Application Bulletin 424/1 e

Titer determination in volumetric Karl Fischer titration

Branch

All branches

Keywords

Titration; Karl Fischer titration; volumetric; titer; titer determination; water standard; sodium tartrate; water

Summary

This Application Bulletin provides information on the titer determination in Karl Fischer titration. It contains information on the types of water standards suitable for a titer determination as well as the correct handling of those standards.

The titer determination of Karl Fischer titrants is a necessary task as the titer can change due to atmospheric moisture. How often the titer needs to be determined mainly depends on the type of titrating agent used and how tight the equipment is.

In Karl Fischer titration, the titer has a unit which is mg/mL. The value determined in a titer determination corresponds to the milligrams of water which react with one milliliter of titrant.

Instruments

- Titrator with a mode for volumetric Karl Fischer titration
- Analytical balance (minimum resolution 0.1 mg)

Accessories

- Plastic or glass syringe and needle with a thickness of approx. 0.8 mm (for liquid standards)
- Glass weighing spoon (for solid standards)
- Plastic syringe with a volume of 1 mL and needle with a thickness of 0.3 to 0.4 mm (for pure water, by weight)
- Microliter syringe (for pure water, by volume)

Electrodes

Double Pt wire-electrode (indicator electrode for volumetric Karl Fischer titration)

Reagents

One- or two-component reagents can be used:

- Titrant for volumetric KF titration
- Solvent for volumetric KF titration

Standards

Liquid water standard	Water standard with certified water content (approx. 10 mg/g)
Solid water standard	Sodium tartrate dihydrate (Na tartrate) with an approximate water content of 15.6%
Pure water	Water can be used as standard

Handling of standard

Liquid water standard

1. Open the ampoule containing the standard as recommended by the manufacturer.
2. Aspirate approximately 1 mL of the standard into the syringe.
3. Take the tip of the needle out of the liquid and pull back the plunger to the maximal volume. Sway the syringe to rinse it with standard. Then eject the standard into the waste.
4. Aspirate the remaining content of the ampoule into the needle (in case air is aspirated, eject the air out of the syringe).
5. Remove excess liquid from the outside of the needle with a paper tissue.
6. Place the needle on a balance and tare the balance.
7. Then start the determination and inject a suitable amount of standard (see table 1 to 3) (not the whole content!) through the septum into the titration vessel. Please take care that the standard is injected into the reagent and not at the electrode or the wall of the titration vessel. This leads to unreproducible results.
8. After injecting the standard, place the syringe again on the balance.

9 Enter the injected sample weight in the software. For the next determination go ahead with step 6.

Repeat step 5 to 8 at least three times. If the complete content of an ampoule has been injected, the needle can be filled with fresh standard (same batch). In this case the needle does not need to be rinsed again. Start directly with step 4.

There are two possibilities to add liquid standard. It can be injected with the tip of the needle above the reagent level. In this case the last drop must be aspirated back into the syringe. Otherwise it is wiped off at the septum and might not be determined although the weight of it is taken into account.

If the needle is long enough, it can be immersed in the reagent directly. In this case there is no last drop and the needle can be pulled out of the titration vessel without aspirating back any liquid.

Solid water standard

1 Place the weighing spoon on the balance and tare the balance. Weigh in an appropriate amount of solid standard. Tare the balance again.

2 Start the titration, quickly remove the stopper with septum, add the solid standard and put the stopper back. When adding the standard, take care that no standard sticks to the electrode or the walls of the titration vessel. In case parts of the solid standard are not dissolved in the reagent, gently swirl the titration vessel to wash down the standard into the reagent solution.

3 After the addition of the standard, place the weighing spoon on the balance again.

4 Enter the added sample weight in the software.

Repeat step 1 to 4 at least three times.

Pure water

By weight

1 An insulin syringe is filled with water. Due to the very small amounts of pure water added for the titer determination, we recommend to use a very thin needle. This helps to add small sample sizes.

2 After filling the syringe, place the syringe on a balance and tare the balance.

3 Then start the titration and inject an appropriate amount of water through the septum into the titration vessel. Aspirate the last drop back into the syringe.

4 Then pull out the needle and place the syringe on the balance again.

5 Enter the sample weight into the software.

Repeat step 2 to 5 at least three times.

By volume

1 A microliter syringe is filled with an appropriate volume of water. Make sure that there are no air bubbles in the syringe. Air bubbles will falsify the result.

2 After filling the syringe, start the titration and inject the content of the syringe through the septum into the titration vessel.

3 Enter the added volume in the software.

Repeat step 1 to 3 at least three times.

Analysis

System preparation

Fill solvent into the titration vessel and make sure that the indicator electrode and the anti-diffusion tip of the buret are immersed properly in the solvent.

Load a method template for the titer determination. If necessary, modify the method according to your needs. Enter the calculation depending on the used standard (formula 1 or 2).

Start the conditioning and wait for the message “conditioning ok”. Then the system is ready for the first standard injection/addition. Please have a look at the following tables, which offer information on suitable standard sizes/volumes depending on the used buret size and titrant.

