

MULTIPLE SPOT PHENOMENON IN INORGANIC CIRCULAR PAPER CHROMATOGRAPHY

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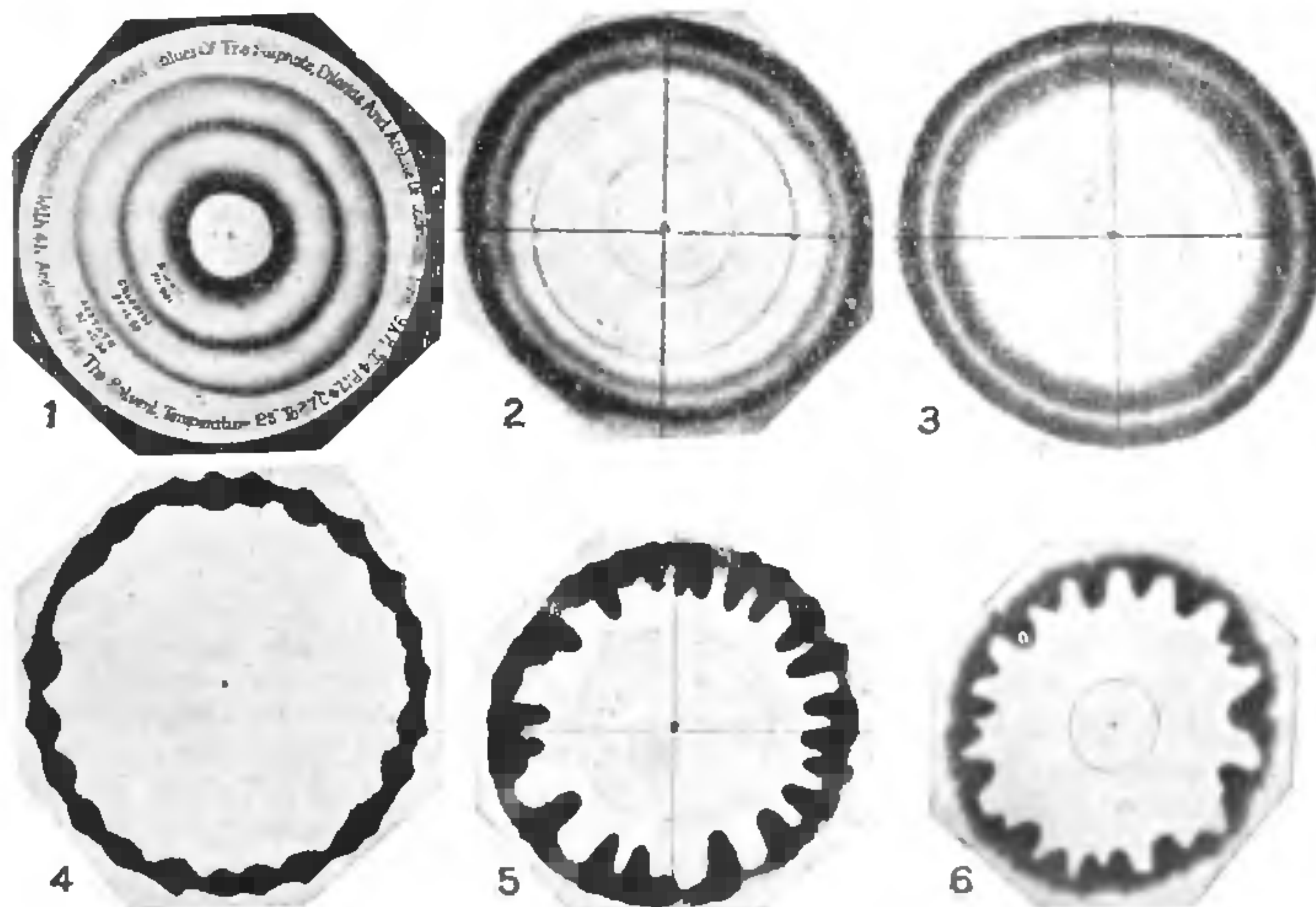
DURING our studies of circular paper chromatography of inorganic ions, certain peculiar results were noticed in some cases (about 10%) although uniform experimental conditions were maintained. A brief account of such results is given in the present communication.

The general technique of chromatography was the same as described earlier.¹ Whatman No. 3 filter-paper discs were used throughout. 0.05 ml. of solution which was 0.05 M. with respect to the salt was used for each experiment. The metallic bands were identified by spraying ammoniacal hydrogen sulphide. The chromatographic experiments were carried out in airtight chambers at $27 \pm 1^\circ \text{C}$.

