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<https://doi.org/10.18297/etd/1357>

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"AN ABBREVIATED SCHEME FOR THE DETECTION OF ACID RADICALS."

A THESIS

SUBMITTED TO THE FACULTY

of the

COLLEGE OF ARTS AND SCIENCES

of the

UNIVERSITY OF LOUISVILLE

through

PROFESSOR CHAS. J. ROBINSON

IN CANDIDACY FOR THE DEGREE OF

"MASTER OF SCIENCE."

by

MARY PRESSLEY SMITH

1912.

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AN
ABBREVIATED SCHEME
FOR THE
DETECTION
OF
ACID RADICALS

Mary Pressley Smith.

In studying qualitative chemistry, two things impress you. The one being, the systematic, inclusive and generally accepted tables for the detection and identification of the several metals; the other, the lack of any agreement as to the method of the identification of acid radicals. The metal analysis tables are so well arranged and so true that even the inexperienced person finds little or no difficulty in working with them. But with the acid radicals, it is an entirely different proposition. There is no generally accepted grouping of the radicals into divisions, some text books giving as many as seven divisions and some none at all. The tests given are, in some instances, not at all satisfactory. And we find dissatisfaction among pupils in regard to their acid radical work.

Now the detection of the non metallic portion of a compound is just as essential to the identification of a substance as that of the metallic. With this idea in view I have been working on the following table compiled by Dr. Robinson for use in the medical and academic laboratories of the University of Louisville.

ANALYTICAL TABLE V. Tests for Acid Radicals.

If the original solution contains metals other than the alkalis, add to about 500 c.c. of it enough Na_2CO_3 to make strongly alkaline, boil 10 to 15 minutes, renewing water lost by evaporation and filter. Use this prepared solution for the acid analysis, except for the carbonate test, and when especially directed to use the original solution.

Perform the tests in the order indicated.

≠ means take fresh portion of the prepared solution.

1. To portion of unacidified original solution, add BaCl_2 . If no precipitate forms, proceed at once to 11. If pree. occurs, or if original solution contains acid, work through A, B, C, D. If solution is acid, omit A.

A ≠ To portion of prepared solution add HCl (to slight ~~excess~~ acid-

ity). Effervescence indicates (unless Na_2CO_3 was added above):

1. $=\text{CO}_3$. Passing gas into lime water gives precipitation.

Gas has no effect on KMnO_4 .

Precipitate of sulphur indicates:

2. $=\text{S}_2\text{O}_3$. Heated gives SO_2 . KMnO_4 when added decolorized.

3. $=\text{S}_x$

4. $=\text{S} +$ oxidizing agent See II E 1.

B Filter clear and add BaCl_2 . White pree. indicates

1. $=\text{SO}_4$.

C. Filter clear, boil to remove CO_2 add CaCl_2 and 1 - 2 grams of sodium acetate. Prec. indicates:

1. $=\text{C}_2\text{O}_4$. Filter, wash, treat pree. with dilute H_2SO_4 , warm and add KMnO_4 . Decolorized.

2. $=\text{Cr}_2\text{O}_7$ if yellow. Filter, wash, dissolve in HCl and add H_2O_2 . Transient blue color.

3. $=\text{SiO}_3$. Metaphosphate bead (microsomic salt) gives "skeleton".

D. Filter clear, make alkaline with $\text{Ba}(\text{OH})_2$ (use litmus).

Pree. indicates:

1. $=\text{PO}_4$. $\neq$ Acidify with HNO_3 . Ammonium molybdate and heat gives yellow pree.

2. $=\text{AsO}_4$. $\neq$ Same as $=\text{PO}_4$. $\neq$ Add conc. HCl and H_2S . Yellow pree. As_2S_5 .

3. $=\text{SO}_3$. $\neq$ H_2SO_4 and heat gives SO_2 . KMnO_4 decolorized.

4. $=\text{BO}_3$ or B_4O_7 $\neq$ Solid material or solution evaporated to very small volume gives with conc. H_2SO_4 and alcohol, a green flame when ignited.

5. $=\text{C}_4\text{H}_4\text{O}_6$. Dissolved pree. in HNO_3 , add AgNO_3 ; NaOH un-

til alkaline: NH_4OH until prec. dissolves and boil. Silver mirror.

E. Silver prec. dark, or darkens when heated, indicates:

1. $=\text{S}$. $\neq \text{H}_2\text{SO}_4$ and heat gives H_2S . Lead acetate paper blackened by vapors.

