

# 1 Chemistry of Milk – Role of Constituents in Evaporation and Drying

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## 1.1 Introduction

This chapter discusses the relevance of major milk components to concentrated and dried products, the chemical composition of the various products and some of the quality issues of the products associated with the various components. Knowledge of the chemical composition of these products is essential for understanding their manufacture, applications, nutritional attributes, essential chemical differences and functional properties, as well as the changes that occur during their manufacture and storage. Several comprehensive reviews of the chemical composition of milk are available in dairy chemistry texts and other publications (e.g. Walstra & Jenness, 1984; Wong *et al.*, 1988; Fox & McSweeney, 1998; Varnam & Sutherland, 2001; Anonymous, 2003; Walstra *et al.*, 2006).

Many factors affect the composition of milk. These include the species and breed of animal from which the milk is derived, the stage of lactation, the season and the nutritional status and health of the animal. In addition, changes to the milk occur after it is harvested and before it is processed, which may affect its processibility. Therefore, it is impossible to provide accurate compositional data. In Table 1.1, 'textbook values' of the major constituents, water, fat, protein, carbohydrate (lactose) and minerals or ash are given for whole milk and skimmed milk, that is, milk from which fat has been removed. Table 1.1 also gives compositional data for a range of concentrated and dried milk products selected from a range of sources. As for the composition of milk, several factors affect the composition of these products also. These include the factors that affect the unprocessed milk and also many processing and storage variables. Therefore, the data in Table 1.1 should be used as a guide only to the composition of particular products. Figure 1.1 shows a graphical comparison of the proximate compositions of the major dried products. For the sake of this illustration, the water content of the powders is assumed to be zero. In practice, however, the water content is approximately 3–5 g 100 g<sup>-1</sup>.

Table 1.1 and Figure 1.1 illustrate a wide range of compositions of the concentrated and dried milk products. In the following sections, these aspects are discussed in relation to the composition and quality aspects of the concentrated and dried products.

## 1.2 Chemical components of liquid, concentrated and dried milk products

### 1.2.1 Protein

Both the protein content and protein composition are important in milk concentrates and powders, with some products being characterised by their protein content. For example,

**Table 1.1** Proximate composition (g 100 g<sup>-1</sup>) of liquid, concentrated and dried milk products.

Product	Water	Fat	Protein	Carbohydrate	Ash/minerals
<i>Liquid milks</i>					
Whole milk	87	3.7	3.3	4.8	0.7
Skimmed milk	90	<0.1	3.4	4.9	0.75
<i>Concentrated milks</i>					
Evaporated whole milk					
American standard	72.7–74.7	7.5–8.0	6.5–7.1	9–10	1.3–1.6
British standard	67–69	9–10	8–9	11.0–12.5	1.9–2.1
Evaporated skimmed milk	79.5	0.3	7.6	11	1.6
Sweetened condensed milk	27	9	8	55	1.8
Sweetened condensed skimmed milk	28	0.3	10	59	2.3
<i>Milk powders</i>					
Whole milk powder	2–4	25–28	25–27	37–38	6–7
Skimmed milk powder	3–5	0.7–1.3	35–37	49–52	7.5–8.0
Buttermilk powder	2.8–3.8	3–6	33–36	47–49	7–8
Cream powder	2.6–3.0	55–70	12–15	13–24	2.0–3.5
<i>Milk and whey protein powders</i>					
MPC 42	3.5	1.0	42	46.0	7.5
MPC 70	4.2	1.4	70	16.2	8.2
MPC 75	5.0	1.5	75	10.9	7.6
MPC 80	3.9	1.8	80	4.1	7.4
MPC 85	4.9	1.6	85	1.0	7.1
High milk protein powder	5.3	2.3	88	0.7	7
Caseinate (Ca, K, Na)	3–5	0.9–1.5	89–95	0.2	3.3–5
Casein (acid)	9.5	0.8	97	0.1	1.8
Casein (rennet)	9.5	0.8	90.5	0.1	8.5
Low-protein WPC	4.6	2–4	34–36	44–53	7–8
Medium-protein WPC	4.3	5	53	35	7
High-protein WPC	3–4	4–6	59–65	21–22	3.5–4
Very high-protein WPC	4–5	0.3–7.0	72–81	2–13	2.5–6.5
Whey protein isolate	2.5–6	0.1–0.7	89–93	0.1–0.8	1.4–3.8
Fractionated whey proteins					
α-fraction	4.5	1.0	81.5	7	3.4
β-fraction	4.5	0.4	87	0.5	3.0

Table 1.1 Continued.

Product	Water	Fat	Protein	Carbohydrate	Ash/minerals
Milk/whey protein hydrolysate	4	5	81.5	3	4.5
<i>Whey powders</i>					
Whey powder (acid)	≤3.5	0.8	9–12	65–69	11–12
Whey powder (sweet)	3–6	0.8–1.5	12–13	70–73	7.5–8.5
Whey powder (demineralised)	≤3	≤1.5	≥11	78–82	≤4
Whey powder (demineralised)	≤3	≤1.5	≥11	80–84	≤1.5
Whey powder (deproteinised)	3	0.2–1	2.5	80–85.5	8.5–10
Whey powder (lactose-reduced)	2–3	1–4	18–25	40–60	11–27
<i>Miscellaneous products</i>					
Lactose (food grade)	0.5	0.1	0.1	99	0.1–0.3
Infant formula	2–3	26–39	10–18	40–60	8

MPC = milk protein concentrate; WPC = whey protein concentrate.

Data compiled from Hargrove & Alford (1974), Posati & Orr (1976), Walstra & Jenness (1984), Morr (1984), Bassette & Acosta (1988), Jensen (1990), Morr & Foegeding (1990), Morr & Ha (1993), Caric (1993), Haylock (1995), Huffman (1996), Early (1998), Australian Dairy Corporation (1999), Pintado *et al.* (1999), Holt *et al.* (1999), O’Malley *et al.* (2000), Mistry (2002), Fox (2002, 2003), Mleko *et al.* (2003), Thomas *et al.* (2004), Kim *et al.* (2005), FSANZ (2006), Walstra *et al.* (2006), Millqvist-Fureby & Smith (2007) and Sinha *et al.* (2007).

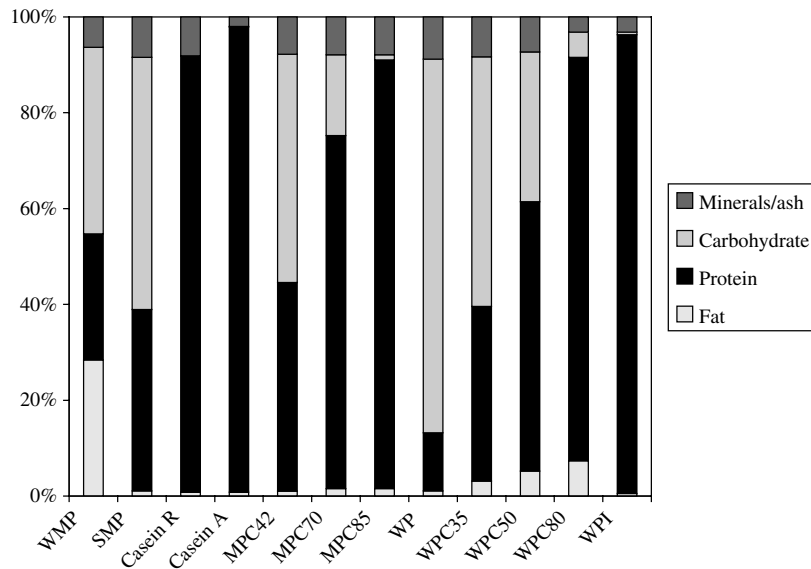


Fig. 1.1 Proximate composition of major milk-derived powders.

WMP = whole milk powder; SMP = skimmed milk powder; MPC = milk protein concentrate; WP = whey powder; WPC = whey protein concentrate; WPI = whey protein isolate; numbers following abbreviations denote approximate protein percentages.

milk protein concentrates (MPC) and whey protein concentrates (WPC) are marketed on the basis of their protein content, for example, WPC80 contains 80 g 100 g<sup>-1</sup> protein powder. In most cases, the nominal protein content is a crude protein figure, not a true protein figure. The non-protein nitrogen components, such as urea, represent the difference between these two values.

The proteins in milk consist of two broad types, the caseins that are insoluble at pH 4.6 and the whey proteins that are soluble at this pH. About 80 g 100 g<sup>-1</sup> of the protein is casein and the remainder is whey proteins. Hence, the casein: whey protein ratio in milk is ~4:1. A third minor class is the membrane proteins that form part of both the milk fat globule membrane and the skimmed milk membrane material. The membrane proteins have only a minor role in the properties of most concentrates and powders.

Table 1.1 and Figure 1.1 also show the difference in the protein contents of different powders. Four types of powder stand out as having a high protein content – casein (both acid and rennet), high-protein MPC such as MPC85, high protein WPC such as WPC80 and whey protein isolate. However, the type of protein differs considerably, with caseins being almost entirely casein, MPC containing both casein and whey protein in the same proportion as the original milk and the whey protein products containing mostly whey protein with only a minor amount of casein. Fractionated whey proteins, such as the alpha and beta fractions contain predominantly the whey proteins  $\alpha$ -lactalbumin and  $\beta$ -lactoglobulin, respectively.

In Table 1.1 and Figure 1.1, the compositions of two different caseins are shown. This is a good example of a product with the same name produced by different methods having different compositions. Rennet casein produced by coagulation of casein by the action of chymosin (in rennet) is depleted in the glycomacropeptide or casein-derived peptide of  $\kappa$ -casein that remains in the whey, while acid casein, produced by the acid precipitation of casein, contains the complete caseins. This also means that the corresponding rennet and acid wheys differ also with rennet whey containing a substantial amount of the glycomacropeptide (~15 g 100 g<sup>-1</sup> of the protein), which is not present in acid whey.

In milk, most of the casein exists in the form of casein micelles that contain the four major caseins,  $\alpha_{s1}$ -,  $\alpha_{s2}$ -,  $\beta$ - and  $\kappa$ -caseins in the ratio of approximately 40:10:35:12. In addition, about 6 g 100 g<sup>-1</sup> of the solid material in the micelle is colloidal calcium phosphate that acts as ‘glue’ to help maintain the integrity of the micelle. If the calcium phosphate is removed from the micelle, for example by acidification, the micelles are disrupted and the casein coagulates into curd. Therefore, the form in which the caseins exist in milk products is determined by the processing procedures used. For example, caseins that are produced by acid precipitation are largely in non-micellar form, while the casein in skimmed milk powder (SMP) or MPC is largely ‘micellar’ (Mulvihill & Ennis, 2003). However, it should be noted that though micelles in milk contain 4–5 g water g<sup>-1</sup>, the dried micelles in powders contain little water and, hence, are quite different from native micelles.

