The Removal of Chlorides and Sulfates by Synthetic Resins.

Lucille Grace Boudreaux
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THE REMOVAL OF CHLORIDES AND SULFATES
BY SYNTHETIC RESINS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

By

Lucille Grace Boudreaux
B.S., Southwestern Louisiana Institute, 1932
M.S., Louisiana State University, 1936
June, 1941
ACKNOWLEDGEMENT

The author wishes to express sincere appreciation for the assistance and advice rendered by Dr. W. R. Edwards and Dr. W. C. Schwartz. She is also grateful to all other persons who have aided her in this undertaking.
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Led by the discovery in 1935 by B. A. Adams and E. L. Holmes, that aldehyde-amine resins would remove anions from water solutions of the corresponding acids or salts, an investigation was undertaken to determine the importance of a number of factors upon the effectiveness of anion removal by a suitable resin. A number of resins were prepared, preliminary tests were run, and it was determined that the resin prepared from m-phenylenediamine, formaldehyde, and hydrochloric acid possessed the most desirable properties. It was, therefore, employed in all subsequent work.

The effects of a number of factors upon the removal of chlorides and sulfates by this resin were determined, and preliminary work was also done on phosphate removal. The solutions tested contained the following substances: (1) hydrochloric acid, (2) sodium chloride, (3) hydrochloric acid and sodium chloride, (4) sodium chloride and sodium hydroxide, (5) sulfuric acid, and (6) phosphoric acid.

To obtain uniform results a rotary shaker accommodating six bottles was immersed in a thermostat. Weighed samples of resin were placed in 500 ml. narrow-mouth bottles. The required amounts of solutions were added, and the bottles sealed with "no air" rubber stoppers and shaken for a definite length of time. The solutions were analyzed before and after extraction. All samples were neutralized to the phenolphthalein end point; the chloride ion was determined volumetrically by the Mohr method, and the sulfate content was
obtained by titration with standard barium chloride solution using disodium tetrahydroxyquinone as an internal indicator.

It was found that the resin and dilute hydrochloric acid (100 p.p.m. HCl expressed as NaCl) reached equilibrium at the end of ten hours; so ten hours was selected as contact time in the remainder of the determinations.

Resin which was prepared and then dried at 92°C. before being rinsed seemed to be slightly superior to resin that was dried at 31°C. or 130°C. Resin rinsed with sodium carbonate and water before drying at 92°C. proved to be more effective in chloride removal but was slightly soluble in dilute acid solution and could not be used. Changing the rate of rotation of the samples (from 17 r.p.m. to 32 r.p.m.) did not influence chloride removal, and the effect of temperature on the samples was also negligible within the range investigated (30°C. to 45°C.).

Reducing the size of the resin particles from that collected between 20-40 mesh sieves to that between 60-100 and 100 to 200 mesh sieves, increased the effectiveness of the resin in removing chlorides, and a similar increase in efficiency was noted when the initial concentration of hydrochloric acid was increased.

A comparison of the amount of hydrogen ions removed, as determined by acidimetric titration, and the quantity of chloride ions removed, as obtained by direct chloride determination, revealed that the entire molecule of hydro-
chloric acid was being removed instead of anion exchange taking place. Keeping the total chloride content constant but increasing the pH of the solution caused a decrease in chloride removal.

More efficient chloride removal was obtained by using smaller volumes of solution with the same weight of resin, provided the weight of resin used was below a certain value. Used resin which was rinsed again was less effective in chloride removal than the fresh resin.

Excellent agreement was obtained in chloride removal when resin of the same batch and the same rinse was used, good agreement was obtained with resin of the same batch but of different rinses, while results that were less consistent were obtained when resin from different batches and different rinses was used. Resin which was rinsed and allowed to stand six months was less efficient than resin which was used a short time after being rinsed.

The 2-phenylenediamine resin prepared was more effective in chloride removal than De Mineralite, a commercial resin. The resin was more efficient in removal of sulfates than in removal of chlorides; and corresponding to the results obtained with hydrochloric acid, the entire molecule of sulfuric acid was recovered and the effectiveness of sulfate removal increased with increasing initial sulfuric acid concentration.
Preliminary work on phosphate removal indicated that the resin was not as effective in phosphate removal as in sulfate or chloride removal.

A study of the results obtained led to the conclusion that the mechanism involved in the removal of chlorides and sulfates by the m-phenylenediamine resin consisted of two factors, salt formation between the acid and the amino groups in the resin and the adsorption, with the first factor playing a much more dominant role.
INTRODUCTION
It has been known for some time that siliceous zeolites possess the property of removing cations from solutions and that these substances can be regenerated by sodium chloride. Carbonaceous materials, such as lignite or brown coal, which can be regenerated by sulfuric acid or sodium chloride are also used in cation removal.

The use of synthetic organic resins in the removal of anions and cations from water solutions has been a comparatively recent development which was instigated by the discovery by Adams and Holmes (5) that resins prepared by the polymerization of phenolic compounds with formaldehyde possessed the property of adsorbing cations from solution, while the polymerization of amines with formaldehyde yielded resins that were capable of removing anions from solutions. However, synthetic organic resins have not yet been employed on full commercial scale in the United States, although a number of test units have been operated.

At the present time, the principal interest in anion and cation removal by the above materials lies in the field of water treatment, especially in the production of boiler feedwater for steam power stations. However, it is very probable that further applications will be found in the chemical industries.

The practical application of the siliceous zeolites has been ahead of theoretical studies on the use of these materials; and this work is initiated in the hope that the
same conditions will not prevail with the newly developed synthetic organic resins.

In the present work were undertaken initial steps in an investigation of the effectiveness of a suitable resin on water samples which contained a variety of dissolved materials. One aim was to determine the effects produced by changing a number of variable factors, in order to show which of these factors were negligible and which were material. With the factors which seemed to play a material part, a second aim was to obtain some conception of the most favorable conditions for efficient removal of dissolved substances. A third aim was to obtain some knowledge of the potential capacity, both qualitative and quantitative, of the resin, and as a final aim it was desired to obtain some information which would attempt to show the actual nature of the removal process.
REVIEW OF LITERATURE
We have been indebted to Adams and Holmes (5) for the discovery that synthetic resins possess adsorptive (or absorptive) properties. They first reported, in 1935, that formaldehyde condensation products of phenolic compounds (such as catechol, resorcinol, quinol, phloroglucinol, and catechol tannins) removed cations from solutions, while formaldehyde condensation products of amines (such as aniline and m-phenylenediamine) yielded resins which removed anions from solution.

Resins prepared by the condensation of formaldehyde and monophenolic or diphenolic compounds were soluble in alkali and could not be utilized, and subsequent work showed that only the polyhydric phenolic resins possessed appreciable adsorptive properties.

