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Miloslav Kalab
Agriculture Canada - Centre for Food and Animal Research

Marijana Caric
University of Novi Sad

Spasenija Milanovic
University of Novi Sad

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COMPOSITION AND STRUCTURE OF DEMINERALIZED SPRAY-DRIED MILK PERMEATE POWDER

Miloslav Kaláb, Marijana Carić*, and Spasenija Milanović*

Centre for Food and Animal Research, Agriculture Canada, Ottawa, Ontario, Canada K1A OC6
*Faculty of Technology, University of Novi Sad, Novi Sad, 21000 Yugoslavia

Abstract

Permeates obtained by the ultrafiltration of milk were demineralized by electrodialysis to demineralization rates (DR, expressed in %) varying from 51 to 93. The demineralized permeates were then concentrated to 55% total solids, cooled to 12°C to crystallize lactose, and spray-dried. Light microscopy and scanning electron microscopy showed that the resulting powders consisted partly of globular and partly of sharp-edged particles. The proportion of the globular particles was highest at DR of 51 and was lowest at DR of 93. The sharp-edged particles were lactose crystals covered with dried collapsed foam consisting of the mother liquor. The globular particles were formed by minute lactose crystals cemented by amorphous material. X-Ray microanalysis (elemental analysis and mapping for potassium, calcium, and phosphorus) of the powders showed that the mineral elements were concentrated in the globular particles.

Lactose, being mostly in the form of α-monohydrate crystals (ratio of α-monohydrate to amorphous lactose was 2.8:1), made the permeate powders resistant to the effects of an atmosphere at 85% relative humidity. Recrystallization of lactose and disintegration of the globular particles occurred only in powders exposed to 100% relative humidity.

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Direct inquiries to M. Kalab
Telephone number: 613 993 6002
Fax number: 613 943 2353

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Introduction

Ultrafiltration separates milk into retentate and permeate. The retentate contains high-molecular substances such as proteins and fat, whereas low-molecular substances such as lactose and mineral salts form the permeate. The composition of the permeate varies depending on the composition of the milk ultrafiltered and the conditions of ultrafiltration, particularly the type of membrane used, the concentration rate, inclusion of diafiltration, and some other factors. On an average, a permeate contains 5-6% total solids of which 80-85% is lactose, 8-10% ash, protein (up to 6% of total solids), fat, non-protein nitrogen, and vitamins [7]. Compared to whey as another by-product rich in lactose, permeates contain considerably less protein.

Lactose, as the major constituent of the permeate is used in the food and pharmaceutical industries but the high ash content prevents the permeate from being used directly. Demineralization [3] followed by spray-drying transforms the permeate into a useful and marketable source of lactose [13]. Changes in the chemical composition of permeates due to demineralization have been studied recently [2, 7]. Precrystallized spray-dried permeate is a free-flowing powder which does not cake as easily as non-instantized spray-dried milk powders when exposed to humid air. This is in agreement with the principle of instantization, *i.e.,* conversion of amorphous lactose into α-lactose in order to reduce caking in milk powders [1].

The objective of this research note was to extend a previous study [7] by examining characteristic structural features of spray-dried permeate powders at various degrees of demineralization. The results had earlier been presented in poster form [2].

Materials and Methods

Preparation of spray-dried permeate

The permeate (6 samples) was produced on an industrial scale by the ultrafiltration of bulk milk at the Somboled Dairy Plant, Sombor. The milk was ultrafiltered in an Ultrafiltration Module Type 35 fitted with GR-61PP membranes (APV Pasilac, Copenhagen, Denmark). The permeate was pasteurized at 76°C for 5 s, cooled to 4°C, evaporated at 70°C to increase the total solids content to 18%, and demineralized by electrodialysis in the Odžačanka Dairy Plant in Odžaci (Yugoslavia). The electrodialysis was carried out at 35-40°C for 15-30 min on an industrial scale using the SRTI equipment (Sodeteg, France). Demineralization rate (DR) was calculated for each permeate according to formula DR = $100(a-b)/a$, where a is the ash content per total solids in the permeate before demineralization and b is the ash content per total solids in demineralized permeate. The demineralized permeates were evaporated at 70°C to further increase the total solids contents to 55%, cooled to 12°C, and crystallized for 10-12 h.

The permeates containing precrystallized lactose were spray-dried in industrial-scale equipment (APV Anhydro, Copenhagen, Denmark). Centrifugal atomization and two-stage spray-drying [4] were used. The inlet and outlet air temperatures were 170°C and 80°C, respectively.

Physico-chemical analysis

Total solids were determined by drying at 102±2°C to constant mass [9], ash was determined by incineration at 550°C [9], lactose according to the IDF method [5], α-lactose and amorphous lactose according to [8], and minerals (K, Na, Ca, Mg, P, Zn, Fe, Mn, and Cu) were determined by emission spectrophotometry using a PGS-2 spectrograph (Carl Zeiss, Wien, Austria). The results of these and additional analyses have been published earlier [7].

