

REVERSED PHASE PAPER CHROMATOGRAPHY OF METAL IONS WITH PHENYLBENZOHYDROXAMIC ACID*

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The reagent phenylbenzohydroxamic acid (PBHA), often named N-benzoyl-phenylhydroxylamine, was first described by BAMBERGER in 1919¹. Structurally PBHA is related to Cupferron, and like Cupferron it precipitates quantitatively a number of metallic elements from strongly acidic solutions. However, PBHA has the advantage of being much more stable than Cupferron.

Phenylbenzohydroxamic acid is used in analytical chemistry as a gravimetric reagent and as a reagent for extractive separations and colorimetry. Fifty papers have been published since 1950 dealing with analytical uses of PBHA. These include the extraction and determination of elements such as vanadium², tungsten³, thorium⁴, titanium⁵, antimony and tin⁶, plutonium⁷, molybdenum⁸, and protoactinium⁹. Much of this work has been reviewed^{10,11}. An interesting separation scheme for Ge, Sn, Ga, In, Pb and Tl with PBHA has been recently described¹².

No research concerning the use of this reagent in extraction (reversed-phase partition) chromatography has been reported. The results below are an initial evaluation of PBHA as a reagent for the paper chromatography of metal ions. Some of the separations obtained are also possible by solvent extraction or precipitation with the reagent, but some have not been previously described.

EXPERIMENTAL

Sheets of Whatman No. 1 chromatography paper were cut to measure 11 in. high by up to 16 in. wide. (Whatman No. 3 MM paper was found to give identical results and speed the solvent flow.) They were impregnated by dipping into a solution of 2% PBHA in 40% 2-octanone, 60% absolute ethanol in a plastic tray. The excess solution was allowed to drip back into the tray and the sheets were dried in a hood on aluminum foil for at least one hour.

Wash liquids were prepared by adjusting the pH of distilled water with HClO₄ or HCl and NaOH, measured with a pH meter. Solutions of pH lower than pH = 0 were prepared by adding the appropriate volume of reagent-grade acid to distilled water. Two liters of solution were poured into a large glass jar (round) lined with

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Whatman No. 3 MM paper and covered with a glass cover. At least one hour was allowed for saturation. At the end of this period, there was a layer of liquid approximately 0.25 in. deep in the bottom of the tank.

Initial zones were applied to premarked spots on the impregnated paper by dabbing with Peerless wood applicator sticks. Approximately $5 \mu\text{l}$ of each test solution was sufficient to allow detection after migration and resultant dilution except for $15 \mu\text{l}$ for cadmium, arsenic and aluminum. Five μl is one average dab from the stick.

Each ion was tested separately with each wash liquid, and selected mixtures (pair, triplets) were developed to check some predicted separations. Mixtures were prepared on the paper by successive spotting of individual solutions on the same area of paper with drying in between. The initial zones were air dried at least thirty minutes before development.

Test solutions of each ion were 0.05 *M* solutions of the nitrate in water, except for the following:

Test solutions

Tin— $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 20% concentrated HCl and diluted to volume with water.

Bismuth— $\text{Bi}(\text{NO}_3)_3$ dissolved in 15% HNO_3 .

Mercury— $\text{Hg}(\text{NO}_3)_2$ dissolved in water; few drops HNO_3 added to remove turbidity.

Vanadium—saturated V_2O_5 in 0.10 *M* H_2SO_4 .

Antimony— SbCl_3 dissolved in 6 *M* HCl.

Arsenic— AsCl_3 in 6 *M* HCl.

Gold—dissolved commercial HAuCl_4 in water.

Platinum—dissolved commercial K_2PtCl_6 in water.

Aluminum— $\text{Al}(\text{NO}_3)_3$ dissolved in water and adjusted to pH 1 with HCl.

Titanium— TiCl_4 dissolved in concentrated HCl, evaporated to fumes with H_2SO_4 and diluted to volume with water.

Zirconium—zirconium oxychloride octahydrate dissolved in 2 *M* HCl with heating.

Uranium—the nitrate plus 1% HNO_3 .

Rare earths—oxides dissolved in HNO_3 and diluted to volume.

When the initial zones were dry, the paper was stapled in the form of a cylinder and stood in the equilibrated jar with the initial zones at the bottom. The wash liquid rose through the origins to a height about 20 cm above the origins in two hours for all solvents.

At the end of two hours, the cylinder was opened, and the paper was hung in a home-made cardboard drying box overnight. It was sprayed with the appropriate reagent(s) the next morning to find the zones.

