Applications of low power monochromatic WDXRF for sulfur and chlorine analysis in petroleum industry --- overview and recent developments

Z.W. Chen and Leslie Johnson

XOS, East Greenbush, 12061 USA

Low power monochromatic wavelength-dispersive x-ray fluorescence (MWDXRF) analysis has become a powerful tool for single/dual element analysis from trace to high concentrations. In a MWDXRF system, a small spot, low power x-ray tube coupled with a doubly curved crystal (DCC) optic [1] provides an intense monochromatic focusing beam on a sample. The emitted x-ray fluorescence photons of an analyte are collected by a large aperture DCC optic and then directed to a detector. The MWDXRF system gives the highest signal/background ratio among any XRF systems due to the combination of monochromatic excitation and high resolution wavelength-dispersive spectrometry.

Low power MWDXRF has been successfully used for sulfur, chlorine, phosphorus, and other analyses. Unprecedented detection limits for sulfur or chlorine in oil matrix have also been achieved by a low power MWDXRF analyzer [2,3]. An ASTM standard test method based on MWDXRF, D7039, was developed for measuring sulfur in petroleum products. This method has been widely adopted by the petroleum industry in both North and South America and China. Ongoing ASTM inter-laboratory cross check sulfur data shows that D7039 gives the best reproducibility at low concentration ranges when compared to UV fluorescence and other WDXRF sulfur methods [4]. The MWDXRF chlorine analyzer can detect 100 ppb chlorine in petroleum products and streams, which is a powerful tool for corrosion monitoring in oil refineries. An ASTM test method, D7536, was also developed for testing trace level chlorine in aromatics [5]. Recently there has been a discussion for the need of an ASTM standardized test method for chlorine in crude oil using MWDXRF.

This paper will review the principle and advantages of MWDXRF. It will also include the results of a recent inter-laboratory round robin study and inter-laboratory cross check study data as well as applications data for diesel, gasoline, biofuel, and gasoline-ethanol fuel. Recent advancement in MWDXRF instrumentation to push the detection limits below 100ppb for sulfur testing will be discussed. Additionally, recent on-line application for trace chlorine monitoring in a refinery process will be illustrated in this paper.

Reference:

1. Zewu Chen, US Patent 6285506, “Curved optical device and method of fabrication,” 2001
2. Z. W. Chen, Fuzhong Wei, Ian Radley, and Berry Beumer, “Low-Level Sulfur in Fuel Determination Using Monochromatic WD XRF – ASTM D7039”, Vol. 2(8), J. of ASTM International (2005).
3. Zewu Chen and David Gibson, US Patent 6,934,359, “Wavelength dispersive XRF system using focusing optic for excitation and a focusing monochromator for collection,” 2005
4. ASTM Standard test method: ASTM D7039-15a, “Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry”, 2015 https://www.astm.org/Standards/D7039.htm
5. ASTM Standard test method: ASTM D7536-16, “Standard Test Method for Chlorine in Aromatics by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry”, 2016 https://www.astm.org/Standards/D7536.htm