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# Determination of total water and surface water in sugars

Heinz-Dieter Isengard*, Petra Heinze

*University of Hohenheim, Institute of Food Technology, Garbenstraße 25, D-70593 Stuttgart, Germany*

## Abstract

A clear distinction between differently bound water fractions by drying techniques is usually not possible. The Karl Fischer titration was used to achieve such a differentiation. As this technique is based on a chemical reaction, water is only determined when it comes into direct contact with the reagents. Surface water can therefore be detected easily. To limit the determination to this fraction, dissolution of the sample must be avoided. If, on the contrary, the total water is to be determined, the sample must either be dissolved completely or measures must be taken to liberate the water from the sample matrix. The aim of this work was to find titration parameters and working conditions that allow the distinction between the total water content and the surface water of sugars.

*Keywords:* Sugars; Total water; Surface water; Karl Fischer titration

## 1. Introduction

Drying techniques do not determine the water content but the mass loss that a sample undergoes under the drying conditions applied. All the volatile substances contribute to this mass loss. A distinction between different water fractions is usually not possible (Rückold, Grobecker, & Isengard, 2000).

The most important method for water content determination is the Karl Fischer titration which is based on a selective chemical reaction:

$$\mathrm{ROH} + \mathrm{SO_2} + \mathrm{Z} \rightarrow \mathrm{ZH^+} + \mathrm{ROSO_2^-}$$

$$\mathrm{ZH^+} + \mathrm{ROSO_2^-} + \mathrm{I_2} + \mathrm{H_2O} + 2\mathrm{Z}$$
$$\rightarrow 3\mathrm{ZH^+} + \mathrm{ROSO_3^-} + 2\mathrm{I^-}$$

$$\text{Total reaction: } 3\mathrm{Z} + \mathrm{ROH} + \mathrm{SO_2} + \mathrm{I_2} + \mathrm{H_2O}$$
$$\rightarrow 3\mathrm{ZH^+} + \mathrm{ROSO_3^-} + 2\mathrm{I^-}$$

In commercial reagents, ROH is methanol or ethanol and Z is often imidazole. Different titration techniques exist. In the so-called two-component technique, the working medium (the "solvent" component) in the titration cell, in which the sample is placed, contains sulphur dioxide and the base dissolved in methanol or ethanol (Solvent E). The titrating solution (the "titrant" component) is a methanolic or ethanolic (Titrant E) solution of iodine. The consumption of iodine is measured.

Before introducing a sample into the working medium, the titration cell is titrated to dryness, it is "conditioned". After analysis, it is kept in this conditioning mode, which means that intrusive water is continuously titrated to make further analyses in the same working medium possible.

The exact water equivalent of the titrant component is determined by titrating known amounts of water.

For the end-point indication two platinum electrodes are submerged in the working medium. In the voltametric technique, they are polarised by a constant current. The voltage necessary to maintain this current is monitored. When the water of the sample is consumed, iodine can no longer react and the redox couple iodine/iodide is then present in the solution. This makes corresponding redox reactions at the electrodes possible, which leads the voltage to drop drastically. This indicates the end point. When the voltage remains below a certain chosen value for a chosen time, the analysis is stopped. This so-called stop delay time is important to allow the detection of water that may not be immediately available, particularly when the sample is not completely soluble and the water reaches the working medium with a certain delay. The end point may also be determined by using the so-called drift. Traces of water

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* Corresponding author. Tel.: +49-711-397-4670; fax: +49-711-397-4674.

*E-mail address:* isengard@uni-hohenheim.de (H.-D. Isengard).

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penetrate into the titration vessel from the exterior through tubes and joints. This rate can be measured before each analysis. Using this technique the determination is ended when the titration rate has reached the value of the drift or a value slightly higher.

## 2. Materials and methods

### 2.1. Materials

Sucrose I ("Kristallzucker", particle size 0.50–1.25 mm), Sucrose II ("Feinstraffinade", particle size 0.10–0.35 mm), D-fructose and α-D-glucose monohydrate were used. The sucrose samples and fructose were from Südzucker, Mannheim, Germany, and glucose from Riedel-de Haën, Seelze, Germany.

The titrator was a KF Titrino 701 (Metrohm, Herisau, Switzerland) with 5- or 10-ml burette, polarising current 50 μA, stop voltage 250 mV, end-point criterion: drift or stop delay time. Chemicals were all from Riedel-de Haën, Seelze, Germany.

### 2.2. General strategy

In the Karl Fischer method the water to be determined must come into direct contact with the reagents.

When total water content is to be determined, the sample should, in the ideal case, be soluble in the working medium. For other samples, several techniques exist to allow a practically complete liberation of the water (Isengard, 1995).

Such measures that are relevant for this investigation are:

- setting a minimal titration time, a so-called extraction time;
- setting of sufficiently long stop delay times;
- setting relatively low maximal titration rates;
- setting small minimal volume increments for reagent addition;
- working at higher temperatures; and
- adding solvents to the working medium to adapt the polarity to the sample.