The following procedure was followed by Adams and Holmes (5) in preparing the phenolic resins. The polyhydric phenol (1 part), water (10 parts), and formalin (2 parts) were heated to the boiling point, and concentrated hydrochloric acid (1 part) was added to the resulting solution. The resin precipitated within a minute or two and was filtered, washed with alcohol and ether, and dried in a vacuum. Drying the product at 25° or 100°, without washing, did not produce any change in properties. With phenols that were not easily oxidized, alkalis (such as sodium hydroxide) or ammonia could be used as catalyst; and with ammonia,
condensation could be carried out at room temperature. Solutions of different salts and alkalis were allowed to flow through beds of resin, and Adams and Holmes noted that the cations alone were removed. The anions seemed to remain in solution, indicating that cation exchange took place. Adsorption was also more complete in alkaline solution, and gaseous ammonia could be adsorbed as the result of passage through a bed of resorcinol resin. Selective adsorption was observed by catechol, resorcinol, quinol, and pyrogallol resins; and the degree of adsorption of the cations by a particular resin was also found to be inversely proportional to the valence of the cation. The resins could be regenerated by treatment with 5% hydrochloric acid, 5% nitric acid, or 5% sulfuric acid and then rinsing with distilled water until free from acid.

Success with the phenol resins led Adams and Holmes to investigate the possibility of anion removal by use of aldehydic condensation products of aromatic bases (5). They found that o- and p-phenylenediamine and 2,4-toluenediamine, when treated with formaldehyde, yielded resins which were soluble in alcohol and dilute acid solution; but the corresponding resin prepared from aniline was only partly soluble, and that obtained from m-phenylenediamine was insoluble in alcohol and dilute acid solution. The m-phenylenediamine was shown to be superior to the aniline resin, in removal of anions as well as in desirable physical
properties, such as hardness and insolubility in the solutions used. Any alkali (including carbonates and bicarbonates) was found to be effective in regenerating the resin.

The following (4) illustrates the procedure followed in preparing a typical resin:

93 grams of aniline were dissolved in a little more than an equivalent amount of hydrochloric acid (in 1000 ml. of water), and 1.5 molecular proportions of 40% formaldehyde solution were added. The mixture was stirred and allowed to remain at room temperature until a gel was formed. It was then cut in pieces and dried around 100°C. After grinding the resin and rinsing it with dilute alkali and distilled water, it was read for use. If the gel was dried above 100°C, the resin obtained lost part of its capacity of adsorption of acid.

Adams and Holmes (4) passed acid solutions (.0033 M) through 10 grams of each of several resins, which had been treated with ammonia and washed free of excess base. The volumes of solutions (in ml.) from which the acid was completely removed were given as follows:

<table>
<thead>
<tr>
<th>Resin</th>
<th>HCl</th>
<th>HNO₃</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>1100</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td>m-Toluidine</td>
<td>2500</td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>m-Xyldidine</td>
<td>1800</td>
<td>1800</td>
<td>2300</td>
</tr>
<tr>
<td>m-Phenylenediamine</td>
<td>2600</td>
<td>1800</td>
<td>2800</td>
</tr>
</tbody>
</table>
Led by the original work of Adams and Holmes, literature on the preparation and use of resins for cation removal expanded rapidly, but a considerable portion of literature available has been limited to patent issues (1, 6, 26-29, 31-35, 38, 40, 41, 48). However, general articles by Akeroyd and Broughton (8), Austerweil (5), Surrall (19), and Griesbach (23) have appeared.

As far as anion removal by synthetic resins was concerned, it was also true that most of the presently available literature has been limited to patent issues (2, 3, 4, 7, 12, 13, 20, 21, 28, 36, 37, 39, 42, 43, 44). The paper of Adams and Holmes was followed by studies of Austerweil and Fiedler (11), Bird, Kirkpatrick, and Melof (17), Austerweil (10), Bird (16), Broughton and Lee (18), Bhatnagar, S. S., Kapur, A. L., and Bhatnagar, A. S. (14, 15), Griesbach (24), Richter (45, 46), and Guodey (22).

Akeroyd and Broughton (8) determined the rates of adsorption of calcium hydroxide by some phenol-formaldehyde resins and obtained results which seemed to indicate that removal of cations from solutions could be explained on the basis of chemical reaction rather than as a pure adsorption phenomenon, since the adsorption maxima approximated those calculated by assuming that on polymerization no linkage occurred through the phenolic hydroxyl groups. The following mode of formation of phenol-formaldehyde resins was suggested:
The resins used by these investigators were prepared as follows:

Two parts (by weight) of phenol, 20 parts of water, and 4 parts of formalin (40%) were heated to boiling, and 1 part of concentrated hydrochloric acid in two parts of water was added. The resin which separated was filtered and washed with hot water and calcium hydroxide solution. The resin was regenerated by treatment with 5% hydrochloric acid and washed with water, alcohol, and ether. It was then dried at 100°C., crushed, and graded through 48-mesh on to 200-mesh. A weighed sample of resin was placed in a bottle with a known volume of standard solution; and after agitation on a rotary shaker, the solution was filtered and analyzed. Adsorption was found to be relatively slow. It was almost complete after about seven days, but it probably proceeded very slowly over a period of months. Typical adsorption isotherms were obtained for short periods of agitation, but for long periods a curve which seemed to indicate chemical
combination was observed. Simple phenolic resins did not seem to adsorb cations from neutral solutions. An alkaline medium was necessary.

Burrell (19) reported results of an investigation conducted on the development of synthetic organic base-exchange materials which showed advantages over the phenol-aldehyde type. These materials were prepared by treating water-soluble wood extracts (particularly those of the tannin type) with concentrated acids—such as sulfuric acid. These substances exchanged sodium or hydrogen ions for calcium or magnesium.

When the tannins were treated with concentrated sulfuric acid, dehydration, oxidation, sulfonation and polymerization probably all took place with the result that a large molecule which possessed sulfonic and hydroxyl groups was formed. These functional groups could then react with the cations involved. When oxidizing agents such as nitric acid and chromium trioxide were substituted for sulfuric acid, most probably the hydroxyl groups were oxidized and materials of zero softening capacity were obtained.

Broughton and Lee (18) obtained low values for adsorption of $\text{H}_2\text{SO}_4$ and $\text{HCl}$ by aniline-formaldehyde and m-phenylenediamine-formaldehyde resins. According to their results, condensation of amine and aldehyde probably occurred through the $\text{NH}_2$ groups as well as through the
nucleus. The following would illustrate the types of linkages to be expected:

\[ \text{H}_2\text{N} - R - \text{CH}_2 - (\text{R}'(\text{NH}_2)\text{CH}_2)_n - R' - \text{NH}_2 \]

\[ \text{NH} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{NH} \quad \text{CH}_2 \quad \text{NH} \quad \text{CH}_2 \quad \text{CH}_2 \]

The method which they used in preparing the resin was found to affect the properties of the resin. The amine was dissolved in dilute hydrochloric acid, and the necessary quantity of formalin was added. The gel was broken up and allowed to stand overnight in normal \( \text{NH}_4\text{OH} \). The mixture was then washed free of \( \text{NH}_4\text{OH} \) and dried at 100°C or some other temperature. The resin was then treated with \( \text{NH}_4\text{OH} \) as before, ground, and graded to pass through 35- on to 100-mesh screen.

They prepared some resins by using a mixture of aniline and acetonilide, in order to protect the amine group during resinification; but these resins were inferior to the simple aniline resin. Small samples of resin (0.2 g.) were weighed out in bottles, and known volumes of standard acid were added. The mixtures were agitated on a rotary shaker at room temperature, and the solutions were filtered and analyzed.

