

# Material Matters

## Limitations of PMI Testing With Portable X-Ray Fluorescence (XRF)

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### Question:

How come the warranty department and casting supplier refuses to accept our claim that the chemistry check on our pump equipment is marginally out of specification based on our field-portable PMI results? What's the difference between the instruments used to create the CMTR, and the portable XRF instrument we use for PMI testing?

### Answer:

Positive material identification (PMI) or alloy verification, and certified materials test reports (CMTR'S), are common requirements placed on purchase orders by customers to provide assurances that they receive the materials specified in pumps, and other industrial products. PMI is usually provided by a relatively inexpensive hand held field-portable device such as an energy-dispersive (ED) X-ray fluorescence (XRF) analyzer or similar instrument offered by a variety of manufacturers. For PMI programs, portable XRF instruments provide a fast, non-destructive method to confirm a material's type and alloy identity. Shown in **Figure 1**, is a typical portable XRF device performing a quality control PMI test.

XRF spectrometry is widely used for the qualitative and quantitative elemental analysis of industrial pump components. However, there are quantitative limitations due to inherent instrument constraints which do not allow for detection of light atomic number elements.

As such, when elements are present in materials that go undetected, test results can only be regarded as semi-quantitative or incomplete. Several limiting factors of PMI instruments are precision and accuracy, inability to detect certain elements, and potential for human error in interpreting analysis results.

It should be recognized that portable XRF equipment is not capable of providing a full quantitative analysis for all elements present in many alloys. Operators must be aware of these limitations when comparing PMI results with CMTR'S. Significant analytical error can occur at all stages in the PMI measurement process, and test analysis variation and precision bias may be substantially larger than one would expect. Detection precision and accuracy are driven by several factors, including X-ray excitation source and strength, type of detector used, time exposure, sample surface conditions, physical and chemical matrix effects, as well as primary elements of interest and inherent x-ray spectral line interference from element overlap.

Variation may come from sample representation, as well as interference effects inherent within the method itself. Improper preparation of samples, if any is performed at all, can impair test accuracy. Without careful preparation to produce a homogeneous and representative sample, an analysis by portable XRF can hardly be considered more accurate than a certified material test report (CMTR).

Some who use portable PMI testers do not understand these limitations and occasionally expect more from the instruments than they can provide. While certain portable XRF instruments

furnish simple readouts as to alloy type, others give a general analysis of the material's "supposed" composition. Few hold the mistaken belief that these PMI test results are quantitative analyses that can be used to scrutinize whether a part meets the composition limits specified in materials standards, and then dispute the suppliers CMTR based upon their findings.

Although some XRF instruments provide fairly good chemical analysis their precision and accuracy are not acceptable for regulatory compliance or certification. Portable XRF instruments are hardly more accurate than more expensive and sophisticated foundry or steel mill metallurgical lab spectrographic instruments used to create the CMTR. While XRF instruments are excellent for alloy verification programs they are not suitable for providing certification; and certainly not accurate enough to declare a CMTR analysis marginally out of material specification limits. Furthermore, due to its inherent detection confines regarding certain elements, portable XRF analyses are not able to certify reports in accordance with regulatory requirements.

Generally PMI or in-situ testing is used to confirm a CMTR heat analyses report. These certified melt reports are made at time of melting and obtained from highly precise instruments such as inductively coupled – optical emission spectrometers [ICP-OES] or arc/spark optical emission spectrometers [OES] as shown in **Figure 2**, which are capable of providing a complete quantitative analysis of all elements present. These instruments are routinely used in metallurgical laboratories to determine chemical compositions and create certified melt test reports.

OES spectrometers are known to be reliable quantitative instruments for determining major,

