For the 0.5 c.c. of the phosphoric acid solution 23.24 c.c. of barium hydroxide solution were required (the actual figures being 23.23, 23.26, 23.22, 23.25, 23.23 c.c. *N/10*) corresponding to 15.19 grms. of phosphoric acid per 100 c.c.

The close agreement with theory (15.17) is very satisfactory. In the later experiments the precaution was always taken of freeing the acid from carbon dioxide—this was done by boiling in Jena glass vessels for a few minutes, cooling, and then transferring to the cylinder, using the sodium acetate solution for rinsing purposes. In the case of the free acid this precaution is scarcely necessary, but with the alkali phosphates it is absolutely essential. All water used must be freed from carbon dioxide.

Disodium orthophosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. The salt used was of a high degree of purity the only impurity present in determinable amount being sulphuric acid; chloride was absent. The crystals were somewhat damp. A solution containing 35.83 grms. per litre was prepared, this solution being decinormal for the hydrogen ion and three times that strength for the phosphoric acid ion. 15 c.c. of this solution was transferred to a small Jena flask, 15 c.c. of *N/10* sulphuric acid added, and the whole boiled for five minutes to expel carbon dioxide. After rapidly cooling the flask contents were transferred to a stoppered cylinder containing 50 c.c. of *N/10* silver nitrate solution, the flask being rinsed with 30 c.c. of *N/5* sodium acetate solution and water; after well shaking the acetic acid produced was titrated as already described, an allowance being made for the sulphuric acid added.

The following results were obtained—given as percentage of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in the salt: ammonium magnesium phosphate method (Schmitz), 96.84 per cent.; sodium metaphosphate method (evaporation and ignition), 96.98 per cent.; volumetric method, 97.03 and 97.07 per cent. The agreement is again good.

Monosodium orthophosphate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. The salt used was in the form of colourless damp crystals and was free from chloride. As with the disodium salt sulphate was present but in smaller amount.

The results obtained with the mono sodium salt were as follows in percentages of NaH_2PO_4 in the salt, the treatment being exactly as for the disodium salt save that in experiment (2) no sulphuric acid was added. Ammonium magnesium phosphate method (Schmitz), 77.28 per cent.; volumetric method, (1) 78.20 (2) 78.33 per cent. (Theory for the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ requires 76.92 per cent.)

The high results obtained by the volumetric method are in all probability due to the presence of free phosphoric acid. This conjecture received confirmation when an attempt was made to determine phosphoric acid as sodium metaphosphate; low results were consistently obtained, no constant weight being obtainable at a bright red heat. In one experiment the first weighing corresponded to 76.92 per cent., and after 30 minutes further ignition this had fallen to 76.28 per cent.

It will be seen that the method as given for mono- and di-sodium phosphates fails in the presence of sodium carbonate. This not unlikely impurity can be readily detected and approximately estimated by slightly modifying the method already given. In the preliminary boiling with sulphuric acid any carbonates present will be converted into sulphates, thus using up some of the acid added, and so low results will be obtained; the full acidity corresponding to the phosphoric acid actually present will not be shown, but the silver consumed in the absence of halogens, etc., will correspond to the actual phosphoric acid content.

Modified method in presence of carbonates. The determination of acetic acid is carried out exactly as already described except that the titration is performed in a 150 c.c. calibrated flask. After noting the alkali consumed, 1 c.c. of normal sulphuric acid is added, the volume is adjusted to 150 c.c. and the contents well mixed. After an hour or so, the flask contents are filtered and the residual silver determined by Volhard's process on 100 c.c. of the filtrate. The results so obtained in all cases have been slightly high, but in the absence of carbonate, the results obtained by the alkali and silver titrations closely agree.

In the modified process alkali chlorides will obviously vitiate the silver, but not the baryta determination; as already mentioned under phosphoric acid, their presence is readily detected in the determination itself when a precipitate of silver chloride will be produced before the sodium acetate is added. This also holds true for the mono-sodium salt, but not for the disodium salt, unless a larger volume of sulphuric acid be added. In any case they can be readily determined by Volhard's method, and a correction applied.

