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Determination of water content in powdered milk

Christoph Reh *, Shrinivasa N. Bhat, Stephane Berrut

Quality and Safety Department, Nestle Research Center, Vers-chez-les-Blanc, P.O. Box 44, Lausanne 1000, Switzerland

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Abstract

The determination of the water content in foodstuff is one of the most frequently performed analyses in the food industry (Isengard, 2001). In dried milk IDF method 26A in which the sample is dried at 102.0 ± 2.0 °C in a standard air drying oven has been used for many years as reference method. The method exhibits excellent repeatability but reproducibility is insufficient. Therefore the IDF working group on water developed an alternative drying method which involves drying the sample in a column at 87.0 ± 1.0 °C under a stream of dried air passing trough the column. The drying conditions were chosen to obtain equivalent results to the standard method. As the physico-chemical properties of the food might influence the outcome it is doubtful that any of the drying techniques allow a well-defined cut between adsorbed and bound water. On the contrary it is possible to define the total water content in milk powder as all water molecules present in whatever form. This is usually measured by the Karl–Fischer (KF) method (Rüegg & Moor, 1987). In this study we measured samples the moisture or water content of a large number of milk powders by several techniques (IDF 26A, desiccation by P_2O_5, KF) and used water activity and near infrared spectroscopy to further understanding. We show how the measurement techniques relate to each other and demonstrate that the KF technique seems to be the most precise and best-defined method. This results, when the KF method is applied properly, in the best reproducibility of the tested methods.

Keywords: Moisture; Water content; Karl Fischer; Isotherm; Milk powder; Drying

1. Introduction

The water content has a strong influence on the physico-chemical stability of milk powder during storage and distribution. Additionally technological functionalities like dissolution or wettability can also be affected by the water content (Mathlouthi, 2001). The oxidative stability of milk powder varies with the water content (Stapelfeldt, Nielsen, & Skibsted, 1997). Legislation imposes strict limits as milk powder or dried milk is an important commodity in international trade. Up to now international standards for moisture content are most commonly based on methods using loss of weight upon drying under controlled conditions in an oven (Rückold, Grobecker, & Isengard, 2000).

According to most common definitions, water can be present in food in at least three forms: free water, adsorbed water and bound water. Free water is present in the void volume or in the pores of the food. It can serve as a dispersing agent, as a solvent for crystalline compounds or for microbiological growth. Adsorbed water is located on the surface of the macromolecules in the food matrices. Bound water is defined as the water of hydration bound to the product by strong H-bonds (Mathlouthi, 2001). Bound water relates to the monolayer of water molecules whereas adsorbed water is present in the form of multilayers in the matrices. This explanation follows the theory of the BET (Brunauer, Emmett, & Teller, 1938) isotherm describing vapour desorption or adsorption isotherms.

Water determination in dried milk can be performed using either direct or indirect methods. The most common direct techniques are either desiccation or oven drying based. In our study we used the desiccation technique with diphosphorus pentoxide (P_2O_5), which is considered to be one of the strongest desiccation agents. The partial pressure of water over this substance can be considered as zero. To separate the water from the product the sample is placed in a tube together with the

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* Corresponding author.
E-mail address: christoph.reh@rdls.nestle.com (C. Reh).

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P_2O_5. To increase the driving force of the drying process the part of the tube where the sample is placed can be heated. It is important not to apply temperatures, which degrade the product or release volatiles. The water content is then determined gravimetrically, usually in several steps up to constant weight.

The most frequently used method is based on the mass loss that dried milk undergoes when heated in an oven. Drying techniques do not measure the water content as such. The result is better defined as the weight loss of the product under the applied drying conditions. Therefore the results achieved with these methods reflect the weight loss caused by the chosen conditions and do not necessarily reflect the true water content. The weight loss can be caused not only by water, but also by the loss of volatiles present in the product or produced by degradation reactions related to heating of the sample. Often vacuum ovens are chosen to reduce these effects. The major weakness of standard oven methods is their unsatisfactory reproducibility. The climatic conditions of the laboratory strongly influence the drying process. As oven drying is a process that involves reaching a final equilibrium an increased relative humidity in the laboratory will automatically lead to lower results. It can be shown that the residual water content is also related to the temperature and relative humidity in the oven. Both parameters are linked to the temperature and relative humidity in the laboratory. This explains the poor reproducibility of the oven method in collaborative studies while repeatability tends to be extremely good.

