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I hereby recommend that the thesis prepared under my supervision by John Weaver

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NEW ORGANIC ANALYTICAL REAGENTS

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INTRODUCTION

New organic analytical reagents are desired to extend the scope of chemical analysis, to make its methods more simple, or more precise, or both. Many modern methods involve troublesome and time consuming separations of interfering substances preliminary to the actual detection or determination of the substance sought, and even when carefully done do not always yield precise results.

Even the detection and determination of many of the elements is not very satisfactory, e.g., the determination of zinc and cadmium in mixtures of the two is by no means simple, Hillebrand and Lundell (1), p. 204, and the precise determination of tantalum and columbium in their mixtures approaches the impossible (loc. cit., pp. 463-485). New reagents of specific reaction are needed to simplify and improve these separations. Analyses for radicals and compounds presents further opportunities for improvements in methods.

The term organic analytical reagent has two definitions, first, the general one of any organic substance used in analysis, and second, the more arbitrary and limited one denoting any organic substance which gives a specific reaction with one or only a few elements, radicals or compounds, and thereby permits the detection or determination of a substance even if it be associated with other substances similar to it in most respects.

The general definition covers many diverse uses of organic compounds and includes the following:

1. Solvents such as alcohols, ethyl ether, etc.

2. Weak acids and bases for acidimetry and alkalimetry and for buffer solutions, e.g., potassium hydrogen phthalate, benzoic and succinic acids and the bases pyridine, urea and ethylamine.

3. Glycerol, mannitol, various sugars and ortho dibasic phenols cause boric acid to become sufficiently strong for accurate titration with strong alkalies.

4. Hydrogen ion indicators, e.g., methyl orange and phenolphthalein.

5. Inert dyes used in conjunction with H-ion indicators to modify the two colors of the indicator and make them more distinguishable, e.g., Xylenole FF with methyl orange can produce a neutral gray in the transition range between the two principal colors, (2), p. 71.

6. Reducing compounds as in the use of oxalic acid (or sodium oxalate) as a primary standard for potassium permanganate solutions.

7. Oxidation-reduction indicators. Diphenylamine (colorless) is oxidized to a blue-violet compound when an excess of potassium dichromate solution is added to an acidified solu-

tion of a ferrous salt and a small amount of the indicator.

8. Adsorption indicators are used to show the end points of certain precipitation titrations. When fluorescein is present in a solution of soluble chloride the addition of a slight excess of silver nitrate solution causes the resulting silver chloride precipitate and suspension to adsorb fluorescein ions and thereby to assume a distinct red color.

9. Protective colloids such as dextrin causes precipitates to remain finely divided and suspended and permits adsorption indicators to show a more distinct end point, (2), p. 127.

10. Precipitates are of various kinds, from the simple formation of calcium oxalate with oxalic acid to the complex crystals formed by cadmium salts with ammonium thiocyanate and pyridine, (3), p. 22.

11. Reagents giving distinctive colors, both of solutions and precipitates, include a wide variety of substances such as p-nitro-benzene-azo-resorcinol which produces a blue solution with magnesium ions, α-Benzoinoxime, which yields a green precipitate with copper salt solutions, rosaniline-sulfurous acid solution (Schiff's reagent), which yields a red color with aldehydes and phenylhydrazine which forms bright yellow osazones with ketonic sugars.

12. Morin, a tetrahydroxylflavanol, was found by F. Goppelsroeder (4) to combine with aluminum ions to give, in the presence of HCl, an intense green fluorescence. This

phenomenon was developed into an analytical method by E. Schantl, (5).

The present problem is concerned chiefly with the precipitates, either distinctively colored or not, and the colored solutions formed by various organic compounds with metal salts. These precipitates have been classified roughly according to their chemical nature by Mitchell and Ward, (3), pp. 17-22, into: (1) saltlike complexes, (2) co-ordination compounds, (3) adsorption complexes, and (4) other complex salts.

1. The compounds of benzidine with sulfate or tungstate ions; of "Cupferron" (ammonium salt of nitrosophenylhydroxylamine) with iron, copper and other ions and of phenylthiohydantoic acid with cobalt are all considered to be true salts.

2. Dimethylglyoxime and other oximes are thought to form co-ordination compounds wih nickel and palladium. Oxime (8-hydroxy quinoline) forms similar precipitates with magnesium, aluminum and other metal ions.

3. Some other precipitates of metals with organic substances are of variable composition, as in the case of aluminum with sodium alizarin sulfonate, and are thought to be produced by the selective adsorption of the organic substance on colloidal hydroxides.

4. More complex salts are formed by pyridine and ammonium thiocyanate with several of the metals. These salts are

quite crystalline and the pyridine contained may be bound only loosely in the crystal as in the case of water of crystallization.

Colored solutions are produced under such diverse conditions that it is difficult to make a general classification of them with respect to products formed. It is possible, however, that some of the colored solutions known are really colloidal suspensions of the hydroxide of the metal on which is adsorbed the organic reagent, producing the distinctive color. It will be shown later that there may be a relation between the formation of the specific color and the value of increasing pH at which metal salts begin to hydrolyze.

A study of tables of the reagents giving more or less specific reactions with metal salts (5,6,7,8) fails to show any pronounced relationship between the structures of the organic reagents employed and the characteristics of the metal or its salts, except that most of them contain weak acid groups and many of them are either colored or are capable of simple transformation into colored compounds. Because of the very fact that the better reagents are quite specific and often peculiar in reaction, it seems unreasonable to expect general, well ordered relationships between their structure and reactions with metals.

Since it then appears impossible to predict by analogy that a given untried compound may produce a specific reaction with a given metallic salt, a search for new organic reagents cannot be directed by a definite set of rules for the choice of possible reagents, except for the general properties of weak acidity and possible color, but must follow a process of trial of a large number of compounds under as widely varying controlled conditions as is practicable, with the possibility that out of a large number of failures a few compounds may give reactions sufficiently specific to merit further investigation.

It was then decided to test a conveniently large number of metal salts with as many organic compounds as time permitted.

Organic compounds were chosen for trial on the bases of availability, possession of acid groups, possible changes of color, solubility, and in some cases by analogy to known reagents. Most of the compounds tried were dyes listed in the Color Index (10). These dyes when mentioned hereafter may be referred to by their numbers in the index, e.g., C.I. 216.

Organic reagents were usually used in neutral 0.1% aqueous solutions, with addition of alkali, or change of solvent, only when necessary to bring the substance into solution.

The choice of metals followed partly their frequency of occurrence, (2) p. 7, and partly their usage for mordants and for lake manufacture, since their mordanting properties may indicate general reactivity with organic compounds possessing acid groups. Weiser, (9) p. 337, lists the hydrous oxides of chromium, aluminum, iron, tin and copper, in the order named, as being the most important metallic mordants, and refers to the use of most of the other metals forming hydrous oxides as being more or less applicable as mordants. The alkali metals were considered to be unworthy of trial because few specific reactions for them are already known, their hydroxides are very soluble and are not hydrated under ordinary conditions and most of their salts are soluble and quite similar to one another.

Twenty-four was arbitrarily chosen as a convenient number of metal salts with which to work. These were chosen from the above considerations and with the purpose of getting, where possible, representatives of the metals of each of the groups and subgroups of the periodic table of the elements. Those chosen were:

$BeCl_2$

$MgSO_4$

$CaCl_2$

$SrCl_2$

$BaCl_2$

$AlCl_3$

$ZrCl_4$

$ThCl_4$

*CbF_5

$CrCl_3$

$MnCl_2$

**$FeSO_4$

$FeCl_3$

$CoCl_2$

$NiSO_4$

$CuCl_2$

Ag_2SO_4

$Zn(C_2H_3O_2)_2$

$CdCl_2$

$HgCl_2$

$SnCl_4$

$Pb(C_2H_3O_2)_2$

$KSbOC_4H_4O_6$

$Bi(NO_3)_5$

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* TaF_5 was substituted in some tests.

** From Mohr's salt.

All except three of the salts (those of Be, Th and Cb were prepared by students) were of standard C.P. grade and were not tested for impurities because of the approximate nature of the tests to be made and because the extreme dilution of the salt solutions, to be discussed below, would make expected amounts of impurities of such low concentration as to escape the limits of sensitivity of most of the known anticipated tests.

Sensitivities of organic reagents for metals as measured by the limits of dilution listed in Mitchell's table, (8), pp. 311-338, range from the extremes of dilution of 1:200 to 1:50,000,000 with most of them falling between 1:5,000 and 1:500,000. This latter range is roughly approximated by making each of the 24 salt solutions 0.0010 molar, and results in dilutions of from 1:110,000 for Be to about 1:5,000 for Bi. Later additions of reagents increase these dilutions about two and one half times. Making all of the solutions of equal molar concentration forms a definite basis for the comparison of the results of each.

EXPERIMENTAL METHOD

In practice, 5 cc. portions of the 24 thousandth molar salt solutions were pipetted into 24 corresponding test tubes. There were then added to each tube equal amounts of the organic reagent solution, usually 5 drops, or sufficient to give a strong but transparent color to the solution, or if colorless, an amount nearly equimolar with the salt present in the test tubes. With the colored compounds the amount used was nearly always only a small fraction of the equimolar amount.

Observations were then made of the appearance of the solution and of any precipitate which may have formed.

0.5 cc. of 6 N. ammonium acetate, adjusted to a pH of 7 by addition of acetic acid and ammonia and comparison with Kolthoff's buffer standards, (11), pp. 147-148, using dibromothymol sulfonphthalein as an indicator, were then added and the solutions were allowed to stand for an hour or longer before a second set of observations were made. The addition of this amount (.003 mole) of ammonium acetate to the 5 cc. of metal salt solution (.000005 mole) served to bring all of the solutions to practically identical values of pH as indicated by the addition of the above indicator to a set of these solutions containing no organic reagents.

2 cc. of 6 N. acetic acid were then added to each tube after the second set of observations and, after standing one hour or more, a third set of observations was made.

5 cc. of 6 N. ammonium hydroxide were added finally and, after another period of standing for an hour or more, final observations were made.

The result is a set of observations in the original solution, at the neutral point, in weakly acid and in weakly alkaline solutions.

The color and solubility of the solutions of organic compounds in 6 N. solutions of hydrochloric acid, acetic acid, ammonium acetate, ammonium hydroxide and sodium hydroxide were also noted with the purpose of finding possible correlations between these characteristics and any unusual results noted in the above sets of observations.

To the objections that conditions of strong acidity and alkalinity are not covered, that the presence of acetic acid or ammonium hydroxide or both may have inhibiting effects on some possible specific reactions, that effects of wide temperature variations are not noted, that only four observations for each case are not enough, it may simply be stated that since the chance of any single reagent proving of value may not be large, and since it is believed that trials of a large number of compounds are most likely to yield good results, it follows that the method of trials must be kept simple in order to make real progress.

The period of standing was found to be quite necessary in the formation of many precipitates and also to be important to the formation of some of the uniquely colored solutions to be described later.

Some of the solutions showed variations in color with different light sources so that a blue "daylight" bulb was used as much as possible.

Originality cannot be claimed for the testing of every compound given, for the time required for an exhaustive search of the literature for each compound would be prohibitive. Hence such searches will be made only for compounds that show promise of value and merit further testing.

In listing results of the tests of each compound, space will not permit the recording of details of the appearance of the tests with each metal. Hence only exceptional appearance contrasted with general non-specific appearance will be noted.

MODE OF LISTING TESTS

In general and where possible the following paragraph mode of listing will be used, in the order given.

Color Index Number. Commercial or chemical name (source). Number of drops of solution per 5 cc. of salt solution and concentration and solvent of the solution (color of this solution in acid, neutral, or alkaline solution, if variable). In neutral, acetic acid and ammoniacal salt solution the normal appearance and the specific appearance if worthy of note. Unless stated otherwise the colors will be those of solutions. Precipitates will be indicated by ppt. Chemical names may in some cases be shortened by using the symbol ⟶ to indicate an azo group, e.g., picramic acid diazotized and coupled to o-cresol is written as picramic acid ⟶ o-cresol.

