

Proposal of a new reference method to determine the water content of dried dairy products

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Abstract

The water content of milk powders is “officially” determined by drying. The result of drying techniques is, however, the mass loss the sample undergoes under the conditions applied. No differentiation between water and other volatile substances is made. A particular problem is the lactose that is present in all dried dairy products. The α -form contains one mole of water of crystallisation per mole. This water fraction is not determined completely by ordinary drying methods. How much of the crystallised water is detected depends very much on the conditions applied. The entity determined by drying is not defined. It is only a tradition to regard the mass loss thus detected as water content. More and more, however, the expression moisture content is used for the result of drying techniques, although this term is also unsatisfactory and misleading. The discrepancy between mass loss on drying and water content becomes more pronounced when the product has high crystalline lactose content, such as whey powders or lactose itself. In these cases the difference between mass loss and water content can be quite significant. The existing reference method for moisture determination in dried milk is therefore not reasonably applicable on dairy products with high crystalline lactose content. It could be shown that the water content of dried dairy products can be determined using the Karl Fischer titration independently of the level of crystallisation water. The results are not only more accurate but also more precise than those obtained by the reference drying method. It is therefore proposed to introduce the Karl Fischer titration as reference method for dried dairy products.

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1. Introduction

Water content of foodstuffs is for several reasons important. This comprises technological, nutritional, logistic, economic and legal aspects. A correct determination of water content is also particularly important in the context of reference materials with respect to the guaranteed values that they are certified for (Rückold, Grobecker, & Isengard, 2001). Water content affects –

via water activity – also enzymatic and microbiological stability and, thus, shelf life. Water activity indicates the degree of “freedom” of the water and the availability for enzymatic and microbiological activities.

In many cases drying methods are applied to determine what is believed to be the water content. It is also often believed that by drying only the free water fraction is detected (de Knecht & v.d. Brink, 1998).

Different drying techniques are in use, ranging from the classical drying oven to rapid methods like infrared, so-called halogen and microwave drying. All of these methods analyse a mass loss caused by drying and principally not the water content. The results depend on the

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parameters applied. The mass loss is caused by evaporation of all volatile matter in the sample, not only by water. This comprises compounds that are originally present in the sample but also those that are formed during the drying process itself by chemical reactions, particularly by decomposition reactions at higher temperatures. This leads to too high results. Strongly bound water, on the other hand, may be retained and escape detection. This effect causes too low results. If the true water content for a given sort of product can be determined by a selective method which then serves as a calibration method, the parameters of a drying technique can be chosen in a way that the two contradictory errors compensate each other (Isengard, 1995). The result of drying methods should not be called water content. The best term would be mass loss on drying (with indication of the parameters). A compromise, which seems to be widely accepted, is “moisture content”.

The Karl Fischer titration is based on a selective reaction of water (Scholz, 1984). Various measures can be taken to bring the water of the sample in contact with the reagents (Isengard, 1995). The result of these analyses is indeed the water content of the sample.

A particular problem exists with dried milk products. They contain more or less high amounts of lactose. In the α -form it contains one mole water per mole. This corresponds to 5.0 g water per 100 g α -lactose hydrate in the pure crystallised form. This crystallisation water can only be separated with a high energy input (Rückold, Isengard, Hanss, & Grobecker, 2003; Rüeegg & Moor, 1987). High energy input brings about the risk to destroy the molecule itself. These reactions may lead to the formation of further volatile material.

2. Background

The water content of dried milk was so far determined in a drying oven according to a standard of the International Dairy Federation (IDF) (1993). Recently, a special oven was designed by the Centraal Orgaan voor Kwaliteitsaangelegenheden in de Zuivel (COKZ) (de Knegt & v.d. Brink, 1998) to determine moisture content in milk powder. The proposed method was approved by IDF and is now a reference method of the International Organization for Standardization (ISO) and the IDF (2003). This type of dryer is therefore referred to as “reference dryer” in the following.

In a previous interlaboratory study it could already be shown that only a part of the crystallised water of α -lactose is detected by this method (Rückold, Grobecker, & Isengard, 2000). This leads to more or less big discrepancies between the “official” results for moisture and the water content, depending essentially on the lactose content of the product. For the typical spray dried

milk such as full cream or skimmed milk powder these discrepancies are normally small as the lactose is in most cases amorphous.

