Fully automated determination of TAN/TBN in industrial samples according to ASTM standards D 664 and D 2896

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Titration

Summary

As manifested by the numerous standard procedures used all over the world, the determination of the total acid number (TAN) and total base number (TBN) of petroleum products is crucial for quality control in the oil industry. These parameters provide invaluable information regarding petroleum degradation (oil aging) as well as the corrosion enhancement properties and alkaline buffer capacity of the material.

The standards ASTM D 664 and ASTM D 2896 describe two simple methods for the determination of TAN and TBN based on potentiometric titration of the acidic and basic constituents, respectively. Despite being relatively simple, these procedures, if carried out manually, are time-consuming and labor-intensive. Further drawbacks are the handling of toxic solvent mixtures and the tedious cleaning of oil-smeared beakers and electrodes.

The 864 Robotic Balance Sample Processor allows to circumvent these drawbacks. The fully automated and computer-controlled TAN/TBN determinations include weighing, solvent addition, waiting times for complete dissolution and optimized electrode conditioning procedures between samples, as well as convenient collection of all data in a sophisticated database. Results are available within minutes and even very low TAN/TBN values can be determined with reproducibilities better than 2%.

Introduction

Depending on age and storage conditions, petroleum products can contain acidic or basic constituents that are either present as additives or as oxidation products that formed by oil degradation during service. The relative amount of these materials defines the oil quality and can be determined by titration with bases or acids.

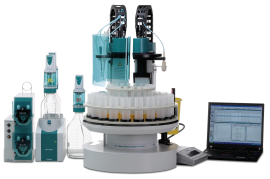
The acid/base number is a measure of the amount of acidic/alkaline substances in the oil. In quality control of lubricating oil formulations, TAN/TBN are determined as standard parameters. While the acid number is the number of mg KOH required to neutralize 1 g sample, the base number is the amount of basic components, expressed as mg KOH, that is contained in 1 g sample.

Depending on the sample, the titration equipment needs a special cleaning and conditioning procedure between individual samples to get rid of sticky oil components. A fully automated system guarantees that these steps are always carried out in the same way to ensure optimum accuracy and reproducibility.

This work describes the automated determination of TAN/TBN in industrial samples according to ASTM D 664 and ASTM D 2896.

Instrumentation

- 864 Robotic Balance Sample Processor
- 809 Titrando
- 800 Dosinos
- Precisa XR 205 A (balance)



Sample preparation and analysis

The 864 Robotic Balance Sample Processor is a fully automated system for determining the total acid or base number in oils. It performs both the preparation of the sample and the determination as such.

- A small amount of sample is put into a beaker and placed on the sample rack.
- All relevant analysis data such as pipetting volume, position and identification of the sample is entered into the sample data table of the ***tiamo***™ software.
- A 10-mL pipetting tip is used to aspirate the amount of sample given in the sample data table.
- The titration beaker is set to tare and the sample is added, after which the used pipetting tip is discarded.
- The weighed sample is transported to the second work station where 60 mL of solvent mixture is added.
- Using the 809 Titrando and the Solvotrode the TAN resp. TBN value is determined by titration with the appropriate titrant.
- At the end of the titration the beakers are emptied and the titration cell equipment is cleaned fully automatically. Depending on the sample an additional cleaning step in the external washing station (option) can be carried out.

Weighing on the sample rack

The patented technique of weighing the sample directly on the rack is unique. There is no simpler way to prepare a sample – just position it and press START. All other steps are carried out fully automatically by the system. This includes taring of the titration beaker as well as transferring the correct sample amount. This technique significantly improves the accuracy and reproducibility of the results.

Calculation

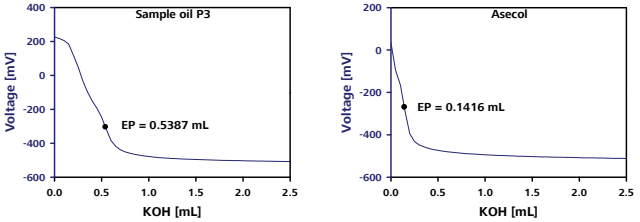
$$\text{TAN / TBN [mg KOH / g sample]} = \frac{(EP1 - Blank) \times Conc. \times 56.106 \times Titer}{\text{Sample size}}$$

EP1:	Titrant consumption up to last endpoint in mL	56.106:	Molecular weight of KOH in g/mol
Blank:	Possible blank value of titrant in mL	Titer:	Titer of the titrant used (dimensionless)
Conc.:	Concentration of the titrant used	Sample size:	Sample size in g

TAN determination

Solvent	Electrolyte	Titrant
Toluene : isopropanol : water 500 495 5	0.4 mol/L TEABr* in ethylene glycol	0.1 mol/L KOH in ethanol/methanol

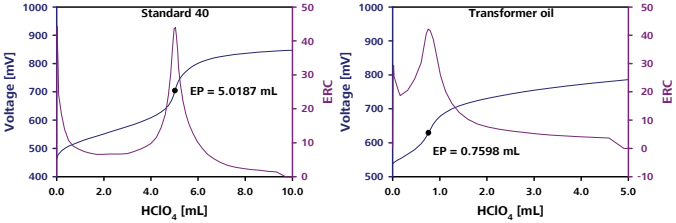
*Tetraethylammonium bromide



	Sample weight [g]	TAN determination no. [mg KOH/g sample] 1	2	3	4	5	Mean	RSD [%]
Oil P3	~15	0.1877	0.1867	0.1885	0.1848	0.1855	**0.1866**	**0.0412**
Asecol	~19	0.0405	0.0406	0.0417	0.0411	0.0419	**0.8157**	**1.5327**

TBN determination

Solvent	Electrolyte	Titrant
a) 1:1 glacial acetic acid : toluene b) 1:2 glacial acetic acid : chlorobenzene	~2 mol/L LiCl in ethanol	0.1 mol/L $HClO_4$ in glacial acetic acid



	Sample weight [g]	TBN determination no. [mg KOH/g sample] 1	2	3	4	5	Mean	RSD [%]
Standard 40	~0.7	39.3472	39.3805	39.3805	-	-	**39.3694**	**0.0488**
Transformer oil	~7.0	0.5625	0.5566	0.5715	0.5507	0.5489	**0.5580**	**1.6535**

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