ELIMINATING INACCURACIES IN PRESENT OFFICIAL METHOD FOR FREE ALKALI

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NO doubt everyone who has had the task of determining the free alkali content of soaps or soap products has had the feeling of the lack of confidence in the results he has obtained. It is in the minds of the members of the soap analysis committee, and also others, that there is room for improvement. Realizing this fact and having observed what appeared to be some sources of possible error, I decided to determine, if I could, what some of the sources of error are.

My first observations were visual, and were not based on comparative figures. Therefore, I set out to substantiate my observations with figures. First, it was necessary to determine as closely as possible just what and where the possible sources of error might be. The sources to be studied were selected by going over the official method and judging, as well as possible, various angles which I felt could have any bearing on the results. It is not unlikely that I may have missed some. However, the entire problem was broken up into smaller problems which were to be settled individually.

Throughout the experimental work, the alcohol used was formula No. 30, denatured, which was obtained from one drum of alcohol. It was prepared for our use in three gallon lots by adding 2 cc. of 1 per cent phenolphthalein and 3 cc. N/2 NaOH per gallon of alcohol.

This was found to give a neutral filtrate at boiling temperature. A study was made of the preparation of the alcohol and we found that varying the quantity of phenolphthalein over wide limits gave a noticeable variation, but if the quantity used is from 1 to 3 cc. per gallon, the variation cannot be measured. The time of aging the alcoholic solution (up to about a week's time) showed that the age has no effect so long as CO_2 is excluded by preserving in a well stoppered bottle. The filters used were Whatman No. 1-15 cm. All titrations were done at the boiling point to insure uniformity as recommended by the members of the soap analysis committee.

The first point I will discuss is the matter of CO_2 solubility, and the part it plays in the official method. We have found that CO_2 is readily soluble in alcohol. This can be shown by the simple experiment of exposing a dish of alcohol containing a small amount of N/10 alkali and a few drops of phenolphthalein while a similar container is kept sealed. After a short time of exposure to the air, the solution will change from pink to colorless. Or if a measured amount of alkali is added and titrated back, one can readily see that the CO_2 is rapidly absorbed in appreciable quantities. The official method states, "Filter through a counterpoised paper, neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes." Theoretically, that is correct, but inasmuch as the exact method of carrying out this point is not stated, one may not provide ample protection. Consequently CO_2 may be absorbed, giving low results. One may cover his flasks and funnels with watch glasses or take other precautions, but during the pouring and filtering operations, CO_2 gets into the containers and is absorbed.

To eliminate this possibility, I set up an apparatus as shown in the diagram. In the diagram (Figure 1) A is a 500 cc. flask, B is a 500 cc. suction flask, C is a 3-in. glass funnel with ground upper edge and fitted with a stopcock G. D is a glass plate about an inch larger in diameter than the funnel and has a ¾-in. hole drilled through the center, which is fitted with a thin cork. E is a container such as a large beaker filled with cold water to condense the alcohol vapors in B. F is a soda lime tube to keep out CO_2. H is a rubber tube fitted with a pinch clamp. All stoppers are corks, inasmuch as rubber stoppers discolor the alcohol, and the corks are boiled with alcohol several hours to extract any alcohol soluble material. Glass plate D is separated about 2 ins. from the top edge of the funnel by raising tube J through the cork. Then the measured quantity of alcohol is run through a filter in funnel C and collects in flask A. The weighed sample is placed into the filter paper and the tube J is lowered until the glass plate rests firmly on the upper ground edge of the funnel, and then connections of the tubes are made at K by means of the short rubber connection. Heat the contents of A to boiling with G and H open, allowing CO_2 and alcohol vapors to pass over to B through the two passages. Regulate the heat to give a slow boil. Then close stopcock G and by closing H force alcohol from A into funnel C, through tube J.

