AIDS TO ANALYSIS OF FOOD & DRUGS

J. R. NICHOLLS

SIXTH EDITION

BAILLIÈRE, TINDALL & COX

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PREFACE TO SIXTH EDITION

THE field of the food and drug analyst becomes wider every year, and the material considered necessary to incorporate in this new edition has increased the size of the book by approximately one-third. Much of this increase is accounted for by sections not previously dealt with; but almost all the sections have been extended. The general plan of the book has been retained and parts still are due to authors of previous editions. The whole has, however, been completely revised and brought up to date as far as possible.

Since the last edition the Food and Drugs Act, 1938, has come into force, and five Addenda to the British Pharmacopœia have been published.

During the war period a large number of Emergency Orders dealing with food have been issued. Some of these are clearly of temporary significance only, and are liable to amendment according to the supply position. Reference has been made to those involving a question of principle or having more than transitory importance.

The Preface to the First Edition stated that this work is not intended to be used as a cram-book for examinational purposes. This still holds; and, although it covers much of the syllabus of the examination of the Institute of Chemistry in Foods and Drugs, the book is primarily written for the use of practising food and drug chemists.

Thanks are due to the Society of Public Analysts and Other Analytical Chemists for permission to make extended use of the comprehensive Reports of the Society's Analytical Methods Committee.

J. R. NICHOLLS.

GOVERNMENT LABORATORY,
July, 1942.

PREFACE TO FIRST EDITION

As no work of moderate size devoted to the analysis of foods and drugs has recently appeared, we venture to hope that this small book may prove of service to those engaged in the examination of foods and drugs. This work is not intended to be used as a cram-book for examinational purposes. We cannot emphasise too strongly the fact that food analysis is not to be taught in a few weeks, as is frequently attempted in the interest of public health students. A competent knowledge of the analysis of food and drugs is only to be attained by some years of active practical laboratory work.

T. H. PEARMAIN.
C. G. MOOR.

September 30, 1895.

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AIDS TO THE ANALYSIS OF FOOD AND DRUGS

MILK.

The Composition of Milk from Different Animals.

Kind of Milk.	*Water.* %	*Fat.* %	*Sugars.* %	*Proteins.* %	*Ash.* %
Ass	90·0	1·3	6·5	1·7	0·5
Buffalo	80·9	7·9	4·5	5·9	0·8
Camel	86·5	3·1	5·6	4·0	0·8
Cat	81·6	3·8	4·9	9·1	0·6
Chimpanzee ..	—	3·75	5·7	2·6	—
Cow	87·35	3·75	4·75	3·4	0·75
Dog	75·4	9·6	3·1	11·2	0·7
Elephant	67·8	19·6	8·8	3·1	0·7
Ewe	79·4	8·6	4·3	6·7	1·0
Goat	86·0	4·6	4·2	4·4	0·8
Guinea-pig ..	82·2	5·5	2·9	8·5	0·9
Human	88·2	3·4	6·4	1·7	0·3
Llama	86·5	3·2	5·6	3·9	0·8
Mare	89·1	1·6	6·1	2·7	0·5
Porpoise	41·1	45·8	1·3	11·2	0·6
Reindeer	68·2	17·1	2·8	10·4	1·5
Sow	89·6	4·8	3·4	1·3	0·9
Whale	48·7	43·7	7·1		0·5

(The above figures are derived from a variety of sources and are subject to variations, which may be very great in non-domesticated animals.)

Cow's milk is most commonly used for human food in civilised countries where animals are bred for milk and flesh. Goat's milk is used in hilly districts in Europe, llama's milk in South America, buffalo's milk in India, Egypt and Hungary, mare's milk in the steppes of Russia and Tartary, and reindeer's milk in northern Europe and Asia. Sheep's milk is used for making cheese—*e.g.*, Roquefort. Ass's milk and mare's milk are low in protein and the casein behaves in a similar manner to that of human milk with acids and rennet; they are sometimes used as substitutes for human milk.

Fermented Milks.

(1) Unsalted, soured—buttermilk, yoghourt, acidophilus milk.

(2) Salted, soured—sostej, tarko.

(3) Alcoholic fermented—kephir, koumiss.

Yoghourt is made from curdled cow's milk, similar products being made from the milk of the buffalo, ewe and goat. It should contain *Bact. bulgaricum*, and the milk must be concentrated to show an increase of one-third in the dry matter—*i.e.*, the fat-free dry matter should be at least 11 per cent. It is a homogeneous, compact mass with an agreeably sour taste. Less concentrated products should be called yoghourt milk.