Scanning electron microscopy (SEM) and X-ray microanalysis

Each powder was spread in a one-particle layer on the sticky surface of a double sticky photo mounting card disk (J. B. EM Service, Inc., Pointe Claire, Dorval, Quebec, Canada) attached to an SEM aluminum stub for SEM [6] or to a carbon disk for X-ray microanalysis. For SEM, the powders were sputter-coated with gold and for X-ray microanalysis they were sputter-coated with carbon.

The coated samples were examined in an ISI DS-130 scanning electron microscope operated at 20 kV. Micrographs were taken on 35-mm film. Energy dispersive spectra and X-ray maps for individual elements were obtained using a Tracor Northern 5500 X-ray spectrometer (Middleton, WI, USA).

Effects of atmospheric humidity on the permeate powders were studied using SEM. The powders, mounted in single-particle layers on SEM stubs as mentioned above or spread on microscope glass slides in layers <0.5 mm thick, were exposed to humid atmosphere in an incubator for 1 to 6 days at 25°C in glass dishes, 55 mm in diameter and 35 mm high, having ground lids. A saturated KCl solution placed on the bottom of the dishes provided 85% relative humidity and distilled water provided 100% humidity [11].

Results and Discussion

Chemical composition

Chemical composition of the six original permeates was in agreement with the data in the literature [12] and confirmed that lactose was the predominant component of the total solids (~87%), followed by ash (~8.1%); there was 4.4 to 7.8% protein in the total solids (Table 1). The fat content was below 0.1%.

Table 1. **Chemical composition of six original permeates**

Parameter:	Mean (%):	Range (%):
Total solids (TS)	5.30	5.03 - 5.53
Ash	0.43	0.38 - 0.45
Ash/TS	8.11	7.23 - 8.58
Lactose	4.59	4.50 - 4.70
Lactose/TS	86.60	83.82 - 89.52
Total nitrogen	0.049	0.037 - 0.068
Total protein	0.31	0.23 - 0.43
Total protein/TS	5.85	4.38 - 7.77
Lactic acid	0.06	0.05 - 0.08
pH	6.55	6.5 - 6.6

Partial concentration by evaporation increased the total solids contents in the permeates from 5.0-5.5% to 16.3-21.6%. The lactose contents were raised from 4.5-4.7% to 14.6-18.3% and the ash contents were increased from 0.39-0.45% to 1.26-1.85%. Subsequent demineralization by electrodialysis affected all constituents, including the water content, to a variable extent depending on the demineralization rate (Table 2).

The contents of the most abundant elements in demineralized permeate powders at DR 51 and 93 are listed in Table 3. However, chlorides and sulfates were not determined although Cl and S were detected in the powders by X-ray microanalysis.

α-Monohydrate lactose contents in the spray-dried permeates were 64.8±5.6% and amorphous lactose was

Table 2. **Chemical composition (%) of partially concentrated permeates before and after demineralization**

No.:	Partially concentrated permeate				Demineralized permeate				
	TS*	Ash	Lactose	Ash/TS*	TS*	Ash	Lactose	Ash/TS*	DR**
1	21.6	1.62	18.3	7.50	17.4	0.64	14.8	3.68	51.1
2	20.5	1.85	17.6	9.02	18.1	0.69	15.5	3.82	57.7
3	17.5	1.24	15.6	7.09	18.4	0.37	12.9	2.56	63.9
4	19.9	1.82	17.2	9.14	18.5	0.41	16.0	2.21	75.8
5	19.4	1.62	16.2	8.35	15.2	0.15	12.8	0.98	88.3
6	16.3	1.26	14.6	7.73	13.4	0.07	12.0	0.52	93.3

* Total solids
** Demineralization rate

Table 3. Contents (mg/kg) of some elements in demineralized milk permeate powders

DR*	K	Na	P	Ca	Zn	Mn
51	4140	4370	2170	765	3.74	2.61
93	1620	2250	1340	517	1.31	1.96

*Demineralization rate

24.8±7.4%. The individual ratios of these two forms of lactose fluctuated between 1.44 and 3.72 with the mean of 2.8±0.8. This indicated that a greater part (~70%) of all lactose was in the form of α-monohydrate.

Structure of demineralized permeate powders

All powders were found to be mixtures of globular and sharp-edged particles (Figs. 1 and 2) and in this respect resembled spray-dried whey powders [10]. The sharp-edged particles were lactose crystals which developed as the result of oversaturation of the concentrated permeate with lactose and crystallization prior to spray-drying. Similar particles were observed by Saito [10] in precrystallized whey powder. Surfaces of many lactose crystals had lace-like ornamentations (Figs. 3 and 4). The ornamentation may have developed as the result of the collapse of foam which consisted of the mother liquor and adhered to the lactose crystals during spray-drying. Protein present in the mother liquor may have contributed to foaming.

