Metrohm

Application Work AW TI US 07/2015

Acidity in Crude Oils and Petroleum Products by Thermometric Titration

Branch

Petrochemistry; Refinery

Keywords

TAN, Thermometric, 859 Titrotherm, Thermoprobe

Summary

Thermometric titration, like other forms of titration, is based on a known chemical reaction between a titrant and species of interest. Many of these reactions are either exothermic (give off heat) or endothermic (take in heat). In Thermometric titration, enthalpy change of the reaction is monitored rather than potential. When all of the species of interest has reacted with the titrant, the solution of the temperature will change in the presence of excess titrant. The titration endpoint is revealed by an inflection in the temperature curve.

In the instance where enthalpy change is small (e.g. weak acids neutralized by strong bases), a catalytic indicator is used to make the titration endpoint apparent.

This application work describes the determination of total acid number in crude oil and refinery process oil samples by catalytic thermometric titration.

Introduction

Success within a petroleum refinery relies heavily on efficient process control and reliable plant operations. Corrosion is a major cause of decreased efficiency throughout the entire refining process and has large economic and production costs.

Sulfur species and naphthenic acids have been shown to be the main contributors to efficiency-decreasing corrosion in the refining process. By monitoring the acidity of crude oil and the associated process oils, billions of dollars are saved annually by avoiding unexpected shutdowns and preserving expensive treatment chemicals.

Titration has long been the preferred method for analysis for total acid number (TAN) in petroleum products. However, traditional methodologies, such as ASTM D664, are not optimal for crude oil, petroleum feed stocks, and refinery fractions. Crude oil is often waxy or contains precipitating asphaltenes that coat the measuring surfaces of the potentiometric electrode used in traditional analysis. When the membrane of a potentiometric electrode is coated, response time of the electrode declines. Additionally, the critical hydration layer required for stable potentiometric readings becomes dehydrated by solvent. This hydration layer can be replenished but doing so extends the analysis time per sample by an addition 2-3 minutes.

In addition to electrode fouling, traditional potentiometric TAN titrations can require up to 120 mL of solvent and may require the analyst to titrate to an alternate buffer endpoint when a true inflection is not apparent.

Thermometric titration improves upon this analysis technique by using a sensor that is insensitive to difficult matrices, requiring lower solvent volumes, and completing sample analysis in often less than two minutes. Additionally, comparison studies show very close data correlation between thermometric TAN titration and traditional potentiometric TAN titration methods making implementation into a refinery with historic data practical.

Samples

Crude Oils – expected concentration 0.8-1.2 mg KOH/g

- Desalted Crude
- Raw Crude

Process Oils – expected concentration 1.2-1.8 mg KOH/g

- Vacuum Light Gas Oil
- Vacuum Heavy Gas Oil
- Atmospheric Heavy Gas Oil
- 650 Endpoint Gas Oil

Instruments

The Metrohm Thermometric TAN Analyzer consists of four main components: Titrotherm thermometric titrator, Thermoprobe sensor, Dosino™ doing system, and tiamo™ Titration Software.

The Titrotherm thermometric titrator provides powerful data processing capabilities necessary to conduct rapid and responsive titrations. The titrator is operated by Metrohm tiamo Titration Software, the only titration software available

that is able to process the large amount of data points (10 measurements per second) necessary for reliable endpoint detection.

The Metrohm Thermoprobe is a highly sensitive and rapid responding sensor that requires no reference system, no maintenance, no calibration (only ΔT is important, not absolute temperature), and has no diaphragm or membrane measuring surface to clog. The sensor is fully integrated with traceability functions making compliance tracking simple. Due to the robust design, the Thermoprobe is simply dipped in stirring solvent between titrations for cleaning. Even with some electrode coating, the sensor will respond as long as the sample can flow through the protective cage.

Metrohm's patented Dosino dosing technology is used to provide the industry's most accurate liquid handling system. With top-down dispensing, the influence of air bubbles is eliminated allowing for truly unattended analysis.

The Metrohm Thermometric TAN Analyzer can be configured as a standalone TAN Analyzer or as an Automated TAN Analyzer. The standalone configuration has a small footprint and is ideal for process areas that may require a walk-up analysis station. In the automated configuration, indicator is combined with solvent and added as a slurry in a single step. Automation is ideal for sample batches, laboratory environments where analysts have multiple responsibilities, and for optimizing safety by reducing analyst contact with solvent, sample, and indicator. Automation is also ideal for achieving the highest levels of precision and accuracy due to a consistent treatment of each sample and the electrode between titrations.

