Traditional Analytical Chemistry of Fatty Acids and Their Derivatives

L.D. METCALFE, Assistant Director of Research, Armak Industrial Chemicals Division,
Akzona, Inc., 8401 W. 47th St., McCook, IL 60525

ABSTRACT

Industrial fatty acids and their derivatives are generally manufactured under strict quality control and sold under rigid specifications. The purchase specifications are normally prescribed by a series of traditional "wet" analytical methods. These methods include acid value, saponification value, iodine value, hydroxyl value, water content, and others. Occasionally, other information is specified; this may include for tall oil fatty acids, rosin content, and free glycerol in monoglycerides, diene value for drying fatty acids, and conjugated fatty acids for specialized fatty acids. The most common fatty acid derivatives of the industrial fatty acids are anionic and nonionic surfactants and the nitrogen derivatives such as amines and quaternary ammonium salts. Rigid quality control is also applied to these compounds. The amine value and the determination of primary, secondary, and tertiary amines are the key analytical methods applied to amine derivatives. Quaternary ammonium compounds present unique problems; these are in a present state of methods improvement. Physical property test methods are often used to characterize fatty acids. Though simple in concept, they are often the most difficult to meet in purchase specifications. Examples of these tests are viscosity, titer, color, color stability, flash and fire point.

INTRODUCTION

All commercial fatty acids and their derivatives such as fatty amines and related nitrogen compounds are sold under rigid specifications. As is generally true of all industrial chemicals of commerce, the manufacturer and the buyer have a mutual interest in the testing of these products. These tests must give a reliable indication as to whether the products meet the specification ranges agreed on by the buyer and the seller.

There are essentially four types of tests that can be performed on the fatty acids and their derivatives to determine their quality and composition: wet chemical tests, physical property tests, application or use tests and instrumental methods including chromatography.

In this discussion we will spend most of the time on the wet chemical tests. We will briefly describe the physical tests and mention only a few of the use application tests. The instrumental methods will be treated at length in the lecture on recent and advanced methods of analysis of fatty acids and derivatives.

TABLE I

Approved Wet Chemical Methods for Fatty Acids

Method	AOCS	ASTM
Acid value	Te la	D 1980
Iodine Value, Wijs method	Tg la	D1959
Saponification value	Tl la	D 1962
Unsaponifiable matter	Tk la	D 1965
Ash	Tm la	D 1951
Hydroxyl value	Cd 13	D 1957
Oxirane oxygen	Cd a	D 1652
Peroxide value	Cd 8	
Thiocyanogen value	Cd 2	
Rosin acids in fatty acid	Ts la	D 1240
Moisture, Karl Fischer method	Tb-2	E 203

There are two organizations which are very active in the development and improvement of analytical and testing methods for fatty acids and their derivatives. These are the American Oil Chemists' Society (AOCS) and the American Society for Testing Materials (ASTM).

Our main discussion concerns itself with official methods developed and recommended by these organizations (1,2). Many of the methods recommended by both organizations are identical because they were developed by joint task force committees. This cooperation between the two groups is most valuable to the industry. It prevents a redundancy of research effort and also prevents possible conflicting "official" methods.

Wet Chemical Test Methods for Fatty Acids

Table I gives a listing of the approved test methods that are recognized by both the AOCS and ASTM. One characteristic of all these methods is that they are relatively simple to perform. The equipment and reagents required are commonly found in even the most rudimentary chemical laboratories. This is in contrast to instrumentation methods that often require very expensive equipment which may not be available to the smaller users of fatty acids. In the following section the most commonly used methods for characterizing fatty acids and derivatives will be dealt with in some detail.

Acid Value

Acid value is the most frequently used method for characterizing fatty acids. This simple titration procedure is defined as the milligrams of KOH required to neutralize the carboxyl groups in one gram of sample. In the AOCS method Te 1A and ASTM Method D 1980 a fatty acid sample is dissolved in alcohol and titrated with standard alcoholic KOH to a phenolphalein end point.

