A working methodology for the total water determination in polysaccharide by the volumetric Karl Fischer titration: the case of inulin, a dietary fibre

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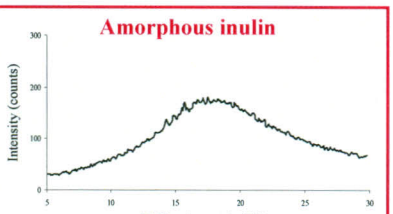
Introduction

In general, water content is determined by oven drying and does not correctly represent the water content of a sample. Indeed, high temperatures can induce the formation and the release of volatile substances (water and others), while water included in the crystals might or might not be completely detected. Moreover, due to the rapid adsorption of water on anhydrous material after oven drying, this technique presents poor reproducibility. The Karl Fischer (KF) titration is a well-established method for the water content determination. This technique allows the determination of the total water of a sample and is now the most important primary method for determining water content in foodstuffs. To determine the water content of a sample, it must be dissolved in the reaction medium, used as solvent. In some cases, the medium does not completely dissolve the sample. In order to increase solubility, some authors used an internal homogeniser, worked at elevated temperatures or modified the polarity of the working medium by adding further solvents to it. These methodologies using the KF titration present some inconveniences as not all titration devices are equipped with an internal homogeniser or a heatable titration vessel which limits the use of these techniques for wider applications. More so, at high temperature, possible evaporation of sulphur dioxide from the boiling working medium makes a reflux condenser necessary.

For these reason, we developed a suitable sample preparation for the total determination of water content and apply it to inulin, a selected dietary fibre. Inulin samples were analysed by KF titration using the usual method of introducing the powder directly in the methanol base working medium, modified or not by formamide (1:3, v/v) in order to increase sample solubility. In addition, an alternative methodology based on the introduction of an inulin solution in pure formamide was developed and compared to the standard KF titration. These methodologies were applied to two inulin sample which presented either an amorphous or a crystalline state.

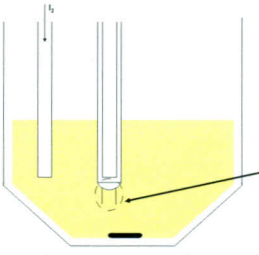
Experimentation and results

Amorphous inulin

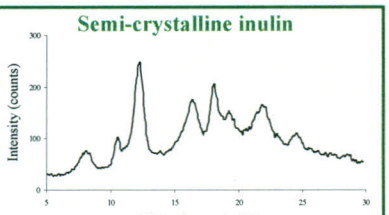


WAXS diffractogram of amorphous inulin

Inulins were stored over P_2O_5 for three weeks at 20°C to obtain a dehydrated product, then analyzed by Wide Angle X-ray Scattering (WAXS).



Semi-crystalline inulin



WAXS diffractogram of semi-crystalline inulin

The determination of the water content is based on the reaction described by R.W. Bunsen in 1853:

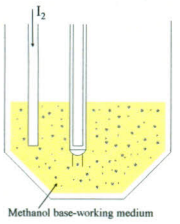
$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

Karl Fischer discovered that this reaction could be used for water determination by a two-step reaction:

$$R\text{-}OH + SO_2 + B \rightarrow BH^+ + ROSO_3^- \quad \text{(Eq. 1)}$$
$$BH^+ + ROSO_3^- + I_2 + H_2O + 2B \rightarrow 3BH^+ + ROSO_3^- + 2I^- \quad \text{(Eq. 2)}$$
$$R\text{-}OH + SO_2 + I_2 + H_2O + 3B \rightarrow BH^+ + ROSO_3^- + 2I^- \quad \text{(Eq. 1+ Eq. 2)}$$

An iodine molecule is attracted to the negatively charged platinum pin. It then acquires two electrons and turns to iodide ($2I^-$). The two negatively charged iodide ions are immediately attracted to the positively charged platinum pin, where they donate the electrons and form an iodine molecule again.
When the reagent consumption rate reaches the same (or a slightly higher) value as immediately before the start of the analysis, it is assumed that all the water of the sample is detected, and the analysis is stopped.
If the sample is not completely dissolved, water diffusion is low, so the analysis is delayed and underestimated.

Analysis of powdered inulin by Karl Fischer titration without formamide in the working medium



The dissolution of inulin was not complete for both semi-crystalline and amorphous inulin.

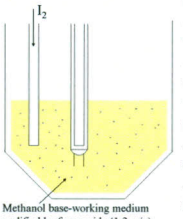
→ Water diffusion was low and delayed.

→ Iodine was continuously consumed.

→ The analysis was stopped by the imposed maximum titration time of 10 min and not by the drift criterion.

→ The water content was underestimated.

Analysis of powdered inulin by Karl Fischer titration with formamide in the working medium (1:3, v/v)



The dissolution of semi-crystalline inulin was increased.

→ An increase of the water content value.

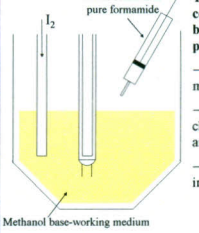
→ The water content was underestimated.

The total dissolution of amorphous inulin was achieved.

→ The analysis was stopped after 4-5 min.

→ The total water content was achieved.

Analysis of inulin dissolved in formamide (2.5:7.5, w/w) by Karl Fischer titration



The dissolution of inulin was completed in pure formamide for both semi-crystalline and amorphous inulin.

→ The analysis was stopped after 1-2 min.

→ The influence of a possible change of the drift during the analysis was reduced.

→ The total water content for both inulin was achieved.

Conventional KF method without formamide	Conventional KF method with formamide	Proposed KF method
1.3 ± 0.3 (>10min)	2.1 ± 0.1 (4-5min)	2.1 ± 0.2 (1-2min)
1.1 ± 0.3 (>10min)	1.8 ± 0.3 (>10min)	2.4 ± 0.1 (1-2min)

Results of the Volumetric Karl Fischer titration (g water / 100 g anhydrous sample) (Amorphous inulin, Semi-crystalline inulin)

Conclusions

The total water content of inulin has been determined by volumetric Karl Fischer titration, using a complete pre-dissolution of the sample in pure formamide, and was compared to the usual introduction of the sample directly in the methanol-based working medium, modified or not by addition of formamide (1:3, v/v) in order to increase sample solubility. The described method allowed the determination of water included in the crystals, as shown by comparing the results for amorphous and semi-crystalline inulin samples.

The titration time for the proposed method was 1 - 2 min, while complete water detection was not achieved after 10 min by the standard method. Dissolving the sample beforehand and transferring an aliquot into the titration cell is time consuming, but this is compensated by the shorter titration time. This advantage is even more important, when routine analyses are carried out and several samples can be dissolved simultaneously. Moreover, the proposed method has the advantage of working at ambient temperature and can be applied to every volumetric KF titrator. This methodology can be applied for the water content determination of other polysaccharides presenting a solubility problem in the working medium.

Acknowledgments

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Reference: S. N. Ronkart, M. Paquot, C. Fougnies, C. Deroanne, J.-C. Van Herck, C. Blecker. (2006). Determination of total water content in inulin using the volumetric Karl Fischer titration. Talanta, 70, 1006-1010.