Comparison of Water Standards for The Volumetric Karl Fischer Titration

Karl Fischer (KF) Titration is the method of choice for the determination of the water content in a vast variety of samples such as pharmaceuticals, petrochemical products, plastics, foods, and beverages. Compared to other analytical methods, KF titration is a simple, quick and unexpensive technique to selectively determine the water amount present in a sample.

Appropriate instrument qualification, calibration and maintenance procedures ensure correct measurement results. The qualification procedure of the titration instrument guarantees customers the accuracy, precision, and uptime in their daily workflow. In particular, the verification of the needed accuracy and precision of the KF titration using certified water standards is the mandatory step to complete the instrument verification.

In this application, this step is performed for the volumetric KF titration using two commonly used water standards, i.e., the 1% liquid water standard and the solid water standard di-sodium tartrate di-hydrate (15.66% water content). Both standards are titrated in two different KF solvents in combination with the 5 mg/mL one-component KF titrant.



Figure 1: The Compact Volumetric KF Titrator V30S is fully controlled by the LabX Laboratory Software.



Introduction

The Karl Fischer titration takes place in a solution mainly consisting of an alcohol, sulfur dioxide, and an organic base. The exact reagent composition used for KF titration influences the speed and accuracy of the analysis. This leads to a continuous development of KF reagents, which helps to further improve the water content determination in terms of accuracy, stability, simplicity, safety, and environmental acceptability.

This application describes the content determination in two certified water standards used to verify the equipment performance. Two different solvents were tested in combination with a 5 mg/mL one-component KF titrant.

Sample Preparation and Procedures

- 1. 50 mL of solvent is added into the titration cell.
- 2. After method start, the pretitration is automatically performed to remove residual water in the titration cell.
- Concentration determination: Approx. 1 g of a 1% water standard is added to the cell.
- Sample determination: Ca. 1 g of 1% water standard or 0.02–0.05 g sodium tartrate dihydrate, respectively is added to the cell.
- Two different methods were used: one with standard parameters (M300), and one with parameters optimized for fast titration.

Chemistry

 $\begin{array}{l} \mathsf{CH}_3\mathsf{OH} + \mathsf{SO}_2 + 3 \ \mathsf{RN} + \mathsf{I}_2 + \mathsf{H}_2\mathsf{O} \rightarrow \\ (\mathsf{RNH})\mathsf{SO}_4\mathsf{CH}_3 + 2 \ (\mathsf{RNH})\mathsf{I} \end{array}$

Analyte:

Water, H_2O , M = 18.02 g/mol, z = 1

Chemicals

• Titrant:

Aquagent[®] Complet 5, free from pyridine; c = 5 mg H_2O/mL (Scharlau, nr. AQ0015)

• Solvents:

- 1. Aquagent® Methanol, dried (ME0304);
- 2. Aquagent® Methanol Fast (nr. AQ0011)

• Water standards:

- 1. HYDRANAL[™] Water Standard 10.0 (34849)
- 2. apura® 15.66% Sodium tartrate dihydrate (1.06664)

Instruments and Accessories

- KF Compact Volumeter V20S/V30S or Titration Excellence T5/T7/T9 with KF Kit
- XP205 Analytical balance (11106027)
- Burette DV1005 5 mL (51107500)
- DM143-SC electrode (51107699)
- LabX software
- 10 mL Syringe (00071482)
- Weighing boats, 5 pcs (00023951)
- Spatula



Figure 2: The waste and solvent bottles of the Compact Volumetric KF Titrator V30S are equipped with the Level Sensor to automatically monitor the volume in both bottles.

Results

Overview:

- Two different KF solvents, i.e., Scharlau Methanol, dried and Aquagent® Methanol Fast were tested.
- Two commonly used water standards have been used as samples for the water content determination:
 - 1. Liquid water standard 10.0 mg/g
 - 2. Sodium tartrate dihydrate solid standard
- The concentration of the one-component titrant was first determined using the liquid water standard. A concentration determination was also performed with sodium tartrate to compare both standards.
- The titrations were performed using two methods with standard and fast control parameters [1, 2].

