

Discover How to Manage Chloride in the Refinery Crude Unit





better analysis counts

Crude Oil Contaminants: Chlorine and the Desalting Process

Crude oil contains many contaminants which present challenges to refiners. Some contaminants occur naturally in the crude oil and others are accumulated in the upstream process. The primary means to remove these contaminants is the desalting process.

In the desalting process, water is mixed with the crude, passing through a mix valve prior to entering the Desalter. The mix valve creates vigorous contact between the water and crude resulting in an environment for contaminants to enter the water phase. Once in the Desalter, a current is applied to help accelerate the separation of the oil and water phase. An emulsion breaker may be used to aid in separation. The water with any solids that might have been in the crude is sent to the wastewater treatment plant for treatment.

Whatever contaminants are not removed by the Desalter must be treated chemically. Of particular importance is chlorine that remains in the desalted crude. Chlorine can exist as either Inorganic Chlorine (Calcium Chloride, Sodium Chloride, and Magnesium Chloride) or Organic Chlorine. Typically the Inorganic Chlorine will be removed in the desalter, but Organic Chlorine will stay with the crude oil.

Chlorine can cause corrosion in the Crude Unit by forming hydrochloric acid. Chlorine can react with amine-based treatments to form ammonium chloride, which can deposit in overhead systems. Heat transfer can be impacted and under-deposit corrosion can result. Treating chlorine in crude units is a balancing act. Too much chemical will increase fouling potential and put downstream equipment at risk. Too little chemical presents a risk of corrosion and fouling in the crude unit. Accurate measurement of Chlorine is vital in protecting your assets.

The XOS Clora On-line analyzer accurately measures total Chlorine in raw crude oil, desalted crude, or both. Real time results give the feedback that is critical in keeping systems running properly. Desalter performance can be monitored to make sure it is working optimally. A properly performing desalter will keep the Crude Unit and downstream units operating well and protect the waste water treatment plant from overload. Desalter upsets can easily be detected and impacts of crude slate changes can be identified.

The XOS Clora On-line analyzer can also measure total Chlorine in water streams giving flexibility based on your needs. Measuring Chlorine in the overhead waters or desalter wash waters can be easily completed, even if they are sour. These measurements can be used to automate chemical feed, protecting systems around the clock.

The desalting process is critical to the refinery. The XOS Clora On-Line analyzer helps ensure quality and avoid issues through the highly accurate measurement of Chlorine in raw crude oil.



*better analysis
counts*

ACCU-FLOW Technology Delivers Efficient, Accurate Liquid Sample Measurement

XOS, a long-time provider of breakthrough elemental analysis solutions for the petroleum industry is proud to introduce readers to ACCU-FLOW technology. Combined with X-Ray Fluorescence (XRF), ACCU-FLOW technology allows for the measurement of continuously flowing samples—a true innovation in benchtop analysis.

ACCU-FLOW technology delivers the direct measurement of liquid samples as they exist in the process as opposed to a static measurement. In a static measurement particulates may settle over time leading to results that reflect inaccurate concentration levels. Significant potential settling effects can occur in just a five to ten minute time span during the static measurement.

By applying ACCU-FLOW technology to an XOS benchtop, we can eliminate the settling of particulates in the sample, resulting in an increased level of accuracy, surpassing traditional benchtop analysis. ACCU-FLOW technology eliminates particulate settling, providing a truly accurate measurement of element concentrations and giving you direct measurement of crude streams as they exist in the refinery.

ACCU-FLOW technology provides unprecedented precision and levels of detection. Beyond precision, XOS analyzers with ACCU-FLOW can operate in tough environments from mobile vans to refinery plants and pipeline terminals.

ACCU-FLOW technology eliminates particulate settling effects with a simple design, optimized for everyday use. It is available on the following XOS analyzers:

- Chlorine benchtop: Clora
- Phosphorus benchtop: Phoebe
- Multi-Element benchtop: Maxine



better analysis counts

Measurement of Aqueous Samples on a Clora Hydrocarbon Calibration Curve

Matrix effects, or differences between the elemental composition of test samples and the calibration standards, can often result in biased chlorine measurements. These effects can be compensated for with the utilization of one of two methods. First, the selection of calibrants that match—as closely as possible—the test sample matrix. This is especially true for materials containing oxygen, for instance E85 (85% ethanol in gasoline). The closer the calibration matrix reflects the actual test samples, the better the results will be. Secondly, one can employ the use of a matrix correction factor. Commonly used in the refining industry, users will typically apply a matrix correction factor for measurement of aqueous samples on a hydrocarbon based calibration curve.

In this procedure, the analyst will pipette 5-8 ml of sample into a sample cup and test in the XOS Clora using Etnom XRF film. The standard analysis time for samples containing >1 ppm chlorine is 300 seconds. 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 is recommended help improve results. If a water-based calibration curve is used when measuring aqueous samples, a matrix correction factor is not needed. When the aqueous sample is measured on a hydrocarbon curve, high oxygen content, when 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% (or 2.50).

In Summary:

Total chlorine of aqueous samples measured on water based calibration curve:

Total chlorine (ppm) = measured chlorine

Total chlorine of aqueous samples measured on hydrocarbon based curve:

Total chlorine (ppm) = 2.5 * measured chlorine



better analysis counts

On-line Chlorine Analyzer for Crude Oil and Petroleum Process Streams

Zewu Chen and Stu Shakshober

XOS

- Background
- Method
 - Monochromatic Wavelength-dispersive XRF
 - Dynamical window module
- Testing Data and field installation
- Conclusion

- High margin for refinery
- More and more OC is used in refinery
- Downside for OC refining
 - Unknown impurities
 - Potential fouling and corrosion effects
 - More on-line process control

Causes of corrosion :

- Inorganic chlorides
- Organic chlorides
- Sulfur compounds
- Organic acids

\$1.3 billion dollars lost a year.

Originally appeared in:
September 2010, pgs 75-79.
Used with permission.