The source, given in each case in parenthesis, will be either "(student)", denoting a student preparation, "(JCW)", denoting a preparation by the author, "(unknown)", or, as in most cases, capital initials, e.g., (NAC), denoting the manufacturer as listed below.

(AAP)	American Aniline Products, Inc., New York
(ADC)	American Dyewood Co., Belleville, New Jersey
(B)	Badische Anilin-und Soda Fabrik, Germany
(CB)	Coleman & Bell, Norwood, Ohio
(CCC)	Calco Chemical Co., Bound Brook, New Jersey
(CCW)	Cincinnati Chemical Works, Norwood, Ohio
(DuP)	E. I. DuPont de Nemours & Co., Wilmington, Del.
(FCL)	Federal Color Laboratories, Norwood, Ohio
(Gy)	Geigy & Co., Basle
(JC)	John Campbell & Co., New York
(K)	C.A.F. Kahlbaum, Berlin
(KP)	Kutroff, Pickhardt & Co., Inc., New York
(Metz)	H.A. Metz & Co., New York
(MOH)	Marden, Orth & Hastings Corp., New York
(NAC)	National Aniline & Chemical Co., New York
(UCP)	United Color & Pigment Co., Newark, N. J.
(WTA)	White Tar Aniline Corp., New York
(Z)	Zinsser & Co., Hastings-on-Hudson, New York

LIST I

1. Dinitrosoresorcin (student). 5 drops of $<0.1\%$ aq. soln. (pale yellow in acid or alkaline). Neutral (colorless): Co-orange; Ni, Cu-yellow; Fe^{++}-green blue. Acetic (colorless): Co-brown ppt.; Ni, Cu-yellow; Fe^{++}- green blue ppt. Ammonia (colorless): Ni-red brown ppt.; Mn-brown ppt.

Like 1. 4-Nitrososalicylic acid (JCW). 5 drops of $<0.1\%$ aq. soln. (pale yellow to bright yellow in NaOH). Various brown ppts.

Like 4. Nitroso R salt (student). 10 drops 0.05% aq. soln. (yellow). Neutral: Co-orange; Cr, Ni, Th-yellow; Fe^{++}-green. Acetic: same. Ammoniacal: Co-orange red.

7. Picric acid (C.P.). 1 cc. 0.1% aq. soln. (yellow).

Like 7. Picramic Acid (JCW). 10 drops 0.1% aq. soln. (orange, pale yellow in acid). Neutral (orange) and acetic (yellow): Cu-yellow ppt.

Like 7. 2-4-6-Trinitroresorcin (student). 1 cc. 0.1% aq. soln. (pale yellow).

Like 7. 2-5-Dinitrohydroquinone (student). 5 drops 0.1% aq. soln. (HCl, acetic-pale yellow; neutral-orange; ammonia, NaOH-purple). Original solution (yellow, red): Pb-pale lavender ppt. Ammoniacal (purple): Co-pale orange; Cu, Mn-yellow.

12. Aurantia (student). 5 drops $<0.1\%$ aq. soln. (yellow).

27. Orange GG (student). 10 drops 0.1% aq. soln. (yellow).

29. Chromotrope 2R (?). 10 drops 0.1% aq. soln. (red, orange). Neutral (orange pink): Al, Be-violet red; Cr, Cu, Zr-red. Acetic (orange pink): Cr-red.

31. Pontacyl Carmine GG (DuP). 5 drops 0.1% aq. soln. (pink).

36. Chrome Yellow G (CCW). 10 drops 0.1% aq. soln. (acid, neutral-yellow; ammonia, NaOH-orange). Many yellow ppts.

40. Chrome Orange R (CCW). 5 drops 0.1% aq. soln. (acid, neutral-yellow ppt.; ammonia-deep red). Many yellow or red ppts.

45. Chromotrope 2B (student). 5 drops 0.1% aq. soln. (acid, neutral-light red; ammonia-violet, NaOH-blue). Neutral (pink): Be, Al, Cr-violet; Th, Cu-violet red. Ammoniacal (red violet): Co-blue violet.

52. Alizarine Yellow 4G (AAP). 10 drops 0.1% aq. soln. (yellow,orange). Many yellow ppts.

53. Acid Violet 4BS (WTA). 5 drops 0.1% aq. soln. (acid-pink, neutral-violet, NH_4OH-orange, NaOH-pink). Neutral (violet): Al, Zr-blue. (May be due to pH change, cf. C.I. 59).

56. Erio Fast Fuchsine 6B (Gy). 5 drops 0.1% aq. soln.

(acid, neutral-red; NH_4OH-orange; NaOH-red. Neutral (red): Be, Al, Th, Cr, Cu-violet; acetic (red): Cr-violet.

57. Fast Crimson 6BL (NAC). 5 drops 0.1% aq. soln. (acid, neutral-pink; NH_4OH, NaOH-pink).

59. Erioazurine 3B (Gy). 5 drops 0.1% aq. soln. (acid-orange red; neutral-blue; NH_4OH-orange; NaOH-red). Neutral (violet red): Be, Al, Cr-pure blue. This merits further investigation as an H-ion indicator.

67. Persian Yellow (student). 5 drops <0.1% aq. soln. (yellow). Various yellow ppts.

Like 67. 1-Hydroxy-2-carboxy-4-nitrobenzene-azobenzene. 5 drops <0.1% aq. soln. (acid-insol., alkaline-yellow). Various yellow ppts.

69. Naphthanil Red G Base (DuP). 0.5 cc. of 0.1% ethereal soln. (yellow).

79. Lake Scarlet R (CB). 5 drops 0.1% aq. soln. (orange pink). Neutral (orange pink): Cu-bright yellow.

87. Fast Red B (student). 0.5 cc. 0.1% aq. soln. (red). Neutral (red): Cu-yellow. (Incomplete tests.)

88. Bordeau R (?). 5 drops 0.1% aq. soln. (pink). Neutral (pink): Cu-yellow, Ni-orange pink.

89. Crystal Ponceau 6RF (?). 5 drops 0.1% aq. soln. (orange-red). Neutral (orange pink): Cu-yellow.

101. Metachrome Brown B (?). 5 drops 0.1% aq. soln. (orange pink). Various ppts.

103. Picramic acid $\longrightarrow$ phenol (JCW). 5 drops 0.1%

aq. soln. (acid, neutral-yellow; NH_4OH, NaOH-orange). Many yellow ppts.

Like 103. Picramic acid ⟶ o-cresol (JCW). 5 drops 0.1% aq. soln. (HCl-pink; acetic-orange; neutral-yellow; NH_4OH, NaOH-orange).

Like 103. Picramic acid ⟶ m-cresol (JCW). 10 drops 0.1% aq. soln. (acid-yellow; alk.-red). Original (yellow, orange): Cu-maroon ppt.; Pb-orange ppt.; other yellow ppts.

104. Picramic acid ⟶ p-cresol (JCW). 5 drops 0.1% aq. soln. (HCl-yellow; acetic-orange; neutral-yellow; NH_4OH, NaOH-orange red). Neutral (yellow): Al, Be, Cu, Ni, Zn-orange pink. Acetic-about same. NH_4OH (pale yellow solns., orange ppts.): Ni-orange pink; Co-brown ppt.

Like 103. Picramic acid ⟶ thymol. 5 drops of <0.1% aq. soln. (acid, neutral-red ppt.; NH_4OH, NaOH-red). Neutral: many red ppts. and solns.; Cu-purple; Mn-green yellow. Acetic (orange ppts.): Mn-green yellow. Ammoniacal (pink): Ag, Co, Mn-yellow.

Like 103. Picramic acid ⟶ catèchol. 5 drops of 0.1% aq. soln. (yellow). Original (yellow): Pb-brown ppts. colorless soln.

Like 103. Picramic acid ⟶ resorcinol. 5 drops of 0.1% aq. soln. (acid-yellow; neutral, NH_4OH-orange; NaOH-red). Many red ppts.

Like 103. Picramic acid ⟶ pyrogallol. 5 drops of 0.1% soln. (yellow or yellow orange). Many yellow and orange ppts. and solns.

Like 103. Picramic acid → phloroglucinol. 3 drops 0.1% soln. (HCl-yellow; acetic to NaOH-orange). Acetic (orange pink): Co-strong orange pink.

Like 103. Picramic acid → salicylic acid. 5 drops 0.1% soln. (HCl-yellow ppt.; acetic, neutral-yellow; NH_4OH, NaOH-yellow orange). Ammoniacal (yellow): Bi, Cr, Fe^{++}, Pb, Th, Zr-yellow ppt.

Like 103. Picramic acid → β-Hydroxynaphthoic acid. 3 drops 0.1% soln. (acid, neutral-red ppt.; NH_4OH-red; NaOH-red brown ppt.). Original soln. (red and violet ppts. and solns.): Mg-blue ppt. Acetic-many pink to blue ppts. Ammoniacal (many lavender and purple ppts.): Ca, Cu, Mg-blue ppts.: Co-no ppt., lavender soln.

Like 103. Picramic acid → β-resorcylic acid. 3 drops 0.1% soln. (HCl-orange ppt.; acetic-red; neutral-red ppt.; NH_4OH-red; NaOH-red ppt.). Various red ppts. and solns.

Like 103. Picramic acid $\xrightarrow{(\text{acid})}$ Schoelkopf's acid. 5 drops 0.1% soln. (orange red). Neutral (orange pink): Many red and brown ppts., and yellow solns. Acetic (pink): Cr, Mn-orange; Cb, Fe^{++}, Fe^{+++}-yellow. Ammoniacal: similar results.

Like 103. Picramic acid $\xrightarrow{(\text{alk.})}$ H-acid. 3 drops 0.1% aq. soln. (HCl-orange; acetic-red; neutral, NH_4OH-

violet red; NaOH-violet). Neutral (violet): Al, Cu, Ni, Th, Zr-blue; Co-green blue. Acetic: same. Ammoniacal (violet): Bi-blue ppt. and soln.; Cu-blue; Co-green blue.

Like 103. Picramic acid ⟶ Schaeffer's Salt. 5 drops 0.1% aq. soln. (red). Neutral, acetic, ammoniacal (red): red ppts. and solns.; Fe^{++}, Fe^{+++}-yellow ppt. and soln.

Like 103. Picramic acid ⟶ Neville and Winther's acid. 3 drops 0.1% aq. soln. (HCl-orange; acetic-orange red; neutral-violet; NH_4OH, NaOH-red). Neutral (red): Cu-blue, blue ppt.; Hg-pale pink. Acetic (red): Co-orange red; Cu-blue ppt.; Fe^{++}, Fe^{+++}-yellow, yellow ppt.; Hg-pale pink. Ammoniacal (pink): Cu-blue ppt.

Like 103. Picramic acid ⟶ G-acid. 5 drops 0.1% aq. soln. (acid-orange; neutral-pink; NH_4OH-orange; NaOH-yellow). Neutral, acetic (pink): Co-yellow pink; Fe^{++}-yellow, yellow ppt. Ammoniacal (pink). Cb-yellow, white ppt.; Mn-yellow, brown ppt.

Like 103. Picramic acid ⟶ R-acid. 3 drops 0.1% aq. soln. (HCl-yellow orange; acetic-orange red; NH_4OH-red; NaOH-red ppt.). Acetic (red): Co, Ni, Cu-orange red; Fe^{++}-yellow; Fe^{+++}-yellow, yellow ppt.

Like 103. Picramic acid ⟶ Chromotropic acid. 5 drops 0.1% aq. soln. (acid-red; neutral-violet; NH_4OH-red; NaOH-deep blue). Neutral (red violet): Al, Cr, Sn, Zr-blue;

blue
ppt.; Ni, Cu-red. Acetic (violet): Cr-blue; Ni, Cu-red. Ammoniacal (violet): Co-green blue; Bi, Th, Zr-blue ppt.

