Phenolphthalein usually gives a satisfactory end point in the titration.

Perform a blank determination on 3·00 ml. of the acetic anhydride-pyridine reagent simultaneously and similar in all respects.

Calculate the percentage of hydroxyl in the sample (see Section **XVI,2**).

XVIII,3. DETERMINATION OF PHENOLS BY BROMINATION

REAGENTS

*Potassium bromate-bromide solution, 0·2*N. Dissolve 5·567 g. of A.R. potassium bromate and 75 g. of pure potassium bromide in water, and dilute to 1 litre in a volumetric flask. (The large excess over 5 equivalents of potassium bromide serves to ensure the complete reduction of the bromate when the solution is acidified and also to increase the solvent power of the solution for free bromine.)

*Sodium thiosulphate solution, 0·1*N. Dissolve about 25 g. of A.R. sodium thiosulphate pentahydrate in 1 litre of freshly-boiled and cooled distilled water. Standardise the solution with A.R. potassium iodate.

Starch indicator solution. See Section **XVII,2**.

Potassium iodide solution, 20 per cent. See Section **XVII,2**.

PROCEDURE

Weigh out accurately about 0·25 g. of the phenol, dissolve it in 5 ml. of 10 per cent. sodium hydroxide solution, and dilute the solution to 250 ml. in a volumetric flask. Pipette 25 ml. of the phenol solution into a 500 ml. iodine flask, followed by 25 ml. of the bromate-bromide solution, and then dilute with 25 ml. of water. Add 5 ml. of concentrated hydrochloric acid, and stopper the flask immediately. Shake the flask for 1 minute to mix the reactants, and allow to stand for 30 minutes with occasional swirling of the contents of the flask. Cool the flask under the tap or in ice water, place 10 ml. of 20 per cent. potassium iodide solution in the cup around the stopper. Slightly dislodge the stopper whereupon the iodide solution is drawn into the flask with no loss of bromine. Shake the flask well for 30 seconds and allow to stand for 10 minutes (1). Remove the stopper and wash the neck of the flask and the stopper with a little water. Titrate the free iodine, which is equivalent to the excess of bromine taken, with 0·1*N* sodium thiosulphate ; add about 1 ml. of starch solution near the end point.

Carry out a blank analysis, using 25 ml. of the bromate-bromide reagent and 25 ml. of water, the procedure being otherwise identical with the analysis proper.

Note.

(1) The precipitate formed with phenol may contain, in addition to tribromophenol, some tribromophenol bromide :

$$C_6H_5OH + 4Br_2 \longrightarrow C_6H_2Br_3.OBr + 4HBr$$

This is of no consequence, as it is converted into tribromophenol when potassium iodide is added to the acid solution :

$$C_6H_2Br_3.OBr + 2KI + 2HCl \longrightarrow C_6H_2Br_3.OH + 2KCl + HBr + I_2,$$

the extra bromine thus combined reacting as if it were free bromine. It is advisable to allow the solution to stand for 5–10 minutes in the presence of potassium iodide solution to ensure that all the tribromophenol bromide is decomposed.

It may be noted that the simple procedure given above is not applicable to **β-naphthol**; the latter (about 0·75 g., accurately weighed) should be dissolved in 10 ml. of 10 per cent. sodium hydroxide solution and diluted to 250 ml. in a volumetric flask. For the titration, use 25 ml. of the β-naphthol solution, 25 ml. of the bromate-bromide solution and 15 ml. of chloroform ; cool in ice for 5 minutes. Add 5 ml. of concentrated hydrochloric acid, stopper the flask, shake gently so that the brominated product dissolves in the chloroform, and cool in an ice bath for a further 5 minutes. Add 10 ml. of 20 per cent. potassium iodide solution, allow to stand for 10 minutes, and titrate with 0·1*N* sodium thiosulphate solution. Shake vigorously before the end point is reached as the chloroform tends to retain the last traces of iodine rather tenaciously. Perform a blank titration under the same conditions and thus compensate for the slight attack on the chloroform by the bromine.

CALCULATION

Calculate the percentage purity of the phenol from the expression :

$$\% \text{ Purity} = \frac{(V_1 - V_2) \times N_1 \times M \times 100}{W \times 2000 \times Z} \qquad (1)$$

where V_1 = ml. of sodium thiosulphate solution used for blank ;
V_2 = ml. of sodium thiosulphate solution used for sample ;
N_1 = normality of sodium thiosulphate solution ;
M = molecular weight of the phenol ;
W = weight (g.) of the sample ; and
Z = number of bromine atoms substituted in the phenol.

Alternatively, the blank analysis may be omitted and the percentage purity of the phenol calculated from formula (2). The student is recommended to perform the blank titration and to calculate the result by both methods.

$$\% \text{ Purity} = \frac{(VN_2 - V_2N_1) \times M \times 100}{W \times 2000 \times Z} \qquad (2)$$

where V = volume (ml.) of bromate solution used for the titration ;
N_2 = normality of bromate solution ;
V_2 = volume (ml.) of sodium thiosulphate solution used ;
N_1 = normality of sodium thiosulphate solution ;
M = molecular weight of the phenol ;
W = weight (g.) of sample ; and
Z = number of bromine atoms substituted in the phenol.

Deduction of formula (2).

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 6KCl + 3H_2O + 3Br_2$$

$$C_6H_5OH + 3Br_2 \longrightarrow Br_3C_6H_2OH + 3HBr$$

The volume of N bromate solution reacting with W g. of the sample is $(VN_2 - V_2N_1)$ ml.

$\therefore$ Weight of bromine used by W g. of sample $= (VN_2 - V_2N_1) \times 80/1000$ g.

