THE TESTING AND ANALYSIS OF SOAPS

by

SIGMUND FLORIAN KIELMA

A Thesis Presented for the Degree of

GRADUATE IN PHARMACY

UNIVERSITY OF WISCONSIN

1924

TABLE OF CONTENTS.

The Testing and Analysis of Soaps.

Soap, of the United States Pharmacopoeia, is of two kinds, hard soap and soft soap. The former is made from olive oil and sodium hydroxide, the latter from cotton-seed oil and potassium hydroxide; both are, therefore, free from animal fats or soaps prepared therefrom.

Soap, like other colloidal substances, is capable, under certain conditions, of adsorbing large quantities of water and still retaining a hard, solid consistency. The water content of soap must, therefore, be carefully controlled. Unless carefully prepared, a large excess of alkali is liable to be found in soaps. A large excess of this uncombined alkali renders soap harsh and unfit for most purposes, especially for medicinal use.

The above mentioned impurities are those which, from the very nature of soaps, might be expected to often be present. In addition to these there are added and accidental impurities, as mineral and organic fillers, resin, metallic compounds, medicinal substances and various other materials. To guard against the presence of added and accidental impurities, many tests have been devised. The United States Pharmacopoeia contains tests which serve to determine the purity of the official soaps.

There is required for the proper formation of soaps, a certain amount of water which enables the particles of

soap to form a compact and yet readily soluble mass. Other things being equal, the solubility and effectiveness of a soap are proportional to the amount of water contained in the soap; therefore a rather high water content is very desirable. A considerable amount of this water is in colloidal combination with the soap substance and is retained by the soap under all ordinary conditions, or even if the soap has been kept for a long time and appears dry. All soaps have the properties of taking water from the air or of giving it off again to the air with changes of external conditions. These properties vary in the different kinds of soaps. The chemical constitution of soaps has the greatest influence on these properties. Thus sodium soaps hold their water less tenaciously and give off more water than do potassium soaps. The fatty acids with which the sodium or potassium are combined have an influence on the power of a soap to retain or give off moisture. Fischer,[1] in his experiments on water in soaps gives the following results:- " A first factor in the amount of water held by different soaps is resident in the nature of the metallic radical combined with the fatty acid. If the radical most effective in this regard is given first, the sequence is about as follows:- NH_4, K, Na, Li, Mg, Ca, Hg, Pb." After experiments performed with various acid radicals

1. Soaps and Proteins, 1921, p. 14.

Fischer reached the following conclusion:- "Under otherwise fixed conditions the water-absorbing power of any soap depends upon the nature of the fatty acid in the soap, increasing with its height in a given series." It is thus seen that there are two chief factors controlling the amount of water which a soap contains.

Though a considerable quantity of water is highly desirable in soaps, the amount must, of course, be within reasonable limits. An excess of water would be considered an adulteration by the consumer. Soaps containing an excess of water become unsightly and light in weight upon loss of this water. The amount of water in a hard soap influences its hardness and the ease with which it rubs away. Commercial hard soap contains a variable amount of water. A good hard soap contains about 20% of water; the amount in various hard soaps varies from 8% or 10% to 25% or 40%. The United States Pharmacopoeia limit of water for solid hard soap is 36% and for the powdered soap 10%. The British Pharmacopoeia allows a limit of 30% for solid hard soap.

Soft soap, or potassium soap, has a great affinity for water. The United States Pharmacopoeia allows 52% of water in soft soap. The United States Pharmacopoeia gives the following method for determining water:-

Dissolve 0.5 Gm. of soap, accurately weighed, in 10 mils

of alcohol, evaporate the solution to dryness in a tared beaker containing 1 Gm. of clean sand, which has been previously dried at 110* C. to constant weight. Dry the residue at 110* C. to constant weight. The loss of weight does not exceed 36% for unpowdered soap and 10% for powdered soap. In evaporating the solution a small flame should be used and the beaker placed on a water-bath, otherwise the sand may be ejected from the beaker.

A commonly employed method for the determination of water is the following:-[2] 10 Gm. of soap is weighed, dissolved in hot water and the volume made up to 100 cc. While still warm 10 cc. is measured out in a pipette and transferred to a weighed flat-bottomed dish. The solution is evaporated to dryness on a water-bath and dried at 100* C. till constant. The loss represents the loss of water in 1 Gm.

