ION EXCHANGE PROPERTIES OF CHROMATOGRAPHIC PAPERS

by

William Jacob Jones

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1966

STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: William J. Jones

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Roy A. Keller

ROY A. KELLER
Associate Professor of Chemistry

September 24, 1965
Date

ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to Dr. Roy A. Keller for his continual guidance and encouragement throughout the course of this work.

TABLE OF CONTENTS

LIST OF TABLES

ABSTRACT

Various methods have been proposed for the determination of the exchange capacity of chromatographic paper and these have lead to conflicting results. A comparison of these methods is made here with a single grade of paper. Exchange capacities were determined by two methods on Whatman #1 paper and two Whatman ion-exchange papers. Some pre-washed papers were used; acetic acid, perchloric acid, EDTA, and a combination base-acid wash.

The exchange capacity generally decreases after acid washing and increases after base washing. The exchange capacities of the special ion-exchange papers were lower than those reported by the manufacturer in both cases.

INTRODUCTION

Paper as an Ion Exchanger

The mechanism of paper chromatographic separation, because of its complexity, is clouded with controversy. It has been regarded as an adsorbtion process, an ion-exchange process, and a partition phenomenon. Ion-exchange is often considered separate from other adsorbtive mechanism[1]. Hanes and Isherwood[2] advocate a mechanism which is a composite of all of these. The mechanism chosen to explain chromatographic results is usually determined by the nature of the species being chromatographed, the chromatographic media, and the nature--especially the polarity--of the solvent or developer.

Ion-exchange reactions were studied by Kolthoff[3] as early as 1921. McLean and Wooten[4] considered exchange reactions in various cellulosic materials and found that ash content is related to the number of exchange sites in the paper. They concluded that the constituents of the ash, present as oxides or carbonates, exist in the paper as organometallic impurities, and that these impurities, not the cellulose, are responsible for the exchange reactions.

Shute[5] contributed further evidence for the ion-exchange mechanism. Using paper chromatography to separate mixtures of alkaloids with hexane as a developer, he found that an irreversible

surface adsorbtion of the alkaloid occurs, which decreases with increasing polarity of the solvent. Swelling of the paper also decreases the adsorbtion. He proposed that for water, a strongly polar and swelling solvent as a developer, little surface adsorbtion should occur. He found, however, that with water, "adsorbtion" indeed took place, and that it had its origin in ion-exchange.

All of these results underscore the importance of the ion-exchange concept in explaining paper chromatographic separations.

Determination of the Exchange Capacity

An early attempt to determine the carboxyl content, equated to the exchange capacity, of chromatographic paper was made by Yackel and Kenyon[6]. The paper was treated with salts of weak acids, e.g. calcium acetate, which react with the carboxyl groups of the cellulose to form the cellulose salt and the corresponding weak acid. The released acid was then titrated with 0.1M sodium hydroxide. Values reported varied from 14.7 to 22.3% carboxyl groups by weight, which corresponds to 3.2 to 5.0 milliequivalents per gram of paper. The major disadvantage of the method is that it may not be used for paper of low exchange capacity since sensitive titrations are impossible. The major pitfall in this method, as Shute[5] later demonstrated, is that all exchange sites are not in the protonated form, but may be occupied by sodium, calcium or magnesium ions. All exchange sites,

then, do not release acid. These same workers later developed a method of decarboxylation followed by collection and measurement of the carbon dioxide evolved. This method is far from simple.

Other methods have involved infrared spectroscopy[7]. With the exception of these and decarboxylation reactions, all other methods have been based on ion-exchange and subsequent titration.

A chromatographic method for the determination of the carboxyl content of filter paper was first proposed in 1955 by Ultee and Hartel[8]. The ion selected for exchange was chosen from the following series of ion affinities for carboxyl groups compiled from the literature:

$$UO_2^{++} \backsim Pb^{++} > Sn^{++} > Cu^{++} > H^+ > \text{methylene blue}^+ > Ba^{++} > Ca^{++} > Ag^+ > Tl^+ > K^+ > Na^+ > Li^+ > N(CH_3)_4^+$$

Lead ion was chosen since, according to this series, it is capable of displacing most other ions, including hydrogen. This series also suggests that acid pre-treatment of the paper should have no effect on the measurement of ion-exchange capacity. In their method a known amount (10 μl) of a lead nitrate solution of known concentration (0.01M - 0.1M) was applied as a spot to the paper strip with a micro-pipet. The strip was chromatographed by the ascending technique for approximately 30 minutes with boiled distilled water as a developer. After location with hydrogen sulfide, the lead spot was traced onto a heavy paper which was then cut out and weighed. From the

weight-per-unit area of the chromatographic and the tracing paper, the carboxyl content of the paper was calculated on assumption that on the final spot a lead ion was attached to each exchange site. The value quoted for Whatman #1 paper is 0.008 milliequivalents per gram of paper and 0.064 milliequivalents per gram for Macherey, Nagel #613.