In this investigation several dried milk products with various compositions were analysed by drying and by Karl Fischer titration.

3. Methods

3.1. Oven drying

The drying oven FD 115 from Binder, Tuttlingen, Germany was used. According to the old standard of the IDF (1993) 1–3 g of the sample – for this investigation approximately 2 g were used – are dried at 102 ± 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. The sample is then dried for another hour and so forth until the difference between consecutive measurements is less than 0.5 mg.

3.2. Reference drying

For “reference drying” according to the new standard of ISO and IDF (2003) the Referenztrockner RD 8 from Funke-Dr. N. Gerber Labortechnik, Berlin, Germany was used. The samples (5.0 ± 0.3 g) are placed in containers with a diameter of 20 mm and a length of 90 mm (plastics syringes without needle) between polyethylene filters and dried (up to eight in parallel per analysis) in a heating block at 87 ± 1 °C for 5 h. An air-flow with a rate of 33 ml/min is passed through the containers with the samples. The mass loss determined by weighing the sample and the containers 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.

3.3. Karl Fischer titration

The KF Titrimo 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. In order to vary the polarity of the working medium titrations were also carried out with additional solvents: formamide, 1-propanol, 1-octanol, chloroform and *tert*-butyl methyl ether. All chemicals were from Sigma-Aldrich, Seelze, Germany. The end point was detected using the voltametric technique with a polarising current of 20 μ A and a stop voltage of 100 mV, the stop criterion being the drift (5 μ l/min above the drift measured before analysis). The minimal titration volume increment was set to 0.5 μ l 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.

3.4. Procedure

The particular focus of this investigation was the comparison of the results obtained by the “reference dryer” and the Karl Fischer titration. The standard parameters for these methods were varied to check the dependence of the methods on these parameters and their robustness.

3.5. Samples

Seventeen dried milk products with various composition (fat content, protein content, carbohydrate nature and content, water content), labelled as full milk powder, skimmed milk powder, whey powder, baby food, coffee whitener or protein concentrate, all provided by Nestlé, Vers-chez-les-Blanc, Switzerland, and α -lactose were analysed.

4. Results and discussion

4.1. Comparison of the results of the different methods

Table 1 gives a juxtaposition of the results obtained by conventional oven drying (according to the former

standard method (IDF, 1993)), the new standard method (International Organization for Standardization, 2003) and the Karl Fischer titration.

The stipulated mass constancy for the drying oven could only rarely be reached. In many cases the mass loss decreased again after several hours, probably due to a water uptake of the dried (and hygroscopic) product during cooling. In such cases the highest value was considered as result. The relative standard deviations (or coefficients of variance) of the oven results range from 1.09% to 17.59% with an outlier of 70.15%, the average being 7.50% (without the outlier). The relative standard deviations of the “reference drying” results range from 2.76% to 21.99% with an average of 11.12%, those of the Karl Fischer titration from 0.13% to 3.69% with an average of 1.56%.

In most of the cases the results of the two oven drying methods are not significantly different. This is due to the relatively imprecise measurements (high standard deviations). The shape of the Karl Fischer titration curves (titrated volume versus time), which were observed during titrations, indicated a complete determination of the water. The Karl Fischer values are also more precise than the mass loss values. When the mass loss is higher than the water content values, other volatile material than water or water produced by chemical reactions during the drying process has obviously contributed to the mass loss. In the opposite situation, not all of the water has been set free by drying. In some cases both phenomena may occur at the same time, but one effect will exceed the other. The effects can be different for the two oven methods, because of the different temperatures (102 and 87 °C) and the different drying times.

Thus, the following interpretations seem to be possible. For sample 27 both drying methods yield too low values, but the higher temperature in the classical oven has a better (yet still incomplete) liberation of the water. The too high results for samples 21 and 26 are caused by other volatiles than water or by additional water formed; this effect is more pronounced at higher temperatures. While the “reference dryer” and the Karl Fischer titration give practically the same results for samples 17 and 18, the temperature in the oven seems to be too high. For sample 11, however, the temperature of the reference dryer seems to be too low. The drying time in the “reference dryer” seems to be too long for samples 1 and 6 for which the oven and the Karl Fischer method yield corresponding values.

