

DETAILED HOW TO MEASURE CHLORIDES IN CRUDE OIL BY ASTM D4929C & WATER EXTRACTION

Organic chlorides do not occur naturally in crude oil; however, they can make their way into crude oil as a result of cleaning operations in pipelines and other refining equipment. Although very small concentrations of organic chloride can typically be handled by refineries with no deleterious effects to the equipment, once they reach a certain threshold, severe damage can ensue¹. The dangers of chloride-contaminated crude oil are well-known to those in the oil industry. Among these dangers is the creation of hydrochloric acid, which can lead to the corrosion and damage of pipelines and refining equipment.

IN RECENT NEWS

A relevant, massive-scale example of the urgency required when monitoring for organic chlorides is the recent instance of the Russian Druzhba Pipeline's crude oil contamination. The Druzhba Pipeline, which is one of the longest oil pipelines in the world, began operating in 1964. It begins in the Russian city of Almet'yevsk and spans the course of 3,400 miles including splits in various directions; meandering through and servicing several European countries including Poland, Germany, Belarus, Slovakia, Ukraine, and the Czech Republic. The Druzhba carries between 1.2 and 1.4 million barrels of oil to these countries on any given day; with the capacity to increase that transport to 2 million barrels should the need arise². Typically, Russian crude exports are considered extremely reliable; but in April of 2019, the oil flowing through the Druzhba was found to have organic chloride concentrations in the naphtha fraction that far exceeded the 10 ppm limits laid out in GOST R 51858, a Russian standard that encompasses organic chloride specifications. Concentrations from the crude that arrived in Belarus were reported to be between 150 and 300 ppm when measured between April 19th and April 22nd of 2019⁴. Given the wide array of countries depending on the Druzhba Pipeline for their oil, it was no surprise that in late April of 2019, the situation made international headlines.

SOLUTION

To avoid the pitfalls of corrosion and other chloride-related concerns, countries throughout the world have implemented standard methods and procedures to ensure that the organic chloride content in their crude is kept below a certain level. Such methods include ASTM D4929 (Russia's GOST R 52247; a modified translation of ASTM D4929-2004, and GOST 33342; a modified translation of ASTM D4929-2007), as well as procedures like water extraction, each to be discussed in further detail throughout this paper.

Since its launch in 2007, Clora[®] Benchtop Analyzer has been widely adopted by refineries and test labs to analyze chlorine. With over 200 systems in the field, XOS customers know they can trust Clora for testing products from crude oil to naphtha cuts and VGO. In this paper, we will discuss two popular Clora benchtop procedures utilized by petroleum laboratories around the world to measure total chlorine:

1. Organic Chlorides by ASTM D4929C
2. Organic and Inorganic Chlorides Using Water Extraction

1 ORGANIC CHLORIDES BY ASTM D4929 – FIRST THERE WAS A & B

ASTM D4929 Standard Test Method for Determination of Organic Chloride Content in Crude Oil was first published with two procedures:

“1.3 Procedure A covers the determination of organic chloride in the washed naphtha fraction of crude oil by sodium biphenyl reduction followed by potentiometric titration.

1.4 Procedure B covers the determination of organic chloride in the washed naphtha fraction of crude oil by oxidative combustion followed by microcoulometric titration.”¹

Both Procedures A and B of the original ASTM D4929 method require users to first distill a crude oil sample to 204°C (400°F), then wash the resulting naphtha fraction with caustic to remove H₂S, and finally, wash with water to remove inorganic chlorides. Afterwards, either Procedure A or B is used to determine chloride content using back calculation.

THE NEED FOR A FASTER & EASIER ALTERNATIVE – AND THEN THERE WAS C

While the distillation of the sample during preparation wasn't something that could be eliminated, the chloride analysis portion of both Procedures A and B were difficult and time-intensive processes. This left room for a simplified process to be created. On October 15th, 2017, ASTM approved the addition of Procedure C to D4929:

“1.5 Procedure C covers the determination of organic chloride in the washed naphtha fraction of crude oil by X-ray fluorescence spectrometry.”

This is an important step forward, as users will be able to officially use XOS' Clora, Clora 2XP, and Sindie +Cl analyzers for organic chloride analysis in crude oil without ASTM method modification.

In order to include Procedure C with Method D4929, an interlaboratory study (ILS) involving eight participants was performed. Each of the participants distilled ten crude oil blends of varying nominal organic chloride concentrations in blind duplicate using the D4929 procedure which is based on the ASTM D86 method for distillation of petroleum products. The D4929 procedure differs in that the 500 ml crude sample was weighed prior to distillation so that the naphtha mass fraction could be calculated. Using a distillation rate of approximately 5 ml/min, the crude oil sample was distilled until 204°C (400°F), and then the resulting naphtha fraction was weighed. The naphtha mass fraction was calculated by dividing the mass of the naphtha fraction by the mass of the crude oil sample prior to distillation.

