CONTROLLING CORROSION:
A NEW METHOD TO MEASURE THE ACID NUMBER IN CRUDE OIL AND REFINERY DISTILLATION FRACTIONS

Many refiners look at discounted opportunity crudes as a means to improve their margin spread. The growing varieties of discounted opportunity crudes on the market contain certain risks for the purchaser, such as high naphthenic acid or sulfur content. Sulfur compounds and naphthenic acids are among the many species that contribute to the corrosive nature of crude oils and refined fractions. Opportunity crudes with high naphthenic acid and sulfur content therefore come with an ongoing risk of increased corrosion. The refiner must balance the cost benefit versus the risk and the cost of corrosion control when processing these crudes.
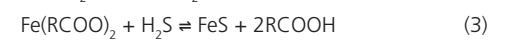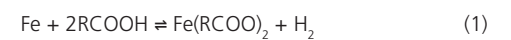
Naphthenic Acids: Occurrence

Naphthenic acids are found in many types of crude oil and can be present at varying concentrations. Their presence is found in crudes of diverse global origin including California, Venezuela, China, India, Mexico, Brazil, West Africa, North Sea, Western Canada, and other regions. Broader availability and higher volume of naphthenic-acid-containing crudes increase the risk of experiencing high-temperature corrosion of refinery equipment in refinery operations. The atmospheric and vacuum distillation columns, side strippers, furnaces, piping, and overhead systems are particularly at risk.

Naphthenic Acid and Sulfur Corrosion

The link between naphthenic acids and refinery corrosion was established by W.A. Derungs[1] who noted it was difficult to differentiate between sulfide and naphthenic acid corrosion. Both produced high corrosion rates at elevated temperatures.

The mechanism of corrosion from combined naphthenic acid and sulfur content has been described by the following chemical reactions:[2, 3, 4]

$$Fe + 2RCOOH \rightleftharpoons Fe(RCOO)_2 + H_2 \qquad (1)$$
$$Fe + H_2S \rightleftharpoons FeS + H_2 \qquad (2)$$
$$Fe(RCOO)_2 + H_2S \rightleftharpoons FeS + 2RCOOH \qquad (3)$$

In the first reaction, iron naphthenates are formed from the reaction of naphthenic acids with steel (Reaction 1). Being soluble in oil, the iron naphthenates are carried in the fluid flow. Simultaneously, hydrogen sulfide or other sulfide-containing species react with the steel to form an iron sulfide coating on the surface (Reaction 2). Hydrogen sulfide reacts with the iron naphthenates to form iron sulfide and liberate the naphthenic acids (Reaction 3).

While these three reactions form the recognized mechanism of corrosion in naphthenic-acid- and sulfur-containing crudes, naphthenic acid corrosion is in fact more complex and affected by many factors such as temperature and velocity as well as acid and sulfur content.[5] Corrosion risk from naphthenic acids is greater at process temperatures over 200 °C. At operating temperatures greater than 420 °C, naphthenic acids are believed to break down into shorter-chain organic acids. These can end up in distillation fractions, and there is concern about their corrosivity.[6] As operating process temperature increases, so does the possibility of corrosion due to these short-chain organic acids.

Physical Parameters Affecting Corrosion

Flow-induced wall shear stress can separately influence the corrosion by naphthenic acid and sulfur species. Refinery units with process stream flow velocities greater than 2.7 m/s and areas of high turbulence are more susceptible to naphthenic acid corrosion. A thin film of iron sulfide – formed through the reaction of hydrogen sulfide in crude and steel refinery units – protects the steel from naphthenic acid attack. High-velocity flow and turbulence can, however, dissolve the sulfide film, leaving the metal vulnerable to attack by naphthenic acid.

Desalter Upsets Caused by Naphthenic Acids

In the crude oil desalter, naphthenic acids can cause upsets through the formation of emulsions: as the pH of the water inside a desalter increases, naphthenic acids can form very stable sodium naphthenate emulsions. Emulsions that are formed must be broken to restore the efficiency of the desalter and reduce fouling.

Corrosion Control: Monitoring the Acid Number

To control corrosion in the processing of crude oil, the acid number and sulfur content of the crude or refinery fraction are measured. The acid number (AN) is defined as the amount of potassium hydroxide in milligrams required to neutralize 1 g of sample. It is not uncommon to find crude or traded fractions such as vacuum gas oil (VGO) with acid numbers up to 4 mg KOH/g. Most crude or refinery fractions have an acid number of less than 1 mg KOH/g. Experience from refineries and corrosion studies shows elevated corrosion risk when the naphthenic acid content is greater than 0.5 mg KOH/g in crude, and greater than 1.0 mg KOH/g in fractions. If the acid number of a crude or fraction exceeds these values it is considered to be a high-acid-number stream.

