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of
Committee on Thesis

The undersigned, acting as a Committee of
the Graduate School, have read the accompanying
thesis submitted by Hugo Ringstrom
for the degree of Master of Science.

They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of Master of Science.

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REPORT
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COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given Hugo Ringstrom final oral examination for the degree of Master of Science..... We recommend that the degree of Master of Science..... be conferred upon the candidate.

Minneapolis, Minnesota

May 30 1917

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A PROXIMATE AND COMPLETE MINERAL
ANALYSIS OF DIFFERENT MARKET
BRANDS OF DESICCATED MILK

A THESIS

Submitted to the
Faculty of the Graduate School
of the
University of Minnesota

by

HUGO RINGSTROM

In partial fulfillment of the requirements
for the degree
of
MASTER OF SCIENCE

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OBJECT. The present investigation was undertaken with the purpose of comparing the proximate and mineral analysis of desiccated with ordinary milk and to determine whether any foreign substances were added before or during desiccation.

HISTORICAL. Desiccated milk has been of technical interest for many years and has lately become quite an item in the commercial world. As early as 1883 two brothers by the name of Beins¹ in Marne (Groningen) succeeded in converting milk to powder form. In 1887 John Carnick² obtained a patent for desiccating skimmed milk, but his method included the addition of foreign substances to the milk.

The first analysis of a desiccated milk was reported in 1890³. The same constituents were determined then that are determined today in a proximate analysis of desiccated milk and the percentage of each constituent found was the same as that found today, so the milk must have been reduced to a powder on a large scale without the addition of foreign substances as early as 1890. But little attention was given to desiccated milks and the method of producing them until about fifteen years ago. Beginning with the year 1906 the reports on investigations and analyses are numerous which in itself is a proof of increased production and utilization. The amount of desiccated milk produced annually at the present time is very large and the demand for milk in the dry form is increasing enormously with the increase in military activities. At the present time, desiccated milk is used chiefly by bakers, ice-cream makers,

1. Vierteljahresbericht und der Fortschritt an der Gebiet der Chemie der Nahrungs - und Gennsmittel, 1890, 5, 14.
2. Chem. Zentr., 1888, 131.
3. Milchindust., 1889-90, V Na 4, 419; Chem. Zentr., 1890, II, 72.

and in the army and navy. Merrell¹ says that in the future it may be as common to handle milk powder as wheat flour, and implies that it is only a question of a few years before the groceryman will supply all the milk needed in the household in dry form and the daily delivery of pasteurized milk will be a thing of the past, especially among people of moderate means living in large cities.

METHOD OF DESICCATION. There are but two general methods used in making desiccated milk. One is drying the milk on steam heated drums, and the other is spraying the milk into a chamber through which a current of hot air is passing. All drum processes of drying the milk are really modifications of the Just-Hatmaker² process, in which the milk is spread in thin films onto drums by a distributing pipe. The drums heated by steam under pressure are set 1-2 mm. apart and rotate towards each other. A paper-like film of milk residue results, which is removed by cutting edges and collected below the drums. In the Ekenberg-Passburg³ process the drums kept at 110-120° C. rotate in a vacuum. In many modifications of the Just-Hatmaker process, the milk is condensed in pans sometimes in vacuum pans one fourth to one fifth of its original volume and then spread onto the drums.

In the spraying process, the milk is pumped through a nozzle and delivered in a fine spray into a chamber through which a current of heated air is passing. A fine powder results which is more soluble than the product from the Just-Hatmaker process. The air is passed into the chamber at 80-200° F. depending on the process used. Generally the milk is first condensed and then sprayed into the chamber. In the Merrell-Soule⁴ process, which is used quite

1. J. Ind. Eng. Chem., 1909, Vol.1, p. 540.

2. J.A. Just. U.S. pat. 712,545 Nov. 4, 1902; J. Soc. Chem. Ind., 21, 1902, p. 1548. And Hatmaker Eng. Pat. 21,617; J. Soc. Chem. Ind., 22, 1903, p. 1145.

3. M. Ekenberg U.S. pat. 764,995 July 12, 1904; J. Soc. Chem. Ind., 23, 1904, p. 797; and E. Passburg U.S. Pat. 1,049,141. Dec. 31, 1912 Chem. Abs., 1913, 7, 668

4. J.S. Merrell U. S. Pat. 985,747 Feb. 28, 1911; J. Soc. Chem. Ind., 30, 407.

extensively, the milk is condensed before spraying and the air is passed into the chamber at 150-200° F. The resulting powder is soluble in cold water and emulsifies well despite the high temperature used.

On the method used in producing the desiccated milk depends largely the extent to which the proteins are coagulated. Orla Jensen¹ states that 88% of the albumin is coagulated in the desiccated milk when it is made by Hatmaker's process, and 55% when it is made by Ekenberg's² process. To increase the emulsifying power of the casein different substances may be added. The use of trisodium citrate³, calcium oxide in a calcium chloride solution⁴, sodium calcium citrate⁴, calcium citrate or phosphate⁵ has been indicated by patent. But the addition of .1-.3% sodium bicarbonate⁴ or 2% sucrose⁵ is more common. It is difficult to tell which one of these is used the more, if used at all, for conflicting statements are made in technical literature⁶.

