

Conclusions. From the statements already made concerning the several variable factors involved in this work, one would predict certain of the results that are apparent in tables 1 and 2. The rate of evaporation should be greater in the 100 ml. burettes than in those of less capacity having a shorter radius of exposed surface; it should be less for water than for benzene which has, for a given temperature, a higher vapor tension; the vapor pressure of a solution 5N is less than that for one 0.25N, hence the rate should be less for the more concentrated solution; and covers over the ends of the burettes should decrease the rate, due to their partial closing of the systems and consequent prevention of freely circulating air from carrying away the gaseous molecules of the liquids.

On account of the rather complex situation prevailing in these experiments, with the several variable factors uncontrolled, it is not possible to point out the effect of each variation. It seems probable that the effects of changes in barometric pressure and relative humidity are relatively small as compared with that for changes in temperature. An inspection of the results in table 2 for the eighth and ninth days shows a small change of the former variables but a distinct increase in the readings of the burettes, even though a decrease in the temperature should have decreased the vapor tension of the water and thus have decreased the rate of evaporation. It seems evident that a change of temperature of the solutions produces a change of volume considerably larger than the change resulting from a change of vapor tension, and in the opposite direction.

It has already been stated that experiments conducted under the conditions prevailing during this work cannot give entirely satisfactory results, but they do furnish a general basis for predicting what may happen when such measurements are made in the usual laboratory. It is evident that caps on burettes do retard the rate of evaporation; but it is also evident that the total loss through evaporation for an aqueous solution is small at the end of a day, even in the open burettes, and one never takes such a length of time for the ordinary titration. Changes of temperature are liable to cause a much greater change in the volume of a standard solution.

THE USE OF SOLUTIONS OF INORGANIC SALTS AS PERMANENT COLOR STANDARDS.

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In the colorimetric determination of certain substances a common procedure consists in comparing, by means of a colorimeter or some other device suitable for the desired accuracy, a definite volume of a solution containing the unknown substance with various standard solutions containing definite amounts either of the constituent being determined, or of some other substance showing the same color as this constituent. When a match is found between the unknown and one of the standards, it is assumed that the amounts of the color-forming constitu-

ent in the two solutions are identical, if of the same composition, or equivalent to each other, if of different compositions. Where frequent determinations are to be made in this manner, it is very desirable to have permanent standards for either of the cases mentioned. Loss of time results if one must prepare a new set for each day or determination; and one's work is uncertain if the colors of the standards change or fade following some reaction affecting the color-forming constituent.

The synthetic organic chemist has supplied us with compounds of every desirable shade of color which might be useful in the preparation of such standards. Unfortunately, many of these compounds do not maintain their color indefinitely when in solution and exposed to the light. In some the color fades; in others the colored solute coagulates and settles out, leaving the solution clear.

In the effort to avoid the difficulty arising from such instability of color with organic substances, occasional work has been done for a number of years involving the use of solutions of inorganic salts. The purpose of the present paper is to review the information available regarding the color of solutions of inorganic substances, to note the requirements of a permanent color standard and the limitations of inorganic substances for such purposes, to mention some of the possible combinations for permanent standards, and to present a résumé of previous work upon the subject. Experimental work is under way relating to certain colorimetric standards but sufficient data is not yet available for any definite conclusions.

The Color of Inorganic Substances in Solution. Compared with the amount that has been written concerning the color of organic compounds, there is a relatively small amount available regarding the color of inorganic compounds. Particularly is this true both for the actual colors of the solutions of the compounds and also for the permanency of such colored solutions.

Recently Bichowsky¹ has discussed the color of inorganic compounds from the standpoint of electronic structure and valence of the atoms. The color exhibited by any compound is the result of its selective absorption of light, and only those substances are capable of such absorption which have an arrangement of electrons free to vibrate in the proper manner. He points out that compounds of invariant valence elements are colorless, due to their high electron stability and consequent absorption of light of short wave lengths—the ultraviolet. According to Bichowsky's table of valence colors for the elements of variable valence, the chief elements we may expect to show color (omitting the rare earth elements and the oxides and sulfides of the variable valence elements) are copper, gold, (silver), titanium, vanadium, chromium, molybdenum, tungsten, uranium, manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum.

