

# Sub-ppm Chloride Monitoring of Hydrocarbons

## Background

Corrosion at petroleum refineries is a critical problem all over the world. In the United States alone, NACE International, a professional association dedicated to reducing the economic impact of corrosion, has shown that \$3.7 billion in direct costs are realized annually from maintenance, vessel expenditures, and fouling as a result of corrosion.<sup>1</sup> This huge figure does not take into account the estimated loss of as much as \$12 billion in profit due to decreased capacity, unit outages, and premature turnarounds that result from corrosion.<sup>2</sup>



Figure 1: Corrosion costs refiners billions of dollars per year.

Since its launch in 2007, the Clora<sup>®</sup> Benchtop Analyzer has been widely adopted by refineries and test labs for monitoring chlorine in petroleum. With over 200 systems in the field, XOS customers know they can trust the Clora for testing products from crude oil to naphtha cuts and VGO. Implementing corrosion mitigation strategies is an important part of ensuring safe refinery operation and maximizing profitability. The Clora has become a critical part of identifying potential corrosion events and monitoring the effectiveness of these mitigation strategies.

As they continue to battle the huge costs of corrosion, leading refiners have found that continuing to lower the chloride content of feedstocks and process streams has significantly extended turnaround times and lowered the costs of corrosion. XOS has responded to the industry's need by introducing the Clora 2XP analyzer. Applying the most recent technical advances in XOS doubly curved crystal (DCC) X-ray optics, the Clora 2XP provides enhanced detection down to 0.07 ppm in hydrocarbon-based samples. This allows the ability to quantify at roughly 0.25 ppm for total chlorine. The increased capability enables the user to better understand and manage the most demanding samples like desalted crude and vacuum gas oil.

## Background

In the US alone, refiners are experiencing \$16 billion in expenses and lost profits due to corrosion. A major cause of corrosion is chlorides in crude feedstocks and process streams. Global refiners are investing in corrosion mitigation strategies that require sub-ppm monitoring of chlorides.

## Experiment

The Clora 2XP analyzer performed repeat measurements of various hydrocarbon samples with low level chloride concentrations.

#### Conclusion

The Clora 2XP is able to quantify subppm concentrations of chlorides in hydrocarbon samples enabling refiners to monitor the effectiveness of their corrosion mitigation strategies and reduce the multi-billion dollar annual costs of corrosion.

## Experiment

Various hydrocarbon samples were prepared and analyzed following a modified ASTM D7536 procedure. The sample types analyzed were:

- Gasoline sample taken from the pump at a local station
- VGO sample from a North American refiner
- A naphtha sample
- A 0.3 ppm chlorine in mineral oil check sample used for typical validation testing

The samples were pipetted into typical XRF sample cups and analyzed for 600 seconds. The standard deviation and average was then calculated based on the results of the sample runs, shown below in Table 1.

Table 1: Clora 2XP Total Chlorine Analysis Results							
Gasoline		VGO		Naphtha		Mineral Oil	
Repeats	Results	Repeats	Results	Repeats	Results	Repeats	Results
#1	0.29	#1	1.41	#1	0.58	#1	0.30
#2	0.31	#2	1.42	#2	0.54	#2	0.33
#3	0.30	#3	1.44	#3	0.40	#3	0.31
#4	0.33	#4	1.36	#4	0.52	#4	0.31
#5	0.36	#5	1.43	#5	0.49	#5	0.30
#6	0.40	#6	1.35	#6	0.55	#6	0.27
#7	0.36	#7	1.44	#7	0.48	#7	0.23
#8	0.32	#8	1.47	#8	0.47	#8	0.34
#9	0.32	#9	1.39	#9	0.50	#9	0.32
#10	0.31	#10	1.46	#10	0.51	#10	0.34
Mean	0.327	Mean	1.417	Mean	0.51	Mean	0.305
Standard Deviation	0.032	Standard Deviation	0.040	Standard Deviation	0.05	Standard Deviation	0.035
All values in parts per million (ppm).							

## Conclusion

The results of this experiment demonstrate the capability of the Clora 2XP to precisely and repeatably monitor sub-ppm chloride concentrations in various hydrocarbon samples. This simple measurement requires just a few minutes to complete and requires no consumable gasses or chemicals. Effectively monitoring chloride concentration in crude feedstocks and process streams is a critical part of any corrosion mitigation strategy. With the capability to quantify chlorides at sub-ppm levels in hydrocarbon samples, refiners will be able to reduce the multi-billion dollar costs of corrosion.

#### **References**

- 1. Koch, Gerhardus H., et. Al. "Corrosion Costs and Preventive Strategies in the United States." NACE International.
- 2. "Petroleum Refinery Gap Analysis." NACE Technical Coordination Committee, 18 Oct. 2008.

For additional information or a demonstration of the Clora 2XP, please contact us at info@xos.com.