Droplets of the mother liquor dried in the form of globular particles. These particles consisted of all solids which had initially been dissolved in the mother liquor, *i.e.*, lactose, mineral and organic salts, protein, and fat. The presence of microcrystalline lactose in the globular particles was noticeable under the scanning electron microscope (Fig. 5). In this respect, also the globular particles resembled spray-dried whey [10].

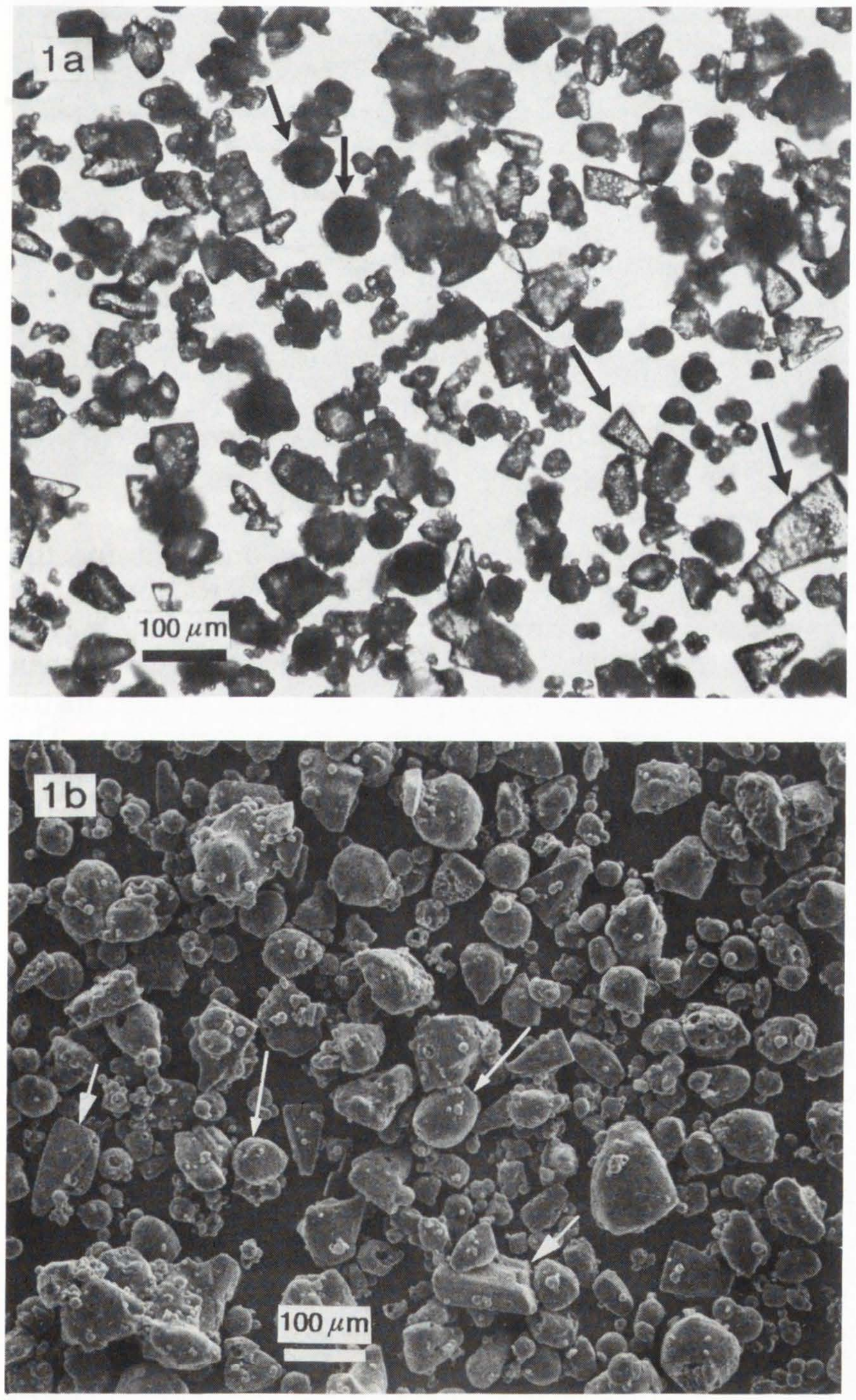


Fig. 1. Permeate powder (DR = 51) consists of globular (small arrows) and crystal-like particles (large arrows).
***a:** Light microscopy, **b:** SEM.*

