paper, with the percentage of alkali in solution as shown in this work, that some of the minerals which give a deep coloration with the former, show in the above table a comparatively small amount of alkali in solution, and *vice versa*. Muscovite for example while giving only a faint coloration with phenolphthalein, contained in solution alkaline compounds equivalent to 0.49 per cent. K_2O; pectolite, with 0.57 per cent. Na_2O, being the only one of the series showing a larger amount.

I hope in the near future to be able to carry this investigation further.

LABORATORY OF THE U. S. GEOL. SURVEY,
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A METHOD OF ANALYSIS FOR CANNED CONDENSED MILK.[1]

BY F. S. HYDE.

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BEFORE proceeding with the analysis, it may be desirable to ascertain the approximate specific gravity of the sample as follows:

Weigh the can with its contents. Then remove contents, replace with water to the top, and weigh again. Weigh empty can (sufficiently dried) and ascertain weights of milk and water separately. Divide the weight of condensed milk by the weight of water as a standard, and the quotient is the specific gravity of the condensed milk (near enough for practical purposes).

The specific gravity, which is not a matter of great importance, may vary from 1.27 to 1.37, according to the quantity of cane-sugar added, or according to the relative amounts of fat and albuminoid material in the milk used for condensation. That is, milk deficient in fat may show an increment in gravity irrespective of the amount of sugar added.

As to the method of analysis: the contents of the can, together with any portions of crystallized sugar, which may adhere to the bottom of the can like a hard mealy mass, are transferred to a beaker and stirred vigorously until the mass

[1] Read before the New York Section of the American Chemical Society, February 10, 1899.

becomes thinner and of the same consistency throughout. Then make stock solution as follows :

Stock Solution.—Weigh out twenty-five grams of the condensed milk and to this add seventy-five cc. water at ordinary temperature. This gives approximately 100 grams solution (of which twenty-five grams are condensed milk) of very nearly the consistency of cow's milk.

The writer attempted to simplify the method by taking aliquot parts of the stock solution for the various determinations, instead of weighing the different portions. Comparisons of the two methods gave discrepancies of three to five per cent. and the method of weighing was adopted as the more accurate, since an error of one-tenth cc. in measuring out five cc. for total solids may involve a difference of from one to two per cent. in the result. All results must be multiplied by four, since the condensed milk is diluted to one-fourth its strength ; *viz.*, each gram of solution should contain one-fourth gram of original condensed milk.

Total Solids.—Weigh out about five grams stock solution in previously weighed lead capsule (bottle cap two and one-half inches in diameter) or platinum dish. Evaporate on the water-bath to dryness. Finally heat in air-bath at 100° C. for fifteen minutes. Cool and weigh. Calculate the percentage and multiply by four.

Fat.—By Adams' coil, weigh quantity (five or six cc.) of stock solution in smallest beaker, recording weight of beaker and solution together. Without removing beaker from balance pan, insert the coil. When a sufficient quantity of solution has been absorbed, withdraw the coil, and reweigh the beaker with its residual contents. The difference is the weight of milk taken up by coil. Dry coil in air-bath at 100° from four to five hours, and extract with ether in the usual manner, employing a Soxhlet or Knöfler apparatus. Multiply the result by four.

Milk-sugar.—Dilute ten grams stock solution to 100 cc. Titrate direct with Fehling's copper solution. Calculate the percentage and multiply by four.

Cane-sugar.—Weigh ten grams stock solution in a No. 2 beaker. Add about fifty cc. water and five cc. (1 : 10) citric acid solution. Boil ten minutes. The citric acid inverts the cane-

sugar, but not the milk sugar. Condensed milk solutions do not coagulate readily with citric acid, hence filtration is superfluous. Cool the solution and neutralize with a solution of caustic potash, using litmus paper, and make up to 250 cc. Titrate direct with Fehling's solution in casserole over low flame. Make a duplicate titration to check results. Calculate reduction as due to cane-sugar, and then deduct milk sugar in terms of cane. The Fehling's copper solution should contain 69.28 grams copper sulphate per liter (five cc. equal to 0.05 gram glucose). On mixing equal volumes of the copper and alkaline tartrate solutions:

Ten cc. should equal 0.0500 gram glucose.

Ten cc. should equal 0.0678 gram milk sugar.

Ten cc. should equal 0.0475 gram cane-sugar (by inversion).

Example:

Suppose 10.16 grams stock solution are taken, inverted, and made up to 250 cc, as above; and suppose, on titration, nine cc. of this diluted solution is found equivalent to 0.0475 gram cane-sugar. Then 250 cc. should contain 1.3194 grams cane-sugar, or 12.98 per cent. (if all sugar in 10.16 grams stock solution be calculated as cane). Since the stock solution is one-fourth the strength of the original condensed milk by dilution, then 12.98 per cent. cane-sugar multiplied by four equals 51.92 per cent. cane-sugar. Now deduct the per cent. of milk sugar in terms of cane-sugar. Assume that milk sugar has been found to be 12.796 per cent., which is equivalent to 8.96 per cent. cane-sugar; then 51.92 per cent. minus 8.96 per cent. equals 42.96 per cent. cane-sugar as such.

It will be observed that while the method of calculation is not new, yet the results obtained are dependent on the manner of making up the milk solution, and weighing the quantities taken for analysis, instead of taking aliquot portions, as in the old methods.

Casein, Albumen and Salts.—The difference between milk solids, and the sum of the milk sugar and fat, is casein, albumen, and salts. For proteids alone, make a nitrogen determination by the Kjeldahl method.

Water.—The difference between 100 per cent. and the per cent. of total solids gives per cent. of water.

Milk Solids.—Subtract cane-sugar from total solids.

