A Distillation Method For Water in Soaps

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DISTILLATION methods for determining water in soaps have been improved from time to time, by applying analytical innovations whenever adaptable.

Distilling water from soaps by means of xylol was not a satisfactory manipulation until Hart (1) showed that foaming could be overcome by adding oleic acid to the contents of the flask before distilling. The distillation method at this time required the collection of the water with a considerable volume of xylol in a single receiver. The large amount of xylol in contact with the water made it necessary to apply a correction for the amount of water absorbed by the organic distillate.

When Dean and Stark (2) introduced their modification of the distillation method for determining moisture in petroleum, oils, tars, etc., analysts recognized the adaptability of this procedure for measuring the amount of water in soaps.

Graham (3) recommended adding a piece of dry rosin to the distillation flask to prevent foaming, when this method was used for determining the amount of water in mineral oil emulsions containing soap. Used in this way, the rosin serves the same purpose as oleic acid, in that it converts neutral soaps into acid soaps.

The method employing oleic acid was in use for a few years until Church and Wilson (4) presented a dissertation in which they described some inherent errors in the distillation method. They showed that oleic acid, added to the soap to prevent foaming, was a cause of error when the soap contained alkaline builders, since oleic acid reacts with these alkalis thereby liberating water, which is in additive error.

Instead of adding oleic acid to the xylol and soap to be distilled, Church and Wilson proposed replacing the oleic acid with anhydrous sodium acetate for an antifoaming agent. Experimental data were offered to show the merit of this modification, which was later accepted by the A.O.C.S. as one method for determining water in soap. The alternative method is oven-drying.

The oven method has its limitations, and does not give accurate results in all instances because temperatures that are high enough to dehydrate some hydrated builders will char or otherwise decompose the soap ingredient.

The present A.O.C.S. method for determining moisture by distillation has some very obvious disadvantages. Among these are its persistent tendency to foam and to boil over and its need for constant watching. Much of this is caused by the thickening of soap in the solvent during some stage of dehydration. Sodium acetate is certainly not a good remedy for this. Furthermore, many tests end with a fused and somewhat charred residue in the flask which is difficult to clean.

The author proposes a new modification in the distillation method that eliminates all of the bad features of the present system. This is accomplished by converting ordinary soaps; that is, water-soluble soaps, into water-insoluble soaps. Soaps insoluble in water do not foam during the distillation test. Such soaps include those of magnesium, calcium, strontium and barium and of some non-alkali metals. Metallic soaps examined were those of zinc, cadmium, aluminum, copper and manganese. Any of these soaps, dissolved or dispersed in benzene, toluene or commercial xylene, to which water has been added, allow perfect distillation without foaming, and generally with complete recovery of water.

Some of these soaps are not sufficiently stable to be used in the distillation test, because they decompose upon heating. Soaps of aluminum, copper, zinc, cadmium, etc. appear to decompose into basic salts of fatty acids. Compared with these are the soaps of magnesium, calcium, strontium and barium, which are not perceptibly altered during prolonged boiling in the previously named solvents.

In conducting the distillation test in this revised manner, ordinary soaps are converted into water-insoluble soaps directly within the distillation flask. A suitable, water-soluble salt whose cation forms soap insoluble in water, is added to the flask containing toluol, or other solvent, and the sample of soap. Some moisture must be present to promote the reaction.

For example, potassium oleate ($KOOC\text{-}C_{17}H_{33}$) is reacted with an excess of barium chloride. The mole-equivalent of soap is not changed, nor is the amount of water, yet these reaction products distill without foaming.

$$2KOOC\text{-}C_{17}H_{33} + BaCl_2 + \text{water} \longrightarrow Ba(OOC\text{-}C_{17}H_{33})_2 + 2KCl + \text{water}$$

Water-insoluble soaps from other water soluble salts are also possible. Both cations and anions may be altered. Examples of these are magnesium sulfate and calcium nitrate, both of which produce nonfoaming soaps,

$$2KOOC\text{-}C_{17}H_{33} + MgSO_4 + \text{water} \longrightarrow Mg(OOC\text{-}C_{17}H_{33})_2 + K_2SO_4 + \text{water}$$

$$2KOOC\text{-}C_{17}H_{33} + Ca(NO_3)_2 + \text{water} \longrightarrow Ca(OOC\text{-}C_{17}H_{33})_2 + 2KNO_3 + \text{water}$$

Sulfates and nitrates are not suitable for use in this moisture test because they oxidize or otherwise react with both soaps and solvents. Not all chlorides satisfactorily serve this purpose, either. Chlorides of a number of metals lose some hydrochloric acid during the water distillation test. Chlorides of zinc, cadmium, aluminum, manganese, magnesium, etc., cannot be used for this reason. Barium chloride proved to be the most suitable.

When builders are present in a soap composition, it may be said that the first reaction to occur is that of one or more of the builders with the salt. Any one of the builders will completely react with barium chloride and probably be-

fore there is any appreciable reaction of the soap ingredient with the $BaCl_2$.