**HYDROCARBON
PROCESSING®**

REFINING DEVELOPMENTS

SPECIAL REPORT

Mitigate corrosion in your crude unit

**Real-time analyzers can provide improved monitoring
of chloride levels and enable better corrosion control practices**

N. P. HILTON, Nalco Energy Services, Sugar Land, Texas; and **G. L. SCATTERGOOD**,
Nalco Energy Services, Beijing, People's Republic of China

In the refining industry, 90% of crude-unit overhead corrosion occurs during just 10% of operating time. These periods of unstable operation may occur during crude tank switches,

Monitoring frequency. Refiners and chemical suppliers use a variety of wet chemistry tests in conjunction with corrosion monitoring tools to track the corrosive environment in crude

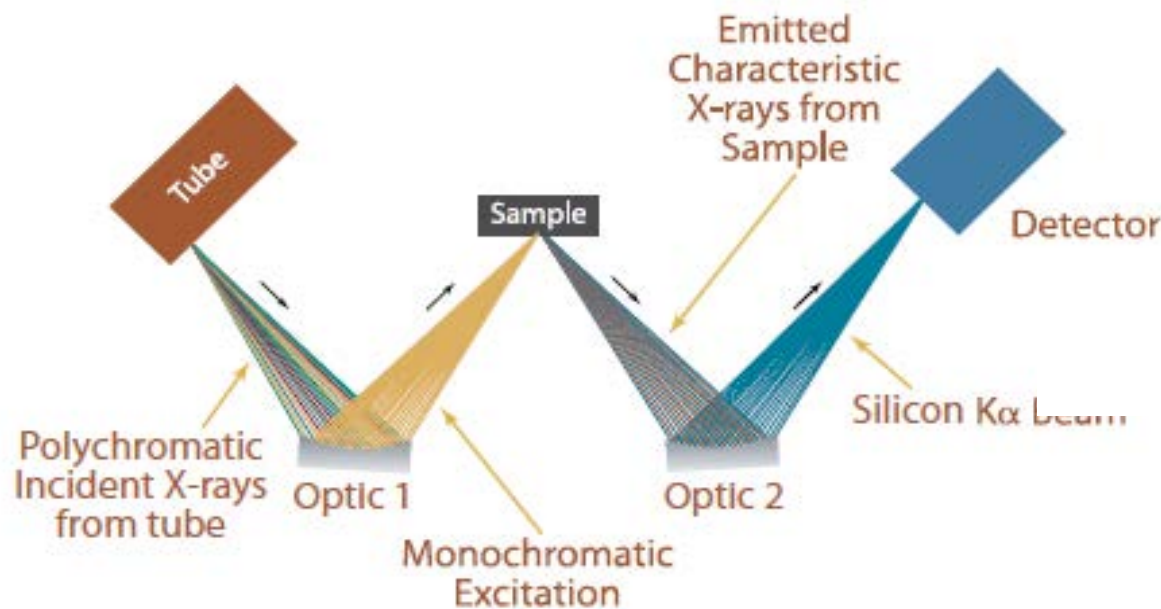
- Chlorides in process stream form HCl
- HCl attacks overhead in distillation tower
- Organic chlorides or non-extractable chlorides are the most problematic
- Chlorine level in process streams < 1ppm

- On-line instrument base on ASTM 3230 – Eletrometric method
- Other wet Chemistry method – Titration
 - Extensive use of reagent chemicals
 - Not able to detect low level chlorides for corrosion control

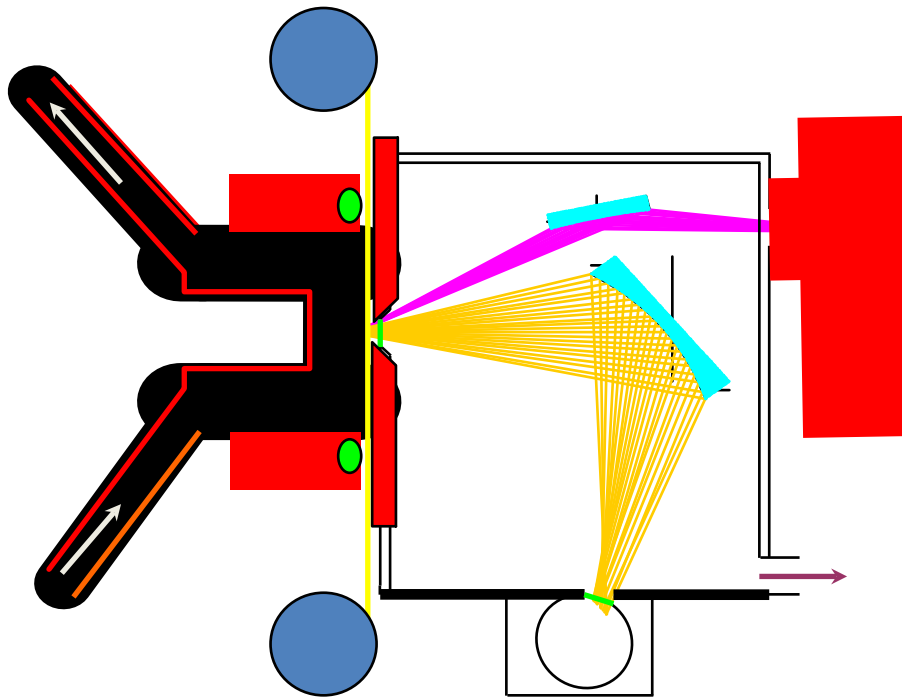


Call for Chlorine Process Analyzer

- Robust and reliable
- No reagent and low maintenance
- Detection limit <0.3 ppm



