SOME MINERAL CONSTITUENTS OF EVAPORATED MILK

by

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INTRODUCTION

There is surprisingly little information concerning the factors which influence the keeping qualities, texture, grain, and other desirable physical qualities of evaporated milk. Unsweetened evaporated milk is rapidly gaining in popularity as food for infants and children. It is therefore desirable that information be gathered which will lead to the perfection of an evaporated milk of finer quality.

It is commonly known among the companies producing evaporated milk that the addition of salts containing one or more of the elements calcium, phosphorus, and magnesium, in quantities less than one part per one hundred thousand to the whole milk often improves the desirable qualities of their product. However, this does not always materially improve its qualities, and trial-and-error is the only method by which they decide which mineral and how much should be added. This experiment was carried on to determine whether or not the elements calcium, phosphorus, and magnesium must be present in constant amount or in constant ratio to each other in order to procure a product of the finest qualities.

The calcium, phosphorus, and magnesium content of cow's milk are necessarily important from the nutrition standpoint.

Also, the relation of magnesium to calcium has been found to be of importance (1), (2), although it has not been determined whether this relation must be quantitative.

According to Mojonnier and Troy (3), the ash does not accurately represent all of the salts as they appear in the milk. Part of the chlorides and sulphates are probably volatilized during the ignition process. Part of the sulphur and the phosphorus in organic combination is probably oxidized during ashing, thus causing a slight increase in weight. The greatest loss occurs in the citrates. Porcher and Chevallier (2) have made a good analysis of this problem.

Evaporated milk is cow's milk condensed by evaporation in vacuo in the ratio of from two to two and one-half parts of fresh milk to one part of evaporated milk. A bulk of 1000 pounds of cow's milk is usually condensed to about 360 to 385 pounds of evaporated milk. It is canned, hermetically sealed, and sterilized by steam under pressure (4).

In regard to the variability of the composition of cow's milk, Rogers (1) says that even the quarter of the udder or the stage of the milking must be considered. Even so, it might be supposed that the analytical results for herd milk would be fairly consistent. They are, so far as orders of magnitude are concerned, except insofar as it

might be desirable to determine minute amounts of mineral constituents. At times of the year when the ration of the herd is changed rather abruptly, the percentages of the various minerals of milk very naturally change more rapidly than under ordinary conditions. At the season when the herd is released on pasture feeding, with supplementary rations, the greatest difficulty is experienced by manufacturers of canned evaporated milk. Soon after it is canned, it develops a "curdy", a "grainy", or a "ropy" texture.

With milk, as with other foods, custom is a large factor in establishing market demands. There is no question but that our retail milk trade calls for a sweet milk of normal consistency and taste. While ropiness ordinarily produces little change in the taste of milk, it does change its consistency so noticeably as to arouse the suspicions of the consumer.

The agitation of recent years for a milk of low germ content has made the consumer very suspicious of any evidence of germ growth in milk, and doubly so of unusual appearances.

While there is no evidence nor any reason to believe that ropy milk is in any way harmful to the consumer, such milk is not acceptable to the American consuming public, and accordingly is neither profitable nor desirable in the

canned evaporated milk.

Broadly speaking, there are two general methods of determining the mineral content of milk: (a) directly, by analysis of the milk; and (b) indirectly, by analysis of the milk ash. The indirect method provides possibility of accuracy in measuring minute amounts of minerals. It was therefore used for this problem.

REVIEW OF THE LITERATURE

In the examination of the literature there was no data found to be available on the mineral analysis of evaporated milk as correlated with its physical qualities. There was considerable data available on the analysis of whole milk, cream, butter, and various other types of milk products, but none of these were correlated with the appearance or keeping qualities of the evaporated milk.

A few experiments of this nature have been carried on independently by individual milk concerns, but none of the data so obtained has been published. As far as could be learned no definite relation was found to exist for any of the minerals for which analyses were made. Considerable stress has been placed upon the alkali chloride content of milk, but no valuable data has been obtained to prove any

definite ratio of the amounts necessary to obtain milk of good physical properties.

Hunziker (5) early discussed and explained the chief defects of evaporated milk under the following classification: (a) curdy, (b) grainy, (c) separated and churned, (d) blown or fermented, (e) brown, and (f) gritty.

The standardizing of evaporated milk is interestingly presented by Mojonnier and Troy (3).