For household use, desiccated milk must have a pleasant smell and must taste like normal milk. Any unpleasant smell or taste would indicate chemical or bacteriological changes. A milk-like emulsion must result without any settling of protein or separation of fat when the powder is mixed with water. Furthermore, it must keep well without any extraordinary precautions being taken to prevent deterioration. Fr. Krull⁷ finds that desiccated milk is commendable as a food even for infants while F. Husppe⁸ recommends it for cooking and baking purposes only.

PROXIMATE ANALYSIS. The composition of the different desiccated skim-

1. Molkerei-Zgt., 1905, 15, 565-6.
2. Reference 3 page II.
3. Chemische Fabrik "Rhenia". D.R.P. 123,622, 1898; Zeit, Unter, Nahr, Genuss., 1902, 5, 178.
4. Reference 2, page II.
5. Reference 3, page II.
6. Fr. Krull: Milch-Ztg., 35, 25-28; And Ballner and Stockert, Zeit, Unter. Nahr. Genuss., 11, 22, 648-51.
7. Milchwirt. Centrall, a, 165-75; Chem. Zentr., 1906, 1, 1708.
8. Zentr. Bakt. I Abt. Orig., 1912, 64, 34-44; Zeit. Unter. Nahr. Genuss., 1913, 25, 63.

4.

milks is surprisingly uniform with the exception of the moisture content, which varies from two to nine per cent or even more. About one-half of the weight of skim-milk powders is made up of lactose and its limits of variation are very narrow - 49-53%. The protein content is more variable. In extreme cases it is as low as 30% and as high as 38% though it usually runs about 33%. The ash content is fairly constant as it is in normal milk and runs between 7 and 8%.

Table I. COMPOSITION OF SKIM-MILK POWDERS.

	Milchindust ¹	Max.Popp ²	"Gallak" ³	Teichert ⁴
Water	4.17%	4.54%	8.96%	8.54%
Fat	1.65	1.25	.57	1.31
Protein	35.56	35.01	30.59	32.71
Lactose	52.37	51.22	48.62	50.24
Ash	7.51	7.98	8.10	7.20

	Fleming ⁵	Teichert ⁶	Goy ⁷	Mohan ⁸
Water	2.53%	7.40%	2.81%	8.3%
Fat	1.81	1.56	2.10	1.7
Protein	38.16	32.50	33.51	33.8
Lactose	49.32	52.57	53.43	49.3
Ash	8.21	6.27	8.04	6.9

1. Milchindust, 1889-90, V Na. 4 419; Chem. Zentr., 1890, II, 72.

2. Chem. Ztg., 33, 647 - 8, 15/6.

3. XVIII Jahresbericht der Unter.-anstalt des Allgem. Oester. Apothiker Vereins, 1905/6, 8; Zeit. Unter. Nahr. Genuss., 1907, 13, 285.

4. Jahr. Milch. Unter. Allgan zu Memmingen, 1911, 11; Zeit. Unter. Nahr. Genuss., 1910, 20 476.

5. Jour. Ind. Chem. Eng., 1912, 4, 543-4.

6. Allgauer Monatschr. Milchwirtsch Viehz., 1913, 1, 31; Zeit. Unter. Nahr. Genuss., 1913, 26, 461.

7. Zeit. Unter. Nahr. Genuss., 1913, 25, 445.

8. Jour. Soc. Chem. Ind., 1915, 34, 109-113.

Table II. COMPOSITION OF SKIM-MILK POWDERS.
AS GIVEN IN TABLE I COMPUTED ON
MOISTURE FREE BASIS.

	Milchindust	Max.Popp	"Gallak"	Teichert
Fat	1.72%	1.31%	.62%	1.43%
Protein	37.09	36.77	33.60	35.76
Lactose	54.65	53.66	53.40	54.90
Ash	7.83	8.36	8.89	7.87
	Fleming	Teichert	Goy	Mohan
Fat	1.85%	1.62%	2.16%	1.85%
Protein	39.03	35.07	34.48	36.86
Lactose	50.44	56.44	54.97	53.76
Ash	8.39	6.77	8.27	7.52

The fat content, of course, depends upon the extent to which the fat had been removed from the milk before it was desiccated. The amount present is very small, rarely exceeding two per cent.

A number of analyses have been made from time to time, but the majority have been made within the last ten years. Of the eight analyses given in Table I, all except the first have been reported since 1905.

NORMAL MILK. Cow's milk has been a popular subject for investigation ever since chemistry became a true science and the average composition of normal milk is known to a fraction of a per cent. The investigations made from time to time by different chemists have been numerous and very thorough. Richmond¹, after making a number of analyses of milk from thousands of cows, computes the average sugar protein and ash to be 4.70, 34.1, and .73% respectively. Leach² compiled the data from eight hundred different analyses of milk and found a slightly higher protein and lactose content, but finds .02% less ash. The figures given by Babcock³ as the average composition of normal milk

1. Analyst, 1899, 24, 197.

2. Leach: Food Inspection and Analysis, 1914, p. 127.

3. Leach: Food Inspection and Analysis, 1914, p. 126.

differ in lactose and protein content materially from that given by Leach. He gives lactose as 4.5 and proteins 3.8%.

Table III. AVERAGE COMPOSITION OF COW'S MILK.