MWD XRF

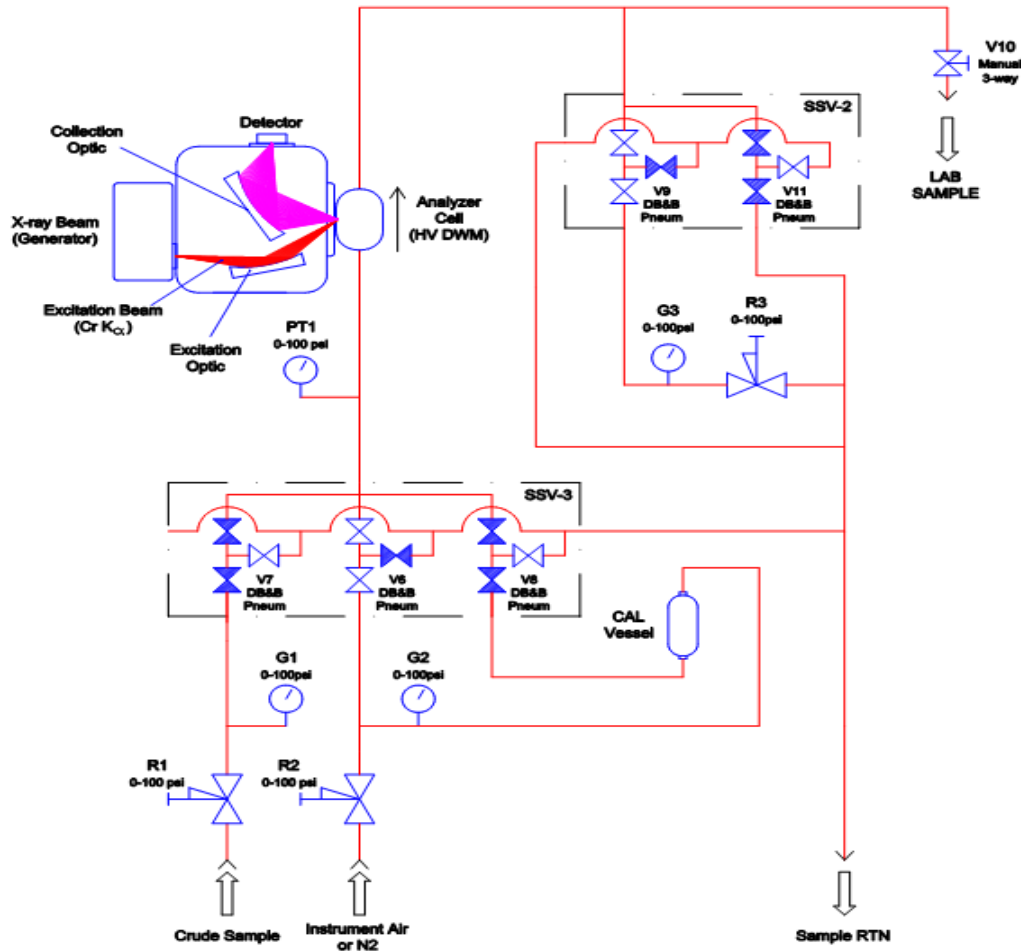


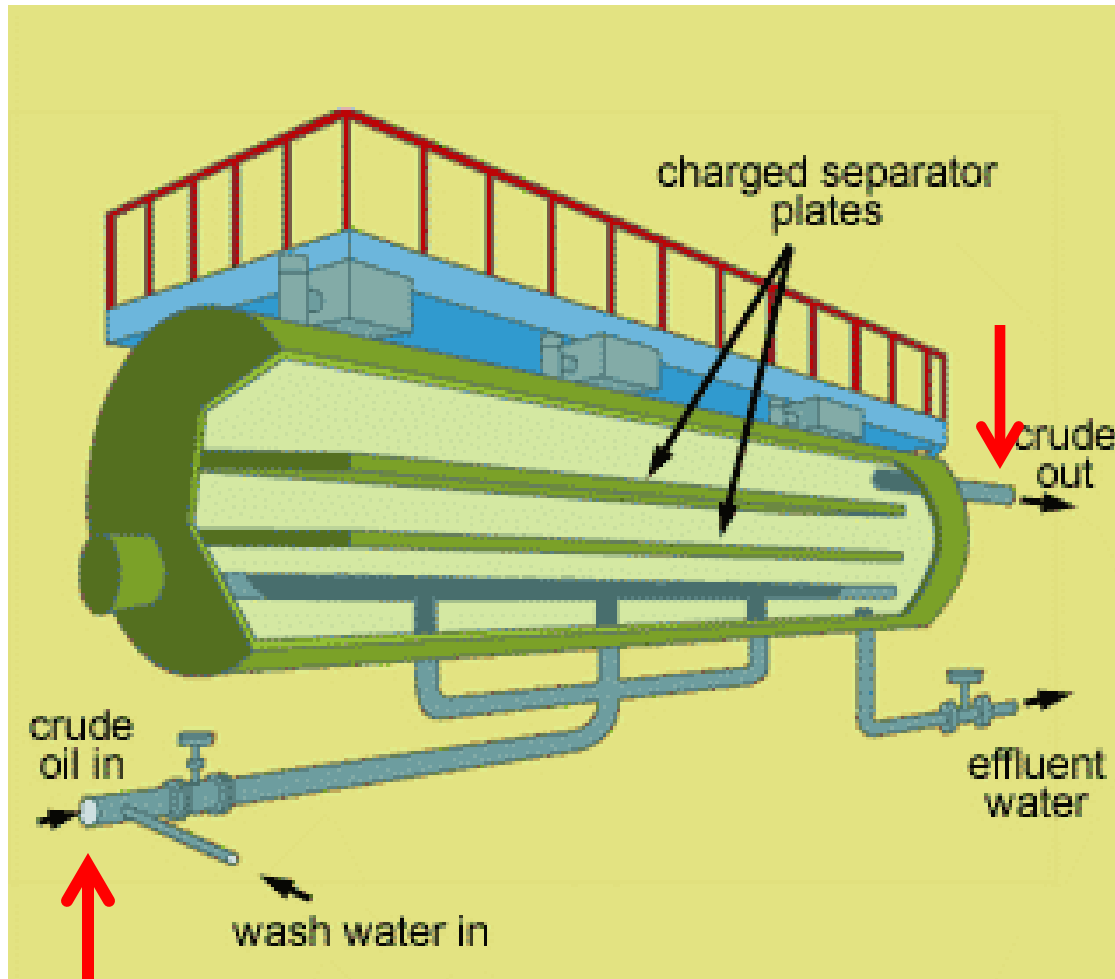
- Monochromatic excitation
- High S/N ratio, >10X better
- Low power, 20-40 x reduction
- Optical efficiency, >10 x
- Limit of detection, 2 x better

