J. Dairy Sci. 96:5455–5464
http://dx.doi.org/10.3168/jds.2012-6497

Protein, casein, and micellar salts in milk: Current content and historical perspectives

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ABSTRACT

The protein and fat content of Dutch bulk milk has been monitored since the 1950s and has increased considerably, by 11 and 20%, respectively, whereas milk yield has more than doubled. The change in protein and fat content of milk is advantageous for the dairy industry, as these are the 2 most economically valuable constituents of milk. Increases in protein and fat content of milk have allowed increases in the yield of various products such as cheese and butter. However, for cheese and other applications where casein micelles play a crucial role in structure and stability, it is not only casein content, but also the properties of the casein micelles that determine processability. Of particular importance herein is the salt partition in milk, but it is unknown whether increased protein content has affected the milk salts and their distribution between casein micelles and milk serum. It was, therefore, the objective of this research to determine the salt composition and protein content for individual cow milk and bulk milk over a period of 1 yr and to compare these data to results obtained during the 1930s, 1950s, and 1960s in the last century. Calcium, magnesium, sodium, potassium, and phosphorus content were determined by inductively coupled plasma atomic emission spectrometry and inorganic phosphate, citrate, chloride, and sulfate content by anion-exchange chromatography in bulk milk and milk ultracentrifugate. In addition, ionic calcium and ionic magnesium concentration were determined by the Donnan membrane technique. We concluded that historical increase in milk yield and protein content in milk have resulted in correlated changes in casein content and the micellar salt fraction of milk. In addition, the essential nutrients, calcium, magnesium, and phosphorus in milk have increased the past 75 yr; therefore, the nutritional value of milk has improved.

Key words: milk protein, casein, calcium phosphate, magnesium

INTRODUCTION

Accurate knowledge of the distribution and total concentration of milk salts is relevant throughout the dairy chain. In nutrition science, great interest exists in the salt content and composition of milk and other dairy food products because they contribute substantial amounts of essential nutrients to the Western diet (i.e., 52–75% of calcium, 30–45% of phosphorus, 19% of potassium, and 16–21% of magnesium; Guéguen and Pointillart, 2000; Huth et al., 2006; Cashman, 2011). Furthermore, milk salt composition is important for the technological properties of milk. The partition of salts, especially the distribution of calcium phosphate between the casein micelle and serum phase, has a large influence on the structure and stability of casein micelles (Holt, 1985; Lucey and Horne, 2009; Dalgleish and Corredig, 2012). The salt partition can be altered by changes in physicochemical conditions, such as heating, cooling, and acidification (de la Fuente, 1998; Gaucheron, 2005) and can, therefore, have major consequences for several dairy processes in which casein micelles are involved, such as acid coagulation of yogurt products and stability of concentrated milk during heating and evaporation (Hardy et al., 1984; Nieuwenhuijse et al., 1988). In addition, colloidal calcium phosphate and free calcium play an essential role during rennet coagulation in the cheese-making process (Lucey and Fox, 1993).

The major fraction of salts in milk is composed of the cations calcium, magnesium, potassium, and sodium and the anions citrate, phosphate, and chloride (Pyne, 1962; Holt, 1985). They can be either dissolved as free ions or ion pairs in milk serum or dispersed in colloidal calcium phosphate nanoclusters bound to caseins (de Kruif et al., 2012). Calcium phosphate nanoclusters are in dynamic equilibrium with milk serum (Holt et al., 1989; Little and Holt, 2004). On average, 70% of calcium, 50% of inorganic phosphate, 30% of magnesium, and 10% of citrate in milk are located in the

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Received December 18, 2012.
Accepted May 23, 2013.
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casein micelle (Holt, 2004) and are of vital importance for casein micelle stability (de Kruif and Holt, 2003; Walstra et al., 2005; Farrell et al., 2006). Because of the close relationship between micellar salts and casein, calcium phosphate in milk varies in proportion to the casein content of milk (Holt and Jenness, 1984, Lucey and Horne, 2009; Holt, 2011).

