

If inspection indicates that every chest of opium in a shipment is quite uniform it is advisable to set aside one chest out of every five for the purpose of sampling. According to this procedure one chest out of a shipment of five chests would be withdrawn for sampling, two out of a shipment of ten, etc., etc.

A quarter section is cut from each piece of opium contained in the sample chest. Ordinarily opium is packed in chests of 150 lbs. or 160 lbs., and the sample will amount to approximately 40 lbs., which is then thoroughly mixed in a Werner & Pfleiderer mechanically driven dough-mixer until a completely uniform mass is produced. As considerable heat, involving loss of moisture, is developed during the mixing, allowance should be made for such loss.

Samples for analyses may then be drawn from the homogeneous mass. These should be at once packed in hermetically sealed tins or bottles, thus precluding a further loss of moisture.

In order to check this method of sampling I have at intervals carried out the above procedure and then have dried the entire lot of opium in question, milled and mixed it and have compared the results (after allowing for the loss of moisture in drying) of the tests with the tests of the original "Gum." The tests were remarkably uniform, and confirm, to my mind, the satisfactory results of the above procedure.

Occasionally lots of opium have been received, which in addition to not being "graded" have been so "crumbly" through age or other reasons, that proper sampling of the drug in its natural condition was precluded. Under such circumstances the entire lot was dried, milled and mixed for the purpose of obtaining uniform samples.

Persian Opium from reliable shippers, packed in bricks, wrapped in waxed paper, is remarkably uniform. It may be sampled by perforating each piece in a case, one case out of five of the same mark, by means of a cork borer of about $\frac{1}{4}$ -inch diameter. The samples thus obtained must, of course, be thoroughly mixed (by hand or in a small power mixer) under the same precautions described earlier in this article, before they are sent to the laboratory for test.

THE STANDARDIZATION OF VOLUMETRIC SULPHURIC ACID SOLUTION.*

BY JOSEPH L. MAYER.

On page 508, the U. S. Pharmacopœia, after stating how volumetric sulphuric acid solution should be prepared says "ascertain its exact strength by titration against freshly standardized normal sodium hydroxide, methyl orange T. S. being used as indicator. The strength may also be ascertained and adjusted after titration against an accurately weighed amount of reagent anhydrous sodium carbonate. It may also be standardized gravimetrically by precipitation and weighing as barium sulphate."

On page 505, the U. S. Pharmacopœia, directs that the sodium hydroxide solution which is employed to standardize the sulphuric acid be standardized as follows: "Determine its strength by titration against a hot solution of an accurately weighed quantity of reagent potassium bitartrate."

* Read before the New York State Pharmaceutical Association meeting, June 1931.

The U. S. Pharmacopœia without directing how these methods should be applied standardizes the sulphuric acid by the three following methods:

1. Sodium hydroxide solution which has been standardized against potassium bitartrate.
2. Anhydrous sodium carbonate.
3. Precipitation as barium sulphate.

These three methods will, respectively, be referred to as the "potassium bitartrate method" the "sodium carbonate method" and the "barium sulphate method."

In order to determine how nearly the results by these methods agreed I made the following experiments, employing a sample of what was approximately $N/10$ sulphuric acid.

(A) Reagent potassium bitartrate was dried in a Freas electric oven at 120 degrees until the weight was constant, after which weighed quantities were dissolved in boiling water and these solutions employed to standardize the sodium hydroxide solution, using phenolphthalein indicator. The sodium hydroxide was freshly prepared from a saturated solution of sodium hydroxide which was free from CO_2 .

This freshly prepared standardized sodium hydroxide solution was used in the presence of methyl orange indicator to standardize the sulphuric acid solution which by this method indicated a $N/10$ factor of 0.998760.

(B) Reagent anhydrous sodium carbonate was dried in a Freas electric oven at 105 degrees until the weight was constant, after which a definite amount was weighed in a 100-cc. flask with a glass stopper, and enough water added to measure 100 cc. Ten-cc. portions of the solution were placed in Erlenmeyer flasks, a drop of methyl orange added to each and the sulphuric acid being standardized slowly added with constant stirring until the end reaction was reached. The $N/10$ factor was 1.00135.

(C) Fifty-cc. portions of the acid were measured into 250-cc. beakers, about 50 cc. of H_2O added, the material heated to boiling on the hot plate and an excess of 10% barium chloride solution added from a 10-cc. pipette, drop by drop, after which the material was heated to boiling for five minutes, placed on the steam-bath for five hours, the supernatant liquid poured through a Gooch crucible the precipitate transferred with 30 cc. of boiling water and the crucible and contents washed with boiling water, until free from chlorides, dried, ignited and weighed. From the weight of BaSO_4 the $N/10$ factor of the acid was calculated and found to be 1.00175.

The simplest method of standardization of volumetric sulphuric acid solution is precipitation as barium sulphate and since "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists" only recognizes it, the U. S. Pharmacopœia should do likewise and in the interest of uniformity abandon the others.

SUMMARY.

1. Sulphuric acid volumetric solution was standardized by the three methods official in the U. S. Pharmacopœia.
2. The $N/10$ factor indicated by the Potassium Bitartrate method was—0.998760.

The $N/10$ factor indicated by the Anhydrous Sodium Carbonate method was—1.00135.

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.

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THE USE OF BARIUM OXIDE FOR ALCOHOL DEHYDRATION.*

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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.