859 Titrotherm	2.859.1010
804 Ti Stand	2.804.0040
802 Propeller Stirrer	2.802.0040
(2) 800 Dosino	2.800.0010
Dosing Unit, 20 mL	6.3032.220
Dosing Unit, 50 mL	6.3032.250

Electrodes

Thermoprobe	6.9011.020

Reagents

- Titrant - 0.1N KOH in IPA
- Sample Solvent - 75:25 Xylene:IPA
- Paraformadehyde - >95% pure, Sigma-Aldrich, Cat. 158127

Standard solutions

- Benzoic acid, dry, 99.5% pure

Sample preparation

For the samples presented in this application work, no additional sample prep was required. However, some samples may require slight warming or pre-dissolution in 10 mL of xylene prior to titration. Warm samples (<60°C) can be titrated without a loss of resolution or precision.

Analysis

The titrant was standardized against dry benzoic acid by weighing a known amount into a plastic beaker, adding 30 mL of sample solvent and performing the titration. The standardization titration was performed on four samples of differing weights and a linear regression was plotted in tiamo. The exact concentration of the titrant was calculated from this regression and stored to the titrant dosing unit.

For each sample, a series of four well-mixed aliquots with masses varying by approximately 2g were weighed into a disposable plastic beaker. Next, 30 mL of solvent was dosed and the sample was mixed. Approximately 0.5g of dry paraformaldehyde was added manually to the sample. The sample was allowed to mix, and then titrated to a thermometric endpoint with 0.1N KOH in IPA. A linear regression was performed on the data, a blank value obtained, and the raw data reprocessed to extract the TAN concentration. This procedure was performed twice for each sample for a total of eight titrations per sample.

Parameters

Titration	TET
Dosing rate	1 mL/min
Filter factor	50-75
Damping until	0.2 mL
Stop volume	2.5 mL
Thermometric evaluation	exothermic
EP criterion	-50

Calculation

Titrant Standardization

mol/L KOH = (1/Slope) x 8.1887

Slope:	Linear regression performed in Tiamo for standard analysis
8.1887:	Factor for converting mL/g to mol/L of benzoic acid

TAN Calculation

$$\text{TAN in mg KOH/g} = \frac{(V_{EP1} - \text{Blk}) \times c(\text{titrant}) \times M[KOH]}{W_S}$$

V_{EP1}:	Titrant consumption in mL
c(titrant):	Concentration of titrant in mol/L
M[KOH]:	Formula mass of KOH 56.11 g/mol
W_S:	Sample weight in g

Results & Discussion

The thermometric blank volumes were similar for all oil types with a mean blank value of 0.073mL over twelve blank determinations (two for each sample). The absolute deviation for these blanks was 0.017mL. This difference equates to a ±0.018 mg KOH/g concentration variance in a 5g sample. This data demonstrates that over a variety of crude oil and process samples, a blank value is not required. Should a blank value be higher than 0.1 mL, the analyst should reanalyze or prepare fresh solvent and titrant.

Titration endpoint selection was automatic and required no manual integration. Tiamo Titration Software quickly applies a second derivative formula that confirms the automatic endpoint selection. Thermometric endpoints were reached very quickly (average of 59.4 s) using minimal volumes of titrant (average 2.15 mL). A stream of solvent from a rinse bottle was used to clean the thermometric sensor.

Conclusion

Thermometric titration is very accurate and reliable alternate method for evaluating acidity in crude and refinery process oils. Thermometric titration provides a very robust technique for these samples documented in the highly repeatable TAN results at the expected concentrations across a range of sample weights. Thermometric titrations are performed rapidly requiring minimal sample, solvent, and titrant compared to traditional techniques and should be considered as a more economical approach to evaluating acidity in crude and refinery process oils.

