

# Preparation of Standard Sodium Hydroxide Solutions by Use of a Strong Anion Exchange Resin

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DAVIES and Nancollas (1) have shown that it is possible to prepare sodium hydroxide solutions essentially free from carbonate ion by passing sodium hydroxide through an anion exchange column filled with a strongly basic exchange resin such as Amberlite IRA-400. By passing a dilute solution of sodium chloride through the column, it should also be possible to prepare a standardized, carbonate-free solution of sodium hydroxide, providing a 100% conversion of chloride into hydroxyl was effected.

To test the response of a column of Amberlite IRA-400 to the passage of sodium chloride, it was decided to pass sodium chloride solution of known normality through the column and collect aliquot fractions of effluent until the hydroxyl form of the resin was exhausted. A plot of the normality of eluted sodium hydroxide against eluant volume collected should indicate a range over which the sodium hydroxide would have a useful concentration. The chloride ion concentration present in each fraction was determined in order to estimate the exchange efficiency of the column. As Davies and Nancollas found that the percentage of carbonate in their sodium hydroxide was directly proportional to the amount of resin in the carbonate form, it was anticipated that the chloride in the eluant would increase as the resin became converted to the chloride form—that is, the normality of sodium hydroxide was expected to reach a maximum value as soon as the dilution effects of the water originally in the column were overcome. Later, as the chloride concentration increased, the sodium hydroxide concentration should fall off. When the column was exhausted, the normality of the chloride should rise to the normality of the influent sodium chloride, and the hydroxide concentration should drop to zero.

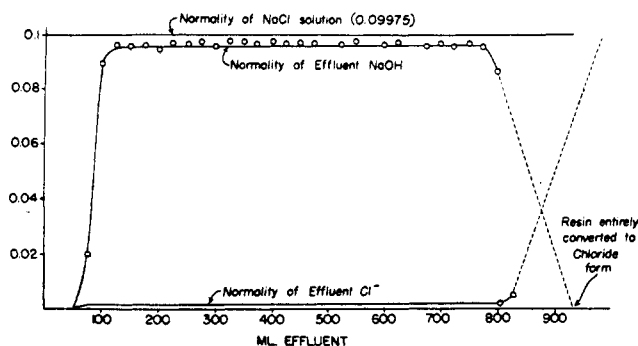


Figure 1. Chloride-Hydroxide Exchange on Amberlite IRA-400

From the information given by such a curve it should be possible to determine how much sodium hydroxide of relatively low chloride content would be obtained from a given amount of fully regenerated resin. A more demanding test of the resin would be to pass through a weighed amount of sodium chloride and determine whether or not the effluent, collected in a volumetric flask, had the expected normality.

The experiments described were conducted to provide the required information.

## MATERIALS

Reagent-grade Amberlite IRA-400 purchased from the Fisher Scientific Co. was employed. Mallinckrodt's reagent grade sodium chloride, dried at 120°C. for 1 hour, was used to prepare

the standard sodium chloride solutions. Mallinckrodt's reagent grade potassium acid phthalate, dried at 110°C. for 1 hour, was used to prepare standard acid phthalate solutions against which the sodium hydroxide was titrated.

## COLUMN PREPARATION

Forty grams of air-dried Amberlite IRA-400 resin in a Jones reductor (18 mm.  $\times$  60 cm.) were washed with dilute hydrochloric acid to remove any carbonate ions. The resin bed was loosened and freed from air bubbles by inverting and shaking the stoppered column. When the resin settled the column was again washed and then regenerated with 2 liters of 1 *N* sodium hydroxide made from 18 *N* sodium hydroxide, so as to be carbonate-free. The resin bed was then washed with about 2 liters of freshly boiled distilled water or until the effluent gave no test for either hydroxyl or chloride ions.

## EXCHANGE STUDIES

A solution of 0.09975 *N* sodium chloride by weight was prepared and passed through the column at a rate of 8 ml. per minute. The effluent was collected in 25-ml. volumetric flasks until 33 samples had been taken. The samples were immediately transferred to 250-ml. bottles and tightly stoppered. At the end of the run the samples were titrated with standard potassium acid phthalate and phenolphthalein indicator. The same samples were also titrated with standard silver nitrate and chromate indicator to obtain the chloride concentration. The results are plotted in Figure 1.