The micelles in milk range in size from 30 to 300 nm diameter (Varnam & Sutherland, 2001). However, after heat treatment they increase in size. Martin *et al.* (2007) found that the size of the micelles increased on average by ~3, 6 and 39 nm after low-heat (79°C for <5 s), medium-heat (90°C for 30 s) and high-heat (120°C for 4 min) treatment of skimmed milk. This increase is due to the attachment of denatured whey proteins onto the micelles (Oldfield *et al.*, 2005). Removal of water by evaporation resulted in much larger

increases of ~60, 78 and 94 nm for low-, medium- and high-heat milks, respectively. These increases in micelle size were attributed to the continued attachment of whey proteins denatured during the heat treatment to the micelles during evaporation and also to soluble casein and calcium moving from the serum to the micelle (Martin *et al.*, 2007). On drying and subsequent dissolution of the powder, the sizes of the micelles from low-, medium- and high-heat treatments were somewhat smaller than those in the concentrated milk, but were still considerably larger than those in the heat-treated milk. The micelles decreased in size after dissolution, up to 24 h, due to a slow re-equilibration of the casein, calcium and denatured whey proteins between the micelles and the serum (Martin *et al.*, 2007).

Caseins are relatively small, amphiphilic, randomly coiled, unstructured open proteins with a high proline content, which prevents them from forming helical structures. By contrast, the major whey proteins  $\alpha$ -lactalbumin and  $\beta$ -lactoglobulin are small globular proteins. Thus, the caseins are quite stable to heat while the whey proteins, especially  $\beta$ -lactoglobulin, which constitutes about 50 g 100 g<sup>-1</sup> of the whey proteins, are heat labile.

$\beta$ -Lactoglobulin exists naturally as a dimer, which unfolds with heat at temperatures above 65°C and exposes a free sulphhydryl group (SH) that is normally buried. This activated form of  $\beta$ -lactoglobulin can then react with other molecules of itself, other whey proteins such as  $\alpha$ -lactalbumin or cow's serum albumin, or  $\kappa$ -casein, which is concentrated on the outside of the casein micelle, via disulphide (S–S) linkages. The heat-induced denaturation of  $\beta$ -lactoglobulin and the subsequent protein–protein interactions are very important reactions with regard to the stability of concentrated and (reconstituted) dried milk products to heat treatment. They are also important in fouling or burn-on when these products are heated in heat exchangers.

The extent of denaturation as measured by the whey protein nitrogen index (WPNI), a measure of the concentration of un-denatured whey proteins, is widely used to classify SMPs according to the intensity of the pre-heat treatment the milk receives before concentration and drying. Thus, low-, medium- and high-heat powders are characterised by WPNI of >6.0, 1.5–6.0 and <1.5 mg kg<sup>-1</sup> [American Dairy Products Institute (ADPI), 1990]; previously the ADPI was known as the American Dry Milk Institute (ADMI). The corresponding heat treatments are of the order of 70°C for 15 s; 85°C for 1 min, 90°C for 30 s or 105°C for 30 s; and 90°C for 5 min, 120°C for 1 min or 135°C for 30 s (Kelly *et al.*, 2006), although industrial conditions vary considerably. Powders are chosen for particular applications on the basis of their WPNI (Kelly *et al.*, 2006). Although heat is applied in the pre-heat, evaporation and drying stages, by far the most denaturation occurs in the pre-heat stage (Oldfield *et al.*, 2005).

Enzymes represent a minor component of milk proteins. However, they can have significant effects on the quality of milk and milk products. By far the most studied enzymes are the lipases and proteases. Raw milk contains one lipase, lipoprotein lipase (Deeth, 2005) and several proteases, the most significant of which is the alkaline protease namely *plasmin* (Kelly & McSweeney, 2003). Lipoprotein lipase is inactivated by high-temperature short time (HTST) pasteurisation conditions (e.g. 72°C for 15 s), the least severe pre-heat treatment used in manufacture of milk powders (Shamsuzzaman *et al.*, 1986). Therefore, action by the native lipase after manufacture of concentrated and dried products can be dismissed. By contrast, milk plasmin is quite heat stable, and is able to withstand high-heat treatments, even some ultra high temperature (UHT) treatments. Consequently, milk

powders, such as low-heat SMP, contain active plasmin that can degrade milk proteins, particularly  $\beta$ - and  $\alpha_s$ -caseins, in products manufactured from milk powder. Newstead *et al.* (2006) demonstrated proteolysis in UHT-treated reconstituted milk produced from low-fat SMP. They showed that the proteolysis could be prevented by employing a pre-heat treatment sufficient to inactivate the plasmin (90°C for 30 or 60 min).

Milk can also contain bacterial enzymes, if psychrotrophic bacteria are allowed to grow to levels sufficient to produce these enzymes, usually  $>10^6$ – $10^7$  colony forming units (cfu)  $\text{mL}^{-1}$ . The most studied of these enzymes are the lipases and proteases. Both types have significant heat resistance and hence, can remain in concentrated and dried milk products, and cause defects in products made from them (Chen *et al.*, 2003; Deeth & Fitz-Gerald, 2006). The lipases can cause hydrolytic rancidity through production of free fatty acids while the proteases can cause bitterness, gelation and sedimentation. Bacterial proteases preferentially attack  $\kappa$ -casein and, hence, their presence can be distinguished from that of milk plasmin which prefers  $\beta$ - and  $\alpha_s$ -caseins (Datta & Deeth, 2003). Enzyme action in milk powder is generally assumed to be extremely slow because of the low water content, usually 1.5–5.5 g 100 g<sup>-1</sup>. However, Chen *et al.* (2003) reported that lipolysis catalysed by bacterial lipase can occur in whole milk powder (WMP) with a moisture content of  $<3$  g 100 g<sup>-1</sup>. They found levels of short-chain free fatty acids (FFAs) in a powder stored for 2 weeks at 37°C, which exceeded the flavour threshold in the reconstituted milk.

Changes to proteins during storage can have marked effects on the properties of some dried dairy products. For example, the solubility of MPC powders decreases with storage time, particularly at elevated temperatures, and can vary widely, between 32% and 98%. The insoluble material has been shown to consist of large particles (100  $\mu\text{m}$ ) in which the casein micelles are joined together by weak non-covalent (hydrophobic) protein–protein interactions. The main individual proteins present are  $\alpha$ - and  $\beta$ -caseins.  $\kappa$ -Casein and  $\beta$ -lactoglobulin are also present in disulphide-linked protein aggregates, but they are not the main cause of the insoluble material (Havea, 2006).

The solubility of casein prepared by acid precipitation can be increased by reaction with alkalis to water-soluble caseinates. If sodium hydroxide is used to solubilise acid casein, it produces sodium caseinate, a common casein product, which is useful in the wide range of industrial application (Mulvihill & Ennis, 2003). Sodium caseinate is also the starting material for producing fractionated caseins (Murphy & Fox, 1991). This procedure is based on the fact that  $\beta$ -casein becomes soluble at low temperature, for example 4°C, and can be separated from the remaining micellar-bound caseins by membrane filtration. It produces two major fractions, one enriched in  $\beta$ -casein and one enriched in  $\alpha_s$ - and  $\kappa$ -caseins.

Caseinates can be highly soluble in water and fairly flavourless if the pH during manufacturing is never higher than 7 (Walstra *et al.*, 2006). During the production of caseinates, the time for which the caseinate solution is held at high temperature should be minimised to limit the extent of browning. The duration for which the casein is exposed to high pH during dissolving should also be reduced, since this may initiate the formation of lysinoalanine and the development of off-flavours.

### 1.2.2 Fat

Most concentrated and dried milk products have low-fat contents. The exceptions are WMP and the speciality and less common cream and butter powders. Whey produced during

cheesemaking contains a small amount of fat even after separation to remove most of the fat. The fat content of whey products tends to increase with an increase in protein content as the processes used primarily to remove lactose, ultrafiltration (UF) and diafiltration (DF), retain the fat as well as the protein.

While the majority of the fat is triglyceride, milk contains fat in the form of phospholipids also, which are present in both the milk fat globule membrane and skimmed milk membrane material in approximately equal amounts. As the membranes are particulate, they are also concentrated by the membrane filtration methods used to concentrate the protein. Buttermilk powder (BMP) contains the highest concentration of phospholipids as the milk fat globule membrane is released into the butter serum (skimmed milk) when the cream is churned.

The fat in milk exists in the form of fat globules 0.2–15  $\mu\text{m}$  in diameter, most in the range 1–8  $\mu\text{m}$ , with an average of about 3  $\mu\text{m}$ . Each globule is enveloped in a biological membrane, known as the *milk fat globule membrane*. This membrane protects the fat from attack by the naturally occurring lipase present in the milk serum and also disperses the hydrophobic fat in the hydrophilic aqueous medium. If this membrane is mechanically disrupted, non-globular or *free fat* is released from the globules. Free fat is defined as that which can be extracted by non-polar organic solvents such as hexane (Evers, 2004). Free fat can be formed if the globules are subjected to shear forces during processing. Therefore, provided the milk has not been subjected to such forces, the fat globules in concentrated and dried products remain largely in globular form. However, in some products, free fat is produced during processing (Fäldt & Bergenstahl, 1995). For example, during drying, the fat of the milk fat globule does not shrink, but that in the milk fat globule membrane does, which causes rupture of the membrane and production of free fat. The free fat is present predominantly on or close to the surface of powder particles and in cracks and fissures in the surface of the particle (Buma, 1971). Free fat has a detrimental effect on some functional properties of powders such as flowability and dispersibility, and is more susceptible to oxidative deterioration than globular fat is during storage. However, a high free fat level in some dried products is beneficial for some applications, such as chocolate manufacture (Liang & Hartel, 2004).

A minor lipid in milk is cholesterol. While its effect on the functional properties of concentrated and dried products is negligible, it has nutritional significance. It is mostly associated with the milk fat globule membrane and skimmed membrane material and, therefore, its proportion of the total fat in a product depends on the relative significance of membrane lipids in the total fat. For example, SMP has  $\sim 30$  mg cholesterol  $100\text{ g}^{-1}$  of powder while WMP has  $\sim 90$  mg  $100\text{ g}^{-1}$ . Since the relative total fat contents of SMP and WMP are  $\sim 1$  and  $26\text{ g } 100\text{ g}^{-1}$ , respectively, the cholesterol as a percentage of the total fat in the SMP is much higher than in the WMP. BMP contains  $\sim 70$  mg cholesterol  $100\text{ g}^{-1}$  (Walstra & Jenness, 1984), over twice the content of SMP because it contains both the milk fat globule membrane and skimmed membrane material.