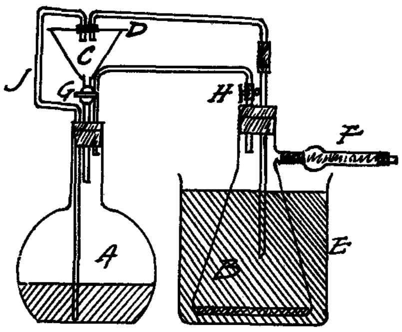

Fig. 1

Open H and G, allowing the dissolving soap to filter back into flask A. After the filter has drained, refill the funnel as before, repeating this procedure until the sample has dissolved (from three to eight washings). Allow the filter to drain, disconnect flask A, and titrate at boiling temperature with N/10 alcoholic HCl. Also, record the measured contents of flask B. Correct results for this evaporated alcohol as indicated later in this paper.

Determinations of free alkali using this apparatus definitely show that lower results are obtained when CO_2 is allowed to enter than when it is excluded. On a sample of kettle soap the filtrate was colorless when CO_2 was admitted and was pink, requiring .2 cc. N/10 acid to neutralize, when CO_2 was excluded.

According to the official method

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TABLE 1
Official Method

	Sample	Filtrate %	+ 100 cc Wash %	+ 300 cc Wash %	New Method %
1	Soap + Free Alkali	.00	.10	.14	.068
2	Soap + F.A. + 5% Na_2CO_3	.06	.10	.17	.088
3	Soap + F.A. + 5% T.S.P.	.02	.08	.16	.062
4	Soap + F.A. + 5% Silicate Alk	.22	.43	.54	.39
5	Soap + F.A. + 5% Silicate	.01	.05	.10	.032
6	Soap + F.A. + all above	.00	.03	.08	.020
7	Regular kettle soap	.00	.008	.02	.010
8	Com'l Silicated flake	.00	.008	.08	.006
9	Cocoa Potash Base	.25	.41	.41	.42

TABLE 2
Soxhlet Extraction

		3 extractions	6 extractions	9 extractions
1	Soap + Free Alkali	.14%	.17%	.18%
2	Soap + F.A. + 5% Na_2CO_3	.18	.18	.19
3	Soap + F.A. + 5% T.S.P.	.14	.16	.20
4	Soap + F.A. + 5% Silicate Alk	.52	.59	.63
5	Soap + F.A. + 5% Silicate	.088	.12	.17
6	Soap + F.A. + all above	.064	.085	.13
7	Regular Kettle Soap	.026	.035	.040

Each extraction = approx. 73 cc.

the sample is to be digested hot with 200 cc. of freshly boiled ethyl alcohol 94 per cent or higher neutral to phenolphthalein. The soap may dissolve slowly or rapidly or it may be difficult to tell by observation when it is dissolved as with a silicated soap. Consequently, varying quantities of alcohol boil away. Alcohol is acid in reaction to phenolphthalein. This leaves the filtrate more basic and the results err to the high side. This is shown by the following experiments: Alcohol distilled from an alkaline solution in the absence of CO_2 is acid in reaction, requiring .23 cc. of N/10 NaOH to neutralize 100 cc. of distillate. Thus also if a neutral alcohol is distilled the distillate will be acid to the above extent and the residue increase in alkalinity a like quantity. It is therefore necessary to prevent the loss of alcohol or to measure the loss and make corrections.

Excerpts from the official method say, "Wash the residue on the paper or in the crucible, with hot neutral alcohol until free from soap. . . . The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates and sulfates as well as starch, and may be used for the approximate determination of these constituents. These salts are not entirely insoluble in alcohol so for accurate determinations separate portions. . . Titrate the filtrate from the above . . . etc." From these excerpts notice that the alkaline salts are slightly soluble in alcohol and that the precipitate is washed free of soap with hot alcohol which dissolves some of the alkaline salts and these are *in turn titrated* in the filtrate and washings. The greater and more intensive the washings the more alkaline salts are dissolved, resulting in variable and high results.