After regeneration of the column, 1.469 grams of sodium chloride were dissolved in 50 ml. of water and transferred to the column. The beaker was washed several times with small amounts of distilled water and the washings were added to the column. About 150 ml. of water were used to wash the column, and the effluent was collected at a rate of 8 ml. per minute until a 250-ml. volumetric flask was filled. The flask was protected from the atmospheric carbon dioxide by an Ascarite drying tube. Fifty-millimeter aliquots of the eluant were titrated with acid phthalate and then with silver nitrate. The normality of the sodium hydroxide was 0.09933. Normality of the chloride was 0.0019. Theoretical normality of the sodium hydroxide on the basis of sodium chloride was 0.1005.

This procedure was repeated using a lower flow rate in an attempt to increase the exchange efficiency. In the next runs, the effluent was collected at a rate of approximately 4 ml. per minute in a 500-ml. volumetric flask. Wash water was added continuously to the column until the flask filled. The following results were obtained:

NaCl, Grams	Normality of NaOH	Theor.	Deviation, Parts per Thousand
2.9199	0.1001	0.0999	+2
2.9221	0.0998	0.1000	-2
2.9244	0.1006	0.1001	+5

## RECOMMENDED PROCEDURE FOR PREPARATION OF STANDARD 0.1 *N* SODIUM HYDROXIDE

A solution of 2.922 grams of sodium chloride (reagent grade) in 50 to 100 ml. of freshly boiled distilled water is passed through the exchange column prepared in the manner described above at a rate of 4 ml. per minute. This is followed by freshly boiled distilled water. The eluate is collected in a 500-ml. volumetric flask by means of an adapter permitting the use of a soda-lime tube to prevent contamination by atmospheric carbon dioxide. The flow rate may be safely increased to about 8 ml. per minute after 250 ml. have collected. Toward the end the flow rate is once again decreased to permit careful adjustment to volume. Should larger quantities of 0.1 *N* sodium hydroxide be desired, larger columns than that described here would be required.

## DISCUSSION OF RESULTS

As shown in Figure 1, both the hydroxyl and the chloride concentrations rose to constant values as soon as the residual water

(ca. 100 ml.) had emerged, and with small deviations remained at these values until the column was nearly exhausted.

The total amount of sodium hydroxide collected before the normality of the effluent began its marked decrease was 70 milliequivalents. Forty grams of resin whose capacity when fully regenerated was 2.3 me. per gram were used in the column. Assuming that the resin was initially 100% regenerated, the maximum amount of sodium hydroxide obtainable was about 90 me. Therefore 78% of the theoretically obtainable sodium hydroxide was collected in a relatively chloride-free state. The normality of the effluent sodium hydroxide was 0.097 and the normality of the chloride solution was 0.0019. This represents a ratio of 0.02 equivalent of chloride per equivalent of hydroxyl or an exchange efficiency of 98%. The exchange efficiency was increased by reducing the rate of flow. When weighed amounts of sodium chloride were passed through the column at the lower flow rate and collected in 500-ml. volumetric flasks, the normality of the sodium hydroxide agreed with the theoretical normality within the experimental error.

If proper precautions are exercised, the sodium hydroxide

solutions prepared in this manner are almost completely devoid of carbonate. To assure this the column should be washed occasionally with dilute hydrochloric acid before regeneration to prevent an accumulation of carbonate in the resin. The distilled water used should be freshly boiled. For most purposes the limited amount of chloride present should not be a detriment, since its effect on the ionic strength is negligible. If solutions of sodium hydroxide less than 0.1 *N* are desired, the amount of chloride will also be correspondingly less.

Sodium salts other than the chloride might also be used in the preparation of sodium hydroxide; an anion such as sulfate which has a high ionic potential might be affixed to the resin more easily and therefore appear in the effluent in lower concentrations.

#### LITERATURE CITED

- (1) Davies and Nancollas, *Nature*, **165**, 237 (1950).

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## Rapid Magnesium Determination in Cement Manufacture in Sweden

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IN THE Swedish cement industry, a method of analysis is used which has proved to be dependably accurate for the control of the manufacturing process.