	Total solids	Fat	Protein	Sugar	Ash	Solids not fat	Citric acid
Richmond	12.51%	3.71%	3.41%	4.70%	.73%	8.84%	
Leach		3.64	3.55	4.88	.71	9.14	
Babcock	12.70	3.60	3.80	4.50	.70	9.10	0.10
Sherman	14.71	5.26	3.66	4.84	.75	9.25	

But even herd milk may differ very much in composition from the averages given by Richmond, Leach, and Babcock. The average composition of the milk as given by Sherman¹, drawn from a herd of 600 cows over a period of two years, illustrates this well. In the herd were 200 pure bred Jerseys and the remainder were "Jersey grades" normally fed and kept. If we compare the figures given by Sherman with those of Richmond, Leach, and Babcock, we find that the amount of protein lactose and ash is only a little higher, but the ratio between these constituents is the same. It is therefore, in the fat content of the milk that the greatest deviation from the normal occurs.

. MINERAL CONSTITUENTS OF NORMAL MILK

The inorganic constituents of the milk, existing as such, together with the inorganic constituents derived from the burning of the organic substances constitutes the milk ash. It is made up principally of potassium, sodium, calcium, and magnesium, sulfur, and phosphorus, and chlorine. Iron is present in small quantities and traces of silica, carbon dioxide, iodine, and fluorine² occur. All these are not combined in the ash in the same form that they exist

1. J. Am. Chem. Soc., 1903, 25, 132.

2. Truntz: Hoppe-Seyler's Zeitschrift für physiol. Chemie, 1903/4, 40, 264.

in the milk. Sulfur and phosphorus exist partly in organic and partly in inorganic combination, and part of the calcium is combined with the casein in the form of a casein salt.

Schweigger¹, Schwartz², Haidlen³, and Weber⁴ determined the mineral constituents of milk ash using different methods from the ones now in use. Hence, their results cannot be compared with those obtained in later investigations. Marchand⁵ made a number of ash analyses on animal and vegetable substances, and among these was the analysis of milk ash, but he does not state the methods used in the analysis. The amount of potassium and chlorine that he found was very low while the amount of phosphorus and iron was considerably higher than any subsequent analyses have shown. Table IV gives the weight of each constituent in thousand parts of milk and per cent in ash as found by him and others. Recent analyses of milk has been made by Schrodt⁶, Richmond⁷, and Babcock⁸. The figures as given in Table V obtained by the two latter investigators represent average composition of milk ash. The chlorine calcium oxide and magnesium oxide found by each agree very closely. In fact, all the figures given by Schrodt and Babcock agree well. The potassium oxide content of Richmond's milk ash is high while the sodium oxide content is lower. He finds only a trace of sulfuric anhydride while all other investigators except Bunge find sulfuric anhydride present to a considerable extent. The carbonic acid content of milk ash is very low. Sherman⁹ states that it is not present in appreciable amounts. Other mineral constituents beside those given in

1. Beitr. zu Chemie und Physik, 1813, 8, 270-2.

2. Diss. inaug. sistens nova experimenta circa lactis principia constitutiva. Kiel 1813.

3. Liebig's Ann. der Chemie und Pharm., 1843, 45, 263.

4. Pogg. Ann. der Physik und Chemie, 1850, 81, 412.

5. Ann. de Chimie et de Physique, 1866, (4), 2, 320.

6. Die landw. Versuchsstation, Bd. 31, s. 55.

7. Dairy Chemistry, p. 32.

8. Leach: Food Inspection and Analysis, 1914, p. 126 - 128.

9. Organic Analysis, 1912, p. 357.

Table IV. COMPOSITION OF MILK ASH.

	Marchand 1000 parts of milk	Bunge ¹ 1000 parts of milk	% in ash	Fleischmann ² % in ash
Potassium oxide	1.071	1.766	22.14	21.539
Sodium oxide	.636	1.110	13.91	11.817
Calcium oxide	1.864	1.599	20.05	20.383
Magnesium oxide	.299	.210	2.63	3.120
Ferric oxide	.127	.0035	.04	.300
Chlorine	.751	1.697	21.27	12.813
Phosphoric anhydride	2.102	1.974	24.75	29.000
Sulfuric anhydride	.323	---	---	2.378
Carbon dioxide	.277	---	---	.533
Silica	.006	---	---	---
Moisture	---	---	---	.300
Carbon and impurities	---	---	---	.350
Loss	---	---	---	.353
Total ash	7.456	8.360	104.79	102.886
Oxygen corresponding to chlorine	.176	.383	4.79	2.886
Corrected ash	7.28	7.977	100.00	100.000

¹Zeitschr. für Biol., 10, 295 - 335.²Ber. Raden, 1885/6, 64.

. Table V. COMPOSITION OF MILK ASH

	<u>Schrodt</u>	<u>Richmond</u>	<u>Babcock</u>	ash per 100 parts milk
	% in ash	% in ash	% in ash	
Potassium oxide	25.42	28.71	25.02	.175
Sodium oxide	10.94	6.67	10.01	.070
Calcium oxide	21.45	20.27	20.01	.140
Magnesium oxide	2.54	2.80	2.42	.017
Ferric oxide	.11	.40	.13	.001
Sulfuric anhydride	4.11	trace	3.84	.027
Phosphoric anhydride	25.11	29.33	24.29	.170
Chlorine	14.60	14.00	14.28	.100
Carbon dioxide	---	.97	---	---
Total ash	103.28			
Oxygen correspond- ing to chlorine	3.28			
Corrected ash	100.00		100.00	.710

Table V are present in minute quantities.

