

OXIDATION-REDUCTION INDICATORS USED IN VOLUMETRIC ANALYSIS¹

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I. A GENERAL DISCUSSION OF INTERNAL ANALYTICAL OXIDATION-REDUCTION INDICATORS

A. HISTORY OF OXIDATION-REDUCTION INDICATORS

In analytical chemistry there are a great many volumetric analyses that depend upon oxidation-reduction reactions. The usual method of running such an analysis is to obtain the unknown constituent in solution as one ion and to change it to a second ion by adding just enough to a standard solution of an oxidizing agent or a reducing agent. The entire determination depends upon knowing when just enough of the standard solution has been added to carry out the desired reaction. It is possible to determine this equivalence point electrically, but the apparatus is costly and the operation is tedious. Fortunately, some of the standard solutions have one color in the oxidized form and another color in the reduced form, or are colorless in one form. When this is the case and the color change is sharp enough, the standard solution will act as the indicator for the reaction. Unfortunately for this method of analysis, the difference in color between the oxidized and the reduced forms of many of the more suitable oxidizing agents is not great, nor is the color change sharp at the equivalence point. In many analyses other colored ions are present and mask the color change at the end point. Furthermore, the presence of certain reagents added during the process of analysis may interfere with the color change, although they have no color of their own.

In the titration of ferrous ion with potassium dichromate solution the color change at the equivalence point is difficult to detect accurately. In studying this reaction in 1906, Brandt (6) proposed that diphenylcarbazide, $\text{CO}(\text{NHNHC}_6\text{H}_5)_2$, which he called diphenylcarbon-hydrazide, be used as an internal indicator. This compound forms a red color with ferric salts

but is colorless in the presence of an excess of potassium dichromate. Barnely and Wilson (3) in 1913, in attempting to reproduce Brandt's experiments, failed to get concordant results. It was found that the results obtained were more dependent upon the conditions of the analysis than upon the amount of iron in the sample. In a later publication (6) Brandt reported his indicator to be only fairly accurate in macrodeterminations of iron and not applicable at all to microdeterminations.

Modern internal oxidation-reduction indicators really began to become prominent in 1924 with the publication by Knop (34) of a discussion of the use of diphenylamine as an internal indicator in the iron-dichromate titration. Sarver and Kolthoff and their coworkers (48) at the University of Minnesota and Young and Willard and their coworkers (74) at the University of Michigan have applied themselves for some time to a study of the use of diphenylamine, diphenylbenzidine, and their derivatives as oxidation-reduction indicators.

Clark and Cohen and their coworkers (8) in the Hygienic Laboratory of the United States Public Health Service from 1924 through 1928 investigated in great detail the properties of oxidation-reduction indicators that change color at low potentials, mainly the indigosulfonates. These indicators at present are of physiological or biological rather than of analytical importance, and are rarely used in analytical work.

In 1931 Hammett and Walden and their coworkers (22) at Columbia University first began work with the phenanthroline ferrous ion complex of Blau as an indicator in titrations with ceric ion. Knop in Europe has continued his work on oxidation-reduction indicators, and of late has been mainly interested in the triarylmethane dyestuffs.

Today we find that the most popular oxidation-reduction indicators in the order of their preference are as follows: the phenanthroline ferrous ion complex, diphenylaminesulfonic acid, diphenylamine, diphenylbenzidine, Erioglaucin A, Erio Green B, and Setoglaucin O. Without these oxidation-reduction indicators the use of ceric sulfate as a standard oxidizing agent would be greatly restricted. In general, the introduction of internal oxidation-reduction indicators has greatly widened the field of oxidimetry by introducing new standard oxidizing agents and increasing the accuracy of older ones.

B. THEORY OF OXIDATION-REDUCTION INDICATORS

If a solution of a reductant is titrated by means of a suitable oxidant, and, during the course of the titration, the oxidation potential is observed by means of a suitable apparatus, values are obtained which, when plotted, give a curve similar to that in figure 1. If an acid is titrated with a suitable base and the hydrogen-ion concentration is determined by means of a

suitable apparatus, values are obtained which, when plotted, give a curve similar to that in figure 2.

A comparison of these two curves indicates that the oxidation potential bears almost the same relation to oxidation-reduction titrations that the pH bears to neutralizations. This conclusion has been established by Kolthoff and other workers (28, 29, 30, 31, 32, 33). As an acid-base

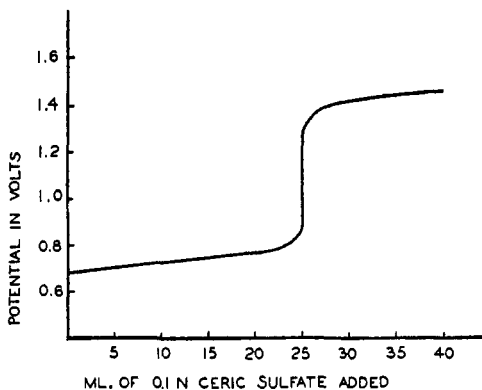


FIG. 1. Titration of ferrous sulfate with standard ceric sulfate

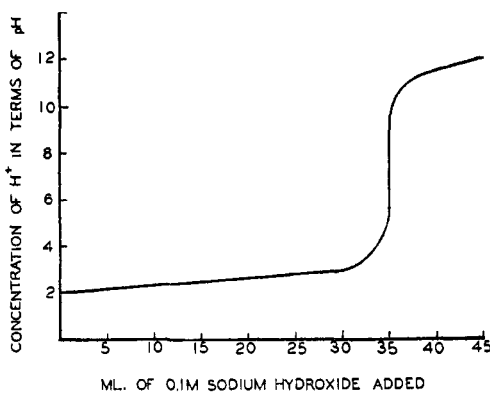


FIG. 2. Titration of sulfuric acid with standard sodium hydroxide

indicator is a compound that produces a marked color change with a certain change of pH, so an oxidation-reduction indicator is a compound that produces a marked change of color with a certain change of oxidation potential. Furthermore, as the ability to change color with change of pH is not the only criterion of the suitability of a compound as an acid-base indicator in a neutralization, so the ability of a compound to change color

with a change of oxidation potential is not the only criterion of its suitability as an indicator in an oxidation-reduction titration.

From the oxidation potential of the constituents titrated and from that of the reducing agent, it is possible to calculate the potential at the equivalence point. Theoretically, therefore, it is possible to calculate the range of oxidation potential in which that of an indicator must be located to be suitable. In the selection of the proper indicator upon the basis of such theoretical considerations, it should be realized that in most cases the oxidation potential at the equivalence point depends upon the hydrogen-ion concentration and the concentration of the other ions present in the solution. Furthermore, it is frequently found that these anions or cations affect the oxidation potential of the constituent titrated, or that of the reagent, or both, usually as a result of complex ion formation. Thus the suitable range in which the color change of the indicator must occur becomes dependent upon the nature of the solution being titrated.

The range of oxidation potential in which the color change of the indicator actually lies also depends upon the solvent medium. As a general rule, oxidation-reduction indicators in their oxidized and reduced forms are donors (acids) or acceptors (bases) of protons, respectively. Their oxidation potentials, therefore, are more or less complicated functions of the hydrogen-ion concentration of the solution and, in addition, depend upon the ionic strength of the medium. That is, the oxidation potential at which the indicator shows a color change varies with different values of the pH and also when different kinds of ions are present. That this is a complicated function is shown by the following equation, which was derived by Cohen and Clark (8, 9) for the variation of the oxidation potential of the simple indophenols at 30°C.:

$$E_h = E_0 - 0.03006 \log \frac{C_r}{C_o} - 0.03006 \log [K_r K_2 (H^+) + K_r (H^+)^2 + (H^+)^3] - 0.03006 \log [K_0 + (H^+)]$$

where E_h = the oxidation potential with respect to the normal hydrogen electrode,

E_0 = the oxidation potential when $C_r/C_0 = 1$ and the pH = 0,

C_r = the concentration of the total reductant,

C_0 = the concentration of the total oxidant,

K_0 = the dissociation constant of the oxidant,

K_r = the acid dissociation constant of the hydrogen in the reductant to which K_0 applies in the oxidant,

K_2 = the acid dissociation constant of the phenolic group, created by the reduction, and

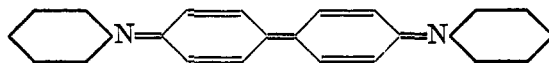
H^+ = the concentration of the hydrogen ion.

As this equation is given for a specific temperature, we know that the oxidation potential of the indicator will vary with the temperature.

The considerations in the two preceding paragraphs are not so very important in cases where the jump in potential near the equivalence point is very great, but they become of primary importance where the useful range of oxidation potential becomes small. Because of these difficulties, most of the investigations of analytical oxidation-reduction indicators have been confined to systems in which the difference in potential just before and just after the equivalence point is fairly great, such as in titrations of ferrous ion with ceric sulfate or potassium dichromate.

The change in the structure or the composition of the indicator that causes the color change is not known in all cases. Blau and later workers have prepared the ferrous phenanthroline complex and found it to be red, while the ferric phenanthroline complex was found to be blue. It is generally accepted that the color change in this indicator is caused by the change from the ferrous to the ferric complex or *vice versa*, and that the ferrous ion held in the complex is not oxidized until an oxidation potential of 1.14 volts with reference to the normal hydrogen electrode is reached.

Kolthoff and his coworkers (28, 29, 30, 31, 32, 33) have investigated thoroughly the color change that takes place in diphenylamine. Their experiments show that the first excess of oxidant changes diphenylamine to diphenylbenzidine. Both of these compounds have been isolated and their composition and structure determined; both are colorless, and the reaction changing the former to the latter is irreversible. This means that this reaction must take place at a lower potential than the equivalence potential or within the useful range. The next portion of oxidant produces a violet coloration in dilute solutions. This violet compound is called diphenylbenzidine violet and is shown, by its absorption spectrum, to be a quinoid salt. Efforts to isolate diphenylbenzidine violet failed, but as a result of spectrographic and other studies the following structure was assigned to it:

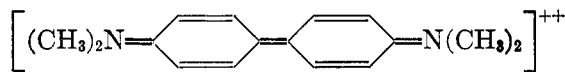


Diphenylbenzidine violet

If the portion of oxidant used to produce the violet color is added slowly to a concentrated solution of the indicator, a green compound is produced which disappears on the addition of more oxidant, giving the violet compound. The investigators called this green compound diphenylbenzidine green. It is assumed to be a molecular compound, called a meriquinoid, the product of the reaction between the oxidized diphenylbenzidine (diphenylbenzidine violet) and the unoxidized portion of diphenylbenzidine.

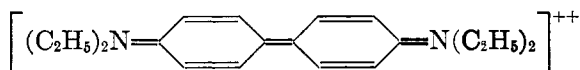
In ordinary titrations diphenylbenzidine green is not produced, because of the small quantity of indicator used and its dilution. However, the oxidation potential of the color change is thought to be the equilibrium potential for the reaction diphenylbenzidine green \rightleftharpoons diphenylbenzidine violet.

Kehrman (26) and his associates established compounds I and II, respectively, as the oxidation products of the two arylmethane dyes Malachite Green and Brilliant Green.



I

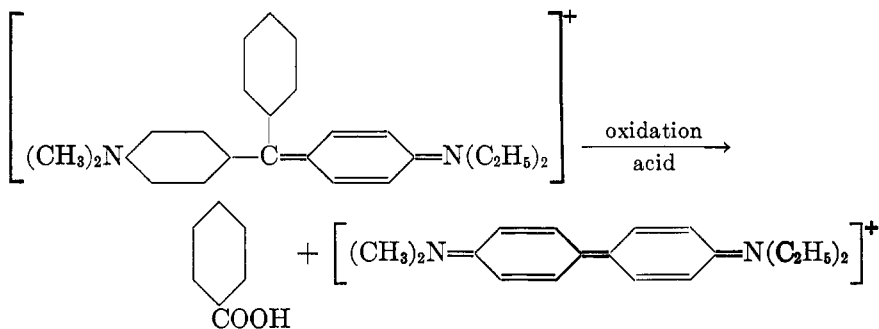
Oxidation product of Malachite Green



II

Oxidation product of Brilliant Green

As can be seen by an examination of the formulas, the compounds are benzidine derivatives and could theoretically be prepared from benzidine. Knop, in attempting to explain the cause of the difference in color of the oxidized and reduced forms of some twenty-five triarylmethane dyes on the basis of this formula, regarded the following reaction as typical:



Absorption spectra studies and comparisons with derivatives of benzidine proved this to be the case in only a few instances, and never when the oxidation product was rose colored. The rose-colored product could not be identified nor is its structure known.

Knop concluded that, when one of the triarylmethane dyes was used as an indicator, during the oxidation there was formed, by an irreversible reaction, a new compound that became the indicator for the reaction. On reduction, this new compound produced a product which was similar

in color to the original dye but was not the original dye. Knop substantiated this contention with experimental evidence, although he was unable to identify definitely the oxidation products. In general, it is thought that the color change in the derivatives and substitution products of diphenylamine is caused by a change similar to that in diphenylamine, and that the color change in the *p*-nitrophenanthroline ferrous complex is similar to that of the phenanthroline ferrous complex. The remaining oxidation-reduction indicators have not been fully studied, and the exact change that causes the color shift has not been determined for every indicator.

Just as with acid-base indicators the color change is sometimes gradual over a range of pH, with a sharp change within certain limits, so with oxidation-reduction indicators there is often more than one color change, but usually one change is sharper between certain limits than any of the others. In the case of oxidation-reduction indicators a single value of the oxidation potential is usually given. This is the potential at which the indicator shows its greatest color change, and it is given with reference to the normal hydrogen electrode, unless otherwise specified. Usually, if the pH is not given, the color change takes place at the given potential in solutions which are between 1 and 2 normal with respect to hydrogen ion.

A system of indicating the range of oxidation-reduction indicators other than that of the oxidation potential which is sometimes, although infrequently, used is that of sensitivity. When it is said that diphenylamine has a sensitivity of 4×10^{-6} to potassium permanganate in 1 *N* sulfuric acid, this means that as soon as the 1 *N* sulfuric acid containing the indicator becomes 4×10^{-6} *N* with respect to potassium permanganate the indicator becomes violet colored. As all oxidizing agents of the same normality do not have the same oxidizing power, this system does not possess the advantage of suggesting the suitability of an indicator for use with different oxidants and reductants that the oxidation potential method does.

