

Thesis Approved

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CHROMATOGRAPHIC FRACTIONATION
OF THE HYDROUS OXIDE IONS

BY
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CHAPTER I

INTRODUCTION

Chromatography is the name given to a technique for the analysis of mixtures by passage of their solutions through an adsorbent column. The different constituents adsorb at different rates, and advantage is taken of this property to separate the components into different sections of the column.

Schoenbein¹⁰ in 1861 was the first to show that, when aqueous solutions rise in strips of filter paper, the water precedes the dissolved material, and the relative height of ascent of solutes can differ enough to make it possible to detect the co-solutes in separate zones. He called this new phenomenon "capillary analysis" and predicted its usefulness in the field of analytical chemistry.

Chromatography was almost completely neglected until 1931, when it was actually re-discovered by Kuhn, Winterstein, and Lederer,⁶ who applied it to the resolution of plant carotene into its components. Then followed a period of rapid development. It was an exceptionally fruitful step which led Consden⁴ in 1944 to resort to the use of filter paper as the inert support for his detection of the amino acids. The ease with which

he was able to make separations was a demonstration of its possibilities--possibilities which have been realized in its application in all fields of analysis.

Large numbers of important separations have been achieved by many workers in the field who have tended to concentrate on special separations rather than on general methods of separating ions. Pollard and co-workers⁷ have concentrated on separations advantageous to the general field of qualitative analysis.

The extensive literature now devoted to paper chromatography illustrates a great number of variations in technique and apparatus, but the method essentially consists in applying a small amount of the solution containing substances to be separated to filter paper. The spot is dried and a developing solution allowed to flow past the spot by capillary action. Solutions containing colored constituents give sharp separations into individual zones. In the case of the colorless ones chromogenic reagents are used for identification.

Student results in the qualitative laboratory show that all ions are not identified with the same ease. In the case of the hydrous oxide ions, aluminum, zinc, chromium, iron, and manganese, extensive coprecipitation makes analysis difficult. In analyzing this group, the principles of chromatography could be illustrated and at

the same time would provide a more successful method of identification than the conventional method now employed. It is therefore the purpose of this study to investigate past chromatographic studies in order to choose or develop a method suitable for the solution of this problem, the separation and identification of these five ions.

CHAPTER II

THEORY

Inorganic separations on filter paper are possible with suitable solvents. It was originally believed that the paper functions solely as an inert support for the aqueous portion of the developing solvent, hence the name paper partition chromatography. It is now generally recognized that commonly paper chromatography functions by a combination of partition, adsorption, and ion exchange. Even though adsorption and ion exchange must be present to some extent, the predominant factor is usually that of partition between two immiscible phases.

Theoretical concepts have been developed in the course of time, but owing to the many variables involved in even the simplest separation, these considerations in the physico-mathematical sense have had singularly little effect on practical procedure. As this study is to be practical in nature, these mathematical concepts need not be included here.

The course of development in a paper chromatogram may be visualized in the following terms:

A zone of the mixture to be separated is placed as a spot or streak on the paper in a position which is to be some relatively small distance away from the surface

of the developer. The edge of the paper is dipped into the developer, or alternatively, the paper is first exposed to the vapors of the developer, then the edge near the zone is dipped into the developer. The developer passes by capillary action along the paper past the zone of the mixture. The rate of movement of the liquid is governed at least by its viscosity, surface tension, and density, and by the porous structure of the paper.

A small element of liquid, say at the advancing edge of the developer, comes into contact with the zone of mixture after rising from the surface of the developer to the region of application of the zone. The liquid picks up the substance(s) in its passage over the zone, possibly reaching saturation, if the zone be a large one. When the element of solution reaches the far edge, it comes into contact with a region of paper empty with respect to solute. Here, in conformity with Le Chatelier's principle, solute passes out of the developer. The small element of developer moving forward progressively loses solute until after a small distance beyond the initial zone it becomes virtually empty of solute. Thus the developer operates as a moving vehicle which transports solute from the rear to the front of a zone.

The next following small element of solution passes through a similar cycle. The summation over a

large number of these cycles represented by the flow of a certain volume of developer results in the movement of the zone in the direction of flow of the developer. The process relies on a distribution taking place between the mobile developer and the nonmobile phase. That component of the mixture which passes to the largest extent into the developer, and which hence tends least to pass into the nonmobile phase, is transported farthest along the paper by a given volume of developer. It shows the highest R_f value. R_f may be defined as the ratio of migration of solute to that of the solvent. If the substance does not pass out of the developer, it travels with the front of the developer and shows an R_f of approximately one. The R_f of a solute reflects its distribution between the two phases.⁵ The distribution depends not only on the nature of the solute, but also on the compositions and chemical natures of the phases. The R_f values are consistent for a given set of variables such as temperature, pH, solvent, time, and complexing agents. They lose their significance when any one of the variables is changed. The R_f values obtained by circular-paper chromatography are somewhat higher than those obtained by linear methods. Surak⁹ suggests the symbol R_{fc} for values obtained in circular-paper chromatography.

