glycerides would therefore give products of differing characteristics.

Summary

Four isomeric octadecenoic acids, oleic, elaidic, petroselinic, and petroselaidic, were prepared and their expansibility determined. The melting dilation of each acid was calculated and found to increase in the order oleic, petroselinic, petroselaidic, and elaidic. In each instance the melting dilation of the trans acid was greater than that of its cis isomer. Of the two cis acids studied, the melting dilation was less for the acid with the double bond farther from the carboxyl end of the carbon chain. The trans acids did not follow this pattern.

At temperatures above 52°C., at which all acids were liquid, the absolute specific volumes of the acids were very nearly equal whereas at temperatures below —7°C. at which all were in the solid state, the specific volumes of petroselinic and elaidic acids were at variance with the specific volumes of oleic and petroselaidic acids. This variance must be attributed to differences in crystal packing.

Oleic acid clearly showed the two polymorphic forms previously recognized and, in addition, apparently reversibly transformed at about —5°C., indicating the possible existence of a third polymorphic form. These transformations of oleic acid occurred regardless of tempering, and without visual melting. The other three acids did not exhibit polymorphism under the conditions employed in the dilatometric measurements.

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Simplified Procedure for Water Determination by the Karl Fischer Method.[1] I. Application to Drycleaning Detergents and Solvents

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PRIOR to 1949 the literature on the Karl Fischer method for determination of water was rather discouraging to one in search of a routine procedure for systems where the oven method could not be used. The discouraging aspects of the method were several. The reagent was unstable, and frequent standardization was necessary; electrometric titrations and apparatus of considerable complexity were usually recommended; the method was overburdened by well-meant but exaggerated precautions.

In 1949 Seaman, McComas, and Allen (5) described a rather drastic modification of the conventional Fischer procedure. This procedure, with the further modifications described in the present paper, appears to meet all of the above objections. The simplified procedure to be described has been in constant use in this laboratory since June 1949 in a variety of research projects and routine analyses. Six different technicians have used it successfully, and none has reported any difficulties.

The principal distinction between Seaman, McComas, and Allen's method and the older ones is that the newer procedure makes use of the reagent in the form of two solutions that are mixed in the presence of the sample during titration.

In the present paper there are offered some simplifications to make the method suitable for routine use where a large number of determinations need to be made. In addition, the method of standardization is improved by substitution of n-propanol for methanol in the standard water solution. Propanol has three advantages over methanol for this purpose. It is less hygroscopic hence the standard solution is more stable on exposure to the air; it is less volatile so that the pipet is not cooled by rapid evaporation of the solvent film; and finally it is more viscous, therefore pipetting is easier.

Propanol could probably be substituted elsewhere in the procedure but for the fact that it is more difficult to dry than is methanol. To obtain satisfactory results with our procedure, we have found that the methanol should be as dry as possible. Methanol can be dried satisfactorily by means of magnesium methylate (3). Fortunately this time-consuming step can be avoided by the purchase of a drum of synthetic methanol. We have found that methanol taken directly from the drum is as dry as we can get it by the magnesium method. This is not generally the case with bottled methanol. The time and expense saved by avoiding the drying operation will amply repay the investment in methanol.

Reagents and Chemicals. The reagents were prepared in the same manner as by Seaman *et al.* (5) except that a number of precautions observed by these workers were found to be unnecessary.

It was not found necessary to cool the methanol before addition of sulfur dioxide. The gas is absorbed very rapidly at room temperature, and the small amount that escapes can be disposed of by using a hood, or an open window and electric fan.

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[1] The Karl Fischer procedure, as modified by Seaman and coworkers, has been further simplified so that it may be used as a routine analytical tool, using merely the visible end-point. Some applications to organic solvents and drycleaning detergents are described.

The most convenient and rapid method of adding the sulfur dioxide is simply to pour it from the cylinder into the methanol. This method avoids long exposure of dry methanol to the air. It is convenient to use the 10-pound cylinder if this method is employed. The cylinder is mounted in an inverted position and a piece of rubber tubing connected to the outlet. The container with the methanol is balanced on a bench balance, and the liquid sulfur dioxide is passed into the methanol until the proper weight has been added. It is important to wrap the tubing from the cylinder with paper towels or some other absorbent. This tube becomes frosted over during the addition of the sulfur dioxide. When the valve is closed, this frost quickly melts and will run into the solution if the towel is not used to absorb it.

It was also not found necessary to cool the mixture of sulfur dioxide and methanol before adding pyridine. When the pyridine is added in about 150-ml. portions at 5-min. intervals, heating of the solution is not excessive. If a Pyrex bottle is used, the pyridine may be added all at one time without danger. In this case the entire operation of preparing Solution A requires only 15 minutes.

