delivered to the detector. Silicon drift detectors can fall prey to several pitfalls based on operational parameters, and failure to accommodate pulses from the detector can negatively affect spectrum generation and, therefore, the analytical chemical information returned. By refining the detector pulse processing, the Vanta analyzer enables the pulse throughput of the silicon drift detector to increase dramatically. This increased pulse throughput increases the overall number of usefully counted, incoming X-rays that reach the detector. In the past, the useful pulse throughput has been a limiting factor to utilizing the full potential power of the instrument’s X-ray tube to generate fluoresced X-rays; by implementing these technological advances, the pulse throughput of the detector no longer functions as a limiting factor. Much higher X-ray count rates can now be quantized accurately. As previously explained, as the count rate increases, the precision value decreases, thereby providing more precise information.
analytically. The user can utilize the precision number to apply statistical methods to the result and derive a confidence interval of the reported value. The Olympus DELTA and Vanta instruments both report precision values as 1-sigma. Due to the improvements highlighted above, the Vanta analyzer reports smaller precision numbers than the DELTA, effectively communicating the calculated degree of confidence of the result to the user.

1.2 Spectral Calculation

The advances detailed up to this point have concerned X-ray detection, pulse processing, and counting accuracy. These upgraded input parameters are then used to construct a detailed spectrum from the sample. While useful in its own right, a spectrum only provides limited information to the human eye at a glance. In order to unlock the full information capacity of a spectrum, complex mathematical analysis of the peak heights and the area under those spectral curves must be performed.

Two common mathematical methods of determining quantitative information derived from a spectrum are the Fundamental Parameters (FP) method and the Empirical Method. While the Empirical Method has merits to quantification, the calibration needed is a very time intensive process that can create calculation errors if the analyte composition is well outside of the empirically calibrated range that is assigned to the instrument. With so many standard compositions in the alloy world, covering a very broad range of alloying elements and compositions, the Empirical Method can fall short of accurate calculations with unknown samples. The Empirical Method, depending on the strength of the calibration samples, can fail to account for inter-elemental effects, such as is observed with transition metals (i.e. titanium through zinc). Additionally, empirically-based calculations require a longer processing time to generate a result, adding time to operator’s use. Oftentimes, maintenance activities requiring PMI functions are time sensitive, so any development that reduces analysis time while returning accurate information is a positive aspect.

Olympus DELTA and Vanta instruments both utilize a strong Fundamental Parameters calculation engine. As expected, the next-generation Vanta analyzer utilizes a refined mathematical model that improves both analytical processing speed and measurement accuracy. Inter-elemental effects are reduced or removed by narrowing the representative elemental energy region and applying these accurate variables to the updated Fundamental Parameters engine.

1.3 Analytical Results Reporting

When integrating a HHXRF device into a Positive Material Identification program, reliable alloy grade determination is a high priority for users. The ability to distinguish similar alloy grades quickly and accurately as part of a large maintenance project adds a measurable time component. Analyzer delay in grade determination lengthens the overall process and may contribute to longer test times. The results reported by the instrument are the culmination of all the contained technologies. All of the advances in technology described to this point highlight how the instrument quickly and accurately displays elemental composition. An advantage of the new Vanta technology is that, with the increased count throughput now available, lower energy X-ray elements, like magnesium through calcium, will display accurate light element results in a shorter time compared to older instruments, as part of the overall reported chemistry.
1.4 Analytical Results Reporting

An often overlooked aspect of HHXRF is the ergonomics of the handheld instrument. This is an area that has also been improved. In the past, even though the instruments were designed to be used in a handheld and portable configuration, there were drawbacks to the devices. The instruments were not tolerant of physical shocks or large temperature changes. These devices could not easily accommodate adverse testing environments, such as high humidity or wet environments, were large and bulky, and oftentimes did not function in harmony with an operator’s required protective personal equipment. Detector safety was also an issue to instrument reliability. The thin-film polymer windows used to provide a dust-barrier to internal components and protect the detector could become damaged and require replacement. During the window replacement process, the detector could inadvertently become damaged, crippling the unit and requiring a costly detector replacement. Vanta utilizes a reinforced polymer window that also features a tool-less changing process, minimizing risk of detector damage from tool mishaps during replacement.

