Separation and Identification of Some Anions by Paper Chromatography

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Summary: Separation and identification of carbonate, acetate, nitrite, nitrate, sulphide, sulphate, chromate and dichromate were carried out by using paper chromatography. Various identifying agents and solvents were tried and R_f values were calculated. A mixture of dioxan, acetone and liquid ammonia was found the most successful solvent for these anions. Different parameters like composition of the solvent, pH and elution time were optimized.

Introduction

Paper chromatography is an important technique for the identification of a large number of inorganic and organic species. Though it has been in practice for a long time, relatively little information is available about its application to inorganic anions.

Halides are among the inorganic anions mostly studied by paper chromatography. Chih [1] separated chloride, bromide and iodide using a mixture of methanol, ethanol and aqueous ammonia as solvents and silver nitrate solution as locating agent. Halides could also be separated on papers impregnated with ferric hydroxide [2]. Canic and co-workers [3] separated a number of inorganic anions by thin layer chromatography. They used butanol, methanol and water system for the separation of nitrite, nitrate and sulphate ions. Very diffused spots with significant tailing were however obtained in this case. Different polyphosphates were also separated and later identified by radiometry [4,5].

The present investigations were carried out because of the lack of sufficient information about the separation and identification of acid group radicals. A number of acid radicals were separated and identified by using different solvent systems and some new locating agents. Different parameters concerned for best results were also optimised.

Experimental

Apparatus

Preliminary separations were made in 250 ml conical flasks using 2x12 cm strips of Grade 3 Chromatographic, B.D.H. paper. For final separations two dimensional glass tanks and 5x25 cm paper strips were employed.

Reagents

All the reagents used were of AnalaR-Grade. Distilled deionized water was used throughout the work.

Solutions of Anions

1% solutions of following salts were separated in distilled deionized water. Sodium nitrite, sodium nitrate, sodium sulphide, sodium acetate, sodium carbonate, potassium chromate, potassium dichromate, sodium sulphate and sodium sulphite.

Solvents

The following solvents were used as such (without any further distillation), acetone, methanol, ethanol, dioxane, isopropanol and ammonia solution (27% by weight).

Locating Reagents

1. Barium-sulphonazo (III) Solution

(Used for sulphate, sulphite and carbonate).

The reagent was prepared by mixing equal volumes of $2x10^{-3}$M solution of barium chloride and $2x10^{-3}$M solution of Sulphonazo (III).

2. Lead acetate solution (Used for sulphide)

1% solution of the reagent was prepared in distilled deionized water.

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Diphenylamine Solution (Used for nitrite and nitrate)

For this reagent, 0.1g of diphenyl amine was dissolved in 10 ml of concentrated sulphuric acid and diluted to 100 ml with acetone.

4. Lanthanum nitrate - iodine - ammonia solution (Used for acetate)

To prepare this reagent 20 ml each of 5% lanthanum nitrate, 0.01 N iodine solution and 1N ammonia solution were mixed.

5. Nickel-DMG Solution (Used for phosphate, carbonate, chromate)

50 ml of 2% nickel sulphate solution was mixed with 50 ml of 1% Dimethylglyoxime ethanolic solution. The red precipitate was filtered off and the clear filterate used as locating reagent.

Procedure

Preliminary Runs

To avoid the wastage of excess reagents, the preliminary runs were made in 250 ml conical flasks. 20 ml of appropriate solvent was taken in the flask. Chromatographic paper was cut to 2x12 cm strips. The end of the paper to be dipped in solvent was marked at 0.5 cm above the margin and spotted with the anion solution to be studied. The upper end of the paper strip was clamped in the groove, specially made in the cork. Now the strip was hanged. The conical flask was tightly closed by cork in such a way that about 0.2 cm of the strip was immersed in the solvent. Elution was continued for half an hour. After which the strips were air dried and movement of the spots was located by spraying with a suitable locating agent. R_f values were then calculated.

Final Runs

For final runs paper was cut to 5x25 cm strips and marked by lead pencil at 1 cm from the edge to be dipped in the solvent. The paper was hanged in the chromatographic tank and covered by the lid. Elution was carried out for two hours after which the papers were air dried and sprayed with appropriate locating reagent.

Results and Discussion

The R_f values for the anions studied have been given in Table 1, along with the solvents and the locating agents used. As shown, a remarkable difference in the R_f values appeared for the best possible solvent mixtures containing dioxane, ethanol and ammonia, and isopropanol, ethanol and ammonia.The best results are however obtained, when these solvents were mixed to 50:20:30 ratio.