Lecithin is a phospholipid, which is sometimes added to concentrated and dried product. The material used in the dairy industry originates from soya bean but has a similar composition to the phospholipids of the milk fat globule membrane. Phosphatidyl choline and phosphatidyl ethanolamine are the major components. One application of adding lecithin is to 'instantise' powders, that is, to improve their dissolution properties, because of its

surfactant properties. A second application is for increasing the heat stability. BMP, which contains milk fat globule membrane material rich in phospholipids, is also useful for this purpose (Singh & Tokley, 1990).

### 1.2.3 Carbohydrate

The carbohydrate in milk is almost entirely lactose which, at about  $5 \text{ g } 100 \text{ g}^{-1}$ , is the single most abundant constituent. Therefore, on direct concentration of milk or whey, the final product contains a high percentage of this compound (Table 1.1 and Fig. 1.1). In the production of high-protein products, such as MPC and WPC, UF and electrodialysis or DF are used primarily to remove the lactose. Consequently, the permeates from these processes are rich in lactose and can be concentrated to produce crystalline lactose, another dried milk derivative.

The nature of lactose in the final product can have a significant effect on the product's properties and quality. Lactose is highly hygroscopic, but its form determines how much water it can absorb. The amorphous form is more hygroscopic than the most common crystalline form,  $\alpha$ -lactose monohydrate. Lactose can be the cause of several problems in milk powders including collapse, stickiness and caking (Listiohadi *et al.*, 2005). The glass transition temperature of lactose-containing milk powders is similar to that of pure lactose, which indicates the importance of lactose in determining the physical state of these powders (Jouppila & Roos, 1994).

During preparation of powders containing high levels of lactose, seed crystals of  $\alpha$ -lactose monohydrate are added to the concentrate before drying to enable the anhydrous  $\alpha$ -lactose to convert to the crystalline monohydrate form before the drying stage. This decreases the risk of caking or clumping in the powder during storage, caused by the conversion of the anhydrous form to the crystalline form. In the production of lactose, concentrates of whey or permeate with  $60\text{--}65 \text{ g } 100 \text{ g}^{-1}$  solids are seeded with  $\alpha$ -lactose crystals to induce crystallisation from a supersaturated lactose solution. After crystallisation, the crystals are separated from the mother liquor, washed and dried to  $\sim 0.5 \text{ g } 100 \text{ g}^{-1}$  water.

In whey derived from cheesemaking, some of the lactose is converted to lactic acid by the starter bacteria. Excessive lactic acid content can lead to a highly sticky and hygroscopic product (Varnam & Sutherland, 2001). However, in some whey products, the lactose is hydrolysed to glucose and galactose. The resulting product is sweeter than whey and can be used as a sweetener. The hydrolysis is usually carried out with the enzyme  $\beta$ -galactosidase, but can also be effected with acid at high temperature in products such as permeates, which contain no protein.

Lactose, being a reducing sugar, can interact with amine groups of proteins, particularly the  $\epsilon$ -amino group of lysine, in the initial reaction of the Maillard series of reactions. The lactose-protein interaction is initiated during heat treatment but continues during storage and, in some products lactosylated proteins constitute a significant proportion of the total proteins.

The other major carbohydrate used in concentrated and dried products is sucrose. The main product containing sucrose is sweetened condensed milk where it constitutes around  $43 \text{ g } 100 \text{ g}^{-1}$ , over half of the dry matter in the product (Walstra & Jenness, 1984).



In this product, it depresses the water activity to a point where the product is shelf stable.

#### 1.2.4 Minerals

Minerals, often determined as ‘ash’, constitute the smallest of the major groups of milk components. Milk contains a wide range of minerals (Table 1.2), the most abundant of which are potassium, calcium, phosphorus and sodium; the levels of these in a range of products are summarised in Table 1.3.

Despite their low total abundance, minerals have a significant effect on many aspects of concentrated and dried products. As for other constituents considered above, the levels of particular minerals in these products are determined by several factors, but the most significant is the process used in manufacture of the product. For example, a concentrated milk prepared by UF has a lower content of minerals than one prepared by reverse osmosis (RO). The former allows (unbound) minerals to pass through the membrane, whereas the latter retains all milk components except water. Similarly, products made by evaporation and/or drying retain all the minerals of the parent milk.

A large proportion of calcium and phosphorus (~two-thirds and a half, respectively) are intimately associated with the casein micelle and as long as the micelle is intact, significant proportions of the calcium and phosphorus are not removed by UF or DF. Conversely, if the micelle is substantially disrupted, for example by acidification, calcium and phosphorus are solubilised and pass through the UF or DF membranes. Similarly, casein prepared by rennet coagulation has substantially more calcium and phosphorus than casein prepared by acid precipitation (Table 1.3).

Calcium has a major role in the functional properties of milk products and so knowledge of the chemistry of this metal in these products can help in understanding its importance. It exists in three forms in milk, *insoluble* calcium in the form of colloidal calcium phosphate

**Table 1.2** Average mineral composition of whole cow's milk.

Minerals	Concentration (mg L <sup>-1</sup> )	Minerals	Concentration (µg L <sup>-1</sup> )
Sodium	530	Manganese	30
Potassium	1360	Iodine	100–770
Chloride	970	Fluoride	20
Calcium	1120	Selenium	10
Phosphorus	890	Cobalt	0.5
Magnesium	110	Chromium	2
Iron	0.5	Molybdenum	50
Zinc	3.9	Nickel	26
Copper	0.09	Arsenic	20–60
		Silicon	700
		Boron	500–1000

After Flynn & Cashman (1997).

**Table 1.3** Mineral composition of liquid, concentrated and dried milk products.

Product	Sodium (mg 100 g <sup>-1</sup> )	Potassium (mg 100 g <sup>-1</sup> )	Calcium (mg 100 g <sup>-1</sup> )	Phosphorus (mg 100 g <sup>-1</sup> )	Total ash (g 100 g <sup>-1</sup> )
<i>Liquid milks</i>					
Whole milk	41–46	152–155	114–123	103	0.7
Skimmed milk	44–49	150–164	117–123	103	0.75
<i>Concentrated milks</i>					
Evaporated whole milk	100–108	300–368	255–263	220–247	1.5–1.7
Evaporated skimmed milk	91–110	324–330	246–290	190	1.5–1.7
Sweetened condensed whole milk	2105–130	357–402	268–300	240–250	1.8
Sweetened condensed skimmed milk	125–130	445–475	335–340	230–280	2.3
<i>Milk powders</i>					
Whole milk powder	310–400	1157–1300	875–910	800	5–6
Skimmed milk powder	428–530	1603–1790	1183–1260	970–1103	7.9–8.5
<i>Casein and whey protein powders</i>					
Ca-caseinate	50–100	100	1000–1500	800	3.5–4.5
K-caseinate	60	1650	300	800	3.3–4.0
Na-caseinate	1200–1300	20	100	800	3.3–4.0
Casein (acid)	100		80	900	2.2
Casein (rennet)	20	30	300	1500	7.5
Low-protein whey protein concentrate (~35 g 100 g <sup>-1</sup> )	460	1190	480	500	5.7–7.8
High-protein whey protein concentrate (65 g 100 g <sup>-1</sup> )	280	650	350	330	3.5–3.9

After Hargrove & Alford (1974), Posati & Orr (1976), Bassette & Acosta (1988), Jensen (1990), Caric (1993), Australian Dairy Corporation (1999), Anonymous (2003), Boumba *et al.* (2001), Fox (2003), Kim *et al.* (2005), FSANZ (2006) and Walstra *et al.* (2006).

associated with the casein micelles, *soluble* or non-micellar calcium and free *ionic* calcium. In cow's milk, the concentrations are ~20, 10 and 1.5 mM, respectively. The ionic calcium is a component of the soluble calcium. These forms are in equilibrium which means that changing the concentration of one form affects the concentration of the others. Milk with a high level of ionic calcium is known to be unstable to heat and hence this component is an important consideration in heat treating milk. For example, goat's milk has a much higher level of ionic calcium than cow's milk, and is much more unstable to high-temperature treatment (Zadow *et al.*, 1983).

### 1.2.5 Water

Water content is an important parameter, which distinguishes between different products, determines several physical properties and affects the stability of products during storage. It is particularly important for powders where the ideal level is  $\sim 3 \text{ g } 100 \text{ g}^{-1}$ . The water contents of various products are shown in Table 1.1.

Water can be present in food in at least three forms: free water, adsorbed water and bound water. Free water occupies the void volume or the pores of the food. It functions as a dispersing agent, as a solvent for crystalline compounds and as a support for microbial growth. Adsorbed water is present on the surface of the macromolecules in the food matrices, whereas bound water is the water of hydration, which is bound to the product by strong hydrogen bonds (Mathlouthi, 2001).

Milk powders are generally hygroscopic and hence increase or decrease in water content according to the environmental relative humidity (RH). At a particular temperature, the water content of a powder is related to its water activity via its sorption isotherm. The water activity is important as it determines the glass transition temperature of the powder, which in turn determines its physical and chemical properties. Physical changes, such as lactose crystallisation and caking generally, occur when the storage temperature is above the glass transition temperature (Thomas *et al.*, 2004).

In the sorption isotherm of lactose-containing powders, an interesting phenomenon occurs between 40 and 50% RH. A break characterised by a sharp decrease in moisture content occurs as water is released when amorphous lactose crystallises as  $\alpha$ -lactose monohydrate (Thomas *et al.*, 2004).

Although in some cases low moisture content may favour fat oxidation, high moisture content in powders is of greatest concern as it has more negative impacts which limit shelf-life. These include protein denaturation, acceleration of the non-enzymatic browning (Maillard) reactions, enzymic reactions, conversion of amorphous lactose to crystalline  $\alpha$ -lactose monohydrate, formation of free fat in whole milk powder, caking of powder during storage and microbial growth (Early, 1992; Verdurmen & de Jong, 2003).

### 1.2.6 Air

While gases including air are present in liquid milk in small amounts, air constitutes a major proportion of some powders. It is occluded into the powder during drying in the form of vacuoles. The air content can increase immediately after drying because a partial vacuum is created in the entrapped air during formation of the particles (Thomas *et al.*, 2004).

The amount of air is inversely proportional to the density of the product. The bulk density of powders is around  $0.6\text{--}0.7 \text{ g mL}^{-1}$  compared with the density of non-fat milk solids of  $\sim 1.6 \text{ g mL}^{-1}$ . The amount of occluded air is influenced by several factors:

- *Processing stages (pre-heat treatment and evaporation)* – These influence the bulk density of powders through the extent of denaturation of the whey proteins in milk. Un-denatured whey proteins increase air occlusion, while denaturation increases particle density.

- *Foaming ability of the concentrate* – Due to its lower degree of protein denaturation, low-heat skimmed milk forms more stable foam than high-heat skimmed milk. A stable foam will hold air to the atomiser and lead to more trapped air in the powder particles produced.
- *Agitation of the concentrate* – Mechanical agitation of the concentrate causes entrainment of air.
- *Drying conditions* – High air temperatures during the critical drying stage promote occlusion of air.
- *Atomisation type* – Pressure rotary atomisers incorporate more air into droplets than atomiser nozzles.
- *Dryer feed concentration* – Low-solid feed materials have lower viscosity and foam more readily and thus lead to more air incorporation (Early, 1992).

