Titration Application Note

# Automated Water Content Determination of Transformer Oils with InMotion KF

## Introduction

Transformer oil or insulating oil is an oil that is stable at high temperatures and has excellent electrical insulating properties.

Limits of 30 to 35 ppm of water in the transformer oil are generally referenced, as water affects the dielectric properties of the insulation and the aging rate of the insulating materials. Low water content in the transformer oil is therefore a very important parameter for safe operation, reliability and aging of a transformer. In the extreme case, transformers can fail because of excessive water in the insulation.

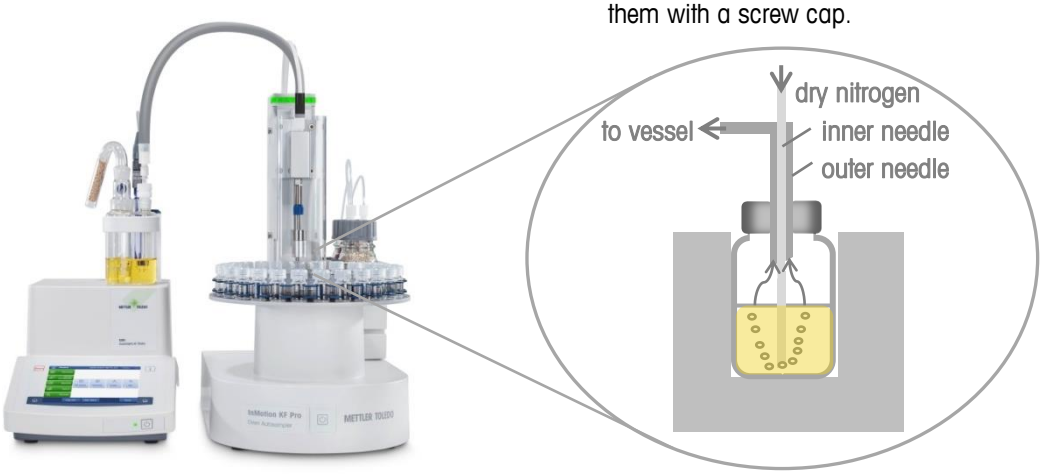
Karl Fischer titration coupled with an oven sample changer is a well-established and accurate technique for the determination of water in transformer oils.

In this application a coulometric C30S Karl Fischer titrator connected to an InMotion KF Pro was used to first perform a temperature scan of the different transformer oil samples in order to identify their ideal gas-phase extraction temperature and to subsequently measure their water content.

As air contains oxygen, which could react with organic samples, an inert gas (nitrogen) was used for the analysis of the transformer oil samples.

## Sample preparation and procedures

1. *Scan principle*: A sample with an unknown water gas-phase extraction temperature is heated with a constant heating rate from a defined start to a defined end temperature. The released water is monitored as function of temperature. The qualitative interpretation of the curve allows to identify the optimal gas-phase extraction temperature.
2. *Gas-phase extraction principle*: Nitrogen from a gas cylinder was used as the purge gas. The two-stage pressure regulator should be used so that the final pressure is in the range of 0.5 – 1 bar. The nitrogen is then passed by a gas stop valve through a drying unit filled with silica gel and subsequently through a drying unit filled with molecular sieve. The nitrogen will transfer the water into the titration cell.
3. *Long Needle:* Use the long needle that is available for the 10 mL vial size for the sample analysis. This long needle will allow purging through the lubricant and, thus, liberating all water from it.
4. *Blank preparation*: Apart from the water in the sample, the sample vial also contains atmospheric humidity; This makes blank value determination necessary.
   Place three empty 10 mL blank vials into positions 1 – 3 of the InMotion KF and close them with a screw cap.



5. *Sample preparation*: Add ~ 6.0 g of the transformer oil sample into a 10 mL vial and close it with the screw cap. Place all filled vials into the corresponding positions of the InMotion KF rack.
6. *Start of analysis*: Place an empty vial into the drift position on the rack. Start M746. The method will first perform a pretitration to remove excess water from the titration cell and will subsequently go into the Standby modus. Perform manual drift determinations until the online drift value is < 5 µg/min. Then press "Start sample". Alternatively you can also select "Automatic" as analysis start and define the "Drift stability" accordingly. The analysis will automatically start as soon as the online drift is below the defined value. The method will usually start with the following sequence: Drift – Blank – Sample. In most cases the drift is determined once before the sample loop and this drift value is used for all subsequent calculations.

