Tech Flash

Using Handheld XRF to Determine Surface Mercury Contamination

Surface Mercury Contamination

Mercury is a naturally occurring element present in virtually all oil and gas products. Mercury levels in crude and gas can vary widely, both between and within reservoirs and geographical areas. Concentrations vary from low ppb (part per billion) to low ppm (part per million) level. Mercury compounds in crude are largely elemental and inorganic compounds such as mercuric sulfide.

In addition to posing environmental and health concerns, mercury is also detrimental to the refining process through amalgamation with other metals, poisoning of catalysts, and liquid metal embrittlement (cracking) with metals such as aluminum. Over time, mercury species from crude oil may accumulate in process equipment over time. During refinery distillation, mercury vapor is predominantly distributed in liquefied petroleum gas (LPG) and light distillate streams. Due to its weight, it can also be found in the residual fraction, which also contains the majority of the insoluble and inorganic mercury salts. Of particular concern are LNG and LPG cryogenic heat exchangers made of aluminum alloy.

Mercury accumulations may require special procedures in many areas:

- Environmental issues and potential waste issues.
- Health and safety issues: volatile sources, surface contamination, particulate contamination during hot work. Assets exposed to mercury must be decontaminated prior to further use. Workplace TWA exposure limits are determined as 0.025 mg/m^3.
- Safety issues: Prevention of corrosion by metal amalgamation or possible liquid metal embrittlement (LME).

Mercury could produce similar conditions inside marine vessels and storage tanks. Wash water could strip out a soluble mercury component. Elemental and inorganic mercury could be a risk in tank bottoms and sludge. Since crude oil tanks are seldom coated, elemental mercury could form an amalgamation with the steel. The partial vapor pressure of mercury could result in a greater concentration in a saturated atmosphere.

Traditionally, surface mercury analysis of metal samples has been performed by laboratory analysis, such as atomic absorption spectroscopy (AAS) which takes time and is not always practical. Portable mercury vapor analyzers are effective for measuring airborne mercury levels, but they do not detect surface contamination such as mercury sulfide deposits.

Handheld XRF Surface Mercury Determination

The Thermo Scientific Niton XL3t series instruments offer two different ways to analyze for the presence of mercury on metal surfaces.In the General Metals analysis mode, the instrument detects the presence of mercury as percent weight or ppm. This mode is best used for a quick pass/fail screening, as it doesn't provide reliable information about mercury levels. Using the Coatings measurement mode, the instrument reports mercury as coating weight (µg/cm^2). The Coatings mode provides accurate coating weight to determine the precise amount of mercury in the contaminated sample. Because common alloys such as iron-, nickel- and copper-based materials do not form alloys with mercury, it remains on the alloy surface, making coating weight analysis the best way to measure the presence of mercury.

Thermo SCIENTIFIC

Coatings Analysis Mode

Thermo Scientific Niton analyzers are capable of coatings thickness or coating weight analysis. Both single layer and multilayer coatings can be analyzed. Metal Coatings mode is an optional mode, available for all Niton XL2 and XL3t models, excluding XL2-100.

Figure 1
Select Sample Type

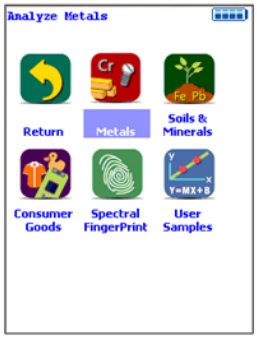

Figure 2
Select Metals mode

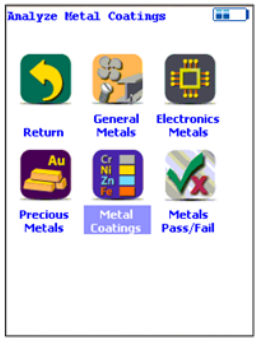

Figure 3
Select Metal Coatings

How to Create a New Coating System for Mercury on Iron

Before you can analyze for thickness, you have to create a Coatings System Entry and define the coating system. Note that the coatings method menu can be accessed via the steps outlined above.

When creating a coating system, click “add” to activate the virtual keyboard and enter the name of a coating system (i.e., Hg on Fe). Once the name is created, use the individual pulldown menus to select the unit (coating thickness or coating weight), substrate (type of metal to be coated) and metal coatings.

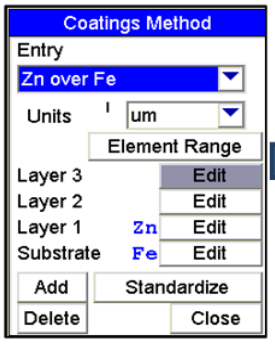

Figure 4
Select Add to create a new method

Figure 5
Enter name of the method:
e.g., Hg on Fe

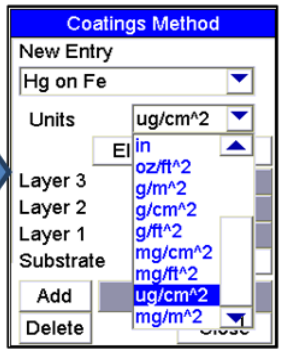

Figure 6
Select preferred unit from the Units list, typically for Hg ug/cm² is used

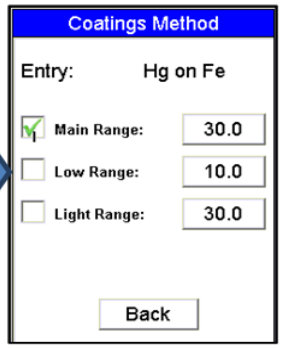

Figure 7
Adjust element range if necessary, only the Main range is needed for Hg of Fe