Fitzpatrick[3] gives the following method for determining water;- 1 Gm. of the soap is weighed into a 200 cc. conical flask, 50 cc. of absolute alcohol is added and heat applied to dissolve the soap completely. The solution is allowed to cool somewhat and is filtered through a filter into another 200 cc. flask. The insoluble material remains on the filter. The filter is washed with alcohol, allowed to cool, and 5 Gm. of anhydrous sodium sulphate added. The flask is corked and allowed to stand for 24 hours. The

2. Soaps, 1921, p. 221.
3. Proceed. A. Ph. A., 59, p. 92.

solution is then filtered into a 200 cc. conical flask which has been previously weighed along with some porous tile. The alcohol is evaporated off on a water-bath and the residual soap dried in a steam oven for 15 minutes. The flask and soap are then cooled in a desiccator, corked and weighed. From this the weight of anhydrous soap is found and the amount of water calculated.

The xylene method which serves so well, in many cases, for the determination of water, does not appear to be applicable to the determination of water in soaps.

The fats employed in making the soaps official in the United States Pharmacopoeia are of vegetable origin. The official soaps should be entirely free from animal fats or soaps made from animal fats. Cottonseed oil and potassium hydroxide are used in making the soft soap and olive oil and sodium hydroxide in the hard soap. The following is the test given for animal fats by the United States Pharmacopoeia:- An alcoholic solution of soap, 1 in 25, should not gelatinize on cooling. This test is based on the fact that animal fats solidify at a much lower temperature than do vegetable fats, containing, as they do, a larger amount of solid acids.

The olive and cottonseed oils used in making the official soaps should be free from other oils and meet the other requirements of the United States Pharmacopoeia. Most of the commercial soft soaps are made from linseed oil, which forms

an odorless and neat appearing soap. Linseed oil has many times been suggested as a substiture for the cotton-seed oil which is at present employed by the Pharmacopoeia and it was formerly used. Sapo Animalis, recognized in the British Pharmacopoeia, is made from animal fats containing principally stearin.

The following is the method of the United States Pharmacopoeia for determining the fatty acids of the official soaps:- Dissolve about 10 Gm. of soap in 200 mils of hot distilled water, add 2 drops of methyl orange T. S. and then diluted sulphuric acid with constant stirring until the aqueous layer becomes red. Boil the mixture until the supernatant layer of the fatty acids is clear and free from solid particles. Separate the aqueous layer with the aid of a siphon and wash the fatty acids by decantation with hot distilled water, until 10 mils of the washings, acidulated with a drop of hydrochloric acid no longer gives a precipitate on the addition of barium chloride T. S. Now place the dish containing the fatty acids on a water-bath and heat until the fatty acids are completely liquefied, then filter the warm acids through a dry filter in a hot-water funnel into a flat dish and dry the acids over sulphuric acid. The iodine number of the acids thus obtained is not less than 84 nor more than 90.

Some soaps contain soluble fatty acids which would not be determined if the usual methods were employed.

Dominikiewitz[4] gives a method for determining insoluble and soluble fatty acids as follows:- 10 Gm. of the soap are dissolved in water and decomposed by a slight excess of sulphuric acid, the flask being heated until the insoluble fatty acids collect as a clear layer on the surface of the aqueous liquid. The vessel and its contents are now cooled and the cake of fatty acids dislodged, while the aqueous layer is filtered through a moistened filter paper. The cake of fatty acids is washed three times with boiling water, cooling and filtering each time. The filtrates are collected together, methyl orange is added as an indicator, and to the liquid a dilute solution of caustic soda is added until the pink color changes to orange. At this stage the whole of the mineral acid is neutralized, but the soluble fatty acids are free. Phenolphthalein is now added and the liquid titrated with N/10 sodium hydroxide.

The various properties desired in the use of soaps are that they should be good detergents both for the removal of dirt and any natural secretion or fat from the skin. To do this without injury to the epidermis it is necessary that the soap should have a very slight amount of free alkali. The free alkali removes a small portion of the natural fats of the skin, leaving the pores clean and open so that they can perform their natural duties. A soap with an excess of fat will not do this.[5]

4. Chem. Zeit., 1909, p. 728.
5. Journ. A. Ph. A., 1916, p. 295.

The hard soap of the United States Pharmacopoeia should contain a very small amount of free sodium hydroxide. To determine whether there is more sodium hydroxide than the limit allowed, the Pharmacopoeia gives the following test:- Dissolve about 10 Gm. of soap accurately weighed, in 100 mils of alcohol, with the aid of heat. Filter off the undissolved residue and wash the filter with boiling alcohol. This alcoholic filtrate and washings are not reddened by 3 drops of phenolphthalein T. S. The exact amount of sodium hydroxide is not determined and the method is inaccurate and indefinite.