Commercial grade sulfur dioxide in 10-pound cylinders was found to be satisfactory and quite anhydrous. No difference in the resulting reagent was detectable when the gas was used directly from the cylinder or when it was first bubbled through concentrated sulfuric acid.

One precaution was found quite important. The pyridine used should be C. P. or a purified grade. Technical grade pyridine is unsatisfactory since it yields a dark colored reagent, making visual detection of the end-point most difficult.

Preparation of Solution A. This solution was made up to the concentration recommended by Seaman: 1 g. sulfur dioxide to 5 ml. methanol and 5 ml. of pyridine. A convenient procedure is as follows. The bottle containing 950 ml. of methanol, taken directly from the drum, is placed on the balance. The sulfur dioxide cylinder is mounted above the bottle. An outlet tube from the cylinder is placed in the bottle in such a way that it does not interfere with the operation of the balance. The valve is then opened, and 190 g. of liquid sulfur dioxide are permitted to run into the methanol. Following this, 950 ml. of C. P. pyridine is added.

If the proper grade of pyridine has been used, the resulting solution will have a light straw color. A water-white solution can be prepared by using redistilled pyridine, but there is no advantage in doing this.

Preparation of Solution B. This is a 45-g. per liter solution of iodine in methanol. The concentration is not too important except that much weaker solutions do not yield as sharp an end-point. Reagent grade resublimed iodine should be used. The proper amount of iodine is placed in a dry g.s. reagent bottle, and this is filled with methanol directly from the drum. The bottle is filled to capacity to prevent absorption of moisture from any air-space over the liquid. This mixture is allowed to stand several days with occasional shaking, and then for at least one day without shaking before transfer to the burette reservoir. The purpose of this one day without shaking is to permit the solution to be decanted from the insoluble particles that contaminate reagent grade iodine. These particles will clog the burette tip if permitted to get into the reservoir.

Apparatus. The apparatus for routine use consists of two side-arm burettes connected to aspirator bottles used as reservoirs. One assembly is for Solution A, the other for Solution B. The nipple of the bottle is connected to the side arm of the burette. Air coming into each reservoir is first passed through sulfuric acid and then through a drying tube containing "Drierite." Beyond the drying tube the air line is split with a T-tube; one branch is attached to the top of the aspirator bottle and the other to the top of the burette. By this device, as the burette is filled with solution, its air passes into the reservoir. As the burette is emptied, outside air is drawn in through the drying train.

One-hole rubber stoppers of the proper size to fit 300-ml. Erlenmeyer flasks are fitted over the burette tips so that the end of the tip extends through the stopper. Titrations are made in 300-ml. Erlenmeyer flasks held against these stoppers. This prevents air turbulence in the neck of the flask and minimizes exposure of the solutions to the air during titration. Flasks are also kept on the stoppers between titrations to minimize evaporation and contamination of the solution in the burette tip.

Three hundred-ml., glass-stoppered Erlenmeyer flasks are used for the titrations. These are thoroughly cleaned, rinsed with distilled water, and dried in an oven at 110°C. before use. For routine work this procedure is too time-consuming. It was also found practical to rinse out the flasks with water after use, then to rinse thoroughly with methanol or acetone to remove the water. It was even found to be practical, after one titration, merely to pour out the old solution, replace the stopper, and use the flask (without cleaning and redrying) for another determination since any residue remaining in the flask was anhydrous.

Initial Standardization of Solution B. Transfer approximately 10 ml. of Solution A into a clean, dry 300-ml., glass-stoppered Erlenmeyer flask. The exact volume is not important—in fact, a burette, although convenient, need not be used for Solution A.

With the flask held against the rubber stopper on the burette, add Solution B until the chrome yellow color changes to a distinct amber. The volume of Solution B added need not be recorded. The amber color should persist for at least 1 minute with the flask held against the rubber stopper and gently swirled. If Solution B has a titer of approximately 3 mg. water/ml., about 0.05 ml. excess is necessary to make a clearly recognizable color change. The visual end-point is thus reproducible to about 0.05 ml. of Solution B or 0.15 mg. of water. The solution in the flask is anhydrous at this point. Weigh 60-70 mg. (2 drops) of water into the flask. A 30-ml., glass-stoppered dropping bottle is convenient for this. This of course restores the chrome yellow color.

