

**Crude Oil Quality Group  
Informational Industry Paper**

**Crude Oil  
Contaminants and  
Adverse Chemical Components  
And Their Effects On  
Refinery Operations**

**Presented on May 27, 2004  
At the General Session  
Houston, Texas**

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## **Introduction**

The Crude Oil Quality Group (COQG) is sponsoring this document as an informational tool to be used by personnel in the petroleum industry. This document is intended to provide basic information on the effects that certain crude oil contaminants have on refinery operations. COQG's goal is for this document to provide beneficial material to all parties involved in the crude oil supply chain - from the wellhead, to pipelines, and to the refinery gate.

This initial document is intended to be the first step in development of a more comprehensive industry report that will cover the effects of additional crude contaminants. On behalf of the COQG, I would like to express thanks for the efforts of Clifford Mills and Aaron Dillard of ConocoPhillips and Bruce Carlile of ITS-Caleb Brett in the initial draft of the document. We are soliciting papers on crude oil contaminants from others in the industry so that the document can more fully cover all contaminants.

If you are interested in submitting a paper, or information in any form, on crude oil contaminants, please contact:

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## ORGANIC CHLORIDES

### SUSPECTED ORIGIN:

Organic chlorides are artificially introduced into the crude. Solvents containing organic chlorides may be used at production sites as a paraffin solvent. Disposal of organic chlorides used as degreasing agents and by some reclaiming operations is another source of this contaminant.

### PROBLEMS CAUSED:

The foremost problem with organic chloride contamination occurs when the naphtha fraction (IBP to ~400°F) is desulfurized at a refinery reformer unit. Hydrochloric acid is produced which can cause extreme and rapid corrosion. Piping and vessels can be rendered dangerously thin and susceptible to leaks and explosions.

When nitrogen compounds are present in the naphtha, ammonium and iron chloride constituents are formed which causes plugging of pumps and exchangers.

This naphtha fraction is also used as military jet fuel. It is unknown as to what extent damage may occur to the jet engine from combustion of organic chlorides.

### MEASUREMENT UNITS:

Organic chlorides are measured as parts per million (ppm), Cl, in the naphtha boiling range (IBP to ~400°F fraction of crude oil).

### DESIRED LEVELS:

Naphtha should contain no organic chlorides.

### ACCEPTABLE LEVELS:

The acceptable concentration of organic chloride is 1 ppm in the naphtha fraction of the crude (IBP to 400°F).

### TESTING METHODS USED:

Organic chlorides are determined using wet analytical chemistry techniques. Organic chlorides are reacted with a sodium compound and an inorganic sodium chloride product is produced. The chloride is titrated with a silver nitrate reagent to determine ppm organic chloride. A gas chromatographic method which utilizes an electron capture detector may be used as a qualitative method only as this method does not quantify all organic chlorides.

### APPROXIMATE LENGTH OF TEST:

This analytical procedure, including distillation of the naphtha fraction, requires 2 1/2 to 3 hours per single test. Several samples may be run simultaneously with a decrease in time required per test to 1 1/2 to 2 hours.

### APPROXIMATE COST OF TEST:

The cost for analysis of a single crude for organic chlorides is \$305.00. (Revised 1/1/04)

### COMPLEXITY LEVEL OF TEST:

The test for organic chloride is fairly difficult and meticulous, requiring the expertise of a trained analytical chemist and good laboratory facilities.

### DEGREE OF ACCURACY:

Organic chlorides may be determined to 20% relative at levels up to 10 ppm. Above 10 ppm the accuracy of the procedure is 10% relative.

### CONCURRENT TESTING POSSIBLE:

The first test in analysis of crude oil for both organic chloride and basic nitrogen contamination is to fractionate a naphtha boiling fraction (IBP to ~350° for organic chloride) and a kerosene boiling fraction (~350°F to ~525°F for basic nitrogen and color) from the crude oil. These two hydrocarbon fractions may be obtained from one laboratory fractionation.

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# VANADIUM

## SUSPECTED ORIGIN:

Vanadium is naturally occurring to varying degrees in virgin crude oil. Another source of vanadium could be blending of resid products into the crude system.

