

65
-23-74

760

RFP-2140

RFP-2140
May 10, 1974

RADIATION EFFECTS ON ION EXCHANGE RESINS
I. GAMMA IRRADIATION OF DOWEX® 50W

Armen R. Kazanjian

David R. Horrell



DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$4.00 Microfiche \$1.45

Printed
May 10, 1974

RFP-2140
UC-4 Chemistry
TID-4500-R60

RADIATION EFFECTS ON ION EXCHANGE RESINS
I. GAMMA IRRADIATION OF DOWEX® 50W

Armen R. Kazanjian

David R. Horrell

PRODUCT INTEGRITY AND SURVEILLANCE

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

SUBJECT DESCRIPTORS

Radiation Effects
Ion Exchange Resins

Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

C O N T E N T S

Abstract	1
Introduction	1
Experimental	1
Results and Discussion	2
Gas Yields	4
Sulfate Production	5
Microscopic Analysis	5
References	5
Appendix	5

RADIATION EFFECTS ON ION EXCHANGE RESINS

I. GAMMA IRRADIATION OF DOWEX® 50W

Armen R. Kazanjian and David R. Horrell

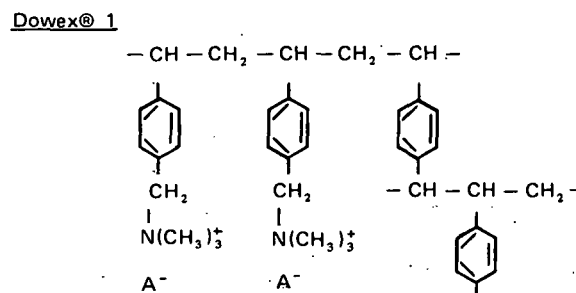
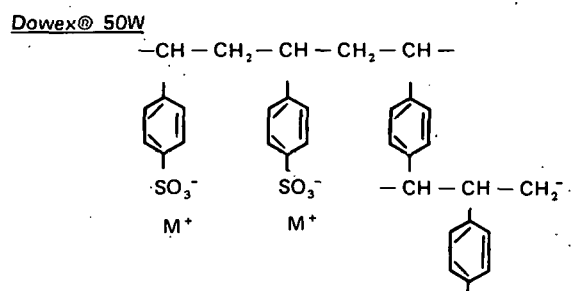
Abstract. Dowex® 50W ion exchange resin was gamma irradiated in the air-dried state and in 0.1N HCl. In both cases, the exchange capacity on a dry-weight basis was reduced about 30% upon absorption of 5×10^8 rads. This loss corresponded to the amount of sulfate ion produced from the sulfonic-acid functional groups by radiation. Changing the cation sorbed on the resin from H^+ to Na^+ had little effect on the degradation.

INTRODUCTION

Ion exchange resins are routinely used for the separation of radioactive materials, and are consequently subjected to high-energy radiation. The effects are detrimental, thereby necessitating a periodic replacement of the resin. Prediction of the useful lifetimes of resins is desirable, especially in these times of increasing emphasis on minimizing radioactive wastes. Although a few studies of the radioactive degradation of ion exchange resins have been made,¹⁻⁴ there is still much information to be obtained because of the many variables involved.

Operations at Rocky Flats include separation of americium-241 with Dowex® 50W, a cation-exchange resin, and separation of plutonium-239 with Dowex® 1, an anion-exchange resin. These resins were chosen for this investigation because of their use at Rocky Flats, and because they are common representatives of strong-acid and strong-base resins. As shown in the following formulas, the copolymer of styrene and divinylbenzene is the skeleton or matrix for both resins. Divinylbenzene, the cross-linking agent, can be attached at the ortho-, meta-, or para-positions. The functional groups (sulfonic acid in Dowex® 50W and quaternary ammonium in Dowex® 1) are

also attached at the ortho-, meta-, and para-positions. The radiation effects on these polymers would be of interest for their own sake regardless of the intended use.



This investigation will include the gamma and alpha irradiation of these two resins. The gamma irradiation of Dowex® 50W has been completed and is reported here.