. EXPERIMENTAL PART

Four different samples of desiccated skimmed milk were purchased on the market or obtained from users of milk powders. Sample I was made by the International Milk Products Company, Detroit, Michigan; Sample II by the Minnesota Dry Milk Company, Anoka, Minnesota; Sample III by the International Milk Company, Plymouth, Michigan; and Sample IV by the California Central Creameries, San Francisco, California.

ODOR AND COLOR. The color of the powders was yellowish white except Sample III which had a brownish tinge and an unpleasant odor. The other three samples had a milk-like odor.

EMULSIFYING PROPERTY. The emulsifying power of the powders was tried with water at room temperature and at 40° C. Approximately two grams of the milk powder was stirred up with a little water to an uniform paste. Water was then added slowly with vigorous stirring until about 20 cc. had been added giving an emulsion of approximately the same consistency and composition as normal skim-milk. Samples I and II emulsified well with water at room temperature giving a milk like emulsion without any settling of protein in four hours. Sample III gave a very poor emulsion, yellowish brown in color. A flocculent precipitate collected on top of the emulsion immediately and a precipitate settled to the bottom in a short time. After four hours the emulsion was stratified, the middle stratum having a serum-like, but turbid appearance. Sample IV gave a fair emulsion from which some protein settled in four hours. With water at 40° C. Samples I, II, and IV gave good emulsions without any settling of protein in four hours. Sample III gave the same kind of an emulsion as with water at room temperature except that stratification proceeded more slowly.

PROXIMATE ANALYSIS

The powders were analyzed for moisture, ash, fat, protein, lactose, and acid content and the acidity recorded as free lactic acid. Moisture was determined on a two gram sample weighed in a glass stoppered vial. The powder was dried in an electrically heated constant temperature oven at 100° C. to constant weight and cooled in a sulfuric acid desiccator. Ash was determined on a two gram sample in a small shallow porcelain dish; incinerated in an electric muffle furnace. The temperature was increased slowly from room temperature to dull redness and kept at this point until the ash was perfectly white. For determining fat the Roesse-Gottlieb¹ method was used, one gram taken for analysis. Protein was determined by Gunning's² modification of Kjeldahl's method and lactose by Soxhlet's³ gravimetric method, the reduced copper sulfate weighed as cuprous oxide. A one gram sample was used in determining protein and a three gram sample in determining lactose. For acidity a three gram sample was dissolved in 50 cc. of distilled water and titrated with one-tenth normal potassium hydroxide using phenolphthalein as an indicator.

1. Roesse: Zeit. Angew. Chemie, 1889, p.100; Gottlieb: Landw. Vers-stats., 1892, 40, 6.
2. Z. anal. Chemie, 1889, 28, 188.
3. J. prakt. Chemie, 21, 266.

Table VI. MOISTURE CONTENT

Sample I				
Analysis	Weight taken	Moisture found	% moisture	Average %
a	1.9218gms.	.1086gms.	5.65	
b	2.1400	.1189	5.55	
c	2.1995	.1231	5.60	
				5.60
Sample II				
a	1.1775gms.	.0561gms.	4.76	
b	1.2025	.0567	4.71	
c	1.0518	.0493	4.68	
				4.68
Sample III				
a	1.9989gms.	.1423gms.	7.11	
b	2.0103	.1423	7.08	
c	1.9744	.1399	7.08	
				7.09
Sample IV				
a	2.0020gms.	.1322gms.	6.60	
b	2.0040	.1332	6.64	
c	2.0029	.1314	6.56	
d	2.0035	.1325	6.61	
				6.60

Table VII. ASH CONTENT

Analysis	Sample I			Average %
	Weight taken	Ash found	% Ash	
a	2 gms.	.1586gms.	7.93	7.89
b	2	.1574	7.87	
c	2	.1576	7.88	
d	2	.1579	7.89	
Sample II				
a	2 gms.	.1595gms.	7.97	7.98
b	2	.1595	7.97	
c	2	.1602	8.01	
d	2	.1598	7.99	
Sample III				
a	2 gms.	.1495gms.	7.47	7.45
b	2	.1488	7.44	
c	2	.1490	7.45	
Sample IV				
a	2 gms.	.1503gms.	7.51	7.49
b	2	.1497	7.48	
c	2	.1501	7.50	
d	2	.1497	7.48	

Table VIII. FAT CONTENT.

Analysis	Sample I			Average %
	Weight taken	Fat found	% fat	
a	1.0790gms.	.0156gms.	1.44	1.42
b	.7283	.0104	1.43	
c	.9783	.0137	1.40	
Sample II				
a	1.2198gms.	.0226gms.	1.85	1.82
b	1.2657	.0227	1.79	
c	.7866	.0142	1.80	
d	.6683	.0125	1.86	
Sample III				
a	1.0947gms.	.0123gms.	1.12	1.01
b	.9679	.0091	.94	
c	1.1192	.0108	.96	
d	.9188	.0095	1.03	
Sample IV				
a	1.0470gms.	.0092gms.	.87	.85
b	1.2115	.0104	.85	
c	1.2498	.0104	.83	

Table IX. PROTEIN CONTENT

Sample I.				
Analysis	Weight taken	Protein found	% Protein	Average %
a	.9193gms.	.3020gms.	32.85	
b	1.5111	.4958	32.81	
c	1.2436	.4093	32.92	
				32.86
Sample II				
a	1.7910gms.	.6056gms.	33.81	
b	1.4081	.4737	33.64	
c	1.0455	.3524	33.72	
				33.72
Sample III				
a	.9763gms.	.3620gms.	37.07	
b	1.0882	.4022	36.96	
c	.8456	.3129	37.00	
				37.01
Sample IV				
a	.9350gms.	.3126gms.	33.43	
b	1.2942	.4327	33.43	
c	1.3470	.4498	33.39	
				33.41

Table X. LACTOSE CONTENT.