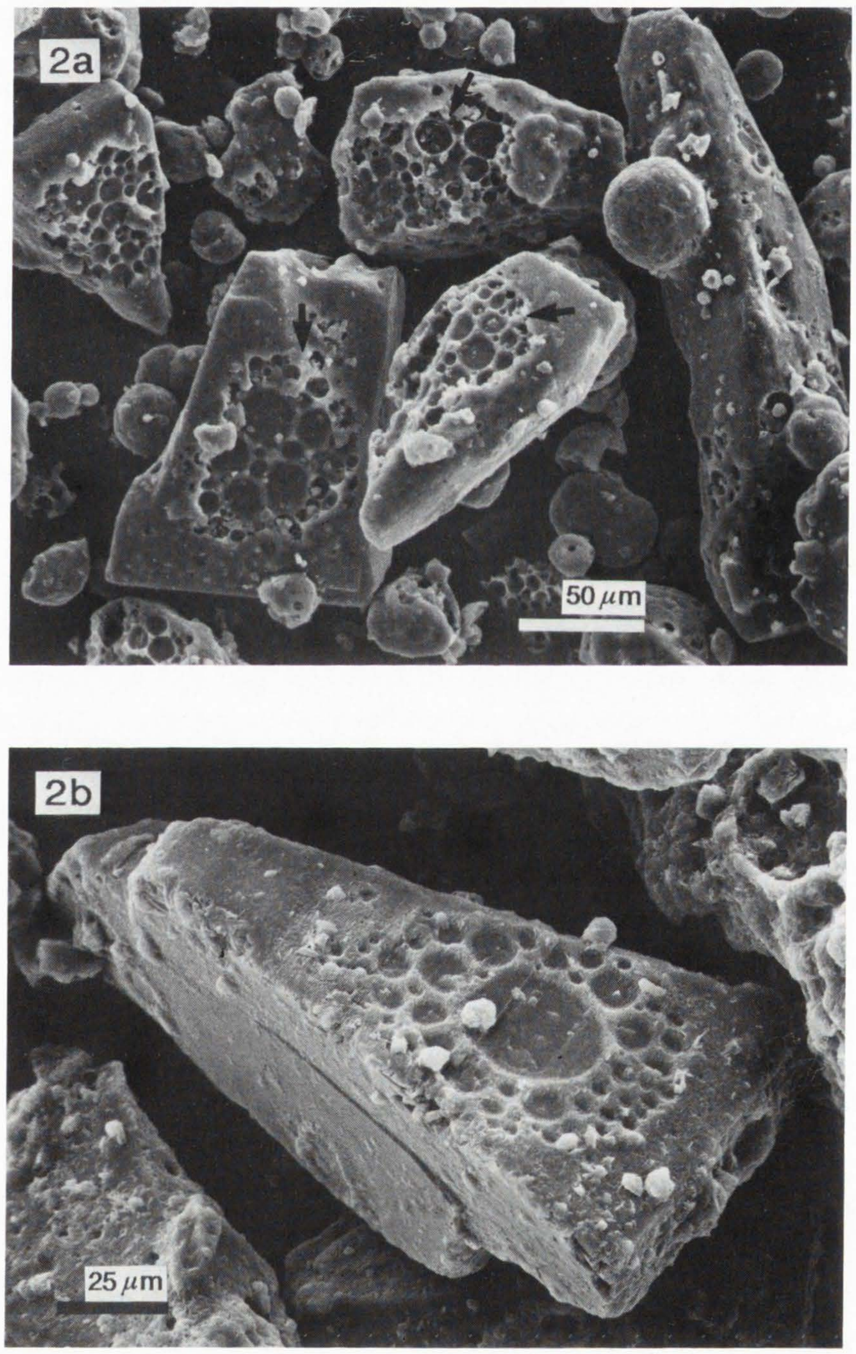


*Fig. 2. Surfaces of crystal-like particles with lace-like ornamentation (arrows). **a:** General view, **b:** Detail.*