The rate of adsorption of anions by the amine resins was greater than the rate of adsorption of cations by the phenol resins, according to the results obtained by Broughton and Lee. They found that adsorption was fairly complete.
within 24 hours with the amine resins, while about seven days were required with the phenol resins. The data that they obtained, also seemed to indicate slightly greater adsorption of hydrochloric acid than sulfuric acid by the aniline resin but greater adsorption of sulfuric acid than hydrochloric acid by the m-phenylenediamine resin. The aniline resin removed 0.40 millimole of HCl per gram of resin and 0.32 millimole of H₂SO₄ per gram of resin, while the m-phenylenediamine resin removed 1.50 millimoles of HCl per gram of resin and 1.55 millimoles of H₂SO₄ per gram of resin.

Drying at low temperatures and using low formaldehyde-amine ratios seemed to discourage condensation through the amine group and, therefore, led to resins of greater adsorptive power. On heating the dry resin a darkening in color resulted along with decreased adsorptive power. This indicated further polymerization. Drying the resin with acid did not seem to have very much effect upon its adsorptive capacity. This was contrary to the results reported by Adams and Holmes (5).

Austerweil and Fiedler (11) described a method of purifying water by passing it first through an exchanger of hydrogen cations (such as lignite treated with H₂SO₄) and then through an insoluble organic base (such as a complex quinonimine). Bird, Kirkpatrick, and Welof suggested a similar process (17).
Bhatnagar, Kapur, and Sarup (14) determined the adsorption of potassium salts of various anions by \( n \)-phenylenediamine-formaldehyde resin. The order of decreasing solubility of some of the salts investigated was 

\[
KCl > KBr > KI; \quad KCIO_3 > KBrO_3 > KIO_3 > KCrE; \quad K_2Cr_2O_7
\]

\( K_3Fe(CN)_6 \) > \( K_2CrO_4 \) > \( K_4Fe(CN)_6 \). In general, adsorption varied inversely with the solubility of the salt, but there were many exceptions.

Richter (46) claimed that resinous ion exchangers were more economical than the old type permutite exchangers.

Griessbach (24) and others (16, 22) have given us a resume of purification of water by synthetic organic resins.
EXPERIMENTAL
In this work the amine-aldehyde resins listed below were prepared by the following procedure: The amine was dissolved in water, the necessary amount of aldehyde was added, and finally hydrochloric acid or ammonium hydroxide solution was added to the solution. The reagents employed were used in the following proportions: 1 mole of the amine (dissolved in 1000 ml. of water) to 2 moles of catalyst to 3 moles of formaldehyde. The resulting gel was cut into small pieces, dried around 100°C., rinsed with sodium hydroxide and then distilled water, and tested for removal of hydrochloric acid.

A. aniline, formaldehyde, hydrochloric acid
B. m-toluidine, formaldehyde, hydrochloric acid
C. m-phenylenediamine, formaldehyde, hydrochloric acid
D. m-phenylenediamine, furfural, hydrochloric acid
E. m-phenylenediamine, furfuryl alcohol, hydrochloric acid
F. m-phenylenediamine, furfural, ammonium hydroxide
G. furfuryl alcohol, hydrochloric acid
H. urea, furfural, hydrochloric acid.

Resins F and G possessed practically no power of removing chlorides from dilute acid solution, and resins B and D were comparatively ineffective. Resins A, D, E, and H showed some solubility in water or acid solution and could
not be utilized, although some of them (particularly E) showed considerable removal properties. Resin C possessed good removal properties, was not soluble in dilute acid, and was comparatively free of any tendency to crumble. It was, therefore, chosen as most desirable for our purposes. All of the resins prepared from furfural were black and crumbly and could not be utilized. Resin E, which was prepared from furfuryl alcohol, was very effective in chloride removal but gave the HCl solution an intense greenish yellow color. On neutralizing the sample to the phenolphthalein end-point with N/50 NaOH, the portion of the resin which had dissolved was reprecipitated. A one gram sample of the resin removed all of the HCl present in 100 ml. of solution containing 198 p.p.m. HCl (expressed as NaCl) within three hours. A one gram sample of resin D removed only 18 p.p.m. HCl (as NaCl) from a 100 ml. sample of the above solution, after the resin had been in contact with the solution three days.
EXPERIMENTAL PROCEDURE

In the following experimental work, the resin obtained by the condensation of m-phenylenediamine and formaldehyde with hydrochloric acid was used entirely (except where indicated). The following illustrates the procedure used in preparing the resin. One-eighth of a mole of technical m-phenylenediamine (13.5 g.) were dissolved in 125 ml. of distilled water. On the addition of 25.7 ml. of formalin (3/8 mole of formaldehyde) to the solution, a milky white suspension resulted. One-fourth of a mole of concentrated hydrochloric acid (21.5 ml.) were added to the suspension, and an orange resin precipitated out. After cutting the resin in small pieces and drying in an oven at 92-94°, a hard black material was obtained. The resin was ground, and the portion that was collected between 20- and 40-mesh sieves was used. The dried, ground resin was rinsed with one small portion of distilled water, next with 5 per cent sodium carbonate solution until free of chlorides, and finally with distilled water to remove the alkali (Table 1). For a 50-gram portion of resin, ten to twelve 100 ml. portions of sodium carbonate and ten to twelve 250 ml. portions of distilled water were used. For the sodium carbonate rinses contact time averaged 30 to 40 minutes; while with the distilled water rinses, contact time averaged 15 minutes. The resin could be regen-
erated to a certain extent by treating with 5% sodium carbonate and rinsing with distilled water, but it was not restored to its original capacity (Table XII). Regenerated resin was not used in the work described here (except where indicated).

A mechanical shaker, which resembled the one developed by Highberger (26), was used so that reproducible results could be obtained. The resin and the solution were placed in 500-ml., narrow-mouth bottles, closed by Sargent "no air" rubber stoppers. The bottles were rotated at 17 r.p.m. in a large thermostat. The apparatus mentioned here is described in detail under "Description of Apparatus." Preliminary work showed that increasing the rate of rotation to 32 r.p.m. did not materially affect the results obtained.

The power of the resin to remove chlorides and sulfates was determined on solutions containing (a) hydrochloric acid, (b) sodium chloride, (c) hydrochloric acid and sodium chloride, (d) sodium chloride and sodium hydroxide, (e) sulfuric acid. Preliminary work was also undertaken with phosphoric acid.

In water treatment work, chlorides are usually expressed in parts per million of sodium chloride, irrespective of the nature of the compound involved. For that reason the chloride contents in this work are expressed as parts per million of sodium chloride. The results with sulfates are listed in parts per million of sulfuric acid since that was the only sulfate used.
The chloride ion was determined volumetrically by the Mohr method. All samples were neutralized to the phenolphthalein end point by the addition of the necessary amount of standard sodium hydroxide solution. When the determination was run with a 100 ml. sample, one ml. of 50 potassium chromate solution was added as the indicator, and the solution was titrated with \( \text{K/58.5 silver nitrate solution} \) until the precipitation of red silver chromate resulted. The sample titrated was compared with a blank, and the necessary correction was made. \( \text{mL. N/58.5 AgNO}_3 \times 10^{-p} \text{mL. NaCl} \) if a 100 ml. water sample was used.

