NOTES ON THE EXTRACTION OF MILK SUGAR FROM WHEY.

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IN view of the efforts which are being made to secure increased production of cheese throughout the country, it is of importance that greater consideration should be given to the problem of the profitable utilisation of the whey, which results as a by product of the cheese industry.

Whey on an average contains 6·5–7·5 per cent. of substance in solution, of which 60–70 per cent. is milk sugar. Its content of albuminoid substance amounts to roughly 1 per cent. and its fat content varies within fairly wide limits according to the method of cheese-making employed, the type of cheese (whole or skimmed milk) made and the efficiency with which the process is carried out.

The following figures give the composition of average samples of fresh whey:

		Fleischmann	Vieth (from skimmed milk)
Water ...	...	93·15 %	93·00 %
Fat ...	...	0·35 „	0·09 „
Sugar ...	...	4·90 „	5·45 „
Protein ...	...	1·00 „	0·92 „
Ash ...	...	0·60 „	0·54 „

The fat content may be as low as 0·04 per cent. in the whey resulting from the making of skimmed milk cheeses and as high as 1·35 per cent. in that obtained from the production of fatty cheeses.

Apart from its use for feeding stock, and where conditions are favourable, probably the most profitable method of disposal of whey is the manufacture of milk sugar, for supplies of which, previous to the war, this country was almost wholly dependent on the Continent. The extraction of the sugar is rendered a matter of difficulty owing to the presence in the whey of acids, lactic and acetic, of protein and of salts, especially those of the alkalies. By the action of the acids and salts, a portion of the milk sugar is converted, during the evaporation of the

whey, into a non-crystalline variety, and is consequently lost. The presence of protein leads to frothing during the concentration of the whey in the vacuum pans and is also liable to retard the crystallisation of the sugar at the later stage. It is of great importance that the final commercial product should be as free from nitrogenous constituents as possible, as the presence of proteins affects the keeping properties of lactose adversely.

Swiss method of preparation of lactose. Lactose has long been prepared from whey in Switzerland by a very simple, though wasteful, process. On the Alps, where the necessary fuel can be obtained cheaply, whey is evaporated over fires in "cheese-kettles." This process yields a residue of yellowish-brown and very impure sugar, known as "sugar-sand." This impure preparation is subsequently sold to the sugar refiners for purification.

Thorpe(1) gives the following details of the method. 50,000 litres of whey are directly evaporated to dryness. The residue (1250 kgs.) is dissolved in water at 65° in copper pans, $\frac{3}{4}$ -1 kg. of alum is added and the liquid is filtered through animal charcoal. The filtrate is boiled down to the syrupy condition and allowed to crystallise on wooden rods. The yield is 55-60 per cent. of the crude sugar.

The main objection to this empirical method lies in the fact that decomposition of lactose in solution begins at temperatures above 70°. Consequently, any method which involves continued boiling of the whey must be uneconomical and result in a considerable wastage of sugar.

Outline of German method(2). To the whey is added dilute caustic soda until the solution shows only a weak acidic reaction. It is then concentrated in vacuum pans at 60-70° to about $\frac{1}{10}$ its original bulk, when it contains about 60 per cent. of substance in solution. The concentrated whey is allowed to cool slowly and the lactose, which crystallises out, is separated from the mother liquor by means of the centrifuge. The yield of moist raw sugar is about 3.85 per cent. of the weight of whey employed or about 75 per cent. of the total sugar originally present.

On boiling the mother liquor for a short time, the protein coagulates. This is worked up into "Ziger" cheese, or is fed along with potatoes to swine. The filtrate is further evaporated and allowed to crystallise. This results in the separation of a further 0.5 per cent. of sugar, making in all an amount of crude sugar equal to 4.35 per cent. of the weight of whey, or about 85 per cent. of the total sugar in the whey. The residual mother liquor contains sugar, protein and mineral salts, including the phosphates of calcium and potassium. It finds application as a fertiliser.

