Lait 82 (2002) 413–421

DOI: 10.1051/lait:2002020

Original article

Lactose crystallization: determination of α-lactose monohydrate in spray-dried dairy products

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Abstract – A new method was used to determine the amount of α-lactose monohydrate present in spray-dried milk products. During the manufacture of spray-dried milk products, the lactose may crystallize (a process during which the α-lactose picks up a molecule of water), while the hygroscopicity and caking properties decrease. In order to determine the degree of crystallization of α-lactose monohydrate, the water bound to the crystals (water of crystallization or hydrate water) is calculated as the difference between total moisture and free moisture or non-hydrate water. The free moisture content is determined in a drying oven at 87 or 105 °C at constant weight. The total moisture is determined by a new method using a vacuum-drying desiccator with dried zeolite powder as a function of temperature, vacuum and time. This new method is then compared to the Karl Fisher method. Results on the percentage of α-lactose monohydrate are also presented for various milk, whey and lactose powders with degrees of crystallinity of α-lactose monohydrate ranging from 0 to 100%. Combining the method for total moisture content using a vacuum-drying oven, and the method for free moisture content makes it easy to determine the amount of α-lactose monohydrate in spray-dried dairy products.

Dairy powder / water / lactose / crystallization / spray drying

Résumé – Cristallisation du lactose : détermination de la teneur en lactose cristallisé α monohydraté dans les poudres laitières obtenues par séchage par atomisation. Une nouvelle méthode a été utilisée pour déterminer la teneur en lactose cristallisé α monohydraté. Après concentration par évaporation sous vide et avant séchage par atomisation, le concentré laitier peut subir une étape de cristallisation au cours de laquelle le lactose cristallisera sous forme α monohydraté permettant ainsi une diminution du collage en chambre d'atomisation et de l'hygroscopicité de la poudre ainsi obtenue. Pour calculer le pourcentage de lactose cristallisé α monohydratée, il est nécessaire de déterminer la teneur en eau liée au cristal par différence entre l'eau libre et l'eau totale. La teneur en eau libre est déterminée par dessiccation à l'étuve entre 87 et 105 °C jusqu'à poids constant. La teneur

Communication at the 1st International Symposium on Spray Drying of Milk Products, Rennes, France, October 16–18, 2001.

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en eau totale est déterminée par une nouvelle méthode par dessiccation sous vide en présence de zéolite en fonction de la durée, de la température et de la pression. Cette nouvelle méthode est comparée avec la méthode de titrage de Karl Fischer. Des résultats de teneur en lactose cristallisé α monohydraté (entre 0 et 100 %) sont présentés dans différentes poudres laitières (lait, lactosérum, caséinate). Ainsi, la détermination de la teneur en eau libre associée à la détermination de la teneur en eau totale par notre nouvelle méthode permet de calculer facilement le pourcentage de lactose cristallisé α monohydraté dans les poudres d'origine laitière.

Poudre laitière / eau / lactose / cristallisation / séchage par atomisation

1. INTRODUCTION

Milk sugar or lactose is a disaccharide ($C_{12}H_{22}O_{11}$) that is found only in milk. This carbohydrate exists in two isomeric forms (α and β). Both forms can crystallize but the physico-chemical relationships between the different forms of lactose are very complex [9]. During the production of milk powders, the water evaporation during spray drying is so rapid that despite saturation, the lactose cannot crystallize but remains in the powder as amorphous lactose, or lactose glass [10, 12–15]. Amorphous lactose is very hygroscopic and can cause caking problems during and after spray drying, in powders such as whey powders which have a high lactose content. To avoid caking, the lactose has to be pre-crystallized as α-lactose-monohydrate, which is non-hygroscopic [4–6, 8]. This is done by lactose crystallization after concentration by vacuum evaporation. The rate of crystallization is controlled by varying the rate of mutarotation of the β-form into the α-form and can be determined on dairy powders by measuring water crystallization. This water content is determined by the difference between the total moisture and the free moisture or non-hydrate water content according to Haugaard et al. [7] and Pisecky [14]. The free moisture content is measured by calculating the loss of weight in about 1.5 g of samples, dried in an oven heated at 102 ± 2 °C to constant weight [7, 13]. The total moisture content, which includes both the free moisture content and the water of crystallization, can be determined by the ADPI [2] or the Karl Fischer titration methods [7]. These methods are very complicated and expensive to operate.

The aim of this paper is to describe a new vacuum desiccator method for the determination of the total moisture content and the amount of α-lactose monohydrate in spray-dried milk products with the help of the physico-chemical relationships between different forms of lactose established by King [10]. It takes into account the bound water or hydrate water in mineral salts, whey proteins and micellar caseins as well as the free moisture content.