Until the release of acid number standard ASTM D8045, the acid number of crude oil and fractions was estimated by using potentiometric method ASTM D664. This test method was originally developed for the analysis of new and used lubricants and presents

the analyst with a number of analytical challenges when applying it to crude oil and fractions. For example, insufficient dissolution of crudes and fractions in the titration solvent can pose a problem: asphaltic, paraffinic (waxy), and bitumen materials are not all readily dissolved in the titration solvent that ASTM D664 stipulates. When the sample is not fully dissolved, the titrant cannot react with all of the acid contained in the sample. Also, the undissolved sample forms a coating on the glass membrane of the electrode in the titration cell, reducing its ability to accurately sense voltage changes during the titration. This subsequently leads to imprecision and poor accuracy.

A colorimetric titration method, namely ASTM D974, has been used to measure some clear refinery fractions. This test method cannot be applied to measure crudes and front-end refinery fractions because of the intense dark color they exhibit when dissolved in the titration solvent.

A New Method for Determining the Acid Number

Since 2008, Metrohm USA has been working with industry partners to overcome the sample and method challenges. This work has resulted in an improved, reliable method to measure acidity in the challenging matrices of crude and refinery fractions. The new titration method is based on thermometric endpoint detection and uses the Metrohm thermometric titrator 859 Titrotherm.

Thermometric Titration: Measuring Principle

Previous acidity measurements of crudes and fractions according to ASTM D664 used a potentiometric titration in which a pH electrode detects the reaction between the titrant and naphthenic acid. During the titration, the sensor often becomes coated with heavier fractions which are difficult to dissolve in the titration solvent stipulated by the standard, leading to measurement imprecision. The new Titrotherm method, ASTM D8045, uses a thermometric sensor which overcomes this issue in two ways: firstly, there is no glass membrane to coat, and secondly, the analyst can vary the solvent composition to aid the dissolution of heavier crudes such as bitumen.

The thermometric sensor developed by Metrohm performs well in the non-aqueous titration of acidity in crude. It employs a thermistor for precise temperature measurements in the titration vessel. The neutralization reaction of naphthenic acid is exothermic; therefore, the temperature increases in the course of the reaction. To obtain a sharp discontinuity in the temperature curve at the endpoint, a thermometric indicator that reacts endothermally with excess hydroxide after the endpoint is added to the sample solution. The thermometric titration gives an inverted V-shaped curve as shown in Figure 1. Evaluation of the titration endpoint is handled by the tiamo software.
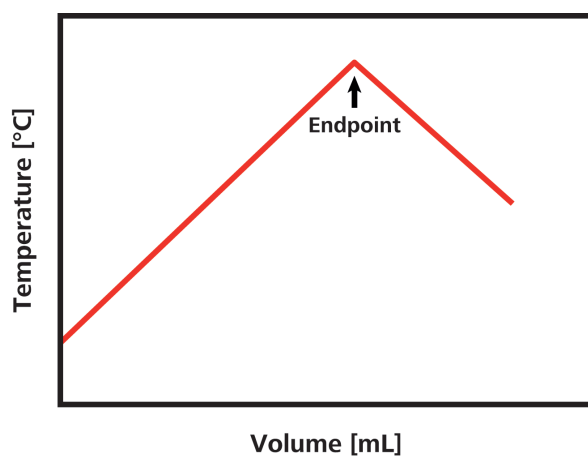

Figure 1: As titrant is added, an exothermic reaction is measured; i.e., the temperature in the titration vessel increases. After reaching the neutralization or endpoint, excess titrant endothermally reacts with the thermometric indicator present in the solvent, resulting in an abrupt temperature decrease.

The measuring response time of the thermistor is less than 0.003 seconds and is much faster than that of a pH glass membrane. This means that, without sacrificing precision or accuracy, thermometric titration by ASTM D8045 can be carried out much faster than the titration according to potentiometric methods which use pH indication. The thermometric sensor also allows the use of nonpolar solvents such as xylene which improves the solubility of many oils, including crude. Thermometric titration does not require an insulated reaction chamber because a relative temperature change is monitored to indicate completion of the reaction.