Detection tests

Ag, Pb, Ni, Cd, Fe, Cu, Sn, Co, Bi, Hg, V, Au, Pt, As, Sb—spray with dark ammonium sulfide followed by 6 *N* HCl.

Uranium—spray with 1% potassium ferrocyanide followed by HCl if necessary.

Titanium—no spray necessary, gives bright yellow zone with reagent.

Scandium, yttrium, lanthanum, thorium, zirconium, aluminum and rare

earths—papers put in NH_3 atmosphere for 10 min, sprayed with alcoholic alizarin followed by 1 *N* acetic acid. Gives blue to purple spots on white background.

Aluminum—aluminon reagent followed by exposure to NH_3 atmosphere. (Aluminon reagent = 1 g aluminon plus 1 g NH_4Ac dissolved in 100 ml H_2O .)

RESULTS

The following elements were chromatographed on PBHA with wash liquids ranging from 5 *M* perchloric acid and 8 *M* hydrochloric acid to sodium hydroxide solutions of pH 11: Ag, Al, As(III), Au(III), Bi(III), Cd, Co, Cu, Fe(III), Hg(II), Ni, Pb, Pt(IV), Sb(III), Sc, Sn(IV), Th(IV), Ti(IV), U(VI), V(V), Y, Zr(IV), La, Ce(III), Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm and Yb. The behavior of the ions in these systems is summarized below followed by a listing of the major predicted separations and the results obtained when the predictions were tested by performing the separations.

5 M and 3 M perchloric acid

At these two acidities, most elements move at or near the solvent front. Typically, the R_F values for the leading and trailing edges of a spot are 1.0 and 0.88, respectively. Titanium and vanadium are strongly complexed and do not leave the origin. Gold, silver and zirconium streak from the origin to about $R_F \sim 0.70$, and antimony and tin streak to $R_F \sim 0.35$. The behavior of lead and bismuth at these acidities is somewhat anomalous and will be discussed below.

1 M perchloric acid

The behavior of most elements is similar to that in 3 *M* and 5 *M* perchloric acid. However, iron now begins to be complexed and has R_F values for the leading and trailing edges of 0.70 and 0.30, respectively. Mercury is also slowed down somewhat in its movement (R_F 0.70 and 0.85). Zirconium is entirely at the origin at this pH.

Perchloric acid, pH 1

The iron spot is nearer the origin (R_F 0.0, 0.45) and thorium is just beginning to show some complexation (R_F 0.65, 0.90). The behavior of other elements shows little change from that noted in the more acidic solutions.

Perchloric acid, pH 2 and pH 3

The mercury zone is now at the origin. Many divalent metals begin to show effects of complexation and approach the origin, especially at pH 3. The rare earth metals are found in rather drawn-out zones ($R_F \sim 0.65, 0.90$ at pH 2 and $\sim 0.20, 0.90$ at pH 3). Thorium, although it forms an elongated zone (R_F 0.0, 0.55), can be separated at pH 2 from many metals which are still at the solvent front at this pH. These include Pb, Ni, Cd, Co, Pt, As, U, Al, Sc, Y, La and all the rare earths. The R_F values of some selected elements at pH 3 are given in Table I.

8 M and 6 M hydrochloric acid

Titanium and zirconium remain at or near the origin, although zirconium gives a comet in 6 *M* acid. Silver and lead move essentially with the solvent front; and tin,

TABLE I

 R_F VALUES FOR SELECTED ELEMENTS IN pH 3 PERCHLORIC ACID

Element	R_F	
	Leading edges	Trailing edges
Hg	0.00	0.00
Sn	0.00	0.00
Ti	0.00	0.00
V	0.00	0.00
Zr	0.10	0.00
Fe	0.06	0.00
Th	0.23	0.00
Cu	0.47	0.00
Ag	0.54	0.00
Pb	0.55	0.22
U	0.61	0.16
Cd	0.80	0.20
Ni	0.80	0.20
Co	0.94	0.20
As	0.88	0.78
Al	0.96	0.25
Nd	0.92	0.43
Tm	0.97	0.29
Yb	0.57	0.21
Pt	1.00	0.90

antimony and vanadium are spread out from the origin to about R_F 0.70 to 0.90. Everything else moves at or near the solvent front.

1 M hydrochloric acid

The following elements are found in reasonably compact spots at or near the origin: Ag, Sn and Zr. Titanium and vanadium are still spread out from the origin to approximately R_F 0.90. Most other elements are at or near the solvent front.

Hydrochloric acid, pH 2 and pH 3

Results for most elements are very similar to those in perchloric acid of the same pH. Vanadium is now entirely at the origin but titanium is still a comet. Unlike the results in HClO_4 , mercury migrates with $R_F \sim 0.70$.

