VOLUMETRIC ANALYSIS.

STANDARDISED SOLUTIONS EMPLOYED IN VOLUMETRIC ANALYSIS

AND

INDICATORS OF NEUTRALITY.

Solutions standardised to contain definite molecular equivalents of various chemical substances are used in the British, United States, and German as well as other Pharmacopœias, for the purpose of determining the quantity of other ingredients with which they enter into reaction in accordance with the laws of chemical equivalence and which are present in unknown quantity.

A Normal Solution is defined as one containing in each 1000 c.c. such an amount of the active constituent as will combine with, replace or oxidise 1 gramme of Hydrogen. The *B.P.* does not define what is meant by a Normal Solution. The *U.S.P.* defines Normal Volumetric Solutions as those which contain in 1 litre in any stated reaction the chemical equivalent of 1 gramme of Hydrogen. It draws attention to the relative weight in grammes required for 1 litre, depending on whether the molecule of the active ingredient is univalent, bivalent or trivalent. The *B.P.* employs measuring apparatus which is adjusted at a temperature of 15·5° C. (60° F.). The *U.S.P.* mentions that it is absolutely necessary that the measuring vessels should agree amongst themselves accurately in their graduation at the standard temperature, but that it is immaterial what standard temperature has been selected for the graduation of the vessels. All the *U.S.P.* Volumetric Solutions must be prepared at a temperature of 25° C. (77° F.), and it is further required that in carrying out titrations with these solutions the temperature should not be below 21° C. (69·8° F.) nor above 29° C. (84·2° F.). The *P.G.* gives no general directions for the temperatures to be observed nor the method to be followed in preparing solutions for Volumetric analysis.

The tabulated list below shows the Volumetric Solutions which are official in the three Pharmacopœias dealt with in this volume, *e.g.*, the *B.P.*, *U.S.P.* and *P.G.*

B.P. Volumetric Sulphuric Acid Solution.
Deci-normal Volumetric Sulphuric Acid Solution.
Volumetric Sodium Hydroxide Solution.
Deci-normal Volumetric Sodium Hydroxide Solution.
Normal Alcoholic Sodium Hydroxide Solution.
Deci-normal Alcoholic Sodium Hydroxide Solution.
Normal Alcoholic Potassium Hydroxide Solution.
Deci-normal Volumetric Alcoholic Potassium Hydroxide Solution.
Volumetric Iodine Solution.
Volumetric Potassium Bichromate Solution.
Volumetric Silver Nitrate Solution.
Volumetric Sodium Thiosulphate Solution.

U.S.P. Normal Volumetric Sulphuric Acid Solution.
Half-normal Volumetric Sulphuric Acid Solution.
Tenth-normal Volumetric Sulphuric Acid Solution.
Fiftieth-normal Volumetric Sulphuric Acid Solution.
Double-normal Volumetric Sodium Hydroxide Solution.
Normal Volumetric Sodium Hydroxide Solution.
Normal Volumetric Potassium Hydroxide Solution.

Tenth-normal Volumetric Potassium Hydroxide Solution.
Fiftieth-normal Volumetric Potassium Hydroxide Solution.
Hundredth-normal Volumetric Potassium Hydroxide Solution.
Half-normal Volumetric Alcoholic Potassium Hydroxide Solution.
Normal Volumetric Hydrochloric Acid Solution.
Half-normal Volumetric Hydrochloric Acid Solution.
Tenth-normal Volumetric Oxalic Acid Solution.
Tenth-normal Volumetric Iodine Solution.
Tenth-normal Volumetric Bromine Solution.
Tenth-normal Volumetric Potassium Dichromate Solution.
Tenth-normal Volumetric Potassium Permanganate Solution.
Tenth-normal Volumetric Potassium Sulphocyanate Solution.
Tenth-normal Volumetric Silver Nitrate Solution.
Tenth-normal Volumetric Sodium Chloride Solution.
Tenth-normal Volumetric Sodium Thiosulphate Solution.
Volumetric Alkali Cupric Tartrate Solution.

P.G. Normal Volumetric Hydrochloric Acid Solution.
Half-normal Volumetric Hydrochloric Acid Solution.
Tenth-normal Volumetric Hydrochloric Acid Solution.
Hundredth-normal Volumetric Hydrochloric Acid Solution.
Normal Volumetric Potassium Hydroxide Solution.
Tenth-normal Volumetric Potassium Hydroxide Solution.
Hundredth-normal Volumetric Potassium Hydroxide Solution.
Half-normal Volumetric Alcoholic Potassium Hydroxide Solution.
Tenth-normal Volumetric Iodine Solution.
Tenth-normal Volumetric Sodium Thiosulphate Solution.
Tenth-normal Volumetric Silver Nitrate Solution.
Tenth-normal Volumetric Ammonium Rhodanate Solution.

Preparing and Setting Solutions for Volumetric Analysis.—For the proper performance of Volumetric work it is necessary to employ the following pieces of apparatus:—

A burette (preferably Mohr's) fitted with a glass stop-cock, graduated from 0 to 50 c.c. and subdivided into c.c. and into $\frac{1}{10}$ c.c.

Pipettes. A series of pipettes graduated to deliver 10, 15, 20, 25, 50 and 100 c.c.

A graduated glass cylinder, preferably stoppered, graduated at 1000 c.c., the intermediate graduations being 100 c.c. subdivided into 10 c.c. It should be capable of holding when filled to the zero mark 1000 grammes of Distilled Water at 15·5° C. (60° F.), and should have preferably an ascending and descending scale.

A stoppered glass measuring flask with single graduation, holding when filled to the mark on the neck 1000 c.c. of Distilled Water, and capable of containing 1000 grammes of Distilled Water at 15·5° C. (60° F.). This flask is commonly known as a litre flask, though it must be borne in mind that a standard litre represents the volume occupied by 1000 grammes (1 kilogramme) of Distilled Water at 4° C. (39·2° F.), the temperature of its maximum density, and at a pressure of 760 mm. of Mercury. 1 millilitre, one-thousandth part of this standard litre, is equivalent to 1·00016 c.c., or 1 c.c. is equivalent to 0·99984 millilitre. The term 'mille' has been suggested as an abbreviation of a millilitre to more accurately describe the one-thousandth part of a litre. Unless marked to the contrary, it is assumed that litre flasks, or any similar graduated glass measuring vessels, have reference to the standard litre graduated at the above-named temperature [4° C. (39·2° F.)]. The *B.P.* gives a caution (which will probably be considered unnecessary), to shake the Volumetric Solutions before use to ensure uniformity, and a note regarding their preservation in stoppered bottles, but omits to mention the necessity of ensuring the cleanliness of the bottles and the necessity for washing thoroughly. The *U.S.P.* directs that all bottles in which Volumetric Solutions are to be kept, as well as the other measuring vessels employed, should before use be thoroughly rinsed in Distilled Water, and then with two or three small portions of the solutions which they are about to contain, and that when not in use the apparatus should be kept

filled with Distilled Water. The *P.G.* does not give directions for the observance of any special precautions. It is extremely important that great attention should be observed in setting Normal Solutions, as any experimental error is greatly magnified when Fiftieth-normal and Hundredth-normal Solutions are prepared from them. These weaker strength solutions should in every case be carefully set before being used for titration, and either adjusted to a strictly correct content, or else a factor ascertained by which the number of c.c. may be converted into those of a strictly correct solution.

VOLUMETRIC SULPHURIC ACID SOLUTION.