C. CHARACTERISTICS OF OXIDATION-REDUCTION INDICATORS

An oxidation-reduction indicator is defined as a substance the oxidized form of which has a color different from that of the reduced form. The character of this color change (when it will take place), the solubility, the reactivity, and the stability of the substance are the main characteristics that must be considered in determining its suitability as a general oxidation-reduction indicator.

(a) The oxidation potential at which the color change takes place is of prime importance. In most of the titrations to which these indicators have been applied this potential must be fairly high,—between 0.7 and 1.3 volts. It is not correct to say that the potential at the transition point (from the

reduced to the oxidized form) must be in the neighborhood of 1.0 volt, because that will depend upon the titrating reagent and the constituent being determined. There is no reason to believe that in the future oxidation-reduction indicators may not be applied to determinations that have a relatively low potential at the equivalence point.

(b) It is essential that the color change at the transition point be sharp. Not only should the difference in color of the oxidized and reduced forms be marked, but the change from one form to the other should be very rapid. Smith (53) gives as the most desirable change one from red to violet or blue. Not all analysts agree with this statement. Some prefer a single-color indicator, believing that a change is best also if this color is so marked that it stands out above colors that might be imparted to the unknown solution by frequently occurring anions or cations.

(c) The end-point color should be fairly permanent. The compound should therefore be stable with respect to both oxidant and reductant. The end color should last for at least 2 min., and it is better if it lasts much longer. Unfortunately, many of the indicators produce colors that last only a few seconds.

(d) In most titrations it is necessary for the indicator to be resistant to the action of the common mineral acids. It is possible that future applications may be made in basic or weakly acidic solutions, but, at present, titrations to which the indicators have been applied are carried out in fairly strong acid solutions (at least 1 to 2*N* with respect to hydrogen ion). It is well, also, if the indicator is resistant to temperatures almost as high as 100°C.

(e) The indicator should not react with the commonly occurring anions and cations. Such action would interfere with the end-point color by forming a new compound or complex that might have different properties.

(f) It is desirable that the indicator reaction be reversible, since this will allow overstepped end points to be back-titrated. However, although certain of the oxidation-reduction indicator reactions are not reversible, they are still used, mainly those used with potassium bromate, most of which are destroyed by the bromine released at the end point. Unfortunately, with an irreversible indicator the end point may be approached from one side only. If the indicator is acceptable in other respects, an irreversible indicator reaction should not cause it to be entirely discarded.

(g) It is preferable that the indicator be water soluble. Limited solubility is just as acceptable as decided solubility, for indicator solutions are seldom stronger than 2 per cent. If the indicator is not soluble in water, the next best property is for it to be soluble in the common acids like sulfuric, hydrochloric, or acetic acid. The indicator is somewhat less desirable if it is soluble in organic solvents only.

(h) The indicator is more acceptable if its solutions are stable for some

length of time, although this is not absolutely essential, as new solutions could be made for each set of determinations. However, if the solutions are stable, the indicator lends itself more readily to routine work.

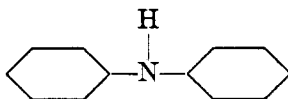
(i) The indicator will be more acceptable if only small quantities are needed for each determination. If a large quantity is needed, this will require a larger quantity of oxidant or reductant to cause the color change and will increase the value of the blank.

(j) It is preferable that the indicator be easily prepared or readily obtainable. Of course, if a compound that proves itself to be a good indicator is difficult to prepare, chemical supply houses will soon make it available.

II. SPECIFIC INTERNAL ANALYTICAL OXIDATION-REDUCTION INDICATORS

A. INDICATORS OF THE DIPHENYLAMINE SERIES

These indicators, at least theoretically, may be formed from diphenylamine by the substitution of different groups for one or more of the hydrogens of the benzene rings. They all contain the structure



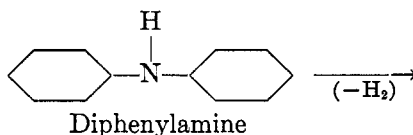
where atoms or groups other than hydrogen may be present on the rings.

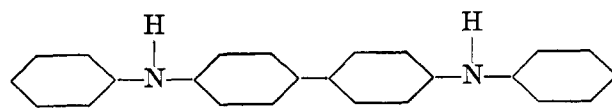
This is the oldest group of oxidation-reduction indicators and one in which investigations are still being carried on. As a general rule, the color changes are from colorless to some shade of blue or pink. Also, as a general rule the introduction of carboxyl or sulfonic acid groups increases the oxidation potential necessary to cause a color change.

In general, for the members of this group as well as for the other indicators, the following five characteristics and conditions will be given in order: (a) structure of the indicator; (b) preparation of the indicator; (c) preparation of the indicator for use; (d) use of the indicator; (e) limitations of the indicator.

1. *Diphenylamine* (1, 15, 18, 19, 20, 21, 24, 28, 32, 33, 34, 41, 46, 48, 50, 52, 66, 68, 74, 75)

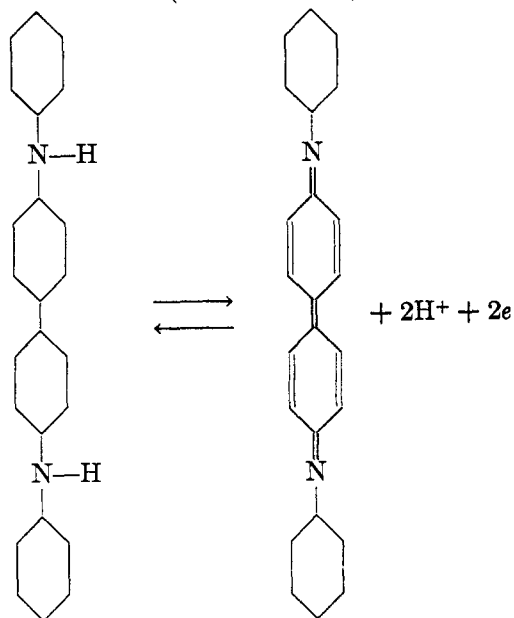
(a) *Structure:*



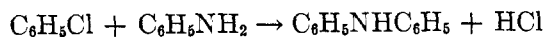


Diphenylbenzidine

(colorless forms)

Diphenylbenzidine
violet

(b) *Preparation of the indicator:* Diphenylamine can be prepared according to the reaction:



Sodium hydroxide is used to bind the hydrogen chloride formed. A mixture of 37 g. of aniline, 44 g. of chlorobenzene, and 40 g. of soda lime is heated for 34 hr. or longer in an autoclave at a temperature of 360–370°C. The mass is dissolved in 800 cc. of water and neutralized with hydrochloric acid. The unchanged aniline dissolves, and the diphenylamine separates as an oil which solidifies overnight and can be filtered off. The product may be further purified by recrystallization from ether.

The indicator is sold in bulk form by most chemical supply houses, by

the Eastman Kodak Company, and by the National Aniline and Chemical Company.

(c) *Preparation of the indicator for use:* Method A—1.69 g. of diphenylamine is melted and is then dissolved, by shaking, in 1 liter of concentrated sulfuric acid. Five or six drops of this solution are used with 0.1 *N* reagents and 0.05–0.02 cc. with weaker reagents. A 0.1 per cent solution in concentrated sulfuric acid is preferred by some analysts.

Method B (preparation of the oxidized form)—According to Young and Willard (74, 75), the correction due to the indicator can be greatly reduced by using the indicator in the oxidized form, which is prepared in the following manner: 0.1 g. of the indicator is dissolved in 10 cc. of sulfuric acid (sp. gr. 1.83) and the solution is diluted with 90 cc. of glacial acetic acid. To about 10 cc. of the above solution in a small beaker is added 5 cc. of phosphoric acid (sp. gr. 1.37) and three or four drops of 0.1 *N* potassium dichromate, followed by very dilute ferrous sulfate solution until a single drop causes the solution to become colorless. Small portions of the indicator so prepared are used.

(d) *Use of the indicator:* The oxidation potential of the indicator at the color change is 0.75 volt and is nearly independent of the hydrogen-ion concentration.

The indicator is one of the best for the determination of iron by titration with potassium dichromate. Knop (34, 35) states that Penny's (41) method for the determination of iron, using potassium dichromate as the standard oxidizing agent with diphenylamine as an indicator, is more accurate than the usual Rheinhardt-Zimmerman method, using potassium permanganate without an indicator. Diphenylamine can be used as an indicator in the determination of cobalt by titration with standard potassium dichromate. It is satisfactory as an indicator in the titration of uranium with potassium dichromate. When hydrofluoric acid is used to suppress the ferrous-ferric potential, accurate results can be obtained on iron in a silicate rock by using the indicator and titrating with standard potassium dichromate. Knop (34, 35) thoroughly investigated the use of the indicator in ferrous-dichromate titrations and found it well suited for use in either macrodeterminations or microdeterminations of iron in ore or in steel. He found that the presence of zinc, nickel, aluminum, cobalt, or chromium has no effect on the determination of iron when this indicator is used. The same investigator also found that dichromate could be employed as the titrating agent when the indicator was used in determining ferrous iron in mixed ferric-ferrous solutions, and that the presence of the ferric ion did not interfere in quantities less than 1 g. in 150–200 cc. of solution.

One of the best methods of determining chromium and vanadium in alloy steels by titrating with ferrous sulfate solution makes use of diphenylamine as the indicator. Ackermann (1) reports using the indicator satisfactorily in the direct titration of used chromeliquor in the tanning of leather. Knop (34, 35) applied the indicator to the determination of chromium in steel. He found that accurate results could be obtained by dissolution of the sample in 1:1 sulfuric acid, oxidation with ammonium persulfate, removal of the manganese as the oxyhydroxide, reduction of the chromic acid so formed with standard ferrous sulfate solution, and back-titration with standard potassium dichromate. Furman (19) found the indicator useful in the determination of vanadium in ores or steels even in the presence of ferric iron, trivalent arsenic, and hexavalent uranium. He employed various methods and titrated with standard ferrous sulfate after oxidizing with potassium permanganate.

Diphenylamine can be used in the titration of hydroquinone with standard ceric sulfate solution, and it can also be applied to the titration of ferrous salt solutions with ceric sulfate. Young and Willard (74, 75) found that the indicator accurately determined the equivalence point in the ferrous-ceric titration even in the presence of arsenious acid and that results so obtained were fully as accurate as potentiometric titrations. They used a buffer solution of sodium acetate solution for all solutions containing free hydrochloric or sulfuric acid. The same investigators substantiated the previous work of Knop on the same indicator.

Diphenylamine is a preferred indicator in the titration of potassium ferrocyanide with standard zinc sulfate.

If diphenylamine is added in the permanganate titration of iron, the end point is sharper and more permanent than when no indicator is used; furthermore, the presence of hydrochloric acid, stannic chloride, or mercurous chloride does not interfere with the end color, although a mixture of 15 cc. each of concentrated sulfuric and phosphoric acids should be used in each 100 cc. of solution. The indicator has been found especially useful in the determination of iron in solutions containing chromium, cobalt, or nickel with standard permanganate; where ordinarily the color of the solution would interfere with the end point, the intense blue color of the diphenylamine prevails.

It has been found that, in general, organic materials do not interfere with titration end points where diphenylamine is used as the indicator.

(e) *Limitations of the indicator:* The oxidation-reduction potential at the color change is so low that in iron determinations the ferrous-ferric potential must be lowered by the addition of fluoride or phosphate to form

a complex. The color of the indicator fades on standing, and the indicator is destroyed by an appreciable excess of oxidant. When the oxidized form of the indicator is used, the indicator correction is negligible, but when the unoxidized form of the indicator is used, it requires a correction in the neighborhood of 0.1 cc. of 0.1 *N* oxidant for each 0.1 cc. of the indicator solution used. Furthermore, it requires different amounts of different oxidants of the same normality to cause the same amount of the indicator to change color. Also, if the titration is not carried out immediately after adding the indicator (within 15 min.), the results will not be accurate. Moreover, there is a reaction between the oxidized and unoxidized forms of the indicator that affects the color at the end point in certain determinations.

The end-point color is not good in the dichromate-iron titration unless the ferric ion is suppressed with phosphoric acid or hydrofluoric acid. The iron-dichromate reaction, using the indicator to denote the end point, is not quantitative in the presence of copper or trivalent arsenic. Copper produces low results unless it is present in quantities less than 1 mg. in 150-200 cc. of the solution being titrated; trivalent arsenic produces high results. Knop (34, 35) found that, in the iron determination with standard dichromate by reduction with stannous chloride and destruction of the excess with mercuric chloride, a small error, equal to about 0.1 per cent of the result, is introduced. He found also that small quantities of platinum affected the results slightly, so care must be exercised where platinum vessels are used in taking the sample into solution. Some investigators find that certain persons have difficulty obtaining accurate results in the potassium dichromate-ferrous ion titrations, as the end point is not as sharp as some writers would lead one to believe.

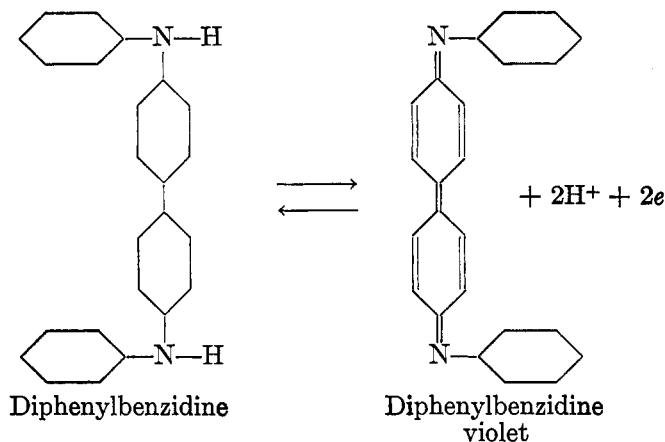
In the hydroquinone-ceric ion titration there is an appreciable blank correction, equivalent to about 0.05 cc. of 0.1 *N* ceric sulfate for each 0.05 cc. of 1 per cent indicator solution used. The indicator is unreliable in the determination of cerium with ferrous sulfate. To secure accuracy in the determination of ferrous iron by ceric ion a suppressing agent must be used, and even then the blank correction is appreciable.

