

Sub-ppm Chloride Monitoring in Hydrocarbons

BACKGROUND

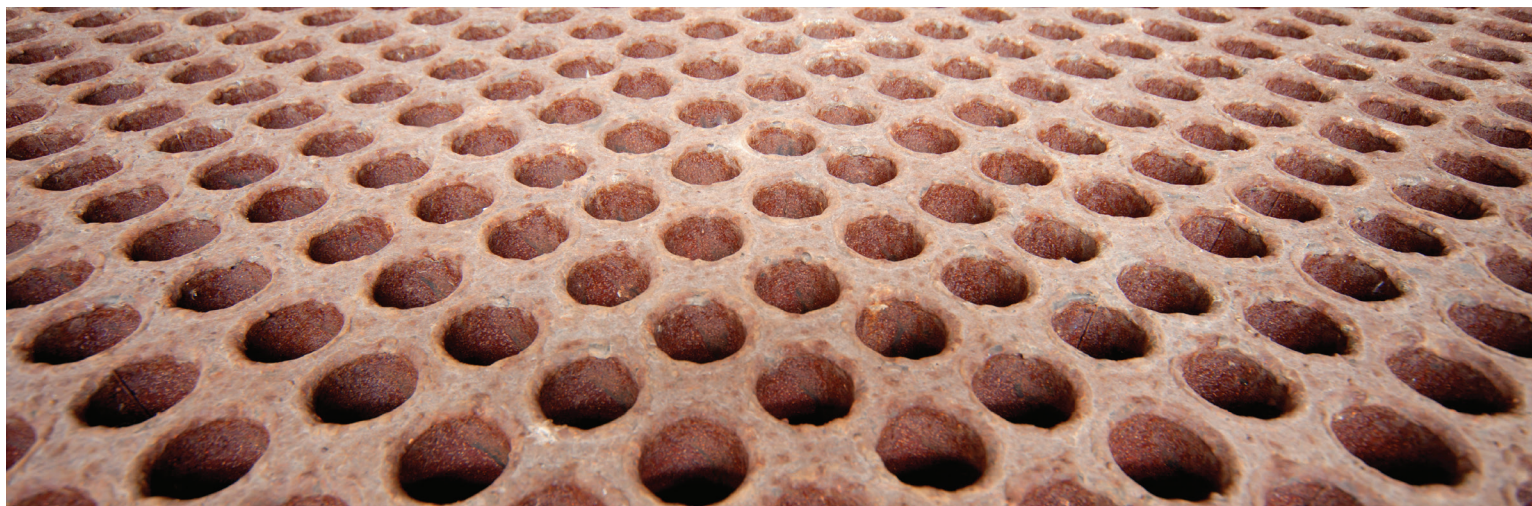
Corrosion at petroleum refineries is a critical problem all over the world. In the United States alone, NACE International, a professional association dedicated to reducing the economic impact of corrosion, has shown that \$3.7 billion in direct costs are realized annually from maintenance, vessel expenditures, and fouling as a result of corrosion.¹ 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.²

Since its launch in 2007, Clora[®] has been widely adopted by refineries and test labs for monitoring chlorine in petroleum. With over 200 units in the field, customers trust Clora for testing products from crude oil to naphtha cuts and vacuum gas oil (VGO). Implementing corrosion mitigation strategies is 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.

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 Clora 2XP analyzer, delivering enhanced detection down to 0.07 ppm in hydrocarbon-based samples. This enables analysis 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.

Clora 2XP delivers twice the precision as Clora, and complies with ASTM D7536 and D4929 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 applications. Powered by MWDXRF, Clora 2XP does not require gasses or high temperature processes, equating to easy operation and minimum maintenance requirements.



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 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 gases 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.