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Application Note

Crude Oil Sample Preparation for CLORA Analysis Water Extraction Methods for Measuring Total, Organic, and Inorganic Chlorine

This document will assist the user in separating chlorine in crude oil into its organic and inorganic counterparts using two different water extraction methods. The primary difference between the two methods is that one makes use of a centrifuge and the other employs a separatory funnel. In addition, this document will assist the user in measuring organic, inorganic, and total chlorine using the CLORA analyzer. This is important because although most of the inorganic chlorine in crude oil coming into a refinery is effectively removed by the desalter, organic chlorides will stay with the crude and downstream processing can break them down into hydrochloric acid which may in turn cause corrosion issues.

Reagents and Materials

- Hot deionized (DI) water
- Reagent grade toluene or xylene – recommended for viscous or asphaltene and bitumen containing crudes

Note 1: DI water and toluene or xylene should be analyzed by the CLORA prior to use to check for chlorine contamination. Any chlorine contamination in the DI should be subtracted from the inorganic chlorine result, and any chlorine contamination from the solvent should be subtracted from the organic chlorine result.

- Centrifuge tubes with caps, 100ml capacity *(extraction method one only)*
- Heated centrifuge *(extraction method one only)*
- Separatory funnel, 250ml capacity *(extraction method two only)*
- Filter paper

Note 2: Some customers using paper filters, such as Whatman 125mm grade 1 filter paper circles, have reported that the filter paper can add to the chlorine content. This can be verified by testing chlorine levels in DI water before and after filtration. Subtract any interferences from the inorganic chlorine result.

- CLORA sample cups
- Etnom XRF film – Etnom film is specifically recommended for CLORA analysis

Crude Oil Sample Preparation

Depending on crude type and composition, it is sometimes hard to obtain a stable homogenous sample. Viscous or asphaltene and bitumen containing crudes are particularly difficult to water extract. Addition of toluene or xylene to these types of crudes will increase the solubility of heavier crude components leading to a more homogenous, less viscous sample that is more efficiently water extracted.

Prepare at least 50 ml of 50/50 wt% crude to solvent (toluene or xylene) mixture per Note 3. A 25 g crude to 25 g solvent mixture will work well for most crudes. Please see Note 1 regarding chlorine contamination in solvents. When analyzing chlorine content on the CLORA remember to multiply the measured results by two to account for this dilution.

Note 3: Be sure to prepare the crude/solvent mixture by *weight*, not volume.

Extraction Method One: Water Extraction Using a Centrifuge

This method is recommended for low viscosity, non-asphaltene and non-bituminous crudes.

Put 25 ml of crude into a centrifuge tube. Add 75 ml of hot DI water. Different amounts of crude and water may be used, but the 3:1 water/hydrocarbon ratio is recommended for effective extraction. Cap the centrifuge tube and shake vigorously for two minutes. Periodically degassing the sample by venting the cap will prevent gas buildup.

Centrifuge the material, with appropriate counter-balance, in a heated centrifuge for ten minutes. This will effectively remove particulates and the inorganic chlorides from the crude into the water layer.

Carefully pipette samples of the crude and water for CLORA analysis, making sure to take the sample from the middle of the sample layer without picking up

contamination from the other phase. When analyzing the water phase it is important to make sure no particulates are present. Filter the sample if necessary (see Note 2).

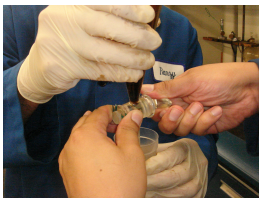
Extraction Method Two: Water Extraction Using a Separatory Funnel

Put 25 ml of crude into a separatory funnel. Add 75 ml of hot DI water. For solvent diluted crudes, use 50 ml of crude/solvent mixture to 150 ml hot DI water. Cap the separatory funnel and shake vigorously for two minutes. Periodically degassing the sample by venting the cap will prevent gas buildup.

Let the sample sit undisturbed for ten to fifteen minutes.

Carefully pipette a sample of the crude for CLORA analysis, making sure to take the sample from the middle of the sample layer without picking up contamination from the water phase.

Drain a water sample from the bottom of the separatory funnel for CLORA analysis. It is important to make sure there are no particulates present in the water sample, so filter if necessary (see Note 2).