Resulting naphtha cuts were triple washed with caustic and water per the method before analysis using XOS' Clora Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) analyzer, among other instruments with varying types of XRF techniques. Because organic chlorides concentrate in the naphtha fraction, in order to obtain the organic chloride in the original crude sample, the measured naphtha chlorine concentration was multiplied by the naphtha mass fraction to obtain the final D4929 result. (Note: this last back-calculation step would not be performed if the desired result is chlorine in the naphtha cut, as in some pipeline specifications.)

The ILS resulted in separate precision statements for differing XRF techniques. In the following figures, the ILS precision is compared with the original method precision statements for Procedures A and B (Figures 1 and 2). The ILS found the following:

- Clora (MWDXRF) has better reproducibility than the other Procedure C XRF techniques and exhibits equivalent or better reproducibility than Procedure B (Figure 1)
- Clora (MWDXRF) consistently exhibited better repeatability than Procedure B (Figure 2)

Figure 1:

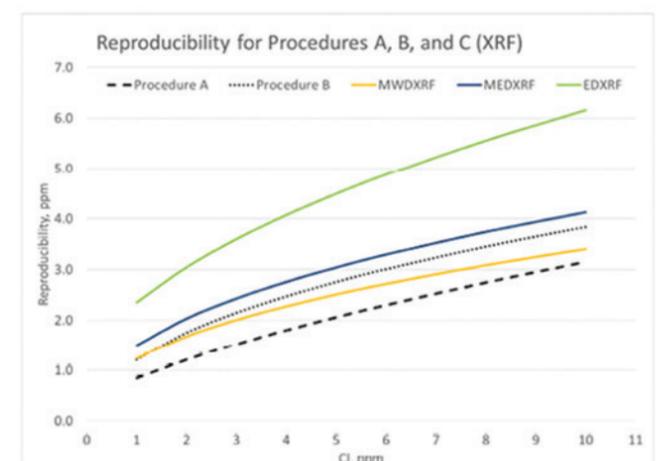
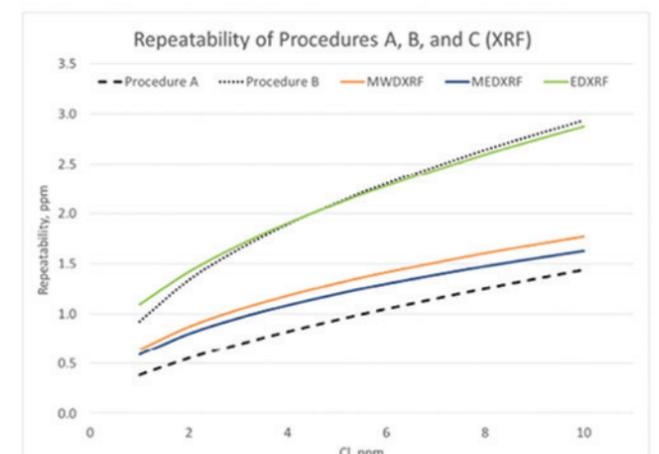


Figure 2:



CONCLUSION

XOS' Clora, Clora 2XP, and Sindie +CI benchtop analyzers comply with ASTM D4929C and are viable solutions for the determination of organic chloride content in crude oil. In addition, ASTM D4929C by XRF has been on the rise and gaining popularity since its approval in 2017, as indicated by information collected from labs by the Crude Oil Proficiency Testing Program (PTP) (**Diagram 1**).

2 ORGANIC AND INORGANIC CHLORIDES USING WATER EXTRACTION

Although all XRF techniques are capable of only total elemental analysis, with some sample preparation, Clora, Clora 2XP, and Sindie +CI 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 technique, unfortunately, this technique has crude-dependent limitations. Not all crude oils are easily extracted, and this sample preparation technique may have variable within-lab repeatability and poor betweenlab reproducibility. **Procedures 1-3** will assist the user in separating chlorine in crude oil into its organic and inorganic counterparts using a water extraction.

Procedure Notes:

- **Note 1:** Be sure to prepare the crude/solvent mixture by weight, not volume.
- **Note 2:** Deionized (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 1: Crude Oil Sample Preparation