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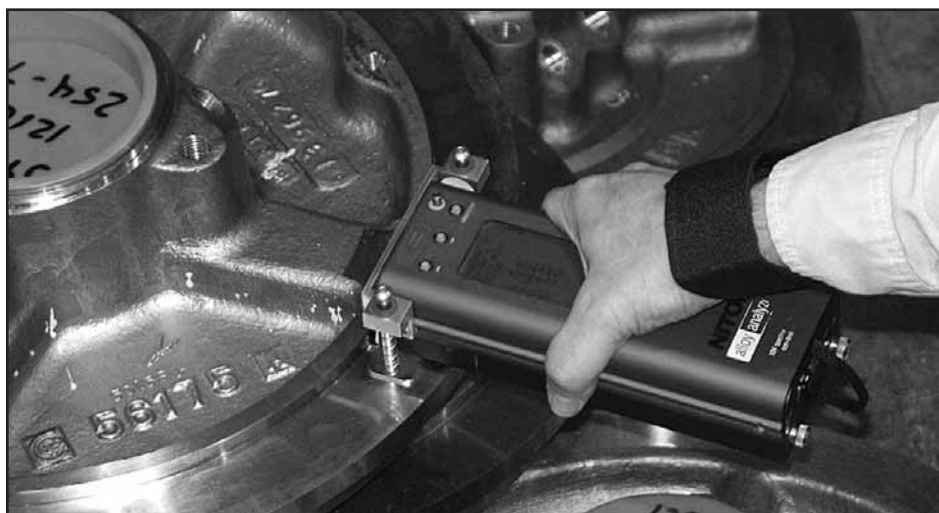


Figure 1. Hand held portable X-ray Fluorescence (XRF) analyzer being used to conduct quality control PMI testing for component verification.



Figure 2. Metallurgical Laboratory ARC/Spark Optical Emission Spectrometer (OES). Used to determine chemical composition and create certified material test reports.

# Material Matters cont'd

minor and trace element analysis over a wide range of alloys produced in foundries and steel mills. OES methods offer a powerful quantitative technique, which provides extensive analytical capability making multi-element analyses possible within approved regulatory standards. While portable XRF is quick and reliable, results are not as precise or accurate as OES laboratory methods.

Since most PMI analyzers are not capable of detecting all elements present in many alloys, XRF analyzers cannot be considered more than a qualitative or limited semi-quantitative instrument at best; unless of course the sample tested consists only of elements that can be detected and measured.

For instance, most radioisotope source XRF analyzers are only capable of detecting elements of atomic number 16 (Sulfur) or higher, while the newer x-ray tube based XRF analyzers are generally limited to elements of atomic number 22 (Titanium) or higher. It is important to note that, elements lighter than sulfur are not measured with portable XRF analyzers because x-rays with energies below 2eV (electron-volts) are largely absorbed in air within a very short distance and never reach the detectors.

Also, XRF analyzers use x-rays emitted from either an x-ray tube or radioisotope sources [e.g., iron<sup>55</sup> (Fe<sup>55</sup>), cobalt<sup>57</sup> (Co<sup>57</sup>), cadmium<sup>109</sup> (Cd<sup>109</sup>), gadolinium<sup>153</sup> (Gd<sup>153</sup>), americium<sup>241</sup> (Am<sup>241</sup>)] to irradiate and excite the atoms of the sample material. These sources emit x-rays of specific energy that are capable of only exciting a limited number of elements efficiently. In order to analyze a broad range of elements, a combination of radioisotopes is needed. Multiple sources can be available with a single analyzer depending upon which elements are of interest. This relationship between instrument source selection and element excitation and detection capability is illustrated in Figure 3.

For example, with a radioisotope source of Cadmium<sup>109</sup> elements below chromium cannot be detected. Instruments adding a secondary Iron<sup>55</sup> source allows for detection of those elements between chromium down to sulfur. No element below sulfur can be detected by any portable XRF instrument. It should be noted that PMI analysis capabilities and reporting limitations vary by instrument, manufacturer, and radiation source types used.

