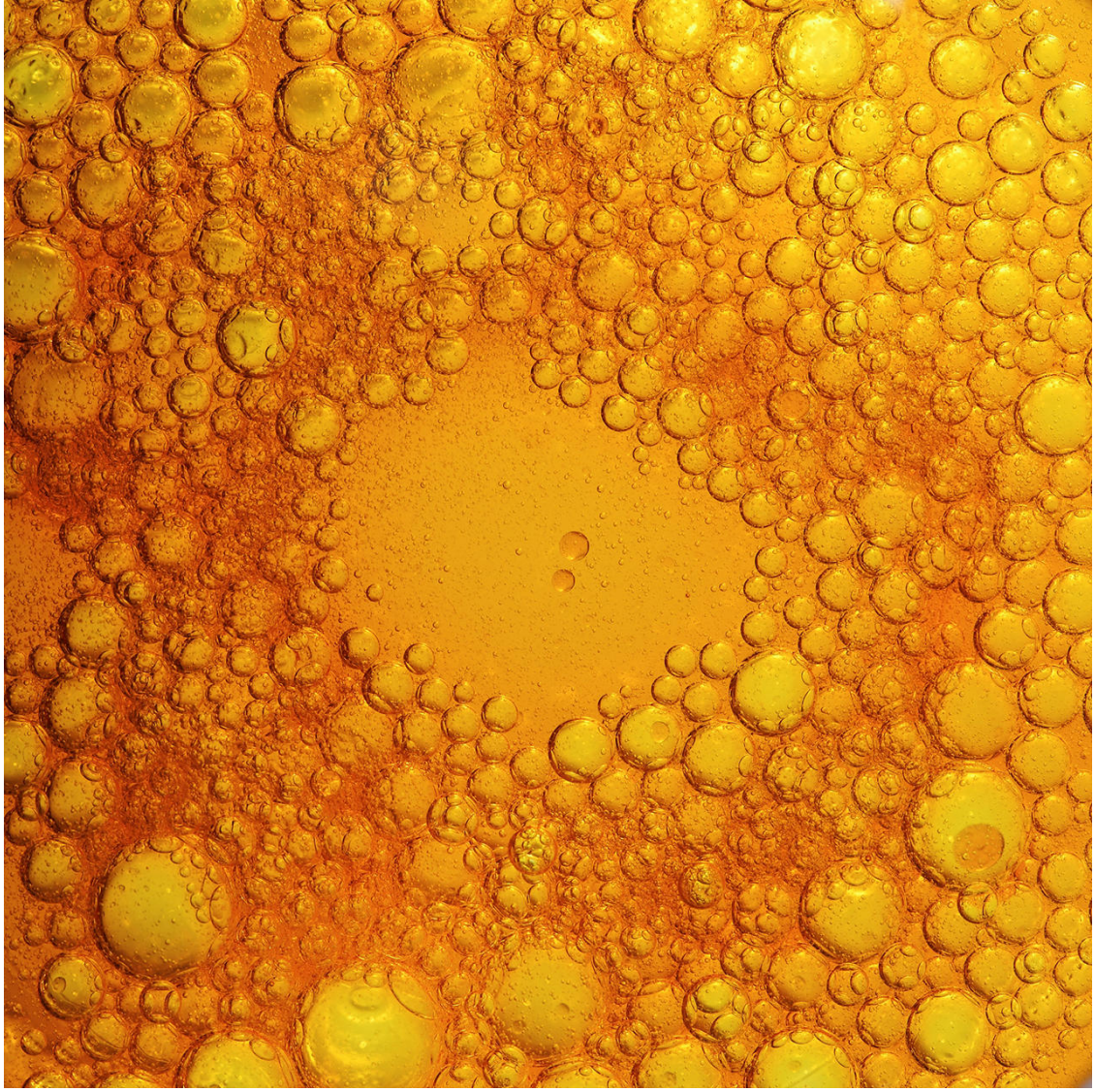

Application Note AN-PAN-1037

Online measurement of the acid number (AN) in oils with thermometric titration (ASTM D8045)

