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NOTE

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Abstract

Reverse phase partition chromatography (RPPC) on paper impregnated with 1-phenyl-3-methyl-4-benzoyl pyrazolone-5 has been studied for several metal ions. Several complex mixtures of 3 to 6 metal ions were separated under different solvent conditions. The solvent mixtures were acetone–hydrochloric acid, methyl ethyl ketone–acetone–hydrochloric acid, methyl isobutyl ketone–hydrochloric acid, acetylacetone–acetone–hydrochloric acid, acetonylacetone–acetone–hydrochloric acid, and dibenzoylmethane–acetone–hydrochloric acid. Beautiful spots of metals, sharply separated from one another, were obtained within a short period of development.

INTRODUCTION

Reverse phase partition chromatography (RPPC) on paper pretreated with β-diketones is of contemporary interest so far as separations of metal ions from mixture are considered. It was Kawamura, Fujimoto, and Izawa (*1*) whose attempt to impregnate a β-diketone (TTA) on ordinary paper with a view to increasing the selectivity of separation of metal ions from mixtures led to the technique of RPPC of metal ions on ketone-impregnated paper. 1-Phenyl-3-methyl-4-benzoyl pyrazolone-5 (PMBP) was used as a chelating agent by Zolotov et al. (*2–5*) during their studies of solvent extraction behavior of metal ions. They reported on the application of

PMBP as an extracting agent for about 40 metal ions (Cu, Ni, Co, Mn, Fe, Pb, Cd, Mo, V, Cr, etc.), the analysis being concluded spectrophotometrically. But no work has yet been reported in the literature on RPPC using PMBP-impregnated paper. Systematic studies of RPPC using 2-thenoyltrifluoroacetone (TTA) have been carried out in our laboratory (*6*). The present work is a systematic study on the RPPC system using filter paper (Whatman No. 1) impregnated with PMBP. Sharp and beautiful well-defined spots were obtained after development in each run. Such well-defined spots were barely observed on ordinary papers in the absence of PMBP.

EXPERIMENTAL PROCEDURE

Apparatus

Development was carried out in 30 × 5 cm glass jars using the technique of ascending chromatography on 25 × 2.5 cm paper strips.

Reagents and Chemicals

The chemicals and solvents used were either of E. Merck or BDH AnalaR except PMBP (obtained as a gift from Prof. Yu. A. Zolotov, Vernadsky Institute of Geochemistry & Analytical Chemistry, Moscow).

Test Solutions

Test solutions of metal ions were prepared by dissolving the respective salts or oxides (A.R., E. Merck) to give a concentration of 1 mg metal ion per milliliter of solution. Such solutions were applied to PMBP-impregnated air-dried filter papers using a very fine glass capillary.

Preparation of Paper Strips Impregnated with PMBP

Paper strips (Whatman No. 1, 25 × 2.5 cm) were allowed to hang freely touching the PMBP solution in benzene (saturated) while the solution ascended along the length of the strip. When the solution reached the upper end the paper was removed, and excess solution from the paper was removed and air dried.

Spraying Reagents

Trisodium pentacyanoaminoferrate (PCAF) was prepared by a standard method (7) and dried with methanol. Other spraying reagents used were rubeanic acid, alizarin Red S, dithiozone, potassium iodide and stannous chloride mixture, potassium ferrocyanide and acetic acid mixture, and oxine and ammonium thiocyanate with stannous chloride.

Procedure

The paper strips impregnated with PMBP were lightly marked with pencil lines to indicate the starting positions of the solvent front and the metal ions and the finishing position of the solvent front. The mixture of metal ions was then spotted on the pencil line and, after drying, was allowed to come in contact with the solvent mixture in each case by ascending paper chromatography. The time of development in each case was fixed as 2 hr. After air drying in the air or over ammonia vapors, development of the spots was accomplished with suitable reagents. The R_f, R_l, and R_t values of the spots were then measured. R_t values were calculated as the ratio of the distance of the upper meniscus of the spot from the starting position to that of the solvent front. R_t values were calculated as the ratio of the distance of the lower meniscus of the same spot to that of the solvent front. R_f values were calculated as the average of R_l and R_t values.

