THE ELECTRICAL CONDUCTIVITY OF MILK.

By J. H. COSTE, F.I.C., AND E. T. SHELBOURN, F.I.C.

(Read at the Meeting, April 2, 1919.)

THE proportion of ash yielded on the incineration of milk is recognised as being fairly constant at rather over than under 0·7 per cent. It therefore appeared probable that the electrical conductivity of milk should yield a fairly exact indication of the amount of dilution with water. Our experiments show that this is the case when a known milk is diluted (*cf.* Fig. 2.), but the examination of upwards of 200 samples of milk which, on the Board of Agriculture standard of 8·5 per cent. of solids-not-fat, appeared to be unwatered, has convinced us that, although the majority of samples fell within fairly close limits of specific conductivity— $K_{15} = 0\cdot0040 - 0\cdot0042$ —the value is not sufficiently well defined to make the determination generally useful for detecting adulteration. It would, however, be useful in a large dairy or institution as a check on watering of milk which had already been examined by the conductivity method, and which had afterwards passed through various hands. Before arriving at these conclusions we investigated the effect of certain factors on the electrical conductivity. We find that—

1. The temperature co-efficient of electrical conductivity in the region of 15° C. is 0·000093, or about 2·3 per cent. of the total conductivity. This agrees fairly with the normal value of 0·026 K for neutral salts.

The electrical conductivity of presumed genuine milks may vary from $K_{15} = 0.0035$ to 0.0047 , but in more than 50 per cent. of the samples it was between 0.0040 and 0.0042 .

3. The electrical conductivity of milks increases, up to a certain point, with the development of acidity, but, owing to the lessened dissociation of the acids formed as their concentration increases, it reaches an almost constant value, whilst the amount of acid is still increasing.

4. There is no correlation between electrical conductivity and total solids.

5. There is no well-defined correlation between electrical conductivity and total "ash."

6. There is a marked correlation between electrical conductivity and chlorine (Cl) content of milk.

7. The specific conductivity of a mixture of milk and water decreases with dilution, but the specific conductivity of the milk in the solution increases greatly as the dilution becomes greater, owing, it may be presumed, to dissociation of phosphates and citrates.

Some of these conclusions seemed to us rather difficult of explanation, but we have found that an investigation on "Milk: its Sugar, Conductivity, and Depression of Freezing Point," by Lillias C. Jackson and A. C. H. Rothera (*Biochem. J.*, 1914, **8**, 1), in which they examined the milk of a great variety of mammals, throws the desired light on the question.

Jackson and Rothera point out that many workers have determined the depression of the freezing point of milk below that of water, and have concurred in the value $\Delta = 0.56^\circ - 0.57^\circ$. They also quote Dreser and Winter, who showed that this value was nearly the same as that found for blood, $\Delta = 0.58^\circ - 0.59^\circ$. This figure is a measure of the osmotic pressure, and is, of course, well known as a convenient, although not very sensitive, means of determining it. The osmotic pressure of milk is due to the milk-sugar and salts which it contains. The fat has no effect, and that of the proteins, if any, is too small for detection by a cryoscopic method. As the osmotic pressure of milk is almost constant, it follows that any variation in the proportion of lactose will be accompanied by such a variation in the salts as will maintain the proper osmotic pressure. That is, an increase in the amount of lactose will lead to a decrease, not necessarily in the amount of salts, but in the total number of their molecules and ions which will be found dissolved in the milk. The osmotic pressure of average milk appears to be made up as follows:

TABLE I.

Constituent.	Percentage.	Osmotic Pressure.	Δ .
Lactose	4.7	3.03	0.25°
Alkali {Cl ions	0.1	1.33	0.11°
Chlorides {Na or K ions}			
Other salts and ions	—	2.42	0.20°
Total	—	6.78 atmos.	0.56°

It will be seen that alkali chlorides, from their relatively low molecular weights and highly dissociated state in only fairly dilute solutions, contribute very largely to the total osmotic pressure. For the same reason they also contribute very largely to the electrical conductivity—from, say, 50 to 80 per cent. of the whole value of K being due to chlorides (reckoned as sodium chloride). As the electrical conductivity of a solution is due to the dissociated solutes—that is, the free ions—it is evident that any variation of the lactose content of milk, accompanied, as it will be, by a compensating variation of the salt content, will cause a variation of the opposite sign in the specific conductivity. So that, although watered milks will show low conductivities, so also will very rich ones. A high conductivity with high lactose content will indicate some abnormality, either pathological or caused by addition of salts. Proteins also have a marked effect on conductivity. Every 1 per cent. protein lowers it 2.76 per cent. According to Jackson and Rothera it is not difficult to increase the conductivity by artificially causing functional disturbances of the

FIG. 1.

mammary gland, but it is unusual for such disturbance to alter Δ . Hence the lactose content is low in such pathological fluids. A low conductivity with low lactose content indicates a hydropathic condition set up in the milk after leaving the udder; it is only compatible with dilution.