Metrohm has partnered with industry leaders to develop an alternative standard for the measurement of acid number (AN) in crude oil and petroleum products to overcome shortcomings in ASTM D664. This standard method (ASTM D8045) describes the use of thermometric catalytic titration for the analysis. Results agree closely with those from ASTM D664, but the thermometric catalytic titration method is far superior in terms of reproducibility and speed of analysis, with complete determinations in one minute. This alternative standard method also decreases the amount of solvent used, reducing waste disposal costs. Comparison studies show very close data correlation between ASTM D8045 and traditional potentiometric AN titration methods, making it possible to seamlessly implement this method into a refinery that relies on historic data.

This Process Application Note presents a method to regularly monitor AN online in crude oil according to ASTM D8045. Online monitoring helps operators avoid corrosion issues in refinery processes.

INTRODUCTION

The success of a petroleum refinery relies heavily on efficient process control and reliable plant operations. Corrosion in refinery processes is a universal disruption factor that can soon result in astronomical production costs. Sulfur species and naphthenic acids (discussed in more detail in AN-PAN-1026) are the main contributors to efficiency-decreasing corrosion in crude refining. These issues can be controlled by monitoring the acid number (AN, or acid value, AV) online and treating the crude oil appropriately. The accuracy of the AN results has a significant influence on the commercial value of crude oil and the profitability of a refinery.

Testing of crude and refined oil products is demanding and requires precise and reliable analysis to meet regulatory demands. Nonaqueous titration has long been the preferred method for analyzing acidity in petroleum and chemical products. AN is expressed in mg KOH per g sample, and it represents the sum of the myriad acid compounds present. Endpoint detection is performed either manually using the color change of an indicator (e.g., ASTM D974) or instrumentally using a pH electrode (e.g., ASTM D664).

However, instrumental methods that use glass membrane pH electrodes suffer from the difficulty of working in a water-free environment which results in dehydration and a decline in electrode response accuracy. Poor electrical conductivity of the titrating medium can lead to imprecise endpoints, particularly with low AN values. To overcome these issues, Metrohm partnered with industry leaders to develop an alternative to ASTM D664 for the measurement of AN in crude oil and petroleum products. The resulting method, ASTM D8045, describes the use of thermometric catalytic titration for this analysis.

Metrohm thermometric titration uses a maintenance-free temperature sensor that does not require calibration nor rehydration and is resistant against fouling and matrix effects. The procedure requires minimal sample preparation and less solvent than traditional methods, which saves on waste disposal costs. Results agree closely with those from the potentiometric titrimetric procedure according to ASTM D664, but the thermometric catalytic titration method is far superior in terms of reproducibility and speed of analysis, with determinations completed within one minute. The thermometric endpoint titration (TET) method utilizes the same titrant (0.1 mol/L KOH in isopropanol) as ASTM D664. Online process analyzers from Metrohm Process Analytics can continuously sample and monitor AN in a refinery (Figure 1) with this fast, robust thermometric technique.

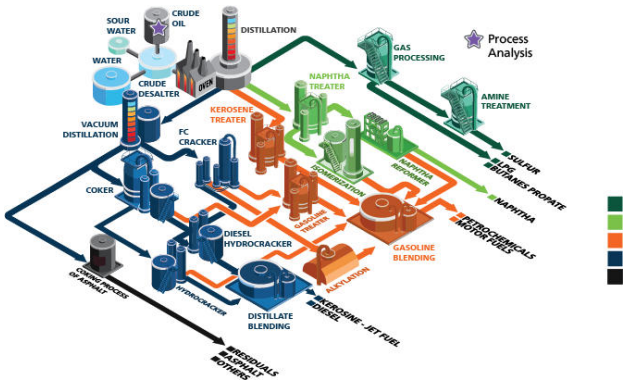

Figure 1. Schematic illustration of a petrochemical refinery. A purple star marks the ideal placement of a process analyzer for this application.