Ash.—The content of ash varies with amounts of cane-sugar present. It may be determined by igniting total solids in a platinum dish.

Degree of Condensation.—This depends on the extent of condensation at factory, as well as the amount of total solids in the original cow's milk used. It is rather an uncertain figure, since skimmed milk might be used. Calculation is usually made by dividing the percentage of milk solids in the condensed milk by 12.5 per cent., the average for ordinary cow's milk. Some recommend calculation based on the percentage of 'solids not fat.'[1]

In regard to the determination of cane and milk sugars in condensed milk with Fehling's solution, when the milk solutions are sufficiently dilute, the end-reaction may be easily determined without the use of the ferrocyanide indicator and the consequent loss of time in preparing ferrocyanide solutions and making filtrations will be avoided.

The condensed milk solution is titrated directly, without coagulation and filtration, in a four-inch casserole over a low Bunsen flame. When the titration is nearly completed it will be noticed that the red precipitate of cuprous oxide and organic matter seems to suddenly collect and settle, on removal of the heat, leaving a clear supernatant liquid which may be either bluish or yellowish, according as the titration is "under" or "overrun." This is all the more apparent in a casserole.

If the supernatant liquid is still slightly bluish, when tilted against the white sides of the casserole, a few drops more of the milk solution will discharge the color, such decolorization being the end-reaction. This end-reaction has been carefully compared with the ferrocyanide indicator, and the difference is too small to be of practical importance, when rapidity is an essential feature of the analysis.

With very little practice, the eye becomes accustomed to the change (discharge of color) and the value of the method can best be appreciated when it is necessary to execute several analyses in a short space of time.

Citric acid employed for the inversion of the cane-sugar, not-

[1] See McGill: *Analyst*, May, 1898, p. 128.

withstanding statements of various authors to the contrary, usually does not produce coagulation in condensed milk solutions, even on boiling. Unless necessary to resort to prolonged operations for coagulation and filtration with special reagents, it is advisable to make use of dilute solutions directly, and avoid any errors in coagulation and filtration, which might not compensate for discrepancies in titration.

It is generally admitted that the presence of organic matter, other than sugar, exerts a reducing action on Fehling's solution while at the same time concentration by evaporation and rapidity of titration also influence the results, so that, whether coagulation and filtration are employed or not, the final results cannot be considered as absolute.

The amount of cane-sugar averages between thirty and forty per cent., and the fat below twelve per cent., which is not surprising in a manufactured article. In the so-called evaporated milks or creams, the cane-sugar is usually absent. The presence of cane-sugar seems to be essential as a preservative and to make the canned condensed milk palatable. Polarimetric methods may be employed for estimating the sugars, but extra reagents are required for clarifying the solutions, besides a correction for the volume of precipitated solids.[1] The old Fehling method is quicker and the results quite satisfactory. Again, it is claimed that the heating during the process of manufacture of condensed milk alters the rotatory power of the milk sugar, while its power to reduce alkaline copper solutions is not seriously affected.

In the Report of the Brooklyn Health Department for *1895*, p. 270, will be found a list of condensed milk analyses, which, with two or three exceptions, were performed by the writer according to the method submitted. The results are hereby appended for ready reference :

[1] See Leffmann and Beam's Analysis of Milk and Milk Products, (*1896*), pp. 70-73.

CONDENSED MILKS ANALYZED DURING 1895.

Brand.	Total solids.	Milk solids.	Milk sugar.	Cane-sugar.	Fat.	Casein, albumen, salts, etc., by difference.	Water.
A.....	77.56	40.78	14.04	36.78	9.53	17.21	22.44
B.....	78.04	44.22	10.14	33.82	10.56	23.51	21.96
C.....	75.12	41.96	15.71	33.16	8.92	17.33	24.88
D.....	75.32	37.36	12.28	37.96	9.04	16.04	24.68
E.....	76.72	36.72	9.50	38.00	8.84	20.38	23.28
F.....	78.82	44.92	10.64	33.90	10.35	23.93	21.18
G.....	74.72	41.71	13.12	33.01	7.84	20.75	25.28
H.....	77.12	42.28	12.80	34.84	9.80	19.68	22.88
I	77.72	45.81	11.96	31.91	9.52	24.33	22.88
J	71.16	38.25	12.52	32.91	9.04	16.69	28.84
K.....	76.40	39.91	11.92	36.49	8.68	19.31	23.60
L	79.12	47.29	11.06	31.83	10.38	25.85	20.88
M	75.64	42.73	17.20	32.91	9.18	16.37	24.36
N.....	74.96	40.37	12.24	34.59	9.92	18.21	25.04
O.....	77.56	43.21	10.76	34.35	8.40	24.05	22.44
P.....	77.72	45.91	12.56	31.81	8.56	24.79	22.28
Q.....	75.76	46.82	10.84	28.94	10.03	25.95	24.24
R.....	73.72	30.76	12.79	42.96	8.07	9.89	26.28
S	35.24	35.24	12.32	none	11.82	11.10	64.76
T	34.33	34.33	11.27	none	9.76	13.30	65.67
U	30.46	30.46	10.15	none	6.73	13.58	69.54

The last three analyses represent so-called "Evaporated Milks," containing no cane-sugar.

A law of New York State,[1] requires that no "condensed milk shall be made * * * * unless the proportion of milk solids shall be, in quantity, the equivalent of twelve per centum of milk solids in crude milk, and of which solids twenty-five per centum shall be fats."

Generally, the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

The original cow's milk used may be considerably above legal standard, and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions, the manufacturer might be liable to prosecution, although the product might be perfectly wholesome.

As to preservatives, the manufacturers seem to depend almost entirely on the use of cane-sugar in sufficient quantity.

[1] Sec. 25, Chap. 143, L., 1894.