In figure 1 is given Mellor's adaptation of the periodic table as arranged by Bayley, in which the atomic weights and the atomic numbers of the elements have been included. The elements of invariant valence (forming colorless compounds) have been indicated with a cross.

¹ *Jr. Am. Chem. Soc.* 40, 500 (1918).

Those forming compounds with pronounced colors are inclosed in the circles. It is of interest to note in connection with the latter series of elements that, (a) the most common ones have the consecutive atomic numbers 22 to 29; (b) two other series of consecutive numbers are included; (c) all the transition elements are included; and (d) those not in the transition groups are substantially the ones adjacent to them. Although there are some colored compounds of the elements not already mentioned, it is probable that few of them will prove of value for the preparation of colored solutions.

PERIODIC TABLE

Rare Earth Elements

57La 58Ce (59Pr) 60Nd 61Pm 62Sm 63Eu 64Gd
138.0 140.2 140.9 144.3 150.4 152.0 157.3

65Tb 66Dy 67Ho (68Er) 69Tm 70Yb 71Lu 72Hf
158.9 162.5 164.5 167.3 168.5 173.5 175.0 (178)

Fig. 1. Showing the location in the periodic table of the chief elements forming colored compounds.

Requirements of a Satisfactory Permanent Color Standard. Any solution to be considered as a possibility for a permanent color standard must first of all possess a color suitable for the purpose in hand, or be capable of giving it through proper blending. The color must be uniform throughout the solution and must not change in intensity or hue. To be suitable for general use the color must be such as to be accurately and readily reproducible. Furthermore, if two or more solutions are to be mixed in order to obtain some blend of the original colors, the solutes and solvents must be of such a nature that no reaction occurs on mixing which destroys the expected, resultant color. The intensity of the color must be sufficient—this requirement would practically eliminate the use of such compounds as manganous salts whose color in solution is very definite but relatively low in intensity. In general it is desirable to have dilution of a colored solution result merely in a decrease in intensity of the color rather than in a real change of color².

² Sheppard—Photo-Chemistry, p. 153, 159 (1914).

Limitations of Inorganic Compounds. When one attempts to select a set of solutions of inorganic materials whose colors include the seven primary, visible colors of the solar spectrum, he is at once confronted with an inherent scarcity of individual colors of a wide variety. The range is fairly well covered from the red of an aqueous solution of cobaltous chloride to the blue of an aqueous solution of cupric sulfate. These, however, do not include deep reds on the one end nor deep blues, indigos nor violets on the other. As will be noted later, deeper reds and blues may be obtained under certain conditions but the stability of the solutions has not been found entirely satisfactory. Some solutions have good colors but cannot be mixed with others, which makes their use limited.

While at certain times one may obtain a closely agreeing match between an unknown, colored solution and an inorganic permanent standard, at other times such a match may be difficult to accomplish, as in tests on such complex systems as the usual surface water. On the one hand, pure or mixed solutions show a clearness and brilliancy of color which many complex samples do not possess. On the other hand, the color produced in the solution to be tested may depend upon a variety of conditions, such as temperature, quantity of reagent added, manner of making reagent, variable quantity of accompanying substances, time elapsing after the preparation of the sample before comparison of the color, and others practically impossible to control closely. Uniformity in preparation and handling both of sample and standard are necessary in such cases.

Elevation of the temperature often changes the color of absorbing media². It is well known, for example, that the red color of an aqueous solution of cobaltous chloride turns blue if the temperature is raised sufficiently. Another red solution, matching the color of the first but having a different composition, probably would not show the same change of color on passing through the same changes of temperature. When such a change of temperature causes a chemical modification, changes in the absorption spectrum occur; but in chemically stable systems, such as potassium bichromate, the alteration is small or nil.³

Another difficulty presents itself. It seems probable that, if one matched the green of a solution of nickelous sulfate with a green produced by blending solutions of cobaltous chloride, ferric chloride and cupric sulfate, the mechanism giving rise to the same color sensation in the two cases for one individual would not do so for another⁴. Arny⁵ has found, for the conditions he studied, that several individuals obtained the same Lovibond readings on a number of different solutions; but Watson⁷ states that the color sensation produced in different persons by the same quality of light may vary considerably.