EXPERIMENTAL

Dowex® 50W-X4 (Baker Analyzed Reagent) resin was used in the H^+ and Na^+ forms, and resin beads were 50 to 100 mesh. The X4 indicated the copolymer contained 4% cross-linking agent, divinylbenzene. The resin was irradiated under two conditions for comparison. One was an air-dried resin containing 66.6% H_2O that was

produced by drying the resin in a Buchner funnel for 15 minutes. The other condition was resin in 0.1N HCl, the medium in which americium is loaded on columns. The resin and aqueous-solution heights were always made equal in the

Table 1. Capacity and Moisture Content of Dowex® 50W Resin.

Dose $\times 10^{-8}$, rads	meq per oven-dried g	meq per air-dried g	meq/ml*	ml/g**	% H ₂ O
Unirradiated Resin					
0	5.35	1.79	1.28	1.40	66.5
H ⁺ form, Irradiated in the Air-Dried State					
0.88	5.06	1.63	1.16	1.40	67.9
1.17	4.77	1.52	1.04	1.46	68.0
2.93	4.22	1.33	0.94	1.42	68.4
3.59	4.06	1.30	0.92	1.41	68.0
5.12	3.77	1.27	0.92	1.39	66.3
7.15	3.44	1.31	0.92	1.42	61.8
H ⁺ form, Irradiated Resin in 0.1N HCl					
1.17	4.85	1.52	1.07	1.42	68.6
1.77	4.68	1.42	1.00	1.41	69.6
2.11	4.46	1.33	0.93	1.42	70.3
3.00	4.18	1.28	0.90	1.42	69.4
3.59	4.00	1.21	0.87	1.39	69.6
5.12	3.72	1.20	0.85	1.39	67.9
Na ⁺ form, Irradiated in the Air-Dried State					
1.77	4.70	1.44	1.02	1.40	69.4
3.85	4.20	1.34	0.96	1.40	68.3
6.32	3.88	1.33	0.84	1.61	65.5
Na ⁺ form, Irradiated Resin in 0.1N HCl					
1.77	4.60	1.37	0.99	1.39	70.2
3.85	4.18	1.28	0.91	1.40	69.4
6.32	3.91	1.12	0.62	1.83	71.3

*milliequivalents per ml of wet-tapped resin.

**ml of wet-tapped resin per air-dried gram.

NOTE: These values are the averages of duplicate results.

irradiation tube, which produced an overall density of 1.07 g/cm³ and resin content of 23.6% by weight.

Irradiations were made with a cobalt-60 gamma source that delivered a dose rate of 1.25×10^6 rads per hour. The temperature in the radiation cell was 45 °C. Various doses up to 7.15×10^8 rads (570 hours) were administered. The energy fraction absorbed by the resin or solution was equivalent to the weight fraction, because the resins and water (or dilute HCl) have approximately the same electron density.

Capacity, moisture content, gaseous product, sulfate ion, and microscopic analyses were made on the irradiated resin. The capacities were determined on the basis of milliequivalents (meq) per ml, air-dried gram, and oven-dried gram of resin. The procedure used, as shown in the appendix, determined the strong-acid or salt-splitting capacity but not the total capacity. All of the capacity of unirradiated Dowex® 50W, however, is of the strong-acid type. Moisture content (% H₂O) was the difference in weight between air-dried and oven-dried (110 °C) resin. Gaseous products were determined by mass spectrometry.

The barium-chloroanilate-colorimetric method was used for the sulfate analysis, and a scanning electron microscope was used to examine the resin beads for structural defects caused by radiation. Break-through capacities would have provided useful data from a practical standpoint, but were not determined because of time considerations.

RESULTS AND DISCUSSION

Results of capacity and moisture determinations are presented in Table 1 and Figures 1–3. The most important parameter is the number of milliequivalents of exchange capacity per gram of oven-dried resin. This indicates the total amount of capacity that is destroyed upon irradiating a given quantity of resin. The other two capacity parameters, meq/air-dried gram and meq/ml, reflect changes in moisture content and packing density; ml/g, in addition to the dry weight capacity. Changes in moisture content

