

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

APPLICATION OF THE FREEZING-POINT TEST TO HEATED MILKS

A NUMBER of samples of hot milk, as served in restaurants, etc., have recently been analysed under the Food and Drugs (Adulteration) Act.

Whilst in certain cases the addition of excessive quantities of water was obvious from all the figures obtained, and successful prosecutions were instituted, in a few cases the freezing-point test indicated the presence of small proportions of added water when the solids-not-fat were in the neighbourhood of 8.5 per cent.

On consideration of the latter results, some doubt arose as to whether the normal inference from the freezing-point could be relied upon when the milk had been heated under unknown conditions.

It has been shown (Barille, *ANALYST*, 1910, **35**, 22; Bell, *id.*, 1925, **50**, 466, *et al.*) that salts, such as citrates and phosphates of calcium and magnesium, are precipitated when milk is heated, and the possibility of an accompanying rise in the freezing-point of the remaining milk had to be considered.

Both Monier-Williams (L.G.B. Report No. 22) and Elsdon and Stubbs (*ANALYST*, 1933, **58**, 7) have clearly shown that pasteurisation and sterilisation have little effect on the freezing-point of milk; the tendency was, however, for a slight rise to occur in the freezing-point after heating.

The heating and boiling of milk in an open or partly open vessel and keeping it hot for unlimited periods, accompanied at times by the formation and separation of skin and sediment, such as might occur in a restaurant where occasional glasses of hot milk are sold, is, however, another matter, and the need for information on the effect of such conditions on the freezing-point was manifest.

The following experiments were therefore carried out with a view to ascertaining the effect of such varying conditions:—A sample pint of fresh milk was purchased and its freezing-point determined; it was then heated in a small covered saucepan to 80° C. (*i.e.* about the lowest temperature suitable for preparing a glass of hot milk), decanted from the skin and sediment which had formed on the pan, and cooled; after determination of the freezing-point, this process was repeated twice on the same sample in the same (cleaned) saucepan, for confirmation.

A second sample was then purchased and, its freezing-point having been taken, it was heated in the same covered saucepan to 90° C., decanted, cooled and tested again; this process was repeated, as before.

A third sample was treated similarly, but heated to the boiling-point each time, and, after the three heat treatments, it was finally boiled for 15 minutes between the tests; it was then no longer suitable for serving, owing to its burnt taste and colour.

A fourth sample was then treated in the same way as the second one, *i.e.* heated to 90° C., except that it was heated in an open saucepan, no precautions being taken to minimise evaporation.

All freezing-points were determined in duplicate by the Hortvet process; in most instances the duplicates were identical, and in the others the means are given to the nearest third decimal place.

	Heated in covered saucepan						In open pan	
	(1) to 80° C.		(2) to 90° C.		(3) to boiling		(4) to 90° C.	
	F.pt.	Differ- ence	F.pt.	Differ- ence	F.pt.	Differ- ence	F.pt.	Differ- ence
Before heating	-0.537		-0.541		-0.544		-0.543	
After once heating	-0.541	-0.004	-0.545	-0.004	-0.555	-0.011	-0.594	-0.051
After twice heating	-0.547	-0.006	-0.551	-0.006	-0.565	-0.010	-0.626	-0.032
After thrice heating	-0.554	-0.007	-0.562	-0.011	-0.575	-0.010	-0.661	-0.035
After boiling for 15 minutes					-0.606	-0.031		

It will be seen that an appreciable lowering of the freezing-point results from heating milk under such conditions. As the greater lowerings follow greater heating, and still more so heating in an uncovered pan, the predominating factor is clearly evaporation.

The various conditions, however, under which milk may be heated and kept hot in cafés and restaurants are hardly reproducible in a laboratory, and it was felt that the only way to discover what changes might arise in those circumstances was to obtain, with the co-operation of the managements, actual samples of such milk, before and after heating.

In small cafés, coffee stalls, etc., where hot milk is infrequently asked for, it is usually heated in a saucepan as required, and the above results would be representative.