The following method of Divine[6] has been found satisfactory in determining free alkali in soaps:- To a solution of 2 Gm. of the soap in 50 cc. of alcohol, contained in a flask provided with a reflux condenser, an excess of N/10 stearic acid is added and the flask heated on a water-bath until a clear solution is obtained. The excess of stearic acid is then determined with N/10 soda solution, the difference giving data for free alkali, both hydrate and carbonate. In a second experiment with the same quantity of soap, the carbonate is removed by means of a 10% solution of $BaCl_2$ and the remaining free alkali estimated as before. The difference between the total free alkali as previously ascertained and the caustic alkali as ascertained in the second experiment gives the amount of free alkali present as carbonate in the sample.

6. Pharm. Central., 1901, p. 589.

F. H. Newington[7] used the following method in determining free alkali in soaps:- 10 Gm. of soap is weighed out in a wide mouth bottle, 50 cc. of water added and the flask heated until solution is effected. The soap is then salted out by addition of 50 mils of a hot saturated solution of sodium sulphate. The mixture is then filtered and the precipitate and washings are titrated with N/10 sulphuric acid, silver nitrate being used as indicator by the spot method.(Brown silver oxide showing as long as free hydroxide remains in the titrated solution.) Carbonates and silicates do not interfere with the process, which is sensitive enough to detect 0.01% of alkali added to a neutral soap.

In the analysis of soap not only is the free alkali determined, but the alkali combined with the fat as soap also. The following is the method of Grelot[8] for determining total alkali:- Dissolve 2 Gm. of soap in 100 mils of boiling water, add 5 or 6 drops of a 1% aqueous solution of Congo Red and titrate with semi-normal hydrochloric acid, maintaining the temperature at 80*C., so that when the fatty acids are liberated they rise and float on the surface; they do not interfere with the titration and the end reaction is very sharp. Another determination is made, this time for the free alkali. The difference between the total alkali and the free alkali will give the percentage of alkali combined

7. Am. Journ. of Pharm., 88, p. 262.
8. Pharm. Journ., 1907, p. 361.

as soap.

The United States Pharmacopoeia gives a method for determining the free alkali in soft soap. The method is the following:- Dissolve about 5 Gm. of Soft Soap, accurately weighed, in 100 mils of hot alcohol, collect the residue, if any, on a filter and thoroughly wash it with alcohol. The combined filtrate and washings, on the addition of 0.5 mil of phenolphthalein T.S. and titration with N/10 sulphuric acid V.S., shows not less than 0.1% nor more than 0.25% of potassium hydroxide. It is seen that soft soap contains much more free alkali than does the hard soap. This probably is due to the large amount of water in the soft soap, hydrolysis taking place.

Sodium carbonate, sodium chloride and silica are found in soaps as impurities. The sodium carbonate may be present because it is sometimes the alkali used in the making of soaps, or it may be formed by the action of carbon dioxide upon sodium hydroxide. Sodium silicate and silica are either added as fillers or may merely be accidental impurities. The United States Pharmacopoeia has devised the following test for the determination of sodium chloride, sodium carbonate and silica in hard soap:- Dissolve about 10 Gm. of soap, accurately weighed, in 100 mils of alcohol, with the aid of heat. Transfer the undissolved residue, if any, to a tared filter which has been dried at 100*C. and wash it thoroughly with boiling alcohol. Its weight, after drying at 100*C.

does not exceed 1% of the weight of dry soap in the original weight taken. The weight of this residue, thoroughly washed with distilled water and dried at 100*C., does not exceed 0.15% of the weight of dry soap in the original weight taken (silica and other accidental impurities.)

The amount of insoluble residue in soft soap is determined in the same manner as that in hard soap, but the amount is 3% of the weight of the soap taken.