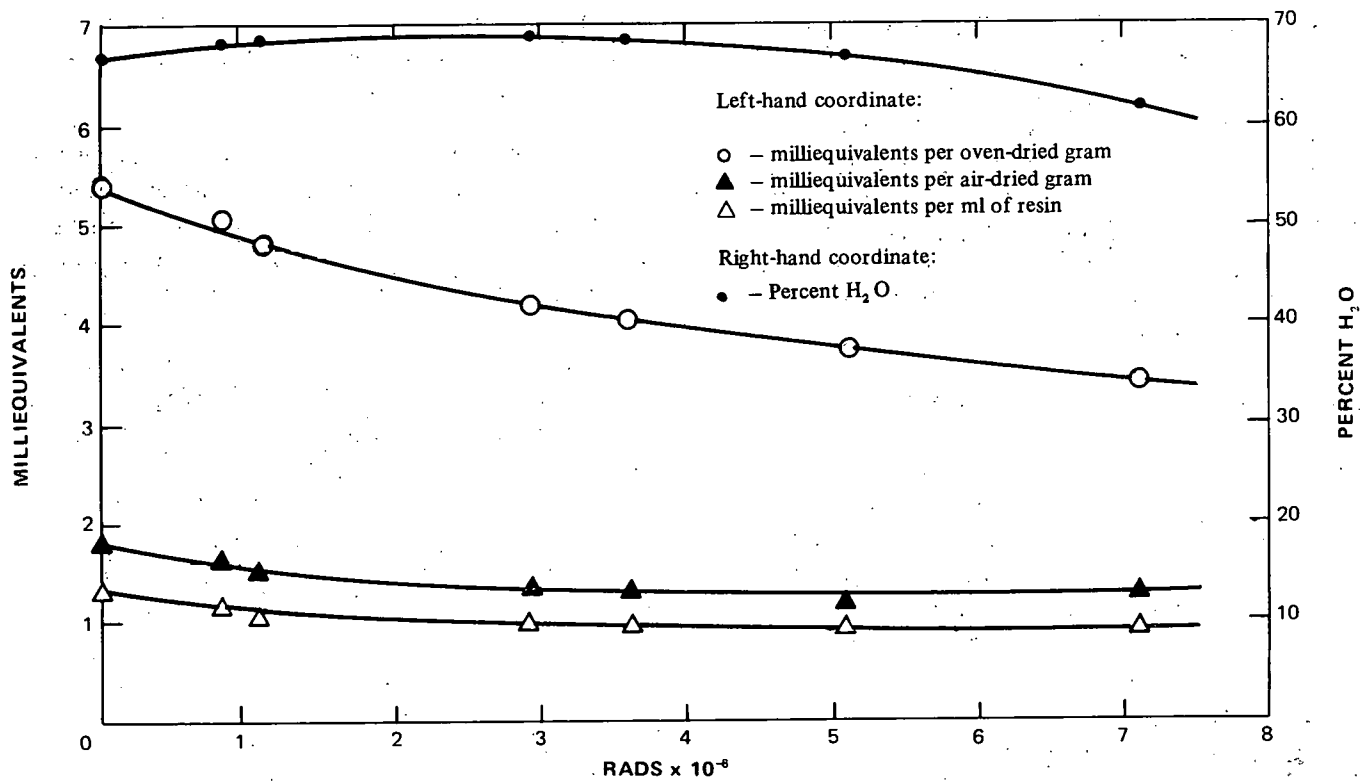


Figure 1. Air-Dried Resin, H⁺ Form.

Figure 2. Resin in 0.1N HCl, H⁺ Form.