What this means is that most PMI testers cannot distinguish between high and low


| Periodic Table with X-Ray Energies   |                          |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          |          |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|--|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|--------|------|------|------|------|------|------|----------|----------|---------|---------|----------|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|    |                          |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          |          |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| IA   | Key To Energy Values     |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          | VIIA     |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| H<br>1   |                          |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          | He<br>2  |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Li<br>3  | Be<br>4                  |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      | B<br>5   | C<br>6   | N<br>7  | O<br>8  | F<br>9   | Ne<br>10 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Na<br>11   | Mg<br>12                 |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      | Al<br>13 | Si<br>14 | P<br>15 | S<br>16 | Cl<br>17 | Ar<br>18 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| 3.31   | 3.61                     | 3.69                     | 4.04                      | 4.09                      | 4.48                      | 4.51                      | 4.93                     | 4.95                     | 5.43   | 5.41 | 5.98 | 5.90 | 6.49 | 6.40 | 7.06 | 6.93     | 7.65     | 7.48    | 8.26    | 8.06     | 8.90     | 8.64  | 9.57  | 9.45  | 10.26 | 9.89  | 10.98 | 10.54 | 11.78 | 11.22 | 12.58 | 11.92 | 13.28 | 12.45 | 14.11 |       |       |       |       |       |       |       |       |       |       |       |       |
| 19   | 20                       | 21                       | 22                        | 23                        | 24                        | 25                        | 26                       | 27                       | 28     | 29   | 30   | 31   | 32   | 33   | 34   | 35       | 36       | 37      | 38      | 39       | 40       | 41    | 42    | 43    | 44    | 45    | 46    | 47    | 48    | 49    | 50    | 51    | 52    | 53    | 54    | 55    | 56    |       |       |       |       |       |       |       |       |       |       |
| 1.69   | 1.75                     | 1.81                     | 1.87                      | 1.92                      | 2.00                      | 2.04                      | 2.17                     | 2.26                     | 2.29   | 2.40 | 2.42 | 2.54 | 2.56 | 2.68 | 2.70 | 2.83     | 2.84     | 2.99    | 2.98    | 3.15     | 3.13     | 3.32  | 3.30  | 3.49  | 3.44  | 3.66  | 3.61  | 3.84  | 3.77  | 4.03  | 3.94  | 4.22  | 4.11  | 4.42  |       |       |       |       |       |       |       |       |       |       |       |       |       |
| 39.07  | 34.98                    | 32.15                    | 35.30                     | 34.4                      | 37.95                     | 37.6                      | 39.75                    | 38.9                     | 41.3   | 39.9 | 42.5 | 40.9 | 43.5 | 41.8 | 44.4 | 42.7     | 45.3     | 43.6    | 46.2    | 44.5     | 47.1     | 45.4  | 48.0  | 46.3  | 48.9  | 47.2  | 49.8  | 48.1  | 50.7  | 49.0  | 51.6  | 50.0  | 52.6  | 51.0  | 53.6  | 52.0  |       |       |       |       |       |       |       |       |       |       |       |
| 86.12  | 97.48                    | 85.49                    | 101.19                    | 89.99                     | 102.85                    |                           |                          |                          |        |      |      |      |      |      |      |          |          | 87.80   | 99.44   | 87.80    | 99.44    | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 | 87.80 | 99.44 |       |       |       |       |       |       |       |       |
| 12.03  | 14.77                    | 12.04                    | 15.20                     | 12.65                     | 15.71                     |                           |                          |                          |        |      |      |      |      |      |      |          |          | 12.03   | 14.77   | 12.04    | 15.20    | 12.65 | 15.71 | 12.03 | 14.77 | 12.04 | 15.20 | 12.65 | 15.71 | 12.03 | 14.77 | 12.04 | 15.20 | 12.65 | 15.71 | 12.03 | 14.77 | 12.04 | 15.20 | 12.65 | 15.71 | 12.03 | 14.77 | 12.04 | 15.20 | 12.65 | 15.71 |
| <b>1 Lanthanide Series</b><br>Ce 58, Pr 59, Nd 60, Pm 61, Sm 62, Eu 63, Gd 64, Tb 65, Dy 66, Ho 67, Er 68, Tm 69, Yb 70, Lu 71<br>4.84, 5.26, 5.53, 5.49, 5.29, 5.75, 5.54, 5.96, 5.64, 6.21, 5.85, 6.46, 6.06, 6.71, 6.29, 6.90, 6.50, 7.25, 6.75, 7.50, 6.91, 7.18, 8.10, 7.41, 8.40, 7.65, 8.71 |                          |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          |          |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| <b>2 Actinide Series</b><br>Th 90, Pa 91, U 92, Np 93, Pu 94, Am 95, Cm 96, Bk 97, Cf 98, Es 99, Fm 100, Md 101, No 102, Lr 103<br>12.97, 16.20, 13.29, 16.70, 13.61, 17.25, 13.95, 17.74, 14.65, 19.28, 14.62, 18.83, 14.99, 19.39, 15.01, 19.97, 15.66, 20.96, 16.02, 21.17, 16.36, 21.79        |                          |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          |          |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| <b>Source Emission Energies</b><br>Fe <sup>55</sup> 5.90keV, Cd <sup>109</sup> 22.16keV, Am <sup>241</sup> 59.5keV, Co <sup>57</sup> 122.0keV<br><b>Source Half-Life</b><br>2.7 Years, 462.3 Days, 432.2 Years, 271 Days   |                          |                          |                           |                           |                           |                           |                          |                          |        |      |      |      |      |      |      |          |          |         |         |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Source   | Fe <sup>55</sup> K-Shell | Fe <sup>55</sup> L-Shell | Cd <sup>109</sup> K-Shell | Cd <sup>109</sup> L-Shell | Am <sup>241</sup> K-Shell | Am <sup>241</sup> L-Shell | Co <sup>57</sup> K-Shell | Co <sup>57</sup> L-Shell | Source |      |      |      |      |      |      |          |          |         | Source  |          |          |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