The amount of sulfate present was determined by direct titration with standard barium chloride solution using disodium tetrachloroquione as the internal indicator (47). Twenty-five ml. of solution were neutralized to the phenolphthalein endpoint, and twenty-five ml. of isopropyl alcohol and the required quantity of indicator were added to the neutralized sample. A yellow color developed in the solution, and the sample was titrated with standard barium chloride solution until the yellow color changed to rose. The amount of indicator employed and the concentration of the barium chloride used were determined by the approximate quantity of sulfate in the solution to be titrated. If the solution contained from 100 to 1000 parts per million of sulfate, then 0.2 gram of indicator was used for each sample titrated, and the standard barium chloride solution
was of such a concentration that one ml. of it was equivalent to one milligram of sulfate. The sample being titrated was compared with a blank and the necessary correction was made. The number of ml. of barium chloride solution used multiplied by 40 gave the parts per million of sulfate. Parts per million of sulfate were converted to parts per million of sulfuric acid by multiplying by the factor 98/96.
DESCRIPTION OF APPARATUS

The shaker (Figure 1) consisted of a base (oak board - 75 x 28 x 2.5 cm.) upon which rested two ball bearing steel shaft hangers. Between the shaft hangers was suspended an oak board (45 x 26 x 2.5 cm.) which rotated about its long axis. Three openings (15 x 5 cm.) were cut (6.5 cm. apart) in the board and rounded to fit 500-ml. narrow-mouth bottles. Two rubber strips 9 cm. wide and cut from automobile tubes were screwed on either side of the board in order to hold the bottles in place. In this manner six bottles could be accommodated at one time. To prevent the rubber strips from tearing through the screws, steel strips (9 x 2 cm. and slightly rounded so that the rubber would not be cut) were inserted between the rubber strips and the screws. On one end of the suspended board a pulley wheel (13 cm. in diameter) was attached. The shaker, also, served as a stirrer for the water bath and was driven by a one-fourth h.p. motor which operated through a speed reducer. The motor and speed reducer were mounted on a shelf above the thermostat, and the shaker was held in position at the bottom of the thermostat by means of vertical iron rods which were clamped to horizontal rods that were fastened above the thermostat.
The heater was constructed of chromel ribbon (350 cm. x 3.3 cm.) which was coiled and inclosed in pyrex glass tubing (1.5 cm. x 100 cm.) bent in the form of a V. The ends of the chromel ribbon were attached to suitable lengths of stiff insulated copper wire, and the copper wire was held in place by means of cork stoppers. The heater was mounted on heavy board.

The theromregulator consisted of a U tube filled with mercury, and the upper portion of one arm of the tube was of capillary size. A piece of platinum wire (attached to a suitable length of insulated copper wire) dipped in the mercury in the arm of regular size, while a platinum wire which was welded to an insulated screw was held in place over the capillary tube by means of a bakelite cap. By manipulating the screw, the desired temperature could be obtained.

The heater and the theromregulator were connected to an electromagnetic relay.

The shaker and other units of apparatus were designed for simplicity and sturdiness so that they could withstand many hours of continuous usage.
EXPERIMENTAL RESULTS
In Table 1, 60 g. of \( m \)-phenylenediamine-formaldehyde-HCl resin were rinsed after the resin had been dried at 92°C. Obviously, chloride removal from the synthetic resin was a gradual process.

### Table 1. Representative Data on Rinsing Resin

<table>
<thead>
<tr>
<th>Rinse No.</th>
<th>Rinse</th>
<th>Contact</th>
<th>ml. dil. NaCl (0.0164N) to ml. AgNO₃ to neutralize sample</th>
<th>Corrected F.P.K. HCl (as NaCl) removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120 ml. H₂O</td>
<td>10 min.</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>120 ml. Na₂CO₃</td>
<td>40 min.</td>
<td>1</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>&quot; &quot;</td>
<td>&quot; 1</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ks H₃SO₄(0.2452N) to neutralize sample</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&quot; &quot;</td>
<td>&quot; 1</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>&quot; &quot;</td>
<td>&quot; 1</td>
<td>1</td>
<td>2</td>
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<tr>
<td>6</td>
<td>&quot; &quot;</td>
<td>&quot; 1</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>&quot; &quot;</td>
<td>&quot; 1</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>8</td>
<td>&quot; &quot;</td>
<td>&quot; 1</td>
<td>1</td>
<td>1.8</td>
</tr>
<tr>
<td>9</td>
<td>&quot; &quot;</td>
<td>&quot; 5</td>
<td>5</td>
<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>&quot; &quot;</td>
<td>&quot; 5</td>
<td>5</td>
<td>1.7</td>
</tr>
<tr>
<td>11</td>
<td>&quot; &quot;</td>
<td>&quot; 5</td>
<td>5</td>
<td>1.8</td>
</tr>
<tr>
<td>12</td>
<td>&quot; &quot;</td>
<td>&quot; 5</td>
<td>5</td>
<td>3.9</td>
</tr>
<tr>
<td>13</td>
<td>&quot; &quot;</td>
<td>&quot; 5</td>
<td>5</td>
<td>9.4</td>
</tr>
<tr>
<td>14</td>
<td>300 ml. H₂O</td>
<td>15 min.</td>
<td>5</td>
<td>9.5</td>
</tr>
<tr>
<td>15-16</td>
<td>&quot; &quot;</td>
<td>&quot; 5</td>
<td>5</td>
<td>1.4</td>
</tr>
<tr>
<td>17</td>
<td>&quot; &quot;</td>
<td>&quot; 10</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>18-22</td>
<td>&quot; &quot;</td>
<td>&quot; 100</td>
<td>2.6,0.7, 7, 4, 1</td>
<td>0.0</td>
</tr>
<tr>
<td>23</td>
<td>&quot; &quot;</td>
<td>&quot; 100</td>
<td>2.6,0.7, 7, 4, 1</td>
<td>0.0</td>
</tr>
<tr>
<td>24</td>
<td>&quot; &quot;</td>
<td>&quot; 100</td>
<td>Neut.</td>
<td>0</td>
</tr>
</tbody>
</table>
EFFECT OF DRYING RESIN AT DIFFERENT TEMPERATURES. Batches of resin were prepared and dried at 31\(^\circ\), 92\(^\circ\), and 130\(^\circ\) C., respectively, before rinsing, to determine the effect of such a variation. Small batches of the resin were prepared, equal weights of resin were rinsed, and all other conditions (except temperature of drying) were kept as identical as possible. Within the limits of experimental error, the drying temperature in the range investigated had very little influence on the effectiveness of the resin in removal of chlorides. There was some indication that drying the resin at 92\(^\circ\) gave a product slightly superior to the other two, but the evidence was not conclusive.