The raw sugar is purified in the following manner: it is dissolved in about three times its weight of warm water (50°) in copper vessels and to the solution is added powdered bone charcoal and about 0.2 per cent. of acetic acid. After bringing to the boiling point, a little magnesium sulphate is added and the boiling is continued for several minutes. The solution is filtered from the sediment of phosphate and protein (which constitutes a valuable fertiliser when treated with sulphuric acid) and the clear filtrate is evaporated in vacuum pans at 65° till it contains about 65 per cent. of sugar. It is then allowed to crystallise in iron pans and the sugar is centrifuged from the mother liquor.

Suggested modification of German method. In the summer of 1918, when attention was being directed to the necessity for encouraging the production at home of certain products which, previous to the war, had been almost entirely imported by this country from foreign sources, it was suggested to me by Professor Crowther that it would be useful to carry out a series of preliminary trials on the preparation of lactose from whey. Accordingly, at convenient intervals during the progress of other work, a number of experiments were made with a view to testing the efficiency of the German method. The results given here are necessarily, under the circumstances, somewhat incomplete; but it was thought, however, that they might furnish information and data of a preliminary character which might prove of value, should a more comprehensive investigation of the subject be undertaken.

In the German method outlined above, it will be observed that no attempt is made to remove the protein from the whey at the outset, so that the first crop of sugar separates from a solution containing approximately 10 per cent. of albuminoid material. Trials were made in order to ascertain whether, by coagulating the protein from the whey before proceeding with the evaporation, the method were capable of improvement. A modification such as this might have beneficial results in several ways. The evaporation of the whey *in vacuo* should proceed without excessive frothing. The sugar should separate from the concentrated whey more readily and should, in addition, be less contaminated with protein. It seemed possible in this manner to increase both the yield and the purity of the product.

Against these advantages, however, must be set certain obvious disadvantages: 1. The extra cost of a process involving initial coagulation arising from the extra labour, fuel and plant required. 2. The loss of a certain amount of sugar carried down by the protein precipitate. 3. The danger of "caramelisation" of sugar during the coagulation

process, owing to the necessity of heating to fairly high temperatures in acidified solutions.

Analysis of sugar fractions. The lactose content was determined according to the Soxhlet(3) modification of the Fehling's reduction method. About 0.5 gm. of the sugar was dissolved in water and the albuminoid matter was removed by the addition of a few drops of lead subacetate solution. After taking out the excess of lead with sodium carbonate, the solution was filtered and made up to 250 c.c. 50 c.c. of the mixed copper reagent were heated to boiling in a beaker and 100 c.c. of the sugar solution run in. The mixture was once more brought to the boil and the boiling was continued for exactly six minutes. The cuprous oxide which separated out was filtered on to a Gooch crucible, ignited and weighed as cupric oxide. The sugar figures represent percentages of hydrated lactose ($C_{12}H_{22}O_{11} + H_2O$).

The protein content of the sugar was determined by the Kjeldahl method. The protein figures were obtained by multiplying the nitrogen content by the factor 6.34. This factor is probably somewhat low, as whey also contains small amounts of "whey protein" with a factor 7.55. Determinations of inorganic matter were made by igniting weighed amounts of the sugar at a dull red heat. In one or two cases, it was also necessary to determine the amount of ether-soluble material. In every case, the estimation was made on material dried for a short time in a steam-oven.

TRIAL I.

2½ litres of whey resulting from the production of Wensleydale cheese were concentrated in a vacuum pan at a temperature of 60–65° to a volume of 250–300 c.c. The acidity of the whey was so slight, that it was unnecessary to add soda before proceeding with the evaporation. No great trouble was experienced with frothing. The concentrated whey was allowed to cool very gradually during a period of 24 hours to the ordinary temperature, and the milk sugar which crystallised out was filtered on to a Buchner funnel and subsequently dried in a vacuum desiccator over H_2SO_4 . The yield of sugar was 87 gm. (3.48 per cent. of the amount of whey employed). It was only very slightly discoloured and gave the following results on analysis:

Crystalline lactose	...	88.42 %
Protein	...	3.75 „
Ash	...	2.85 „
Ether extract	...	4.70 „

The large percentage of ether soluble material is explained by the fact that the fat was not separated from the whey previous to evaporation and was consequently carried down during the crystallisation process by the sugar. This would not, however, occur in actual factory practice, as the whey would be run through a cream separator before undergoing concentration. A portion of the sugar was extracted with ether and the percentage of lactose in the product was then found to be 93 per cent.