To locate spots on a completed chromatogram, any

reagent which produces a color or fluorescence or quenches fluorescence may be used.

In order to insure results there are certain simple rules to be followed:

1. The composition of the flowing solvent should be kept constant throughout the development. This is done by keeping the chromatogram in an enclosed chamber, the space of which is saturated with the developing solvent at constant temperature.
2. The developing solvent should move at a relatively slow rate. The rate of solvent flow is dependent on the type of paper used, on the ratio of the width of the "wick" to that of the paper chromatogram, on the composition of the solvent, and on the temperature of the chromatogram chamber.
3. The choice of a solvent should be one in which the components to be separated have a small but definite solubility. If the substances are too soluble then they will appear at or near the solvent "front" of the chromatogram. If they are too insoluble in the solvent they will remain at the point of application. If the factors of adsorption and ion exchange are neglected, the movement of a substance in a paper chromatogram is a function of its solubility in the developing solvent. Thus, solvents for water-soluble

substances are usually water-containing organic compounds, while solvents for substances soluble in organic solvents but insoluble in water are often aqueous solutions of organic solvents.

4. Sample spot must be dry before placing in the developing solvent or it will be diluted, resulting in a poor separation.¹
5. The air must be free of H_2S gas or precipitation of zinc, iron, and manganese will occur immediately after sample solution is placed on the paper with no resulting migration. Aluminum and chromium do not form sulfides, or if they do, the sulfides are soluble.³

CHAPTER III

METHOD

Circular-filter paper chromatography is a very simple and rapid method of qualitative analysis which lends itself particularly well to the separation under study. Rutter⁸ is generally credited with originating this technique. The method has greater sensitivity, resolving power, and reproducibility than other methods of paper chromatographic analysis. The principle of this technique is that the substances to be analyzed are resolved into circular zones instead of bands and spots. A tail is cut from a circular filter paper disk and immersed into the developing solvent after a drop of the substance to be analyzed has been deposited on the paper at the joint.

Apparatus

A large mayonnaise jar may be used for the chromatogram chamber and a #0 crucible, 15 ml., set in an evaporating dish is used for the solvent. These form a support for the filter paper. A disk of Whatman #1 filter paper 12.5 cm. in diameter is very suitable. A tail is fashioned by making two parallel cuts, about 1.2 cm. apart from the same edge up to the center of a circular

filter paper, and the tail is bent at the joint perpendicular to the plane of the paper and cut down to about 1.5 cm. in length. Care must be taken that the cuts are of equal lengths, because otherwise the development may not result in truly circular zones. Pipettes made from capillary tubing are used to apply both sample solution and chromogenic reagents to the disk.

Experimental Procedure

Sample Solution

In preparation of the solution to be analyzed, nitrates or chlorides should be used since salts of these metals are soluble and show little tendency to hydrolyze. Mixture of the cations used in this study were present as chlorides. Ten ml. of the unknown mixture were prepared. The concentration was made 4% in respect to each cation present, then the 10 ml. were acidified with 1 ml. of concentrated HCl. A concentration of 2% to 5% can be separated. Above 5% the ions begin to overlap.

Developing Solvent

The separation of Al, Cr, Fe, Mn, and Zn was obtained by using a developer consisting of dioxane-anti-pyrine-HCl. This system is similar to that used by Pollard.⁷ This system contains a complexing agent, and the solubility of the metal complexes in the organic

solvent determines the rate of movement of a zone along the paper rather than the solubility of the metal ion of the salt itself. To prepare the solvent 0.1 g. antipyrine was dissolved in a mixture of 18 ml. pure dioxane, 1 ml. concentrated HCl and 4 ml. H₂O. This solution was then placed in the crucible and enclosed in the chromatogram chamber.

Chromogenic Reagents

These were prepared as follows:²

Hypochlorite Solution.--This solution was purchased but it could be freshly prepared. Eight ml. of chlorine water, plus 2 ml. 5 N sodium or potassium hydroxide, plus 2 g. sodium or potassium chloride.

Dithizone.--Solution contained 1 to 2 mg. diphenylthiocarbazone in 100 ml. carbon tetrachloride.