These workers also employed infrared spectroscopy to the possibility of opening lactone rings present in the paper with this treatment. They concluded that carboxyl groups may be formed from the lactone rings if an alkaline medium is used.

In 1957, Schröder[9] modified the work of Ultee and Hartel. He proposed that, since lead acetate tends to hydrolyze and lead nitrate may act as an oxidizing agent, a lead chloride solution is more appropriate to the determination. Specifically, fifty microliters of 0.01M lead chloride was applied to a paper strip with a micropipet and the strip chromatographed ascending with water in a vapor saturated tank. The spots were located by spraying the strip with a dithizone solution (0.01% in acetone) and the area measured with a planimeter. The value reported for Whatman #1 paper is 0.0066 milliequivalents per gram of paper and for Macherey, Nagel #613, 0.036 milliequivalents per gram -- different by about a factor of two from the results of Ultee and Hartel.

An extensive treatment of the subject by Ackermann and Krüger[10] appeared in 1962. The exchange capacity of various

papers, including some acid and base washed papers, was determined, also by the chromatographic method. This group substituted nickel ion for Ultee and Hartel's lead ion. Sample values reported are 0.0039 milliequivalents per gram for Scheicher and Schüll 2043a and 0.0043 for Macherey, Nagel & Company's 2214 as compared to Schröder's reported 0.0057 and 0.005 milliequivalents per gram.

Epstein and Lewin[11] reverted to the earlier method of treating the cellulose with a salt solution followed by estimation of the liberated anion or of the cation remaining in solution. These methods, however, remain unsatisfactory for measuring small exchange capacities.

Exchange Capacity of Pre-treated Paper

Shute reported results of chromatographing weak acids with water as a developer on pre-washed paper. He proposed that the cations in the paper (M_P^+) were exchanged for hydrogen ions from the weak acid, H^+, to form the protonated exchange site, H_P^+, and the free metal ion, M^+, i.e.,

$$M_P^+ + H^+ \rightleftharpoons H_P^+ + M^+$$

When the paper was washed with water prior to chromatography of the weak acid, a larger spot resulted. This was presumably because the water supplies hydrogen ion to some of the exchange sites during the washing process, making fewer available for exchange during the chromatographic process.

Ultee and Hartel expected that the acid pre-washings would replace any cations occupying exchange sites with hydrogen ions. If the so-called "affinity series" were valid, there would be no change in the exchange capacity since lead ion has one of the highest affinities for carboxyl groups. They reported no essential change in the value after the acid wash.

The findings of Ackermann and Krüger seriously contradicted these results. Using paper designated as VEB Spezial-papierfabrik Niederschlag WF 1 (unwashed) and WF 11 (acid washed), they found that the exchange capacity dropped from 0.0057 milliequivalents per gram for the unwashed to 0.0044 milliequivalents per gram for the acid washed paper. If the paper is washed first with hydrochloric acid and then with sodium hydroxide, the exchange capacity returns to nearly the unwashed value (0.0054 milliequivalents per gram of paper). The explanation offered is that the acid wash causes lactone ring formation by reaction of the hydroxyl and carboxyl groups which are present in the paper, thus decreasing the number of exchange sites. The lactone rings are then cleaved by treatment with sodium hydroxide, making the carboxyl groups again available for exchange. No infrared spectral data were reported to confirm this hypothesis.

Ultee and Hartel applied infrared spectroscopy to investigate the possibility of splitting the lactone rings which may be present in untreated and in oxidized cellulose. They found that lactone rings

are cleaved during the chromatographic process, thus causing errors in carboxyl determinations in papers of high lactone concentration. This would indicate that, if rings are formed during the acid treatment as was reported by Ackermann and Krüger, they should be broken during the chromatographic process with the lead solution so the exchange capacity is always independent of the lactone content. Ultee and Hartel made no investigation of the presence of lactone rings on acid washed paper.