Within limits the exact amount of silver nitrate added is immaterial, but with excessive silver the end point is obscured by precipitated silver hydroxide which does not completely redissolve. The quantities given have been found to work well, and of course the silver solution is not of necessity truly decinormal or even of known value unless carbonates are to be determined.

The author is at present extending the process to calcium phosphates.

The silver nitrate solutions used, when largely diluted, were neutral to phenolphthalein. The sodium acetate was the ordinary trihydrated salt; it was neutral to phenolphthalein.

The author desires to express his indebtedness to Messrs. Boots, Ltd., for the use of their laboratory, in which the work was carried out.

ADDENDUM.

In determining the factor of an approximately decinormal baryta solution the importance of freeing the acid used as standard from carbon dioxide cannot be too strictly insisted on. In the author's opinion this is a point that is often overlooked; his practice is to use *N/10* sulphuric acid for the purpose, boiling for a few minutes, cooling, and then proceeding as usual; the precipitated barium sulphate does not in any way mask the end point.

Baryta solutions often cause grave inconvenience by crystallizing in the burette owing to changing temperature—an effect specially noticeable in the winter months. This source of trouble and annoyance can be completely eliminated by using a mixed alkaline earth hydroxide solution. A saturated calcium hydroxide solution is prepared and the requisite amount of barium hydroxide, dissolved in a limited amount of boiling water, is then added. After standing a day the solution is decanted and is ready for use.

Scottish Section.

Meeting held at Glasgow on Tuesday, December 8th, 1908.

MR. D. J. PLAYFAIR IN THE CHAIR.

THE VALUE OF THE POLENSKE TEST IN THE ANALYSIS OF OILS AND FATS.

BY R. R. TATLOCK AND R. T. THOMSON.

This method of analysis was introduced by Polenske, whose object was to detect cocoanut oil, and if present, to determine its proportion, in butter. This was the primary intention, but it has also been attempted to utilise it, in conjunction with other constants, for the detection of animal fat, such as beef fat or lard, in butter. It is with these two points, and with a reference to the application of the method to other oils and fats that we shall deal in this paper. The method of procedure, and the precise form of apparatus employed, were exactly as described in Vol. II., page 853, of Lowkowitz's book on Oils and Fats. Of course we had in view, and were in agreement with Lowkowitz's dictum "that it is absolutely necessary to follow the process in all its minutest details, in order to obtain concordant results." There is one detail, however, which has not been generally referred to, and that is the exact amount, and the condition

as regards fineness, of the pumice employed in the process. In Lewkowitsch's volume it is stated that "some powdered pumice" is added, but Harris ("Analyst," Vol. XXXI., page 358) adopts 0.1 gm. as being nearly the amount recommended by Polenske, which was a quantity sufficient to cover the point of a pocket-knife blade. The results Harris gives are only with "three pieces of pumice-stone about 1.5 c.m." and "0.1 gm. of powdered pumice-stone," but still we have no idea of the degree of fineness of the powdered pumice. In the following table are stated results of two butters for insoluble volatile acids which we have obtained with pumice of varying degrees of fineness, and when employed in different quantities:—

	Insoluble volatile acids.	
	Butter A.	Butter B.
With two small lumps pumice	2.0	not done
" 0.1 gm. of No. 1 pumice powder	2.3	3.7
" 0.1 gm. of No. 2 pumice powder	2.5	4.1
" 0.5 gm. " " "	2.75	4.4
" 1.0 gm. " " "	2.9	not done.

The No. 1 pumice powder referred to above was ground so as to pass through a sieve with 100 meshes and remain on one with 400 meshes to the square inch, while No. 2 pumice powder was treated in the same way with sieves having 2500 and 3600 meshes, respectively, to the square inch. The soluble volatile acids were practically the same in each experiment, being 29 for butter A and 31 for butter B. In all further tests we have adopted 0.1 gm. of No. 2 pumice powder, as that is quite sufficient to prevent priming, and results can be obtained within 0.1 of each other. In our opinion, however, it is inadvisable to depend upon getting results closer than 0.2 to the truth, as there is a danger of obtaining higher results when the filtration of the alcohol takes longer than usual. Thus an exposure of five minutes may account for 0.1 c.c. of decinormal alkali. Taking everything into consideration, it is apparent that the Polenske method requires delicate handling, and above all it is necessary not to be dogmatic with regard to the bearing of slight differences from the maximum or minimum of insoluble volatile acids found in oils or fats.