Therefore the IDF working group reviewed the IDF 26A standard method and worked out a technique using a stream of dried air. This eliminates residual moisture in the product related to the relative humidity of the air. In the method a test portion of 5.0 ± 0.3 g is dried for 5 h at 87.0 ± 1.0 °C (De Knegt & van den Brink, 1998). The sample is placed in a column and a controlled stream of 33 ml/min of dried air is passed through it. This air is prepared by passing it through a tube containing silica gel. The drying conditions were chosen to match the results of the method of IDF 26A standard (1993). This is aimed to work with the same norms, while improving the reproducibility of the method. The principal open question is whether under the given new conditions a clear distinction between adsorbed and bound water is obtained. The final weight loss in a drying process is determined by the drying conditions and the physico-chemical status of the product. This means that the structure of the product can influence the result.

2. Materials and methods

The present work is based on the comparison of the following methods and practices. Water activity and near infrared spectroscopy measurements are used to support conclusions on the selectivity of the moisture determination methods.

3. Drying method IDF standard 26A (ODM)

This standard gravimetric method consists of drying 1–3 g of a test sample at 102.0 ± 2.0 °C under atmospheric pressure for 2 h. Constancy of mass is tested by additional drying steps of 1 h until the difference in mass does not exceed 0.5 mg. For this study two further improvements were applied to the oven drying method. First, all air drying ovens were placed in an air-conditioned laboratory with controlled temperature (23.0 ± 2.0 °C) and relative humidity (40 ± 5). Second, the number of samples in the oven was limited to six to provide comparable amounts of released volatiles during all measurement series. We used model T6060 ovens (Heraeus AG, Germany). The temperature in the ovens was measured using a temperature controller (Hamster 2000, Herni AG, Switzerland), which is checked twice a year against a certified thermometer. Analyses were performed at least in duplicate measurement and results averaged.

4. Desiccation method using P_2O_5 (DES)

The samples (ca. 2 g) were desiccated under a water pump vacuum in the presence of phosphorpentoxide (P_2O_5) at 48.0 ± 1.0 °C up to weight constancy. The weight was determined after 10 days and then every second day up to weight constancy. The P_2O_5 was changed when the glass tube was opened. These conditions were applied to the first set of instant milk powder samples (see Section 8). As alternative, approximately 2 g of the product was dried for 2 h at 102.0 ± 1.0 °C in the presence of phosphorpentoxide. These conditions were applied to the set of skimmed milk powder samples (see Section 8). A constant temperature was guaranteed by placing the end of the tube where the sample is placed into an oil bath. Due to the large heat capacity of the oil the temperature is very stable. The analysis was performed at least in duplicate and the results averaged.

5. Volumetric Karl–Fischer titration

The Karl–Fischer (KF) method is performed by automatic titration and determines the water content of a sample by means of a two step chemical reaction where iodine reacts with water in the presence of sulphur dioxide.

$$CH_3OH + SO_2 + RN \leftrightarrow [RNH]SO_3CH_3$$

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

The parameter measured in the volumetric KF method is the amount of iodine reduced in the second reaction step. The analyses were carried out using a Mettler DL18 apparatus. About 0.5 g of product was analyzed at room temperature with Hydranal composite 5 as reagent and methanol as the solvent. The solvent was changed at every replicate. The analysis was performed at least in duplicate and the results averaged. More information on how to optimize the KF method can be found elsewhere (Thomasow, Mrowetz, & Delfs, 1972).

6. Water activity

Water activity (WA) measurements were carried out with a Rotronic Hygroskop model DT following our internal procedure. All water activity values were measured at 25 °C and corrected using a quadratic equation obtained using five standard (reference) calibrating salts as shown in the table below. The linearity of the calibration curve was used to determine the proper functioning of instrument and the good preparation of the reference salts used. The samples were equilibrated at around 25 °C before measurement. The results are the average of duplicate measurements.

No.	Name	Chemical formula	Merck reference number	aw value at 25 °C
1	Lithium chloride	$LiCl \cdot H_2O$	1.05679.1000	0.113
2	Potassium acetate	CH_3COOK	1.04820.1000	0.225
3	Magnesium chloride	$MgCl_2 \cdot 6H_20$	1.05833.1000	0.328
4	Potassium carbonate	K_2CO_3	1.04928.1000	0.432
5	Magnesium nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	1.05853.1000	0.529

7. Near infrared spectroscopy

All the samples were scanned using a NIRSystems model 6500 scanning near infrared spectroscopy (NIR) spectrometer from FOSS NIRSystems. The instrument scans from 400 to 2500 nm, using a silicon detector for wavelengths between 400 and 1100 nm and a lead sulphide detector from 1100 to 2500 nm. The measurements were done according to the standard operating procedure using a small ring cup. Samples were scanned in duplicate over the whole range of wavelength (400 to 2500 nm) with a resolution of 2 nm. However, an averaged spectrum was used for further work.

