Determination of Acid Number (AN) with Titration and NIR Spectroscopy

Iris Kalkman and
Andreas Agerer

The acid number (AN) is a measure for the quality of oils and their potential to enhance corrosion. When analyzing fresh, unused oils, the AN is used to ensure the specified quality from the manufacturer, whereas for used oils the AN is determined to observe its increase until a critical level is reached. Although it is generally assumed that the AN correlates to the corrosive potential of the oil, this is not exactly correct, as it is the change of the AN value which indicates this issue. Therefore it is necessary to determine the AN on a regular basis. Several standards already exist to determine AN via titration methods, however it is also possible to measure this parameter via spectroscopic (NIRS) methodology. No matter which technique you choose, Metrohm has you covered with high-performance instruments suitable for these published norms.

Metrohm International Headquarters; Herisau, Switzerland

Determination of the AN according to ASTM standards

Determination of the acid number is normally done according to ASTM D664 via potentiometric titration with potassium hydroxide (KOH) in isopropanol as the titrant. A new ASTM standard released in 2017, ASTM D8045, describes the thermometric titration of the AN value.

The results obtained from either type of titration may be used for the method development and subsequent routine analysis with near-infrared spectroscopic (NIRS) technology according to ASTM E1655.

Potentiometric titration according to ASTM D664

In potentiometric titration, potential changes during the titration are measured by an electrode system. In case of AN, a combined pH electrode suitable for non-aqueous media is used. The equivalence point is indicated by an inflection of the titration curve. The advantage of this method is the possibility to distinguish between the concentrations of stronger and weaker acids within a single sample.

For the analysis, the oil is dissolved in a solvent mixture of toluene, isopropanol, and water, and afterwards is titrated with KOH in isopropanol. The detection of the equivalence point is done by indication with a non-aqueous electrode (e.g., Solvotrode easyClean). More than one equivalence point may occur as the acid compounds present in the oil may have different acid dissociation constants. Accordingly, the calculation of the acid number is performed with the last occurring equivalence point.

Figure 1. Potentiometric titration

Thermometric titration according to ASTM D8045

Thermometric titration is a technique based on the fact that every titration produces a reaction enthalpy which leads to a difference in temperature of the titration mixture. When analyzing the AN, the reaction enthalpy is not large enough, and a catalyst must be used. This enhances the reaction enthalpy of the titration. The advantage of this method is the fast analysis time in comparison to potentiometric titration. Additionally, the solvent mixture allows a better dissolution of some oils (e.g. crude oil).

For this method, the oil sample is dissolved in a mixture of anhydrous isopropanol with mixed xylenes and then titrated after an addition of paraformaldehyde (the catalyst) with KOH in isopropanol. The endpoint is indicated with a thermistor, which is a very accurate type of thermometer. Only one endpoint is obtained with this type of titration, as first all the acidic components react, followed by the catalyst. Only the reaction enthalpy of the KOH with the catalyst is high enough to accurately monitor the change in temperature.

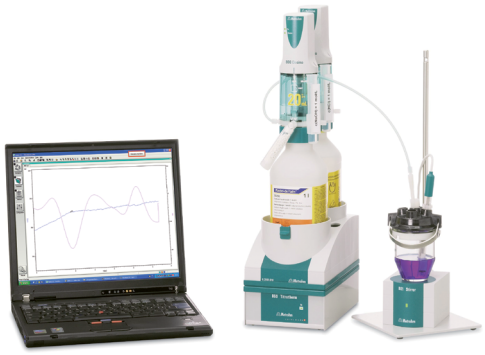


Figure 2. Thermometric titration

Results

These different methods of titration could lead to slightly different reported AN values, as the technique itself is not the same. This difference is not discussed further here, but rather in our other related White Paper: **Metrohm WP-012** "*Avoid corrosion: A new method for TAN determination in crude oil and petroleum products*".

