TP-TM-007C
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Determination of Hydroxyl Value

Principle:

Hydroxyl value is the number of milligrams of potassium hydroxide equivalent to the acetic anhydride consumed by one gram of sample. The sample is acetylated with acetic anhydride; the excess acetic anhydride is converted to acetic acid by boiling with water, and then is titrated with aqueous KOH.

Apparatus and Reagents:

1. Acetylating Reagent: Acetic anhydride/Pyridine = 1/3 (V/V). **Prepare freshly.**

   CAUTION: *See cautions below*.
2. 0.7 N Alcoholic KOH
3. 3A Alcohol
4. Phenolphthalein indicator (1.0% in 3A Alcohol)
5. 250 mL Round bottom flask
6. 50 mL Burette
7. Air condenser, 4 ft.

Procedure:

1. Into a 250 mL round bottom flask with ground neck, weigh a sample (see *Sample Size* below) to the nearest 0.1 mg. Use another 250 mL RB flask with ground neck as the blank flask.
2. Pipette 5 mL of acetylating mixture into the sample flask, lubricate the neck with silicone grease and connect both flasks to ground glass tip air condensers.
3. Swirl the flasks thoroughly and put the flasks on a steam bath (previously heated to 100°C). Maintain the bath temperature between 100°C - 120°C for 1 hour. At the end of 1 hour, add 10 mL D.I. water from the top of condenser and continue heating for 10 min.
4. Allow the flasks to cool below 50°C and rinse from the top of condensers with 25 mL 3A alcohol (previously neutralized with 0.1 KOH to phenolphthalein end point). Remove condensers from the flasks and allow the flasks to cool further to room temperature.
5. If the solution is cloudy, or if an insoluble residue is present, add 50 mL of a 50/50 (V/V) mixture of toluene and 3A alcohol.

   CAUTION: Toluene is flammable and toxic. Wear safety glasses and gloves.
6. Add 1 mL of phenolphthalein indicator solution and titrate to a pink endpoint with 0.7 N alcoholic KOH.

   CAUTION: Phenolphthalein is a carcinogen and irritant. Handle with care. Wear safety glasses and gloves.

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Calculations:

$$\text{Hydroxyl Value} = \frac{[\text{mL(blank)} - \text{mL(sample)}] \times \text{N(KOH)} \times 56.1}{\text{Wt of sample in gms}} + \text{(Acid Value)}$$

Size of Sample:

Unless specifically mentioned, the following size of sample is recommended:

Hydroxyl Value Range	Weight of Sample In Grams
300 - 350	0.75
250 - 300	1.0
200 -250	1.25
150 - 200	1.5
100 - 150	2.0
50 -100	3.0
20 -50	5.0
0 - 20	10.0

References:

Extracted from USP23/NF18 (401), 1995.