For the normalization procedure all NIR spectra were exported as JCAMP (JCM) format from the instrument and converted into absorption values corresponding to each peak using a home made program. Further, these absorption values were normalized to eliminate texture effects. The normalization was performed using an EXCEL sheet at 1680 and 2232 nm (0.359 and 0.688 Abs, respectively). The selected range of wavelengths contains peaks of fat (1728 nm), water (1940 nm) and carbohydrates (2100 nm), from which we are only using the water band at 1940 nm in this report.

8. Samples

Two sets of instant milk powder and one set of skimmed milk powder were used. The first sample set consisted of 24 samples of instant milk powder produced on a pilot plant-scale during three hours of production. Samples were taken at several locations in the spray dryer installation to obtain varying moisture contents. Low moisture content samples were obtained by additional drying in a desiccator. The fat content was relatively constant at about 28 wt% and the water content (KF) ranged from 1.2 to 5.3 wt%.

The second sample set of instant milk powders included eighty-one samples from various factories with water contents (KF) ranging from 2.5 to 4.2 wt%. These samples also had a wide distribution of fat content between around 26 and 30 wt%. Additionally included in the sample set were milk powders containing different levels of crystallized lactose due to technological differences or modification during storage or transport of the product.

The set of skimmed milk powder consisted of 69 samples from various factories with moisture content (KF) ranging from 2.0 to 6.5 wt%. The desiccation method with P_2O_5 was performed on a selected number of 24 samples. The oven method was also only applied to 24 samples with a partial overlap with the sample set undergoing the desiccation method. The only criteria for selecting samples was to achieve an almost even distribution over the water content range. This should allow to check the linearity between the methods and to identify any bias.

9. Results and discussion

The first sample set of instant milk powders showed very consistent results. In Table 1 the results and the

Table 1
Comparison of different methods for instant milk powder

Sample no.	Oven (ODM)	P_2O_5 (DES)	Karl–Fischer (KF)	DES–ODM	KF–ODM	KF–DES
	Content in wt%					
1	4.89	5.15	5.30	0.26	0.41	0.15
2	4.89	5.12	5.27	0.23	0.38	0.15
3	2.38	2.62	2.79	0.24	0.41	0.17
4	2.16	2.40	2.47	0.24	0.31	0.07
5	2.95	3.18	3.37	0.23	0.42	0.19
6	4.98	5.15	5.38	0.17	0.40	0.23
7	3.23	3.41	3.57	0.18	0.34	0.16
8	3.71	3.92	4.05	0.21	0.34	0.13
9	5.28	5.49	5.68	0.21	0.40	0.19
10	3.46	3.68	3.84	0.22	0.38	0.16
11	1.19	1.49	1.55	0.30	0.36	0.06
12	5.18	5.43	5.63	0.25	0.45	0.20
13	4.68	4.85	4.96	0.17	0.28	0.11
14	2.17	2.41	2.47	0.24	0.30	0.06
15	1.93	2.19	2.36	0.26	0.43	0.17
16	4.64	4.90	5.03	0.26	0.39	0.13
17	4.13	4.37	4.49	0.24	0.36	0.12
18	1.76	2.03	2.09	0.27	0.33	0.06
19	4.54	4.78	5.03	0.24	0.49	0.25
20	3.59	3.84	4.01	0.25	0.42	0.17
21	2.10	2.33	2.54	0.23	0.44	0.21
22	5.10	5.31	5.51	0.21	0.41	0.20
23	2.23	2.44	2.62	0.21	0.39	0.18
24	2.92	3.15	3.36	0.23	0.44	0.21
Average	3.50	3.74	3.89	0.23	0.39	0.16
Minimum	1.19	1.49	1.55			
Maximum	5.28	5.49	5.68			

differences between the three methodologies are listed. The aim of this study was to establish differences between the three methodologies under ideal conditions. Especially samples were analysed by the standard drying method (ODM) in a very short period of time in a climatisised laboratory. It is known that varying climatic conditions in a laboratory cause a loss of reproducibility and sometimes of repeatability. Only precise measurements allow conclusions on the occurrence of a bias to be drawn.

