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I hereby recommend that the thesis prepared under my supervision by Leora E Straka

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A STUDY OF OXIDATION-REDUCTION INDICATORS

A dissertation submitted to the

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Table of Contents

Introduction

The purpose of this study was the possible discovery of one or more compounds or classes of compounds which are easily oxidized by slight traces of oxidizing agents producing highly colored products whose color is sufficiently in contrast with that of the mother substance so that the change can be easily observed. In short, these materials were to be used as internal indicators in oxidation-reduction titrations. Particular emphasis was laid on such materials as are oxidized in acid solution by traces of dichromate since the quantitative employment of this excellent oxidizing agent has until recently required the use of an external indicator. A few internal indicators are now used more or less successfully, but the field has hardly been touched. With few exceptions these indicators are difficult to prepare and most of them are not readily soluble in water. The color change at the equivalence point in the majority of cases is not sharp either because the change extends over a range or because the color of the oxidation product is not sufficiently in contrast with the green of the chromic solution. The present study has dealt entirely with the preparation of derivatives or closely related homologues of materials already suggested for indicator use. We hoped that our preparations might lack in whole or in part the undesirable characteristics listed above. We have been partially successful. The unsuccessful as well as the immediately useful findings are embodied in this thesis so that others may profit by both our negative and positive results.

History

Until rather recently the generally accepted reagent for determining the endpoint of ferrous-dichromate titrations has been potassium ferricyanide used externally. This gives satisfactory results but its use is tedious and cumbersome. Consequently the search for practicable oxidation-reduction indicators was begun, and the findings thus far have been fairly satisfactory.

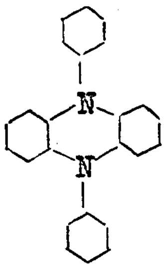
In 1900 Cazeneuve (1) found that diphenylcarbazide $CO(NHNHC_6H_5)_2$ can be used in the colorimetric determination of mercuric, mercurous, cupric and chromate ions. The latter can be detected by this reagent at a dilution of one part in one million. This carbazide was used in the form of an indicator paper by Oddo (2) for the determination of mercurous ions and also in the determination of lead by precipitating the lead with standard dichromate until a drop of the solution gives a positive test for chromate with diphenylcarbazide paper. Brandt (3) was the first to use diphenyl carbazide internally in the titration of iron with dichromate. The first drop of the oxidizing agent produces a red color which persists until the end of the main reaction when it is discharged by a slight excess of dichromate. This endpoint results from the destructive oxidation of the dye. Barneby and Wilson (4) investigated this reaction more closely and determined the optimum conditions for the use of diphenylcarbazide as indicator in the titration of iron with dichromate. They found that the color changes were very sharp but the rate of adding the dichromate must be carefully controlled. This indicator, a reducing agent, is oxidized by the dichromate and a blank determination must be made for accurate work. Numerous oxidizing agents give a blue coloration with benzidine and Kolthoff (5) found that this color appears at a definite potential. However, the color change is not reversible and therefore benzidine is not a satisfactory indicator in oxidimetry. Benzidine and some of its derivatives were further investigated by Feigl (6) and he recommended these for qualitative reactions. The application of benzidine acetate as internal indicator in the titration of ferrocyanide by dichromate was studied by Sierra and Burriel (7). Haary and Rudge (8) have described the use of benzidine and tolidine as indicators.

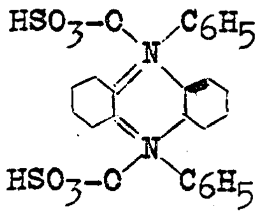
Even Hofman (9), the discoverer of diphenylamine in 1864, knew that a solution of this amine in concentrated sulfuric acid gives an intense blue coloration with a wide variety of oxidizing agents. This fact was rediscovered by Merz and Weith (10). Kopp (11) used this amine in the colorimetric determination of nitric acid in sulfuric acid, a procedure modified and improved by Tellmans and Sutthoff (12) and Smith (13). Later Tellmans used diphenylamine-sulfuric acid for the colorimetric determination of nitrates in milk.

Hinrichs (15) continued and confirmed Kopp's work and found that diphenylamine is also oxidized by vanadic acid, a discovery which was applied to the colorimetric determination of vanadium in water by Meaurio (16).

