Acidity in crude oil and refined petroleum products by ASTM D8045

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Acid number (AN) is a critical parameter in the quality control and valuation of crude oil and other refined petroleum products. Directly affecting how the oil is processed, a minor shift in acidity can result in corrosion within the refining process and significant barrel pricing adjustments. Until now, ensuring the accuracy of acid number in these samples has been challenging and inefficient. Find out how Metrohm titration and ASTM D8045 overcome these challenges.

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Balancing risk with opportunity

Discounted opportunity crude oils have the potential to dramatically improve refinery operating margins and bring a significant increase in profitability to the refining industry overall. By mixing opportunity crude with well-defined samples, refineries can cut raw material costs and drive up margins on refined products. Despite their potential economic advantages, these opportunity crudes are discounted due to the risk associated with processing petroleum products that contain increased levels of naphthenic acid. More and more opportunity crudes are introduced to the market every year illustrating the need for a better method to reduce the transactional risk between buyers and sellers.

Even if a refinery is not interested in rolling the dice with opportunity crudes, their own operation is continuously at risk from damaging corrosion. A NACE-sponsored federal corrosion report remains the landmark study, estimating annual cost of corrosion in U.S. refineries at $3.7 billion. The report's gap analysis estimates a direct profit loss ranging from $2 to $12 billion due to interruption in refinery operations caused by corrosion-related shutdowns.1 Refinery and terminal management is tasked with balancing potential revenue with the refinery infrastructure risk and cost of corrosion control when choosing to accept opportunity crudes or certain petroleum products.

The need for a better acid number test

Monitoring acid number (AN) in crude oil and petroleum products remains the benchmark for evaluating the risk of processing opportunity crude oils and for adjusting refinery protocol to accommodate corrosive petroleum products. Traditional potentiometric methods, written to address acidity in lubricant products, require large amounts (up to 120 mL) of solvent and extensive electrode care procedures. Poor solubility of crude products, especially asphaltic, paraffinic, and bitumen materials, causes electrode fouling and inaccurate acid number results via potentiometric techniques. In 2008, key petroleum industry leaders requested a new test method from ASTM. As a member of ASTM, Metrohm partnered with the industry to develop method D8045, a thermometric titration standard that addresses these challenges while improving analysis time and reagent expenditure.

Figure 1. ASTM D8045 was developed using the Metrohm 859 Acidity Analyzer.

What is thermometric titration?

Rather than measuring a potential difference, thermometric titration uses a sensitive thermistor device to detect the enthalpy change in an endothermic or exothermic reaction initiated by the constant dosing of a titrant. Much like traditional titration techniques, when the targeted unknown sample species have been neutralized by titrant, the endpoint is indicated at the point of excess titrant. While enthalpy changes down to ±0.001°C are detectable due to the high resolution and fast response time of the sensor, some applications benefit from the use of a catalytic indicator to make the titration endpoint apparent. Thermometric titration improves upon traditional titration techniques with a maintenance-free sensor that requires no calibration, no reference solution, and minimal total sample volume. Solvent resistant construction makes the sensor unaffected by difficult samples or harsh solvents.

Accurate evaluation of thermometric titration data requires algorithms unique from other types of titration (i.e., potentiometric and conductometric). Up to 30-times more data is collected for thermometric measurements compared to potentiometric. Metrohm instrument algorithms filter out noise to produce a smooth curve with a single, well-defined endpoint (Figure 2).