If the air content is too high, the product is too bulky and difficult to handle. For this reason, many powders are instantised by agglomeration to increase the average particle size and increase the bulk density of the product. Agglomeration is a process in which small particles coalesce to create large relatively permanent masses, where the original particles are still identifiable. The agglomerates produced are porous clusters of particles 250–750  $\mu\text{m}$  in diameter, and have a high level of entrapped air. Agglomeration improves the rehydration behaviour of the powder since the open porous configuration of the agglomerates allows water to penetrate into the particles, forcing the particle to sink. In spray dryers, agglomeration may occur within the atomiser spray, between sprays of various atomisers, between sprays and dry material introduced into the drying chamber or on a fluid bed outside the spray chamber.

As air in contact with powder particles can cause oxidation during storage, particularly if the powder contains readily accessible fat, powders are often flushed with and stored under nitrogen, or vacuum packaged. This is particularly important in high fat powders.

The bulk density of SMP is generally higher than WMP due to the lower density of milk fat relative to protein and lactose. However, this difference is somewhat counteracted by the presence of fat in whole milk powder which may hinder foaming and reduce the amount of occluded air.

### 1.3 Surface composition of powders

Many properties of milk powders, which are important in their storage, handling and final application (e.g. dispersibility, wettability, flowability and oxidative stability), are influenced by the surface composition rather than the bulk composition of the powder (Hindmarsh *et al.*, 2007). If one of the milk components is preferentially present on the powder surface, the properties can be changed dramatically. Of particular importance is the amount of fat on the powder surface. The presence of fat renders the powder surface hydrophobic, thus decreasing its wettability and dispersibility.

During the drying process, evaporation and drying simultaneously promote the migration of milk constituents, particularly fat, protein and lactose toward the particle surface. Nijdam

& Langrish (2006) studied the migration of these components within milk droplets and particles in a spray dryer and found that the surface fat coverage is much higher than the average fat content of the powder. This implies a higher concentration of fat accumulated at the surface of each milk particle than in the interior leading to a non-uniform distribution of fat throughout the solid matrix. For instance, the surface fat coverage may reach as high as 50%, when the average fat content of the milk powder is only 15%. The fat begins to appear on the powder surface even at very low-fat contents and between 0 and 5% it increases up to 35% (Nijdam & Langrish, 2006). Kim *et al.* (2002) found that the fat on the surface was mostly free fat, and that fat globules protected by proteins were preferentially located underneath the surface fat. The next dominant milk component on the surface of powders is protein, possibly because of its surface-active nature, then lactose (Kim *et al.*, 2002, 2005; Nijdam & Langrish, 2006; Shrestha *et al.*, 2007) (Table 1.4).

The flowability of powders is a surface-related property and is, therefore, controlled by the powder surface composition. Of special importance is the surface fat which renders the surface of fat-containing powders sticky and causes the particles to adhere to one another thus decreasing the flowability of the powder. By contrast, SMP whose surface is made up mostly of lactose and protein flows well (Kim *et al.*, 2005). Kim *et al.* (2005) have concluded that the surface fat content rather than free-fat and total fat content correlates best with flowability. The fact that high surface fat coverage is responsible for poor flowability of powders was clearly demonstrated when flowability was significantly increased by removal of the fat from the surface with petroleum ether. The dissolution rate of the powder in water also decreased with increasing surface fat (Millqvist-Fureby *et al.*, 2001).

Millqvist-Fureby *et al.* (2001) used WPC to examine the effect of heat treatment of whey proteins on the powder surface composition and some functional properties of spray dried protein-stabilised emulsions. The heat-treated (denatured) protein has fewer active

**Table 1.4** Surface composition<sup>a</sup> of industrial spray dried dairy powders and skimmed milk powders with different lactose levels.

Powders	Bulk composition (g 100 g <sup>-1</sup> )			Surface composition <sup>b</sup> (%)			References
	Lactose	Protein	Fat	Lactose	Protein	Fat	
SMP	58	41	1	36	46	18	Kim <i>et al.</i> (2005)
WMP	40	31	29	2	—	98	
CP	13	12	75	1	—	99	
WPC	8	86	6	6	41	53	
SMP:lactose (3:1)	63	26	0.8	29	61	10	Shrestha <i>et al.</i> (2007)
SMP:lactose (1:1)	75	17	0.5	31	58	11	
SMP:lactose (1:3)	88	9	0.25	39	57	5	

WMP = whole milk powder; SMP = skimmed milk powder; CP = cream powder; WPC = whey protein concentrates.

<sup>a</sup>Assuming that dairy powders are composed of three main components, namely, lactose, protein and fat.

<sup>b</sup>Based on data from X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA).

surface sites and competes less favourably for the interface than the untreated protein. Thus the powder surface coverage of protein decreases with increasing degree of protein denaturation before the emulsification. This leads to more leakage of fat onto the powder surface.

Nijdam & Langrish (2006) proposed that higher drying temperatures accelerate the formation of a surface skin which hampers the migration of surface-active protein towards the surface; this results in the preferential presence of lactose over protein at the surface of the milk powder particle. At the lower drying temperature of 120°C, the surface has a higher concentration of protein than lactose, even though there is more lactose than protein in the bulk powder. However, at the higher drying temperature of 200°C, this trend is reversed and more lactose appears at the surface of the powder than protein, although the ratio of lactose to protein on the surface is still generally lower than the average value in the powder. This phenomenon occurs because protein has more time to drift to the surface of the droplet at lower drying temperatures, before sufficient moisture is evaporated to cause formation of the skin (Nijdam & Langrish, 2006). The relative amounts of lactose and protein on the surface of powder particles are important as the proportion of lactose strongly influences the caking of milk powders during storage at high RH when the glass transition temperature is exceeded (Jouppila & Roos, 1994; Lloyd *et al.*, 1996).

Modifying the protein content of SMP by addition of lactose affects the surface composition, sorption behaviour and glass transition temperature of spray dried powder (Shrestha *et al.*, 2007). As shown in Table 1.4, as the lactose:protein ratio increases, there is no a proportional increase in the lactose content on the surface of the powder. This suggests that the lactose migrates to the surface slower than protein and fat. Shrestha *et al.* (2007) reported that increases in lactose concentration in SMP significantly increased the water adsorption in milk powders and also lowered the water activity range at which the crystallisation occurred.

## 1.4 Quality issues

### 1.4.1 Heat stability

The major issue associated with concentration and drying of milk is the heat stability of the concentrated milk during sterilisation processes, in-container or UHT, and the heat stability of the powders when reconstituted. Heat instability is manifested in gelation or coagulation during heating, sedimentation after heating and burn-on or deposit formation in heat exchangers during continuous UHT treatments. Concentrated milks may also thicken and gel during storage; this may be initiated by the heating process but is considered to be a storage-related issue.

Heat stability of milk has been studied extensively in both single-strength and concentrated milks. Despite this research effort, the scientific basis of heat instability has not been completely elucidated. The effects of many compositional factors on the heat stability of unconcentrated milk are now well known, but many of these do not hold for concentrated milks. Conversely, a knowledge of the heat stability of unconcentrated milk, determined by the classical heat coagulation time (HCT) test (time to coagulate at 140°C) is not a reliable

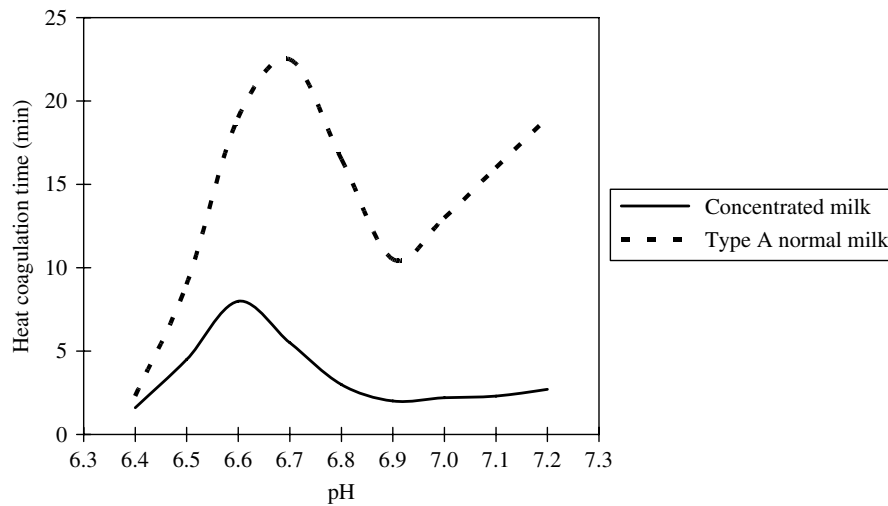
guide to the heat stability of concentrated milk (Williams, 2002). The desired HCT of milk is 20 min at its natural pH ( $\sim 6.7$ ).

The HCT test is carried out by heating milk in a closed tube in an oil bath and observing the first signs of coagulation. For normal milk the test is performed at  $140^{\circ}\text{C}$ , but for concentrated milk,  $120^{\circ}\text{C}$  is used. The test is quite subjective and requires some experience to obtain consistent results. For this reason, alternative methods of estimating heat stability have been sought. Lehmann & Buckin (2005) observed the heat stability of recombined evaporated milk (REM) subjected to different pre-heat treatments using high resolution ultrasonic spectroscopy. They observed four stages. In the first stage, ultrasonic velocity decreases sharply while the attenuation increased due to the thermal equilibration of the sample (the time required by the sample to achieve the holding temperature) together with the fast denaturation of whey protein and precipitation of calcium phosphate onto the micelles that occurs during the first few minutes of heating. The second stage, called the pre-coagulation stage, showed small changes in ultrasonic velocity, the slope of which depended on the nature and pH of the samples. In the third stage, ultrasonic velocity and attenuation declined sharply and the attenuation profile reached a peak. This stage was identified as the coagulation point when the gel network is formed. The last stage demonstrated small changes in ultrasonic velocity and attenuation and was attributed to the end of the coagulation process.

A major factor in the heat stability of both unconcentrated and concentrated milk is pH. The HCT–pH curves for unconcentrated milk are of two types, A and B, where type A curves exhibit a distinct maximum (pH  $\sim 6.7$ ) and minimum (pH  $\sim 6.9$ ); while type B milks show no maximum or minimum, there is a gradual increase in HCT with pH. The majority of milks are of type A. Concentrated milk shows a much different curve with a maximum at lower pH and no minimum; the height of the maximum is much lower than the height of the maximum for type A milk. Concentrated milk is less heat stable than unconcentrated milk at all pH values, especially at pH values higher than the heat stability maximum. Since the heat stability decreases with increasing solids content, the classic heat coagulation test for concentrated milk is performed at  $120^{\circ}\text{C}$  rather than  $140^{\circ}\text{C}$  as used for unconcentrated milks. Typical HCT–pH curves for unconcentrated milk type A and concentrated milk are shown in Figure 1.2 (Singh *et al.*, 1995). This shows the maximum for concentrated milk at  $\sim 6.6$ ; however, the actual pH of maximal heat stability depends on several factors including the pre-heat treatment and concentration level. A corresponding heat stability curve for concentrated milk given by O'Connell & Fox (2003) shows a maximum at pH  $\sim 6.45$ .

