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# The Determination of Moisture in Sodium Alkyl Aryl Sulfonates

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THE determination of water in commercial synthetic detergents of the sodium alkyl aryl sulfonate type is frequently desired in these laboratories. In our opinion the literature is lacking in methods which have been carefully investigated for such materials. The sodium alkyl aryl sulfonates are available in many grades and forms, covering a range of active agent content. Sodium sulfate is a major constituent of the finished products with minor constituents, such as unsulfonated oil and moisture, being present in the range of 1% or less. Commercial products from several sources were investigated so that the results obtained can be considered reliable for the sodium alkyl aryl sulfonates in general.

Five methods for the determination of water in sodium alkyl aryl sulfonate products were investigated. Two methods, drying at 110°C. for four hours and desiccation for eight days over concentrated sulfuric acid, were selected as the former had been used as a control procedure and the latter had been used in these laboratories in previous work. After a consideration of other methods three were selected which appeared to be most readily applicable to the problem. One of these, Official Method F 1a-44 of the American Oil Chemists' Society (3), involves azeotropic distillation followed by measurement of the volume of water separating from the distillate. The second method selected was developed in this laboratory by Suter (6) for the determination of water in solid caustic. As in the A.O.C.S. method, this procedure involves removal of the water by azeotropic distillation, but the determination of the water in the distillate is made by titration with Karl Fischer reagent rather than by volumetric measurement. The third method selected was direct titration with Karl Fischer reagent without prior removal of water by other means.

## Experimental

The samples of sodium alkyl aryl sulfonate used in this work were obtained from several different manufacturers and were selected in some cases for wide variation in active agent and unsulfonated oil content. None was known to contain any admixed compound which would react with Karl Fischer reagent.

*Karl Fischer Method.* The Karl Fischer method for the determination of water has been extensively investigated. It is not generally applicable to all materials as a number of compounds have been found to interfere with the reagent. A literature survey did not disclose any instance of the application of the Karl Fischer reagent to sodium alkyl aryl sulfonates as a class; however no theoretical objection to its use could be found. As detergents of this type usually contain sodium sulfate, consideration was given to the applicability of this method to hydrates of sodium sulfate. Smith and Mitchell (5) reported the water of hydration in sodium sulfate to be determined quantitatively by the Karl Fischer reagent, a fact readily confirmed in this laboratory.

The Karl Fischer apparatus used for this work employed standard taper flasks which fitted into a turned bakelite stopper carrying the stirrer and electrodes as recommended by Almy, Griffin, and Wilcox (2). The end point was determined by the dead stop method of Foulk and Bawden (4) and detected by a G. F. Smith Electron Beam Sectrometer.[1] The Fischer reagent and standard water solutions were dispensed from ordinary automatic burettes suitably protected from atmospheric moisture. It was found advantageous in this instance to add an excess of Karl Fischer reagent and titrate the excess with a standard water solution. The water solution was prepared by the addition of water to anhydrous methanol and may be standardized by any of the recognized methods.[2] The Karl Fischer reagent was prepared as directed by Wernimont and Hopkinson (7).

Preliminary tests made by adding the Karl Fischer reagent directly to a weighed sample indicated the desirability of suspending the material in a solvent prior to analysis. Spent Karl Fischer reagent was used as a suspending medium, and excellent results were obtained for samples containing 40-50% sodium alkyl aryl sulfonate, but erratic results were obtained for samples containing greater amounts. This difficulty was eliminated by using anhydrous methanol as the suspending medium. The procedure adopted is as follows:

> Weigh the sample by transferring three to five grams into a dried, tared weighing bottle. Cap the bottle immediately and reweigh. Introduce into a 250 ml. Erlenmeyer flask, 15-25 ml. of anhydrous methanol and add a small excess of Karl Fischer reagent. Titrate with the standard water solution to the exact end point. Remove the flask immediately and transfer the sample from the weighing bottle into the flask. If any sample remains in the weighing bottle, it may be reweighed later and the sample weight corrected. Add an excess of Karl Fischer reagent at once to the sample in the pretitrated methanol solution and record the amount. Then titrate in the usual manner to the end point with standard water solution, recording the amount required.