Koumiss, a preparation of mare's or ass's milk in a partly fermented condition, is largely used in Russia. It is prepared as follows: The milk is allowed to cool and deprived of a part of its cream; a little yeast is then added which sets up a slow fermentation, the milk-sugar being converted into alcohol and lactic acid Bell found Russian koumiss to have the following percentage composition: Lactic acid, 1·96; casein, 2·11; sugar, 0·40; fat, 1·10; alcohol, 2·12; ash, 0·34; water, 91·97.

Kephir, a preparation of cow's or goat's milk, very similar to koumiss, is produced by a special ferment. It is used largely by the tribes of the Caucasus.

Human Milk.

Human milk has a watery appearance and the taste is slightly saline. The average yield is about 0·4 litre. It is rather more alkaline than cow's milk, the *p*H being about 7·0. The average composition of 529 samples examined by Elsdon (*Analyst*, 1928, **53**, 78) showed:

Fat	3·27 per cent.
Solids-not-fat	8·80 ,, ,,
Proteins	1·8 ,, ,,
Ash	0·29 ,, ,,

Specific Gravity—The usual range is 1·029 to 1·035, but abnormal samples may vary from 1·017 to 1·036.

Fat.—The fat is generally between 3 and 4 per cent., but may be below 1 or over 9 per cent. The globules are generally smaller, and the melting-point of the fat lower than with the fat of cow's milk.

The first portion of human milk to exude is poor in fat, the bulk of which comes in the end milk. An analysis of a particular fraction of the milk available at one time is of little value as far as the fat content is concerned; a specimen representative of the whole of a feed should be examined. Further, as the fat content varies to some extent, not with the time of the day but with the relative period since previous feeding, it is well where fat is abnormal to examine specimens given at various times during the twenty-four hours.

The fat has the following characteristics (Elsdon, *Analyst*, 1916, **41**, 74; *ibid.*, 1928, **53**, 78):

	1916.	1928.
Refractive index (40° C.) ..	1·4568	—
Reichert value	2·0	3·4
Polenske value	2·2	1·9
Kirschner value	1·9	2·0
Iodine value	—	35·9

Non-Fatty Solids.—These are usually between 8 and 9·5 per cent.

Proteins.—Proteins vary greatly in quantity, depending much on the stage of nursing. Two per cent. is a common figure during the first week, but any value between 1 and 5 may be found.

On clotting, human casein is loose and flocculent, and is more easily digested by the child than cow casein, but the lower amounts both of casein and lime salts may be the factors responsible for this difference. Cow casein clots in large masses. Human milk is slightly richer in lactalbumin than cow's milk. By precipitin tests, it has been shown that both the casein and the albumin of human milk are biologically different from the analogous proteins of cow's milk.

Lactose is between 4 and 8 per cent. and remains fairly constant throughout lactation.

Ash shows a diminution as lactation advances. Human milk contains 1·6 to 1·7 milligrammes of ferric oxide (Fe_2O_3) per litre.

The trace of boric acid sometimes to be found in human milk generally comes from a dusting powder or from glycerin and borax used on the nipples.

Chlorine amounts to approximately one-fifth of the ash.

Reaction.—The *p*H is 6·9 to 7·3, the titratable acidity being usually between 0·025 and 0·050 per cent. Partridge (*Analyst*, 1933, **58,** 88) has recorded instances of exceptionally high acidities associated with abnormal compositions.

Goat's Milk.

Composition.—See page 1. It contains about double the chlorine present in cow's milk.

Fat.—

Reichert Value	23-28
Polenske Value	4-9
Kirschner Value	16-19
Saponification Value	228-231
Iodine Value	24-37
Butyro-refractometer reading at 40° C.	40-42

Detection of Goat's Milk in Cow's Milk (Krenn, *Analyst*, 1933, **58,** 349). Shake 5 ml. of milk with 15 ml. of a solution of ammonium sulphate (sp. gr. 1·134) and 10 ml. of ether for one minute. The layer of serum which separates after a further fifteen minutes is turbid with goat's milk and clear with cow's milk. The test is unaffected if the milk is twenty-four hours old, or has a high acid value, or is preserved with up to 1 per cent. of formalin or if obtained from ill or otherwise abnormal animals.