2. $=\text{S}_2\text{O}_3$. $\neq \text{H}_2\text{SO}_4$ and heat gives prec. of S and SO_2 . KMnO_4 when ~~heated~~ added decolorized.

F. $\neq$ gives marked color with HCl and FeCl_3 .

1. $-\text{SCN}$. Blood red solution with FeCl_3 and HCl .

2. $=\text{Fe}(\text{CN})_6$. Dark blue prec. with FeCl_3 and HCl .

3. $=\text{Fe}(\text{CN})_6$. Dirty brown. prec. HCl and FeSO_4 deep blue precipitate.

4. $-\text{I}$. Brown with HCl and FeCl_3 . Chloroform added and shaken assumes violet color. $\neq$ Silver prec., Yellow.

G. $\neq$ Neutral solution with FeCl_3 alone. Brown color indicates

1. $-\text{C}_2\text{H}_3\text{O}_2$. Brownish-red solution. Prec when boiled. See III 4;

2. $-\text{NO}_2$. Reddish brown. Prec. on shaking, hastened by heat. See III 2.

H. $\neq$ With NaOH , FeSO_4 , FeCl_3 and HCl , blue prec. indicates

1. $-\text{CN}$. (Not applicable in presence of F 2 and 3).

I. $\neq$ gives Cl with acids and heat (Starch-iodide paper in vapors turns blue) indicates:

1. $-\text{ClO}$. $\neq$ Acidified, bleaches indigo solution.

K. $\neq$ Chlorine water and chloroform added to slightly acidified solution; color in latter indicates:

1. $-\text{Br}$ gives chloroform brown color.

2. $-\text{I}$ " " violet color. Carefully add excess of chlorine water until violet disappears. (ICl_3). If brown remains, both $-\text{Br}$ and $-\text{I}$ are present.

L. If all previous tests in Section II are negative, the silver pree. must be AgCl , indicating Cl . Pree. readily soluble in NH_4OH . If other acid radicals of this section are present, mix a portion of dry substance (or residue left by evaporation of solution) with powdered $\text{K}_2\text{Cr}_2\text{O}_7$ in dry test-tube, add 5 cc. conc. H_2SO_4 and warm. Pour brown fumes into water, shake and add H_2O_2 . Blue color indicates $-\text{Cl}$. (Dangerous if chlorates are present. Apply test III 3 to detect chlorates).

III. Acid radicals not pree. by Ba or Ag.

1. $-\text{NO}_3 \neq$ Add equal volume conc. H_2SO_4 , mix well, cool; on this stratify FeSO_4 . Brown ring. If test is positive, either $-\text{NO}_2$ or NO_3 may be present.

2. $\text{NO}_2 \neq$ Effervesces with acids. $\neq$ Acetic acid and FeSO_4 produces brown color. $\neq$ Acid, KI and starch paste: blue.

3. $-\text{ClO}_3$ Small particles of dry substance (or of residue left by evaporation) gives sharp explosion with conc. H_2SO_4 .

4. $-\text{C}_2\text{H}_3\text{O}_2$. Warmed with H_2SO_4 , and alcohol gives fruity odor of ethyl acetate. $\neq$ IF NEUTRAL, solution gives brownish red color with FeCl_3 , pree. on boiling.

5. $-\text{MnO}_4$. Characteristic purple color destroyed by H_2SO_4 and a sulphite.

6. $-\text{BO}_3$ (Not pree. by Ba in very dilute solutions). See I D 4.

7. H_2O_2 . HCl and few drops $\text{K}_2\text{Cr}_2\text{O}_7$ gives blue color.

Absence of acid radical indicates that substance being analyzed is an element, oxide or hydroxide.

The nature of the subdivisions and the reasons why such subdivisions have been made are as follows.

In Group I of those substances which from unacidified solutions form

a precipitate on the addition of Barium chloride.

Group I, Division A. Substances which decompose on the addition of hydrochloric acid

Division B. Substances which form a precipitate with barium chloride in the presence of hydrochloric acid .

Division C. Substances which form barium or calcium salts insoluble in acetic acid.

Division D. Substances which form barium or calcium salts, soluble in acetic acid, insoluble in alkaline medium.

Group II, substances which form a precipitate with silver nitrate in the presence of nitric acid.

Division E. Substances forming silver precipitates which are dark, or darken on heating.

Division F. Substances which, in solutions made acid with hydrochloric acid, give marked color with ferric chloride.

Division G. Place in this group due to an error.

Division H. Substances which with sodium hydroxide, ferrous sulphate, ferric chloride, and hydrochloric acid (to acidity) give a blue color.

Division I. Substances which, with acids and heat liberate chlorine.