Figure 3 (Source EDAXppd.com) Periodic Table Showing Element X-Ray Energy References and XRF Excitation Associated Elemental Analysis Coverage Range for Various Radioisotope Sources.

carbon content in any alloy or stainless steels, nor verify important nitrogen levels in many high alloy stainless steels. XRF has some striking limitations with regard to aluminum-bronzes and silicon-bronzes because of its inability to detect the key elements aluminum (atomic number 13) and silicon (atomic number 14). Furthermore carbon, silicon or magnesium levels in cast irons, or sulfur levels that distinguish the free machining grades of many alloy and stainless steels cannot be determined at all. Instruments that provide no information on important alloying elements such as carbon, nitrogen, magnesium, aluminum, silicon, phosphorous or sulfur can hardly question or dispute a certified laboratory CMTR regarding specification limits.

### Why Use PMI Testing?

Portable XRF devices are not intended to replace the more rigorous and precise stationary spectrographic instruments used to provide certified CMTR analyses. Rather, portable testing provides in-situ PMI which can be used to validate a CMTR or complement the certified test analysis to avoid material mix-ups when identities are lost.

Regardless of what manufacturers of portable analyzers advertise and claim, certified quantitative chemical composition analyses cannot be made by portable XRF test instruments that are unable to detect important alloying elements. The quality of portable XRF test results varies with alloy, surface conditions and even make or type of analyzer used. Since

XRF is completely non-destructive, any sample tested and measured in the field can be verified by other approved laboratory methods in the event of an analysis dispute, provided a sample can be removed for destructive analysis.

XRF is perfectly suited to provide verification and confirmation when used properly as part of a PMI program. Since PMI instruments only provide a semi-quantitative verification of alloy type they should not be used to reject a CMTR materials certification or check for elemental compliance within standards limits.

### X-Ray Fluorescence (XRF) - A Closer Look

X-ray fluorescence spectroscopy is a technique that can be used for direct analysis of solid metal samples, and very popular for portable PMI instruments. Compared to other competitive laboratory techniques, XRF has the advantage of being non-destructive, multi-elemental, fast and cost-effective. It is frequently used for PMI analyses performed in the field and for industrial quality control. Its main disadvantage is that analyses are generally restricted to elements heavier than sulfur for isotope based instruments or titanium for tube based instruments.

PMI is an important part of many process safety and non-destructive quality validation management programs. In response to a number of incidents resulting from materials mix-ups, companies recognizing the importance of minimizing errors have implemented PMI test requirements, or alloy verification programs using a variety of techniques. In some instances

customers require suppliers conduct PMI testing to verify materials prior to shipment; in others customers perform their own PMI testing before equipment goes into service.

If a material composition identity is lost or a materials certification is missing, then PMI offers a way to reassure that proper materials are furnished, and ensures materials are what they are believed to be. Furthermore, on-site testing using X-ray Fluorescence (XRF) analysis provides non-destructive in-situ PMI confirmation of certified laboratory analyses, testing is quick and can identify situations that may require a more thorough investigation.

Field portable X-ray fluorescence (XRF) continues to gain acceptance as a complement to traditional laboratory testing, but is not intended to replace the more rigorous lab-based spectrographic instruments. Rather, XRF complements these methods by providing near real-time or in-situ analysis in the field or shop without relying on time consuming and costly laboratory analysis, and is versatile enough to provide field screening analysis with accuracy approaching that of certified laboratory analyses.

The method of X-ray fluorescence (XRF) spectrometry is a mature technology, having origins dating back to the beginning of the 1900's. The test method has undergone significant improvements since then to bring the technology from the lab to the field, including the introduction of field portable XRF a little more than 30 years ago. As electronics and computer

technology advances continue, analytical instrumentation will continue to become smaller, allowing us to bring the laboratory to the sample.