2. MATERIALS AND METHODS

2.1. Vacuum desiccator method

Total moisture or total water content was measured in a vacuum desiccator (Fig. 1). In order to do this, 1 ± 0.1 g powder was placed in a stainless steel support on top of 95 ± 5 g of pre-dried zeolite powder (WE 291, Bayer, Puteaux, France) while the temperature, vacuum, time and zeolite content were varied (3 replicates).

2.2. Skim milk, whey, whey proteins, casein suspension and lactose powders and mineral salt solutions

The experiment on skim milk, casein suspension and whey protein powders was performed at Bionov (Rennes, France) in a 3-stage pilot-plant spray dryer (GEA, Niro Atomizer, Saint-Quentin-en-Yvelines,

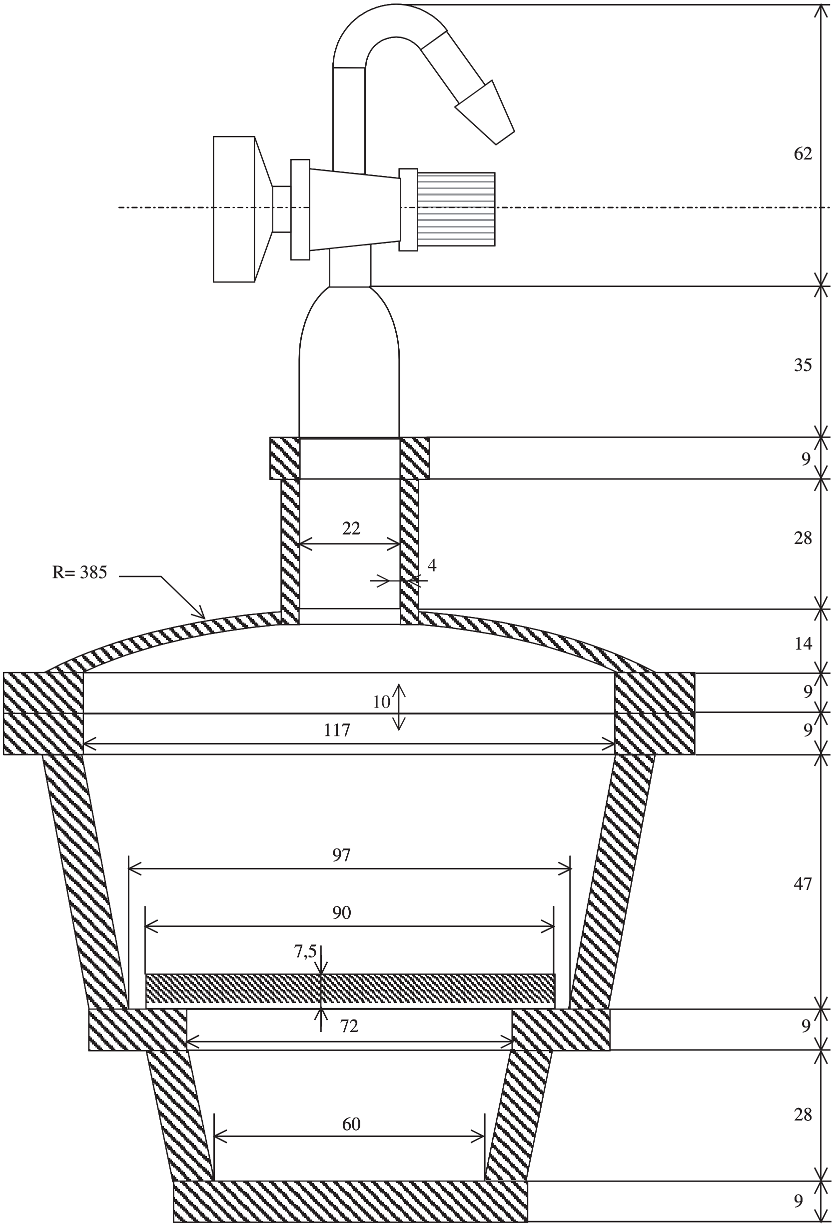

Figure 1. Vacuum desiccator.

France) according to Schuck et al. [17, 18]. This atomizer was equipped with a pressure nozzle (0.73 mm orifice diameter) and a 4 slot core (0.51 mm nominal width), that gave a 60° spray angle. The evaporation capacity was 70 to 120 $kg \cdot h^{-1}$ (depending on inlet and outlet air temperature and air flow). The α-lactose monohydrate was bought at Sigma-Aldrich Chemie Gmbh (Steinheim, Germany). The mineral salt solution (I and II) was created according to Jenness and Koops [9]. Whey powders were obtained from Uclab (Landerneau, France) and Laiterie Nouvelle de l'Arguenon (Créhen, France).