Repeatabilities for the three methods were determined based on duplicate measurements. For the standard drying method (ODM) the standard deviation of repeatability was 0.019 wt%. The KF method gave a standard deviation of repeatability of 0.019 wt% and the standard deviation of repeatability for the desiccation method was 0.030 wt%. The repeatability can, therefore, be judged as excellent for all three methodologies.

All three methods were highly correlated as shown in Fig. 1. For the samples with moisture content ranging between 1.2 and 5.3 wt% (based on ODM) we find a regression R^2 values of 0.999 and a slope of nearly 1. The intercepts indicate the presence of a bias between each of the methods. The KF method gives the highest results with a bias of 0.39 wt% versus the standard drying method (ODM) and a bias of 0.16 wt% versus the desiccation method (DES) at 48 °C. The bias between the standard drying method (ODM) and the desiccation method (DES) is, therefore, 0.23 wt%. This difference could either result from an incomplete drying process or water molecules, which are bound as crystallization water in the lactose of the milk powder. Assuming that the KF method determines the total water content we must conclude that the two other methods have water remaining in the sample.

The second sample set of instant milk powders gave results in line with those of the first set. The repeatability for the KF method calculated as the standard deviation of the repeatability for all eighty-one instant milk powders gave 0.04 wt%. Due to the measurement plan some additional information can be drawn. The moisture isotherm between 0.1 and 0.3 water activity and between 2.5 and 4.2 wt% water content can be constructed. This is the area of the moisture isotherm most often related to adsorbed water and the isotherm should be linear in this region. The results indeed include a linear regression shown in Fig. 2. To develop a complete moisture isotherm following either the BET (Brunauer et al., 1938) or the GAB (Guggenheim, 1966) model more data points at lower and higher water activities are needed. Some spread can be seen around the linear regression line. Some of this spread can be explained by

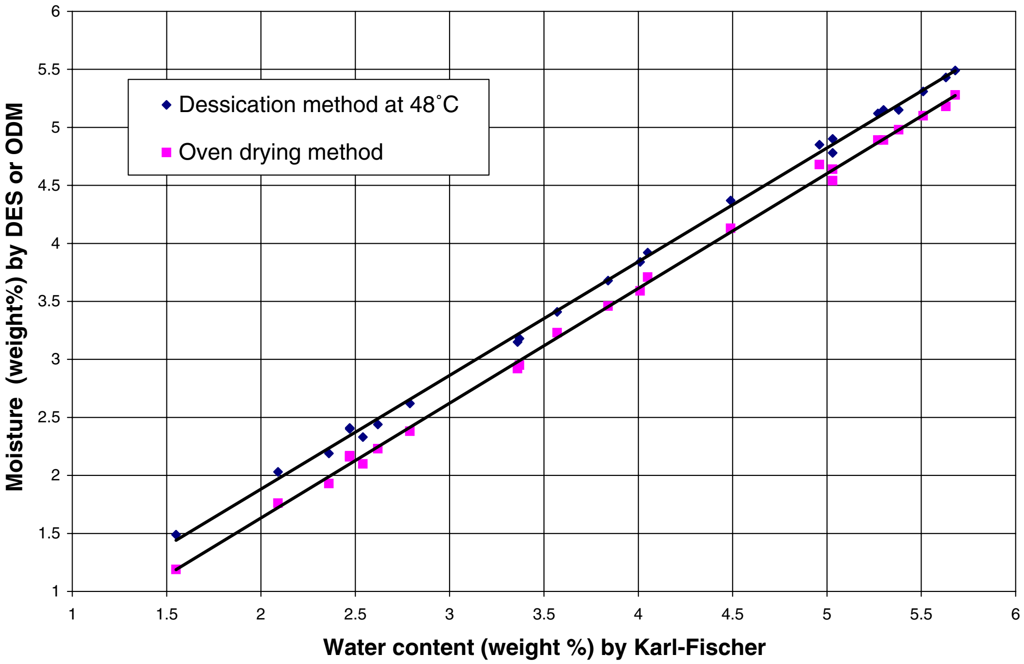

Fig. 1. Moisture determination in instant milk powder.

