

# The HBr Scheme of Qualitative Analysis

by Ronald Rich

The main use of qualitative analysis nowadays is to teach the fundamentals of chemical processes in solution. The most widely used scheme in the world is still basically that proposed by Fresenius in 1840; some of its weaknesses are briefly outlined below.

The main part of this article is an extremely condensed report of the results of research done, during most of the years from 1947 to 1978, in order to develop a new system, which is presented here for use in the laboratories of beginning chemistry courses in universities.

## Classical Problems

The qualitative analysis scheme to be described deals with the following difficulties, and is claimed to be the first and / or the most successful in ameliorating greatly at least the first three:

*Non-periodicity.* "..... the fragmentary remains of the classical qualitative scheme do not satisfactorily illustrate chemical periodicity." (1) "..... students do not carry from the course much feeling for the chemical properties of the ions ..... In part, this may be due to the fact that in the H<sub>2</sub>S scheme most widely used, the analytical groupings do not follow the periodic table groupings ....." (2)

*Interference.* Previous schemes largely break down unless various common complexing agents (e.g., sugars, P<sub>2</sub>O<sub>7</sub><sup>4-</sup>, Edta) and

precipitants ( $F^-$ ,  $HPO_4^{--}$  etc.) are destroyed or removed first; many of these require relatively high temperatures and/or tedious procedures (3). It is seldom noted that even  $Br^-$  and rather low concentrations of  $I^-$  can complex and partly or completely prevent the normal precipitation of the sulfides of many heavy metals, including Hg. For many years the usual result has been that students receive very artificial unknowns, untainted by such important parts of reality as are found in, say, orange juice.

*Duplication of effort.* It has normally been necessary to look twice for Pb, Hg, As (as "cation" and anion) and Tl (if included).

*Impracticality.* "..... the number of available (but unused) reactions and tools has greatly increased ..... courses in qualitative analysis, particularly those in inorganic, bear little resemblance to practice," (1)

### The HBr Scheme

The version presented here is brief and gives attention mainly, though not exclusively, to Ca, Cr, Fe, Co, Cu, Zn, Hg and Pb. Table 1 shows the group separations, which call for both inorganic and organic reagents.

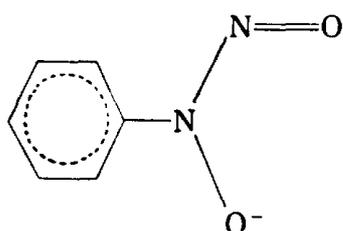
*Concerning organic reagents.* Some chemists, though accepting  $(CH_3-C=NOH)_2$ , i. e. dimethylglyoxime, in a confirmatory test, prefer to avoid any organic reagents in more prominent positions in work intended for beginning students. On this, several points should be made:

1: Only two or three of the total of 26 solutions and solvents (or 24 distinct substances) called for here contain sequences of more than two carbon atoms. Two or three more (depending on the reductant in Pcd 1) are simply derivatives of acetic acid. In addition we use just one indicator. This is similar to the statistics for other established systems, excluding, in fact, those that use organics really heavily.

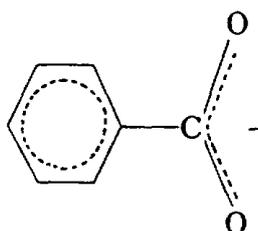
2: The only presently *required* group reagents are:  $H^+$ ,  $Br^-$ ,  $I^-$ ,

$\text{Co}(\text{CN})_6^{---}$ ,  $\text{C}_6\text{H}_5\text{-N}_2\text{O}_2^-$  and  $\text{F}^-$ ; and these do make it possible to remedy most of the problems already listed. The extracting cation in Pcd 1 does not have to be  $\text{CH}_3(\text{C}_6\text{H}_5)_3\text{P}^+$  (an analog of  $\text{NH}_4^+$ , after all) although this seems to be better than others.