XRF has developed over the last few decades from the first commercial instruments into a powerful, affordable, fast, non-destructive, and relatively accurate technique for qualitative as well as semi-quantitative chemical analysis. Ease of use and portability of hand held XRF instruments has increased in popularity. Chemical analysis for knowing the composition of a material is important and essential for evaluation of raw materials and finished products. However, the labor and expensive testing associated with classical wet chemical methods or delay in sending samples to outside labs cannot provide the speed, economy or effectiveness required for quality control PMI testing.

Constant technology developments, particularly recent ones in computer microchip and detector electronics technology, has led to the design and introduction of small battery powered, portable X-Ray fluorescence analyzers that can attain analytical performance approaching that of conventional laboratory instruments. The continued miniaturization, speed and increasing power of micro-computers, allows the packaging of more complex electronics and potent software into portable instruments.

Current trends in PMI testing are towards continued technological developments in metal

analyzers, increased analysis speed, improved accuracy, durability, portability and ease of use. Technology improvements have yet to change many of the fundamental instrument limitations with regard to detection capabilities. The search for a suitable PMI metals analyzer should begin by asking the principal question; which elements must be determined and what alloys must be identified? The analysis test requirements once clearly understood, can then be carefully matched with an instruments capabilities. ■

### Select References

- [1] Goldstein J.I., Newbury D.E., Echlin P., Joy D.C., Fiori C., Lifshin E., (1981). *Scanning Electron Microscopy and X-Ray Microanalysis*. Plenum Press, New York. 205 – 299
- [2] Jenkins Ron. (1999). *X-ray Fluorescence Spectrometry*. Wiley, John & Sons, New York.
- [3] Lachance G.R., Claisse F. (1994). *Quantitative X-ray fluorescence analysis: theory and application*. John Wiley & Sons, New York.
- [4] Villescas Julie., (June 12, 2003). *What's that Material? Using XRF technology to identify alloys*. [www.thefabricator.com/Articles/Fabricating-Article.cfm?ID=604](http://www.thefabricator.com/Articles/Fabricating-Article.cfm?ID=604)
- [5] XRF laboratory – *Elemental analysis using the XRF technique*. <http://omega.physics.uoi.gr/xrf/english/index.htm>
- [6] X-Ray Fluorescence (XRF) *Spectrometry*. [www.innov-xsys.com/technology/xrayflour.html](http://www.innov-xsys.com/technology/xrayflour.html)
- [7] *Niton Sample Analysis Via Energy Dispersive X-Ray Fluorescence (EDXRF)*. [www.niton.com/how\\_xrf\\_works.asp](http://www.niton.com/how_xrf_works.asp)
- [8] *Periodic Table with X-Ray energies*. [www.edaxppd.com/applications/period.html](http://www.edaxppd.com/applications/period.html)
- [9] *Basic Theory of X-Ray Fluorescence*. [www.learnxrf.com/BasicTheory.htm](http://www.learnxrf.com/BasicTheory.htm)

## Solutions

### Growth in China Flue Gas Desulphurization Market

Goulds China Team won two orders total value more than US\$1 million consisting of 12 units of heavy duty process pumps. These pumps will be installed in the flue gas desulphurization (FGD) construction of two thermal power plants located in Neimenggu and Henan provinces respectively.

Plants burning coal account for more than 80 per cent of China's electricity output. Although mined in China, the coal is contributing to serious air pollution that is blighting the quality of life in many areas and posing a threat to public health.

Thermal power plants are the main source of pollution in China currently. Studies have shown that over 50 per cent of sulphur dioxides in China are from thermal power plants. Unfortunately, only a very small fraction of them are equipped with anti-pollution equipment.



Recently, China's National Environment Bureau started to take action on pollution management. The initiative is being referred to as the "Environment Protection Storm." Forty-six thermal power plants have been cited and requested to begin FGD construction by the end of 2005. With China's expanding power sector as well as the increasing focus on

environment protection, especially for reducing the pollution of sulphur dioxide, the FGD industry is entering into a rapid growth period. It is expected to cost about US \$4 billion over the next five years with pumps accounting for approximately 6 percent. Goulds is well positioned to supply the pumping needs for the industry. ■