Sheep's Milk.

Composition.—See page 1.

Fat.—

Reichert Value	23-31
Polenske Value	2-8
Kirschner Value	17-24
Saponification Value	227-236
Iodine Value	28-32
Butyro-refractometer reading at 40° C.	40-43

Cow's Milk.

Commercial milk should be the normal, clean, and fresh secretion obtained by completely milking the udders of healthy cows properly fed and kept, excluding that yielded during fifteen days immediately before and ten days immediately following parturition.

Genuine milk is an opalescent white liquid, with a sweetish, bland taste. It contains:

(1) Compounds characteristic of milk—fat (including carotinoids and fat-soluble vitamins), casein, lactose, citric acid.

(2) Subsidiary compounds generally found in biological fluids—water, albumin, globulin, non-protein nitrogenous compounds, mineral salts, enzymes and various cells, dissolved gases (including carbon dioxide, oxygen and nitrogen).

The average composition is given on page 1.

Milk is unsuitable as the sole diet of adults, but in many districts it is the chief source of fat-soluble vitamins, of protein of good quality and of calcium salts. A minimum of ½ pint daily has been recommended for each adult, 1-2 pints for children and 2 pints for nursing and expectant mothers.

The fat is suspended in the aqueous portion of the milk (milk plasma) in the form of globules, from 0·0015 to 0·01 mm. in diameter. Small numbers of epithelial cells, leucocytes, and blood-corpuscles are frequently present, and in some cases colostrum. On standing for some time, a separation of part of the fat takes place, the larger fat globules of the milk naturally rising first.

Colostrum.—The first secretion in the udder immediately following parturition is a thick liquid, called colostrum, which differs from that subsequently secreted. Its composition is variable, being particularly high in albumin and globulin during the first few hours after calving. Elsdon (*Analyst*, 1934, **59,** 665) found

Fat	1-15	per cent.
Non-fatty solids	9-22	,, ,,
Protein	4-17	,, ,,
Ash	0·84-1·20	,, ,,

Freezing-point (Hortvet), Δ 0·54-0·59° C.

Reaction.—Absolutely fresh milk is amphoteric in reaction—*i.e.*, blue litmus is turned reddish, and red litmus bluish (due to the phosphates and citrates present). Its *p*H may be as low as 6·0, but the usual range is 6·4-6·6. A value over 6·8 may be regarded as abnormal. It usually reaches the consumer faintly acid, owing to some slight production of lactic acid through bacterial fermentation of lactose.

When the fermentative change has resulted in the production of about 0·4 per cent. of lactic acid, the milk can be distinctly recognised by the taste to be sour. When the acidity reaches 0·6 per cent., the milk curdles spontaneously, separating into a solid known as 'curd,' which consists of the fatty and protein constituents of the milk, and a clear liquid known as 'whey' which is essentially a solution of milk-sugar and mineral salts. This change is also brought about artificially by the addition of rennet. The further changes which take place in the composition of the milk after curdling depend upon the nature of the bacteria which have gained access, various organisms giving rise to different fermentations.

Titratable acidity is usually determined by titrating with standard sodium hydroxide solution, using phenolphthalein as indicator. The amount of indicator should be about 0·1 g. per 100 ml. of milk, otherwise the colour is indistinct and the end point passed. The usual end-point is 'a faint but definite pink,' and some workers use a colour standard made by adding a rosaniline salt to milk. One firm supplies a pink coloured stirring rod. The result may be expressed as a percentage of lactic acid, and it is convenient to use N/9 alkali—*i.e.*, 4·5 g. sodium hydroxide per litre, since 1 ml. = 0·01 g. lactic acid. Sometimes the result is given as 'degrees of acidity,' which is the number of ml. of N/10 alkali required to neutralise 10 ml. of milk. Soxhlet-Henkel used N/4 alkali, and the number of ml. required to neutralise 100 ml. of milk was called Soxhlet-Henkel degrees. To avoid ambiguity it is better to express the result as per cent. lactic acid.

Milk-Fat.—This is considered under 'Butter-Fat,' with which it is of course identical.

Milk-Proteins.—The nitrogenous bodies in milk consist of—

(1) Casein (2·2 to 3·5 per cent.).
(2) Lactalbumin (0·4 to 0·7 per cent.).
(3) Lactoglobulin (0·05 to 0·2 per cent.).
(4) Non-proteins (traces).