Division K. Substances which with chlorine water and chloroform, added to the acidified solution, give marked color in the chloroform.

Division L. Substances which give a precipitate with silver nitrate in the presence of nitric acid but do not fall into any of the groups mentioned above.

Group III. Substances which form no precipitates with barium chloride, nor with silver nitrate in the presence of nitric acid, or form such precipitates only in solutions of a concentration unusual in qualitative

analysis.

The above table, which was compiled by Dr. Robinson, and used by him in his classes, though it worked well in the main still in many particulars proved unsatisfactory. It lacked experimental foundation, and it was not known what concentrations of some acid radicals were required for the fulfillment of the tests indicated. So, in order to supply this foundation, to give accurate knowledge of what strength solutions are required, to ascertain whether or no the individual tests as given were distinct and definite enough for the identification of the separate radicals, to eliminate what errors might be present and to give such tests or the discussion of given tests as would make the scheme more accurate, clearer and easily followed by the student. With the thought in mind that it must be an abbreviated scheme, only as long as needed for clearness, and for accuracy of test, the experimental work described in this paper was undertaken.

In testing solutions of the individual substances, special note has been made of percentage and of any unusual circumstance arising. A discussion of mixtures, with in some instances a fuller discussion of the individual radical, is given later. The substances are considered in the order given in the table above. Ammonium, sodium or potassium salts were used in every case and percentages are stated in terms of these salts, generally the sodium salt. Colors are identified and named according to the Bradley color standard (Mulliken's "Identification of Pure Organic Compounds" pp 232)

I A 1 =CO_3 $1/2\%$ salt solution of carbonate gives a heavy gelatinous precipitate with barium chloride. Some effervescence on the addition of hydrochloric acid, with the slight effect on lime water. The 5% solution worked splendidly.

I A 2, 3, 4 will be treated in II E where they more properly be-

long.

I B $=\text{SO}_4$ In $1/2\%$ salt solution of sulphate, the formation of barium sulphate as a white precipitate was decided and immediate.

I C 1 $=\text{C}_2\text{O}_4$ $1/2\%$ salt solution gives no immediate precipitate under the conditions of the table. The 1% and 5% solutions work satisfactorily. A fuller discussion of oxalates is given later.

I C 2. $=\text{Cr}_2\text{O}_7$ or Cr_2O_4 $1/2\%$ salt solution worked very well.

I C 3. $=\text{SiO}_3$. 5 cc. of 1% salt solution evaporated to small volume gives skeleton in microcosmic salt.

I B 1. $=\text{PO}_4$ $1/2\%$ salt solution is apt to form a precipitate in C, but if precipitate comes in C, it is dissolved by the addition of acetic acid. The molybdate test gives a heavy normal yellow precipitate, immediately with heat.

I D 2. $=\text{AsO}_4$ $1/2\%$ salt solution with nitric acid and ammonium molybdate gives a yellow coloration, a slight precipitate forms on standing some hours. Concentrated hydrochloric acid and hydrogen sulphide give a canary yellow precipitate As_2S_5 . This precipitate forms quickly on heating but takes sixty minutes if cold.

I D 3. $=\text{SO}_3$ From freshly prepared solution ($1/2\%$) slight effervescence. Concentrated sulphuric acid and heat give SO_2 . Sulphite changes on standing to sulphate.

I D 4. $=\text{BO}_3$ or $=\text{B}_4\text{O}_7$ 5cc. 1% salt solution forms a precipitate with barium chloride. 5 cc. 1% solution evaporated on ignition gives with concentrated sulphuric acid and alcohol a normal green flame.

I D 5. $=\text{C}_4\text{H}_4\text{O}_6$. 5 cc. of 1% solution evaporated to dryness gives heavy charring. A burnt sugar odor and syrupy liquid are present just before charring.

The silver mirror test as given in the table, as well as a number of other tests were tried with varying degrees of success. The resorcin test is the most satisfactory. Add three or four drops of two per cent resorcin to tartrate solution, stratify on concentrated sulphuric acid and heat on hot water bath. A violet red ring forms at the intersection of the two liquids, within from three to eight minutes.

II E 1. =S One half percent salt solution gives with silver nitrate and nitric acid a heavy, immediate and dark precipitate. Sulphides with sulphuric acid and heat give off hydrogen sulphide which can be detected by its odor, and by the blackening of lead acetate paper.

II E 2. =S₂O₃. One-half percent salt solution works satisfactorily under the conditions in the table. The precipitate does not turn dark as quickly as the sulphides. Thiosulphates with sulphuric acid and heat give off sulphur dioxide which can be detected by the odor.

