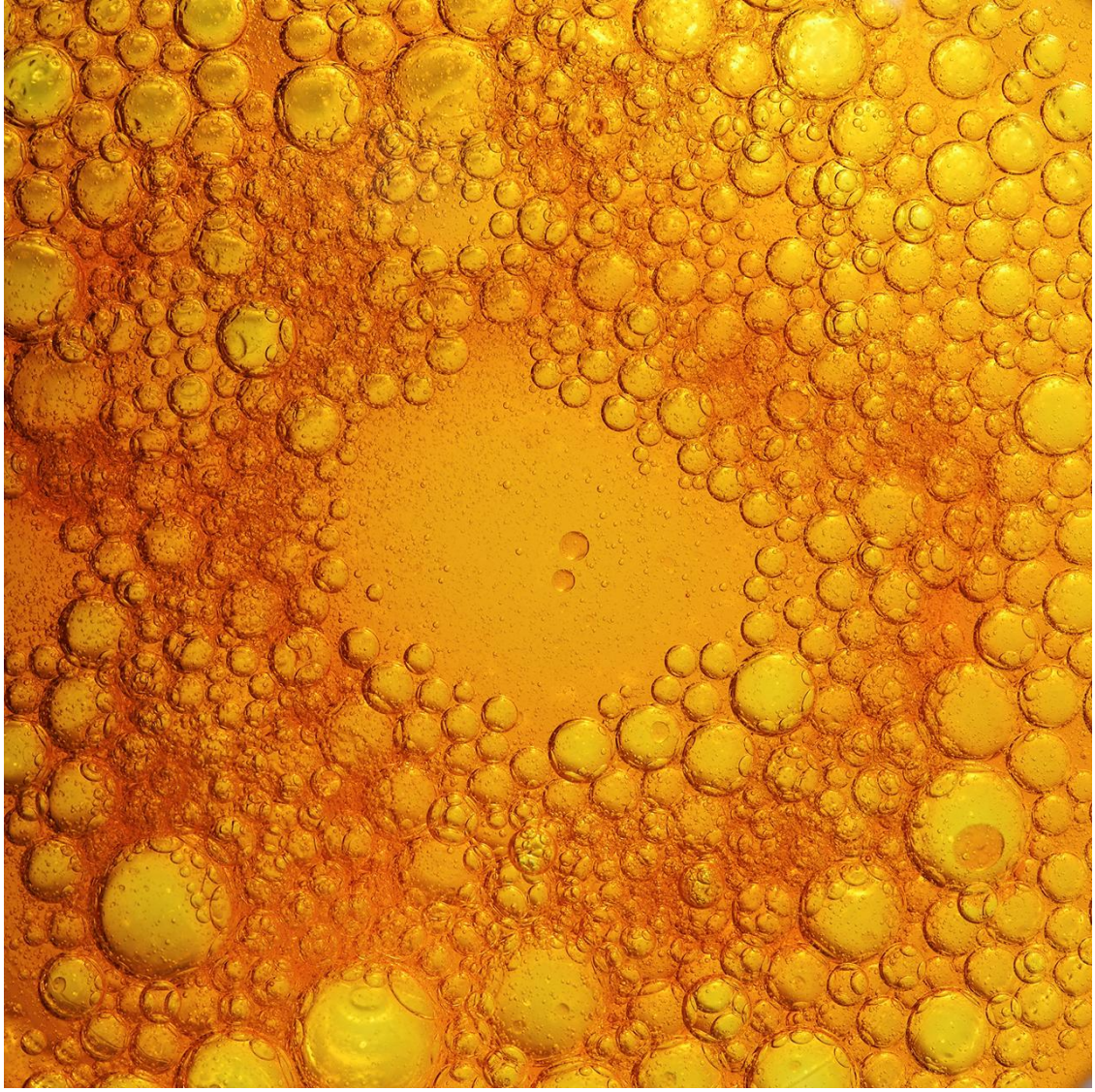

Application Note AN-PAN-1037

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

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 the current method (ASTM D664). This new standard method (ASTM D8045) describes the use of thermometric catalytic titration for this 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 determinations being complete in one minute. Solvent usage is much less compared to older methods, saving on waste disposal costs. Comparison studies show very close data correlation between ASTM D8045 and traditional potentiometric AN titration methods, making implementation into a refinery with historic data practical.

This Process Application Note presents a method to regularly monitor AN online in crude oil to avoid corrosion issues in refinery processes.

INTRODUCTION

Success within a petroleum refinery relies heavily on efficient process control and reliable plant operations. Corrosion in refinery processes is a universal disruption factor and one that can soon result in astronomical production costs. Sulfur species and naphthenic acids (discussed in more detail in AN-PAN-1026) have been shown to be 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. Nonaqueous titration has long been the preferred method for analysis of acidity in petroleum and chemical products. AN is expressed in mg KOH per g sample, and represents the sum of the myriad acid compounds present. In standard methods, 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 using a glass-membrane pH electrode suffer from the difficulty of working in a water-free environment, resulting in dehydration and a declining response of the electrode. Poor electrical conductivity of the titrating medium can lead to imprecise endpoints, particularly with low AN values.