Statement of Problem

Earlier work by Keller and Rommel[12] concerning the appearance of multiple spots during the chromatography of phosphate species made it desirable to know the exchange capacity of Whatman #1 paper. This thesis attempts to clarify the reported values and techniques of carboxyl group determinations in filter paper. The problem was attacked as follows:

a) Determination of the exchange capacity of Whatman #1 paper by the method proposed by Ultee and Hartel and by Schröder's modification.

b) Application of the above methods for the determination of the exchange capacity to commercial papers of very high, known exchange capacity to determine the reliability of the methods.

c) Determination of exchange capacity of pre-treated papers to investigate the effect thereof. Pre-treatment included pre-washes

of acetic acid, perchloric acid, EDTA (disodium salt), ammonium hydroxide, and an acid followed by a base.

EXPERIMENTAL

The paper used in this research was commercially available Whatman #1. The 47 x 55 centimeter sheets of filter paper were cut into strips 2.8 centimeters wide and 55 centimeters long. The solution to be chromatographed was applied three centimeters from one end with a standard Misco microliter pipet calibrated to deliver. The strips were then hung in a water vapor saturated chromatographic tank and immediately chromatographed in the ascending manner. The developer was boiled distilled water. In order not to disturb the tank's equilibrium when the papers were hung, the top was displaced as slightly as possible. When pre-treated papers were used, the chromatograms were run in sets with one chromatogran of each kind of paper constituting a set. This procedure was followed so that conditions would be the same for each set of results. The strips were allowed to hang in the tank until the solvent front had progressed to about twenty centimeters from the bottom, requiring 1 1/2 - 2 hours. The strips were removed and allowed to hang in a stream of hydrogen sulfide gas to make the spots visible. In later experiments, the spots were located by spraying with dithizone (0.03% in acetone). The latter method was more effective in the production of well-defined spots. The chromatograms were allowed to dry in air and the spots were

traced on to the heavy weight biology paper. The spots were then cut out and weighed. A planimeter was found to be unsatisfactory. The weight-per-unit area of this paper and the Whatman #1 paper were then determined by drawing and weighing several 2 x 2 centimeter squares. With this data the exchange capacity in milliequivalents of lead per gram of paper was calculated.

For example:

$$\frac{0.0874 \text{ gm. biol. paper}}{0.01621 \frac{\text{gm. biol. paper}}{\text{cm}^2}} = 5.3917 \text{ cm}^2$$

$$5.3917 \text{ cm}^2 \times \frac{.0086025 \text{ gm. Whatman \#1}}{\text{cm}^2} = 4.638 \times 10^{-2} \text{ gm. Whatman \#1}$$

$$\frac{2 \times 10^{-4} \text{ meq of } Pb^{++}}{4.638 \times 10^{-2} \text{ gm Whatman \#1}} = 4.312 \times 10^{-3} \frac{\text{meq}}{\text{gm}}$$

Solutions used were made from AR grade lead chloride and lead nitrate manufactured by Mallinckrodt. Concentrations varied from 0.01M to 0.1M and sample volumes varied from 5 to 100 microliters. The volume and concentration were chosen in order to produce a traced spot weight of 0.1 - 0.2 grams (6 - 12 square centimeters). For example, combinations used on Whatman #1 paper (exchange capacity of 0.005 meq/gm) were 10 microliters of 0.01M lead nitrate and 10 microliters of 0.02M lead nitrate. The data on the two papers of high and known exchange capacity follow:

1) Whatman Paper Chromedia CM81 - Ion Exchange Cellulose
   Carboxymethyl Cellulose
   Basis Weight - 85 grams per square meter
   Nominal Capacity - 0.5 milliequivalents per gram
   Catalogue Number 22811
   Batch Number 1000/1

2) Whatman Ion-Exchange Cellulose - Cellulose Phosphate P81
   Basis Weight - 85 grams per square meter
   Nominal Total Capacity - 2.1 milliequivalents per gram
   Catalogue Number 21811
   Batch Number 64/78/2

The pre-washing of the papers consisted of placing five strips into a two-liter beaker filled with the washing solution. The solutions used were 2M acetic acid, 1M perchloric acid, 0.1M EDTA (disodium salt), and 2M ammonium hydroxide. After being washed for about 15 minutes, the papers were removed and again washed in successive two-liter distilled water washes to remove the excess solution. When the pH of the water wash was the same as the distilled water (4.5) (using narrow range pH paper), washing was discontinued; usually three rinses were sufficient. The papers were then hung in a chromatographic oven and dried at room temperature. The oven served to speed drying by circulating air around the hanging strips by forced draft.

