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Water determination – Scientific and economic dimensions

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Abstract

Water content is for a number of reasons one of the most important properties of foodstuffs. The determination of water content is therefore a very important analysis. This is not only the case for scientific or technical reasons. The water fraction in food is sometimes regarded as a component without commercial value. The price is based on dry matter, which makes water content determination an analysis with economic consequences. Different existing methods often yield different results. This entrains the problem that vendor and buyer, for economic reasons, prefer different methods to favour their role in trade. The situation would be easier if the method to be applied would be the same and would be agreed upon by both parties. International standards and reference methods are established by bodies that consist not only of neutral scientists but also of representatives of industry. These will usually see the interest of their respective company and will rather try to introduce methods which "improve" their profit rather than accepting methods scientifically correct but with lower profit. Milk powder trade is given as an example to illustrate such a situation.

Keywords: Water determination; Karl Fischer titration; Mass loss by drying; Dairy powders; Economic aspects

1. Introduction

1.1. Analytical methods and international trade

When goods are sold beyond international borders, they must meet the requirements of the receiving country. These may differ from the regulations existing in the delivering country. When, however, the laws or traditional consumer expectations are not the same in the countries involved, a compromise or an agreement between the trade partners is necessary. The best solution would of course be to have the same regulations in both countries and, by general extrapolation, in all countries.

These considerations are particularly relevant for the trade with agricultural products and food. Certain components may be characteristic for a given product and may also be decisive for the price. The content or concentration of such compounds must then be analysed. The method of determination may possibly be not the same in the countries concerned. Again, an agreement is necessary. A conflict may arise when the methods legal in the two countries favour the respective partner. In such situations both partners will have the tendency to insist on their national regulation for economic reasons.

Still another problematic situation is possible. A commonly accepted or internationally established method may exist, which may, however, turn out to be incorrect from the scientific point of view. Thus, the results would be legally correct, but would not reflect the true value. In this case, one of the partners would have an advantage, whereas the other would rather prefer the scientifically sound method to be applied, which, of course, would make it necessary to replace the existing method by another – scientifically correct – method.

Such a situation is described. Dairy powders are sold on the basis of dry matter. Water determination is therefore an important analysis in this field.

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1.2. Water content

Water content – and thus dry matter – is often determined by drying techniques, particularly by drying the product at a certain temperature for a certain time in a drying oven.

Drying techniques, be it the "classical" oven drying, vacuum drying, freeze drying, infrared or microwave drying, do not distinguish between water and other volatile substances. The result of all of these methods is not water content but the mass loss the product undergoes under the conditions applied. These conditions (sample size, temperature, pressure, time, energy input, criteria to stop the analysis) can principally be freely chosen. The result depends very much on these conditions but may be very reproducible. This alone shows that this technique, leading to different results when the parameters are changed, cannot be the correct one, because water content is a sample property which has a certain, though unknown value. From the scientific point of view, the results of drying methods should therefore not be called "water content" but rather "mass loss on drying" with indication of the drying conditions. In the past years the term "moisture content" was introduced as a compromise. It means the relative mass loss by evaporation of water (though possibly not all of the water) and other volatile compounds under the drying conditions.

The problem with all drying techniques is that they do not measure water specifically. All the compounds volatile under the analytical conditions contribute to the mass loss, even compounds that are not originally contained in the sample but are formed by chemical reactions during the analysis, particularly by decomposition reactions at higher temperatures. But, on the other hand, strongly bound water may escape detection.

These conflicting errors, inclusion of other volatiles on the one hand and water not detected on the other hand, may account for each other when the drying parameters are chosen in an appropriate way (Isengard, 1995). The appropriate choice of the parameters necessitates, of course, that the true water content has been analysed before with a method selective for water as a primary method. The parameters of the secondary method must then be chosen in a way that the result corresponds to the water content determined with the primary method. Once the secondary method is calibrated in this way, it can be applied for this particular type of product. The calibration is product-specific and the same parameters cannot be applied for other types of samples.

The most important primary method to determine water content is the Karl Fischer titration. It is based on a chemical reaction selective for water:

$$\mathrm{ROH} + \mathrm{SO_2} + \mathrm{Z} \rightarrow \mathrm{ZH^+} + \mathrm{ROSO_2^-} \tag{1a}$$

$$\mathrm{ZH^+} + \mathrm{ROSO_2^-} + \mathrm{I_2} + \mathrm{H_2O} + 2\mathrm{Z} \rightarrow 3\mathrm{ZH^+} + \mathrm{ROSO_3^-} + 2\mathrm{I^-} \tag{1b}$$

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

Z is a base (very often imidazole), ROH is an alcohol, usually methanol.

