In the case of ether for anaesthetic purposes, some pharmacopoeial tests are unnecessarily rigid; some are open to improvements; others should be replaced entirely by improved methods of detection; and several should be incorporated for detecting impurities not considered.

Furthermore, the demand for a good ether for anaesthesia involves difficulties inherent in the practical application of chemical methods by hospitals and physicians. As has been stated, anaesthetic ether should be provided in small containers, and it is impracticable, and should be unnecessary, to test the contents of each container before use; hence, reliance, as is the common practice now, must be placed on the experience and integrity of the manufacturer and on the uniformity of his product, for we have found that some ethers of the market vary not only in specific gravity and absolute ether content, but also in impurities, from time to time, yet they may comply with the requirements of the Pharmacopoeia.

Finally, in regard to anaesthetics in general, there is no doubt that, though even the most improved chemical and physical tests may be stated ever so clearly in print, and may properly serve to eliminate low-grade material, yet clinical experience must have the final word.

COLLEGE OF THE CITY OF NEW YORK,
1910.

THE ESTIMATION OF LIME AND POTASH IN THE ASH OF CEREALS.

By FIRMAN THOMPSON AND H. H. MORGAN, JR.

Received January 25, 1911.

In the course of some experimental work with cereals being carried on at this station the analysis of a large number of samples of the ash of corn and wheat grains was found to be necessary. During the prosecution of this work it was found that the A. O. A. C. methods, as given in *Bull. 107* of the Bureau of Chemistry, left much to be desired with respect to accuracy as well as rapidity of execution. Our efforts were then directed to removing these defects by modifications of these or other existing methods with a view to increasing the speed while not sacrificing any of the accuracy of the standard methods. We have met with such success in the estimation of potash and lime that we are prompted to publish them at this time, and while not claiming originality for the basic principle involved, we believe that our modifications are very vital to their rapid and accurate execution and trust that they may receive a thorough testing in laboratories other than our own.

CALCIUM OXIDE.

In the A. O. A. C. method for the determination of CaO in plant ash it is necessary to add sufficient FeCl_3 to combine with all of the P_2O_5 present, and the combined phosphates of iron and aluminum are then removed by precipitation with ammonia or an alkali acetate. The ash of cereal grains consists in great part of potassium phosphate, the P_2O_5 amounting to from 40 to 50 per cent. and the K_2O to about 30 per

cent. while the CaO is comparatively low. It is quite obvious that a sample containing sufficient CaO for accurate determination would require a large amount of FeCl_3 to combine with all of the P_2O_5 . In an ash containing 40 per cent. P_2O_5 and 2 per cent. CaO, which is about the average for wheat grains, the amount of iron required to combine with the P_2O_5 would be about fifteen times the amount of CaO and the resultant precipitate of ferric phosphate would amount to about forty times the amount of CaO present. Granting that none of the CaO would combine with the P_2O_5 , under such conditions the danger of mechanical loss by absorption is quite apparent to say nothing of the inconvenience of handling such a large precipitate and filtrate. That this danger is a very real one has been the experience of every chemist in this laboratory who has used the method, the results being uniformly low even after repeated re-solution and reprecipitation, as some of the following figures will show.

In devising a method for the determination of CaO which would be free from these objections, advantage was taken of the fact that calcium and magnesium phosphates are very easily soluble in dilute acetic acid while the phosphates of iron and aluminum are quite insoluble.

Method.—50 cc. of the hydrochloric acid solution of the ash, corresponding to 0.500 g., are heated to boiling, made slightly ammoniacal and then acidified again with acetic acid, adding about 10 cc. of 50 per cent. acetic acid in excess, making the total volume not more than 75 cc. The precipitate is boiled for a few minutes, allowed to settle and the combined phosphates of iron and aluminum filtered off and washed thoroughly with hot water. Since this precipitate is usually very small a reprecipitation has not been found necessary. About 10 cc. of saturated ammonium oxalate solution are added to the filtrate while still hot and the CaO determined in the usual way, either by ignition or titration with permanganate.