DISCUSSION OF RESULTS

The calcium method for the determination of exchange capacity proposed by Yackel and Kenyon was tried with Whatman #1 paper. The amount of acid released was so small that the method was immediately discarded as wholly unsuitable for the determination, due to the insensitivity of titrations.

The exchange capacity of the Whatman #1 paper was further determined by the procedure proposed by Ultee and Hartel and also by this same method with the modifications suggested by Schröder. The results of these experiments are summarized in Tables 1 and 2 respectively, which gives the exchange capacity in milliequivalents per gram of paper; n is the number of determinations made, i.e., the sample size. For each type of paper, there is essentially no difference in the results of exchange capacity and standard deviation, i.e., the exchange capacities and the standard deviations for the untreated paper by the methods of Ultee and Hartel and Schröder are comparable; the same is true for the acetic acid washed papers, etc. The conclusion is that the differences observed are not due to the different methods. Differences arise for different pre-treatments with the same method. The results with acid washed paper are consistent with those of Ackermann and Krüger rather than Ultee

TABLE 1

EXCHANGE CAPACITIES OF WHATMAN #1 PAPER WITH VARIOUS PRE-TREATMENTS BY THE METHOD OF ULTEE AND HARTEL

Pre-treatment	Exchange Capacity	Number of Samples	Standard Deviation
Untreated	4.382×10^{-3}	10	0.2424×10^{-3}
Acetic Acid Washed	3.220×10^{-3}	10	0.2649×10^{-3}
Perchloric Acid Washed	2.456×10^{-3}	10	0.480×10^{-3}
Na_2EDTA Washed	3.233×10^{-3}	10	0.430×10^{-3}

TABLE 2

EXCHANGE CAPACITIES OF WHATMAN #1 PAPER WITH VARIOUS PRE-TREATMENTS BY THE METHOD OF SCHRÖDER

Pre-treatment	Exchange Capacity	Number of Samples	Standard Deviation
Untreated	4.091×10^{-3}	10	0.172×10^{-3}
Acetic Acid Washed	3.320×10^{-3}	10	0.362×10^{-3}
Perchloric Acid Washed	2.735×10^{-3}	10	0.493×10^{-3}
Na_2EDTA Washed	3.606×10^{-3}	10	0.461×10^{-3}

and Hartel, i.e., the exchange capacity decreased with paper pre-washed with acid. The explanation proposed by Ackermann and Krüger for these results is lactone ring formation. The decrease of exchange capacity is greater with the perchloric acid than the acetic acid, possibly because of the relative strengths of the two acids and their ability to form lactones. The acid was not expected to oxidize the paper for it is difficult to see how exchange capacity could be decreased by an oxidative reagent which would produce carboxyl groups. The EDTA washed paper was used to determine the effect of the possible presence of heavy metal cations. If these cations were occupying the exchange sites, they should be replaced by sodium or hydrogen ions from the EDTA, to make the sites more available and increase the exchange capacity. The exchange capacity dropped slightly, however. This might be due to some lactone ring formation from the very weak acid groups present in EDTA. The presence of heavy metals would then seem to have no major effect on the exchange capacity.

Table 3 shows the results of determinations of exchange capacities of special ion-exchange paper, Whatman CM 81 (carboxymethyl cellulose) with various pre-treatment. The results follow the same trends as the Whatman #1 paper, but far more dramatically. The exchange capacity is reduced by about a factor of ten after acid pre-washing, much greater than the effect in the Whatman #1 paper. Most pronounced, however, is the difference between the reported

TABLE 3

EXCHANGE CAPACITIES OF WHATMAN CM-81 PAPER WITH VARIOUS PRE-TREATMENTS BY THE METHOD OF ULTEE AND HARTEL

Pre-treatment	Exchange Capacity	Number of Samples	Standard Deviation
Untreated[a]	0.2093	18	0.00814
Acetic Acid Washed	0.02034	8	0.00157
Perchloric Acid Washed	0.02050	9	0.00207
Na_2EDTA Washed	0.2827	10	0.02134
NH_4OH Washed	0.4544	9	0.00628
$HClO_4$ - NH_4OH Washed	0.3770	7	0.01701

[a]Manufacturer's reported exchange capacity is 0.5 meq/gm

value of 0.5 milliequivalents per gram and the determined value of 0.2093 milliequivalents per gram, less than half the reported value. The determinations approached the reported value only when the paper is pre-washed with ammonium hydroxide. To test the lactone formation explanation, the paper was washed with perchloric acid, decreasing the exchange capacity, and then with ammonium hydroxide to see if the capacity is restored. The results show that the exchange capacity returns to a value greater than that of untreated paper, but less than just base washed paper. Presumably, there are lactone rings present in the unwashed paper which are broken on treatment with base, and the rings formed with acid treatment are not all broken with the following basic wash.