The calculations are made by determining the ratio of Karl Fischer reagent to the standard water solu-

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[1] Smith, G. F., and Sullivan, V. R., "The Electron Beam Sectrometer," G. Frederick Smith Chemical Company, Columbus, Ohio.

[2] The various standardization methods available may be found in Mitchell-Smith "Aquametry," pp. 69-71.

tion. This ratio must be determined daily and should be reproducible before analyses are attempted.

The precision obtained by the above method is very good when the total water determined is in the range 20-200 mg. It was planned to establish the accuracy of the method by adding known amounts of water to the thoroughly dried material. This approach had to be abandoned when it was found that the material retained moisture even when dried for considerable periods of time. Water added in addition to that found by analysis can be recovered quantitatively; however the determination of the original water content is open to question. In an effort to establish the accuracy of the method comparative results were obtained by two different but generally acceptable methods. The methods used for comparison were the azeotropic distillation method of the A.O.C.S. (3) and the distillation titration procedure of Suter (6).

The Karl Fischer method has the obvious advantages of being precise as well as rapid. An examination of the sodium alkyl aryl products showed that there were no strong acids or bases present which would react with the reagent. Methyl alcohol used in the procedure will not esterify with the material, therefore no error from water from this source is possible, and it was found that iodine would not react under the conditions of the test. It appears therefore that the results obtained by this method can be accepted with confidence.

*Azeotropic Distillation.* The azeotropic distillation of water from sodium alkyl aryl sulfonate products and measurement of the volume of water distilled cannot be recommended. All of the usual difficulties in operation are encountered, such as water holdup in the condenser and difficulty in separation of the distillate. These difficulties are magnified by the fact that due to the low moisture content small losses cause large percentage errors. The low moisture content necessitates the use of large samples. The large samples are difficult to handle as there is a tendency for gel formation and the sodium sulfate is insoluble, causing poor heat transfer at the bottom of the flask. Some constituent, which has been assumed to be unsulfonated oil, distills with and clouds the water and causes difficulty in separation of the two phases in the measuring tube. This is particularly pronounced in the materials containing high concentrations of the sulfonate. It was found that several hours were necessary for a good separation of the water and hydrocarbon solvent. Both xylene and toluene were used with little difference being noted between the two. The agreement of the results obtained with those by the Karl Fischer method are no doubt attributable to the care and patience with which each determination was made.

On account of the difficulties described and the time involved for a single determination there was little interest in this method. For this reason only a few determinations were made by this method.

The distillation-titration method of Suter provides an excellent method for the determination of water when it may be removed by distillation from compounds interfering with the usual Karl Fischer procedure. The distillation is accomplished in an all-glass apparatus. The receiver, which also serves as a condenser, is a standard taper flask suitable for carrying out the Karl Fischer titration.

It was expected from the work of Suter that the results obtained by this method would be high. He found that results tended to be about 5% greater than the actual water content. The data obtained leaves this point in doubt, half of the samples agreeing well with the Karl Fischer method and half being high in comparison. The high results could not be correlated with any controllable factor. Both xylene and toluene were used as the organic solvent with very little difference in results. It would appear that the samples are not sensitive to 140°C. temperature.

A comparison of the results of the Karl Fischer and Suter method are shown in Table I.