109. Dutch Yellow (student). 0.5 cc. of 0.1% alc. soln. (yellow). Many yellow and orange ppts., and yellow solns.

110. Diamond Flavine G (student). 5 drops of <0.1% aq. soln. (HCl-brown ppt.; acetic, neutral-yellow; NH_4OH, NaOH-orange). Many yellow ppts. and solns.

120. Coccinine (?). 5 drops 0.1% aq. soln. (orange-red). Neutral (red): Co, Cu-orange.

124. Chromazone Red N (Gy). 5 drops 0.1% aq. soln. (red). Neutral (orange red): Al-red, Be, Cr-violet red.

148. Resorcin Yellow (student). 5 drops 0.1% aq. soln. (HCl to NH_4OH-yellow, NaOH-orange). Neutral, acetic, ammoniacal (yellow): yellow; NaOH (orange): orange.

Like 148. p-Nitrobenzene-azo-resorcin (student). 5 drops 0.1% aq. soln. (HCl acetic, neutral-yellow; NH_4OH-red; NaOH-purple). Neutral, acetic, ammoniacal (yellow): yellow ppts. and solns.: NaOH (violet): Mg-blue ppt.; other ppts. not blue.

150. Orange I (CB). 5 drops 0.1% aq. soln. (HCl-violet red; acetic, neutral-orange yellow; NH_4OH, NaOH-red).

151. Orange II (Gy). 5 drops 0.1% aq. soln. (HCl, acetic, neutral-yellow; NH_4OH, NaOH-orange).

157. p-nitro-orthanilic acid ⟶ salicylic acid

(student). 10 drops 0.1% aq. soln. (HCl, acetic, neutral-yellow; NH_4OH-orange, NaOH-pink). Yellow ppts. and solns.

Like 157. 2,6 dichloro,4 nitroaniline ⟶ salicylic acid (student). 5 drops 0.1% aq. soln. (HCl, acetic-colorless; neutral, NH_4OH, NaOH-yellow). Yellow solns.

159. Fast Orange S (?). 5 drops 0.1% aq. soln. (orange-yellow). Neutral (orange pink): Ni-red; Sn-orange ppt., colorless soln. Acetic and ammoniacal-orange red ppts.

163. Rubrex Red (CCW). 5 drops of $<0.1\%$ soln. (orange red). Many orange and red ppts. and solns.

169. Superchrome Violet B (NAC). 5 drops of 0.1% soln. (HCl-red ppt.; acetic-yellow orange; neutral, NH_4OH-red; NaOH-orange). Neutral, acetic (orange red): Fe^{++}, Fe^{+++}-yellow; ammoniacal (pink): Fe^{++}, Fe^{+++}, Mn-yellow; Bi-violet ppt.; Co, Ni, Cu-orange pink; Th, Zr-orange ppt.

170. Superchrome Black PV (NAC). 5 drops 0.1% aq. soln. (HCl, acetic, neutral-red; dil. NH_4OH-blue; NH_4OH-violet; NaOH-pink). Neutral (violet pink): Fe^{++}, Fe^{+++}-yellow. Acetic (pink): Fe^{++}, Fe^{+++}-yellow. Ammoniacal (blue): Fe^{++}, Fe^{+++}-turbid yellow; Cr, Mg, Ni-red violet; Th, Zr red ppt.

175. Echtbraun G (K). 1 cc. 0.1% aq. soln. (orange and yellow). Incomplete tests.

176. Fast Red A (DuP). 5 drops 0.1% aq. soln. (HCl-yellow; acetic-pink; neutral-yellow; NH_4OH, NaOH-pink).

179. Azo Rubine Extra (NAC). 5 drops 0.1% aq. soln. (red). Neutral (red): Cu-yellow.

184. Amaranth (?). 5 drops 0.1% soln. (pink). Neutral (pink): Cu-yellow; Ni-orange.

185. Ponceau 4 R (K). 0.5 cc of 0.1% aq. soln. (red). Neutral (red): Cu-yellow. Tests incomplete.

189. Lithol Red R (CCW). 0.3 cc. of 0.1% alc. (with HCl) soln. (red).

194. Scarlet 2 R (FCL). 5 drops of 0.1% aq. soln. (orange). Neutral (orange): Cu-yellow.

195. Chromaven Yellow LSW (AAP). 5 drops 0.1% aq. soln. (yellow).

201. Eriochrome Blue Black B (CCW). 5 drops 0.1% aq. soln. (HCl-red violet, acetic-red; neutral-violet; very dilute NH_4OH-blue; NH_4OH, NaOH-red). Original: Mn-green blue. Neutral (violet red). Acetic (red): Mn-yellow. Ammoniacal (blue): Mn-yellow; several violet and red ppts. and solns.

202. Pontachrome Blue Black R (DuP). 10 drops 0.1% aq. soln. (No color-pH tests made). Variety of shades of red to blue in acetic and ammoniacal solns. Bleaches in ammoniacal solution with speed varying with metal present.

203. Eriochrome Black T (CCW). 5 drops of 0.1% aq. soln. (HCl-red violet; acetic-red; neutral-violet blue; very dilute NH_4OH-pure blue; NH_4OH, NaOH-red). Neutral

(violet): Co, Th, Zn-red; Mn-yellow; Cd-colorless, white ppt. Acetic (pink): Co, Cu-red; Mn-yellow; Sr-yellow-lavender. Ammoniacal (blue or green blue): Al, Be, Mg, Sr, Ni-pink; Mn-yellow green; Ca-yellow, orange ppt.; Fe^{++}, Fe^{+++}-yellow; Th-yellow, red ppt.; Zr-green, violet ppt.; Cd-green blue, blue ppt.

204. Eriochrome Black A (CCW). 5 drops 0.1% aq. soln. (HCl-red violet; acetic-pink; Neutral-blue; NH_4OH-violet; NaOH-red). Solns. and ppts. of many colors from yellow through red to blue appear to be formed under various conditions of acidity and alkalinity.

209. Pontacyl Fast Blue SB (DuP). 5 drops 0.1% aq. soln. (HCl, acetic-blue; neutral-violet; NH_4OH, NaOH-red).

211. Methyl Red (student). 0.5 cc. of 0.1% aq. soln. (HCl, acetic-red; neutral, NH_4OH, NaOH-yellow).

212. Anthranilic acid $\longrightarrow$ p-cresol (student). 5 drops 0.1% aq. soln. (HCl, acetic-orange ppt.; neutral-yellow orange; NH_4OH, NaOH-orange). Neutral (yellow): Co-pale green; Cr, Fe^{++}, Ni, Cu-orange pink; Th, Pb-pink ppts. Acetic (yellow): Co-brown green; Cr, Fe^{++}, Cu-orange pink; Th-yellow ppt.; Fe^{++}- pink ppt. Ammoniacal (yellow): Co-violet; Cr, Fe^{++}-pink yellow.

Like 212. Anthranilic acid $\longrightarrow$ m-cresol (student). 5 drops 0.1% aq. soln. (yellow).

Like 212. Anthranilic acid ⟶ phenol (JCW). 5 drops 0.1% aq. soln. (yellow).

Like 212. Anthranilic acid ⟶ p-chlorophenol (JCW). 5 drops 0.1% aq. soln. (yellow). Neutral (yellow): Co-greenish yellow; Be, Al, Th, Cr-orange; Ni, Cu-red orange; Zr, Th, Ta, Cr, Cu-red ppt. Acetic (yellow): Cr, Mn, Cu-orange. Ammoniacal (yellow): Co-violet red.

Like 212. Anthranilic acid ⟶ resorcinol (JCW). 5 drops 0.1% aq. soln. (yellow). Neutral (yellow): Co-brown orange. Acetic (yellow): Co-red orange; Hg-orange ppt. Ammoniacal (yellow): Co-deep orange; Cr-orange.

Like 212. Anthranilic acid ⟶ pyrogallol (JCW). 5 drops of <0.1% aq. soln. (yellow). Ammoniacal (yellow): Co-pale violet yellow; several orange ppts.

213. Anthranilic acid ⟶ salicylic acid (student). 5 drops of 0.1% aq. soln. (yellow).

214. Anthranilic acid ⟶ β-Naphthol (student). 1 cc. of <0.1% alc. soln. (yellow orange). Neutral (orange): Co, Fe^{++}-yellow; Ag-red ppt. Acetic (pink orange): Co-green yellow. Ammoniacal (orange): Co-pale violet red.

215. Anthranilic acid ⟶ Schaeffer's acid (student). 5 drops of 0.1% aq. soln. (orange). Neutral (yellow orange): Co-brown green. Acetic (yellow orange): Co-green yellow. Ammoniacal (yellow orange): Co-violet red.

Like 215. Anthranilic acid ⟶ Neville and Winther acid (JCW). 5 drops 0.1% aq. soln. (HCl, acetic, neutral-orange; NH_4OH, NaOH-yellow). Neutral (orange): Co, Fe^{++}-brown. Acetic (orange): Co-brown; Cr-red orange. Ammoniacal (orange): Co-violet red.

216. Pigment Scarlet 3B (CCW). 5 drops 0.1% aq. soln. (orange). Neutral, acetic (orange): Co-green orange; Cu-yellow orange; Ammoniacal (orange): Co-violet pink.

223. Cotton Yellow R (B). 5 drops 0.1% aq. soln. (acid, neutral-yellow; alkaline-orange). Various yellow and orange solns. and ppts.

234. Resorcin Brown B (CCW). 5 drops 0.1% aq. soln. (HCl, acetic-orange; neutral-yellow; NH_4OH, NaOH-dark orange). Various yellow solns. and ppts.

235. Resorcin Brown RN (NAC). 5 drops 0.1% aq. soln. (orange, red). Many orange and red ppts.

246. Naphthol Blue Black B (Gy). 3 drops 0.1% aq. soln. (blue). Ammoniacal (blue): Co-bleached.

248. Oil Scarlet (?). 0.5 cc. of <0.1% aq. soln. (pink). Precipitates.

252. Croceine Scarlet MOO Conc. (WTA). 10 drops 0.1% aq. soln. (orange red). Orange red solns. only.

277. Croceine Scarlet (JC). 5 drops 0.1% aq. soln. (orange red).

294. Buffalo Black 10B (NAC). 2 drops 0.1% aq. soln. (blue). Neutral (blue): Al, Cr, Fe^{+++}-turbid lavender;

Zr, Cb-blue ppt.

299. Chrome Fast Black FW (CCW). 3 drops 0.1% aq. soln. (HCl, acetic, neutral-red violet; alkaline-blue). Mostly violet and red ppts. and solns. Ammoniacal (red ppt., colorless): Bi-blue ppt., colorless.

307. Durol Black B (NAC). 5 drops 0.1% soln. (acid-green; alkaline-violet). Some purple ppts., lavender solns.

315. Naphthol Black B (?). 3 drops 0.1% aq. soln. (purple). Neutral (purple): Cu-yellow; Ag, Al, Cr, Fe^{++}, Fe^{+++}-turbid lavender; Zr-purple ppts.

326. Erie Fast Scarlet 4BAP (NAC). 3 drops 0.1% soln. (pink). Various orange and pink ppts.

336. Chromaven Black SE (AAP). 5 drops 0.1% soln. (HCl-purple ppt.; acetic-bright red; neutral-pale blue, blue ppt; NH_4OH-dark blue; NaOH-red). Acetic (violet ppts.): Cd, Cr, Zn-red, red ppt.; Cb, Co, Cu, Ni-blue, blue ppt. Ammoniacal (blue ppt.): Co-violet, violet ppt.; Th-violet red ppt.; Mn-green ppt.

346. Pontamine Fast Yellow 5GL (DuP). 10 drops 0.1% aq. soln. (HCl-red; acetic, neutral, NH_4OH-yellow; NaOH-orange). Yellow, yellow ppts.

Like 354. α-Naphthol ⟷ p,p': diaminodiphenylmethane ⟶ α-Naphthol. 0.5 cc. of <0.1% alc. soln. (acid-violet; neutral, alkaline-pink). Pink, pink ppts.