In the first step the alcohol is esterified with sulphur dioxide to form alkyl sulphite. The base provides for a practically complete reaction (Eq. (1a)). In the second step this alkyl sulphite is oxidised by iodine to form alkyl sulphate; this reaction requires water (Eq. (1b)). The overall reaction (Eq. (2)) shows that the consumption of iodine is stoichiometrically equivalent to water present in the sample.

1.3. The lactose problem – scientific background

Lactose exists in different forms. The α-anomer is the more stable form at temperatures below 93 °C. It crystallises with one mole of water per mole lactose. At higher temperatures the anhydrous β-anomer is more stable. Lactose occurs also in amorphous form which may include small amounts of water. Depending on the production conditions dried dairy powders contain mixtures of these polymorphs. In addition to included water and water of crystallisation, the product usually contains small quantities of surface water.

The usual drying temperature for moisture determination of dairy products in drying ovens is 102 °C. At this temperature the water of crystallisation of α-lactose is not evaporated completely during the usual drying times. The separation of this water fraction from the matrix needs a high energy input (Rückold, Isengard, Hanss, & Grobecker, 2003; Rüegg & Moor, 1987). After 2 h, the standard drying time, only a part of this water is detected. The consequence is that drying techniques yield results that differ more or less from the true water content.

As lactose occurs in practically all dairy products and is also used in the pharmaceutical industry, this problem affects a wide range of products, particularly those with high lactose content like whey powders or lactose itself.

Usually the drying results are lower than water content. In special cases, however, they can be higher. This is possible if the lack in water detection is over-compensated by other volatile substances which are contained in special products or which are formed by decomposition of components during the drying process.

1.4. The lactose problem – economic aspects

Dairy powders are sold on the basis of dry matter, DM. This should be the mass, m_0, of the product minus the mass of the water, m_W, contained in it (Eq. (4)). The mass of water can be calculated from water content, WC, (Eq. (3)):

$$\mathrm{WC} = m_\mathrm{W}/m_0 \quad \Rightarrow m_\mathrm{W} = \mathrm{WC} \cdot m_0 \tag{3}$$

$$\mathrm{DM} = m_0 - m_\mathrm{W} = m_0 - \mathrm{WC} \cdot m_0 = m_0 \cdot (1 - \mathrm{WC}) \tag{4}$$

Dry matter becomes smaller with increasing water content. If the analytical method yields a result lower than the true water content, dry matter is calculated too high than its real value. This would give the vendor of the product an unjustified advantage and the buyer would pay too much for the product. This is just the situation likely to happen in the trade with dairy powders.

2. Material and methods

2.1. Reference method for determining moisture in milk powders

The International Dairy Federation (IDF) has established a method for determining the moisture content in dried milk. For this purpose a new drying device was specially designed (de Knegt & Brink, 1998). The method was also adopted by the International Organization for Standardization (ISO) (ISO 5537 | IDF 26, 2004).

This method was strongly supported by the dairy industry. Scientific arguments brought forward and results of an international inter-laboratory test (Rückold, Grobecker, & Isengard, 2000) were pushed aside. There were – apart from possible economic interests (see above) – particularly two arguments to introduce and establish this method.

The first argument was that the results obtained by this new technique (description see below) were practically the same (but with smaller standard deviation for replicate samples) as those received by drying the samples according to the former method using an ordinary drying oven, independently from the geographic situation (altitude, air pressure, relative humidity of the environment).

The second argument (against the objection that the result of this method is not the complete water content) was that the complete water content would not be the interesting property of milk powders. This would rather be the free water of the product.

2.2. Mass loss, moisture content, water content – comparison of results obtained by different methods for various dairy powders

Several dairy powders (lactose, skimmed milk powder, full cream milk powder, whey powder and calcium caseinate) were analysed for mass loss by drying and for water content.

Two drying techniques were used: The "classical" oven drying (OD) and the new "reference drying" method (RD).

Water content was determined by Karl Fischer titration (KFT).

2.3. Oven drying (OD)

The experiments were carried out according to the former IDF standard method "Dried milk and dried cream, Determination of water content" (IDF 26A, 1993). It is remarkable that at that time the mass loss measured was defined as "water content", whereas the new method, which has officially replaced this one, determines "moisture content".

One to three grams of the sample – for this investigation, approximately 2 g were used – was dried at 102 °C ± 2 °C in a ventilated drying oven. The mass loss is measured by weighing before and after 2 h drying and cooling in a desiccator. According to the method, the sample is then to be dried for another hour and so forth until the difference between consecutive measurements is less than 0.5 mg. In this investigation the samples were analysed after different drying times to follow the drying process more closely (see below). The result after 2 h was however used to compare the results with each other. The analyses were carried out with the drying oven FD 115 from Binder, Tuttlingen, Germany.