**TABLE II. EFFECT OF DRYING RESIN AT DIFFERENT TEMPERATURES**

<table>
<thead>
<tr>
<th>Weight of Resin Grams</th>
<th>Residual HCl Expressed as H(_2)Cl</th>
<th>Resin dried at 31(^\circ)</th>
<th>Resin dried at 92(^\circ)</th>
<th>Resin dried at 130(^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>83</td>
<td>80</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>64</td>
<td>52</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
<td>36</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>27</td>
<td>17</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>18</td>
<td>6</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>14</td>
<td>4</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

\* m-phenylenediamine resin, 250 ml. of 100 p.p.m. HCl expresses as H\(_2\)Cl, 30\(^\circ\) C., 10 hr. reaction time.
EFFECT OF DRYING RESIN BEFORE OR AFTER RINSING. When the resin was rinsed with sodium carbonate and water before drying at 88°C., it was considerably more effective in removal of chlorides, as shown in Table III. Unfortunately, it also developed considerable solubility, imparted a distinct yellow color to samples treated with it, and thus proved unsatisfactory.

<table>
<thead>
<tr>
<th>Weight of Resin Grams</th>
<th>F. P. M. Residual HCl Expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resin dried at 92°C., Rinsed before drying then rinsed at 92°C.</td>
</tr>
<tr>
<td>0.25</td>
<td>83</td>
</tr>
<tr>
<td>0.50</td>
<td>66</td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
</tr>
<tr>
<td>1.50</td>
<td>27</td>
</tr>
<tr>
<td>2.00</td>
<td>20</td>
</tr>
<tr>
<td>2.50</td>
<td>16</td>
</tr>
</tbody>
</table>

*o-phenylenediamine resin, 250 ml. of 100 p. p. m. HCl expressed as NaCl, 30°C., 10 hr. reaction time.
EFFECT OF VARIATION OF ROTATION OF SAMPLES ON CHLORIDE REMOVAL: From Table IV a comparison of the results obtained when the bottles were rotated at 17 r. p. m. and 32 r. p. m. showed that the effect of the rate of rotation on chloride removal was negligible.

TABLE IV. EFFECT OF VARIATION OF ROTATION OF SAMPLES ON CHLORIDE REMOVAL*

<table>
<thead>
<tr>
<th>Wt. of Resin</th>
<th>F. P. E. Residual HCl expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td>Rotary shaker adjusted to 16 r. p. m.</td>
</tr>
<tr>
<td></td>
<td>to 32 r. p. m.</td>
</tr>
<tr>
<td>0.25</td>
<td>79</td>
</tr>
<tr>
<td>0.50</td>
<td>63</td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
</tr>
<tr>
<td>1.50</td>
<td>27</td>
</tr>
<tr>
<td>2.00</td>
<td>22</td>
</tr>
<tr>
<td>2.50</td>
<td>19</td>
</tr>
</tbody>
</table>

*—m-phenylenediamine resin, 250 ml. of 100 p. p. m. HCl expressed as NaCl, 30°C., 10 hr. reaction time.
EFFECT OF TEMPERATURE OF WATER SAMPLE. Chloride removal was determined at 30°C, 40°C, and 45°C. From the results obtained in Table V, it is apparent that within the limits of experimental accuracy, the temperature coefficient within this range is zero.

TABLE V. EFFECT OF TEMPERATURE ON CHLORIDE REMOVAL*

<table>
<thead>
<tr>
<th>Reaction Time Minutes</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>83</td>
<td>82</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>60</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*One gram of m-phenylenediamine resin, 350 ml. solution containing 100 p. p. m. HCl expressed as NaCl.
EFFECT OF REACTION TIME. The rate at which chloride was removed was an important factor. The data in Table VI and Figure 2 showed that the reaction reached equilibrium slowly. The system seemed to attain equilibrium at the end of ten hours, so the time used for obtaining equilibrium was ten hours.

**Table VI. Effect of Reaction Time on Chloride Removal**

<table>
<thead>
<tr>
<th>Reaction Time (Hours)</th>
<th>F. P. M. Residual HCl Expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>82</td>
</tr>
<tr>
<td>0.50</td>
<td>74</td>
</tr>
<tr>
<td>1.00</td>
<td>69</td>
</tr>
<tr>
<td>2.00</td>
<td>60</td>
</tr>
<tr>
<td>6.00</td>
<td>48</td>
</tr>
<tr>
<td>10.00</td>
<td>41</td>
</tr>
<tr>
<td>14.00</td>
<td>40</td>
</tr>
</tbody>
</table>

*One gram of m-phenylenediamine resin, 30°C., 250 ml. solution containing 100 p. p. m. HCl expressed as NaCl.
EFFECT OF PARTICLE SIZE. When the size of the particles of resin was reduced from that collected between 20-40 mesh sieves to that between 60-100 and 100-200 mesh sieves, the efficiency of chloride removal was increased as is shown in Table VII. However, particles smaller than the 20-40 mesh sieve size would not be practical for use in commercial units because the loss of material would be too great. In all other runs, particles of 20-40 mesh size were used.

TABLE VII. EFFECT OF PARTICLE SIZE ON CHLORIDE REMOVAL

<table>
<thead>
<tr>
<th>wt. of Resin Grams</th>
<th>Mesh Size</th>
<th>F. P. M. Residual HCl Expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>20-40</td>
<td>83</td>
</tr>
<tr>
<td>0.50</td>
<td>20-40</td>
<td>66</td>
</tr>
<tr>
<td>0.25</td>
<td>60-100</td>
<td>70</td>
</tr>
<tr>
<td>0.50</td>
<td>60-100</td>
<td>53</td>
</tr>
<tr>
<td>0.25</td>
<td>100-200</td>
<td>68</td>
</tr>
<tr>
<td>0.50</td>
<td>100-200</td>
<td>47</td>
</tr>
</tbody>
</table>

*m-phenylenediamine, initial concentration 100 ppm. HCl expressed as NaCl, 250 ml. solution, 30°C., 10 hr. reaction time.
EFFECT OF INITIAL CONCENTRATION OF HYDROCHLORIC ACID ON CHLORIDE REMOVAL. As the result of a study of the effect of initial concentration of hydrochloric acid on the removal of chlorides, it was seen that the effectiveness of chloride removal increased with increasing concentration of acid (Table VIII and Figure 3). The data also indicated that more efficient chloride removal could be obtained by using several small samples of resin rather than one large sample.

By using the values obtained in Table VIII and plotting the logarithm of the parts per million of HCl (as NaCl) removed per gram of resin against the logarithm of the parts per million of residual HCl (as NaCl), it was seen that true adsorption isotherms were not obtained (Figure 4).
## TABLE VIII. EFFECT OF INITIAL CONCENTRATION OF HYDROCHLORIC ACID ON CHLORIDE REMOVAL*

<table>
<thead>
<tr>
<th>Wt. of Resin</th>
<th>P. F. M. Residual HCl</th>
<th>P. F. M. HCl as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td>Expressed as NaCl</td>
<td>Removed per gram resin</td>
</tr>
</tbody>
</table>

### Initial Concentration 100 p. p. m. HCl expressed as NaCl

| 0.25 | 88 | 68 |
| 0.50 | 66 | 60 |
| 1.00 | 40 | 40 |
| 1.50 | 27 | 40 |
| 2.00 | 20 | 34 |
| 2.50 | 16 | 34 |

### Initial Concentration 75 p. p. m. HCl expressed as NaCl

| 0.25 | 61 | 56 |
| 0.50 | 48 | 54 |
| 1.00 | 28 | 47 |
| 1.50 | 18 | 35 |
| 2.00 | 14 | 31 |
| 2.50 | 12 | 26 |