Scott (52) observed that when diphenylamine is used in the permanganate-iron titration to sharpen the end point, more than 0.4 cc. of the indicator affects the results. Sarver (46) found that end points with diphenylamine are often passed without the formation of color. Watson proved that mercuric chloride has a powerful inhibiting effect upon color formation with the indicator.

Diphenylamine cannot be used to detect the end point in determining iron when tungstate ion is present.

2. Diphenylbenzidine (32, 35, 47, 48, 71, 75)

(a) Structure:



(b) *Preparation of the indicator:* To a mixture of 1 liter of concentrated sulfuric acid, 2 liters of glacial acetic acid, and 12 liters of water is added slowly, and with constant stirring, a solution of 50 g. of diphenylamine in 500 cc. of acetic acid. If diphenylamine separates, it may be redissolved by heating not higher than 50°C. To the resulting solution at 15–25°C. is added slowly and with vigorous stirring a solution of 22 g. of potassium dichromate in 500 cc. of water; after 15 min. the excess dichromate is reduced with a solution of 10 g. of sodium bisulfite in water. The colloidal precipitate is collected on a filter with the aid of a filter medium. The greenish black precipitate is placed, while still wet, in a warm concentrated solution of sodium bisulfate; when it turns light brown it is filtered off, washed with hot water, thoroughly dried, pulverized, and extracted with the same solvent. The pure diphenylbenzidine separates on cooling. It is filtered off, washed with alcohol until the washings fail to yield a white cloud upon dilution with water, and dried at 110°C. The yield is 60 to 65 per cent.

(c) *Preparation of the indicator for use:* Method A—A 0.1 per cent solution in concentrated sulfuric acid is prepared. One drop of this solution is mixed with 10 cc. of a mixture of equal parts of glacial acetic acid and sirupy phosphoric acid. The entire amount is used in an iron determination with 0.01 *N* or stronger reagents for good sharp end points.

Method B—A 0.005 *M* solution is prepared by dissolving 1.68 g. of diphenylbenzidine in 1 liter of 9 parts of glacial acetic acid and 1 part of concentrated sulfuric acid. Five or six drops are used when titrating with

0.1 *N* oxidant in 100–200 cc. of volume. When 0.01 *N* or 0.001 *N* solutions are to be titrated, 0.02–0.05 cc. of the solution is used in 10–50 cc. of volume.

Method C (preparation of the partially oxidized form)—0.1 g. of diphenylbenzidine is dissolved in 10 cc. of sulfuric acid (sp. gr. 1.83), and the solution is diluted with 90 cc. of glacial acetic acid. To about 10 cc. of the above solution in a small beaker are added 5 cc. of phosphoric acid (sp. gr. 1.37), three or four drops of 0.1 *N* potassium dichromate, and then very dilute ferrous sulfate solution until a single drop causes the solution to become colorless. Small portions of this solution are used.

(*d*) *Use of the indicator*: In general, the indicator may be used in the same determinations as diphenylamine. According to the theory of oxidation-reduction indicators, diphenylamine is oxidized by the first excess of oxidant to diphenylbenzidine; therefore the oxidation potential at the end point will be the same for both indicators,—namely, 0.73 volt.

As would be expected from the above, the indicator correction with diphenylbenzidine is less than that with diphenylamine. It amounts to about 0.1 cc. of 0.01 *N* oxidant for each 0.1 cc. of diphenylbenzidine prepared by method B, and about twice this quantity when diphenylamine is used. In titrating dichromate or vanadate with ferrous sulfate the correction is about the same. This is not true with diphenylamine.

Diphenylbenzidine can be used in ceric titrations of iron, even in the presence of arsenious acid; however, it is less satisfactory than diphenylamine. Diphenylbenzidine is also applicable to the determination of vanadium by titration with ceric sulfate.

(*e*) *Limitations of the indicator*: Diphenylbenzidine is subject to essentially the same limitations as diphenylamine, since it is the partially oxidized form of diphenylamine. Young and Willard (74, 75) report less success with the partially oxidized form of diphenylbenzidine than with the partially oxidized forms of either diphenylamine or diphenylamine-sulfonic acid. This is to be expected from the theory, as the next step in the oxidation of diphenylbenzidine would produce the color change; this is not true with diphenylamine or diphenylaminesulfonic acid. The same investigators report that when diphenylbenzidine is used in the ceric titration of iron in the presence of arsenious acid a heavy white precipitate is formed, which is not formed with diphenylamine in the same determination.

3. Diphenylaminesulfonic acid (33, 48, 74)

(*a*) *Structure*: The position of the sulfonate radical in this compound has not been established. The formula usually given is $\text{HSO}_3\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5$.

(*b*) *Preparation of the indicator*: 170 g. of diphenylamine is mixed with 95 ml. of acetic anhydride and 10 ml. of concentrated sulfuric acid, and the

mixture is refluxed for 1 hr. The excess acetic acid is removed by washing with cold water. The acetyldiphenylamine is recrystallized from ether and dried at 100°C. Two hundred grams of 20 per cent fuming sulfuric acid is cooled to 5°C. and to this is added 100 g. of pulverized acetyldiphenylamine in small portions with constant stirring. The mixture is then warmed for 2 hr. on a water bath at 45°C. with constant stirring. It is poured into 250 cc. of water and boiled for 3 hr. to hydrolyze the acetyl compound. The mixture is then poured into a large volume of water, and the unchanged diphenylamine is filtered off. The filtrate is neutralized with barium carbonate, and the barium sulfate is filtered off. The white barium diphenylaminesulfonate and the barium acetate are separated by fractional crystallization.

(b) *Preparation of the indicator for use:* Method A—A 0.005 *M* solution of the barium salt of the acid is prepared by dissolving 3.17 g. of the anhydrous salt in water.

Method B—A 0.01 *M* solution of sodium diphenylaminesulfonate is prepared by dissolving 3.2 g. of the barium salt in water, adding sodium sulfate in excess, and decanting from the barium sulfate. One hundred cubic centimeters of this solution and 25 cc. of concentrated sulfuric acid are placed in a volumetric flask and diluted to 900 cc. To this is added 25 cc. of 0.1 *N* potassium dichromate, slowly and with frequent stirring, and then 0.1 *N* ferrous sulfate with repeated shaking until one drop causes a visible color change from bluish green to a clear deep green in the liquid when viewed through the neck of the flask; this requires about 6.5 cc. of ferrous sulfate solution. This solution is used as the indicator, but it settles on standing and requires frequent shaking.

Method C—A mixture of 100 cc. of the 0.01 *M* sodium diphenylamine-sulfonate and 5 cc. of concentrated sulfuric acid is diluted to about 300 cc. To this is added about 25 cc. of 0.1 *M* potassium dichromate, 8 cc. of 0.1 *N* ferrous sulfate, and 5 cc. of concentrated sulfuric acid. The mixture is allowed to stand 3 or 4 days, until the supernatant liquid gives no color when added to 100 cc. of water containing 2 cc. of 0.1 *N* potassium dichromate and 5 cc. of concentrated sulfuric acid. The supernatant liquid is siphoned off slowly, care being taken not to disturb the green precipitate, which is the indicator. After the addition of 300 cc. of water and 15 cc. of concentrated sulfuric acid, the material is allowed to settle again. The siphoning and washing are repeated. More rapid washing can be obtained by means of the centrifuge. The precipitate is then shaken up with 100 cc. of water, in which, in the absence of an electrolyte, it remains in colloidal suspension. For most titrations 0.5 cc. of this solution is sufficient.

Method D—A stock solution is prepared containing 0.2 to 0.5 per cent of either sodium or barium diphenylaminesulfonate in water.

(c) *Use of the indicator:* Diphenylaminesulfonic acid is one of the best of all indicators in the titration of ferrous ion with potassium dichromate, the color change being so brilliant and so sharp that it can be carried out even in brilliantly colored solutions. The indicator may be used in the presence of tungstate ion; this is not true of diphenylamine or diphenylbenzidine. Sarver and Kolthoff (48) also used the indicator in permanganate or vanadate titrations in acid solutions. It can be used also as the reverse indicator, that is, in titrating vanadate or dichromate with ferrous ion. The indicator can be used internally in the titration of zinc with potassium ferrocyanide or the reverse. It can be used in almost every dichromate titration and in many ceric titrations, especially in the ceric titration of iron.

(d) *Limitations of the indicator:* None of the diphenylamine derivatives is very resistant to excess oxidant, as previously stated. However, diphenylaminesulfonic acid resists it better than the other members of the series. The color change is inhibited by mercury salts. The color change in dichromate titrations other than that of iron is somewhat slow; apparently it is catalyzed by ferrous ion. The indicator cannot be used in all ceric titrations. When ferrous ion is titrated with either ceric sulfate or potassium dichromate, the ferrous-ferric potential must be lowered by adding about 10 cc. of 25 per cent phosphoric acid for each 50 cc. of titrating volume.

The indicator correction with this indicator is appreciable. The correction amounts to about 0.1 cc. of 0.01 *N* oxidant or its equivalent for each 0.25 cc. used. In back-titrations with ferrous ion, the correction is somewhat greater. Practice dictates that the indicator correction be determined by running a blank along with the determination.

4. *Monosulfonate of diphenylamine (11)*

(a) *Structure:* The exact structure of this compound is not known. The formula given is $C_6H_5NHC_6H_4SO_3Na$. It is probable that the compound is the sodium salt of an isomer of the diphenylaminesulfonic acid of Kolthoff and Sarver (33).

(b) *Preparation of the indicator:* A mixture of 21 g. of di-*n*-butyl sulfate and 16.9 g. of diphenylamine is heated on a boiling water bath for 1 hr. and then on a metal bath at 130–140°C. for 1 hr. A solution of sodium ethylate (4.8 g. of sodium and 200 cc. of ethanol) is added, and the mixture is refluxed until the tarry reaction mass becomes white. The alcohol is distilled off, the residue is taken up in water, the mixture is filtered, and the filtrate is thoroughly extracted with ether to remove residual diphenylamine. The ether is removed by warming and aeration. Concentrated sodium hydroxide is added cautiously until a faint turbidity appears. The

desired sodium salt precipitates slowly. After 24 hr. the suspension is filtered off, and the salt is sucked as dry as possible. The salt is redissolved in warm ethyl alcohol and precipitated with an excess of ether. Purification is completed by dissolving again in warm alcohol, passing in carbon dioxide until no more sodium carbonate separates, filtering, and concentrating the filtrate to incipient crystallization on the water bath.

(c) *Preparation of the indicator for use:* A 0.1 per cent solution of the sodium diphenylaminesulfonate in water is prepared. Four or five drops of this solution are used in 400 cc. of titrating solution.

(d) *Use of the indicator:* The indicator has been applied to the iron-dichromate titration. The indicator correction is negligible. The color change is from colorless in the reduced form to deep purple in the oxidized form, and the end color lasts about 15 min. Mercury salts do not inhibit the color change. Analyses of iron and chromium ores show it to be reliable.

(e) *Limitations of the indicator:* In the one determination to which the indicator has been applied, the usual sulfuric-phosphoric acid mixture must be used,—25 cc. of the mixed acids in each 400 cc. of titrating solution. This indicator has possibilities, but has not been thoroughly investigated or applied to enough determinations.

5. *Product of the action of ethyl sulfate on acetyldiphenylamine (25, 57)*

(a) *Structure:* The structure is undetermined. The substance is probably the sodium salt of a monosulfonated diphenylamine which, in turn, is probably an isomer of diphenylaminesulfonic acid.

(b) *Preparation of the indicator:* A mixture of 50 g. of acetyldiphenylamine, prepared by the method of Kaufmann (25), and 40 g. of ethyl sulfate is heated on a water bath for 5 hr. The reaction mixture is refluxed with 7 g. of sodium in 200 cc. of ethanol until the original dark-colored mass is converted into a white mass. The alcohol is removed by distillation, and the solid residue is dissolved in water. The solution is extracted thoroughly with ether to remove any diphenylamine. The ether is removed from the water layer by aeration, and the solution is treated with concentrated sodium hydroxide until a permanent turbidity appears. A voluminous precipitate appears within 12 to 24 hr. and may be recrystallized from water.

(c) *Preparation of the indicator for use:* A 2 per cent aqueous solution is used, and three drops per 250 cc. of titrating volume are sufficient for a determination.

(d) *Use of the indicator:* The discoverers of the indicator claim that it can be used wherever diphenylaminesulfonic acid can be used. They state that it is very soluble in water, is unaffected by mercury salts, and is stable

toward excess oxidant, and that the indicator blank is small. The color change, which is from colorless to very red, is very sharp, permanent, and very mobile.

(e) *Limitations of the indicator:* It has been applied only to the titration of ferrous solutions with standard dichromate solution and to the titration of dichromate solutions with standard ferrous sulfate solution.

6. Diphenylbenzidinesulfonic acid (49)

(a) *Structure:* Analysis indicates that when the indicator is prepared as directed, ten sulfonate groups are introduced in most cases. If 25 per cent fuming sulfuric acid is used instead of the specified 60 per cent acid, only four sulfonate groups are introduced. The positions of the groups are unknown and would be difficult to determine.

(b) *Preparation of the indicator:* 1 g. of dry powdered diphenylbenzidine is added, little by little over a period of about 2 min., to 10 cc. of 60 per cent fuming sulfuric acid in a shallow dish. The mixture heats up but should not be allowed to become warmer than 40°C. As complete solution as possible is obtained by stirring and mashing the lumps with a rod; then, after not more than 3 min., the mixture is poured on ice. It is not desirable to work with larger quantities, because the reaction is difficult to control. However, as many portions as desired can be combined at this point. For each gram of diphenylbenzidine used, the solution is diluted to a volume of 200 cc.

The solution is heated to boiling and the green color is reduced with a stream of sulfur dioxide. The excess sulfur dioxide is removed by boiling, and the solution is filtered to remove any tarry matter. The filtrate is carefully neutralized with sodium carbonate, more water being added if any precipitation occurs. Four volumes of ethyl alcohol are added to precipitate the sodium sulfate. After filtration, the filtrate is retained. The residue is redissolved in water and reprecipitated with alcohol as often as necessary to remove the yellow color from the precipitate. The separate filtrates are combined, the volume being about 5 liters for each gram of diphenylbenzidine used. The alcohol is boiled off rapidly; the evaporation is completed on the steam bath, long exposure or overheating of the residue being avoided. The sodium diphenylbenzidinesulfonate should be a light yellow in color. The yield is 4 g. (approximately) for each gram of diphenylbenzidine used.