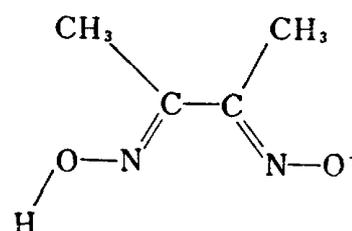
3: Cupferrate, a relative of hyponitrite and not a nitrosamine, is hardly more "complex" than the well-accepted group reagent, benzoate (4, 5), or dimethylglyoximate; note structural formulas:



Cupferrate



Benzoate



Dimethylglyoximate

We can hope that most students have heard of the benzene ring; if not, this may be a good time just to mention it. Ascorbic acid,  $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ , has a more complex structure but is not required here. (An alternative,  $\text{CH}_2\text{SH-CO}_2\text{H}$ , is not as malodorous as expected.)

The non-poisonous (and non-organic?)  $\text{Co}(\text{CN})_6^{---}$  is much more symmetrical, and therefore simpler in an important sense, than  $\text{CH}_3\text{-CO}_2\text{H}$ . The equally complex  $\text{Hg}(\text{SCN})_4^{--}$  is accepted in confirmatory tests.

4: The avoidance of even such two-carbon complexing agents as  $\text{CH}_2\text{OH-CO}_2\text{H}$  is obligatory for all but one (6) other scheme and is not necessarily a virtue.

5: Do the problems of "understanding" dimethylglyoxime or cupferrate really depend on their roles as group reagents or confirmatory tests?

*Periodicity.* Table 2 shows the arrangement of new analytical groups in the periodic chart. Even the rare metals have been checked, except for some rare earths and some radioactive ones, but including Tc, Th and U. Some would call for procedural

changes, but these make good special projects for students.

Fig. 1 shows one version (7) of the conventional grouping. Table 2 should clearly be better for teaching basic relationships among the metals.

*Non-interference.* Nearly all interferences disappear if, as here, we use higher acidities (to mask basic ligands) together with the less basic anions in group separations. With care in the choice of anions and their sequences we can also improve some other aspects.

In a test of interference, half of the 28 students received the same unknowns as the other half, but with about 50% of the solution volume coming from orange juice (minus solids). There was no difference at all in the number of errors in the two groups.

Chelating agents can now be added even purposely, for example to help dissolve various solids. (If these were allowed in other schemes, they could prevent there the hydrolysis and premature precipitation of, say,  $\text{SbOCl}$  or  $\text{BiOCl}$  in the first group.)

Very inert complexes such as  $\text{Co}(\text{CN})_6^{4-}$ , however, are still not broken down, and  $\text{HC}_2\text{O}_4^-$  would still prematurely precipitate  $\text{Ca}^{++}$  in Pcd 3. (Fortunately, however, the pH adjustment in Pcd 3 that may yield mainly  $\text{CaC}_2\text{O}_4$  does not also bring down  $\text{Cr}(\text{OH})_3$ ; this scheme thus has the advantage of permitting easy separation of any  $\text{CaC}_2\text{O}_4$  from the later  $\text{CrCfr}_3$ .)

Our freedom from interference is thus already very extensive as to the *identity* of potential trouble makers. As with (all?) other chemical operations, however, there are *quantitative* limitations. A solution in aqua regia would still have to be boiled down considerably, preferably with  $\text{HBr}$ , and then diluted. Large amounts of  $\text{Cl}^-$  would decrease the extractability of  $\text{Zn}$ , and oxidants like  $\text{HNO}_3$  would destroy the first portions of reductant in Pcd 1. Solutions of unknowns, as with other schemes, preferably contain less than 2% total solutes. It would be helpful, as recommended elsewhere (8a), to have information from anion tests or other sources before

starting on the metals. The origins of real unknowns reveal a lot, but such a discussion would go beyond our present purpose.

*Non-duplication of effort.* If the analyst is looking for As (a metalloid) it, plus Ge and Se, can be removed as a bromide subgroup by distillation from concentrated HBr (9) before Pcd 1. If ignored, it causes no trouble and does not appear in any group of metals.

Of the "common" metals, only Mn persists appreciably in aqueous solution after the removal of its group, although much less so than Pb in the classical and most other schemes. Optionally,  $MnO_2$  may be precipitated once and completely (8b) between Pcds 1 and 2. It thus appears possible to deal with each metal, or at least each "common" one, just once. (The others are less well known.)