II F 1. -SCN. One-half percent salt solution gives with silver nitrate a heavy precipitate. With hydrochloric acid and ferric chloride the blood red color is instantaneous.

II F 2. =Fe(CN)₆. One-half salt solution gives with nitric acid and silver nitrate a heavy precipitate which turns blue on heating. The dark blue precipitate with ferric chloride and hydrochloric acid is satisfactory.

II F 3. =Fe(CN)₆. One-half/salt solution gives with nitric acid and silver nitrate a normal yellow orange precipitate. With hydrochloric acid and ferric chloride a green yellow shade 2 coloration was given. With hydrochloric acid and ferrous sulphate a heavy inky blue precipitate forms. The one percent solution works the same excepting that with hydrochloric acid and ferric chloride a yellow orange shade 2 was given. The five percent solution gives with hydrochloric acid and ferric chloride a red brown coloration.

II F 4. -I. One-half percent salt solution gives a yellow precipitate with nitric acid and silver nitrate, With chlorine water and chloroform, a violet coloration appears in the chloroform.

II G $\begin{matrix} -\text{CH}_3\text{COO} \\ -\text{NO}_2 \end{matrix}$ do not belong in Group II.

II H 1. -CN. One-half percent salt solution gives a heavy white precipitate with nitric acid and silver nitrate. With sodium hydroxide ferrous sulphate, ferric chloride, and hydrochloric acid to acidity gives a blue precipitate.

II I 1. -ClO. One-half percent salt solution gives the test of this table in a decided and immediate manner.

II K 1. -Br. One-half percent salt solution gives test satisfactorily according to the table.

II K 2. -I. See II F 4.

II L 1. -Cl. One-half percent salt solution gives a heavy white precipitate with nitric acid and silver nitrate. Hydrogen dioxide added to the water in which the brown fumes arising from the mixture of the chloride and concentrated sulphuric acid and potassium dichromate are poured, gives a transient blue color. The test works beautifully.

III 1. -NO₃. One percent salt solution mixed with concentrated sulphuric acid stratified with ferrous sulphate heated slightly gives on standing a brown ring.

III 2. -NO₂. One-half percent salt solution effervesces with acids. When mixed with concentrated sulphuric acid and ferrous sulphate stratified thereon, a brown ring is given. A brown color forms on the addition of acetic acid and ferrous sulphate to the nitrite solution. The salt solution when acidified turns iodine starch paper blue.

III 3 -ClO₃. Five cc. of one percent solution evaporated to dry-

ness gives if concentrated sulphuric acid is dropped upon it disagreeable brown fumes. of chlorine dioxide, and chlorine fumes. If the temperature is above 60° , a sharp explosion occurs.

III 4 $-\text{CH}_3\text{COO}$: The ferric chloride test for reasons given later is omitted. 10 cc. of one-half percent or five cc. of one percent salt solution evaporated to dryness gives with a mixture of 3 cc of ethyl alcohol and 3 cc. of concentrated sulphuric acid fruity odor of ethyl acetate; if an excess of acid, acetic acid odor is given. 5 cc. of one per cent salt solution gives a slight charring.

III 5. $-\text{MnO}_4$. One-half per cent solution works satisfactorily.

III 6. $-\text{BO}_3$. Not precipitated by barium chloride in dilute solutions. See I B 4.

III 7. H_2O_2 . One-half per cent solution gives with hydrochloric acid and potassium dichromate a transient blue color.

From the foregoing data, and other considerations, various changes in the analytical table were seen to be necessary, and the following revised table embodies these corrections.

Analytical Tables. Tests for Acid Radicals.

If the original solution contained metals other than the alkalies, add to about 50 cc. of it enough sodium carbonate to make strongly alkaline, boil ten to fifteen minutes, renewing water lost by evaporation, and filter. Use this prepared solution for the acid analysis, except for the carbonate test, and when specially directed to use the original solution.

Perform the tests in the order indicated.

~~/~~means take fresh portion of prepared solution.

I. If the original solution contains acid, work through B, C, D. If unacidified, add to a portion of it barium chloride and heat. If no precipitate forms proceed at once to II. If precipitate occurs, work

through A, B, C, and D.

A. $\neq$ To a portion of the prepared solution add hydrochloric acid (one to ten drops) to slight acidity. Effervescence indicates (unless sodium carbonate was added above)

1. $=\text{CO}_3$. Passing gas into lime water gives precipitate. Gas has no effect on KMnO_4 .