Aluminon.--0.1 g. aurintricarboxylic acid and 1 g. ammonium acetate were dissolved in 25 ml. of 10% glacial acetic acid and was filtered.

Development

A streak of the unknown to be analyzed was placed along the wick joint of the filter paper disk and air-dried. (See Plate I.) The disk was then laid on the crucible so that its surface was about 8 mm. above the surface of the solvent and so that its tail was immersed

in the solvent. The circle was developed to a diameter of 6 cm. and required about an hour.

Identification of zones

After development, the chromatogram was air-dried and the individual zones were identified with chromogenic reagents applied with capillary pipettes. For the chromatogram in Plate III, the individual zones were identified according to the order given here.

The iron formed an orange complex with the developer, which when treated with aluminon formed a purple colored zone. By streaking dithizone from the outer edge of the disk, a pink circle indicated the position of zinc on the outer edge of the iron zone. Chromium was visible as a very faint green just inside the orange circle made by the iron. NaOCl was applied to this circle and the chromic ions were oxidized by the alkali hypochlorite to chromate ions and formed a yellow zone. Brown manganese dioxide was formed and its position was indicated when NaOCl was streaked from the chromium zone towards the center. Aluminum produced a red circle with aluminon just inside the manganese circle.

Alternatively test sectors could be cut from a chromatogram, and the positions of the ions could be determined separately by using the test sectors as a guide to mark their positions on the main chromatogram.

CHAPTER IV

CONCLUSION

In a review of the literature several methods and various solvents suggested themselves as possible instruments for the satisfactory analysis of this group by chromatography. The ascending-descending technique of Block¹ was chosen as it seemed to offer the simplest method of approach. The filter paper sheet containing the spots to be analyzed was draped over a glass rod, the long end was immersed into the solvent in such a manner that the solvent climbed by capillary action up the paper past the support rod and down the other side.

Some of the solvents tried were: butanol-benzoylacetone, collidine-water, methylethylketone, formic acid, and dioxane-antipyrine. The last mentioned gave some satisfactory results. The results were quite satisfactory for zinc, aluminum, and manganese, whereas for chromium and iron the results were nil. Iron was not too difficult to identify, but in all instances there was much diffusion and tailing. Chromium proved to be the most difficult because it also diffused and no suitable reagent could be found to identify it.

Other methods tried were: two-dimensional chromatography, multiple development, and circular and

horizontal chromatography. The circular and horizontal technique proved to have greater resolving power than the other methods tried and the excess diffusion and tailing were eliminated. The concentrations of the components of the solvent were adjusted until a satisfactory separation was obtained.

According to the results of this study, paper chromatography places the application of chromatography within the capabilities of beginning chemistry students and at the same time gives a satisfactory method for the analysis of a group difficult to analyze by other conventional methods.

Plates I and II (pages 16 and 17) are pictures of the apparatus used. Plate III (page 18) is a picture of a completed chromatogram.

The Table (page 15) contains data which were obtained in the separation of these cations. The R_{fc} value, chromogenic reagent, and color are listed for each cation. The determination of R_{fc} values is not necessary for qualitative procedure. Not too much attention should be paid to the actual R_{fc} values, but rather to their relative values. These indicate that separations will occur and the relative positions the cations will occupy after their separation.

TABLE 1
 CATIONS USED, TYPE OF PAPER, DEVELOPER, CHROMOGENIC
 REAGENT, COLORS PRODUCED, R_fC VALUES OBTAINED,
 AND TIME OF RUNNING

Type of paper	Whatman #1		
Time	1-1½ hrs.		
Solvent	dioxane-antipyrine-HCl		
Cation	Identifying Reagent	Color	R _f C
Al	Aluminon	Red	0.61
Cr	NaOCl	Yellow	0.71
Fe	Aluminon	Purple	0.76
Mn	NaOCl	Brown	0.84
Zn	Dithizone	Pink	0.89

The simplest procedure has been devised and can be carried out by the most inexperienced. The separations desired can be obtained as long as care is taken to keep constant all the conditions which have been pointed out to have an effect on the separations.