### Initial Concentration 50 p. p. m. HCl expressed as NaCl

| 0.25 | 39 | 44 |
| 0.50 | 30 | 40 |
| 1.00 | 16 | 34 |
| 1.50 | 10 | 27 |
| 2.00 | 8  | 21 |
| 2.50 | 7  | 17 |

*m-phenylenediamine resin, 250 ml. solution 30°C., 10 hr. reaction time.
FIGURE 4

- C: INITIAL CONC. 50 PPM. HCl AS NACI
- A: INITIAL CONC. 75 PPM. HCl AS NACI
- D: INITIAL CONC. 100 PPM. HCl AS NACI

LOG RPM. RESIDUAL HCl AS NACI
SIMULTANEOUS REMOVAL OF ANION AND CATION FROM HYDROCHLORIC ACID. In the experiments described above, the changes in chloride content alone were noted. Two possibilities existed: either that ion exchange took place, or that the whole hydrochloric acid molecule was removed. In Table IX are given the results obtained from acidometric titration as well as volumetric chloride determination. It is evident that, within the limits of experimental accuracy, the entire molecule was being removed, since the acidity of the solution decreased in amount equivalent to the chloride ion concentration.

TABLE IX. SIMULTANEOUS REMOVAL OF ANION AND CATION FROM HYDROCHLORIC ACID*

<table>
<thead>
<tr>
<th>Gr. of Resin</th>
<th>Removed as Indicated by Neutralization of Sample after Chloride Removal</th>
<th>Removed as Indicated by Direct Determination of Chloride Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P. P. M. HCl, as NaCl</td>
<td>P. P. M. HCl, as NaCl</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>0.25</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>0.50</td>
<td>35</td>
<td>29</td>
</tr>
<tr>
<td>1.00</td>
<td>62</td>
<td>48</td>
</tr>
<tr>
<td>1.50</td>
<td>74</td>
<td>61</td>
</tr>
<tr>
<td>2.00</td>
<td>82</td>
<td>64</td>
</tr>
<tr>
<td>2.50</td>
<td>87</td>
<td>65</td>
</tr>
</tbody>
</table>

*m-phenylenediamine resin, 250 ml. solution containing, A-100 p. p. m., B-75 p. p. m., C-50 p. p. m. HCl expressed as NaCl, 330°C., 10 hr. reaction time.
EFFECT OF ACIDITY ON CHLORIDE REMOVAL. In Table X are shown the results of a series of experiments, in which the total chloride contents of the initial samples were nearly the same, but the pH values were different. This was attained by using appropriate solutions of sodium chloride with varying amounts of hydrochloric acid or sodium hydroxide. In one case sodium chloride alone was used, and in another hydrochloric acid alone was used. It was found that a rather regular decrease in total chloride removal resulted with decreasing acidity of samples that possessed the same total chloride content. However, there was some removal from the neutral solution, although the presence of free alkali reduced this still more. This showed that the activity of the resin was not entirely exerted toward the free acid; though in the case of the alkaline solutions, the amounts of chloride removed were too nearly of the same order of magnitude as the probable experimental error to receive very great consideration.
### Table X. Effect of Acidity on Chloride Removal

<table>
<thead>
<tr>
<th>Ft. of Resin</th>
<th>P. P. M. Residual NaCl</th>
<th>P. P. M. NaCl Removed per G. Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Conc. 75 P. P. M. HCl, as NaCl; pH 3.9</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>61</td>
<td>56</td>
</tr>
<tr>
<td>0.50</td>
<td>48</td>
<td>54</td>
</tr>
<tr>
<td>1.00</td>
<td>28</td>
<td>47</td>
</tr>
<tr>
<td>1.50</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>2.00</td>
<td>14</td>
<td>31</td>
</tr>
<tr>
<td>2.50</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td><strong>Initial Conc. 75 P. P. M. (31.5 HCl 43.5 NaCl) as NaCl; pH 3.5</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>63</td>
<td>48</td>
</tr>
<tr>
<td>0.50</td>
<td>63</td>
<td>44</td>
</tr>
<tr>
<td>1.00</td>
<td>42</td>
<td>33</td>
</tr>
<tr>
<td>1.50</td>
<td>36</td>
<td>26</td>
</tr>
<tr>
<td>2.00</td>
<td>32</td>
<td>22</td>
</tr>
<tr>
<td>2.50</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td><strong>Initial Conc. 75 P. P. M. (7 HCl 68 NaCl) as NaCl; pH 4.3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>0.50</td>
<td>66</td>
<td>18</td>
</tr>
<tr>
<td>1.00</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>1.50</td>
<td>56</td>
<td>13</td>
</tr>
<tr>
<td>2.00</td>
<td>51</td>
<td>12</td>
</tr>
<tr>
<td>2.50</td>
<td>48</td>
<td>11</td>
</tr>
<tr>
<td><strong>Initial Conc. 75 P. P. M. NaCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>72</td>
<td>12</td>
</tr>
<tr>
<td>0.50</td>
<td>68</td>
<td>12</td>
</tr>
<tr>
<td>1.00</td>
<td>68</td>
<td>12</td>
</tr>
<tr>
<td>1.50</td>
<td>59</td>
<td>11</td>
</tr>
<tr>
<td>2.00</td>
<td>54</td>
<td>11</td>
</tr>
<tr>
<td>2.50</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td><strong>Initial Conc. 75 P. P. M. NaCl - Soln. Alkali by Adding NaOH; pH 10.2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>72</td>
<td>4</td>
</tr>
<tr>
<td>0.50</td>
<td>72</td>
<td>2</td>
</tr>
<tr>
<td>1.00</td>
<td>72</td>
<td>1</td>
</tr>
<tr>
<td>1.50</td>
<td>71</td>
<td>1</td>
</tr>
<tr>
<td>2.00</td>
<td>71</td>
<td>1</td>
</tr>
<tr>
<td>2.50</td>
<td>69</td>
<td>1</td>
</tr>
</tbody>
</table>

*m-phenylenediamine resin, 250 ml. solution, 30°C., 10 hr. reaction time, solutions contain progressively decreasing amounts of HCl.*
EFFECT OF INITIAL VOLUME OF WATER SAMPLE ON CHLORIDE REMOVAL.

By using 125 ml. of solution instead of 250 ml., the efficiency of HCl removal was increased with the smaller samples of resin but not with the larger samples. This would indicate that, with the larger samples of resin, sufficient material was present to take care of 250 ml. of solution; but with the smaller samples, insufficient resin was present to obtain maximum efficiency with the larger volume of solution. It was possible that the same degree of effectiveness would have been obtained if volumes of solution greater than 250 ml. had been used with the larger samples of resin; and there was, also, the possibility that greater efficiency would have been obtained by using even smaller volumes of solutions with the smaller samples of resin.

