Total Organic Chloride (MCT) in Crude Oil ASTM D4929

The ASTM D4929 is a common international test method to analyze the amount of organic chloride content in crude oil. Refineries often allow no more than 1 ppm (mg/kg) organic chloride in their crude charge, which is reflected in the naphtha cut. Primary sources of organic chlorides are contaminated tankers and transportation pipelines, the consequence of chemical solvents used to clean the equipment or "dumping" of contaminated crudes in the stream.

Organic chloride is difficult to control in the refining process. It causes various forms of corrosion at different temperatures and pressure levels, downstream of the distillation unit. Besides the corrosive effects, chloride also deteriorates the quality of the final product. Several pipelines have set specification limits at <1 mg/kg organic chlorides in the whole crude, and <5 mg/kg in the light naphtha fraction, based on the naphtha fraction being 20% of the original sample. Most chlorides concentrate in the boiling range of the naphtha cut, therefore the amount of organic chloride is generally 5 to 6 times higher compared to the whole crude.

The ASTM D4929 - Procedure B covers the determination of organic chloride (above 1 µg/g organically-bound chloride) in crude oils, using distillation and oxidative microcoulometry.

Solution

- XPLORER-TX
- ARCHIE Liquids Autosampler

- Liquids Introduction Module

- Collision Flow Combustion Tube

Sample information

Sample Type	Crude Oil / Naphtha Fraction
Component	Organic Chloride
Concentration	1 – 5 µg/g
Method Applicable	ASTM D4929

Summary

The XPLORER-TX elemental combustion analyzer equipped with Liquids Introduction Module, has been used to perform the analysis of total organic chloride (MCT) in crude oil by analyzing the light naphtha cut. All samples were introduced by the ARCHIE liquids auto sampler. The relative standard deviation (RSD) of results is well within the repeatability limits stated in the ASTM D4929, which are calculated by the following formula: $r=1.01\ (X-0.17)^{0.467}$. Refined Naphtha samples were analyzed during the same sample run. The results demonstrate a high sensitivity of the XPLORER-TX, even at concentrations below the scope of the ASTM D4929.

Results

Sample	Volume	Density	Concentration Cl (µg/g)	RSD (%) n=5
Refined Naphtha 1	40 µL	0.7	0.32	4.17
Refined Naphtha 2	40 µL	0.7	0.30	4.72
Light Naphtha Fraction 1	40 µL	0.7	7.16	1.32
Light Naphtha Fraction 2	40 µL	0.7	2.36	1.00
Light Naphtha Fraction 3	40 µL	0.7	5.73	0.63
Chlorine Standard Solution 10 mg/L Chlorobenzene in Isooctane	40 µL	-	10.42	0.60

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Method

A crude oil distillation must be performed to obtain the naphtha cut from the whole crude. The international test method ASTM D86 can be used for the distillation of petroleum products. After distillation, the naphtha cut is washed repeatedly with caustic solution until all hydrogen sulfide is removed. Thereafter, the naphtha cut is washed again with water to remove the inorganic chlorides. The washed naphtha has been analyzed according to procedure B – 'Combustion and Microcoulometry'. This procedure has several advantages over the other procedures:

- Microcoulometry is an absolute detection technique. All (organic) chloride components are converted to hydrochloric acid (HCl). The XPLORER-TX achieves a 100% recovery. The analyzer can be calibrated, but it is not required.
- Sulfur is another harmful component which is commonly present in petroleum products. Microcoulometry does not experience interferences of sulfur to the chloride signal. No sulfur analysis or dilution is required prior to chloride analysis.
- At trace level (<1 ppm), the performance in terms of precision and reproducibility is unrivaled within the industry.

System Description

Introduction - The ARCHIE liquids XYZ auto sampler automatically introduces the sample at controlled rate into the temperature-controlled liquids module (500 °C). This module is specifically designed for the introduction of liquid samples with a final boiling point up to 420 °C.

Combustion - The XPLORER-TX is fitted with a dual-zone furnace, which enhances combustion performances. The temperature is adjustable up to 1150 °C. The Collision Flow Tube has a secondary oxygen flow that collides with the oxidizing gas stream and replaces some of the depleted oxygen. Resulting in more oxidation power for samples which are difficult to oxidize.