Measuring AN via near-infrared spectroscopy (NIRS)

Near-Infrared Spectroscopy (NIRS) uses the NIR segment of the electromagnetic spectrum to induce molecular vibrations in the sample structure. The detection of these overtones and combination vibration bands provides information about the sample chemistry and physical parameters. This spectral information can be used for either qualitative or quantitative analysis.

For quantitative determinations, a prediction model is necessary, which links the spectral information to the results obtained from primary methods such as titration. These models are built with the help of chemometric software packages. After validation is completed, the models can be used to measure AN in routine analysis independent of the primary method.

Compared to the primary method, NIRS achieves results with similar accuracy, yet without the need of sample preparation and in less time. In addition to AN analysis, further parameters can be determined with a single measurement. This white paper illustrates how the combination of NIRS and titration achieves higher sample throughput in routine analysis.

Data Acquisition

For the analysis of liquid samples, Metrohm offers cuvettes and disposable glass vials. Cuvettes are available with a small path length, so even highly absorbing samples can be accurately measured. Flow cell cuvettes offer the possibility to automate measurements, further increasing sample throughput. For convenient sample handling, disposable vials are recommended, as their use eliminates the need for a separate cleaning step.

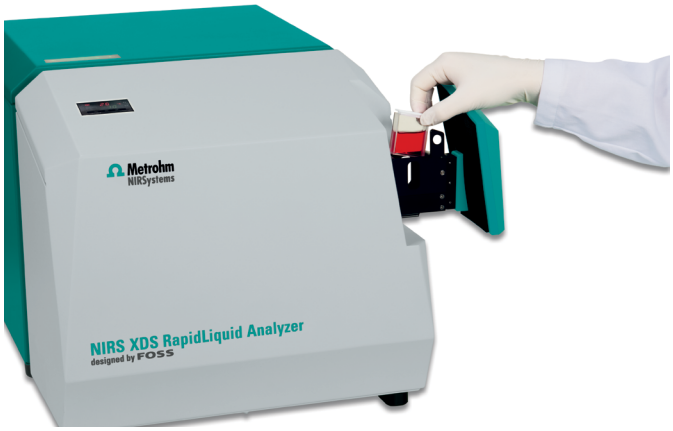


Figure 3. Data acquisition with the NIRS XDS RapidLiquid Analyzer

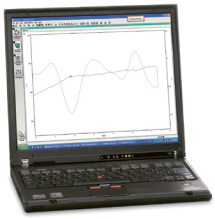
Since temperature fluctuations have a large influence on the measured NIR spectrum, it is crucial that the instrument maintains a stable temperature during data acquisition. Metrohm NIR instruments continuously monitor the temperature during the measurement to provide the most reliable results.

Method development

The combination of AN values obtained by titration and the acquired NIR spectra of the same samples enables the development of a prediction model. The Vision Air 2.0 complete package uses well-established Partial Least Squares (PLS) algorithms, and the logical software structure helps to easily develop a model. After validating robustness of the model, it is ready to use for routine analysis.

Easy to use NIRS routine analysis

Vision Air 2.0 includes a straightforward routine software that allows even unskilled users to be successful from the beginning. Only two clicks are required to select the method and start the analysis. Prior to the sample measurement, automatic internal wavelength standardization measurements are performed. Within 60 seconds from the start of the measurement, the acid number is displayed, and if required, an indication is shown regarding whether the sample is within user defined limits.



Summary

NIRS is an easy to use analysis tool, while titration gives you ultimate confidence in the results. It is clear that both techniques offer unmatched performance when it comes to AN determination.

Metrohm analyzers are highly versatile and find use in QC, R&D, and the production lab environment. Different accessories for both instruments enable AN determination for nearly all oil types.

Benefit now from our extensive experience with titration instruments and our convenient to use NIRS lab analyzers, to bring your laboratory to the next level.

WP-053EN by Metrohm, published 12-2019

Contact: info@metrohm.com

Metrohm