CHEMISTRY AND TESTING OF DAIRY PRODUCTS

Fourth Edition

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Preface to the Fourth Edition

The authors are very pleased with the continued acceptance of this text by dairy students and by field and laboratory personnel in the dairy industry. While most of the basic information remains valid in modern milk quality control, we feel the need to update several parts of this material and to expand the discussion to include new concepts in testing procedures which have been accepted by the dairy industry since publication of the Third Edition.

Our dialogue with students and industry personnel have shown the desirability of retaining the background information which has been presented in earlier editions. Developments described in simple terms allow the reader to better understand how the tests included in this book relate to quality control of milk and dairy products in a changing dairy industry.

We recognize the growing importance of the metric system in technical literature. On the valued advice of workers in the dairy industry, we have continued to report data in common units in this edition with the exception of temperatures, which have been converted to Centigrade units. This necessarily results in some inconsistency. Information is presented in the Appendix to enable the interested reader to convert these data to or from the metric system if this is desired.

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Preface to the Third Edition

This book is a complete revision and expansion of the original "Testing and Chemistry of Dairy Products" by J. A. Newlander. Information on the composition and properties of milk has been brought up to date and related to modern methods for making the physical and chemical tests which are so important in quality control of milk and milk products.

It is the intent of the authors to prepare a somewhat detailed discussion of the chemistry of the dairy products and the testing procedures to give an insight into the composition of milk and its derivatives, and the reasons for the special conduct of the different tests.

The revisions and additions which have been made in this book recognize the many changes which have taken place in the field of quality control during the years since World War II. The literature has been carefully reviewed and those contributions are presented which have importance in assessing the compositional quality of milk.

Additional chapters have been added to summarize information in several areas not covered in present texts or else receiving only piecemeal treatment. Experience in teaching agricultural students, fieldmen, regulatory workers and laboratory personnel has demonstrated the need for an organized presentation of this material.

This text is designed to discuss the several aspects of dairy testing and quality control in such a manner that the beginning student can appreciate the varied physical and chemical properties of milk and their influence on consumer acceptance of the resulting dairy products. Suggested laboratory tests are presented to illustrate the principles discussed. At the same time, the more advanced students and those responsible for quality control in the dairy industry will find this a valuable reference to the methods of conducting the different tests in the dairy laboratory.

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Contents

1

Composition of Milk

DEFINITION

Milk is the lacteal secretion, practically free from colostrum, obtained by the complete milking of one or more healthy cows, which contains not less than 8¼ percent milk solids-not-fat and not less than 3¼ percent milkfat. The word "milk" shall be interpreted to include goat milk.

The main constituents of milk are water, fat, proteins (such as casein and albumin), lactose (milk sugar), and ash. The constituents other than the water are known as total solids (TS) and the total solids minus the fat as solids not fat (SNF). Other common terms are milk plasma which consists of all the substances except the fat, and milk serum which consists of all the constituents except the fat and casein. Thus, the former corresponds practically to skimmilk and the latter to whey, the watery product left in cheese making.

COMPOSITION

The composition of normal cows' milk varies to a great extent. There are any number of tables giving the average composition of milk and each one differs slightly, but for all practical purposes the composition of normal whole milk corresponds closely to the figures in Table 1.1. Table 1.2 illustrates the factors affecting concentrations of components in cow's milk.

Table 1.1 represents the average analyses of a large number of samples of normal milk. The composition of individual samples of cow's milk would vary greatly, especially the fat and water. In general, the water will range from 82 to 90 percent; the fat from 2.5 to 8.0 percent; the casein from 2.3 to 4.0 percent; the sugar from 3.5 to 6.0 percent; the albumin from 0.4 to 1.0 percent and the ash from 0.5 to 0.9 percent.

