

Thermo. Titr. Application Note No. H-088

Title: Automated determination of Total Acid Number in oils

Scope: Automated determination of Total Acid Number in new and used lubricating oils and crude oils using the 814 USB Sample Processor

Principle: Dissolve oil sample in mixture of toluene and 2-propanol, add paraformaldehyde and titrate with 0.1 mol/L or 0.01 mol/L KOH in propan-2-ol. The endpoint is indicated by an endothermic response caused by the base-catalyzed depolymerization of paraformaldehyde.

Reference:

1. M. J. D. Carneiro, M. A. Feres Júnior, and O. E. S. Godinho. Determination of the acidity of oils using paraformaldehyde as a thermometric end-point indicator. *J. Braz. Chem. Soc.* **13** (5) 692-694 (2002)

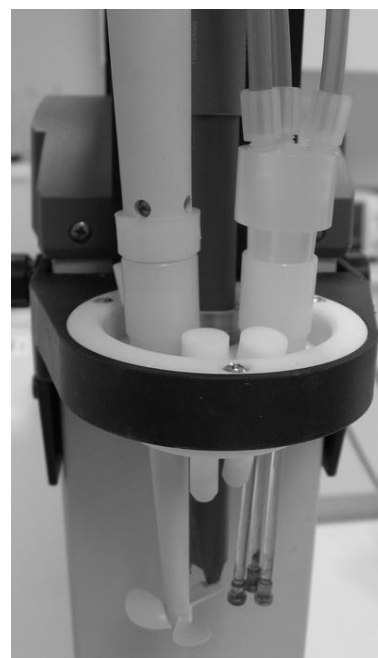
Reagents: 0.1 mol/L KOH in propan-2-ol (standardized)
Paraformaldehyde (eg, Sigma-Aldrich cat. no. 158127)
75% A.R. toluene: 25% A.R. propan-2-ol

Equipment List:

	859 Titrotherm	2.136.0010
	Thermoprobe	6.9011.020
	Dosino, 10 mL	2.800.0010
	Dosino, 50 mL	2.800.0050
	802 Propeller rod stirrer for 804	2.802.0040
	814 USB Sample Processor	2.814.0030
	Sample rack, 14 place	6.2041.370
	Macro titration head	6.1458.040
	3-way stopper	6.1453.210
	Long SGJ sleeve (2 required)	6.2709.060
	Intermediate SGJ sleeve	6.2727.010

**Equipment List
(cont.)**

Polypropylene cup, 100 mL (medical specimen cup, fits holes perfectly in 6.2041.370 rack, H = 74 mm, top i.d. = 56.5 mm, bottom i.d. = 45 mm

**Titration head setup:**

Note the use of the long SGJ sleeve with the 3-way stopper, a combination of long SGJ sleeve and intermediate SGJ sleeve with the 802 stirrer. The tips of the Thermoprobe guards have been trimmed to reduce the protection to the thermistor element to about 1.5 mm. The Thermoprobe is placed as close to the stirrer blades as possible without touching. The length of the titrant inlet tubes has also been reduced, so that they too are as close to the stirrer blades as possible. This was done by removing the anti-diffusion tips, and cutting the tubes squarely with a very sharp blade (e.g., a new scalpel blade). After re-forming the ends of the tubes to a round shape, the anti-diffusion tips are refitted.

Method:
Basic Experimental Parameters:

Titrant delivery rate (mL/min.)	8 (0.1 mol/L KOH)
Titrant delivery rate (mL/min)	15 (0.01 mol/L KOH)
No. of exothermic endpoints	1
Data smoothing factor	55
Maximum dose (mL)	5
Stirring speed (802 stirrer)	15
Solvent pre-dose (mL)	35
Pre-dose rate (mL/min)	40
Delay before start after pre-dose (secs.)	30

Create a Titrotherm titration program which incorporates the above parameters

Automation Program "Dip Rinse"

Step	Command	Parameters
1	Goto Current Sample	1
2	Move Head	231
3	Run Method	
4	Goto Sample	0,14
5	Move Head	231
6	Stirrer Start	15
7	Wait	15
8	Stirrer Stop	
9	Move Head	1

Sample Preparation

According to the oil type, weigh accurately approximately 2-5 g of oil into a 100 mL polypropylene beaker. Add ~0.5-0.6 g paraformaldehyde (*a level 1/8th kitchen teaspoon measure is ~ 0.5 g*). Place in the sample rack of the 814 USB Sample Processor.