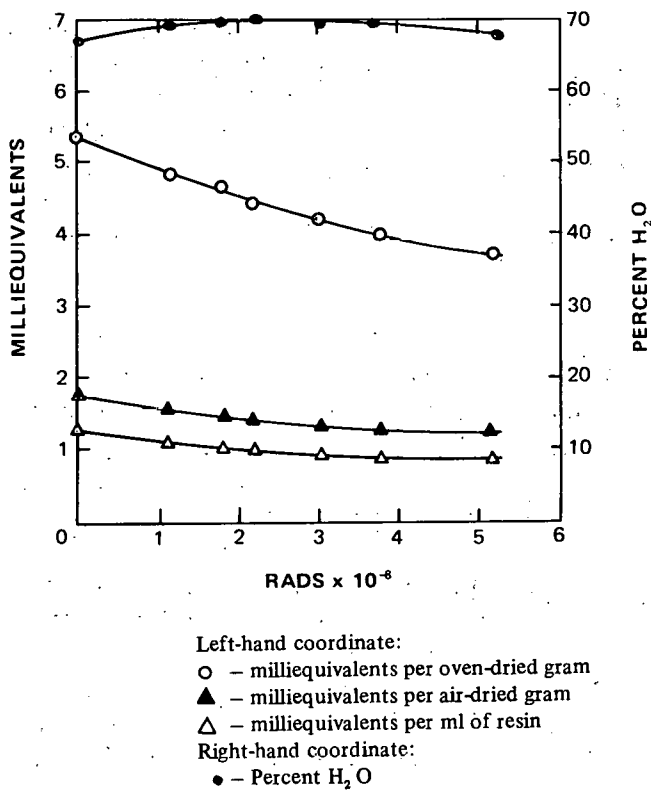
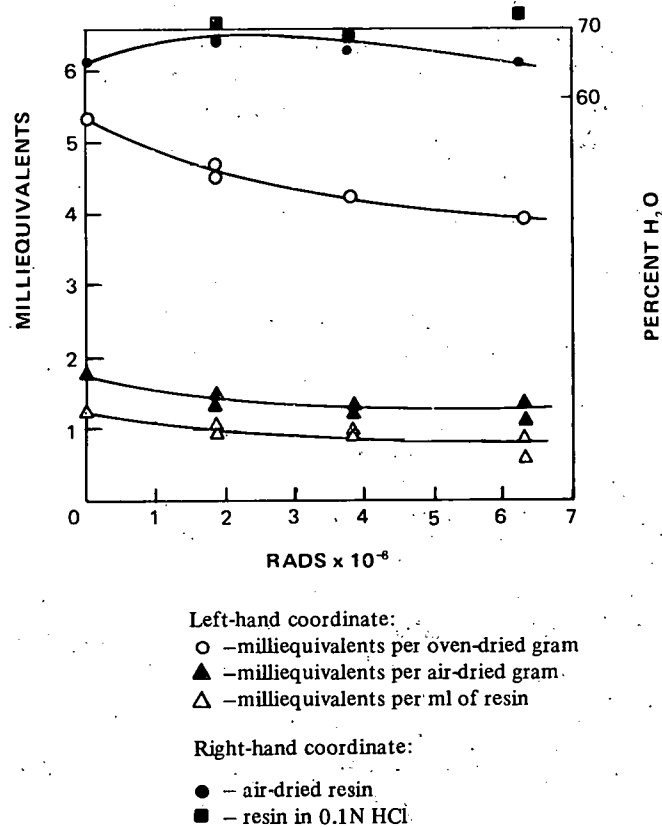


Figure 3. Na⁺ Form.



and packing density are important in ion-exchange kinetics and column operation.

Results show radiation of air-dried resin and resin in 0.1N HCl produces an equivalent change in capacity. Air-dried resin contains 66.5% H₂O (initially), so 66.5% and 33.5% of the gamma energy are absorbed by the water and resin, respectively. The weight percent of resin in 0.1N HCl is 23.6%, so 76.4% and 23.6% of the energy are absorbed by dilute HCl and resin, respectively. In each case, energy absorption by the resin (direct effect) is less than energy absorption by water (indirect effect). In the indirect effect, the radiolysis products of water react with the resin. The most likely reactive species are the solvated electron (or the hydrogen atom in acid solution), the hydroxyl radical, OH, the perhydroxyl radical, HO₂, existing in oxygenated solutions such as these, and hydrogen peroxide.

In dilute HCl, the hydroxyl radical is scavenged according to the following reaction:⁵ $\text{OH} + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl} + \text{H}_2\text{O}$.

Since OH is postulated to be one of the main precursors of H₂O₂, the above reaction would also greatly reduce the H₂O₂. Radiation effects in acid solution may also be different from those in water because of the formation of H atoms from solvated electrons (e_{aq}⁻). These two reducing species (H and e_{aq}⁻) undergo identical reactions, but the H atom usually reacts at a slower rate. Our experiments demonstrate that although most of the energy deposition is in the aqueous solution, changing the aqueous solution so the reactive radiolytic products are greatly altered does not affect the overall radiolytic degradation of the resin. No further inferences will be drawn from this result.