Sample I.				
Analysis	Weight taken	Lactose found	% Lactose	Average ¹ / _p
a	2 gms.	.9705gms.	48.52	
b	2	.9695	48.47	
				48.49
Sample II.				
a	2 gms.	.9520gms.	47.60	
b	2	.9550	47.75	
				47.67
Sample III				
a	2 gms.	.8275gms.	41.37	
b	2	.8280	41.40	
				41.38 ¹
Sample IV				
a	2 gms.	.9425gms.	47.12	
b	2	.9430	47.15	
				47.13

1. Note: Two more determinations were run on this sample with similar results.

Table XI. FREE AND APPARENT ACIDITY AS LACTIC ACID.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Weight taken (in grams)	3.9809	3.6780	2.7765	3.4795	3.0320	2.9721	3.5702	4.5520
CC. Potassium hydroxide ¹	7.3	6.9	5.1	6.4	5.1	4.95	7.1	8.9
% Lactic acid	1.57	1.60	1.57	1.57	1.44	1.42	1.70	1.68
Average %	1.58		1.57		1.43		1.69	

1. One cubic centimeter of the alkali contained .00536 grams potassium hydroxide which is equivalent to .00857 grams lactic acid.

Table XII. SUMMARY OF THE PROXIMATE ANALYSIS

	Sample I	Sample II	Sample III	Sample IV
Ash	7.89%	7.98%	7.45%	7.49%
Fat	1.42	1.82	1.01	.85
Protein	32.86	33.72	37.01	33.41
Moisture	5.60	4.71	7.09	6.60
Lactose	48.49	47.67	41.38	47.13
Acidity	<u>1.58</u>	<u>1.57</u>	<u>1.43</u>	<u>1.69</u>
	97.84	97.47	95.35	97.17
Hydration of lactose	<u>2.43</u>	<u>2.38</u>	<u>2.07</u>	<u>2.37</u>
Total	100.27	99.85	97.42	99.54

Table XIII. AVERAGES OF THE PROXIMATE ANALYSIS
ON MOISTURE FREE BASIS.

	Sample I	Sample II	Sample III	Sample IV
Ash	8.36%	8.37%	8.02%	8.02%
Fat	1.50	1.91	1.08	.91
Protein	34.81	35.38	39.83	35.68
Lactose ¹	53.94	52.52	46.76	53.00
Acidity	<u>1.67</u>	<u>1.64</u>	<u>1.54</u>	<u>1.81</u>
Total	100.28	99.82	97.23	99.42

1. With one molecule of water of crystallization.

The proximate analysis of the powders compares favorably with the analyses made by others on skim-milk powders with one exception. The lactose found in Sample III was low and repeated analysis gave the same results. The ash content is uniform varying between 8.37 and 8.02% and agrees closely with the average of the analyses. The lactose and protein content on samples I, II, and IV vary little, being close to 35 and 53% respectively. The lactose in Sample III is about seven per cent lower and the protein content about four per cent higher than the average of other analyses.

Table XIV. PROXIMATE ANALYSIS COMPUTED ON MILK CONTAINING.
NINE PER CENT "SOLIDS NOT FAT".

	Sample I	Sample II	Sample III	Sample IV
Ash	.78 %	.79%	.77%	.75%
Fat	.14	.18	.10	.08
Protein	3.25	3.33	3.82	3.35
Lactose	4.80	4.71	4.27	4.74
Acidity	.16	.16	.14	.17

Table XV. ASH, PROTEIN, AND LACTOSE CONTENT COMPARED
WITH THE AMOUNT FOUND IN NORMAL MILK.

Richmond	.73 %	3.41%	4.70%
Leach	.71	3.55	4.88
Babcock	.70	3.80	4.50
Sample I	.78	3.25	4.80
Sample II	.79	3.33	4.71
Sample III	.77	3.82	4.27
Sample IV	.75	3.35	4.74

From Table XV may be observed two peculiarities in the constituents of the desiccated milk, computed on the basis of normal milk having nine per cent "solids not fat". The ash in each sample is a little higher than the ash content of normal milk. The difference ranging from .04 to .08 of one per cent. The protein content is considerably lower than that of ordinary normal milk except on Sample III. The protein content of Samples I, II and IV was 3.25, 3.33, and 3.35 per cent respectively, being from .25 to .35 per cent lower than the average protein content of normal milk. Sample III, however, contained 3.82 per cent protein which is about .22 per cent higher than the average protein content of normal milk. Lactose ran close to the average content of milk except in Sample III in which it was about one half per cent low.