(c) *Preparation of the indicator for use:* A 0.1 per cent solution of the sodium diphenylbenzidinesulfonate in water is recommended and can be kept for several months. One drop or less is used with 0.01 or 0.001 *N* oxidizing or reducing solutions and 10 drops with 0.1 *N* solutions.

(d) *Use of the indicator:* The article (49) gives no specific determina-

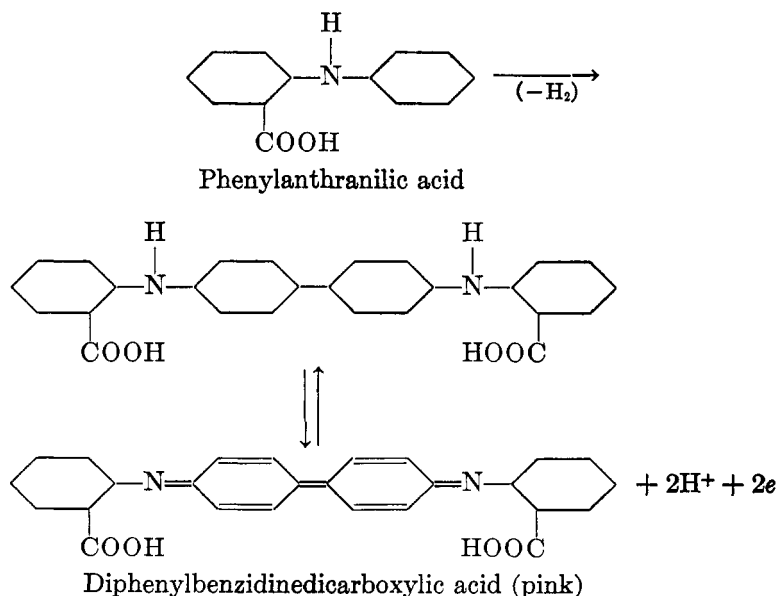
tions in which the indicator has been used, but indicates that it can be used wherever diphenylaminesulfonic acid can be used. Apparently the potential is slightly above that of diphenylaminesulfonic acid at the color change, as substituted sulfonic acid groups in general raise the oxidation potential at the color change. This would make the indicator applicable to titrations of potassium dichromate, potassium permanganate, and ceric sulfate. The color change is pale yellow to deep yellow to violet. The reaction is reversible by reduction.

The indicator is unchanged by contact for 10 min. with an appreciable excess of potassium dichromate. The green half-oxidized form is stable, but the reddish violet form fades after a long time.

(e) *Limitations of the indicator:* The indicator has not been thoroughly enough reported to determine all its limitations. The investigators state that the indicator correction is negligible except in microanalysis. They report, however, that in potassium dichromate determinations back-titration with ferrous sulfate is more reliable than direct titrations. The indicator probably has the limitations of diphenylbenzidine and diphenylamine, modified by greater resistance to excess oxidant and greater resistance to acids, along with increased solubility in water.

7. Phenylanthranilic acid (*o*-diphenylaminocarboxylic acid) (10, 48, 58)

(a) *Structure:*



There is no mention in the literature of specific experiments to establish the above mechanism as that of the color change, but it is established on the basis of Sarver and Kolthoff's theory of indicators which are derivatives of diphenylamine.

(b) *Preparation of the indicator:* A mixture of 10 g. of *o*-chlorobenzoic acid, 10 g. of potassium carbonate, 40 cc. of aniline, and 0.1 g. of precipitated copper is boiled, in a round-bottom flask fitted with a short upright air condenser, at such a rate that a little water may escape from the top of the condenser. The mixture gradually darkens, and the reaction is complete in about 3 hr. The unchanged aniline is removed by steam distillation and the residue is filtered hot. The latter is boiled with animal charcoal and the mixture is filtered. Upon the addition of concentrated hydrochloric acid to the hot filtrate, a nearly colorless precipitate of phenylanthranilic acid is thrown down. This is filtered off when cold, washed with cold water, and dried. The yield is about 13 g. The product may be further purified by recrystallization from acetic acid and alcohol.

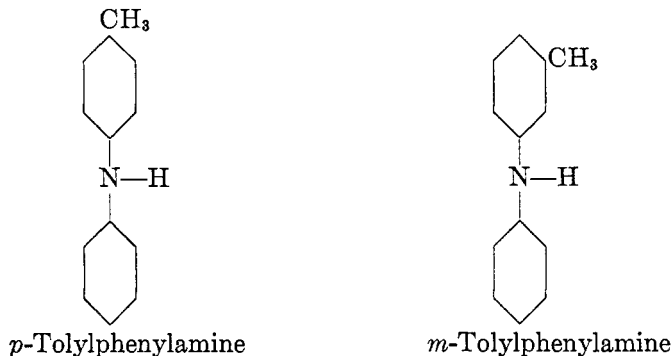
(c) *Preparation of the indicator for use:* A stock solution of the sodium salt (0.005 *M*) is prepared. The sodium salt is prepared by dissolving the acid in an equivalent quantity of sodium carbonate. Three to five drops of this solution are sufficient for most determinations.

(d) *Use of the indicator:* The color change is from colorless in the reduced form to pink in the oxidized form at an oxidation potential of 1.08 volts in sulfuric acid solutions of low acidity. Only one set of investigators has used the indicator, but they report it satisfactory for ceric sulfate and potassium permanganate titrations in sulfuric acid solutions, and fairly satisfactory for dichromate titrations. They reported using it for the determination of iron in ore, of vanadium in titanium-magnetite ore, of vanadium in pig iron and steel, and of vanadium in vanadium slags, using a modified Land and Jurz method and titrating with both ceric sulfate and potassium permanganate. The results were exceedingly accurate.

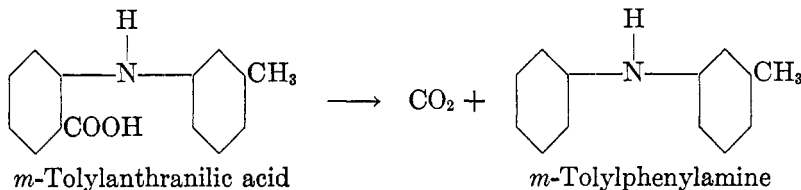
(e) *Limitations of the indicator:* The indicator has been reported completely enough to determine many of its limitations. In titration with potassium dichromate, the solutions must be at least 2 *N* in acid; also, in such titrations the color change is slow but is catalyzed by traces of ferrous iron. The color change does not seem to be any too intense, as pink is a rather pale color.

8. *p*-Tolylphenylamine and *m*-tolylphenylamine (57, 65)

(a) Structure:



(b) *Preparation of the indicator:* The basis for the preparation is the fact that, when phenylanthranilic acid is warmed to a fairly high temperature, it undergoes a decomposition in which the carboxyl group splits off carbon dioxide and the diphenylamine derivative remains. The reaction proceeds in this manner:



Specific details for preparing *m*-tolylphenylamine are as follows: A mixture of 2 g. of *o*-chlorobenzoic acid, 8 g. of *m*-toluidine, 2 g. of potassium carbonate, and about 1 mg. of precipitated copper is boiled for 2 hr. and then cooled. The brown fused mass is boiled with dilute hydrochloric acid and filtered; the filtrate is discarded. The residue is dissolved in alkali, filtered to remove traces of resin, and reprecipitated with hydrochloric acid. This material is *m*-tolylanthranilic acid and may be purified by recrystallization from benzene. The yield thus far is about 65 per cent of the theoretical. To produce the tolylphenylamine, the *m*-tolylanthranilic acid is distilled; this brings about the decomposition previously mentioned. The *m*-tolylphenylamine may be further purified by redistillation or by recrystallization from benzene.

p-Tolylphenylamine is prepared similarly, using *p*-toluidine in place of *m*-toluidine.

(c) *Preparation of the indicators for use:* The indicator solution is a 1 per cent solution in sulfuric acid. About three drops are used per determination.

(d) *Use of the indicators:* The indicators have been applied to dichromate titrations and especially to the determination of iron or chromium. The solutions should contain the usual 20 cc. of the sulfuric acid-phosphoric acid mixture, and 15 cc. of 6 *N* hydrochloric acid in a total volume of 250 cc. One drop of 0.1 *N* dichromate will produce a deep blue coloration that is easily visible and lasts for 10 to 15 min. The indicator reaction is easily reversed, and in the determination of chromium the chromic acid formed can be directly titrated with ferrous sulfate, using either indicator. The indicators may also be used in permanganate titrations.

(e) *Limitations of the indicators:* The indicators have not been reported for titrations other than ferrous ion-dichromate titrations. However, in this reaction the color development is greatly inhibited by the presence of mercury salts. The color also does not develop except in the presence of ferric ion, which leads one to suspect that the color is really due to complex formation.

9. Other indicators of the diphenylamine series (23, 27, 66)

(1) *p-Nitrodiphenylamine:* The indicator solution is a 0.01 *M* solution of the indicator in glacial acetic acid, of which two or three drops are used per determination. The indicator has been applied to ceric sulfate-ferrous sulfate titrations, but it is irreversibly oxidized by an excess of oxidant; therefore back-titrations or the reverse titrations are impossible. Dichromate-ferrous ion titrations are unsatisfactory with the indicator because of the slow development of color. The potential is high at the color change, being 1.03 volts in acid solutions.

(2) *2,4-Diaminodiphenylamine:* The indicator is prepared by the reduction of the dinitro compound with tin and hydrochloric acid. The method of preparing the indicator solution has not been reported, but the indicator is probably dissolved in acetic or sulfuric acid. It has an oxidation potential at the color change of 0.70 volt in 2 *N* sulfuric acid. It has been used satisfactorily in ceric sulfate-ferrous sulfate titrations and in potassium dichromate-ferrous sulfate titrations.

The indicator has also been used satisfactorily in ceric sulfate-titanous chloride titrations, in which the reverse reaction is good. The indicator is stable toward excess oxidant and strong acids.

(3) *Two amino substitution products of diphenylamine:* 2,4-Dinitro-4'-aminodiphenylamine and 2,4-dinitro-4'-methoxydiphenylamine, when reduced with tin and hydrochloric acid, yield products having indicator properties over the same range as diphenylamine and 2,4-diaminodiphenylamine, but possessing no particular advantages over the latter.

(4) *Diphenylaminedicarboxylic acids:* 2,2'-, 2,3'-, and 2,4'-dicarboxylic acid derivatives of diphenylamine are compounds with indicator properties. The introduction of the two carboxyl groups increases the oxidation po-

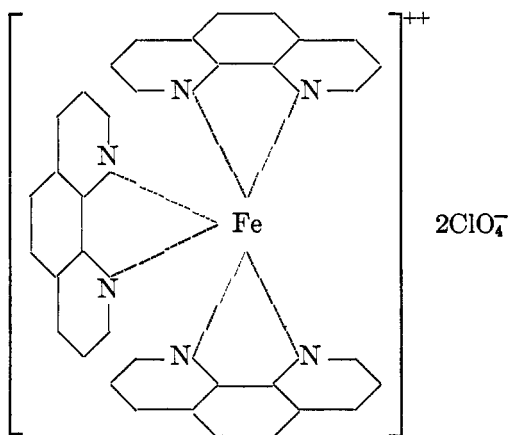
tential at the color change. The three indicators are useful in solutions that are strongly acidic and indicate the end of oxidation-reduction reactions in solutions 16 to 20 *N* in sulfuric acid.

B. COMPLEX COMPOUNDS USED AS INDICATORS

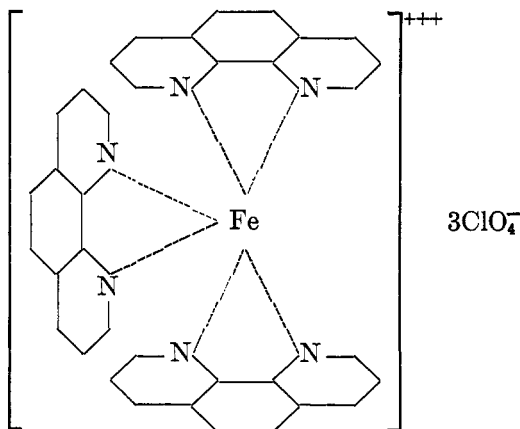
This group includes only two types of compounds,—*o*-phenanthroline ferrous ion, which is used as the sulfate or perchlorate, and nitrophenanthroline ferrous ion, which is used as the sulfate only. *o*-Phenanthroline ferrous ion is the most successful of all the oxidation-reduction indicators that have been thoroughly investigated and reported.

1. The *o*-phenanthroline ferrous complex (5, 32, 38, 53, 55, 66, 67, 69, 71, 72)

(a) Structure:



o-Phenanthroline ferrous perchlorate (red)



o-Phenanthroline ferric perchlorate (blue)

(b) *Preparation of the indicator:* To a freshly prepared mixture of 125 g. of glycerol, 125 g. of 100 per cent sulfuric acid, and 50 g. of arsenic oxide, contained in a 1-liter flask provided with a thermometer, stirrer, and reflux condenser and maintained at a temperature of 115°C., is added all at once 25 g. of *o*-phenylenediamine. The temperature rises about 10°C. The mixture is heated carefully at 140°C. for 2 hr., care being taken to avoid all higher temperatures. The material is poured into water, made strongly alkaline, and allowed to stand for at least 1 day. The tarry product is separated, washed, and dried at 110°C. until hard and brittle. The mass is pulverized and extracted with benzene in a Soxhlet until the residue no longer gives a red color with ferrous sulfate (this requires from 10 to 20 hr.). For the purification of the crude phenanthroline which crystallizes on the evaporation of the benzene, it is dissolved in dilute acid, and alkali is added until a small tarry precipitate appears; the precipitate is discarded, and the base is entirely precipitated by adding excess alkali. The solid may be recrystallized from water (with decolorizing carbon) as the monohydrate.