Now titrate with Solution B to the same end-point as before. The water equivalence of the iodine solution (Solution B) is calculated from the weight of water added and the volume of Solution B used. Water and iodine react mole for mole according to the equation:

$$H_2O + I_2 + SO_2 \longrightarrow SO_3 + 2\,HI$$

This equation was confirmed by Seaman *et al.* (5) and has also been confirmed in this laboratory. The formation of the pyridinium complexes (4, 6) is not shown as this concerns only the mechanism of the reaction—not the iodine-water stoichiometry.

Preparation and Standardization of Water-in-Propanol Solution

Immediately after Solution B has been standardized by the method described, it is used to determine the amount of water in an n-propanol solution of water. The n-propanol solution is then used for subsequent standardizations of Solution B due to greater convenience.

The propanol solution of water is prepared by pipetting 10.00 ml. of water into a 1-liter, volumetric flask containing n-propanol and then making up to the mark with additional n-propanol (isopropanol may be substituted if desired, of course).

The exact water content of the water-in-propanol solution is determined by titration with Solution B, observing the precautions pointed out above under "Initial Standardization of Solution B." The procedure is identical with that subsequently used for daily standardization of Solution B with the water-in-propanol solution:

a) Transfer 10 ml. of Solution A to a 300-ml., g.s. Erlenmeyer flask.
b) Add Solution B until an amber color is obtained that persists for 1 minute.
c) Pipete 5.00 ml. of water-in-propanol solution into the flask.
d) Titrate with Solution B to the same end-point as in b).

The following result is typical and also serves to illustrate the accuracy possible by this method:

Wt. of 10.00 ml. of water at 24°C.	9.97 g.
Amt. of water in 990.0 ml. propanol	1.35 g.
Calculated titer—mg. water per ml. soln	11.32
Found by titration—mg. water per ml. soln	11.31

In Table I are given data on the stability of a standard solution of water in propanol.

TABLE I

Stability of Solution of Water in n-Propanol

Days	Water content
	mg./ml.
0	11.5
66	11.7
111	12.2

On the basis of this observation we recommend restandardization of the water-in-propanol solution about once a month. Toward the end of the period, during which this solution was being used, the volume of liquid in the bottle was small compared to the volume of air. This probably accounts for the more rapid increase in titer during this period. It should be emphasized that this bottle was being opened almost daily for the removal of samples.

We recommend daily standardization of Solution B against duplicate 5.00-ml. samples of water-in-propanol. However the data in Table II are given to show how well Solution B maintains its titer in the described apparatus. The solution was used intermittently over the period covered by the data and was restandardized on the indicated days.

TABLE II

Change in Titer of Solution B on Standing

Days	Titer
	(mg. H_2O/ml.)
0	2.79
2	2.77
10	2.72
15	2.69
16	2.68
17	2.68
20	2.65
21	2.62
22	2.63
23	2.62
24	2.59

Determination of Water in Solvents

The same procedure is used as outlined above for the standardization of Solution B with water-in-propanol solution except that the appropriate volume of solvent to be tested is added instead of water-in-propanol.

If the solvent is thought to contain only a trace of water, it is best to pipet 100-ml. samples. In the case of hydrocarbon solvents, such as Stoddard solvent (7), even a 100-ml. sample may require only a few ml. of Solution B. Hydrocarbon solvents of this type are not miscible with Solution A so a two-phase titration is encountered. This offers no difficulties however if fairly vigorous agitation is used and Solution B is added in 0.05 ml. increments near the end-point. Since the color change occurs in the pyridine-methanol phase at the bottom of the flask, the phases are allowed to separate and the lower phase is examined for color after each addition. The phase separation is usually very rapid and does not cause undue delay. The hydrocarbon phase protects the lower one from the air so the color change is sharp and permanent. Values obtained on typical solvents used in this laboratory are given in Table III.

TABLE III

Water Content of Various Solvents

Solvent	% H_2O (by wt.)
Benzene (saturated at 27.1°C.)	0.075
Pyridine C. P.	.16
Methanol (from drum)	.027
Methanol dried[a]	.035
Stoddard solvent (saturated at 22°C.)	.010
Stoddard solvent (from plant rag filter)	.0105
Stoddard solvent (freshly distilled)	.0070
Perchlorethylene (freshly distilled)	.0077
Cyclohexanol	.32

[a] Distilled from Mg. and collected under anhydrous conditions (3).

The values shown for methanol in this table illustrate why we abandoned our efforts at drying the methanol. Every reasonable precaution was taken in this operation, but the amount of water after distillation was greater than before.

Determination of Water in Drycleaning Detergents

In the determination of water in drycleaning detergents, most of which are liquid, we employ the same technique as described under "Initial Standardization of Solution B," except that the detergent, instead of water, is weighed into the neutralized solution from a dropper bottle. The size of the sample taken must of course be governed by the order of magnitude of the water content as estimated by a rough preliminary determination.