Concentration Determination and Titrant Stability:

The titrant concentration was determined by titrating series of six samples over one week to verify its stability. All results were in the range between 5.2 and 5.5 mg H₂O/mL, which was significantly higher than the nominal value of 5 mg H₂O/mL. Tests with sodium tartrate dihydrate confirmed these findings. These values are expected since the KF one-component titrant is always produced with a slightly higher concentration than then nominal value to increase the storage lifetime. The default lower acceptance limit of 4.5 mg H₂O/mL is therefore justified.

| Day 1 | | | Day 4 | | | Day 7 | | |
|-------------------------|--------------------------|--------|-------------|--------------------------|--------|-------------|--------------------------|--------|
| H ₂ O Std 10 | R1 | Sample | Na-tartrate | RI | Sample | Na-tartrate | R1 | Sample |
| | Concentration | Weight | | Concentration | Weight | | Concentration | Weight |
| | [mg H ₂ O/mL] | [g] | | [mg H ₂ O/mL] | [g] | | [mg H ₂ O/mL] | [g] |
| 1 | 5.462 | 0.8431 | 1 | 5.444 | 0.0590 | 1 | 5.320 | 0.0586 |
| 2 | 5.436 | 1.2018 | 2 | 5.449 | 0.0556 | 2 | 5.377 | 0.0548 |
| 3 | 5.456 | 1.2405 | 3 | 5.426 | 0.0552 | 3 | 5.425 | 0.0499 |
| 4 | 5.457 | 0.9109 | 4 | 5.418 | 0.0519 | 4 | 5.481 | 0.0498 |
| 5 | 5.461 | 1.4938 | 5 | 5.434 | 0.0543 | 5 | 5.493 | 0.0443 |
| 6 | 5.478 | 1.1356 | 6 | 5.442 | 0.0560 | 6 | 5.489 | 0.0457 |
| Mean | 5.458 | | Mean | 5.436 | | Mean | 5.431 | |
| S | 0.014 | | s | 0.012 | | s | 0.071 | |
| srel | 0.248% | | srel | 0.217% | | srel | 1.302% | |

Titration Application Note

Overview of All Results:

| | | | Standard P | arameter Me | thod | | | | | Fast Parame | eter Method | | | | | |
|------------------------|----------------|------------------------|------------|-------------|----------|---|-------|---------|---------------|-------------|-------------|----------|---|-------|---------|---------------|
| | | | average | s | srel (%) | = | STIR | E | TIME | average | s | srel (%) | ۲ | STIR | E | TIME |
| Water standard 10 mg/g | Methanol Dried | CONC (mg/mL) | 5.459369 | 0.027251 | 0.499 | 9 | 10 s | 1-1.5 g | 5.52-6.03 min | 5.481897 | 0.017369 | 0.317 | 9 | 10 s | 1-1.5 g | 2.95-3.83 min |
| 10.00 +/- 0.15 mg/g | | Sample (%) | 1.000 | 0.002 | 0.232 | 9 | 25 s | 1-1.5 g | 4.55-5.65 min | 1.006 | 0.003 | 0.335 | 9 | 10 s | 1-1.5 g | 2.20-2.85 min |
| (1.000 +/- 0.015 %) | | | | | | | | | | | | | | | | |
| | | | average | s | srel (%) | ۲ | STIR | | TIME | average | s | srel (%) | L | STIR | | TIME |
| | Methanol Fast | CONC 1 (mg/mL) | 5.199093 | 0.203556 | 3.915 | 9 | 10 s | 1-1.5 g | 2.47-3.10 min | 5.470506 | 0.022634 | 0.414 | 9 | 10 s | 1-1.5 g | 1.20-1.47 min |
| | | CONC 2 (mg/mL) | 5.458367 | 0.013685 | 0.251 | 9 | 10 s | 1-1.5 g | 2.91-3.17 min | | | | | | | |
| | | Sample 2.1 (%) | 1.001 | 0.004 | 0.398 | 9 | 25 s | 1-1.5 g | 3.00-3.58 min | 1.004 | 0.005 | 0.449 | 9 | 15 s | 1-1.5 g | 1.25-1.53 min |
| | | Sample 2.2 (%) | 1.000 | 0.003 | 0.259 | 9 | 25 s | 1-1.5 g | 3.27-3.48 min | | | | | | | |
| | | | | | | | | | | | | | | | | |
| | | | average | s | srel (%) | = | STIR | | TIME | average | s | srel (%) | E | STIR | ε | TIME |
| Na-tartrate dihydrate | Methanol Dried | | | | | | | | | | | | | | | |
| 15.66% | | Sample (Na-Tartrate) | 15.706 | 0.157 | 0.999 | 9 | 25 s | 0.02 g | 4.63-5.17 min | 15.471 | 0.161 | 1.038 | 9 | 15 s | 0.02 g | 2.52-2.65 min |
| (15.61-15.71 %) | | | | | | | | | | | | | | | | |
| | | CONC (Na-tartrate) | 5.424890 | 0.028196 | 0.520 | 9 | 120 s | 0.05 g | 6.58-7.90 min | | | | | | | |
| | | Sample (Na-tartrate) | 15.640 | 0.096 | 0.615 | 9 | 120 s | 0.05 g | 6.30-7.70 min | | | | | | | |
| | | | | | | | | | | | | | | | | |
| | | | average | s | srel (%) | = | STIR | | TIME | average | s | srel (%) | E | | E | TIME |
| | Methanol Fast | CONC | 5.465792 | 0.020419 | 0.374 | 9 | 10 s | 1-1.5 g | 3.12-3.33 min | 5.430755 | 0.070632 | 1.301 | 9 | 120 s | 0.05 g | 4.43-5.23 min |
| | | Sample 1 (Na-tartrate) | 15.641 | 0.152 | 0.971 | 9 | 25 s | 0.02 g | 2.67-2.90 min | 15.646 | 0.094 | 0.602 | 9 | 120 s | 0.05 g | 4.15-5.30 min |
| | | Sample 2 (Na-tartrate) | 15.746 | 0.149 | 0.947 | 9 | 25 s | 0.02 g | 2.62-2.95 min | | | | | | | |
| | | | | | | | | | | | | | | | | |
| | | CONC (Na-Tartrate) | 5.435483 | 0.011750 | 0.216 | 9 | 120 s | 0.05 g | 6.22-7.52 min | | | | | | | |
| | | Sample (Na-Tartrate) | 15.454 | 0.329 | 2.129 | 9 | 120 s | 0.05 g | 6.72-7.68 min | | | | | | | |

