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

- Boiling 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 water 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)
- Clora sample cups
- Etnom or Prolene XRF film – Use the correct sample film for your analysis; Etnom film for the Clora/Clora XR and Prolene film for the Clora 2XP
- Filter paper (use only if needed, see Note 2)

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.

Extraction Method One: Water Extraction Using a Centrifuge

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

Weigh 25 grams of crude into a centrifuge tube. Make sure to shake or homogenize crude oil sample before obtaining a specimen. Add 75 ml (see Note 3) 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.

Note 3: Assuming the density of water = 1 g/ml, then weight equals volume. Therefore, 75 ml water = 75 g.

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).

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. 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 4. 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. 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 4: Be sure to prepare the crude/solvent mixture by weight, not volume.

Extraction Method Two: Water Extraction Using a Separatory Funnel

Weigh 25 grams of crude into a separatory funnel. Make sure to shake or homogenize 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 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 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 2).

Organic, Inorganic, and Total Chlorine Analysis on the Clora

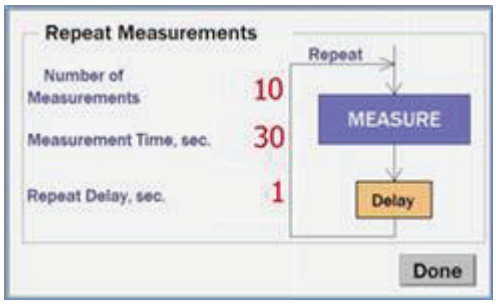
In general, pipette 5-8 ml of sample into a sample cup and test on the Clora using XRF film (Etnom for Clora, Prolene for Clora 2XP). Remember to punch a vent hole in the sample cup. The standard analysis time for samples containing >1 ppm chlorine is 300 sec. If the sample contains <1 ppm chlorine, a 600 sec measurement time is suggested for optimal results on the Clora. For samples containing <0.5 ppm chlorine measured on a Clora 2XP, measure two samples (new sample cup each time) for 300s 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% sulfur (≥0.1 wt% sulfur when measuring on a Clora 2XP), use of sulfur 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 1).

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 on the Clora/Clora 2XP analyzer 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 on the right, if the recommended measurement time is 300 seconds, run (10) 30 second repeats on one sample and examine the individual repeat measurements for upward trending.



If the total measurement time is 600 seconds, run (10) 60 second repeats. Keep the repeat delay at 1 second. Don't forget to use sulfur correction if necessary.

Settle time hh:mm:ss	Sample repeat	Crude A Cl (ppm)	Crude A cts/30s	Crude B Cl (ppm)	Crude B 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	76.87	2024
Average		2.84		52.81	

If the measurement results indicate trending (crude B in the table), 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), use the average measurement result and the following equations to calculate organic chlorine.

For undiluted crude samples:

Total organic chlorine (ppm) = measured organic chlorine (ppm)

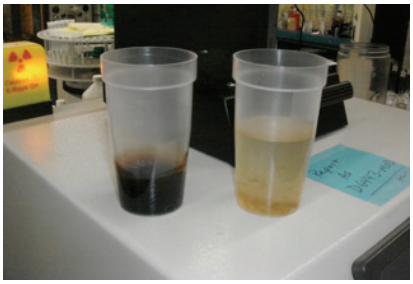
For 50/50 wt% diluted crude samples:

Total organic chlorine (ppm) = [2 * measured organic chlorine (ppm)] – solvent chlorine interferences (ppm)

An industry rule of thumb is that organic chlorine results less than two ppm indicate that the chlorine level is acceptably low enough to minimize corrosion issues. In the future, this level is expected to be lower as measurement capability improves.

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).

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.



Particulate matter, if present in the sample, will often be in the water layer. Filter the sample if necessary (see Note 2). 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 chloride 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, use the following equations to calculate inorganic chlorine. If running multiple extractions, combine the extraction water, mix well, and measure sample per directions above. Use the following equations to calculate inorganic chlorine. 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.

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

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

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

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

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.

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.

Appendix A: Crude Prep and Clora Analysis Example:

Procedure highlights:

- 12.5 g crude/12.5 g toluene mixture (by weight) added to separatory funnel
- Add 75 ml hot DI to extract in separatory funnel, shake, then allow to settle
- 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 (filter the same amount of water used in the inorganic chlorine calculation)
- 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/solvent 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 (ppm) = [2 * measured organic chlorine (ppm)] – solvent chlorine interferences (ppm)

Total organic chlorine = (2 * 1.23) – 0.38 = 2.08 ppm

Inorganic chlorine calculation:

For 50/50 wt% diluted crude samples on hydrocarbon based curve:

(Assuming density of water = 1 g/ml, then weight (g) = volume (ml). This also assumes that the solvent contains no inorganic chlorine This may be confirmed by extracting a solvent blank with water.)

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

Total inorganic chlorine = [2.5 * (1.98 – 1.77) * 75] / 12.5 = 3.15 ppm

Total chlorine = total organic chlorine + total inorganic chlorine:

Total chlorine = 2.08 + 3.15 = 5.23 ppm