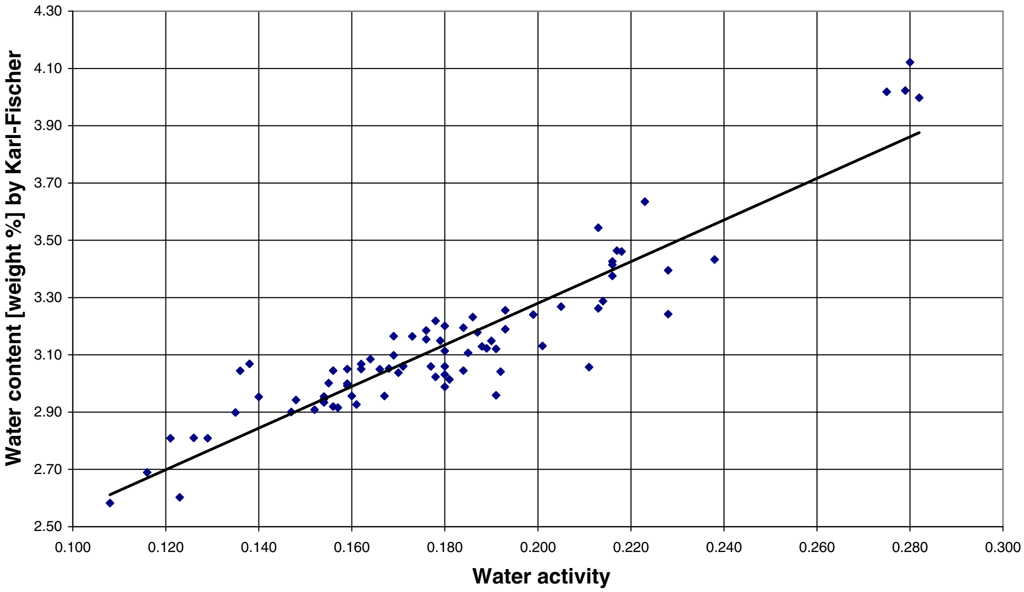

Fig. 2. Moisture isotherm for instant milk powder.

the variation in the total fat content. The rest relates to variations of other chemical or physico-chemical parameters.

The normalized NIR absorbance at 1940 nm was determined for the same set of samples and is plotted in Fig. 3. The regression shows a very good correlation between both parameters with an R^2 of 0.94 and a standard deviation of differences of 0.07 wt%. This shows the ability of near infrared spectroscopy to predict water content in milk powders. It also illustrates the ability of the KF method to measure properly the water content. The major advantage of NIR absorbance at 1940 nm is the almost complete absence of interference from other food ingredients. The peak of water is principally only influenced by the texture of the product. Most of the residual variation can be explained by the analytical error of the KF method and the instrumental error of the near infrared spectroscopy method.

The set of skimmed milk powder samples gave comparable results to those obtained for instant milk

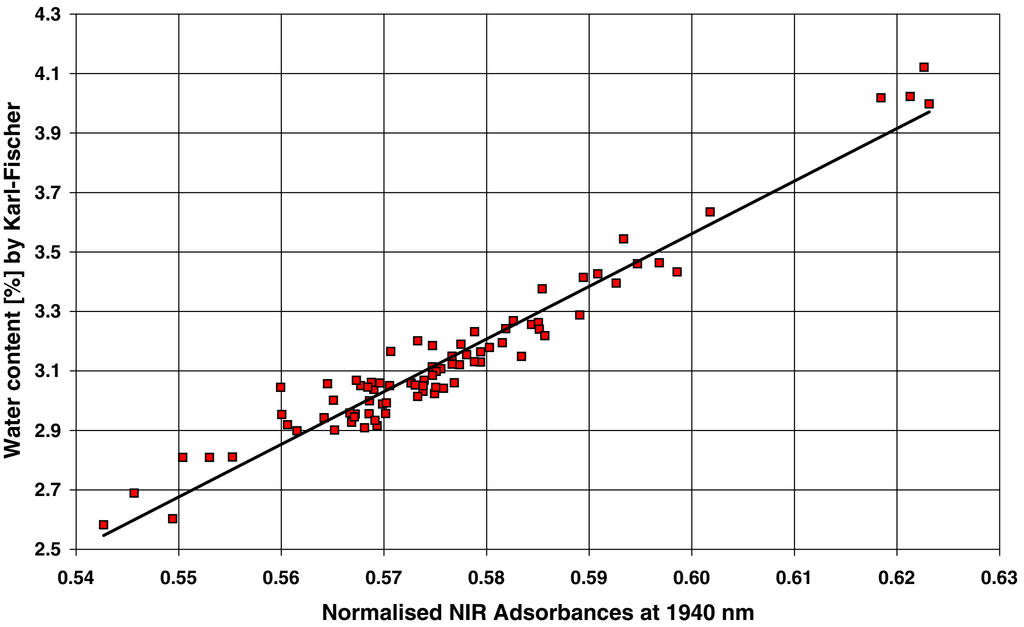

Fig. 3. Water content versus NIR adsorbance.