In medium-sized cafés, buffets, snack bars, etc., apparently the usual practice is for the milk to be heated and kept hot in a water- or steam-jacketed earthenware urn; whilst in the larger multiple restaurants, it appears to be the practice to fill and replenish from time to time a water-heated urn, kept at an almost constant temperature, with milk heated first in a saucepan.

Samples of milk, before and after heating, were accordingly obtained from various restaurants in the last two categories, and the results of analyses were as follows:

Source	No.	Fat PerCent.	S.N.F. PerCent.	F.pt.	Differ- ence	Observations
Dairy snack bar	1a	2.89	8.85	-0.541	-0.003	Before filling urn
	1b	2.02	8.94	-0.544		After 2 hours' heating in urn; thick skin formed
Dairy snack bar	2a	3.81	8.84	-0.543	-0.002	Before filling urn
	2b	3.73	8.89	-0.545		After $\frac{1}{2}$ hour's heating in urn; slight skin formed
Railway refreshment buffet	3a	4.02	9.03	-0.543	+0.023	Before filling urn
	3b	3.91	8.70	-0.520		Half-hour's heating; found to contain water from cleaning
The same, later	4a	3.87	8.94	-0.543	-0.003	Immediately after last filling
	4b	3.79	9.02	-0.546		After $1\frac{1}{4}$ hours' heating
Dairy snack bar	5a	3.81	8.82	-0.545	-0.001	Before heating
	5b	1.76	9.05	-0.546		After $1\frac{1}{2}$ hours' heating; thick skin formed

Source	No.	Fat Per Cent.	S.N.F. Per Cent.	F.pt.	Differ- ence	Observations
Public house	6a	3.71	8.72	-0.544	+0.039	Before filling urn
	6b	3.29	8.00	-0.505		After $\frac{3}{4}$ hour's heating; contained condensed steam
Large multiple restaurant	7a	3.67	8.47	-0.525	-0.001	Before heating
	7b	3.63	8.45	-0.526		Kept hot for an hour
Large multiple restaurant	8a	3.82	8.93	-0.545	-0.008	Before heating
	8b	3.83	9.02	-0.553		Kept hot for $1\frac{1}{2}$ hours
Large multiple restaurant	9a	3.64	8.34	-0.516	0	Before heating
	9b	3.49	8.39	-0.516		Kept hot for an hour

In two cases, Nos. (3) and (6), where the results departed from the general trend, investigation proved that water had accidentally found its way into the hot milk; in (3) this was due to the outlet tap incompletely emptying the urn, with the result that a small amount of water was introduced into the first filling of the urn after cleaning, from which filling the sample had been taken; a second pair of samples, numbered (4), taken from the same urn (*a*) immediately after the last filling of the day, and (*b*) after heating for $1\frac{1}{4}$ hours, gave normal results. In the other case, (6), the flat earthenware lid covering the milk compartment was found to be broken, and steam from the outer jacket was condensing on the outer lid and percolating through the broken lid into the milk; as no new lid was provided, further samples were not taken.

The series of analyses showed several points of interest; in some instances, particularly where much skin had formed, the fat-content was lowered considerably by the heating; in others, only slightly—showing that from this aspect the method of heating adopted is of the greatest importance; and, further, that practically no fat need be lost when milk is heated under suitable conditions, and even kept hot for an hour or more.

In most cases, and even when a thick skin was observed, the solids-not-fat are slightly higher in the heated sample; the percentages, however, agree closely with figures which may be calculated from the solids-not-fat in the corresponding unheated sample, allowance being made for the difference in fat and the evaporation suggested by the freezing-points; this indicates but little loss in solids-not-fat through heating, in spite of skin and sediment formation.

As may be seen, the samples could not all have been considered genuine, but they serve nevertheless for the purposes of comparison, and show no instance where the heated sample gave a higher freezing-point than the unheated milk, excepting where it was proved to contain added water.

To summarise, therefore, it would appear that the normal inference from the freezing-point can be relied upon when a milk has been heated in any of the ways usual where hot milk is sold; except that under some conditions when the milk has been re-heated or allowed to evaporate to any extent, a proportion of added water may be somewhat under-estimated by this means.