2.3. Chemical analyses

Free moisture, free water or non-hydrate water content was estimated by weight loss after drying 1.5 g of the sample mixed with sand in a forced air oven at 105 °C for 5 h (powder) or 7 h (liquid). Total moisture content was determined by Karl Fischer titration according to Haugaard [7]. Bound moisture or hydrate water content was determined by calculating the difference between total moisture and free moisture content. Nitrogen fractions were determined according to the methods of Rowland [16] and Aschaffenburg and Drewy [3]: non-casein nitrogen (NCN), non-protein nitrogen (NPN), total nitrogen matter (TNM) with a 6.38 conversion factor, casein (TNM – NCN) and whey protein (NCN – NPN), by Kjeldahl. Lactose was determined by the Acton method [1]. Nir Infrared Reflectance (NIR) (Infralyzer 500, Bran+Luebbe, Plaisir, France) was used to characterize the state of lactose (amorphous or crystallized) according to Vuataz [19]. Ashes were measured after incineration at 550 °C for 5 h. The chemical composition of the different powders and solutions are reported in Table I.

3. RESULTS AND DISCUSSION

3.1. Vacuum desiccator method

In order to determine the optimal conditions of this new method and the total moisture content of α-lactose monohydrate (theoretically 50 $g \cdot kg^{-1}$; that is 950 $g \cdot kg^{-1}$ of total dry content) in skim milk and whey powders, we have modified some of parameters (the temperature, vacuum, time and zeolite).

Table I. Chemical composition of the different powders and solutions.

Products	Free moisture	Casein	Whey proteins	Ashes	Lactose	α-Lactose monohydrate
	($g \cdot kg^{-1}$)					
Skim milk powder	53.0	282.2	63.3	80.2	510.0	Absence
Whey powder (0% fat)	26.1	nd	95.1	73.0	725.0	Presence
Whey powder (50% fat)	13.4	nd	49.0	36.3	371.2	Absence
Casein suspension powder	86.2	758.4	41.1	78.5	18.0	Absence
Whey protein powder	40.6	nd	853.9	21.1	nd	Absence
Milk salt solution I [8]	776.1	nd	nd	218.2[1]	nd	nd
Milk salt solution II [8]	894.2	nd	nd	107.6[1]	nd	nd

nd: non determined.
[1]: theoretical value [8].

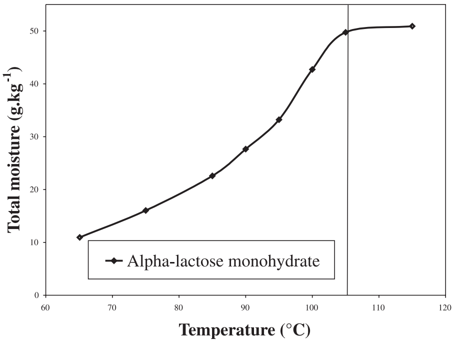

Figure 2. Total moisture versus temperature under 40 Pa of vaccum and for 7 h.

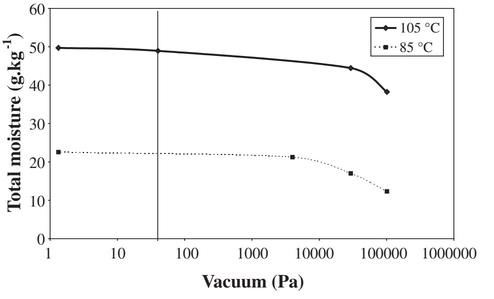

Figure 4. Total moisture versus vacuum for 7 h, at 85 °C and 105 °C.

3.1.1. Effect of temperature

An increase in temperature from 60 to 115 °C, under 40 Pa of vacuum and for 7 h, increased the total moisture content (Fig. 2). The temperature which gave the result nearest to the theoretical total moisture content of α-lactose monohydrate was 105 °C.

3.1.2. Effect of vacuum

An increase of vacuum from 1.33 Pa to 101325 Pa, at 85 °C and 105 °C and for 7 h gave a higher total moisture content (Fig. 3). The vacuum that gave the result closest to the theoretical total moisture content of α-lactose monohydrate (50 g·kg^{-1}) was under 40 Pa.