Shocks to analytical instruments, such as HHXRF devices, can cause electronic component connection failure, misalign key geometrically-designed functions of the analyzer, and provide other stresses to the envelope of the instrument that can eventually affect fit, form, and function. Despite the dangers, shocks to portable, handheld devices are inevitable. The Vanta analyzer features a complete envelope redesign that helps protect the instrument against shocks. Vanta analyzers have been drop tested from a height of 4 feet and are built to survive this shock with no adverse effects to operation.

Demanding operational environments are often unavoidable for portable, handheld instruments. Accurate reporting is expected whether the device is used in a laboratory or in wet, dusty or hot environments. In the past, drips, mists, sprays, and other liquids were a hazard to operating a portable HHXRF instrument, and users were recommended to avoid environments where these hazards might be present. Vanta analyzers have achieved an IP65 rating due to an improved outer envelope and casing design.

As recently as ten years ago, HHXRF devices may have weighed 4 kg (8.8 lb) or more. Instruments in this weight range can cause fatigue after an operator has used the device over an entire shift. In addition to the weight of the unit, the functional device controls, miniaturized for handheld operation, became difficult to reliably operate using required personal protective equipment, such as leather gloves. Vanta analyzers have a capacitively coupled touch screen that enables operators wearing safety equipment to easily operate the unit so that operator safety remains uncompromised. Along with the user-friendly touch screen, the overall weight of the instrument has been reduced so an operator can utilize the device over the course of an entire shift without marked fatigue.

1.5 Connectivity

Once a HHXRF instrument generates accurate results, the data needs to be easily disseminated. The ability to provide real-time analytical information is now possible by equipping the Vanta analyzer with Wi-Fi and Cloud-accessible connectivity. A user-interface software export feature enables the device to transmit data to remote data analysis terminals.
Handheld XRF Application Studies

2.1 API Recommended Practice 578
Material Verification Program for New and Existing Alloy Piping Systems

For component suppliers or plant operations/maintenance, Positive Material Identification (PMI) and material verification are important concerns. Whether for corrosion resistance, temperature tolerance, or mechanical characteristics, alloys are specified by design. An alloy material mix-up can result in component failure. Component failure costs include downtime, repair and replacement, lost or leaked material, environmental and fire hazards, or batch contamination.

Utilizing handheld X-ray fluorescence as a fast, non-destructive testing technique for measuring alloy composition, an operator can confirm alloy grades and perform PMI duties as part of an established program per API RP 578. At any point in the alloy material fabrication process—producing components, receiving fabricated materials, installing pipes, valves, or other mission critical items, or a confirmation check of in-service process systems, HHXRF provides rapid, definitive material confirmation.

HHXRF is a near-surface measurement, only penetrating approximately 10 microns into alloy samples. Because of the sampling depth, painted, plated, corroded, or peened surfaces may require some preparation. After preparation, XRF provides quick in situ testing, even on process devices operating at an elevated temperature. The test time needed to identify most grades is, on average, two seconds. To verify a grade, it is only necessary to distinguish it from other similar grades. Grades that are nearly compositionally identical, such as AISI 303, 304, and 321 stainless steel grades or 9 chromium (ASME Grade 9) and 9 chromium + vanadium (ASME Grade 91) alloy steels, are sorted by grade specific differences visible to HHXRF. These differences can be as small as 0.05% for a transition metal alloying element.