This one useful method gives all kinds of information. Examples of the various calcualtions are:

$$\text{Acid value} = \frac{\text{N.X mL} \times 56.1}{\text{wt (grams)}}$$

$$\begin{array}{l}\text{Free Fatty Acid (FFA)} \\ \text{(as oleic acid)}\end{array} = \frac{\text{N} \times \text{mL} \times 28.2}{\text{wt (grams)}}$$

$$\text{Neutralization equivalent} = \frac{\text{Sample wt. gram} \times 1000}{\text{N} \times \text{ml.}}$$

The latter, often abbreviated as N.E., is also the apparent molecular weight or reacting weight. Variations on these calculations can give useful interchangeable information.

$$\text{Acid value} = 1.986 \times \text{FFA}$$

$$\text{N.E.} = 56100/\text{A.V.}$$

Some typical acid values for common commercial fatty acids are shown in Table II.

Iodine Value

Probably the second most important analytical procedure used for fatty acids is the Wijs procedure for the measurement of unsaturation. This is the official AOCS method and is designated Tg 1a; the ASTM designation is Method D 1959. The iodine value or result from the Wijs method is expressed in terms of *Centigrams of Iodine taken up per gram of sample.* The analytical procedure measures the absorption of iodine monochloride by the sample. It is useful for measuring most of the double bond types encountered in fatty acids and their derivatives. However, the method is not applicable to conjugated or hindered double bonds.

The iodine value is run by weighing a sample (the sample size depends on the amount of unsaturation expected), and dissolving it in carbon tetrachloride. An excess of iodine monochloride reagent is added. The sample and a reagent blank are placed in the dark for 1 hr. The unabsorbed iodine is then titrated with sodium thiosulfate. It is possible to lower the reaction time by using mercuric acetate as a catalyst. However, care must then be taken in disposing of the samples so that the mercury catalyst does not become an environment problem. It is possible in some states to cause the waste water in a plant to go out of compliance with respect to mercury by throwing the reagent from iodine value determinations that use mercuric acetate catalyst down the sewer.

The Iodine Value (IV) is calculated as follows:

$$\text{IV} = \frac{(\text{B}-\text{S N} \times 12.69)}{\text{Sample Wt. G.}}$$

Typical Iodine Values for some commercial fatty acids are shown in Table II.

Calculation of a theoretical IV for a fatty acid can be made by using the following equation.

$$\text{Theoretical IV} = \frac{253.8 \times 100 \times \text{No. of Double Bonds}}{\text{M.W.}}$$

Saponification Value

Saponification value is defined as the milligrams of KOH required to react with all reactive groups in one gram of sample. This analysis is performed by refluxing alcoholic KOH with the sample for 30–60 min. A reagent blank must also be run at the same time. At the end of reaction any unreacted KOH is titrated with standard acid. All the ester and carboxylic acid groups will react with the base.

If the acid is free of ester, the saponification value will be identical to the acid value. The difference between the "Sap value" and the acid value is a measure of any ester present. This difference is sometimes called the ester value.

$$\text{Calculation: Saponification Value} = \frac{\text{B}-\text{S} \times 56.1 \times \text{N}}{\text{Wt. G.}}$$

where B is the titration of the blank and S is the titration of sample.

The use of these methods described gives a surprising amount of information about a given fatty acid or fat. Some typical values for a number of fatty acids are essentially the same as those for acid values shown in Table II.

Other important chemical tests commonly used for fatty acid specifications can only be briefly mentioned. Hydoxyl value is a measure of hydroxyl groups in fatty acids and is performed by acetylating the hydroxyl group. The consumption of acetylating reagent is measured to obtain the desired information. Oxirane oxygen is a measure of epoxy groups in fatty acids. This is obtained by measuring the addition of hydrogen bromide to the oxirane ring.