EXPERIMENTAL.—Most of our determinations of conductivity were made with a metre bridge with a platinum wire of about 12 ohms resistance (0.1 mm. diameter), using 100 ohms comparison resistance and obtaining the current from the secondary of a small medical coil. The telephone was of the “watch” form, having a resistance of about 40 ohms. Later we used a Kohlrausch universal bridge with a high-frequency coil and 100 ohm resistance. The wire was of platinum iridium. The method of making the determination is described in most books on practical physical chemistry. The electrodes were of the pattern shown in Fig. 1. The cork was paraffined, and the space above it filled in with sealing-wax to make the arrangement rigid. The platinised platinum electrodes were 19 mm. $\times$ 3 mm., and 4 mm. apart. The constant of the system—about 0.35—allowed the reading to come fairly near the middle of the bridge wire. The determination was made at the temperature of the milk and corrected to 15°.

1. *The Temperature Coefficient*, as already stated, was found to be approximately 0.000093 or $0.024K_{15}$, the value which might be expected of a dilute saline solution.

2. *The Electrical Conductivity of presumed Genuine Milks.*—Two hundred and three in all were examined, of which nine were from individual Jersey and Short-horn cows belonging to our colleague, Dr. F. N. K. Menzies, who kindly supervised

the collection of these samples, and the remainder were obtained commercially from retailers in various districts of London. The following table shows the percentage numerical incidence of the values found within each ten units in the fifth place of decimals, the observed third and fourth places being shown (*e.g.*, 40 includes $K = 0.00400-409$).

TABLE II.

$K_{15} \times 10^4$	...	...	...	35	36	37	38	39	40	41	42	43	44	45	46	47
Percentage number of samples	...	...	...	1.5	0.5	3.4	4.4	10.3	26.6	26.1	16.3	5.9	3.4	0	0	1.0
Solids-not-fat ...	...	...	...	9.3-10	9.9	8.5-9.7	8.5-9.7	8.5-9.5	8.5-9.8	8.5-9.5	8.5-9.7	8.6-9.6	8.5-9.0	—	—	8.7-8.8

3. *The Influence of Free Acid* was first noted in a milk which on examination gave $K_{15} = 0.00521$. The acidity was found to be $56.2^\circ = 0.056$ N. This was kept for a week, during which the acidity went up to $87^\circ = 0.087$ N, reaching this point in six days. The conductivity was stationary at 0.00572 in two days. Formalin had been added to this sample. Another untreated "nursery" milk had an acidity of 20° about twenty-four hours after delivery, which went up to 80° in four days, and in eleven days reached 93° . The conductivity, originally 0.00411, went up to 0.00530 in four days, and did not materially increase in eleven days.

The grouping around the position of greatest density—*i.e.*, between $K \times 10^4 = 400$ and $= 420$ —is normal.

4. *The Relation between Non-Fatty-Solids and Conductivity* follows no law. The range of solids-not-fat for the above conductivities is shown in Table II. One hundred and twenty-four samples containing solids-not-fat 8.5 to 8.9 inclusive had conductivities from 0.0037 to 0.0047, and seventy-nine containing solids-not-fat 9.0 to 10.0 had an exactly similar range, the position of greatest density in each series being approximately the same—0.0040-42.

The nine samples from individual cows contained from 9.3 to 10.0 per cent. solids-not-fat. Average 9.6. The conductivity varied from $K_{15} = 0.00350$ to 0.00388—all very low, illustrating Jackson and Rothera's generalisation.

5. *Relation between "Ash" and Conductivity.*—The percentage of ash in 195 samples varied from 0.62 to 0.85, the mean being 0.72. This was also the position of greatest density.

TABLE III.

Percentage of ash (below) ...	...	...	0.66	0.66-7	0.68-9	0.70-1	0.72-3	0.74-5	0.76-7	0.78-9	0.80-1	0.82-3	0.84-5
Percentage number of samples ..	...	...	1	4.1	11.8	23.1	25.2	15.4	13.3	3.6	1.5	0.5	0.5
$K_{15} \times 10^4$...	...	...	39	37-42	37-44	37-44	37-43	35-47	35-42	42	40-44	35-38	38

The ash in the milks of individual cows varied from 0.73 to 0.85 per cent., the average being 0.79, and the median 0.80 per cent.

