Workshop 4

# Water Determination in Ethanol

## by Karl Fischer Titration

### Background

Water content is an important parameter for a wide range of processes (e.g. chemical reactions) and products (e.g. food products). Its determination in raw and finished products is therefore a standard method in many laboratories, often by means of Karl Fischer titration. This method is based on a selective reaction between water and the Karl Fischer reagent, ideally using an automated titrator. It has excellent precision, accuracy and selectivity, which can be achieved with a short analysis time for water contents from 100 % to a few ppms. Karl Fischer is the method recommended by international standards for different matrices in liquid, solid and even gaseous samples.

### Reaction

$$CH_3OH + SO_2 + 3\ C_3H_4N_2 + I_2 + H_2O \rightleftharpoons (C_3H_4N_2H)\cdot SO_4CH_3 + 2\ (C_3H_4N_2H)I$$

From this reaction it can be seen that water ($H_2O$) reacts with iodine ($I_2$) - in the presence of sulfur dioxide ($SO_2$), a base ($C_3H_4N_2$, imidazole) and methanol ($CH_3OH$) - attaining 1:1 stoichiometry.

### Safety

Karl Fischer titrant and solvent are toxic. Remember to follow general laboratory safety procedures. Always wear a lab coat, gloves and protective goggles during this workshop.

### Tasks

<u>1. Titrant concentration determination:</u>

Use an automated titrator to determine the concentration of the Karl Fischer one-component titrant with a nominal concentration of 5 mg/mL. Fill the titration vessel with 50 mL of dry methanol and start the titrant concentration determination. The pretitration is performed automatically; the titrator switches to standby mode as soon as it is finished. Wait for a low and stable drift (< 25 µg/min). Rinse a 10 mL syringe with 2 mL of certified water standard (10 mg/g) and then aspirate ca. 5 mL of this standard. Start the concentration determination on the titrator and inject about 1 mL of the water standard into the titration vessel. Use the back-weighing technique to determine the amount of sample injected:

1. Place the syringe containing the water standard on the balance.
2. Tare.
3. Start the concentration determination and inject the sample into the titration vessel through one of the vessel stoppers.

4. Place the syringe again on the balance. The amount of sample added into the titration vessel will be given on the balance as the negative weight.

5. Enter the weight into the titrator.

Wait until the titration is finished. The result will be displayed on the screen (or printed out). Repeat the concentration determination two times. The mean value, standard deviation (*s*) and relative standard deviation (*srel*) will be calculated automatically by the titrator.

2. Water content determination:

Calculate the optimal sample size from the estimated water content of the ethanol sample, such that about 20 mg of water are injected into the titration vessel. Start the titration. Note that this is a water content determination and not a concentration determination. Wait until the pretitration is finished and the drift in the standby mode is low and stable. Rinse the syringe with 1 mL of sample and then aspirate the amount of sample needed. Start the measurement and add the calculated amount of sample. Use the back-weighing technique as described above to determine the amount of sample injected.

Perform this analysis at least three times. The results (water content in %) mean value, standard deviation (s) and relative standard deviation (*srel*) will be displayed on the screen (or printed out).

Stop the titration and remove the solvent from the vessel.

## Waste disposal:

Collect all solutions and dispose of as organic solvents.

Teacher Information

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### Equipment

- 1x Analytical balance
- 1x Mettler-Toledo Easy KFV titrator with 10 mL burette, tubing, drying tubes, bottle heads and EasyPump for solvent replacement
- 1x EG43-BNC pH Electrode
- 1x Magnetic stirrer bars

### Chemicals

The quantities below were roughly estimated for 5 concentration determinations and 5 water content determinations.

- 200 mL of Karl Fischer one-component titrant 5 mg/mL
- 100 mL of dry methanol (for Karl Fischer titration)
- 10 mL of certified water standard 10mg/g
- 10 mL of ethanol containing about 1 % of water as sample
- 100 g molecular sieve

### Preparation

- Install the titrator and fill all drying tubes with fresh (or regenerated) molecular sieve.
- Rinse the burette of the automatic titrator with titrant at least twice to dispel any air bubbles trapped in the burette and tubing.

### Comments

- This method may be slightly adapted depending on the water content of the sample.

## Solution

1. Concentration determination:

Expected result:

The concentration of the titrant should be between 4.5 mg/mL and 5.5 mg/mL. Use fresh titrant if the concentration lies outside this limit.

2. Water content determination:

The optimum sample size of the titrant can be calculated by using the following formula:

$$m = \frac{m_{opt}}{R \cdot 10}$$

| | |
|---|---|
| *m:* | Optimum sample size (in g) |
| $m_{opt}$: | Optimum amount of water which should be put into the titration vessel (in mg, here: 20 mg) |
| *R:* | Expected water content for the sample (in %, here: 1 %) |
| *10:* | Unit conversion factor from % to mg/g (in mg/(g·%)) |

Expected result:

Depending on the sample the water content should be around 1 %.

## Example

<u>1. Concentration determination:</u>

Three concentration determinations were performed and the following titrant concentrations ($c$) were obtained for the three samples ($m$: Sample size):

| *Nr.* | *m* | *c* |
|---|---|---|
| 1 | 2.136 g | 5.1975 mg/mL |
| 2 | 1.783 g | 5.2089 mg/mL |
| 3 | 2.234 g | 5.2175 mg/mL |

The statistics for these results are:

Mean: 5.2080 mg/mL
*s*: 0.0100 mg/mL
*srel*: 0.19 %

<u>2. Water content determination:</u>

The optimum sample size was calculated using the following formula, estimating a water content of 1 % and an optimum amount of water of 20 mg. It is expected that around half of the burette volume will be used for this amount of water.

$$m = \frac{m_{\text{opt}}}{R \cdot 10} = \frac{20 \text{ mg}}{1 \% \cdot 10 \frac{\text{mg}}{\text{g} \cdot \%}} = 2 \text{ g}$$

The calulated sample size was used to measure the water content of ethanol three times. The following water contents (R) and statistics were obtained:

| *Nr.* | *m* | *R* |
|---|---|---|
| 1 | 2.136 g | 0.8753 % |
| 2 | 1.783 g | 0.8739 % |
| 3 | 2.234 g | 0.8761 % |

Mean: 0.8751 %
*s*: 0.0011 %
*srel*: 0.13 %