TABLE II

Typical Acid Values and Iodine Values Obtained with Some Common Commercial Fatty Acids

Acid	Acid value	Iodine value
Caprylic	390	0.7
Capric	325	0.5
Lauric	280	0.5
Myristic	240	0.5
Palmitic	218	0.5
Stearic	198	1.0
Hydrogenated tallow	205	4.0
Coco	270	90
Tallow	204	12
Oleic	202	45
Soya	195	130
Corn	193	115

TABLE III

Approved Physical Test Methods for Fatty Acids

	Designation	
Methods	AOCS	ASTM
Titer test	Tr 1a	D 1982
Viscosity	tq 1a	D 1545
Flash and fire point	Tn 1a	D 92
Specific gravity	To 1a	D 1963
Color Gardner	Td 1a	D 1544
Color platinum-cobalt	Td 1b	D 1204
Photometric index	Td 2a	D 1469
Moisture and volatile matter, hot plate method	Tb 1a	—

The peroxide value is a measure of peroxide content in fatty acids. This is defined as the milliequivalent of peroxide per 1000 g of sample that oxidize KI under the conditions of the test. Free iodine under acidic conditions is released and titrated with standard thiosulfate solution.

Rosin acids in fatty acids are usually determined by esterifying the fatty acids which readily form methyl esters. The unesterified rosin acids are then titrated with standard base.

Physical Property Tests for Fatty Acids

A large variety of physical property tests have been developed to characterize fatty acids. These tests also give valuable information on use performance and use application for given fatty acids. The approved test methods are shown in Table III with their AOCS and ASTM designations. Very often these tests are used in customer specifications. Most of the tests are pretty much self explanatory. However, the conditions under which they are performed are very strictly controlled so that reproducible results are possible. Time does not permit a description or emphasis of these physical test methods. This does not mean they are less important than the chemical methods since many of them have a longer history than many of the wet analytical methods.

Nitrogen Derivatives of Fatty Acids

Many derivatives of fatty acids have been made. The greatest commercial impact of derivatives of fatty acids has been made by the fatty nitrogen compounds. In the same way as the fatty acids, the fatty nitrogen derivatives are

TABLE IV

Approved Wet Chemical Test Methods for Fatty Nitrogen Compounds

Method	Designation AOCS	Designation ASTM
Total amine value of fatty amines:		
Potentiometric method	Tf 1a	D 2073
Indicator method	Tf 1b	D 2074
Primary, secondary, and tertiary amines values of fatty amines:		
Potentiometric method	Tf 2a-64	D 2073
Indicator method	Tf 2b-64	D 2074
Percent, primary, secondary and tertiary amines in fatty amines	Tf 30-64	D 2083
Iodine Value of Fatty amines, modified Wijs method	Tg 2A	D 2075
Iodine Value of fatty quaternary ammonium chlorides modified Wijs method	Tg 3a	D 2078
Average molecular weight of fatty quaternary chloride	Tv 1a	D 2080

TABLE V

Data Calculated from a Single Titration of an Amine

$$\text{Amine value} = \frac{\text{ml x N x 56.1}}{\text{wt. grams}}$$

$$\text{meq/g} = \frac{\text{N x ml}}{\text{wt. g}}$$

$$\text{N.E. or apparent mol. wt.} = \frac{\text{Wt. g x 1000}}{\text{N. ml.}}$$

$$\text{\% Amine} = \frac{\text{ml x N. x Mol. Wt.}}{\text{wt. g x 10}}$$

manufactured and sold on rigid specifications. The nitrogen compounds differ from the fatty acids in that they are not single functional group compounds such as a simple carboxylic acid. They may be nitriles, amides, primary, secondary, tertiary amines, diamines, quaternary ammonium compounds or amidoamines. As with fatty acids, the test methods used can be divided in the wet chemical methods and the physical test methods. Table IV lists the wet chemical methods used to characterize the various fatty nitrogen compounds. Many of these methods were developed by task force committees of the AOCS and ASTM. Emphasis will be made on these wet methods in this discussion. Some of the analytical chemistry involved is much more elegant and complex than that associated with the parent fatty acids.