RESULTS AND DISCUSSION

The mixtures of metal ions used for separation were:

Manganese(II), iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) (Table 1).

Zinc(II), cadmium(II), and mercury(II) (Table 2).

Arsenic(III), antimony(III), and bismuth(III) (Table 2).

Aluminum(III), chromium(III), and zirconium(IV) (Table 3).

Niobium(V), lanthanum(III), and cerium(IV) (Table 3).

Chromium(III), molybdenum(VI), tungsten(VI), and uranium(VI) (Table 4).

Copper(II), palladium(II), and platinum(IV) (Table 4).

TABLE 1

R_{f}, R_l, and R_t values of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) on PMBP-Impregnated Paper. Time of development: 2 hr

Solvent system	Separations achieved
Dibenzoyl methane (0.1 *M* in acetone): HCl (6 *N*) = 9.5: 0.5	Mn, 0.28 $\binom{0.29}{0.27}$; Fe, 0.91 $\binom{0.93}{0.89}$; Co, 0.58 $\binom{0.59}{0.57}$; Ni, 0; Cu, 0.80 $\binom{0.81}{0.79}$; Zn, 1
DBM (0.1 *M*): HCl (6 *N*) = 7.5:2.5	Mn, 0.35 $\binom{0.37}{0.32}$; Fe, 0.88 $\binom{0.89}{0.87}$; Co, 0.52 $\binom{0.54}{0.50}$; Ni, 0.15 $\binom{0.17}{0.13}$; Cu, 0.73 $\binom{0.76}{0.70}$; Zn, 1
DBM (0.1 *M*): HCl (6 *N*) = 6.5:3.5	Mn, 0.4 $\binom{0.42}{0.38}$; Fe, 0.85 $\binom{0.87}{0.83}$; Co, 0.52 $\binom{0.54}{0.48}$; Ni, 0.3 $\binom{0.32}{0.28}$; Cu, 0.65 $\binom{0.67}{0.63}$; Zn, 1
AcAc (10%): HCl (6 *N*) = 7.5:2.5	Mn, 0.19 $\binom{0.21}{0.17}$; Fe, 0.80 $\binom{0.82}{0.78}$; Co, 0.37 $\binom{0.39}{0.35}$; Ni, 0.05 $\binom{0.07}{0.03}$; Cu, 0.52 $\binom{0.54}{0.57}$; Zn, 0.93 $\binom{0.95}{0.91}$
AcAc (10%): HCl (6 *N*) = 6:4	Mn, 0.41 $\binom{0.53}{0.38}$; Fe, 80 $\binom{0.82}{0.78}$; Co, 50 $\binom{0.51}{0.48}$; Ni, 0.33 $\binom{0.35}{0.31}$; Cu, 0.60 $\binom{0.62}{0.58}$; Zn, 1
MIBK: Ac: HCl (6 *N*) = 3: 5.3: 1.7	Mn, 0.37 $\binom{0.39}{0.35}$; Fe, 0.80 $\binom{0.84}{0.77}$; Co, 0.50 $\binom{0.53}{0.48}$; Ni, O; Cu, 0.63 $\binom{0.65}{0.61}$; Zn, 1
MEK: Ac: HCl (6 *N*) = 7: 2.6: 0.4	Mn, 0.1 $\binom{0.12}{0.07}$; Fe, 0.66 $\binom{0.67}{0.65}$; Co, 0.37 $\binom{0.39}{0.35}$; Ni, O; Cu, 0.50 $\binom{0.53}{0.48}$; Zn, 1
MEK: Ac: HCl (12 *N*) = 5: 4.6: 0.4	Mn, 0.17 $\binom{0.19}{0.15}$; Fe, 0.90 $\binom{0.92}{0.88}$; Co, 0.45 $\binom{0.47}{0.43}$; Ni, O; Cu, 0.7 $\binom{0.73}{0.68}$; Zn, 1