Besides the effect of a change of temperature just mentioned, several

² Wood—Physical Optics, p. 441 (1911).

³ Sheppard *Loc. cit.*, p. 163.

⁴ Richards and Ellms—*Jr. Am. Chem. Soc.* 18, 75 (1896).

⁵ Arny—Report 8th. Intr. Congr. Appl. Chem. 26, 319 (1912).

⁷ Watson—Textbook of Physics, p. 559 (1919).

Sheppard—*Loc. cit.* p. 150.

other factors may affect the permanency of the color of a solution. Among these may be mentioned the possibility of changing a color's hue or intensity, or both, through the reaction of the solvent and the solute, through the action of the solvent on the container, or through the action of light upon the solution. Many qualitative observations have been made bearing upon these reactions, but little data of a quantitative nature is available.

In discussing the photo-sensitiveness of salts of metals, Sheppard⁵ states that "the greater proportion of ordinary crystallizable salts of the metals, whether in the solid state or dissolved, are comparatively stable in respect to light. But this stability is certainly relative rather than absolute, being an inverse function of the absorption of light of the bodies, and is, practically, not disconnected with the fact that it is rare for these bodies to be exposed without intermission. . . . It has been observed that aqueous solutions of the salts of the heavier, polyvalent metals undergo a gradual change of character on keeping. This change is apparently of the nature of a hydrolytic cleavage of the metal salt, leading by a series of reactions in stages, with concomitant side reactions fixing each stage enduringly and irreversibly as evolved, to the deposition of structurally conformed aggregates of insoluble oxides, sulfides, and ternary and quaternary complexes of varying composition."

Inorganic Substances Available for Colored Solutions. There are recorded many more or less isolated statements to the effect that various inorganic substances give a certain color in a given solvent, but no general summary or collection of such data has been found. Many of these colors, and particularly certain of those used as qualitative tests, are too transitory to merit consideration in this paper. Others are apparently permanent for a considerable period of time. The original intention was to present a list of those which seemed to offer the most promise of meeting the requirements already stated. The time available has proven too limited for the accomplishment of this compilation; but mention will be made of some of the types of substances which seem to have possibilities, even though their application may be limited. The solutions mentioned are at present being investigated. It is hoped that special apparatus will be available later so that quantitative data may be collected for them.

Aqueous solutions seem to be by far the most important. Those containing the color-forming elements mentioned in connection with the periodic table, in the form of simple cations, include our most familiar, colored solutions, such as cupric sulfate, ferric chloride, etc. The color of some of these solutions is markedly changed through the formation of complex cations under certain conditions, as the strongly ammoniacal solutions of cupric, cobaltic, and nickelous salts. It should be mentioned that pronounced changes of color of solutions of salts of some of the elements takes place on changing the solvent from 1 per cent hydrochloric acid to 30 per cent acid. The most common anions giving colored solutions are chromate, dichromate, permanganate, ferrocyanide, ferricyanide, and chloroplatinate.

⁵ *Loc. cit.* p. 318.

Little can be stated at present regarding the colors of non-aqueous solutions of salts of the color-forming elements. In some cases there is a profound change in the color with the change from water as the solvent, as, for example, the change from the red of cobaltous chloride in aqueous solution to the deep blue with the salt dissolved in absolute ethyl alcohol. A solution of the same salt in acetone is a deeper red than an aqueous solution. A number of these solutions are being investigated.

A very limited class of solutions consists of those in which the elements as such are dissolved. A saturated, aqueous solution of bromine in water has a marked orange-red color. Iodine in carbon tetrachloride gives a beautiful pink colored solution, while in ethyl alcohol it shows a yellowish color. In certain other solvents these elements give somewhat different colors.