## PROBLEMS CAUSED:

Off-specification coke may be produced when levels of vanadium are too high in the crude oil. Vanadium deactivates cracking catalysts. When products containing vanadium are burned, corrosion of turbine blades may occur. Vanadium also fuses, during burning, with refractory to form low melting "alloys".

## MEASUREMENT UNITS:

Vanadium is measured as ppm in coke or crude oil.

## DESIRED LEVELS:

The desired level of vanadium in crude oil is <5 ppm.

## ACCEPTABLE LEVELS:

The acceptable level of vanadium in crude oil is approximately 7 ppm.

The acceptable level of vanadium in petroleum coke at the Ponca City Refinery is approximately 300 ppm. Acceptable levels at other refineries depend on the ultimate use of the petroleum coke.

## TESTING METHODS USED:

Vanadium in crude oil may be determined by dilution and atomic absorption or ICP analysis.

Vanadium in crude oil and in coke may also be determined by an ashing technique with atomic absorption or ICP finish.

## APPROXIMATE LENGTH OF TEST:

Crude oils analyzed by dilution require approximately 1/2 hour from receipt of sample.

Crude oils and coke analyzed by ashing techniques require approximately 1 day from receipt of sample.

## APPROXIMATE COST OF TEST:

The cost as part of the base metal test plus 2 (Fe, Ni, Van) is \$240.00. (Revised 1/1/04)

## COMPLEXITY OF TEST:

The analysis of vanadium in crude oil is difficult requiring the expertise of a trained analytical chemist and good Laboratory facilities.

## DEGREE OF ACCURACY:

Vanadium in crude may be determined by dilution with atomic absorption finish to  $\pm 1$  ppm at levels below 10 ppm. At levels above 10 ppm vanadium may be determined to  $\pm 10\%$  relative.

Vanadium in crude and coke may be determined by ashing techniques with atomic absorption finish to  $\pm 0.5$  ppm at levels below 10 ppm. At levels above 10 ppm vanadium may be determined to  $\pm 5\%$  relative.

## CONCURRENT TESTING POSSIBLE:

Vanadium and iron may be determined concurrently when using the ashing technique.

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# IRON

## SUSPECTED ORIGIN:

Iron is predominately introduced into the crude as corrosion products (iron oxide and iron sulfide) in the field and during pipelining. Another source could be blending of resid materials back into the crude. Trace amounts of iron may be naturally occurring in some crudes.

## PROBLEMS CAUSED:

High levels of iron cause coke production to be off specification. Also, this material is particulate and may cause pump and exchanger fouling.

## MEASUREMENT UNITS:

The iron is measured as ppm Fe in the coke or crude oil.

## DESIRED LEVELS:

The desired level of iron in both coke and crude oil is none.

## ACCEPTABLE LEVELS:

At present coke production at the Ponca City Refinery is limited to a maximum of 300 ppm iron by specifications. This corresponds to approximately 7 ppm in the crude with the crude slate at present (i.e., coke is approximately 1/32 to 1/40 of the crude charge).

## TESTING METHODS USED:

Iron is determined using an ashing technique followed by dissolution and analysis by inductively coupled plasma. (ICP or AA)

Iron in coke may also be determined by x-ray analysis, however, varying sulfur levels of the coke may cause a reduced degree of accuracy.

## APPROXIMATE LENGTH OF TEST:

Analysis of coke from production by ICP requires one day (approx. 24 hours) after receipt of the prepared sample (sample preparation requires approximately 7 hours). Analysis of crude for iron also requires one day after receipt of sample.

Analysis of coke by x-ray requires about one hour for the coke cars from one drum of coke. (after receipt of samples)

## APPROXIMATE COST OF TEST:

The cost as part of the base metal test plus 2 (Fe, Ni, Van) is \$240.00. (Revised 1/1/04)

## COMPLEXITY LEVEL OF THE TEST:

The analysis of iron in coke and crude oil is difficult, requiring the expertise of a trained analytical chemist, and good laboratory facilities.