When only the surface water is to be determined, the dissolution of the sample must be prevented. Therefore, opposite measures must be taken:

- short titration times;
- setting of a short or even no stop delay time;
- setting high maximal titration rates;
- setting higher minimal volume increments;
- working at lower temperatures; and
- adding solvents with an "inappropriate" polarity for the sample.

The difference between total water and surface water is included water.

## 3. Results and discussion

### 3.1. Determination of the total water content

The two-component technique was used, with Hydranal-Titrant 2 or Hydranal-Titrant 5 as titrating solution and Hydranal-Solvent:formamide 2:1 by volume as working medium; temperature was room temperature for fructose and glucose, 45 °C for sucrose; maximal titration rate: 5 ml/min; minimal volume increment: 1 μl for 10-ml burette, 0.5 μl for 5-ml burette; sample sizes: ~1.5 g for fructose and sucrose, ~0.25 g for glucose monohydrate.

The results are given in Table 1.

### 3.2. Determination of the surface water content

The two-component technique was used, with Hydranal-Titrant 2, Hydranal-Titrant 5 or Hydranal-Titrant 5E as titrating solution and Hydranal-Solvent (or Hydranal-Solvent E):chloroform 2:1 and 1:5 by volume as working medium; temperatures between 20 and −25 °C; maximal titration rate: 5 and 15 ml/min; minimal volume increment: 0.5 and 5 μl; sample size: ~5 g.

#### 3.2.1. Sucrose I (particle size 0.50–1.25 mm)

Table 2 shows the results of the surface water content determinations of sucrose I with a total water content of 0.0556±0.0021 g/100 g.

The values found, using one third of chloroform in the working medium, were significantly higher than those using five sixths. This higher amount is necessary to prevent traces of the sample from being dissolved. The stop criterion is less important, but titration times are shorter when a fixed stop delay time is used. The

Table 1
Water content (WC) of sugar samples, 10 replicates each, determined by Karl Fischer titration using different titrating solutions

| Titrating agent: | Titrant 2 | Titrant 5 |
|---|---|---|
| | WC [g/100 g] ; coefficient of variation | |
| Sucrose I (0.50–1.25 mm) | 0.0556±0.0021; 3.69% | 0.0552±0.0021; 3.86% |
| Sucrose II (0.10–0.35 mm) | 0.0469±0.0016; 3.47% | 0.0464±0.0023; 5.01% |
| Fructose | 0.0800±0.0018; 2.29% | 0.0803±0.0026; 3.29% |
| Glucose monohydrate | Not used | 8.839±0.016; 0.19% |

Table 2
Surface water content (SWC) of sucrose (particle size 0.50–1.25 mm), five replicates each, using different titration parameters, sample size 5 g

| Titration agent | Working medium (v/v) | Stop criterion | SWC (g/100 g) | Duration (s) |
|---|---|---|---|---|
| Titrant 2 | Solvent:chloroform 2:1 | Drift 5 μl/min | 0.0050±0.0006 | 19 |
| Titrant 2 | Solvent:chloroform 1:5 | Drift 5 μl/min | 0.0033±0.0004 | 21 |
| Titrant 2 | Solvent:chloroform 1:5 | Time 5 s | 0.0035±0.0004 | 13 |
| Titrant 5E | Solvent E:chloroform 2:1 | Drift 5 μl/min | 0.0043±0.0005 | 28 |
| Titrant 5E | Solvent E:chloroform 1:5 | Drift 5 μl/min | 0.0032±0.0003 | 21 |
| Titrant 5E | Solvent E:chloroform 1:5 | Time 5 s | 0.0034±0.0004 | 14 |

results obtained with methanol-based reagents are practically the same as those obtained with ethanol-based chemicals. The surface water content of 0.0034 g/100 g represents 6.1% of the total water content of 0.0556 g/100 g.

### 3.2.2. Sucrose II (particle size 0.10_0.35 mm)

Table 3 shows the results of surface water content determinations for sucrose II with a total water content of 0.0469±0.0016 g/100 g. As the particle size is smaller than that of sucrose I, the danger of dissolution during the titration is greater. Determinations were therefore also carried out at lower temperature.

No significant differences exist between the different methods. The temperature had no influence on the results, but for a slight prolongation of the titration times. The surface water content of 0.0054 g/100 g represents 11.5% of the total water content of 0.0469 g/100 g. It is higher than that of sucrose I with bigger particles and thus a smaller surface.

### 3.2.3. Fructose

Fructose has a higher solubility in methanol than sucrose. Titrations were also carried out at very low temperatures and the stop delay time, as well as a set extraction time, was varied.