TABLE XI. EFFECT OF INITIAL VOLUME OF WATER SAMPLE ON CHLORIDE REMOVAL

<table>
<thead>
<tr>
<th>wt. of Resin</th>
<th>F. P. T. Residual HCl expressed as NaCl</th>
<th>Initial Volume</th>
<th>Initial Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td></td>
<td>250 ml.</td>
<td>125 ml.</td>
</tr>
<tr>
<td>0.25</td>
<td>79</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>63</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>27</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>22</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>19</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

*m-phenylenediamine resin, original solution contained
100 p. p. m. HCl expressed as NaCl, 30°C., 10 hr. reaction time.
EFFECT OF USING REGENERATED RESIN ON CHLORIDE REMOVAL

Resin which had been used in chloride removal was re-generated by treatment with 5% Na₂CO₃ solution until free of chlorides and then rinsed with distilled water until free of alkali (see Table I)

From the comparison given in Table XII, it is apparent that used resin, which was rinsed with sodium carbonate solution, was only partially regenerated.

**TABLE XII. EFFECT OF USING REGENERATED RESIN ON CHLORIDE REMOVAL**

<table>
<thead>
<tr>
<th>wt. of Resin (Grams)</th>
<th>P.P.E. Residual HCl Expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh Resin</td>
</tr>
<tr>
<td>0.25</td>
<td>79</td>
</tr>
<tr>
<td>0.50</td>
<td>63</td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
</tr>
<tr>
<td>1.50</td>
<td>27</td>
</tr>
<tr>
<td>2.00</td>
<td>22</td>
</tr>
<tr>
<td>2.50</td>
<td>19</td>
</tr>
</tbody>
</table>

*m-phenylenediamine resin, 250 ml. of 100 p.p.m. HCl expressed as NaCl, 30°C., 10 hr. reaction time.
REPRODUCIBILITY OF RESULTS. Excellent agreement was obtained when samples were run using resin of the same batch and the same rinse; rather good agreement was obtained with resin of the same batch but different rinse, although the unrinased resin was allowed to stand six months (A and B, Table XIII); while results that were less consistent were obtained when resin from different batches as well as different rinses was used. (A, C, and D, Table XIII).

Another observation made showed that resin which had been rinsed and allowed to stand six months was less efficient in chloride removal than resin which was used a short time after being rinsed. (A and E, Table XIII) Rinsing the unused resin again (regeneration) did not increase the efficiency of the resin. (E and F, Table XIII)

Technical m-phenylenediamine was used in the preparation of the resin. On standing, the m-phenylenediamine became black and gummy, and portions used at different intervals could possibly give resins of slightly different properties.
### TABLE XIII. REPRODUCIBILITY OF RESULTS

<table>
<thead>
<tr>
<th>Wt. of Resin</th>
<th>P. P. M. Residual HCl Expressed as NaCl</th>
<th>P. P. M. Residual HCl Expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resin from same batch but different resin</td>
<td>Resin from different batch and rinse</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>0.25</td>
<td>73</td>
<td>75</td>
</tr>
<tr>
<td>0.50</td>
<td>55</td>
<td>54</td>
</tr>
<tr>
<td>1.00</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>1.50</td>
<td>11</td>
<td>--</td>
</tr>
<tr>
<td>2.00</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>2.50</td>
<td>4</td>
<td>--</td>
</tr>
</tbody>
</table>

*m-phenylenediamine resin, 250 ml. of 100 p. p. m. HCl expressed as NaCl, 30°C., 10 hr. reaction time.
COMPARISON OF m-PHENYLENEDIAMINE-FORMALDEHYDE - HCl RESIN
WITH DE MINERALITE (A Commercial Resin). From the results obtained in Table XIV, m-phenylenediamine resin was superior to De Mineralite in chloride removal, but the solution containing De Mineralite reached equilibrium more rapidly than the solution containing m-phenylenediamine resin. However, apparently some of the De Mineralite dissolved and gave the solution a pinkish lavender tint.

TABLE XIV. COMPARISON OF m-PHENYLENEDIAMINE RESIN WITH DE MINERALITE

<table>
<thead>
<tr>
<th>Reaction Time (Hours)</th>
<th>P. F. M. Residual HCl Expressed as NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>De Mineralite</td>
</tr>
<tr>
<td>1.00</td>
<td>66</td>
</tr>
<tr>
<td>2.00</td>
<td>62</td>
</tr>
<tr>
<td>6.00</td>
<td>62</td>
</tr>
<tr>
<td>10.00</td>
<td>62</td>
</tr>
<tr>
<td>14.00</td>
<td>62</td>
</tr>
</tbody>
</table>

*One gram of resin, 30°C., 260 ml. solution containing 100 p. p. m. HCl expressed as NaCl.
EFFECT OF INITIAL CONCENTRATION OF SULFURIC ACID ON REMOVAL OF SULFATES. From the results obtained in Table XV and Figure 5, it is seen that the resin was more effective in the removal of sulfuric acid than in the removal of hydrochloric acid. As with hydrochloric acid, the effectiveness of sulfate removal was found to increase with increasing initial sulfuric acid concentration; but with the solution containing 759 p.p.m. sulfuric acid (Table XV), very slight solution of the resin took place with a few samples, since a faint straw color was detected in the solution that was in contact with portions of resin weighing one gram or more.

According to work done recently by E. Garrett (done at Louisiana State University, and as yet unpublished) the approximate equilibrium time for sulfates was found to be about three hours; so in Table XV it was safe to assume that equilibrium had been reached within ten hours.

It was found that a true adsorption isotherm could not be obtained by plotting the results obtained in Table XV.
TABLE XV. EFFECT OF INITIAL CONCENTRATION OF SULFURIC ACID ON REMOVAL OF SULFATES *

<table>
<thead>
<tr>
<th>Weight of Resin</th>
<th>P. P. M. Residual H₂SO₄</th>
<th>P. P. M. H₂SO₄ Removed per Gram Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Concentration 171 p. p. m. H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>98</td>
<td>292</td>
</tr>
<tr>
<td>0.50</td>
<td>57</td>
<td>228</td>
</tr>
<tr>
<td>1.00</td>
<td>2</td>
<td>166</td>
</tr>
<tr>
<td>1.50</td>
<td>2</td>
<td>113</td>
</tr>
<tr>
<td>2.00</td>
<td>0</td>
<td>86</td>
</tr>
<tr>
<td>2.50</td>
<td>0</td>
<td>66</td>
</tr>
<tr>
<td>Initial Concentration 396 p. p. m. H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>264</td>
<td>408</td>
</tr>
<tr>
<td>0.50</td>
<td>208</td>
<td>376</td>
</tr>
<tr>
<td>1.00</td>
<td>106</td>
<td>260</td>
</tr>
<tr>
<td>1.50</td>
<td>57</td>
<td>228</td>
</tr>
<tr>
<td>2.00</td>
<td>16</td>
<td>150</td>
</tr>
<tr>
<td>2.50</td>
<td>2</td>
<td>157</td>
</tr>
<tr>
<td>Initial Concentration 750 p. p. m. H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>632</td>
<td>508</td>
</tr>
<tr>
<td>0.50</td>
<td>534</td>
<td>450</td>
</tr>
<tr>
<td>1.00</td>
<td>347</td>
<td>412</td>
</tr>
<tr>
<td>1.50</td>
<td>220</td>
<td>353</td>
</tr>
<tr>
<td>2.00</td>
<td>139</td>
<td>310</td>
</tr>
<tr>
<td>2.50</td>
<td>102</td>
<td>263</td>
</tr>
</tbody>
</table>

*m-phenylenediamine resin, 250 ml. solution, 30°C., 10 hr. reaction time.*
SIMULTANEOUS REMOVAL OF ANION AND CATION FROM SULFURIC ACID.