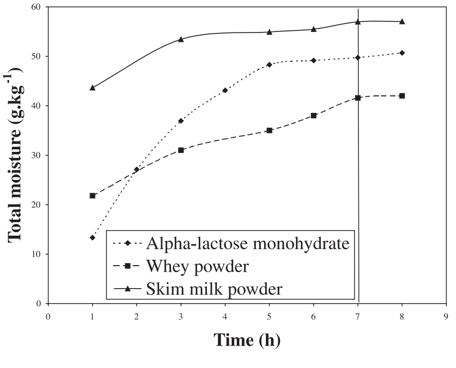

Figure 3. Total moisture versus time under 40 Pa of vacuum and at 105 °C.

3.1.3. Effect of time

An increase in the duration of the experiment from 1 to 8 h, under 40 Pa of vacuum and at 105 °C, increased the total moisture content (Fig. 4). The time which gave the result closest to the theoretical total moisture content of α-lactose monohydrate was 7 h. We have similar results with whey and skim milk powder.

3.1.4. Effect of zeolite (presence or absence)

Table II shows that to obtain a result of total moisture content close to the theoretical total moisture content of α-lactose monohydrate (50 g·kg^{-1}), the presence of zeolite was essential under 40 Pa of vacuum.

3.1.5. Method

All the above results made it possible to define a new method of dosage of the total moisture, the methodology of which is the following.

3.1.5.1. Apparatus and reagents

Analytical Balance – Desiccator (Fig. 1) – Oven – Zeolite – Vacuum pump – Metal round, flat-bottomed, 54 ± 1 mm in diameter.

Table II. Effect of the presence or absence of zeolite on the total moisture of α-lactose monohydrate, at 105 °C, for 7 h.

Zeolite (95 g)	Pressure (< 40 Pa)	Free moisture ($g \cdot kg^{-1}$)
Absence	Absence	1.3
Absence	Presence	1.6
Presence	Absence	38.3
Presence	Presence	49.7

3.1.5.2. Procedure

Weigh accurately and put 1 ± 0.1 g of sample in a round flat-bottomed metal dish. Place the dish directly on the shelf, on top of 95 ± 5 g dried zeolite powder in the desiccator under 40 Pa of vacuum and keep it at 105 ± 1 °C in an oven. Dry for approximately 7 h until constant weight is reached. Remove the desiccator from the oven and cool to room temperature for 1/2 h. Remove the vacuum, open the desiccator slowly and weigh the dish. Calculate percent loss in weight as moisture.

3.2. Repeatability

Table III shows the repeatability of the new vacuum desiccator method for determination of total moisture content in skim milk, whey and lactose α-monohydrate powders. The relative standard deviation ($p < 0.05$) for 10 analyses (n = 10) is 2.9, 5.4 and 2.9% for the skim milk, whey and lactose α-monohydrate powder, respectively.

3.3. Relation between vacuum desiccator method and Karl Fischer titration

Figure 5 shows the relation between the new vacuum desiccator method and Karl Fischer titration for the determination of total moisture content in lactose α-monohydrate. The determination coefficient r^2 was 0.97 which showed a significant relationship between these two methods.

3.4. Applications

Table IV shows the amount of total, free and bound moisture in casein suspension powder, whey protein powder and mineral salt solutions.

3.4.1. Casein suspension and whey protein

Using the chemical composition of casein suspension and whey protein powder (Tab. I) and the results in Table IV, the quantity of bound water per 100 g of protein

Table III. Repeatability of the new vacuum desiccator method.

Powder	Average ($g \cdot kg^{-1}$)	Standard deviation ($g \cdot kg^{-1}$)	Relative standard deviation $p < 0.05$ (%)
Skim milk	58.82	0.86	2.9
Whey	32.33	0.88	5.4
α-Lactose monohydrate	49.74	0.72	2.9

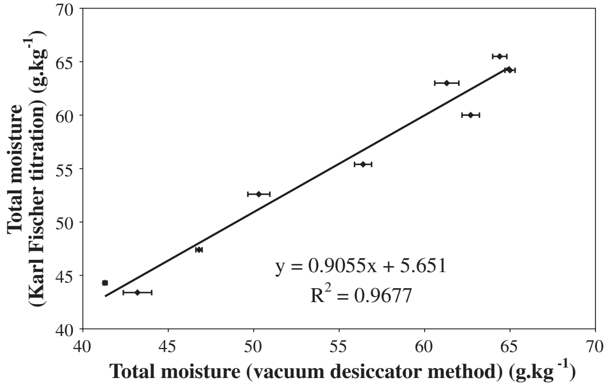

Figure 5. Relation between vacuum desiccator method and Karl Fischer titration.

Table IV. Rate of the free, total and bound moisture.