This point may be illustrated with the hypothetical treatment of a powder containing soap, sodium carbonate and trisodium phosphate. The following reactions take place in the presence of moisture:—

(1) $2Na_3PO_4\text{-}12H_2O + 3BaCl_2 \longrightarrow 6NaCl + Ba_3(PO_4)_2 + 12H_2O$

(2) $Na_2CO_3 + BaCl_2 \longrightarrow 2\,NaCl + BaCO_3$

(3) $2NaOOC\text{-}C_{17}H_{33} + BaCl_2 \longrightarrow 2NaCl + Ba(OOC\text{-}C_{17}H_{33})_2$

The end products are neither hydrated nor hygroscopic. They are easy to free from water by the distillation method.

The foregoing equations indicate the need of sufficient reacting salt. It is almost impossible to weigh out just enough $BaCl_2$ to exactly convert all of the constituents of a saponaceous composition into water-insoluble products. It is also obvious that an excess of the reacting salt should be used to assure complete reactions. This imposes another requirement upon the salt chosen for this purpose, and that is, that the salt itself can be easily dehydrated under the conditions of the distillation test, and that it shall not interfere with the dehydration of other products. Barium chloride fulfills these requirements in every detail.

It is to be noted that the water obtained by this test includes the water of all of the components of the material tested, and therefore also water of hydration. A quantitative analysis of the composition is required before water of hydration can be allotted to its proper place.

The conversion of neutral and basic salts into insoluble barium salts makes this method quite generally applicable, with the exception of bicarbonates, in which case there is an additive error of water, according to the following equation:

$$2NaHCO_3 + BaCl_2 \longrightarrow 2NaCl + Ba(HCO_3)_2 \downarrow$$
$$BaCO_3 + CO_2 + H_2O$$

Excepting the occurrence of a sesqui-carbonate and rarely a bicarbonate, all other agents for compounding with soap can be treated by this method without corrections.

METHOD FOR APPLYING MOISTURE TEST

The method for making moisture determinations upon soaps and saponaceous compounds proposed in this paper, is essentially the same as the usual distillation method.

The distillation flask was the ordinary 500 m.l. short neck pyrex flask. The receiver was a 25 m.l. Bidwell-Sterling burette, graduated to o.1.m.l. divisions.

Ten grams of the soap to be analyzed are carefully weighed into the flask and immediately covered with 250 m.l. of toluene. Since the method permits precise measurements, the operator should weigh his sample with accuracy to the second decimal place whenever possible.

About ten grams of anhydrous powered $BaCl_2$ is next added. If it is definitely known that the sample of soap contains less than 30% water, ten m.l. of additional water should be added to the contents of the flask by means of a pipette. A blank run upon the amount of water delivered by the pipette should be made so that the quantity of water obtained from this source can be deducted from the burette reading.

Prior to distillation, the contents of the flask should be heated just below boiling for from ten to thirty minutes. If the sample of soap contains 40% of water, or if an additioial 10 m.l. of water has been added, the time for preliminary heating will seldom exceed fifteen minutes. The complete conversion of water-soluble soaps into barium soap is clearly indicated by the behavior of the boiling liquid, and after this point is reached, distillation may be as rapid as the operator desires. The precautions and recommendations made in the regular A.O.C.S. method should otherwise be observed.

Anhydrous barium chloride was prepared by heating a quantity of pure $BaCl_2\text{-}2H_2O$ in an evaporating dish, or in a suitable crucible over a hot flame. The salt should be stirred during heating, and a stainless steel spatula will serve this purpose. The $BaCl_2$ while still hot, should be moderately pulverized in a mortar, transferred to a beaker and thence stored in a dessicator for use.

All liquids used in the distillation tests were first dehydrated by distillation.

Since corks were used to connect the flask, burette and condenser, a precautionary provision for preventing either gain or loss of moisture, was obtained by coating the corks with flexible collodion*. These were coated after they had been bored to proper size so that all surfaces could be made water-tight. The flexible collodion also provides a coating impervious to toluene, so that the cork fittings may be used for many hours of service before replacement.

In observing the meniscus during the calibration of the moisture burette, it was found that its shape was not exactly the same in frequent instances. Since the reading is usually made at the lowest part of the meniscus, this irregularity gives rise to error.

For ordinary readings, the error is negligible. If readings with an accuracy of 0.1 of a division are desired, the round meniscus makes this difficult to attain.

However, if the interface between the toluene and water is made flat, it is possible to duplicate readings with an accuracy of 0.1 division. The flat interface is obtained by introducing a minute amount of a surface tension depressant. This is accomplished by barely dipping the end of a fine (B & S gauge 22) copper wire into a 25% solution of Aerosol OT, and lowering this to the water-toluene junction.* The burette used in the experiments described herein, was calibrated for flat menisci.

The reading of the burette can be facillitated by coloring the toluene above the water. A little oil-soluble dye,** preferably red, can be added to the burette after distillation as a dry powder, or in a concentrated solution in toluene. In the latter case, the dye is added by means of the copper spiral which is used for dislodging water within the burette.[4] The spiral may first be dipped into the concentrated dye solution.***

The use of stained xylol (or other solvent) for aiding the reading of the moisture trap (burette) is not altogether new, for Fuchs [5] recommended adding a few drops of a solution of asphalt in benzol to the burette to make more visible any drops of water that might be adhering to the side.