Resin in the H⁺ form experiences a 30% decrease in capacity after absorbing 5×10^8 rads of gamma energy. The rate of decrease is not constant, however. The resin becomes somewhat less susceptible to degradation with energy absorption. The resin in the Na⁺ form is almost the same, losing 25% of its capacity after absorbing 5×10^8 rads.

Results of the Na⁺-form resin, irradiated air-dried or in 0.1N HCl, were almost identical. For this reason, Figure 3 contains single curves for both sets of data.

The last measurement of ml/g and the high moisture content of 71.3% for the Na⁺-form resin are disregarded because of their anomaly.

As shown in Figures 1 through 3, water content of the resin increases and peaks at an energy absorption of 2 to 3×10^8 rads. The increased water content, accompanied by an increased amount of swelling, is usually due to a decreased amount of cross-linking. Irradiation of polymers produces degradation and cross-linking, so the above results indicate that degradation is the predominant effect up to 2 to 3×10^8 rads, followed by a predominance of cross-linking. Since the packing density (ml/g) remained constant, the meq/ml and meq/air-dried gram curves are governed by the moisture content and dry-weight capacity. The slopes of these curves are initially greater than those of the meq/oven-dried gram based on percentage capacity loss, (this is not easily discerned in Figures 1 through 3) because of increased moisture content. In the latter part of the curves where the percent water is decreasing, the opposite effect occurs and the curves show no loss in capacity per wet ml or air-dried gram of resin.

As previously mentioned, the measured exchange capacities were of the strong (sulfonic) acid type. Two tests were also made in which the total capacity was measured. This was done by adding a strong base after the NaCl addition (see appendix) and back-titrating with 0.1N HCl. These tests involved air-dried resin and resin in 0.1N HCl irradiated to a dose of 5.72×10^8 rads. Total capacities were about 7% higher than the strong-acid capacities, indicating that 7% of the total capacity was then of the weak-acid type. This can be explained by the presence of carboxylic-acid functional groups formed by the radiolytic oxidation of the polymer matrix. There was no further work done in this area.

GAS YIELDS

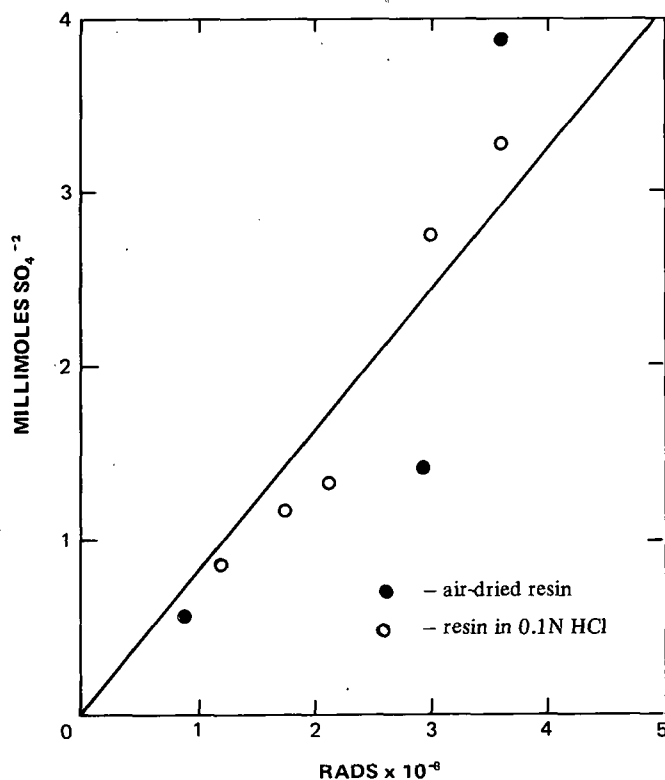
Samples of air-dried resin, resin in 0.1N HCl, and 0.1N HCl were gamma irradiated in evacuated vials and the product gases analyzed by mass spectrometry. The only gas produced in significant quantities was hydrogen. In all three cases, there was a relatively small yield of about 0.1

molecule per 100 eV of absorbed energy. The H_2 could be formed either in the aqueous solution or from the straight chain portion of the polymer molecules. The latter mechanism leads to increased cross-linking.