Like 354. H-acid $\xleftarrow{\text{(alk.)}}$ p,p'; diaminodiphenylmethane $\xrightarrow{\text{(alk.)}}$ H-acid. 5 drops 0.1% aq. soln. (red).

Like 354. H-acid $\xleftarrow{\text{(alk.)}}$ p,p'; diamino, o,o'; dinitrodiphenylmethane $\xrightarrow{\text{(alk.)}}$ H-acid. 5 drops 0.1% aq. soln. (acid, neutral-brown red; alkaline-violet). Red brown solns.

364. Brilliant Paper Yellow (CCC). 10 drops 0.1% aq. soln. (strong acid-intense blue; acid, neutral-yellow; alkaline-orange).

365 Chryrophenine Y (KP). 10 drops 0.1% aq. soln. (yellow).

382. Pontamine Scarlet B (DuP). 5 drops 0.1% aq. soln. (orange red). Neutral (orange red): Cu-yellow. Many orange ppts.

386. Heliotrope BB (K). 5 drops 0.1% aq. soln. (Conc. HCl-blue; HCl-violet blue; acetic-red; neutral-violet; NH_4OH, NaOH-red). Neutral (pink): Cu-orange.

394. Pontamine Violet N (DuP). 10 drops 0.1% aq. soln. (acid, neutral-red; alkaline-violet). Acetic (red ppts): Cu-orange violet.

401. Pontamine Diazo Black BH (DuP). 5 drops 0.1% aq. soln. (acid-blue; alkaline-violet). Purple, purple ppts.

406. Pontamine Blue BBF (DuP). 5 drops 0.1% aq. soln. (violet).

410. Chrysamine G (student). 5 drops 0.1% aq. soln. (HCl-pink; acetic, neutral-yellow; alkaline-orange).

415. Benzo Orange R (CCW). 5 drops 0.1% aq. soln. (acid-violet; neutral-yellow; alkaline-orange). Many orange and yellow ppts.

419. Pontamine Fast Red F (DuP). 5 drops 0.1% aq. soln. (HCl-violet; acetic-orange; neutral, NH_4OH-orange red; NaOH-orange). Orange red ppts.

420. Direct Browm M (CCW). 5 drops 0.1% aq. soln. (HCl, acetic-red ppt. and soln.; neutral-yellow; alkali-red). Red, red ppts.

463. Azo Blue (student). 10 drops 0.1% aq. soln. (acid-violet red; neutral-yellow brown; NH_4OH-orange; NaOH-pink). Neutral (violet): Cu-orange violet. Many violet and purple ppts.

466. Dianil Blue B (K). 5 drops 0.1% aq. soln. (acid, neutral-violet blue; NH_4OH-violet red; NaOH-blue). Blue, blue and purple ppts.

478. Erie Orange Y (NAC). 5 drops 0.1% aq. soln. (acid-orange ppt; alkali-orange). Yellow and orange ppts. and solns.

502. Pontamine Blue AX (DuP). 5 drops 0.1% aq. soln. (HCl, acetic-blue; neutral-violet; NH_4OH, NaOH-red). Many blue and violet ppts. and solns.

512. Pontamine Blue RW (DuP). 5 drops 0.1% aq. soln. (HCl-blue; acetic-violet; neutral, NH_4OH-blue; NaOH-red). Blue, blue ppts.

515. Niagara Blue R (NAC). 5 drops 0.1% aq. soln. (HCl-violet red; acetic, neutral-violet; NH_4OH, NaOH-red). Neutral, acetic (violet): Al-violet ppt.; Ag-turbid blue.

518. Pontamine Sky Blue 6BX (DuP). 5 drops 0.1% aq. soln. (blue). Neutral (blue): Al-turbid blue with red reflection; Ag, Cb, Cr, Cu, Fe^{++}, Fe^{+++}, Zr-blue ppts. Ammoniacal (blue): Co, Pb, Cr-pink lavender; Al, Bi, Cb, Ni, Th, Zr-blue ppts.

520. Niagara Sky Blue (NAC). 5 drops 0.1% aq. soln. (blue). Neutral (blue): Al, Cr-turbid red violet; Cu-red violet. Acetic (blue): Cu-red, violet.

581. Pontamine Black EX (DuP). 5 drops 0.1% aq. soln. (HCl, acetic-purple; neutral-green blue; NH_4OH, NaOH-blue).

593. Pontamine Green BX (DuP). 5 drops 0.1% aq. soln. (green). Neutral (green): Cu-brown. Many blue green ppts.

594. Direct Green GB (CCW). 5 drops 0.1% aq. soln. (green). Green, green ppts.

596. Direct Brown T (CCW). 5 drops 0.1% aq. soln. (orange red). Orange, orange ppts.

598. Congo Brown G (CCW). 5 drops 0.1% aq. soln. (orange). Orange, orange ppts.

601. Pontamine Brown CR (DuP). 5 drops 0.1% aq.

soln. (orange red). Orange red, red ppts.

603. Alizarine Yellow FS (JCW). 5 drops of $<0.1\%$ aq. soln. (yellow). Yellow, yellow ppts.

636. Fast Light Yellow (?). 5 drops 0.1% aq. soln. (yellow).

639. Xylene Yellow (CCW). 10 drops 0.1% aq. soln. (yellow).

640. Tartrazine (NAC). 5 drops 0.1% aq. soln. (yellow).

652. Eriochrome Red B (CCW). 5 drops 0.1% aq. soln. (orange). NH_4OH (yellow): Co, Ni, Cu, Th-orange; Cr-pink.

666. Acid Green L Extra (NAC). 5 drops 0.1% aq. soln. (HCl-yellow; acetic, neutral-green; alkaline-colorless.

674. Chrome Green pdr. (WTA). 10 drops 0.1% aq. soln.(HCl-orange pink; acetic-pink violet; neutral, NH_4OH, NaOH-purple). Neutral (purple): Al-blue; Co-green blue; Ni, Zn-blue purple. Acetic (violet): Al, Cu, Zr-blue; Co-green blue. Ammoniacal (violet): Co-green blue; Cu-blue by transmitted light, pink by reflected light.

720. Alizarole Azurine ECH (NAC). 5 drops 0.1% aq. soln. (HCl-pink; acetic-orange; neutral-yellow; NH_4OH-green by transmitted, red by reflected light; NaOH-blue by transmitted, violet red by reflected light). Neutral (yellow): Be, Al, Th, Cr, Cu, Sn, Bi-blue by transmitted, red by re-

flected light; Zr-violet red soln. and ppt.; Fe-blue; Pb-green yellow. Acid (pink): Be-red, blue ppt.; Al, Zn-violet ppt. and solns. by transmitted, violet red by reflected light; Cr-blue by transmitted, violet red by reflected light; Fe^{++}, Fe^{+++}- blue ppt. and soln. Ammoniacal (yellow): Be, Th-red violet ppt.; Cr, Co-pink.

722. Alizarole Cyanine RG (NAC). 5 drops 0.1% aq. soln. (HCl-pink; acetic, neutral-yellow; NH_4OH-orange; NaOH-red). Neutral (yellow): Be, Al, Th, Cr, Cu, Pb, Bi-red; Zr, Sn-red ppt.; Cr-violet red ppt.; Fe^{++}-blue ppt. and soln. Acetic (pink): Be, Al-red; Cr-violet red. Ammoniacal (yellow): Cr-pink; Be, Th-pink ppt.

724. Aurin (K). 10 drops of 0.1% aq. soln. (acid-yellow; neutral-orange; alkaline-pink).

749. Rhodamine B (DuP). 5 drops of 0.1% aq. soln. (HCl-orange; acetic, NH_4OH-pink with orange fluorescence; NaOH-violet).

758. Violamine R (DuP). 5 drops 0.1% aq. soln.(red).

766. Fluorescein (student). 5 drops of 0.1% aq. soln. (yellow with greenish fluorescence). Neutral: Pb, Hg, Mn, Th-orange ppt.

768. Eosin (student). 5 drops of 0.1% aq. soln. (acid-yellow; neutral, alkaline-pink, all with green fluorescence). Many orange and pink ppts.

769. Methyl Eosin (K). 5 drops 0.1% aq. soln.

(HCl-yellow; acetic, neutral, alkaline-orange pink with green fluorescence).

772. Erythrosin (K). 10 drops 0.1% aq. soln. (acid-yellow; neutral, alkaline-pink). Neutral, acetic (pink): Ag-red ppt. All fluoresce somewhat.

773. Erythrosin (student). 5 drops 0.1% aq. soln. (HCl-yellow; acetic, neutral, alkaline-pink, pink ppt.). Neutral, acetic (pink): Ag, Bi-red ppt.

781. Gallein (student). 3 drops of <0.1% aq. soln. (acid-yellow; nuetral-red $\xrightarrow{\text{time}}$ yellow; NH_4OH-violet red $\xrightarrow{\text{time}}$ yellow; NaOH-blue). Neutral (yellow): Ag-green ppt.; Bi, Th-violet ppt.; Al, Cr, Sn, Zr-red ppt.; Al, Bi, Sb, Zn-red. Acetic (yellow): Ag-green ppt.; Al, Bi, Cb, Sb, Sn, Zr-red ppt.; Al, Bi, Cr, Sb, Sn, Zr-pink. Ammoniacal (yellow): Be, Cb-pink; Cr, Th, Zr-pink ppts.

783. Coerulein (Z). 5 drops 0.1% aq. soln. (acid-turbid black; neutral-blue green; alkaline-green). Neutral (green and grey ppts.): Ag, Mn-brown, brown ppts. Acetic (grey ppts.); Ag-red ppts.; Mn-brown. Ammoniacal (green ppts.): Ag, Ni-brown ppts.; Mn-brown.

801. Quinoline Yellow (K). 5 drops 0.1% aq. soln. (yellow).

878. Chrome Blue GD (NAC). 10 drops 0.1% aq. soln. (HCl-pink; acetic-green blue; neutral-blue; NH_4OH, NaOH-violet). A variety of blue and violet ppts. and solns.

883. Chrome Blue GCB (NAC). 5 drops 0.1% aq. soln. (HCl-red; acetic-red violet; neutral-blue; NH_4OH, NaOH-violet). A variety of blue and violet ppts. and solns. Acetic (violet): Mn-pale orange.

893. Prûne Pure (AAP). 5 drops 0.1% aq. soln. (HCl, acetic-red; neutral-blue; NH_4OH, NaOH-violet). Many blue and violet ppts. and solns. Ammoniacal (violet): Co-yellow brown.

931. Calcochrome Brilliant Blue G (CCC). 10 drops 0.1% aq. soln. (HCl-violet, acetic-blue; neutral-lavender blue; NH_4OH-green blue; NaOH-blue). Variety of very pale yellow (with red reflection) and blue solns. and ppts.

1013. Gallacetophenone (JCW). 0.5 cc. 0.1% alc. soln. (acid-colorless; neutral, NH_4OH, NaOH-yellow; saturated NaOH-green ppts.). Acetic (pale yellow): Zr, Mn, Co, Ni, Hg-bright yellow; Sr, Ta, Fe^{++}-yellow ppt.

Like 1013. 2:4-Dihydroxyacetophenone (JCW). 0.5 cc. 0.1% alc. soln. (colorless). Neutral (colorless): Ag, Zn-pale pink.

Like 1013. Pink crystals, possibly triacetyl resorcin (JCW). 0.5 cc. 0.1% alc. soln. (acid-yellow; neutral, NH_4OH-pink with green fluorescence; NaOH-colorless).

1014. 1:2:3-Trihydroxybenzophenone (JCW). 0.5 cc. 0.1% alc. soln. (acid-colorless; neutral, NH_4OH-yellow; NaOH-yellow green; saturated NaOH-green ppt.). Neutral (yellow): Be, Al, Zr, Th, Ta, Cu, Hg, Pb-yellow ppt.; Ag, Fe^{+++}-brown ppts.; Fe^{++}-violet brown ppts. and solns. Acetic (yellow): Ta, Co-orange ppts.; Al, Zr, Th, Ni, Hg-yellow ppts.; Ag, Fe^{+++}-brown ppts.; Fe^{++}-violet black ppts. and soln. Ammoniacal-many ppts.