2.4. Reference drying (RD)

The samples (5.0 g ± 0.3 g) are placed in containers with a diameter of 20 mm and a height of 90 mm (plastics syringes without needle) between polyethylene filters and dried (up to eight in parallel per one analysis) in a heating block at 87 °C ± 1 °C for 5 h. Dry compressed air is passed with a rate of 33 ml/min through the containers with the samples. The mass loss determined by weighing the sample and the container before and after the drying process (after cooling in a desiccator) is defined as moisture content. It is not controlled if a constant mass has been reached. For this reference drying according to the new standard method the Referenztrockner RD 8 from Funke-Dr. N. Gerber Labortechnik, Berlin, Germany was used.

2.5. Karl Fischer titration (KFT)

The KF Titrino 701 from Metrohm, Herisau, Switzerland with titration stand 703 and titration cell with thermostatic jacket was used. The two-component technique was applied with Hydranal-Titrant 2 as titrating solution and Hydranal-Solvent as working medium. All chemicals were from Sigma-Aldrich Laborchemikalien, Seelze, Germany. The end point was detected using the voltametric technique with a polarising current of 20 µA and a stop voltage of 100 mV, the stop criterion being the drift (5 µl/min above the drift measured before analysis). The minimal titration volume increment was set to 0.5 µl and the maximal titration rate to 5 ml/min. In order to obtain a more rapid dissolution or dispersion of the samples in the working medium and, consequently, shorter titration times, the analyses were carried out at 50 °C.

2.6. General procedure

The different samples were analysed on the same day by the three methods. Five Karl Fischer titrations were carried out for every sample. The "reference drying" was started with eight portions of each sample, two of each were analysed as duplicates after 3, 4, 5 and 6 h (the "official" drying time being 5 h). Twelve portions of each sample were placed in the drying oven. Two each were analysed in parallel after 60, 80, 100, 120, 150 and 180 min (the "official" drying time being 120 min).

3. Results and discussion

Table 1 (from Isengard, Felgner, Kling, & Reh, 2006b) gives a juxtaposition of the results obtained by Karl Fischer titration (KFT), by conventional oven drying (OD) according to the former standard method and by the new standard method ("reference drying", RD). The OD results are – for better comparison – those obtained after 2 h, the RD results are the values after the "official" time of 5 h. Values for other drying times both for oven drying and for "reference drying" are given below. The shape of the Karl Fischer titration curves indicated a complete and correct determination of water for all the samples.

The results for the two milk powders are very close to each other. The KFT and the RD results are not significantly different. The OD results (obtained after 2 h drying time) come closer to the KFT results when the drying times are longer: (3.90 ± 0.01) g/100 g after 2.5 h for skimmed milk powder and (2.58 ± 0.01) g/100 g after 3 h for full cream milk powder (see below). In the other cases the results for water content and mass loss differ clearly. For lactose and whey powder the differences are very high.

The drying times were varied for the two drying methods to receive information on the evolution of the results in the course of time. The results of these experiments are depicted in Figs. 1–5 (from Isengard et al., 2006b).

The lactose sample (Fig. 1) was a technical product and obviously contains not only α-lactose but also anhydrous polymorphs. The water content found by Karl Fischer titration is therefore slightly below 5 g/100 g. This value is by far not reached by the drying techniques because the water of crystallisation is strongly bound.

A very important finding is that the drying techniques do not detect the "free" water only (which is usually in the range of 0.1 g/100 g) but also a part of the "bound" water. It cannot be claimed therefore that the new reference method detects only free water. The measured entity is in

Table 1
Results for water content by Karl Fischer titration (KFT) and for mass loss by oven drying (OD) after 2 h and by "reference drying" (RD); n = number of replicates

Sample	Water content by KFT ($n = 5$) [g/100 g]	Mass loss by OD ($n = 2$) [g/100 g]	Mass loss by RD ($n = 2$) [g/100 g]
Lactose	4.45 ± 0.19	2.45 ± 0.13	1.04 ± 0.03
Skimmed milk powder	3.92 ± 0.07	3.85 ± 0.00	3.94 ± 0.13
Full cream milk powder	2.65 ± 0.05	2.46 ± 0.02	2.72 ± 0.14
Whey powder	4.46 ± 0.05	2.12 ± 0.01	2.24 ± 0.07
Calcium caseinate	6.19 ± 0.11	5.62 ± 0.03	5.73 ± 0.02