The Amine Value

The amine value is to fatty amines what the acid value is to fatty acids. It is by far the most fundamental analytical method for primary, secondary, and tertiary amines, and the diamines. The fatty amines are chemicals with relatively high base strength that are easily titrated using acid titrants. The fatty amines are best titrated in nonaqueous solvents such as isopropyl alcohol with standard hydrochloric acid. A potentiometric or indicator end point can be used. In the official AOCS procedures, methods using both indicator and potentiometric end points are approved. The definition of the amine value is the number of milligrams of KOH equivalent to the basicity in one gram of sample. This definition has its roots in fat and oil analytical chemistry. The fact that there are both a potentiometric method and an indicator method approved by AOCS was a concession to laboratories that preferred the more rapid indicator method or to small companies that did not have the proper equipment. This simple acid titration gives not only the amine value but also milliequivalents per gram, neutralization equivalent, or apparent molecular weight, and percentage of amine if the molecular weight is known.

TABLE VI

Calculations for Determining Meq./g.of Primary, Secondary and Tertiary Amine Using Differential Titrations

1.	mew/g	total tit. = 1° + 2° + 3°	$= \frac{\text{ml x N}}{\text{wt. g}}$
2.	meq/g	tit. S = 2° + 3°	$= \frac{\text{ml x N}}{\text{wt. g.}}$
3.	meq/g	tit. T = 3°	$= \frac{\text{ml x N}}{\text{wt. g.}}$
	meq/g	Primary amine	= Total –S
	meq/g	Sec. amine	= S–T
	meq/g	Tertiary amine	= T

All of these can be calculated from one titration. Table V shows the various values that can be obtained from one titration.

Primary, Secondary, and Tertiary Amine Analysis

The fatty primary amines that are commercially available usually contain small amounts of secondary and tertiary amines. The commercial secondary amines contain small amounts of primary and tertiary amines. Likewise, the tertiary amines will contain some primary and secondary amines. It is important to know the amounts of each type of amine present during amine manufacture and also in their commercial applications. This information is obtained by doing a series of differential acid titrations.

Again the AOCS has two official methods, one potentiometric, the other an indicator method. In each case a total amine titration is performed. This titration includes the primary, secondary and tertiary amines present. A second sample is weighed and this sample is reacted with salicylaldehyde.

Any primary amine present forms a very weakly basic Schiff's base. The sample is titrated with standard HCl, and only the secondary and tertiary amines will titrate under the conditions of the analysis. A third sample is weighed, and in the case of the potentiometric method acetic anhydride is added. This will react with the primary and secondary amines present to form nonbasic amides. The sample is then titrated with standard perchloric acid, and then only tertiary amine present will titrate. In the case of the indicator method, the third sample is weighed and reacted with phenylisothiocyanate. Any primary and secondary amines will form a nonbasic substituted thioureas. On titration with HCl only the tertiary amine will be titrated. Thus, with a series of three differential titrations, one can calculate the amine value, milliequivalent per gram, or percent of primary, secondary, and tertiary amine in a given sample. Table VI shows the equations used to calculate the milliequivalents per gram of each amine present. Once this is known, then both amine values and percentages can be determined by simple arithmetic.

Iodine Value of Fatty Nitrogen Derivatives

The iodine value is also used to measure the unsaturation of the fatty nitrogen compounds. However, the Wijs method is modified somewhat from that used for fatty acids. The definition is the same as before and is expressed in terms of centigrams of iodine absorbed per gram of sample. The method is applicable to fatty amines, diamines, amidoamines except those containing conjugated unsaturation. The IV method for amines differs in that glacial acetic acid is used as a solvent instead of carbon tetrachloride, and mercuric acetate is used as a catalyst. Wijs reagent or iodine monochloride is used as in determining the iodine value of the fatty acid. Somewhat more care must be taken than when determining the iodine value of fatty acids. The precision is not as good as with the fatty acids. It is interesting to note that some amines are sold with IV specifications that are tighter than the precision of the method is able to deliver. However, the method is very useful in helping to identify amines and characterize them for certain applications.

