SIMPLE, FAST, AND ACCURATE CHLORINE ANALYSIS IN VGO AND VLSFO

WHY MEASURE CHLORINE IN VGO AND VLSFO?

Vacuum gas oil, more commonly referred to as VGO, is primarily used as a feed for cracking units such as the fluid catalyst cracker (FCC) or the hydrocracker. The FCC and hydrocracking units transform VGO into more desirable products – specifically, gasoline and gasoil (diesel). While VGO is worth more as a feedstock for producing these higher-value fuels, another potential – but uncommon – use for VGO is to blend it into residual fuel oil.

Since VGO is most likely to be used as a feedstock, it is paramount to measure and control its chlorine content. Higher chlorine content in feedstocks will impair and diminish catalyst performance by deactivating the catalyst more rapidly than it would in the absence of chlorine. In addition, chlorine in VGO feedstock can be transformed into hydrochloric acid (HCl), which causes corrosion damage, leading to repair needs, in turn causing an increase in both downtime and turnaround time.

Very low sulfur fuel oil, commonly abbreviated to VLSFO, is mainly used as a marine fuel and is compliant with the new 2020 International Maritime Organization (IMO) regulations for marine fuels. For VLSFO, accurate chlorine determination is important for storage reasons: VLSFO is stored in shore tanks and on ships in bunker tanks. These tanks hold the fuel for varying amounts of times and are connected to hoses, pipelines, manifolds, and other pipes or tubes that connect the ship to shore. Because chlorine is an oxidizer and high levels of chlorine can accelerate chloride corrosion of stainless steel, as with VGO, the ramifications of having elevated chlorine levels are not ideal.

In short, chlorine content in VGO and VLSFO is measured so that it can ultimately be reduced or adjusted to prevent catalyst deactivation, corrosion damage, and unwanted reactions with free radicals during chemical processes. Each of the aforementioned items lead to increased operating costs, increased maintenance hours, and a reduction in the amount of time between turnarounds.

MICROCOULOMETRY

Traditionally, when the chlorine levels in VGO and VLSFO are analyzed, this is done by using microcoulometry. Microcoulometry is a well-accepted method to determine chloride and/or organic halogens in petroleum products, and while this is certainly a good technique for analyzing the chloride or halogen content, there are some drawbacks – mainly: 1) these samples cannot be analyzed directly, and 2) they have to be diluted from either 5-times dilution or 20-times dilution, with heavier fractions needing to be diluted even further. Diluting samples often leads to error, leading to different values from those expected. Additionally, if a sample isn't properly diluted, incomplete combustion occurs, fouling the unit and rendering it inoperable until it's been cleaned or the fouled parts have been replaced.

Other microcoulometry methods may require the sample be refluxed with xylene, water, and a nitric acid solution for 15 minutes or more – then, the flask must be allowed to cool, and the organic and inorganic layers must separate. It is only after all of this that the analysis can begin.

Ultimately, microcoulometry, though effective at providing accurate chloride analysis, is a time-intensive process that requires gasses, acids (sulfuric acid, acetic acid, and nitric acid – the latter of which is only for extraction purposes), continuous observation and maintenance with regards to the liquid volumes in the reaction vat and scrubber, and a combustion tube at roughly 1000°C. Due to these drawbacks and the safety concerns of working with both acids and extremely high temperatures, a growing number of labs and refineries are moving away from combustion techniques and solutions that require extra sample preparation, and are instead seeking safer alternatives for obtaining fast, accurate, and reliable solutions for measuring chlorine in petroleum fuels.

Luckily, such an alternative exists in the form of Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF), a variation of standard XRF that requires minimal sample preparation without the use of gasses or acids, delivering precise results within five minutes.

The main benefit of XOS's patented monochromatic excitation technology is that the signal to noise ratio is decreased significantly in relation to traditional XRF, focusing on only one specific section of interest instead of the entire spectrum. Due to this decreased signal to noise ratio, the detection limit of analyzers using this technology is typically very low. XOS' Clora series, which includes Clora, Clora 2XP, Sindie + Cl, and Clora Online, all use MWDXRF technology, providing refiners, producers, and laboratories with a safe and reliable chlorine-measuring solution that adequately meets their needs.

EXPERIMENT

XOS performed the following experiment to showcase the precision and reliability of MWDXRF using Clora 2XP by acquiring two real-world samples: One VGO sample and one VLSFO sample. Both samples have been analyzed under repeatability conditions, defined here as 10 measurements obtained using 10 unique cups containing 10ml aliquots from a single sample container, analyzed by the same device, on the same day, in the same location, by the same operator.

For this experiment, Clora 2XP has been calibrated with a mineral oil calibration standard set that includes the following data points: 0, 0.5, 1, 2, 5, and 10 mg/kg. Both the VGO and the VLSFO samples have been heated to 50°C/122°F in a warm water bath, which is continuously kept at 50°C/122°F.

After heating, the samples were vigorously shaken horizontally for 10 seconds and then shaken again, this time vertically, for 10 seconds. After the first 20 seconds of shaking, the sample would then be inverted and shaken again – vertically for 10 seconds and then horizontally for 10 seconds; ensuring that the sample has been completely liquified and properly homogenized. In total, the sample has been shaken for 40 seconds: 10 seconds with the cap facing up, 10 seconds with the cap facing right, 10 seconds with the cap facing down, and finally, 10 seconds with the cap facing left. After this, each sample was poured into a standard XRF sample cup, sealed with Prolene film, and placed in the analyzer. Each sample was analyzed for 300 seconds with Clora 2XP's sulfur correction feature enabled.