TABLE I

Comparison of the Determination of Water in Sodium Alkyl Aryl Sulfonates by the Karl Fischer Method, Azeotropic Distillation Method of A.O.C.S., and the Distillation-Titration Method of Suter

| Sample | Water by the Karl Fischer method, % | Water by A.O.C.S. F 1a-44, % | Water by method of Suter, % |
|---|---|---|---|
| A | 1.98<br>1.98 | 2.0<br>1.5 | 2.12<br>2.14 |
| B | 1.59<br>1.61 | 1.60 | 1.65 |
| C | 2.00<br>2.00 | 2.0 | 2.18 |
| D | 3.04<br>3.06 | 3.3 | 3.15 |
| E | 1.85<br>1.85 | ...... | 2.12<br>2.14 |
| F | 1.40<br>1.48 | ...... | 1.43<br>1.47 |
| G | 1.23 | ...... | 1.23 |

*Oven Drying.* Samples were analyzed for water content by drying four hours at 110°C. The water content was also determined by the Karl Fischer method as outlined above. It was found that in general the results obtained by oven drying were lower than the results obtained by the Karl Fischer method. This indicated the possibility of residual water. Tests were then made by drying for four hours at 110°C. and determining the residual moisture by the Karl Fischer method. Results are given in Table II. For samples with low unsulfonated oil content the total water content as determined by oven drying plus the residual water by the Karl Fischer method compared favorably with the total water content as determined by the Karl Fischer method. For the other samples

TABLE II

Comparison of the Oven Drying and Karl Fischer Methods

| Sample | Unsulfonated oil | Weight loss at 110°C. 4 hours, % | Residual water by Karl Fischer, % | Total, weight loss at 110°C.+ residual water, % | Water by Karl Fischer method, % |
|---|---|---|---|---|---|
| D | 1.6 | 2.29 | 0.99 | 3.28 | 3.06<br>3.04 |
| H | 1.2 | 1.15 | 0.50 | 1.65 | 1.69<br>1.64 |
| I | 4.3 | 1.37<br>2.02 | 0.96<br>0.49 | 2.33<br>2.51 | 1.35<br>1.38 |
| J | 0.8 | 1.56 | 0.36 | 1.92 | 1.81<br>1.87 |
| K | 2.5 | 0.94 | 0.41 | 1.35 | 1 02<br>0.97 |

the loss by drying at 110°C. plus the residual water gave a total water value much higher than the water content as determined by the Karl Fischer method. From these data it was concluded that water is not entirely removed from the material by oven drying and that oil is lost simultaneously.

To determine if loss of unsulfonated oil was a factor adversely affecting the results by oven drying a sample was selected which was high in unsulfonated oil and the oil content determined on the original material and then after drying for four- and 24-hour periods. The data tabulated in Table III show that unsulfonated oil is lost during drying at 110°C.

TABLE III

Volatilization of Oil by Oven Drying

| Sample | Oil, % | Weight loss at 110°C. 4 hours, % | Weight loss at 110°C. 24 hours, % | Oil after drying 110°C., % | Oil Calculated loss at 110°C., % | Water calculated loss at 110°C., % |
|---|---|---|---|---|---|---|
| I-1 | 4.3 | 1.39 | ...... | 3.4 | 0.9 | 0.5 |
| I-2 | 4.3 | 2.43 | ...... | 2.4 | 1.9 | 0.5 |
| I-3 | 4.3 | ...... | 3.21 | 2.0 | 2.3 | 0.9 |
| I-4 | 4.3 | ...... | 3.60 | 1.4 | 2.9 | 0.7 |

*Drying Over Concentrated Sulfuric Acid.* Samples were dried over concentrated sulfuric acid for eight days by enclosing each sample in a separate desiccator and storing. The results were compared with those obtained by the Karl Fischer method. The samples after drying were analyzed for residual moisture by the Karl Fischer method as was done for the oven dried samples. The data are summarized in Table IV.

TABLE IV

Comparison of Results by Dehydration Over Sulfuric Acid for Eight Days and the Karl Fischer Method

| Sample | Oil, % | Water by dehydration over conc. $H_2SO_4$ for 8 days, % | Residual water by Karl Fischer, % | Total water dehydration + residual water, % | Water by Karl Fischer, % |
|---|---|---|---|---|---|
| D | 1.6 | 1.78 | 1.30 | 3.08 | 3.05[a] |
| H | 1.2 | 0.92 | 0.67 | 1.59 | 1.67[a] |
| I | 4.3 | 0.53 | 0.86 | 1.39 | 1.37[a] |
| M | 4.3 | 0.48 | 0.85 | 1.33 | 1.33[a] |
| N | 3.1 | 1.92 | 1.23 | 3.15 | 3.15[a] |

[a] Average of two or more determinations made at start of test.