## DEGREE OF ACCURACY:

Iron in crude may be determined by ICP to  $\pm 0.5$  ppm at levels below 10 ppm. At levels above 10 ppm iron may be determined to  $\pm 5\%$  relative.

Iron in coke may be determined by ICP to  $\pm 5\%$  relative.

Iron in coke may be determined by x-ray analysis to  $\pm 10\%$  relative.

## CONCURRENT TESTING POSSIBLE:

Iron and vanadium may be determined concurrently using the ashing technique.

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## **BASIC NITROGEN**

### **SUSPECTED ORIGIN:**

Some basic nitrogen constituents are found naturally occurring in virgin crude oil. Basic nitrogen constituents may also be introduced by addition of cracked products into the crude system.

### **PROBLEMS CAUSED:**

The primary problem occurring from crudes containing high basic nitrogen levels is off-specification products. The basic nitrogen in combination with phenols or other substituents of the crude form color-bodies and promote gum formation in the naphtha fraction (IBP to ~350°F) and in the kerosene fraction (~350°F to ~525°F).

### **MEASUREMENTS:**

Basic nitrogen is measured as ppm (parts per million) in the kerosene fraction of the crude. (may also be measured in the naphtha fraction)

### **DESIRED LEVELS:**

Basic nitrogen should be found in the kerosene fraction of crude oil at levels of one ppm or less.

### **ACCEPTABLE LEVELS:**

At present the generally accepted maximum for basic nitrogen in the kerosene fraction of crude oil is five ppm. However, this level is by no means all-inclusive. Of more importance is the susceptibility of the kerosene fraction to form color-bodies and gums. For example, some crudes have kerosene fractions which form color-bodies with as little as 2 ppm basic nitrogen while others may not form color-bodies with 7 or 8 ppm basic nitrogen.

### **TESTING METHODS USED:**

Basic nitrogen in the kerosene fraction of crude oil is determined by titration with perchloric acid.

The kerosene is dissolved in acetic acid prior to determination of basic nitrogen.

### **APPROXIMATE LENGTH OF TEST:**

This analytical procedure, including fractionation of the kerosene boiling range (~350°F to ~525°F) from the crude, requires 1 1/2 to 2 hrs. Several samples may be run simultaneously with a decrease in time required per test to approximately 1 hour.

### **APPROXIMATE COST OF TEST:**

The cost for analysis of a crude for basic nitrogen in the kerosene fraction is approximately \$165.00. (Revised 1/1/04)

### **COMPLEXITY LEVEL OF THE TEST:**

This test for basic nitrogen is not too difficult but requires the expertise of trained personnel and good laboratory facilities.

### **DEGREE OF ACCURACY:**

Basic nitrogen may be determined to  $\pm 0.3$  ppm.

### **CONCURRENT TESTING POSSIBLE:**

The first step in analysis of crude oil for both organic chlorides and basic nitrogen contamination is to fractionate a naphtha boiling fraction (IBP to 350°F-organic chloride) and a kerosene boiling fraction (350 to 525 °F-basic nitrogen and color forming tendency) from the crude oil. These two hydrocarbon fractions may be obtained from one laboratory fractionation.

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## NAPHTHENIC ACID

### SUSPECTED ORIGIN:

Naphthenic acids are naturally occurring in some virgin crudes.

### PROBLEMS CAUSED:

Naphthenic acids may cause operational problems such as foaming in the desalter or other units. Naphthenic acids are corrosive especially at high temperatures. Off-specification products, JP-4 and Kerosene, may be produced. Odor problems with products may be caused. Naphthenic acids may also carry cations through the desalting process which can cause deactivation of catalysts.

### MEASUREMENT UNITS:

Naphthenic acids are measured as mg of KOH/gram of crude oil.

### DESIRED LEVELS:

The desired level of naphthenic acids in the crude oil is less than 0.05 mg of KOH/gram of oil.

### ACCEPTABLE LEVELS:

The current acceptable maximum level of naphthenic acid in crude oil received at the Ponca City Refinery is 0.15 mg of KOH/gram of oil. This maximum may vary from refinery to refinery according to treatments and processes used in the refinery.