. MINERAL CONSTITUENTS OF THE DESICCATED MILK

Sodium and Potassium. For determining sodium and potassium a three gram sample was weighed into a platinum evaporating dish and burned in an electric muffle furnace. The temperature was raised slowly to dull redness and kept there until only a trace of carbon remained. The ash was taken up with a little water and concentrated hydrochloric and evaporated to dryness. The residue was then taken up with water, a drop or two of concentrated hydrochloric acid added and the solution diluted to about 50 cc. and heated on a boiling water bath. A saturated solution of barium hydroxide was then added slowly to the hot solution until no more precipitate formed. After standing for a time the solution was filtered and the precipitate thoroughly washed with hot water. Lawrence Smith's method was followed from this point.

Table XVI. POTASSIUM OXIDE IN ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Weight of powder	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.
Total chlorides	.1274	.1270	.1388	.1390	.1200	.1197	.1257	.1258
Pot. oxide	.05707	.05676	.06103	.06103	.05017	.05019	.05803	.05797
Per cent	24.11	24.00	25.49	25.49	22.44	22.45	25.82	25.80
Average %	24.05		25.49		22.44		25.81	

Table XVIII. SODIUM OXIDE IN ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Weight of powder	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.
Total chlorides	.1274	.1270	.1388	.1390	.1200	.1197	.1257	.1258
Sodium oxide	.01979	.01974	.0224	.0225	.02154	.02186	.01797	.01807
Per cent	8.32	8.34	9.35	9.40	9.64	9.57	8.00	8.05
Average %	8.33		9.37		9.60		8.02	

The per cent of sodium oxide varied between 8.02 and 9.60 which is lower than any other investigators have found except Richmond. Potassium oxide varied between 22.44 and 25.81 per cent which is close to the figures given by Schrodt and Babcock. Sample III which had the highest sodium oxide content had the lowest per cent of potassium oxide. And Sample IV which had the lowest sodium oxide content had the highest potassium oxide content.

Calcium and Magnesium. Three grams of the powder was burned in the electric muffle furnace. The ash was taken up with water and a little hydrochloric acid and the solution filtered. In determining the calcium and magnesium oxides the method of Francis H. McCrudden¹ was used. This method is adapted for determining calcium in the ash of foods which contains magnesium, phosphates, and small amounts of iron.

The amount of calcium oxide varied more than any other constituent of the ash. The ash of Sample II contained 21.99 per cent while Sample III contained 25.86 per cent. In the ash of the other two samples 23.15 and 23.32 per cent calcium oxide was found. The amount of magnesium oxide was nearly the same in the four samples. The highest per cent found was 3.18 on Sample I and the lowest 2.91 on Sample II which is an unusually close agreement.

1. J. Biol. Chem., 10, 187-99.

Table XVIII. CALCIUM OXIDE IN ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Weight of powder	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.
Calcium oxide	.0559	.0557	.0527	.0526	.0578	.0578	.0524	.0524
Per cent	23.19	23.11	22.01	21.97	25.86	25.86	23.32	23.32
Average %	23.15		21.99		25.86		23.32	

Table XIX. MAGNESIUM OXIDE IN ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Weight of powder	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.	3 gms.
Magnesium oxide	.00753	.00756	.00699	.00699	.00688	.00684	.00688	.00698
Per cent	3.18	3.19	2.91	2.91	3.08	3.06	3.06	3.10
Average %	3.18		2.91		3.07		3.08	

Sulfur and Phosphorus. The sulfur and phosphorus were not determined in the ash. The organic matter in the powders was destroyed with sodium peroxide in a Parr¹ cartridge. The procedure was essentially the same as that described by Leclerc and Dubois². .7 gram of the powder was weighed into the cartridge after one half gram dry powdered potassium chlorate had been added. A charge of sodium peroxide was added; the top put on immediately; and the cartridge shaken for two minutes. Particles adhering to the top and sides were shaken down by tapping the cartridge. It was then immersed in enough water to cover the main part of the cartridge and the charge ignited with a red hot brass wire slug. After the cartridge had cooled it was opened and the fused mass washed into a beaker with hot water. In order to obtain sufficient sulfur three ignitions were made for each determination. The solution was acidified with hydrochloric acid, filtered, brought to boiling and the sulfur precipitated with 10% hot barium chloride. The barium sulfate was then determined by the usual gravimetric method. The filtrate from the barium sulfate precipitate was evaporated almost to dryness and the crystallized sodium chloride dissolved in a little water. 20 cc. of concentrated nitric acid was then added and the solution again evaporated almost to dryness. The phosphoric acid was precipitated by Woy's³ method, and after dissolving the yellow precipitate the last time the solution was made up to 250 cc. 50 cc. were titrated according to Emmerton's⁴ method with one modification, i.e., 10-11 grams of granulated zinc were used instead of fifteen and were dissolved completely. The solution was cooled under the water tap to a moderate temperature and titrated without being filtered. A Bunsen trap was used on the Erlenmeyer flask

1. J. Am. Chem. Soc., 1900, 22, 646; same 1904, 26, 1139.

2. J. Am. Chem. Soc., 1904, 26, 1108.

3. Chem. Zeit., 21, 442.

4. Trans. Am. Ins. Min. Engs., Vol. XV, p. 93.

Table XX. SULFURIC ANHYDRIDE IN THE POWDER CALCULATED ON THE ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Powder taken	2.1 gm.	1.4 gm.	2.2. gm.	1.4 gm.	2.0 gm.	2.1 gm.	1.4 gm.	1.4 gm.
Sulfuric Anhydride	.01886	.01258	.02108	.01372	.0203	.02154	.01279	.01272
Per cent	11.38	11.39	12.34	12.28	13.69	13.76	12.21	12.14
Average %	11.38		12.31		13.73		12.17	