TABLE 2

R_f, R_l, and R_t Values of Zn(II), Cd(II), Hg(II), As(III), Sb(III), and Bi(III). Time of Development: 2 hr

Solvent system	Separations achieved
MEK : Ac : HCl (12 *N*) = 8.3 : 0 : 1.7	Zn, 0.95$\binom{0.98}{0.92}$; Cd, 0.81$\binom{0.82}{0.80}$; Hg, 0.73$\binom{0.74}{0.73}$
Methyl isobutyl ketone : acetone : HCl (12 *N*) = 8.6 : 0 : 1.4	Zn, 0.28$\binom{0.31}{0.25}$; Cd, 0.17$\binom{0.19}{0.15}$; Hg, 0.09$\binom{0.12}{0.06}$
Acetone : HCl (6 *N*) = 9 : 1	Zn, 0.97$\binom{0.99}{0.95}$; Cd, 0.93$\binom{0.95}{0.91}$; Hg, 0.88$\binom{0.91}{0.87}$
DBM (0.1 *M*) : HCl (6 *N*) = 9.5 : 0.5	Zn, 0.98$\binom{1.0}{0.96}$; Cd, 0.91$\binom{0.93}{0.89}$; Hg, 0.81$\binom{0.82}{0.81}$
AcAc (10%) : HCl (6 *N*) = 9.0 : 1.0	Zn, 0.94$\binom{0.95}{0.93}$; Cd, 0.82$\binom{0.85}{0.80}$; Hg, 0.64$\binom{0.65}{0.63}$
Acetonylacetone (10%) : HCl (12 *N*) = 8.5 : 1.5	Zn, 0.91$\binom{0.93}{0.90}$; Cd, 0.84$\binom{0.88}{0.80}$; Hg, 0.65$\binom{0.70}{0.60}$
Acetone : HCl (12 *N*) = 9 : 1	As, 0.89$\binom{0.90}{0.80}$; Sb, 0.82$\binom{0.85}{0.79}$; Bi, 96$\binom{0.98}{0.94}$
MIBK : Ac : HCl (12 *N*) = 9.6 : 0 : 0.4	As, 0.48$\binom{0.51}{0.44}$; Sb, 0.32$\binom{0.38}{0.24}$; Bi, 0.93$\binom{0.98}{0.88}$
AcAc (10%) : HCl (6 *N*) = 9.5 : 0.5	As, 0.83$\binom{0.83}{0.82}$; Sb, 0.66$\binom{0.70}{0.62}$; Bi, 0.94$\binom{1.0}{0.87}$
DBM (0.1 *M*) : HCl (6 *N*) = 9 : 1	As, 0.81$\binom{0.82}{0.80}$; Sb, 0.72$\binom{0.74}{0.71}$; Bi, 0.97$\binom{1.0}{0.95}$

TABLE 3

R_f, R_l, and R_t Values of Al(III), Cr(III), Zr(IV), Nb(V), Ce(IV), and La(III). Time of Development: 2 hr