Normal Solution of Sulphuric Acid should contain in each litre a weight equivalent in grammes to one half its molecular weight, that is to say, it should contain $97{\cdot}34 \div 2 = 48{\cdot}67$ grammes of pure Hydrogen Sulphate. In preparing the solution a useful method is to carefully weigh out in a clean, dry, stoppered weighing bottle 1 gramme of the Sulphuric Acid to be used in the preparation of the solution, pour it carefully into a small volume of Distilled Water, rinse out the weighing bottle with several small successive quantities of Distilled Water, and determine the weight of pure Hydrogen Sulphate present by titration with Normal Volumetric Sodium Hydroxide Solution, using a few drops of Phenolphthalein Solution as an indicator of neutrality. The Normal Volumetric Sodium Hydroxide Solution is prepared and set in a manner to be hereafter described. Having ascertained the quantity of Hydrogen Sulphate present, the quantity necessary to produce a solution containing a slight excess of the normal amount is weighed out and poured gradually and in small portions at a time into about 500 c.c. of the Distilled Water, the mixture being kept well cooled during the addition. When thoroughly mixed the solution is made up to 1000 c.c., and the mixture well shaken. A portion of the solution is then transferred to a burette, and the exact number of c.c. required to neutralise the molecular equivalent of pure dry Sodium Carbonate determined, Methyl Orange Solution being used as an indicator of neutrality. The balance of the acid remaining in the burette is returned to the original vessel, its volume ascertained, and it is then diluted in the proportion of the number of c.c. which it has actually required to the number of c.c. which it should have required had it been strictly normal. As an example, assuming that the titration of the 1 gramme of Sulphuric Acid has shown that the acid contains 98 p.c. of pure Hydrogen Sulphate; then the quantity necessary to produce a solution containing a little over 48·67 grammes per litre would be the following proportion—as 98 is to 100 so is 48·67 to x, viz., 49·66 grammes, so that in round numbers about 50 grammes should be weighed out, or, if it be preferred to measure the quantity, about 27 c.c. It should be mixed as described above, and the solution set against the pure dry Sodium Carbonate obtained by igniting pure powdered Sodium Bicarbonate. A quantity of 1·0531 grammes of the pure dry Sodium Carbonate is weighed out, and the Sulphuric Acid Solution added from a burette. The number of c.c. required is noted, and the solution diluted accordingly. Assuming that 950 c.c. of the solution remain after titration, and that x represents the number of c.c. of Sulphuric Acid Solution required to neutralise the above weight of pure dry Sodium Carbonate, it will be required to be diluted in the proportion of x is to 20 so is 950. In order to ensure the correctness of the dilution the solution should be reset.

B.P.—The *B.P.* employs a weighed quantity of 50 grammes of Sulphuric Acid, which it dilutes with 900 c.c. of Distilled Water, presumably adding the Distilled Water to the acid, which is a dangerous method of proceeding. It employs titration against pure dry Sodium Carbonate (obtained from the ignition of Sodium Bicarbonate) as a means of setting the acid, but presumably refers to Litmus as an indicator of neutrality, as it inserts a caution to boil off the Carbonic Anhydride. The use of Methyl Orange Solution as an indicator, as described above, obviates the necessity of boiling off Carbonic Anhydride and shortens the time required for the titration.

U.S.P.—The *U.S.P.* prepares Normal Volumetric Sulphuric Acid Solution by carefully mixing 30 c.c. of pure concentrated Sulphuric Acid of the *U.S.P.* official strength (see p. 80) with sufficient Distilled Water to produce about 1050 c.c., and sets a measured quantity of this strong solution by titration with

Normal Volumetric Potassium Hydroxide Solution, using 2 drops of Methyl Orange Solution as an indicator of neutrality. Having ascertained the number of c.c. required it proceeds to dilute the strong solution in the proportion of the volume actually required to the proportion which should have been required were the solution of strictly normal strength. As an additional safeguard against error it directs that a second determination of the strength should be made to ensure the exact correspondence of the solution, and if it be still found that solutions differ a new adjustment is directed to be made.

P.G.—Not included. See Table.

DECI-NORMAL VOLUMETRIC SULPHURIC ACID SOLUTION.

This solution may be prepared from the Normal Solution by diluting a measured quantity of the stronger solution with sufficient Distilled Water to produce ten times the volume of liquid. Thus 100 c.c. of Volumetric Sulphuric Acid Solution may be diluted with sufficient Distilled Water to produce 1000 c.c. of Deci-normal Volumetric Sulphuric Acid Solution. It should be carefully set against pure dry Sodium Carbonate in the same manner as described under Volumetric Sulphuric Acid, except that the weight of substance there indicated may be dissolved in Distilled Water and diluted with a further sufficient quantity of Distilled Water to produce 200 c.c., 10 c.c. of this solution may be employed and should correspond exactly to 10 c.c. of Deci-normal Volumetric Sulphuric Acid Solution. In the event of the solutions not strictly corresponding, the number of c.c. should be noted and the solution diluted accordingly, and should be again reset with a further 10 c.c. of the pure dry Sodium Carbonate Solution.

B.P.—The *B.P.* prepares the Deci-normal Solution from the Volumetric Sulphuric Acid Solution in a similar manner to that described above, but does not mention the necessity of setting the finished product.

U.S.P.—The Tenth-normal Volumetric Sulphuric Acid of the *U.S.P.* is prepared by diluting 100 c.c. of Normal Volumetric Sulphuric Acid Solution with sufficient Water to measure 1000 c.c. at 25° C. (77° F.). As will be seen from the monographs on the standardised preparations, *e.g.*, Belladonna, Ipecacuanha, Nux Vomica, etc., this solution is most frequently employed together with Fiftieth-normal Volumetric Potassium Hydroxide Solution (*U.S.P.*) in the titration of alkaloids, and in the various instances different indicators of neutrality are used, *e.g.*, Hæmatoxylin Solution, Cochineal and Iodeosin Solution. The *U.S.P.* authorities have consequently inserted a requirement to the effect that a special experiment should be made, in order to ensure the correspondence of these two solutions towards these indicators of neutrality. In the event of the solutions not corresponding they should be so adjusted that they do exactly correspond.

P.G.—Not included. See Table.

HALF-NORMAL VOLUMETRIC SULPHURIC ACID SOLUTION.

Half-normal Volumetric Sulphuric Acid Solution may be prepared by diluting a measured volume of Normal Volumetric Sulphuric Acid Solution with sufficient Distilled Water to produce 2 volumes, that is to say 500 c.c. of the stronger solution may be diluted with sufficient Distilled Water to produce 1000 c.c. of the weaker solution, and may be set against a solution prepared by dissolving 2·6327 grammes of pure dry Sodium Carbonate in Distilled Water and adding a further sufficient quantity of Distilled Water to produce 100 c.c. 10 c.c. of the Semi-normal Volumetric Sulphuric Acid should be equivalent to 10 c.c. of the Sodium Carbonate Solution, Methyl Orange Solution being employed as an indicator of neutrality. If the solutions do not correspond, the number of c.c. required should be accurately noted and the corresponding adjustment made; they may then be again re-titrated to ensure strict correspondence.

B.P.—Not included. See Table.

U.S.P.—The Half-normal Volumetric Sulphuric Acid Solution of the *U.S.P.* is prepared on lines similar to those indicated above. The measurements are made at 25° C. (77° F.). The solution is chiefly used for the titration of the organic salts of Potassium and Sodium, and for this purpose Methyl Orange Solution is usually employed as an indicator of neutrality. The

U.S.P. directs that a measured quantity of 10 c.c. of Normal Volumetric Potassium Hydroxide Solution should be titrated with the above solution, using 2 drops of Methyl Orange T.S. as an indicator of neutrality; exactly 20 c.c. of the Half-normal Solution should be required. In the event of a divergence between the above solutions, an adjustment should be made in order to ensure their exact correspondence.

P.G.—Not included. See Table.

FIFTIETH-NORMAL VOLUMETRIC SULPHURIC ACID SOLUTION.

This solution may be prepared by diluting 1 volume of Volumetric Sulphuric Acid Solution with sufficient Distilled Water to produce 50 volumes, or 1 volume of Deci-normal Volumetric Sulphuric Acid Solution with sufficient Distilled Water to produce 5 volumes. Thus 20 c.c. of Volumetric Sulphuric Acid Solution may be diluted with sufficient Distilled Water to produce 1000 c.c., or 200 c.c. of Deci-normal Volumetric Acid Solution may be diluted with sufficient Distilled Water to produce 1000 c.c. It may be set against a solution of pure dry Sodium Carbonate prepared by dissolving a weighed quantity of 0·10531 gramme of pure dry Sodium Carbonate in Distilled Water, and adding a further sufficient quantity of Distilled Water to produce 100 c.c. 50 c.c. of this solution exactly corresponds to 50 c.c. of the Fiftieth-normal Solution, Methyl Orange Solution may be used as an indicator of neutrality.

B.P.—Not included. See Table.

U.S.P.—The *U.S.P.* Fiftieth-normal Volumetric Sulphuric Acid Solution is prepared on similar lines to those above indicated, except that the measurements are made at a temperature of 25° C. (77° F.). It is chiefly employed for alkaloidal titration, and for this purpose Hæmatoxylin, Cochineal or Iodeosin T.S. are generally employed as indicators of neutrality. The *U.S.P.* does not in this instance require that a special test should be made to ensure correspondence between the solutions with which these indicators are used.

VOLUMETRIC SODIUM HYDROXIDE SOLUTION.

A solution of Sodium Hydroxide containing in each 1000 c.c. 39·76 grammes of pure Sodium Hydroxide (NaHO, eq. 39·76). The solutions should be kept in well-closed glass bottles, fitted with a vaselined stopper, an indiarubber stopper, or, preferably, fitted with a tube containing Soda-lime, or it may be kept under a layer of pure liquid Paraffin.