Table XXI. PHOSPHORIC ANHYDRIDE IN POWDER CALCULATED ON THE ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Powder taken	1.4 gm.	1.4 gm.	2.2. gm.	2.1 gm.	2 gm.	1.4 gm.	2.1 gm.	2.1 gm.
Phosphoric Anhydride	.03604	.03618	.05504	.05285	.04874	.03426	.05401	.05378
Per cent	32.63	32.77	31.35	31.54	32.79	32.85	34.34	34.19
Average %	32.70		31.44		32.82		34.26	

to prevent diffusion of the air. To determine the amount of potassium permanganate required to produce a pink coloration a blank determination was made and this correction applied for each determination.

The sulfur content as determined in the powder and computed as sulfuric anhydride on the ash gives results which cannot be compared with the amount found in the ash by other investigators, for most of the sulfur in organic combination in the milk is undoubtedly lost when the solid material is ashed. And most of the sulfur found in the milk is in organic combination. Steinegger and Allemann¹ found 24.3 to 40.6 per cent of the sulfuric anhydride determined in milk ash to occur as sulfates in the milk. Tillman and Sutthoff² made a more thorough study of the sulfur in milk and found it to be present as sulfates to the extent of 1.23 per cent calculated as sulfuric anhydride on the ash. But the sulfur present as sulfates was only 10.4 per cent of the total sulfur present in the milk. Thus, total sulfur calculated as sulfuric anhydride on the ash would give 11.8 per cent.

The sulfuric anhydride varied between 11.38 and 13.63 per cent and is directly proportional to the amount of protein present. On the ash of Sample I which contained 32.86 per cent protein was found 11.38 per cent sulfuric anhydride and on Sample III containing 37.01 per cent protein 13.73 per cent sulfuric anhydride.

The phosphorus is present in the form of phosphates in the milk serum and of organic phosphorus compounds. But only a small part of the phosphorus is combined organically in the milk. Of the phosphoric anhydride found by Bordas and Tomplain³ in a liter of milk 1.279 grams were present in the serum and .219 grams in the coagulate. Therefore, the variations that occur in the

1. Zeit. Unter. Nahr. Genuss., 1906, 11. 456.
2. Zeit. Unter. Nahr. Genuss., 1910, 20. 49-63.
3. Compt. rend., 1911, 152, 899-900.

Table XXII. CHLORINE IN THE POWDER COMPUTED ON THE ASH.

	Sample I		Sample II		Sample III		Sample IV	
	a	b	a	b	a	b	a	b
Weight of powder	3 gm.	3 gm.	3 gm.	3 gm.	3 gm.	3 gm.	3 gm.	3 gm.
Weight of chlorine	.02943	.02956	.03407	.03431	.03129	.03149	.02791	.02771
% chlorine	12.42	12.49	14.23	14.33	14.00	14.09	12.42	12.33
Average %	12.45		14.28		14.04		12.37	

amount of protein effect the phosphoric anhydride very little. And the amount present in the desiccated milk varied but little - between 31.44 and 34.26 per cent. The agreement is much closer than the figures given by Richmond and Babcock for the average per cent in milk ash. But the amount found is about four per cent higher than the average given by Richmond and about nine per cent higher than that given by Babcock.

Chlorine. The determination of chlorine was carried out on the powder and not on the ash. H.E. Davies¹ has shown that chlorine is lost on ignition of organic substances, and that such loss takes place at a temperature below redness. He further shows that the loss of chlorine can be prevented by mixing the dry substance with enough 20% sodium carbonate solution to make the sodium carbonate equal to five per cent of the sample taken. But the method worked out by Paul Peetschke² for chlorine in milk is much shorter and just as accurate as the ignition with sodium carbonate. Three grams of the powder was weighed into a dry 250 cc. graduated flask and mixed well with a little water. The volume was brought up to about 200 cc.; 10 cc. of Fehling's copper sulfate was added then 7 cc. of half normal sodium hydroxide to partly neutralize the copper sulfate. The volume was brought up to the 250 cc. mark and the solution well mixed. The solution was then filtered through a dry ribbed filter, the first few cubic centimeters discarded and 200 cc. titrated by Volhardt's³ method. But before titrating back the excess of silver nitrate, the silver chloride was coagulated by briskly stirring and warming the solution and then filtering. Correction was made for the volume occupied by the protein precipitate and for the chlorine present in the reagents.

Chlorine is present in milk to the extent of 12-14 per cent computed on the ash. Sample IV contained 12.37; Sample II, 14.28; Sample I, 12.42; and

1. J. Soc. Chem. Ind., 1901, 20, p. 98.
2. J. Ind. Eng. Chem., 1910, 2, 210-2.
3. A.O.A.C., Bull. 107, p. 23.

Sample III, 14.99 per cent. The chlorine present in milk is proportioned to the amount of sodium present in the ash. An ash low in sodium oxide is low also in chlorine. Sample I which had 8.33 per cent sodium oxide contained 12.42 per cent chlorine and Sample II containing 9.37 per cent sodium oxide contained 14.28 per cent chlorine. The ratio of sodium oxide to chlorine is nearly the same for the other two samples.