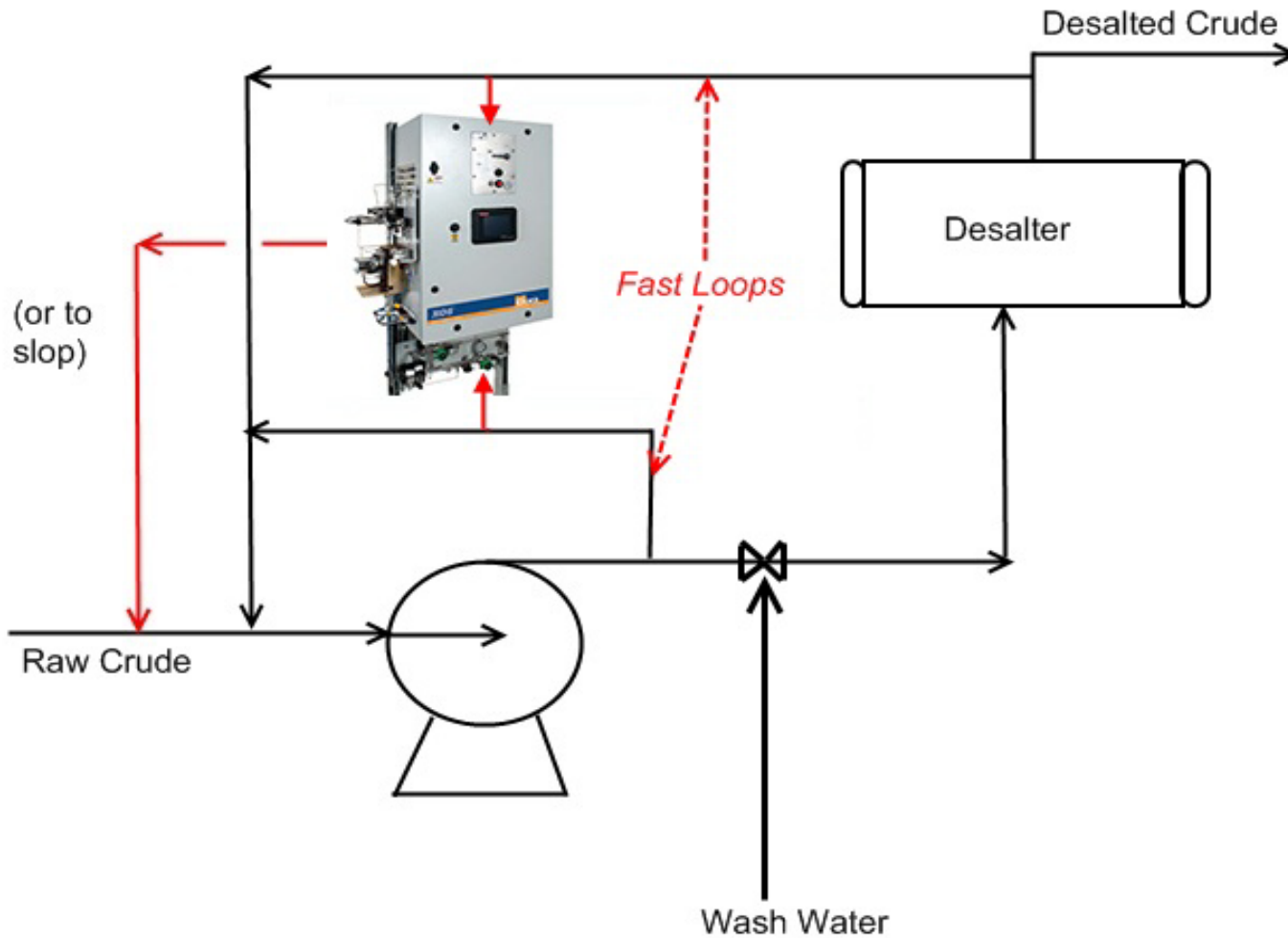
- No reagent
- Low maintenance
- Lower LOD for corrosion control