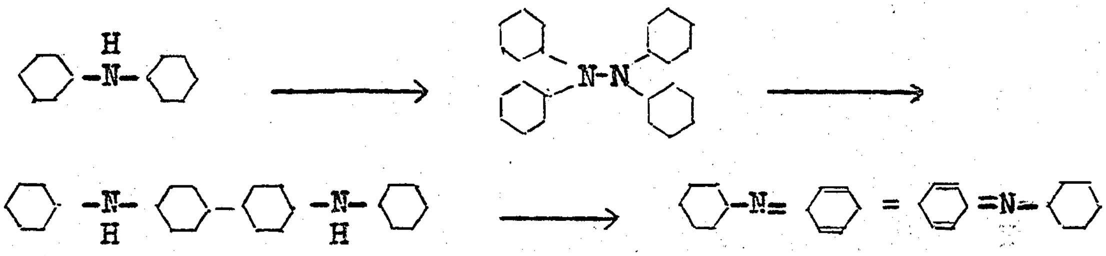
Knop (17) (1924) suggested the use of diphenylamine and diphenylbenzidine in the titration of iron with dichromate and both of these indicators hve been found to be fairly satisfactory under most conditions. An acidified solution of diphenylamine is oxidized by ferric salts to form a blue solution only after long standing, but an excess of one drop of decinormal dichromate immediately produces a dark blue coloration which completely hides the green color of the chromic salts formed during the titration. The color change is easily reversible, the addition of ferrous salt dispels the blue color and there is a sharp contrast as the green due to the chromic ions then becomes apparent. Knop found that the yellow color resulting from a high concentration of trivalent iron interferes with the sharpness of the endpoint; he overcame this difficulty by adding a concentrated sulfuric-phosphoric acid mixture. The indicator is used as a 1% solution in concentrated sulfuric acid; 0.20 cc. is most satisfactory and more than 0.40 cc. gives aberrant results. The acidity of the solution being titrated may vary over a rather wide range. Knop also found that when titrating solutions in which ferric iron had been reduced by the usual stannous-mercuric chloride procedure the color changes are not so striking as those observed when ferrous salts alone are present, i.e. in the absence of suspended mercurous chloride. Since the oxidation of ferrous salts by the oxygen of the air is catalyzed by the presence of copper, low results were obtained with samples of iron ores containing this element. The presence of trivalent arsenic increases the consumption of dichromate. The reliability of the color change is not impaired by high concentrations of ferrous salts and consequently Knop recommended the use of this indicator when determining chromium in chromium steels.

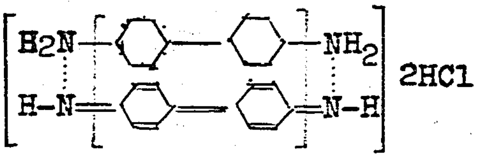
Not much was known about the mechanism of the formation of this blue oxidation product. Baeyer (18) suggested that it was possibly due to the transient production of diphenylhydroxylamine, at that time still unknown. This view was later found to be incorrect. Wieland's (19) first explanation of this reaction was that it is due to a series of oxidations in which the diphenylamine is oxidized to tetraphenylhydrazine which in turn gives diphenyldihydrophenazine and the latter is further oxidized to a blue derivative, diphenylperazonium sulfate.



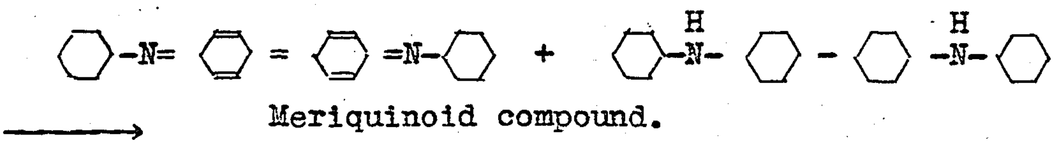


The mechanism of the reaction was further investigated by Kehrman and Micewicz (20) and Kehrman and Roy (21). They believed the first stage of the reaction is the formation of tetraphenylhydrazine which is transformed in acid solution into diphenylbenzidine and this then is oxidized into a quinoid compound of intense blue color. They also believed that there was an intermediate green meriquinoid compound of some unknown condensation reaction between the benzidine and the quinoid compound.