Titration Program

It is critical that the solvent is added just before the titration commences. Performance of the paraformaldehyde deteriorates, if left in contact with the dissolved sample too long before titrating. To avoid poor results, solvent and paraformaldehyde should not be added to the oil sample

prior to placing in the sample rack. Titrate to an inflection characterized by a reduction in temperature.

Determination of titration blanks.

Titration blanks should be determined separately for each type of oil under analysis, e.g., crude oil, engine oil, hydraulic oil. For a particular oil type, weigh at least 5 samples of oil into beakers. For example, for the oil sample reported here, a range of 6 masses from approximately 0.8 – 2 g in approximately 0.25 g increments was used. After adding paraformaldehyde, the weighed samples were put in the sample rack and titrated automatically.

Standardization of KOH.

It has been shown that extremely precise calibrations can be performed, if a Dosino is used to dispense aliquots of benzoic acid in favour of using manual pipetting. Individual titration methods were constructed to automatically pre-dose 1, 2, 3, 4 and 5 mL of 0.1 mol/L benzoic acid. These methods were then specified in the automation set-up. Titration vessels containing 0.5 g paraformaldehyde only were placed in the sample rack. The required 35 mL of 2-propanol solvent was pre-dosed automatically.

Example:

Used oil sample submitted by major oil company

Automated titration with 814 USB Sample Processor:

TAN = 5.33±0.13 mg KOH/g sample (n=7)

(Comparison: result by “semi-auto” (no sample processor)

TAN = 5.48±0.16 mg KOH/g sample (n=7)

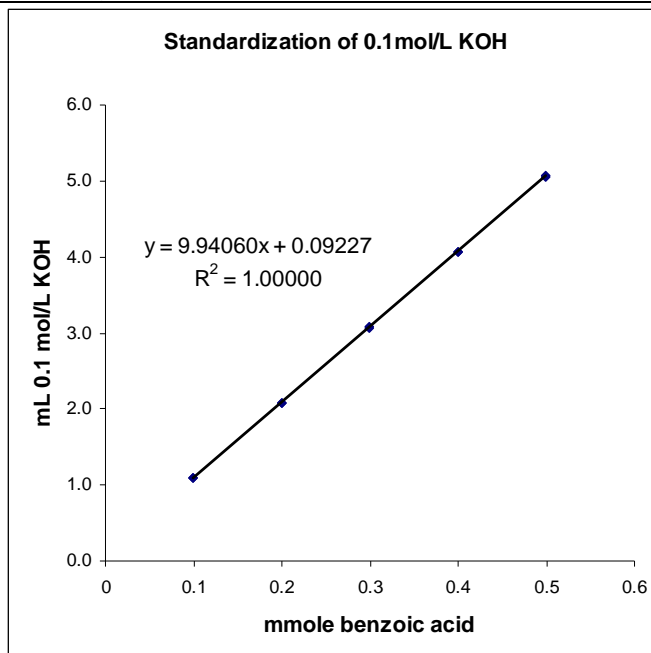
Calculation:

$$\text{TAN} = \frac{((\text{titre, mL} - \text{blank, mL}) \times \text{MKOH} \times 56.11)}{\text{sample mass, g}}$$