In several cases (samples 4, 9, 22, 24, 26 and 28) a slight browning of the sample after drying in the oven could be observed. This confirms the risk of decomposition reactions to take place during the drying process and the forming of volatile products that contribute to the mass loss. For all of these samples the mass loss was indeed higher than the water content. Browning was, however, also observed for sample 27 which yielded a mass loss lower than the water content. This sample (a

Table 1

Moisture content (MC) determined in the drying oven (DO) and the “reference dryer” (RD) and water content (WC) determined by Karl Fischer titration (KFT) at 50 °C with a working medium of 20 ml Hydranal-Solvent and 10 ml formamide, all results in g/100 g, n = number of replicates

Sample	MC by OD (n)	MC by RD (n)	WC by KFT (n)
1	2.49 ± 0.25 (3)	2.88 ± 0.33 (5)	2.52 ± 0.09 (10)
3	4.64 ± 0.05 (3)	4.57 ± 0.82 (3)	4.81 ± 0.07 (10)
4	3.63 ± 0.22 (3)	3.54 ± 0.41 (5)	2.88 ± 0.04 (10)
6	3.08 ± 0.03 (3)	3.80 ± 0.28 (5)	3.02 ± 0.08 (10)
9	4.01 ± 0.54 (3)	4.10 ± 0.49 (5)	3.26 ± 0.03 (3)
11	3.03 ± 0.26 (3)	2.64 ± 0.31 (3)	2.97 ± 0.07 (9)
14	2.64 ± 0.37 (3)	2.78 ± 0.26 (5)	2.30 ± 0.04 (8)
17	3.18 ± 0.56 (3)	2.44 ± 0.54 (3)	2.59 ± 0.07 (10)
18	4.47 ± 0.46 (3)	3.38 ± 0.17 (3)	3.36 ± 0.03 (10)
21	4.15 ± 0.19 (3)	3.26 ± 0.34 (5)	2.80 ± 0.00 (3)
22	2.72 ± 0.27 (3)	2.49 ± 0.55 (3)	2.21 ± 0.03 (4)
24	3.90 ± 0.32 (3)	3.26 ± 0.25 (3)	2.43 ± 0.03 (3)
26	4.22 ± 0.05 (3)	3.55 ± 0.39 (5)	2.91 ± 0.02 (4)
27	3.19 ± 0.33 (3)	1.96 ± 0.13 (8) ^a	4.47 ± 0.09 (7)
28	6.44 ± 0.15 (3)	5.91 ± 0.40 (3)	5.76 ± 0.14 (4)
30	2.19 ± 0.20 (3)	1.88 ± 0.34 (3)	4.75 ± 0.04 (3)
32	6.77 ± 0.46 (3)	6.31 ± 0.17 (3)	7.16 ± 0.14 (4)
Lactose 1	0.67 ± 0.47 (3)	1.08 ± 0.14 (3)	4.48 ± 0.02 (4)
Lactose 2	0.67 ± 0.11 (3)	1.46 ± 0.07 (3)	5.05 ± 0.06 (4)

^a All replicates in one single assay.

wey powder) obviously underwent degradation reactions, but this effect was less pronounced than the amount of water not detected (see below).

The most obvious discrepancies between the oven methods and the Karl Fischer titration were observed for lactose and samples 27 and 30. Obviously the Karl Fischer titration detects the total (crystallised and “free”) water content of lactose. Lactose 1 seems to contain, besides α -lactose, anhydrous modifications. The results of the drying techniques do neither reflect the total nor the free water content. Samples 27 and 30 are wey powders and contain, therefore, much lactose. Here, too, the water of crystallisation is only incompletely detected.

These results reveal that drying techniques are not capable to determine water content in products containing lactose correctly. This concerns more or less nearly all (dried) dairy products and makes drying techniques problematic in this domain.

The discrepancy between the methods was underlined by the following experiment: A wey powder was analysed by the “reference dryer” and yielded a mass loss of 2.20 g/100 g. The obtained “dried” product was then titrated and water content of 3.58 g/100 g was found.

4.2. Variation of parameters

In order to check the dependence of the results on the parameters and thus the robustness of the “reference method” and the Karl Fischer titration, parameters were varied for these techniques.