*Suitable flexible collodion can be obtained from any chemical supply house.
*Aerosol OT, made by American Cyanamicl Co.
**Any oil soluble sudan red dye will serve this purpose.
***A description of this method was given by the author at the October 1938 meeting of the A.O.C.S.

EXPERIMENTAL PART

Experiment No. 1

Approximately 10 g. of anhydrous $BaCl_2$ were weighed into a distillation flask to which was added toluene and exactly ten m.l. of water. The contents were distilled for one hour. Exactly 10.00 m.l. of water were recovered.

It was thereby shown that $BaCl_2$ does not interfere with the complete recovery of water by the distillation method.

Experiment No. 2

Similar tests to determine the completeness of the recovery of water were made upon anhydrous sodium acetate (10.0 g.). Exactly 10.00 m.l. of water were distilled with (1) benzene and (2) toluene. The results shown below indicate that anhydrous sodium acetate also relinquishes all water during the test.

	Benzene	Toluene
Time required	5 hrs	45 minutes
Water recovered	9.95 m.l.	10.02 m.l.

Experiment No. 3

A series of distillation tests were made upon a variety of soaps for the purpose of comparing the percents of water found by the two methods. In certain cases of dry soaps and those low in water content an additional 10 m.l. of water was added for the test and in these instances corrections have been made in the table.

Test No.	Kind of Soap	Percents of Water Found A.O.C.S. Method		Barium Chloride Method	
1	Liquid Coconut Oil Soap	59.2 59.6	Av. 59.4	59.8 59.2	Av. 59.5
2	Soybean Oil Soap +5% borax	59.3 59.2	Av. 59.25	60.1 60.4	Av. 60.25
3	Corn Oil Jelly Soap	68.2 68.0	Av. 68.1	68.2 67.8	Av. 68.0
4	Hard Vegetable Paste Soap	35.4 35.6	Av. 35.5	35.2 35.4	Av. 35.3
5	Corn Oil Soap (+10 m.l. H_2O)	19.4		19.6	
6	Powdered Tallow Soap (+10 m.l. H_2O)	4.3 4.6	Av. 4.45	4.7 4.6	Av. 4.65
7	Soap Powder containing 50% T.S.P. (+10 m.l. H_2O)	2.3 2.2	Av. 2.25	2.3 2.3	Av. 2.3

Test No. 2 indicates that borax is difficult to dehydrate by the A.O.C.S. distillation method, while this is not experienced in the $BaCl_2$ Method since the borax is converted into the non-hydrated barium meta-borate. This suggests that there may be other builders similarly difficult to dehydrate when the sodium acetate method is used.

Conclusion

The use of anhydrous barium chloride for an anti-foaming agent in the distillation method for determining the amount of water in soap, is superior to sodium acetate in respect to speed, ease of handling the test, and finally in respect to leaving more cleanable apparatus. It offers another advantage in that anhydrous $BaCl_2$ is more easily prepared than is anhydrous sodium acetate.

REFERENCES

(1) Hart, J. Ind. Eng. Chem. 10,598 (1918).
(2) Dean & Stark, J. Ind. Eng. Chem. 12,486-90 (1920).
(3) Graham, J. Assoc. Offic. Agri. Chem. 9,-127-37 (1925).
(4) Church & Wilson, Soap 7, No. 11, 3507 (1931).
(5) F. C. Fuchs, Eng. Mining J. 106,357 (1918).

Report of the Uniform Methods and Planning Committee

OCTOBER 4, 1939

THE Uniform Methods and Planning Committee have considered the recommendations of the Soap Analysis Committee and have concurred in their recommendations, which follow:

1. That the McNicoll method for rosin, as modified by the committee, be adopted as a tentative method of the A.O.C.S.
2. That the method for determination of iodine number, prescribed by the Fat Analysis Committee, be included in the Soap Analysis Methods for use on soap fatty acids. Preparation of fatty acids for iodine number determination will be essentially the same as for titer.
3. *Matter volatile at 105° C.* (Oven Method) specifies drying to "constant weight." It was agreed to define this as follows: "Constant weight is attained when successive heating for one hour periods shows a loss (or gain) of not more than 0.1%."
4. *Matter Insoluble in Water.* Some confusion has existed in the interpretation of this method. Some laboratories have been proceeding with this determination on the sample used under "Matter Insoluble in Alcohol," that is, after drying and weighing the latter. The method will be revised to emphasize the fact that a *new sample* should be taken for the water insoluble determination.
5. *Screen Test.* The Committee has approved the deletion of the reference to the Ro Tap machine and the method will refer to the use of any suitable type screen test machine. Also, since specifications may call for use of sieves other than those now specified in the method, it was agreed to add a note that, when called for, other sieves may be used in the determination as now written.

Upon motion, duly seconded, the recommendations were adopted by a vote of the Society.

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E. B. Freyer
C. P. Long
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A. K. Schwartz
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