Determination of Free Alkali in Soaps

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THIS relatively simple determination is fraught with difficulty when only small amounts of free alkali are present as is usually the case in modern soaps.

The accepted A.S.T.M. standards for free alkali are not more than 0.1% as sodium hydroxide for toilet soaps and not more than 0.2% as sodium hydroxide for chip and powdered soaps. On a 5 gram sample these maximum percentages would require only 1.25 ml. and 2.50 ml. of tenth normal acid.

The method of determination which is recommended by the A.O.C.S. is to dissolve 2 to 10 grams of the soap in 200 ml. of freshly boiled ethyl alcohol, filter through a filter paper neutral to phenolphthalein or through a Gooch crucible with suction, protecting the solution from carbon dioxide and other acid fumes during the operation by covering with a watch glass. The paper or Gooch is washed with hot neutral alcohol until free from soap and the filtrate and washings heated to incipient boiling and titrated with standard acid after the addition of 0.5 ml. of a 1 per cent solution of phenolphthalein.

Considerable experience has shown that much depends on the neutrality to phenolphthalein of the filter paper and on how well the whole is protected from carbon dioxide and other acid fumes.

The first requirement may be met by previously washing the filter paper with alcohol which has a faint pink coloration after being titrated to just on the alkaline side using phenolphthalein as indicator. As filter paper apparently adsorbs alkali to an extent that is very considerable when compared to the small amounts present in good soaps, it will be necessary to wash the filter paper with sufficient slightly alkaline alcohol until the filtrate is the same tint of pink as the wash alcohol. A final washing with neutral alcohol is then needed. Alternatively the filter paper may be washed with definitely alkaline alcohol and finally with neutral alcohol until colorless.

In either case this procedure is tedious and somewhat indefinite.

The second requirement—to protect the whole from carbon dioxide and other acid fumes—is not easy to accomplish and at best is not 100 per cent effective.

A simple technic which obviates both of these difficulties consists in dissolving the soap in hot neutral alcohol and at once centrifuging until the alcohol solution is clear, which is readily accomplished. For most purposes the alcohol solution may then be decanted without disturbing the precipitate, heated to conform with the standard method and titrated. In general the titration is so small that it is unnecessary to wash the precipitate with neutral alcohol and centrifuge. However, for extreme accuracy this may be done.

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OUR last report (1) indicated that the Bertram-Rutgers method (2) of analysis for glycerin appeared to be more of "a principle than a method of analysis." The interest of our committee in this rather novel procedure has been sufficient to motivate further attempts to improve the method and its precision. After studying the results obtained by our committee, Dr. Bertram has made several valuable suggestions. Careful experiments have been conducted by a number of our committee (in particular by Dr. A. F. Nelson of the Lever Brothers Company at Cambridge) which have enabled the formulation of a workable procedure. This method has been applied to the "A.O.C.S. Standard Crude Glycerin" and to other selected samples.

While results by the revised method show a great improvement over those obtained by the original procedure, it is obvious that the precision is still considerably short of that demanded by commercial transactions or cost accounting. Your committee is unanimous in this opinion and accordingly the procedure is *not* recommended for adoption as a tentative method of the Society. The improved procedure, however, does afford a rapid and easy means of determining the approximate glycerin content of materials which are grossly contaminated with substances which seriously interfere with the standard acetin and bichromate procedures. Among these may be mentioned sugars; trimethylene and diethylene glycol; the glycol ethers, such as cellosolve, carbitol, etc.; hydroxy-acids, such as tartaric and citric; and oxalic acid. None of these substances shows as much as one per cent apparent glycerol. Ethylene glycol, propylene glycol and the hexahydric alcohols, such as mannitol and sorbitol, show apparent glycerol from two to five per cent. Polyglycerol ethers and the alkanol-amines are interfering substances. Ammonia, present in amount not exceeding about one gram of NH_3, shows no interference. Above this rather sharply-defined "threshold" a soluble cuprammonium compound is readily formed.

One of our members obtained results which led him to conclude that the glycerol percentage is dependent upon the size of sample used for analysis. This conclusion could not be substantiated by other members of the committee.

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(1) Oil & Soap *16*, 19-20 (1939).
(2) Rec. trav. chim. *57*, 681-87 (1938).