Even at 0 °C and using a stop delay time of only 5 s, the total water content was found. The titration curves showed that the voltage dropped to the stop value after about 40 s for the first time. The stop delay was therefore set to 0 s, and, in order not to end the titration immediately after the start, an extraction time and thus a minimal duration of the titration was set (40 s). The temperature was varied. Previous experiments with water standards had shown that the electrical parameters (polarising current and stop voltage) had to be changed for very low temperatures. At 0 °C the usual combination 50 μA/250 mV can be applied, but at −10 and −20 °C the combination 40 μA/250 mV and at −25 °C the combination 35 μA/250 mV were used.

Table 4 shows the results of the surface water content determinations of fructose with a total water content of 0.0800±0.0018 g/100 g.

Lower temperatures (and lower solubility) lead to lower values of water content. A comparison of titration curves at −25 °C shows that the stop voltage is reached only slowly when Titrant 2 is used, resulting in longer determination times and probably a higher amount of fructose dissolved. The shape of the curve for Titrant 5 is better in this sense. In the case of the ethanol-based reagents the solubility of fructose is lower because of the lower polarity of the working medium. The stop voltage is obviously reached before the minimal duration of 40 s. The water content found is about 0.029 g/100 g and it is therefore the most reliable value.

### 3.2.4. Glucose monohydrate

Glucose monohydrate is even more soluble in methanol than fructose and contains one mole of water of crystallisation per mole. The theoretical content of 9.09 g/100 g is often not reached as most samples contain anhydrous glucose.

Table 5 gives the result for a sample of glucose monohydrate with a total water content of 8.839±0.016 g/100 g obtained with experimental parameters set with the experience from the previous experiments.

Table 3
Surface water content (SWC) of sucrose (particle size 0.10–0.35 mm), 10 replicates each, using different titration parameters, sample size 5 g, stop criterion: time 5 s

| Titration agent | Working medium (v/v) | Temp. (°C) | SWC (g/100 g) | Duration (s) |
|---|---|---|---|---|
| Titrant 2 | Solvent:chloroform 1:5 | 20 | 0.0051±0.0002 | 21 |
| Titrant 2 | Solvent:chloroform 1:5 | 10 | 0.0054±0.0003 | 28 |
| Titrant 5E | Solvent E:chloroform 1:5 | 20 | 0.0054±0.0002 | 27 |
| Titrant 5E | Solvent E:chloroform 1:5 | 10 | 0.0057±0.0007 | 34 |

Table 4
Surface water content (SWC) of fructose, 10 replicates each, using different titration parameters, sample size 5 g, stop criterion: time 0 s, extraction time: 40 s

| Titration agent | Working medium (v/v) | Temp. (°C) | SWC (g/100 g) | Duration (s) |
|---|---|---|---|---|
| Titrant 2 | Solvent:chloroform 1:5 | 0 | 0.0499±0.0012 | 48 |
| Titrant 2 | Solvent:chloroform 1:5 | −10 | 0.0487±0.0015 | 68 |
| Titrant 2 | Solvent:chloroform 1:5 | −20 | 0.0352±0.0013 | 54 |
| Titrant 2 | Solvent:chloroform 1:5 | −25 | 0.0357±0.0016 | 71 |
| Titrant 5 | Solvent:chloroform 1:5 | 0 | 0.0445±0.0012 | 40 |
| Titrant 5 | Solvent:chloroform 1:5 | −10 | 0.0345±0.0016 | 41 |
| Titrant 5 | Solvent:chloroform 1:5 | −20 | 0.0348±0.0016 | 42 |
| Titrant 5 | Solvent:chloroform 1:5 | −25 | 0.0330±0.0012 | 50 |
| Titrant 5E | Solvent E:chloroform 1:5 | 0 | 0.0382±0.0010 | 43 |
| Titrant 5E | Solvent E:chloroform 1:5 | −10 | 0.0345±0.0009 | 59 |
| Titrant 5E | Solvent E:chloroform 1:5 | −20 | 0.0298±0.0007 | 46 |
| Titrant 5E | Solvent E:chloroform 1:5 | −25 | 0.0289±0.0006 | 40 |

Table 5
Surface water content of glucose monohydrate and the used parameter set, 10 replicates, sample size 5 g

| | |
|---|---|
| Titrating agent | Titrant 5E |
| Working medium (v/v) | Solvent E:chloroform 1:5 |
| Temperature | −25 °C |
| Maximal titration rate | 15 ml/min |
| Minimal volume increment | 5 µl |
| Stop delay time | 0 s |
| Extraction time | 0 s |
| Average titration time | 10 s |
| Surface water content | 0.0146±0.0009 g/100 g |

## 4. Summary and conclusion

The total water content of sugars can easily be determined by the Karl Fischer titration. The working medium should contain formamide (one third of its volume). When the solubility is low, the temperature can be slightly elevated to accelerate the analyses.

For the determination of surface water content, an addition of chloroform (five sixths of the volume) is necessary. Ethanol-based reagents are advantageous. The lowering of the temperature to −25 °C is imperative for sugars with higher solubility. In case of highly soluble sugars the stop delay time must be set to 0 s and no extraction time should be programmed. In addition, the titration rate should be high and also the minimal volume increment should be increased.

## References

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