TABLE 1.1. COMPOSITION OF MILK OF VARIOUS MAMMALS

	H_2O %	Fat %	Sugar %	Protein %	Ash %
Cow	87.00	4.00	5.00	3.30	.70
Human	87.41	3.78	6.21	2.00	.30
Goat	85.71	4.78	4.46	4.29	.76
Sheep	83.00	5.30	4.60	6.30	.80
Mare	90.18	1.59	6.73	2.14	.42
Ass	91.23	1.15	6.00	1.50	.40
Rat	68.30	14.79	2.83	11.77	1.50
Monkey	...	3.93	5.89	2.09	.26
Buffalo	82.05	7.98	5.18	4.00	.79
Camel	87.61	5.38	3.26	2.98	.70
Reindeer	65.32	19.73	2.61	1.91	1.43
Llama	86.55	3.15	5.60	3.90	.80
Hog	81.82	6.85	5.00	6.19	.98
Dog	79.26	8.17	4.00	7.53	1.36
Cat	82.17	3.33	4.91	9.08	.51
Rabbit	69.50	10.45	1.95	15.54	2.56
Elephant	68.00	19.60	8.80	3.10	.50
Whale	70.10	19.60	...	9.50	1.00
Porpoise	41.11	45.80	1.33	11.19	.57
Fox	81.88	5.42	5.11	...	.88
Hippo	90.43	4.51	4.40	...	.11
Dolphin	48.76	43.71	...	...	.46
Porcupine	...	31.00	...	...	...

Historically, milk fat has served as the basis for most pricing systems for milk. Consequently, many studies have been made to evaluate the factors which affect the fat content of a milk supply. However, the value of the non-fat milk solids must not be overlooked. Nutritional studies showing the importance of these milk solids in the diet, coupled with increased awareness of the economic consequences of variations in the solids-not-fat (SNF) content of milk on the yield of the many manufactured dairy products, have resulted in widespread interest in the factors which influence the SNF content of milk.

Seasonal variations in the amount of each milk constituent are less than variations in total milk produced. However, the relative composition of milk varies many times during the year while total milk received usually increases and decreases once each year. Table 1.3 indicates the relationship of protein and lactose to fat during the year.

Hereditary and environmental factors influence the SNF content of milk from breeds. There are definite and systematic effects of age, pregnancy, and stage of lactation. Seasonal variations are attributed to the combined effects of temperature and feeding since both high temperatures and poor quality feeds result in milk with low SNF content while good feed and low temperatures tend to raise the SNF concentration. SNF content is high at the start of the lactation period, then sharply decreases to the lactation low point at 40 to 60 days. It then rises gradually until the sixth month of lactation, followed by a sharp increase until the end of the lactation period. However, the latter rise is attributed to gestation effects since the SNF content of milk from animals which were not bred increases little, if any, during the final stages of lactation. Heredity has an important influence on SNF content.

TABLE 1.2. FACTORS AFFECTING CONCENTRATIONS OF COMPONENTS OF COWS' MILK

Factor	Ash	Fat	Protein	Lactose
Mastitis	Total ash increased; Na, Cl increased; K, Mg, Ca, P decreased	Decreased	Albumin increased; casein decreased; with possible changes in ratio of different caseins	Decreased
Lactation Colostrum	All components increased, except K	Increased	Increased	Generally constant
First 2 months	Generally constant	Decreased	Reaches minimum	Generally constant
Middle	Generally constant	Gradual increase	Gradual increase	Generally constant
Last 2 months	Total ash, Cl, Na, Ca, and Mg increased	Sharp increase at end	Sharp increase at end	Slight decrease at end
Season	Changes generally related to feed and stage of lactation. Total solids show decrease in June and July, with decrease distributed among the ash, protein and lipid components.			
Feed				
Underfeeding	Reduces solids-not-fat by 0.5–0.6% with more supression of protein than lactose.			
Excess feeding	Causes a slight increase in solids-not-fat, with change primarily reflected by protein level.			
Composition	The composition of the ash components and milk-fat can be affected by alterations in the mineral and lipid components of feed, respectively.			

Sources: Webb *et al.* (1974).

Reports from England agree that underfeeding and breeding are the common causes of low SNF content in milk. Similar studies from Kentucky reveal that the "seasonal" variations noted in the literature were more likely due to the general pattern of freshening and availability of suitable feeds within an area rather than to changes on the calendar. Studies from Missouri on the effect of controlled diurnal environmental temperature cycles on milk composition show that both fat and SNF content of milk increase during high 21 to 38° C or 16 to 43° C and low −12 to 4° C temperature cycles. Total nitrogen content of milk increases

TABLE 1.3. GRAMS OF PROTEIN AND LACTOSE PER 100 GRAMS OF FAT IN THE COWS' MILK RECEIVED BY TWO NORWEGIAN DAIRIES

Grams per 100 grams fat	Gausdal		Misvaer	
	Protein	Lactose	Protein	Lactose
January	96	139	94	136
February	94	137	91	134
March	91	131	95	138
April	92	136	85	128
May	91	133	86	131
June	85	117	78	112
July	79	119	84	125
August	82	113	79	113
September	86	116	85	122
October	91	127	92	126
November	92	131	89	116
December	92	125	95	126
Average	89	127	88	125

during the low temperature cycles. Low temperatures do not affect the chloride content but high temperature cycles give increased chloride values. Changes in milk composition occur very slowly following a change in environmental temperature.