The movement of lead in concentrated perchloric acid is anomalous. In perchloric acid solution pH 1 lead moves near the solvent front, but as the concentration of perchloric acid is increased, the lead moves more and more slowly (see Table II). Bismuth is considerably spread out at low acidities, but in 1 M and 5 M perchloric acid is found in a compact zone from R_F 0.50 to 0.70. Gold in hydrochloric acid moves roughly half way from the origin over a wide range of acidities (see Table II). The behaviour of lead, bismuth and gold does not appear to be caused by the complexing effect of PBHA because similar results have been obtained for these elements using untreated paper^{13,14}. Nevertheless, these phenomena make it possible to separate lead from a large number of metal ions in concentrated perchloric acid and to separate gold from many other elements using a hydrochloric acid eluent (Table III).

At pH > 3 virtually every zone was a comet from the origin. Exceptions were

TABLE II

R_F VALUES (LEADING, TRAILING EDGES) FOR LEAD(II) WITH PERCHLORIC ACID AND FOR GOLD(III) WITH HYDROCHLORIC ACID ELUENTS

Element	Acid concentration			
	5 M	3 M	1 M	pH 1
Pb	0.52, 0.40	0.76, 0.59	0.87, 0.81	0.95, 0.78
Au	0.51, 0.32	0.54, 0.43	0.57, 0.42	double spot

platinum and arsenic which had high R_F values and compact zones, and the metals which were complexed strongly (Fe, Hg, Sn, Th, Ti, V and Zr). The runs with these wash liquids were not valid because some acidic constituent was dissolved from the paper as it stood in the wash liquid, and the pH of the solution changed. This was no problem in the pH range which proved to be of interest, at pH 3 and below. These solutions showed no change in pH after several runs. With strongly basic wash liquids, many of the ions were precipitated by hydroxide ions. Also, the PBHA reagent was stripped from the paper, especially near the origin. This was especially noticeable in a few runs performed by descending development. This led also to mostly elongated and cometed zones.

The major separations that appear to be feasible are summarized in Table III. By selective qualitative tests, it should often be possible to identify members of a group not separated from each other. For example, vanadium is easily identified by the intense brown violet color of its PBHA complex. In the absence of vanadium, titanium may be identified by its bright yellow color. Silver may be confirmed by the formation of a black precipitate with the sulfide spotting reagent.

In Table IV, results are compiled for the separations which were actually attempted. These data confirm the validity of the separations predicted from the behavior of individual metal ions. In all cases the separations predicted in Table III were successful when attempted. Only rarely was an R_F value different when an ion was part of a mixture rather than alone.

In many cases it was possible to separate a given metal from every other metal

TABLE III

SUMMARY OF PREDICTED MAJOR SEPARATIONS

Element or group separated*	Conditions	R_F range	Interferences
Pb	3 M HClO ₄	0.76, 0.59	Ag, Au, Bi, Pt, Zr
Ti, V, Zr	1 M HClO ₄	0.00, 0.00	Sn, Au, Sb, Ag
Bi	1 M HClO ₄	0.70, 0.60	Ag, Hg, Fe
Fe	1 M HClO ₄	0.70, 0.30	Ag, Sn, Bi, Au, Sb
Hg	pH 2 HClO ₄	0.00, 0.00	Th, Ag, Fe, Sn, V, Au, Sb, Zr
As, Pt	pH 3 HClO ₄	1.00, 0.78	Al, Cd, Ni, Co, most rare earths
Ag	1 M HCl	0.00, 0.00	Sb, Sn, Ti, V, Zr
Au	1 M HCl	0.60, 0.40	Sb, Ti, V
Sn	1 M HCl	0.00, 0.00	Ag, Sb, V, Ti, Zr

* Separation is predicted from all elements studied except for the interferences noted.

TABLE IV

SEPARATIONS ACTUALLY ATTEMPTED

Numbers below each element are the R_F values obtained in the actual separation. The number at the right is the distance of separation between the trailing edge of the faster moving zone and the leading edge of the slower moving zone.