Schlenk, (22) in his work upon benzidine and its derivatives which are closely related to diphenylamine considers the colored oxidation product as a compound in which meriquinoid linkages are active joining one mole of imide, one mole of the benzidine and two mols of acid. In the light of Kehrman's results Wieland (23) abandoned his original hypothesis and accepted that of Kehrman in its essentials. He, however, eliminated the intermediate formation of tetraphenylhydrazine. Marqueyrol and Muraour (24) postulated essentially the same reaction as that of Wieland just stated but they insisted that some intermediate compound must be formed between diphenylamine and diphenylbenzidine. They based this idea on the fact that the hydrogen of the imino group is active and also because acetylated diphenylamine is not oxidized to the corresponding benzidine. In reply Wieland (25) insisted that the para carbon is the point of attack. He also gives a reaction mechanism for the oxidation of tertiary amines. This argument will be presented somewhat later in this thesis. In 1927, Madelung, Reiss and Herr (26) declared that the blue compounds are not the oxidation products of the benzidines but are due to complicated addition products which suffer dehydrogenation. Although diphenylamine was highly recommended by Knop, Kolthoff and Sarver (27) found that the endpoint is not always as sharp as Knop had asserted. The masking of the color change is due to the formation of a green insoluble meriquinoid compound of unknown structure. This is an intermediate oxidation product between diphenylbenzidine and diphenylbenzidine violet.



Meriquinoid compound.

These writers also state that in titrations of ferrous solutions with dichromate a correction must be applied because diphenylbenzidine violet is never completely reduced to colorless diphenylbenzidine but only to the green insoluble meriquinoid. Recently Theil(28) has given a new interpretation to this mechanism. He assumes that not the amines but the corresponding cations enter into the reaction.

Scott (29) showed that diphenylamine offers considerable advantage as an indicator in permanganate titrations of iron. The titrations may be made in the presence of mercurous chloride and the endpoint is more pronounced and permanent than that obtained from the self-color of permanganate. Further commendation of this indicator has been given by Core (30) and Thomas (31). The Statements of Knop in regard to the determination of small amounts of iron by means of dichromate and diphenylamine were also confirmed by Pichler (32) who used extremely accurate volumetric apparatus. Mehlig (33) made a comprehensive study of the use of diphenylamine in dichromate titrations and his verdict was favorable. He found that the diphenylamine gives a very satisfactory result for both high and low iron content and is especially valuable in the determination of chromium in chromite. Kolthoff (34) showed that this indicator is not specific for the reacting ions but behaves as an oxidation-reduction indicator. His evidence was derived from the following experiment. When a small quantity of ferricyanide is added to an acidified solution of ferrocyanide the addition of diphenylamine produces no color reaction because the solution does not have a sufficiently high oxidation potential. If now a zinc solution is added, the ferrocyanide ions are removed, the oxidation potential is raised and the indicator is oxidized as evidenced by the appearance of a deep blue. A Potentiometric study of the oxidation of diphenylamine was carried out by Watson (35). He found that the purple oxidation color appeared at the stoichiometric endpoint and that Knop's arbitrary deduction of 0.05 cc. as a corrective factor is not warranted. He has also shown that mercuric chloride has an inhibiting effect on the oxidation of diphenylbenzidine. Kolthoff and Sarver (36) in 1930 made further studies of the properties of diphenylamine and diphenylbenzidine as oxidation-reduction indicators. They showed that the rate of the color developement is greater in the presence of hydrochloric acid than when sulfuric acid was present and that the rate increased with rise in temperature. They also found that diphenylbenzidine violet is decomposed irreversibly by an excess of the oxidizing agent. They measured the light absorption of diphenylbenzidine violet, the solubility of this compound in water, sulfuric acid, sodium chloride, and mercuric chloride solutions, and the order of its ionization constant. Potentiometric experiments demonstrated that the oxidation of diphenylamine to diphenylbenzidine takes place almost stoichiometrically. Diphenylbenzidine can be further oxidized to the violet color and this in turn can either be further oxidized to yellow or red compounds, or it can react with unchanged diphenylbenzidine to form the green meriquinoid. These writers believe that this green compound is an equimolecular complex of oxidized and unoxidized diphenylbenzidine. Theil (28) who studied the colorimetric determination of diphenylamine has suggested another possible reaction mechanism. A critical review of the methods of determining iron was made by Bennett and Campbell (37). They recommended a prodedure with permanganate followed by reduction with stannous chloride and subsequent titration with dichromate using diphenylamine as indicator.