Water

As seen from the composition, water is the constituent that gives bulk to milk. It holds the solids either in solution or in suspension.

Fat

Composition of Milk Fat.—The fat in milk is spoken of as milk fat, butterfat or simply fat. It is present in minute droplets or globules which vary in diameter from 0.001 to 0.01 millimeter (mm) or 1/25,000 to 1/2500 of an inch depending on the breed, stage of lactation and the individual cow. The higher testing breeds have the largest fat globules. On an average the volume of the fat globule in Guernsey milk is 80 percent greater than one in Holstein milk. The fat globules are usually largest during the first two weeks of lactation with the most rapid rate of decline occurring during the next two months. Thereafter the rate of decline in size is slow, but usually continues to the end of the normal lactation period.

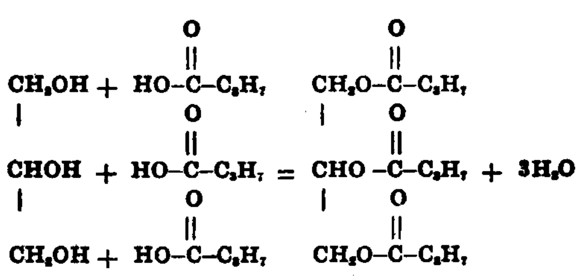
The globules float around in the milk in a true emulsion, oil-in-water, the fat being in the dispersed phase. The spherical shape is due to the force of surface tension, or the affinity one molecule has for the other. Hence, there is a tendency for the molecules to move toward the center one, which results in the milk fat globule assuming the smallest surface area possible in relation to its volume. This form must necessarily be spherical.

The fat globules are kept apart by the viscosity of the liquid, and by the layer of colloidal substance around the outside of the globule. This layer consists of both protein and phospholipids, and has to be removed or broken before two fat globules can unite. A negative electric charge is present in the globules and this also tends to keep them apart. Agitation as in churning breaks the absorbed layer and the globules coalesce with a final result of butter.

Milk fat, like most other animal fats, is a triglyceride. That is, one molecule of glycerol is joined chemically to three molecules of fatty acids. However, milk fat differs from other animal fats in that it has many more kinds of fatty acids. The principal ones are butyric, capric, caproic, caprylic, lauric, myristic, oleic, palmitic, stearic, and linoleic. Thus, butterfat is a mixture of different fats, each of which is made up of a molecule of glycerol and three molecules of fatty acids. For example, glycerol plus three molecules of butyric acid gives the fat butyrin; glycerol plus oleic acid gives olein. In most case, however, a molecule of glycerol, instead of being united to three molecules of the same acid, is joined to two or three different fatty acid molecules, such as stearic, oleic, and palmitic acids. The resulting fat in this case would be termed stearyl olyl palmitin. The following chemical equations illustrate the above examples:

1.	$C_3H_5(OH)_3$ Glycerol	+	$3C_3H_7COOH$ Butyric acid	=	$C_3H_5(C_3H_7COO)_3$ Butyrin	+	$3H_2O$ Water
2.	$C_3H_5(OH)_3$ Glycerol	+	$3C_{17}H_{33}COOH$ Oleic acid	=	$C_3H_5(C_{17}H_{33}COO)_3$ Olein	+	$3H_2O$ Water
3.	$C_3H_5(OH)_3$ Glycerol	+	$\left\{\begin{matrix} C_{17}H_{35}COOH \\ C_{17}H_{33}COOH \\ C_{15}H_{31}COOH \end{matrix}\right\}$ Stearic, oleic and palmitic acids	=	$C_3H_5\left\{\begin{matrix} C_{17}H_{35}COO \\ C_{17}H_{33}COO \\ C_{15}H_{31}COO \end{matrix}\right\}$ Stearyl olyl palmitin	+	$3H_2O$ Water

The structural formula of a fat is as follows:



Glycerol + Butyric acid = Butyrin

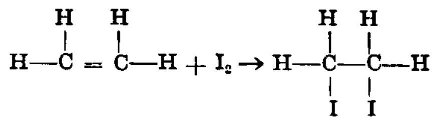
New methods of analysis in recent years have enabled workers to provide a much more comprehensive picture of the composition of milk fat than was possible in early texts. There are at least 64 different fatty acids in milk (as compared with <20 in most edible fats); about 23 are saturated and the remainder unsaturated. The saturated acids account for about 60 to 65 percent of the total fatty acids and the unsaturated acids the remaining 35 to 40 percent.