### TESTING METHODS USED:

Naphthenic acids are determined according to ASTM Method D-664, using an automatic titrator and standard KOH solutions.

### APPROXIMATE LENGTH OF TEST:

This procedure requires 15 to 20 minutes to perform.

### APPROXIMATE COST OF TEST:

The approximate cost of this procedure is \$660.00. (Revised 1/1/04)

### COMPLEXITY LEVEL OF TEST:

This procedure is not difficult but requires good laboratory facilities.

### DEGREE OF ACCURACY:

The naphthenic acid content of a crude oil may be determined to  $\pm 0.02$  mg KOH/gram of oil.

### CONCURRENT TESTING POSSIBLE:

No preparation (distillation or ashing) is required. Therefore, no concurrent testing is possible.

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## PHENOLIC COMPOUNDS IN CRUDE OIL

### SUSPECTED ORIGIN:

The suspected origin of phenolic compounds in crude oil is disposal of cracked products into the crude. Another source of phenolic compounds is disposal of spent cresylic acid into the crude.

### PROBLEMS CAUSED:

Off-specification products may be produced (unstable color and excess gum formation). Also, these phenolic compounds may cause problems in downstream treating units.

### MEASUREMENT UNITS:

Phenolic compounds are measured as % phenolics in the kerosene fraction of crude oil.

### DESIRED LEVEL:

The desired level of phenolic compounds in kerosene fraction of crude oil is less than 0.01%.

### ACCEPTABLE LEVEL:

The acceptable level of phenolic compounds in the kerosene fraction of crude oil is 0.03%.

### TESTING METHOD USED:

The amount of phenolic compounds in the kerosene fraction of crude oil is determined by using a caustic extraction and ultraviolet instrumental method finish and requires fractionation of the crude oil.

### APPROXIMATE LENGTH OF TEST:

Determining of phenolic compounds in the kerosene fraction of crude oil requires approximately 30 minutes after obtaining the kerosene fraction.

### APPROXIMATE COST OF TEST:

The cost of determining phenolic compounds in the kerosene fraction of crude oil is \$485.00. (Revised 1/1/04)

### COMPLEXITY LEVEL OF TEST:

The analysis of phenolic compounds in the kerosene fraction of crude oil is difficult requiring the expertise of trained personnel and good laboratory facilities.

### DEGREE OF ACCURACY:

The phenolic compounds in the kerosene fraction of crude oil can be determined to  $\pm 10\%$  relative.

### CONCURRENT TESTING POSSIBLE:

Requires a fractionation to be performed. The same fractionation can be used to obtain fractions for organic chlorides, basic nitrogen and phenolic compounds.

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## **ZINC (USED LUBRICATING OILS)**

### **Suspected Origin:**

Zinc is artificially introduced into the crude. No sources of naturally occurring zinc have been identified. Used lubricating oil reclaiming is almost always the source of zinc in crude oil (zinc- phosphorous compounds are utilized extensively in formulating motor and hydraulic oils). The testing for zinc is used as a marker for possible surfactants being present from detergent additives in lubricating oils.

### **Problems Caused:**

The main problem encountered when zinc is found in crude oil occurs during desalting of the oil. The surfactants present with the zinc can cause emulsion problems in the desalter which leads to poor desalting and carryover of water and salts into the crude tower.

The water carryover causes safety problems in the heaters and crude tower where it is converted to steam abruptly and could cause excessive pressures to occur.

A portion of the salts can hydrolyze to HCl which causes corrosion throughout the refinery. The remainder of the salts concentrate in the resid which is fed to the coker and causes premature coking in the furnace tubes. These salts also cause coke to be downgraded when specifications cannot be met.

### **Measurement Units:**

Zinc is measured as ppm in crude oil.

### **Desired Levels:**

Crude oil should contain no zinc.

### **Acceptable Levels:**

The maximum acceptable concentration of zinc in crude oil is <2 ppm.