According to Leach (6), the composition of the ash of a typical whole milk sample is as follows:

K_2O	25.02%
Na_2O	10.01
CaO	20.01
MgO	2.42
FeO	0.13
SO_3	3.84
P_2O_5	24.29
Cl	14.28

According to Mojonnier and Troy (3), the higher specific gravity of cow's milk over that of water is due to the constituents classified as solids-not-fat, the specific gravity of which is about 1.615.

VanSlyke and Bosworth (7) state that, of the constituents of milk, the sugar, citric acid, potassium, sodium, and chlorine are wholly in solution, and that the albumin, inorganic phosphates, casein, calcium, and magnesium are partly in solution and partly in suspension. About 0.7% of

the whole milk is ash (1).

In this research, the individual elements were determined by a refined procedure drawn from the methods proposed by Scott (8) and from methods as outlined by the A. O. A. C. (9). These methods are not especially adapted to quantitative determinations of minute amounts of minerals. No definite temperature for ashing the milk is required by those methods. In this problem, it was found necessary to ash the sample and precipitates within very narrow limits of temperature in order to get results to check. This is exemplified on page 9 of this paper.

EXPERIMENTAL

Apparatus

For this experiment a micro-balance which permits weighing fifty grams to 0.00001 gram, was used. The temperature of the balance room was kept nearly constant, and each weight was very carefully checked and standardized. The swing of the pointer was observed through a small, powerful telescope.

The instrument which was used to control and record the temperature of the muffle furnace used in all the ashing and ignition processes was a Leeds and Northrup potentiometer

pyrometer, which is described and fully discussed on pages 3, 42, and 43 of their catalog No. 87(1930).

The thermocouple used to control temperature was accurately calibrated by observing several temperature readings of a total-immersion mercury thermometer (recently standardized by the U. S. Bureau of Standards), with the mercury bulb placed on the thermocouple connection within the muffle furnace.

Platinum dishes were used for all the ashing and ignition processes. The glassware used consisted of 250-cc. beakers of high-grade pyrex glass.

Materials

Milk. Only unsweetened evaporated milk of proven quality and texture was used. Three brands were selected, on two of which were run four sets of triplicate determinations, and on the other, only two sets. This was a sufficient number to prove the facts as found from the experiment.

Reagents

The hydrochloric acid and the ammonium hydroxide used were of the same high quality as used for all determinations made by the Experiment Station, and were known to be calcium-, phosphorus-, and magnesium-free.

Blank determinations were made on the ammonium oxalate

reagent and the magnesia mixture and they were found to be free from those minerals which were to be determined.

The magnesia mixture referred to was prepared as follows: 11 grams of MgO were dissolved in HCl (1+4), a little MgO added in excess, the solution boiled and filtered, and to the filtrate were added 140 grams of NH_4Cl and 130.5 cc. of NH_4OH. This resulting solution was diluted to one liter.

All the distilled water used was special redistilled water from a copper still, and known to be free from the minerals to be determined.

Throughout the determinations, a filter paper of known ash content must be used for filtering the solutions, and corrections made in the weight of ignited precipitate. In this problem the filter paper used was that of Carl Schleicher & Schull, No. 589, blue ribbon grade.

Procedure

The samples were secured as follows: An accurately weighed platinum dish was used. Into the dish was weighed fifty grams of sample, at room temperature, from a pipette with large tip; the sample having been thoroughly agitated and mixed. Later, in the calculations, corrections were made for the error of the balance weights.

The platinum dishes were reweighed after each deter-

mination. Before weighing the empty dishes, they were carefully warmed to a temperature slightly below boiling in 1+1 HCl, carefully rinsed with distilled water, and ignited to constant weight at the same temperature as the next precipitate was to be ignited.

The sample was heated in an electric oven at 110° C. until it was thoroughly dried and partially charred. It was then placed in a muffle furnace at room temperature and slowly heated to 550° C., at which temperature it was ashed to constant weight.

Considerable caution must be exercised in ashing the sample to prevent swelling and spattering. The same is true of the ignition of all the precipitates to be subsequently ashed.