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THE DETERMINATION OF NITRATE BY MEANS OF DEVARDA'S ALLOY

THE determination of nitrate, according to Devarda's original instructions,¹ is unsatisfactory because of the tendency of the hydrogen, which is being evolved from the alloy, to carry over an extremely fine alkaline fog during distillation. This fog is very difficult to remove by scrubbing, even with complicated bubble scrubbers.² The method of reducing nitrate to ammonia has obvious advantages over alternative methods from the theoretical point of view, since reduction with ferrous sulphate in carbon dioxide or steam is troublesome to operate and, moreover, Chilian nitrate, its liquors and raw caliche also contain other oxidising agents, such as iodates. The nitrometer method is not safe, on account of the pressures which may be developed with the strong acids in the mercury vessel. Further, if the amount of sodium chloride in the sample exceeds 17 per cent. of the weight of sodium nitrate, the method gives high results.³

The object of this research was to determine the easiest and most economical method of determining nitrate as a routine operation. Most writers appear to have substituted sodium hydroxide for the more expensive potassium hydroxide specified by Devarda, who required 40 ml. of potassium hydroxide solution of sp.gr. 1.3 and 2 to 2.5 g. of alloy (50 per cent. of copper, 45 per cent. of aluminium, 5 per cent. of zinc) for 0.5 g. of sodium nitrate.

The other extreme was advocated by Valmari,⁴ quoted by Allen,⁵ who used *N*/10 alkali and 6.5 g. of alloy per g. of nitrate. (The concentration given by Devarda works out at about 2 *N*, or twenty times as large.)

Butt⁶ found that the particle-size of the alloy was immaterial so long as it would all pass through a 20-mesh sieve, and that about 200 ml. had to be distilled to ensure that all the ammonia had been transferred from the distilling flask into the standard acid. These results were confirmed in the present investigation.

EXPERIMENTAL.—The sodium hydroxide, which was guaranteed to contain less than 0.0015 per cent. of ammonia, was made up to give a solution of sp.gr. 1.32 (381 g. per l.). The distillation was carried out in litre flasks connected by means of Davisson scrubbers with condenser tubes made of tin, to eliminate any possibility of soda being dissolved from a glass tube by steam condensing on it. The quantity of sodium nitrate taken for analysis was 1 g. of the purest quality obtainable; the standard acid and alkali were made of the same normality, and were equivalent to 0.02 g. of nitrate ion per ml.; and the indicator was methyl red dissolved in alcohol. In the first test, 250 ml. of distilled water were distilled, and the blank test gave zero readings. The result of adding varying quantities of alkali and alloy is given in Table I. In every test the amount of water used was 250 ml.

TABLE I

Sodium hydroxide solution		Percentage reduction of the nitrate		
ml.	Normality	3.00 g. of alloy	2.5 g. of alloy	2.00 g. of alloy
1	0.035	35.2		
2	0.069	90.8	84.0	61.7
3	0.104	100.0	100.0	86.3
4	0.139	100.0	100.1	86.7
5	0.173	100.0	98.9	79.5
6	0.208	99.9	95.2	79.6
7	0.243	100.0		
8	0.277	97.7		69.7
9	0.312	95.0		
10	0.347	95.8		
20	0.694			66.2
30	1.040	92.5		
50	1.735	88.5		

The effect of doubling the quantity of water in the reaction was next tried, 525 ml. of water being added to the reaction flask. The results are given in Table II.

TABLE II

Sodium hydroxide solution		Percentage reduction of the nitrate	
ml.	Normality	3.00 g. of alloy	2.50 g. of alloy
2	0.035	85.1	
3	0.052	98.2	86.1
4	0.069	100.0	91.0
5	0.086	96.3	87.1
6	0.104		81.7
7	0.121		77.3
8	0.139	71.0	

These figures show that the only method of obtaining correct results with the original Devarda proportions of reagents was to get just sufficient alkaline spray to balance the lack of ammonia due to incomplete reduction of the nitrate. On comparing Table II with Table I it will be seen that it is also inadvisable to specify *N/10* alkali, because the reduction depends, not on the concentration of alkali, but on the quantity of it used per g. of alloy.