In addition to their use on fabricated items, HHXRF can identify the composition of the welding wire that is selected for a project. The user can analyze the material prior to the welding process. In addition, after the weld is deposited, the weld material can be identified via HHXRF using the collimated beam function on the Olympus DELTA and Vanta analyzers. Collimation of the beam narrows the analysis spot size, enabling the operator to generate results on the base material, weld material, and any joining material if present. Figure 3 shows the Olympus DELTA in practical use, during weld inspection of a structural beam.

Figure 3. The Olympus DELTA in use for weld analysis.
2.2 API Recommended Practice 939-C
Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries

Corrosion as a result of sulfur compounds in crude oil is typically thought to occur at temperatures above 450 °F (230 °C), in environments absent of hydrogen. The petroleum industry relies on a set of curves (modified McConomy) to predict corrosion rates in this environment. These curves show that, at a given temperature and total sulfur level, steels with increasing chromium content (from carbon steel grades, to 5Cr to 9Cr low alloy steels, and finally, stainless steels) will experience lower corrosion rates. Additionally, in these hydrogen-free process streams, carbon steel piping with less than 0.1% silicon (Si) can exhibit significant accelerated/non-uniform corrosion. Silicon detection in the Olympus DELTA and Vanta instruments at that level of 0.1% has benefited from technology advancements, in that the silicon X-ray intensity is well-resolved.

When hydrogen is present in the process stream in combination with sulfur, i.e. \( \text{H}_2/\text{H}_2\text{S} \) corrosion, corrosion starts to increase at temperatures above approximately 450 °F (230 °C). A similar set of curves (Couper-Gorman curves) is used to predict the corrosion rate in this environment. These curves relate the amount of \( \text{H}_2\text{S} \) present with temperature to determine the corrosion rate. At a given \( \text{H}_2\text{S} \) content and temperature, increasing Cr content of low to medium alloys makes little or no difference in corrosion rates and alloyed materials in that range will exhibit significant corrosion. It is recommended to use 18Cr-8Ni stainless steels in order to achieve a significant improvement in corrosion resistance. Positive Material Identification Recommended Practices that encompass such stainless steel identification are implemented with success when using an Olympus DELTA or Vanta instrument.

2.3 Flow Accelerated Corrosion

In power generation, there exists a possibility that in carbon steel process lines at a high flow rate, the native protective oxide (magnetite or hematite) formed by the piping material may be removed by the rate of flow. As the material attempts to renew the native oxide layer, the resulting attempt is also removed due to the flow rate. This is called Flow Accelerated Corrosion (FAC). FAC frequently occurs at flow disturbances and process direction changes often affecting elbows, tees, and reducing couplings.

The Ducreaux model specifies that carbon steels containing less than 0.04% Cr in the composition of the steel are susceptible to FAC. This monitoring threshold is well above the LOD for chromium in iron-based steels for both the Olympus DELTA and Vanta instruments. The advancements in place for Vanta analyzers make the compositional analysis of steels containing chromium below this threshold accurately quantifiable.

2.4 Residual Alloying Elements

In gasoline refining, hydrofluoric acid alkylation units are often required. Hydrofluoric acid is an extremely corrosive media, having a pH of 2.1. The carbon steel piping used in these units can undergo advanced corrosion if not properly specified, analyzed, and installed. Carbon steel containing a combined total residual level of copper, nickel, and chromium greater than 0.2% will accelerate localized corrosion when entered into service. The very low limits of detection on the Olympus DELTA and Vanta analyzers quantify these trace...
elements accurately to provide the desired information to calculate the combined total residual level for this type of service.

Conclusions

With analytical performance now rivaling many laboratory-based instruments, Handheld X-ray fluorescence continues to evolve and benefit with improvements to core technological aspects, which allow the technique to yield parallel improvements in reporting results with respect to accuracy and precision. Additional strengthening of trace level analysis of elements from Magnesium through Uranium provide even more preciseness in Positive Material Identification efforts. Robust external envelope design criteria provide operators of HHXRF instruments increased quantitative confidence and reliable portability.

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References