Like 1014. 2:4-Dihydroxybenzophenone (JCW). 0.5 cc. of 0.1% alc. soln. (acid, neutral-colorless; NH_4OH, NaOH-yellow). Neutral (colorless): Cu-yellow ppts.; Fe^{++}-pink orange suspension.

Like 1014. 2:4, 2':4'-Tetrahydroxybenzophenone (JCW). 0.5 cc. 0.1% alc. soln. (acid-pale yellow; neutral, NH_4OH,NaOH-colorless, but with bluish reflection). Ammoniacal (pale blue green): Th-blue ppt.; Th, Cu, Pb-bright blue; Co-violet purple.

1018. Styrogallol (JCW). 5 drops of <0.1% aq. soln. (acid-yellow, yellow ppt.; neutral-red; NH_4OH-green; NaOH-violet blue). Acetic (yellow, yellow ppts.): Zr, Sb, Ta-orange red ppts.

Like 1019. Alizarine Black RB Pdr. (Z). 5 drops 0.1% aq. soln. (HCl-orange red ppt. and soln.; acetic-brown; neutral, alkaline-violet). Violet ppts. and pale yellow solns.

1026. Chromotropic Acid (Technical) (CB). 10 drops of <0.1% aq. soln. (very pale pink and yellow attributed to impurities). Neutral (very pale pink): Cu-red brown. Acetic (pale yellow): Cu-orange. Ammoniacal (very pale pink): Co, Cu-pink; Mn-yellow ppt.

Like 1027? Turkey Red #143 Pulp (UCP). 10 drops

0.1% soln. (pink). Neutral (pink): Many orange ppts. Acetic (pink): Co-yellow; a few orange ppts. Ammoniacal (pink): Co-yellow; many ppts.

1027. Alizarine (NAC). 2 drops of $<0.1\%$ aq. soln. (acid-yellow; neutral-orange; NH$_4$OH-red violet; NaOH-violet blue). Neutral (orange red ppts.): Fe^{++}, Co, Ni-purple ppts.; Th, Zn-red purple ppts. Acetic (yellow): yellow, orange and red ppts.; Ni-violet ppt.). Ammoniacal (red ppts.): Co-red; Bi, Fe^{++}, Fe^{+++}, Th-purple ppt.

1028. Quinizarin (student). 5 drops of $<0.1\%$ aq. soln. (acid, neutral-yellow; NH$_4$OH-green blue; NaOH-purple). Ammonia (violet): Be, Mg-pink; Mg-pink ppt.; Co-blue green; Mn-yellow, yellow brown ppt.

1033. Alizarine Orange AP (NAC). 5 drops 0.1% aq. soln. (HCl-yellow; acetic, neutral-orange; NH$_4$OH-red, NaOH-red ppt.). Orange and red ppts. and solns.

1034. Alizarine Red S (CB). 2 drops 0.1% aq. soln. (acid-yellow; neutral-orange; alkaline-purple). Neutral (orange): Ag-yellow, yellow ppts.; Al, Cb, Cr, Sb, Sn-orange ppts.; Co, Fe^{+++}, Pb, Th, Zn, Zr-red ppts.; Fe^{++}, Cu, Ni-violet ppts. Acetic (yellow): Al, Ba, Ca, Cb, Fe^{++}, Fe^{+++}, Mg, Sb, Sn, Zn-orange ppts.; Co, Cr, Zr-red ppt.; Al, Cb, Cr, Th-orange. Ammonia (pink, pink or orange ppts.): Bi-purple ppt.; Co, Fe^{++}, Fe^{+++}, Th, Zr-red ppts.

1035. Anthragallol (student). 10 drops of ca. 0.1% aq. soln. (HCl-yellow; acetic, neutral-orange; alkaline-purple).

Brown and yellow ppts. and solns.

1037. Purpurin (K). 5 drops 0.1% aq. soln. (HCl-yellow, red ppt.; acetic, neutral-orange; alkaline-red). Red solns. and ppts. Ag, Mn-yellow ppts. and solns.

1040. Alizarine Red SX (NAC). 5 drops of <0.1% aq. soln. (acid-yellow, orange ppt.; neutral-orange, orange ppt.; alkaline-red). Neutral (orange, orange and red ppts.): Fe^{++}, Co, Ni-purple ppt.; Cu-dark red ppt.; Th-violet red ppt. Acetic (yellow, yellow and orange ppts.): Ni-purple ppt.; Fe^{++} brown ppt.; Th-violet red ppt.; Cb, Cr, Fe^{+++}, Zr-red ppts.; Al, Cu-orange ppts. Ammonia (orange, red ppts.): Fe^{++}-purple ppt.; Co-dark red soln.

1045. Quinalizarine (student). 5 drops 0.1% aq. soln. (acid-yellow; neutral-orange; NH_4OH-purple; NaOH-violet). Original soln. Fe^{++}, Co, Ni, Cu-violet ppts.; other yellow and red ppts. Acetic (yellow, orange ppts.): Cr-pink suspension; Zr-red ppt.; Ni-green. Ammoniacal (red ppts. colorless soln.): Bi-purple ppt.; Fe^{++}-violet red ppt.; Cd-red.

1052. Ruffigallol (JCW). 5 drops 0.1% aq. soln. (acid, nuetral-yellow; NH_4OH-orange brown; NaOH-violet). Original (yellow, orange red): Ba-green, black ppt.; Fe^{++}-blue, violet blue ppt.; Be-violet ppt. and soln.; Ca-green brown, brown ppt.; Sr-dark violet. Acetic (yellow, yellow and orange ppts.): Fe^{++}-violet, violet black ppts.; Mg-green yellow. Ammoniacal-brown ppts. (with much opportunity for aerial oxidation).

1053. Alizarine Sapphire SE (NAC). 5 drops 0.1% aq. soln. (HCl-violet, acetic, neutral, alkaline-blue). Ammoniacal (blue): Mn-yellow, yellow ppt.; Co-green.

1054. Alizarine Sapphire (NAC). 5 drops 0.1% aq. soln. (HCl-purple; acetic, neutral, alkaline-blue). Original (blue): Ag, Al, Co, Ni, Th-green blue; Cr-turbid lavender; Cu-blue ppt. Neutral (blue): Be, Cu-green blue; Al, Th, Zr-blue ppt.

1062. Alizarine Blue 2 RC (NAC). 5 drops 0.1% aq. soln. (HCl-violet red; acetic-red, neutral-violet; NH_4OH-violet blue; NaOH-blue). Neutral, acetic (violet ppts.): Fe^{++}-black ppt.; Ta, Sn-red ppts. Ammoniacal (violet, violet blue ppts.): Co-violet, violet green ppt.

1066-1067. Alizarine Blue S (AAP). 5 drops 0.1% aq. soln. (acid-pink; neutral-blue ppt.; alkaline-blue ppt., blue soln.). Blue ppts. and solns.

1073. Oil Sol. Fast Heliotrope R (AAP). 0.3 cc. of <0.1% aq. soln. (acid, neutral-violet; alkaline-blue violet). Violet ppts. and solns.

1085. Alizarine Blue Black B (AAP). 5 drops of <0.1% aq. soln. (HCl-red violet; acetic-violet red; neutral, alkaline-red violet). Red violet solns. and a few violet ppts.

1090. Benzoin Yellow (JCW). 5 drops 0.1% aq. soln. (acid, neutral-turbid yellow; NH_4OH-turbid orange; NaOH-turbid red. Yellow ppts. and solns.

NATURAL COLORING MATTERS

1231 Young Fustic (ADC). Crude "crystals".

1232. Osage Orange Powder (MOH). Crude powder.

1233. Quercitron (ADC). Crude "crystals".

1234. Persian Berries (ADC). Crude "crystals".

These four substances contain, according to the Color Index (10) and Schultz Farbstofftabellen (12), the five flavonols: fisetin, morin, quercetin, and rhamnetin with rhamnazin, respectively. Morin has been proposed as a reagent for aluminum by F. Goppelsroeder (4), and E. Schantl (5). Goppelsroeder found that morin forms with aluminum a compound which gives off a bright green fluorescence in the presence of alcohol and HCl. It then appears interesting to look for similar results with the other flavonols.

The four crude dye products listed above were used without purification so that neither the presence of only the desired flavonol nor the absence of aluminum can be guaranteed. Using 10 drops of 0.2% aq. solns. of the commercial dye products tests were made in the prescribed manner with the result that all four dyes behaved quite similarly in giving yellow solutions with all metals, and green fluorescence with many metals in neutral and acid solution. Four sets of 3 cc. portions of the metal salt solutions were treated with 2 cc. of 0.1% alc. solns. of the four dyes with the result that in both neutral and strong HCl solution, several metals produced fluorescence, particularly Cr, Sb and Zr.

1238. Curcumin or Turmeric (?). 10 drops 0.1% alc. soln. (yellow). Yellow ppts. and solns.

1239. Carmine or Cochinial (?). 5 drops 0.1% aq. soln. (HCl-orange; acetic, neutral-red; NH_4OH-deep red; NaOH-red violet). Neutral (pink, pink ppts.): Co-very pale pink; Mn-pale yellow. Acetic (orange pink): Al, Cr-pink; Cb, Fe^{++}, Hg, Sn-pink ppt.; Zr-violet pink ppt.; Mn-colorless. Ammoniacal (pink, including Mn): Al, Be, Bi, Cb, Sn-pink ppts.; Zr-violet pink ppts.

1242. Orseille Extract (ADC). 10 drops of a soln. of 2 cc. extract in 100 cc. alcohol (acid-orange; neutral-red; alkaline-violet red). Original (pink, violet pink): Hg-pale violet, violet ppt.

1243. Hypernic Crystals (ADC). 5 drops of $<0.1\%$ aq. soln. (HCl-pink; acetic-yellow; neutral-orange pink; alkaline-red). Neutral(orange): Al, Be, Bi, Cb, Cu, Hg, Sb, Th, Zr-pink; Cr-violet pink; Fe^{++}-turbid lavender; Fe^{+++}-purple ppt.; Sn, Zr-pink ppt. Acetic (yellow): Al-orange; Cb, Cr, Zr-pink; Cb, Zr-pink ppt.

1246. Haematoxylin (?). 5 drops 0.1% aq. soln. (HCl-pink; acetic-yellow; neutral-orange; NH_4OH-dark red; NaOH-violet blue). Neutral (orange, yellow): Fe^{++}, Fe^{+++}, Pb-violet black ppt.; Al, Bi, Cb, Cr-purple ppts.; others - yellow to violet ppts. Acetic (yellow): Fe^{++}, Fe^{+++}-violet black ppts.; Cb, Cr, Th, Zr-purple ppts.; Al, Bi, Sb-orange solns. Ammonia (yellow): Fe^{++}, Fe^{+++}-black ppts.; Cb, Th, Zr-purple ppts.; Co-red brown.

1249. Gambier (ADC). Crude crystals. 5 drops 0.1% aq. soln.

1249. Cutch (ADC). crude crystals. 5 drops 0.1% aq. soln.

1249. Quebracho (ADC). crude crystals. 5 drops 0.1% aq. soln.

All these are yellow in acid, orange in neutral or alkaline solution, and behave quite similarly, and are all said to contain the compound catechin. They all give yellow solutions and with several metals form orange or brown ppts. The alkaline solution with copper is a lighter yellow.

Like 1249. Virginia Sumac (?). 10 drops $<0.2\%$ aq. soln. (yellow). Yellow solns., and yellow and brown ppts.

Like 1249 ? Dragon's Blood (?). 0.5 cc. of $<0.1\%$ alc. soln. (acid-yellow; neutral, alkaline-yellow orange). Orange pink ppts. and solns.

UNCLASSIFIED AZO DYES

Phenol-azo-phenol (?). 10 drops 0.1% aq. soln. (HCl-orange; acetic, neutral, alkaline-yellow). Yellow ppts. and solns.

