Application note

Rapid analysis of residual elements in carbon steel piping from hydrofluoric acid alkylation units

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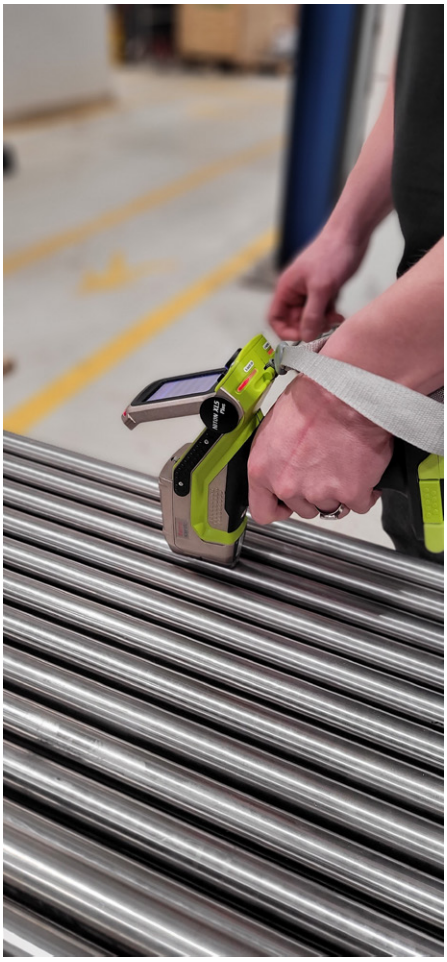

Application

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 Nb, Mo, Sn, V, Ti, Sb, As, and Pb.

The manufacturing of carbon steel is becoming more dependent on recycled scrap metal. As more recycled metal is used, residual element (RE) concentrations in finished materials increase. Residual materials can adversely affect final material properties, and the level of RE can be a strong indicator of the strength of key properties such as corrosion resistance. In addition, RE concentrations are difficult to remove or decrease using simple metallurgical techniques during the melting process. As a result, the detection of RE in products made of carbon steel is a major concern in both installed assets and newly purchased materials.

A case study cited in *Hydrocarbon Processing* showed that hydrofluoric acid (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[1]. The American Petroleum Institute (API) in the recommended practice (RP) 751[2] specifies that material verification programs including positive material identification shall include chemical analysis of RE. The level of the RE (sum of Cr, Cu, Ni) shall not exceed 0.15% in carbon steel weld and base metals according to API RP 571[3].

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Niton XL5 Plus Handheld XRF Analyzer

The Thermo Scientific™ Niton™ XL5 Plus analyzer is the smallest and lightest high-performance X-ray fluorescence (XRF) metal analyzer in the market. The light weight and small size of the analyzer reduce operator fatigue and enable access to more test points. Compact measurement geometry, a powerful 5W miniaturized X-ray tube and a large area silicon drift detector with a window made of graphene provide high performance and ideal sensitivity for the most demanding applications, such as the measurement of RE.

The Niton XL5 Plus analyzer was selected for this analysis due to its:

- Enhanced sensitivity for Cr, Cu and Ni for fast and reliable RE testing
- Flexible user interface enabling custom workflow solutions and easy optimization for specific applications
- A pseudo-element feature and a pass/fail setting to be used respectively to calculate the sum of RE and assess if the level is above or below 0.15% threshold (Figure 1)
- Integrated micro and macro camera and small spot analysis for accurate sample positioning and image capture
- Splashproof, dustproof and rugged housing for harsh environments

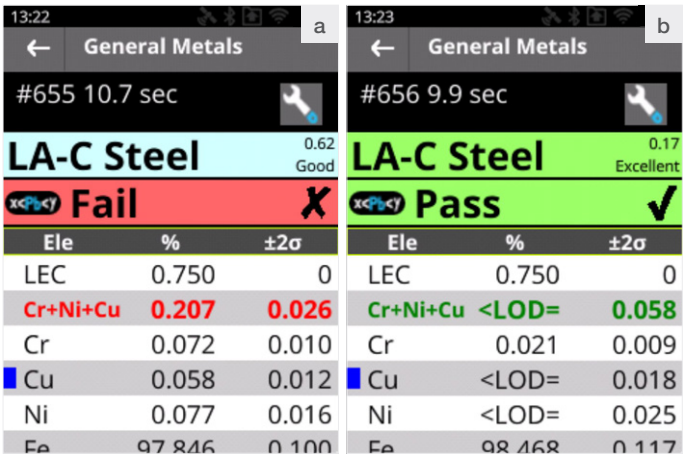

Figure 1. measurement of RE in carbon steel. Sample containing RE both a) above and b) below the threshold of 0.15%.