In the experiments at our laboratory we found, as stated in the official method, that the alkaline salts are appreciably soluble in hot alcohol. This was done by boiling the various salts in alcohol, filtering off a measured quantity and drying to constant weight. The residue was taken up in water and titrated. We also extracted some of the salts in a Soxhlet extractor (Table 2) and after a few extractions the alcohol becomes supersaturated in the flask below, throwing out of solution the dissolved carbonate. The amount thrown out of solution is a surprising quantity.

TABLE 3
Variation of $Na_2O \div SiO_2$

$\frac{Na_2O}{SiO_2}$	Free Alk
1 ÷ 1 approx.	2.39%
1 ÷ 2 approx.	.55%
1 ÷ 3 approx.	.14%
1 ÷ 4 approx.	.037%

Have you ever had a filtrate from a free alkali determination filter colorless up to the time of washing and after washing turn pink? Inasmuch as the sample is dissolved in alcohol and the washings are also hot alcohol, one would expect the washings to be the same color as the filtrate. Or in other words, if the washings are pink, why should not the original filtrate be pink also?

The reason for this is that the alkaline salts are practically insoluble in a soap solution of high concentration; that is, one containing over 2.5 per cent of soap. When soda ash is boiled with a neutral 2.5 per cent soap solution with a reflux condenser and filtered the filtrate is colorless. With these facts in mind you can see why the original filtrate, which contains a large quantity of soap, may filter colorless and the washings by dissolving the salts turn pink. From this it is apparent that it is better to titrate without washing the precipitate to obtain a more correct free alkali content. The loss due to that solution which is retained in the paper and funnel amount to less than 2 cc. in a 15 cm. filter paper by actual test, which with 200 cc. amounts to less than 1 per cent error.

The official method calls for a 2 to 10 gm. sample dissolved in 200 cc. of alcohol. In view of my experiments, the sample must be sufficiently large to give a 2.5 per cent soap solution or else neutral alcoholic soap solution should be used to make up the deficiency.

We have done some work on soaps containing silicates of various Na_2O to SiO_2 ratios. (See Table 3.) However, I feel that this is a separate problem on which we expect to do more work later. I feel that the results of this work will probably be quite interesting, and may report on this at some later date.

Table 1 shows the free alkali obtained on various samples of prepared soaps together with commercial kettle and filled soap samples. In addition, a sample of cocoa potash soap is shown. The first sample had only free alkali together with a small per cent of carbonate normally in soap. The second is the same as the first with 5 per cent soda ash added; the third, with 5 per cent trisodium phospate; the fourth, 5 per cent silicate plus caustic soda; the fifth, 5 per cent regular commercial silicate; the sixth, a mixture of 1 per cent each of the previous materials. The seventh sample is a regular pure dried kettle soap; the eighth, a commercial silicated flake, and the ninth a potash base cocoanut oil soap.

Notice that in every case the washes in the official method increase the free alkali content considerably due to the solubility of the salts in the alcohol.

Notice also that the original filtrate in every case is lower than that obtained by the so-called new method, due to CO_2 absorption.

The method is equally effective on potash base soaps as on soda soaps using the same concentration of soap in alcohol.

Although the figures are not shown here, difficulty was experienced in checking results by the official method when the samples were washed with equal quantities of alcohol. With the new method check results were readily obtained.

The samples extracted three times in the Soxhlet extractor show approximately the same results as by the official method with a 300 cc. wash. The samples washed six and nine times show still higher results. In practically all samples the solution in the flask becomes cloudy.

From the data obtained there are several sources of possible error in the official method. The results obtained are dependent upon the technique of the analyst; consequently, variable results are obtained by various analysts.

To obtain consistent results, therefore, it is necessary to have a concentration of soap in alcohol of not less than 2.5 per cent. The residue in the filter should not be washed with alcohol, and consequently the free alkali determination should be subordinated from the alcohol insoluble determination. The entire operation should be excluded from CO_2 by some positive prescribed method.