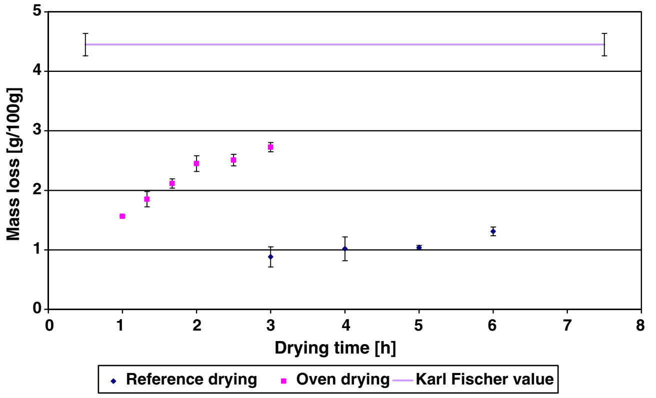

Fig. 1. Mass loss by "reference drying" and oven drying after various drying times of crystallised lactose and – for comparison and reference – the water content by Karl Fischer titration (also in g/100 g).

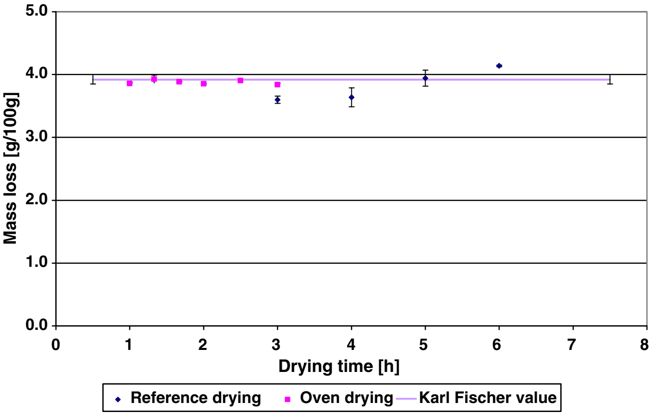

Fig. 2. Mass loss by "reference drying" and oven drying after various drying times of skimmed milk powder and – for comparison and reference – the water content by Karl Fischer titration (also in g/100 g).

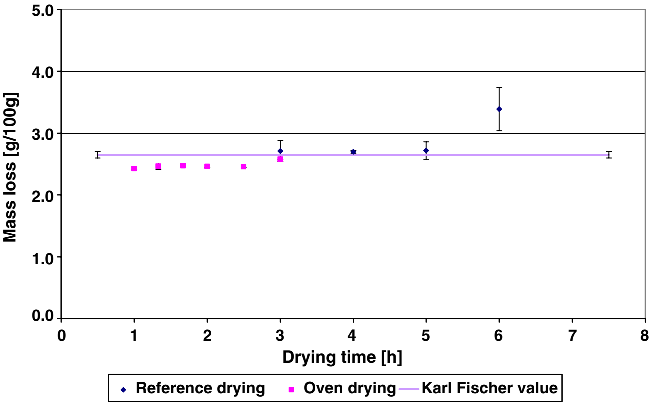

Fig. 3. Mass loss by "reference drying" and oven drying after various drying times of full cream milk powder and – for comparison and reference – the water content by Karl Fischer titration (also in g/100 g).

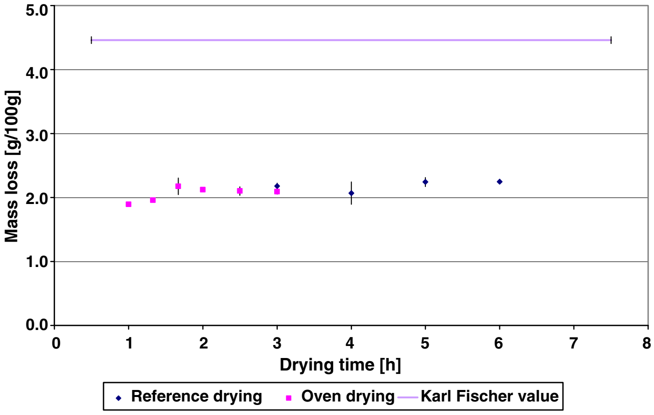

Fig. 4. Mass loss by “reference drying” and oven drying after various drying times of whey powder and – for comparison and reference – the water content by Karl Fischer titration (also in g/100 g).

