

# Mechanism of Paper Chromatography of Inorganic Ions on Impregnated Papers: Separation of Ag(I), Cu(II), Ni(II), Co(II), Hg(II), Pb(II) & Fe(III)

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Migration of ions on filter papers impregnated with aqueous glycine (2%, w/v) and ammonium thiocyanate (4%, w/v) solutions has been studied. Organic solvents like alcohols, ketones and chloroform have been used as mobile phases to get the  $R_f$  data. The migration tendencies of different ions have been explained on the basis of a new mechanism of paper chromatography with impregnated papers using polar and non-polar solvents. The migration of inorganic ions in polar solvents (with donor properties) on untreated papers has also been studied.

MANY attempts have been made to explain the mechanism of paper chromatography<sup>1-10</sup>. Recently Janardhan and Paul<sup>11</sup> have tried to explain the migration of inorganic ions by proposing a stepwise mechanism involving (i) adsorption of the metal ion on the cellulose through ion association leading to ion-associated metal-cellulose complex, (ii) desorption of the ion due to its displacement by the proton of the acid present in the solvent and (iii) washing away of the desorbed ions by the irrigating solvent.

In view of the increased emphasis laid in recent years on the use of impregnated papers and the use of complexing agents in the mobile phase to get better separations, we have studied the paper chromatography of some inorganic ions on papers impregnated with aqueous glycine and ammonium thiocyanate solutions with a view to explaining the mechanism of paper chromatography. Comparative studies have also been carried out using untreated papers and solvents with donor properties (such as alcohols and ketones) and chloroform.

## Materials and Methods

To prepare the impregnated papers, filter paper discs (diameter = 11 cm, Whatman No. 1) were soaked in an aqueous solution of glycine (2%, w/v) or ammonium thiocyanate (4%, w/v). These were then dried in an inert atmosphere at room temperature and stored in polythene bags and properly sealed.

Nitrates (BDH, AR reagents) of Ag(I), Pb(II), Hg(II), Fe(III), Ni(II), Co(II) and Cu(II) were dissolved in doubly distilled water to get stock solutions of the ions (0.05M).

All organic solvents (except ethanol) used were of AR grade and were distilled once. Absolute ethanol was used. All mixed solvents were prepared on volume to volume basis from the required pure solvents.

For all the studies Rutter's technique of radial development<sup>12</sup> was adopted, but the wicks with

tapering free end (width 2 mm; length 2-3 cm) were prepared as described earlier<sup>13,14</sup> from untreated as well as treated (impregnated) papers. Spotting of the metal ions was done by micropipette (~0.02 ml or 30-50  $\mu$ g per drop). After the spots had been dried, development was carried out by irrigating with the required solvent system (~2 hr) in airtight chambers previously saturated with the vapours of the solvent concerned and water. The discs were taken out and after marking the solvent front these were dried by a cold air blast.

With glycine and ammonium thiocyanate impregnated papers, Fe(III), Co(II), Ni(II) and Cu(II) formed coloured glycinates and thiocyanates and could be detected without spray reagents but Ag(I), Hg(II) and Pb(II) were detected by spraying aqueous H<sub>2</sub>S solution. For detecting Cu(II), Co(II) and Ni(II) ions on untreated papers, rubeanic acid (0.5% in 90% ethanol) was used; while Fe(III) was detected by the spray of aqueous potassium ferrocyanide (5% w/v).

## Results and Discussion

$R_f$  data have been collected using seven different solvents with untreated and impregnated papers of the two types (Tables 1 and 2). With untreated

TABLE 1 —  $R_f$  DATA USING UNTREATED PAPER

Ion	$R_f \times 100$						
	A	B	C	D	E	F	G
Fe(III)	84*	94*	*	T	49	*	T
Co(II)	94*	96*	*	T	65	*	T
Ni(II)	74*	79*	*	T	T	*	T
Cu(II)	93*	94*	*	T	70	*	T
Ag(I)	33*	46*	*	T	26	*	T
Hg(II)	93*	92*	*	T	90	*	T
Pb(II)	59*	77*	*	T	58	*	T

\*Diffusion.

A = methanol, B = ethanol, C = isopropanol, D = *n*-butanol, E = acetone, F = methyl ethyl ketone, G = chloroform, T = tailing.

TABLE 2 —  $R_f$  DATA USING IMPREGNATED PAPERS

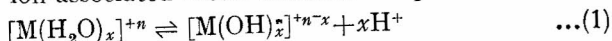
Ion	$R_f \times 100$						
	A	B	C	D	E	F	G
GLYCINE IMPREGNATED PAPER							
Fe(III)	95	87	93	—	90	72	—
Ni(II)	91	83	88	—	71	90	87
Co(II)	97	85	92	—	93	94	90
Cu(II)	85	*	93	—	80	78	88
Ag(I)	*	—	—	—	75	70	*
Pb(II)	60	—	—	—	79	73	*
Hg(II)	27	—	—	—	56	63	*
AMMONIUM THIOCYANATE IMPREGNATED PAPER							
Fe(III)	54	52	—	60	38	46	—
Ni(II)	72	60	—	97	63	34	—
Co(II)	87	64	—	90	93	81	—
Cu(II)	28	42	—	35	16	37	—
Ag(I)	16	24	23	30	27	15	—
Pb(II)	14	4	—	—	—	6	—
Hg(II)	63	41	37	46	92	49	—

\*Diffusion.