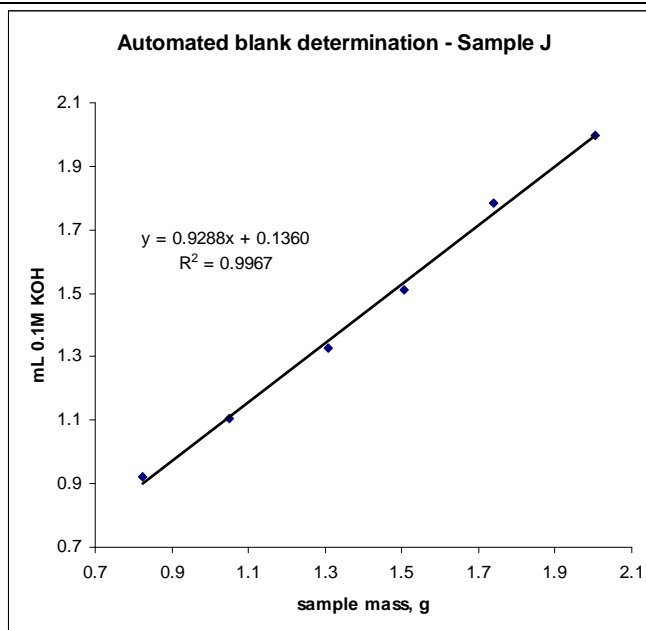
Titration standardization: Molarity = 1/gradient = 0.1006 mol/L

Titration results using
814 USB Sample
Processor:

mmole benzoic acid	mL 0.1 mol/L KOH
0.1000	1.088
0.1000	1.088
0.2000	2.079
0.2000	2.080
0.3000	3.072
0.3000	3.073
0.4000	4.068
0.4000	4.067
0.5000	5.059
0.5000	5.069

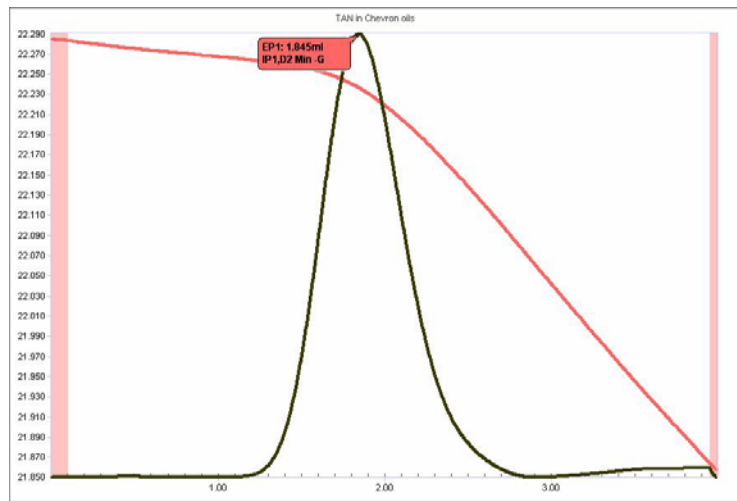


Titration blank determination:

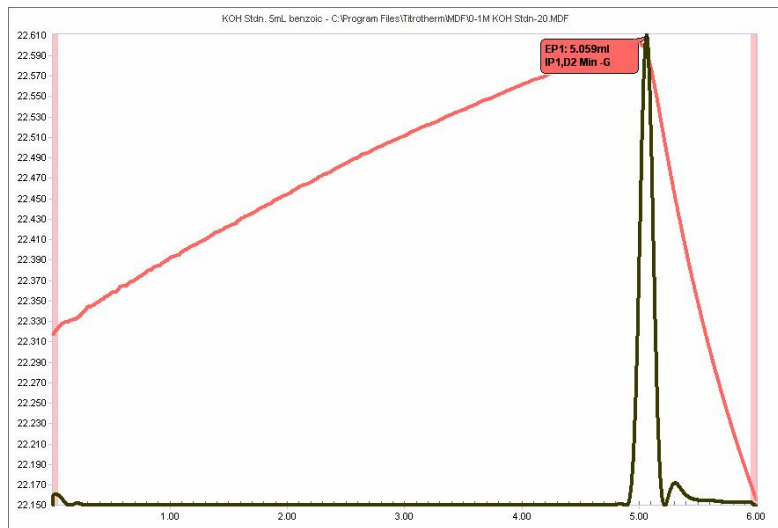


Thermometric Titration Plots:

Legend:
 Red = solution temperature curve
 Black = second derivative curve (for endpoints)



Automated titration of used oil sample using 814 USB Sample Processor



Automated titration of standard benzoic acid using 814 USB Sample Processor