



We're Going Global

Chlorides...

Organic vs. Inorganic...what's the difference?

Organic Chlorides are an undesired contamination in crude oils. The presence of even a very small amount (a few ppm) of chlorides can be catastrophic during crude oil fractionation in the refineries which can cause considerable damage to the refinery equipment.

These organic chlorides during the refining process become hydrochloric acid which is highly corrosive and can cause severe corrosion in crude distillation overhead systems. There are commercially available additives which are used to help minimize such corrosion by organic chlorides.

An organic chloride is a compound containing at least one "covalently bonded" atom of chlorine. Their wide structural variety and divergent chemical properties lead to a broad range of names and applications. Organic chlorides are those compounds where one or more chlorine atoms are directly connected with Carbon atom.

Examples are Methylene dichloride (CH_2Cl_2), Methyl chloride (CH_3Cl), Chloroform, also called trichloro methane (CHCl_3), Carbon tetrachloride (CCl_4), 1,1,1 trichloroethane ($\text{CH}_3\text{-CCl}_3$) dry-cleaning solvent. Ethylene dichloride ($\text{CH}_2\text{Cl-CH}_2\text{Cl}$) Carbonyl chloride (COCl_2) and more. All of these solvents have a boiling range below 400 degF.

Inorganic Chlorides are not a major concern as a desalter unit in the refinery can easily remove salt and hence the inorganic chlorides.

Inorganic chlorides are those compounds where one or more chlorine atoms are directly connected with metals like sodium, calcium, aluminum, iron copper, magnesium, lithium and many more.

Examples are Sodium chloride or common salt (NaCl), Lithium chloride (LiCl), Aluminum chloride (AlCl_3), Calcium chloride (CaCl_2) and many more.

Products Containing Chlorides

In general, chlorides are used in the production of certain goods such as:

- PVC
- Pesticides
- Chloromethane
- Teflon
- Insulators
- Carbon tetrachloride (CCl_4): Chlorinated rubber manufacture, semiconductor manufacture, metal recovery
- Tetrachloroethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$): Dry Cleaning, degreasing, textile, printing, soap, paint removal
- Vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$): Monomer for PVC
- Chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$): Degreasers, refrigerants
- Chloroprene ($\text{CH}_2=\text{CClCH}=\text{CH}_2$): Monomer for polychloroprene used as wire and cable cover, gaskets and automotive components
- Dichloromethane (CH_2Cl_2): Paint and varnish removers (being phased out)
- Trichloroethylene ($\text{CHCl}=\text{CCl}_2$): Industrial cleaner, solvent in paint and glue manufacture

Damaging Effect of Organic Chlorides

The presence of organic chlorides in crude oils is extremely damaging during refining. Organic chlorides are chloride-containing organic compounds that are generally not naturally occurring. They are extensively used in the oil field as a wax dissolver but can have a negative impact based on environmental issues that they cause. Organic chlorides are not naturally present in crude oils and are usually derived from cleaning operations at production sites, pipelines and tanks.

During hydro treating or reforming, organic chlorides are converted into hydrochloric acid and this acid accumulates in condensing regions of the refinery causing rapid corrosion.

It is extremely important for the refineries to have a good knowledge of the organic chlorides in crude oils, particularly when transfer of custody is involved. This information is furnished by laboratories capable of testing organic chlorides.

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Organic chlorides in crude oil during distillation concentrate in heavy naphtha fractions and can cause extreme damage if not properly analyzed and reported. Correct reporting of organic chlorides before refining helps engineers to take proper corrective action.

The results must be obtained by use of the proper method, right equipment and trained technician. AmSpec Laboratory personnel involved with testing organic chlorides are highly trained in the testing procedures of organic chlorides.

Although they're useful in production, organic chlorides can cause corrosion in pipelines, valves and condensers, and cause catalyst "poisoning". The refining, transportation and storage industries are unfortunately affected by damage caused by these substances. Below is a brief explanation of the many methods used for Chloride laboratory testing.

Lab Testing of Organic Chlorides in Crude Oil

There are several approved ASTM & UOP methods for testing total, inorganic and organic chlorides. Selection of the best method for a given crude oil or its naphtha fraction depends on the agreement between the lab and the customer requesting it.

Common Industry Test Methods

ASTM D 4929 can be D 4929a or D 4929b

This is the test method for organic chloride in crude oil.

ASTM D 5808

This method determines organic chloride in aromatic hydrocarbons and related chemicals by microcoulometry.

UOP 588 & UOP 779 (similar to D 4929a & D4929b)

This method determines total, inorganic and organic chloride in hydrocarbons by potentiometric titration.

ASTM D 7536

This method determines chlorine in aromatics by wavelength dispersive x-ray fluorescence.

ASTM D 4929a Potentiometric Titration

In this method naphtha fraction of crude oil are washed repeatedly with caustic to remove H₂S and treated with sodium biphenyl which converts organic chlorides to inorganic chlorides. The excess sodium biphenyl is decomposed. The mixture is acidified and the aqueous phase separated and evaporated to a desired volume. The aqueous solution is then titrated potentiometrically.

ASTM D 4929b Combustion and Microcoulometric Titration

The washed naphtha fraction of crude oil is injected into a flowing stream of oxygen through a combustion tube maintained at 800 degC. The chlorine is converted into chlorides and oxychlorides, which then flow into a titration cell where they react with silver ions. The silver ions thus consumed are coulometrically replaced. The current required to replace the silver ions is a measure of the chlorine present in the sample.

ASTM D 5808 Organic Chloride by Microcoulometer

This is used for cleaner products. The liquid sample is injected into a combustion tube maintained at 900 degC having a flowing stream of 50% oxygen and 50% argon gas. Oxidative pyrolysis converts organic chlorides to hydrogen chloride that then flow into a titration cell where it reacts with silver ions. The silver ions thus consumed are coulometrically replaced and the current required in this case is a measure of the organic chlorides.

UOP 588

This method is the same as ASTM D 4929a / UOP 779 is the same as ASTM D 4929b. The estimated completion time for any of the above methods is about 3-4 hours.

ASTM D 7536

This is a nondestructive method based on x-ray fluorescence technique. This is essentially for total chlorine, requires minimum sample preparation and can be completed in 5-10 minutes for each analysis. The method can be extended to measure organic chlorides by careful washing of the naphtha fraction and separating the organic chlorides by extraction.

For more specific information regarding chlorides and chlorides testing, please contact AmSpec's Ken Nabi PhD @ ken.nabi@amspecgroup.com

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