Metrohm has partnered with industry leaders to develop an alternative to ASTM D664 for the measurement of AN in crude oil and petroleum products to overcome the above-mentioned shortcomings. 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 or rehydration and is free of fouling and matrix effects. The procedure requires minimal sample preparation and less solvent than traditional methods, saving 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 being complete in **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. Comparison studies show very close data correlation between ASTM D8045 and traditional potentiometric AN titration

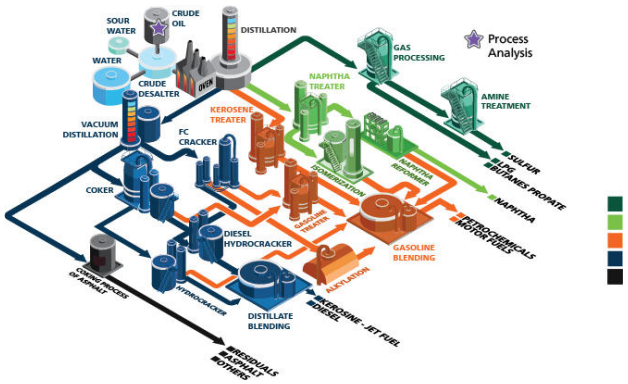

Figure 1. Schematic illustration of a petrochemical refinery.

Additionally, testing of crude and refined oil products is demanding and requires precise and reliable analysis to meet regulatory demands. Metrohm Process Analytics is actively involved with international standard bodies to help drive method development. The ADI 2045TI Ex proof Analyzer (Figure 2) can monitor acidity of crude oil according to ASTM D8045 testing procedures. By monitoring the acidity of crude oil and the associated products, billions of dollars are saved annually by avoiding unexpected shutdowns and preserving expensive treatment chemicals.

Figure 2. ADI 2045TI Ex proof Analyzer suitable for ASTM D8045.

APPLICATION

ASTM D8045 describes the nonaqueous thermometric catalytic titration of weakly acidic species in crude oil. A defined amount of sample is introduced via sample loop and dissolved in a 30–35 mL 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.

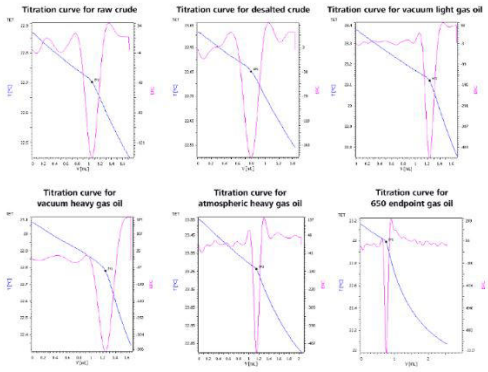

Figure 3. Acidity in crude oils and petroleum products by Metrohm thermometric catalytic titration according to ASTM D8045.

Table 1. Typical range for AN in petroleum.

Parameters	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 of the reaction is monitored rather than potential. Catalytically enhanced titrations using paraformaldehyde as catalyst are based on the endothermic hydrolysis of the 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 ADI 2045TI Ex proof 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 Online determination of salt in crude oil by automated process analysis

AN-PAN-1026 Mercaptans and hydrogen sulfide in raw oil in accordance with ASTM D3227 and UOP163

RELATED DOCUMENTS

8.000.5367 Petroleum and Petrochemicals Industry

8.000.5370 Brochure 2045 TAN Analyzer

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

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CONFIGURATION

ADI 2045TI Ex proof Analyzer

L'appareil d'analyse ADI 2045TI Ex proof Process Analyzer a été étudié pour une utilisation dans des environnements à risques d'explosion où apporter la preuve de la protection contre les explosions est une exigence de sécurité critique. Cet appareil d'analyse est conforme aux directives EU 94/9/CE (ATEX95) et est homologué pour les Zone-1 et Zone-2. La conception de cet appareil d'analyse associé un système de purge/pressurisation à des appareils électroniques de sécurité intrinsèque. La phase de purge d'air et la surpression permanente empechent qu'une quelconque atmosphère explosible potentielle de l'air ambiant ne pénètre dans l'enveloppe de l'analyseur. La conception intelligente de l'appareil d'analyse évite la nécessité d'avoir à purger de grands abris pour analyseurs. Il peut etre placé dans la ligne de production en zone à risques d'explosion.

Titrage, titrage Karl Fischer, photométrie, mesures avec électrodes ioniques spécifiques et mesures directes sont tous réalisables avec ce modèle Ex-p.