

## Quantitative Determination of Certain Cations by Paper Chromatography

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**Summary:** Qualitative and quantitative analysis of iron, zinc, cobalt, copper and nickel using paper chromatography is reported. Qualitative analysis was done by measuring  $R_f$  values of these metal cations whereas the quantitative estimation was done by colour comparison technique using Lovibond Tintometer.

### Introduction

Paper chromatography is a powerful tool for the separation of cations. It has been used as a group separation technique for qualitative analysis of these ions. Different people have used this technique for the separation of nickel, cobalt, copper, cadmium, lead, zinc, mercury, silver and manganese using different types of developing solvents [1-10]. All these methods were used for qualitative analysis.

Agrinier [11] used ascending paper chromatographic technique for the separation of nickel, in presence of cobalt, tantalum, copper and titanium and has determined nickel semi-quantitatively.

Estimation of metal ions in a mixture have been tried, by separation on a paper and then estimating the individual spot quantitatively by techniques such as spectrophotometry, densitometry, micro-analysis titration, by the measurement of the area of the spot and by visualizing with eye, or U.V. lamp etc. [12]. None of these methods was found successful for quantitative estimation. Most of them were used as semi-quantitative methods. The

present work is an attempt to develop a cheap quantitative technique for the estimation of iron, zinc, cobalt, copper and nickel in presence of each other from soil, ore and mild steel samples etc., by first separation by paper chromatography and then their estimation (on the strip) by Lovibond Tintometer. Such technique would thus simplify the method of determination of such metals present in traces and thus reduce the expenses and the time taken for such determination.

### Experimental

All reagents used were of A.R. grade. Distilled water was used for dilution purpose unless otherwise mentioned.

#### *Preparation of Reagents*

For preparation of 100 ppm standard mixture solution 4.04 g.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 3.53 g.  $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ , 4.03g.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 3.73g.  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  and 4.83g.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were accurately weighed and dissolved in 0.15M HCl in 1000

ml measuring flask. The volume was made upto the mark with 0.15M HCl. This would give 1000 ppm solution. 10 ml of this solution was further diluted to 100 ml with 0.15M HCl to obtain 100 ppm solution.

For different denominations of this solution 5ml, 10ml, 15ml, 20ml, and 25ml of the 100 ppm solution were taken in 100ml measuring flask and volume made upto the mark with 0.15M HCl to give 5, 10, 15, 20 and 25 ppm standard solution respectively which were used for calibration.

#### *Rubeanic acid*

0.5% (w/v) solution of rubeanic acid was prepared by dissolving 0.5g. of rubeanic acid in 60 ml of ethanol and the volume was made upto 100ml with distilled water.

#### *Dithiazone*

0.2g. of dithiazone was dissolved in 100 ml chloroform.

#### *Preparation of Soil Sample*

Soil samples from 3 different places of Cholistan Desert were collected. Each sample was mixed thoroughly and then heated at 105-110°C to a constant weight. It was then pulverized. 0.1g. of this ground soil was fused with 0.6g. of  $\text{Na}_2\text{CO}_3$ , 0.05g. of  $\text{Na}_2\text{O}$  in a platinum crucible as described by Vogel [13]. The contents after fusion were dissolved in 0.15M HCl to a 100 ml volume. Small quantity of this solution was used for determination of iron and manganese by the present method and the rest of it were used for estimation of iron [13] and manganese [15] by photometric methods. Results are given in Table-IV.

#### *Preparation of Steel Sample Solution*

Weighed 0.1g. of sample into a small beaker and to it was added 2 ml of conc. HCl. Heated the contents gently till the sample dissolved. The upto volume was made 100 ml. with distilled water. The results alongwith the certified values are given in Table-V.

#### *Quantitative Analysis*

35 x 5 cm strips of Watman No. 1 paper were used. With the help of a micro pipette about 0.0075 ml of the test solution was placed at a distance of 2 cm from the lowest edge of the paper strip. The strips were dried. Appropriate solvent was taken in a trough and was placed in chromatography chamber for 30 minutes to saturate it with the vapours of the solvent. The lower end of the strips was immersed in the solvent trough and the lid replaced. Six to eight strips were used at a time. After the solvent front had moved about 13 cm from base-line the strips were neutralized by passing it over an ammonia jar. Developing reagents, rubeanic acid and dithiazone [13] were then sprayed on the strips for establishment of colour complexes for visualization. Qualitative estimation of each metal ion was made by measuring  $R_f$  values.

#### *Quantitative Estimation*

Five different standard solutions were prepared from 1000 ppm stock solution of every cation (Table-III). Known quantity of each solution was applied to a strip. Same quantity of solution of unknown sample was applied to the sixth strip. All the six strips were simultaneously eluted with the solvent No. VIII. After the solvent had moved to the requisite length,

they were taken off the tank, dried neutralized and sprayed with the appropriate reagent as explained for qualitative work. Colour intensity of the spot was measured with a Lovibond Tintometer by colour adjustments (Table-III). The colour intensity of the spot (which was directly proportional to concentration of metal ion) was plotted against the concentration to obtain a calibration graph. The concentration of unknown sample was calculated from this calibrated graph. Different solvent mixtures tried with the time of elution are given below:-

*Solvent No. I*

Acetic acid 30 ml, 7.2N HCl 10ml, time of elution 3 hours, Temp. 23°C.