In order to test the method, known amounts of calcium carbonate and calcium phosphate and potash alum were dissolved and the CaO determined in the solution according to the above method with the following results:

CaO present. Gram.	CaO found. Gram.
0.13475	0.1353
0.13517	0.1348
	0.1345

When large amounts of Al_2O_3 are present a reprecipitation of the AlPO_4 will be necessary as is shown by the analysis of a solution containing 0.0273 g. Al_2O_3 and CaO in the form of chloride and phosphate.

CaO present. Gram.	CaO found with one precipi- tation of AlPO_4 . Gram.	CaO found with reprecipi- tation of AlPO_4 . Gram.
0.1460	0.1383	0.1462
0.1460	0.1329	0.1462

A comparison of the percentages of CaO found in a number of samples of the ash of wheat grains by the two methods is shown in the following table:

FeCl ₃ method.	Acetic acid method.
1.55	2.27
1.24	2.43
1.34	2.43
1.33	2.56
1.03	2.43
0.93	2.68
0.83	2.76
1.14	2.96
0.72	2.88
0.62	2.43
0.83	2.47
0.72	2.27

It will be noted that while the results are considerably higher by the acetic acid method they also show a greater uniformity, as might be expected with samples of such similar origin.

It should also be stated here that, although aluminum is commonly supposed to be a comparatively rare constituent of plant ash, we have found a quite appreciable amount in every sample of ash of wheat straw and grains examined by this method. A more complete account of its occurrence will be given later.

POTASSIUM OXIDE.

As is well known the standard method for the determination of K₂O, although quite accurate, is a very long and tedious one, involving as it does the removal of all other bases with the exception of sodium and also requiring, where a large number of determinations are to be made, a large stock of platinum chloride. For these reasons a shorter, more inexpensive method is very much to be desired and our attention was directed to the cobaltinitrite method of Adie and Wood¹ as possibly overcoming the faults mentioned. In working with this method it was found that the best results were secured by allowing the precipitate of potassium cobaltinitrite to crystallize out from the cold acetic acid solution by standing for at least twelve hours, decomposing the precipitate with an alkali, filtering off the cobaltic hydroxide thus formed, cooling the solution and titrating with acidified permanganate. A serious difficulty was met with in the fact that in using a fixed alkali for the decomposition it was almost impossible to effect a complete precipitation of the cobalt, which presumably passed the filter as soluble double salts. As the presence of any cobalt would vitiate the titration with permanganate, it seemed necessary that some other means for the decomposition of the cobaltinitrite should be found. Since the alkaline earths do not have the same tendency to form double salts with cobalt, a saturated solution of Ba(OH)₂ was substituted for the NaOH, and it was found that the precipitation was very complete and the barium sulphate formed in the subsequent treatment interfered in no way with a sharp end reaction. It was also found advisable to titrate by allowing the alkaline solution of the nitrite to run into the hot, acidified, standard permanganate. While this procedure has the disadvantage that the end point must be judged by the disappearance of the color, this is more than compensated for by the elimination of danger of loss of nitrous acid. With a little practice it has been found that it is quite easy to determine the end within one or two drops.

¹ Jour. Chem. Soc., 77, 1076-80 (1900).

Method.—The hydrochloric acid solution of 0.500 g. of ash is neutralized with NaOH and acidified again with acetic acid, adding 10 cc. of 50 per cent. acetic acid in excess. The solution is boiled and the precipitate of iron and aluminum phosphates filtered off and washed thoroughly with hot water. The filtrate is concentrated to about 75 cc. and allowed to cool. 25 cc. of cobaltinitrite solution, made according to the method of Adie and Wood, given below, are now added. Allow to stand over night at the room temperature and filter on an asbestos felt in a Gooch crucible, washing several times with cold, 10 per cent. acetic acid and finally once with cold water. The asbestos and precipitate are transferred with water to a small beaker, 40 cc. of a saturated Ba(OH)₂ solution added and heated to boiling when a copious precipitate of cobaltic hydroxide will be formed. Allow the precipitate to settle and while still hot filter into a 200 cc. graduated flask, washing thoroughly with hot water. Cool and make up to 200 cc.