*Practicality.* Some aspects of practicality have been discussed, but here we note others. It is useful to introduce one important organic reagent used for quantitative separations, namely cupferron. One such reagent is not overwhelming, and yet it lets us show something of this part of modern chemical practice. It may be omitted, simply by substitution with phosphate (10), although subject to some of the previously mentioned interferences and with incomplete precipitation of V, if included.

Various techniques, such as solvent extraction, are also important in practice and yet generally excluded from the qualitative analysis of metals. Not all can be introduced, but solvent extraction is used here for the group that includes the most poisonous common metals and offers the possibility of later detecting even traces of them (with modified subsequent procedures).

No special claim, in general, is made for sensitivity. The 2 ml of unknown should probably contain at least 0.4 mg of each metal that is to be found without special care. (Comparisons based on amount of substance, instead of mass, would not allow for the heavy metals' usually greater visibility in reactions (3b), poisonousness, rarity and cost.)

## On the Procedures

One way to avoid the cook-book approach is to omit details that can be thought through or checked with knowns. Another is to present ionic formulas where possible; these also emphasize the really important species. A handbook, if not the reagent shelf, would show that 5 M  $\text{CO}_3^{--}$  or 2 M  $\text{F}^-$  are not the  $\text{Na}^+$  salts. Some confirmatory tests should be looked up elsewhere.

*Group 1.*  $\text{CH}_2\text{Cl}_2$  is preferred over  $\text{CHCl}_3$  for lower toxicity, greater extraction, and less dependence of extraction on  $c(\text{HBr})$ .

A disadvantage of solvent extraction is the absence of visual evidence for the presence or absence of the group. Here the precipitation before the extraction gives evidence, but small amounts of the Zn complex may not appear, although they are extracted. Lack of visible precipitation thus does not quite prove the absence of the entire group. Centrifuging, however, promotes visibility.

For most of these metals except Zn,  $\text{I}^-$  is better than  $\text{Br}^-$  as a ligand.  $\text{I}^-$  is used only to finish the extractions, however, because of several problems of working mainly with HI, which perhaps need no discussion here.  $\text{I}^-$  also helps remove the excess  $\text{Mtp}^+$ , which would otherwise precipitate  $\text{Co}(\text{CN})_6^{--}$  and  $\text{Cfr}^-$  in Pcds 2 and 3.  $\text{Hg}_2^{++}$  apparently becomes  $\text{Mtp}_2\text{HgI}_4$ , with dismutation and/or help from any oxidized form of the reductant, so that, as with other metals, no special tests are required (or permitted!) for the different oxidation states.

Table 3 presents the separations within the group. Students previously indoctrinated with " $\text{NH}_4\text{OH}$ " should learn that this (i. e. aqueous  $\text{NH}_3$ ) is *not* included in the formula  $\text{OH}^-$  for the strong base used in Pcd 1.1 and elsewhere.

Pcd 1.2 introduces a little kinetics in the different rates of precipitation of PbS and ZnS. Thiourea is a suitable reagent, cheaper than thioacetamide, and perhaps less "organic" and complex for students too. The volume of thiourea added is important partly

for its effect on the final  $c(\text{OH}^-)$ .

*Group 2.* The inertness of  $\text{Co}(\text{CN})_6^{4-}$  prevents any confusion with  $\text{Co}^{++}$ . If no reductant had been added,  $\text{Fe}^{+++}$  would react very slowly in Pcd 2. Also, the high ionic strength there lowers the previously noted (10) tendency to form semi-colloidal sols; a minimum excess of  $\text{Co}(\text{CN})_6^{4-}$  must be used, however, and the finely divided precipitates must be centrifuged longer and more carefully than others. The prior removal of  $\text{Hg}^{++}$  eliminates the slight Hg-catalyzed decomposition of  $\text{Co}(\text{CN})_6^{4-}$  that was also noted previously (10). Table 4 shows a separation and identification of Fe and Co.