*Solvent No. II*

Acetone 20 ml, ethyl acetate 20 ml, ethyl-methyl ketone 3 ml, phosphoric acid 4 ml. Elution time 9 hours, Temp. 23°C.

*Solvent No. III*

Acetic acid 25 ml, Acetone 20 ml, ethyl acetate 20 ml, ethyl methyl ketone 3 ml, conc. HCl 10 ml. Elution time 2.3 hours, Temp. 23°C.

*Solvent No. IV*

Acetic acid 25 ml, acetone 20 ml, ethyl acetate 20 ml, ethyl methyl ketone 8 ml, conc. HCl 10 ml. Time of elution 2.9 hours. Temp. 23.5°C.

*Solvent No. V*

Acetic acid 10 ml, acetone 10 ml, ethyl acetate 10 ml, ethyl methyl ketone 8 ml, formic acid 10 ml, conc. HCl 10 ml. Elution time 4 hours, Temp. 23.5°C.

*Solvent No. VI*

Acetic acid 40 ml, acetone 20 ml, ethyl acetate 20 ml, ethyl methyl ketone 3 ml, conc. HCl 15 ml. Elution time 4.07 hours. Temp. 24°C.

*Solvent No. VII*

Acetic acid 50 ml, acetone 20 ml, ethyl acetate 20 ml, ethyl methyl ketone 3 ml, formic acid 5 ml, conc. HCl 10 ml. Elution time 2.45 hours. Temp. 30°C.

*Solvent No. VIII*

Acetic acid 60 ml, acetone 20 ml, ethyl acetate 20 ml, ethyl methyl ketone 3 ml, formic acid 10 ml, conc. HCl 10 ml. Elution time 1.45 hours. Temp. 30°C.

In another experiment when solvent VIII was used at 45°C the time of elution was reduced to 40 minutes and all the ions ran very close to each other showing a very poor resolution.

## Results and Discussion

The  $R_f$  values of various cations obtained by using solvents mentioned above are given in Table-I. Locating agents used and colours developed with different ions are given in Table-II. Solvent I is highly acidic and acidic conditions favour the separation of iron. However, the other 4 cations were poorly resolved. In solvent II, phosphoric acid being a heavy acid drastically reduced the rate of elution, so that in 9 hours, the solvent front moved only 13 cm. Viscosity of the mobile phase affects the rate of flow [14]. All the five cations appeared as one spot 4 cm from the base line. With solvent III, when acetone, ethyl

Table-1: Cation  $R_f$  value, Room temp. 20-30°C

Solvent R.T.	Iron	Zinc	Cobalt	Copper	Nickel
I	0.82	0.76	0.69	0.69	0.56
II	0.30	0.30	0.30	0.30	0.30
III	0.98	0.86	0.77	0.71	0.39
IV	0.99	0.86	0.76	0.71	0.15
V	0.99	0.65	0.58	0.46	0.11
VI	0.99	0.90	0.83	0.77	0.42
VII	0.99	0.55	0.49	0.38	0.10
VIII	0.97	0.52	0.42	0.31	0.06
VIII *	0.98	0.96	0.89	0.89	0.84

\*  
at 45°C.

Table-II: Locating Agents

Metal ion	Spraying reagent	Colour obtained
Iron ( $\text{Fe}^{+3}$ )	Dithiazone	Yellow brown
Zinc ( $\text{Zn}^{+2}$ )	Dithiazone	Pink
Cobalt ( $\text{Co}^{+2}$ )	Rubeanic acid	Yellow green
Copper ( $\text{Cu}^{+2}$ )	-do-	Olve green
Nickel ( $\text{Ni}^{+2}$ )	-do-	Blue purple

acetate and ethyl methyl ketone were used alongwith acetic acid and conc. hydrochloric acid, all the five cations were separated. Iron appeared as a band running with the solvent front while other 4 cations appeared as spherical spots.

The lower edge of the zinc and upper edge of the cobalt spots were slightly diffused. This diffusion however disappeared when quantity of ethyl methyl ketone was increased from 3 ml in solvent No. III to 8 ml in solvent No. IV and spots of zinc and cobalt were clearly separated. Still better resolution of the cations was obtained by slight adjustment of the quantities of contents in solvent No. IV and introduction of 10 ml of formic acid (solvent No. V). Spots of all the metal ions became more intense, spherical and their tailing effect was also minimized. Experiments were carried out with 6,7,8,9,10,20 and 25 mls, of formic acid in solvent V. Best results were obtained with 10 ml formic acid. For solvent No. V the ratio of acetic acid and conc.HCl in solvent No. III were slightly increased which caused all the cations to move slightly upward. Zinc instead of giving a clear

spot got diffused between the spots of iron and cobalt. By doubling the quantity of acetic acid and introduction of 5 ml of formic acid (solvent No. VII) in solvent No. III, resulted in a low  $R_f$  value for zinc, cobalt and copper which appeared like a single big spot divided into three differently coloured portions while iron appeared as a band along the solvent front.