Certain colloidal systems consisting of a solid dispersed through a liquid show marked colors, such as the red of ferric hydroxide in water. It is distinctly questionable as to whether such a system would be of any value for permanent color standards.

Previous Work. An attempt has been made to collect the references relating to the use of solutions of inorganic salts as permanent color standards. The following résumé includes a statement of the principles and methods involved in the work for which reports have been located.

Crookes, Odling and Tidy⁹ devised an instrument for comparing the colors of waters with solutions of inorganic salts. This instrument consisted of a pair of 24-inch tubes, one of which contained the water under examination, while the other remained empty. Behind the latter were placed two hollow wedges, one containing a 1 per cent solution of cupric sulfate, the other a solution of ferric and cobaltous chlorides containing 0.7g. of iron and 0.3g. of cobalt per liter, with a slight excess of free hydrochloric acid. These wedges were pushed over the empty tube until their color matched that of the water under examination in the other tube, and the color was recorded as equal to so many millimeters of blue and red solutions.

Hazen¹⁰ proposed the use of a mixture of potassium chloroplatinate and cobalt chloride as a color standard for natural waters. The stock solution contained 1.246g. of potassium chloroplatinate (0.5g. Pt) and 1g. of crystallized cobaltous chloride (0.25g. Co) and 100ml. of concentrated hydrochloric acid, the whole being diluted to one liter. Solutions for comparison were made by diluting 1, 2, 3, . . . ml. to 50. This solution was found to be unaltered after one year, even when standing in the light.

Jackson¹¹ reported the use of permanent color standards for the colorimetric determination of several constituents in water. The various standards used consisted of mixtures of solutions of the following salts:

⁹ Chem. N. 43, 174 (1881).

¹⁰ Am. Chem. Jr. 14, 309 (1892).

A.P.H.A.—Standard Methods of Water Analysis, p. 9 (1917).

¹¹ Tech. Quar. 13, 514 (1900).

A.P.H.A.—*Loc. cit.* p. 17 (1917).

for ammonia, potassium chloroplatinate (2g. per L.) and cobaltous chloride hexahydrate (12g. per L.); for nitrites, cobaltous chloride hexahydrate (24g. per L.) and cupric chloride dihydrate (12g. per L.); and for iron, cobaltous chloride hexahydrate (24g. per L.) and potassium chloroplatinate (12g. per L.). In the preparation of each solution the salt was dissolved in water, 100ml. of concentrated hydrochloric acid added, and the whole diluted to one liter.

Kendall and Richards¹² discussed the factors preventing a perfect match between permanent color standards and the colors obtained with many samples of water. As standards for routine work they do recommend the use of a neutral solution of potassium chromate in connection with the Grandval and Lajoux test for nitrates, and of various dilutions of Tidy's formula (0.25g. potassium dichromate and 9.05g. cobaltous sulfate heptahydrate per L.) for the determination of ammonia.

Washburn¹¹, by combining "in the proper proportions" solutions of ferric chloride, cobaltous nitrate and cupric sulfate, prepared permanent color standards for use in determining the proper iodometric end point in the determination of arsenious acid.

McBain¹¹, in his study on the use of phenolphthalein as an indicator, employed as permanent standards solutions containing mixtures of copper and cobalt salts, acidified with nitric acid to prevent hydrolysis. The most dilute solution contained 0.50g. cobalt nitrate hexahydrate and 0.62g. cupric sulfate pentahydrate per liter; the others contained 2, 3, etc., times these amounts. The difference between any two standards was planned to be equivalent to the color change caused by the addition of one drop of N/250 acid or base.

Army¹, following Washburn's suggestion for blending solutions colored by the cobaltous, ferric and cupric ion, proposed the adoption of solutions containing these ions as "international standards for colored fluids". By mixing these three primary colors, red, yellow and blue, in the proper proportions he obtained 88 blends, ranging from the red through to the blue. These solutions are designated as the "Co-Fe-Cu" standards. In the preparation of the standards, 0.5 N solutions were made of cobaltous chloride, ferric chloride and cupric sulfate by dissolving the salts in 1 per cent hydrochloric acid. All of the work was checked by means of a Lovibond tintometer, and the acidified solutions were found to give the same readings after standing for a year.