SULFATE PRODUCTION

After irradiation, the resins were washed with a 5% NaCl solution. These solutions were analyzed for sulfate ions formed by the radiolytic degradation of the sulfonic-acid functional groups on Dowex® 50W. Results are shown in Figure 4. Although the points are scattered, the best line-fit establishes that the production of sulfate ion corresponds almost exactly to the loss in exchange capacity. For example, absorption of 5×10^8 rads of energy produces 4.1 moles of SO_4^{-2} per 10 ml of resin, which corresponds to a 32% decrease $[(4.1/12.8) \times 100]$ in exchange capacity. This indicates the functional groups are attacked directly by a scission of the carbon-sulfur bond. Every such

Figure 4. Sulfate Ion Production.



rupture results in a sulfate ion rather than any kind of an organic entity. The calculated value for sulfate production is 0.74 molecule per 100 eV of absorbed energy.

MICROSCOPIC ANALYSIS

Photomicrographs of the irradiated beads were taken at 50X and 500X with a scanning electron microscope. There was no visible evidence of any physical changes caused by radiation. The polymeric matrix was obviously not altered to a great extent.

REFERENCES

1. I. R. Higgins, "Radiation Damage to Organic Ion Exchange Materials," ORNL-1325, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1953.
2. S. A. Fisher, "Effect of Gamma Radiation on Ion Exchange Resins," RMO-2528 (1954).
3. J. L. Ryan and E. J. Wheelwright, *Ind. Eng. Chem.*, 51, 60, 1959.
4. L. L. Smith and H. J. Groh, "The Effect of Gamma Radiation on Ion Exchange Resins," DP-549, United Kingdom Atomic Energy Authority, Research Group, Atomic Energy Establishment, Winfrith, Dorset, England, February 1961.
5. J.W.T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, 1964, p. 267.

APPENDIX

Sulfonic Cation Exchangers (Strong Acid)*

Procedure

1. Place about 10 ml of wet swollen sample in a 0.50-in. column.

*Dowex: Ion Exchange, The Dow Chemical Company, Midland, Michigan, 1964, p. 35.

2. Pass 200 ml of 5% hydrochloric acid through the resin at a relatively constant flow rate for one hour.
3. Rinse the resin with deionized or distilled water at the same flow rate until the effluent is neutral to pH paper (200 ml is normally satisfactory).
4. Remove the sample from the column and tap and settle two 4 to 5-ml aliquots of resin.
5. Attach the vacuum flask with sintered glass filter to a vacuum and wash one aliquot into the filter. Apply the vacuum for ten minutes (no more).
6. Carefully remove the entire sample and place it in a previously tared weighing bottle. Reweigh and leave overnight in an oven set at 105 to 115 °C. Be sure to vent the weighing bottle.
7. Repeat steps 5 and 6 for the other aliquot.
8. Remove the samples from the oven, cool in a desiccator, and reweigh.
9. Wash and dry sample into a 400-ml beaker and dilute to 200 ml with deionized or distilled water. Allow the sample to rehydrate for one-half hour.
10. Add approximately 5 grams of CP sodium chloride to the beaker and titrate the liberated

acid with 1N sodium hydroxide to a pH of 7, following the pH with a pH meter while stirring vigorously. Record the ml of sodium hydroxide required. The phenolphthalein end point can be used.

11. Calculate the wet volume total capacity

$$\begin{aligned} &\text{Capacity, H}^+, \text{ wet} \\ &= \frac{\text{ml NaOH} \times \text{normality NaOH}}{\text{ml wet sample}} = \text{meq/ml} \end{aligned}$$

12. Calculate the dry weight total capacity

$$\begin{aligned} &\text{Capacity, H}^+, \text{ dry} \\ &= \frac{\text{ml NaOH} \times \text{normality NaOH}}{\text{g dry sample}} = \text{meq/dry g} \end{aligned}$$

13. Calculate the wet weight total capacity

$$\begin{aligned} &\text{Capacity, H}^+, \text{ wet} \\ &= \frac{\text{ml NaOH} \times \text{normality NaOH}}{\text{g wet sample}} = \text{meq/wet g} \end{aligned}$$

14. Calculate the moisture content

$$\begin{aligned} &\% \text{ moisture, H}^+ \\ &= \frac{(\text{g wet sample} - \text{g dry sample}) \times 100}{\text{g wet sample}} \end{aligned}$$