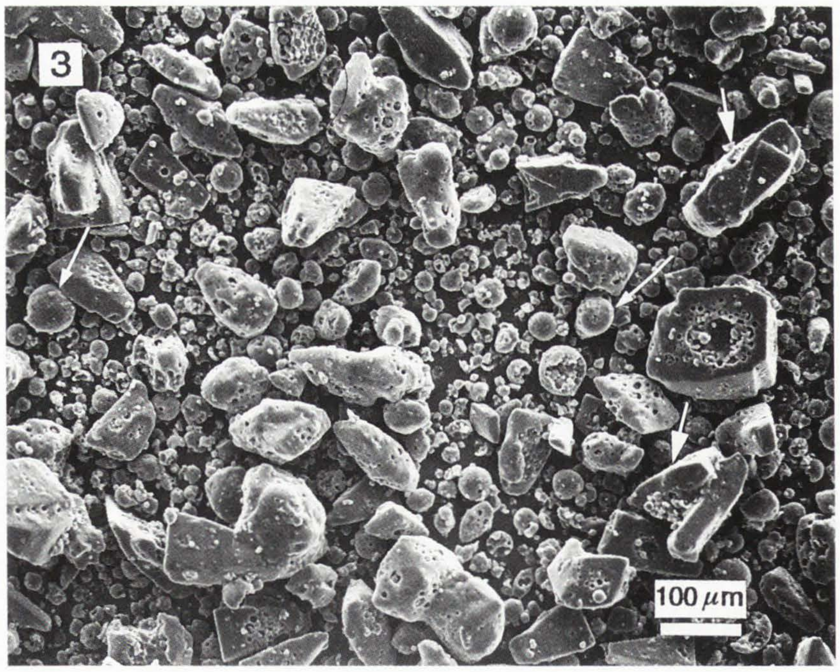


Fig. 3. Extended demineralization (DR = 75.8) decreases the proportion of globular particles (small arrows) and increases the proportion of crystal-like particles (large arrows) in the powders (SEM).

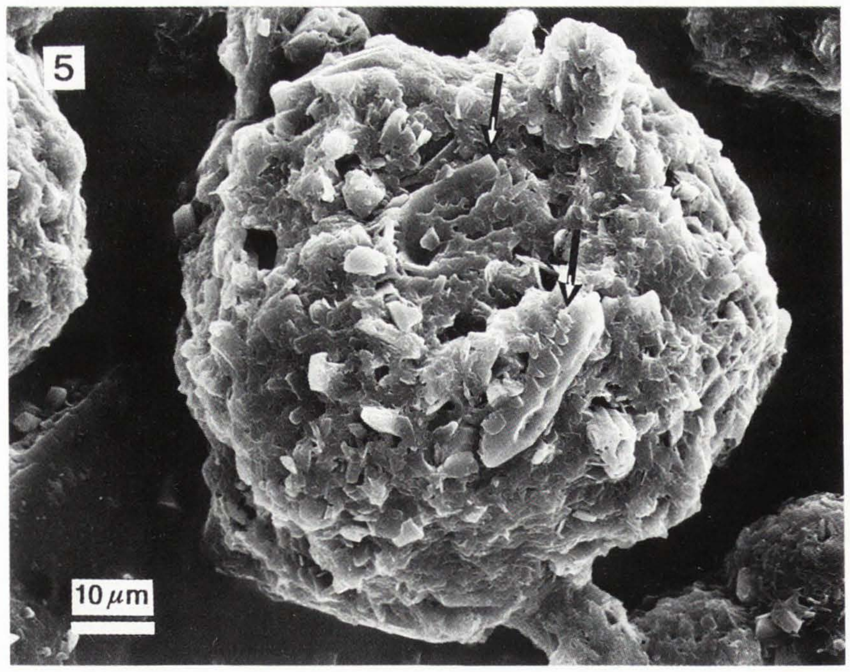
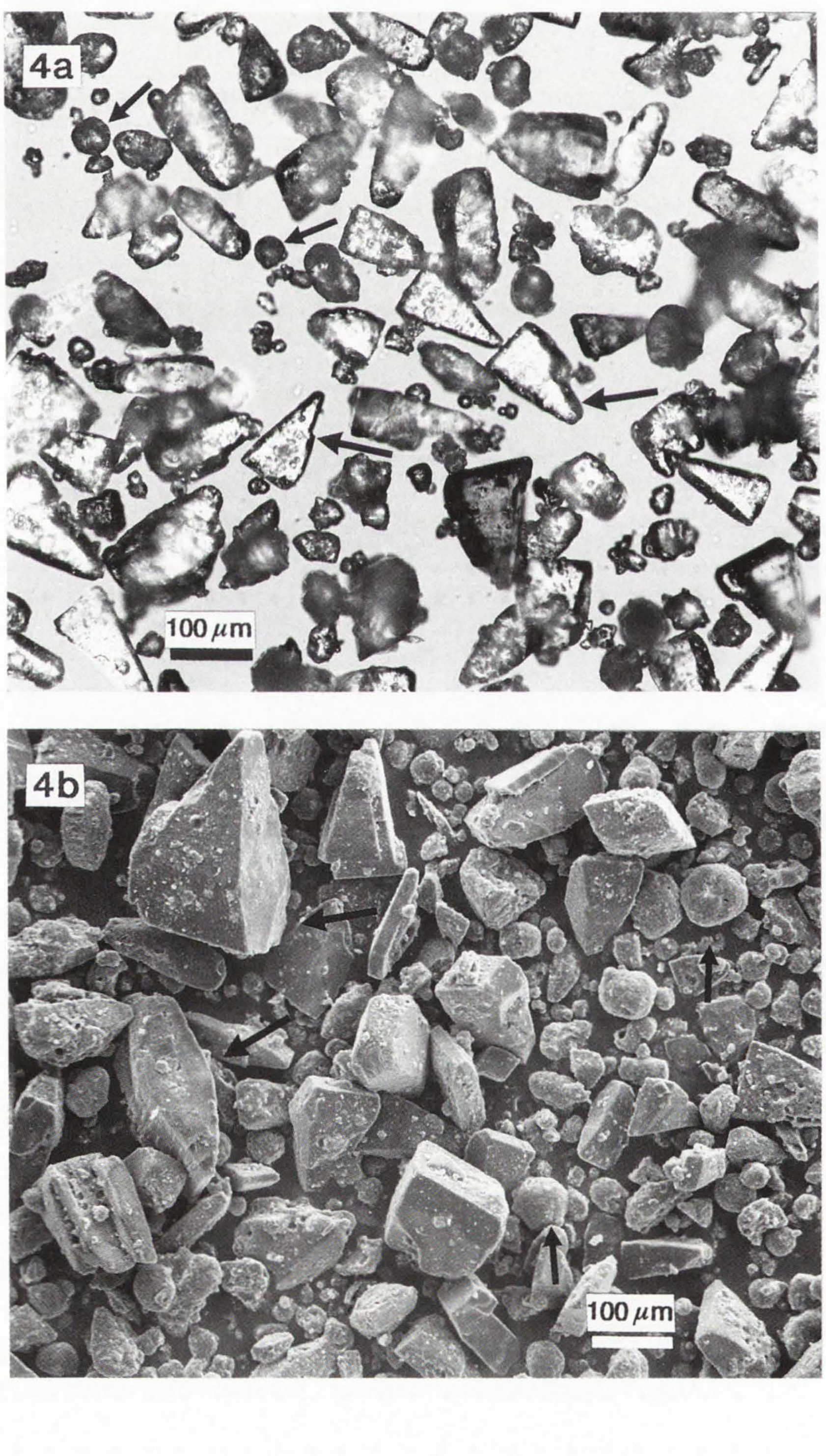