2:4 Dinitrobenzene-azo-α-naphthol-4-sulfonic acid (student). 5 drops of $<0.1\%$ aq. soln. (acid-orange; neutral-yellow; alkaline-purple). Neutral (yellow orange): Co, Cu, Ni, Pb-orange; Bi, Cb-orange pink ppt. and soln. Ammoniacal (purple): Ni-pale purple, Bi-blue ppt.

Alizarole Black 3 G (NAC). 5 drops 0.1% aq. soln. (acid-red; neutral, alkaline-violet red). Neutral, acetic (red): Co-orange red; Fe^{++}, Fe^{+++}-yellow brown soln.

Brilliant Croceine FL (DuP). 5 drops 0.1% aq. soln. (acid-pink, alkaline-orange). Neutral (orange): Co, Cu-yellow orange.

Chrome Green CB (?). 5 drops 0.1% aq. soln. (HCl-purple ppt.; acetic-blue; neutral-red purple ppt.; alkaline-blue. Red to blue ppts. and solns.

Erie Brown CG (NAC). 5 drops 0.1% aq. soln. (yellow, brown). Brown ppts.

Pontachrome Yellow SW (DuP). 10 drops 0.1% aq. soln. (yellow).

Pontachrome Green Glo (DuP). 5 drops 0.1% aq. soln. (HCl-red; acetic-violet; neutral-orange red ppt.; alkaline-violet). Original (violet): Al, Co, Mn-blue; Be-red; Cr, Fe^{++}, Fe^{+++}-pink. Neutral (red ppts.): Bi, Ca, Cd, Hg, Mg-pale blue; Co-intense blue; Ba, Fe^{++}, Fe^{+++}, Mn-pink. Acetic (violet): Co-intense blue; Fe^{++}, Fe^{+++}-pink; Be, Sr, Zn-red ppts. Ammonia (violet, red ppts.): Co-intense blue; Fe^{++}- pale blue.

OTHER COMPOUNDS

Catechol (Recrystallized - JCW). 10 drops 0.1% aq.

soln. (colorless). Neutral (colorless): Cb-pale yellow; Hg, Ni, Th-green, Co, Cu-blue; Fe^{++}-violet. Acetic (colorless): Co, Cu, Fe^{++}, Hg-green. Ammonia (colorless): Cu-green; Fe^{++}-violet.

Resorcinol (Recrystallized - JCW). 10 drops 0.1% aq. soln. (colorless). Ammonia (colorless): Co-pale green.

Quinol (Mallinckrodt). 10 drops 0.1% aq. soln. (colorless). Neutral, acetic (colorless): Co, Hg-pink; Cu-green.

Salicylic, p-Hydroxybenzoic, β-Resorcylic and β-Hydroxynaphthoic acids tested under the same conditions, showed no reactions of interest.

Phloroglucinol (CB). 10 drops 0.1% aq. soln. (colorless).

Pyrogallol (Mallinckrodt). 10 drops 0.1% aq. soln. (colorless, pale yellow). Neutral (pale yellow). Fe^{++}-deep purple; Cu-green blue ppt.; several brown ppts. Acetic, ammoniacal (pale yellow): several yellow to black ppts.

Gallic acid (Merck). 10 drops 0.1% aq. soln. (colorless to yellow). Neutral (pale yellow): Fe^{++}-deep violet; Mg, Ca, Sr, Ba-green blue; Cd, Sn-pale green blue; Cu-yellow, yellow ppt.; other ppts. Acetic (yellow): Fe^{++}-blue. Ammoniacal (yellow): Fe^{++}-red.

Methylene digallic acid (student). 10 drops of 0.1% aq. soln. (yellow): Original (pale yellow): Ni-pink;

Fe^{++}-purple. Neutral, acetic (colorless, or pale yellow): Fe^{++}-purple; Cb-yellow. Ammoniacal (pale yellow). Fe^{++}-dark red; Fe^{+++}-red ppt.

Methylene disalicylic acid (JCW). 10 drops 0.1% aq. soln.

Tetrabrompyrocatechin (student). 10 drops 0.1% aq. soln. (colorless): Neutral (colorless): Ag, Fe^{++}-black ppt.; Mn-pale pink. Acetic (colorless): Cb-orange ppt.; Ag-black ppt.; Fe^{++}-pale blue; Mn-pale pink. Ammoniacal (colorless): Ag-black ppt.; Fe^{++}-brown blue ppt.

Dicyanhydroquinone (student). 10 drops 0.1% aq. soln. (acid, neutral-colorless; acetic-blue fluorescence; neutral-yellow green fluorescence; alkaline-pale yellow, yellow green fluorescence). Neutral, acetic (colorless, blue fluorescence): Mn, Fe^{++}, Fe^{+++}, Cu, Hg-yellow, no fluorescence.

p-Dihydroxyphthalimide (JCW). 10 drops of ca. 0.1% aq. soln. (HCl-colorless; acetic to NaOH-yellow soln., green fluorescence). Neutral (yellow, green fluorescence): Co, Ni-orange ppt. and soln., no fluorescence. Various other yellow and brown ppts. and solns.

Succinylosuccinic ester (student). 10 drops 0.1% aq. soln. (colorless).

Aesculine (K). 10 drops 0.1% aq. soln. (colorless; neutral, alkaline-blue fluorescence.

From the results of the tests of the 216 compounds and commercial products described in the preceding list, the more outstanding instances of specific reactions will be selected and presented in an abbreviated tabular form, from which may be made selections for further consideration.

In the following table, the third column may contain the words: original, neutral, acetic or ammonia, which refer, as in the preceding list, to the original .001 molar salt solution, this solution plus successive additions of 0.5 cc. of 6 N neutral ammonium acetate, 2 cc. of 6 N acetic acid and 5 cc. of 6 N ammonium hydroxide solution respectively.

TABLE I

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
7	Picramic acid	Neutral; acetic	Yellow soln.	Cu	Yellow ppt.
29	Chromotrope 2R	Neutral	Orange pink	Al, Be	Violet red
45	Chromotrope 2B	Neutral	Pink	Be, Al, Cr	Violet
				Cu	Violet red
		Ammonia	Violet	Co	Blue violet
53	Acid Violet 4BS	Neutral	Violet	Al, Zr	Blue
56	Erio Fast Fuchsine 6B	Neutral	Red	Be, Al	Violet
				Cr, Th	Violet
59	Erioazurine 3B	Acid		H^+	Red - blue
		Alkaline		H^+	Blue-orange
79	Lake Scarlet R	Neutral	Orange Pink	Cu	Yellow
87	Fast Red B	Neutral	Red	Cu	Yellow
88	Bordeaux B	Neutral	Pink	Cu	Yellow
				Ni	Orange pink
89	Crystal Ponceau 6RF	Neutral	Orange pink	Cu	Yellow
103	Picramic a. →m-cresol	Original	Yellow;	Cu	Maroon ppt.
			orange	Pb	Orange ppt.
104	Picramic a. →p-cresol	Ammonia	Yellow;	Ni	Orange pink
			orange ppts	Co	Brown ppt.
103	Picramic a. →thymol	Neutral	Red;	Cu	Purple ppt.
			red ppts.	Mn	Green yellow
		Ammonia	Pink	Ag, Co, Mn	Yellow
103	Picramic a. →catechol	Original	Yellow	Pb	Colorless; brown ppt.
103	Picramic a.→ →phloroglucinol	Acetic	Orange pink	Co	Strong orange pink
103	Picramic a.→ β-OH-naphthoic acid	Original	Red, violet ppts. & solns	Mg	Blue ppt.
		Ammonia	Purple ppts.	Ca, Cu, Mg	Blue ppts.
				Co	Lavender

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
103	Picramic a.	Acetic	Violet	Al,Cu,Ni,Th,Zr	Blue
	→H-acid			Co	Green blue
		Ammonia	Violet	Bi,Cu	Blue
				Co	Green blue
103	Picramic a.	Neutral	Red	Cu	Blue; blue ppt.
	→NW acid			Hg	Pale pink
		Acetic	Red	Co	Orange red
				Cu	Blue ppt.
		Ammonia	Pink	Cu	Blue ppt.
103	Picramic a.	Acetic	Red	Fe^{++}	Yellow
	→R-acid			Co,Ni,Cu	Orange red
103	Picramic a.→	Neutral	Red violet	Al,Cr,Sn,Zr	Blue
	chromotropic			Ni,Cu	Red
	acid	Acetic	Violet	Cr	Blue
				Ni,Cu	Red
		Ammonia	Violet	Co	Green blue
				Bi,Th,Zr	Blue ppts.
169	Superchrome	Neutral	Orange red	Fe^{++};Fe^{+++}	Yellow
	Violet B	Ammonia	Pink	Mn,Fe^{++};Fe^{+++}	Yellow
				Bi	Violet ppt.
				Co,Ni,Cu	Orange pink
				Th,Zr	Orange ppt.
170	Superchrome	Neutral	Violet red	Fe^{++};Fe^{+++}	Yellow
	Black PV	Ammonia	Blue	Fe^{++};Fe^{+++}	Yellow
				Cr,Mg,Ni	Red violet
				Th,Zr	Red ppt.
		Neutral		H^{+}	Pink to blue
179	Azo Rubine Ex	Neutral	Red	Cu	Yellow
184	Amaranth	Neutral	Pink	Cu	Yellow
				Ni	Orange
185	Ponceau 4R	Neutral	Red	Cu	Yellow
194	Scarlet 2R	Neutral	Orange	Cu	Yellow
201	Eriochrome	Ammonia	Blue	Mn	Yellow
	Blue Black B				
203	Eriochrome	Neutral	Violet	Co,Zn,Th	Red
	Black T			Mn	Yellow
				Cd	Colorless

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
203	Eriochrome Black T	Ammonia	Blue	Al,Be,Mg,Sr,Ni	Pink
				Mn	Yellow green
				Ca,Th,Fe^{++};Fe^{+++}	Yellow
				Zr	Green
				Cd	Green blue
204	Eriochrome Black A		Solns. of many colors, from yellow, thru red to blue		
212	Anthranilic acid →p-cresol	Acetic	Yellow	Co	Brown green
				Cr,Fe^{++};Cu	Orange pink
				Th	Yellow ppt.
		Ammonia	Yellow	Co	Violet
				Cr,Fe^{++}	Pink yellow
212	Anthranilic	Acetic	Yellow	Cr,Mn,Cu	Orange
	→p-Cl-phenol	Ammonia	Yellow	Co	Violet
212	Anthranilic →resorcinol	Acetic	Yellow	Co	Red orange
				Hg	Orange ppt.
		Ammonia	Yellow	Co	Deep orange
				Cr	Orange
212	Anthranilic →pyrogallol	Ammonia	Yellow	Co	Violet yellow
214	Anthranilic —β-naphthol	Ammonia	Orange	Co	Violet red
215	Anthranilic →Schaeffer's acid	Ammonia	Yellow orange	Co	Violet red
215	Anthranilic	Ammonia	Orange	Co	Violet red
	→NW acid	Neutral	Orange	Co,Fe^{++}	Brown
216	Anthranilic	Acetic	Orange	Cr	Red orange
	→R salt	Ammonia	Orange	Co	Violet red
294	Buffalo Black 10 B	Neutral	Blue	Al,Cr,Fe^{++};Zr	Lavender
				Cb	Blue ppt.
315	Naphthol Black B	Neutral	Purple	Cu	Yellow
336	Chromaven Black SE	Acetic	Violet ppt.	Cd,Cr,Zn	Red
				Cb,Co,Cu,Ni	Blue
		Ammonia	Blue ppt.	Co	Violet
				Th	Violet red ppt.
				Mn	Green ppt.

