

The $N/10$ factor indicated by the Barium Sulphate method was—1.00:75

3. In view of the fact that the barium sulphate method is the only one recognized by the Association of Official Agricultural Chemists, is accurate and easily applied, it should be the one official in the United States Pharmacopœia.

RESEARCH AND ANALYTICAL LABORATORY,
LOUIS K. LIGGETT Co.,
NEW YORK.

THE USE OF BARIUM OXIDE FOR ALCOHOL DEHYDRATION.*

BY B. L. MEREDITH AND W. G. CHRISTIANSEN.

The purpose of this work was to investigate the claim of Smith (1) that BaO may be considered a commercial possibility for the dehydration of alcohol. There are many commercial operations in which an alcohol of 97.5% (by weight) may be used, and it is from the near-absolute angle that we have approached the problem of dehydration. The author cited above refluxed a liter of 93% alcohol (by weight) with 500 Gm. of BaO for two hours and obtained a product, in one instance, as high as 99.61%. He records no assay for the BaO.

In the following experiments the 190-proof alcohol assayed 91.90% (by weight) by the specific gravity method. The BaO, which was obtained from the same company (2) which supplied the above experimenter, was not assayed. Instead of tabulating our results, the successive experiments are recorded, because major changes were made in experimental procedure and because it is desirable to comment on each experiment in turn.

EXPERIMENTAL PART.

Experiment A.—One liter of alcohol was refluxed with 500 Gm. BaO for 2 hours at a bath temperature of 83–85° C. The alcohol was then distilled off, using a Hempel trap, and 750 cc. distillate was obtained. An hour and a half was consumed in the distillation, and the bath temperature at the end had been brought to 96° C. Vacuum was then applied and a second fraction of 75 cc. was obtained.

TABLE I.

	Yield, cc.	Sp. gr. at 20° C.	Per cent alcohol by weight.
First fraction	750	0.79316	98.75
Second fraction	75	0.79424	98.39

The liter of alcohol contained 65.8 Gm. of water, and to hydrate 500 Gm. of 95% BaO only 56.1 Gm. of water is required. However, Ba(OH)₂ is known to hold an extra molecule of water of crystallization very tenaciously, and its further dehydrating power was expected to operate in our favor. Assuming that, at normal pressure, and at the boiling point of alcohol, the entire liter of alcohol had been dehydrated to the extent of the first 750-cc. fraction, the BaO had removed only 56.9 Gm. of water. This does not indicate the formation of much Ba(OH)₂.H₂O. These indications, however, in all probability do not conform with the facts, since Ba(OH)₂ paradoxically possesses a greater affinity for water than BaO. Hence

* Scientific Section, A. P. H. A., Baltimore meeting, 1930.

an equilibrium was reached between the chief components: BaO, Ba(OH)₂, Ba(OH)₂.H₂O, C₂H₅OH and C₂H₅OH.H₂O. We believed that the dehydrating power of Ba(OH)₂ would become operative when smaller proportions of BaO were used, and further experiments were carried out.

Experiment B.—This experiment was carried out in exactly the same manner as *Experiment A* but only half (250 Gm.) the weight of BaO was used to 1 liter of alcohol.

TABLE II.

	Yield, cc.	Sp. gr. at 20° C.	Per cent alcohol.
First fraction	900	0.79675	97.57
Second fraction	38	Sp. gr. not determined. . . .	

If no Ba(OH)₂.H₂O had been formed, only 28 Gm. of water would have been removed, but we find that the BaO had taken up 47.2 Gm. indicating that the Ba(OH)₂ was hydrated to Ba(OH)₂.H₂O to the extent of 68.6%. The excellent yield obtained constitutes a recovery of 97.8% of the C₂H₅OH, as against 86.5% in Experiment A.

Experiment C.—Again the BaO was halved, but this time after refluxing the liter of alcohol with 125 Gm. BaO, the reaction flask was allowed to cool (5½ hours) and the alcohol filtered off from the hydrated BaO before distilling. After this had been distilled, the residue which had been filtered off was reintroduced into the first flask and the remainder of the alcohol distilled off under vacuum.

TABLE III.