## Chemistry

Water, M = 18 g/mol.

$ROH + SO_2 + 3\ RN + I_2 + H_2O = (RNH)\bullet SO_4\ R + 2\ (RNH)I$

## Solutions

- **Chemicals**: 100 mL HYDRANAL® Coulomat AG Oven.
- **Standard**: 1 % oven water standard
- **Sample**: Transformer oils

## Instruments and accessories

- Compact line titrator C30S, titration cell without diaphragm (30252662)
- Titration Excellence T7 (30252675) or T9 (30252676) with coulometric Karl-Fischer kit (30267113)
- XPE205 Analytical balance (30087653)
- InMotion KF Pro Oven Autosampler with 10 mL rack (30407502)
- Gas stop valve SV2 (30407442)
- LabX software
- Spatula

## Results

*Scan:*

For best results, the gas-phase extraction temperature needs to be high enough to ensure fast and complete water release. However, if the measurement temperature is too high organic molecules are liberated by decomposition and react with the titrant (i.e. with iodine), ultimately leading to an overestimation of the water content.
A major increase in drift, i.e. cumulative water content at high temperature is an indication of decomposition. For the investigated transformer oil samples decomposition started between 150 to 210 °C. Optimal gas-phase extraction temperature (oven temperature) was chosen approx. 30 °C below the decomposition temperature.

*Water content determination*:

Water content determination of the NYTRO transformer oil sample at an oven temperature of 170 °C and a measurement time of 600 s:

| | R2: Water content<br>Blank: [µg], NYTRO Sample: [ppm] |
|---|---|
| Blank 1 | 38.6 |
| Blank 2 | 35.7 |
| Blank 3 | 41.4 |
| 1 | 8.67 |
| 2 | 9.34 |
| 3 | 8.43 |
| 4 | 7.45 |
| 5 | 8.62 |
| **Mean** | 8.50 ppm |
| **s** | 0.68 ppm |
| **srel** | 8.013 % |

Oven temperature, measurement time and water content of three transformer oil samples:

| | Oven T | Time | Water content | | |
|---|---|---|---|---|---|
| | [°C] | [s] | Mean [ppm] | s [ppm] | srel [%] |
| NYTRO | 170 | 600 | 8.50 | 0.68 | 8.013 |
| T22 | 120 | 600 | 23.27 | 0.83 | 3.561 |
| T400 | 145 | 600 | 61.24 | 0.73 | 1.184 |

## Remarks

Coulometric reagents have a limited water capacity. Water capacity of the HYDRANAL® Coulomat AG Oven is 700 mg $H_2O$ per 100 mL reagent.

