DETERMINE ORGANIC AND INORGANIC CHLORIDES IN CRUDE OIL

Although all XRF techniques are capable of only total elemental analysis, with some sample preparation, Clora, Clora with Accu-flow, Clora 2XP, and Sindie +Cl can also be used to characterize inorganic and organic chlorides in crude oil. Using a hot water extraction, crude oil may be separated into its organic chloride and inorganic chloride constituents with the organic chlorides staying in the crude oil layer and the inorganic chlorides precipitating into the water layer. Clora can then be used to measure each layer to determine organic and inorganic chlorides. While many laboratories have successfully used this sample preparation technique, unfortunately, this technique has crude-dependent limitations. Not all crude oils are easily extracted and this sample preparation technique has variable withinlab repeatability and poor between-lab reproducibility.

Procedures A-C will assist the user in separating chlorine in crude oil into its organic and inorganic counterparts using water extraction methods.

Procedure Notes:

- **Note 1:** Be sure to prepare the crude/solvent mixture by weight, not volume.
- **Note 2:** DI water and toluene or xylene should be analyzed by Clora prior to use to check for chlorine contamination. Any chlorine contamination in the DI water should be subtracted from the inorganic chlorine result, and any chlorine contamination from the solvent should be subtracted from the organic chlorine result.
- **Note 3:** Assuming the density of water = 1 g/ml, then weight equals volume. Therefore, 75 ml water = 75 g.
- **Note 4:** Some customers using paper filters, such as Whatman 125 mm 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.
- **Note 5:** When pipetting the water sample, expel air from the pipette when initially putting it into the water sample to keep oil (often present as a thin film on the surface of the water) out of the measured sample cup.
- **Note 6:** When calculating inorganic chlorine, use the weight of the crude in the calculation. Do not use the combined weight of the solvent and crude.

PROCEDURE A: Crude Oil Sample Preparation

Depending on crude type and composition, it may be hard to obtain a stable homogenous sample. Viscous or asphaltene and bitumen containing crudes are particularly difficult to water extract. The 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 approximately 25 ml of 50/50 wt% crude to solvent (toluene or xylene) mixture per **Note 1**. Shake or homogenize the crude oil sample prior to obtaining a specimen for dilution. A 12.5 g crude to 12.5 g solvent mixture will work well for most crudes. See **Note 2** regarding chlorine contamination in solvents. When analyzing chlorine content with Clora, remember to multiply the measured results by 2 to account for this dilution.

PROCEDURE B: Water Extraction Using a Separatory Funnel

Weigh 25 grams of crude into a separatory funnel. Make sure to shake or homogenize the crude oil sample before obtaining a specimen. Add 75 ml (**see Note 3**) of boiling DI water. For solvent diluted crudes, use 25 grams of crude/solvent mixture (as prepared in the Crude Oil Sample Preparation section) to 75 ml boiling DI water.

Cap the separatory funnel and shake vigorously for two minutes. Periodically degassing the sample by venting the stopcock 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 the 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 4**).

PROCEDURE C: Organic, Inorganic, and Total Chlorine

Separatory Funnel

Analysis with Clora

In general, pipette 5-8 ml of sample into a sample cup and test with Clora using XRF film (Etnom for Clora and Sindie +Cl, Prolene for Clora 2XP). Remember to punch a vent hole in the sample cup. The standard analysis time for samples containing >1 ppm chlorine is 300 s. If the sample contains <1 ppm chlorine, a 600 s measurement time is suggested for optimal results with Clora and Sindie +Cl. For samples containing <0.5 ppm chlorine measured with Clora 2XP, measure two samples (new sample cup each time) for 300 s each and use the average of the two results. If the two results have a ≥0.2 ppm difference, measure a third sample to determine which of the two samples is an outlier. Discard any outlier measurement results.

In addition, if the sample contains >0.5 wt% sulphur (>0.1 wt% sulphur when measuring with Clora 2XP), use of sulphur correction may improve the accuracy of the results.

Analyze a blank solvent sample (if diluting crude sample) and a blank DI water sample to account for any diluent interferences (**see Note 2**).

Analyze the crude phase to quantify the amount of organic chlorine (and non-extractable inorganic chlorine) in the crude sample. In order to ensure the extraction process has been successful, check the crude or crude/solvent mixture for settling while performing the measurement. To do this, divide the recommended measurement time (as described above) into 30 or 60 second repeats, noting that the maximum repeat input with Clora and Clora 2XP analyzers is 10 repeats. Run the sample accordingly and look for increasing measurement values within the individual sample repeats. Continually increasing measurement values indicate an incomplete extraction. A second (or third) extraction may be necessary.

For example, on the repeats screen below, if the recommended measurement time is 300 s, run (10) 30-second repeats on one sample and examine the individual repeat measurements for upward trending. If the total measurement time is 600 s, run (10) 60-second repeats. Keep the repeat delay at 1 second. Don't forget to use sulphur correction if necessary.