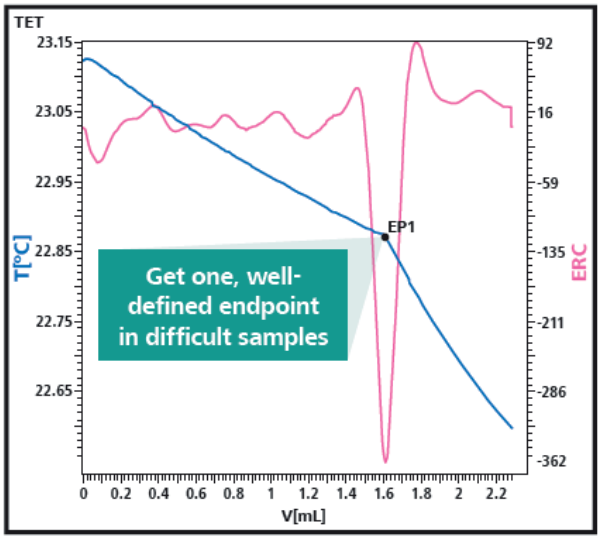

Figure 2. Typical thermometric acid number titration curve demonstrating a single, well-defined endpoint.

Acid number: Thermometric vs. Potentiometric

There are several benefits to performing acid number analysis using thermometric titration. Thermometric acid number by ASTM D8045 eliminates solubility challenges by using a solvent mixture of xylene and 2-propanol in a ratio designed to adequately disperse difficult crude oils. This optimized solvent mixture allows for a 75% reduction in solvent used for acid number analysis, creating an instant cost per analysis improvement. The average laboratory running 20 samples per day saves approximately $30,000 annually in solvent expense alone.

In addition to material savings, thermometric titration guarantees laboratory efficiency gains over potentiometric titration. Thermometric titration time averages around 60 seconds or less while potentiometric titrations can require more than 3X the time for the same sample. Additionally, potentiometric method D664 requires electrode cleaning and regeneration time while thermometric titration via D8045 requires no additional sensor regeneration. See a full method comparison in Table 1.

Table 1. Comparison of acid number techniques.

Parameter	ASTM D664 (Potentiometric)	ASTM D8045 (Thermometric)
Titrant	0.1 mol/L KOH in IPA	0.1 mol/L KOH in IPA
Solvent	Toluene/IPA/water	Xylene/IPA
Solvent volume	120 mL	30 mL
Titration time	~220 s	~60 s
Conditioning of electrode	3-5 min	None
Sensor maintenance	Solvent wash, rehydration, IPA dip, refill with electrolyte, store in LiCl in ethanol	Solvent wash is sufficient
Sample size (expected AN of 0.05–1.0 mg KOH/g)	20 ± 2 g	~10 g

Improve commerce and prevent corrosion

According to petroleum industry leaders, thermometric acid number by D8045 offers the highest accuracy for analysis of acid number in crude oil and refinery fractions.2 The benefits to this accuracy are actualized in both improved commerce and corrosion prevention.

In refinery operations, quick decisions based on accurate acid number must be made to prevent corrosive damage to valuable infrastructure. For example, the catalytic cracking units combine high temperature, pressure and expensive catalyst to convert heavy vacuum gas oil fractions into revenue generating gasoline products. Quick acid number assessment using D8045 allows for adjustment of expensive acid inhibitor chemicals and catalyst to prevent unexpected damage from the presence of corrosive acids. A shutdown in this process is one example in which quick acid number results can save the refinery millions of dollars.

With the crude and petroleum product prices weighing heavily on acid number, ASTM D8045 is the only internationally approved standard for evaluating acidity in both of these product types. By solving sample solubility and acidity accuracy issues, this thermometric method offers increased agreement between buyers and sellers of petroleum products and is a recommended standard to add to these agreements.

Future of thermometric titration

For the first time, the industry has control of its most valuable testing parameter. Metrohm's partnership with the ASTM to develop method D8045 and the acceptance of thermometric titration as an international standard opens the door for the adoption of other standards where reduced solvent toxicity, increased accuracy, and faster analysis times are desperately needed.

Labs analyzing total base number by today's approved standard, ASTM D2896, are faced with using higher volumes of toxic solvents such as chlorobenzene. Application research has been completed to document how thermometric titration can be leveraged to bring reduced solvent toxicity, consumption and faster titration times to total base number analyses.3 Industry demand within ASTM will be the driving force behind the adoption of thermometric titration for determination of total base number.

References

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WP-013EN, published October, 2016

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