Precipitate of Sulphur indicates

2. $=\text{S}_2\text{O}_3$. Heated gives off SO_2 . Recognizable by odor, KMnO_4 when added decolorized.

3. $=\text{S}_x$

4. $=\text{S} +$ oxidizing agent. See II, E, 1.

Gelatinous precipitate indicates

5. $=\text{SiO}_3$. See C 3.

B. Filter clear add BaCl_2 , white precipitate.

1. $=\text{SO}_4$.

C. Filter clear, boil to remove CO_2 , add CaCl_2 (a few crystals) and one to two grams sodium acetate. Boil, Reaction must remain acid, precipitate (insoluble in acetic acid) indicates:

1. $=\text{C}_2\text{O}_4$. Filter, wash, treat pree. with dilute H_2SO_4 , warm and add KMnO_4 , decolorized.
2. $=\text{Cr}_2\text{O}_7$. $=\text{CrO}_4$. If yellow. Filter, wash, dissolve in HCl , add H_2O_2 , a transient blue color.
3. $=\text{SiO}_3$. Evaporate 5 cc. of acidified solution to dryness. Residue metaphosphate bead (microcosmic salt) gives a skeleton.

D. Filter clear, make alkaline with $\text{Ba}(\text{OH})_2$ (use litmus, if necessary evaporate to original concentration) Precipitate indicates:

1. $=\text{PO}_4$ $\neq$ acidify with nitric acid, add ammonium molyb-

date, on heating (not above 60°) heavy normal yellow prec.

2. $\equiv \text{AsO}_4$. $\neq$ Add conc. HCl , H_2S and heat. A canary yellow prec.

$\neq$ Molybdate test, on heating and standing some hours.

3. $\equiv \text{SO}_3$. $\neq$ H_2SO_4 and heat gives SO_2 . KMnO_4 decolorized.

4. $\equiv \text{BO}_3$, or $\equiv \text{B}_4\text{O}_7$. Solid material or material evaporated to very small volume gives with conc. H_2SO_4 and alcohol a green flame when ignited.

5. $\equiv \text{C}_4\text{H}_4\text{O}_6$. $\neq$ Evaporate 5 cc. of solution to dryness and heat the residue, heavy charring, burnt sugar odor, syrupy liquid just before charring. $\neq$ To 3 cc. add from two to four drops 2% resorcin solution stratify on conc. H_2SO_4 . A violet red ring forms in from three to eight minutes if heated on the water bath.

II. $\neq$ Acidify with HNO_3 and add AgNO_3 . If no prec. forms, proceed at once to III. If prec., work through E to L.

E. Silver prec. dark, or darkens when heated.

1. $\equiv \text{S}$. Silver prec. darkens immediately. $\neq$ H_2SO_4 and heat give H_2S detected by odor, and by lead acetate paper being blackened in vapors.

2. $\equiv \text{S}_2\text{O}_3$. $\neq$ H_2SO_4 and heat give prec. of S and SO_2 . detected by odor and decolorization of KMnO_4 .

F. $\neq$ Gives marked color with HCl and FeCl_3 .

1. $-\text{SCN}$ blood red solution with HCl and FeCl_3 .

2. $\equiv \text{Fe}(\text{ox})_3$. Dark blue prec. with HCl and FeCl_3 . Silver prec blue on heating.

3. $\equiv \text{Fe}(\text{CN})_6$. Dirty brown. $\neq$ HCl and FeSO_4 deep blue prec. Silver prec. orange.

4. $-\text{I}$ brown with HCl and FeCl_3 . Chloroform added and shaken assumes violet color. $\neq$ Silver prec. yellow.

G. $\neq$ NaOH , FeSO_4 , FeCl_3 , and HCl to acidity, blue prec. indicates

1. $-\text{CN}$ (not applicable in F_2 and F_3 .)

H. $\neq$ gives Cl with acids and heat (starch-iodide paper in vapor turns blue)

1. $-\text{ClO}$ $\neq$ acidified bleaches indigo solution.

I. $\neq$ Chlorine water and chloroform added to slightly acidified solution.

Color in latter indicates,

1. $-\text{Br}$ gives chloroform brown color.

2. $-\text{I}$ gives chloroform violet color. Carefully add excess of chlorine water until violet disappears (ICl_3). If brown remains, both Br and I are present.,

K. If all previous tests in section II are negative, the silver precipitate must be AgCl , indicating $-\text{Cl}$. Precipitate readily soluble in NH_4OH . If other acid radicals of this section are present, mix portion of dry substance or residue left by evaporation of solution with powdered $\text{K}_2\text{Cr}_2\text{O}_7$ in dry test tube, add 5 cc. H_2SO_4 and warm. Pass bromine fumes into water mixed with H_2O_2 . Transient blue color indicates Cl . (Dangerous if chlorates are present, apply test III, 3, to detect chlorates).