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
382	Pontamine Scarlet B	Neutral	Orange red Orange ppt.	Cu	Yellow
386	Heliotrope BB	Neutral	Pink	Cu	Orange
394	Pontamine Violet N	Acetic	Red ppts.	Cu	Orange violet
463	Azo Blue	Neutral	Violet	Cu	Orange violet
515	Niagara Blue R	Neutral	Violet	Al	Violet ppt.
				Ag	Turbid blue
518	Pontamine Sky Blue 6BX	Neutral	Blue	Al	Red reflection
				Ag,Cb,Cr,Cu, Fe^{++},Fe^{+++}	Blue ppts.
		Ammonia	Blue	Co,Pb,Cr	Pink lavender
				Al,Bi,Cb, Ni,Th,Zr	Blue ppts.
520	Niagara Sky Blue	Neutral	Blue	Al,Cr,Cu,	Red violet
		Acetic	Blue	Cu	Red violet
652	Eriochrome Red B	Ammonia	Yellow	Co,Ni,Cu,Th	Orange
				Cr	Pink
674	Chrome Green	Neutral	Purple	Al	Blue
				Co	Green blue
				Ni,Zn	Blue purple
		Acetic	Violet	Al,Cu,Zr	Blue
				Co	Green blue
		Ammonia	Violet	Co	Green blue
				Cu	Blue(transmit) Pink(reflect)
720	Alizarole	Neutral	Yellow	Be,Al,Th,Cr	
				Cu,Sn,Bi	Blue(transmit) Red (reflect)
				Fe	Blue
		Acetic	Pink	Be	Red; blue ppt.
				Al,Zr	Violet
				Cr	Blue
				Fe^{++},Fe^{+++}	Blue ppt.,soln
		Ammonia	Yellow	Be,Th	Red violet ppt.
				Cr,Co	Pink

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
722	Alizarole Cyanine RG	Neutral	Yellow	Be,Al,Th,Cr,Cu,Pb,Bi	Red
				Zr,Sn	Red ppt.
				Cr	Violet red ppt.
				Fe^{++}	Blue ppt.,soln.
		Ammonia	Yellow	Cr	Pink
				Be,Th	Pink ppt.
781	Gallein	Neutral	Yellow	Ag	Green ppt.
				Al,Sn,Zr,Cr	Red ppts.
				Al,Bi,Sb,Zn	Red
		Acetic	Yellow	Ag	Green ppt.
				Several	Red ppts.,solns.
883	Chrome Blue GCB	Acetic	Violet	Mn	Pale Orange
1013	Gallacetophenone	Acetic	Yellow	Zr,Mn,Co,Ni,Hg	Bright Yellow
				Sr,Ta,Fe^{++}	Yellow ppt.
1014	Alizarine Yellow A	Neutral	Yellow	Fe^{++}	Violet brown
				Be,Al,Zr,Th,Ta,Cu,Hg,Pb	Yellow ppts.
		Acetic	Yellow	Ta,Co	Orange ppts.
				Al,Zr,Th,Ni,Hg	Yellow ppts.
1014	2:4-Di-OH-benzophenone	Neutral	Colorless	Cu	Yellow ppt.
				Fe^{++}	Pink orange
1014	2:4,2':4' Tetra-OH-benzophenone	Ammonia	Blue green	Th	Blue ppt.
				Th,Cu,Pb	Bright blue
				Co	Violet purple
1018	Styrogallol	Acetic	Yellow	Zr,Sb,Ta	Orange red ppts.
1026	Chromotropic Acid	Neutral	Pale pink	Cu	Red brown
		Acetic	Pale Yellow	Cu	Orange
		Ammonia	Pale pink	Cu,Co	Pink
				Mn	Yellow ppt.
1027	Turkey Red #143 Pulp	Acetic	Pink	Co	Yellow
		Ammonia	Pink ppts.	Co	Yellow
1027	Alizarine	Neutral	Orange ppt.	Fe^{++},Co,Ni	Purple ppts.
				Th, Zn	Violet red ppts.
		Acetic	Yellow	Ni	Violet ppt.
		Ammonia	Red ppts.	Co	Red
				Bi,Fe^{++},Fe^{+++}	Purple ppts.

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
1028	Quinizarin	Ammonia	Violet	Be,Mg	Pink
				Mg	Pink ppt.
				Co	Blue green
				Mn	Yellow
1034	Alizarine Red S	Neutral Acetic	Variety of colors of ppts. and solns.		
1037	Purpurin	Neutral	Orange	Ag,Mn	Yellow ppts.& solns.
1040	Alizarine Red SX	Neutral	Orange	Fe^{++},Co,Ni	Purple ppts
				Cu	Dark red ppt.
				Th	Violet red ppt.
		Acetic	Yellow	Ni	Purple ppt.
				Fe^{++}	Brown ppt.
				Th	Violet red ppt.
				Cb,Cr,Fe^{+++},Zr	Red ppts.
				Al, Cu	Orange ppts.
		Ammonia	Orange ppts.	Fe^{++}	Purple ppt.
				Co	Dark red
1045	Quinalizarine	Acetic	Orange ppts.	Cr^{++}	Pink suspension
				Zr	Red ppt.
				Ni	Green
		Ammonia	Red ppts	Bi	Purple ppt.
				Fe^{++}	Violet red
				Cd	Red
1052	Ruffigallol	Original	Orange	Ba	Green: black ppt.
				Fe^{++}	Blue; violet ppt.
				Ca	Green brown
				Be	Violet ppt,,soln.
				Sr	Dark violet
		Acetic	Yellow	Mg	Green yellow
				Fe^{++}	Violet
1053	Alizarine Sapphire SE	Ammonia	Blue	Mn	Yellow
				Co	Green
1054	Alizarine Sapphire	Original	Blue	Ag,Al,Co, Ni,Th	Green blue
				Cr	Turbid lavender
				Cu	Blue ppt.
		Neutral	Blue	Be,Cu	Green blue
				Al,Th,Zr	Blue ppt.
1062	Alizarine Blue 2AC	Neutral Acetic	Violet ppts.	Fe	Black ppt.
				Ta,Sn	Red ppts.
		Ammonia	Same	Co	Violet,violet green ppt.

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
1231	Young Fustic	Acid	Yellow	Cr,Sb,Zr and others	Green fluorescence
1232	Osage Orange	Acid	Yellow		
1233	Quercitron	Acid	Yellow		
1234	Persian Berries	Acid	Yellow		
1243	Hypernic	Neutral	Orange	Al,Be,Bi,Cb,Cu,Hg, Sb,Th,Zr	Pink
				Cr	Violet pink
				Fe^{++}	Turbid lavender
				Sn,Zr	Pink ppt.
		Acetic	Yellow	Al	Orange
				Cb,Cr,Zr	Pink
				Cb,Zr	Pink ppt.
		Ammonia	Yellow	Cr,Sb	Pink
				Al,Be,Th,Zr	Pink ppt.
1246	Haematoxylin	Neutral	Orange	Fe^{++};Fe^{+++};Pb	Violet;black ppt.
				Al,Bi,Cb,Cr	Purple ppts.
		Acetic	Yellow	Fe^{++};Fe^{+++},	Violet;black ppts.
				Cb,Cr,Th,Zr	Purple ppts.
				Al,Bi,Sb	Orange
		Ammonia	Yellow	Fe^{++};Fe^{+++}	Black ppts.
				Cb,Th,Zr	Purple ppts.
				Co	Red brown
	Alizarole Black 3G	Neutral Acetic	Red	Co	Orange red
				Fe^{++};Fe^{+++}	Yellow brown
	Brilliant Croceine FL	Neutral	Orange	Cu,Co	Yellow orange
	Pontachrome Green Glo	Original	Violet	Al,Co,Mn	Blue
				Be	Red
				Cr,Fe^{++};Fe^{+++}	Pink
		Neutral	Red ppts.	Be,Ca,Cd, Hg,Mg	Pale blue
				Co	Intense blue
				Ba,Mn,Fe^{++};Fe^{+++}	Pink
		Acetic	Violet	Co	Intense blue
				Fe^{++};Fe^{+++}	Pink
				Be,Sn,Zn	Red ppts.
		Ammonia	Violet; red ppts.	Co	Intense blue
				Fe^{++}	Pale blue

DYE NO.	DYE NAME	ACID OR ALKALINE	NORMAL BEHAVIOR	ELEMENT	SPECIFIC BEHAVIOR
	Catechol	Neutral	Colorless	Cb	Pale Yellow
				Hg,Ni,Th	Green
				Co,Cu	Blue
				Fe^{++}	Violet
		Acetic	Colorless	Co,Cu,Fe^{++},Hg	Green
		Ammonia	Colorless	Cu	Green
				Fe^{++}	Violet
	Resorcinol	Ammonia	Colorless	Co	Pale green
	Quinol	Neutral	Colorless	Co,Hg	Pink
		Acetic		Cu	Green
	Pyrogallol	Neutral	p.Yellow;	Fe^{++}	Purple
			brown ppts.	Cu	Green blue ppt.
	Gallic Acid	Neutral	p.Yellow	Fe^{++}	Deep violet
				Mg,Ca,Sr,Ba	Green blue
				Cd,Sn	Pale green blue
		Acetic	Yellow	Fe^{++}	Blue
		Ammonia	Yellow	Fe^{++}	Red
	Methylene digallic acid	Original	p.Yellow	Ni	Pink
		Neutral	Colorless	Cb	Yellow
		Acetic	p.Yellow	Fe^{++}	Purple
		Ammonia	p.Yellow	Fe^{++}	Dark red
				Fe^{+++}	Red ppt.
	Tetrabrom-pyrocatechin	Neutral	Colorless	Ag,Fe^{++}	Black ppt.
				Mn	Pale pink
		Acetic	Colorless	Cb	Orange ppt.
				Ag	Black ppt.
				Fe^{++}	Pale blue
				Mn	Pale pink
		Ammonia	Colorless	Ag	Black ppt.
				Fe^{++}	Brown blue ppt.

LIST II

There may be noted in the preceding list and table, several items of particular interest.

1. A group of similar azo dyes giving a yellow color only with copper.

2. A group of similar azo dyes giving a violet red color only with cobalt.

3. Several azo dyes showing color changes of strong contrast at various ranges of acidity or alkalinity:

a. C.I. 59. p-Dimethylaminoaniline → 1:8-dihydroxynaphthalene sulfonic acid. Blue to red with acid; blue to orange with alkali.

b. C.I. 170. p-Hydroxy-m-aminobenzenesulphonic acid → 1,5 dihydroxynaphthalene. Blue to pink with alkali.

c. C.I. 201, 202, 203, 204. Various substituted α-amino-β-naphthols, diazotized and coupled to α-or β-naphthol, give with alkali a change from red to blue.

d. C.I. 336. β-Naphthol ← 0,0' diaminophenol-p-sulfonic acid → β-naphthol. Blue to red with weak acid <u>or</u> strong alkali.

e. Many others, including C.I. 386, 394, 502.

4. The picramic acid salts of copper appears to be more insoluble than those of other metals tested.

5. The group of dyes made from picramic acid appear to give several more or less specific reactions of interest

a. Picramic acid——β-OH-naphthoic acid gives a blue precipitate with Mg.

b. Picramic acid→NW acid gives a blue precipitate with Cu.

c. Picramic acid→R-salt gives a yellow color with Fe^{++}.

6. C.I. 201. α-Amino-β-naphthol-4-sulfonic acid→α naphthol gives a yellow color with Mn, as does also the similar dye, C.I. 203.

7. C.I. 720 and 722, both substituted triphenylmethane dyes, give a considerable variety of colored precipitates and solutions, and they and similar compounds might yield worthwhile results by further investigation. They are, of course, somewhat similar to the aluminum reagent, aurintricarboxyacid.

8. 2:4-Dihydroxybenzophenone gives a yellow precipitate with copper and a pink orange suspension with ferrous iron.

9. 2:4, 2': 4'-Tetrahydroxybenzophenone, an impure sample, give bright blue solutions with several metals. This needs to be duplicated and investigated further.

10. Chromotropic acid, C.I. 1026, impure, gives an orange color with copper which may be of theoretical interest from its relation to β-Nitrosochromotropic acid which is used as a reagent for copper.

