Karl Fischer titration in boiling methanol

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Summary. Karl Fischer titration is a very precise and rapid chemically based method to determine the water content specifically. The found values are more reliable than those for the loss on drying (often incorrectly called water content, too). On the one hand, the drying process leads to the loss of all compounds volatile under the applied conditions, even of those which might be produced during the process itself; on the other hand, strongly bound or included water may be retained by the product. It is shown that titrations can be carried out even at the boiling point of methanol. The stoichiometry of the reaction is not altered and the water equivalent of the reagent remains the same as at room temperature. A simple multinecked round-bottomed flask with ground joints proved to be a very tight titration vessel.

This “boiling point titration” leads to considerably shorter determination times, sharper end points, more complete water detection and more reproducible results. Interferences by decomposition of sugars, as were reported for “classical” reagents, are not observed when using modern ones. Moreover this method makes products accessible to a quick and easy (and real!) water determination, which undergo a decomposition at temperatures applied for drying methods.

1 Introduction

Being based on a specific chemical reaction Karl Fischer titration is certainly the most precise method for the determination of water. The stoichiometry in a methanolic media is [1, 2]:

\[
\text{CH}_3\text{OH} + \text{SO}_2 + R_3\text{N} \rightarrow R_3\text{NH}^+ + \text{CH}_3\text{OSO}_2^- , \\
R_3\text{NH}^+ + \text{CH}_3\text{OSO}_2^- + I_2 + H_2O + 2 R_3\text{N} \rightarrow 3 R_3\text{NH}^+ + \text{CH}_3\text{OSO}_2^- + 2 I^- .
\]

R, N is an organic base, in modern reagents usually imidazol. According to the overall reaction 1 mol of H\(_2\)O is indicated by 1 mol of I\(_2\). This ratio must not be changed, if a quantitative titration is to be undertaken. An interference of this sort may be caused by any substances in the sample which consume or produce water by a reaction between themselves or with a component of the Karl Fischer reagent(s), notably with methanol. Another source of difficulties are substances which interfere with the redox system I\(^-\)/I\(_2\).

For its detection the water of the sample must be delivered into the methanolic media. If the sample is not soluble in methanol, a quantitative extraction is necessary. Its rate — and with it the duration of the titration — depends on the physical and chemical properties of the sample. The particle size should be as small as possible, but during necessary processes to achieve this state no water must be lost. The extraction may be accelerated by additional solvents, but in this case it must be assured that the stoichiometry of the Karl Fischer reaction is not altered. Another means of improvement is the titration at increased temperatures, again under the condition that the molar ratio of the reacting components H\(_2\)O and I\(_2\) remains unchanged.

Whereas so far many applications exist for titrations at temperatures up to about 50° C, only a few experiments have been undertaken at the boiling point [3]. We have examined this method for several foodstuffs which are problematic when titrated at room temperature.

2 Materials for Karl Fischer titration

Chemicals. Hydranal-Composite 5 and methanol from Riedel-de Haën, Seelze, FRG. This one-component reagent was preferred to the corresponding two-component system Hydranal-Titrant 5/Hydranal-Solvent (which gives faster titrations and sharper end points) because of the danger that the sulphur dioxide dissolved in the Hydranal-Solvent might evaporate during titration at boiling point.

A pyridine containing reagent from Riedel-de Haën was additionally used to check a possibly occurring decomposition of sugars.

Titrator. KF-Processor 658\(^1\) with standard equipment ( burette, double platinum electrode, magnetic stirrer) and pen writer Labograph E 586 from Metrohm, Herisau, Switzerland.

Titration vessel. The standard titration vessel and its separate upper part with holes for the burette tip, the electrodes, the drying tube and the sample inlet could not be used because of the increased working temperature. We used a specially produced 100-ml-round-bottomed flask with a central joint

\(^1\) Since some time we use the Titrino 701 from Metrohm
powder, gravy powder and cocoa. All of these were bought whose water content cannot be determined by a simple drying method due to decomposition. These products were cheese, milk powder, sultanas, honey, vegetable stock rye flour, wheat flour and semolina, rusk, noodles, permesan 3.1 Tightness of the apparatus

To test the tightness of the specially developed titration vessel, 40 ml of methanol were dried by the usual pre-titration. Then a titration without sample was started. To make the titrator not end the determination after 30 s (chosen as equal stop delay for all the titrations of this work) an “extraction time” of 60 min was programmed. So the drift (the amount of reagent used to keep the cell dry) could be measured during 1 h. This was performed at 25, 50 and 65°C, the boiling point of methanol.