	Yield, cc.	Sp. gr. at 20° C.	Per cent alcohol.
First fraction	810	0.80512	94.66
Second fraction	60	0.80055	96.25

In this experiment 664 Gm. C₂H₅OH obtained constitutes a recovery of 88.9% of the original C₂H₅OH content of the aqueous alcohol used. The water extracted calculates to 23.7 Gm. which means a hydration of 69.3% of the Ba(OH)₂ to Ba(OH)₂.H₂O. This is practically the same hydration obtained in Experiment B, and we are therefore reasonably safe in concluding that under these conditions there is formed no Ba(OH)₂.3H₂O or any hydrate higher than the mono.

Experiment D.—Distillation under vacuum, at a low temperature seemed to produce better results, hence a second experiment using only 125 Gm. BaO was tried. The alcohol and the BaO (this time finely ground) were refluxed together for three hours, then cooled to 40° C. and distilled under vacuum, the receiver being chilled with ice and salt. The vacuum was approximately 28.5 inches, and toward the end of the distillation the temperature of the bath had been raised to 65° C.

Yield 750 cc., sp. gr. 0.80411, corresponding to an alcohol content of 95.02%.

From these figures it is found that a recovery of 573 Gm. C₂H₅OH was obtained, which is a yield of 76.7%. Calculation also reveals that the water held by the BaO (based, as before, on a 100% recovery) was 26.6 Gm. which would indicate a 90% formation of Ba(OH)₂.H₂O. This greater efficiency of the BaO is more than offset by the inefficiency of condensation of the distillate.

Experiment E.—Since the dry barium hydroxide residue had caked to some extent in all the preceding experiments, mechanical agitation was now used in

duplicating *Experiment B*, which was the most promising of the first four. Two hundred and fifty grams BaO were ground to pass a 16-mesh sieve and were added to 1 liter of the same lot of alcohol used in all the foregoing work. A mechanical agitator with mercury seal and side-neck for reflux (and subsequently for distillation condenser) was used and agitation was continued not only for the two hours of refluxing, but during distillation until the residue became pasty. The last 26 cc. of distillate was taken, using vacuum, after the removal of the agitator.

TABLE IV.

	Yield, cc.	Sp. gr. at 20° C.	Per cent alcohol.
First fraction	918	0.79616	97.75
Second fraction	26	Sp. gr. not determined . . .	

This means that out of a possible 747 Gm. C₂H₅OH were obtained 734.6 Gm., a yield of 98.6%. Also, the same calculations used on the other four experiments shows the BaO to have combined with 48.6 Gm. of water, or that 73.6% of the Ba(OH)₂ was hydrated to Ba(OH)₂.H₂O.

CONCLUSIONS.

An "absolute" alcohol of 97.5% or over may be obtained by using 250 Gm. of commercial BaO per liter of alcohol as low as 91.9% ethyl alcohol (by weight).

A yield of 94% by volume, which is an actual yield of 98% of the C₂H₅OH originally present, may be obtained.

Using less than 250 Gm. BaO per liter gives a product assaying less than 97.5%, while more than 250 Gm. reduces the yield.

Vacuum distillation increases the efficiency of the BaO but greatly decreases the yield. It should, however, be applied to the residue after the regular distillation (and after cooling somewhat), since the yield may be increased 3-4% thereby.

REFERENCES.

- (1) *Ind. & Eng. Chem., Analytical Ed.*, Vol. 1, No. 2, page 72.
- (2) J. H. R. Products Co., O. Willoughby.

RESEARCH DEPARTMENT, CHEMICAL AND PHARMACEUTICAL LABORATORIES,
E. R. SQUIBB & SONS, BROOKLYN, N. Y.

OLIVE OIL—FLUORESCENCE IN ULTRAVIOLET LIGHT.*

BY J. LEWIS DEUBLE AND R. E. SCHOETZOW.

A number of writers¹ have discussed the fluorescence of various types of olive oil when viewed under the ultraviolet light. Some months ago we had an opportunity to examine some samples of olive oil which we believe to be authentic. Our results corroborating those already published may be of interest. The samples examined were:

- I. Pure Virgin Italian Olive Oil.
- II. Pure Virgin Spanish Olive Oil.
- III. Pure Virgin Tunisian Olive Oil.

(All three oils are of first pressing and are unfiltered.)

* Scientific Section, A. Ph. A., Rapid City meeting, 1929.

¹ See Bibliography at end of article.