Solvent system	Separations achieved
MEK:Ac:HCl (6 *N*) = 5:3:2	Al, $0.92\begin{pmatrix}0.93\\0.90\end{pmatrix}$; Cr, $0.53\begin{pmatrix}0.55\\0.51\end{pmatrix}$; Zr, 0
MIBK:Ac:HCl (6 *N*) = 2:7:1	Al, $0.87\begin{pmatrix}0.88\\0.86\end{pmatrix}$; Cr, $0.70\begin{pmatrix}0.72\\0.67\end{pmatrix}$; Zr, 0
Acetone:HCl (6 *N*) = 9:1	Nb, $0.77\begin{pmatrix}0.80\\0.74\end{pmatrix}$; La, $0.85\begin{pmatrix}1.0\\0.77\end{pmatrix}$; Ce, $0.03\begin{pmatrix}0.07\\0.00\end{pmatrix}$
MEK:Ac:HCl (6 *N*) = 6:2:2	Nb, $0.75\begin{pmatrix}0.78\\0.72\end{pmatrix}$; La, $0.61\begin{pmatrix}0.63\\0.60\end{pmatrix}$; Ce, $0.05\begin{pmatrix}0.09\\0.00\end{pmatrix}$
AcAc (10%):HCl (6 *N*) = 9:1	Nb, $0.81\begin{pmatrix}0.83\\0.80\end{pmatrix}$; La, $0.95\begin{pmatrix}0.99\\0.92\end{pmatrix}$; Ce, $0.12\begin{pmatrix}0.16\\0.07\end{pmatrix}$
Acetonyl acetone (10%):HCl (6 *N*) = 8.5:1.5	Nb, $0.77\begin{pmatrix}0.78\\0.76\end{pmatrix}$; La, $0.85\begin{pmatrix}0.89\\0.81\end{pmatrix}$; Ce, $0.06\begin{pmatrix}0.09\\0.03\end{pmatrix}$

TABLE 4

R_f, R_l, and R_t Values of Cr(VI), Mo(VI), W(VI), U(VI), Cu(II), Pd(II), and Pt(IV). Time of Development: 2 hr

Solvent system	Separations achieved
Acetone:HCl (12 *N*) = 8:2	Cu, $0.73\begin{pmatrix}0.75\\0.70\end{pmatrix}$; Pd, $0.97\begin{pmatrix}0.98\\0.96\end{pmatrix}$; Pt, $0.82\begin{pmatrix}0.84\\0.81\end{pmatrix}$
MEK:Ac:HCl (6 *N*) = 3.5:5:1.5	Cr, $0.82\begin{pmatrix}0.85\\0.80\end{pmatrix}$; Mo, $0.94\begin{pmatrix}0.98\\0.90\end{pmatrix}$; W, $0.10\begin{pmatrix}0.14\\0.07\end{pmatrix}$; U, $0.72\begin{pmatrix}0.74\\0.70\end{pmatrix}$
MEK:Ac:HCl (6 *N*) = 8.5:0.5:1	Cu, $0.33\begin{pmatrix}0.35\\0.32\end{pmatrix}$; Pd, $0.87\begin{pmatrix}0.90\\0.84\end{pmatrix}$; Pt, $0.62\begin{pmatrix}0.65\\0.60\end{pmatrix}$
AcAc:HCl (6 *N*) = 8:2	Cu, $0.49\begin{pmatrix}0.52\\0.46\end{pmatrix}$; Pd, $0.98\begin{pmatrix}1.0\\0.96\end{pmatrix}$; Pt, $0.77\begin{pmatrix}0.80\\0.74\end{pmatrix}$

The seven mixtures were tried for separation using several solvent compositions, the principal solvent systems being:

Acetone-hydrochloric acid.
Methyl ethyl ketone–acetone–hydrochloric acid.
Methyl isobutyl ketone–acetone–hydrochloric acid.
Acetyl acetone (10% in acetone)–hydrochloric acid.
Acetonyl acetone (10% in acetone)–hydrochloric acid.
Dibenzoyl methane (0.1 *M* in acetone)–hydrochloric acid.