Sample Preparation

The heterogeneous nature of crude oil can affect determinations, particularly when measuring relatively small sample sizes of 3 to 5 g. Studies by the work group have shown that, to improve the precision of the new test method, it is necessary to homogenize the crude before analysis using a shear mixer.

To optimize the solvent system in ASTM D8045, a solvent study was conducted. It was found that a mixture of xylene and 2-propanol (also called isopropyl alcohol or IPA) in the ratio of 75:25 by volume worked best to dissolve the variety of crudes and refinery fractions. The xylene–2-propanol titration solvent is efficient enough that only 30 to 40 mL of solvent is required compared to 120 mL for ASTM Method D664. The reduction in total solvent volume and waste disposal saves substantial operating costs.

Crudes and refinery fractions that are liquid at room temperature are weighed directly into a beaker. 30 mL of titration solvent containing the thermometric indicator is added to dissolve the sample, which is then titrated with 0.1 molar potassium hydroxide in 2-propanol. Samples that are not liquid at room temperature, such as asphalt and high-paraffin-content fractions, require sample preparation.

High Paraffin Content: Particularly Challenging Samples

The analyst may encounter crude oils with high paraffinic content which are referred to as «waxy crudes». These samples can be challenging because the paraffins are often solid at room temperature. Samples with high paraffinic content should be fluidized and homogenized by heating them to 80 °C so that a representative aliquot is obtained and analyzed. The warm sample is weighed into the titration beaker and 10 mL of solvent is added (toluene or xylene). The majority of crudes analyzed, including bitumen samples, did not require this first dissolution step. Approximately 30 mL of the xylene–2-propanol titration solvent is added and the sample aliquot is reheated to 65 °C to ensure the dissolution of the paraffin content. The warm sample may be analyzed immediately without adversely affecting endpoint resolution, further supporting the method ruggedness of D8045.

Recommended Sample Weights

Crudes and distillation fractions with an expected acid number less than 1 mg KOH/g should be analyzed using a sample mass of 10 to 20 g. If the acid number is greater than 1 mg KOH/g, the analyst should use 5 g of sample for the measurement. The amount used can be adjusted to accommodate for solubility limitations. For unknowns, it is advised to start with 5 g and adjust the sample size as needed for subsequent measurements. The volume of titrant consumed must be at least 0.15 mL. A titrant volume smaller than 0.15 mL indicates that additional sample is required. A titrant volume greater than 5.0 mL suggests that less sample is needed. Recommended sample weights according to the expected value of the acid number are presented in Table 1.

Table 1: Recommended sample weights

Expected Acid Number (mg KOH/g)	Recommended Sample Mass (g) +/- 10%
0.05–0.99	10–20
0.00–4.99	5
5.00–15.00	1

Table 2:
Thermometric titration method correlated to the ASTM D664 Method

Blank Determination

It is important to determine a blank periodically. This should consume less than 0.1 mL titrant, in particular when measuring samples with acid numbers less than 1.0 mg KOH/g. To ensure that the blank value is less than 0.1 mL, only ACS Reagent grade solvents should be used. To determine the blank, a stable sample with a known acid number is measured three or more times, using a different sample mass each time. The largest sample size must not use a titrant volume greater than the volume of the burette. The example below shows a blank calculation for a crude oil sample with an acid number of approximately 0.9 mg KOH/g. In a plot of the titrant volume consumed until the endpoint against the sample mass, the blank value is equal to the value of the titrant volume y when the sample mass x is set to zero (Figure 2). In this particular example, it equals 0.039 mL. tiamo titration software can be configured to fit the data and calculate the slope automatically.
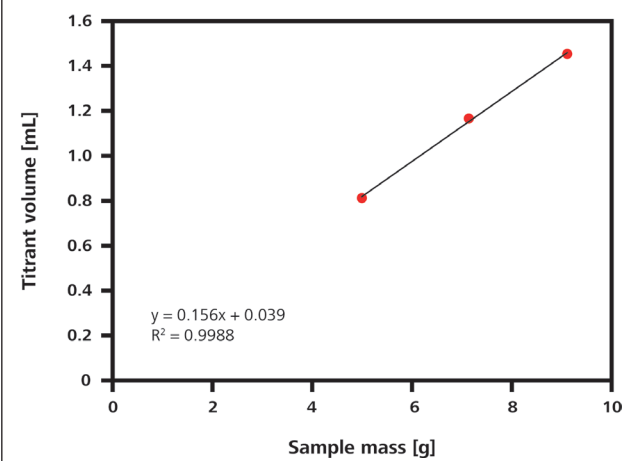

Figure 2: The blank value is determined from three or more determinations of the same sample, each of which is done using a different sample mass. The titrant volume required in these determinations is plotted against the respective sample mass. After a linear fit is applied, the blank value, equal to the titrant volume when the sample mass is 0 g, is extrapolated.