Measure off 25 cc. of standard permanganate solution into a casserole, add 5 cc. of 1 : 1 H₂SO₄ and 150 cc. of hot water and run in the alkaline nitrite solution slowly from a burette until the color disappears.

On the basis of the formula K₂NaCo(NO₂)₆·H₂O, 1 cc. of tenth-normal permanganate is equivalent to 0.000785 g. K₂O. It has, however, been found to be more convenient to use a permanganate solution of such strength that 1 cc. is equivalent to 1 milligram of K₂O, which would be 0.1274 normal.

Sodium Cobaltinitrite Solution.—113 grams of cobalt acetate are dissolved in 400 cc. of 20 per cent. acetic acid. 220 grams of sodium nitrite are dissolved in 400 cc. of water. The two solutions are mixed, allowed to stand at the ordinary temperature for 24 hours, removing the nitric oxide formed by evacuation with a filter pump, and then filtered.

In order to test the method a stock solution was made by dissolving chemically pure K₂CO₃, MgSO₄ and Ca₃(PO₄)₂ in HCl and determining the K₂O by the platonic chloride method. 20 cc. of this solution gave the following amounts of K₂O in grams:

Calculated from K ₂ CO ₃ taken.	Found by platonic chloride method.
0.19856	0.1990
0.19856	0.1984

In testing the method 20 cc. of the stock solution were precipitated and the precipitate decomposed with 20 cc. of saturated Ba(OH)₂ solution, the filtrate made up to 250 cc. and 20 cc. taken for analysis. The titration was made by adding the permanganate from a burette after first making a preliminary titration to ascertain the approximate amount of permanganate required. This feature has been improved upon in the final procedure adopted. The following results were obtained:

K ₂ O present. Gram.	Tenth-normal KMnO ₄ , cc.	K ₂ O found. Gram.
0.015896	20.1	0.01578
0.015896	20.2	0.01586
0.015896	20.2	0.01586
0.015896	20.1	0.01578

Another determination was made using exactly the

same method but with 30 cc. of $\text{Ba}(\text{OH})_2$ solution to determine the effect of an excess of alkali, with the following results:

K_2O present. Gram.	Tenth-normal KMnO_4 , cc.	K_2O found. Gram.
0.015896	20.1	0.01578
0.015896	20.1	0.01578

The effect of different amounts of NaOH used for the decomposition of the cobaltinitrite precipitate is shown by the following results. The method used was exactly the same as before, but 50 cc. of the alkaline nitrite solution were used for the titration.

With 25 cc. of five per cent. NaOH .		
K_2O present. Gram.	Tenth-normal KMnO_4 , cc.	K_2O found. Gram.
0.03974	41.6	0.03266
0.03974	41.8	0.03281
0.03974	41.8	0.03281
With 50 cc. of five per cent. NaOH .		
0.03974	48.4	0.03799
0.03974	48.4	0.03799
0.03974	48.4	0.03799
With 75 cc. of five per cent. NaOH .		
0.03974	52.8	0.04145
0.03974	52.9	0.04153
0.03974	52.9	0.04153

With still larger amounts of NaOH the cobalt was taken into solution to such an extent that the blue color was quite perceptible in the filtrate and no determinations were made. It is quite evident from the above results that NaOH is very unsuitable as a precipitant of the cobalt and its use was therefore abandoned.