It is noted that in every instance the results obtained by drying over sulfuric acid are lower than by the Karl Fischer method. The agreement is good when the residual water is added to the drying loss.

*Precision and Accuracy of the Karl Fischer Method.* Establishment of the accuracy of the Karl Fischer method is difficult as no absolute methods were found for determining the amount of water in the material under investigation and it could not be dehydrated so that added water could be determined. As the Karl Fischer method gives results comparable with those of other established methods and water added plus that found by analysis can be determined with good accuracy, it can be expected that the accuracy will be the same as for the Karl Fischer method for the determination of water in other materials. It has been found in these laboratories that by standardizing against known water contents the water can be determined within one part per hundred, which is the expected accuracy of the Karl Fischer method for the determination of water in sodium alkyl aryl sulfonates.

In an effort to establish the precision of the method in various laboratories a disinterested person prepared a composite sample which was analyzed by four different laboratories with agreement within 0.04%. The results submitted were 1.57%, 1.58%, 1.59%, and 1.61%. This agreement is much better than was attained with any of the other methods. It has been found in evaluation of a large amount of data obtained by the Karl Fischer method for sodium alkyl aryl products that the average deviation is 0.02%.

TABLE V

Comparative Analyses of Two Laboratories on Analysis of Sodium Alkyl Aryl Sulfonates by the Karl Fischer Method

| Sample | Laboratory No.1, % $H_2O$ [a] | Laboratory No. 2, % $H_2O$ [b] |
|---|---|---|
| 1 | 1.57 | 1.61 |
| 2 | 1.63 | 1.56 |
| 3 | 1.56 | 1.53 |
| 4 | 0.72 | 0.72 |
| 5 | 1.69 | 1.67 |
| 6 | 1.91 | 1.82 |
| 7 | 2.21 | 2.21 |
| 8 | 1.34 | 1.40 |

[a] Average of duplicate determinations made by experienced personnel.
[b] Single determinations reported by control technician.

Table V presents data of various samples of sodium alkyl aryl sulfonates analyzed by two different laboratories. The results reported by Laboratory No. 1 were made by experienced personnel whereas the results reported by Laboratory No. 2 were made by a technician who made only a single analysis for each sample.

## Discussion

On the basis of the experimental work the Karl Fischer method was selected as the most satisfactory for the determination of water in sodium alkyl aryl sulfonates. The procedure is accurate and rapid with good precision. The method is readily adaptable to control work and requires little training to perform satisfactorily. Oven drying and desiccation over sulfuric acid has been shown to give erroneous results. The azeotropic distillation method of A.O.C.S. is not satisfactory for either routine determinations or more critical examinations. The determination is severely limited by the amount of water distilled and the determination of this volume. The azeotropic distillation of Suter is not justified for the type of materials under examination. The amount of time and technique involved is considerably greater than for the Karl Fischer method; however this method has been of great value in determining the moisture content of mixtures of sodium alkyl aryl sulfonate where an admixed compound was known to react with the Karl Fischer reagent.

The Karl Fischer method has been in use in these laboratories for nearly a year and has been very satisfactory. For control laboratory work it has been found advantageous to discard the standard taper flask arrangement and substitute a titration flask similar to that recommended by Aepli and McCarter (1). This flask has an opening in the top for the stirrer, and on the sides for the burettes and electrodes. A stopcock in the bottom allows the discharge of the sample and titrating media.

