



better analysis counts



Summary of Product Evaluation by Shell

Intro

The Clora 2XP from XOS was evaluated for a 4-month period by the Shell Pernis refinery lab for the analysis of organic chlorides and total chlorides in hydrocarbons, ranging from crude to short residue.

In general, the system was found to be very operator friendly. And with the introduction of double open ended sample cups analysis of residual fuels was also possible. The LOD was found to be in good agreement with the manufacturer specification of 0.07 mg/kg. The sulphur correction works well for low concentrations though for samples with 3% (m/m) sulphur an error up to 10-15% was found. But it should be noted that the amount of data is limited. Repeatability and reproducibility were found to be on par with oxidative microcoulometry. Analysis of organic chlorides in crude according to ASTM D4929* yielded comparable results to micro coulometry. However, a direct comparison with analysis of organic chlorides in the crude itself cannot be made. This was found to be inherent to the composition of crude itself.

** ASTM D4929 compliance is pending. XOS is leading the effort to get a Procedure C for XRF included in the D4929 methodology.*



The LOD was determined with several approaches. It was calculated as 3 times the standard deviation (SD) of 8 analyses of paraffin oil. The LOD was also calculated from the slope of the calibration curve and the standard deviation, following the ICH Q2(R1) guideline. And the LOD was calculated from the standard deviation at several concentrations [1]. Analyses were spread over several weeks and the secondary window replaced daily. All analyses were done at 300 and at 600 seconds.

	300 seconds	600 seconds
LOD as 3* SD blank (mg/kg)	0.0720	0.0485
LOD from the calibration curve (mg/kg)	0.1327	0.0868
LOD from regression of SD (mg/kg)	0.1070	0.1844

The correction for the sulphur interference was tested by adding potassium polysulfide in varying concentrations to organic chloride standards in paraffin oil. The polysulfide itself was analyzed with combustion IC for presence of organic chloride. The polysulfide was found to contain 1.0 mg/kg of chloride and this was corrected for in the final chloride concentration on the samples.

% Sulphur (m/m)	Total Chloride (mg/kg)	Measured Chloride (mg/kg)
0.00	0.51	0.50
0.36	0.38	0.35
2.41	0.48	0.43
0.00	2.27	2.28
0.48	2.55	2.44
2.71	2.79	3.19

An estimate of reproducibility and repeatability was made by 8 repeated analyses of an organic chloride in paraffin oil. At a concentration of 1 mg/kg and with an analysis time of 600 seconds the repeatability was found to be 0.1 and the reproducibility 0.26.

	average result (mg/kg)
Distilled fraction (Clora 2XP)	0.15
Distilled fraction (coulometer)	0.21
Distilled fraction + spike (Clora)	0.94
Distilled fraction + spike (coulometer)	0.93

A direct comparison with oxidative micro coulometry was made for analysis of organic chlorides in crude according to ASTM D4929. The normal procedure for distillation and washing of the naphta were followed. Part of the naphta was spiked with 0.795 mg/kg organic chloride. All samples were analyzed in triplo on the Clora 2XP (600 second analysis) and on a coulometer.

Attempts to analyze organic chlorides directly in crude were also made. Crude was diluted with toluene and repeatedly washed with equal volumes of hot distilled water to remove inorganic chlorides. After repeating this three times there was no significant amount of chloride in the water phase. However analysis of the remaining crude yielded significantly higher results than expected on the organic chloride content of the fraction with a boiling point below 204° C.

[1] http://www.eraqc.com/Portals/0/PDF%20documents/ERA_LOD-LOQ_White_Paper_R2.pdf