Fig. 5. Globular particles consisting of microcrystalline lactose (arrows) (SEM).



The incidence of the globular particles decreased and the sharp-edged particles became predominant as the demineralization rate was increased. This would be in agreement with the change in the composition of the permeate because most of the minerals had been reduced by extensive demineralization. Total nitrogen and protein were also decreased but fat contents remained unchanged. Lactose concentration was increased from 85% to 89.5% as DR was increased from 51 to 93 [7].

X-Ray microanalysis

The globular particles were firstly analyzed for the presence of mineral elements using their K_α lines. This analysis revealed the presence of P, S, Cl, K, and Ca. The globular and crystal-like particles (Fig. 6a) were then mapped for the distribution of K, Ca, and P. Similar distributions were obtained with each of these 3 elements. The map shown in Fig. 6b is a combination of all the 3 elements. It indicates that their highest concentrations were in the globular particles. Crystal-like particles showed considerably weaker signals for the mineral elements and the patterns were not clearly outlined. It is probable that the amorphous material adhering to the crystal-like particles (Fig. 6a), apparently consisting of the mother liquor, was the source of the signals. Thus it may be concluded that the mineral elements present in the spray-dried permeate powders were concentrated in the globular particles and were also present on the surfaces of lactose crystals.

Exposure to humid atmosphere

The high incidence of α-monohydrate lactose crystals (~70%) in the powders suggested that the powders may have a very low susceptibility to recrystallization in a humid atmosphere. Exposure of the powders to an atmosphere

*Fig. 4. At DR = 93, the proportion of crystal-like particles (large arrows) in the permeate powders is markedly increased and the proportion of globular particles (small arrows) is reduced. **a:** Light microscopy, **b:** SEM.*