Milk in which acidity develops due to bacterial growth before heat treatment can produce concentrated and dried products, which are unstable to heat treatment because of the pH–heat stability relationship. Similarly, milk powders which have been stored for some time, especially if stored under unfavourable conditions (i.e. elevated temperature and/or water activity) may have a lower pH than normal and be less heat stable than fresh powders (Zadow & Hardham, 1978). The stability of powders to the relatively low pH and high temperature of coffee solutions is the basis of the coffee stability test (Oldfield *et al.*, 2000).

The heat stabilities of milks, concentrates and reconstituted powders show a seasonal or stage of lactation trend although the corresponding variation in the levels of relevant



**Fig. 1.2** Heat coagulation times at 140°C as a function of pH for normal (single-strength) milk and concentrated milk.

milk components is not often obvious. Singh *et al.* (1995) reported that, in New Zealand, low-heat stability corresponded with the beginning and the end of the dairying season. The seasonal variation seems to be associated with changes in the pH of maximal stability, which is also affected by the nature of the pre-heat treatment. According to Newstead *et al.* (1975), the pH of maximal stability of REM was lower than its natural pH for much of the year in New Zealand. Thus, judicious pH adjustment can improve the heat stability.

The type and sequence of processing steps have a significant effect on the heat stability of concentrates. Pre-heat treatment of the milk prior to concentration is the most important of these steps. More severe heat treatments lead to more heat-stable concentrates. The major effect of pre-heat treatments is denaturation of whey proteins to form whey protein aggregates and whey protein–casein complexes, formed largely through disulphide linkages between  $\kappa$ -casein and  $\beta$ -lactoglobulin. Concentrates with a high level of un-denatured  $\beta$ -lactoglobulin are significantly less stable than those with lower concentrations. This destabilisation occurs over the entire pH range. By contrast, addition of  $\kappa$ -casein can enhance the heat stability of concentrates (Muir & Sweetsur, 1978).

The significant effect on heat stability of denaturation and subsequent aggregation of  $\beta$ -lactoglobulin is clearly demonstrated by the addition of SH blocking or oxidising agents; both improve heat stability. Blocking agents include N-ethyl maleimide and iodoacetamide, and oxidising agents include hydrogen peroxide and  $\text{Cu}^{2+}$  (Walstra & Jenness, 1984). However, addition of these compounds is not practised commercially as they are not legal additives in most countries. Addition of urea to unconcentrated milk increases its heat stability (Dalglish *et al.*, 1987), but it has no beneficial effect in concentrated milk (Muir & Sweetsur, 1978).

Homogenisation, an important step when whole milks are concentrated, decreases the heat stability of the concentrated milk. However, the effect of homogenisation is minimised



by pre-heating the milk before concentration and homogenisation. Pre-heating can be in the UHT range (145°C for 5 s) (Sweetsur & Muir, 1982) or at a lower temperature (120°C for 120 s) (Newstead *et al.*, 1979). Sweetsur & Muir (1983) found that the sulfhydryl interactions between  $\beta$ -lactoglobulin and  $\kappa$ -casein have a more marked effect on the heat stability of homogenised than on unhomogenised concentrated milk.

The minerals in concentrated milk have a major role in heat stability. Reduction in the mineral content before concentration (Muir & Sweetsur, 1978) or concentration by UF, which results in loss of minerals through the membrane (Sweetsur & Muir, 1980), increase the heat stability of the concentrates. The so-called salt balance theory, which was first developed over 50 years ago (Sommer & Hart, 1922), suggests that, apart from whey proteins, the ratio of calcium and magnesium to phosphate and citrate controls heat stability. The influence of other factors such as pH may be largely through their effects on the salt balance.

High ionic calcium levels are associated with low-heat stability. Thus, addition of stabilising salts, such as disodium hydrogen phosphate and trisodium citrate which reduce the calcium ion activity, can enhance the HCT of evaporated milk (de Jong & Verdurmen, 2001). They also increase the pH of the product. The heat stability can also be improved by decreasing the calcium content of the milk before evaporation by means of ion exchange (Walstra *et al.*, 2006) or by adding phosphate prior to pre-heating (Horne & Muir, 1990). Hardy *et al.* (1984) suggested that heat stability relied on the mineral equilibrium which determined the concentration of soluble calcium. During processing, both calcium and phosphate tend to migrate from the serum to the colloidal phase.

Thus, in addition to pre-heat treatment, adding salts, such as phosphates and citrates, is a major means of controlling the heat stability. However, the choice of additives is not straightforward. Sometimes addition of the acidic phosphate, sodium dihydrogen phosphate, is most appropriate and sometimes addition of the basic disodium hydrogen phosphate is most appropriate. In general, if the natural pH of the milk is higher than the pH of maximal stability, addition of sodium dihydrogen phosphate may be beneficial while, if the natural pH of the milk is lower than the pH of maximal stability, addition of disodium hydrogen phosphate or trisodium citrate is recommended (Singh *et al.*, 1995). In practice, use of a pilot plant to test the most appropriate additive is the best test available to the processor as data from traditional heat stability tests are poorly correlated with behaviour of the product in commercial processing.

Hardy *et al.* (1985) reported that a heat-stable concentrate can be achieved by means of lecithin incorporation without addition of inorganic phosphate and can be processed at a higher than usual homogenisation pressure. The addition of lyophilised salted butter serum to concentrated skimmed milk shifted the pH of maximum heat stability to a higher value and, at certain concentrations, increased the maximum HCT. It was suggested that the beneficial effects of the butter serum on the heat stability may be due to the sodium chloride present. The role of sodium chloride in shifting the pH of maximum stability may be through a reduced micellar charge. Addition of sodium chloride to milk may increase the level of non-sedimentable calcium, as sodium can replace the calcium in colloidal form. This results in an increased level of soluble calcium which will reduce the micellar charge; a higher pH will then be required to gain the same net negative charge (Huppertz & Fox, 2006).

### 1.4.2 Fouling

Fouling or deposit formation occurs at the surface of heat exchangers used for heating milk and milk products. The build-up of deposit reduces the heat transfer rate and, hence, the heating medium temperature has to increase to maintain the same product temperature. This increase in temperature exacerbates the fouling. The fouling deposit also blocks the flow of product through plate and tubular heat exchangers, and increases the back pressure in the plant. When the temperature of the heating medium and/or the back pressure in the plant becomes excessive, the plant has to be shut down for cleaning. Overall, fouling is costly for the dairy industry because of the down time required for cleaning, the loss of milk, the increased cost of detergents required and the greater quantity of wastewater produced (Walstra *et al.*, 2006).

Fouling is more significant at high temperatures than at low temperatures and, hence, is a significant issue with UHT processing. At heating temperatures of  $\sim 80\text{--}115^\circ\text{C}$ , the fouling layer is relatively soft and consists mainly of proteins ( $50\text{--}70\text{ g } 100\text{ g}^{-1}$ ), but at higher temperatures – up to  $150^\circ\text{C}$  – encountered in UHT plants, the fouling layer is harder and is predominantly mineral ( $\sim 70\text{ g } 100\text{ g}^{-1}$ ). The mineral is mostly calcium phosphate as this becomes less soluble at higher temperatures. The lower-temperature deposit is known as type A, while the higher-temperature deposit is known as type B. Type A is yellowish in colour, voluminous and curd-like while type B, often called milk stone or scale, is greyish in colour, hard and gritty (Burton, 1988; Walstra *et al.*, 2006).

Fouling is influenced by several factors, but a major one of significance here is the solids content. Concentrated milks foul more readily than single-strength milks. There are several possible explanations for this; these include: (a) the higher content of  $\beta$ -lactoglobulin (Tissier *et al.*, 1984), (b) higher content of calcium (Jeurnink & de Kruijff, 1995), (c) higher lactose levels which cause Maillard reactions (Jeurnink *et al.*, 1996), (d) lower pH (Singh *et al.*, 1995) and (e) higher viscosity (Kastanas, 1996) of concentrated milk compared with single-strength milk. In a recent study of fouling in concentrated reconstituted skimmed milk up to  $20\text{ g } 100\text{ g}^{-1}$  solids, Prakash (2007) concluded that denaturation of  $\beta$ -lactoglobulin was most significant as the use of the SH blocking agent iodoacetamide markedly reduced fouling. High lactose levels, lower pH and high viscosity had comparatively little effect on fouling. Similarly, reduction of ionic calcium with trisodium citrate or sodium hexametaphosphate did not reduce fouling in the concentrated milk in contrast to its beneficial effect in single-strength cow's and goat's milk (Prakash, 2007; Prakash *et al.*, 2007).

Denaturation of  $\beta$ -lactoglobulin during heat treatment is considered to be significant in most fouling situations. In fact, the intermediate unfolded form is considered the most adhesive form, and the faster the  $\beta$ -lactoglobulin passes this intermediate stage and aggregates with itself, other whey proteins or  $\kappa$ -casein, the less severe is the fouling (Grijpspeerdt *et al.*, 2004). Milk or whey that has been heated to such an extent that  $\beta$ -lactoglobulin is completely aggregated produces minimal protein fouling (Walstra *et al.*, 2006). However, mineral deposits of largely calcium phosphate still occur in the high-temperature sections of the plant.

Another type of fouling occurs in evaporators and in the regeneration section of plate heat exchangers (Lehmann *et al.*, 1992). This is known as microbial fouling or bio-fouling. During processing at temperatures below  $80^\circ\text{C}$ , thermophilic bacteria, such as *Streptococcus*

*thermophilus*, can attach to the surface walls of heat exchangers and grow as a film. These biofilms can subsequently detach and contaminate the products when plants are run for extended times. The bacterial growth, adherence and amount of bacteria released into the product have been modelled as a function of operating time. This enables plant conditions to be optimised to minimise bio-fouling and for the amount of contamination of product by thermophilic bacteria to be predicted (de Jong & Verdurmen, 2001). Knight *et al.* (2004) devised a successful method of minimising biofilm build-up by using a temperature cycling procedure. This system effectively interrupts the growth cycle of the bacteria and prevents their rapid growth typical of the logarithmic phase.

### 1.4.3 Age thickening

Age thickening is a further ramification of protein instability. During storage the viscosity of shelf-stable milk increases and this may lead to gelation in the product. It occurs in both single-strength and concentrated milk but the mechanism of the change appears to be different for both types of milk. In single-strength milk it is largely initiated by proteolysis, whereas in concentrated milk it occurs without proteolysis (Datta & Deeth, 2001).