Smith and Getz (55) have described in detail a process for producing the indicator on a large scale, using vats holding 40 and 50 gallons of solution and employing complicated stirrers and thermostats.

(c) *Preparation of the indicator for use:* Method A (preparation of *o*-phenanthroline ferrous sulfate)—A 0.025 *M* solution of the sulfate is prepared by dissolving the stoichiometric amount of the monohydrate (14.85 g. per liter) in a 0.025 *M* ferrous sulfate solution. One drop is used in 100–150 cc. of volume for each titration.

Method B (preparation of *o*-phenanthroline ferrous perchlorate)—The 0.025 *M* solution of the sulfate is prepared as directed in method A. To a portion of this solution (100 or 1000 cc.) is added dropwise, with vigorous stirring, a dilute solution of perchloric acid until the bright red precipitate which is formed leaves, after settling, an almost colorless supernatant liquid. The colorless liquid is decanted from the precipitate as completely as possible. Centrifuging accelerates the process. The precipitate is washed four or five times with small additions of water, centrifugal separations being used to remove the excess perchloric acid. Finally the precipitate is filtered through a glass filtering crucible or funnel and dried at 80–90°C. A saturated solution of the perchlorate is prepared; it contains about 0.795 g. per liter. In each determination 1 cc. of this solution is used.

Method C (alternative method of preparing *o*-phenanthroline ferrous perchlorate)—0.94 g. of c. p. iron filings in a 300-cc. flask is dissolved by the addition of 10 cc. of 70 per cent perchloric acid that has been diluted with water to 60–75 cc. The flask is fitted with stopper and tubes so that a stream of carbon dioxide can be passed through the solution. The

liquid is heated almost to a boil, carbon dioxide being passed through the solution continuously and water being replaced as it evaporates, until the iron has completely dissolved. The solution is cooled, with the gas stream still passing through it, and is then diluted to 1000 cc. in a 1.5-liter beaker, with filtration if necessary. To 500 cc. of distilled water which has been heated to boiling is added slowly, with constant stirring, 10 g. of *o*-phenanthroline monohydrate. The ferrous perchlorate solution containing excess perchloric acid is cooled to 0°C., and the hot solution of dye base is added to it slowly with constant stirring. The mixture is allowed to cool and the solid to settle out for 30 min. The colorless supernatant liquid is poured through a 30-cc. glass filtering crucible, using reduced pressure. Finally, the red crystalline precipitate is transferred to the crucible and filtered dry. It is washed five or six times with small portions of distilled water and then dried at 80–90°C. For a stock solution, a saturated solution of the ferrous perchlorate of *o*-phenanthroline is prepared by dissolving 0.795 g. of the solid in 1 liter of water. In determinations using 0.01 *N* reagents, 1 cc. of this stock solution is employed.

(d) *Use of the indicator:* The indicator shows a color change from red in the reduced form to blue in the oxidized form at an oxidation potential of 1.20 volts in 1 *M* sulfuric acid. This corresponds to a 90 per cent oxidation of the indicator. The end point is reached with 0.01 per cent excess of oxidant. The color change is vivid and intense, as well as reversible and mobile. The indicator is non-reactive with many commonly occurring anions and cations, and is not inhibited by mercury salts. The oxidized color does not fade on standing. Most investigators report the indicator correction to be negligible, except in microanalysis.

The indicator is used in almost all ceric sulfate titrations and in many dichromate titrations. It can be used in the determination of vanadium and in the determination of vanadium in the presence of iron, chromium, or molybdenum. It is used in the titration of arsenious oxide and of potassium ferrocyanide with ceric sulfate. It may be used as the indicator in the determination of chromium and vanadium in steel by the use of potassium permanganate and perchloric acid. It can be employed when ceric sulfate is used as the titrating agent in the determination of chromium in iron ore and of iron in ferrovandium by using the Walden silver reductor or in the determination of chromium in a chromite. The indicator may be used in the standardization of ceric sulfate by means of sodium oxalate or arsenious oxide, using iodine monochloride as a catalyst. It may be used as the indicator in the ceric sulfate titration of ferrocyanide ion, thallos ion, antimonite ion, uranyl ion, hydrogen peroxide, and sodium nitrate.

In the presence of acetone and sulfuric acid, iodides may be titrated

quantitatively with ceric sulfate to a visible end point, using *o*-phenanthroline ferrous ion as the indicator. In this titration bromides interfere only slightly and chlorides less. Their effect may be almost entirely removed by diluting while keeping the acid concentration constant.

(e) *Limitations of the indicator*: The indicator is limited by its high oxidation potential to reactions producing the potential at the equivalence point. When dichromate is titrated with ferrous sulfate solution the color change requires a little time, and therefore the end point must be approached drop by drop from that direction. In the determination of iodides too little acid leads to high results and is time-consuming, while too much acid leads to low results and a fleeting end point. The indicator is not as suitable in titrations with the ceric nitrate and ceric perchlorate ions, as a momentary preferential oxidation of the indicator takes place and some time is required for the pink color to develop. Some students in the laboratories of the University of Georgia have reported that the indicator correction is not always negligible and is quite considerable in microdeterminations.

2. Nitrophenanthroline ferrous complex (23,55)

(a) *Structure*: Chemical analysis shows that the structure of this complex corresponds to the formula $C_{12}H_7N_3O_2$. The position of the nitro group has not been established.

(b) *Preparation of the indicator*: 1 g. of *o*-phenanthroline is dissolved in 10 cc. of concentrated nitric acid and the solution is added to 25 cc. of 95 per cent sulfuric acid. After 1 hr. at 115–120°C. the product is precipitated by dilution with water and neutralization with sodium hydroxide. It can probably be purified by redissolution in dilute acid, partial neutralization, filtration, and reprecipitation with alkali.

(c) *Preparation of the indicator for use*: The ferrous complex can be formed by direct reaction between the ferrous salt and the dye base. In all probability a 0.025 *M* solution is prepared by dissolving the stoichiometric proportion of the nitrophenanthroline base in 0.025 *M* ferrous sulfate, although specific quantities or concentrations are not mentioned in the reference (23), nor are the quantities to be used in each determination stated.

(d) *Use of the indicator*: There is some confusion in the literature as to just what oxidation potential is necessary to cause the color change. Hammett, Walden, and Edmonds (23) give the potential as 0.11 volt higher than the value for the phenanthroline ferrous complex under the same conditions, which would make it 1.31 volts; Smith and Getz (55) give it as 1.55 to 1.6 volts. The former say that it can be used in ceric sulfate titrations, while the latter do not agree. The color change is from red in the reduced form to greenish blue in the oxidized form, and is reversible.

According to Smith and Getz (55), the indicator is applicable to titrations using ceric perchlorate or nitrate ions, $(\text{Ce}(\text{ClO}_4)_3)^{--}$ or $(\text{Ce}(\text{NO}_3)_6)^{--}$, in the form of the free acids or of their ammonium or potassium salts; with these, arsenite and oxalate may be determined.

(e) *Limitations of the indicator:* Smith and Getz (55) state that the nitrophenanthroline ferrous complex cannot be used in sulfate titrations on account of the high oxidation potential necessary to cause the color change. The greenish blue color of the oxidized form is of low intensity. Immediate additions of ferrous sulfate to oxidized portions of the indicator regenerate the red color instantaneously, but if it is allowed to stand before the addition of the ferrous solution the color is regenerated more slowly. Apparently the ferric complex decomposes into ferric ions and nitrophenanthroline ions; the addition of ferrous ions before this reaction is complete produces the ferrous complex by reaction with the ferric complex, but later additions produce it by the action between the ferrous and the nitrophenanthroline ions.

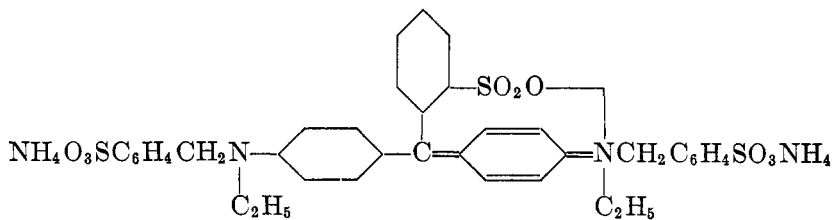
The indicator would be limited mainly by the high potential necessary to cause the color change.

C. COMMERCIAL DYES USED AS OXIDATION-REDUCTION INDICATORS

In this group an attempt has been made to include dyes that are used only under their trade names. In an article of this type it would be impossible to include all such dyes. Readers further interested in this group are referred to an article by Smith and Bliss (54) for dyes usable with bromate and to two articles by Knop (35) on commercial dyes used as indicators. The dyes from these three reports which are given in this group have been selected as the best in the opinion of the original investigator and of later writers.

1. *Erioglaucin A* (4, 19, 32, 34, 35, 36, 51)

(a) *Structure:*



Ammonium 4,4'-bis(ethyl(4-sulfobenzyl)amino)triphenylmethylsulfonate

(b) *Preparation of the indicator:* Erioglaucin A has a number of trade names, of which "Erioglaucin" is the best known. It is a patented product,

but the exact details of its manufacture are secret. However, Schultz (51) makes the following statements concerning its preparation: It is prepared by the condensation of benzaldehyde-*p*-sulfonic acid with ethylbenzylanilinesulfonic acid (perhaps with ethylbenzylaniline and additional sulfonation) to form a leucosulfonic acid, which is oxidized and then converted to the ammonium salt.

Beilstein (4) is only slightly more complete, stating that the dye is prepared by the condensation of benzaldehydesulfonic acid(2) with ethyl-(4-sulfobenzyl)aniline and oxidation of the resulting leuco compound with lead dioxide in hydrochloric acid solution.

This indicator is obtainable through the National Aniline and Chemical Company.

(c) *Preparation of the indicator for use:* A 0.1 per cent aqueous solution of the indicator is used and keeps well. From 0.5 to 1 cc. of the indicator solution is used per determination.

(d) *Use of the indicator:* The indicator has a blue color in water solution, a green color in acid solution, and at an oxidation potential of 0.71 volt is oxidized to a bluish red in acid solutions under 1.5 *N* in sulfuric acid. The indicator change is sharp, intense, and reversible.

The indicator is best applied to permanganate titrations. It is used in the titration of ferrocyanide with permanganate,—a titration having an end point which it is difficult to determine accurately without the indicator. In the standardization of permanganate against Mohr's salt the end point is much more brilliant if Erioglucin A is used. It can be used in either sulfuric or hydrochloric acid solution. The indicator is effective in the determination of iron with permanganate, even in the presence of considerable amounts of nickel and cobalt. No correction is necessary in the iron determination. The use of phosphoric acid can be omitted, as the color change is so brilliant that it is not disturbed by the ferric ion present.

Kolthoff (28, 29) states that the indicator is not very satisfactory in ceric sulfate titrations, while Knop (34, 35) does not agree. The latter says that it is an excellent indicator for the titration of ferrous ion with ceric sulfate or *vice versa*. Furthermore, he states that the indicator works equally well in hydrochloric acid and sulfuric acid solutions, and that in the presence of calomel and of an excess of mercuric chloride the transition is very sharp. A very slight excess of ceric sulfate turns the indicator rose-red in the presence of ferric salts; in the unoxidized form it is orange or pale rose in acid solution.

(e) *Limitations of the indicator:* The indicator cannot be used with dichromate. While it can be used in hydrochloric acid solution, there are other triarylmethane dyes that perform better. The indicator in the oxidized form is rather unstable, especially in the presence of an excess

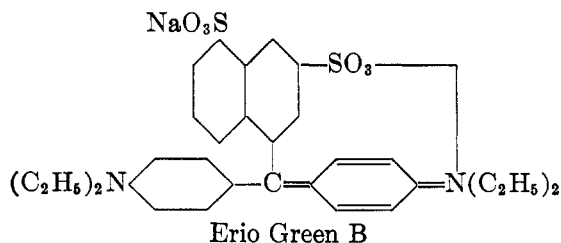
of oxidant; moreover, the color change becomes less pronounced in strongly acid media.

The titration of iron which has been reduced with zinc by means of the indicator and permanganate is not so satisfactory; the titration of iron which has been reduced with stannous chloride is better; the titration of electrolytic cadmium is best of all. The oxygen dissolved from the air interferes in microdeterminations.

In ceric titrations there is a short time interval necessary for the full color change at the end point, but the chance of overtitration is slight. In almost all titrations the end-point color fades slowly, but it lasts sufficiently long for most determinations.

2. Erio Green B (19, 32, 35, 51)

(a) Structure:



(b) *Preparation of the indicator:* This indicator is also a triarylmethane dye that is manufactured by patented processes. Schultz (51) gives three methods of preparation: (1) by the condensation of tetraalkyldiaminobenzhydroxide with naphthalene, chloronaphthalene, or their monosulfonic acid derivatives, followed by sulfonation of the resulting leuco acid and oxidation; (2) by the condensation of tetramethyldiaminobenzhydroxide with naphthalenedisulfonic acid, followed by oxidation; (3) by the condensation of *p*-alkylaminobenzaldehyde with 1 mole of alkylated xenylamine or its sulfonic acid derivative and 1 mole of an aromatic hydrocarbon or its halogen, sulfo, or halogensulfo derivatives.

(c) *Preparation of the indicator for use:* The indicator solution is a 0.1 per cent aqueous solution, of which from 0.5 to 1 cc. is used in each 150–200 cc. of titrating volume.

(d) *Use of the indicator:* The indicator is bluish green in water solution, a yellow color in acid solution, and orange colored when oxidized. The last color change takes place in acid solutions at an oxidation potential of 0.72 volt and is sharp and distinct.

The indicator may be used in the permanganate-ferrocyanide titration where the end point would not ordinarily be sharp. It can be used in the ferrous-permanganate titration to sharpen the end point; when nickel or

cobalt is present, the color change of the indicator prevails over the color of these ions. The color change is not disturbed by the ferric ions formed and the use of phosphoric acid may be omitted. In this titration the end point is determined within one drop of 0.05 *N* potassium permanganate.