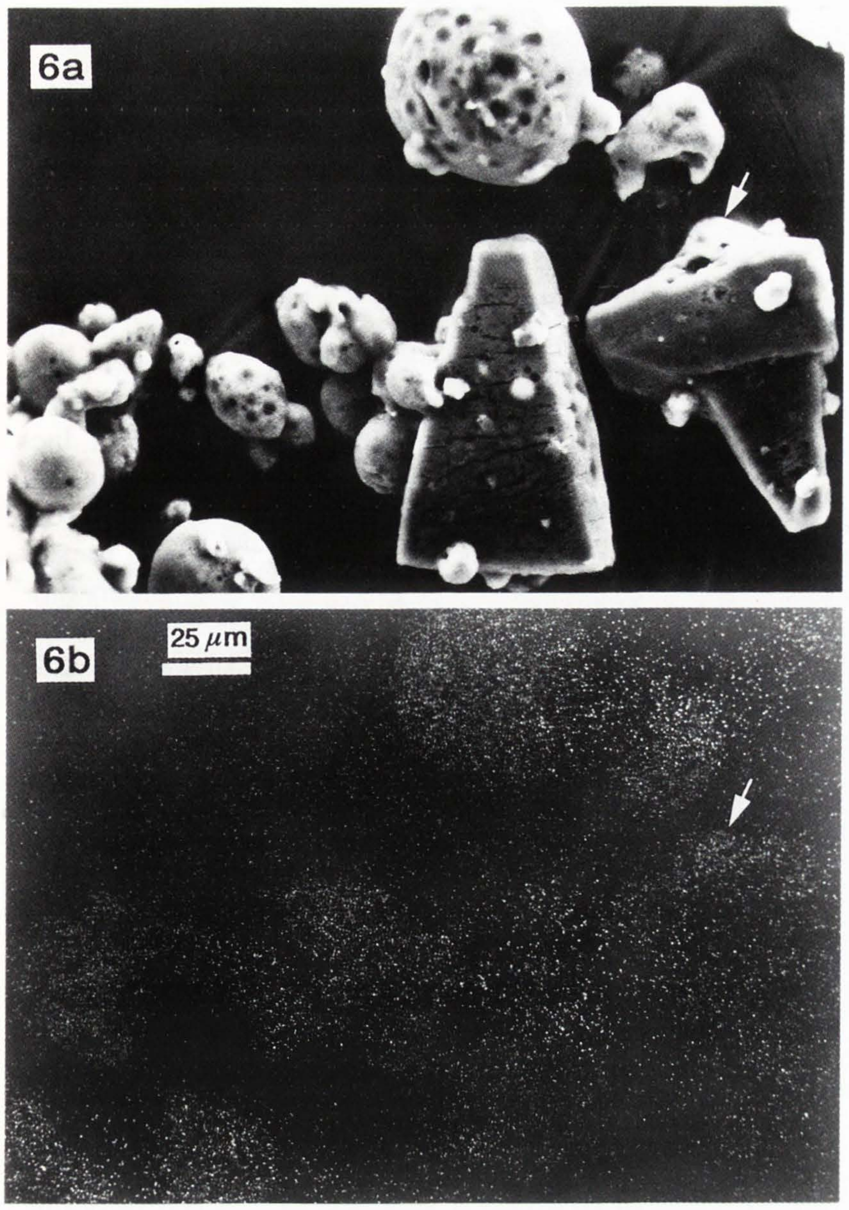


Fig. 6. Crystal-like and globular particles (SEM, ***Fig. 6a****) in a powder (DR = 76) subjected to X-Ray microanalysis mapping (****Fig. 6b****) show that K, Ca, and P have become concentrated in the globular particles. A combination of scans for all three elements is shown in* ***Fig. 6b****. Arrows point to mother liquor dried on the surface of crystal-like particles.*

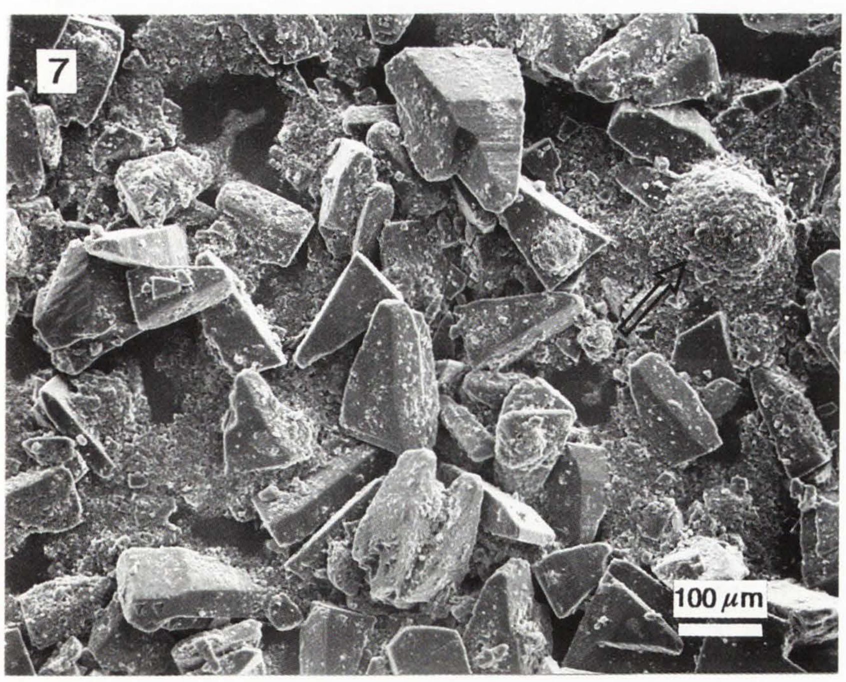


Fig. 7. Lactose recrystallized in a permeate powder (DR = 76) exposed to 100% relative humidity for 24 h at 25°C and the globular particles (asterisk) disintegrated.

with 85% relative humidity for 6 days confirmed this assumption. The powders remained unchanged. Structural features of the powders changed only following exposure to 100% relative humidity at 25°C for 24 h (Fig. 7). The globular particles disaggregated and microcrystalline lactose recrystallized.

