fluoric acid. If a single treatment by (*b*) does not effect complete decomposition, and this will be very often the case, the procedure that has thus far commended itself is the following: Having titrated (according to the directions in *Bull.* **305**, *U. S. Geol. Survey*, p. 142) with permanganate to the first more or less transient pink blush throughout the whole body of liquid, let settle, decant and wash once by decantation with water, rinse the residue into a small agate mortar, decant most of the water after again allowing to settle, grind the residue for a short time, under what water remains, transfer it by a stream of hot water to the large crucible from which it was taken and repeat the treatment by hydrofluoric and sulphuric acids used in smaller amounts than the first time. The final titration may be made in the crucible itself if this is of at least 80 cc. capacity and the bulk of liquid in it is small, after quickly diluting with cold water till the crucible is nearly full.

This manner of treatment has afforded thus far satisfactory results and is in most cases to be preferred to that given as (*a*). Not only are the double determinations of water avoided, but also the error that often arises from oxidation by long grinding under alcohol. The very short grinding under water of the small fraction of the original iron-bearing mineral or minerals that remains after the first treatment with hydrofluoric acid can not conceivably lead to any detectable error.

In conclusion a few remarks are in place regarding the comparative merits of the Pratt and Cooke methods of decomposing minerals for the ferrous iron determination. In *Bull.* **305**, p. 138, it was said that indications seemed to slightly favor the former method, and this expression is strengthened by the comparative data contained in the foregoing table on pp. 1124–26. Although in some instances (2, *b*, *e*, 5, *a*, *b*, *d*) the two methods appear to be of equal merit, in others (2, *a*, *f*) they differ materially in favor of that of Pratt, and in the rest there is evident a general tendency toward lower results by that of Cooke.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C., May 25th.

A NEW APPARATUS FOR THE QUANTITATIVE DISTILLATION OF AMMONIA.

BY PHILIP ADOLPH KOBER.

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In *Z. physiol. Chem.*, **37**, 161, Folin describes a new method for the determination of free ammonia in physiological solutions, or solutions which decompose easily when subjected to any temperature above 50°. Essentially, his method consists of passing a current of air through the solution whose ammonia is to be determined and through a standard acid solution, which is then titrated back with a standard alkali solution.

For this purpose there is required a vertical cylinder, 45 cm. high and 5 cm. in diameter for the solution to be determined, and another absorption cylinder for the standard acid (shown in the sketch below). The addition of sodium chloride to decrease the solubility of the ammonia and the addition of 5–10 cc. of toluene or petroleum to decrease the foaming are recommended.

Since this method requires practically no attention when once started, it can be used simultaneously on a large number of determinations and gives accurate results, it seemed desirable to me to try the application of this idea to other determinations, *e. g.*, nitrogen determinations the Kjeldahl process, urea determinations according to Folin and according to Mörner-Sjöqvist.

The first attempt when a Kjeldahl determination was subjected to an air current distillation, under usual conditions, *i. e.*, with 200–300 cc. of water in the flask, resulted in a failure. The solution was much too voluminous, too dilute, and too cold. The next step, using very little water with the sulphuric acid, showed that the alkali could not be added in the usual way, and that a special arrangement was necessary in order that no ammonia should be lost during the addition of the saturated caustic soda. After considerable experimentation it was found that enough water must be added so that the sulphuric acid, when almost neutralized by the alkali, would heat the resulting solution to boiling by its own heat of neutralization. As this heat was generated so quickly it was necessary to use considerable skill and judgment in adding the alkali by means of a dropping funnel.