In order to determine the ratio of N_2O_3 to K_2O in the cobaltinitrite precipitate a solution of 0.500 g. of K_2CO_3 in HCl was precipitated as before and the precipitate decomposed with $\text{Ba}(\text{OH})_2$. The filtrate was made up to 200 cc. and N_2O_3 and K_2O determined in 25 cc. portions by titration with tenth-normal permanganate and precipitation with platinic chloride with the following results:

K_2O in original solution.	K_2O found.	N_2O_3 found.	Ratio found.	Ratio theor.
0.04189	0.04285	0.1027	0.4173	0.4130

AGRICULTURAL EXPERIMENT STATION,
DELAWARE COLLEGE.

TREATMENT OF CREAMERY SEWAGE BY THE SEPTIC TANK PROCESS.¹

By JAMES TEN BROECK BOWLES.²

Received January 20, 1911.

In the manufacture of butter and cheese there is a comparatively large amount of waste product, part of which can be returned to the farmer for stock-feeding, but a considerable amount cannot be so disposed of, and it is liable to create a nuisance when discharged into a stream or run upon land. That such a nuisance is created is shown by the following court decisions:

"The deposit of refuse from a creamery into the bed of a stream flowing through plaintiff's land and

¹ This research work was carried on while Chemist of Wisconsin State Hygienic Laboratory, University of Wisconsin.

² Sanitary Chemist, Cristobal, Canal Zone.

near his buildings, polluting the water and giving off noxious gases affecting the use and enjoyment of the plaintiff's property, is a nuisance."

"A creamery company will be enjoined from causing offensive waste matter to flow upon another's pasture to its injury." (Price vs. Oakfield Highland Creamery Co., 87 Wis., 536.)

The question of how creamery waste can be disposed of so as not to create a nuisance is therefore one of considerable importance, and although some work has been done on this subject in Europe and America the best method of treating such waste is a problem that still remains to be solved, and the following investigation was undertaken in the hope of throwing a little more light upon the subject.

Composition of Creamery Wastes.—Creamery waste consists of, pieces of cheese, butter, skim milk, whey, buttermilk, etc., diluted by washing from the floor, churns and pasteurizers. This mixture was found to be full of acid-producing bacteria which give the medium more or less acid reaction at first. After decomposition sets in and fermentation and putrefaction are well started, the medium gradually changes to a neutral rather than an acid one. It is plain to see that one is dealing with an undigested product, putrefaction not having yet started. In municipal sewage we have what is called a predigested product, that is, when the waste leaves the body it is full of putrefying bacteria, putrefaction and fermentation having already started. Thus when municipal sewage enters the septic tank decomposition has already set in and liquefaction goes on rapidly, while with creamery waste a long time elapses before putrefaction has even started.

The flow of creamery waste is not constant and for that reason is difficult to manage. In the mornings a large amount is received soon after churning, towards noon another large amount is received consisting largely of water used in cleaning up the floor where milk and cream are spilt. In the afternoon buttermilk and skim milk and washings are often turned into the tank.

Most of the cooling water has been cut off from the septic tank as the water is clean and there is no need of it going through the tank.

TABLE I.—CHEMICAL COMPOSITION OF CREAMERY SEWAGE FROM UNIVERSITY DAIRY AS COMPARED WITH OTHER CREAMERIES AND WITH MUNICIPAL SEWAGE.

	PARTS PER MILLION.			
	University dairy.	Elkhorn creamery.	Garnet creamery.	Madison City sewage.
Free ammonia.....	26.98	32.2	47.0	39.25
Alb. ammonia.....	38.55	43.8	105.5	6.0
Nitrates.....	0.0	0.0	0.0	0.0
Nitrites.....	0.0	0.0	0.0	0.0
Total solids.....	1702.8	2121.5	7575.0	896.4
Loss on ignition.....	169.3	1200.0	2216.0	201.0
Oxygen cons.....	396.2	311.6	261.0	79.6
Suspended matter.....	134.16	521.0	668.0	130.0
Putrescibility.....	7.9 hrs.	6 hrs.	4 hrs.	1/2 day

The free ammonia figures of the creamery sewage do not vary a great deal from those of the municipal sewage. The University Dairy sewage figures are much lower than those of the other creameries.