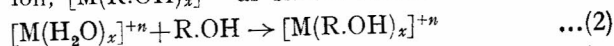
A, B, C, D, E, F and G refer to the solvents methanol, ethanol, isopropanol, *n*-butanol, acetone, methyl ethyl ketone and chloroform respectively.

papers, the ions showed considerable migration with the solvents, methanol, ethanol and acetone. However, migration was accompanied with diffusion for some ions. Solvents like methyl ethyl ketone and chloroform (which has no donor properties) failed to induce migration. The ions moved very efficiently in all the solvents (polar or non-polar) on impregnated papers indicating the possibility of many binary or ternary ionic separations (Table 3). On the basis of the mechanism of Janardhan *et al.*<sup>11</sup>, ions cannot migrate with organic solvents in the absence of dissociable protons (or acid). If this is true, the migration results with polar donor molecules and on papers impregnated with glycine or ammonium thiocyanate remain unexplained. A modification in working hypothesis of Janardhan *et al.*<sup>11</sup> is thus required for untreated papers and a new mechanism is required to explain the process on impregnated papers.

As per the mechanism suggested by Janardhan *et al.*<sup>11</sup> the aquo cation can release a proton (Eq. 1) and this temporarily released proton associates with the hydroxyl groups of the cellulose to form ion-associated metal-cellulose complex.



On irrigating the paper disc (or strip) with a polar solvent (A-F), a high concentration of the solvent molecules around the adsorbed metal ion is obtained and bound water molecules are replaced by the solvent molecules either partially or wholly. If this polar molecule is an alcohol (R.OH), then ion-association may lead to the formation of the ion,  $[M(R.OH)_x]^{+n}$  as shown below:



But the species formed cannot undergo dissociation of the type (1) to provide the hydrogen ions for linkage to cellulose structure and the metal ion gets desorbed from the cellulose base. The cation now

TABLE 3 — SEPARATION POSSIBILITIES OF IONS ON IMPREGNATED PAPERS WITH PURE SOLVENTS WITHOUT ACID IN THE SYSTEM

Ions separated	Glycine impregnated papers	Ions separated	Ammonium thiocyanate impregnated papers
	Useful solvents		Useful solvents
Ni(II), Co(II)	Methanol	Cu(II), Hg(II)	Methanol
Ag(I), Co(II)	do	Pb(II), Hg(II)	do
Pb(II), Hg(II)	do	Pb(II), Ni(II), Cu(II), Fe(III)	<i>n</i> -Butanol
Ag(I), Hg(II), Pb(II)	do	—	—
Ag(I), Hg(II)	Acetone	Pb(II), Cu(II)	Acetone
Ni(II), Co(II)	do	Ag(II), Hg(II), Pb(II), Cu(II), Hg(II)	do

present as desorbed material in the solvent-soaked filter paper competes for the free mobile solvent. Thus the nature of chromatographic mechanism changes to partition from adsorption. This is the type of expected mechanism in the case of a polar solvent with donor properties. But in the case of solvents having no donor properties, formations of ion-associated complexes are not possible and hence desorption of metal ion does not take place. This appears to be the reason for migration not taking place with chloroform or carbon tetrachloride as the solvents.

The lower alcohols and ketones, though sufficiently polar and having donor characteristics, move the metal ions with diffusion only. On the other hand a weakly polar solvent like *n*-butanol fails to bring about any movement of inorganic ions without the presence of a proton donor, i.e. acid in the medium.

In the cases of impregnated papers containing some complexing agent in the stationary phase, the process can be described in terms of metal-ligand complex formation.<sup>12</sup> The aquocation does not form the hydrogen-bonded ion-associated metal-cellulose complex and the fixing of the metal ion after spotting on the paper is due to metal-ligand complex formation. Hence the process of desorption is much easier in this case as no breaking of cellulose complex takes place. The irrigating solvent washes the complex compounds on account of its solvating tendencies for them.

In the case of glycine impregnated paper, protons will be released on complex formation with the metal ions. The released protons may also help in the desorbing process as indicated above. Similar release of protons is not possible in the case of ammonium thiocyanate impregnated paper. Hence it is expected that the migration of ions should be facilitated more on glycine impregnated paper as compared to that on ammonium thiocyanate impregnated paper. The metal-thiocyanate complexes thus appear to move only due to their solvation tendencies in polar organic solvents. The differential migration tendencies are displayed due to difference in solubilities of the complexes in organic solvents. Separations achieved on glycine impregnated

and ammonium thiocyanate impregnated papers (Table 3) with simple pure solvents (without the addition of acid) prove the utility of such papers.

Thus, the mechanism of chromatography on impregnated papers can be explained without involving the concept of ion-associated metal-cellulose complex. If the solvent is polar enough to replace the bound water in the aquocation, the presence of an optimum concentration of protons may not be essential for migration. Of course, the presence of protons will always be useful in getting compact bands or spots and better separations.

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