# Contributed and Selected

## DIRECT TITRATION OF ACIDS IN ALKALOIDAL SALTS.

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It is a familiar fact that certain indicators for alkalies (e. g. phenolphthalein) are not affected by most alkaloids, so that the combined acids of alkaloidal salts behave in titration almost as if they were free acids. It is also well known that attempts to determine such combined acids by titration with volumetric alkali solutions fail because in a certain concentration the alkaloids after all show an alkaline reaction so that the end point of the titration is not sharp enough for an exact quantitative determination.

I have recently hit upon a little expedient by which it is possible to make such a titration with a pretty close approximation to exactness in the case of many alkaloids. The indicator which has given me the most promising results is methyl red, changed by alkalies to yellow.

If 0.301 gm. of crystallized morphine be dissolved in 12 cc. of decinormal hydrochloric acid and methyl red indicator be added, it will require just 10 cc. of N/50 alkali to change the color of the solution to yellow. If now there be added to the solution 10 cc. of neutral chloroform, and the mixture be shaken, the indicator will be taken up by the chloroform, leaving the aqueous solution colorless. If now volumetric alkali be added to the mixture, little by little, shaking well after each addition, no apparent change will be produced until enough of the alkali has been added to more than saturate the whole of the combined acid present. As soon as there is excess the aqueous solution will appear yellow instead of colorless after shaking. The quantity of volumetric alkali required to produce this effect (in this case 50 cc. N/50) is a measure of the amount of combined acid, and so of the amount of alkaloid present.

The effect of the chloroform must be to withdraw the alkaloid from the aqueous solution as fast as it is set free by the alkali.

This gives us a new principle to act upon in titrations of alkaloidal salts, and one which promises to work out satisfactorily in the case of many alkaloids.

When chloroform is used for the solvent and methyl red for the indicator, the end reaction is reasonably sharp with morphine, quinine and strychnine. It is possible that some other solvent might be better, and that another indicator may be still better suited for the titration.

There is a field here for experimentation that may develop useful results. Of course, the behavior of each alkaloid must be studied, since these vary greatly in their degree of alkalinity. I have not tried atrophine sales, and should not expect to find that their behavior is like that of the salts of morphine.

The plan will enable us to titrate a solution containing a mixture of alkaloidal

and alkaline salts, (e. g. chlorides) without previously reporting the alkaloid, giving at least an approximate determination of the vegetable base. If free acid is present, this may also be determined in the same operation.

## A PLAN FOR DETERMINING BY TITRATION BOTH ACID AND BASE IN BENZOATES OR SALICYLATES OF THE ALKALIES.

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Dissolve 0.25 gm. of the salt (e. g. Sodium Benzoate) in 10 cc. of distilled water in a separator. Add 25 cc. of decinormal sulphuric acid. Shake out the benzoic acid with four successive portions of chloroform, which must be proved to be free from alkalnity or acidity. The chloroform must be drawn off each time into a second separator in which it is to be shaken with 20 cc. of distilled water, to wash out any sulphuric acid which may have accompanied the chloroform. After washing thus, transfer the chloroform to a suitable flask, in which the free acid is to be titrated with N/25 volumetric alkali (lime water answers well), using as indicator methyl red. The end point of the titration is indicated by the appearance of a yellow color in the aqueous stratum after shaking with the chloroform.

The water in separator No. 2 is to be transferred to separator No. 1 and the residual acid is to be determined by titration with N/25 volumetric alkali. This excess deducted from the volumetric sulphuric acid originally taken, gives a measure of the benzoic acid which has been extracted, and consequently of the base with which that acid was combined.

Evidently this second titration is all that is usually required, but the first serves as a check on the result obtained.

The method should be tried in comparison with that of the U. S. P. VIII to test the question which of the two is the more exact on the one hand, and the more rapidly executed in practice on the other.

## NOTES ON CHEMICAL TESTS OF THE UNITED STATES PHARMACOPŒIA.*

CARL E. SMITH.

(Continued from page 301.)

ACONITINA.—Requires 26 to 28 parts of alcohol for solution ("22 parts." U. S. P.). The melting point is not a good criterion of purity, as the alkaloid decomposes and melts at temperatures varying with the rate of heating. About 0.2 gm. should leave no weighable residue on incineration. Not all solutions of aconitine are laevogyrate, as B. L. Murray has pointed out; alcohol-solutions are dextrogyrate, water-solutions inactive, and benzene-solutions laevogyrate. Market products are variable in composition, frequently not responding to the perman-

*Analytical Laboratory of Powers-Weightman-Rosengarten Company.