The mother liquor from the first crystallisation was next heated to 75° in the water bath for a few minutes and the coagulated protein was filtered off and well washed with warm water. The washings were added to the main bulk of liquid.

Yield of dried crude protein, 24.8 gm. (about 1 per cent. of whey).

After making the filtrate from the protein almost neutral by the addition of soda, it was further concentrated *in vacuo* at 65°. On cooling, a second crop of sugar separated out.

Yield: 10 grams (0.4 % of whey).

Composition:

Crystalline lactose	...	92.29 %
Protein	...	3.67 „
Ash	...	3.70 „

Appearance: slightly discoloured.

The mother liquor was again brought almost to neutrality with soda, evaporated to a syrupy consistency on the water bath and inoculated with a crystal of lactose. After standing 24 hours, a further 20 gm. (0.8 per cent.) of impure brown sugar crystallised out.

Composition:

Crystalline lactose	...	84.42 %
Protein	...	6.15 „
Ash	...	9.10 „

The residual brown mother liquor was analysed with the following results:

Lactose	...	9.25 grams
Protein	...	7.21 „
Ash	...	7.20 „
{P ₂ O ₅	...	1.50 „
{K ₂ O	...	3.01 „

The figures indicate that the separation of the protein by coagulation of the concentrated whey after the removal of the greater part of the sugar was by no means complete.

TRIAL II.

In this trial, the bulk of the protein was removed from the whey before concentrating *in vacuo*. As a preliminary, several trials were made in order to ascertain the best method of coagulating the protein, keeping in mind the fact that working at high temperatures would result in the decomposition of some of the sugar.

It was found possible, especially when dealing with sour wheys, to effect coagulation by heat alone at 85–90°. When working with fresh sweet whey, however, coagulation was brought about more readily and at a somewhat lower temperature in the presence of a little acetic acid. A sample of fresh Wensleydale whey was heated to 82° in a water bath, at which temperature no sign of coagulation was to be observed. On the addition of a few drops of acetic acid, however, the protein immediately separated out. In no case was the removal of protein anything like complete, due partly to a protective action exerted by the sugar in the whey.

The coagulation was carried out in the following manner: The whey was heated to 75° in a water bath and to it was added acetic acid (0.5 c.c. glacial acid to every litre of whey). At this temperature, the coagulation began and it was completed by raising the temperature gradually to about 82°.

An interesting observation was made in tests where acetic acid was replaced by phosphoric acid. Coagulation of protein occurred if only small amounts of phosphoric acid were added; if the amount of phosphoric acid were increased, however, coagulation was prevented altogether. In two tests with 300 c.c. of whey, 2 c.c. and 3 c.c. of 50 per cent. phosphoric acid were added respectively. In neither case was coagulation brought about even at the temperature of boiling water and the addition of a little acetic acid at this stage also failed to cause the separation of the protein.

The protein was removed from 2500 c.c. of fresh Wensleydale whey by the method outlined above. After filtering off the protein (yield 23 gm.) on a folded filter paper, the clear filtrate was made almost neutral by the addition of dilute caustic soda and evaporated to $\frac{1}{10}$ its bulk in a vacuum pan at 65°. The sugar, which crystallised out on allowing the concentrated whey to cool slowly, was filtered off and dried on a porous plate placed in a vacuum desiccator.

Weight of crude sugar, 96 gms. (3.84 per cent. of whey).

The analysis of the dried sample gave the following results:

Crystalline sugar	...	93.65 %
Protein	...	2.15 „
Ash	...	4.00 „

After making the mother liquor almost neutral, it was further concentrated *in vacuo* at 65°. The sugar which came out on cooling was of a pasty nature and was separated from the mother liquor by means of the centrifuge. It was then washed with a little alcohol and the discoloured mass was allowed to harden on a porous plate. After powdering and drying, it was submitted to analysis.

