CXVIII. THE RELATION OF SODIUM TO CHLORINE IN THE MILK OF SHORTHORN AND GUERNSEY COWS.

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The determination of the distribution of the cations in milk has, until recent years, been rendered difficult by the lack of a rapid and convenient method for the determination of sodium. The description by Barber and Kolthoff [1928] of an accurate gravimetric method by which micro-quantities can be determined by a macro-technique was followed by the description of a colorimetric method by McCance and Shipp [1931]. Earlier methods for the determination of sodium in milk have been described by Blanchetière [1923] and Barthe and Dufilho [1926; 1928, 1]. The method for the determination of sodium described in this paper consists of the application of the gravimetric method of Barber and Kolthoff to milk. Owing to the uncertainty of the temperature at which sodium is volatilised as chloride and the prolonged time necessary for complete ashing at the maximum allowable temperature, it was decided to adopt the method of wet ashing with nitric acid.

Few values for the sodium content of cow's milk have appeared in the literature and these are usually given as mean values together with the ranges in which they occur. Little attempt has been made to correlate the sodium and chloride values except to state that the chloride in milk is more than equivalent to the sodium and that the excess is probably combined with calcium. Indeed it has been stated [Barthe and Dufilho, 1927] that the sodium content of the milk of healthy cows is never greater than 50 mg. per 100 ml. and that the Na : Cl ratio is never higher than 0·339. The idea however is presented that the sodium content of cow's milk increases as the period of lactation advances [Barthe and Dufilho, 1928, 2].

The milk of 20 cows of the Shorthorn and Guernsey breeds has been examined in an attempt to correlate the sodium and chloride contents of their milk and their stages of lactation. The results of duplicate, and in some cases triplicate, determinations are given in Table I together with the length of time during which the cows had been in lactation. The values for sodium and chloride have ranged from 39·2 to 139·2 and 70 to 193 mg. per 100 ml. respectively, with mean values of 76·8 and 113·4 mg. per 100 ml. respectively. The calculation of the correlation coefficient for the collected data has resulted in the high value of 0·91 and the straight line representing this correlation, calculated by the method of least squares, is represented by the equation

$$Cl = 1{\cdot}24\ Na + 18{\cdot}09$$

where Cl and Na are expressed in mg. per 100 ml. This is the straight line drawn in the graph (Fig. 1). This correlation is given independently of the breed of the cow, no significant difference having been found between the milks of the two breeds investigated.

When expressed in milli-equivalents, the relation takes the form

$$Cl = 0{\cdot}805\ Na + 0{\cdot}51$$

from which it is evident that chloride is always in excess. This holds for values of Cl from 70 to 193 mg. per 100 ml., the higher value being well into the region of abnormality preceding "drying off". It is not certain that the equation

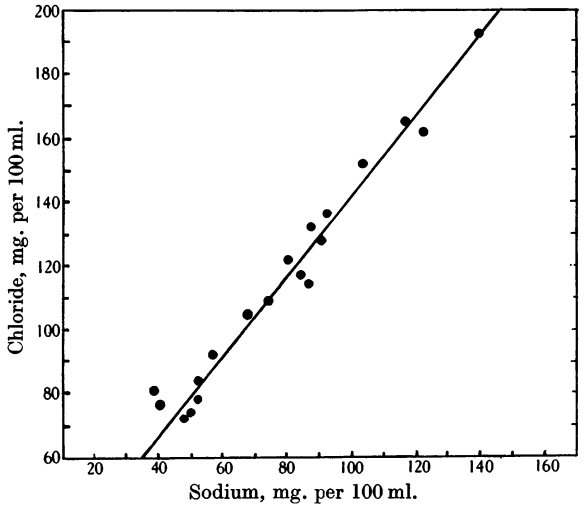

Fig. 1. Relation of sodium to chloride. $Cl = 1{\cdot}24\,Na + 18{\cdot}09$; $r = 0{\cdot}91$.

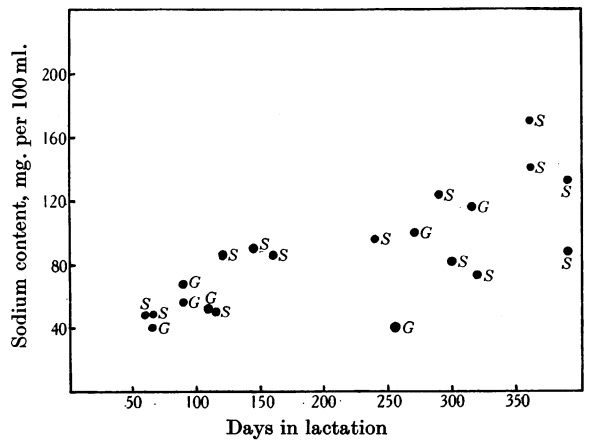

Fig. 2. Sodium content and duration of lactation.

holds for values of chloride below 70 mg. per 100 ml. (or sodium below 39·2 mg. per 100 ml.) since samples of cow's milk of lower chloride content are rarely encountered. The Na : Cl ratio is evidently not a fixed quantity for milk, but is a function of the value of either element, so the statement of Barthe and Dufilho [1927] is incorrect. Indeed, in no cases were values as low as 0·339 found for this ratio in the milk of the cows of our herd, which is to be regarded as typical of English herds of their breeds. The value given for the mean of the

chloride contents of the milks examined is somewhat higher than the value found for over a thousand samples [Davies, 1935] which was 100 mg. per 100 ml. The latter corresponds to a sodium value of 66·0 mg. per 100 ml. which can be regarded as the mean sodium content for cow's milk.