The experience gained from these results was embodied in some instructions to assayers, published in 1928.⁷ The quantity of reagents then recommended was 4 g. of alloy and 8 to 10 ml. of 25 per cent. caustic soda solution (sp.gr. 1.28) for 1 g. of sodium nitrate. In view of the fact that papers are still being published which indicate that it is not generally recognised that the amount of caustic soda originally recommended by Devarda is excessive and leads to inaccurate results, it was thought that the publication of the experimental work on which these instructions were based might serve a useful purpose. Thus, Cattelain⁸ recommends for 0.5 g. of nitrate the use of 2.5 g. of alloy and 25 ml. of 30 per cent. caustic soda solution (sp.gr. 1.33) and 5 ml. of ethyl alcohol with 125 ml. of distilled water. Similarly, Meurice and Martens,⁹ for 0.25 g. of nitrate, recommend 40 ml. of 40 per cent. caustic soda solution and 3 g. of Devarda alloy with 250 ml. of water. Both these papers are misleading, and the quantities that are now put forward are recommended as being productive of more accurate results, as well as being more economical.

SUMMARY.—The determination of nitrate by reduction to ammonia by means of Devarda alloy has been investigated by varying all the conditions and reagents one by one. As a result, it has been found that the limits are very different from those specified by Devarda in his instructions. The reduction is best accomplished by using only one-twentieth of the amount of alkali originally specified. It is inadvisable to specify concentration of alkali, because the reduction depends upon the quantity of alkali to a given amount of alloy. The optimum amount for the reduction of 1 g. of nitrate is 3 g. of alloy and 2 g. of caustic soda in about 250 ml. of distilled water.

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THE COMPOSITION OF SCOTTISH RASPBERRIES

At first sight it appears to be a simple matter to determine whether the composition of a sample of jam complies with the standards agreed upon between the Society and the Food Manufacturers' Federation (*cf.* ANALYST, 1930, **55**, 694), but one must remember that we are dealing with a natural product subject to wide variations in composition, and that only a limited number of analyses of Scottish raspberries have been published.

The insoluble solids or the number of seeds in the raspberries are usually taken for computing the fruit-content of a jam, but both constituents vary within wide limits depending on various factors, such as the strain of cane, the climate and the soil conditions.

Macara (ANALYST, 1931, **56**, 39) found the insoluble solids to range from a minimum of 4.4 per cent. to a maximum of 9.2 per cent., with an average of 6.17 per cent. He also found that the number of seeds per 10 g. of fruit varied from 356 to a maximum of 490, with an average of 419.

Since this experiment was made I find that Macara (ANALYST, 1935, **60**, 592) has found a minimum of 3.29 per cent. of insoluble solids in Blairgowrie fruit.

In a disputed case before the Law Courts regarding the fruit content of a sample of raspberry jam taken under the Food and Drugs (Adulteration) Act, the above figures were taken as a basis of calculation of the fruit-content. From my experience of Scottish raspberries I was not satisfied that these figures represented their average composition. Accordingly, I arranged to visit a few fruit farms in Essendy and Craigie, near Blairgowrie, and collected the fruit direct from the canes. The raspberries were just in the right condition for pulling, and there had been no rain for a week previously. The samples were kept overnight in screw-capped glass jars, and the analyses were carried out next morning.

The results are as follows:

					Insoluble solids Per Cent.	Soluble solids Per Cent.	Seeds per 10 g.
Lloyd George	4	years	canes	..	3.99	8.43	246
" "	5	"	"	..	4.95	8.20	326
Devons	2	"	"	..	4.71	8.67	332
"	6	"	"	..	4.80	10.70	402
"	6	"	"	..	4.65	11.18	400
"	10	"	"	..	4.36	10.61	334
Antwerp	10	"	"	..	3.93	8.21	288
Mitchells	3	"	"	..	4.24	9.34	284
Pynes Red Cross	3	"	"	..	4.94	9.23	274
Pynes Royal	10	"	"	..	3.94	8.64	287
Maximum	4.95	11.18	402
Minimum	3.93	8.20	246
Average	4.45	9.32	317

It is quite true only 10 samples were taken, but at least they indicate appreciably lower values than those published at the time.

