

## Preparation of Very Dilute Standard Base by Ion Exchange

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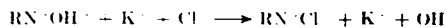
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IN DEVELOPING a method for titration of microgram quantities of fatty acids from fractions of biopsy specimens of liver, a major problem was the difficulty of obtaining a constant normality of standard alkali of about 0.001 *N*. Solutions were carefully prepared with boiled, redistilled water and saturated caustic from which the carbonate had been allowed to precipitate. On storage of such solutions in the usual manner in bottles well coated with paraffin, and without contact with glass or rubber, the strength of the solutions was found to differ from day to day and even during the course of the day from storage, handling, or other cause.

Schubert (1), describing analytical applications of ion exchange separations, quotes the suggestion of a simple means for preparing standard acid by stoichiometric release of hydrogen ions from organic cation exchange resins. The preparation and storage of very dilute mineral acid is certainly less critical than is that of very dilute alkali, but the suggestion indicated the possibility of a similar preparation of alkali by means of anion exchanging resins to obtain stoichiometric release of hydroxyl ions.

Since this paper was submitted, Steinbach and Freiser (2) have described a similar technique for preparation of batches of 0.1 *N* sodium hydroxide with Amberlite IRA-400. It is clear that the technique is of general application but with special advantage in titration of microgram quantities.

This idea was satisfactorily developed by means of a simple apparatus in which a strong base anion exchange resin was reacted with 0.0010 *N* potassium chloride solution to provide the corresponding standard potassium hydroxide solution according to the reaction

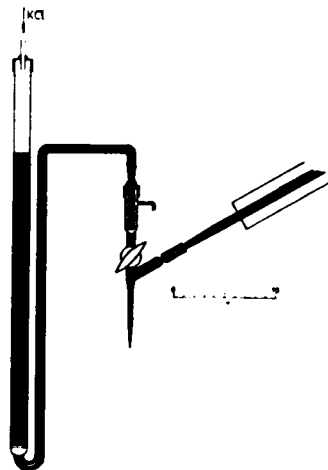


The reaction apparently proceeds without attention for months and shows a remarkable constancy of normality of the solution delivered.

### EXPERIMENTAL

**Apparatus.** The apparatus consisted of a glass tube, 40 cm. in length and 16 mm. in outside diameter, attached at the lower end to a 1-mm. bore heavy-wall capillary tube bent as shown in the diagram. A sintered-glass filter sealed in the larger tube served to retain the resin with which the tube was filled. The constricted end of the capillary was led to the bottom of a reservoir

vessel with an outlet about 1 cm. below the top. Solution flowing from this outlet was led to a drain by a rubber catheter tube. To the lower end of the vessel was attached a capillary stopcock, below which was an angular side connection and delivery tip as shown. The side connection was attached by means of a gum rubber tube to the capillary tip of a capillary buret (2) which could be filled after opening the stopcock. When the stopcock was closed, the incoming standard solution was forced out of the outlet and led to the drain.



Above the column was placed a separatory funnel containing 0.0010 *N* potassium chloride solution which was led through a length of Tygon tubing to a tip in the top of the column. Notches were filed in the stopcock plug to allow fine control of the flow rate which could also be altered by the height of the funnel.

**Procedure.** The column was charged with the strong base anion exchange resin, Amberlite XE-67. The resin has been previously saturated with a 4% sodium hydroxide solution and washed with redistilled water until a neutral reaction was obtained. The separatory funnel filled with 0.0010 *N* potassium chloride solution was connected and about 200 ml. of solution allowed to flow rapidly through the column to displace water, after which the rate was adjusted to about 2 ml. per hour. The

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excess alkali generated was allowed to waste to the drain because interference with the rate of flow appeared to alter the normality slightly. The buret was filled after opening the stopcock, during which the delivery tube could be flushed by raising the catheter tube drain. On closing the stopcock and adjusting the solution meniscus in the buret, the titration could be performed.

After the system reached equilibrium the only attention required was to replenish the stock of 0.0010 *N* potassium chloride in the upper separatory funnel from time to time.

#### DISCUSSION OF RESULTS

Numerous titrations were performed against a known standard acid solution and against potassium biphthalate and benzoic acids as primary standards, with both color indicator and potentiometric end points. A closed-chamber titration vessel similar to that previously described (3) was employed. Stirring was performed with a rotating magnetic stirrer. Carbon dioxide that remained in the chamber on closing was absorbed by means of a little saturated sodium hydroxide solution kept in the bottom of the chamber.

Over a period of 45 days, the alkali resulting from the ion exchange process was titrated with standard acid using a mixture of bromoresol green and methyl red as indicator. A total of 56 titrations during this period gave an average titer of 43.34 microliters of acid with a maximum deviation of  $\pm 0.50$  microliter and a standard deviation of  $\pm 0.171$  microliter. A small positive deviation of normality of the alkali from that of the potassium chloride solution was noted. The reason for this is not clear, and may be related to the difficulties of employing primary standards in minute quantities. Benzoic acid, titrated in alcoholic medium, yielded the most consistent values for absolute standardization, with a value for the alkali of 0.00105 *N*.

It had been noted by Sheldon Rosenberg of this laboratory in

connection with other investigations that as hydroxyl ion was replaced by chloride ion with this resin, the color of the resin was altered noticeably. The color change apparently serves as a reliable index of the degree of exhaustion of the material. The rate of change noted in these experiments indicates that the column described will function with this concentration of solution for a period of at least 8 to 10 months. Using the manufacturer's figures that 1 ml. of wet resin will exchange 1 milliequivalent of chloride for hydroxide ion, it follows that the amount of material used in this experiment should last for at least 1 year at the rate of flow employed. The ion exchanger XE-67 is stated to operate best with dilute solutions—e.g., not over 0.01 *N*. It appears probable that within this limitation, any normality of alkali solution may be readily obtained without interference of carbonate or other ions and over a period long enough to be convenient as a general technique.

#### ACKNOWLEDGMENT

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