As is well known, the chloride content of milk increases with advance in the period of lactation. Consequently, the value for the sodium content of milk must increase. Fig. 2 shows the scatter diagram for sodium against the period of lactation in days. Again it is evident that there is no significant difference between Shorthorn and Guernsey types. There appears to be a general upward trend but the number of determinations is not large enough for statistical treatment.

Methods.

The milk samples used were taken from individual cows either at the a.m. or p.m. milking and represent the whole of the milk at that particular milking (fore milk being rejected).

Chloride was determined by the method of Davies [1932]. Sodium was determined by the triple acetate gravimetric method as follows:

Reagents. (1) Concentrated nitric acid (sp. gr. 1·4).

(2) Alcoholic zinc acetate with zinc hydroxide. This is prepared from sodium-free zinc sulphate according to the method of McCance and Shipp [1931].

(3) Zinc uranyl acetate solution: (*a*) 10 g. of uranyl acetate (A.R.) are dissolved in 50 ml. of boiling water containing 2 ml. of glacial acetic acid; (*b*) 30 g. of zinc acetate are dissolved in 50 ml. of boiling water containing 1 ml. of glacial acetic acid. (*a*) and (*b*) are mixed while boiling, re-boiled for a few minutes, cooled, allowed to stand overnight and filtered. This solution is always kept saturated at working temperature with sodium zinc uranyl acetate, prepared by mixing some of the reagent with an alcoholic solution of sodium chloride, and filtered before use.

(4) 95 % alcohol saturated with the triple acetate. The alcohol is kept in contact with the triple acetate at working temperature and filtered before use.

Procedure. 25 ml. (or if the milk is known to contain less than 80 mg. Na per 100 ml., 50 ml.) of milk are measured into a 150 ml. silica flask, 10 ml. of concentrated nitric acid are added, and the mixture is heated on a sand-bath. When the solution has been almost reduced to dryness the mass chars and the carbon ignites and burns in the nitric fumes. By the cautious addition of nitric acid it is possible to obtain a white ash in a few minutes. This ash is dissolved in a small amount of dilute nitric acid and transferred with the aid of 10 ml. of water to a 25 ml. graduated flask. For removal of phosphate 15 ml. of the zinc acetate-zinc hydroxide reagent are added, mixed with the solution and allowed to stand 24 hours. The solution is made up to the mark and filtered. 2 ml. portions of the filtrate are measured into 10 ml. of the zinc uranyl acetate reagent contained in a 10 G 4 Jena filter of 15 ml. capacity which is stoppered at the bottom in the manner described by Peters and Van Slyke [1932]. After vigorous stirring by means of a short, thin rod, the latter is washed down by two successive portions of 1 ml. of the reagent and the filter is covered and set aside for 1 hour. After removal of the stopper, the fluid contents are sucked through by means of the pump and the precipitate is washed five times with 2 ml. portions of alcohol saturated with the triple acetate and twice with 5 ml. portions of ether. The outside of the filter is then wiped dry, the filter is placed in a desiccator for 1 hour and weighed, an ordinary analytical balance being

sufficiently accurate. The precipitate weighs 66·9 times its content of sodium, so that using 25 ml. of milk, and 2 ml. of filtrate, the mg. Na per 100 ml. milk are

$$\frac{100 \times \text{mass of precipitate (mg.)}}{2 \times 66{\cdot}9}.$$

The agreement between triplicates is usually well within 1 % and often identical values are obtained.

Excess of potassium interferes with the determination, but this element does not occur in milk to such an extent that special precautions have to be taken as is the case with certain urines, feeding stuffs *etc.*

Table I.

Cow No.	Guernsey (G) or Shorthorn (S)	Days in milk	Milk Cl mg./100 ml.	Milk Na mg./100 ml.
1	G	255	81	39·2
2	G	88	92	56·3
3	G	87	105	68·0
4	S	118	117	86·0
5	S	239	140	97·2
6	G	314	165	116·5
7	S	351	193	139·2
8	S	324	109	73·7
9	S	297	122	82·2
10	S	64	70	48·8
11	S	145	128	90·7
12	S	160	116	85·8
13	S	288	162	121·6
14	G	66	77	39·9
15	S	387	132	87·4
16	G	268	152	100·8
17	G	109	84	52·1
18	S	116	74	50·0
19	G	108	78	52·1
20	S	64	70	48·2

SUMMARY.

1. A detailed account of the determination of sodium in cow's milk is given.
2. In the milk of 20 cows the average values of Cl and Na were 113·4 and 76·8 mg. per 100 ml. respectively.
3. The relation between chloride and sodium in milk of Shorthorn and Guernsey cows is given by the equation

$$Cl = 1{\cdot}24\ Na + 18{\cdot}09$$

where Cl and Na are expressed in mg. per 100 ml.

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