3.2 Water equivalent of the Karl Fischer reagent

The water equivalent (often named “titre”) of the reagent was determined by titrating known amounts of water (about 40 mg) and of sodium tartrate-2-hydrate (about 300 mg).

3.3 Heat stability of sugars

As sugars might decompose and produce additional water at higher temperatures, we verified a possible falsification of the results for products with a high sugar content. 1 to 1.5 g of sugar (we examined the behaviour of glucose, fructose and sucrose) were titrated in 60 ml of pre-dried methanol for 30 min at 25°C (to be sure to have titrated their normal water content) and consequently for 5 h at 65°C to determine water which might be produced by partial decomposition reactions.

3.4 Samples and sample handling

Liquids were added by disposable plastic syringes and solids by small sample spoons. Sample amounts were always measured by back weighing with an accuracy of 0.01 mg.

Titrations were carried out at 25, 50 and 65°C. In the case of the boiling point the samples were introduced at about 50°C during the heating period. The boiling point was reached about 30 s later. Flour, honey, cocoa and milk powder were added directly into the titration vessel, whereas samples with a greater particle size were ground in a laboratory mill which can be chilled by ice water (IKA Analysenmühle A10 from Janke & Kunkel, Staufen, FRG). Sultanas were passed four times through a metal sieve for homogenisation.

3.5 Alternative methods

To compare the results obtained, the samples were also dried in a drying oven (Heraeus electronic from Heraeus, Hanau, FRG) according to existing standard methods. Flour, cheese and sultanas (the latter two in a mixture with dried sand) were also desiccated in an infrared drier (Moisture Analyzer MA50 from Sartorius, Göttingen, FRG) to be able to follow the loss of mass continuously. It must, however, be stressed that drying methods do not yield the water content of a substance, at least as far as most natural products are concerned, but the loss on drying, which is not necessarily the same! The water content of honey was determined by its refractive index \( n_{313} \) at 40°C and the wavelength of 589 nm (Abbe Refractometer from Atago, Japan) as second method, the dry substance D (in mass percent) being calculated by the empirical formula \( D = 78.0 + 390.7 \cdot (n_{313} - 1.4768) \).

4 Results

4.1 Drift and water equivalent

The results of the drift experiments are shown in Table 1. To calculate the amount of intruding water from the amount of reagent used a water equivalent of 5 mg/ml is assumed. The titration cell proved to be very tight. The differences seem to have rather statistic than systematic reasons.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Reagent volume [µl/min]</th>
<th>Intruding water [µg/min]</th>
<th>Intruding water [mg/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.3</td>
<td>1.5</td>
<td>0.09</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>2.5</td>
<td>0.15</td>
</tr>
<tr>
<td>65</td>
<td>0.4</td>
<td>2.0</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The water equivalent of 4 different titration solutions was determined at 25°C and 65°C each, for 2 of them using water and for the other 2 sodium tartrate-2-hydrate as standard. The number of samples in each case was 4. The results are listed in Table 2. The water equivalents found for the four reagent solutions in boiling methanol are practically the same as those determined at room temperature; each value lies in the range of the standard deviation of the cor-

<table>
<thead>
<tr>
<th>Solution (number of samples)</th>
<th>Standard</th>
<th>Water equivalent (mg H₂O/ml) at 25°C</th>
<th>Water equivalent (mg H₂O/ml) at 65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (4)</td>
<td>Water</td>
<td>5.161 ± 0.017</td>
<td>5.170 ± 0.020</td>
</tr>
<tr>
<td>B (4)</td>
<td>Water</td>
<td>5.358 ± 0.011</td>
<td>5.359 ± 0.025</td>
</tr>
<tr>
<td>C (4)</td>
<td>Tartrate</td>
<td>5.556 ± 0.017</td>
<td>5.549 ± 0.014</td>
</tr>
<tr>
<td>D (4)</td>
<td>Tartrate</td>
<td>5.531 ± 0.018</td>
<td>5.524 ± 0.009</td>
</tr>
</tbody>
</table>