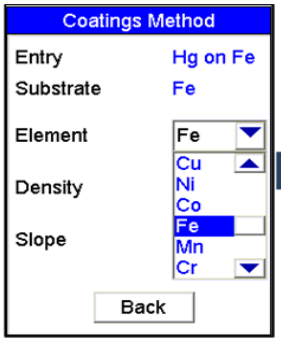

Figure 8
Select Substrate: Fe

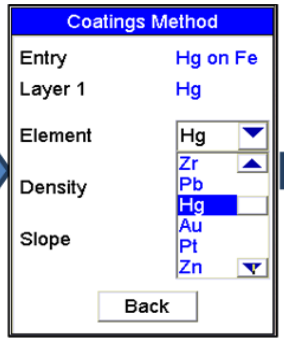

Figure 9
Select Coating Layer 1: Hg

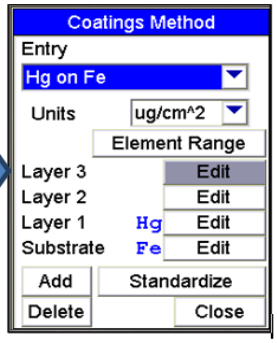

Figure 10
Completed Coating System setup

Standardization

The Standardize feature is a single point type standardization routine that corrects for any bias when compared to another analytical technique, e.g., bench-top X-ray, strip and weight or Eddy current. To perform standardization, you must introduce a single known sample for analysis and enter the known thickness value for that sample. Following the analysis of that sample, the slope is calculated based on the value and the response of the measured sample. This provides the basis for a very accurate calibration in the target thickness range. Once the standardization measurement is finished, you can either accept or reject the new slope calculation.

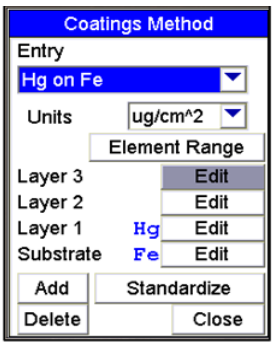

Figure 11
Select Standardize

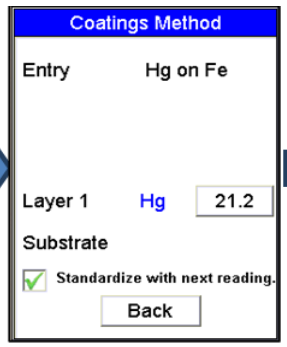

Figure 12
Enter known thickness and check Standardize checkbox

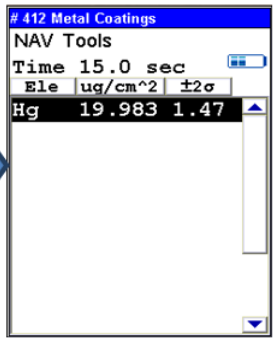

Figure 13
Return to Measurement screen to measure the standardization sample

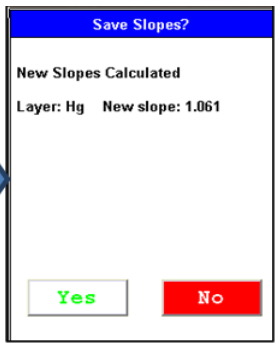

Figure 14
Save new slope

The standardization sample used should be consistent with the target thickness value for your application. Use a representative mercury surface contamination sample that has been analyzed in the laboratory or a reference sample with a known mercury coating weight.

One source for mercury coating weight standards is Micromatter (www.micromatter.com). Micromatter standards have a known coating weight of silver-mercury alloy on Mylar plastic film. Since the Coatings mode is designed for pure element coatings, this type of binary coating sample is not ideal for standardization, but it can be used for an approximate calibration adjustment and as a check sample measured periodically for quality control purposes.

When this type of sample is measured, it is essential to place a steel plate underneath the sample, so that it represents an actual measuring situation (mercury on steel).

Micromatter Mercury Silver reference standard.
www.micromatter.com

How to Change the Active Coating System

Note: Coatings Entry list includes only methods that have been created by the user.

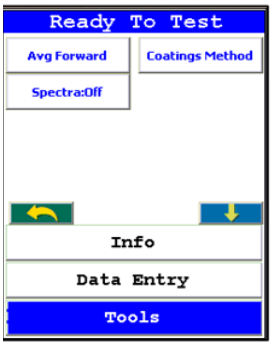

Figure 15
Select Tools/Coatings Method

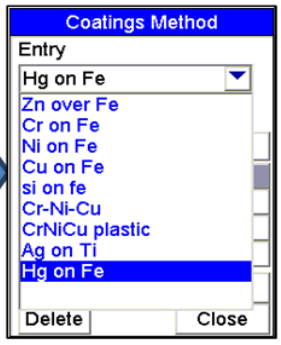

Figure 16
Select method from the Entry list

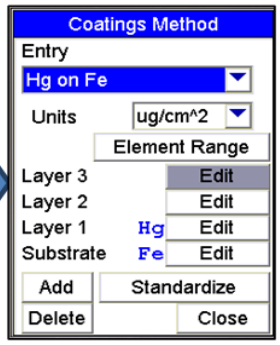

Figure 17
Select Close to return measurement screen

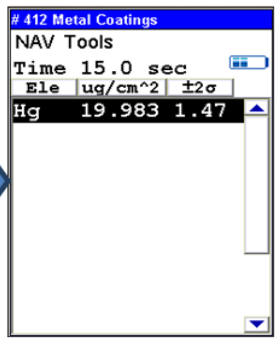

Figure 18
Make a coating weight measurement

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