Casein is a phosphoprotein and contains sulphur. It occurs as a calcium salt and is not coagulable by heat. The casein nitrogen is about 77 per cent. of the total nitrogen, and amounts to 15·7 per cent. of the casein; the conversion factor is 6·38.

Lactalbumin contains $2\frac{1}{2}$ times as much sulphur as casein. It is heat coagulable (at 70°-75° C.) and is similar to blood serum albumin.

Lactoglobulin is also heat coagulable.

Of the **non-proteins** urea is present in largest amount.

In average milk the nitrogen is distributed as follows:

Protein N	95 per cent.
Casein N	77 ,, ,,
Albumin N	13 ,, ,,
Globulin N	5 ,, ,,
Non-protein N	5 ,, ,,

Abnormality in milk lowers the casein N, raises the albumin and non-protein N, and considerably raises the globulin N.

Milk-Sugar, or Lactose ($C_{12}H_{22}O_{11}+H_2O$).—This sugar is peculiar to the milk of the Mammalia and is the most constant constituent of milk. There is no other carbohydrate ordinarily present in milk, except possibly in traces. Lactose has only a faint degree of sweetness, and is gritty when chewed. It is soluble in water, but insoluble in dry ether and in absolute alcohol. It is a disaccharide which yields *d*-glucose and *d*-galactose on hydrolysis.

Lactose exists in two modifications, viz., alpha-lactose, the usual form, which may be hydrated or anhydrous, and beta-lactose, which contains no water. Both types are present in milk in the proportion of 1 part of alpha to 1·65 parts of beta. This is the equilibrium mixture which always results finally from the solution of either modification. When water is removed from the solution transference to the beta modification takes place at 93·5° C. On heating alpha-lactose hydrate the water is driven off between 110° and 130° C.

Lactose is dextro-rotatory to a ray of polarised light, and reduces Fehling's solution but not Barfoed's reagent.

Citric acid, which readily inverts cane-sugar, has no action on lactose.

Lactose is an official preparation in the British Pharmacopœia, being used as a nutrient and diluent, and in the preparation of 'humanised milk' from cow's milk. The Pharmacopœia stipulates that it shall not leave more than 0·1 per cent. of ash when incinerated, and that, as well as satisfying limit tests for copper, lead, arsenic and more soluble sugars, 5 g. in distilled water shall not require more than 0·5 ml. of decinormal sodium hydrate solution for neutralisation, using phenolphthalein as indicator.

Citric Acid is present up to 0·3 per cent.

Mineral Matter.—The mineral matter varies from 0·70 to 0·85 per cent., the average being 0·75 per cent. Its composition is:

Potash as K_2O	26 per cent.	(18-29)
Soda as Na_2O	9 ,, ,,	(3-11)
Lime as CaO	22 ,, ,,	(20-28)
Magnesia as MgO	3 ,, ,,	(2-5)
Phosphoric acid as P_2O_5 ..	26 ,, ,,	(22-29)
Chlorine as Cl	14 ,, ,,	(12-16)
Sulphuric acid as SO_3 ..	3 ,, ,,	(2-4)
Carbon dioxide	trace	
Iron	trace	
	103	
Less oxygen equivalent to chlorine	3	
	100	

In milk, iron is about 2 parts per million, colustrum containing about double; copper about $\frac{1}{4}$ part per million; zinc about 3 parts per million; iodine about 24-30 μ g. per litre.

Vitamins.—Milk contains practically all the known vitamins, but except for vitamin A is a poor source. Vitamin C is the one most affected by heat. Pasteurisation is detrimental to it, but flash methods less so than holder processes. Sterilisation causes rapid destruction. Vitamin A is hardly affected by pasteurisation and vitamin D is heat-resistant.

The amount of reserve vitamin A stored in the tissues of a grass-fed animal is usually much higher than that stored in the tissues of a stall-fed animal.

Milk Enzymes.—Milk contains peroxidase, catalase, reductase and some hydrolytic enzymes—*e.g.*, lipase (fat splitting), phosphatase (hydrolysing phosphoric esters), galactase (a protease), lactase and amylase (hydrolysing carbohydrates).

Peroxidase is capable of liberating active oxygen from hydrogen peroxide and organic peroxides, and is concerned with oxidative effects in metabolism. *Catalase* can break down hydrogen peroxide into