In the procedure employed to determine the correct temperature at which to ash the milk and its mineral components, it was found that at any temperature below 490° C., the milk or any of the precipitates would apparently never ash to whiteness, while the maximum temperatures for the several ignitions at which reproducible results could be obtained varied. At temperatures above 560° C. the ash of the milk was decomposed in some way such that results obtained would not check. All temperatures of ignition, as given hereafter, are those which were found to be best suited to that

individual ignition process. Results checked to the fifth decimal place, or to 0.001%; which, in most cases, was the fourth significant figure in the final result.

Determinations

(a) Calcium. The ash was dissolved in a slight excess of dilute HCl(1+1), fifty cc. of water added, heated to boiling, filtered and washed thoroughly with hot water. The filtrate was then heated to boiling and twenty cc. of a saturated solution of ammonium oxalate added. This solution was allowed to come almost to boiling and then cooled to room temperature. Ammonium hydroxide was added drop by drop, until precipitation was complete, the solution heated to boiling and tested with a few drops of ammonium oxalate and ammonium hydroxide to insure complete precipitation of calcium oxalate and calcium phosphate. The solution and precipitate was allowed to stand at room temperature overnight, filtered, and the precipitate washed thoroughly with a hot, two percent solution of ammonium hydroxide, saturated with calcium oxalate. The filtrate, which we shall call Solution A, was covered and set aside.

The precipitate was thoroughly dried in the oven at 110° C. and heated slowly in the controlled muffle to 570° C., at which temperature it was ignited to constant weight.

To the resulting ash was added ten cc. of a saturated

solution of ammonium carbonate, again dried at 110°, and then heated to constant weight at 150°, and weighed as $CaCO_3$ + $Ca_3(PO)_4$.

The ash from above was dissolved in a slight excess of 1+1 HCl, heated to boiling, allowed to cool, and made strongly ammoniacal with ammonium hydroxide. This solution was allowed to stand for twenty-four hours at room temperature, the precipitate filtered off and washed with hot water, and dried as above. It was then heated slowly in the muffle furnace to 535° C., at which temperature it was ignited to constant weight and weighed as $Ca_3(PO)_4$. This weight, multiplied by 0.3874492, gives the weight of the calcium contained in it. The weight of the $Ca_3(PO)_4$, subtracted from the previous weight of $CaCO_3$, gives the actual weight of the $CaCO_3$ which, multiplied by 0.4004197, gives the calcium contained in it. The total calcium is the sum of the two results. The weight of the $Ca_3(PO)_4$, multiplied by 0.2000064, gives the weight of the phosphorus contained in it.

(b) Magnesium. The filtrate designated above as Solution A was evaporated slowly to about 100 cc, made strongly ammoniacal, and allowed to stand in a covered beaker for twenty-four hours. The precipitate was then filtered off, washed several times with ammoniacal hot water. The filtrate, combined with the washings is later referred to as

Solution B. The precipitate was dried at 110°, heated very slowly in muffle furnace to 585°, at which temperature it was ignited to constant weight and weighed as $Mg_2P_2O_7$, which, multiplied by 0.2184163, gives the magnesium contained in it. The weight of the $Mg_2P_2O_7$, multiplied by 0.2786514, gives the weight of the phosphorus contained in it.

(c) Phosphorus. Magnesia mixture was slowly added, with constant stirring, to the solution from above, designated as Solution B, until precipitation was complete, the solution then allowed to stand for twenty-four hours. The resulting precipitate was filtered, washed with hot, very dilute ammonium hydroxide, slowly dried at 110°, ignited to constant weight at 600°, and weighed as $Mg_2P_2O_7$, which, multiplied by 0.2786514, gives the phosphorus contained in it. The total phosphorus is the sum of the three results.

RESULTS

The percentages of the elements are given in Table I.

Since this research was carried on in order to gain some definite information concerning the ratios of the various elements to each other and to the ash, it is necessary to calculate all of the possible ratios which exist, in order to determine whether or not any of these elements need