Army and Pickhardt¹³ discussed the requirements of satisfactory color standards and reported further observations on the "Co-Fe-Cu" series proposed earlier. This series lacks deep reds and deep blues.

Army and Ring¹⁴, in the effort to provide for the deficiencies of the "Co-Fe-Cu" series, proposed a new series of 0.1 N ammoniacal solutions of chloropentammine cobaltic chloride (red), ammonium chromate (yel-

¹² *Tech. Quar.* 17, 277 (1904).

¹³ *Jr. Am. Chem. Soc.* 30, 31 (1908).

¹⁴ *Jr. Chem. Soc.* 101, 814 (1912).

¹⁵ Report 8th Int. Congr. Appl. Chem. 26, 319 (1912).

Jr. Am. Pharm. Assoc. 2, 76 (1913).

¹⁶ *Druggist's Circular* 58, 131 (1914).

¹⁷ *Jr. Franklin Inst.* 180, 199 (1915).

low) and ammonio-cupric sulfate (blue)¹⁸. When mixed in various proportions, these salts were found to produce all hues except a few delicate pinks and violets. The tints which could not be produced by this "Co-Cro-Cu" series were obtained by means of mixtures of 0.001 N potassium permanganate and 0.01 N potassium dichromate, known as the "Cro-Mn" series. In the "Co-Cro-Cu" series the red and yellow solutions were found to remain unchanged in color if kept well stoppered. The blue solution, however, precipitates within a few weeks and must be prepared frequently. In the "Cro-Mn" series each solution is stable alone, but they begin changing an hour after mixing.

Arny and Ring¹⁹ reported further use of the above mentioned solutions in connection with certain pharmaceutical work.

Arny and Ring²⁰ reported the application of the three series of solutions in the preparation of permanent standards for use in the colorimetric determination of ammonia, nitrates, nitrites, vanillin, uric acid, salicylic acid and phosphates. They state that practically every tint desired in colorimetric work can be obtained with the three series of colors. The original acidified "Co-Fe-Cu" solutions and their blends neither fade nor precipitate until at least two years old; the ammoniacal cobalt and chromate solutions show no fading after a year. The ammoniacal copper solution precipitates and undergoes change of color within a few weeks, but the blends keep satisfactorily when sealed in ampules or kept in well filled, rubber stoppered bottles which are not opened. The concentration recommended in this paper for the "Co-Cro-Cu" series is 0.02 N.

Arny, Kish and Newmark²¹ discussed the unreliability of the Lovibond tintometer for the testing of cottonseed oil, and proposed the use of the "Co-Fe-Cu" and "Co-Cro-Cu" color standards.

Kolthoff²² was the first to propose the use of permanent color standards instead of the usual buffer solutions and indicators in the colorimetric determination of hydrogen ion concentration. By means of M/4 cobaltous nitrate and M/6 ferric chloride he prepared solutions which match the colors of buffer solutions through the pH range of certain indicators. Matches were made showing the change in color of neutral red, methyl orange, tropaeolin 00 and partially for methyl red.

Snell²³ recommends the use of Arny's "Co-Fe-Cu" series for the preparation of permanent standards for the colorimetric determination of carbon, lead, chlorine, and possibly for aluminium. He states further, that for the determination of bismuth, permanent standards may be made using the same reagents as in the case of the unknown sample. Solutions of potassium chromate, potassium chloroplatinate and ammoniacal cupric chloride may be used for permanent standards for the determination of chromium, potassium, and oxygen, respectively.

¹⁸ Note—Salts of copper and cobalt are M 20 and the dichromate M 120.

¹⁹ *Jr. Am. Pharm. Assoc.* 4, 1294 (1915).

²⁰ *Jr. Ind. Eng. Chem.* 8, 309 (1916).

²¹ *Ibid.* 11, 950 (1919).

²² *Pharm. Weekblad* 59, 104 (1922).

²³ *Colorimetric Analysis* (1921).