powders. Based on a set of 24 samples with moisture contents ranging between 1.8 and 4.9 wt% (based on ODM) we found a high correlation between the standard drying method (ODM) and the KF method. The R^2 was 0.997 and the slope very nearly 1. The intercept value indicates the presence of a bias between the two methods. The KF method gave higher results with a bias of 0.43 wt% versus the standard drying method.

Using a second sample set of 24 samples with moisture contents ranging between 2.22 and 5.02 wt% (based on KF) we found a high correlation between the KF method and the desiccation method (DES) with P_2O_5 at 102 °C. The R^2 was 0.999 and the slope very nearly 1. The intercept indicates the presence of a bias between the two methods. The two regression curves are illustrated in Fig. 4. The KF method gives higher results with a bias of 0.06 wt% versus the desiccation method. This result indicates some residual water after applying the desiccation method assuming that the KF method determines the total water content. One explanation could be the presence of crystallization water in the lactose. Nevertheless the bias observed is smaller with the desiccation method at 102 °C than at 48 °C. This illustrates that the temperature is important to draw the water out of the product. On the other side a too high temperature might lead to degradation of the product.

As for instant milk powder, we also determined part of the moisture isotherm for the set of skimmed milk powders. We also assumed an almost linear relationship between 0.1 and 0.37 for water activity and water contents between approximately 2 and 6.4 wt%. Compared to instant milk powder less spread was observed which results in a better fit of the regression as shown in Fig. 5. This can be partially explained by the absence of fat in skimmed milk powder and better repeatability of the KF method for skimmed milk powder compared to instant milk powder. At water activities around 0.1 we observed a trend of water content values smaller than the regression line. This can be interpreted as corresponding to a change in the moisture isotherm when going from the multilayer into the monolayer absorption region.

Repeatability's of the three methods were determined based on duplicate measurements. For the standard drying method (ODM) the standard deviation of repeatability was 0.034 wt%. The repeatability for the KF method calculated as standard deviation of repeatability for all 69 skimmed milk powders was 0.018 wt%. The standard deviation of repeatability for the desiccation method (DES) was 0.032 wt%, but this was calculated with a smaller number of samples than the other two methods. The repeatability can be judged as excellent for all three methodologies.

The differences found between the standard drying method (ODM) and the desiccation method (DES) under the two conditions illustrate the importance of keeping the drying conditions as narrow as possible. The final result can be significantly modified by choosing the temperature, the relative humidity, the gas flow over the product and the residence time. Additionally it is clear that it is impossible to differentiate adsorbed from bound water by the oven drying or desiccation techniques. Depending of the chosen conditions part of the bound water will be determined or part of the adsorbed water will not be included. To optimize the conditions it is important to understand the process of removing the water from a food product. This loss of water is influ-

