



Apr 02, 2019

Working

## Determination of the total acid number (TAN) in crude oils

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Reservoir Fluids Characterization

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### ABSTRACT

#### Description

Titrimetric determination of total acid number (TAN) in crude oil. Protocol is applicable to crude oils of medium acidity (approximately 0.5 mg KOH/g). Sample and reagent volumes should be adjusted if the TAN value is expected to be outside of this range.

#### Instrumentation

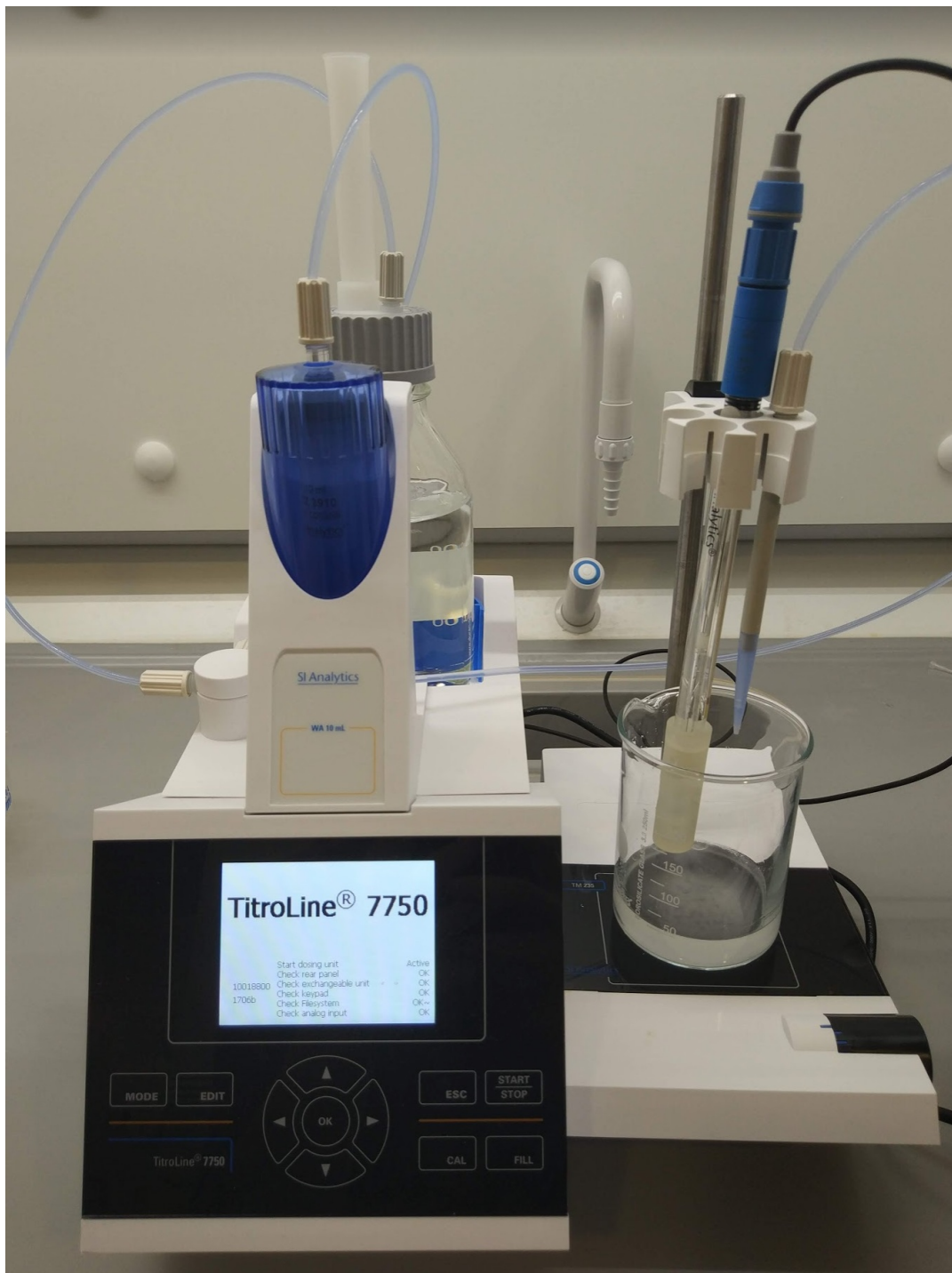
The analysis is carried out using a slightly modified version of ASTM 664 using a SI Analytics TitroLine 7750 (see attached documents for details of the original procedure).