In conclusion, this research note shows that the high lactose content and crystallization prior to spray-drying are reflected in the appearance of spray-dried permeate powders. Precrystallization resulting in most lactose being in the form of α-monohydrate crystals made the powders resistant to lactose recrystallization in an atmosphere having 85% or lower relative humidity.

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References

1. Carić M, Kaláb M. (1987). Effects of drying techniques on milk powders quality and microstructure. *Food Microstruc.* **6**(2), 171-180.
2. Carić M, Milanović S, Kaláb M. (1990). Production and physico-chemical quality of demineralized permeate powder. *Brief Commun. Abstr. Posters XXIII Int. Dairy Congress, Dairying in a Changing World,* Montreal, Canada, Oct. 8-12, 1990, Vol. I, 384 (Poster P725). Can. Nat. Com. Int. Dairy Fed. c/o Livestock Devel. Div., Agriculture Canada, Ottawa.
3. Evans M. (1985). Electrodialysis and ion exchange as demineralisation methods in dairy processing. In: *Evaporation, Membrane Filtration, Spray-Drying in Milk Powder and Cheese Production.* R. Hansen (ed.), North European Dairy Journal, Vanlose, Denmark, 55-78.
4. Hall CW, Hedrick TI. (1975). Drying of Milk and Milk Products, AVI Publishing Co., Inc., Westport, Connecticut, USA, 59-93.
5. International Dairy Federation (1974). Document No. 28, Int. Dairy Fed., Brussels, Belgium, 28-30.
6. Kaláb M, Carić M, Zaher M, Harwalkar VR. (1989). Composition and some properties of spray-dried retentates obtained by the ultrafiltration of milk. *Food Microstruc.* **8**(2), 225-233.
7. Milanović S, Carić M. (1990). Production and quality of demineralized permeate, concentrated permeate and permeate powder. *Milchwissenschaft* **45**(5), 303-308.
8. Niro Atomizer A/S. (1978). Analytical Methods for Dry Milk Products, 4th ed., A/S Niro Atomizer, Copenhagen, 66-68.

9. Pejić O, Djordjević J. (1973). Dairy Laboratory Handbook. Textbook Publishing House of the Serbian SR, Beograd, Yugoslavia, 44-46 (in Serbian).
10. Saito Z. (1988). Lactose crystallization in commercial whey powders and in spray-dried lactose. *Food Microstruc.* 7(1), 75-81.
11. Saltmarch M, Labuza TP. (1980). SEM investigation of the effect of lactose crystallization on the storage properties of spray-dried whey. *Scanning Electron Microsc.* **1980/III**, 659-665.
12. Shay LK, Wegner GH. (1986). Nonpolluting conversion of whey permeate to food yeast protein. *J. Dairy Sci.* **69**, 676-683.
13. Zadow JG. (1986). Utilisation of milk components: Whey. In: *Modern Dairy Technology.* Vol. 1. RK Robinson (ed.), Elsevier Applied Science Publishers, London, UK, 273-316.

Discussion with Reviewers

J. Fincher: Could you explain more fully what you mean by precrystallization preventing recrystallization, as given in your last sentence?

E. Parnell-Clunies: While this research clearly shows the need for demineralization in order to obtain the more stable α-monohydrate form, the added cost of processing may preclude demineralization unless the end product has enhanced value. Given the distinct size and morphological differences in the crystal form, do the authors think that a physical separation (sizing) of the end product would be relevant to obtain a high-value, stable permeate? If so, what would the approximate yields be of the stable and unstable permeate powders?

Authors: Evaporation of the permeate, which increases the total solids content to 55% as mentioned in the Materials and Methods section, produces an oversaturated lactose solution. Cooling to 12°C leads to the formation of α-monohydrate lactose crystals and facilitates spray-drying by reducing viscosity of the evaporated permeate. Omission of the crystallization procedure would produce part of the lactose present in the anhydrous form in the finished powders. Anhydrous lactose is hygroscopic and recrystallizes on absorption of water. Uncontrolled recrystallization of lactose is associated with caking of milk powders. Thus, partial precrystallization of lactose before spray-drying reduces susceptibility of the resulting spray-dried powder to recrystallization of lactose and to caking. Naturally, precrystallization is only partial, because part of the lactose present stays in the form of a saturated solution. This lactose may be converted into the anhydrous form during multi-stage drying.

Demineralization reduces the mineral contents in the permeates. Removal of the minerals enhances the value of the permeates so that they may be used in the food and pharmaceutical industries. Since the minerals in spray-dried permeate powders are concentrated in globular particles, the incidence of such particles is an indicator of the ash content. As the extent of demineralization is increased, the incidence of the globular particles is decreased and would be very low in a high-value, demineralized, stable spray-dried permeate powder.