Viscosity is a very important parameter for concentrated milks and high-temperature processing. Controlling the viscosity is imperative in the manufacture of sweetened condensed milk. The viscosity needs to be high enough to prevent sedimentation and creaming of the fat, but not excessively high for ease of processing.

The steps taken to minimise age thickening are essentially the same as those to minimise protein instability problems during processing, that is, pre-heating of the milk prior to concentration to denature whey proteins (de Jong & Verdurmen, 2001; Walstra *et al.*, 2006), and addition of stabilising or buffering salts, such as sodium and potassium hydrogen carbonate, calcium chloride, sodium and potassium phosphate, sodium and potassium diphosphate, disodium or trisodium phosphate, sodium and potassium citrate, sodium and potassium orthophosphate (Caric, 1993; Spreer, 1998; Brennan, 2006). Sterilisation of the concentrated product under intense conditions delays thickening and gelation as it does for unconcentrated milk (Datta & Deeth, 2001).

### 1.4.4 Maillard reactions

Maillard reactions are initiated by the reaction of a reducing sugar, such as lactose with amino residues on proteins, chiefly the  $\epsilon$ -amino group of lysine. The final products of the reactions are brown-coloured melanoidins, which impart a brown colour to affected products. In addition, several intermediate compounds are formed, such as hydroxymethylfurfural and formic acid, the latter responsible for some of the pH reduction in stored dairy products. Maillard reactions cause flavour and colour changes in milk products, such as concentrated and dried products, and also reduce their nutritive value. An extreme case of Maillard browning occurs in so-called scorched particles in powders, which are a significant defect.

The first step in milk products, lactosylation, results in lactose adducts of proteins and reduces the availability of lysine, an essential amino acid. The reaction is initiated during

heating but continues during storage. Lactosylation produces  $\epsilon$ -N-deoxylactulosyl-*D*-lysine or lactulosyl lysine, the most stable product of the Maillard reactions. Lactosylation occurs readily in the dry state. In fact, Morgan *et al.* (1998) found an average of six lactose units attached to  $\beta$ -lactoglobulin after storage of powder with a water activity of 0.65 for 20 h at 50°C compared with only one when left in solution at the same temperature. In both cases, the lactosylated forms were highly heterogeneous.

Guyomarc'h *et al.* (2000) reported that the degree of lactosylation of proteins can be reduced by modifying the spray drying operating condition. A low outlet temperature, preferably <80°C, together with a relatively high inlet temperature of 170–175°C was the optimal condition for producing a low degree of lactosylation and a high drying rate.

The extent of Maillard reactions in milk products is often determined by measurement of furosine, a product of the acid hydrolysis of lactulosyl lysine formed during the analysis. The furosine content is largely influenced by the processing conditions. For pasteurised milk, furosine concentration is 4–7 mg 100 g<sup>-1</sup> protein, but it is much higher in more severely heated products, such as UHT-sterilised milk; Elliott *et al.* (2005) reported an average of 183 mg 100 g<sup>-1</sup> protein for 16 commercial indirectly heated UHT milks. In SMP, the concentration can be in the range of 170–600 mg 100 g<sup>-1</sup> protein, depending on the drying process. However, extreme pre-heating conditions can have a significant effect. At pre-heating temperatures below 105°C, the furosine content of the powders ranges between 170 and 300 mg 100 g<sup>-1</sup> protein, but at 115°C it is up to 600 mg 100 g<sup>-1</sup> protein. Furosine levels increase during storage of all milk powders containing lactose with levels increasing faster with increasing water activity, up to 65%, and increasing temperature (Van Renterghem & De Block, 1996).

Evaporated milk is susceptible to Maillard reactions, which influence its colour and flavour during storage, particularly at an elevated temperature. However, the brown discolouration is more marked in sweetened condensed milk as the milk is concentrated to a higher concentration. Adding sugar before evaporation leads to faster browning than adding it after evaporation (Walstra *et al.*, 2006).

Maillard reactions are a major cause of quality deterioration of whey powders during storage as they contain a relatively high concentration of lactose and protein. During storage, browning increases over time and is more obvious at a higher temperature and lower pH. The shelf-life of whey powder can be predicted by the use of models based on the kinetics of the browning reaction and the conditions and time of storage (Dattatreya *et al.*, 2007).

Lysine and the sulphur-containing amino acids are the main amino acids that are affected by Maillard reactions during the high-temperature treatments. In dried products produced by efficient spray drying, the availability of lysine is high, ~90–97% (Rolls & Porter, 1973). Significant destruction of lysine only occurs in severely heated samples, when a loss of methionine up to 10% also occurs. Although Maillard reactions are known to be more important in milk powders during storage, Jones *et al.* (1998) speculated that the reactions are initiated during spray drying.

#### 1.4.5 Oxidation

Lipid oxidation during storage is a significant issue for fat-containing powders, such as whole milk powder. The fat can react easily with oxygen in the air to produce off-flavours,

especially at higher storage temperatures ( $>30^{\circ}\text{C}$ ). Hydroperoxides, the primary products of lipid oxidation are colourless, tasteless and odourless, but they are transformed into a complex mixture of low-molecular-weight compounds with distinctive odour, colour and flavour characteristics. These include alkanes, alkenes, aldehydes, ketones, alcohols, acids and esters. These compounds impart off-flavours to the milk powder, and limit its shelf-life (Fenaille *et al.*, 2001; see also Liang, 2000).

The rate of oxidation in milk powders increases with increasing temperature. McCluskey *et al.* (1997) reported that the rate increases 10-fold for every  $10^{\circ}\text{C}$  increase in temperature. The oxidation rate also increases when the powder particles disintegrate as the amount of fat exposed to the air increases. It is interesting to note that powders are prone to oxidation largely at extremely low moisture content because under these conditions, the powder particles disintegrate and increase the area of exposed fat (Early, 1998). Conversely, the oxidation rate decreases when the milk powder collapses as this lowers the access of the air to the fat (Thomas *et al.*, 2004).

Reducing the oxygen content in the package also reduces oxidation of milk fat. When oxygen in milk powder or infant formula packages is replaced by nitrogen and/or carbon dioxide, oxidation is significantly decreased. Whole milk powder has a shelf-life of more than 12 months if packed in cans under vacuum or with an inert gas, such as nitrogen. Milk powders stored in cans or drums for medium- to long-storage times are generally packaged in a modified atmosphere of normal air mixed with additional  $\text{CO}_2$  and  $\text{N}_2$ , 100%  $\text{N}_2$  or reduced  $\text{O}_2$  atmospheres. Driscoll *et al.* (1985) investigated the sensory quality of instant and regular SMPs after 4 years' storage in cans or polybags at 10, 21 and  $32^{\circ}\text{C}$  and in atmospheres of normal air, air modified with 100%  $\text{CO}_2$  or 100%  $\text{N}_2$ . They found that powder stored under air had a much lower sensory quality than those stored under either  $\text{N}_2$  or  $\text{CO}_2$  at the same temperature. Packaging techniques have also been developed for dry milk powders to eliminate or reduce  $\text{O}_2$  and, hence, reduce fat oxidation. These include gas flushing and use of oxygen absorbers (Hotchkiss *et al.*, 2006).

Addition of antioxidants can extend the shelf-life of powders. Antioxidants do not improve the quality of the product, but they maintain it by preventing oxidation of labile lipid components. Examples of antioxidants are  $\alpha$ -tocopherol, ascorbic acid and  $\beta$ -carotene (McCluskey *et al.*, 1997). The same authors also reported that milk from cows fed on a vitamin E-supplemented diet produced a powder that was less susceptible to oxidative deterioration.

Baldwin & Ackland (1991) found that higher pre-heat treatment increased the antioxidant activity of whole milk powder. Heating of milk leads to denaturation of whey proteins, especially  $\beta$ -lactoglobulin, thus exposing SH groups and generating SH compounds, such as hydrogen sulphide and methanethiol (Al-Attabi *et al.*, 2009), which can react with free radicals of the unsaturated fatty acids and decrease the oxidation rate. These compounds also absorb some oxygen, and also help to protect the anti-oxidative vitamins, such as ascorbic acid and vitamin E. The effect of pre-heat treatment was supported by the finding of Stapelfeldt *et al.* (1997) that low-heat milk powder had lower storage stability than medium- and high-heat powders as it was subject to severe oxidative changes. During accelerated storage at  $45^{\circ}\text{C}$  and with full contact to atmospheric oxygen, the medium- and high-heat powders were less affected than the low-heat

powder. The rate of autoxidation increased steadily as water activity increased from 0.11 to 0.33.

## 1.5 Conclusions

Concentrated and dried milk products represent a diverse range of dairy products. They vary considerably in chemical composition, which is determined by the composition of the original milk as well as the various heating and dehydration processes involved in their manufacture. There is also variation in the distribution of chemical components within products, for example between the surface and the interior of powder particles and between the colloidal and soluble phases, which affects the products' properties. Chemical and enzymic changes continue to occur during storage of the concentrated and dried products, which can significantly affect their functional properties and organoleptic qualities. The most important chemical changes that occur or can occur during processing and storage are denaturation of whey proteins, coagulation of caseins, lactosylation of proteins and subsequent Maillard reactions, oxidation of milk fat and crystallisation of lactose. Knowledge of the chemical components of the products, their relationship to functional properties, and the changes that can occur in these components is essential for determining the optimal production and storage conditions for these products.

## References

- ADPI (1990) *Standards for Grades of Dry Milks Including Methods of Analyses*, Bulletin No. 916 (revised). American Dry Products Institute, Chicago, Ill.
- Al-Attabi, Z., D'Arcy, B.R. & Deeth, H.C. (2009) Volatile sulphur compounds in UHT milk. *Critical Reviews in Food Science and Nutrition*, **49**, 29–47.
- Anonymous (2003) *Dairy Processing Handbook*, 2nd and revised edn. of G. Bylund (1995). Tetra Pak Processing Systems AB, Lund.
- Australian Dairy Corporation (1999) *Proximate Composition of Australian Dairy Foods*. Australian Dairy Corporation, Melbourne.
- Baldwin, A.J. & Ackland J.D. (1991) Effect of pre-heat treatment and storage on the properties of whole milk powder – changes in physical and chemical properties. *Netherlands Milk and Dairy Journal*, **45**, 169–181.
- Bassette, R. & Acosta, J.S. (1988) Composition of milk products. In: *Fundamentals of Dairy Chemistry*, (ed. N.P. Wong), 3rd edn. pp. 39–79. Van Nostrand Reinhold, New York.
- Boumba, V.A., Voutsinas, L.P. & Philippopoulos, C.D. (2001) Composition and nutritional value of commercial dried whey products from feta cheese manufacture. *International Journal of Dairy Technology*, **54**, 141–145.
- Brennan, J.G. (2006) Evaporation and dehydration. In: *Food Processing Handbook*, (ed. J.G. Brennan). pp. 71–124. Wiley-VCH Verlag, Weinheim.
- Buma, T.J. (1971) Free fat in spray-dried whole milk X. A final report with a physical model for free fat in spray dried milk. *Netherlands Milk and Dairy Journal*, **25**, 159–174.
- Burton, H. (1988) *Ultra High Temperature Processing of Milk and Milk Products*. Elsevier Applied Science Publishers, London.
- Caric, M. (1993) Concentrated and dried dairy products. In: *Dairy Science and Technology Handbook 2: Product Manufacturing*, (ed. Y.H. Hui). pp. 257–300. VCH Publishers, New York.