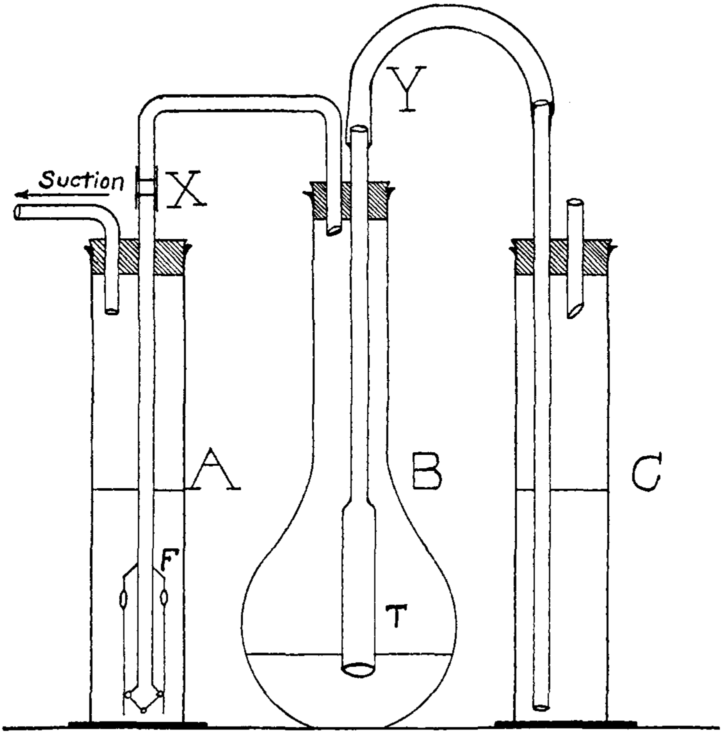
The use of another cylinder, which automatically added the alkali as the pressure of the Kjeldahl flask permitted, proved to be very successful.

The widened tube "T" in the Kjeldahl flask "B" was found necessary in order to prevent sodium sulphate from closing off the air, by crystallization in the tube. Experience has shown that this tube must be at least 12.5 mm. in diameter. Results on some 400 determinations have shown that the method will give all the accuracy of the old distillation process with condenser and gas, that it is as easily handled, and requires no attention once the suction is started. It is especially adapted in distilling off ammonia where heavy precipitates and solutions that foam considerably, are used.

Directions.—After digesting the substance in the usual way, allow the melt to cool sufficiently to add distilled water comfortably and after adding a definite amount of water (95 cc. to 25 cc. of concentrated sulphuric acid; 40 cc. to 10 cc. of concentrated sulphuric acid) cool to room temperature.

Set up the flask as in the sketch, having the standard acid in the cylinder

"A" with a Folin tube "F;" the melt and the required water, at room temperature, in the Kjeldahl flask "B;" and the saturated caustic soda necessary to make the solution in "B" decidedly alkaline, in cylinder "C." Start suction at such a rate that it takes about 1–2 minutes to add the alkali, while at the same time shaking the Kjeldahl flask for a few seconds, just long enough to insure thorough mixing of the acid and the alkali, or in other words to prevent the caustic soda from forming a layer at the bottom of the flask, which might act too vigorously when once the action has begun. The flask "C" can be safely disconnected after all the alkali has been drawn from it, and the apparatus connected to a supply of ammonia-free air, provided that the rate of suction has been increased as much as is possible without losing some of the acid in the cylinder "A," by excessive foaming. It is hardly necessary to mention the precaution to continue the suction as long as the contents of the Kjeldahl flask are above room temperature. It is well to avoid caustic soda that contains too much carbonate, as this at the neutral point might cause the contents to boil over, owing to the excessive gas formation.



Tube "T" should not extend more than 1 cm. below the level of the solution.

Caustic soda made by the electrolytic process is quite free from carbonate and is for this purpose the best and the cheapest.

The distillation is completed within an hour, but the continuation of the suction until it is convenient to titrate, will have no effect on the determination.

In addition to the values given in the last part of this paper, the following made by Dr. Leo Kristeller, of the Montefiore Home Laboratory, will suffice to show that the method gives very satisfactory results even on first trial.

cc. NH_4Cl.	Old distillation.	New method.
8.00	10.10	10.00
9.00	11.40	..
8.00	..	10.15
5.75	...	7.30
In terms of		
1.00 cc.	1.26	1.25
	1.27	1.27
		1.27
Average,	1.265	1.263

The results are expressed in terms of N/10 ammonia.

