CCXXXVI. THE PREPARATION, STORAGE AND USE OF STANDARD CARBONATE-FREE SODIUM HYDROXIDE SOLUTIONS.

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WHEN adapting the urease aeration-titration method for very accurate determinations of blood-ureas [Kay and Sheehan, 1934] it became evident that the primary essential for accuracy was that the *N*/75 or *N*/100 NaOH used for titrations should be absolutely free from carbonate. Dilution of strong or saturated solutions of NaOH failed to give good enough solutions; the method described in this paper was therefore devised, and has given complete satisfaction throughout a long period. It appears to be a new application of a well-known simple chemical reaction, though Sutton [1904], to precipitate carbonates from caustic soda solutions, recommended the cautious addition of baryta.

Barium hydroxide is allowed to react with excess of carbonate-free sodium sulphate in aqueous solution: after settling, a solution of carbonate-free NaOH containing sodium sulphate is obtained.

The presence of Na_2SO_4 in the alkali does not interfere with titrations.

The possible significant impurities in reagents are chlorides and carbonates in the sodium sulphate, barium carbonate in the baryta, and CO_2 in the distilled water. The chloride plays no significant part in the reaction, as any barium chloride which it may form gives barium sulphate, so that all barium is precipitated. Carbonate is removed from the sodium sulphate by making the solution very faintly acid with H_2SO_4 and boiling vigorously before adding the baryta. CO_2 is removed from distilled water by boiling. The slight traces of barium carbonate suspended in the baryta solution might theoretically cause difficulty but do not in practice.

Preparation of concentrated alkali.

The method is carried out as follows:

A flat-bottomed litre flask (monax or other resistance glass) is fitted with a tight rubber stopper through which pass

(a) a short bent glass tube connected to two wash-bottles in series, each containing 40 % NaOH. These serve as CO_2 traps for air entering the flask;

(b) one limb of a long glass siphon preferably of resistance glass. This is a fairly tight fit in the stopper but can be forced up or down as required; in the preliminary stages it is pulled up so that it only projects a short distance below the stopper. The other limb of the siphon is sealed into a good glass tap, the delivery tube of which is about 5 cm. long, drawn out into a jet about 2 mm. bore, and protected from air by being enclosed in a small removable test-tube.

Details can be seen in Fig. 1.

800 ml. of distilled water and 300 g. of pure sodium sulphate crystals are placed in the open flask and boiled vigorously for 10–15 minutes. The solution is made faintly acid with dilute H_2SO_4 (usually 1–2 ml. N H_2SO_4 are ample) and boiling is continued for several minutes.

Fig. 1. CO_2 -free NaOH solutions. Preparation and storage apparatus.

Meanwhile in another flask a solution is made of 280 g. of pure barium hydroxide crystals in 200 ml. of distilled water, and boiled vigorously. There is usually a slight precipitate of barium carbonate.

The boiling baryta solution is added to the boiling sulphate solution. There is an immediate precipitation of barium sulphate, which causes a tendency to boil over. When all the baryta is added, boiling is continued for a few minutes to help granulation of the precipitate. The flask is then stoppered, thus connecting it to the CO_2 traps, removed immediately from the source of heat and allowed to settle and cool. The siphon tap must of course be closed and, to avoid fouling of the siphon with precipitate, the uptake limb should not yet enter the solution.

The barium sulphate settles rapidly and leaves a perfectly clear solution of carbonate-free NaOH, about 1.2–1.3 N and containing Na_2SO_4 . The solution is ready for standardisation and use as soon as clear and cold. The uptake limb of the siphon is then pushed down into the solution and the siphon started either by suction at the jet or by blowing gently through the CO_2 traps.

Prepared and stored in this way, carbonate-free NaOH keeps perfectly for 4–5 months. Solid carbonate should not be allowed to form round tap or jet (the tube enclosing the jet prevents this) and the jet is cleaned and dried externally before and after use. The solution in the tap and siphon is rejected when withdrawing solution for use.

Preparation of dilute alkali.

For the preparation of $N/100$ NaOH, the calculated amount of concentrated solution is drawn into a narrow measuring cylinder and added at once to the requisite amount of boiling distilled water in a flat-bottomed resistance glass flask, the water having been boiled vigorously for some time to expel CO_2 . The flask is then stoppered and removed from the source of heat, the stopper having a connection with a wash-bottle containing 40 % NaOH, through which air is admitted to the flask in cooling.

When the solution is cold, the flask is connected to a burette fitted up as in Fig. 2. The flask is supported on a movable shelf. The solution is then standardised for use.

Attention may be called to the following points:

(a) The burette is filled from the top; this eliminates inaccuracies through faulty 3-way taps, and grease is not carried up the burette from the tap. The tap through which the burette is filled hardly ever needs greasing. The jet which discharges the solution into the burette is bent slightly to direct the stream against the burette side in order to avoid bubble formation.

(b) The small amount of air making contact with the solution is never greater than the volume of the solution used. It passes through two wash-bottles containing 40 % NaOH solution, followed by one containing distilled water, when entering to replace solution run out of the burette; when the burette is filled again the air from it is displaced into the reservoir. If all the joints are satisfactorily air-tight the burette cannot be emptied completely owing to the head of fluid in the CO₂ traps. This is not important as only the upper half of the burette need be used for titrations.

(c) The standard solution never comes into contact with rubber.

(d) The glass of ordinary burettes has a deleterious effect on *N*/100 NaOH, the strength of which is changed by as much as 0.1–0.2 % on standing for 1–2 hours in the burette. Solutions left in the burette therefore must be rejected and thoroughly changed before use.

On the other hand, under the conditions described, dilute alkali can be stored in monax vessels for at least 10 days without change of strength or loss of sharpness of end-point. The critical colour change of methyl red in 40–50 ml. of fluid is produced by less than 0.01 ml. *N*/75 NaOH [see Kay and Sheehan, 1934].

(e) When placing a new dilute alkali solution in position above the burette, the ascending limb of the siphon is wiped dry with clean cotton-wool and a little solution run out of the siphon to break contact between old and new solutions.

Fig. 2. CO₂-free NaOH solutions. Ordinary burette fitted for use with diluted standard solutions. The flask serves as dilution flask and as reservoir for the diluted solution.

SUMMARY.

1. Very satisfactory carbonate-free NaOH solutions can be prepared by the interaction of barium hydroxide and pure sodium sulphate.

2. A description is given of the technique of preparing and storing such solutions and of their dilution and use in a burette.

REFERENCES.

- Kay and Sheehan (1934). *Biochem. J.* **28**, 1784.
 Sutton (1904). *Systematic handbook of volumetric analysis*, 9th edition, p. 48.