(1) 1 M HClO ₄					
A	Ti	plus	U	13.0 cm	
	0.0, 0.0		0.70, 1.0		
B	Zr	plus	Th	17.8 cm	
	0.0, 0.0		0.90, 1.0		
C	V	plus	Bi	11.0 cm	
	0.0, 0.0		0.58, 0.70		
D	Zr	plus	Al	17.0 cm	
	0.0, 0.0		0.85, 1.0		
E	Fe	plus	Hg	0.60 cm	
	0.28, 0.68		0.71, 0.86		
(2) 3 M HClO ₄					
A	Pb	plus	Cu	3.0 cm	
	0.60, 0.74		0.89, 1.0		
B	Pb	plus	U	1.7 cm	
	0.60, 0.74		0.85, 1.0		
(3) 5 M HClO ₄					
	Bi	plus	Fe	7.0 cm	
	0.50, 0.72		0.85, 1.0		
(4) pH 2 HClO ₄					
A	Zr	plus	Al	13.5 cm	
	0.0, 0.0		0.74, 0.92		
B	Hg	plus	Co	17.0 cm	
	0.0, 0.0		0.84, 0.92		
(5) pH 3 HClO ₄					
A	Au	plus	Pt	7.7 cm	
	0.0, 0.50		0.88, 0.97		
B	Ag	plus	Pt	1.5 cm	
	0.0, 0.75		0.85, 0.99		
C	Sn	plus	As	10.5 cm	
	0.0, 0.21		0.76, 0.87		
D	Pb	plus	Pt	8.0 cm	
	0.22, 0.55		0.90, 1.0		
(6) 1 M HCl					
A	Ag	plus	Au	plus	Cu
	0.0, 0.0		0.43, 0.54		1.0, 0.87
	Sepn. by 7.6 cm		Sepn. by 6.2 cm		
B	Sn	plus	Fe	17.0 cm	
	0.0, 0.0		0.85, 0.98		
C	Sn	plus	Pb	11.5 cm	
	0.0, 0.0		0.61, 0.81		
D	Ag	plus	Hg	16.8 cm	
	0.0, 0.0		0.86, 0.98		
E	Au	plus	Hg	6.0 cm	
	0.42, 0.57		0.86, 0.98		
F	Sn	plus	Hg	16.6 cm	
	0.0, 0.0		0.84, 0.99		
G	Ag	plus	Pb	11.2 cm	
	0.0, 0.0		0.60, 0.80		
(7) 6 M HCl					
	Au	plus	Pb	7.0 cm	
	0.31, 0.51		0.85, 0.98		

by employing several different wash liquids. For example, Table III indicates that iron could be separated from everything except Ag, Au, Bi, Sb and Sn in 1 *M* HClO₄. However iron was separated from Sb in 3 *M* HClO₄, from Bi in 5 *M* HClO₄ and from Sn and Au in 1 *M* HCl. Mercury was separated from the interferences shown in Table III in 1 *M* HClO₄, except for Ag, Au and Sn which separated from Hg in 1 *M* HCl. Lead was separated from Au and Zr in 6 *M* HCl, from Ag in 1 *M* HCl, from Bi in 1 *M* HClO₄ and from Pt in pH 3 HClO₄.

DISCUSSION

Some runs were made at first in which the impregnation was made with 2% reagent in ethanol alone (1 *M* HClO₄ wash liquid). There were only minor differences when compared with results on sheets impregnated with 2-octanone. These differences involved slightly sharper (less diffuse) zones in several cases, and favored the use of 2-octanone. This method was used the rest of the time.

At HClO₄ concentrations greater than 5 *M*, the paper disintegrated during the run. This is also true at greater than 8 *M* HCl.

It is possible that there is frontal analysis of some of the wash liquids during development. It would be difficult to test for the HCl or HClO₄ acid front, because the paper is already impregnated with acid. Indications of this frontal analysis were: (1) In some runs, collections of impurities from the paper (the so-called "brown front") were noted slightly behind the bulk solvent front. (2) Ions often migrated with this brown front. If this occurred it was a small effect and was reproducible and should not in any way alter the validity or usefulness of these separations.

Although no extensive study of reproducibility was made, it was evident that the movement of the zones was quite reproducible. For example, lead was developed on four different papers with 3 *M* HClO₄ and gave *R_F* values of 0.59, 0.74; 0.60, 0.74; 0.56, 0.75; and 0.59, 0.79. This was typical of the reproducibility when checks were made (see also Table IV).

Beginning at pH 3 and above, the rare earths showed long zones streaking from the origin with double trails. In some cases the middle part of this zone was not visible. Development of the rare earths with the same wash liquids on unimpregnated Whatman No. 1 paper gave very similar zones indicating that PBHA is a poor extractant for these elements and that mutual separations by chromatography with PBHA are improbable.

Separations comparable to those obtained here would undoubtedly be obtained on columns or thin layers of cellulose impregnated with PBHA.

SUMMARY

The chromatographic behavior of some 35 different metal ions has been studied using paper impregnated with phenylbenzohydroxamic acid and 2-octanone. A number of selective separations can be accomplished using eluents varying in acidity from pH 3 to 5 or 6 molar acid.

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