*Groups 3 and 4.* If the neutralization with  $\text{CO}_3^{2-}$  in Pcd 3 produces a precipitate (a useful indication of enough base), the buffering  $\text{CH}_2\text{Cl}-\text{CO}_2\text{H}$  should be added in a minute or so if we want to keep any  $\text{Cr}(\text{OH})_3$  from becoming hard to dissolve in it. To keep the  $\text{Cr}^{+++}$  dissolved, then, we don't allow it to stand very long.

In spite of cupferron's well-known sensitivity to heat and light, it can be heated briefly with  $\text{Cr}^{+++}$  to overcome the latter's inertness.

If Group 3 elements beside Cr are being considered, a Ti subgroup can be removed with  $\text{Cfr}^-$  before the adjustment of pH. During that adjustment an Al subgroup appears in the cold solution. This, as with  $\text{H}_2\text{S}$ , can illustrate the importance of pH. The reductant remaining from Pcd 1 puts  $\text{UCfr}_4$ , for example, into the Al subgroup. As with other parts of this scheme, further information is obtainable on writing; the additional procedures, however, have been tested less thoroughly.

Table 5 shows some further steps for Cr and Ca. The alkaline earths might be good candidates for introducing some kind of chromatographic separation, but we have not yet incorporated these methods. The final steps for these elements can be the conventional ones.

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Fig. 1 The Classical Analytical Groups

Li	Be										B	C	N	O	F	
Na	Mg	Al										Si	P	S	Cl	
K	Ca	Sc	Ti	V	Cr	(Mn)	Fe	(Co)	(Ni)	Cu	(Zn)	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	(Ag)	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	(W)	Re	Os	Ir	Pt	Au	(Hg)	(Tl)	(Pb)	Bi	Po	At
Fr	Ra	Ac	Th	Pa	U											
group VI plus NH <sub>4</sub> <sup>+</sup>	group V	group III									group II					anions
					Complex equilibria lead to a separation into groups I (○), & IV (○)											

Table 1 Separation into Groups

<p>Unknown soln : 2.0 ml. <b>Ped 1</b> : Add 8.8 M HBr, 0.9 ml (final <math>c(\text{HBr}) = 2.5\text{-}3.0\text{ M}</math>). Add satd MtpBr in 3 M HBr, 5 d excess after any precipitation. Add 2 n reductant<sup>a, b</sup> aq excess. Extract with <math>\text{CH}_2\text{Cl}_2</math>, 0.8-1.0 ml. <sup>c</sup> Add 6 M <math>\text{I}^-</math>, 1 d. Extract with <math>\text{CH}_2\text{Cl}_2</math>, ca 1 ml.</p>	<p>Reject all <math>\text{CH}_2\text{Cl}_2</math> ext. <b>Ped 2</b> : Add 0.5 M <math>\text{Co}(\text{CN})_6^{3-}</math>, only 1-2 d soln <math>2\frac{1}{2}</math>-<math>3\frac{1}{2}</math><sup>e</sup>. Heat with 0.4 soln excess. 