WHY DOES SULFUR CORRECTION MATTER?

Without correcting for sulfur during XRF sample analysis, secondary excitation of sulfur by the chlorine fluorescence will lead to biased results. Clora 2XP comes equipped with an automatic sulfur-correcting feature that can be enabled during measurement. Fortunately, automatic correction does not require a known sulfur content as the sulfur concentration is measured concurrently with chlorine. However, standard Clora models require the user obtain prior knowledge of the sample's sulfur concentration in order to manually correct for it.

Table 1: Sample Information

	Aromatic Content	Asphaltene Content	Sulfur Content
VGO	48.8 wt.%	203 mg/kg	1.64 wt.%
VLSFO	75.4 wt.%	2.2 wt.%	0.47 wt.%

__Table 2: VGO Sample Results.__ Each measurement aliquot has been measured for 300 seconds with Clora 2XP's automatic sulfur correction feature enabled.

Measurement	Result in mg/kg
1	1.30
2	1.34
3	1.29
4	1.35
5	1.30
6	1.32
7	1.41
8	1.34
9	1.31
10	1.38
Average	1.33
stdev	0.04
%RSD	2.88

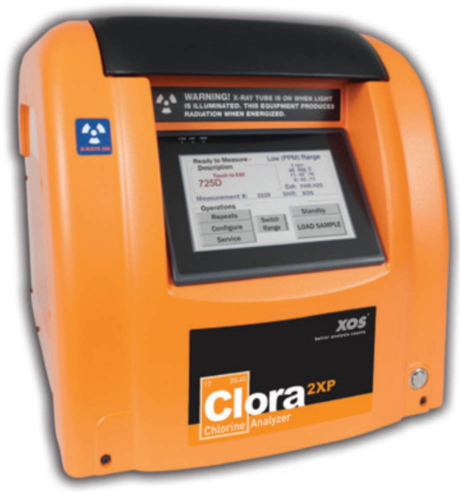
__Table 3: VLSFO Sample Results.__ Each measurement aliquot has been measured for 300 seconds with Clora 2XP's automatic sulfur correction feature enabled.

Measurement	Result in mg/kg
1	1.98
2	2.10
3	2.19
4	1.95
5	2.00
6	2.12
7	2.00
8	2.19
9	2.12
10	2.23
Average	2.09
stdev	0.10
%RSD	4.77

CONCLUSION

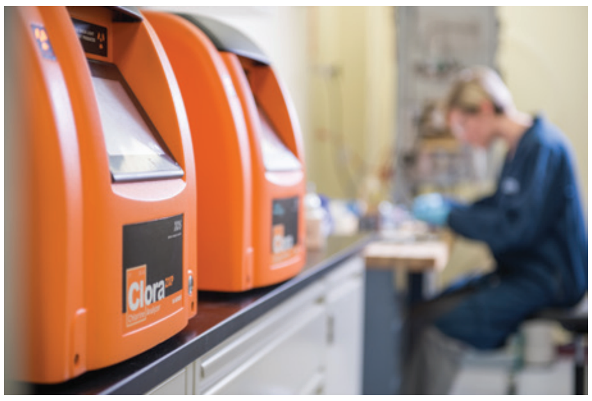
Chlorine analysis continues to be an important measurement for refiners, producers, and laboratories around the world. Global trends to reduce chlorine in feedstocks, or to accurately determine the chlorine in a feedstock or product, highlight the need for a simple, fast, and accurate analysis solution.

Based on the data presented herein, XOS' Clora series provides a viable solution for such needs. Utilizing the most advanced optics technology, the Clora series delivers accurate measurements across various matrices such as hydrocarbons, biofuels, vegetable oils, animal fats, water and more without the need for complex sample preparations, acids, or gasses.



PRODUCT HIGHLIGHT

Clora 2XP delivers better precision for total chlorine analysis in liquid hydrocarbons such as aromatics, distillates, heavy fuels, crude oils, and aqueous solutions. Compliant with ASTM D7536 and D4929 methodology, Clora 2XP is ideal for testing related to catalyst poisoning in reformers and sites with catalytic crackers and hydrocrackers. In addition, its automatic sulfur correction is perfect for high-sulfur and low-chlorine applications, such as crude oil and VGO. Powered by MWDXRF, Clora 2XP does not require gasses or high-temperature processes, equating to easy operation and minimal maintenance requirements.



TECHNOLOGY BRIEF: MONOCHROMATIC WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE (MWDXRF)

Monochromatic Wavelength Dispersive X-Ray Fluorescence (MWDXRF) utilizes state-of-the-art focusing and monochromating optics to increase excitation intensity and dramatically improve signal-to-background ratio compared to traditional WDXRF instruments. This enables significantly improved detection limits, precision, and a reduced sensitivity to matrix effects. A monochromatic and focused primary beam excites the sample, and secondary characteristic fluorescent X-rays are emitted from the sample. A second monochromating optic selects the chlorine characteristic X-rays and directs these X-rays to the detector. MWDXRF is a direct measurement technique and does not require consumable gasses or sample conversion, delivering robust and lowmaintenance analyzers with dramatically lower detection limits and faster response times.