Urea Determinations.—In the *Z. physiol. Chem.*, **30**, 504 and **37**, 333, Folin describes a new method for the estimation of urea, which consists essentially in digesting urine with 20 grams of $MgCl_2$ in an acid solution at 160–170° for one and a half hours, distilling off the ammonia in a Kjeldahl flask after the addition of about 20 cc. of 15 per cent. caustic soda, and then titrating back a standard acid solution of the distillate. This method gives satisfactory results and with certain reservations (on which we hope to report soon) can be safely used for urinary analysis.

For the distillation of Folin urea determinations this suction apparatus will also give good results, if a few precautions are taken. In a separate paper the reasons for some of these precautions will be fully discussed, but sufficient for actual determinations are the following:

(1) Transfer the magnesium chloride solution to a Kjeldahl flask, so that the resulting solution will not be over 50 cc., disregarding the solution in the Folin condenser.

(2) Add an excess of caustic soda, *i. e.*, more than enough to completely precipitate the magnesium chloride.

(3) Shake the Kjeldahl flask after all the alkali has been added, until all of the lumps of magnesium hydroxide have disappeared.

(4) Continue the suction for about 2 hours.

Folin Ammonia Determination.—This suction apparatus can be conveniently used for Folin's ammonia determination by substituting the Kjeldahl flask for the tall cylinder, if 5–10 cc. of saturated potassium carbonate are added by means of a pipette at "Y" instead of adding 1 gram of dry carbonate in the usual way.

The following figures are taken from our laboratory note-book, on metabolism. They are expressed in terms of $N/10$ ammonia.

	cc. solution taken.	Specimen A.			Specimen B.			Specimen C.	
Free NH_3	25	0.65	0.70	...	0.60	0.60	...	9.00	9.05
Gross urea	10	19.60	19.65	19.60	43.30	43.20	43.20	33.80	33.75
Total nitrogen...	10	20.50	20.50	20.60	44.30	44.30	44.10	35.60	35.70

My thanks are due to Dr. P. A. Levene and to Dr. G. W. Heimrod for their advice and encouragement in developing this method and to Mr. Wm. W. Crawford for assistance in preparing this paper for publication.

ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH,
NEW YORK CITY, April 20, 1908.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 154.]

4-AMINO-*o*-PHTHALIC ACID AND SOME OF ITS DERIVATIVES.[1]

BY MARSTON TAYLOR BOGERT AND ROEMER REX RENSHAW.

Received April 23, 1908.

In a previous paper,[2] the authors described dimethyl 4-aminophthalate and certain of its acyl derivatives. The present article deals with the free acid, its salts, and various other derivatives or experiments not reported in the earlier paper.

The literature on the subject of the free 4-amino-*o*-phthalic acid is meagre and confusing.

Miller[3] subjected 4-nitrophthalic acid to the action of tin and hydrochloric acid. The reduction proceeded smoothly, no carbon dioxide was evolved, and presumably the double salt of tin chloride and aminophthalate was formed. This double tin salt remained in solution and could not be separated by freezing (differing in this respect from the corresponding 3-aminophthalic compound). When the tin was precipitated from this solution by hydrogen sulphide and the filtrate from the tin sulphide concentrated, only the hydrochloride of *m*-aminobenzoic acid remained.

Bodé[4] reduced 4-nitrophthalic acid to the double zinc acetate and aminophthalate by the Bernthsen and Semper method[5] but found the yield inferior to that obtained from the 3-nitro acid. These double zinc acetates and aminophthalates can be diazotized direct and thus used for the preparation of other substituted phthalic acids or for direct coupling. Apparently, he did not attempt the isolation of the free aminophthalic acid.

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[1] Read at the New York meeting of the Society, Dec. 28, 1906.

[2] THIS JOURNAL, **28**, 617 (1906).

[3] *Ber.*, **11**, 992 (1878); *Ann.*, **208**, 223 (1881).

[4] Inaug. Dissertat., Heidelberg (1898).

[5] *Ber.*, **19**, 164 (1886).