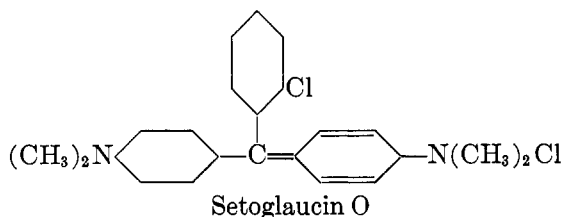
The indicator is applicable to the ceric-ferrous titration or *vice versa*. No blank correction is necessary. A very slight excess of ceric sulfate turns the indicator a rose color, which in the presence of ferric salt becomes orange. The indicator is equally satisfactory in hydrochloric and sulfuric acid solutions, and in the presence of mercury salts.

(e) *Limitations of the indicator:* The indicator cannot be used in dichromate titrations. It is less sensitive in the permanganate-ferrous titration than is Erioglaucin A. As with Erioglaucin A, Erio Green B is rather unstable in the oxidized form, especially in the presence of excess of oxidant; also, the color change becomes less pronounced as the acid concentration increases.

In the ceric titrations the same difficulties are encountered with Erio Green and Erioglaucin.

3. Setoglaucin O (35, 51)

(a) *Structure:*



(b) *Preparation of the indicator:* Setoglaucin O is also a patented dye-stuff. Schultz gives its preparation as follows: The dye is prepared by the condensation of *o*-chlorobenzaldehyde with dimethylaniline and oxidation of the resulting tetramethyldiamino-*o*-chlorotriphenylmethane.

The indicator is sold by the National Aniline and Chemical Company.

(c) *Preparation of the indicator for use:* The stock solution is a 0.1 per cent aqueous solution and 0.5-1 cc. is used per determination in each 150-200 cc. of titrating volume.

(d) *Use of the indicator:* In neutral solutions the dye has a blue color, which becomes yellow in acid solutions. The dye is oxidized to a yellow red in acid solutions at a potential of 0.72 volt. The indicator works in either hydrochloric or sulfuric acid solution; the solution should be about 2 *N* with respect to acid.

Knop (35) reports, "the sensitiveness of the indicator, the convenience

of the color change potential for the iron titration, as well as its resistance to the oxidative action of permanganate, make it ideal for the micropermanganate titration of iron. The error in determining 1 mg. of iron is less than 0.1 per cent (of the result)."

Knop further reports that the indicator is unaffected by the presence of tin and mercury salts, and that it is especially useful in determining iron in the presence of nickel or cobalt, although it produces a color change not greatly different from that of the solution, which is sharp and distinct. The indicator is reported as being used in the standardization of permanganate against oxalic acid or sodium oxalate, without any correction, after the usual preliminary titration.

Knop (35) reports that the indicator is the best of the triarylmethane dye indicators in hydrochloric acid solution.

(e) *Limitations of the indicator:* While accurate results can be obtained with the indicator over wide ranges of hydrochloric acid concentration, best results are obtained when this concentration is low. Unfortunately, very little has been accomplished toward applying the indicator to determinations other than permanganate determinations of iron, but it is possible that it has the same weakness as the other triphenylmethane dyes,—namely, lack of resistance to excess oxidant, inapplicability to dichromate titrations, and poor color change in strongly acid solutions

4. Cyanine B (35, 36, 51)

(a) *Structure:* The structure of the dye has not been established.

(b) *Preparation of the indicator:* Cyanine B is prepared from Patent Blue V.

Schultz (51) gives for the preparation of Patent Blue V the following methods: (1) Reduction of the *m*-nitrotetraethyl-diaminotriphenylmethane resulting from the condensation of *m*-nitrobenzaldehyde with 2 moles of diethylaniline, and the conversion of the amino compound thus formed to the hydroxy compound by diazotization. The last-named product is sulfonated, converted to its calcium, magnesium, or sodium salt, and oxidized.

(2) Condensation of *m*-hydroxybenzaldehyde with diethylaniline and treatment of the resulting hydroxy compound, which is identical with that obtained in method 1, as described above.

Schultz gives the following preparation of Cyanine B from Patent Blue V: "Oxidation of Patent Blue V with chromic acid et cetera, whereby a C_2H_5 group is probably joined on."

(c) *Preparation of the indicator for use:* A 0.1 per cent aqueous solution is prepared, and from 0.5 to 1.0 cc. is used per 150–200 cc. of final titrating volume.

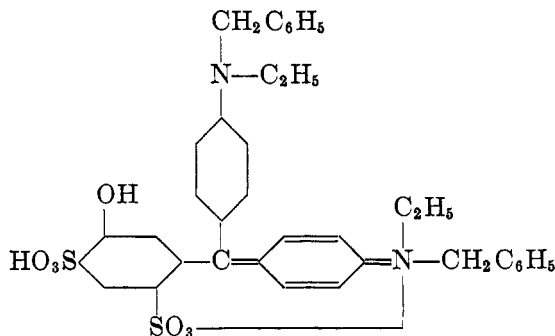
(d) *Use of the indicator:* At an oxidation potential of 0.73 volt in a solution which is 1 *N* in either hydrochloric or sulfuric acid the indicator shows a color change. In sulfuric acid the color change is from yellow in the reduced form to orange in the oxidized form; in hydrochloric acid solution the color change is from yellow to brownish orange. The color change is reversible in both cases to a greenish yellow. The color change is sharp and the end-point color is long lasting.

The indicator has been applied only to sharpening the end point in the permanganate-ferrous titration. It is very satisfactory for this, producing accurate results in either hydrochloric acid or sulfuric acid solution, even in the presence of considerable nickel or cobalt. It is especially good in microdeterminations.

(e) *Limitations of the indicator:* The indicator cannot be applied to dichromate titrations, and is probably not resistant to excess oxidant. It is not satisfactory for use in the presence of zinc. However, tin and mercury salts do not affect the end point or the color development. Care must be taken either to remove dissolved oxygen or to carry out the titration in an atmosphere of carbon dioxide.

5. Patent Blue A (35, 51)

(a) *Structure:*



Patent Blue A

(b) *Preparation of the indicator:* Schultz gives the following information concerning the manufacture of the dye: (1) The *m*-nitro compound resulting from the condensation of *m*-nitrobenzaldehyde with 2 moles of ethylbenzylaniline is reduced, and the amino compound thus formed is converted to the hydroxy compound by diazotization. The product is sulfonated, converted to the calcium compound, and oxidized.

(2) *m*-Hydroxybenzaldehyde is condensed with ethylbenzylaniline and

the resulting hydroxy compound (which is identical with that described in method 1) is worked up by the procedure described in method 1.

This dye is available through the National Aniline and Chemical Company.

(c) *Preparation of the indicator for use:* A 0.1 per cent aqueous solution is prepared, and from 0.5 to 1.0 cc. is used per determination in 150-200 cc. of final volume.

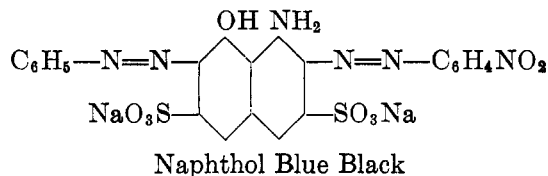
(d) *Use of the indicator:* At an oxidation potential of 0.71 volt in a solution which is 1 *N* in either hydrochloric or sulfuric acid the indicator shows a change from a greenish yellow color in the reduced form to a rose color in the oxidized form. The color change is very sharp and easily reversed.

The indicator has been applied only to sharpening the end point in titrations of iron with permanganate. It is very satisfactory for this, producing accurate results in both hydrochloric acid and sulfuric acid solutions.

(e) *Limitations of the indicator:* The indicator cannot be applied to dichromate titrations; hence one may conclude that it is not resistant to an excess of oxidant. In fact, Knop (35) states that the end color fades rapidly, so that the first alteration of color indicates the equivalence point.

6. Naphthol Blue Black (13, 51, 54)

(a) *Structure:*



(b) *Preparation of the indicator:* Schultz (51) gives the following information regarding its preparation: 13.8 kg. of *p*-nitroaniline is diazotized and the product is combined with 32 kg. of H acid (1-amino-8-naphthol-3,6-disulfonic acid) in acid solution. The solution is made faintly alkaline with soda and into it is led the solution resulting from the reaction between 9.3 kg. of aniline and diazobenzyl chloride. The precipitated dye is filtered off and dried.

(c) *Preparation of the indicator for use:* 0.2 cc. of a 0.2 per cent water solution is used to each 100 cc. of titrating solution.

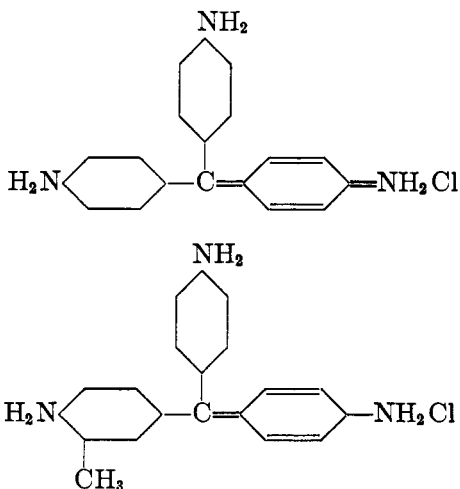
(d) *Use of the indicator:* Smith and Bliss (54) report the dye as being quite satisfactory in bromate determinations under ordinary conditions. This must mean that fairly weak acidities and room temperature are necessary. The color change is from bright blue to colorless and is very

sharp. As the indicator can be used with bromate, it is applicable to the determination of many metals by means of 8-hydroxyquinoline.

(e) *Limitations of the indicator:* The indicator is irreversibly oxidized by an excess of oxidant. It is not satisfactory in strongly acidic media.

7. Fuchsin (7, 51, 54)

(a) *Structure:* The commercial dye is a mixture of the two chemical compounds below.

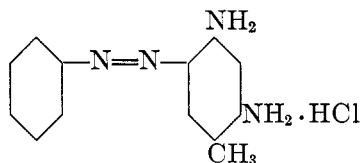


(b) *Preparation of the indicator:* Schultz (51) gives the following methods of preparing the dye: (1) A mixture of aniline, *o*- and *p*-toluidines, and their hydrochloride salts is heated with nitrobenzene or nitrobenzene and nitrotoluene in the presence of iron and zinc chloride. (2) A mixture of aniline, *o*-toluidine, and *p*-toluidine is heated with arsenic acid.

(c) *Preparation of the indicator for use:* A stock solution is prepared by dissolving 2 g. in 1 liter of water, and 0.2 cc. of this solution is used for each 100 cc. of final volume.

(d) *Use of the indicator:* The indicator is recommended for the determinations using bromate as the titrating agent at low temperature. The color change is from a reddish yellow to a lavender. Using the indicator, the investigators were able to determine 100 mg. of arsenic or antimony with an error of only 0.2 per cent; mercuric salts were used to guide the reaction.

(e) *Limitations of the indicator:* The indicator is oxidized from the lavender color to colorless by an excess of reagent and the reaction is irreversible. It is not applicable to high temperatures or to titrations in strongly acid solutions.

8. *Chrysoidine R* (13, 32, 51, 54)(a) *Structure:*

Chrysoidine R

(b) *Preparation of the indicator:* 20 g. of aniline is dissolved in a solution of 63 g. of hydrochloric acid in 1.5 liters of water. This is cooled with 500 g. of ice and diazotized with a solution of 14.8 g. of sodium nitrite (100 per cent) in 1 liter of water. To this solution is added slowly a solution of 26 g. of 4-*m*-tolylenediamine in 250 cc. of 10 per cent hydrochloric acid. The liquor turns faintly reddish orange but scarcely any dye separates. After stirring for 15 min., a dilute solution of sodium acetate (about 1 *N*) is run in slowly; this causes a much richer color to develop. Not too much acetate solution should be allowed to run in, only enough to bind the excess acid; addition of the acetate should be stopped while the solution is still weakly acidic with mineral acid. The reaction mixture is stirred for at least 1 to 2 hr. and as much longer as it takes for the diazo compound to disappear. The liquid is heated to boiling and filtered; 250 g. of solid common salt is added and the liquid is again heated to boiling until the jelly-like precipitate first formed changes to a crystalline one. The solid dye is filtered off by suction and dried.

(c) *Preparation of the indicator for use:* A 0.2 per cent aqueous solution is prepared. Two or three drops of this are sufficient in a volume of 100 cc.

(d) *Use of the indicator:* The indicator is useful in bromate titrations where a color change from reddish yellow to colorless is desired. Kolthoff and Sandell (32) give it as a preferred indicator in bromate titrations. Smith and Bliss (54) report that the color is bleached by reducing agent, is restored at the end point, and is then destroyed by an excess of oxidant.

(e) *Limitations of the indicator:* The indicator is destroyed by excess oxidant and has not been applied to titrations other than the bromate titration.

9. *Brilliant Ponceau 5R and Bordeaux* (13, 32, 54)

(b) *Preparation of the indicators:* The preparation of the indicators is not given by Schultz, but can probably be found in reference 13. Both dyes can be obtained from most dye manufacturers.

(c) *Preparation of the indicators for use:* A 0.2 per cent aqueous solution is used as the indicator solution.

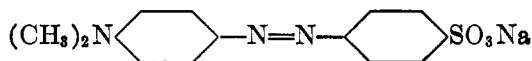
(d) *Use of the indicators:* Both are applicable to bromate titrations. Brilliant Ponceau 5R is recommended by Smith and Bliss (54) as being very advantageous because it resists fading and reacts moderately rapidly at room temperature and low acidities, and the color change is accelerated by increased temperatures and acidities. The best conditions are a normality of about 1.0 with respect to hydrogen ion and a temperature of 50–60°C. With Ponceau the color change is from scarlet red to colorless.

Kolthoff and Sandell (34) prefer Bordeaux in bromate titrations. Smith and Bliss discuss the dye, saying that the color change is from red to colorless and that the dye is suitable at moderate pH and low temperatures.

(e) *Limitations of the indicators:* Both indicators are irreversibly oxidized by an excess of oxidant.

10. Methyl orange (10, 32, 44, 63, 73)

(a) *Structure:*



Methyl orange

(b) *Preparation of the indicator:* 10 g. of sulfanilic acid is dissolved in a solution of 2.5 g. of anhydrous sodium carbonate in 100 cc. of water. A solution of 3.5 g. of sodium nitrite in 20 cc. of water is then slowly added. The mixture is cooled in ice, a solution of 6 cc. of concentrated hydrochloric acid in 20 cc. of water is poured into it, and the liquid is made alkaline with caustic soda. The separation of methyl orange begins at once and is assisted by the addition of about 20 g. of common salt. The precipitate is filtered by suction and recrystallized from hot water. The yield is almost theoretical.