#### Reporting

TAN values are reported in milligram of potassium hydroxide per gram of sample (mg KOH/g).

#### Quality control (QC) / system suitability test (SST)

A synthetic oil containing a mixture of C<sub>13</sub>, C<sub>15</sub> and C<sub>17</sub> linear fatty acids (in 80:20 hexadecane:toluene) corresponding to 0.5 mg KOH/g is prepared and analyzed with each batch (maximum 6 oils). The value should be within 10% of the true value.



SIA-ApNote-ASTM-664-  
Total-Acid-4477.pdf



QC\_TAN\_ASTM\_664\_31\_  
01\_19-10\_58\_53.pdf

#### PROTOCOL STATUS

#### Working

We use this protocol in our group and it is working

## MATERIALS

NAME ▾	CATALOG # ▾	VENDOR ▾
2-Propanol	190764	Sigma Aldrich
Hexadecane	H6703	Sigma Aldrich
Toluene	1.07019	Sigma Aldrich
Potassium hydroxide	1.05012	Sigma Aldrich
Potassium hydrogen phthalate	1.04874	Sigma Aldrich
Tridecanoic acid	91988	Sigma Aldrich
Pentadecanoic acid	91446	Sigma Aldrich
Heptadecanoic acid	H3500	Sigma Aldrich

## SAFETY WARNINGS

## BEFORE STARTING

Check availability of the following standards and consumables:

- Titrant solution (6 g/L KOH in 2-propanol)
- Titration solvent (500:495:5 toluene:2-propanol:H<sub>2</sub>O)
- Potassium hydrogen phthalate
- Quality control sample (C<sub>13</sub>+C<sub>15</sub>+C<sub>17</sub> fatty acid in 80:20 hexadecane:toluene)
- Crude oil(s) (approximately 25 mL per sample)



For preparation of standards, select "Appendix Preparation of consumables and standards" under Setup below.

Dissolution of KOH in 2-propanol proceeds slowly; titrant solution should be prepared *one day in advance*.

## Setup

1 Assemble the titrator inside a ventilated fume-hood as samples are stored in open containers.

- Keyboard is optional, but highly recommended for entering of sample details.
- To store results as a PDF document, insert a USB memory stick (*without encryption*) into a USB-port in the back of the titrator. To avoid data loss, record results manually on paper.
- To ensure proper mixing, stirring should be used during all steps of the analysis. The stirrer bar should not touch the electrode, and spin at a low speed while stimulating proper mixing.



TitroLine 7750  
Titrator  
SI Analytics TL7750

step case

Analysis

**Prepare instrument for analysis**

- 2 The system is stored under H<sub>2</sub>O. Remove water bottle, and replace with bottle filled with a suitable amount of titrant solution (6 g/L KOH in 2-propanol).



Approximately 50 mL of titrant is used in calibration and blanking, followed by 5-6 mL per sample.


**3 Rinse syringe, tubing and pipette with titrant solution**


1. Click 'MODE'.
2. Select 'Rinsing'.
3. Place empty beaker under pipette.
4. Perform three consecutive rinses (10 mL each).
5. Discard titrant waste.