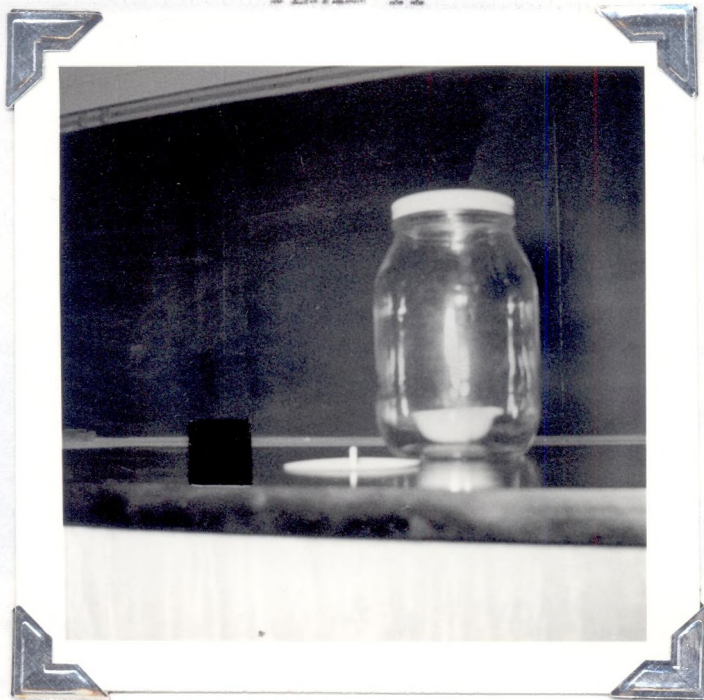
PLATE I



The Orange coloring along the wick joint indicates the position of the ion mixture prior to separation.

PLATE II

PLATE II



Apparatus Used

Completed Chromatogram.--Fig. 2. The colors produced--from the outer to the inner edge are: Yellow, Orange, Red, Purple, Blue, Green, and White.

PLATE III

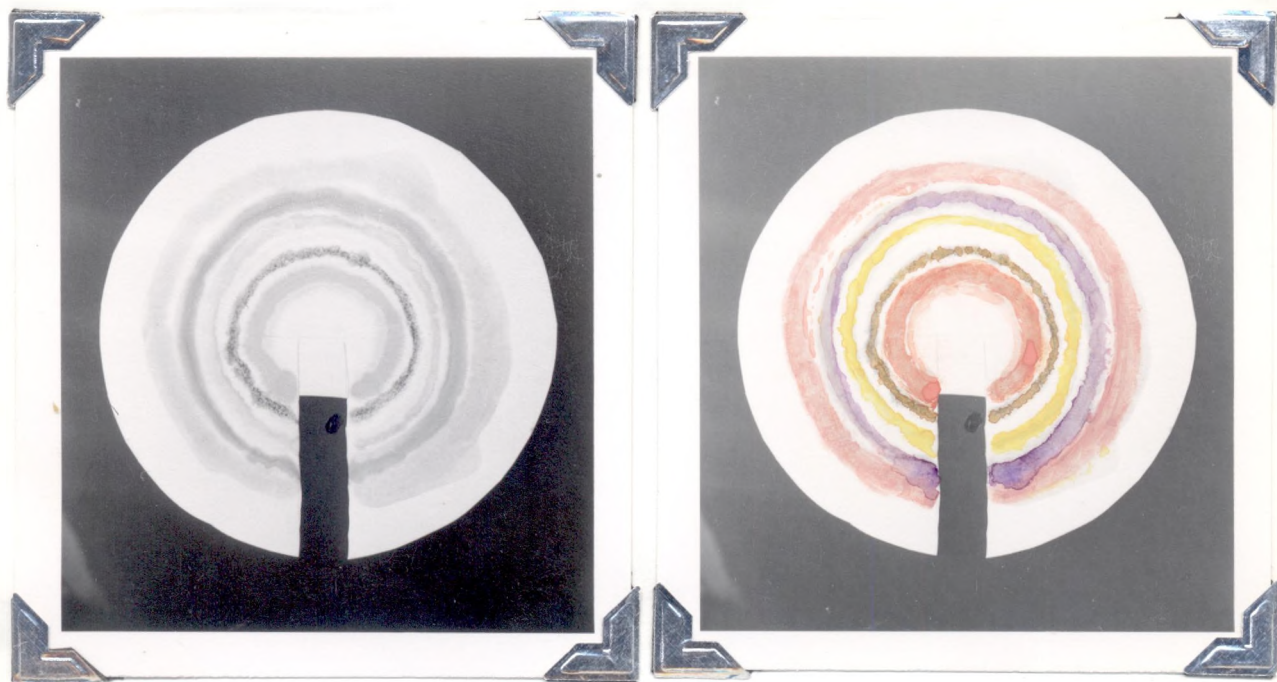


Fig. 1

Fig. 2

A Completed Chromatogram.--Fig. 2 has been tinted to show the colors produced--from the outer circle to the inner circle: Pink, Zn; Purple, Fe; Yellow, Cr; Brown, Mn; Red, Al.

B I B L I O G R A P H Y

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