The unsaturation of fatty quaternary ammonium compounds is also measured using a modified Wijs method. Chloroform is used as a solvent. Sodium lauryl sulfate is also added to prevent the free iodine from being held tenaciously by the nonaqueous phase. The technical reason for this is that sodium lauryl sulfate reacts with the quaternary and prevents formation of a quaternary triiodide. Although this latter compound is quite soluble in chloroform, it releases the iodine slowly. The last wet methods I would like to discuss are those involving the determination of long chain quaternary ammonium compounds. This is one of the most interesting areas in the analytical chemistry of fatty nitrogen derivatives. There is only one official AOCS for quats involving their quantitative analysis. This is a method for the average molecular weight of fatty quaternary ammonium compounds (TV 12-64). This is rather misleading because this method using perchloric acid as a titrant combined with mercuric acetate as an anion transfer agent is really a method for halides (3). It is not applicable to sulfate quats. When all the corrections are made for nonquaternary components, the molecular weight can be calculated.

A great deal of analytical talent and effort has gone into methods for determining quaternary ammonium compounds. The best known are those that use solvent partition systems in which a long chain anionic surfactant is used to titrate a quat in the presence of anionic dye or indicator (3–5). The anionic indicator which is normally water soluble complexes with the quat to be solubilized in a water immiscible solvent such as chloroform. The anionic titrant replaces the dye in the quaternary complex. When there is no longer any color in a water immiscible solvent, the titration is complete.

Recently the AOCS has been testing a system for titrating quaternaries that uses sodium tetraphenylboron (TPB) as a titrant (6). The titration is performed in water in the presence of dichlorofluorescein indicator. This indicator normally is yellow in aqueous solution, but in the presence of a long chain quaternary a pink complex is formed. As TPB is added to the system the quaternary precipitates. When all the quat is precipitated, the indicator suddenly changes from pink to yellow. The method can be used not only to determine the chloride quats but also the quaternary ammonium sulfate salts.

There are AOCS official methods for ash, pH, solids, nonamines, flash point, and moisture in the various nitrogen derivatives. The criteria for these determinations are self evident and won't be discussed at this time.

There exists a great deal of literature on the analytical chemistry of fatty acids (7) and their derivatives for those who would seriously pursue the subject. In this short presentation it is possible to discuss only some of the analytical highlights but not go into the subject in great depth.

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GENERAL READING

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Pollution Control in the Fatty Acid Industry

G.N. McDERMOTT, Senior Engineer, Procter and Gamble Company, Winton Hill
Technical Center, 6105 Center Hill Road, Cincinnati, OH 45224

ABSTRACT

Operations of the fatty acid industry create wastewaters, emissions to the air, and solid wastes which have the potential of insulting the quality of the environment in a number of ways. Some of the controversy and the problems that are current in the national environmental effort are discussed. As to the fatty acid industry prospects, some attention may come to the industry if toxics are found to be in the industry's wastewaters. New air emissions permit will be difficult if not impossible to obtain. Long delays and expensive data gathering will be involved. Disposal of solid waste classified as hazardous materials will become extremely costly and involve much paperwork. Wastewaters can originate from any of the process steps: spills and tank bottoms from receiving and storage, foots from alkaline extraction pretreatment, condensate from pressure reduction after fat splitting, condensing water and condensate from fatty acid distillation, and condensing water from glycerine evaporation and distillation. The organic matter in the wastes is biologically degradable so one pollutional effect is reduction of the oxygen level in receiving streams. Oil not in soluble or finely dispersed state is objectionable for the additional reason that it forms slicks or films in the water surface. Fatty acids in soluble forms are toxic to fish in fairly low concentrations. Heavy metal catalysts used for fat splitting or hydrogenation such as zinc are objectionable at trace levels. Source control methods include good operator attention to minimize avoidable losses, optimum recovery of fatty acids and