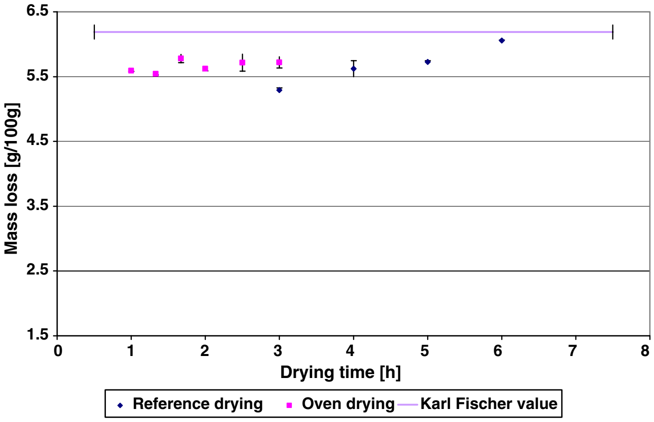

Fig. 5. Mass loss by “reference drying” and oven drying after various drying times of calcium caseinate and – for comparison and reference – the water content by Karl Fischer titration (also in g/100 g).

fact not defined, it is neither free nor total water. This is a serious disadvantage for a reference method.

For the two milk powder samples (Figs. 2 and 3), the mass loss by drying corresponds approximately to the water content determined by Karl Fischer titration. The “lack” of water detection can be compensated by the determination of volatile substances formed by decomposition at higher temperatures (see above). This is obvious from the results by “reference drying” which rise to numbers above the Karl Fischer results when the drying process is longer than the “official” 5 h. The value for both milk powders after 5 h is, however, in very good consistence with the water content.

The whey powder (Fig. 4) contains approximately 85% lactose by mass. A part of it is crystallised. Consequently, the mass loss by drying does not reach the water content determined by Karl Fischer titration. Other components with high water binding capacity may contribute to this effect.

The calcium caseinate sample (Fig. 5) does not contain lactose. The reason for the too low drying results may therefore be a slow diffusion of the water from the core of the particles to the surface. The airflow in the “reference dryer” is obviously advantageous for the drying process as it keeps the partial pressure of water above the sample extremely low. The Karl Fischer value would probably be reached if the drying time was longer.

4. Concluding considerations

Results obtained for mass loss by drying and for water content by Karl Fischer titration can differ clearly. With increasing α-lactose content the difference increases and is extreme for pure lactose. The drying techniques do neither determine the total water nor the free water fraction alone. The defenders of the new reference method argue that the water of crystallisation is of no practical importance, because it has no influence on the flowability of the powders and nearly no importance for the microbiological stability and thus the shelf life of the product. This argumentation does not consider the fact that this “bound” water is set free when the product is dissolved. This has to be accounted for when recipes are designed. The total water content (including water of crystallisation) is therefore of importance.

The results of the “reference method” depend very strongly on the drying time and also other parameters (de Knegt & Brink, 1998; Isengard, Kling, & Reh, 2006a, 2006b). Only for ordinary milk powders are they close to Karl Fischer results. For products with other compositions other product-specific parameters would have to be found. This makes the method limited.

The Karl Fischer method detects the total water content selectively and is independent from the lactose content. The precision of the Karl Fischer results is very good, even though the sample sizes are much smaller than those of the drying techniques. The precision of the new reference method is not better than that of oven drying.

The drying techniques are more time consuming than the Karl Fischer method. Conventional drying takes several hours and real mass constancy is only rarely reached. Experience shows that it is recommendable to terminate the measurement after a fixed time of 2 h. This makes results more comparable, because in many cases additional mass loss may be due to decomposition processes and/or to the Maillard reaction which consists of condensation and dehydration reactions. The “reference drying” is very time consuming (practically one day for a set of eight samples). The Karl Fischer method is by far the most rapid method for a sample (a couple of minutes). A disadvantage of the Karl Fischer technique is the use of chemicals.

These and other investigations (Isengard et al., 2006a, 2006b; Rückold et al., 2000) have shown that the “reference drying” method is correct only for ordinary milk powders but not necessarily for other dried dairy products. The Karl Fischer titration, on the contrary, can generally be applied on these products and would be a more reasonable reference method.

These considerations are clear and straightforward from the scientific point of view and cannot be doubted. Nevertheless, attempts to introduce the Karl Fischer titration as reference method for water determination in dairy powders meet the resolute resistance of the dairy industry. The reason is obviously the economic interest not to "find" all the water in the product that they sell to their customers. The detection of the true water content would lower the price of the product if it is calculated on the basis of dry matter.

Scientific facts are – at least so far – not strong enough against economic arguments. A harmonisation of scientific truth and correctness with economic power and interest is necessary. Such a harmonisation should, for ethical reasons, be aimed at in the interest of honest and correct trade.

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