A convenient method for preparing Volumetric Sodium Hydroxide Solution is to first prepare a concentrated Sodium Hydroxide Solution by dissolving 50 grammes of good stick or good powdered Sodium Hydroxide in 50 c.c. of Distilled Water, the resulting solution is kept under a layer of pure liquid Paraffin. 1 gramme of this concentrated solution is carefully weighed and diluted with about 10 c.c. of Water, a few drops of Phenolphthalein Solution added and the liquid titrated with Volumetric Sulphuric Acid Solution, using Phenolphthalein Solution as an indicator of neutrality. The number of c.c. of Volumetric Sulphuric Acid Solution required is noted, and the amount of pure Sodium Hydroxide corresponding to this number of c.c. is ascertained by multiplying by 0·03976; having ascertained the percentage of Volumetric Sodium Hydroxide present in each gramme a sufficient weight of the solution is removed to represent about 41 or 42 grammes of pure Sodium Hydroxide, and this quantity is mixed with sufficient Distilled Water to produce 1000 c.c.; this will give a solution somewhat greater in strength than the Normal. This solution is set against 20 c.c. of Volumetric Sulphuric Acid Solution prepared as described under that heading, Phenolphthalein Solution being used as an indicator, and the number of c.c. required noted. The balance of the liquid in the burette is returned to the vessel holding the main quantity of liquid. Its volume is carefully ascertained, and is then diluted in the proportion of this number of c.c. to 20 (the number of c.c. which should have been required had the solution been strictly normal); thus, as an example, if x represents the number of c.c. required to neutralise the 20 c.c. of Volumetric Sulphuric Acid Solution and 950 c.c. of liquid are available, it should be diluted in the proportion of x is to 20 so is 950. After this dilution has been made the finished product should be checked against Volumetric Sulphuric Acid Solution, and if it be

found that the solution should still not correspond a further adjustment of the solution is necessary until they are in exact agreement. It may be noted that the *B.P.* employs Litmus and not Phenolphthalein Solution as an indicator of neutrality. It is generally conceded that Phenolphthalein is the more sensitive indicator.

B.P.—The *B.P.* Volumetric Sodium Hydroxide Solution is prepared by dissolving 42 grammes of purified Sodium Hydroxide in 1000 c.c. of Distilled Water. It is set by titration against Volumetric Sulphuric Acid Solution, the excessively large quantity of 100 c.c. being employed for the titration, and Litmus is used as an indicator of neutrality. The number of c.c. of the strong solution required to neutralise this quantity is noted, and the solution diluted in the ratio between this number of c.c. and 100. The *B.P.* makes no requirement that the solution should again be checked after the adjustment has been made, and apparently assumes that the solution is correct.

U.S.P.—Normal Volumetric Sodium Hydroxide Solution (*U.S.P.*) is prepared by dissolving 54 grammes of Sodium Hydroxide (*U.S.P.*) in sufficient Distilled Water to measure 1050 c.c. The solution is standardised by titration against Potassium Bitartrate Solution. The Potassium Bitartrate used is a specially purified Bitartrate obtained from Potassii Bitartras (*U.S.P.*), the following process being adopted. A weighed quantity of 100 grammes of the salt is digested in a covered beaker on a water-bath with a mixture of 85 c.c. of Distilled Water and 25 c.c. of diluted Hydrochloric Acid, the digestion being carried on with intervals of occasional stirring for 3 hours, the mixture is quickly cooled, the solution drained from the precipitate, which is washed by decantation with two successive quantities each of 100 c.c. of Water, the precipitate is collected upon a plain filter, the washing with cold Water is continued until a few drops of the filtrate, when acidified with Nitric Acid, afford no opalescence on the addition of Silver Nitrate T.S. The purified Bitartrate is dissolved in the smallest possible quantity of boiling Water, filtered, and the filtrate constantly stirred whilst being repeatedly cooled. The crystalline precipitate is removed by filtration, when cold washed with 300 c.c. of cold Water and allowed to drain thoroughly. It it then dried until constant in weight at 120° C. (248° F.). It should be kept in dry, well-stoppered glass bottles. A weighed quantity of 9·339 grammes of this salt and 160 c.c. of Distilled Water are introduced into a glass flask, the liquid boiled until solution has taken place and the strong Potassium Hydroxide Solution is added, a few drops (3 to 5) of Phenolphthalein Solution being added as an indicator of neutrality. The number of c.c. of Potassium Hydroxide Solution is noted, and, assuming that this number of c.c. is represented by x, the solution is diluted in the proportion of x to 50. The *U.S.P.* requires that, subsequent to adjustment, the solution should be reset against the solution of a similar quantity of a purified Potassium Bitartrate in a similar manner to that described above, and if still found to be in want of agreement, that a fresh adjustment should be made and the solutions made to strictly correspond. A special precaution is inserted with regard to the liability of solutions of Potassium or Sodium Hydroxide to absorb Carbonic Anhydride from the air, and it is required that these Volumetric Solutions should be preserved in bottles provided with well-fitting rubber stoppers, or with tubes filled with Soda-lime, which latter provision is also to be observed if the solution is allowed to remain for any considerable time in a burette. The use of Volumetric Sodium Hydroxide in place of Volumetric Potassium Hydroxide is permitted, but as the latter solution is stated to foam less and to attack glass more slowly it has a preference over the former.

P.G.—Not included. See Table.

DECI-NORMAL VOLUMETRIC SODIUM HYDROXIDE SOLUTION.

The Deci-normal Solution may be prepared by diluting 1 volume of Normal Solution with sufficient Distilled Water to produce 10 volumes, that is to say, 100 c.c. of Normal Volumetric Sodium Hydroxide Solution is diluted with sufficient Distilled Water to produce 1000 c.c. The finished solution should be set against a Tenth-normal Volumetric Sulphuric Acid Solution prepared as described under that heading, and the solutions adjusted to correspond, Phenophthalein Solution may be used as an indicator of neutrality.

The solution should be kept in well-closed glass bottles, preferably fitted with a tube containing Soda-lime, or it may be kept under a layer of pure liquid Paraffin.

B.P.—The *B.P.* Deci-normal Volumetric Solution is prepared in a similar manner to the solution described above, but no reference is made to a method of ensuring the accuracy of the finished product, nor is any reference made to precautions to be observed for storage.

U.S.P., *P.G.* } Not included. See Table.

DOUBLE NORMAL VOLUMETRIC SODIUM HYDROXIDE SOLUTION.

A solution containing in each 1000 c.c., 79·52 grammes of pure Sodium Hydroxide (NaHO).

B.P., *P.G.* } Not included. See Table.

U.S.P.—The *U.S.P.* prepares this solution by dissolving 90 grammes of Sodium Hydroxide (*U.S.P.*) in sufficient Distilled Water to produce about 1000 c.c. The solution is finally set against purified Potassium Bitartrate in a similar manner to that described under Normal Volumetric Sodium Hydroxide Solution (*U.S.P.*), and is adjusted so that a measured quantity of 25 c.c. exactly neutralises the quantity of Potassium Bitartrate there mentioned. It is equally important that the same precaution should be observed for keeping this solution, as in the case of the Normal Volumetric Sodium Hydroxide Solution.

NORMAL ALCOHOLIC SODIUM HYDROXIDE SOLUTION.

A solution containing 39·76 grammes of pure Sodium Hydroxide (NaHO) in each 1000 c.c. It is prepared on similar lines to the Volumetric Sodium Hydroxide Solution, except that Alcohol (90 p.c.) is used in the place of Distilled Water and set against Normal Volumetric Hydrochloric Acid Solution, to be hereafter described, Phenolphthalein Solution being used as an indicator of neutrality. It may be adjusted on the same lines as the solution referred to, so that the solutions may be strictly in agreement, or, preferably, a factor may be calculated, by which the number of c.c. used during a titration may be at once converted into terms of strictly Normal Solution.

It should be kept in glass bottles provided with well-fitting rubber stoppers.

B.P.—The *B.P.* information respecting Normal Volumetric Alcoholic Sodium Hydroxide Solution is very meagre. It appears as a footnote to Volumetric Sodium Hydroxide Solution, and officially directs the use of Alcohol (90 p.c.) as a solvent. It may also be presumed that the solution is intended to be standardised in a similar manner to the aqueous solution, but no definite statement to this effect appears. No precautions to be observed for storing the solution are given.

U.S.P., *P.G.* } Not included. See Table.

DECI-NORMAL VOLUMETRIC ALCOHOLIC SODIUM HYDROXIDE SOLUTION.