Various observers have given the results of their examination of butters by the Polenske method, and have endeavoured to trace a more or less close relationship between the soluble and insoluble volatile acids, but we have not been so fortunate as Polenske himself, for example. That no close relationship existed was plain from the analysis of several hundreds of samples received mainly from sanitary inspectors, but in addition we examined 24 samples, of which 21 were extracted by ourselves from milks from different districts, including the counties of Aberdeen, Dumbarton, Perth, Lanark, and Ayr, while the other three were butters from reliable sources. In order to show the variations in this comparatively small number of butter fats, we may quote the following:—

TABLE I.

showing the variable nature of the relationship between the soluble and insoluble volatile acids in genuine butter fat.

	Soluble volatile acids.	Insoluble volatile acids.
Butter fat No. 1	30.0	2.1
do. No. 2	27.1	2.1
do. No. 3	25.2	2.1
do. No. 4	29.5	2.3
do. No. 5	29.4	4.2
do. No. 6	26.0	1.0
do. No. 7	26.5	2.3

It is scarcely necessary to do more than quote these, the variations being so striking, and especially so as they represent about one-third of the samples tested. It must

also be particularly borne in mind that these are good average specimens of butter fat, as five or six samples of milk (which were undoubtedly mixed milks to begin with) were mixed together for extraction of the fat. The other samples showed very considerable variations, but not so great as those quoted above. The general results are given in

TABLE II.

Number of samples.	Variations in soluble volatile acids.	Average soluble volatile acids.	Variations in insoluble volatile acids.	Average insoluble volatile acids.
6	30 —32.4	30.0	2.1—3.2	2.7
10	28.1—29.7	28.8	1.8—4.2	2.6
5	26.0—27.1	26.6	1.0—2.3	1.9
3	24.1—25.2	24.0	1.2—2.1	1.7

The average for the 24 samples was 28.5 of soluble and 2.4 of insoluble volatile acids.

We shall now deal with the effect of various proportions of cocoanut oil on the Polenske test for butter, the results of our experiments being stated in

TABLE III.

	Soluble volatile acids.	Insoluble volatile acids.
Butter alone	28.1	1.8
Cocoanut oil alone	7.5	18.0
Butter with 5% cocoanut oil ..	27.4	2.4
do. 10% do.	26.2	3.2
do. 20% do.	24.4	4.2
do. 30% do.	22.5	5.7
do. 40% do.	20.0	7.4

The cocoanut oil used in the above trials was extracted in the laboratory from the cocoanut, so that its genuineness is undoubted, and the same oil has been employed in the trials of which the results are recorded later. It is apparent from these results that the possibility of the detection of even 10 per cent. of cocoanut oil in a butter by the Polenske method is very doubtful. One of the genuine butters, extracted from milk in our laboratory, gave 29.4 of soluble and no less than 4.2 of insoluble volatile acids, and, reasoning from analogy, it is most probable that butter fats having about 25 of soluble and 3.5 of insoluble volatile acids may occur in that class of butter. In this connection it ought to be noted that comparatively few butters with low soluble volatile acids have been examined by the Polenske method, so that before giving a final decision on this matter, a much larger number of such butters ought to be analysed. Among the genuine butters we have one showing 25.2 of soluble and 2.1 of insoluble acids, which, on Polenske's original figures, might be regarded as containing at least 10 per cent. of cocoanut oil.

If we now examine the results recorded in Table III., we shall find that the soluble volatile acids in the mixtures are higher, and the insoluble volatile acids lower, than the average of those given by the butter and cocoanut oil separately. Take for example the mixture containing 20 per cent. of cocoanut oil. If we calculate simply on the basis of the butter and cocoanut oil results, we find that the average for soluble and insoluble volatile acids is 24.0 and 5.0 respectively, but the actual results are 24.4 and 4.2, and the same holds good for the other mixtures. It is evident, however, that this is not a true average, as the mixture operated upon was 4 grms. of butter and 1 gm. of cocoanut oil, and it is therefore necessary to know what these quantities will give separately. In making these tests the full quantity (20 grms.) of glycerin was employed, but the amount of caustic soda used was proportionate to the quantity of fat saponified. When the full amount (2 c.c.) of the caustic soda solution required for 5 grms. was employed for 1 gm. of the fat, the mixture

would not clear up, so that the point of complete saponification could not be determined satisfactorily. The following Table (IV.) gives the results obtained:—

TABLE IV.