If the measurement results indicate trending (crude B in **Table 2**), return the crude or crude/solvent sample to the separatory funnel or centrifuge tube and extract again using a new aliquot of hot DI water. If the measurement results indicate a successful extraction (crude A in **Table 2**), use the average measurement result and the following equations to calculate organic chlorine:

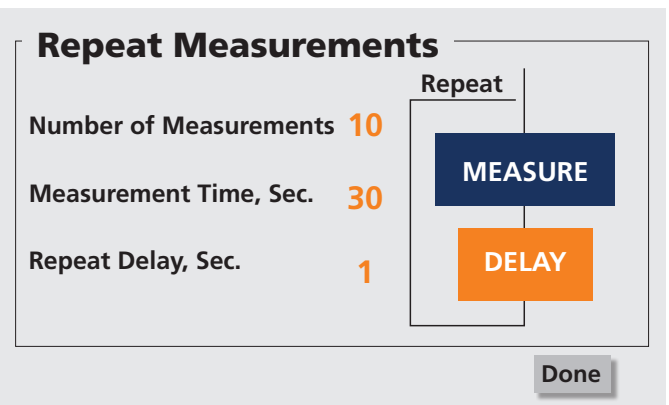

Table 2

Settle Time	Sample	Crude A		Crude B	
hh:mm:ss	Repeat	Cl (ppm)	cts/30s	Cl (ppm)	cts/30s
0:00:30	1	2.51	81	36.15	960
0:01:00	2	3.28	101	35.31	938
0:01:30	3	2.59	83	37.91	1006
0:02:00	4	2.51	81	44.76	1185
0:02:30	5	2.51	81	52.00	1374
0:03:00	6	3.39	104	55.52	1466
0:03:30	7	2.47	80	59.88	1580
0:04:00	8	3.24	100	63.86	1684
0:04:30	9	2.97	93	65.85	1736
0:05:00	10	2.90	91	76.87960	2024
Average		2.84		52.81	

EQUATIONS TO CALCULATE ORGANIC CHLORINE

• For undiluted crude samples:

$$\text{Total Organic Chlorine (ppm)} = \text{Measured Organic Chlorine (ppm)}$$

• For 50/50 wt% diluted crude samples:

$$\text{Total Organic Chlorine (ppm)} = \left[2 \times \text{Measured Organic Chlorine (ppm)} \right] - \text{Solvent Chlorine Interferences (ppm)}$$

The water phase of the sample is measured to quantify the amount of inorganic chlorine in the crude sample. Pipette a water sample for analysis (**see Note 5**).

Particulate matter, if present in the sample, will often be in the water layer. Filter the sample if necessary (**see Note 4**). Cloudy water is normal and does not require filtration.

It is best to use a water based calibration curve to test low chlorine concentration water samples in order to compensate for oxygen absorption effects. High oxygen content, if not accounted for, will result in reduced counts and a falsely low chlorine value. If a dedicated water curve has not been developed, multiply the results obtained using a hydrocarbon calibration curve by 250% (i.e. 2.50).

To account for the dilution of the inorganic crude chlorine into the water phase of the sample, we will use the following equations to calculate inorganic chlorine. If running multiple extractions, combine the extraction water, mix well, and measure sample per directions above. Remember to use the total weight of water used for extraction. See **Note 3** regarding the weight of water used for this calculation. See **Note 6** regarding the use of crude weight vs. crude/solvent weight in the following inorganic chlorine calculations.

EQUATIONS TO CALCULATE INORGANIC CHLORINE

• For 50/50 wt% diluted crude or undiluted crude oil samples on water based curve:

$$\text{Total Inorganic Chlorine (ppm)} = \frac{\left[\text{measured inorganic chlorine (ppm)} - \text{DI water and filter interferences (ppm)} \right] \times \text{weight of water used (g)}}{\text{Weight of crude used (g)}}$$

• For 50/50 wt% diluted crude samples or undiluted crude oil samples on hydrocarbon based curve:

$$\text{Total Inorganic Chlorine (ppm)} = \frac{2.5 \times \left[\text{measured inorganic chlorine (ppm)} - \text{DI water and filter interferences (ppm)} \right] \times \text{weight of water used (g)}}{\text{Weight of crude used (g)}}$$

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

CONCLUSION

Corrosion mitigation strategies are an important part of ensuring safe refinery operation and maximizing profitability. Clora has become a critical part of identifying potential corrosion events and monitoring the effectiveness of these mitigation strategies. With over a decade of experience supporting refiner's needs to monitor chlorine, XOS can provide many different solutions for monitoring organic, total, and inorganic chlorine in crude oil.

17 35.45 **Clora 2XP** Chlorine Analyzer

Clora 2XP delivers twice the precision for total chlorine analysis in liquid hydrocarbons such as aromatics, distillates, heavy fuels and crude oils, as well as 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 sulphur 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.

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