Yield: 25 gm. (1 % of whey)

Composition:

Crystalline lactose	...	84.30 %
Protein	...	6.40 „
Ash	...	9.12 „

The mother liquor from this crystallisation failed to yield a third crop of crystalline sugar after being further concentrated.

TRIAL III.

This was a repetition of Trial II with 2½ litres of another sample of Wensleydale whey. The following results were obtained:

1st crop.

Yield of crude sugar: 77 gm. (3.08 % of whey)

Composition:

Crystalline lactose	...	93.43 %
Protein	...	3.12 „
Ash	...	2.72 „
Ether soluble	...	0.45 „

2nd crop.

Yield of crude sugar: 10 gm. (0.4 % of whey)

Composition:

Crystalline lactose	...	77.80 %
Protein	...	4.20 „
Ash	...	17.75 „

It was not possible to isolate a third crop of sugar in the crystalline state.

From these trials, it would appear that little is to be gained regarding yield and purity of sugar by initial coagulation of the whey protein. The sugar from Trials II and III contained very little less protein than that obtained from Trial I. The results of Trials II and III (especially of III) gave evidence of partial "caramelisation" of the lactose during

the coagulation process, as it was difficult to obtain more than one crop of sugar in the crystalline state. In Trial I, the sugar crystallised quite satisfactorily from the concentrated protein-containing whey and the subsequent coagulation of the protein was brought about readily at a fairly low temperature and without addition of acid.

TRIAL IV.

The details of working were altered somewhat in this test. To $2\frac{1}{2}$ litres of fresh sweet whey were added 50 c.c. of Derby whey which had been allowed to sour. The mixture was heated in a water bath. The protein began to separate out when the temperature of the whey was $80-83^{\circ}$ and the process was completed by gradually raising the temperature to 93° during a period of ten minutes.

The albuminoid matter was removed by filtration and the filtrate was neutralised by the addition of alumina cream. After shaking the mixture vigorously and filtering, the clarified liquid was concentrated to a volume of 500 c.c. in a vacuum pan at 60° . To the concentrated whey was added animal charcoal and the mixture was brought to the boil. 2 gm. of MgSO_4 and 1 gm. $\text{Al}_2(\text{SO}_4)_3$ were then added and the boiling was continued for three minutes. After filtering, the solution was clear and almost colourless.

The filtrate was further concentrated to about 200 c.c. *in vacuo* at 60° and the residual liquor was allowed to cool slowly. The lactose was filtered off on a Buchner funnel and washed with a concentrated solution of lactose. The sugar was then brought on to a porous plate and dried in a vacuum desiccator over H_2SO_4 .

Yield: 80 gm. (3.2 % of whey)

Composition:

Crystalline lactose	...	96.20 %
Protéin	...	1.50 „
Ash	...	1.60 „
Ether extract	...	trace

This method gives a sugar of very fine appearance and of greater purity than that obtained from any of the other trials. There is, however, an increased danger of partially “caramelising” the sugar during the process.

Purification of sugar samples. Tests were made with fuller’s earth as a decolorising agent in the place of animal charcoal. Below 60° , fuller’s earth only effected slight improvement of a brown lactose mother liquor; if the solution were shaken for about 10 minutes with a little

fuller's earth at a temperature of 70–75°, a marked improvement resulted on filtering. Under the same conditions, the turbidity of a solution of lactose crystals was removed.

At all temperatures, however, animal charcoal proved more efficient in this respect than fuller's earth. Alumina cream at the ordinary temperature also effected a slight improvement in the appearance of turbid solutions of crude sugar.

(1) 20 gm. of the first crop of fat-containing sugar obtained in Trial I were dissolved in 120 c.c. of hot water. After adding a little MgSO_4 and fuller's earth, the solution was placed in a water bath at 70–75° for 10 minutes, during which time the flask was frequently shaken. The solution was filtered and evaporated *in vacuo* at 60°. On cooling, 15 gm. of sugar separated out, which when dried gave the following results on analysis:

Crystalline lactose	...	95.58 %
Protein	...	0.49 "
Ash	...	3.45 "
Ether extract	...	0.59 "

Most of the protein and fat had in this manner been removed. The high ash content arose from having added more MgSO_4 than was necessary.