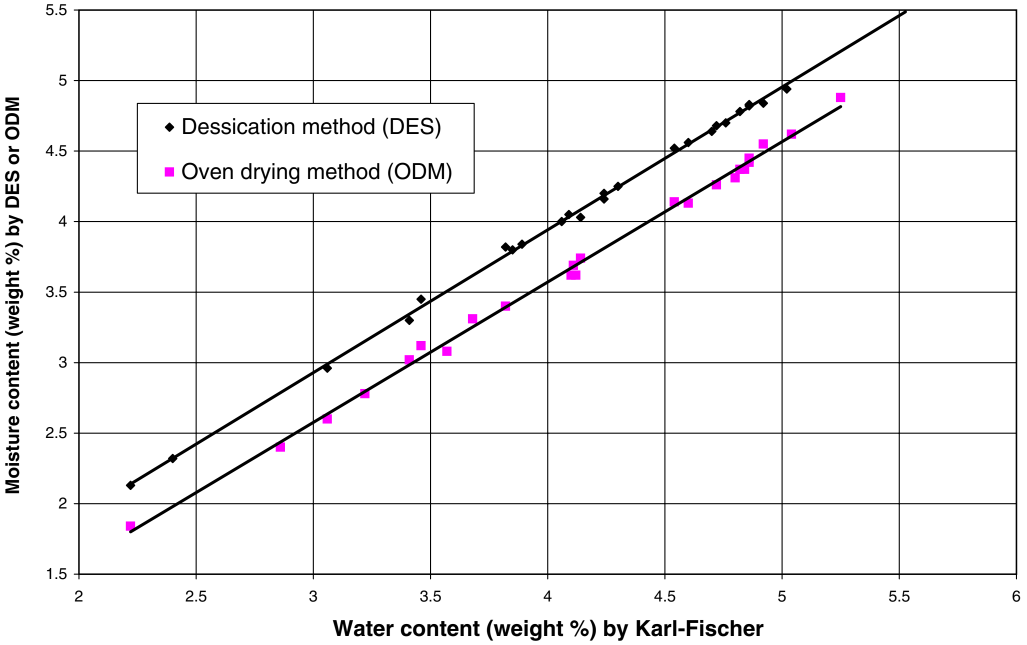

Fig. 4. DES and ODM versus KF for skimmed milk powder.

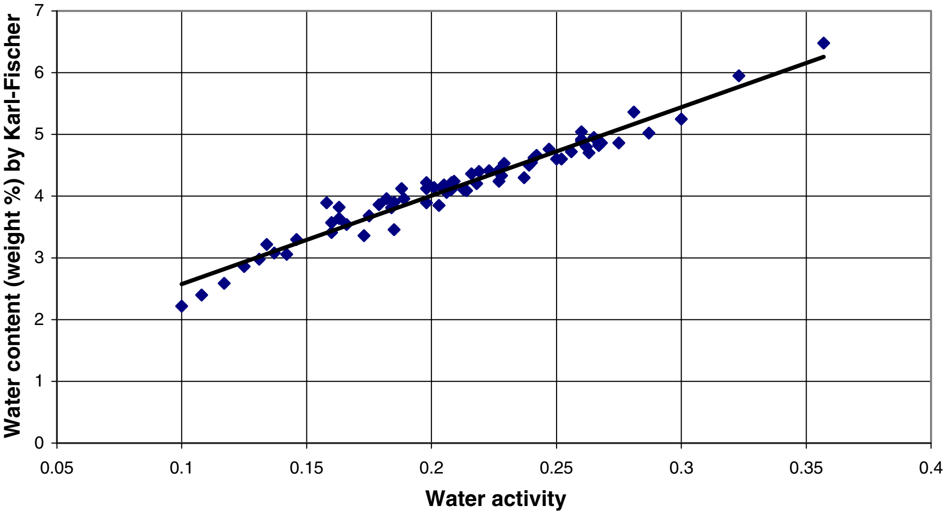

Fig. 5. Moisture isotherm for skimmed milk powder.

enced by the diffusion of water molecules in the food, the transfer of the water molecule from the food into the gas phase and convection of the gas removing the water molecule from vicinity of the food. Diffusion of water molecules out of food is mainly influenced by temperature, it's geometry and it's structure. Increasing temperature and decreasing particle size of the sample will speed up the drying process. Transfer of water molecules into the gas phase is influenced by the surface area (e.g., particle size of the product), temperature, pressure in the drying chamber and relative humidity of the gas phase. Increased convection over the product keeps the relative humidity over the product low and facilitates drying by removing the water molecules from near-by the product.

10. Conclusions

The KF method determines the total water content of dried dairy products like milk powders with high accuracy and good reproducibility. It is, therefore, the best choice as basic reference method and for calibrating indirect methods widely used in the food industry for process control purposes such as near infrared spectroscopy. It can additionally be used for a wide range of other food ingredients, which are used in the dairy industry. The principal risk of the KF method is the reactivity of the reagent with other ingredients. However so far no major interference was reported for standard dried milk powders. Only vitamin C, an ingredient in some dairy products, is known to react.

No drying or desiccation technique is able to determine a clearly defined water portion in the product. The results of these techniques depend on the applied parameters and reflect loss upon drying under defined conditions. The reproducibility of all drying techniques depends on how well the conditions can be controlled. Temperature, time, relative humidity, pressure and gas flow over the sample are the most important parameters. Several studies have shown that especially the standard drying method (ODM) exhibits limited reproducibility.

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