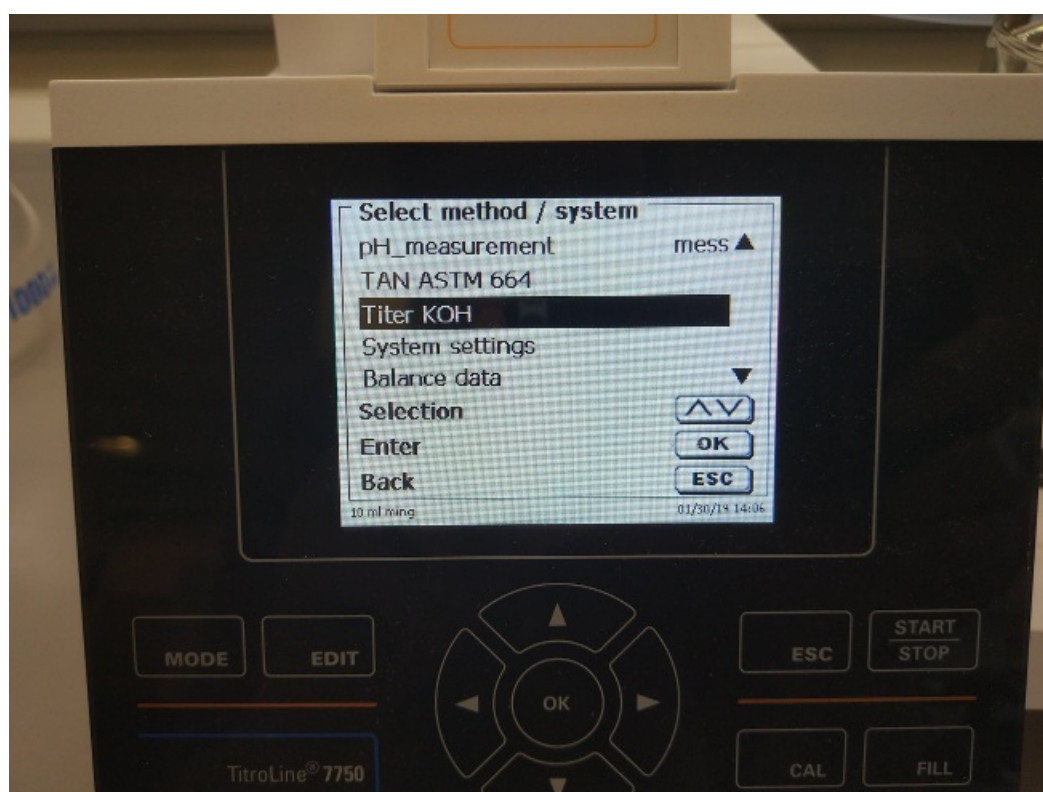
**4 Calibrate titrant solution against freshly prepared KHP (aq., 12 mM)**

1. Prepare three separate solutions of approximately 125 mg potassium hydrogen phthalate (KHP) in H<sub>2</sub>O (50 mL) in 100 mL beakers.  
*Record the exact mass to two decimals.*
2. Irrigate the beakers in a ultrasonic bath to facilitate dissolution.
3. When fully dissolved, place the first beaker on the titrator base.
4. Click 'MODE'.
5. Select 'Titer KOH'.
6. Click 'START'.
7. Enter the exact measured weight of KHP.
8. After the measurement is finished, discard the solution and rinse the electrode with water.

9. Repeat the calibration measurement on all three solutions. *The average value is automatically saved in the unit.*

 0.09 - 0.11 M (%RSD < 5)

 The experimentally measured value should be 0.1 M. A large deviation indicates an issue with either the titrant / KHP solution or instrument. Troubleshoot and continue when the issue has been identified and fixed.



## 5 Blank instrument against titration solvent (500:495:5 toluene:2-propanol:H<sub>2</sub>O)

1. Transfer 100 mL of titration solvent to a 250 mL beaker with a stirring rod.
2. Click 'MODE'.
3. Select 'Blank TAN-TBN'.
4. Click 'START'.
5. After the measurement is done, discard the solution and rinse the electrode with titration solvent, water and titration solvent again.
6. Repeat the blank measurement twice.

## 6 Validate instrument performance using QC sample

1. Weight 20 grams (approximately 25 mL) of QC sample in a 250 mL beaker with a stirring rod. *Record the exact mass to two decimals.*
2. Dissolve the sample in 100 mL of titration solvent.
3. Click 'MODE'.
4. Select 'TAN ASTM 664'.
5. Click 'START'.
6. Enter 'YYMMDD\_QC' as sample name.
7. After the measurement is done, discard the solution and rinse the electrode with titration solvent, water and titration solvent again.