Titer determination

Table 1: Suitable sample sizes/volumes for different titrants for a 5 mL buret

	Titrant 1*	Titrant 2+	Titrant 5§
Water standard 5 mg/g	0.025-0.225 g	0.05-0.45 g	0.125-1.12 g
Water standard 10 mg/g	0.05-0.45 g	0.1-0.9 g	0.25-2.25 g
Na tartrate	-	0.02-0.057 g	0.03-0.27 g
Water (back weighing)	-	-	~ 0.02 g
Water (volume)	-	-	~ 20 µL

Table 2: Suitable sample sizes/volumes for different titrants for a 10 mL buret

	Titrant 1*	Titrant 2+	Titrant 5§
Water standard 5 mg/g	0.05-0.45 g	0.1-0.9 g	0.25-2.25 g
Water standard	0.1-0.9 g	0.2-1.8 g	0.5-4.5 g

10 mg/g			
Na tartrate	0.02-0.057g	0.02-0.115 g	0.03-0.287 g
Water (back weighing)	-	~ 0.02 g	~ 0.025 g
Water (volume)	-	~ 15 µL	~ 25 µL

Table 3: Suitable sample sizes/volumes for different titrants for a 20 mL buret

	Titrant 1*	Titrant 2+	Titrant 5§
Water standard 5 mg/g	0.1-0.9 g	0.2-1.8 g	0.5-4.5 g
Water standard 10 mg/g	0.2-1.8 g	0.4-3.6 g	1-9 g
Na tartrate	0.02-0.175 g	0.026-0.23 g	0.065-0.58 g
Water (back weighing)	-	0.02-0.35 g	0.02-0.09 g
Water (volume)	-	15-35 µL	15-90 µL

* Titrant 1: 1 mL of titrant reacts with approximately 1 mg H_2O

+ Titrant 2: 1 mL of titrant reacts with approximately 2 mg H_2O

§ Titrant 5: 1 mL of titrant reacts with approximately 5 mg H_2O

Calculation

Titer

By weight

$$\text{Titer} = \frac{m_{standard} \times w(standard)}{V_{EP}} \quad (1)$$

Titer: Titer of the selected titrant in mg/mL

$m_{standard}$: Mass of standard in g

w(standard): Certified water content of standard in mg/g (for pure water = 1000)

V_{EP}: Titrant consumption up to the end point in mL

By volume:

$$\text{Titer} = \frac{V_{standard} \times \rho \times w(standard)}{V_{EP}} \quad (2)$$

Titer: Titer of the selected titrant in mg/mL

$V_{standard}$: Volume of standard in mL

ρ: density of water in mg/mL

w(standard): Certified water content of standard in mg/g (for pure water = 1000)

V_{EP}: Titrant consumption up to the end point in mL

Table 4: Density of water at a pressure of 100 kPa (1 bar)

Temperature / [°C]	Density / [g/cm^3]
15	0.99910
20	0.99982
25	0.99705
30	0.99565
35	0.99404

Example

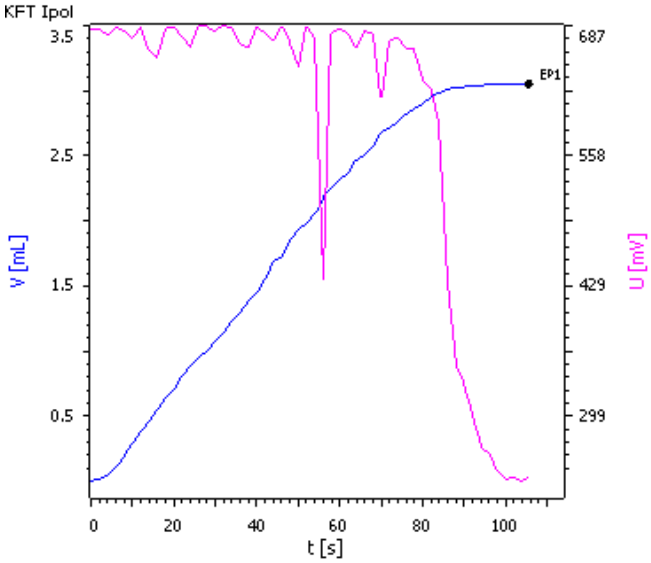

Figure 1: Titration curve of a titer determination with water standard 10 mg/g (blue = added volume of titrant in mL, pink = measured value in mV)

Comments

- Use fresh and certified water standards for the titer determination.
- Carry out the titer determination at the same temperature as the water content determination of the sample. A temperature increase of 1 °C results in a titer decrease of approximately 0.1%.
- Always aspirate the whole content of a liquid standard ampoule into the syringe. If this is not possible, give the remaining standard into the waste.
  In an open ampoule the standard will change its water content and lead to wrong results.
- The solubility of sodium tartrate dihydrate in methanol is poor. Therefore, the limit for the sample size mentioned in table 1 to 3 should not be exceeded.
- Due to the poor solubility of sodium tartrate dihydrate the solvent has to be exchanged frequently.
- When working with pure water and the determination of the sample size is done by weighing, it is essential that

a balance suitable for small weights is used. Otherwise the balance error can have a significant influence on the result.

- Usually the density of water is assumed to be 1, which is not absolutely true. In fact, the density of water depends on the temperature. The values in table 4 can be used to correct the sample size depending on the temperature.
- We recommend comparing titer values with the titer history of the same titrant bottle. If there are unexpected variations, the system needs to be checked.

Reference

- CRC Handbook of Chemistry and Physics (data of table 4)

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