4.7 Determination of hydroxyl value

The hydroxyl value of a substance is the amount, in milligrams, of potassium hydroxide required to neutralize any acid when combined by acylation in 1 g of the substance under examination.

Recommended procedures

Method A

To the quantity of the substance being examined (as specified in the individual monograph) add 12 g of stearic anhydride R and 10 mL of xylene R and heat gently under a reflux condenser for 30 minutes. Allow to cool, add a mixture of 40 mL of pyridine R and 4 mL of water, and heat again under a reflux condenser for 30 minutes. Titrate the hot solution with carbonate-free sodium hydroxide (1 mol/l) VS, using phenolphthalein/ethanol TS as indicator. Repeat the procedure, omitting the substance under examination.

The hydroxyl value is calculated from the expression 56.10 *v/m,* where *v* is the difference, in mL, between the two titrations and *m* is the quantity, in g, of the substance taken.

Method B

Unless otherwise indicated in the individual monograph, weigh accurately the quantity of the substance to be examined shown in the table under 4.7 Determination of hydroxyl value, place it in a 150-mL acetylation flask fitted with an air condenser and add the corresponding volume of pyridine/acetic anhydride TS.

Presumed hydroxyl value	Quantity of substance (g)	Volume of pyridine/acetic anhydride TS (mL)
10-100	2.0	5.0
100-150	1.5	5.0
150-200	1.0	5.0
200-250	0.75	5.0
250-300	0.60 or 1.20	5.0 or 10.0
300-350	1.0	10.0
350-700	0.75	15.0
700-950	0.5	15.0

Heat the flask for 1 hour in a water-bath, maintaining the level of the water 2-3 cm above the level of the liquid in the flask. Remove the flask and condenser, allow to cool, and add 5 mL of water through the top of the condenser. If a cloudiness appears, add sufficient pyridine R to produce a clear liquid, noting the volume added. Shake the flask, place it in a water-bath for 10 minutes, remove, and allow to cool. Rinse the condenser and the walls of the flask with 5 mL of neutralized ethanol TS. Titrate with potassium hydroxide/ethanol (0.5 mol/l) VS, using 0.2 mL of phenolphthalein/ethanol TS as indicator. Repeat the procedure, omitting the substance under examination.

Calculate the hydroxyl value from the expression ($a + 28.05$) *v/m*, where *v* is the difference, in mL, between the two titrations, *a* is the acid value determined for the substance, and *m* is the quantity, in g, of the substance taken.