Furman (38) found diphenylamine to be a sensitive indicator of the endpoint of the reaction between ferrous and vanadic acid in which case the color change is from a deep blue to a greenish shade. He applied this indicator to the determination of vanadium and chromium in steels and vanadium in ores. Willard and Young (39) also found diphenylamine and diphenylbenzidine satisfactory for the titration of vanadic acid with ferrous sulfate. Since these indicators were shown to be suitable for ferrous-dichromate titrations, these same writers (40) extended the use of diphenylamine and diphenylbenzidine to the determination of iron by ceric sulfate and found them most satisfactory. However they found these indicators could not be used for the determination of cerium, a finding that was later confirmed by Furman and Wallace (41). These indicators were used in the oxidation of trivalent chromium with ceric sulfate by Willard and Young (42). In their study of cerimetry, Vanossi and Ferramola (43) state the conditions under which diphenylamine may be used in such titrations.

Cone and Cady (44) investigated the possibilities of diphenylbenzidine in the titration of zinc with ferricyanide. A small quantity of ferricyanide must be present. They found that in the presence of zinc salts the diphenylbenzidine violet product is formed by the ferricyanide and is then reduced by the first excess drop of ferrocyanide. The blue oxidation product first appears after the addition of 1-2 cc. of ferrocyanide. The color deepens during the course of the titration and within a few drops of the endpoint a purple color appears which gives way at the endpoint to a pale green. A comparison of the results obtained with diphenylamine and diphenylbenzidine are quite interesting. With diphenylamine there is an average decrease in the amount of ferrocyanide used of about 0.03 cc. for each additional drop of indicator. With diphenylbenzidine the amount of indicator has little effect although when twelve drops of indicator are used the sharpness of the color change is diminished. Two to four drops were recommended. An extended series of trials yielded consistent results thus confirming the sharpness of the endpoint. Closer checks were obtained with diphenylbenzidine than with uranium nitrate, the usual indicator, which must be used externally. Kolthoff(15) continued the work of Cone and Cady, studied the variables involved and recommended diphenylamine as indicator in zinc titrations providing the analysis is made under the conditions which he has specified. He found that the endpoint is easily overrun if the titration is made at room temperature. If, however, a few grams of ammonium sulfate is added and if the titration is begun at 60°C., just before the endpoint is reached the color changes from blue to greenish yellow and then after a few seconds to blue violet again. The titration is continued until the greenish color is permanent. Later Kolthoff (46) worked out a method for the titration of ferrocyanide with zinc sulfate using this same indicator. A further systematic examination of the titration of zinc with ferrocyanide was made by Kolthoff and Pearson (47). They found that although the indicator correction for diphenylamine was greater than that for diphenylbenzidine and subsequent corrections for this had to be made nevertheless diphenylamine is preferable because the color change is more pronounced.

Sarver (48) has advocated the use of diphenylamine for the determination of ferrous iron in silicates. He found that the color produced at the endpoint is frequently quite faint but nevertheless unmistakeable. He also noticed that is an excess of several drops of dichromate is added there is no increase in the intensity of the color, but if one drop of ferrous solution is added to this overtitrated solution, an intense blue color appears and the doubtful endpoint can then be definitely fixed. His titrations were carried out in the presence of a hydrofluoric-sulfuric acid mixture. The hydrogen fluoride seems to have no effect other than to brighten the color. A new improved procedure for the determination of ferrous and ferric iron in silicates using diphenylamine is described by Schollenberger (49). Potentiometrically he has shown that hydrofluoric and also phosphoric acid increase the sharpness of the endpoint due to a lowering of the oxidation potential.

Druce (50) has successfully used diphenylamine in the determination of tin in the presence of phosphoric-sulfuric acid mixture. Saz (51) determined tin in cassiterite by reducing the tin and then reoxidizing it with dichromate in the presence of diphenylamine. Someya (52) found that diphenylamine is a suitable indicator in dichromate titration of tri and quadrivalent uranium, trivalent titanium and hydrochloric acid solutions of the ferroacetates.

