

so far as "white arsenic" is concerned. Even if the latter were not itself rather readily soluble in ammonia, the fact stated in all books of reference that it is easily soluble in ammonium arsenite (which is of course formed when Paris green is dissolved in ammonia) fully disposes of any claim of this test to acceptance.

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A METHOD OF DETERMINING FREE ALKALI IN SOAPS.

BY R. E. DIVINE.

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THE usual method of making this determination prescribes a separation of caustic from carbonated alkali by drying the soap, dissolving in absolute alcohol, and after filtering and washing the undissolved carbonate with alcohol and dissolving in water to titrate the solutions containing caustic and carbonate, respectively, with standard acid. This method is open to several objections, aside from the amount of time consumed. If it is desired to obtain accurate results on the caustic and carbonate separately, the preliminary drying of the soap introduces an error since the caustic alkali will take up carbon dioxide from the air unless the drying is done out of contact with air. It is quite a troublesome process to filter an alcoholic soap solution if one is not provided with appliances to keep the funnel hot during filtration. Dudley and Pease¹ use an alcoholic solution of stearic acid for titrating the caustic, but still filter from undissolved carbonate, and determine the latter in the usual manner. In the following process the writer has succeeded in eliminating filtration. For this method it is necessary to provide three standard solutions:

1. Hydrochloric acid, N/10 (for standardizing 2).
2. Caustic soda, N/10, in alcohol.
3. Stearic acid, N/10, in alcohol.

2 and 3 should be exactly equivalent one to the other, titrated warm with phenolphthalein indicator.

Two grams soap (which needs no drying) is weighed into a round-bottomed flask, of about 300 cc. capacity, and 50 cc. alcohol poured upon it. N/10 stearic acid is now run in from a

¹ *Engineering and Railroad Journal*, (1891), 551.

burette in amount judged to be sufficient to neutralize the free alkali in 2 grams of the soap, some phenolphthalein added, and the flask then stoppered with a cork stopper, through which passes a glass tube about 30 inches long and of about $\frac{1}{4}$ inch internal diameter, the lower end ground to a point on a grindstone, and the purpose of which is to serve as a reflux condenser. The flask and contents are placed on a steam-bath and heated thirty minutes, at the expiration of which time the solution should be quite clear and show no alkali with the phenolphthalein. If the solution turns red during the boiling, showing that an insufficient quantity of stearic acid has been added at first, add more of that solution until the color disappears, then several cubic centimeters in excess, and heat twenty minutes further. The flask is now removed from the bath and, after a few minutes' cooling, titrated with N/10 caustic soda. The difference between the number of cubic centimeters stearic acid solution added and the number of cubic centimeters caustic soda used to back titrate is equivalent to the total free alkali present.

While the first flask is heating, weigh out in a similar flask 2 grams of soap and add 50 cc. alcohol and place on the steam-bath. When the first test is finished, calculate roughly the total alkali, assuming the total quantity to be carbonate. Now add to the second flask an amount of 10 per cent. barium chloride solution sufficient to precipitate alkali found,¹ heat a few minutes, add phenolphthalein, and titrate with N/10 stearic acid. The titration must take place slowly and with thorough agitation of the liquid for the reason that the sodium or potassium hydroxide reacts with the barium chloride added and forms sodium chloride and barium hydroxide. The latter is not very soluble in the alcoholic liquid and sufficient time and pains must be taken to ensure its complete neutralization by the stearic acid. A blank test should be made on 50 cc. of the alcohol, since this frequently contains carbon dioxide, and the number of tenths cc. N/10 caustic soda necessary to neutralize the free acid in this quantity of alcohol added to the reading of the stearic acid burette in the second test. This corrected reading gives the number of cubic centimeters N/10 stearic acid used to neutralize the caustic alkali in 2 grams of soap. The difference between the total

¹ 1 cc. N/10 stearic acid = 0.0122 gram $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ or 0.122 cc. 10 per cent. barium chloride solution.

alkali found and the caustic will, of course, give the carbonate. For example : 2 grams of soap and 15 cc. N/10 stearic acid ; run in 3.2 cc. N/10 caustic soda to back titrate. Consequently, $15 - 3.2 = 11.8$ cc. N/10 stearic acid equivalent to total free alkali.

To neutralize the caustic in the sample treated with barium chloride was required 4.1 cc. N/10 stearic acid. Fifty cc. of the alcohol used required 0.2 cc. N/10 caustic soda, then $4.1 + 0.2$.

4.3 cc. N/10 stearic acid to neutralize free caustic alkali.

$11.8 - 4.3 = 7.5$ cc N/10 stearic acid to neutralize carbonated alkali.

1 cc. N/10 stearic acid = 0.004 gram caustic soda or 0.0053 gram sodium carbonate.

The above figures calculated to percentage would be :

0.86 per cent. caustic soda and 1.99 per cent. sodium carbonate.

It is to be noted that a rubber stopper cannot be used in the flasks for dissolving the soap on account of the sulphur in the rubber, which decolorizes an alcoholic solution of phenolphthalein. The method is applicable to all soaps which do not contain fillers which react with the standard solutions employed.

BUFFALO, July 24, 1900.

INVESTIGATIONS ON THE DETERMINATION AND COMPOSITION OF HUMUS AND ITS NITRIFICATION.

BY CHARLES RIMBACH.

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THE investigation on the nitrification of the *matière noire* of Grandeau, here discussed, was undertaken on the suggestion of Prof. Hilgard, to test the question whether or not that substance is to be regarded as a source of nitrates under the influence of nitrifying bacteria as has been assumed, but never definitely proved. The method of preparation consists in treating the soil with dilute hydrochloric acid to remove the lime and magnesia with which the humus substance forms insoluble compounds ; and after washing with distilled water, until the filtrate is neutral, extracting it with 6 per cent. ammonia. On evaporation the solution leaves the *matière noire* behind.

As a medium containing the carbonates of lime and magnesia is most favorable to nitrifying bacteria, the compound of the