Laboratory 3: Determination of the Acid Number of Vegetable Oils by Titration

Topics Covered

- pH vs. acid number
- Acidity and acid values in organic solutions
- Titration techniques
- How to obtain acid values of vegetable oils

Equipment Needed (per pair or group)

- One graduated titration burette with stand, 50 mL
- Three Erlenmeyer flasks, 250 mL each
- Weighing scale (readable to 0.01g)
- Pipette

Reagents Needed (per pair or group)

- Titrant solution (prepared by instructor)
- Titration solvent (prepared by instructor)
- Phenolphthalein indicator solution (prepared by instructor)
- 2 grams vegetable oil

Background Information -- Acid number

To make biodiesel, triglycerides (fats and oils) react with an alcohol (such as methanol) to produce methyl fatty acid esters and glycerol. A catalyst such as potassium hydroxide or sodium hydroxide is added to speed up the process. However, if the oil or fat is degraded and has a lot of free fatty acids (fatty acids not attached to a glycerol backbone), these free fatty acids can react with the catalyst first to create soap, which must be removed. Therefore, before making biodiesel it is necessary to determine the amount of free fatty acids in the oil or fat, in order to know how much catalyst to add.

Fats and oils with high free fatty acid levels include waste vegetable oil and animal fats. These feedstocks are cheaper to use than food-grade vegetable oil, and so are often desirable as feedstocks for making biodiesel.

You are probably familiar with the concept of "pH" to measure the acidity or alkalinity of an aqueous solution (a solution of a substance dissolved in water). pH can be measured using pH paper or a pH meter. The pH number indicates the strength of the acid. The stronger the acid, the lower the pH number.

Can we use pH paper or a pH meter to figure out how much free fatty acids are in a sample of oil or fat? Unfortunately, we cannot, because pH will not tell us *how much* acid we have—it will only tell us the strength of the acid.

When making biodiesel, we need to know not the strength of the acid, but the *amount* of free fatty acids (FFAs) present.

In addition, pH is not applicable in a fat or oil, because the hydrogen in organic solutions does not dissociate into hydrogen ions. Acidity exists in organic solutions containing acidic functional groups such as carboxyl groups (-COOH), which are found in fatty acids[1].

Instead of pH, we have to use a measure called the acid number. The acid number is a measure of the acidity in a non-aqueous solution (non-water solution) such as an organic solution.

The acid number is expressed as the quantity of a known concentration of potassium hydroxide (KOH) consumed by titrating one gram of a sample in the units of milligrams (mg) of KOH per gram of sample, i.e., *mg KOH /g* of sample.

Since organic solutions are not usually miscible with aqueous potassium hydroxide solutions, the addition of another solvent that helps the organic chemical dissolve in an aqueous solution is typically needed.

With manual titration, a color indicator, such as phenolphthalein, is needed.

Background Information -- Acid-Base Titration

Titration is a wet-chemistry practice to determine the concentration of an unknown chemical in a solution. An acid-base titration is a titration that uses a known concentration of an acid (or base) solution, such as hydrochloric acid (or potassium hydroxide), to react with an unknown base (or acid) in solution.

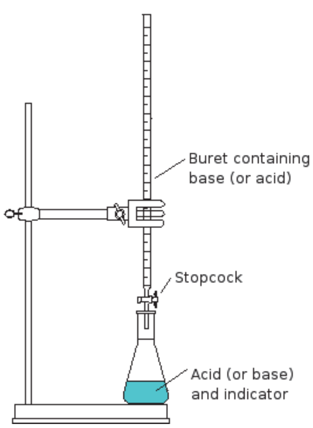

Figure 1 Illustration of a titration set-up

After the base (or acid) is all consumed, the solution is neutral. Any small amount of acid (or base) added after this point will cause the solution to rapidly become acidic (or basic).

Based on the acid (or base) consumed, the concentration of the unknown base (or acid) can be calculated. The originally known concentration solution is then called the standard solution of titrant, which is used to titrate the unknown.