Powder	Free moisture ($g \cdot kg^{-1}$)	Total moisture ($g \cdot kg^{-1}$)	Bound moisture ($g \cdot kg^{-1}$)
Casein suspension powder	86.2	97.7	11.5
Whey protein powder	40.6	44.9	4.3
Milk salt solution I [8]	776.1	782.0[a]	5.9
Milk salt solution II [8]	894.2[b]	892.0[a,b]	≈ 0
Skim milk powder	53.0	58.8	5.8
Whey powder (0% fat)	26.1	61.3	35.2
Whey powder (50% fat)	13.4	14.7	29.8

[a]: theoretical value [8].
[b]: no significant difference ($p < 0.01$).

can be deduced. So, we found about 1.52 g and 0.50 g of bound water per 100 g of casein suspension and whey protein, respectively. These results can be compared with those of Kinsella and Fox [11] which showed that the structural water content (water activity < 0.05) could be situated under 2 g per 100 g of protein or 10 to 20 H_2O molecules / protein.

3.4.2. Milk salt solution

Using the results of Tables I and IV and knowing that the milk salt solution I represents 2% of the milk salt solution and that the quantity of total solids of the milk salt solution is 7.622 $g \cdot kg^{-1}$, we find that the bound water content per 100 g of milk salt solution is 1.55.

3.5. Determination of α-lactose monohydrate in spray-dried milk powders

The content of α-lactose monohydrate (% C°) in spray-dried milk powder was calculated according to the following formula:

$$\%C^o = \left(\frac{BWL \cdot 19}{L}\right) \cdot 100 \qquad (1)$$

where

BWL: bound water content in the lactose ($g{\cdot}kg^{-1}$);

L: lactose content ($g{\cdot}kg^{-1}$).

The bound water content in lactose was calculated according to the following formula:

$$BWL = TW - FW - (0.0152.CC) - (0.005.WPC) - (0.0155.MSSC) \quad (2)$$

where

BWL: bound water content in lactose ($g{\cdot}kg^{-1}$);

TW: total water content ($g{\cdot}kg^{-1}$);

FW: free water content ($g{\cdot}kg^{-1}$);

CC: casein content ($g{\cdot}kg^{-1}$);

WPC: whey protein content ($g{\cdot}kg^{-1}$);

MSSC: milk salt solution content ($g{\cdot}kg^{-1}$).

Using equations 1 and 2 and the results of Tables I and IV, we find that the percentage of α-lactose monohydrate (% C°) in skim milk powder, free fat whey powder and whey powder with 50% of fat was about 0%, 88.0% and 2.5%, respectively. These results agreed with those obtained by the Near Infrared Reflectance method [19] which showed that there was a negligible amount of crystalline α-lactose in the whey powder with 50% of fat.

3.6. Standard addition method with α-lactose monohydrate

Figure 6 shows the theoretical and measured quantity of α-lactose monohydrate added to skim milk powder without crystalline α-lactose. The determination coefficient r^2 was 0.99 which showed a high degree of agreement between the figures calculated during the experiment and the theoretical rate of α-lactose monohydrate. The standard deviation of the method for calculating the percentage of crystalline α-lactose in skim milk powder varied between 3.7 and 6.9% for content in α-lactose monohydrate varying from 0 to 100%.

4. CONCLUSIONS

This measurement of total moisture content by the new vacuum desiccator method helps to estimate easily and accurately the percentage of crystallized lactose (standard deviation between 3.7 and 6.9%) in dairy powders by taking into account the free moisture content and the moisture content bound to the casein suspension (1.52 g of

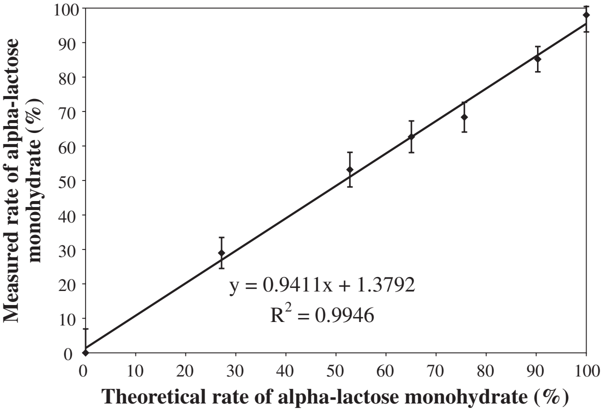

Figure 6. Standard addition method with alpha-lactose monohydrate.

bound water per 100 g), whey protein (0.50 g of bound water per 100 g) and mineral salt solutions (1.55 g bound water per 100 g). This non-destructive method also helps to almost eliminate the total water contained and so to get back an anhydrous sample useful for other possible analyses (X-ray and sorption isotherm …).

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