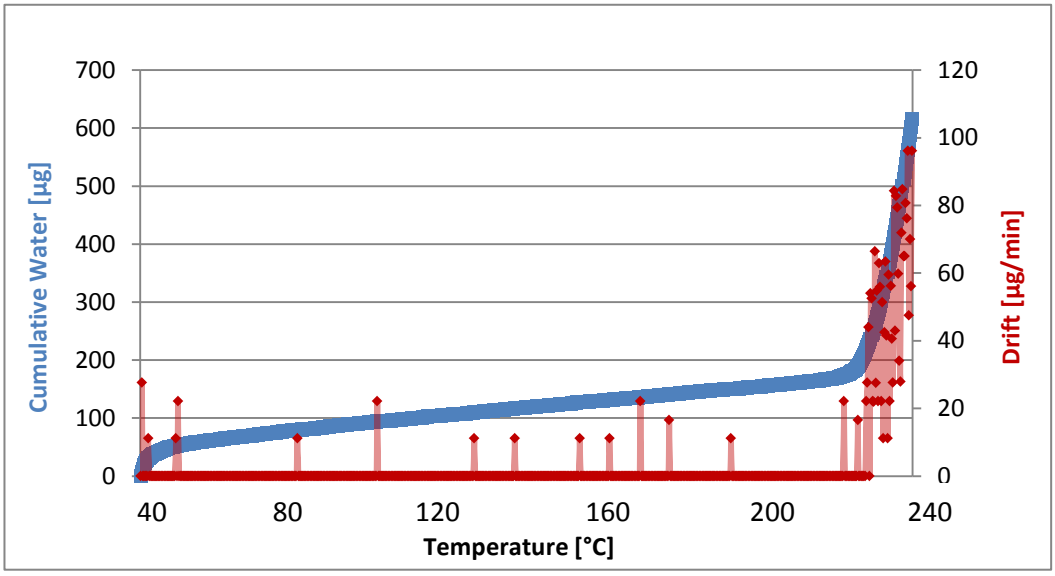
## Waste disposal and safety measures

Dispose as organic solvent

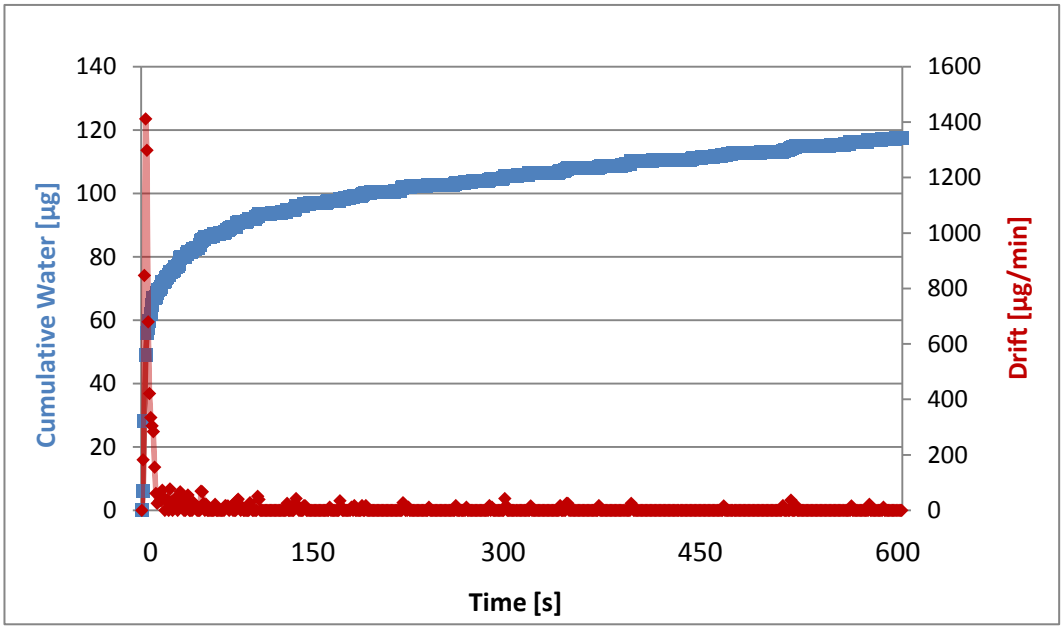
## References

http://www.mt.com/global/en/home/products/Laboratory_Analytics_Browse/Product_Family_Browse_titrators_main/automated-titration-systems/KF-oven-autosampler.html