The 2060 TI Ex Proof Process Analyzer (Figure 2) can monitor acidity of crude oil according to ASTM D8045 testing procedures. By monitoring the acidity of crude oil and associated products, billions of dollars are saved annually by avoiding unexpected shutdowns and preserving expensive treatment chemicals.

Figure 2. 2060 TI Ex Proof Process Analyzer, suitable for ASTM D8045.

APPLICATION

ASTM D8045 describes the nonaqueous thermometric catalytic titration of weakly acidic species in crude oil. A defined sample amount is introduced via the sample loop and dissolved in 30–35 mL of a 3:1 xylene/isopropanol mixture. Paraformaldehyde is added as a catalytic indicator before the titration is performed with 0.1 mol/L KOH in isopropanol. The endpoint, indicated by a temperature change with the robust Metrohm Thermoprobe, is identified by the second derivative (Figure 3). Benzoic acid is used as a standard in this method.

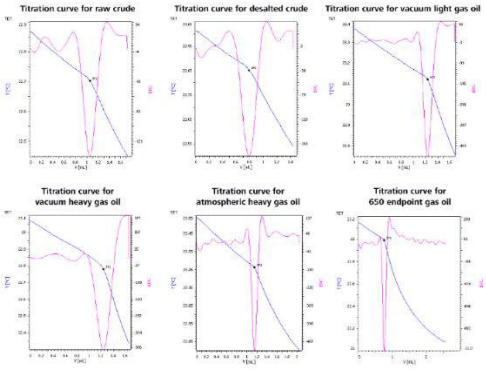

Figure 3. Acidity in crude oils and petroleum products by Metrohm thermometric catalytic titration, according to ASTM D8045.

Table 1. Typical range for AN in petroleum.

Parameter	Range [mg KOH/g]
AN	0.1–16

REMARKS

If the sample is not in liquid form, preconditioning at 65 °C is permitted to decrease sample viscosity. In thermometric titration, enthalpy change rather than potential of the reaction is monitored. Catalytically enhanced titrations using paraformaldehyde as catalyst are based on the endothermic hydrolysis of paraformaldehyde in the presence of an excess of hydroxide ions. It is recommended to use the paraformaldehyde specified in the given ASTM method, as not every type is suited for the catalysis of this reaction.

CONCLUSION

The Metrohm Process Analytics **2060 TI Ex Proof Process Analyzer** can reliably measure the acid number in crude oil and petroleum products according to ASTM D8045. Additionally, it offers automated analysis results for different parts of a refinery process and helps to safeguard plant operations.

RELATED APPLICATION NOTES

AN-PAN-1014 Automated online determination of salt in crude oil according to ASTM D3230

AN-PAN-1026 Analysis of hydrogen sulfide and mercaptans derived from crude oil – Online determination according to ASTM D3227 and UOP163

BENEFITS FOR ONLINE ANALYSIS IN PROCESS

- **More savings per measurement**, making results more cost-effective.
- **Increased product throughput**, reproducibility, production rates, and profitability.
- **Guarantee compliance** with government standards.
- **Protection of company assets** with built-in alarms at specified warning limits to prevent corrosion.

CONTACT

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CONFIGURATION

2060 TI Ex Proof Process Analyzer

The **2060 TI Ex Proof Process Analyzer** is an intrinsically safe wet chemistry process analyzer for process monitoring in gas or dust zoned hazardous environments rated as zone 0, 1 and 2, or 20, 21, and 22. It complies with EU Directives 94/9/EC (ATEX95) and is certified for Zone 1 and Zone 2 areas. Its design combines a purge and pressurization system with intrinsically safe electronic devices. The air purging phase and permanent overpressure prevent potentially explosive atmospheres from entering the analyzer enclosure.

The analyzer's design eliminates the need for purging large analyzer shelters, allowing for direct installation at the production line within hazardous zones. It supports various kinds of techniques, including titration, Karl Fischer titration, photometry, ion-selective electrode measurements, and direct measurements.