A NON-FATTY OIL FROM JOJOBA SEED*

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JOJOBA oil is obtained from the seed of Simmondsia californica, Nutt, of the family Buxaceae. The plant is known also as the joboba, while the fruits are known in this country as goat, pig, sheep, or quinine nuts. The shrub is found in Arizona, southern California, and western Mexico, ranging in height from 3 to 15 feet. This thickly branched boxwood-like evergreen shrub is commonly found growing on rocky hillsides. Sheep men in the locality where it grows state "that it is one of the most important of the browsing plants. It is one of the few green things during a dry winter and is eaten freely." It is probably eaten at times also by cattle, pigs and goats. It bears both staminate and pistillate flowers. The fruit is a thin, brown, 3-valved capsule which contains a single seed, having a tough reddish-brown testa. The somewhat egg-shaped seeds average about 0.8 gram in weight but range from .4 to 1.4 grams and are about one-half inch long and three-eighths of an inch in diameter.

For the present investigation a sample of about twenty-five pounds of the seed from the State of Senora, Mexico, was sent to us by L. Kishlar, Manager of Research, Ralston Purina Company, St. Louis, Missouri. These seeds were found to contain 51.2 per cent of oil and 4.7 of moisture. S. Ivanov (Bull. Appl. Botany 32, 129, 1930) reported an oil content of 44.5 per cent for the seed investigated by him.

The seeds were ground in a Hobart mill, and the oil was extracted by cold percolation with petrolic ether. The solvent was removed as far as practicable by distillation at atmospheric pressure. Most of the remaining solvent was removed by heating the oil in an evaporating dish on the steam bath. The last traces were removed at 135° C. under diminished pressure. Over 3 liters of a light yellow limpid oil was obtained.

Table I gives the chemical and physical characteristics of the oil.

TABLE I

Refractive index at 25° C.	1.4648
Specific gravity 25°/25°	0.8642
Iodine number (Hanus)	81.7
Saponification value	92.2
Acid value	0.32
Unsaponifiable matter, per cent	48.3
Iodine number of unsapon. (Rosenmund-Kuhnhenn)	77.2
Acetyl value of unsapon.	171.8
*Saturated acids (Bertram), per cent	1.64
Iodine number (Hanus) — total fatty acids	76.1
Neutralization value of total fatty acids	172.0
Glycerine	0.0

*It should be observed that no separation of the saturated acids could be effected by the lead-salt ether method.

The acetyl value and iodine number of the unsaponifiable matter indicated that it consisted very largely of unsaturated alcohols. A portion of the unsaponifiable matter was brominated at 5° C. and subjected to frictional distillation under diminished pressure, but no saturated alcohols or hydrocarbons were detected. Another portion of about two grams was treated with cold concentrated sulphuric acid. No observable quantity of saturated hydrocarbon separated from this solution upon standing.

About two grams of the unsaponifiable matter was completely hydrogenated using the Adams platinum catalyst, and a 0.90-gram portion of the resulting product was subjected to oxidation with chromium trioxide in a glacial acetic acid solution according to the method of Chibnall and Piper (Biochem. J. 25, 215, 1931). The acids (0.45 grams) were converted into their calcium salts, which were extracted with ether in order to remove any non-acid constituents. The calcium salts were decomposed with hydrochloric acid in the usual manner. The recovered fatty acids after repeated crystallization from alcohol melted at 68.4-69.0°. They gave a neutralization value of 167.5, indicating a mean molecular weight of 335, which is approximately that of behenic acid, but the low melting point indicates that the product is a mixture of acids.

A 100-gram portion of the original oil was saponified by treatment with a solution of sodium ethylate in absolute alcohol. The acids were converted into their calcium salts by treatment with a solution of calcium chloride. The major portion of the unsaponifiable matter separated as an upper liquid phase. This was removed as completely as possible by centrifuging, and further portions were separated by repeated extraction of the remaining calcium salts with ether. The extracted calcium salts were decomposed by treatment with hydrochloric acid, the liberated acids were taken up in ether and the ethereal solution washed with water until free from mineral acid. On removal of the ether 43.2 grams of acids were obtained. This low yield indicated either an imperfect saponification or an incomplete separation of the saponification products. Therefore the unsaponifiable fraction, which had been separated from the calcium

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