Table 2

Moisture content determined by “reference drying” at different flow rates, n = number of replicates

Sample	Moisture content in g/100 g at gas flow rate	
	33 ml/min	>33 ml/min
17	2.44 ± 0.54 (n = 3)	2.83 (n = 2)
18	3.38 ± 0.17 (n = 3)	4.35 (n = 2)
21	3.26 ± 0.34 (n = 5)	3.93 (n = 2)
28	5.91 ± 0.40 (n = 3)	6.06 (n = 2)

Table 3

Moisture content (MC) by “reference drying” for the same sample using different sample sizes; 2 replicates for sample sizes 2, 3, 4 and 6 g, 5 replicates for sample size 5 g

Sample size in g	2	3	4	5	6
MC in g/100 g	5.31	4.21	4.43	4.10	3.73

Table 4

Moisture content (MC) of a lactose sample by “reference drying” at 102 °C in dependence on drying time, n = number of replicates

Drying time in h	2	3	4	5	6	7
MC in g/100 g (n)	1.79 (2)	2.37 ± 0.56 (4)	2.65 ± 0.51 (6)	3.00 ± 0.32 (6)	3.17 ± 0.30 (4)	3.35 (2)

4.2.1. Parameter variation for reference drying

Increase of gas flow. With an increased gas flow the results become higher as is shown in Table 2. The regulation knob was set two revolutions higher. The exact flow rate was not measured. As the drying process is often not yet completed under standard conditions the increase of flow rate increases the water transfer into the gas phase and leads to a higher mass loss.

Variation of sample size. Table 3 shows that the sample size has a great influence on the results. The effect is probably explained by the larger amount of water to be removed. The differences are nevertheless quite significant. It also shows the importance of controlling well the sample size for drying methods.

Variation of temperature and drying time. A lactose sample was dried at 102 °C (the temperature of the drying oven method). The mass loss was measured after different drying times. The result obtained for this sample at standard conditions (87 °C for 5 h) was 1.08 ± 0.14 (n = 3). The results increase with drying time (Table 4).

4.2.2. Parameter variation for the Karl Fischer titration

Polarity of the working medium. Because of the carbohydrate content of the samples it proved to be advantageous to add formamide to the standard working

Table 5

Results for water content by Karl Fischer titration (50 °C, sample size 5 g) in pure Hydranal-Solvent as working medium and in a mixture of 20 ml Hydranal-Solvent and 10 ml formamide, n = number of replicates

Sample	Water content in g/100 g using as working medium	
	Pure Hydranal-Solvent	Hydranal-Solvent/formamide
1	2.63 ± 0.06 (n = 10)	2.52 ± 0.09 (n = 10)
3	4.87 ± 0.03 (n = 3)	4.81 ± 0.07 (n = 10)
4	3.00 ± 0.05 (n = 10)	2.88 ± 0.04 (n = 10)
6	3.14 ± 0.10 (n = 10)	3.02 ± 0.08 (n = 10)
9	3.42 ± 0.02 (n = 3)	3.26 ± 0.03 (n = 3)
11	3.11 ± 0.10 (n = 3)	2.97 ± 0.07 (n = 9)
14	2.09 ± 0.04 (n = 10)	2.30 ± 0.04 (n = 8)
17	2.58 ± 0.02 (n = 3)	2.59 ± 0.07 (n = 10)
18	3.39 ± 0.02 (n = 3)	3.36 ± 0.03 (n = 10)
21	2.97 ± 0.05 (n = 3)	2.80 ± 0.00 (n = 3)
22	2.30 ± 0.02 (n = 4)	2.21 ± 0.03 (n = 4)
24	2.49 ± 0.02 (n = 3)	2.43 ± 0.03 (n = 3)
26	3.05 ± 0.04 (n = 4)	2.91 ± 0.02 (n = 4)
27	4.44 ± 0.04 (n = 5)	4.47 ± 0.09 (n = 7)
28	5.98 ± 0.13 (n = 3)	5.76 ± 0.14 (n = 4)
30	4.89 ± 0.03 (n = 4)	4.75 ± 0.04 (n = 3)
32	7.04 ± 0.14 (n = 3)	7.16 ± 0.14 (n = 4)
Lactose 1	4.46 ± 0.10 (n = 4)	4.48 ± 0.02 (n = 4)
Lactose 2	5.10 ± 0.01 (n = 3)	5.05 ± 0.06 (n = 4)