- Chen, L., Daniel, R.M. & Coolbear, T. (2003) Detection and impact of protease and lipase activities in milk and milk powders: a review. *International Dairy Journal*, **13**, 255–275.
- Dalgleish, D.G., Pouliot, Y. & Paquin, P. (1987) Studies on the heat stability of milk II. Association and dissociation of particles and the effect of added urea. *The Journal of Dairy Research*, **54**, 29–37.
- Datta, N. & Deeth, H.C. (2001) Age gelation of UHT milk – a review. *Transactions of the Institute of Chemical Engineers C. Food and Bioproducts Processing*, **79**, 197–210.
- Datta, N. & Deeth, H.C. (2003) Diagnosing the cause of proteolysis in UHT milk. *Lebensmittel-Wissenschaft und Technologie*, **36**, 173–182.
- Dattatreya, A., Etzel, M.R. & Rankin, S.A. (2007) Kinetics of browning during accelerated storage of sweet whey powder and prediction of its shelf-life. *International Dairy Journal*, **17**, 177–182.
- Deeth, H.C. (2006) Lipoprotein lipase and lipolysis in milk. *International Dairy Journal*, **16**, 555–562.
- Deeth, H.C. & Fitz-Gerald, C.H. (2006) Lipolytic enzymes and hydrolytic rancidity. In: *Advanced Dairy Chemistry 2 Lipids*, (eds P.F. Fox & P.L.H. McSweeney), 3rd edn. pp. 481–556. Springer, New York.
- de Jong, P. & Verdurmen, R.E.M. (2001) Concentrated and dried dairy products. In: *Mechanisation and Automation in Dairy Technology*, (eds A.Y. Tamime & B.A. Law). pp. 152–203. Sheffield Academic Press, Sheffield.
- Driscoll, N.R., Brennand, C.P. & Hendricks, D.G. (1985) Sensory quality of nonfat dry milk after long-term storage. *Journal of Dairy Science*, **68**, 1931–1935.
- Early, R. (1992) Milk powders. In: *The Technology of Dairy Products*, (ed. R. Early). pp. 167–196. Blackie, Glasgow.
- Early, R. (1998) Milk concentrates and milk powders. In: *The Technology of Dairy Products*, (ed. R. Early), 2nd edn. pp. 228–300. Blackie Academic and Professional, Glasgow.
- Elliott, A.J., Datta, N. & Deeth, H.C. (2005) Heat-induced and other chemical changes in commercial UHT milks. *The Journal of Dairy Research*, **72**, 442–446.
- Evers, J.M. (2004) The milkfat globule membrane-methodologies for measuring milkfat globule (membrane) damage. *International Dairy Journal*, **14**, 747–760.
- Fäldt, P. & Bergenstahl, B. (1995) Fat encapsulation in spray-dried food powders. *Journal of the American Oil Chemists Society*, **72**, 171–176.
- Fenaille, F., Mottier, P., Turesky, R.J., Ali, S. & Guy, P.A. (2001) Comparison of analytical techniques to quantify malondialdehyde in milk powders. *Journal of Chromatography A*, **921**, 237–245.
- Flynn, A. & Cashman, K. (1997) Nutritional aspects of minerals in bovine and human milks. In: *Advanced Dairy Chemistry 3: Lactose, Water, Salts and Vitamins*, (ed. P.F. Fox), 2nd edn. pp. 257–302. Chapman & Hall, London.
- Food Standards Australia New Zealand (FSANZ) (2006) *NUTTAB 2006 Australian Food Composition Tables*. Food Standards Australia New Zealand, Canberra.
- Fox, P.F. (2002) Milk – introduction. In: *Encyclopedia of Dairy Sciences*, (eds H. Roginski, J.W. Fuquay & P.F. Fox). pp. 1805–1812. Academic Press, London.
- Fox, P.F. (2003) Milk proteins: general and historical aspects. In: *Advanced Dairy Chemistry 1: Proteins*, (eds P.F. Fox & P.L.H. McSweeney), 3rd edn. pp. 1–48. Kluwer Academic, London.
- Fox, P.F. & McSweeney, P.L.H. (1998) *Dairy Chemistry and Biochemistry*. Chapman & Hall, London.
- Grijpspeerd, K., Mortier, L., De Block, J. & Van Renterghem, R. (2004) Applications of modelling to optimise ultra high temperature milk heat exchangers with respect to fouling. *Food Control*, **15**, 117–130.
- Guyomarc'h, F., Warin, F., Muir, D.D. & Leaver, J. (2000) Lactosylation of milk proteins during the manufacture and storage of skim milk powders. *International Dairy Journal*, **10**, 863–872.

- Hardy, E.E., Muir, D.D., Sweetsur, A.W.M. & West, I.G. (1984) Changes of calcium phosphate partition and heat stability during manufacture of sterilized concentrated milk. *Journal of Dairy Science*, **67**, 1666–1673.
- Hardy E.E., Sweetsur, A.W., West, I.G. & Muir, D.D. (1985) Heat stability of concentrated milk: enhancement of initial heat stability by incorporation of food grade lecithin. *Journal of Food Technology*, **20**, 97–105.
- Hargrove, R.E. & Alford, J.A. (1974) Composition of milk products. In: *Fundamentals of Dairy Chemistry*, (eds B.H. Webb, A.H. Johnson & J.A. Alford), 2nd edn. pp. 58–86. AVI Publishing, Westport, CT.
- Havea, P. (2006) Protein interactions in milk protein concentrate powders. *International Dairy Journal*, **16**, 415–422.
- Haylock, S.J. (1995) Dried dairy ingredients for confectionery. *Manufacturing Confectioner*, **6**, 65–73.
- Hindmarsh, J.P., Russell, A.B. & Chen, X.D. (2007) Fundamentals of the spray freezing of foods – microstructure of frozen droplets. *Journal of Food Engineering*, **78**, 136–150.
- Holt, C. (1997) The milk salts and their interaction with casein. In: *Advanced Dairy Chemistry 3: Lactose, Water, Salts and Vitamins*, (ed. P.F. Fox), 2nd edn. pp. 233–256. Chapman & Hall, London.
- Holt, C., McPhail, D., Nevison, I. *et al.* (1999) Apparent chemical composition of nine commercial or semi-commercial whey protein concentrates, isolates and fractions. *International Journal of Food Science and Technology*, **34**, 543–556.
- Horne, D.S. & Muir, D.D. (1990) Alcohol and heat stability of milk protein. *Journal of Dairy Science*, **73**, 3613–3626.
- Hotchkiss, J.H., Werner, B.G. & Lee, E.Y.C. (2006) Addition of carbon dioxide to dairy products to improve quality: a comprehensive review. *Comprehensive Reviews in Food Science and Food Safety*, **5**, 158–168.
- Huffman, L.M. (1996) Processing whey protein for use as a food ingredient. *Food Technology*, **50**, 49–52.
- Huppertz, T. & Fox, P.F. (2006) Influence of added lyophilized butter serum on the heat stability of unconcentrated and concentrated bovine milk. *International Journal of Dairy Technology*, **59**, 18–21.
- Jensen, G.J. (1990) Milk powders: Specifications in relation to the products to be manufactured. *Recombination of Milk and Milk Products*, Special Issue 9001. pp. 104–125. International Dairy Federation, Brussels,
- Journink, T.J.M. & de Kruif, K.G. (1995) Calcium concentration in milk in relation to heat stability and fouling. *Netherlands Milk and Dairy Journal*, **49**, 151–165.
- Journink, T.J.M., Walstra, P. & de Kruif, C.G. (1996) Mechanisms of fouling in dairy processing. *Netherlands Milk and Dairy Journal*, **50**, 407–426.
- Jones, A.D., Tier, C.M. & Wilkins, J.P.G. (1998) Analysis of the Maillard reaction products of  $\beta$ -lactoglobulin and lactose in skimmed milk powder by capillary electrophoresis and electrospray mass spectrometry. *Journal of Chromatography A*, **822**, 147–154.
- Jouppila, K. & Roos, Y.H. (1994) Glass transitions and crystallization in milk powders. *Journal of Dairy Science*, **77**, 2907–2915.
- Kastanas, P. (1996) *Studies on the fouling of heat exchangers during the sterilization of Cows' and Goats' milk*. PhD thesis, University of Reading, Reading, MA.
- Kelly, A., Datta, N. & Deeth, H.C. (2006) Thermal processing of dairy products. In: *Thermal Food Processing: New Technologies and Quality Issues*, (ed. D.-W. Sun). pp. 265–298. CRC Press (Taylor & Francis Group), Boca Raton, FL.
- Kelly, A.L. & McSweeney, P.L.H. (2003) Indigenous proteinases in milk. In: *Advanced Dairy Chemistry 1: Proteins*, (eds P.F. Fox & P.L.H. McSweeney), 3rd edn. pp. 495–521. Kluwer Academic, London.