11. Turkey Red #143 Pulp, a commercial dye product of composition unknown to this writer, gives uniformly pink solutions with all metal solutions except that of cobalt which

is yellow.

12. Quinizarin, C.I. 1028, gives distinctively colored solutions with several elements which might compare favorably in specificity with the similar compound quinalizarin, C.I.1045.

13. Ruffigallol (1,2,3,5,6,7 hexahydroxynaphthoquinone), C.I. 1052, gives an interesting variety of colored precipitates with various metals, particularly green precipitates with the alkaline earths.

14. The five natural dyes, Fisetin, Morin, Quercetin, Rhamnetin and Rhamnazin, from C.I. 1231, 1232, 1233 and 1234 need to be obtained in a pure state and they and their analogues tested for comparative results with respect to the morin reaction with aluminum whereby a green fluorescence is produced. Also it should be ascertained what other metals do or do not give this reaction.

15. Cobalt was observed to give a blue green color with many dyes of diverse nature. No generalization concerning this has yet been made by this writer.

16. Tetrabrompyrocatechin gives with Cb an orange precipitate, probably due to adsorption of the above compound on the precipitated columbium hydroxide. This needs to be tried with tantalum. With ferrous iron a pale blue was produced and with manganese a pale pink.

YELLOW COLOR PRODUCED BY COPPER

A yellow color was produced by the 10 following orange or red dyes: C.I. 79, 87, 88, 89, 120, 179, 184, 185, 194 and 216, and an orange color by the violet dyes C.I. 315, and 386, these effects being observed with no other metal. Furthermore, this color, occurring at neutrality was replaced by the normal dye color upon the addition of quite small amounts of either hydrochloric acid, acetic acid, ammonium hydroxide, or sodium hydroxide. No instance of similar colors produced by Cu have been found in the literature by the author, though Georgievics (13), p. 110, does mention the use of similar dyes containing <u>two</u> hydroxy groups, one on each ring, adjacent to a single azo group, which dyes are made more soluble by "coordinating" with copper and other metal salts to form soluble derivatives giving very fast direct dyeings.

The dyes giving this yellow color with copper all contain substituted α-or β-naphthols to which have been coupled diazotized naphthylamines or anilines. But other dyes containing quite similar groups and possessing quite similar colors did not appear to give this reaction.

It was then decided to determine the pH range over which this yellow color is stable, partly as an end in itself and partly to make sure of the apparent paradox stated in the preceding paragraph.

.001 molar solutions of $CuCl_2$ were buffered by the addition of relatively large amounts (several cc's.) of 6 N ammonium hydroxide and acetic acid until the several solutions had pH values of 4.0, 4.4, 4.8, 5.2, 5.6, 6.0 and 7.5 respectively as determined by comparison with Kolthoff's succinic acid - borax and potassium dihydrogen phosphate-borax buffer mixtures (11), using brom cresol green, brom cresol purple, and brom thymol blue as indicators. These solutions, containing a large amount of ammonium acetate showed no precipitate of cupric hydroxide. To 5 cc. portions of each of these buffered $CuCl_2$ solutions were added 5 drops of 0.1% solutions of the following dyes: C.I. 79, 88, 89,120, 179, 184, 194, 216, 315, 382, 386, 29, 159, 169, 170, 202, 252, 394, 466, 502, picramic acid → NW-acid, picramic acid (alk.) → H-acid and picramic acid → chromotropic acid. Except for the dyes mentioned above giving the specific reaction, only C.I. 382 and 502 showed any sign of a specific reaction with copper and these gave only a slight lessening of intensity of color.

Of the dyes giving the reaction, all but two, C.I.120 and C.I. 216, changed gradually from the normal dye color to the yellow or orange color over a pH range of 5.2 to 6.0. The two dyes, C.I. 120 and 216, were yellow even at pH 4.0, although their normal dye color is orange. All of the ten dyes were yellow at pH 7.5 but the addition of 1 to 10 drops of 6 N ammonium hydroxide changed all of the yellow colors to the normal dye color. Hydrolysis of the copper salt prevented a more accurate determination of the alkaline transition range by the above method.

It is interesting to note that the acid transition range of the yellow color, pH 5.2 to 6.0, is approximately that given by Britton (14), as the minimum pH value for the hydrolysis of copper salts.

That ammonium hydroxide is not specifically necessary to the formation or disappearance of the yellow color is shown by repeating some of the tests, e.g., with C.I. 88, which was quite pure, and using, in addition to an unbuffered 0.001 molar $CuCl_2$ solution, only acetic acid and sodium hydroxide solutions, with the result that the yellow color could be caused to appear and disappear at will by the appropriate addition of the acid or base.

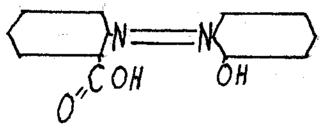
Some sort of quantitative relation, as yet undetermined, appears to exist between the amounts of dye and copper salt used. Gradual addition of an excess of dye solution caused the yellow to become gradually obscured by the normal dye color, after which subsequent addition of copper salt solution gradually restored the pure yellow color. Perhaps this phenomenon could be utilized for the volumetric determination of small amounts of copper as is done with nitrosochromotropic acid by Ansbacher et al (15).

A GROUP OF SPECIFIC REAGENTS FOR COBALT

A series of similar dyes appears to give a specific characteristic reaction with cobaltous ion. These dyes consist of anthranilic acid, diazotized and coupled to certain phenols and naphthols. Six dyes, consisting of anthranilic acid, diazotized and coupled to p-cresol, p-chlorophenol, β-naphthol, β-naphthol-6-sulfonic acid, α-naphthol-4-sulfonic acid and β-naphthol-3:6-disulfonic acid, give, on addition to a weakly ammoniacal cobaltous chloride solution, after standing, a violet color, the shades of which vary slightly with the individual dye. But three other dyes, consisting of anthranilic acid, diazotized and coupled to m-cresol, salicylic acid and phenol give no indication of such a color formation, while two dyes, consisting of anthranilic acid, diazotized and coupled to resorcinol and pyrogallol, give, under similar conditions, only a deep orange and a very pale violet respectively (their normal dye colors both being yellow).

Anthranilic acid itself is known (7) to give characteristic precipitates with cobalt, copper and nickel, but neither it nor a solution of diazotized anthranilic acid gives the specific reaction for cobalt herein described.

From these observations, it appears that the specific reaction is due to a certain group:



i.e., the hydroxyl group of the phenol or naphthol coupled to the diazotized anthranilic acid must be in a position ortho to the azo group in order to obtain the characteristic color. Furthermore, the substitution of additional hydroxyl groups, as in the case of resorcinol and pyrogallol above, appears to alter this specific reaction considerably, whereas the substitutions in the other compounds cited above, containing methyl, chloro and sulfonic groups did not appear to cause a major variation in the specific reaction. The author was unsuccessful in coupling the diazotized anthranilic acid to p-nitrophenol in an attempt to observe the effect of the nitro group on the reaction.

The author has not found mention of this reaction in the literature.

Simultaneous tests of the six positively reacting dyes listed above show that at room temperature the differently soluble dye containing β-naphthol reacts much slower than the other, the two containing p-chlorophenol p-cresol produce only an intermediate brown color in two hours, while the dyes from R-salt, NW acid and Schaeffers acid reach almost a maximum value of the specific color in one hour. On standing 17 hours to permit all six dyes to reach a maximum color, these tests show that the dyes from p-cresol and p-chlorophenol both give a much bluer shade of violet than the similar red violet colors produced by the dyes from R-salt, NW acid and Schaeffer's acid.

Of the six dyes listed, that from NW acid (α-naphthol-4-sulfonic acid) appears most satisfactory as a reagent for cobalt since it is quite soluble in water, even in acid solution, it develops the violet color a little faster than those from R- and Schaeffer's acids, it is normally a bright orange in both acid and alkaline solutions and according to preliminary tests gives practically no other unique reactions

The time required for the formation of the color by this dye is reduced from one hour to a few minutes by boiling the solution.

The concentration of cobalt in the .001 molar solution is, of course, 59 parts per million, but the characteristic color is still distinguishable at a concentration of about 5 parts per million.

In order to further test the specificity of the reagent, 5 cc. samples of the twenty-four .001 molar salt solutions were pipetted into test tubes, 2 cc. of 6 N ammonium hydroxide and 10 drops of .01 molar dye solution (anthranilic acid ⟶ NW acid) were added to each, thus making approximately equimolar quantities of dye and metal salt. The tubes were placed in a boiling water bath for 1 hour, were removed and water was added to make up for evaporation, and the following observations were made. All but four of the tubes retained the original bright orange color of the dye, with precipitates of the metal hydroxides appearing in some cases. Chromium, nickel and copper gave a reddish orange and cobalt gave an intense violet red, stronger than in previous tests because of the much greater amounts of dye used.

That the presence of a definite amount of ammonia is required is shown by the following. To nine 5 cc. portions of .001 molar $CoCl_2$ were added: one, two, and three drops of 6 N ammonium hydroxide and one, two, three, five, seven and ten drops of 6 N sodium hydroxide respectively, and then to each portion was added 5 drops of the .01 molar reagent mentioned above. Each portion was boiled a few seconds, was allowed to cool, and was diluted to 10 cc. On standing only the portion to which had been added 3 drops of ammonium hydroxide showed the characteristic violet color, while all the others showed only brown precipitates and brown or yellow solutions.

But ammonia does not seem to be necessary to the formation of the intermediate brown color which appears almost immediately after the addition of the reagent to the .001 molar $CoCl_2$ solution. From this it appears that the characteristic violet color is produced in two successive stages, first between the dye and the metal salt and then with ammonium hydroxide.

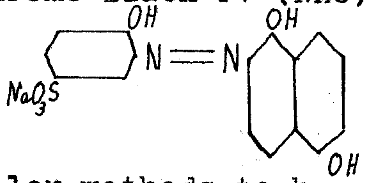
The possibility of the necessity of aerial oxidation of the cobaltous ion to cobaltic ion in ammoniacal solution as a prerequisite to the characteristic color formation is shown to be unwarranted by repeating the test with boiled solutions in a closed vessel.

HYDROGEN ION INDICATORS

Two commercial dye products were tested to determine the pH ranges of the color transition.

Erioazurin 3B (Geigy), C.I. 59, is listed as consisting of p-dimethylaminoaniline ⟶ 1:8-dihydroxynaphthalene sulfonic acid, and has two principal color transitions. By use of Kolthoff's buffer mixture (11, pp. 147-8) of borax with succinic acid and potassium dihydrogen phosphate the pH ranges of the two transitions were determined. 5 drops of a 0.1% solution of the commercial dye were added to 20 cc. portions of the buffer mixture. The dye changed from a clear pink at pH 3.2 to a nearly pure blue at pH 4.8, and from this same blue at pH 6.4 to a yellow at pH 7.8. The acid transition is almost identical with that of the similar methyl orange and offers the possibility of replacing it in some cases. Both the pink and the blue are quite free of dichroism, thus making a favorable comparison with brom phenol blue. In the alkaline transition range the change from blue to yellow requires several minutes to attain equilibrium in the buffer solution.

Superchrome Black PV (NAC), C.I. 170 of formula



was found by similar methods to have a color transition from violet pink at pH 7.2 to violet blue at pH 9.2.

SUMMARY

Tests for specific reactions between dilute solutions of 24 metal salts and 216 commercial dye products and organic compounds (of which 36 were prepared by the author) were made in the original salt solutions, at the neutral point, in acid, and in alkaline media. Results of these tests are listed, and from this list a table of the more interesting reactions is derived. Sixteen cases of specific reactions are cited as being of particular interest and worthy of further investigation.

A series of azo dyes giving a specific yellow color with copper salts is investigated and discussed.

A series of azo dyes made from anthranilic acid giving a characteristic color only with cobalt in the presence of ammonia is investigated and discussed.

The pH ranges of the color transition of two azo dyes are determined, and one of these, Erioazurin 3B, is suggested as a possible replacement for methyl orange as a hydrogen ion indicator.

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