Results

Correlation of Thermometric and Potentiometric Methods

A variety of crude types and refinery fractions have been analyzed using the new thermometric ASTM D8045 titration standard. A study comparing this method to the ASTM D664 potentiometric method shows good correlation (Table 2).

In a three-laboratory study, 89 samples were analyzed using potentiometric and thermometric methods to compare the method results. The results showed that the new thermometric ASTM Method D8045 produces equivalent results to ASTM Method D664 as shown in Figure 3.

Repeatability

The acid number repeatability of the thermometric method was studied for low-TAN samples in a single laboratory. A crude oil, a mineral oil, and a refinery fraction were analyzed. The results are shown in Table 3, Table 4, and Table 5. ASTM D8045 demonstrates excellent method precision for low TAN values.

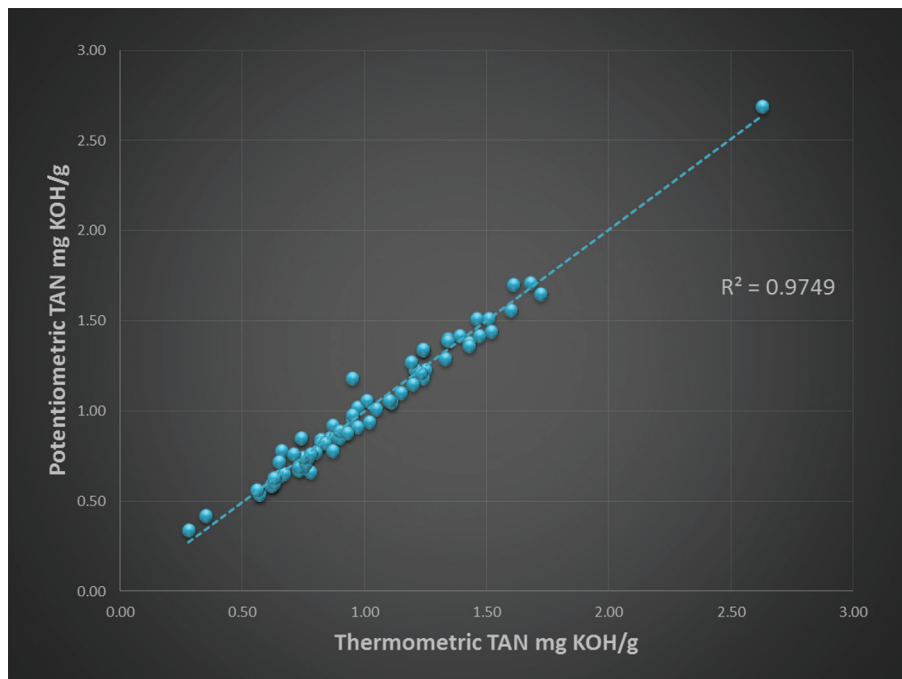| Sample	Mean Thermometric TAN (mg KOH/g)	%RSD (n=8)	Potentiometric TAN Result (mg KOH/g)	% Difference
Desalted Crude	0.76	2.1%	0.73	4.0%
Raw Crude	0.73	1.1%	0.67	8.6%
Vacuum Light Gas Oil	1.23	0%	1.20	2.5%
Vacuum Heavy Gas Oil	1.25	0.8%	1.23	1.6%
Atmsp. Heavy Gas Oil	1.15	1.2%	1.10	4.4%
650 Endpoint Gas Oil	0.73	1.1%	0.69	5.6%

Figure 3: Correlation of the results of the thermometric TAN determination according to ASTM D8045 and the potentiometric TAN determination according to ASTM D664

Table 3: Repeatability of the acid number determination in crude oil by thermometric titration