0.5 mg KOH/g

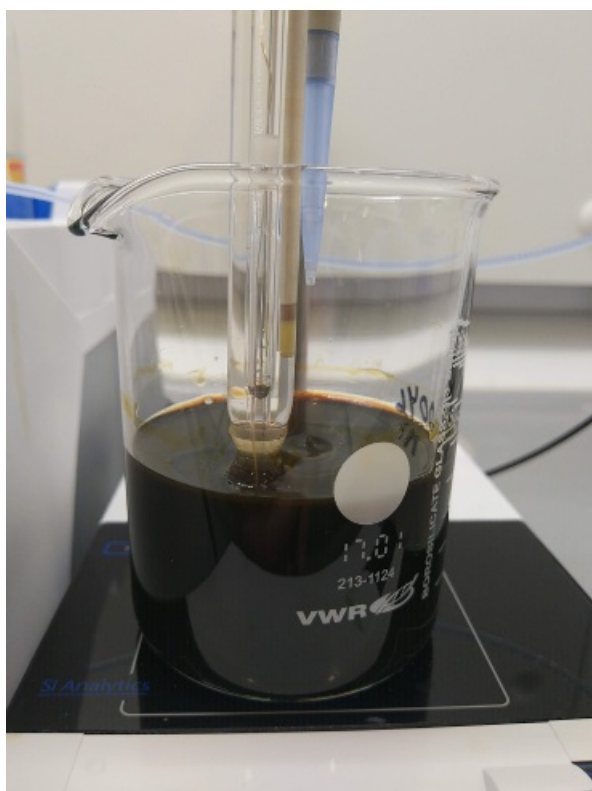


The measured value must be within 10% of 0.5 mg KOH/g. If the value deviates, identify the issue before continuing. See attached documents under protocol description for a example QC titration.

## Sample measurement

### 7 Determine TAN for crude oil(s)

1. Weight 20 grams (approximately 25 mL) of crude oil sample in a 250 mL beaker with a stirring rod. *Record the exact mass to two decimals.*
2. Dissolve the oil in 100 mL of titration solvent.
3. Click 'MODE'.
4. Select 'TAN ASTM 664'.
5. Click 'START' to start.
6. Enter weight, date and sample information.
7. After the measurement is done, discard the solution and rinse the electrode with titration solvent, water and titration solvent again.
8. Repeat until all samples have been measured.



## Finishing

- 8 When all samples have been measured, proceed with the following steps to prepare the instrument for storage:
  1. Rinse electrode with titration solvent and water. If any (semi)-solid material have deposited on the electrode, remove it *carefully* using a lint-free Kimwipe.
  2. Remove the titrant bottle and replace with bottle containing freshly prepared H<sub>2</sub>O (Milli-Q).

3. Place empty beaker under pipette.
4. Click 'MODE'.
5. Select 'Rinsing'.
6. Click 'START'.
7. Perform three consecutive rinses (10 mL each).
8. Turn off and disconnect system.

#### Titrant

step case

#### Appendix

Preparation of consumables and standards.

- 2 Measure 6.0 grams of potassium hydroxide (KOH) and transfer to a 1 L glass flask. Use a volumetric flask to measure 1000 mL of 2-propanol and transfer to the flask containing KOH. Stir overnight at room temperature. If the solution is cloudy or a precipitate is visible, filter through glass filter funnel. Label flask according to contents and date of preparation.



The solution has limited shelf-life, and should be used within a month or discarded.

#### Titration solvent

- 3 Measure 500 mL of toluene in a 500 mL volumetric flask and transfer to a 1 L glass bottle. Using a pipette, transfer 5.0 mL of de-gassed H<sub>2</sub>O (Milli-Q) to a 500 mL volumetric flask and top up with 2-propanol. Transfer contents to the toluene containing flask. Label flask according to contents and date of preparation.



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