	Soluble volatile acids.	Insoluble volatile acids.
4 grms. butter fat	22.6	1.7
1 grm. cocoanut oil	4.4	9.1
Mixture of 4 grms. butter with 1 grm. cocoanut oil	24.4	4.2

It will be here observed that there is a deficiency in the soluble volatile acids of 2.6 and in the insoluble of no less than 6.6, and this is most probably due to the retention of the less volatile acids by the non-volatile acids. Another point which calls for remark is with regard to the very high proportion, namely 4.4, of soluble volatile acids obtained from 1 grm. of cocoanut oil as compared with 7.5 from 5 grms. of the same oil. In order to throw some light on this apparent discrepancy, we saponified 1 grm. of butter and 1 grm. of cocoanut oil, respectively, distilled off the usual 110 c.c. which was titrated in the ordinary way, then added 110 c.c. of water to the distilling flask, distilled off 110 c.c. again, and repeated this four times, with the results given in Table V.

TABLE V.

	1 grm. butter.		1 grm. cocoanut oil.	
	Soluble volatile acids.	Insoluble volatile acids.	Soluble volatile acids.	Insoluble volatile acids.
1st distillation ...	6.2	1.0	4.4	9.1
2nd " ...	.6	.8	.7	5.0
3rd " ...	.2	.6	.2	4.3
4th " ...	.1	.6	.15	3.0
5th " ...	.05	.5	.10	2.7
6th " ...	.05	.5	.05	2.3

If we add together all the soluble volatile acids data 7.2 is obtained, and this is equal to 36 for total soluble volatile acids in 5 grms. As the 5 grm. quantity actually gave 28.1, it is plain that there is practically no discrepancy between the results, when the nature of the method is taken into account. With the 1 grm. of cocoanut oil the figure is 5.6, which is equal to 28 in 5 grms., whereas the actual figure from the latter quantity is only 7.5. This difference cannot be accounted for by the proportion of soluble volatile acids in the residual mixture in the distilling flask when 5 grms. are operated upon, but is manifestly due to the fact that the insoluble volatile acids are only insoluble under the conditions of the process. If these so-called insoluble volatile acids are not quite insoluble, but in reality slightly soluble, then the higher soluble volatile acids in the 1 grm. quantity are accounted for. That this is the case is proved by an experiment made with 5 grms. in the usual way, diluting the 110 c.c. distillate to 550 c.c. with water, shaking thoroughly, filtering and titrating 500 c.c. of the filtrate. Treated in this way the soluble volatile acids were 12 c.c. and the insoluble 13.7 c.c., and although this does not account for the whole difference in the soluble volatile acids, it clearly shows that the so-called insoluble volatile acids are not quite insoluble in water. If the distillate, after dilution, had been heated to boiling and then cooled it is certain that considerably more of the acids would have been dissolved, but it was not necessary to pursue the matter further.

A series of trials was next made with margarine containing various percentages of cocoanut oil, which was the same as was employed in the mixtures with butter, and the following results were obtained:—

TABLE VI.

	Soluble volatile acids.	Insoluble volatile acids.
Margarine alone	.4	.5
do. with 5% cocoanut oil	1.4	.7
do. do. 10% do.	2.2	1.3
do. do. 20% do.	3.0	2.6
do. do. 30% do.	5.0	3.0
do. do. 40% do.	5.8	5.7
do. do. 50% do.	6.5	7.6

Taking, as before, the margarine containing 20 per cent. of cocoanut oil, it is apparent that the soluble volatile acids are 0.8, and the insoluble volatile acids, 6.9, lower than would be expected from the mixture, thus showing, as in the case of butter, that these acids are retained to the extent stated, by the non-volatile fatty acids. Identical results were obtained with olive oil and beef fat when mixed with the cocoanut oil, after allowing for the slight differences in the composition of the two former oils. This shows that the almost liquid fatty acids of olive oil have quite as great an effect as the more solid fatty acids of beef fat, in retaining the volatile acids.