Conditioning - The combustion gas, carrying halide ions is led into a sulfuric acid scrubber for rapid water and interference removal.

Detection - The amount of Total Chloride (MCT) is analyzed by Oxidative Microcoulometry, which is an absolute detection technique. No calibration required. The halide ions react with the silver ions present in the titration cell. The amount of charge (the integral of the re-generation current over the measuring time) used to regenerate the lost silver ions, represents the Total Chloride content of the sample.

System Settings

Oxygen Injection	300 mL/min
Argon Injection	100 mL/min
Oxygen Collision Flow	100 mL/min
Oxygen Bypass	50 mL/min
Furnace Temperature I	1000 °C
Furnace Temperature II	1000 °C
Gain	Auto gain
Cell Cooling	15 °C
Sample Volume	40 µL
Sample Injection Speed	0.5 µL / s

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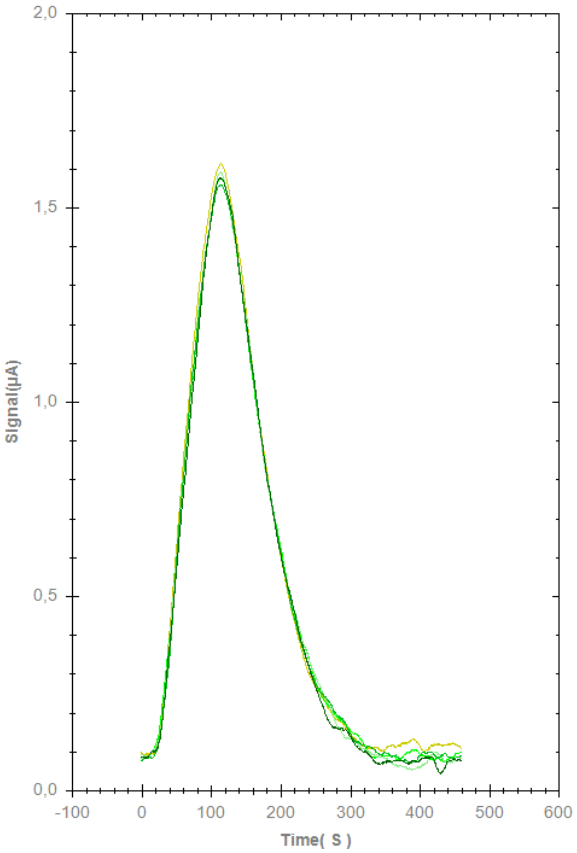
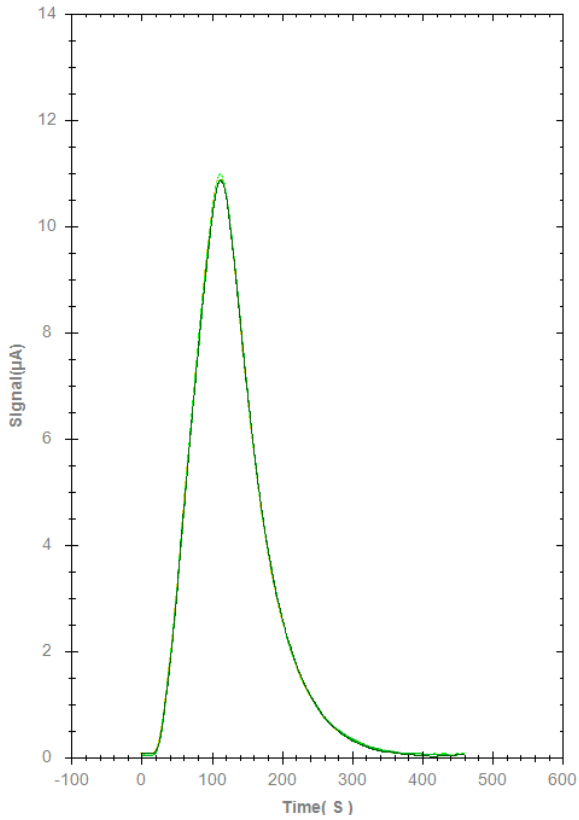
Example Peaks



Light Naphtha Fraction 2 - TX
Concentration: 2.36 µg/g
Replicates: 5
RSD: 1.00%



Chlorine Standard Solution 10 mg/L
Concentration: 10.42 mg/L
Replicates: 5
RSD: 0.60%

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