One of the manufacturers concentrates limestone by flotation, which increases the calcium carbonate content and reduces the magnesium silicate content. To obtain fully satisfactory control of the concentration process, the author has developed a rapid colorimetric method which reveals both the carbonate and silicate compounds of magnesium.

For this purpose a high-frequency generator was obtained from the Reeve Electronic Co., 609 West Lake St., Chicago, Ill. The output of the generator is 750 watts; the induction coil, in which a crucible of platinum was heated, has only a few turns. The voltage drop across the coil is therefore so low that it can be touched safely while in operation. The currents induced in the bottom of the crucible produce a temperature of about 1300° C., which is generally high enough to render the raw mix and limestone soluble in hydrochloric acid. The material is then only sintered, so that for the determination of magnesium the sintered cake is transferred to a beaker for further treatment. If the limestone is low in calcium the material will melt; to prevent this (as it takes considerable time to dissolve the melted substance) calcium carbonate is added.

#### MAGNESIUM DETERMINATION WITH BRILLIANT YELLOW

The reagent brilliant yellow (2), produced by Coleman & Bell, Norwood, Ohio, has been used in America for determination of magnesium in water. The addition of aluminum prevents the presence of this element from deranging the analysis; neither is the method affected by the presence of iron in small quantities. With the use of organic reagents for magnesium such as hematoxylin, curcumin, Titan yellow, hydroquinone, and the like, it has usually been the great sensitivity of the reagent to sesquioxides which has prevented the method from being used in practice. As it was thought that this disadvantage could be eliminated, and the method was believed to be rapid, there was reason for further investigation of this reagent for use in the concentration plant, where a rapid test for magnesium was urgently needed.

A Lumetron Model 402E colorimeter was available. The instrument was equipped with a mercury vapor lamp, monochromatic filters, and circular cuvettes.

Earlier work with colorimetric methods has shown that no reproducible values can be obtained unless the indicator and sta-

bilizer are introduced below a pH of 5 or 6, and then the pH is rapidly raised by adding sodium hydroxide, and the colloidal magnesium hydroxide which is then instantly formed is absorbed by the indicator (1). The stabilizer prevents precipitation. Examination of a number of materials revealed that a cellulose product from Mo- and Domsjö in Sweden was an excellent stabilizer with very good keeping properties. This product is ethyloxyethylcellulose, sold as Tylose SL/100.

Preliminary tests to find the proper wave length and sensitivity showed that 550 mμ was best. The series of experiments which followed revealed clearly the need of a stabilizer. Without the stabilizer, the samples precipitated immediately, regardless of whether magnesium was present in large or in small quantities. Here it proved, however, that the zone of measurement extends up to about 0.5 mg. of magnesium oxide; therefore the change in transmittancy would be too small in relation to the variation in magnesium content to allow sufficient accuracy in the analysis.

Test runs with variations in the calcium oxide and aluminum oxide content showed that both these compounds strengthen the dye, giving lower transmittance values. When 8 mg. of calcium oxide and 0.1 mg. of aluminum oxide are added per 100 ml. of the solution to be analyzed, the method is rendered insensitive to variations in these quantities.

**Variation of Tylose and Stabilization with Time.** Table I shows that the color intensity reached its maximum after 5 minutes and that 2 ml. of 1% Tylose make the method insensitive to large errors in titration.

**Variation of Sodium Hydroxide.** Five milliliters of 20% sodium hydroxide are used hereafter to make the method insensitive

Table I. Variation of Tylose and Variation of Stabilization with Time

Additions.	8 mg. of CaO 0.1 mg. of Al <sub>2</sub> O <sub>3</sub> 2 ml. of 0.05% dye 5 ml. of 20% NaOH	diluted to 80 ml. diluted to 100 ml.				
MgO, Mg.	1% Tylose, Ml.	Transmittancy				Remarks
		5 min.	10 min.	15 min.	30 min.	
0.000	1	100	100.9	100.9	100.9	Precipitation
0.500	0.1					
0.500	0.5	57.4	57.7	58.0	57.1	
0.500	1.0	44.6	45.0	45.4	45.4	
0.500	2.0	43.0	44.4	43.2	41.9	
0.500	5.0	44.0	44.0	43.4	43.4	