A solution containing 3·976 grammes of pure Sodium Hydroxide (NaHO) in each 1000 c.c. It may be prepared by diluting 1 volume of Normal Volumetric Alcoholic Sodium Hydroxide Solution with sufficient Alcohol (90 p.c.) to produce 10 volumes. It may be standardised against Deci-normal Volumetric Hydrochloric Acid Solution (to be hereafter described), and the solution may be either adjusted to a strictly Deci-normal strength, or a factor may be obtained from which the number of c.c. used during the titration may be converted into strictly Deci-normal strength. This factor is obtained by dividing the number of c.c. which should have been required to neutralise, by the number of c.c. actually required. The solution should be preserved in glass bottles fitted with well-fitting stoppers, or, preferably, with a rubber stopper containing a tube filled with Soda-lime.

B.P.—The *B.P.* solution is prepared, presumably, in a similar manner to the Tenth-normal Volumetric Sodium Hydroxide Solution, with the exception that Alcohol (90 p.c.) is used as a diluent in place of Water. No definite directions

are given for the standardisation of the finished solution, nor are any precautions directed to be observed in the storage of the solution. The quantity of solution prepared on each occasion should be only sufficient to last for a short period.

U.S.P., *P.G.* } Not included. See Table.

NORMAL VOLUMETRIC POTASSIUM HYDROXIDE SOLUTION.

A solution containing 55·71 grammes of pure Potassium Hydroxide (KOH) in each 1000 c.c. It may be prepared by dissolving 100 grammes of good commercial Potassium Hydroxide in sticks in 100 c.c. of Distilled Water. The resulting solution is cooled and kept under a layer of pure liquid Paraffin. A quantity of 1 gramme is weighed out in a weighing bottle, diluted with Distilled Water, and the quantity of Potassium Hydroxide present determined by titration with Volumetric Sulphuric Acid Solution, using a few drops of Phenolphthalein Solution as an indicator of neutrality. Having ascertained the quantity present in 1 gramme, a sufficient quantity is weighed out to yield about 58 grammes, and diluted with sufficient Distilled Water to produce 1000 c.c. The solution is standardised by titration with Volumetric Sulphuric Acid Solution, and adjusted to its requisite strength in a similar manner to the method adopted for Volumetric Sodium Hydroxide Solution. The same precautions are necessary with regard to the storage of the solutions when made.

B.P.—Not included. See Table.

It is presumed that the *B.P.* does not intend to include Volumetric Potassium Hydroxide Solution, unless the small type note under alcoholic solutions is intended to refer to both the aqueous and alcoholic solutions, which is scarcely likely. The note accords permission to use an equivalent proportion of Potassium Hydroxide in some instances instead of Sodium Hydroxide.

U.S.P.—The *U.S.P.* Normal Volumetric Solution is required to contain 55·74 grammes of pure Potassium Hydroxide (KOH) in 1000 c.c. at 25° C. (77° F.), and is prepared by dissolving 75 grammes of Potassium Hydroxide (*U.S.P.*) in sufficient Water to measure about 1050 c.c. It is standardised by methods similar to that described in the *U.S.P.* process for setting Normal Volumetric Sodium Hydroxide Solution. The *U.S.P.* requires that the strength of the finished solution shall be freshly determined after adjustment has been made, and that if required a readjustment shall be instituted in order that there may be strict correspondence between the solutions. It directs similar precautions to those mentioned under Sodium Hydroxide Solution to be observed in storage.

P.G.—The Normal Volumetric Potassium Hydroxide Solution of the *P.G.* is required to contain 56·16 grammes of Potassium Hydroxide in 1 litre. No method is given for its preparation or standardisation, nor are precautions for its storage stated.

DECI-NORMAL VOLUMETRIC POTASSIUM HYDROXIDE SOLUTION.

A solution containing 5·571 grammes of Potassium Hydroxide (KOH) in 1000 c.c. It is prepared by diluting 1 volume of Normal Volumetric Potassium Hydroxide Solution with sufficient Distilled Water to produce 10 volumes; *e.g.*, 100 c.c. of Normal Volumetric Potassium Hydroxide Solution is diluted with sufficient Distilled Water to produce 1000 c.c. It may be standardised against Deci-normal Volumetric Sulphuric Acid Solution, and in the event of its being found not to correspond should be readjusted till the solutions are in strict accordance.

It should be kept in glass bottles fitted with well-fitting rubber corks, preferably fitted with a Calcium Chloride tube containing fragments of Soda-lime, or it may be kept under the surface of a layer of pure liquid Paraffin.

B.P.—Not included. See Table; see also note under *B.P.* Volumetric Potassium Hydroxide Solution.

U.S.P.—The *U.S.P.* solution is prepared on similar lines to that given above, with the exception that the Normal Potassium Hydroxide Solution (*U.S.P.*) is required to be freshly standardised, and the measurements are made at 25° C. (77° F.). The solution is set against purified Potassium Bitartrate. A weighed quantity of 0·9339 gramme should require for neutralisation 50 c.c. of the

Tenth-normal Volumetric Potassium Hydroxide Solution. The *U.S.P.* requires the same precautions to be taken in the preservation of this solution as are recommended under Normal Volumetric Potassium Hydroxide Solution.

P.G.—The *P.G.* solution is required to contain 5·616 grammes of Potassium Hydroxide in 1 litre, and is prepared by mixing 10 c.c. of Normal Volumetric Potassium Hydroxide Solution (*P.G.*) and 90 c.c. of Water. It is standardised by titration against Deci-normal Volumetric Hydrochloric Acid Solution. No precautions are stated for its preservation.

FIFTIETH-NORMAL VOLUMETRIC POTASSIUM HYDROXIDE SOLUTION.

A solution containing 1·1142 grammes of Potassium Hydroxide (KOH) in 1000 c.c. prepared by diluting 1 volume of the Normal Solution, or 10 volumes of the Deci-normal Solution with sufficient Distilled Water to produce 50 volumes, *e.g.*, 20 c.c. of the Normal or 200 c.c. of the Deci-normal Solution is diluted with sufficient Distilled Water to produce 1000 c.c. It should be standardised against the Fiftieth-normal Volumetric Sulphuric Acid Solution described on p. 1296, and in the event of its being found incorrect the solution should be readjusted until the solutions are in strict accord. The same precautions which are observed in dealing with the Normal Solution should be also observed here.

U.S.P.—A solution containing 1·1148 grammes of Potassium Hydroxide (KOH) in 1000 c.c. prepared in a similar manner to the above, measurements being made at 25° C. (77° F.). The *U.S.P.* does not in this instance require that the solution should be standardised after preparation in order to ensure its correctness, although it states that it is for use together with Tenth-normal Volumetric Sulphuric Acid Solution in such delicate determinations as the titration of alkaloidal residues with Hæmatoxylin, Cochineal or Iodeosin T.S. as indicators of neutrality. It inserts cautions respecting its preservation which are virtually those given under the Normal Solution, with the addition of a recommendation that the solution should be renewed at frequent intervals.

P.G.—Not included. See Table.

HUNDREDTH-NORMAL VOLUMETRIC POTASSIUM HYDROXIDE SOLUTION.

A solution containing 0·5571 gramme of Potassium Hydroxide (KOH) in 1000 c.c., prepared by diluting 1 volume of the Normal Solution or 10 volumes of Deci-normal Solution with sufficient Distilled Water to produce 100 volumes. It should be standardised against Hundredth-normal Volumetric Sulphuric Acid Solution, prepared by diluting the Fiftieth-normal Solution with an equal volume of Distilled Water, the solution being in turn standardised against pure dry Sodium Carbonate.

B.P.—Not included. See Table.

A **Centi-normal Volumetric Sodium Hydroxide Solution** is officially described under Extractum Belladonnæ Liquidum, but is not included in the list of official Volumetric Solutions. It is stated to contain 0·3976 gramme of Sodium Hydroxide per litre. No method of preparation, standardisation, or preservation is given.

U.S.P.—A solution containing 0·5574 gramme of Potassium Hydroxide in 1000 c.c., prepared by diluting 10 c.c. of the Normal or 100 c.c. of the Tenth-normal Solution with sufficient Water to measure 1000 c.c. The measurements are made at 25° C. (77° F.). The usual notice respecting the precautions to be observed for the preservation of the solution is here omitted, but the solution is recommended to be frequently renewed.

P.G.—The *P.G.* solution contains 0·5616 gramme of Potassium Hydroxide in 1 litre, and is prepared by mixing 10 c.c. of the Tenth-normal Solution with 90 c.c. of Water. It is stardardised against Hundredth-normal Volumetric Hydrochloric Acid Solution, to be hereafter described.

NORMAL VOLUMETRIC ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION.

Normal Volumetric Alcoholic Potassium Hydroxide Solution is rarely if ever employed, and is not official in either the *U.S.P.* or the *P.G.* The *B.P.* description of it is brief.