## Measured values




Scan NYTRO sample




Water content determination NYTRO sample 1/5

| Consumption mC | Meas. value mV | $H_2O$ µg | Drift µg/min | Time s |
|---|---|---|---|---|
| 0.0 | 340.3 | 0.0 | 0 | 0 |
| 64.7 | 334.2 | 6.0 | 182.2 | 1 |
| 300.3 | 290.9 | 28.0 | 846.1 | 2 |
| 522.6 | 177.2 | 48.8 | 1411.2 | 3 |
| 597.2 | 118.1 | 55.8 | 1297.6 | 4 |
| 616.7 | 118.7 | 57.6 | 679.7 | 5 |
| 637.7 | 124.6 | 59.5 | 420.5 | 6 |
| 663.2 | 118.4 | 61.9 | 334.3 | 7 |
| 694.6 | 112.5 | 64.8 | 304.6 | 8 |
| 717.0 | 99.7 | 66.9 | 283.2 | 9 |
| 717.1 | 101.2 | 66.9 | 155.2 | 10 |
| 718.8 | 104.9 | 67.1 | 60.9 | 11 |
| 732.3 | 105.3 | 68.4 | 25.4 | 12 |
| | | | | |
| 1255.8 | 96.5 | 117.2 | 0 | 594 |
| 1255.8 | 97.5 | 117.2 | 0 | 595 |
| 1255.8 | 103.1 | 117.2 | 0 | 596 |
| 1257.3 | 101.7 | 117.4 | 0 | 597 |
| 1257.4 | 101.7 | 117.4 | 0 | 598 |
| 1257.4 | 101.6 | 117.4 | 0 | 599 |
| 1257.6 | 97.1 | 117.4 | 0 | 600 |
| 1257.6 | 99.9 | 117.4 | 0 | 600 |

NYTRO sample 1/5

# Method

## 001 Title

| | |
|---|---|
| Type | InMotion KF Coul. |
| Compatible with | C30S / T7 / T9 |
| ID | M746 |
| Title | NYTRO |
| Author | Administrator |
| Date/Time | 11/07/2017 04:07:23 pm |
| Modified on | 11/07/2017 04:07:23 pm |
| Modified by | Administrator |
| Protect | No |
| SOP | None |

## 002 Drift determination

| | |
|---|---|
| Wait time | 60 s |
| Duration | 3 min |

## 003 Sample (Blank)

| | |
|---|---|
| **Sample** | |
| Sample type | Blank |
| Number of IDs | 1 |
| ID 1 | Blank |
| Entry type | Fixed pieces |
| Pieces | 1 pcs. |
| Weight per piece | 1.0 g |
| Correction factor | 1.0 |
| Temperature | 25.0 °C |
| Analysis start | Manual |

## 004 Titration stand (InMotion KF)

| | |
|---|---|
| Type | InMotion KF |
| Titration stand | InMotion KF/1 |
| Temperature ramp | No |
| Oven temperature | 170 °C |
| Source for drift | Determination |
| Max. start drift | 10 µg/min |
| Carrier gas source | InMotion KF |
| Flow rate | 80 mL/min |
| Transfer tube heating | No |

## 005 Mix time

| | |
|---|---|
| Duration | 60 s |

## 006 Titration (KF Coul) [1]

| | |
|---|---|
| **Sensor** | |
| Type | Polarized |
| Sensor | DM143-SC |
| Unit | mV |
| Indication | Voltametric |
| Ipol | 5.0 µA |
| **Stir** | |
| Speed | 45 % |
| **Control** | |
| End point | 100.0 mV |
| Control band | 250.0 mV |
| Rate | Normal |
| Generator current | Automatic |
| **Termination** | |
| Type | Delay time |
| Delay time | 10 s |
| Min. time | 600 s |
| Max. time | 600 s |

## 007 Calculation R1

| | |
|---|---|
| Result | InMotion blank value |
| Result unit | µg |
| Formula | R1=(ICEQ/10.712-TIME*DRIFT)/C |
| Constant C = | 1 |
| Decimal places | 1 |
| Result limits | No |
| Record statistics | Yes |
| Extra statistical functions | No |

## 008 End of sample

## 009 Record

| | |
|---|---|
| Summary | Yes |
| Results | No |
| Raw results | No |
| Resource data | No |
| Method | No |
| Series data | No |

## 010 Blank

| | |
|---|---|
| Name | Blank IMKF Coul |
| Value B= | Mean[R1] |
| Unit | µg |
| Limits | No |

## 011 Sample

| | |
|---|---|
| **Sample** | |
| Sample type | Sample |
| Number of IDs | 1 |
| ID 1 | NYTRO |
| Entry type | Weight |
| Lower limit | 0.0 g |
| Upper limit | 5.0 g |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Temperature | 25.0 °C |
| Entry | Arbitrary |