Iron. The quantity of iron found in milk ash is very small - so small that it cannot be determined gravimetrically unless large quantities of milk solids are reduced to ash. Dilute potassium permanganate¹ has been used to titrate the iron, but the quantity of milk required makes the method tedious. Colorimetrically the iron can be determined rapidly and accurately on small quantities of material. Pulsifer² has proposed acetylacetone for determining small amounts of iron and found the method very sensitive. The potassium sulfocyanate method, however, is simpler and gives concordant results. A number of modifications³ of this method have been made, but the principle of each method is the same. Lachs and Friedenthal⁴ have shown that the maximum intensity of color is obtained when the mixed solution contains a concentration of hydrochloric acid in the standard and in the sample.

The method used is as follows: A standard solution of iron containing one tenth of a milligram of iron, equivalent to .143 mg. ferric oxide, was prepared from pure ferrous ammonium sulfate; a solution of hydrochloric and six times normal free from iron and nitric acid; and a strong solution of potassium sulfocyanate. One gram of the powder was ignited in a silica evaporating dish

1. Fendler, Frank und Stüber: Zeit. Unter. Nahr. Genuss., 1910, 19, 369-70.
2. J. Am. Chem. Soc., 26, 967-75.
3. Standard Methods of Water Analysis: Am. Public Health Ass., 1912;
. F. Gothe: Zeit. Unter. Nahr. Genuss., 1914, 27, 576-83;
Lachs und Friedenthal: Biochem. Zeitschr., 1911, 32, 120-6.
4. Given under reference 3, this page.

at dull redness until white. The ash was taken up with strong hydrochloric acid, a drop of concentrated nitric acid added and evaporated to dryness. The residue was taken up with a little water; hydrochloric acid added and again evaporated to dryness. The residue was then washed into a 50 cc Nessler jar with 17 cc of the prepared hydrochloric acid and a little water. 17 cc of the sulfocyanate solution was added and the volume brought up to the 50 cc mark. At the same time a comparison solution was prepared with the standard iron solution by adding small quantities at a time from a pipette graduated to .02 cc until the colors were matched.

Table XXIII. FERRIC OXIDE IN THE ASH.

	Sample I		Sample II	
	a	b	a	b
Weight of powder	1 gm.	1 gm.	1 gm.	1 gm.
Weight of ferric oxide	.0286 mg.	.0271 mg.	.0300 mg.	.0271 mg.
% ferric oxide	.036	.034	.038	.033
Average %	.035		.035	
	Sample III		Sample IV	
	a	b	a	b
Weight of powder	1 gm.	1 gm.	1 gm.	1 gm.
Weight of ferric oxide	.0257 mg.	.0257 mg.	.0357 mg.	.0386 mg.
% ferric oxide	.034	.034	.047	.051
Average %	.034		.049	

The ferric oxide found in the ash was very small compared to the per cent given by Fleischmann and Babcock. The former gives the ferric oxide content of milk ash as .30 and the latter .13 of one per cent. Sample III contained .034; Sample IV, .049; and Samples I and II, .035 per cent ferric oxide. Bunge in his analysis found only .04 per cent ferric oxide in the ash and Fendler, Frank, and Stüber found .0004-.0012 per cent ferric oxide in the milk corresponding to .055 and .16 of one per cent respectively in the ash on the basis of .75 per cent ash in the milk. And the lowest figures are probably

more correct than the higher ones for the milk may easily be contaminated with iron from outside sources.

Table XXIV. SUMMARY OF THE MINERAL CONSTITUENTS
IN THE POWDER.

	Sample I	Sample II	Sample III	Sample IV
Potassium oxide	24.05%	25.49%	22.44%	25.81%
Sodium oxide	8.33	9.37	9.60	8.02
Calcium oxide	23.15	21.99	25.86	23.32
Magnesium oxide	3.18	2.91	3.06	3.08
Ferric oxide	.035	.035	.034	.049
Sulfuric anhydride	11.38	12.30	13.73	12.17
Phosphoric anhydride	32.70	31.44	32.82	34.26
Chlorine	12.42	14.28	14.05	12.37

Table XXV. MINERAL CONSTITUENTS OF THE POWDER
COMPUTED ON MILK HAVING NINE PER CENT
"SOLIDS NOT FAT".

	Sample I	Sample II	Sample III	Sample IV
Potassium oxide.	.1876%	.2014%	.1728%	.1936%
Sodium oxide	.0650	.0740	.0739	.0602
Calcium oxide	.1806	.1737	.1991	.1749
Magnesium oxide	.0248	.0230	.0236	.0231
Ferric oxide	.00027	.00027	.00025	.00036
Sulfuric anhydride	.0888	.0972	.1057	.0813
Phosphoric anhydride	.2551	.2484	.2527	.2569
Chlorine	.0969	.1138	.1082	.0928

.CONCLUSION

The proximate analysis of samples I, II, and IV showed that they were made up of the "solids not fat" in skimmed milk plus a little fat and moisture in the same proportion as found in normal skimmed milk. The protein was somewhat below the normal protein content of milk and the ash somewhat higher. Of Sample III, the protein and lactose content varied considerably from the normal content of these constituents and may have been adulterated.

The mineral constituents in the desiccated milk were found to be normal except the calcium and phosphorus content, which were both high. The high percentage of these constituents may be due to the addition of some calcium salts and phosphates. It is probable that these substances were added to increase the emulsifying property of the powder.