It is a solution containing 55·71 grammes of Potassium Hydroxide in 1000 c.c. of Alcohol (90 p.c.). The *B.P.* permits its use in 'certain' cases instead of Alcoholic Sodium Hydroxide, but does not state what these certain cases are.

SEMI-NORMAL VOLUMETRIC ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION.

A solution containing 27·855 grammes of Potassium Hydroxide (KOH) in Alcohol (90 p.c.). It may be conveniently prepared in the following manner: A weighed quantity of good commercial Potassium Hydroxide in sticks is dissolved in about 20 c.c. of Water and titrated with Normal Volumetric Sulphuric Acid Solution, using Phenolphthalein Solution as an indicator. From the results of this titration the percentage of pure Potassium Hydroxide in the sample is calculated, and a sufficient quantity taken to ensure a slight excess over the calculated weight; thus, assuming the sample to have indicated 85 p.c. of the pure Hydroxide, the quantity required for the solution should be as 85 : 100 : : 27·855, corresponding to about 33 grammes. Weigh out about 35 grammes of the specimen, dissolve in 20 c.c. of Water and dilute with sufficient Alcohol (90 p.c.) to produce 1000 c.c. The solution may be standardised against Semi-normal Volumetric Hydrochloric Acid Solution, using Phenolphthalein Solution as an indicator of neutrality. A measured quantity of 50 c.c. of the Semi-normal Volumetric Hydrochloric Acid Solution may be taken and the number of c.c. required to neutralise it carefully noted. The solution may then be diluted with Alcohol (90 p.c.) in the proportion between the number of c.c. actually required, to the number of c.c. which should have been required had the solution been strictly Semi-normal. In the event of the solution being only of little more than Semi-normal strength a good plan is to obtain a factor by which it may be converted into terms of strictly Semi-normal Solution, and to allow the extra strength for deterioration on keeping. The solution will be required to be set freshly at each time of using if employed at more than short intervals.

The same precautions which are observed with the Normal Volumetric Potassium Hydroxide Solution should be observed in the case of this solution, and in addition the glass bottles should be of a dark amber tint.

B.P.—Not included. See Table.

U.S.P.—A solution containing 27·87 grammes of Potassium Hydroxide in 1000 c.c. prepared by dissolving about 40 grammes of Potassium Hydroxide (*U.S.P.*) in about 20 c.c. of Water, and adding sufficient Alcohol (94·9 p.c.) to produce 1000 c.c. One day is allowed to elapse for the solution to clear, and the supernatant solution is quickly decanted into another bottle. The solution is standardised against a purified Potassium Bitartrate, using Phenolphthalein T.S. (5 drops) as an indicator of neutrality. A weighed quantity of 1·8678 grammes of the purified Bitartrate representing 20 c.c. of a Semi-normal Solution is employed. The number of c.c. required to exactly neutralise is noted and the solution diluted with Alcohol (94·9 p.c.) in the proportion between this number of c.c. and 20. 20 c.c. of the finished solution being required to exactly neutralise 1·8678 grammes of purified Potassium Bitartrate. An alternative method of standardising the solution is with Half-normal Volumetric Hydrochloric Acid Solution, the dilution being made in a similar manner; the finished solution being required to exactly neutralise an equal volume of the Half-normal Volumetric Hydrochloric Acid, the measurements are made at 25° C. (77° F.). The *U.S.P.* inserts precautions respecting the preservation of the solution, and requires that it should be kept in bottles provided with well-fitting rubber stoppers, and that it should be protected from the light. The solution decreases in strength somewhat rapidly, and it is required in addition that blank tests should be performed whenever it is employed in titration.

P.G.—A solution containing 28·8 grammes of Potassium Hydroxide in 1 litre of Alcohol (90 p.c.). No method of preparation is given. It is standardised against Semi-normal Volumetric Sulphuric Acid Solution. The *P.G.* describes it as a colourless or but slightly yellow-coloured liquid. No precautions respecting its preservation are included.

DECI-NORMAL VOLUMETRIC ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION.

A Deci-normal Alcoholic Solution of Potassium Hydroxide is seldom if ever employed in official volumetric work. Neither the *U.S.P.* nor the *P.G.* includes such a solution. The *B.P.* in the vaguest possible terms as a footnote to Volumetric Sodium Hydroxide Solution. From this description it may be taken to mean a solution containing 5·571 grammes of Potassium Hydroxide in 1000 c.c. of Alcohol (90 p.c.) which is for use in 'certain cases' instead of Sodium Hydroxide Solution.

NORMAL VOLUMETRIC HYDROCHLORIC ACID SOLUTION.

A solution containing 36·19 grammes of Hydrogen Chloride (HCl) in 1000 c.c. It may be prepared by a method similar to that described under Volumetric Sulphuric Acid Solution, except that Hydrochloric Acid is substituted for Sulphuric Acid; it may be set against pure dry Sodium Carbonate as there described.

B.P.—Not included. See Table.

U.S.P.—A solution containing 36·18 grammes of absolute Hydrochloric Acid in 1000 c.c. It is prepared by mixing 130 c.c. of Hydrochloric Acid [sp. gr. 1·158 at 25° C. (77° F.)] with sufficient Water to measure 1000 c.c., the measurements being made at 25° C. (77° F.). It is standardised with Normal Volumetric Potassium Hydroxide Solution, using Methyl Orange T.S. as an indicator of neutrality. The number of c.c. of Normal Volumetric Potassium Hydroxide Solution required to neutralise 10 c.c. of the above solution mixed with about 20 c.c. of Water is noted and the acid solution diluted so that the solutions are in strict accord. After the dilution has been made the *U.S.P.* directs that a further trial of its neutralising power should be made, and if still found to be incorrect it should be readjusted.

P.G.—A solution containing 36·46 grammes of absolute Hydrochloric Acid in 1 litre. No directions are given for its preparation or standardisation.

SEMI-NORMAL VOLUMETRIC HYDROCHLORIC ACID SOLUTION.

A solution containing 18·095 grammes of Hydrogen Chloride in 1000 c.c. prepared by mixing 1 volume of the Normal Solution with sufficient Distilled Water to produce 2 volumes, *e.g.*, 500 c.c. of the Normal Solution is diluted with sufficient Distilled Water to produce 1000 c.c. It may be standardised by titration against Normal Volumetric Sodium Hydroxide Solution, of which 10 c.c. should exactly neutralise 20 c.c. of the Semi-normal Acid. In the event of its not being so, it should be readjusted and a fresh titration should be made in order to ensure the solutions being strictly in accord.

B.P.—Not included. See Table.

U.S.P.—A solution containing 18·09 grammes of absolute Hydrochloric Acid in 1000 c.c. prepared by diluting 500 c.c. of Normal Volumetric Hydrochloric Acid Solution with sufficient Distilled Water to measure exactly 1000 c.c., the measurements are made at 25° C. (77° F.). No directions are given to ensure the finished solution being of the correct strength.

P.G.—A solution containing 18·23 grammes of absolute Hydrochloric Acid in 1 litre. No method of preparation or standardisation given.

DECI-NORMAL VOLUMETRIC HYDROCHLORIC ACID SOLUTION.

A solution containing 3·619 grammes of Hydrogen Chloride in 1000 c.c. prepared by diluting 1 volume of the Normal Solution with sufficient Distilled Water to produce 10 volumes, *e.g.*, 100 c.c. of the Normal Solution is diluted with sufficient Distilled Water to produce 1000 c.c. It may be standardised against Deci-normal Volumetric Sodium Hydroxide Solution, using Phenolphthalein Solution as an indicator of neutrality. In event of the solutions not strictly corresponding, a readjustment should be made in order that they may be in strict accord.

B.P.—Not included. See Table.

Although not included in the official list of Volumetric Solutions it is used

in the titration of the residual alkaloid from the assay of Liquid Extract of Belladonna and is described under Extractum Belladonnæ Liquidum, as containing 3·619 grammes of HCl per litre. No method of preparation, standardisation, or preservation is given.

U.S.P.—Not included. See Table.

P.G.—A solution containing 3·6464 grammes of absolute Hydrochloric Acid in 1 litre prepared by mixing 10 c.c. of the Normal Solution and 90 c.c. of Water. No directions for its standardisation are included.

CENTI-NORMAL VOLUMETRIC HYDROCHLORIC ACID SOLUTION.

A solution containing 0·3619 gramme of Hydrogen Chloride in 1000 c.c. prepared by diluting 1 volume of Normal or 10 volumes of Deci-normal Solution with sufficient Distilled Water to produce 100 volumes, *e.g.*, 10 c.c. of Normal or 100 c.c. of Tenth-normal Solution is diluted with sufficient Distilled Water to produce 1000 c.c. The solution is standardised with Centi-normal Volumetric Potassium Hydroxide Solution, and in the event of the solutions not strictly corresponding, a readjustment should be made, so that they may be in strict accord. The solution requires to be carefully standardised as it is used in alkaloidal titrations.