## 012 Titration stand (InMotion KF)

| | |
|---|---|
| Type | InMotion KF |
| Titration stand | InMotion KF/1 |
| Temperature ramp | No |
| Oven temperature | 170 °C |
| Source for drift | Determination |
| Max. start drift | 10 µg/min |
| Carrier gas source | InMotion KF |
| Flow rate | 80 mL/min |
| Transfer tube heating | No |

## 013 Mix time

| | |
|---|---|
| Duration | 60 s |

## 014 Titration (KF Coul) [2]

| | |
|---|---|
| **Sensor** | |
| Type | Polarized |
| Sensor | DM143-SC |
| Unit | mV |
| Indication | Voltametric |
| Ipol | 5.0 µA |
| **Stir** | |
| Speed | 45 % |
| **Control** | |
| End point | 100.0 mV |
| Control band | 250.0 mV |
| Rate | Normal |
| Generator current | Automatic |
| **Termination** | |
| Type | Delay time |
| Delay time | 10 s |
| Min. time | 600 s |
| Max. time | 600 s |

### 015 Calculation R2

| | |
|---|---|
| Result | Cont. blank comp. (B in µg) |
| Result unit | ppm |
| Formula | R2=(ICEQ[2]/10.712-TIME[2]*DRIFT-B[Blank IMKF Coul])/(C*m) |
| Constant | C = 1 |
| Decimal places | 3 |
| Result limits | No |
| Record statistics | Yes |
| Extra statistical functions | No |

### 016 End of sample

### 017 Record

| | |
|---|---|
| Summary | Yes |
| Results | No |
| Raw results | No |
| Resource data | No |
| Method | No |
| Series data | No |

## Method (Scan)

### 001 Title

| | |
|---|---|
| Type | Scan KF Coul. |
| Compatible with | C30S / T7 / T9 |
| ID | Scan |
| Title | Scan NYTRO |
| Author | Administrator |
| Date/Time | 04/25/2017 11:05:28 am |
| Modified on | 04/25/2017 11:05:28 am |
| Modified by | Administrator |
| Protect | No |
| SOP | None |

### 002 Sample

| | |
|---|---|
| **Sample** | |
| Sample type | Sample |
| Number of IDs | 1 |
| ID 1 | NYTRO |
| Entry type | Weight |
| Lower limit | 0.0 g |
| Upper limit | 5.0 g |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Analysis start | Manual |
| Entry | Arbitrary |

### 003 Titration stand (InMotion KF)

| | |
|---|---|
| Type | InMotion KF |
| Titration stand | InMotion KF/1 |
| Max. start drift | 10 µg/min |
| Carrier gas source | InMotion KF |
| Flow rate | 80 mL/min |
| Transfer tube heating | No |

### 004 Mix time

| | |
|---|---|
| Duration | 20 s |

### 005 Titration (KF Coul) [1]

| | |
|---|---|
| **Sensor** | |
| Type | Polarized |
| Temperature sensor | DM143-SC |
| Unit | mV |
| Indication | Voltametric |
| Ipol | 5.0 µA |
| | |
| **Temperature program** | |
| Start temperature | 40 °C |
| Heating rate | 2 °C/min |
| End temperature | 240 °C |
| | |
| **Stir** | |
| Speed | 35 % |
| | |
| **Control** | |
| End point | 100.0 mV |
| Control band | 250 mV |
| Generator current | automatic |

### 006 Calculation R1

| | |
|---|---|
| Result | Sample size |
| Result unit | g |
| Formula | R1=m |
| Constant C= | 1 |
| M | M[None] |
| z | z[None] |
| Decimal places | 4 |
| Result limits | No |
| Record statistics | Yes |
| Extra statistical functions | No |

**007 Record**

| | |
|---|---|
| Summary | Per sample |
| Results | Per sample |
| Raw results | Per sample |
| Table of meas. values | Yes |
| Sample data | Per sample |
| Resource data | Per sample |
| $H_2O$ - T | Yes |
| Drift - T | Yes |
| $H_2O$ - T & Drift - T | Yes |
| Method | Yes |
| Series data | Yes |

**008 End of sample**

**009 Record**

| | |
|---|---|
| Summary | Yes |
| Results | Yes |
| Raw results | Yes |
| Resource data | Yes |
| Method | Yes |
| Series data | Yes |