To check the accuracy of this method a drycleaning soap was prepared of known water content. This soap was prepared from oleic acid, potassium hydroxide, cyclohexanol, water, and Stoddard solvent. The calculated water content of this mixture was corrected for the hygroscopic water in the potassium hydroxide, the water in the solvents, and for the water formed upon neutralization of the potassium hydroxide by oleic acid. The water content calculated thus was 10.4% by weight. Analysis of three samples by the K-F method gave values of 10.4, 10.0, and 10.0 for an average of 10.1% water found.

The water content of drycleaning detergents cannot always be determined with any confidence by the conventional distillation apparatus (2) due to foam formation or to the presence of water-soluble solvents, such as alcohols that distill over with the water. However in some cases these objections were not present, and the two methods were compared. Data on 16 commercial soaps are given in Table IV.

TABLE IV

Soap No.	Moisture content by weight	
	Distillation	Titration
	%	%
1	2.4	2.0
2	0.0	0.046
3	19.1	20.0
4	0.4	0.45
5	0.3	0.48
6	24.4	25.3
7	3.2	3.2
8	0.6	0.38
9	3.5	3.9
10	24.7	23.4
11	0.67	0.83
12	0.75	0.64
13	9.7	9.1
14	0.43	0.65
15	5.1	5.2

As shown in Table IV, the agreement is fairly good between the methods. In a number of other cases high values were obtained by the distillation method. In all such cases the presence of alcohols could be deduced by the odor and by the low flash point of the liquid. When alcohols or other volatile and water-miscible solvents are present, the distillation method is, of course, inaccurate.

The values given in Table IV are the averages of three separate determinations by titration and of two separate determinations by distillation.

Accuracy of Method

The procedure as described above is very rapid and convenient. The question will naturally arise as to whether this advantage is purchased at the price of accuracy. We do not believe so for the reasons that follow.

In our procedure the accuracy is limited by the reproducibility of the end-point. We have observed that this reproducibility is roughly inversely proportional to the volume of liquid in the flask at the end point. For example, we find that titrations of duplicate samples requiring about 20 ml. of Solution B are reproducible to about 0.05 ml. Duplicate samples requiring about 40 ml. of Solution B are reproducible to about 0.1 ml. Thus our procedures have been developed on the principle of keeping the titration volume as small as possible, consistent with accuracy of volume measurements. For this reason our standard water solution is made with 11 mg./ml., and 5.00-ml. aliquots are taken rather than the easier way of taking 50.00 ml. of the propanol as it is purchased (1.36 mg./ml.).

There is no question but that the end-point in the Fischer titration can be determined with greater precision electrometrically than visually. If the end-point can be determined electrometrically with a precision of 0.015 ml. as shown by Almy, Griffin, and Wilcox (1) and the water in the standard solution is weighed with a precision of 1 part per 1,000, then one has a right to expect analytical results to exhibit a precision of this order. The fact is that they do not. We have found no paper in the literature where such precision is claimed for any modification of the Fischer method. It is quite probable, then, that the limiting factor in all procedures is absorption of atmospheric moisture. This absorption is minimized when a rapid procedure is used. The procedure described above meets this condition. The analysis consists in three steps: neutralization of Solution A, weighing or pipetting the sample, and final titration. The total time required for an analysis is 3 to 4 minutes. No serious amount of atmospheric moisture will be absorbed in this time if reasonable care is taken.

Our experience with standardizing Solution B yields data for determining the precision of the method when used for routine work. We have analyzed the data for 25 consecutive standardizations, each run in duplicate using 5.00 ml. of water-in-propanol. The volumes of Solution B required ranged between 19 and 25 ml. The largest deviation from the mean was 0.10 ml., which occurred twice in the 25 standardizations. The average deviation from the mean was 0.029 ml. The median volume in this set of data was 21.95 ml. Thus the average deviation was about 1.3 parts per 1,000. This is within the probable range of precision of measuring consecutive samples of 20 ml. with a burette.

It should also be emphasized that the success of our procedure depends in a large part upon the use of quite dry methanol taken directly from the drum. The use of very dry methanol minimizes the volumes required at each stage and permits optimum precision to be realized.

The procedure, as here described, permits one to determine water in most systems to two significant figures with confidence. Most of the complications that have been piled upon the Karl Fischer method have been the result of a vain effort to obtain one additional significant figure. It is our contention that for most purposes this third figure—even if attained—is purchased at too dear a price. If the water content of a solvent is 0.65%, how often is one concerned with whether the true value is 0.653 or 0.654?

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