B.P., *U.S.P.* Not included. See Table.

P.G.—A solution containing 0·3646 gramme of absolute Hydrochloric Acid in 1 litre. It is directed to be prepared by mixing 10 c.c. of Tenth-normal Volumetric Hydrochloric Acid Solution and 90 c.c. of Water.

DECI-NORMAL VOLUMETRIC IODINE SOLUTION.

A solution containing 12·59 grammes of pure Iodine prepared by the resublimation of Iodine answering the official tests, mixed with 25 p.c. of its weight of dry Potassium Iodide; the resulting crystals being freed from moisture by drying over fused Calcium Chloride or over Sulphuric Acid in a desiccator. A weighed quantity of 12·7 grammes is mixed with 18 grammes of pure Potassium Iodide (free from Iodate) and dissolved in about 25 c.c. of Water. When completely dissolved the solution is diluted by the cautious addition of Water to measure 1000 c.c. It is standardised against Deci-normal Volumetric Sodium Thiosulphate Solution (to be hereafter described), using, if necessary, Starch Mucilage as an indicator. The solution may also be standardised by titration with pure Arsenious Anhydride. The number of c.c. of the Iodine Solution required to completely react with the Deci-normal Volumetric Sodium Thiosulphate Solution employed is noted, and the solution diluted accordingly (as described under Volumetric Sulphuric Acid Solution), so that it shall be strictly Deci-normal, or a factor may be obtained by dividing the number of c.c. which should have been required, by the number of c.c. actually required, and this factor used to interpret the solution into strictly Deci-normal terms.

It should be kept in well-stoppered glass bottles of a dark amber tint in a cool atmosphere and protected as far as possible from the light.

B.P.—A solution containing 12·59 grammes of pure Iodine and 18 grammes of pure Potassium Iodide in 1000 c.c. The official method of setting the solution is by titration against Arsenious Anhydride, pure Barium Thiosulphate, or other suitable substance, and it is permitted to either use the solution as it is with a correction for difference in strength between it and Deci-normal, or to convert it into a strictly Deci-normal Solution. The *B.P.* gives no instructions regarding the preservation of the solution.

U.S.P.—A solution containing 12·59 grammes of pure Iodine in 1000 c.c. of Water. It may be prepared by two methods:—1. By dissolving 12·59 grammes of pure Iodine and 18 grammes of pure Potassium Iodide in 300 c.c. of Water and diluting with sufficient Water to measure exactly 1000 c.c. The measurements are made at 25° C. (77° F.). The pure Iodine is prepared from Iodine (*U.S.P.*) by careful re-sublimation, first over boiling Water to remove moisture, Cyanogen Iodide, Bromide and Chloride, and then by mixing it with 5 p.c. of its weight of dry Potassium Iodide and re-sublimation on a sand-bath; any moisture still adhering is removed by drying over Calcium Chloride. A determination of

the strength of this solution is made at the time of using, unless it is freshly prepared. 2. A weighed quantity of 14 grammes of Iodine (*U.S.P.*) and 18 grammes of Potassium Iodide (*U.S.P.*) are dissolved in about 300 c.c. of Water and the solution diluted to 1000 c.c. The resulting solution is standardised by titration with 10 c.c. of Tenth-normal Volumetric Sodium Thiosulphate Solution, the number of c.c. recorded, the ascertained volume of the solution diluted in the ratio of the number of c.c. actually required to the number of c.c. which should have been required (namely 10). After dilution the strength is again verified to ensure strict accordance between the solutions, and in the event of their still differing a fresh adjustment is made followed by re-determination in order to ensure the solutions being strictly correct.

The solution is directed to be kept in glass-stoppered bottles, but no other precaution specified.

P.G.—A solution containing 12·685 grammes of Iodine and 20 grammes of Potassium Iodide in 1 litre. The Iodine is directed to be dissolved by the aid of 20 grammes of Potassium Iodide, but otherwise no instructions are given respecting the preparation or standardisation of the solution; no directions are inserted regarding the preservation of the solution when made.

DECI-NORMAL VOLUMETRIC BROMINE SOLUTION.

B.P., *P.G.* Not included. See Table.

The solution is only employed in the determination of Phenol.

U.S.P.—A solution containing 7·936 grammes of pure Bromine in 1000 c.c. It is prepared by dissolving 3·2 grammes of Potassium Bromate and 50 grammes of Potassium Bromide in sufficient Water to measure 900 c.c. The solution is standardised by means of Potassium Iodide Solution. A measured quantity of 20 c.c. of the above solution is transferred into a 250 c.c. glass-stoppered bottle mixed with 75 c.c. of Water, 5 c.c. of pure Hydrochloric Acid and 5 c.c. of Potassium Iodide T.S. The liberated Iodine is titrated with Tenth-normal Volumetric Sodium Thiosulphate Solution. The number of c.c. required is noted, and an ascertained volume of the solution diluted in the ratio of the number of c.c. of Tenth-normal Solution actually required to the number of c.c. of Tenth-normal Solution which should have been required. A re-determination of the strength of the solution is made, and in the event of the solutions still not agreeing it is readjusted so that the solutions shall be strictly in accord.

The solution is directed to be kept in well-stoppered bottles of a dark amber tint.

DECI-NORMAL VOLUMETRIC SODIUM THIOSULPHATE SOLUTION.

A solution containing 24·644 grammes of crystallised Sodium Thiosulphate ($Na_2S_2O_3 . 5H_2O$) in 1000 c.c. of Distilled Water. It may be prepared by dissolving about 30 grammes of the crystallised salt in about 250 c.c. of Distilled Water, and diluting with a further quantity of Distilled Water to measure 1000 c.c. It may be set against a weighed quantity of the re-sublimed Iodine described under Deci-normal Volumetric Iodine Solution, or, preferably, by means of Deci-normal Volumetric Potassium Bichromate Solution (hereafter described), and Potassium Iodide Solution. A measured quantity of 20 c.c. of Deci-normal Volumetric Potassium Bichromate Solution is introduced into a solution of 1 gramme of Potassium Iodide in 50 c.c. of Water, and 10 c.c. of diluted Sulphuric Acid added. The liberated Iodine is titrated with the above solution, the number of c.c. accurately noted, and an ascertained volume of the approximately Deci-normal Thiosulphate Solution diluted in the ratio between the number of c.c. actually required, and the number of c.c. which should have been required, namely 20. After dilution, the solution is reset in a similar way to that described above. In order to ensure accuracy, and if found not to be in agreement, it should be readjusted so that the solutions should be in strict accord.

It should be kept in well-stoppered glass bottles of a dark amber tint and in a cool atmosphere.

B.P.—A solution containing 24·644 grammes of crystallised Sodium Thiosulphate ($Na_2S_2O_3 . 5H_2O$) in 1000 c.c. of Distilled Water. It is officially directed

to be prepared by dissolving 28 grammes of the salt in 1000 c.c. of Distilled Water, and to be set against Volumetric Iodine Solution, Mucilage of Starch being employed as an indicator. An excessively large quantity of Volumetric Iodine Solution is employed for titration, namely 100 c.c. The solution is diluted in accordance with the result of this determination, and adjusted to contain the above-mentioned amount of crystallised Sodium Thiosulphate. No directions are given with regard to the preservation of the solution.

U.S.P.—A solution containing 24·644 grammes of crystallised Sodium Thiosulphate in 1000 c.c. at 25° C. (77° F.). It is prepared by dissolving 30 grammes of the salt in sufficient Distilled Water to measure 1000 c.c. The Sodium Thiosulphate employed must be free from Sulphates and Sulphites, free alkalis and Calcium salts. The solution is standardised with Tenth-normal Volumetric Potassium Bichromate Solution and Potassium Iodide. The solution is diluted in accordance with the result obtained with this Volumetric determination, and a fresh determination is made to ensure the accuracy of the solution. In the event of the solutions being still found lacking in agreement a fresh adjustment is made in order to render them in strict accord.

The solution is required to be kept in glass-stoppered bottles carefully protected from dust.

P.G.—A solution containing 24·832 grammes of Sodium Thiosulphate in 1 litre of Water. No directions are given for its preparation, standardisation, or preservation.

DECI-NORMAL VOLUMETRIC SILVER NITRATE SOLUTION.

