Residual element concentrations in carbon steel can be a critical indicator in the expected life and performance of pipes and components used in petrochemical applications. Particular elements of interest include Cr, Cu, and Ni, as well as Mo, Sn, V, Sb, As, and Pb.

The manufacturing of carbon steel is becoming more dependent on recycled metal scrap. As this happens, residual element concentrations in finished materials increase. Further, residual elements are difficult to remove or lower using simple metallurgical techniques during the melting process. Because residual levels can be strong indicators and affecters of material properties, including corrosion resistance, residual element analysis is increasingly a major concern in both installed and newly purchased materials.

A case study cited in Hydrocarbon Processing showed that HF alkylation units can be subject to selective corrosion in a unique manner resulting from elevated levels of residual Cr, Cu, and Ni. In this case study, a failure in the form of a pressure leak caused by internal corrosion was discovered at a weld between a 90° elbow and a straight section of pipe. Chemical testing determined that the sum of Cr, Cu, and Ni was greater than 0.50%. The article’s authors suggest a maximum allowable value of 0.20% for the sum of these three elements.

The Thermo Scientific Niton XL5 is the latest offering in our market-leading family of Niton handheld XRF analyzers. The Niton XL5 is specifically designed for low detection limits, high accuracy and the fastest analysis time for trace elements, such as Cr, Cu, and Ni.

Key Words
Niton XL5, Residual Elements, HF Alkylation, Corrosion, Petrochemical, Niton, XRF

**Application**
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**Niton XL5 handheld XRF**
The new Thermo Scientific™ Niton™ XL5 is the smallest and lightest high-performance X-ray fluorescence (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 sensitivity for the most demanding applications, such as residual element measurement. The Niton XL5 offers the following key benefits:

- Unparalleled chemistry and metal-grade identification accuracy for confident results every time
- Excellent trace element detection (Cr, Cu and Ni) for fast and reliable residual elements testing
- Small size and light weight improve productivity and enable testing in tight spots, without operator fatigue
- Flexible user interface enables custom workflow solutions and easy optimization for specific applications
- A pseudo-element feature can be used to automatically calculate the sum of residual elements
- Integrated micro and macro camera and small spot analysis for accurate sample positioning and image capture
- Waterproof, dustproof and rugged housing for harsh environments

The Niton XL5 Pseudo-element feature enables automatic calculation of the sum of residual elements.

Esa Nummi, Thermo Fisher Scientific, Tewksbury, MA USA
Test Method and Results
Using the Niton XL5 XRF analyzer, certified reference standards and samples were analyzed after ensuring the surface was clean of any contaminants. Carbon steel alloys oxidize easily when exposed to atmospheric conditions. This oxide coating can affect the accuracy of the reading when performing an XRF analysis. It is important 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. All surface contamination must be removed in the area to be analyzed.

Data quality objectives dictate the sample preparation requirements and the minimum analysis time used. Ten individual XRF readings were collected, using a total measurement time of 30 seconds. The objective of the residual element analysis is to discern whether the material contains Residual Element (RE) Sum (Cu+Ni+Cr) less than 2000 ppm (0.20%).

Table 1 shows the results obtained with the Niton XL5 analyzer. The certified reference material results are reported on the top line of the table (Material Test Report). The XRF average analysis is the average of ten individual test results using the 30 second test times. The two sigma standard deviation was calculated from the ten individual results.

<table>
<thead>
<tr>
<th>Niton XL5 Test Result of carbon steel samples</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>SUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Test Report</td>
<td>0.111</td>
<td>0.051</td>
<td>0.107</td>
<td>0.269</td>
</tr>
<tr>
<td>Niton XL5 average result</td>
<td>0.125</td>
<td>0.059</td>
<td>0.099</td>
<td>0.283</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.004</td>
<td>0.011</td>
<td>0.004</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Table 1: Niton XL5 test result of carbon steel sample.

As can be seen from Table 1, there is good agreement between laboratory results and the Niton XL5 results. Limits of detection (LODs) for the Niton XL5 are listed in Table 2 below. LODs are calculated as three standard deviations (99.7% confidence interval) for each element for several different measurement times. Limit of detection improves as a function of measurement time.

<table>
<thead>
<tr>
<th>Niton XL5 Test Result of carbon steel samples</th>
<th>Measured time, in seconds</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>SUM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 sec</td>
<td>0.0050</td>
<td>0.0600</td>
<td>0.0120</td>
<td>0.0770</td>
</tr>
<tr>
<td></td>
<td>30 sec</td>
<td>0.0035</td>
<td>0.0424</td>
<td>0.0085</td>
<td>0.0544</td>
</tr>
<tr>
<td></td>
<td>60 sec</td>
<td>0.0025</td>
<td>0.0300</td>
<td>0.0060</td>
<td>0.0385</td>
</tr>
</tbody>
</table>

Table 2: Detection limits for Niton XL5.

Conclusion
Refinery inspectors need confidence in residual chemistry analysis. Residual concentrations can be critical to hundredths of a percent, in order to accurately predict variances in material strength, hardness and corrosion resistance. HF alkylation is an increasingly central process in the refining industry for the production of petrochemical products. As gasoline requirements have evolved, so, too, has the dependence on this process that offers a very clean burning product.

The Niton XL5 analyzer provides excellent trace element precision and sensitivity for residual element analysis. Given appropriate sample preparation, the analyzer is able to quickly and reliably verify whether the sum of residual element (RE) content is lower or higher than the critical 0.2% level. The Niton XL5 unique pseudo-element feature makes this task easy by automatically calculating RE content.

When low detection limits or the highest sample throughput are critical, the combination of Thermo Scientific hardware and software, along with our direct industry experience, provides the ideal solution for the most difficult analytical requirements. The improved analytical capability for trace quantities of Cr, Cu, and Ni and other unique capabilities make Niton XL5 the ideal tool for residual element analysis. In addition to residual elements, the analyzer can quickly generate full chemical analysis and positive material identification (PMI) for a wide range of alloy grades used in the oil and gas industry.

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.