It is clearly relevant for many disciplines within the field of dairy science and for the dairy industry to have an accurate understanding of the casein content and salt composition of the milk used on a daily basis. However, the detailed salt composition and casein content is currently not monitored on a regular basis. Although it is recognized that the salt composition in milk of individual cows is influenced by breed, season, stage of lactation, diet, and mastitis within the time frame of a lactation period (Gaucheron, 2005), until now insufficient data have been available to determine variation over a longer time frame of decades. During the past 50 yr, several trends between casein, salt fractions, and several other factors have been observed using individual milk samples, bulk milk, mineral-depleted milk, and even interspecies analysis. White and Davies (1958) examined the bulk milk of 1 herd of Ayrshire cows during 1 yr as well as individual milk samples of cows at different stages of lactation. The analysis of differences in milk composition between cows showed multiple direct and inverse correlations between different salt fractions, pH, lactose, and stage of lactation. Correlations between lactose, sodium, and potassium were also observed in milk from 8 individual Friesian cows that were followed during the first 90 d of their lactation (Tsioulpas et al., 2007a). In addition, correlations between calcium in serum and citrate in serum were found after analysis of bulk milk from 5 creameries in Scotland during 1 yr (Holt and Muir, 1979). Mineral depletion of bulk milk and 3 individual cow milk samples showed a strong correlation between colloidal calcium and colloidal phosphate (Holt, 1982) and were later also found between species (Holt and Jenness, 1984).

The protein and fat content of Dutch bulk milk has been monitored yearly since the 1950s and it can be seen that both have increased considerably (Figure 1). Also milk yield per cow has approximately doubled and the average milk protein yield in the Netherlands has increased from 148 kg in 1960 to 331 kg in 2010 per lactation per cow (CRV, 2012). These changes are the result of changes in management, especially feed composition, and breeding strategies (Heck et al., 2009). Breeding goals in most countries consist of milk yield and milk composition. Selection might result in correlated changes in other traits. For example, selection for a higher fat content resulted in more saturated and less unsaturated FA (Stoop et al., 2008). Similarly, selection for higher protein content can alter milk protein composition (Schopen et al., 2009). Breeding and payment schemes for the dairy industry have been aimed at increasing the protein content or protein yield of milk (Boland et al., 2001; Schopen et al., 2009). The change in protein and fat content of milk is advantageous for the dairy industry, as these are the 2 most economically valuable constituents of milk. Increases in protein and fat content of milk have allowed increases in the yield of various products derived from milk, including cheese, butter, as well as milk protein- and milk fat-based ingredients. However, for the applications listed above, particularly those where casein micelles play a crucial role in structure and stability, it is not only casein content, but also the properties of the casein micelles that determine processability. Of particular importance herein is the mineral balance in milk, but it is unknown whether increased protein content has affected the milk salts and their distribution between casein micelles and milk serum. These changes could influence the structure and stability of casein micelles as well as processes in which casein micelles play a crucial role, such as rennet coagulation, acid coagulation, and concentration of milk. Besides that, changes in salt composition might have an effect on the nutritional value of milk.

The objective of this research was, therefore, to determine salt composition and protein content for individual cow milk and bulk milk over a period of 1 yr and to place these recent data in a historical perspective, using results from milk salt analysis performed during the 1930s, 1950s, and 1960s of the last century. This was done by creating 2 data sets containing informa-

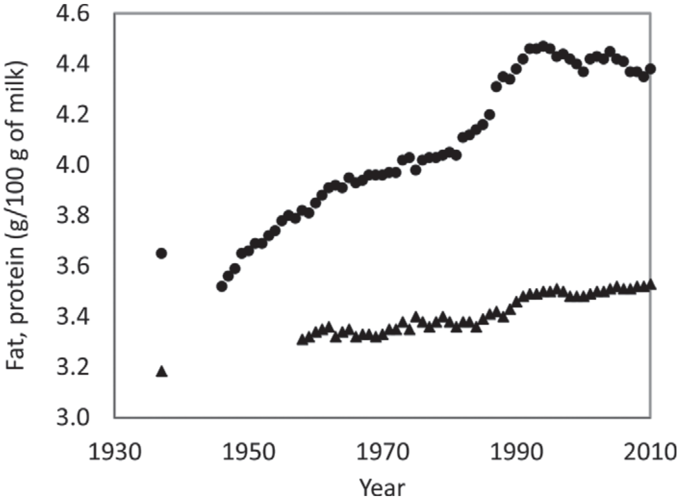

Figure 1. Historical trend for fat (●) and protein (▲) content (g/100 g of milk) of Dutch bovine raw milk from 1945 to 2010 (CRV, 2012). Data for 1937 are from Ter Horst (1963).