Sample ID	Run#	Sample weight (g)	Titration rate (mL/min)	Solvent volume (mL)	End point (mL)	TAN (mg KOH/g)
crude oil	1	5.1924	2	30	0.1367	0.15
crude oil	2	5.1623	2	30	0.1333	0.14
crude oil	3	5.0474	2	30	0.1400	0.16
crude oil	4	5.0192	2	30	0.1400	0.16
crude oil	5	5.0100	2	30	0.1333	0.15
crude oil	6	5.0643	2	30	0.1333	0.15
crude oil	7	5.0858	2	30	0.1400	0.15
crude oil	8	5.0956	2	30	0.1333	0.15
crude oil	9	5.0278	2	30	0.1467	0.16
crude oil	10	5.1419	2	30	0.1367	0.15
					mean	0.1520
					SD	0.0063

Table 4: Repeatability of the acid number determination in a refinery fraction by thermometric titration

Sample ID	Run#	Sample Weight (g)	Titration rate (mL/min)	Solvent volume (mL)	End point (mL)	TAN (mg KOH/g)
refinery stream	1	20.152	2	30	0.1733	0.05
refinery stream	2	19.9484	2	30	0.1633	0.05
refinery stream	3	20.0509	2	30	0.1600	0.04
refinery stream	4	20.2944	2	30	0.1533	0.04
refinery stream	5	19.3136	2	30	0.1467	0.04
refinery stream	6	20.1019	2	30	0.1567	0.04
refinery stream	7	20.1044	2	30	0.1467	0.04
refinery stream	8	20.2357	2	30	0.1533	0.04
refinery stream	9	20.1517	2	30	0.1533	0.04
refinery stream	10	20.3568	2	30	0.1567	0.04
					mean	0.0420
					SD	0.0042

Precision

The single-laboratory precision as well as the precision between multiple laboratories have been studied in the development of the ASTM D8045 thermometric acid number standard. This was done in a ten-laboratory study of twelve crudes and refinery fractions. Both the single-laboratory precision, or repeatability, and the precision between multiple laboratories, or reproducibility, proved to be much better than those of method D664 when measuring crudes and refinery fractions. These improvements are attributed to an improved solvent system that makes the sample fully accessible for reaction to the titrant as well as the use of a precise, enthalpy detecting sensor that is unaffected by difficult samples or harsh solvents.

Table 5: Repeatability of the acid number determination in mineral oil by thermometric titration

Sample ID	Run#	Sample Weight (g)	Titration rate (mL/min)	Solvent volume (mL)	End point (mL)	TAN (mg KOH/g)
mineral oil	1	10.2058	2	30	0.1267	0.07
mineral oil	2	10.1955	2	30	0.1300	0.07
mineral oil	3	10.3425	2	30	0.1267	0.07
mineral oil	4	10.1028	2	30	0.1167	0.06
mineral oil	5	10.307	2	30	0.1167	0.06
mineral oil	6	10.0383	2	30	0.1200	0.07
mineral oil	7	10.0328	2	30	0.1200	0.07
mineral oil	8	10.0974	2	30	0.1200	0.07
mineral oil	9	10.0852	2	30	0.1167	0.06
mineral oil	10	10.1142	2	30	0.1333	0.07
					mean	0.0670
					SD	0.0048

Conclusion

The new thermometric standard ASTM D8045 offers the highest accuracy for the analysis of the total acid content in crudes and refinery fractions. By solving sample solubility and measuring accuracy issues, ASTM D8045 offers increased precision between buyers and sellers of petroleum products and is a recommended standard to add to these agreements. By using 75% less solvent and reducing the analysis time, the new solvent system also considerably lowers the cost of testing. Table 6 provides on overview of the new method's most important improvements for the analyst compared to ASTM D664.

From crude feedstock to refinery fractions, extensive testing and method development using the Metrohm Titrotherm for acid number determination by ASTM D8045 proves to be simple and precise. With improved measurement, refiners can better adjust their plant operation to control and mitigate corrosion risk from naphthenic acid while ensuring fair trade and commerce throughout the industry.

Table 6: Method parameters of ASTM D8045 and ASTM D664

	D664	D8045
Solvent system	Toluene/IPA/H2O (120 mL)	Xylene/IPA (30 mL)
Reagent cost per titration	$ 4.09/sample	$ 1.07/sample
Titration time	~ 220 s	~ 60 s
Sample size for expected TAN of 0.05–1.0 mg KOH/g	20 g ± 2.0 g	~ 10 g
Sensor maintenance procedure	1. Solvent rinse 2. Two minute rehydration 3. IPA dip Fill with electrolyte fill solution. The probe must not dry out during storage.	1. Solvent rinse No rehydration No fill solution Store dry.

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