Remarks

Titration Time

- The water content determination was compared using standard control parameters [1] and optimized parameters for a faster titration [2].
- The results obtained with the faster method parameters show that the titration time can be shortened to approximately 50–60% of that achieved with the standard method.
- Note that the parameter TIME refers to the duration of a sample analysis from the end of standby mode to the end of the titration method function, thus including waiting for sample addition as well as the stir time before titration.

KF Titrant Stability

- The concentration determination has been repeated over seven days to monitor the stability of the KF titrant, i.e., how fast its concentration is decreasing with time.
- The results show that the KF titrant concentration is almost constant during seven days, independent of the water standard, the stir time, and the sample size.

Accuracy and Precision

- The accuracy of the standard method is better with the Methanol, dried solvent. On the other hand, the use of Methanol, fast solvent yielded even more accurate results with the adjusted method.
- The recovery of both water standards agrees well with the certified values, especially for the liquid water standard since the liquid standard is completely dissolved.
- On the other hand, di-sodium tartrate dihydrate has a limited solubility in methanol, i.e., approx. 150 mg in 50 mL methanol. Hence, the sample size was

reduced to 20 mg to enable a series of 6 samples in the same solvent. The rather small sample size may affect the precision of the determination since the relative weighing error is larger.

 Alternatively, when using a sample size of 50 mg, the KF solvent amount was increased to 100 mL–120 mL to accommodate 6 samples of sodium tartrate. Note that after 4 samples the KF solvent becomes turbid. This leads to a slightly lower repeatability.

Waste Disposal and Safety Measures

Wear personal protection at all times while in the laboratory, i.e., safety glasses, lab coats and gloves. Read and understand the appropriate MSDS's when using chemicals prior to use.

Dispose the sample solutions as non-chlorinated organic solvents.

Literature

- [1] "Concentration and Content Determination with Water Standard 10.0 mg/g", METTLER TOLEDO Titration Application no. M300.
- [2] "Volumetric Determination of Water Standard Samples in Different KF Solvents", METTLER TOLEDO Titration Application no. M794.

Further Information

Titrator Compact V30S - Overview - METTLER TOLEDO (mt.com)

Measured Values

Concentration Determination - Standard Method – Methanol Dried:

HYDRANAL[™] Water Standard 10.0



Figure 3: Karl Fischer E-t titration curve (blue) and accumulated water H₂O-t (grey) of 1% water standard sample in Methanol, dried (Series 01-sample 4/6, standard parameters).