Table 6

Results for water content by Karl Fischer titration at 50 °C in pure Hydranal-Solvent as working medium using different sample sizes, n = number of replicates

Sample	Water content in g/100 g	
	Sample size 0.5 g	Sample size 0.1 g
1	2.63 ± 0.06 ($n = 10$)	2.82 ± 0.07 ($n = 4$)
3	4.87 ± 0.03 ($n = 3$)	4.55 ± 0.06 ($n = 11$)
4	3.00 ± 0.05 ($n = 10$)	2.99 ± 0.04 ($n = 10$)
6	3.14 ± 0.10 ($n = 10$)	3.16 ± 0.10 ($n = 10$)
9	3.42 ± 0.02 ($n = 3$)	3.63 ± 0.04 ($n = 3$)
11	3.11 ± 0.10 ($n = 3$)	2.93 ± 0.15 ($n = 10$)
14	2.09 ± 0.04 ($n = 10$)	2.20 ± 0.06 ($n = 10$)
17	2.58 ± 0.02 ($n = 3$)	2.48 ± 0.06 ($n = 10$)
18	3.39 ± 0.02 ($n = 3$)	3.37 ± 0.08 ($n = 10$)
21	2.97 ± 0.05 ($n = 3$)	3.10 ± 0.04 ($n = 4$)
22	2.30 ± 0.02 ($n = 4$)	2.27 ± 0.04 ($n = 10$)
24	2.49 ± 0.02 ($n = 3$)	2.63 ± 0.02 ($n = 3$)
26	3.05 ± 0.04 ($n = 4$)	3.13 ± 0.06 ($n = 5$)
27	4.44 ± 0.04 ($n = 5$)	4.57 ± 0.03 ($n = 10$)
28	5.98 ± 0.13 ($n = 3$)	5.52 ± 0.04 ($n = 10$)
30	4.89 ± 0.03 ($n = 4$)	4.82 ± 0.06 ($n = 10$)
32	7.04 ± 0.14 ($n = 3$)	6.99 ± 0.14 ($n = 10$)
Lactose 1	4.46 ± 0.10 ($n = 4$)	4.58 ± 0.04 ($n = 3$)
Lactose 2	5.10 ± 0.01 ($n = 3$)	5.07 ± 0.06 ($n = 3$)

medium to achieve a quicker dissolution or dispersion of the samples and, consequently, shorter titration times. It is, however, also principally possible to work with pure Hydranal-Solvent as can be seen from Table 5. The average difference between the two working media is very low and was calculated as 0.06 mass% for the whole sample set.

Variation of sample size. The results do not change very much when the sample size is decreased from 0.5 to 0.1 g. This is demonstrated in Table 6 even for titrations in pure Hydranal-Solvent as working medium.

5. Summary and conclusion

Results obtained for mass loss by drying and for water content after Karl Fischer differ in many cases. With increasing level of crystallisation water 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 entity determined by drying techniques is not defined.

The results of the “reference method” depend very strongly on the drying parameters. Only for ordinary milk powders are they close to the Karl Fischer results. For products with other compositions other product-specific parameters must be found. This makes the

method very limited for industrial use. Dairy ingredients are widely used in all types of foods and water content often affects the properties of those products.

The Karl Fischer method detects the total water content selectively and is independent of any content of crystallisation water. The precision of the Karl Fischer results is clearly better than that of the drying results, even though the sample sizes are much smaller.

The drying techniques are more time consuming than the Karl Fischer method. Conventional drying takes 6–7 h for 10 samples and real mass constancy is only rarely reached. The “reference dryer” needs 7–8 h for eight samples. Ten samples can be analysed in 1 h by the Karl Fischer method. A disadvantage of the Karl Fischer technique is the use of chemicals. As reference methods are often used as calibration methods for indirect methods like near infrared spectroscopy a method with high specificity for water is required. Based on the presented results the Karl Fischer method exhibits the highest selectivity to water.

As a consequence of the findings it is proposed that the Karl Fischer titration be established as a standard and reference method for the determination of water content in dried dairy products.

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