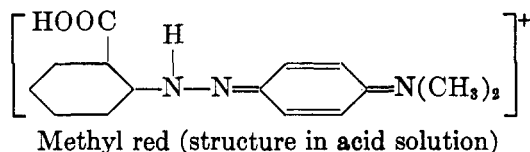
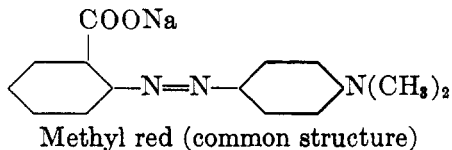
(c) *Preparation of the indicator for use:* A 1 per cent aqueous solution is prepared, and one or two drops of this are used per determination.

(d) *Use of the indicator:* The indicator is best applied to bromate titrations. It is irreversibly oxidized in such cases, however. It is the indicator commonly used in the determination of arsenite and antimonite by means of bromate. Methyl orange may be satisfactorily used as the indicator in the determination of trivalent antimony with ceric sulfate, whereby it is irreversibly oxidized.

(e) *Limitations of the indicator:* The main fault of the indicator is that it is not sufficiently stable toward an excess of oxidant to be used with the stronger oxidants. Even with bromate it is irreversibly oxidized. The color change with methyl orange is not good and is hindered by high concentrations of acids.

11. Methyl red (14, 19, 20, 31, 32, 44, 45, 70, 76)

(a) Structure:



The structure of the violet-colored compound has not been determined.

(b) *Preparation of the indicator:* Method A—20 g. of anthranilic acid is dissolved in 50 cc. of 2 *N* sodium hydroxide and a solution of 8 g. of sodium nitrite in 100 cc. of water is added. The mixture is cooled in ice and poured into 50 cc. of 2 *N* hydrochloric acid. The solution so obtained is mixed with a prepared solution of 12 g. of dimethylaniline in 100 cc. of 1 *N* hydrochloric acid. The mixture is made distinctly alkaline with sodium hydroxide. The sodium salt separates shortly and is filtered by suction. If desired, it can be recrystallized from water.

Method B—12 g. of dimethylaniline is dissolved in a suspension of 20 g. of anthranilic acid in 100 cc. of water, the mixture is cooled in ice, the sodium nitrite mixture described in method A is added, and the dye is precipitated.

Conant (14) describes in detail a method of making the dye base in large quantities.

(c) *Preparation of the indicator for use:* 0.2 g. of methyl red is dissolved in 100 cc. of 1.2 *N* sulfuric acid. Two drops of this solution are used in most titrations. In bromate titrations a 1 per cent aqueous solution is used.

(d) *Use of the indicator:* The indicator may be used in certain ceric sulfate titrations. In the titration of ceric sulfate with ferrous sulfate, the color change is from yellowish to violet. The indicator may be used in the titration of a fluoride ion solution with thallium salts, using a modified Willard and Winter (70) method. Methyl red can be used as the indicator in the titration of trivalent antimony with ceric sulfate, and in determining hydroquinone by using ceric sulfate as the titrating agent. In the ferrous sulfate-ceric sulfate titration the indicator is satisfactory in both sulfuric and hydrochloric acid solutions and the color change is more rapid than

that of diphenylamine. It is not affected by the presence of mercury or tin salts. The color change is reversible.

The indicator may be used in bromate titrations, but it is irreversibly oxidized by the reagent. However, in spite of this it is quite satisfactory if the temperature is kept at about 40–50°C. and the acid concentration between 0.7 and 1.0 *N* with hydrochloric acid. It is sensitive to 2 or 3×10^{-5} *N* bromate.

(e) *Limitations of the indicator:* The indicator is not stable to excess oxidant, as bromate, permanganate, and chlorine all oxidize it beyond the reversing point. It is not as satisfactory in the ceric sulfate–hydroquinone titration as is diphenylamine. There is a slight indicator correction in its use. Apparently there are two separate color changes, one from deep orange to violet in ferrous–ceric titrations and the other from orange to yellow in the ceric–hydroquinone titration.

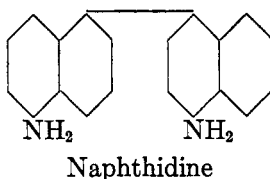
D. MISCELLANEOUS COMPOUNDS USED AS OXIDATION–REDUCTION INDICATORS

In this group are included all reported indicators that did not fall in either of the other three groups. It does not include any very widely used indicators but does include some that show promise.

The indigophenols and their substitution products are not given, since their oxidation potentials at the color change are too low to be of value at present in analytical work. Readers who are investigating indicators that change color at low potentials are referred to the work of Clark and his coworkers (8, 9) and the work of L. Michaelis (40).

1. Naphthidine (12, 16, 57)

(a) *Structure:*



(b) *Preparation of the indicator:* The first workers with the compound used the method of Cumming and Steel (16), which is method 1 below, but later workers prepared it by method 2, which is the preferred method.

Method 1—20 g. of α -nitronaphthalene, 175 cc. of 90 per cent alcohol, 50 cc. of water, and 40 g. of ammonium chloride are heated together at 70°C. on the water bath; the nitronaphthalene goes into solution, but some of the ammonium chloride remains undissolved. To this is added

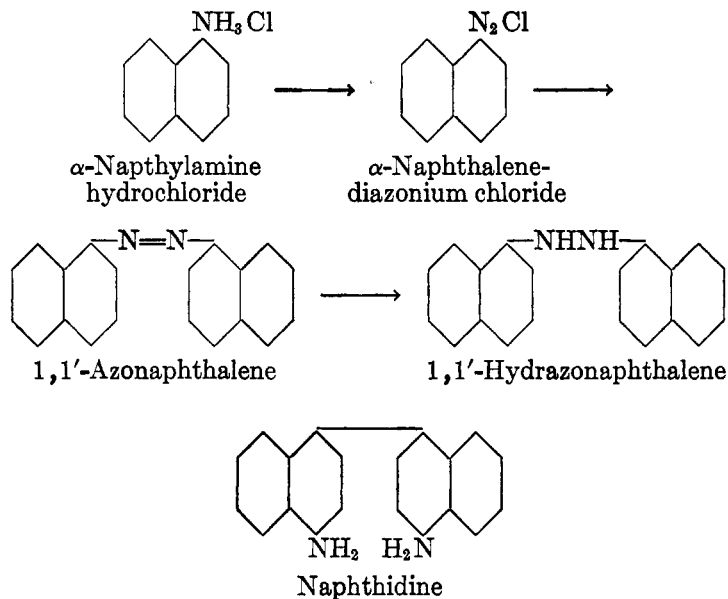
28 g. of zinc dust at such a rate that the temperature remains at 70–75°C. The hot solution, which gradually changes from red to yellow, is filtered, the residue is extracted with 90 per cent alcohol, and the combined filtrate and extract are cooled. The crystalline precipitate is removed, and a further deposit is obtained by concentrating the filtrate under reduced pressure. The α -azoxynaphthalene is purified by washing with warm water and 90 per cent alcohol. It is then dissolved in glacial acetic acid and reduced with stannous chloride in hydrochloric acid. Reduction takes place easily. Concentrated hydrochloric acid is added and the product is dissolved in water. Treatment with sodium hydroxide causes the dye to crystallize. It may be recrystallized from alcohol in white silvery plates.

Method 2—35 g. of α -naphthylamine hydrochloride is stirred into 500 cc. of water, 17.5 cc. of concentrated hydrochloric acid is added, the mechanical stirrer is started, and the solution is cooled on the ice bath to 0°C. Cold dilute sulfuric acid (21 cc. of acid of sp. gr. 1.84 plus 200 cc. of water) is then stirred in. The suspended amine salt is diazotized by slowly adding a cold solution of 14 g. of sodium nitrite in 80–100 cc. of water. The reddish brown mixture is allowed to stand for 5 min. in an ice bath, and filtered by suction, the filtrate being received in a precooled flask surrounded by an ice bath. The cold filtrate is transferred to a 2-liter beaker (ice bath), the stirrer is started, and a cold solution of 66 g. of sodium acetate (anhydrous) in 300 cc. of water is slowly added, the temperature being kept between 0° and 5°C. A cooled solution of 31 g. of sodium sulfite in 200 cc. of water is then run in slowly; a vigorous evolution of nitrogen ensues, and 1,1'-azonaphthalene begins to separate. After the addition of sodium sulfite, the stirring is continued for 5 min. The suspension is then taken out of the ice bath and warmed on the water bath. The tan or orange precipitate is filtered off and dried on a porous plate.

Twenty grams of the crude moist filter cake of 1,1'-azonaphthalene is suspended in 200 cc. of ethanol, and the mixture is brought to a weak boil. A solution of 40 g. of stannous chloride in 100 cc. of concentrated hydrochloric acid is slowly run in, with occasional stirring, until the suspended solid has turned light tan. The heating is immediately discontinued, the suspension is cooled to room temperature, and 100 cc. of concentrated hydrochloric acid is added to precipitate the rest of the naphthidine hydrochloride. Under no conditions must the solution be heated with the acid, since the dinaphthylene (or 1,1'-diamino-2,2'-dinaphthyl) present in the solution, when heated with hydrochloric acid, loses ammonia, forming dinaphthocarbazole, which precipitates with the naphthidine hydrochloride and greatly impedes its purification.

The naphthidine hydrochloride is removed from the suspension, sucked as dry as possible, and suspended in 200 cc. of water; 20 per cent sodium hydroxide solution is then added in slight excess. The mixture is kept warm for 10 min. at 40°C. with frequent stirring. The crude naphthidine is filtered, washed with water until free of alkali, and sucked as dry as possible. The crude base is boiled with 120 cc. of ethanol, and pyridine (40-45 cc.) is slowly run into the boiling suspension until the solid has dissolved. The solution is filtered hot. The filtrate is allowed to cool slowly; the naphthidine separates in well-formed crystals.

The equations for the synthesis given under method 2 are as follows:



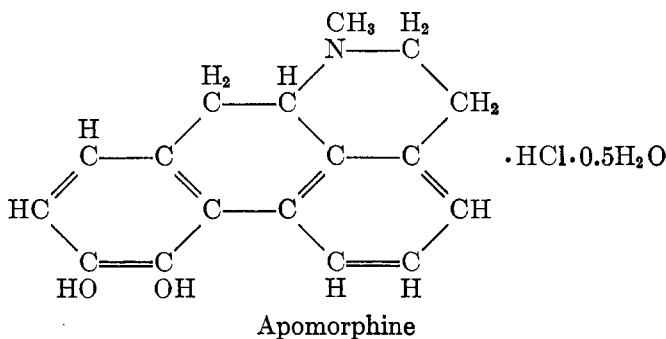
(c) *Preparation of the indicator:* The stock solution is a 1 per cent solution of the indicator in sulfuric acid. Three drops of this solution per 250 cc. give the color change.

(d) *Use of the indicator:* The indicator has been applied to the ferrous-dichromate titration only and works excellently for either direction. It gives a deep red with a slight excess of dichromate, and the color is sharply discharged by ferrous ion. Mercury salts do not interfere in the least. The deep red color is in sharp contrast to the green color of chromium salts, much more so than the blue color of most of the diphenylamine derivatives.

(e) *Limitations of the indicator:* The indicator has not been applied to titrations other than that of ferrous-dichromate. The color at the end point lasts only for 1.5 to 2 min. and then fades; this would make it of little value in permanganate titrations, as permanganate alone does this.

2. Apomorphine (39, 42, 62)

(a) *Structure:*

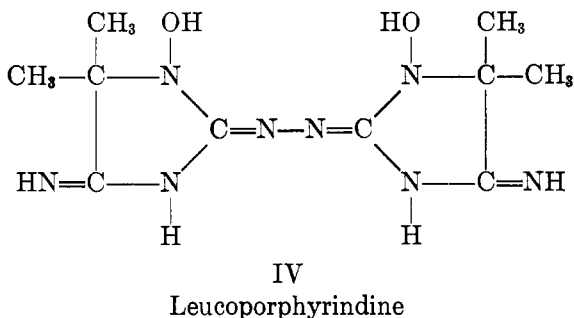
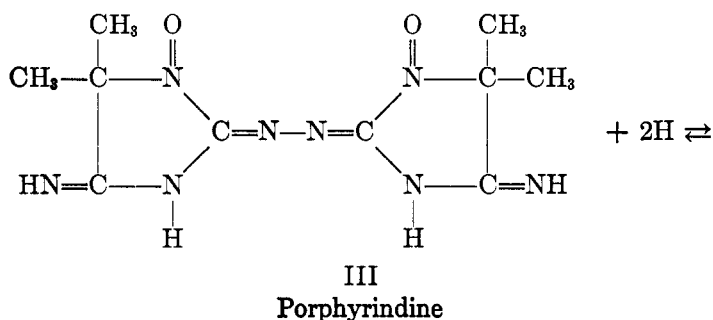
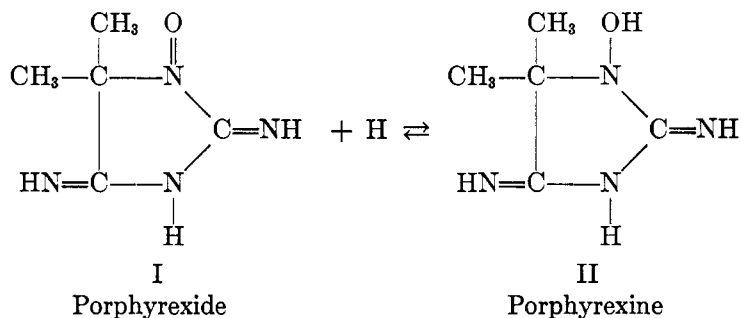


(b) *Preparation of apomorphine:* Apomorphine hydrochloride is obtained from morphine by heating it with hydrochloric acid in sealed tubes.

(c) *Preparation of the indicator for use:* A 0.1 per cent aqueous solution of apomorphine hydrochloride is used for the indicator solution; 0.3 cc. of this is used per determination.

