Whether or not this method is a true index to its quality, or whether an assay for pure filicic acid should be devised, the writer is not prepared to state, but it would seem desirable to have a standard for this preparation, in order to secure a more reliable product.

ASSAY OF OPIUM AND ITS PREPARATIONS.

The present U. S. P. directions for assay read: Collect morphine crystals on a pledget of cotton in the neck of funnel.

In many cases the crystals obtained are so small that they pass through cotton and are lost, and the results vitiated.

A substitute for cotton is offered in the form of an Alundum or Gooch crucible; with the aid of suction either will retain all of the precipitate. By this method the morphine crystals may be weighed, thus providing a check on the volumetric titration.

A porous crucible of this type is even more suitable than filter paper, which is liable to rupture if suction is used. This is quite necessary when a slower filtering medium than cotton is used, else the rapid evaporation of ether leaves behind some of ether-soluble alkaloids, which would, of course, give higher results.

ABSTRACT OF DISCUSSION.

J. P. Snyder has used the method of Lyman F. Kebler for assaying Aromatic Spirit of Ammonia, with success. (See p. 615, July, 1917, THIS JOURNAL.—Editor.)

L. E. Warren regretted that the Pharmacopoeia gave the melting point for any of the alkaloids, because this is not definite for any of them.

Responding to a question of Arno Viehoever relative to Mr. Berg's view relative to assay of opium, the latter stated that his views coincided with those of H. W. Jones. (See January, 1920, JOURNAL A. PH. A., p. 51.) The use of filter paper is not satisfactory, owing to the slow filtration, he said. L. F. Kebler opposed the use of oak sawdust, he had found sand much more satisfactory. He contended that Mr. Berg's criticism of the assay of copaiba was not well taken, that it was almost impossible to obtain pure copaiba at present.

E. H. Grant stated that there was now very little, if any, copaiba imported, which would meet all the requirements of the United States Pharmacopoeia.

Mr. Berg stated that the sample of copaiba used in his work was passed by the Bureau of Chemistry. But that did not necessarily mean that they had erred—as he realized that they must often admit samples such as this which it is impossible t o obtain in absolute purity. Mr. Kebler's correction as to quality of commercial Balsam Copaiba is accepted.

ASSAY OF AROMATIC SULPHURIC ACID.*

BY E. F. KELLY AND J. C. KRANTZ, JR.

Having occasion recently to examine a commercial sample of Aromatic Sulphuric Acid, the writers employed the method suggested in an article published in 1916 by the Maryland State Board of Health. This article criticized the Pharmacopoeial method of assay on the ground that the boiling for six hours of the water and acid mixture in a flask connected with a reflux condenser prevented the decomposition of the acid ethyl suphate through the constant return of the alcohol to the solution instead of its removal. The modification suggested was to heat the mixture of aromatic sulphuric acid and water in an open beaker on a water-bath from three and a half to four hours. By this method, three assays

*Read before Section on Practical Pharmacy and Dispensing, A. Ph. A., City of Washington meeting, 1920.

showed only 14.9 percent of sulphuric acid. Two assays of the sample were then made by the Pharmacopoeial method and showed 18.4 and 18.5 percent, respectively, of sulphuric acid, indicating that the ester was not reformed to any considerable extent by the condensation of the alcoholic vapors.

In view of these varying results, a standard aromatic sulphuric acid was made from a strictly U. S. P. Sulphuric Acid, the calculated strength of the finished preparation being 20.49 percent of acid. An open beaker assay of this standard preparation with six hours' heating gave only 16.3 percent of acid. Three assays by the Pharmacopoeial method gave 17.8 percent of acid. Increasing the time of boiling from six to seven hours, three assays gave 17.2, 18.7, and 18.81 percent, respectively, of acid. Increasing the amount of water used for dilution from 60 to 120 mils had no effect upon the decomposition of the ester, the results of three assays being 17.2, 17.1 and 18 percent, respectively, of acid. These results indicate that the fault lies with the methods tried.

The next method employed contemplated the decomposition of the ester by concentrated hydrochloric acid, with the formation of ethyl chloride, and the determination of the sulphuric acid gravimetrically as barium sulphate. The hydrochloric acid did not decompose the ester, however, the soluble barium ethyl sulphate passed through the filter, and the amount of barium sulphate obtained, calculated as sulphuric acid, evidently corresponded only to the amount of free sulphuric acid present in the preparation.

We next attempted to saponify the ester by the usual method of adding an excess of standardized alkali hydroxide solution, heating on a boiling water bath for six hours and titrating the excess of alkali with standardized acid solutions. Three determinations showed only 14.4, 14.5 and 14.9 percent, respectively, of sulphuric acid.

The method finally adopted, and which yielded very satisfactory results, was to evaporate a weighed quantity of the aromatic sulphuric acid to dryness in the presence of an excess of standard alkali, and titrating the excess of alkali with a standard acid solution. The results obtained by this method were very concordant and the percents of acid corresponded closely to the amount present in the preparation. A series of five determinations showed the following percents of acid calculated as sulphuric: 20.47, 20.39, 20.39, 20.47 and 20.31. The advantage of this method, in addition to its being strictly quantitative, is the short period of time required to carry it out. In this laboratory, 45 minutes was sufficient to complete the assay.

The writers suggest that the present Pharmacopoeial method of assay for aromatic sulphuric acid be modified as follows:

Accurately weigh about 5 mils of aromatic sulphuric acid and transfer to a tall beaker. Add 30 mils of normal sodium hydroxide and evaporate the mixture to complete dryness on a sand bath. Dissolve the residue in 20 mils of distilled water and titrate the excess of alkali with normal sulphuric acid-methyl orange T. S. as indicator. Each mil of normal sodium hydroxide used corresponds to 0.049045 Gm. H_2SO_4.

Since all alkali solutions absorb a small amount of carbon dioxide when evaporated over an open flame, we wish to caution against the use of phenolphthalein as an indicator unless the titration is carried on at boiling temperature.