TABLE I

PERCENTAGES OF ELEMENTS

Sample No.	Ash %	Calcium %	Magnesium %	Phosphorus %
A-1(a)	1.63674	0.28971	0.02629	0.21314
A-1(b)	1.63622	0.28924	0.02602	0.21300
A-1(c)	1.63693	0.28934	0.02650	0.21304
B-1(a)	1.56481	0.26341	0.02275	0.20859
B-1(b)	1.56443	0.26321	0.02241	0.20880
B-1(c)	1.56462	0.26325	0.02276	0.20874
C-1(a)	1.59387	0.28186	0.02459	0.20206
C-1(b)	1.59403	0.28166	0.02421	0.20217
C-1(c)	1.59379	0.28164	0.02404	0.20210
A-2(a)	1.60477	0.26874	0.02599	0.23137
A-2(b)	1.60484	0.26911	0.02602	0.23120
A-2(c)	1.60455	0.26903	0.02587	0.23132
B-2(a)	1.55991	0.25487	0.02341	0.23026
B-2(b)	1.55933	0.25451	0.02323	0.23004
B-2(c)	1.56004	0.25463	0.02347	0.22988
C-2(a)	1.59111	0.26694	0.02616	0.22206
C-2(b)	1.59143	0.26659	0.02671	0.22221
C-2(c)	1.59091	0.26714	0.02651	0.22218
A-3(a)	1.59760	0.29141	0.02541	0.21491
A-3(b)	1.59773	0.29177	0.02561	0.21447
A-3(c)	1.59747	0.29180	0.02575	0.21459
C-3(a)	1.59126	0.27867	0.02541	0.20659
C-3(b)	1.59150	0.27823	0.02571	0.20627
A-4(a)	1.58881	0.28459	0.02526	0.20983
A-4(b)	1.58907	0.28433	0.02578	0.21009
C-4(a)	1.58476	0.28386	0.02523	0.20634
C-4(b)	1.58522	0.28422	0.02509	0.20586

TABLE II

RATIOS AMONG ELEMENTS

Sample	Ash/Ca	Ash/P	Ash/Ca,P,Mg	Ca/P
A-1	5.65	7.68	0.309	1.36
B-1	5.94	7.50	0.316	1.26
C-1	5.66	7.89	0.314	1.40
A-2	5.96	6.94	0.305	1.16
B-2	6.12	6.78	0.307	1.11
C-2	5.96	7.61	0.309	1.20
A-3	5.48	7.44	0.301	1.36
C-3	5.71	7.71	0.312	1.35
A-4	5.59	7.57	0.306	1.35
C-4	5.58	7.70	0.308	1.39

Sample	Mg/P	Ca,Mg/P	Ca/Mg	Ash/Mg	Ca,P/Mg
A-1	0.123	1.48	11.02	62.29	19.13
B-1	0.108	1.37	11.62	69.10	20.85
C-1	0.120	1.51	11.60	65.64	19.92
A-2	0.112	1.28	10.36	61.81	19.27
B-2	0.102	1.21	10.90	66.73	20.74
C-2	0.119	1.32	10.08	60.12	18.48
A-3	0.119	1.48	11.40	62.43	19.79
C-3	0.124	1.48	10.90	62.27	18.97
A-4	0.122	1.48	11.15	62.26	19.37
C-4	0.122	1.50	11.29	62.99	19.48

be present in any constant ratio to any of the others in evaporated milk of excellent physical qualities.

Table II gives the ratios (averages) of the various constituents.

CONCLUSION

It is very evident from the data obtained in this problem that there need be no definite and strict amounts of the elements calcium, phosphorus, and magnesium, in order to produce an evaporated milk of excellent physical qualities. Neither need there be any definite ratio between any two of these elements, or between any one of them and the ash content of the milk.

Definite information concerning the factors which influence the grain, texture, or "ropiness" of evaporated milk must await further study.

SUMMARY

1. It is known that the addition of salts containing one or more of the elements calcium, phosphorus, and magnesium, in quantities less than one part per one hundred thousand, to the whole milk often improves the physical pro-

perties of the canned evaporated milk.

2. The elements calcium, phosphorus, and magnesium were gravimetrically determined on ten individual samples of evaporated milk of satisfactorily proven physical qualities.
3. Three retail brands of canned, unsweetened, evaporated milk were involved in the determinations.
4. A method of analysis for these three mineral elements was perfected by which quantities as small as one part per one hundred thousand may be determined.
5. The temperatures of ignition were definitely fixed and were controlled by means of a Leeds & Northrup Potentiometer Pyrometer.
6. Results were obtained which show that there need be no definite amounts or ratios of the three minerals in order to produce a product of good physical qualities.
7. The factors which directly influence or control the textural qualities of canned evaporated milk must await further study.

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