(2) 50 gm. of the same sample of sugar were recrystallised by dissolving in 250 c.c. of warm water, adding animal charcoal, and after bringing the solution to the boil, a pinch of MgSO_4 and 0.5 c.c. of glacial acetic acid. The boiling was prolonged for three minutes and the solution was then filtered and evaporated to crystallising point *in vacuo* at 60°.

Yield of sugar: 39 gm.

Composition:

Crystalline lactose	...	98.63 %
Protein	...	0.66 "
Ash	...	0.61 "

(3) 47 gm. of the first crop of crude sugar from Trial III were recrystallised in a similar fashion, using animal charcoal, MgSO_4 and acetic acid. A yield of 37 gm. sugar was obtained, with the following composition:

Crystalline lactose	...	98.53 %
Protein	...	0.64 "
Ash	...	0.41 "

(4) 20 gm. of the same sample of crude sugar were purified by boiling the solution for three minutes with a little fuller's earth and MgSO_4 . A yield of 14.5 gm. of sugar separated out from the filtered liquid, after

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concentration *in vacuo* and subsequent cooling. The dry sugar was analysed and gave the following results:

Crystalline lactose	...	98.84 %
Protein	...	0.34 „
Ash	...	0.49 „

(5) 15 gm. of the third crop of impure sugar from Trial I gave 10 gm. of recrystallised sugar after purification with the use of animal charcoal, MgSO_4 and acetic acid. A great improvement resulted in both appearance and purity, the content of protein and ash having been reduced to 1.04 per cent. and 0.68 per cent. respectively.

Iron content of commercial milk sugar. The question arose as to whether, during the evaporation of the slightly acid whey in iron vacuum pans, any appreciable amount of iron would be dissolved. In order to settle this point, the iron content of whey after separation of the butter fat was determined and the same determination was carried out on the semi-solid crystalline mass, which was obtained on evaporating the same sample of whey to $\frac{1}{10}$ its bulk in an iron vacuum pan.

The dry matter was determined first on a weighed amount of the sample. The residue was then ignited at a dull red heat and the last traces of carbon removed with the aid of a few drops of concentrated nitric acid. The amount of ash was determined.

About 0.1–0.2 gm. of the ash was weighed out and dissolved in a little dilute nitric acid. The volume was made up to 100 c.c. Into each of two Nessler glasses were pipetted 10 c.c. of 10 per cent. HNO_3 and 5 c.c. of 5 per cent. potassium sulphocyanide. Into the one glass was then run 5 c.c. of the ash solution and the volume was made up to the 50 c.c. mark with distilled water. The latter was also added to the contents of the other glass until just short of the 50 c.c. mark and then a freshly made solution of ferrous sulphate (0.01 gm. Fe per litre) was added drop by drop from a pipette measuring to 0.01 c.c. until the pink colour in the first glass was matched. From the volume of FeSO_4 solution added, the amount of iron in the sugar ash was estimated.

Sample 1. (Whey after separation of butter fat):

Dry matter	...	6.35 %
Ash	...	0.70 %
Iron	...	0.00005–0.0001 %

Sample 2. (After evaporation to about $\frac{1}{10}$ bulk):

Dry matter	...	67.00 %
Ash	...	7.65 „
Lactose	...	46.84 „
Iron	...	0.00161 „

It will be seen that the original whey contains the veriest trace of iron. After evaporation to somewhat less than $\frac{1}{10}$ the initial volume, the value of the iron content indicated that an extremely small and negligible amount of iron had been dissolved from the vacuum pan.

In conclusion, I should like to express my indebtedness to Professor Crowther, who not only suggested this work, but also offered helpful advice during the carrying out of the trials.

REFERENCES.

- (1) *Thorpe's Dictionary of Applied Chemistry*, 2, p. 619.
- (2) G. ZIRN, *Milch. Ztg.*, 1895, pp. 481 and 497.
- (3) SOXHLET, *Journ. f. prakt. Chemie*, 21, 1880, 227.

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