References

- Metrohm Application Bulletin No. 80/3e, Determination of the acid and base number in petroleum products.
- Practical Titration, Monograph created by Metrohm
- ASTM D664 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- AW TI US 7/2015, Acidity in Crude Oils: Comparison of Thermometric and Potentiometric Titration

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Appendix

Figure 1: Metrohm Thermometric TAN Analyzer

Figure 2: Metrohm Automated Thermometric TAN Analyzer

Table 1: Titrant standardization result

0.1M KOH in IPA Titrant Standardization	0.0966 mol/L

Table 2: Thermometric TAN results

Sample	Mean Thermometric TAN (mg KOH/g)	%RSD (n=8)
Desalted Crude	0.76	2.1%
Raw Crude	0.73	1.1%
Vacuum Light Gas	1.23	0%
Vacuum Heavy Gas	1.25	0.8%
Atmsp. Heavy Gas	1.15	1.2%
650 Endpoint Gas	0.73	1.1%

Table 3: Thermometric blank titration results and statistics

Sample	Average Thermometric Blank (mL)	R^2
Desalted Crude	0.082	1.000
Raw Crude	0.097	1.000
Vacuum Light Gas	0.071	1.000
Vacuum Heavy Gas	0.050	1.000
Atmsp. Heavy Gas	0.069	1.000
650 Endpoint Gas	0.067	1.000
Potentiometric Blank	0.084	NA

Figure 3: Titration curve for raw crude

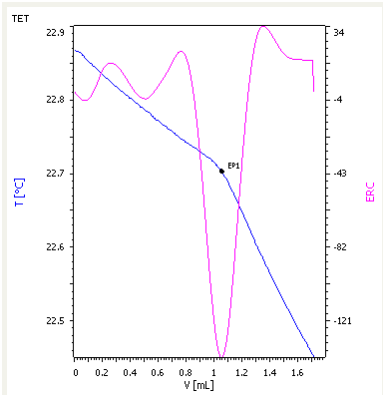


Figure 4: Titration curve for desalted crude

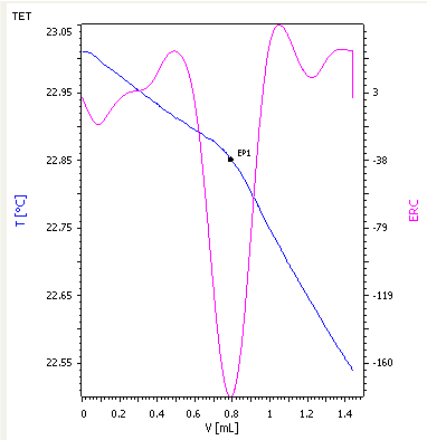


Figure 5: Titration curve for vacuum light gas oil

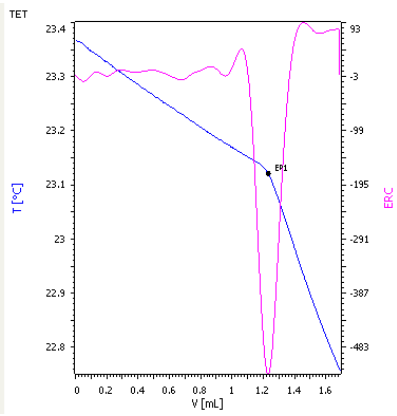


Figure 6: Titration curve for vacuum heavy gas oil

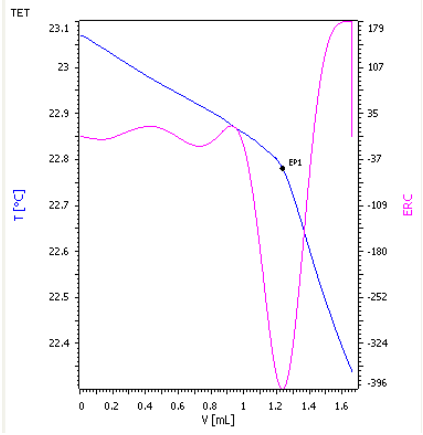
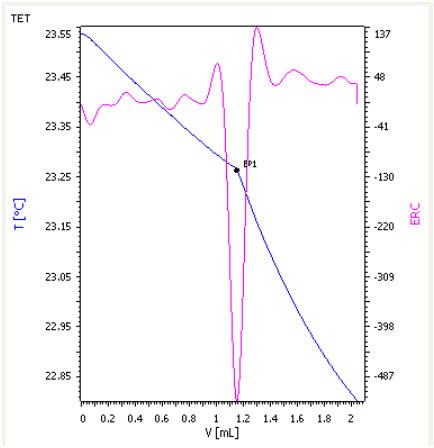


Figure 7: Titration curve for atmospheric heavy gas oil



Titration curve for 650 endpoint gas oil