III. Acid radicals not precipitated by Ba or Ag .

1. $-\text{NO}_3$ $\neq$ add equal volume conc. H_2SO_4 , mix well, cool, On this stratify with pipette FeSO_4 . Brown ring. If test is positive, either $-\text{NO}_2$ or $-\text{NO}_3$ may be present.

$-\text{NO}_2$ $\neq$ acid + KI starch paste, blue. If both $-\text{NO}_3$ and NO_2 are present add acetic acid and urea crystals. Boil till a few drops give no color with FeSO_4 , showing that NO_2 is no longer present. Cool, apply ring test.

2. $-\text{ClO}_3$ Dropping conc. H_2SO_4 on particles of dry substance (or residue left by evaporation) liberates disagreeable brown fumes ClO_2 , also Cl . Sharp explosion may occur.

4. $-\text{C}_2\text{H}_3\text{O}_2$. Evaporate 5 to 10 cc. to small volume in evaporating dish. Add 3 cc. ethyl alcohol and 3 cc. conc. H_2SO_4 (well mixed so that

odor of alcohol in annihilated), heat, fruity odor, ethyl acetate. If excess of sulphuric acid, acetic acid odor.

5. -MnO_3 . Characteristic purple color destroyed by H_2SO_4 and a sulphite. Add a sulphite crystal, for the solution changes rapidly to sulphate.

6. =BO_3 . (Not precipitated by barium salt in very dilute solutions)
See 1 D 4.

7. $\text{=C}_4\text{H}_4\text{O}_6$. (May not be precipitated by BaCl . See 1 D 5.)

8. H_2O_2 . HCl and a few drops of $\text{K}_2\text{Cr}_2\text{O}_7$ gives a blue color.

Absence of acid radical indicates that the substance being analyzed is an element, oxide, or hydroxide.

I have substituted the charring and resorcin tests for tartrates in the place of the silver mirror test, for the latter does not work satisfactorily. Some authorities give only the charring test for the detection of tartrates. But as other organic acids also char, it is wise to have the resorcin test for confirmation. The resorcin test gives with ~~tartrates~~ the normal violet red coloration -with lactic acid, one percent salt solution gives a normal gray yellow, with five percent gives yellow shade one -with citric acid one percent solution gives no coloration and five percent gives orange yellow shade two.

As some substances do not precipitate readily with barium chloride, but do so more readily when hot than cold, the word "heat" was inserted in the directions for group one. Then in directions for precipitating division C group one the words "insoluble in acetic acid," because the phosphates are nearly always precipitated in division C, their precipitates thus formed are dissolved upon the addition of acetic acid. In the test for acetates the words, "if neutral solution gives brownish red color

with ferric chloride, precipitate on boiling " were omitted. Because ferric chloride alone gives a normal orange red coloration, due to the hydrolysis of ferric chloride and the formation of the precipitate ferric hydroxide, this, however, on boiling changes to normal yellow orange. The solution of ferric chloride and an acetate is normal red which on boiling yields a red orange shade one precipitate. While the two precipitates differ several shades in color, still the two solutions differing by only one shade (red for acetate solution and orange red for the ferric chloride solution) and the fact that both on boiling yield precipitates, are apt to mislead the student.

As sulphites in solution are changed so rapidly to sulphates, I have found in testing permanganates, III 5, it is most satisfactory to add a sulphite crystal than ~~to~~ a solution.

Division G group II was omitted. Because group two was to consist of substances which gave a precipitate with silver nitrate in the presence of nitric acid. If fifty percent acetate solution with pure silver nitrate crystals formed a precipitate, which was partially dissolved upon the addition of dilute nitric acid to the test tube containing it. A twenty-five percent acetate solution to which was added pure silver nitrate crystals yielded a precipitate which dissolved in dilute nitric acid. A fifty percent acetate solution with dilute nitric acid and silver nitrate (one-half percent, the same as used throughout the experiments) yielded a faint cloudiness but no precipitate. A fifty percent nitrite solution yielded with nitric acid and silver nitrate brown fumes and a precipitate, as did the twenty-five percent and twelve and one half percent, in each case the precipitate was decreasing in amount. Below twelve and one half percent solutions, there was a very faint precipitate due in all probability to a chloride, as no chloride-free nitrite was obtainable. In general, the solutions used for qualitative analysis are not more than five percent, if

that strong; and as neither acetates nor nitrites of that percentage yield a precipitate with nitric acid and silver nitrate, it is advisable to omit division G group II of the original table.