### **Testing Methods Used:**

Zinc in crude oil may be determined by dilution and atomic absorption or ICP analysis. Zinc in crude and coke may also be determined by ashing techniques using atomic absorption or IOP finish.

### **Approximate Length of Analysis:**

Crude oils analyzed by dilution require about 1/2 hour to complete.

Samples analyzed by ashing techniques require approximately 1 day from receipt of the sample.

### **Approximate Cost of Analysis:**

The cost of analysis of a single crude for zinc is \$50.00. (Revised 1/1/04)

### **Complexity of the Analysis:**

The analysis of zinc in crude oil is difficult, requiring the expertise of a trained analytical chemist and good laboratory facilities and equipment.

### **Degree of Accuracy:**

Zinc in crude oil may be determined by dilution with IOP finish to +/- 1 ppm at levels below 10 ppm. At levels above 10 ppm, zinc may be determined to +/- 10% relative.

Zinc in crude oil or products may be determined by ashing techniques with atomic absorption or IOP finish to +/- 0.1 ppm at levels below 2 ppm. At levels above 2 ppm, zinc may be determined to +/- 5% relative.

### **Concurrent Testing:**

Zinc, vanadium, iron and other metals may be determined concurrently when using the ashing technique.

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## Methanol

### SUSPECTED ORIGIN:

Methanol is artificially introduced into crude. Methanol is used in deepwater production to prevent the formation of hydrates in crudes exposed to cold temperatures when wells are shut in or when rates are slowed. Methanol contamination is more common in late summer and early fall as this is peak hurricane season when Gulf of Mexico storms cause unexpected shut-ins.

### PROBLEMS CAUSED:

The foremost problem related to methanol contamination is its impact on Refinery Wastewater Treatment systems. Because methanol is miscible in water, it gets carried with the water in the crude to the refinery. When the refinery processes crude containing methanol in the desalter the methanol is removed with the water and sent to the water treatment system where it can drastically upset the balance of the system leading to EPA permit excursions. This happens because the bacteria used to breakdown other components prefer the methanol instead, leaving other hydrocarbons & toxins untreated. A big enough upset can also lead to a "bug kill" which renders the treatment system useless and typically requires major remediation to get the system back in balance. Refineries will typically opt to cut runs vs. risking a permit excursion and future penalties. Methanol is not believed to cause problems downstream of the desalters or beyond the wastewater treatment system.

### MEASUREMENT UNITS:

Methanol is measured as parts per million (ppm) using various analytical measurement techniques.

### DESIRED LEVELS:

Tolerance levels will vary from refinery to refinery as this is dictated by the capabilities of the refinery site Wastewater Treatment System.

The desired level of Methanol is 0. However in deep water production this is not usually possible when methanol is used in the production process. Resolution capabilities of the test method also make a 0 limit difficult to measure.

### ACCEPTABLE LEVELS:

Acceptable levels will vary depending on specific refinery constraints.

### TESTING METHODS USED:

Methanol measurement can be done using different analytical techniques. The industry accepted and most common method used is the direct injection multidimensional GC method ASTM D 7059. Other GC Separation methods have been developed to measure methanol but any of these methods should adhere to applicable QA/QC controls and demonstrate correlated results.

### APPROXIMATE LENGTH OF TEST:

Testing can usually be completed in about 45 minutes with times varying by method employed

### APPROXIMATE COST OF TEST:

Test costs are relatively inexpensive but can vary depending on technique used (\$20 - \$50 per single sample analysis)

### COMPLEXITY LEVEL OF TEST:

Nominal/Minimal complexity with GC methods.

### DEGREE OF TEST ACCURACY:

The degree of accuracy will vary depending on the concentration of methanol in the sample. Also, the lower end resolution of this method doesn't allow results below 5 ppm to be quantified. Following are the accuracy parameters (Repeatability, Reproducibility):

<u>Methanol conc. ppm</u>	<u>Repeatability</u>	<u>Reproducibility</u>
15	5	8
50	7	12
100	10	17
300	23	39
900	60	103

### CONCURRENT TESTING POSSIBLE:

Additional testing for alcohols or related components may also be performed concurrently with certain GC techniques.