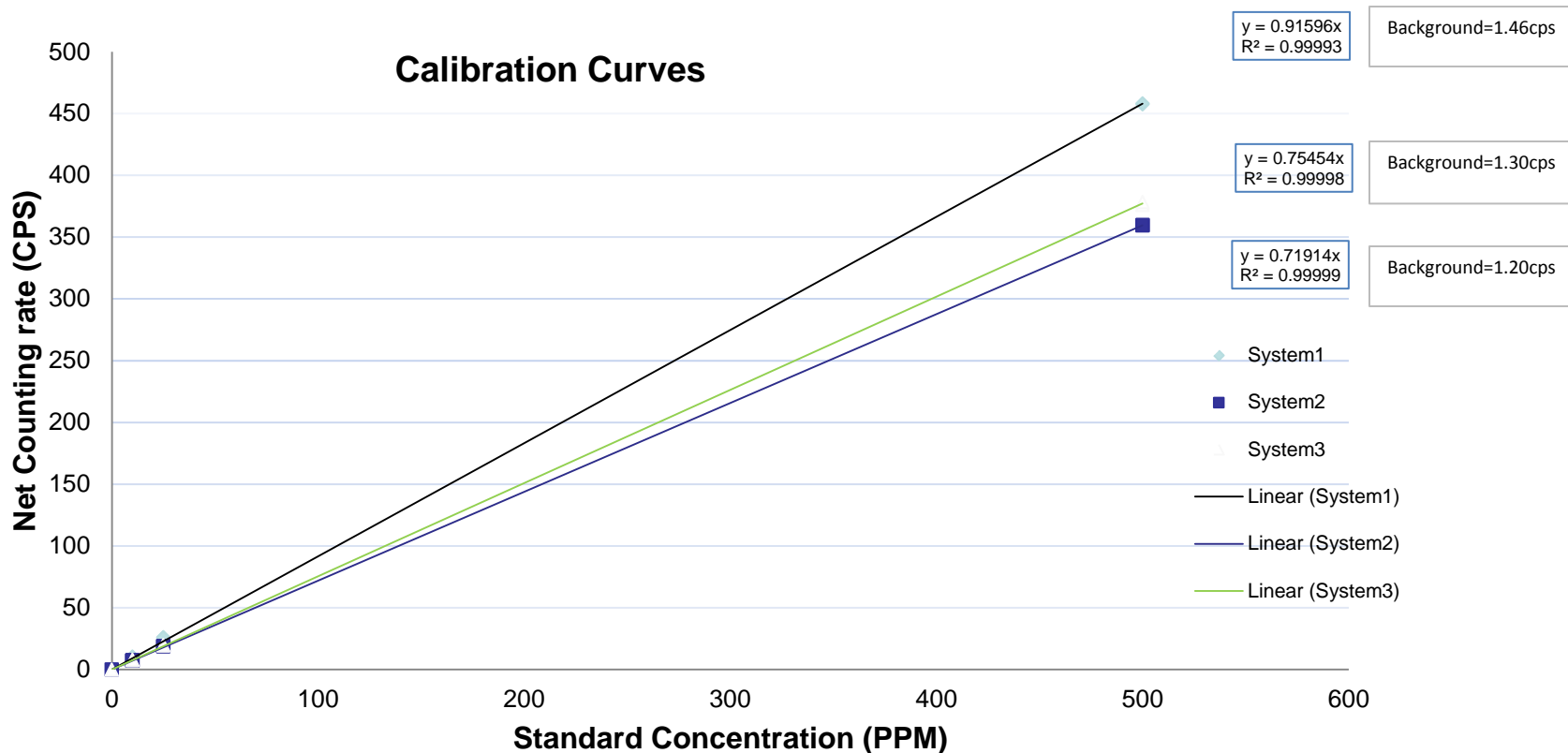
- Total Chlorine
 - LOD: 0.2 ppm @ 600s – hydrocarbon matrix
 - LOD: 0.4 ppm @ 600s – aqueous matrix
- Analysis Time: 10 - 900s – user adjustable
- Range: 0.2 ppm/wt – 3,000 ppm/wt
- Continuous Measurement