Test method and results

Carbon steel alloys oxidize easily when exposed to atmospheric conditions. This oxide coating can affect the accuracy of readings collected during XRF analysis. It is important to remove any corrosion to ensure an accurate reading. In addition to oxidation, there can often be paint, oil or grease on the surface of a sample. All surface contamination must be removed in the area to be analyzed. In the analysis described in this note, certified reference standards and samples were analyzed with the Niton XL5 Plus XRF analyzer after ensuring the surface was clean of any contaminants.

The goal of the residual element analysis is to discern whether the material contains (RE) sum (Cu+Ni+Cr) more or less than the threshold of 0.15%. Hence, data quality objectives dictate the minimum analysis time used. For this purpose, limits of detection (LODs) and limits of quantification (LOQs) for the Niton XL5 Plus analyzer were determined (Table 1). LODs and LOQs are calculated as 3, respectively 10 standard deviations (σ) of the background for each element for several different measurement times. LODs and LOQs improve as a function of measurement time. The results indicate that the operator should measure for at least 10 seconds when the sum the concentration of RE is close to or below the threshold of 0.15%.

	LOD Cr	LOD Cu	LOD Ni	Sum
5 seconds	0.022 %	0.025 %	0.028 %	0.074 %
10 seconds	0.013 %	0.014 %	0.019 %	0.045 %
15 seconds	0.010 %	0.011 %	0.015 %	0.036 %
20 seconds	0.009 %	0.009 %	0.012 %	0.030 %
	LOQ Cr	**LOQ Cu**	**LOQ Ni**	**Sum**
5 seconds	0.072 %	0.082 %	0.093 %	0.25 %
10 seconds	0.043 %	0.045 %	0.062 %	0.15 %
15 seconds	0.034 %	0.036 %	0.049 %	0.12 %
20 seconds	0.029 %	0.030 %	0.042 %	0.10 %

Table 1. Limits of detection (LOD) and limits of quantification (LOQ) in carbon steel for different testing times with the Niton XL5 Plus handheld XRF analyzer.

In the analysis described in this note, ten individual XRF readings were collected using a total measurement time of 10 seconds each (Table 2). The certified reference material results are reported on the bottom line of the table (Material Test Report). The XRF average analysis is the average of ten individual test results using the 10-second testing time. As can be seen in Table 2, there is good agreement between laboratory results and the Niton XL5 Plus analyzer readings for a relatively short measurement time of 10 seconds, which appears to be sufficient to accurately differentiate between material at risk which contains more than 0.15% of RE.

Reading #	Cr (%)	Cu (%)	Ni (%)	Sum
1	0.059	0.047	0.080	0.186
2	0.067	0.048	0.069	0.184
3	0.059	0.056	0.072	0.186
4	0.065	0.039	0.077	0.181
5	0.060	0.051	0.071	0.182
6	0.062	0.046	0.072	0.180
7	0.067	0.046	0.068	0.181
8	0.067	0.051	0.073	0.190
9	0.063	0.036	0.077	0.176
10	0.062	0.047	0.067	0.175
Average	**0.063**	**0.047**	**0.072**	**0.182**
Std. Dev	**0.003**	**0.006**	**0.004**	**0.005**
MTR*	**0.062**	**0.051**	**0.069**	**0.182**

*Material test report (MTR) result

Table 2. Test results of carbon steel sample from 10 seconds readings with the Niton XL5 Plus analyzer.

Conclusion

Refinery operators and inspectors need confidence in residual chemistry analysis. Residual concentrations can be critical to hundredths of a percent to accurately predict variances in material strength, hardness and corrosion resistance. RE is also a concern in HF alkylation which is an increasingly central process in the refining industry for the production of gasoline from isobutane and light alkenes.

The Niton XL5 Plus analyzer proved it could deliver excellent trace element precision and sensitivity for residual element analysis. Given appropriate sample preparation (cleaning the sample surface), the analyzer is able to quickly and reliably verify whether the sum of RE content is lower or higher than the critical 0.15% level. The analyzer's pseudo-element feature makes this task easy by automatically calculating RE content. In addition to RE, 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. The Niton XL5 Plus analyzer delivers unparalleled chemistry and metal-grade identification accuracy yielding confident results and fast analysis time for trace elements, such as Cr, Cu, and Ni.

References

1. Tim Munsterman and Anelsy G. Mayorga, "Preferential Corrosion of Welds in HR Service," Hydrocarbon Processing (September 2004): 113-119.
2. API RP 751-2021 Safe Operation of hydrofluoric acid alkylation units, American Petroleum Institute, Washington, DC
3. API RP 571-2020 Damage mechanisms affecting fixed equipment in the refining industry, American Petroleum Institute, Washington, DC

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 **thermoscientific.com/pmi**