There may also be present in soaps metallic compounds which were present in the fats used or were added to color the soap. The United States Pharmacopoeia gives under Soap the following test for metallic impurities:- Ten mils of an aqueous solution of Soap (1 in 20) remains unchanged in color upon the addition of ammonium sulphide T.S., and upon acidulating another portion of 10 mils of the solution with hydrochloric acid and filtering, the filtrate remains unchanged in color when an equal volume of hydrogen sulphide T.S. is added and the mixture allowed to stand well-stoppered, in a warm place, for half an hour.

It is seen that soaps which would be used in Pharmacopoeial preparations must conform with the high requirements set down by the United States Pharmacopoeia. It is of utmost importance that the Pharmacopoeia should set such standards because inferior soaps might ruin the preparations in which they are used and not give the desired effects. Some of the preparations containing Soap are intended for internal use and

foreign substances in the soap might be injurious to the patient. The United States Pharmacopoeia as for all the other medicinal substances it contains, maintains a high standard for Soaps.

Pharmacopoeial History of Soap.

1820--First Edition.

Soap--Not official.

1830--New York.

Sapo Albus--White Soap.

1830--Philadelphia.

Sapo--Soap.

1840--Second Revision.

Sapo--Soap.

1850--Third Revision.

Sapo--Soap.

1860--Fourth Revision.

Sapo--Soap.

1870--Fifth Revision.

Sapo--Soap.

1880--Sixth Revision.

Sapo--Soap.
Sapo Viridis--Green Soap (Soft Soap).

1890--Seventh Revision.

Sapo--Soap.
Sapo Mollis--Soft Soap (Green Soap).

1900--Eight Revision.

Sapo--Soap.
Sapo Mollis--Soft Soap.

1910--Ninth Revision.

Sapo--Soap.
Sapo Mollis--Soft Soap.

BIBLIOGRAPHY.

Sienier, A. 1874.

Am. Journ. of Pharm., 46, p. 353.
Analysis of Soaps.

Wright, C.R.H.
Thompson, C. 1886.

Estimation of Resins in Soaps:-
Yr. Bk. Brit. Pharm. Conf., 1886,p.141.

Napier, H. 1887.

Determination of Free Alkali in
Soft Soap:-
Proceed. A. Ph. A., 35, p. 66.

Braithwaite, J. O. 1888.

Procedure for the Determination of
Copper in Soaps:-
Yr. Bk. Brit. Pharm. Conf., 1888,p.122.

Spencer, L. J. 1891.

Tests for Glycerin:-
Yr. Bk. Brit. Pharm. Conf., 1891,p.139.

Sanpe, M. 1891.

Determination of Fatty Acids in Soap:-
Yr. Bk. Brit. Pharm. Conf., 1891,p.139.

Dietrich, E. 1893.

A Point in the Analysis of Soap:-
Proceed. A. Ph. A.,42, p. 608.

Klopine, ---. 1898.

Assay for Phenol in Carbolic Acid Soap:-
Proceed. A. Ph. A., 46, p. 718.

Silker, F. A. 1898.

Examination of Typical Commercial Samples of Soap:-
Proceed. A. Ph. A. 46, p. ---.

Divine, ---. 1901.

Method for Determination of Free Alkali:-
Proceed. A. Ph.A., 49, p. 589.

Martin, E. 1905.

Detection of Glycerin in Soap:-
Proceed. A. Ph. A., 53, p. 584.

Hassern, A. 1905.

Detection of Sodium Silicate:-
Proceed. A. Ph.A., 53, p. 585.

Grelot, P. 1907.

Determination of Total and Free Alkali in Soap:-
Pharm. Journ., 1907, p. 361.

Saus, J. 1909.

A Simple Test for Rosin in Soap:-
Proceed. A. Ph. A., 1909, p. 321.

Fitzpatrick, R. M. 1911.

Chem. News, 1911, p. 247.

Mayer, J. L. 1913.

Analysis of Castile Soap:-
Journ. A. Ph. A., 2, p. 734.

Hewington, F. H. 1916.

Determination of Free Alkali in Soap:-
Yr. Bk. A. Ph. A., 5, p. 80.

Slack, H. F. 1918.

Determination of Fatty Acids in Soap:-
Yr. Bk. A. Ph. A., 7, p. 115.

Book Literature:-

Fischer, M. L. 1921.

Soaps and Proteins.

Hurst, G. 1921.

Soaps.

Approved Nellie Wakeman

Inst in Pharm. Chem.