The chromatograms when sprayed with suitable reagents revealed well-defined differently colored beautiful spots as follows. PCAF + rubeanic acid: Mn(II), light blue; Fe(III), deep blue; Co(II), yellowish brown; Ni(II), blue; Cu(II), apple green, Zn(II), red. Alizarin Red S:La(III), brown; Ce(IV), violet; Zr(IV), red; Th(IV), reddish violet; Al(III), reddish violet. Dithizone: Zn(II), red; Cd(II), purple; Hg(II), pink; As(III), yellow; Sb(III), red; Bi(III), purple. KI + $SnCl_2$: Pt(IV), brownish yellow; Pd(II), pink. $K_4Fe(CN)_6$ + CH_3COOH:U(VI), light brown; Mo(VI), deep brown. Oxine: Nb(V), pink; Ta(V), brown. NH_4CNS + $SnCl_2$: Cr(III), red; W(VI), red.

PMBP forms chelates with most of the metal ions at low pH. RPPC studies with PMBP also revealed the same fact. Therefore, the optimum acidity of the developing solvent was maintained within the range of 0.48 to 2.4 *N* with respect to hydrochloric acid. Separation of metal ions gradually become poorer as the acidity was increased or decreased beyond this limit. The important results may be summarized as follows.

(1) At higher acidity, the 3d-transition metal ions, viz., Fe(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), generally have higher R_f values. When the developing solvent mixture is dibenzoyl methane (0.1 *M* in acetone)–hydrochloric acid (6.0 *N*), the R_f values of Fe(III) and Cu(II) decreases with increasing acid strength. When the developing solvent mixture is acetone–HCl (6 *N*) or methyl ethyl ketone–acetone–HCl (6 *N*), the R_f values of aluminum increase and these of chromium decrease. The R_f values of Nb(V) increase while that of La(III) decrease with increasing acidity.

(2) Increased R_f values are obtained with increased acetone content in the developing solvent mixture. This fact is more pronounced when acetone–hydrochloric acid is the solvent. These increased R_f values

indicate that a polar solvent such as acetone increases the ability of PMBP for metal extractions.

(3) It was the experience with TTA-impregnated paper that Fe(III) in all instances showed maximum R_f values. But PMBP-impregnated papers revealed that it is Zn(II) that exhibits maximum R_f values. Moreover, on TTA-impregnated paper Al(III) gave the smallest R_f value in the mixture of Al(III), Cr(III), and Zr(IV). In contrast, on PMBP-impregnated paper Zr(IV) give minimum R_f values, those of Al being the maximum under identical conditions.

(4) Except for a very few ions such as Ni(II), Mn(II), Ce(IV), and Zr(IV), the R_f values of all the metal ions were uniformly high. Indications that PMBP gives rise to chelate compounds in the acid region used were experimentally confirmed by the R_f values.

(5) On TTA-impregnated paper the R_f values of both Cr(III) and Fe(III) were reported to be unity. But in the case of PMBP-impregnated paper neither of the two shows a R_f value of unity. The maximum R_f values are reported by such metals as Zn(II), Bi(III), Al(III), La(III), Mo(VI), and Pd(II). The most significant separations are:

Mn–Fe–Co–Ni–Cu–Zn [methyl ethyl ketone–acetone–hydrochloric acid (12 *N*) = 7:2.6:0.4].

Cu–Pd–Pt [methyl ethyl ketone–acetone–hydrochloric acid (6 *N*) = 8.5:0.5:1].

Zn–Cd–Hg [methyl isobutyl ketone–acetone–hydrochloric acid (12 *N*) = 8.6:0:1.4].

As–Sb–Bi [methyl ethyl ketone–acetone–hydrochloric acid (6 *N*) = 9:0:0.1].

Nb–La–Ce [methyl ethyl ketone–acetone–hydrochloric acid (6 *N*) = 6:2:2].

A rapid and clean-cut separation of the above-mentioned mixtures of common metal ions was possible using this RPPC technique. For comparison, several runs were made with identical solvent compositions using ordinary filter paper Whatman No. 1. During these studies it was observed that in most cases the periods of development were long and the separations of the metal ions were poor. Wider bands instead of well-defined spots were generally obtained with ordinary filter paper. Thus a prompt and convenient device for separation of metal ions in a complex mixture has been achieved by RPPC on PMBP-impregnated papers.

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