Solvent No. VIII was prepared by increasing the amounts of acetic acid and formic acid in solvent VII to 60 and 10 mls respectively. This solvent gave the best resolution in our experiments. The spots were clear, symmetrical and symmetrically arranged. This solvent mixture proved to be most suitable for qualitative and quantitative determination of these metal ions.

When the experiment was repeated with solvent VIII at 45°C, the time of elution was drastically reduced. No resolution of cations was observed, rather they appeared as one big spot.

Many factors influence the separation of a mixture in partition chromatography. Solubility of the solute in the solvent has a foremost effect. Inorganic salts like Ni, Cu, Co, Zn and Fe are less soluble in organic liquid than in water. In the mixture of two solvents the solubility of a salt often but not always lies between its solubilities in the pure solvents [14]. Compounds that are soluble and highly ionized in water may not be so in another solvent [14]. From the results explained above, it was observed that these five cations in separation, always, appeared in order of Ni, Cu, Co, Zn, and Fe from the base line under the conditions employed. Solutes that remain near the base line do so because they are polar and their retention is favoured by the

polar aqueous stationary phase. Such solutes are made to move by increasing the polarity of the mobile phase. This is clear by comparing the  $R_f$  values of Ni, Cu, Co and Zinc in solvent I, which is highly polar and other solvents which are not so polar.

Rate of movement of a given component of the mixture also depends on its solubility in the stationary phase. More soluble substances travel more slowly than the less soluble ones. During their passage the substances undergo partition between the two phases and separation occurs due to their difference in partition coefficient. Rate of flow of the mobile phase depends on the viscosity of the phase too. Introduction of phosphoric acid (solvent II) a heavy acid, reduced the rate of flow of the mobile phase and hence the mixture was poorly resolved.

Repetition of experiment with solvent VIII at a higher temperature (from 30 to 45°C) showed interesting results. The time of elution was reduced to 40 minutes (from 1.45 hours) and no resolution of the cations was observed. This may be due to the fact that concentration in the two phases at equilibrium depend on the partition coefficient and since viscosity and partition coefficient are temperature dependent the separation of cations is drastically effected and solvent moves at a higher speed, with the rise of the temperature.

It was also observed that neutralization of the strips before spraying of the locating agent is a must. This is because the metal complexes formed with the chromogenic reagent are relatively more stable in neutral conditions.

Table-III: Quantitative determination of ions with Tintometer

	Concentration (ppm)										
	50	60	70	80	90	100	150	200	250	300	unknown
<u>Iron</u>											
Major colour yellow						0.1	0.2	0.3	0.4	0.5	0.2
Adj.colour Red.						0.1	0.1	0.3	0.3	0.3	0.1
Light Red.						0.8	0.9	0.9	0.8	0.9	0.9
Light Red						0.8	0.9	0.9	0.8	0.9	0.9
<u>Zinc</u>											
Major Colour (No adujst-ment required).	0.5	0.6	0.7	0.8	0.9						0.6
<u>Cobalt</u>											
Major colour light yellow	0.4	0.5	0.6	0.7	0.8						0.7
Adj.colour light pink	0.3	0.4	0.4	0.5	0.5						0.4
<u>Copper</u>											
Maj: Light Yellow	0.2	0.3	0.4	0.5	0.6						0.5
Adj.colours Light blue.	0.1	0.2	0.2	0.3	0.4						0.3
Light Pink	0.2	0.2	0.3	0.3	0.4						0.3
<u>Nickel</u>											
Maj: Light blue	0.1	0.2	0.3	0.4	0.5						0.3
Adj: Light Pink	0.1	0.1	0.2	0.3	0.3						0.2

Table-IV: Soil Samples Analysis

No.	Present Method		Standard Method	
	iron %	Mn%	iron%	Mn%
1.	3.12	0.265	3.128	0.28
2.	1.50	0.112	1.52	0.12
3.	0.89	0.301	0.86	0.32

Table-V: Standard Steel Samples Analysis

No.	Present Method %	Certified value%
1. BCS No. 3221 SS52	0.190	0.194
2. BCS No. 329 SS59		
Mn	0.125	0.120
Cu	0.068	0.072
Co	0.064	0.07

For quantitative determination of these cations experiments were run with known concentration of a metal using solvent VIII. The colour intensity was measured with a Lovibond Tintometer by colour adjustments (Table-III) and was directly proportional to the concentration of that metal ion. This colour intensity was plotted against the concentration to obtain a calibration graph. The concentration of the unknown sample was obtained from this calibration graph.

Results of metal ions in soil samples from Cholistan Desert are given in Table IV and that of British Steel Corporation standard sample in Table V. The values compare favourably with those obtained with standard photometric methods. The method is thus reliable, simple and could be applied for determination of these metal ions in soil, ore and mild steel samples etc.

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