The question now arises as to the value which is to be attached to the Polenske numbers for the detection and determination of cocoanut oil in butter and in margarine. It must be admitted without qualification that the Polenske test is purely empirical, and it is hedged round by so many conditions that extreme caution must be exercised before coming to a decision as to the presence of cocoanut oil in a butter. It is all very well, as some analysts have done, to show what small proportions can be detected on the condition that one knows the exact composition of the butter which has been mixed with cocoanut oil. But unfortunately for the analyst, he is not in a position to know this, and therefore the Polenske test simply brings him, in some cases, to the doubtful point. This occurs, as far as our experience goes, when there is found a ratio of 9 of insoluble volatile acids to 100 of soluble volatile acids. In such cases resort must be had to the phytosteryl acetate test, and if this proves the presence of a vegetable oil, the probability will then be that it is cocoanut oil, although certainty is out of reach. Where a positive result is obtained, it will probably be safe to regard any excess of insoluble volatile acids as being due to cocoanut oil, and to state always the minimum proportions that may be present. We may add that so far as our trials have gone, we cannot place any reliance on the methods of detecting cocoanut oil which are dependent on silver, copper or baryta values.

As regards the detection and estimation of cocoanut oil in margarine, the Polenske number appears to be quite reliable within limits of say 5 per cent. Basing our calculations on the figures given in Table VI., we have tested margarines of known composition, and obtained results within 3 per cent. of the truth, where there was 35 per cent. of cocoanut oil present. In this connection there is a danger of the analyst reporting a margarine, say on a soluble volatile acids of 6.4, as containing 16 per cent. of butter, if he only determined the soluble volatile acids which seems to be all that he is legally required to do. In a sample of margarine tested by ourselves, the soluble volatile acids were 6.2, and the insoluble 6.6, but this we reported as genuine, as practically the whole of the former was due to cocoanut oil and not to butter. This is a pitfall which analysts must avoid, as they may otherwise wrongly accuse manufacturers of margarine of an infringement of the Sale of Food and Drugs Act, 1899.

As already stated, it has been attempted to utilise the Polenske number as a factor for the determination of animal fat, such as beef fat or lard, in butter. But for this purpose two principles must be established beyond doubt, and these are (1) that a greater proportion of insoluble volatile acids, as compared with the soluble acids, is to be found in butters when the latter acids are high than when they are low, and (2) that the other constants are so affected as to throw them out of their usual relationship to each other. The first of these propositions is founded upon insufficient data, and in our experience facts are

entirely against it, as is shown by the figures already referred to. It may be said that Butter No. 5 in Table I. does not support our contention, but this is an exceptional case, and its composition is probably due to the cow which produced it having been fed partly on cocoanut cake or meal. In fact, the only butters we have found to give such results were from the milk of cows which we had fed in this way, by a farmer, for experimental purposes. It is therefore to be expected that butters having low soluble volatile acids, say about 25, will have a corresponding proportion of the insoluble variety, if the cows received cocoanut meal as a portion of their food. The first proposition therefore remains unproved, or rather is practically disproved, and without it the second proposition is of little account. It is not necessary to enter into an elaborate argument on this point, but we may just put on record the following analysis of a genuine Scotch butter, which, according to the two propositions referred to, would be regarded as containing animal fat:—

Soluble volatile acids	25.2
Insoluble volatile acids	2.1
Saponification value	227.2
Zeiss at 40° C.	43.7
Specific gravity at 100° F.	.9113
Iodine value	42.71

It is sometimes inconvenient, as occasionally in cheese analysis, to obtain 5 grms. for the determination of the volatile acids, and it is therefore of interest to know the relationship between the results with this and smaller quantities of butter. With this object in view, tests were made with 1, 2.5 and 5 grms., respectively, of two samples of butter, the results being embodied in:—

TABLE VII.