In each of the more frequent ranges of ash the greatest density was around $K = 0.0040$. "Ash" is, of course, a rather unmeaning figure in such a case as milk, and has not any necessary exact relation to the salts actually dissolved in the milk.

6. *Relation between Cl Ions and Conductivity.*—The concentration of Cl ions in milk is about 0.03 N = 0.1 per cent. Cl'. Between this concentration and infinite dilution the molecular (or specific) conductivity of alkali chlorides increases only about 11 per cent., so that the specific conductivity of their solutions will be fairly

proportional to the concentration. We have determined the chlorine in sixty-nine milks by the following process: 1 c.c. of milk is added to 0.028 gm. of pure lime (obtained by evaporating and igniting to decomposition 0.5 c.c. of a solution formed by dissolving 100 grms. of calcium carbonate in nitric acid and diluting to a litre). It is then rapidly evaporated and gently ignited. The cooled ash is then extracted with water, a drop of phenolphthalein solution added, and then sufficient sodium-bicarbonate to render the solution colourless; a suitable volume of potassium chromate solution (to make the liquid contain at least 0.1 per cent. potassium chromate), is added and the chlorine determined by Mohr's method. A small correction dependent on the volume (v) of liquid at the end of the titration should be made. Hazen's value $0.003 v + 0.02$ c.c. is applicable if 1 c.c. silver nitrate = 0.0005 gm. Cl. It is subtracted from the volume of silver nitrate solution used, which is about 2 c.c. This method gives appreciably higher results (0.00 to 0.002 per cent. on a total of about 0.1 per cent.) than titration of the carefully determined ash. It is very rapid. We had hoped that a mixture of milk and calcium nitrate could be ignited, but found that chlorine was lost.

The chlorine in sixty-nine presumably unwatered milks varied from 0.068 per cent. to 0.143 per cent.—i.e., from 0.019 N to 0.04 N. On calculating the specific conductivity for solutions of sodium chloride of the same strength, we found that more than half of the conductivity of milk was attributable to chlorides. There was a strong correlation between the proportion of Cl ions and the conductivity of the milks (see Table IV.).

TABLE IV.

Number of Milks.	Percentage of Cl'.	Specific Conducting K_{15} .		Mean Conductivity due to NaCl.	Mean Percentage of Conductivity due to NaCl.
		Range.	Mean.		
1.	0.06-0.69	0.00350	0.00350	.00172	49
2.	0.07	0.0035-38	0.00372	.00193	52
17.	0.08	0.0035-41	0.00388	.00220	57
27.	0.09	0.0037-41	0.00399	.00245	61
18.	0.10	0.0039-43	0.00410	.00271	66
3.	0.11	0.0038-42	0.00403	.00296	73
0.	0.12	—	—	—	—
0.	0.13	—	—	—	—
1.	0.14	0.00477	0.00477	.00375	78

The chlorine in the samples from individual cows varied from 0.068 to 0.113, the average being 0.086 and the median 0.088.

7. *The Effect of Dilution.*—When milk is diluted with water the specific conductivity decreases, but at a less rate than would be attributable to mere dilution without dissociation. A series of dilutions of a milk ($K_{15} = 0.00409$) with London tap-water

of such strength that each contained 0.9 of the milk in the preceding one was examined (Table V. and Fig. 2).

FIG. 2.

A further series, diluted with distilled water, to contain $\frac{1}{2}, \frac{1}{4}, \frac{1}{8} \dots \frac{1}{128}$ milk, was also examined. In the latter series the specific conductivity of the milk itself more than doubled, owing to dissociation of phosphates and citrates.

TABLE V.

Milk per cent.	...	100	90	81	72.9	65.6	59.0	53.1	47.8
$10^5 K_{15}$	...	409	379	351	333	310	288	268	235

164 MASTERS: NOTE ON SOLUBLE LEAD IN THE GLAZE OF CASSEROLES

TABLE VI.

Milk	...	...	...	$\frac{1}{1}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
$10^5 K_{16}$	...	...	...	406	244	137	74	42	23	13	8
$10^5 K_{16}$ of milk in liquid	...			406	488	548	584	661	704	781	909

The conductivity falls off linearly to about 40 per cent., but in each series 50 per cent. dilution would correspond to about 60 per cent. of the original conductivity. The determination of conductivity would be useful to a milk distributor in checking the operations of a staff, but not, by itself, to the analyst dealing with milk of unknown origin.