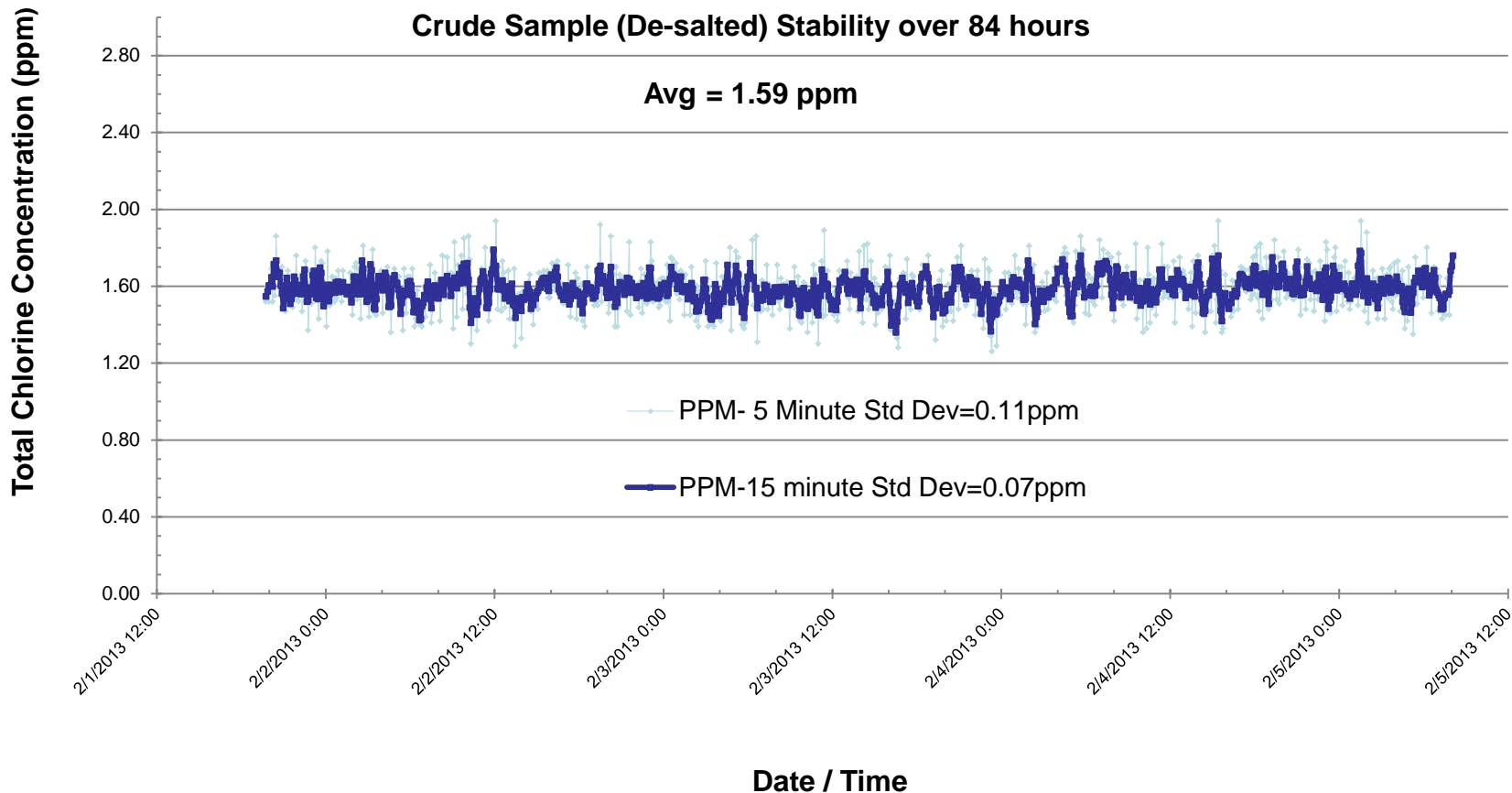






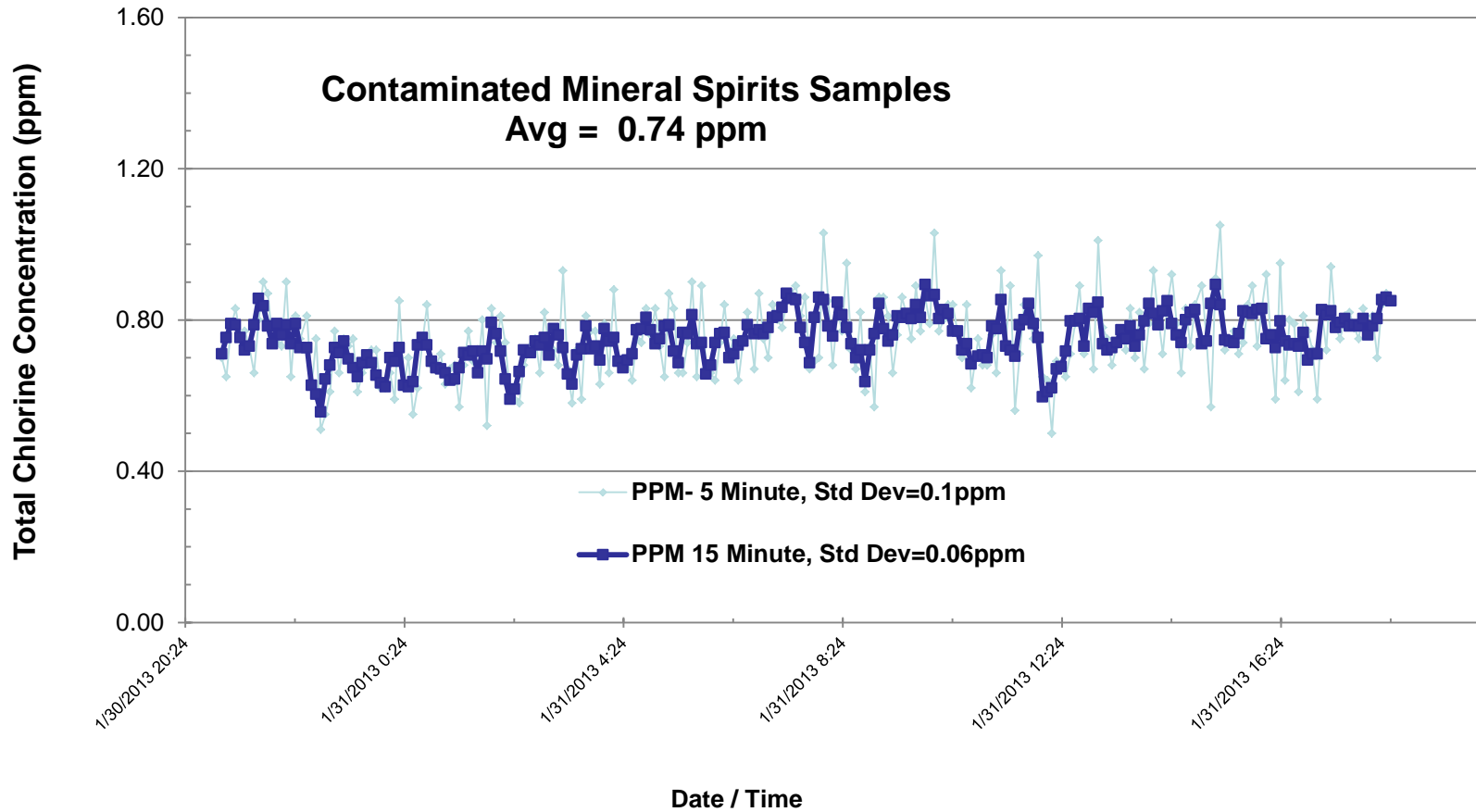


Desalted Crude -- Stability Testing

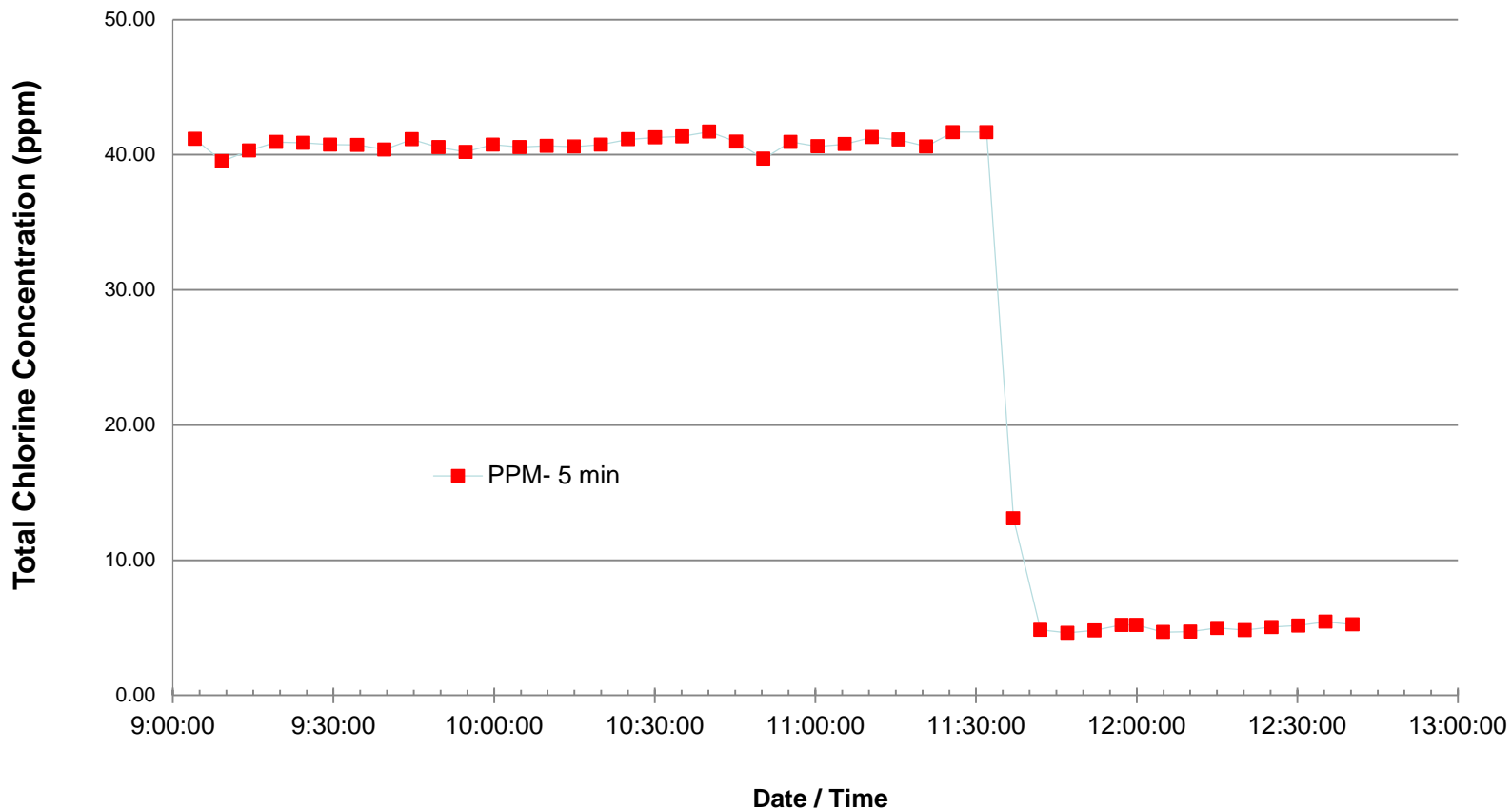




Sample Cl Level Close to Detection Limit



**Analysis of total Cl during a transition from raw crude to de-salted crude
(Western Canadian blend)**





Stability and Detection Limit