2 M Cfr<sup>-f</sup> 40-50 s with stirring. Cool.</p>	<p><b>Ped 3</b> : Neutralize with 5 M <math>\text{CO}_3^{--d}</math>. Add 6 M <math>\text{CH}_2\text{Cl-CO}_2\text{H}</math> until pH = <math>\text{M F}^-</math>, 5 d</p>	<p><b>Ped 4</b> : Add 1-2 M <math>\text{F}^-</math>, 5 d</p>
<p><math>\text{CH}_2\text{Cl}_2</math>, ext 1 (combined) ↓</p>	<p>↓ ppt 2 ↓</p>	<p>↓ ppt 3 ↓</p>	<p>↓ ppt 4 ↓</p>
<p>Mtp<sub>x</sub>Met(Br, I)<sub>y</sub>. Met = <math>\text{Cu}^I</math>, <math>\text{Zn}^{\text{II}}</math>, <math>\text{Hg}^{\text{II}}</math>, <math>\text{Pb}^{\text{II}}</math> etc. Go to Table 3.</p>	<p>ca <math>\text{KMetCo}(\text{CN})_6</math>. Met = <math>\text{Fe}^{\text{II}}</math> (yellow or whitish), <math>\text{Co}^{\text{II}}</math> (pink) etc. Go to Table 4.</p>	<p><math>\text{CrCfr}_3</math> (gray-green), HCfr, <math>\text{C}_6\text{H}_5\text{NO}</math> etc. Go to Table 5.</p>	<p><math>\text{CaF}_2</math> etc. Go to Table 5.</p>
<p><sup>a</sup> either (1) 1 M <math>\text{H}_2\text{C}_6\text{H}_4\text{O}_6</math>, ascorbic acid or the cheaper optical isomer, araboascorbic acid;</p>	<p><sup>b</sup> Colored <math>\text{Fe}(\text{III})</math> and <math>\text{Cu}(\text{II}) \rightarrow \text{Fe}(\text{II})</math> and <math>\text{Cu}(\text{I})</math>.</p>	<p><sup>c</sup> May repeat addition of Mtp<sup>+</sup> and extraction, especially for complete removal of Zn.</p>	<p><sup>d</sup> Congo-Red paper → red, and fizzing decreases.</p>
<p>or (2) 2 M <math>\text{CH}_2\text{SH-CO}_2\text{H}</math>, mercaptoacetic (thioglycolic) acid;</p>	<p><sup>e</sup> Congo-Red paper → purple.</p>	<p><sup>f</sup> up to 1-2 ml, if there is much color of <math>\text{Cr}(\text{III})</math>.</p>	
<p>or (3) 1 M <math>\text{PH}_2\text{O}_2^-</math>, phosphate (I) (hypophosphite). Phosphates of other metals such as Ti may ↓; <math>\text{Hg}_2\text{Br}_2</math> ↓. (1) or (2) is preferred. (Phosphate in the unknown is OK since incompatible ions would not be in the same solution.)</p>			
<p>The <math>c(\text{HBr})</math> must be kept at 2.5-3.0 M by adding half as much 8.8 M HBr as reductant, or by dissolving the reductant in 3 M HBr (volume effects are successfully disregarded), which may require making fresh solutions more often, say at least every week in the case of <math>\text{H}_2\text{C}_6\text{H}_4\text{O}_6</math>.</p>			