Effect of Solvent Composition

Pure Solvents

No significant ascending of anions was observed when pure solvents like ethanol, isopropanol, dioxane, acetone and methanol were employed.

Two Component Mixtures

Two component mixtures were prepared by adding different volumes of ammonia solution into pure solvents. Addition of ammonia considerably enhanced the elution rate of anions. Ammonia concentration was varied over a range 10-90% in each organic solvent. With ammonia-solvent mixtures, tailing effect was observed in almost all cases except sulphide, acetate and carbonate ions which gave relatively less diffused spots. Mixtures consisting 30-50% ammonia along with dioxan and isopropanol, separately, yielded better results. Hence these systems were further explored to get clear separations.

Three Component Mixtures

Different amounts of dioxan or isopropanol were mixed with varying quantities of other organic solvents and ammonia. Very clear spots were identified in the cases where dioxane, ethanol, ammonia were mixed in 50:20:30 volume ratios respectively. A 40:40:20 ratio of isopropanol: ethanol: ammonia also gave relatively better results but less remarkable than former system. Therefore the final elution was made by using these compositions in regular chromatographic apparatus.

Table 1: % Rf Values for the anions studied.

Sr. No.	Anions	% Rf Diox: Eth: NH_3 50: 20: 30	% Rf Iso-Pro: Eth: NH_3 40: 40: 20	Locating agents
1.	CO_3^-	29%	27%	Barium-sulphonazo (III) Nickel-DMG Soln.
2.	S^-	54	48	Lead Acetate Soln.
3.	CH_3COO^-	32	41	Lanthanum nitrate-iodine-Amm. Soln.
4.	SO_4^-	30	25	Barium-Sulphonazo (III)
5.	SO_3^-	38	22	Barium Sulphonazo (III)
6.	NO_3^-	86	76	Diphenyl amine solution
7.	NO_2^-	81	68	Diphenyl amine solution
8.	CrO_4^-	32	16	
9.	$Cr2O_7^-$	40	26	

Effect of Elution Time

Separation of various anions was made for different times of elution. The R_f values for the anions studied at time intervals of 30, 60, 90, 120, 150 and 180 minutes. The R_f values became stable after 90 minutes, therefore, a time interval of two hours was thought appropriate for separation of the anions studied.

An anomaly was observed in the case of sulphide ions, which could not be located after 60 minutes. No reason could be suggested for this exceptional behaviour. However for sulphide ions the time of elution was selected as one hour.

Effect of Cations

Initially all the anions separated were taken as their sodium salts except chromate and dichromate, which were taken as potassium salts. R_f values were also calculated for anions when taken with other cations like potassium and ammonium. No significant change appeared in the R_f values therefore the cations were considered to have a very little impact on the ascending chromatography of the anions studied.

Locating Reagents

Different locating agents were used for various anions. An equimolar solution of barium-sulphonazo (III) gave very good spots for carbonate, sulphate, sulphite and sulphide. Colour of the reagent is blue but the spots were developed in violet colour giving a very clear demarkation.

Solution of diphenylamine was used for nitrite and nitrate ions. A brown coloured spot indicated nitrite and a less brown nitrate.

Lead acetate gave dark brown spot for sulphide ions. Chromate and dichromate ions did not need an extra locating agent and were identified due to their own colours.

Lanthanum and iodine solution gave a red circle for acetate ions.

Pink spots were achieved for carbonate, phosphate and chromate when saturated solution of nickel-dimethyl glyoxime was sprayed. A problem, however, is that the background colour of the paper also gets pink so it becomes rather difficult to identify the spots properly.

Separation of Anions

Cross mixtures of various anions were spotted to study the effectiveness of their separation. A mixed solvent containing dioxane: ethanol: ammonia in 50:20:30 ratio respectively was employed for this purpose. Sulphide, sulphite, and sulphate could easily be identified. But a problem was encountered in the case of carbonate and sulphate which have almost the same R_f values. Other anions like nitrate, nitrite, chromate, dichromate and acetate were also separated from each other very effectively.

Conclusion

The present work offers a very attractive method for the separation and identification of a number of inorganic anions, often required in routine analysis. Some new locating agents have been introduced. The bicarbonate ion could not be studied so far, because no appropriate locating agent had been reported for this ion. The solvents applied are easily available and gave a clear separation for the anions studied. The same solvent mixture could be used for separation of all the anions studied in the present work. Problem was however encountered for the separation of sulphide ion whose identification became suspicious if more than 60 minutes is used for its elution.

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