$\therefore$ Weight of bromine used by M g. of sample $= \dfrac{(VN_2 - V_2N_1) \times 80 \times M}{W \times 1000}$ g.

But 1 mol of pure phenol would react with 3 mols of bromine or 6×80 g. of bromine,

$$\therefore \quad \% \text{ Purity} = \frac{(VN_2 - V_2N_1) \times 80 \times M \times 100}{W \times 1000 \times 6 \times 80}$$

$$= \frac{(VN_2 - V_2N_1) \times M \times 100}{W \times 2000 \times 3}$$

For a phenol which reacts with Z mols of bromine :

$$\% \text{ Purity} = \frac{(VN_2 - V_2N_1) \times M \times 100}{W \times 2000 \times Z} \qquad (2)$$

Equation (2) may be written in the form :

$$\% \text{ Purity} = \left(\frac{VN_2}{N_1} - V_2\right) \times \frac{N_1 \times M \times 100}{W \times 2000 \times Z}$$

This is identical with equation (1), VN_2/N_1 representing the theoretical value of the blank.

XVIII,4. DETERMINATION OF PHENOLS BY TITRATION AS ACIDS IN NON-AQUEOUS SOLVENTS

REAGENTS

Sodium methoxide in methanol, ca. *0·1*N. Weigh out about 2·4 g. of freshly-cut, clean sodium metal and add it to 100 ml. of methanol contained in a 500 ml. flask fitted with a reflux condenser ; if necessary, cool the flask momentarily in cold water to prevent the reaction becoming too violent. When all the sodium has reacted, add benzene until the solution remains cloudy upon swirling ; add methanol and benzene alternately in this manner until the volume is 1 litre and the solution is clear. Store the solution in a Pyrex glass bottle provided with a soda-lime guard tube to prevent entry of carbon dioxide. Standardise the solution daily with A.R. benzoic acid dissolved in benzene-methanol and use thymol blue as indicator. The benzoic acid (about 0·25 g.) may also be dissolved in dimethylformamide (50 ml.). The standardisation may also be effected with pure *p*-aminobenzoic acid.

Thymol blue indicator. Dissolve 0·3 g. of thymol blue in 100 ml. of methanol. The colour change is from yellow to blue.

o-Nitroaniline indicator. Dissolve 0·15 g. of *o*-nitroaniline in 100 ml. of benzene. The colour change is from yellow to orange-red.

Azo violet indicator. Prepare a saturated solution of *p*-nitrobenzene-azo-resorcinol in benzene. The colour change is from red to blue.

Dimethylformamide. A grade of dimethylformamide (DMF) suitable for titration purposes is available commercially. This compound decomposes slightly at its normal boiling point (153° C.) to give small amounts of dimethylamine and carbon monoxide. The technical dimethylformamide may be purified by mixing it with about 10 per cent. by volume of sodium-dried benzene and distilling at atmospheric pressure to remove the benzene; the temperature does not rise above 80° C. and most of the water is removed in the benzene-water azeotrope. The resulting product is shaken mechanically for several hours with anhydrous magnesium sulphate previously heated at 300–400° C. (25 g. per litre), distilled at 15–20 mm. pressure through an efficient fractionating column and the middle fraction collected.

Ethylenediamine. A product suitable for titrations is available commercially; its purity is 95–100 per cent. It may be dried, if necessary, by warming with sodium hydroxide pellets, cooling to permit the facile separation of water, and then distilling from sodium.

PROCEDURE

Titration in dimethylformamide. *Determination of the purity of vanillin.*

Place 25 ml. of dimethylformamide in a 250 ml. conical flask and add three drops of azo violet indicator. Stir the contents of the flask by means of a magnetic stirrer (Fig. *XV*, *5*, 2). Run in the 0·1*N* sodium methoxide solution from a burette until the colour of the solution in the flask just changes from pink to blue: close the mouth of the flask by a small square of cardboard and insert the burette tip through a small hole in the cover. This preliminary titration serves to neutralise any acidic impurities in the dimethylformamide. An equivalent result is obtained by performing an independent blank titration.

Weigh out accurately about 0·35 g. of vanillin and dissolve it in the dimethylformamide. Add the 0·1*N* sodium methoxide solution until the pink colour of the solution changes to blue. The colour should persist for 30 seconds.

The end point may also be determined by potentiometric titration using antimony and glass electrodes (compare Fig. *XV*, *4*, 3) and a commercial *p*H meter.

Calculate the purity of the vanillin from the relationship:

$$\text{Percentage purity} = \frac{\text{Volume of NaOMe solution} \times \text{Normality} \times \text{Equivalent weight}^* \times 100}{\text{Weight of sample (g.)} \times 1000}$$

* This is the equivalent weight of the vanillin.

Titration in ethylenediamine. *Determination of the purity of β-naphthol.*

Precautions must be taken to protect the solvent and the solution from carbon dioxide and moisture. Place 25 ml. of ethylenediamine in a 250 ml. conical flask and add 2–3 drops of *o*-nitroaniline indicator ; stir with a magnetic stirrer. Add 0·1*N* sodium methoxide solution until the colour of the solution just changes from yellow to orange red (compare Fig. *XV*, *5*, 2) ; this will neutralise acidic impurities in the solvent. Immediately add an accurately weighed sample (about 0·20 g.) of β-naphthol, stir until dissolved, and titrate until the colour changes from yellow to orange red. A reference standard contained in a stoppered conical flask prepared from a known weak phenol and the theoretical volume of titrant may be helpful. Alternatively, the " EEL " absorptiometer (Fig. *XV*, *5*, 6) may be used for detecting the colour change at the end point.

The end point may also be determined potentiometrically ; a 100 or 250 ml. three-necked flask should be used.

Calculate the purity of the β-naphthol.