| Time | Volume | Signal | H ₂ O | Drift |
|------|---------|--------|------------------|----------|
| [S] | [mL] | [mV] | [mg] | [µg/min] |
| 0 | 0.00000 | 608.2 | 0.0000 | 6.3 |
| 0 | 0.00000 | 608.1 | 0.0000 | 6.3 |
| 1 | 0.00075 | 608.9 | 0.0039 | 0.0 |
| 2 | 0.00200 | 608.8 | 0.0104 | 119.7 |
| 3 | 0.00350 | 608.7 | 0.0182 | 210.3 |
| 4 | 0.00475 | 608.6 | 0.0247 | 274.1 |
| 5 | 0.00625 | 608.6 | 0.0325 | 296.6 |
| | | | | |
| 61 | 0.18625 | 611.1 | 0.9683 | 1636.1 |
| 62 | 0.19225 | 611.0 | 0.9995 | 1659.3 |
| 63 | 0.19850 | 610.9 | 1.0320 | 1690.1 |
| 64 | 0.20450 | 610.9 | 1.0632 | 1931.5 |
| 65 | 0.21025 | 610.9 | 1.0931 | 1946.7 |
| 66 | 021675 | 611.5 | 1.1269 | 1985.7 |
| | | | | |
| 144 | 1.55075 | 94.9 | 8.0625 | 46.7 |
| 146 | 1.55075 | 90.7 | 8.0625 | 38.9 |
| 146 | 1.55075 | 85.2 | 8.0625 | 23.4 |
| 148 | 1.55075 | 85.2 | 8.0625 | 23.4 |
| 148 | 1.55075 | 84.5 | 8.0625 | 23.4 |
| 149 | 1.55075 | 93.6 | 8.0625 | 7.8 |

Method

Standard Parameters / Fast Method Parameters:

001 | Title

| Туре | KF Volumetric |
|-----------------|--------------------|
| Compatible with | V20S/V30S/T5/T7/T9 |
| ID | M886 |
| Title | KFVol 1-comp 5 |
| | |

002 | Sample

| Joumpie | |
|-----------------------|---------------------|
| Sample | |
| Number of IDs | 1 |
| ID 1 | |
| Entry type | Weight |
| Lower limit | 0 g |
| Upper limit | 5 g |
| Density [g/mL] | 1.0 |
| Correction factor | 1.0 |
| Temperature | 25.0 °C |
| Autostart | Yes |
| Entry | After addition |
| Concentration | |
| Titrant | Scharlau aquagent 5 |
| Nominal concentration | 5 mg/mL |
| Standard | Water-Standard 10.0 |
| Entry Type | Weight |
| Lower limit | 0 g |
| Upper limit | 2 g |
| Mix time | 10 s |
| Autosttart | Yes |
| Entry | After addition |
| Conc. Lower limit | 4.0 mg/mL |
| Conc. Upper limit | 5.6 mg/mL |
| End of Sample | - |
| Open series | Yes |

| 003 | Titration | stand |
|-----|-----------|-------|
| 000 | | Juliu |

| •• | | |
|----|------------------|-----------|
| | Туре | KF stand |
| | Titration stand | KF stand |
| | Source for drift | Online |
| | Max. start drift | 25 μg/min |

004 | Mix time

| Duration | 25 s / 15 s |
|----------|-------------|

005 | Titration (KF Vol) [1]

| Titrant | |
|-----------------------|---------------------|
| Titrant | Scharlau aquagent 5 |
| Nominal concentration | 5 mg/mL |
| Reagent type | 1-comp |

| Sensor | |
|-------------------------|------------------------|
| Туре | Polarized |
| Sensor | DM143-SC |
| mV | mV |
| Indication | Voltametric |
| Ipol | 24 μΑ |
| Temperature Acquisition | |
| Temperature Acquisition | No |
| Stir | |
| Speed | 35% |
| Predispense | |
| Mode | None |
| Wait time | 0 s |
| Control | |
| Endpoint | 100.0 mV / 80.0 mV |
| Control band | 400.0 mV |
| Dosing rate (max) | 5 mL/min / 15 mV/min |
| Dosing rate (min) | 80 µL/min / 400 µL/min |
| Start | Cautious |
| Termination | |
| Туре | Drift stop relative |
| Drift | 15.0 µg/min |
| At Vmax | 10.0 mL |
| Min. time | 0 s |
| Max. time infinite | Yes |

006 | Calculation R1 (Content)

| Result | Content |
|-----------------------------|----------------------|
| Result unit | % |
| Formula R1 = | (VEQ*CONC- |
| | TIME*DRIFT/1000)*C/m |
| Constant | C = 0.1 |
| Decimal places | 3 |
| Result limits | No |
| Extra statistical functions | No |
| Send to buffer | No |
| Condition | No |

007 | Calculation R2 (Titration duration)

| | , |
|-----------------------------|--------------------|
| Result | Titration duration |
| Result unit | min |
| Formula | R2 = TIME |
| Constant | C = 1 |
| Decimal places | 3 |
| Result limits | No |
| Extra statistical functions | No |
| Send to buffer | No |
| Condition | No |
| | |

008 | End of sample

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