There is consequently no definite standard upon which to found an opinion, and one is left to decide what figure to adopt for purposes of calculation. This will be obvious if the respective minima stated above be taken in order to calculate the fruit-content of a jam, containing, say, 1.80 per cent. of insoluble solids. Macara's minimum of 4.4 would indicate 40.9 per cent. of fruit, and his later minimum of 3.29 indicates 54.7 per cent. of fruit. The minimum of 3.93 found in my experiments is intermediate, with 45.8 per cent. of fruit.

The difference between the highest and lowest result thus obtained is 13·8 per cent., and brings one to the conclusion that the amount of fruit in a raspberry jam can only be determined with accuracy if the composition of the raspberries from which the jam is made is known.

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THE CHLORINE-CONTENT OF FEATHERS

(Read at the Meeting of the North of England Section, February 1, 1936)

IN 1935 rumour spread among a section of the upholstery trade that the limit of chlorine, prescribed by the Rag Flock Act Regulations, 1912, was applicable to such articles as feathers, feather pillows, feather beds, down cushions, etc.

In spite of assurances to the contrary, the fear of legal action persisted, and it was decided to ascertain the amount of chlorine extracted with water in the usual way from feathers actually being used at the time.

As I was unable to discover any figures relative to this point in the literature, the results obtained in the investigation may be of interest to analysts.

The feathers from pillows (purchased locally) manufactured by rival firms, showed the possibility of fairly wide differences.

Pillow No. 1	yielded chlorine	..	499	parts per 100,000	(cf. Grade 6 below)
„ No. 2	„	..	102	„	„

By the courtesy of the Scott Feather Co. I was enabled to obtain samples of the feathers as purchased wholesale and of the various grades in general use after treatment. Feathers are purchased from many sources and stored in a warehouse until wanted. To keep down offensive odours when in store, they are sometimes sprayed with dilute ammonia while awaiting treatment. Before being washed they are graded according to size, each grade being dealt with separately.

The treatment consists in a thorough washing with boiling water in a large tank fitted with a stirrer, the time of washing varying with the grade of feather. The feathers are then screened off and stoved to complete their sterilisation.

A sample of the untreated feathers direct from a warehouse yielded:

Chlorine	609	parts per 100,000
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After treatment, the following figures were obtained for the various grades:

				Chlorine (parts per 100,000)
Grade 1 (down)	68
„ 2	51
„ 3	68
„ 4	85
„ 5 (larger whole feathers)	..			398
„ 6	„	„	..	406

As the above results represented a mixture of feathers from all kinds of birds, I procured, from the C.W.S. Poultry Department, Armagh, samples of feathers plucked from selected birds during their preparation for the Christmas market, and a second lot a few weeks later. These had not been washed or treated in any way.

The results were as follows:

				Chlorine (parts per 100,000)	
				Lot 1	Lot 2
Duck feathers	176	209 (grey duck)
Goose feathers	242	267
Chicken feathers	342	350
Turkey feathers	359	359
Pheasant feathers (Lancashire)	..			367	
Goose feathers from old feather bed				409	

The method adopted for the tests was that used for rag flock. The chlorine in the extracts was present chiefly as potassium and sodium chlorides, any excess being presumably due to ammonium chloride.

The following figures (expressed as percentages on the extracts) were obtained in the course of the work:

				Potassium chloride	Sodium chloride
Duck feathers	0.25	0.05
Geese feathers	0.24	0.21
Geese feathers (old bed)	..			0.23	0.26
Chicken feathers		0.24	0.15
Turkey feathers		0.28	0.28
Pheasant feathers		0.20	0.24

A comparison of the figures for fresh and old geese feathers indicates that the increase in the chlorine-content of the old feathers is mainly in the form of ammonium chloride.

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