Most of the fatty acids in milk fat have an even number of carbon atoms. The saturated acids range from butyric acid with 4 carbon atoms to cerotic acid with 26 carbons. Palmitic acid, stearic acid and myristic acid (the C_{14}, C_{16}, and C_{18} saturated acids) comprise 72 to 78 percent of the total saturated acids and 45 to 50 percent of the total fatty acids present in milk fat. Table 1.4 gives the formulae, melting points, and percentage of the different acids in milk fat. This shows that the remaining saturated acids are present in only small amounts. The presence of butyric acid in milk fat serves as a distinguishing characteristic since no other fats contain this low molecular weight fatty acid. Branch-chain acids, straight-chain acids with an uneven number of carbon atoms, and straight-chain acids with 20 to 26 carbon atoms have been reported in trace amounts.

TABLE 1.4 FATTY ACIDS IN MILK FAT

Acid	Carbon atoms	Formula	Melting point °C	Average percentage
		Acetic Series $C_nH_{2n}O_2$		
Butyric	4	C_3H_7COOH	8 4	2.93
Caproic	6	$C_5H_{11}COOH$	10 1	1 90
Caprylic	8	$C_7H_{15}COOH$	15 4	0 79
Capric	10	$C_9H_{19}COOH$	31 0	1.57
Lauric	12	$C_{11}H_{23}COOH$	48 0	5 85
Myristic	14	$C_{13}H_{27}COOH$	58 0	19 78
Palmitic	16	$C_{15}H_{31}COOH$	64 0	15 17
Stearic	18	$C_{17}H_{35}COOH$	70 0	14 91
		Oleic Series $C_nH_{2n-2}O_2$		
Oleic	18	$C_{17}H_{33}COOH$	14 0	31 90
		Linoleic Series $C_nH_{2n-4}O_2$		
Linoleic	18	$C_{17}H_{31}COOH$	−17 8	4 50

The acids in the acetic series are saturated while those in the other series are unsaturated. A hydrocarbon which unites with oxygen or such monovalent elements as bromine, chlorine, iodine or hydrogen is spoken of as an unsaturated compound. This union is possible because of the double linkage between two adjacent carbon atoms. This is the unsaturation point and here an atom may be added and the compound thus pass into the single linkage class. The saturated hydrocarbons have single linkage and therefore do not have this particular property of combination.



Unsaturated Compound — Saturated Compound

The unsaturated fatty acids in milk present many problems for the chemist attempting to fractionate and identify them. They range in chain length from 10 to 24 carbons. They exist in different geometrical configurations. The fatty acid may exist with isomers having the double bond in different positions in the carbon chain. In addition, there are small quantities of polyunsaturated fatty acids in milk fat, these having 2, 3, 4, or 5 double bonds.

The lower members of the monounsaturated fatty acids (C_{10} to C_{16}) have the double bond in the 9, 10 position. These are present only in limited concentration. The C_{18} monounsaturated acid (oleic acid) exists in a number of isomeric forms and is one of the major constituents of milk fat. Oleic acid accounts for approximately 30 percent of the total fatty acid content. It is apparent that most of the early analyses include the lower molecular weight unsaturated acids along with oleic acid and thus values for oleic acid appear a little high. The polyunsaturated acids account for approximately 3 to 5 percent of the fatty acid content in milk fat.

The major fatty acids of milk may be divided into two groups, volatile and non-volatile.

Volatile	*Non-Volatile*
1. Butyric	6 Myristic
2 Caproic	7 Palmitic
3 Caprylic	8 Stearic
4. Capric	9 Oleic
5. Lauric	10 Linoleic

The first four fatty acids are soluble and the rest insoluble. All are saturated except oleic and linoleic which are unsaturated. Fats from the volatile fatty acids are rather unstable compounds and are quite easily decomposed. They have considerable influence on the flavor (and off-flavors) in milk. The unpleasant odor from rancid butter is due to freed fatty acids, mainly butyric. Normal processing and storage methods employed in the dairy industry do not produce any marked chemical changes in the saturated fatty acids. The unsaturated fatty acids, on the other hand, are of particular significance in the oxidative deterioration of milk and its products.