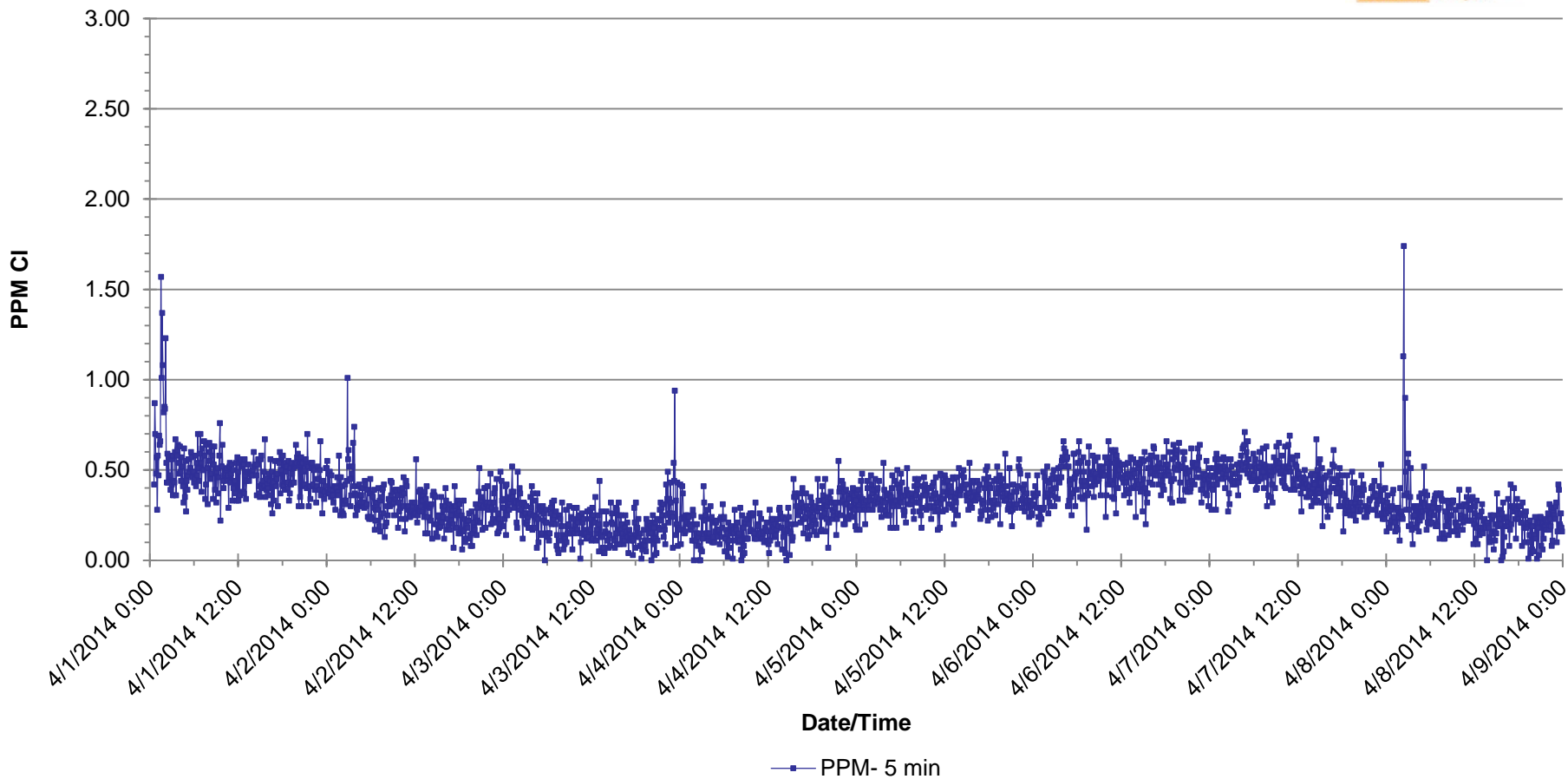
	RAW CRUDE	DESALTED CRUDE		MINERAL SPIRITS	
Integration time	5 min	5 min	15 min	5 min	15 min
Overall run time	82 hrs	84hrs	84 hrs	21 hrs	21 hrs
Average (ppm)	34.4	1.59	1.59	0.74	0.74
Standard Dev (ppm)	0.57	0.11	0.07	0.10	0.06
RSD (%)	1.7	6.9	4.4	13.5	8.1
LOD (ppm)	NA	NA	NA	0.30	0.18
LOQ (ppm)	NA	NA	NA	1.0	0.6