As described in a previous section, the sulfate ion was determined by direct titration with standard barium chloride solution, using disodium tetrahydroxyquinone as an internal indicator. The results obtained were expressed in parts per million of sulfate; and to convert the readings to p.p.m. of sulfuric acid, the conversion factor 98/36 was utilized. The acidity of the samples was determined by titrating with standard sodium hydroxide solution to the phenolphthalein endpoint. From Table XVI it is obvious that, as with hydrochloric acid, the entire molecule of acid was removed from solution. However, agreement was not as uniform as with hydrochloric acid. Perhaps the reason for this was that the results obtained with sulfate determinations were not as accurate as the results with chlorides.

TABLE XVI. SIMULTANEOUS REMOVAL OF ANION AND CATION FROM SULFURIC ACID.

<table>
<thead>
<tr>
<th>Weight of Resin</th>
<th>P.p.m. H₂SO₄ Removed as indicated by Neutralization of Sample after Sulfate Removal</th>
<th>P.p.m. H₂SO₄ Removed as indicated by Direct Determination of Sulfate Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>0.25</td>
<td>72</td>
<td>104</td>
</tr>
<tr>
<td>0.50</td>
<td>108</td>
<td>117</td>
</tr>
<tr>
<td>1.00</td>
<td>145</td>
<td>286</td>
</tr>
<tr>
<td>1.50</td>
<td>153</td>
<td>331</td>
</tr>
<tr>
<td>2.00</td>
<td>160</td>
<td>380</td>
</tr>
<tr>
<td>2.50</td>
<td>160</td>
<td>386</td>
</tr>
</tbody>
</table>

* _m_-phenylenediamine resin - 250 ml. solution containing: A 171 p.p.m., B 386 p.p.m., C 750 p.p.m. H₂SO₄; 50°C., 10 min. reaction time.
PRELIMINARY WORK ON PHOSPHATE REMOVAL. Preliminary work on
the removal of phosphoric acid by the m-phenylenediamine resin
seemed to indicate that the resin was less effective in
taking up the phosphoric acid than in taking up the sulfuric
acid or hydrochloric acid (Table XVII). However, insuffi-
cient data were obtained to draw any conclusion.

In each determination a 25 ml. sample was neutralized
to the phenolphthalein endpoint. 25 ml. of the original
solution required 25 ml. of 0.019 N sodium hydroxide solution
for neutralization to the phenolphthalein endpoint. This
would indicate that the phosphoric acid solution was 0.019 N
as a dibasic acid. \((\text{H}_3\text{PO}_4 \quad 2\text{H} \\text{H}_2\text{PO}_4)\). \(98/2\) times 0.019
.931 g. of \(\text{H}_3\text{PO}_4\) per liter or .931 mg. per ml. .931 mg.
times 25 ml. \(\text{NaOH}\) times 40 .931 p.p.m. phosphoric acid in
the original solution. The other values in Table XVII were
calculated in the same manner.

TABLE XVII. PRELIMINARY WORK ON PHOSPHATE REMOVAL*

<table>
<thead>
<tr>
<th>Weight of m-phenylenediamine resin, 250 ml. solution, 30°C., 10 hr. reaction time.</th>
<th>Initial Concentration 931 p. p. m. (\text{H}_3\text{PO}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Concentration 931 p. p. m. (\text{H}_3\text{PO}_4)</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
</tr>
</tbody>
</table>

*Volume of NaOH (.019N) to neutralize 25 ml. sample after phosphate removal.
DISCUSSION OF RESULTS AND CONCLUSIONS
It appears from the results obtained that chemical reaction rather than adsorption was definitely the determining factor in the removal of acids by the m-phenylenediamine resin. A true adsorption isotherm was not obtained when the necessary data was plotted. The fact that the entire molecule of acid was removed would also discredit the theory of ion-exchange. The small amount of free alkali that could possibly have been held by the resin after rinsing could not have been the reactive substance because the decrease in acidity of the solution was accompanied by a corresponding decrease in chloride ion content. It is, therefore, logical to assume that salt formation took place between the free amino groups present in the resin and the acid being removed from solution.

\[ \text{RNH}_2 + \text{HCl} \rightarrow \text{RNH}_2\text{HCl} \] (insoluble salt)

This is further substantiated by the fact that equilibrium was reached fairly slowly and that the resin that was rinsed before being dried was more effective in the removal of hydrochloric acid than the resin that was dried before being rinsed. The last statement is in agreement with the results obtained by Adams and Holmes (5) but at variance with the data reported by Broughton and Lee (18). Drying the resin in the presence of excess acid and formaldehyde would tend to increase the degree of polymerization or condensation at the amino groups and thus yield a resin that would possess a smaller number of free amino groups and less affinity for acids.
However, the removal of small quantities of sodium chloride from neutral solution cannot be explained on the basis of salt formation. The observation that increasing the amount of resin surface exposed, by varying the size of the particles, increased the effectiveness of the resin also seems to point to the fact that some adsorption as well as chemical reaction took place.

It therefore seems likely that removal of chlorides and sulfates from solutions can be attributed primarily to salt formation, in which the amine groups of the resin are involved, and to a minor extent to surface adsorption.
SUMMARY
water solutions of chlorides and sulfates were treated with a resin prepared from m-phenylenediamine, formaldehyde, and hydrochloric acid. The effects of a number of factors upon the efficiency of the resin in removing solutes were determined. Some of the factors included were: effect of drying resin at different temperatures, drying before or after rinsing, variation in rotation of samples, temperature of water sample, reaction time, particle size, initial concentration, acidity, initial volume of water sample, and using regenerated resin. From the data obtained, it seemed that removal of the chlorides and sulfates could be attributed chiefly to salt formation, and to a minor extent to adsorption.
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(39) Ibid., 832,726 (Oct. 3, 1938).
(40) Ibid., 838,332 (March 2, 1939).
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BIOGRAPHY
Lucille Grace Boudreaux was born in Scott, Louisiana on August 11, 1913. She graduated from Scott High School in May, 1929 and entered Southwestern Louisiana Institute during the summer of that same year. In May, 1932 she received the degree of Bachelor of Science, after being a student assistant in Chemistry during the session 1931-32. She taught mathematics at Scott High School from 1932 to 1934 and entered Louisiana State University as a fellow in chemistry in September, 1934. She received the degree of Master of Science in August, 1936 and has been teaching chemistry at Mississippi State College for Women since the fall of 1939. At present she is a candidate for the degree of Doctor of Philosophy with a major in chemistry.
EXAMINATION AND THESIS REPORT

Candidate: Lucille Grace Boudreaux

Major Field: Chemistry

Title of Thesis: The Removal of Chlorides and Sulfates by Synthetic Resins

Approved:

[Signatures of Major Professor and Chairman and Dean of the Graduate School]

EXAMINING COMMITTEE:

[Signatures of committee members]

Date of Examination:

May 3, 1941