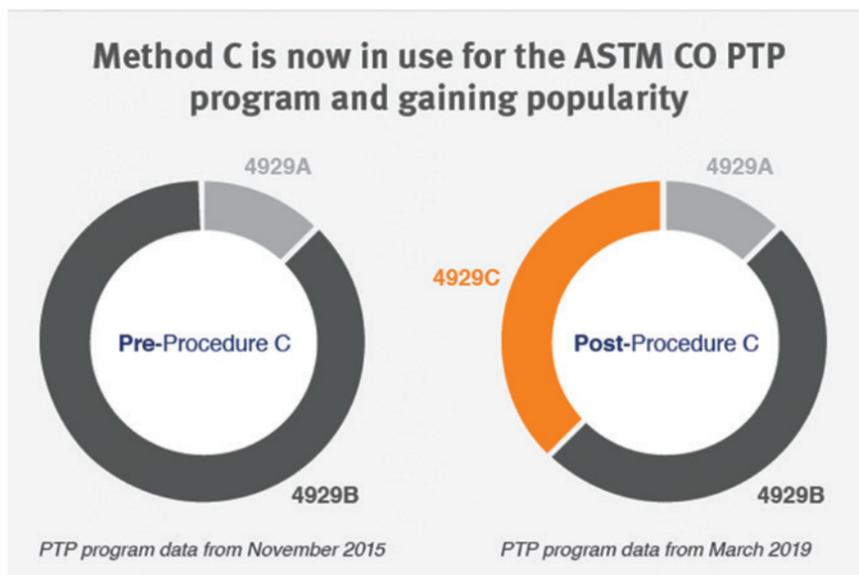
Depending on crude type and composition, it may be hard to obtain a stable homogenous sample. Viscous or asphaltene and bitumen containing crudes are particularly difficult to extract. The addition of toluene or xylene to these types of crudes will increase the solubility of heavier crude components 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 2: Water Extraction Using a Separatory Funnel

Weigh 25 grams of the crude/solvent mixture into a separatory funnel. Add 75 ml (**see Note 3**) of boiling DI water.

Diagram 1



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/solvent mixture 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**).

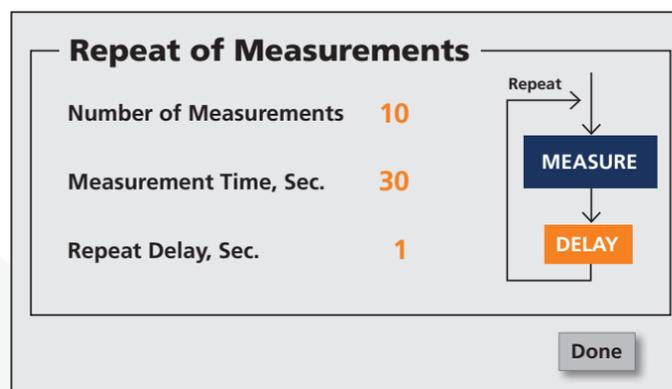
PROCEDURE 3: Organic, Inorganic, and Total Chlorine Analysis with Clora

In general, pipette 5-8 ml of sample into a sample cup and test with Clora using XRF film (Etnom for Clora and Sindie +CI, 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 +CI. 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% sulfur (>0.1 wt% sulfur when measuring with 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 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 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 sulfur correction if necessary. If the measurement results indicate trending (Crude B in **Table 1**), return the crude or crude/solvent sample to the separatory funnel and extract again using a new aliquot of hot DI water. If the measurement results indicate a successful extraction (Crude A in **Table 1**), use the average measurement result and the following equations to calculate organic chlorine:



Settle Time	Sample	Crude A		Crude B		
		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	

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:

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

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

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

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:

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

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.

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

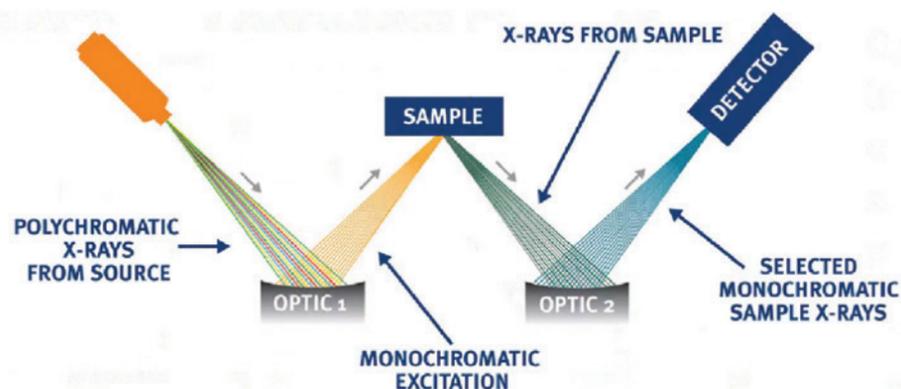
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ADVANCED ANALYSIS WITH MWDXRF

Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) utilizes state-of-the-art excitation 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 fluorescence 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 low maintenance analyzers with dramatically lower detection limits and faster response times.



Clora 2XP complies with ASTM D4929C and D7536 and is a viable solution for the determination of organic chloride content in crude oil.

Because Clora 2XP delivers a significantly lower limit of detection, it delivers better precision below 1ppm for total chlorine analysis in liquid hydrocarbons such as aromatics, distillates, heavy fuels, and crude oils, as well as aqueous solutions. 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.

REFERENCES:

- 1 ASTM D4929, Standard Test Method for Determination of Organic Chloride Content in Crude Oil (<https://www.astm.org/Standards/D4929.htm>)
- 2 Koch, Gerhardus H., et. Al. "Corrosion Costs and Preventive Strategies in the United States." NACE International