If the indicator be left long in a solution which is even slightly alkaline, as indicated by a reddish color in the solution, or the color of more intense alkalinity, decomposition occurs and the color fades. This destruction occurs too slowly however to cause any trouble. It should be noted that the color varies greatly with the temperature, thus the purple color of high alkalinity may be converted into almost pure blue by warming.

With the aid of this substance it is, accordingly, possible to estimate the concentration of ionized hydrogen and hydroxyl in an unknown solution rapidly and accurately to about one power of ten between hundredth normal concentration of ionized hydrogen and hundredth normal concentration of ionized hydroxyl. In all, eleven different intensities of reaction may be thus differentiated. To this end it is necessary to prepare a series of standard solutions corresponding to those above described. The process then consists merely in the matching and interpolation of colors.

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THE QUANTITATIVE DISTILLATION OF AMMONIA BY AERATION.

(SECOND PAPER.)

BY PHILIP ADOLPH KOBER.

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In a previous paper[1] a new apparatus for the quantitative distillation of ammonia was described, which, since, has been tried in several laboratories. In three cases the results have been published and it is the object of this paper to summarize, and to discuss, the criticisms that have been made, and to record the experience accumulated during the past two years.

In a recent article[2] J. Sebelien in conjunction with A. Brynildsen and O. Haavardsholm developed and reported independently the identical process devised by the writer over a year before.

They proved by many experiments that ammonia can be liberated from solutions quantitatively, even if a slow stream of air and a large volume of solution (200 cc.) are employed. They concluded that the aeration procedure has many advantages over the old method and eliminates several sources of error.

Davis[3] found that the method, using an ordinary water pump, gave good results provided the flask was insulated with asbestos. He also makes the statement that if 30 cc. of acid are digested, the flask would require additional heat during distillation.

[1] THIS JOURNAL, **30**, 1131 (1908).

[2] Read by J. Sebelien in the Section for Analytical Chemistry, Congress of Applied Chemistry, June, 1909, printed in *Chemiker-Zeitung*, **1909**, No. 87.

[3] THIS JOURNAL, **31**, 56 (1909).

An asbestos insulator can hardly be of any service in keeping the contents of a flask warm, while a rapid stream of cool air is passing through it. Doubtless, the good results recorded were not dependent on the use of asbestos. That 30 cc. of sulphuric acid can be handled in the process is shown by the figures of J. Sebelien and collaborators. Gill and Grindley have quite recently reported[1] favorably on the process in application to many substances but concluded that the elements magnesium and phosphorus when present together in relatively large amounts cause a slight retention (3.2 per cent.). This conclusion, based on the analysis of cottonseed, wheat bran, and magnesium ammonium phosphate, involves the assumption that magnesium ammonium phosphate, supposedly formed during the digestion, somehow or another, in the strongly alkaline solution holds back the ammonia.

According to modern views of chemistry concerning ions and their concentration it is hard to conceive of magnesium, in a large excess of sodium hydroxide, being in solution at all. In their paper they refer to Steel and Gies[2] having proven it impossible to liberate ammonia quantitatively when the urine contained magnesium and sodium carbonate, but omit to mention that these authors settled the point in question, namely, that sodium hydroxide liberates quantitatively ammonia from magnesium ammonium phosphate. They also refer to a previous paper of mine on the influence of magnesium and calcium salts in retarding ammonia distillation, but surely calcium and magnesium salts cannot come into consideration in an excess of sodium hydroxide.

The figures given by Gill and Grindley record a retention of 3.2 per cent. of the ammonia in magnesium ammonium phosphate, which means that 96.8 per cent. of the ammonia in magnesium ammonium phosphate was distilled and determinable. Taking this value and calculating the amount of ammonia that would be retained from the data given in regard to the content of magnesium and phosphorus in food, etc., we would have in the most unfavorable case a decrease of 0.02 in the per cent. of nitrogen. In order, however, to leave no doubt as to the accuracy of the preceding theoretical discussion the following comparisons[3] were made. A few of them will suffice as they have, apparently, but one interpretation.

	Old distillation with heat, etc.	Aeration after the addition of 5 grams $MgHPO_4$.
Urine No. 1	11.50	11.55
Urine No. 2	11.60	11.60
Urine No. 3	17.35	17.37

The results are expressed in terms of $n/4$ ammonia after making suitable blank determinations, using all the reagents. This amount of magnesium

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[1] THIS JOURNAL, **31**, 1249.

[2] *J. Biol. Chem.*, **5**, 71 (1908).

[3] These distillations were made in the laboratory of Dr. C. A. Herter.

phosphate, being practically ten times more than is sufficient to combine with all the ammonia, does not show the slightest retention.

The statement by the authors that it was necessary to keep the solution warm, gives us a key to the source of error, *e. g.*, insufficient excess of alkali.

Experience with the Method.

Since the first publication nearly two years ago the writer has gained considerable experience with the method in the analysis of foods and allied products, particularly in distilling large numbers of solutions in series, using but a single ordinary water pump. The time required for complete distillation of ammonia from the long-necked Kjeldahl flask (of 500 cc. capacity) is about two hours, whereas with a large wash bottle (of 700 cc. capacity) the time required is three hours. The time required for aeration varies, as Folin pointed out, with the temperature, alkalinity, volume, and height of the solution.

Saturated alkali in large excess should always be used (about 40 per cent. more than necessary to neutralize the acid). The application of an open-screw pinchcock has made it possible to control the aeration process completely in all respects. Before the addition of the concentrated alkali, this screw pinchcock is applied (at X in the original illustration) at the junction between the Kjeldahl flask and the absorption bottle and the rate of aeration reduced (about 100 bubbles a minute). As the alkali enters the Kjeldahl flask it is shaken in a rotatory fashion until all of the alkali has been drawn over. By decreasing the aeration in this manner it was possible with perfect ease to start a distillation while the contents were still quite hot.

If the aeration is closed off completely at the junction indicated above, the absorption bottle in question can easily be temporarily removed or reinserted, for the purpose of adding more acid, titrating, etc. To avoid accidents a safety valve should be inserted in the system, between the source of vacuum and the first absorption bottle, so that the Kjeldahl flasks are not exposed to too great a vacuum.

Summary of Directions.

The melt in the Kjeldahl flask after digestion is diluted with four parts, by volume, of ammonia-free water and allowed to cool to about room temperature. After connecting to the absorption bottle and reducing the rate of aeration the alkali is added, shaking the Kjeldahl flask at the same time in a rotatory fashion. Should there be any serious back pressure in adding the alkali the rate of aeration is too rapid, and therefore should be reduced to a more suitable rate. The adding cylinder (see first paper) is then disconnected, and the second distillation attached, etc.