- Kim, E.H.J., Chen, X.D. & Pearce, D. (2002) Surface characterization of four industrial spray-dried dairy powders in relation to chemical composition, structure and wetting property. *Colloids and Surfaces B: Biointerfaces*, **26**, 197–212.
- Kim, E.H.J., Chen, X.D. & Pearce, D. (2005) Effect of surface composition on the flowability of industrial spray-dried dairy powders. *Colloids and Surfaces B: Biointerfaces*, **46**, 182–187.
- Knight, G.C., Nicol, R.S. & McMeekin, T.A. (2004) Temperature step changes: a novel approach to control biofilms of *Streptococcus thermophilus* in a pilot plant-scale cheese-milk pasteurisation plant. *International Journal of Food Microbiology*, **93**, 305–318.
- Lehmann, L. & Buckin, V. (2005) Determination of the heat stability profiles of concentrated milk and milk ingredients using high resolution ultrasonic spectroscopy. *Journal of Dairy Science*, **88**, 3121–3129.
- Lehmann, F.L., Russel, P.S., Solomon, L.S. & Murphy, K.D. (1992) Bacterial growth during continuous milk pasteurisation. *Australian Journal of Dairy Technology*, **47**, 28–32.
- Liang, J.H. (2000) Kinetics of fluorescence formation in whole milk powder during oxidation. *Food Chemistry*, **71**, 459–463.
- Liang, B. & Hartel, R.W. (2004) Effects of milk powders in milk chocolate. *Journal of Dairy Science*, **87**, 20–31.
- Listiohadi, Y.D., Hourigan, J.A., Sleight, R.W. & Steele, R.J. (2005) Properties of lactose and its caking behaviour. *Australian Journal of Dairy Technology*, **60**, 33–52.
- Lloyd, R.J., Chen, X.D. & Hargreaves, J.B. (1996) Glass transition and caking of spray-dried lactose. *International Journal of Food Science and Technology*, **31**, 305–311.
- Martin, G.J.O., Williams, R.P.W. & Dunstan, D.E. (2007) Comparison of casein micelles in raw and reconstituted skim milk. *Journal of Dairy Science*, **90**, 4543–4551.
- Mathlouthi, M. (2001) Water content, water activity, water structure and the stability of food stuffs. *Food Control*, **12**, 409–417.
- McCluskey, C., Connolly, J.F., Devery, R. *et al.* (1997) Lipid and cholesterol oxidation in whole milk powder during processing and storage. *Journal of Food Science*, **62**, 331–337.
- Millqvist-Fureby, A., Elofsson, U. & Bergenstahl, B. (2001) Surface composition of spray-dried milk protein-stabilised emulsions in relation to pre-heat treatment of proteins. *Colloids and Surfaces B: Biointerfaces*, **21**, 47–58.
- Millqvist-Fureby, A. & Smith, P. (2007) In-situ lecithination of dairy powders in spray-drying for confectionery applications. *Food Hydrocolloids*, **21**, 920–927.
- Mistry, V.V. (2002) Manufacture and application of high milk protein powder. *Lait*, **82**, 515–522.
- Mleko, S., Janas, P., Wang, T. & Lucey, J.A. (2003) Rheological properties of reduced lactose whey dispersions. *International Journal of Dairy Technology*, **56**, 157–161.
- Morgan, F., Bouhallab, S., Mollé, D., Henry, G., Maubois, J.L. & Léonil, J. (1998) Lactolation of  $\beta$ -lactoglobulin by electrospray ionisation mass spectrometry. *International Dairy Journal*, **8**, 787–792.
- Morr, C.V. (1984) Manufacture, functionality, and utilization of milk-protein products. In: *Proceeding of the International Congress on Milk Proteins*, (eds T.E. Galesloot & B.L. Tinbergen). pp. 171–182. Pudoc, Wageningen.
- Morr, C.V. & Foegeding, E.A. (1990) Composition and functionality of commercial whey and milk protein concentrates and isolates: a status report. *Food Technology*, **44** (4), 100–112.
- Morr, C.V. & Ha, E.Y.W. (1993) Whey protein concentrates and isolates – Processing and functional properties. *Critical Reviews in Food Science and Nutrition*, **33**, 431–476.
- Muir, D.D. & Sweetsur, A.W.M. (1978) The effect of concentration on the heat stability of skim-milk. *The Journal of Dairy Research*, **45**, 37–45.
- Mulvihill, D.M. & Ennis, M.P. (2003) Functional milk proteins: production and utilization. In: *Advanced Dairy Chemistry 1: Proteins*, (eds P.F. Fox & P.L.H. McSweeney), 3rd edn. pp. 1175–1228. Kluwer Academic, London.

- Murphy, J.M. & Fox, P.F. (1991) Fractionation of sodium caseinate by ultrafiltration. *Food Chemistry*, **39**, 27–38.
- Newstead, D.F., Conaghan, E.F. & Baldwin, A.J. (1979) Studies on the induction of heat stability in evaporated milk by preheating: effects of milk concentration, homogenization and whey proteins. *The Journal of Dairy Research*, **46**, 387–391.
- Newstead, D.F., Paterson, G., Anema, S.G., Coker, C.J. & Wewala, A.R. (2006) Plasmin activity in direct-steam-injection UHT-processed reconstituted milk: effects of preheat treatment. *International Dairy Journal*, **16**, 573–579.
- Newstead, D.F., Sanderson, W.B. & Baucke, A.G. (1975) The effects of heat treatment and pH on the heat stability of recombined evaporated milk. *New Zealand Journal of Dairy Science and Technology*, **10**, 113–118.
- Nijdam, J.J. & Langrish, T.A.G. (2006) The effect of surface composition on the functional properties of milk powders. *Journal of Food Engineering*, **77**, 919–925.
- O’Connell, J.E. & Fox, P.F. (2003) Heat-induced coagulation of milk. In: *Advanced Dairy Chemistry 1: Proteins*, (eds P.F. Fox & P.L.H. McSweeney), 3rd edn. pp. 879–945. Kluwer Academic, London.
- Oldfield, D.J., Taylor, M.W. & Singh, H. (2005) Effect of preheating and other process parameters on whey protein reactions during skim milk powder manufacture. *International Dairy Journal*, **15**, 501–511.
- O’Malley, A.M., Mulvihill, D.M. & Singh, T.K. (2000) Proteolysis in rennet casein-based cheese analogues. *International Dairy Journal*, **10**, 743–753.
- Oldfield, D.J., Teehan, C.M. & Kelly, P.M. (2000) The effect of preheat treatment and other parameters on the coffee stability of instant whole milk powder. *International Dairy Journal*, **10**, 659–667.
- Pintado, M.E., da Silva, J.A.L. & Malcata, F.X. (1999) Comparative characterization of whey protein concentrates from ovine, caprine and bovine breeds. *Lebensmittel-Wissenschaft und Technologie*, **32**, 231–237.
- Posati, L. & Orr, M.L. (1976) Composition of foods, dairy and egg products, raw, processed, prepared. In: *Agriculture Handbook No. 8-1*. ARS, US Department of Agriculture, Washington, DC.
- Prakash, S. (2007) *Burn-on in Ultra High Temperature Processing of Milk*. PhD thesis, University of Queensland, Brisbane.
- Prakash, S., Datta, N., Lewis, M.J. & Deeth, H.C. (2007) Reducing fouling during UHT treatment of goats’ milk. *Milchwissenschaft*, **62**, 16–19.
- Rolls, B.A. & Porter, J.W.G. (1973) Some effects of processing and storage on the nutritive value of milk and milk products. *Proceedings of the Nutrition Society*, **32**, 9–15.
- Shamsuzzaman, K., Modler, W. & McKellar, R.C. (1986) Survival of lipase during manufacture of nonfat dry milk. *Journal of Dairy Science*, **70**, 746–751.
- Shrestha, A.K., Howes, T., Adhikari, B.P., Wood, B.J. & Bhandari, B.R. (2007) Effect of protein concentration on the surface composition, water sorption and glass transition temperature of spray-dried skim milk powders. *Food Chemistry*, **104**, 1436–1444.
- Singh, H., Creamer, L.K. & Newstead, D.F. (1995) Heat stability of concentrated milk. In: *Heat Induced Changes in Milk*, (ed. P.F. Fox), Special Issue 9501. pp. 256–274. International Dairy Federation, Brussels.
- Singh, H. & Tokley, R.P. (1990) Effects of preheat treatments and buttermilk addition on the seasonal variations in the heat stability of recombined evaporated milk and recombined concentrated milk. *Australian Journal of Dairy Technology*, **45**, 10–16.
- Sinha, R., Radha, C., Prakash, J. & Kaul, P. (2007) Whey protein hydrolysate: functional properties, nutritional quality and utilization in beverage formulation. *Food Chemistry*, **101**, 1484–1491.
- Sommer, H.H. & Hart, E.B. (1922) The heat coagulation of milk. *Journal of Dairy Science*, **5**, 525–543.
- Spreer, E. (1998) *Milk and Dairy Product Technology*. Marcel Dekker Inc., New York.

- Stapelfeldt, H., Nielsen, B.R. & Skibsted, L.H. (1997) Effect of heat treatment, water activity and storage temperature on the oxidative stability of whole milk powder. *International Dairy Journal*, **7**, 331–339.
- Sweetsur, A.W.M. & Muir, D.D. (1980) The use of permitted additives and heat treatment to optimize the heat stability of milk and concentrated skim milk. *Journal of the Society of Dairy Technology*, **33**, 101–105.
- Sweetsur, A.W.M. & Muir, D.D. (1982) Manipulation of the heat stability of homogenized concentrated milk. *Journal of the Society of Dairy Technology*, **35**, 129–132.
- Sweetsur, A.W.M. & Muir, D.D. (1983) Influence of sulphhydryl group interactions on the heat stability of homogenized concentrated milk. *The Journal of Dairy Research*, **50**, 301–308.
- Thomas, M.E.C., Scher, J., Desobry-Banon, S. & Desobry, S. (2004) Milk powders ageing: Effect on physical and functional properties. *Critical Reviews in Food Science and Nutrition*, **44**, 297–322.
- Tissier, J.P., Lalande, M. & Corrieu, G. (1984) A study of milk deposit on heat-exchange surface during UHT treatment. In: *Engineering and Food I. Engineering Sciences in the Food Industry*, (ed. B.M. McKenna). pp. 49–58. Elsevier Applied Science, London.
- Van Renterghem, R. & De Block, J. (1996) Furosine in consumption milk and milk powders. *International Dairy Journal*, **6**, 371–382. &
- Varnam, A.H. & Sutherland, J.P. (2001) *Milk and Milk Products: Technology, Chemistry and Microbiology*. Aspen Publishers, Gaithersburg, MD.
- Verdurmen, R.E.M. & de Jong, P. (2003) Optimising product quality and process control for powdered dairy products. In: *Dairy Processing – Improving Quality*, (ed. G. Smit). pp. 333–390. Woodhead Publishing, Cambridge.
- Walstra, P. & Jenness, R. (1984) *Dairy Chemistry and Physics*. John Wiley & Sons, New York.
- Walstra, P., Wouters, J.T.M. & Guerts, T.J. (2006) *Dairy Technology*, 2nd edn. CRC Press (Taylor & Francis Group), Boca Raton.
- Williams, R.P.W. (2002) The relationship between the composition of milk and the properties of bulk milk products. *Australian Journal of Dairy Technology*, **57**, 30–44.
- Wong, N.P., Jenness, R., Keeney, M. & Marth, E.H. (eds) (1988) *Fundamentals of Dairy Chemistry*, 3rd edn. Van Nostrand Reinhold, New York.
- Zadow, J.G. & Hardham, J.F. (1978) The influence of milk powder, pH and heat treatment on the reflectance and stability of recombined milk sterilized by the ultra high temperature process. *Australian Journal of Dairy Technology*, **33**, 6–10.
- Zadow, J.G., Hardham, J.F., Kocak, H.R. & Mayes, J.J. (1983) The stability of goats milk to ultra high temperature processing. *Australian Journal of Dairy Technology*, **38**, 20–23.