A solution containing 16·869 grammes of Silver Nitrate in 1000 c.c., prepared by dissolving this quantity of the salt in about 250 c.c. of Distilled Water, and diluting the solution with a further quantity of Distilled Water to measure 1000 c.c. It may be standardised with Deci-normal Volumetric Hydrochloric Acid Solution or with Deci-normal Volumetric Sodium Chloride Solution. A measured quantity of 10 c.c. of either solution may be employed. The number of c.c. required is accurately noted and an ascertained volume of the solution is diluted with Distilled Water in the ratio between the number of c.c. of Deci-normal Volumetric Silver Nitrate Solution actually required, and the number of c.c. which should have been required, namely 10. In order to ensure that the dilution is correct a re-determination of the strength of the solution should be made, and in the event of the solutions still not agreeing a further adjustment should be made so that the solutions may be in strict accord.

When finished the solution should be kept in well-stoppered glass bottles of a dark amber tint in a cool atmosphere and protected as far as possible from contact with dust and light.

B.P.—A solution containing 16·869 grammes of Silver Nitrate in 1000 c.c. of Water prepared by dissolving the salt in a sufficient quantity of Water and further diluting with Distilled Water to produce 1000 c.c. The strength of the solution is officially directed to be checked by titration against pure Sodium Chloride or pure Hydrochloric Acid Solution of definite strength, and the solution adjusted according to the result of this Volumetric determination or the real strength of the solution recorded in order that the requisite correction may be made. No directions are contained for the verification of the solution after dilution.

Opaque stoppered bottles are recommended for its preservation, but amber-tinted glass bottles are preferable.

U.S.P.—A solution containing 16·869 grammes of Silver Nitrate in 1000 c.c. of Water prepared by dissolving the pulverised and dried salt, completely dehydrated at 130° C. (266° F.), in sufficient Water to measure 1000 c.c. In this instance it appears to be assumed that the solution will be found correct when made, as no directions are given for its standardisation, although the various methods in which the solution may be employed for titration are recorded: thus, there is the method of direct titration where the Volumetric Solution is added direct to the solution of a weighed quantity of the salt with Potassium Chromate T.S. as an indicator; there is the Volhard method of indirect titration where an accurately measured excess of the Tenth-normal Volumetric Silver Nitrate Solution is added to the solution to be determined, acidified with Nitric Acid, and the uncombined excess of Tenth-normal Volumetric Silver Nitrate Solution is determined

by titration with Tenth-normal Volumetric Potassium Sulphocyanate Solution, using Ferric Ammonium Sulphate T.S. as an indicator; and the method of titration generally employed for the assay of Hydrocyanic Acid and Cyanides where the formation of a permanent precipitate indicates the end of the reaction.

The solution is recommended to be kept in glass-stoppered vials of a dark amber colour, and to be carefully protected from dust and sunlight.

P.G.—A solution containing 16·977 grammes of Silver Nitrate in 1 litre. No directions are given for either its preparation, standardisation, or preservation.

VOLUMETRIC POTASSIUM BICHROMATE SOLUTION.

A solution containing 4·87 grammes of pure Potassium Bichromate ($K_2Cr_2O_7$, eq. 292·3) in 1000 c.c. of Water, that is to say a solution containing one-sixth of the molecular equivalent of the salt as 1 molecule of Potassium Bichromate liberates 3 atoms of Oxygen which are capable of oxidising 6 atoms of Hydrogen.

It may be prepared by dissolving the above-named quantity of the well-dried and finely powdered salt in about 250 c.c. of Distilled Water and diluting the solution with a further quantity of Distilled Water, sufficient to produce the above volume. It may be standardised against Deci-normal Volumetric Sodium Thiosulphate Solution, using Potassium Iodide Solution and Sulphuric Acid, or by titration with Deci-normal Volumetric Sodium Hydroxide Solution; in this latter case it must be recollected that the solution is Deci-normal, when the solution contains one-half its molecular equivalent per litre of Potassium Bichromate. It may also be set against pure Ferrous Ammonium Sulphate, in the latter case a solution containing one-sixth molecular equivalent per litre corresponds to the Deci-normal solution. If found too strong the solution may be diluted in a similar manner to other volumetric solutions, and re-standardised after dilution.

It should be kept in well-stoppered glass bottles of a dark amber colour and protected as far as possible from contact with dust and direct sunlight.

B.P.—A solution containing 4·87 grammes of Potassium Bichromate in 1000 c.c. It is prepared by dissolving this weight of the salt in about half the required volume of Water, and diluting the solution so obtained with a further quantity of Distilled Water to measure exactly 1000 c.c. It is officially directed to be standardised by titration with pure Ferrous Ammonium Sulphate, or 'other reliable substance,' and either dilution of the solution to a strictly Deci-normal strength or the ascertainment of its true strength is recommended.

U.S.P.—A solution containing 4·8713 grammes of pure Potassium Bichromate in 1000 c.c. of Distilled Water. It is prepared by dissolving the above-named quantity of pulverised salt dried at 120° C. (248° F.) in sufficient Water to measure exactly 1000 c.c. at 25° C. (77° F.). A method of standardising the solution is not given, but references are made to its uses, it is further pointed out that when used with Phenolphthalein as an indicator the solution is Tenth-normal when it contains 14·614 grammes in 1000 c.c., but when used as an oxidising agent a solution containing the amount stated at the commencement of the paragraph is the value of a Tenth-normal Solution. When employed for titrating various compounds it is added gradually from a burette to a solution of the Ferrous Salt in Water rendering it acid if necessary with Sulphuric Acid, Potassium Ferricyanide T.S. being used as an indicator, it is also employed in conjunction with Potassium Iodide and Sulphuric Acid in standardising Tenth-normal Sodium Thiosulphate Solution.

P.G.—Not included. See Table.

DECI-NORMAL VOLUMETRIC OXALIC ACID SOLUTION.

A solution containing 6·255 grammes of pure crystallised Oxalic Acid ($H_2C_2O_4H_2O$, eq. 125·10) in 1000 c.c. of Distilled Water. It may be prepared by dissolving 6·5 grammes of the crystallised salt in about 100 c.c. of Distilled Water and adding a further sufficient quantity of the Distilled Water to produce 1000 c.c. It may be standardised by titration against Deci-normal Volumetric Sodium Hydroxide Solution. A measured quantity of 20 c.c. of the latter solution is introduced into a porcelain basin, and the Oxalic Acid Solution run in from a burette, Phenolphthalein Solution being used as an indicator of neutrality.

The number of c.c. required is accurately noted, and an ascertained volume of the solution is then diluted in the ratio of the number of c.c. actually required to the number of c.c. which should have been required (20 c.c.). After dilution it is again standardised in order to ensure the correctness of the solution, and if found to be still lacking in agreement the solution should be further adjusted until it is in strict accord. It is employed in standardising Deci-normal Volumetric Potassium Permanganate Solution.

B.P.—Not included. See Table.

U.S.P.—A solution containing 6·255 grammes of pure crystallised Oxalic Acid in 1000 c.c. at 25° C. (77° F.). It may be prepared by dissolving 6·4 grammes of pure Oxalic Acid in sufficient Water to measure 1000 c.c. It is standardised by titration against 10 c.c. of a freshly-standardised Tenth-normal Volumetric Potassium Hydroxide Solution diluted with twice its volume of Water, Phenolphthalein T.S. being used as an indicator of neutrality, the titration being conducted at a boiling temperature. The solution is diluted in accordance with the usual instructions for the dilution of volumetric solutions. A fresh determination being made to ensure the accuracy of such dilution, and a readjustment being made should the solution be found to be still inexact, to render them in strict accord. The *U.S.P.* mentions that it deteriorates on standing. It is used for standardising Tenth-normal Volumetric Potassium Permanganate Solution.

P.G.—Not included. See Table.

DECI-NORMAL VOLUMETRIC POTASSIUM PERMANGANATE SOLUTION.

A solution containing 3·1374 grammes of pure crystallised Potassium Permanganate in 1000 c.c. It may be prepared by dissolving 3·5 grammes of the pure crystallised salt in about 250 c.c. of Distilled Water, and when solution is complete, diluting it with sufficient Distilled Water to measure 1000 c.c. It may be standardised by titration with Deci-normal Volumetric Oxalic Acid Solution, a measured quantity of 20 c.c. of the latter solution is introduced into a glass flask, mixed with about 1 c.c. of Sulphuric Acid, heated over a Bunsen flame, and the Permanganate Solution run in from a burette until a faint pink colour (permanent for about 30 seconds) is produced. The number of c.c. required is accurately noted, and an ascertained volume of the approximately Deci-normal Permanganate Solution is diluted in the ratio between this number of c.c. and 20. To ensure correctness the solution is re-standardised with a further quantity of the Volumetric Oxalic Acid Solution, and in the event of the solutions not agreeing a further adjustment is made until the solutions are in strict accord.

The finished solutions should be kept in well-stoppered glass bottles of a dark amber colour and protected as far as possible from contact with dust and light.

B.P.—Not included. See Table.