A soap is formed by the union of a non-volatile fatty acid, usually palmitic or stearic with sodium (or potassium). Animal fats and vegetable oils are boiled with sodium hydroxide and a soap is formed according to the following reaction:

$$\underset{\text{Stearin}}{C_3H_5(C_{17}H_{35}COO)_3} + \underset{\text{Sodium hydroxide}}{3NaOH} = \underset{\text{Sodium stearate (soap)}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}$$

A similar reaction will take place if a fat is heated with steam under pressure in which case the resulting products will be the free fatty acid and glycerol.

$$\underset{\text{Stearin}}{C_3H_5(C_{17}H_{35}COO)_3} + \underset{\text{Water}}{3H_2O} = \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}$$

Factors Affecting Composition of Milk Fat.—Milk fat varies in composition, the principal changes being in the amounts of the butyric, palmitic, stearic and oleic acids. This variation is due mainly to breed of animal, kind of feed and season of year.

The fat from Jerseys and Guernseys is usually firmer than that from Holsteins and Ayrshires, as the former contains less of the volatile and unsaturated fatty acids than does the latter. The fatty acids have varied melting points which affect the firmness of the milk fat. An increase in the low melting point acids such as oleic and butyric will give a soft milk fat, while an increase in stearic acid produces a hard fat.

Such feeds as linseed oil meal and pasture grass increase the oleic and linoleic acids with the production of soft fat. Cotton-seed meal produces a firm fat because it lowers the amount of butyric acid, which has a low melting point, and thus indirectly increases the percent of higher melting point acids. In general, feeds rich in carbohydrates and low in oils produce the firmer fats, while succulent roughages and oily concentrates give the softer fats.

Milk fat contains more of the volatile and of the unsaturated fatty acids during the spring and summer than in the fall and winter. This, however, is more a feed factor than a seasonal one.

Properties of Milk Fat.—*Melting Point.*—The melting point of milk fat varies normally between 32° C and 36° C with an average of 34° C. This wide variation in melting point is to be expected because of the change in proportions of the several fatty acids in milk fat due to feed and breed, etc. Because of the different melting points of the various fatty acids, butter softens slowly instead of melting suddenly. The melting point increases slightly (0.6 to 2.2° C) toward the end of the lactation period. The greater increases apply especially to the Holstein breed.

Specific Gravity.—The specific gravity of milk fat at 21° C is 0.93, while at 57° C to 60° C, the temperature at which fat tests are tempered, it is 0.892. However, a specific gravity of 0.9 is used in calculating what the capacity of the graduated portion of the Babcock test bottle should be. This will be explained later under the Babcock test.

Solubility.—Milk fat is readily dissolved by either ethyl ether, carbon tetrachloride, chloroform or benzene. It is moderately soluble in acetone, slightly so in alcohol and insoluble in water.

Iodine Number.—The iodine number measures the amount of unsaturated glycerides in a fat. It is the grams of iodine combining with 100 grams of fat. Since unsaturated fatty acids have double linkages at certain points in the carbon chain, iodine will join at these points and the amount of the halogen absorbed will determine the degree of unsaturation. Table 1.5 gives some typical iodine numbers.

TABLE 1.5. IODINE NUMBER OF SOME FATS AND OILS (NORMAL RANGE)

Butter	30-34	Olive oil	77- 91
Tallow	35-40	Cottonseed oil	104-116
Lard	48-64	Linseed oil	175-201

It will be noted that the oils have a greater degree of unsaturation than the fats, being higher in such fatty acids as oleic and linoleic. Butter contains less of the unsaturated fats than tallow or lard and therefore has a lower iodine number.

The iodine number of milk fat increases quite sharply during the pasture season and when oily feeds are fed in quantities. It also rises during the last few weeks of the lactation period, and to some extent during fasting. Thus, any factor that increases the proportion of unsaturated fatty acids, raises the iodine number.

Reichert-Meissl Number.—Milk fat differs from other common fats in having a larger percentage of volatile fatty acids. Therefore, a method of measuring the amount of these acids gives a means of distinguishing milk fat from other fats. The Reichert-Meissl number is used for this purpose. Specifically, the Reichert-Meissl number is equivalent to the number of milliliters of N/10NaOH required to neutralize the volatile fatty acids in 5 grams of fat.