It was shown² that cations like copper and cadmium can be separated into different bands corresponding to several anions associated with the metal such as sulphate, chloride, nitrate

acetic acid (1, 2, 3 N) (Fig. 2). Similarly when copper nitrate was chromatographed with the solvent, butanol saturated with 3 N acetic acid, the metallic band separated into two rings corresponding to nitrate and acetate (Fig. 3). Copper chloride also exhibited two rings, one of which was due to chloride and the other to acetate. Lead acetate irrigated with a solvent containing ethyl alcohol acetic acid and water developed two rings similar to copper salts. It was also noted that no such clear separations occurred when the irrigating solvent contained hydrochloric acid (3 N) instead of acetic acid.

In some other instances, the metallic bands exhibited a peculiar shape in the contour. Fig. 4 was obtained with copper chloride irrigated by *n*-butanol-6 N acetic acid (1:1). Fig. 5 is a chromatogram developed by copper chloride with the solvent butanol-5 N acetic

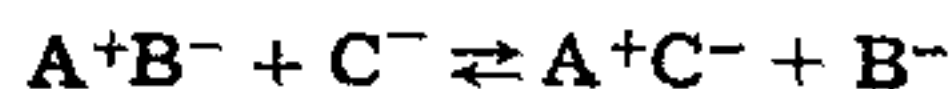


and acetate (Fig. 1) when irrigated with a solvent like butanol saturated with 4 N acetic acid. It was found subsequently that even a pure single substance such as copper acetate gave rise to two rings after irrigating the spotted disc with butanol saturated with dilute

acid (1:1). Cadmium sulphate gave rise to a star-shaped picture (Fig. 6) when chromatographed with butanol-5 N acetic acid (1:1). It is difficult to explain how these distorted pictures are obtained. Surface tension and differential wetting would play an important role

in the spreading of the solution at the initial stages but it has not been possible to identify the surface active substance which influences such a course of development.

The possibility of such a separation of metallic bands corresponding to different anions associated with the cation has been accounted for³ on the basis of the equilibrium in the process of elution of a salt A^+B^- by a mobile phase containing C^- which can compete with B^- for A^+



When the acid H^+C^- is present in the irrigating solvent, the formation of AC depends on its strength and on its concentration. The hydrogen-ion concentration of the solvent medium influences the mobility of the ions to a considerable extent. While this can explain partly the separation of copper chloride or nitrate into two bands corresponding to (1) chloride and acetate, (2) nitrate and acetate in the abovementioned cases it is very difficult to account for the separation of copper acetate or lead acetate into two bands with the same solvent, viz., butanol-acetic acid.

The formation of double zones in partition⁴ chromatography has been attributed to the water-logging of the kieselguhr column when the solvent containing butanol was slightly undersaturated with water or held an excess of water in fine suspension. The composition of the solvent mixture is likely to alter as a result of such logging of water in the partition chromatography with substances like kieselguhr, silica gel or paper. Difference in temperature may also alter the composition of the solvent and introduce changes in R_f value. In the present series, multiple spots could not be obtained in every experiment conducted with butanol-acetic acid solvent containing different amounts of suspended water. Only two chromatograms out of 20 exhibited two rings corresponding to nitrate and acetate when copper nitrate was used to spot on the filter-paper. In a few trials, water was eliminated in the solvent by using only glacial acetic acid along with butanol. Even under such conditions there were a few instances where there was the formation of double rings of copper associated with nitrate and acetate. It was noticed that a wide halo surrounded the metallic band in a few

cases. In the light of the present observations it is extremely difficult to say that water content of the mobile phase greatly influences the chromatogram.

It has been observed that multiple spots are developed when the solvent used for irrigation contained a complex forming reagent with the metal under test, such as ammonia in the case of cadmium⁵ or aceto-acetic ester in the case of cobalt⁶ or benzyl acetone with copper.³ Such a separation of a single metal into different zones is attributed to the formation of different complexes which move with different R_f values. It should be noted that the present authors have obtained such clearly separated metallic bands even in the case of single common ion between the test solution and the solvent without the presence of any complexing reagent. "Ghosts" and "shadow" spots found along with the metallic spots were attributed to the alkaline earth and heavy metal impurities⁷ in paper in the case of the separation of phosphoric esters. In the present case, however, the analysis was mainly with metals such as Cu, Cd or Pb which remain unaffected even in the presence of such impurities in the paper.

It may be concluded from the present work that multiple spots can be obtained with a metal moving as two or more species. For quantitative analysis particularly, it is essential that a metal should move as a single band and give sharply defined boundary. It therefore becomes necessary to run a large number of experiments in order to be certain of the species obtained by chromatographic analysis.

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