Analysis of silicon in steel using the Thermo Scientific Niton XL5 analyzer to prevent sulfidic corrosion failures

Esa Nummi, Thermo Fisher Scientific, Tewksbury, MA USA

Key Words
Niton XL5, Sulfidic Corrosion, Silicon, XRF, Niton, Refinery

Introduction
Sulfidic corrosion of piping and equipment within the refining industry continues to be a significant cause of leaks and issues that can lead to early replacements, unplanned outages, and incidents potentially resulting in loss of property and injury to workers. Carbon steels with low-silicon (<0.10%) content can corrode at an accelerated rate when exposed to hydrogen-free sulfidation corrosion conditions. According to the American Petroleum Institute (API) Recommended Practice 939-C (Guidelines for Avoiding Sulfidation Corrosion Failures in Oil Refineries), one-third of high-temperature sulfidic corrosion failures are the result of low silicon content. API RP 939-C is a subcomponent of the larger API RP 578 PMI program – the verification of correct alloy installation in all sulfidation surfaces, both proactive and reactive. Examples of equipment where hydrogen-free sulfidation occurs include crude/vacuum, fluid catalytic cracker, coker, and visbreaker units. Hydroprocessing and hydrocracking units experience hydrogen-free sulfidation corrosion in their feed and distillation sections. To help prevent these incidents from occurring, silicon analysis of such piping and equipment with portable X-ray fluorescence (XRF) is an ideal choice. The new Thermo Scientific™ Niton™ XL5 allows for fast, accurate, and precise analysis of silicon and other elements in the field.

Thermo Scientific Niton XL5 XRF Analyzer
The new Niton XL5 is the smallest and lightest high performance XRF metal analyzer in the market. The light weight and small size of the Niton XL5 reduce operator fatigue and enable access to more test points. Compact measurement geometry and a new powerful 5W X-ray tube provide highest performance and best light element sensitivity for the most demanding applications such as low silicon measurement. Niton XL5 delivers fast, accurate elemental analysis in demanding refinery environments. The Niton XL5 provides the refining industry with the following key benefits:

• Excellent light element detection (Mg, Al, Si, P, S) without vacuum or helium (He) purge
• Small size and light weight improves productivity and enables testing in tight spots without operator fatigue
• Flexible user interface enables custom workflow solutions and easy optimization for specific applications such as low silicon measurement.
• Integrated camera and small spot analysis for accurate sample positioning and image capture
• Waterproof, dustproof and rugged housing for harsh environments

The Thermo Scientific Niton XL5 in use, analyzing finished welds in steel piping.

Method
Certified reference standards and samples were analyzed after ensuring the surface is clean and clear of any contaminants that could introduce silicon or other elements to our analysis. Data quality objectives dictate the sample preparation requirements and the minimum analysis time used.

• Unparalleled chemistry and grade identification accuracy for confident results every time
Typical metal alloys that are at risk of sulfidation corrosion are carbon and low alloy steels. These alloys will oxidize when exposed to atmospheric conditions. This oxide coating can affect the accuracy of the reading when performing an XRF analysis. As the chromium concentration in the metal gets lower, the oxidation will get worse. It is imperative to remove any corrosion in order to ensure an accurate reading.

In addition to oxidation, there can often be paint or oil or grease on the surface. Paint typically contains metals, such as titanium, zinc or cadmium, that can interfere with the analyzer’s readings. Grease can contain molybdenum and other additives.

In order to get the accurate silicon readings, all surface contamination must be removed in the area to be analyzed. The fastest way to prepare an oxidized surface is to use a right angle die grinder equipped with the proper abrasive media, such as a ZrAlO grinding disc. For low silicon analysis, the samples were analyzed for 20 to 60 seconds using both the main filter (5 seconds) and light filter (15 to 55 seconds) after thorough surface preparation.

Results
Figure 1 shows the correlation curve and certified results vs. the Niton XL5 analyzer results. The coefficient of determination \( R^2 \) value is a measure of how closely the data sets correlate with each other, where a perfect correlation would have an \( R^2 \) of 1. As can be seen from the data agreement between laboratory results and the XL5, the results are very good.

Figure 2 shows the measurement repeatability data for a low Silicon standard (0.058% Si) and higher Silicon standard (0.20% Si) using 30 second measurement time. The data in Table 1 demonstrates the improvement in precision based on used measurement time.

Conclusion
Results achieved using the Niton XL5 analyzer demonstrates excellent agreement with the laboratory results. The Niton XL5 provides the best light element precision and sensitivity, and enables faster and more reliable low silicon measurement. Given appropriate sample preparation, the analyzer is able to reliably detect Si levels in steel at less than 0.05%. Extended measurement time can be used to achieve even better results. As can be seen from Figure 2, Niton XL5 has excellent silicon measurement repeatability, and it can quickly and reliably identify low Si steel which has elevated risk of sulfidation corrosion from higher silicon steel.

To discuss your particular applications and performance requirements, or to schedule an on-site demonstration and see for yourself how Thermo Scientific portable XRF analyzers can help save you time and money, please contact your local Thermo Scientific representative or visit our website at www.thermoscientific.com/portableid.

Table 1: Effect of measurement time on silicon in steel measurement repeatability using the Niton XL5

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<thead>
<tr>
<th>Run Number</th>
<th>15 Seconds</th>
<th>30 Seconds</th>
<th>60 Seconds</th>
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<td>0.093</td>
<td>0.095</td>
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<tr>
<td>2</td>
<td>0.099</td>
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<td>0.108</td>
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<td>3</td>
<td>0.082</td>
<td>0.099</td>
<td>0.103</td>
</tr>
<tr>
<td>4</td>
<td>0.098</td>
<td>0.103</td>
<td>0.101</td>
</tr>
<tr>
<td>5</td>
<td>0.102</td>
<td>0.110</td>
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</tr>
<tr>
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<td>0.093</td>
<td>0.105</td>
</tr>
<tr>
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<td>0.104</td>
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<tr>
<td>10</td>
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<td>0.104</td>
</tr>
</tbody>
</table>

**Reference Value**
0.100
0.100
0.100

**Average Result**
0.094
0.102
0.103

**Standard Deviation**
0.007
0.006
0.004

Figure 1: Silicon in steel accuracy using the Niton XL5 analyzer

Figure 2: Silicon in steel measurement repeatability using the Niton XL5 analyzer