The third paper tested was Whatman P 81, cellulose phosphate paper. The results, shown in Table 4, are particularly interesting because the pre-wash has essentially no effect on the exchange capacity. The arithmetic means differ slightly, but the differences are within the standard deviations. The consistancy of results even after acid treatment indicates that the phosphate does not form the internal ester as in the other papers. But, most important, the exchange capacities vary from 0.6652 - 0.7682 as compared to a reported 2.1 milliequivalents per gram from the manufacturer. The method of determination of this value by Whatman Company is unavailable.

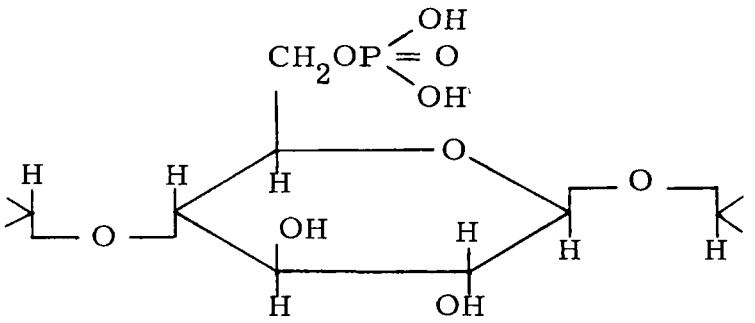
TABLE 4

EXCHANGE CAPACITIES OF WHATMAN P 81 PAPER WITH VARIOUS PRE-TREATMENTS BY THE METHOD OF ULTEE AND HARTEL

Pre-treatment	Exchange Capacity	Number of Samples	Standard Deviation
Untreated[a]	0.7682	8	0.02612
Acetic Acid Washed	0.7247	7	0.06783
Perchloric Acid Washed	0.6925	7	0.04887
Na_2EDTA Washed	0.7682	8	0.03470
NH_4OH Washed	0.7774	8	0.03927
NH_4OH - $HClO_4$ Washed	0.6652	7	0.02094

[a]Manufacturer's reported exchange capacity is 2.1 meq/gm

The assumption was made by all the earlier mentioned workers that the cation used for exchange occupied every available exchange site because these cations had high affinities for carboxyl groups. There is no reason to assume this is true for the phosphate paper where the exchange site is a phosphoric acid, i.e., the cellulose phosphate structure proposed by Knight.[13]



The low exchange capacities obtained with the Whatman CM 81 challenges the validity of this assumption.

LIST OF REFERENCES

1. Lederer, S. and M. Lederer, Chromatography, Elsevier Publishing Co., New York, 1953

2. Hanes, Charles S. and F. A. Isherwood, Nature, 164, 1107(1949)

3. Kolthoff, I. M., Pharm. Weekblad, 58, 233(1921)

4. McLean, D. A. and L. A. Wooten, Ind. Eng. Chem., 31, 1138(1939)

5. Shute, J. B., Nature, 171, 839(1953)

6. Yackel, Edward C. and William O. Kenyon, J. Am. Chem. Soc., 64, 121(1942)

7. Forziati, F. H., J. W. Rowen, and E. K. Pyler, J. Research Natl. Bur. Standards, 46, 4(1950)

8. Ultee, A. J., and J. Hartel, Anal. Chem., 27, 557(1955)

9. Schröder, Karl Heinz, Chemiker-zeitung. Cothen, 81, 558(1957)

10. Ackermann, G., and G. Krüger, Z. Anal. Chem., 191, 17-30(1962)

11. Epstein and Lewin, Textile Research J., 30, 652-5(1960)

12. Rommel, M. A., Ph. D. dissertation, University of Arizona, Tucson, Arizona, (1964)

13. Knight, C. S., Chromatographic Reviews, 4, 69(1962)