Compared to Lab Results

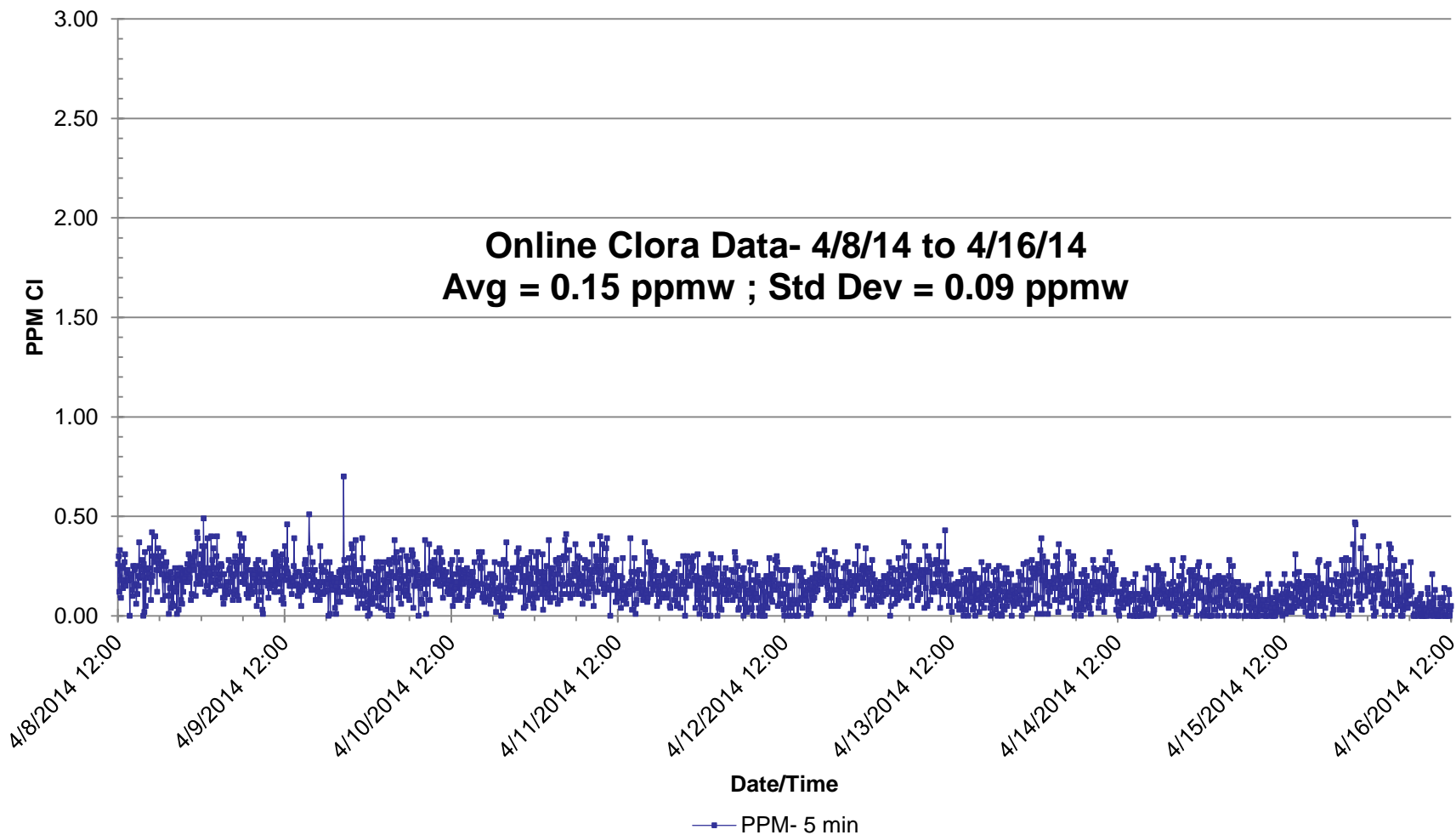
	WESTERN CANADIAN RAW CRUDE	WESTERN CANADIAN DESALTED CRUDE
D3230 Salt content (lb/1000bbl)	25	2.8
D3230 Converted to Cl (ppm)	49	5.5
Clora Lab bench average (ppm)	44.5 (Avg of 43.5, 45.2, 44.8)	5.1 (Avg of 5.1,5.2,4.9)
Online average (ppm)	40.8	4.98

Online Clora Data- 4/1/14 to 4/9/14





Refinery installation data – low level



- Corrosion is a major issue for refineries and mitigation is critical
- The XOS Clora OL allows for robust and reliable chloride detection down to $<0.3\text{ppm}$ with no reagents and low maintenance