	Soluble volatile acids.	Insoluble volatile acids.
5 grms. No. 1 butter fat	32.4	2.7
2.5 grms. do. do.	16.7	2.4
1 gm. do. do.	7.3	1.8
5 grms. No. 2 butter fat	28.1	1.8
2.5 grms. do. do.	14.7	1.5
1 gm. do. do.	6.2	1.1

These results show that the soluble volatile acids for 5 grms. of butter fat may be obtained approximately by multiplying the result from 2.5 grms. by 1.92, and that from 1 gm. by 4.5. Similarly the insoluble volatile acids for 5 grms. may be approximately obtained by multiplying the result from 2.5 grms. by 1.16, and that from 1 gm. by 1.6.

We have also been making trials with regard to the application of the Polenske test to other oils and fats, so far without finding it of any positive value, but we intend going further into the matter. In the meantime we append the results obtained with several oils and fats:—

TABLE VIII.

	Soluble volatile acids.	Insoluble volatile acids.
Beef fat	.35	.3
Lard	.35	.4
Cottonseed oil	.4	.4
Olive oil	.2	.2
Arachis oil	.4	.35
Cod liver oil	.5	.4
Dogfish liver oil	.3	.0
Porpoise oil	81.4	1.4
Japan wax	3.0	.0

Yorkshire Section.

Meeting held at Leeds on Monday, December 14th, 1908.

PROF. W. M. GARDNER, M.Sc., IN THE CHAIR.

THE FIFTH REPORT OF THE ROYAL COMMISSION ON SEWAGE DISPOSAL.

BY JOHN T. THOMPSON, M.Sc.

After ten years of deliberation the Commissioners have issued this Report, which deals chiefly with the relative merits of the methods available for the purification of the sewage of towns.

As a result of this delay in publication, the Report is very important as an official confirmation of facts that have been known for some years amongst those working on the sewage problem, but it contains little recent investigation. During the last two or three years, authorities who were compelled to carry out schemes may have spent considerable sums of public money, for example, on storm filters, whilst the Royal Commission held back information showing that these were costly and inefficient. At the same time one must bear in mind the difficulty of the task which the Commissioners have successfully carried out, namely, the collecting of a large mass of evidence and collating with it observations and experiments of their own. They have interpreted their terms of reference wisely and in broad outline the conclusions they have arrived at are excellent, consequently they deserve the gratitude of all engineers and chemists who are responsible for the sewage disposal and general sanitation of our towns. Some of the experiments and methods by which these conclusions were arrived at are open to criticism; the general arrangement of the Report is also somewhat confusing. There is very scanty reference to work done in other countries on this subject.

The following paragraph is noteworthy, and reveals the main principle underlying the whole report:—

"We are satisfied that it is practicable to purify the sewage of towns to any degree required, either by land treatment or by artificial filters, and that there is no essential difference between the two processes, for in each case the purification, so far as it is not mechanical, is chiefly effected by means of micro-organisms. The two main questions, therefore, to be considered in the case of a town proposing to adopt a system of sewage purification are, first, what degree of purification is required in the circumstances of that town and of the river or stream into which its liquid refuse is to be discharged; and, second, how the degree of purification required can, in the particular case, be most economically obtained."

The Commissioners realise that local circumstances vary to such an extent that "the necessary control cannot be provided by direct enactment which could be enforced by the ordinary courts," therefore, statutory provisions in regard to questions of pollution and public health must be of an elastic character. This important principle will be received with general satisfaction.

The Report will be extremely useful in the hands of those who have intimate expert knowledge of all the varied local factors which enter into the question of the sewage treatment of any place, but the danger of misuse by the inexperienced cannot be too strongly emphasised, for it may lead to an increase of the waste of public money which is continually going on, especially in small communities, by the employment of architects and surveyors who have no personal experience of sewage disposal.

PART I.—PRELIMINARY PROCESSES.

Par. 21.—Dr. McGowan's formula for "strength of sewage" seems too empirical, but as Appendix IV. is not yet available one cannot judge how it has been arrived at. It is significant that the Report says that "no statement can be made as to its precise accuracy."

Par. 24.—"Screening" might have been dealt with more fully. It is essential, not only where the sewage has to be pumped, but also where it is necessary to press the sludge.