U.S.P.—A solution containing 3·1396 grammes of pure crystallised Potassium Permanganate in 1000 c.c. of Water, measured at 25° C. (77° F.). It is prepared by dissolving 3·3 grammes of pure crystallised salt by the addition of 1000 c.c. of Distilled Water. The solution being boiled for about 5 minutes, the flask is then plugged with Cotton-Wool and the suspended matter allowed to deposit; the clear portion of the solution being poured off, the Water used for dilution is Water that has been distilled over Potassium Permanganate. The solution is standardised against 10 c.c. of an accurately standardised Tenth-normal Volumetric Oxalic Acid Solution with the addition of 1 c.c. of pure concentrated Sulphuric Acid; the Permanganate Solution being diluted in the usual manner with sufficient Distilled Water to produce a strictly Tenth-normal Solution. An alternative method of standardisation is also mentioned. A measured quantity of 20 c.c. of the approximate Permanganate Solution is introduced into a solution of about 1 gramme of Potassium Iodide in 10 c.c. of diluted Sulphuric Acid, and the mixture diluted with 200 c.c. of Distilled Water. The liberated Iodine is titrated with an accurately standardised Tenth-normal Volumetric Sodium Thiosulphate Solution. The number of c.c. of the latter solution is noted carefully and the solution diluted in the ratio between the number of c.c. of Permanganate Solution which should have been required and the above number. The *U.S.P.* requires that a fresh trial in the manner described immediately

above should be made after dilution, and if necessary a new adjustment should be made to render the correspondence between the solutions perfect.

P.G.—Not included. See Table.

TENTH-NORMAL VOLUMETRIC SODIUM CHLORIDE SOLUTION.

This solution is very little used, and is chiefly employed for the titration of Silver salts or for the standardisation of Volumetric Silver Nitrate Solution. The *U.S.P.* describes the method of preparing pure Sodium Chloride, but a very pure salt may be obtained so cheaply that it is questionable whether it is worth while to specially prepare the pure Chloride in the laboratory.

B.P.—Not included. See Table.

U.S.P.—A solution containing 5·806 grammes of pure Sodium Chloride in 1000 c.c. It is obtained by dissolving 5·806 grammes of pure Sodium Chloride in sufficient Water to measure exactly 1000 c.c. at 25° C. (77° F.). No method is indicated for the standardisation of the solution, and when prepared with the pure Sodium Chloride may be assumed to be correct.

P.G.—Not included. See Table.

TENTH-NORMAL VOLUMETRIC POTASSIUM SULPHOCYANATE SOLUTION.

This solution is also known under the name of Volhard's Solution, and is chiefly used for the indirect titration of the Silver salts, according to Volhard's method. It is mentioned under Tenth-normal Volumetric Silver Nitrate Solution. Ferric Ammonium Sulphate Solution is usually employed as an indicator.

B.P.—Not included. See Table.

U.S.P.—A solution containing 9·653 grammes of pure Potassium Sulphocyanate in 1000 c.c. of Water. It is prepared by dissolving 10 grammes of pure crystalline Potassium Sulphocyanate (which is required to be free from Antimony, Arsenic, Cadmium, Copper, Iron, Lead, Zinc and Sulphates) in 1000 c.c. of Water. It is standardised with Tenth-normal Volumetric Silver Nitrate Solution. A measured quantity of 10 c.c. of the latter solution, together with 3 c.c. of Nitric Acid (free from Nitrous Acid), being diluted with about 100 c.c. of Distilled Water. The Volumetric Sulphocyanate Solution is added from the burette until a perceptible reddish-brown tint is acquired. Ferric Ammonium Sulphate Solution is employed as an indicator. The number of c.c. is accurately noted and an ascertained volume of the remaining solution diluted in the ratio between the number of c.c. actually required to the number of c.c. which should have been required. After dilution a fresh determination should be made, using a measured quantity of 50 c.c. of Tenth-normal Volumetric Silver Nitrate Solution, 5 c.c. of Ferric Ammonium T.S., 5 c.c. of Nitric Acid and 200 c.c. of Water, and the solution should be so adjusted that exactly 50 c.c. of the Potassium Sulphocyanate Solution should be required to produce the above-mentioned tint. If necessary, a further adjustment should be made until the solutions strictly correspond.

P.G.—Not included. See Table.

ALKALINE CUPRIC TARTRATE SOLUTION.

Potassio-cupric Tartrate Solution, Alkaline Cupric Tartrate Solution, or Fehling's Solution, consists of two solutions. The first solution contains 69·28 grammes of crystallised Copper Sulphate and 1 c.c. of Sulphuric Acid in 1000 c.c. of Water, and is prepared by dissolving 34·64 grammes of crystallised Copper Sulphate in sufficient Water to effect solution, adding 0·5 c.c. of Sulphuric Acid and sufficient Distilled Water to produce 500 c.c. The second solution contains 352 grammes of Sodium Potassium Tartrate and 154 grammes of Sodium Hydroxide in 1000 c.c. of Distilled Water, and is prepared by dissolving 176 grammes of Sodium Potassium Tartrate and 77 grammes of Sodium Hydroxide in a sufficient quantity of Water to effect solution, and diluting with sufficient Distilled Water to produce 500 c.c. When required for use the solution of Copper Sulphate is mixed with an equal quantity of the alkaline Tartrate; the above solution is seldom employed volumetrically. Pavy's Solution, described

on p. 468, is more convenient, and is more generally employed in volumetric work.

B.P.—The *B.P.* solution is on the lines indicated above. It is not employed volumetrically in the official volume.

U.S.P.—The *U.S.P.* alkaline Cupric Tartrate Solution is employed volumetrically. It consists of two solutions:—1. The Copper Solution, which is prepared by dissolving 34·67 (more correctly 34·6663) grammes of carefully selected uneffloresced pure Cupric Sulphate, free from adhering moisture, in a sufficiency of Distilled Water, and diluting to measure 500 c.c. at 25° C. (77° F.). The solution is directed to be kept in small, well-stoppered bottles. 2. The Alkaline Tartrate Solution, which is prepared by dissolving 173 grammes of crystallised Potassium Sodium Tartrate together with 75 grammes of Potassium Hydroxide in a sufficiency of Water to measure exactly 500 c.c. at 25° C. (77° F.). This solution is directed to be kept in small bottles fitted with rubber stoppers. When required for use the solutions are mixed in equal volumes.

P.G.—A weighed quantity of 3·5 grammes of Copper Sulphate is dissolved in 30 c.c. of Water, and the solution mixed with a solution of 17·5 grammes of Sodium Potassium Tartrate in 30 c.c. of Water, the latter solution having been previously mixed with 40 grammes of Sodium Hydroxide Solution (15 p.c.).

TENTH-NORMAL VOLUMETRIC AMMONIUM RHODANATE SOLUTION.

This solution is employed by the *P.G.* instead of Tenth-normal Volumetric Potassium Sulphocyanate Solution for the determination of the excess of Volumetric Silver Solution in the indirect Silver titration. Almost the only instance in which it is used in this volume is in the determination of Volatile Oil of Mustard.

B.P., *U.S.P.* Not included. See Table.

P.G.—A solution containing 7·618 grammes of Ammonium Rhodanate in 1 litre. No method of preparation, standardisation, or preservation is indicated.

INDICATORS OF NEUTRALITY.

The following list shows at a glance the Solutions employed by the three Pharmacopœias as indicators in Volumetric Analysis.

B.P.	Cochineal Tincture.		Phenolphthalein T.S.
	Litmus.		Rosolic Acid T.S.
	Methyl Orange.		Starch T.S.
	Phenolphthalein.		Turmeric Tincture.
	Starch Mucilage.	*P.G.*	Hæmatoxylin.
	Turmeric Tincture.		Iodeosin Solution.
U.S.P.	Brazil Wood T.S.		Litmus paper.
	Cochineal T.S.		Phenolphthalein Solution.
	Hæmatoxylin T.S.		Rosolic Acid Solution.
	Iodeosin T.S.		Starch Solution.
	Litmus paper and T.S.		Turmeric paper.
	Methyl Orange T.S.		Turmeric Tincture.

BRAZIL WOOD SOLUTION.

Brazil Wood solution is coloured yellow by acids and crimson-red by alkalis. It is used chiefly as an indicator of neutrality in the titration of alkaloids.

B.P., *P.G.* Not included. See Table.

U.S.P.—A solution obtained by boiling 50 grammes of finely cut Brazil Wood for 30 minutes with 100 c.c. of Water, the evaporated Water being replaced from time to time. The mixture is allowed to cool, strained, 100 c.c. of the strained liquid are mixed with 25 c.c. of Alcohol (94·9 p.c.), the solution filtered. It is required that the solution be excluded from contact with ammoniacal vapours.