Organic, Inorganic, and Total Chlorine Analysis on the CLORA

Pipette 5-8 ml of sample into a sample cup and test in the CLORA using Etnom XRF film. Remember to punch a vent hole in the sample cup. The standard analysis time for samples containing >1 ppm chlorine is 300 sec. If the sample contains <1 ppm chlorine, a 600 sec measurement time is suggested for optimal results. In addition, if the sample contains >1 wt% sulfur, use of a sulfur correction table may help improve results.

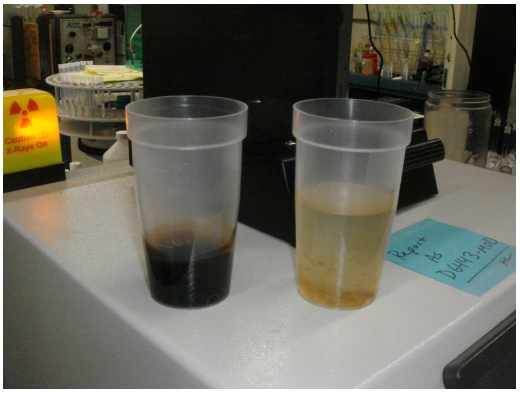
Analyze the crude phase to quantify the amount of organic chlorine in the crude sample.

For undiluted crude samples:
Total organic chlorine = measured organic chlorine

For 50/50 wt% diluted crude samples:
Total organic chlorine = 2 * (measured organic chlorine – solvent chlorine interferences)

Because no water extraction procedure is 100% effective, any organic chlorine result less than two ppm should ensure that the measured crude sample is not contaminated by organic chlorine.

The water phase of the sample is measured to quantify the amount of inorganic chlorine in the crude sample. Be sure to use a water based calibration curve to test this sample to rule out oxygen adsorption effects. High oxygen content, if not accounted for, will result in reduced counts and a falsely low chloride value. If a dedicated water curve has not been developed, multiply the results obtained using a hydrocarbon calibration curve by 250% (or 2.50).



For undiluted crude samples on water based curve:
Total inorganic chlorine = measured inorganic chlorine – DI water and filter interferences
For undiluted crude samples on hydrocarbon based curve:
Total inorganic chlorine = 2.5 * (measured inorganic chlorine – DI water and filter interferences)

For 50/50 wt% diluted crude samples on water based curve:
Total inorganic chlorine = 2 * (measured inorganic chlorine – DI water and filter interferences)
For 50/50 wt% diluted crude samples on hydrocarbon based curve:
Total inorganic chlorine = 5 * (measured inorganic chlorine – DI water and filter interferences)

To obtain total chlorine, simply add inorganic and organic results together.

References

NACE International, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International Publication 34105, Item 24226.

Application Note

Appendix A: Crude Prep and CLORA analysis example:

Procedure highlights:

25 g crude/25 g toluene mixture (by weight)
50 ml crude/solvent to 150 ml hot DI to extract in separatory funnel
Pipette crude sample from top of funnel for organic chlorine analysis
Filter sample from bottom of funnel for inorganic chlorine analysis

Analysis of blanks on CLORA:

0.07 ppm – unfiltered DI water
1.77 ppm – filtered DI water
0.38 ppm – toluene

Interferences:

-1.77 ppm from inorganic chlorine result for filter and DI water
-0.38 ppm from organic chlorine result for toluene

CLORA sample measurements:

1.23 ppm – crude phase on hydrocarbon calibration
1.98 ppm – water phase on hydrocarbon calibration

Organic chlorine calculation:

For 50/50 wt% diluted crude samples:
Total organic chlorine = 2 * (measured organic chlorine – solvent chlorine interferences)

Total organic chlorine = 2 * (1.23 – 0.38) = 1.70 ppm

Inorganic chlorine calculation:

For 50/50 wt% diluted crude samples on hydrocarbon based curve:
Total inorganic chlorine = 5 * (measured inorganic chlorine – DI water and filter interferences)

Total inorganic chlorine = 5 * (1.98 – 1.77) = 1.05 ppm

Total chlorine = total organic chlorine + total inorganic chlorine:

Total chlorine = 1.70 + 1.05 = 2.75 ppm