(d) *Use of the indicator:* The indicator is used for the determination of antimony with potassium bromate. Small quantities of the indicator in hydrochloric acid solution are colored rose by free bromine, and the solution is decolorized when potassium antimonyl tartrate is added. The reaction is reversible. The same color change is produced by an antimonite with the indicator and potassium bromate. The results agree with potentiometric titrations.

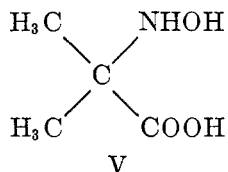
(e) *Limitations of the indicator:* The indicator can be used only with potassium bromate. *Merck's Index* (39) reports the compound as being very unstable to even moderate oxidation. It cannot be used in strong acid solutions, and the temperature must be kept between 45° and 50°C. for accurate results. Near the end point of the titration 10-20 sec. must elapse between the addition of each drop of standard solution to see if the color develops. Too much apomorphine disturbs the sharpness of the end point.

3. *Porphyrexide-porphyrexine and porphyrindine-leucoporphyrindine*(a) *Structures of the two indicators and their indicator reactions:*

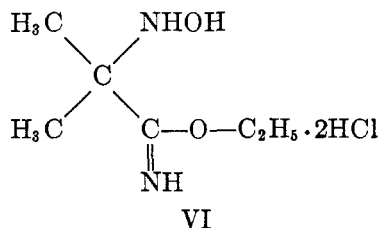
Compounds I and III are very unusual in that they have a nitrogen atom with four valence bonds in an organic compound. These equations are given by both sets of investigators. Undoubtedly I and III are theoretical compounds that cannot be isolated, but are the most likely modifications of compounds II and IV that differ from the latter only by the hydrogen ions that are present in the solutions.

(b) *Preparation of porphyrexide and of porphyrindine:* A mixture of 180 g.

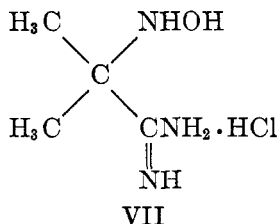
of acetoxime, 150 g. of 70–80 per cent hydrocyanic acid, and 30 g. of water is stirred for 2 days at 4°C. The temperature is raised to 15°C. and the stirring is continued for 2 more days. The product formed is α -hydroxylaminoisobutyric acid and, according to Kuhn and Franke (37), has the following structural formula:



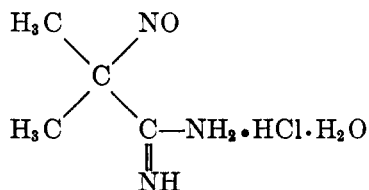
The next product in the synthesis is given by Kuhn and Franke as prepared by the method of Piloty (one of these references was not available). Piloty's directions for the preparation of the hydrochloride (VI) are as follows: The α -hydroxylaminoisobutyric acid is crystallized from ether. About 5 g. of it is suspended in 50 g. of absolute alcohol, and, while stirring and keeping the temperature at 0°C., well-dried hydrogen chloride is led in until the solution is saturated. The hydrochloride (VI) is formed on standing, the yield being almost theoretical. Evaporation is carried out *in vacuo*.



Ten grams of the above salt is dissolved in 50 cc. of absolute alcohol and 28.5 cc. of 4 *N* alcoholic ammonia (2.5 moles) is added. This requires about 4 hr. with constant shaking at 15–20°C. The ammonium chloride formed is filtered off by suction and the alcoholic filtrate is evaporated *in vacuo*. The product so formed, according to Kuhn and Franke, has the following structure:



Seven grams of the hydroxylamino amide is dissolved in 40 cc. of water containing 1 cc. of concentrated hydrochloric acid. Chlorine gas is led in slowly (about two bubbles per second) until the white nitroso material deposited on the bottom fails to increase; on the top of the supernatant chlorine solution a violet colored oil is noticed. The product formed is α -nitrosoisobutyric-amido hydrochloride and has the following structural formula:



VIII

The condensation of compound VIII with potassium cyanide takes place between very narrow temperature limits. Over a period of 2 min. 2.0 g. of α -nitrosoisobutyric-amido hydrochloride is added in small portions to a solution of 1.00 g. of potassium cyanide in 3.5 cc. of water, at a temperature of 55–60°C. The mixture is kept at this temperature for 1 more min., with constant stirring, and then cooled immediately with ice water. The crystals can be separated from the mother liquor on a porous plate or the whole can be brought to dryness over phosphorus pentoxide in a vacuum. In the latter case the mass is extracted with alcohol, thus leaving the potassium chloride on the filter. On evaporation of the alcohol, the porphyrexide separates as fine white needles.

The leucoporphyrindine can be prepared from the porphyrexide by treatment with hydrazine, using 0.5 mole of hydrazine for each mole of porphyrexide (for details see Piloty and Vogel (43)).

(c) *Preparation of the indicators for use:* The method of preparation has not been determined. The indicators are soluble in alcohol and probably in mineral acids.

(d) *Use of the indicators:* The porphyrexide–porphyrexine system shows a color shift from the red in the reduced form to colorless in the oxidized form at a potential of 0.97 volt at pH 7 and 1.34 volts at pH 0.

The porphyrindine–leucoporphyrindine system shows a color shift from blue in the reduced form to colorless in the oxidized form at an oxidation potential of 0.81 volt at pH 7 and 1.2 volts at pH 0.

The indicators have not as yet been applied to titrations.

(e) *Limitations of the indicators:* The limitations are unknown, but it is probable that the indicators are unstable toward an excess of oxidant.

4. *Some inorganic indicators (59, 60, 61, 63, 64)*

(1) *Sodium bromoaurate and sodium bromoaurite.* Sodium bromoaurite (NaAuBr_2) gives a colorless aqueous solution, but sodium bromoaurate (NaAuBr_4) dissolves in water with a deep yellow color. Either compound is suitable as an indicator in the determination of arsenites with ceric sulfate; they give sharp end points and can successfully replace iodine monochloride.

The yellow compound is easily reduced to the colorless one and free bromine oxidizes the colorless one to the colored. Either can be used as the indicator in the determination of antimony with bromate. The results are good.

(2) *Manganese salts.* Manganese salts may be used as catalyzers and indicators in the oxidation of oxalates with ceric sulfate.

(3) *Phosphomolybdic acid.* Hydrazine sulfate solutions react with phosphomolybdic acid to give a deep blue reduction product of molybdic acid. The addition of oxidizing agent causes the disappearance of the blue color as a result of the oxidation of the molybdenum to the hexavalent state; this reaction is reversible. The compound may therefore be used as an indicator in the titration of hydrazine salts with potassium bromate. The solution to be titrated may contain the equivalent of 10–30 cc. of 0.1 *N* hydrazine salt. It is diluted with water to about 40 cc.; 0.3 g. of powdered sodium molybdate and 10 cc. of 25 per cent phosphoric acid are then added. The solution is heated to 60–80°C. and titrated with standard potassium bromate solution until the solution becomes colorless within 30–40 sec. after the addition of the last drop. Potentiometric titrations which have been performed show the results to be reliable.

(4) *Osmic acid.* A solution of arsenite in dilute sulfuric acid gives a deep blue-black color when treated with a little osmic acid. The color is believed to be caused by colloidal osmium. The solution becomes colorless on the addition of potassium bromate. The procedure is to make the solution slightly acid with sulfuric acid, to add 0.25 g. of potassium bromide and 2 cc. of 0.25 per cent osmic acid, and to titrate with standard bromate. In the above determination the total volume should be increased if the amount of arsenic is large.

(5) *Selenium.* Potassium bromate titrations of arsenious arsenic require no indicator in bright sunlight. Methyl orange is ordinarily used. However, selenious acid may be used as follows: 5 g. of sodium bromide is added to the arsenite solution, the solution is diluted to 35 cc., 25 cc. of concentrated hydrochloric acid is added, the solution is heated to 55–60°C., 1 cc. of 1 *M* selenious acid is added, and the titration is performed. When the selenious acid is added, dark red colloidal selenium is formed

TABLE 1

Compounds reported as unsatisfactory for use as oxidation-reduction indicators

NO.	COMPOUND	COMMENT
1a. Substitution products of diphenylamine		
1	<i>p</i> -Acetylamino-diphenylamine	Is not stable enough against excess oxidant to warrant its use
2	<i>p</i> -Amino-diphenylamine	Is easily destroyed by excess oxidant
3	2,4,6-Triaminodiphenylamine	Has no indicator properties
4	2,4,6,3'-Tetraaminodiphenylamine	Has no indicator properties
5	2,4,2',4'-Tetrabromodiphenylamine	Has no colored oxidation products
6	2,4-Dichlorodiphenylamine	Has no colored oxidation products
7	2,4,2',4'-Tetrachlorodiphenylamine	Has no colored oxidation products
8	2,4,6,2',4',6'-Hexachlorodiphenylamine	Has no colored oxidation products
9	<i>m</i> -Nitrodiphenylamine	Has no colored oxidation products
10	2,4-Dinitrodiphenylamine	Requires too high an oxidation potential for ceric ion, permanganate ion, or sodium bismuthate to cause a visible color change
11	2,4-Dinitro-4'-aminodiphenylamine	Requires too high an oxidation potential for ceric ion, permanganate ion, or sodium bismuthate to cause a visible color change
12	2,4-Dinitro-4'-methoxydiphenylamine	Requires too high an oxidation potential for ceric ion, permanganate ion, or sodium bismuthate to cause a visible color change
13	2,4,6-Trinitrodiphenylamine	Requires too high an oxidation potential for ceric ion, permanganate ion, or sodium bismuthate to cause a visible color change
14	2,4,6,3'-Tetranitrodiphenylamine	Requires too high an oxidation potential for ceric ion, permanganate ion, or sodium bismuthate to cause a visible color change
15	Sodium methyl-diphenylaminesulfonate	Produces a long range of intermediate colors preceding the development of the full red, and the establishment of an end point is obscured
16	Sodium ethyl-diphenylaminesulfonate	Produces a long range of intermediate colors preceding the development of the full red, and the establishment of an exact end point is thereby obscured
1b. Substitution products of diphenylbenzidine		
17	2,4-Diaminodiphenylbenzidine	Is too easily destroyed by an excess of oxidant

TABLE 1—*Continued*

NO.	COMPOUND	COMMENT
1b. Substitution products of diphenylbenzidine— <i>Concluded</i>		
18	<i>N,N</i> -Dimethyl- <i>N,N'</i> -diphenylbenzidine	Although it gives a colored oxidation product, is of too little merit to warrant its use
19	2,4-Dinitrodiphenylbenzidine	Requires too high an oxidation potential for ceric ion, permanganate ion, or sodium bismuthate to cause a visible color change
2. Complex compounds		
20	Cadmium complex of phenanthroline	Has no color in either the oxidized or the reduced state
21	Chromium complex of phenanthroline	Has a low color intensity and the color contrast is not great at the end point
22	Cobalt complex of phenanthroline	Has no color in either the oxidized or the reduced state
23	Copper complex of phenanthroline	Has no color in either the oxidized or the reduced state
24	Ferrous dipyridyl complex	Reacts too rapidly with acids, and its potential is not different from that of the ferrous phenanthroline complex
25	Nickel complex of phenanthroline	Has no color in the oxidized or the reduced state
26	Zinc complex of phenanthroline	Has no color in the oxidized or the reduced state
3. Commercial dyes		
27	Acid Green GV	Is strongly oxidized by an oxidant and the end-point color fades rapidly
28	Acid Violet 5B	Has an irreversible indicator reaction and is unstable toward an oxidant
29	Acid Violet 6 BN	Is rapidly oxidized by an oxidant and the indicator reaction is not reversible
30	Acid Violet 7B	Is rapidly attacked by an oxidant and the indicator reaction is only weakly reversible
31	Fast Acid Blue B	Is strongly attacked by an oxidant and gives a color change too soon
32	Fast Green Extra	Is partially oxidized as the oxidant is added, and the end color fades rapidly

TABLE 1—*Concluded*

NO.	COMPOUND	COMMENT
3. Commercial dyes— <i>Concluded</i>		
33	Methyl Violet B	Is strongly attacked as an oxidant is added; the color vanishes quickly and is not reversible
34	Turkish Blue BB	Is not very resistant to an oxidant and the end color fades rapidly
35	Victoria Blue B	Produces a fleeting end-point color and is strongly attacked as an oxidant is added
36	Victoria Blue 4R	Is very strongly attacked as an oxidant is added
37	Wool Green S	Produces an end color that fades too rapidly
4. Miscellaneous compounds		
38	Benzidine	Gives too many colors on oxidation to establish an end point
39	<i>N,N'</i> -Dimethylbenzidine	Produces color changes that are not striking enough to warrant its use
40	Benzidinemonosulfonic acid	Produces color changes that are not striking enough to warrant its use
41	Dinaphthocarbazole	Produces color changes that are not striking enough to warrant its use
42	Chromotropic acid	Has no colored oxidation products
43	1-Naphthylamine	Has no colored oxidation products
44	β,β -Dinaphthylamine	Has no colored oxidation products
45	<i>m</i> -Tolyl-1-naphthylamine	Has no colored oxidation products
46	<i>o</i> -, <i>m</i> -, and <i>p</i> -Tolyl-2-naphthylamines	Have no colored oxidation products
47	Phenylhydrazonaphthalene	Produces colored oxidation products
48	Diaminodiphenetole	Has no colored oxidation products
49	<i>o</i> - and <i>m</i> -Tolidines	Have no colored oxidation products
50	Tetrabromo- <i>m</i> -tolidine	Has no colored oxidation products
51	<i>o</i> -Tolylphenylamine	Produces colored oxidation products of too little merit to warrant its use
52	Sodium <i>m</i> -tolylphenylaminesulfonate	Has no indicator properties
53	Sodium <i>p</i> -tolylphenylaminesulfonate	Has no indicator properties

in the solution; this acts as the indicator. The results agree with potentiometric titrations.

E. COMPOUNDS REPORTED AS BEING UNSATISFACTORY FOR
USE AS OXIDATION-REDUCTION INDICATORS

In table 1 each compound which has been reported as being unsatisfactory for use as an oxidation-reduction indicator is listed and the reason for its unsuitability is given. In general, the indicators are arranged in alphabetical order in each of the following groups: (1) the diphenylamine series; (2) the complex ions; (3) the commercial dyes; (4) miscellaneous compounds.

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