In the table as revised all the individual tests have been proven. So that the scheme will afford no trouble whatever in the detection of the acid radical of a single salt. Now we will give the results obtained with this table in using a mixture of two salts, and in some instances more detailed information concerning the individual acid radicals.

In all the following tests one percent salt solutions were used.

Carbonates may be successfully detected when mixed with sulphides, thiosulphates, sulphocyanides, ferrocyanides, ferricyanides, iodides, cyanides, hypochlorites, bromides, chlorides, nitrates, nitrites, chlorates, acetates, permanganates, and hydrogen peroxide.

Oxalates may be detected with sulphides, thiosulphates, sulphocyanides, ferrocyanides, ferricyanides, iodides, cyanides, hypochlorites, bromides, chlorides, nitrates, nitrites, chlorates, acetates, and hydrogen peroxide; but not very successfully with permanganates.

Phosphates may be detected with sulphides, thiosulphates, sulphocyanides, ferrocyanides, ferricyanides, iodides, bromides, cyanides, hypochlorites, bromides, chlorides, nitrates, nitrites, chlorates, acetates, permanganates, borates, and hydrogen peroxide.

In all the above cases phosphate precipitate was formed in division group I, this precipitate dissolved upon the addition of acetic acid, otherwise the tests were satisfactory. With ferrocyanide a red brown precipitate formed in trying the molybdate test, on heating, however, the color disappeared leaving the characteristic yellow. With sulphides and thiosulphates a green color is obtained with molybdate test, these too disappear on heating leaving the canary yellow precipitate due to the presence of phosphates. With iodides and molybdate test a dark green coloration is

formed, which with heating gave off purple fumes (iodine) on boiling hard for five minutes an orange solution and yellow precipitate appear, on boiling several more minutes we obtain the desired canary yellow precipitate. If color other than phosphate yellow is present, the addition of nitric acid help to drive it off more quickly.

Arsenates may be successfully tested for when mixed with sulphides, thiosulphates, sulphocyanates, ferrocyanides, ferricyanides, iodides, cyanides, hypochlorites, bromides, chlorides, nitrates, nitrites, chlorates, acetates, permanganates, borates, and hydrogen peroxide.

A number of tests often used for tartrates were tried out, with the following results. 1. Add ferrous sulphate or chloride, a little sodium peroxide, and excess of sodium or potassium hydroxide, a purple color is given. This color is given only when saturated or very concentrated solutions of tartrates are used. 2. The silver mirror test with nitric acid, silver nitrate, and ammonium hydroxide is not dependable. 3. A tartrate solution plus dilute sulphuric acid one or two drops of potassium chromate, heated some time gives a yellow color which changes to blue violet. The five percent solution gave a good green violet coloration, the one percent a greenish. This reaction is given by other organic acids. 4. Add weakly acid ammonium molybdate to tartaric acid, one or two drops of hydrogen peroxide or a trace of sodium peroxide (not more), heat gently color changes from wine to green then to blue. This test did not work satisfactorily. 5. A few drops of resorcin in concentrated sulphuric acid warmed until the sulphuric acid vapors just begin to escape, the liquid assumes a wine color. This last test with five percent tartrate solution gave a bead of normal red which charred on standing, the one percent solution gave a bead of violet red tint one which changes to red tint one. Modifying the above method of the resorcin test, in that a two percent

resorcin solution, was used, mixed with the tartrate solution, and the mixture stratified upon concentrated sulphuric acid and heated gently. One drop of two percent resorcin to one percent tartrate solution was sufficient to give a slight violet red ring, on being heated to a slight boil. Two drops of the resorcin solution gave a more decided test on being heated. The ring increasing on standing. While three or four drops of resorcin solution are added there would be no doubt as to the identification of the tartrate. All of the above char on standing. In a hot water bath the violet red ring was formed with the one, two, three, or four drops of resorcin in from three to eight minutes.