Most titrations are conducted in aqueous solutions, such as acid-base titration. If the sample to be titrated is water insoluble (such as oil), a co-solvent or a different solvent other than water is needed.

[1] Sometimes, the acidity of an organic solution can be also contributed by Lewis acids, which do not contain carboxyl groups but behave like an acid due to the fact that they are electron receivers or proton donors. A Lewis acid is any specie that accepts electrons.

The equipment for performing titrations manually can be simply a calibrated burette for the standard titrant solution, and a volumetric flask that contains a precise volume of the unknown solution. An indicator, such as phenolphthalein, is needed to provide visual indication for the endpoint.

Automated titration devices are also available to perform titrations with high efficiency and accuracy, and are widely used in commercial applications.

Fig. 2: Auto-titrator

Pre-Lab Questions

- How is pH different from acid value?
- Why is pH not used when measuring the amount of acid in an oil or fat?

Safety Note: In this lab you will be using solutions containing isopropyl alcohol and toluene, which are both highly flammable. Keep these away from heat or flames. The titrant contains potassium hydroxide, which is caustic and can burn skin and harm eyes. Wear gloves, a lab coat or apron, and eye protection when using potassium hydroxide.

Laboratory Procedure

1. Weigh flask and record the weight on Table 1.
2. Weigh approximately 1 g of oil sample to the nearest 0.01 g [2] and transfer to the titration flask.
3. Record the sample size in Table 1.
4. Add 125 mL of titration solvent into the flask containing the sample.
5. Add a couple of drops of the phenolphthalein indicator into the solution.
6. Swirl the solution vigorously for approximately 1 minute to ensure the uniformity of the solution.
7. Prepare a second sample for titration by repeating the steps a) though f)
8. Prepare a blank/ reference with only titration solvent and phenolphthalein indicator (no oil) by repeating steps a) through f).
9. Fill the burette with the titrant solution.
10. Record the starting volume of titrant on Table 1.
11. Carefully introduce the titrant from the burette into the flask while swirling the solution vigorously but without spattering.
12. Stop introducing titrant if the solution changes color to pink.
13. Record the ending volume of titrant on Table 1.
14. Repeat the steps i) through m) for the second sample.

[2] This is based on an expected acid number of between 5 and 20; if acid number is higher than 20, a sample size of 0.25 g is recommended; if the acid number is lower than 5, a sample size of 5.0 g is recommended.

15. Repeat the steps i) through m) for the blank (please note that the blank requires a much smaller volume of titrant because of its low acidity).

Table 1 Raw data recoding

Category	Variable	Quantity	Sample #1	Sample #2	Blank #b
Sample size	$\mathbf{W_{ini}}$	Flask weight (g)			--
	$\mathbf{W_{end}}$	Flask + sample (g)			--
	W	Net sample size (g)			--
Titrant volume	$\mathbf{V_{ini}}$	Starting vol. (mL)			
	$\mathbf{V_{end}}$	Ending vol. (mL)			
	V	Net volume (mL)			

Data Processing

Acid number calculation:

$$A_1 = 56.1 \cdot \frac{(V_1 - V_b) \times C}{W_1} \qquad A_2 = 56.1 \cdot \frac{(V_2 - V_b) \times C}{W_2} \qquad \text{and}$$

$$A = \frac{A_1 + A_2}{2}$$

Where: A_1, A_2, and A are the acid numbers of sample #1, sample #2, and average, respectively (*mg KOH/g*)

V_1 , V_2 and V_b are the net titrant volumes for titrating sample #1, sample #2 , and blank, respectively (*mL*)

W_1 and W_2 are the net sample sizes of sample #1 and sample #2 (*mL*)

C is the concentration of the standard solution (*M* or *mol/L*) provided by the instructor

Relative precision of the titration: [3]

$$p\% = \left| 1 - \frac{A_1}{A_2} \right| \times 100\%$$

Where: $p_{\%}$ the relative precision of the titration (in %)

[3] If the relative precision is less than a certain value, e.g., 2%, conducting another sample titration is typically recommended.

A_1 and A_2 are the acid numbers of sample #1 and sample #2 (*mg KOH/g*)