## Conclusions

1. The oven drying method for the determination of water in sodium alkyl aryl sulfonates results in incomplete removal of water and may result in the loss of unsulfonated oil and other volatile products.
2. The determination of water in sodium alkyl aryl sulfonates by desiccation over concentrated sulfuric acid results in incomplete removal of the water.
3. The determination of water in sodium alkyl aryl sulfonates by azeotropic distillation and subsequent measurement of the water distilled is not recommended because of the operational difficulties and lack of sufficient accuracy.
4. The azeotropic distillation of Suter (6) is applicable for the determination of water in sodium alkyl aryl sulfonates, but comparable results may be determined more readily by the proposed Karl Fischer method.
5. The determination of water in sodium alkyl aryl sulfonates by the Karl Fischer method is the most satisfactory of the methods investigated.

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# Some Observations on the Solubility of Sulphonated Castor Oil in Organic Solvents

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RESEARCH on the solubility of soap in organic solvents plus water and the study of different phases encountered has made much progress in recent years (1). The study of the solubility of sulphonated castor oil (commercially known as turkey red oil) has not progressed in a similar manner. This subject however is of great practical importance for the textile industry. The author has undertaken some experimental work on these lines. Results of these experiments may help to initiate further research on this subject.

It was found that the solubility of most commercially available turkey red oils in organic solvents of the aromatic type such as benzene, xylene, and toluene, and of the paraffinic type, such as kerosene and light petroleum fractions was rather poor. The reason for this was that the water content of most commercial products was much higher than 30%. In order to obtain better results a sulphonated castor oil with water content below 30% was specially prepared in the laboratory and the experiments carried out with this product. This highly concentrated turkey red oil is as easily prepared on a plant scale as the more dilute types.

## Experimental

150 g. castor oil were sulphonated with 37.5 g. sulphuric acid at a temperature not exceeding 30°C. After the sulphonation was completed, which took about 30-45 minutes, the mixture was allowed to stand for about 20 hours. The sulphonation product was washed free of uncombined sulphuric acid with 150 g. of a 10% sodium chloride solution. After another period of 12 hours' settling the wash solution was drained off and the washed sulphonation product neutralized with 60 g. of a 20% caustic soda solution. The final product was a viscous clear liquid with pH about 7.5 in 1:1 dilution with distilled water. The product has a water content of 28%, organic $SO_3$ content of 9.0%, and 58.0% total fatty matter.

This sulphonated castor oil was the material with which all solubility tests were carried out. The first observation was that in all solvents used in the experiments the sulphonated oil was more soluble when less solvent was used for dilution. This observation was quite in accordance with similar observations with triethanolamine oleate, which is not completely soluble in gasoline below 2% (2).

## Results

*Petrol Ether as Diluent.* 100 g. sulphonated oil were completely soluble in 50 ml. petrol ether (boiling range 50-70°C.). When 100 g. sulphonated oil were diluted with 66 ml. petrol ether, the mixture became turbid. On standing for 10 hours, a clear liquid separated at the top of the mixture (40 ml. = 24% of the total).

*Kerosene as Diluent.* 100 g. sulphonated oil were completely soluble in 66 ml. kerosene (140-230°C. boiling range with about 18% aromatic and olefinic constituents). A mixture of 100 g. sulphonated oil with 100 ml. kerosene became turbid and after 10 hours a clear liquid separated on top (80 ml. = 40% of the total).

*Benzene as Diluent.* 100 g. sulphonated oil were completely soluble in up to 400 ml. benzene. A mixture of 100 g. sulphonated oil and 500 ml. benzene became turbid and a clear liquid separated after 10 hours' standing (110 ml. = 18.3% of the total).

*Xylene as Diluent.* 100 g. sulphonated oil were completely soluble in up to 400 ml. xylene. A mixture of 100 g. sulphonated oil with 500 ml. xylene became turbid and a clear liquid separated on top of the mixture on standing for 10 hours (120 ml. = 20% of the total).

*Toluene as Diluent.* 100 g. sulphonated oil were completely soluble in up to 500 ml. toluene. A mixture of 100 g. sulphonated oil in 600 ml. toluene became turbid and a clear liquid separated on top after 10 hours' standing (280 ml. = 46.5% of the total.)