Tartrates may be tested for, according to the above scheme with no alterations in the case of the mixture of tartrates with, sulphocyanates, thiesulphates, chlorides, acetates, borates, and cyanides. In the case of the cyanides the concentrated sulphuric acid has to be added carefully as the formation of hydrocyanic acid and its evolution as a gas spoils the test. Tartrates with ferrocyanides, ferricyanides, and iodides, form little or no precipitate with barium chloride. With sulphides, ferrocyanides, ferricyanides, iodides, and bromides the tartrate is precipitated in division C. With ferricyanide the perception of the violet red ring of the resorcin test is marred by the presence of a heavy dark precipitate. With a mixture of tartrates and iodides there is this difficulty, for while the tartrates give the violet red color, with resorcin and concentrated sulphuric so do iodides. If only the two are present, the precipitate in division D group one would show the presence of tartrates and precipitation in group two the presence of an iodide. But there may be other radicals of division D present so we have to resort to the charring test for tartrates. 2 cc. of one percent tartrate solution in a crucible cover gives an extremely heavy char. So much so that this test is often given as the only test for

the detection of tartrates in mixtures. Acetates give a slight char, exalates a very slight one if any. With bromides and the resorcin test, the ring instead of being violet red is blue, (though in one instance the ring is violet red) due to bromine interference. If an excess of bromide be added the violet red ring changes to blue, this was shown by other experiments to be due to the liberation of bromine. In mixtures of tartrates and hypochlorites the hypochlorites act on the resorcin giving an evanescent purple color. If a mixture of one percent hypochlorite and one percent tartrate is used the resorcin test is still good. But if the mixture contains twice as much hypochlorite as tartrate a brown ring is formed. The resorcin test is of no avail with nitrates, nitrites, chlorates, permanganates, and hydrogen peroxide.

Sulphites may be detected in the presence of carbonates, exalates, phosphates, arsenates, tartrates, bromides iodides, and nitrates.

Thiosulphates may be detected in the presence of exalates, phosphates, arsenates, tartrates, bromides, iodides, and nitrates.

Sulphocyanides may be detected in the presence of carbonates, exalates, phosphates, arsenates, tartrates, and borates.

Ferrocyanides may be detected in the presence of carbonates, exalates, phosphates, arsenates, tartrates, and borates.

Ferricyanides may be detected in the presence of carbonates, exalates, phosphates, tartrates, borates, and arsenates.

Iodides may be detected in the presence of carbonates, exalates, phosphates, arsenates, tartrates, borates, and nitrates by the chloroform, chlorine water test. But if the iodides be mixed with either a sulphide or a thiosulphate the chloroform, chlorine water test is no good. If you heat a mixture of sulphides and iodides with concentrated nitric acid to destroy the sulphide, purple iodine vapors will be given off before all the sulphide is destroyed. If to a mixture of

an iodide and thiosulphate you add concentrated nitric acid and chlorine the iodine coloration is given.

Cyanides may be detected in the presence of carbonates, oxalates, phosphates, arsenates, and tartrates.

Hypochlorites may be detected in the presence of carbonates, oxalates, phosphates, arsenates, and tartrates.

Bromides may be detected in the presence of carbonates, oxalates, phosphates, arsenates, tartrates, and nitrates. If the bromide is mixed with a sulphide or a thiosulphate the chlorine water test will not work until the sulphide or thiosulphate has been destroyed; this may be done with concentrated nitric acid.

Chlorides may be detected in the presence of carbonates, oxalates, phosphates, arsenates, and tartrates.

Nitrates may be detected in the presence of carbonates, oxalates, phosphates, arsenates, tartrates, bromides, and iodides. Nitrates when mixed with sulphides and thiosulphates are changed to nitrites.

Nitrites may be detected in the presence of carbonates, oxalates, phosphates, arsenates, and tartrates.

Chlorates may be detected in the presence of carbonates, oxalates, phosphates, arsenates, and tartrates.

Acetates may be detected in the presence of carbonates, oxalates, phosphates, arsenates, and tartrates.

Permanganates may be detected in the presence of carbonates, oxalates, arsenates, and tartrates. If the permanganate is mixed with a phosphate, the permanganate will not be decolorized by a sulphite, but will be by a sulphide.

Borates may be detected in the presence of phosphates, arsenates, tartrates, sulphocyanides, ferrocyanides, ferricyanides and iodides.

Hydrogen peroxide may be detected in the presence of oxalates,

phosphates, arsenates, tartrates, and freshly prepared solutions of carbonates. If the mixture of hydrogen peroxide and carbonates is allowed to stand for a day or so, the hydrogen peroxide test will not be given.

In working the foregoing experiments reagents of the following strengths were used, unless otherwise specified. Sodium hydroxide, ammonium hydroxide, ammonium chloride, sulphuric acid, hydrochloric acid, and nitric acid were three-normal. Ammonium carbonate and acetic acid twice-normal. Sodium carbonate was a normal solution. Barium chloride, ferric chloride, potassium dichromate, and lead acetate were half-normal. Potassium ferrocyanide was fourth-normal and the silver nitrate was one-half of one percent.