(list of abbreviations : next page)



Table 3 Analysis of Group 1

<p><math>\text{CH}_2\text{Cl}_2</math> ext 1: <math>\text{Mtp}_x</math> (<math>\text{Cu}^I</math>, <math>\text{Zn}^{II}</math>, <math>\text{Hg}^{II}</math>, <math>\text{Pb}^{II}</math>) (Br, I)<sub>y</sub>. Reject all aq soln 1, <b>Ped 1.1</b>: Put into evap dish without washing. Add 4 M <math>\text{OH}^-</math>, 2 ml. Heat and stir (<math>\text{CH}_2\text{Cl}_2</math> ↑). Cool 1 min.</p>	<p><math>\text{Zn}(\text{OH})_4^{--}</math>. <b>Ped 1.3</b>: Add 1 M <math>\text{S}^{--}</math> or <math>\text{HS}^-</math>. Heat. (Discard soln.)</p>	<p><math>\text{Zn}(\text{OH})_4^{--}</math>. <b>Ped 1.3</b>: Add 1 M <math>\text{S}^{--}</math> or <math>\text{HS}^-</math>. Heat. (Discard soln.)</p>
<p>ppt and oil 1.1 ↓</p> <p>Orange <math>\text{CuOH}</math>, yellow or white <math>\text{Mtp}_2\text{HgI}_4</math>.</p> <p><b>Ped 1.5</b>: Ww <math>\text{H}_2\text{O}</math>. Acidify with <math>\text{HBr}</math> or 6 M <math>\text{HCl}</math>. Add 6 M <math>\text{NH}_3</math>, excess.</p>	<p>soln 1.1 →</p> <p>60-70 s. Cool.</p>	<p>White ppt: <math>\text{ZnS}</math>. <b>Ped 1.31</b>: Ww <math>\text{H}_2\text{O}</math>. Dslv in 0.5 M <math>\text{HCl}</math>, no heat. (Discard any dark res.) Add 0.5 M <math>\text{Fe}(\text{CN})_6^{4-}</math>. White ppt: e.g., <math>\text{K}_2\text{Zn}_3(\text{Fe}(\text{CN})_6)_2 \cdot 8\text{H}_2\text{O}</math>; insoluble in 6 M <math>\text{NH}_3</math> or 6 M <math>\text{HCl}</math>.</p>
<p>res 1.5 ↓</p> <p><math>\text{Cu}(\text{NH}_3)_2^+</math>.</p> <p><b>Ped 1.6</b>: soln Air → blue 1.5 → <math>\text{Cu}(\text{NH}_3)_4^{++}</math>.</p> <p><b>Mtp}_2\text{HgI}_4</b>. <b>Ped 1.7</b>: Ww <math>\text{NH}_3</math>. Add 1 M <math>\text{CS}(\text{NH}_2)_2</math>, 1 ml. Add 6 M <math>\text{NH}_3</math>, 10 d. Heat 30 s (in 15 s, → black). Ppt: <math>\text{HgS}</math>. (Discard soln.) <b>Ped 1.71</b>: Ww <math>\text{H}_2\text{O}</math>. Confirm by insolubility on heating in 2 M <math>\text{HNO}_3</math>, 2 min, and by <b>Ped 1.72</b>: (Discard soln.) Dslv in warm 1 M <math>\text{I}^-</math>, + 6 M <math>\text{HCl}</math>, 4-6 d. Extract with <math>\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5</math>. Evaporate ext. Res: <math>\text{HgI}_2</math>, red or yellow; yellow → red on rubbing!</p>	<p>ppt 1.2 ↓</p> <p>Black <math>\text{PbS}</math>. <b>Ped 1.4</b>: Ww <math>\text{H}_2\text{O}</math>. Dslv in hot 6 M <math>\text{HClO}_4</math> if small (since <math>\text{Pb}^{++}</math>-<math>\text{NO}_3^-</math> complexing decreases sensitivity) or 2 M <math>\text{HNO}_3</math>. (Optional: Discard any insoluble <i>MetS</i>.) Cool. Add 1 M <math>\text{I}^-</math>. Yellow ppt: <math>\text{PbI}_2</math>.</p>	<p>soln 1.2 →</p>

Table 4 Analysis of Group 2

<p>Ppt 2: ca <math>K(Fe^{II},Co^{II})Co(CN)_6</math>. Pcd 2.1: Ww 0.5 M HCl, 1 ml, + 0.5 M <math>Co(CN)_6^{3-}</math>, 1 d. Add 10 M KSCN satd with <math>Na_4P_2O_7</math>, 2 ml. Extract twice with <math>CH_3CO_2C_2H_5</math> (EtAc).</p>	<p>Blue  <math>\xrightarrow{EtAc}</math> organic  soln 2.1:  <math>Co(NCS)_4^{--}</math>.</p>
<p>↓ aq soln 2.1 ↓</p>	
<p><math>Fe(P_2O_7)_2^{6-}</math> ? Pcd 2.2: Add 1 M <math>S^{--}</math> or <math>HS^-</math>. Dark ppt: <math>FeS</math>. (Discard soln.) Ww <math>H_2O</math>. Dslv most in hot 0.5 M HCl, mim. Boil <math>H_2S</math> ↑. Add 1 M <math>H_2O_2</math>, 2 d. Add 0.5 M <math>SCN^-</math>, 1 d. Deep red soln: <math>Fe^{3+}(SCN^-)_x</math>.</p>	

Table 5 Dissolution of Cr and Ca

Ppt 3:  $CrCfr_3$ . Pcd 3.1: Ww  $NH_3$ . Heat to dslv in 4 M  $OH^-$  + 1 M  $H_2O_2$ , 1:2, mim. (Discard any dark res.) Yellow soln:  $CrO_4^{--}$ .

Ppt 4:  $CaF_2$ . Pcd 4.1: Ww  $OH^-$ . Ww  $H_2O$  (thoroughly if for future flame tests). Dslv in 0.8 M (satd)  $H_3BO_3$  + 6 M HCl, 2:1, mim.