Another interesting application of diphenylamine is the use of diphenylamine blue as an adsorption indicator in the volumetric determination of chloride, bromide, and silver ions in acid solution. This is due to Lang and Messinger (53). Gillis and Cuelier (54) used diphenylamine in the volumetric determination of cobalt. This indicator was also applied in the oxidation of hydroquinone by ceric sulfate, an investigation studied by Furman and Wallace (55). The endpoint is very sharp but an indicator correction must be made.

The green meriquinoid compound which is formed during a titrating involving diphenylamine and diphenylbenzidine has been found objectionable. Szebelledy (56) avoided this difficulty by using para-phenetidine, $C_2H_5O.C_6H_4.NH_2$ as the inside indicator for the titration of iron with dichromate and adding ammonium chloride to bind the ferric ions. Weeks (57) also investigated para-phenetidine and para-anisidine, $CH_3O.C_6H_4.NH_2$, as oxidation-reduction indicators for titration of iron with dichromate. Recent study has led Weeks (58) to suggest bi-ortho-anisidine $(NH_2.C_6H_3.OCH_3)_2$ as internal indicator in the dichromate method for iron. Ten drops of 1% indicator solution are prescribed and the color passes through brownish green to red brown. Although the color change is not sharply reversible, iron determinations which have been overtitrated may be treated with a measured volume of standard solution and the true endpoint established with dichromate.

Sarver and Kolthoff (59) in 1931 recommended diphenylamine sulfonic acid, $H.N(C_6H_4.SO_3H)(C_6H_5)$, as a new internal indicator. The mechanism of its reaction is similar to that of diphenylamine. Divalent iron has a great accelerating effect upon the speed of its oxidation to the reddish violet diphenylbenzidine sulfonic acid violet. The reactions are reversible and the accompanying color changes are more sharp and brilliant than those observed with diphenylamine. This is particularly recommended in the titration of ferrous iron by dichromate because the intensity of the color is so great that titrations may be made in even highly colored solutions. They also determined the indicator corrections for diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid and although these values for diphenylamine and diphenylbenzidine are smaller than those for diphenylamine sulfonic acid the latter is so obviously superior in other respects that it is nevertheless recommended. It also may be used in the presence of tungstate, which is not true of the other two. A discussion of the use of oxidized diphenylamin sulfonic acid and oxidized diphenylamine as indicators for the determination of chromium and vanadium in steels has been given by Willard and Young (60).

A new series of oxidation-reduction indicators of the tri-aryl methane type was investigated by Knop (61). He used permanganate as the oxidant. Because of the striking colors produced by some of these indicators they are particularly appliçable to the titration of ferrous solutions which are highly colored by nickel or cobalt. Brucine, $C_{23}H_{26}O_4N_2.4H_2O$, has recently been advocated by Miyagi (62) for use in dichromate titrations. It can be used in the titrations of iron and tin salts. The colorless sloution becomes permanently red in the presence of excess of dichromate. Szebelledy and Schick (63) have recently proposed selenium as an oxidation-reduction indicator in the determination of arsenite by bromate. Dark red colloidal selenium is formed in the solution which serves as indicator. Results by this method are said to agree well with those obtained by potentiometric titrations.

Walden, Hammett, and Chapman (64) have investigated phenanthroline ferrous iron, $(C_{12}H_8N_2)_3Fe$, as a new reversible oxidation-reduction indicator of high potential. It is recommended as an ideal indicator because it exhibits an intense, reversible color change and makes possible a high degree of precision. A number of new procedures involving the use of ceric sulfate with ortho-phenanthroline ferrous complex as indicator have been described by Willard and Young (65): the titration of $Fe(CN)_6^{----}$, Tl^{+}, Sb^{++++}, U^{++++} and hydrogen peroxide and the titration of hydrogen peroxide or sodium nitrite. They also proposed (66) a new method for the direct determination of chromium and vanadium in steels by means of a differential titration with permanganate using this ferrous complex as indicator. Research on the oxidation potentials relative to each other of the ferric-ferrous system, of the phenanthroline indicator, and the stages of the vanadate reduction have been measured by Walden, Hammett and Edmonds(67)and the necessary conditions for the titration of iron and vanadium have been stated.

Experimental

The foregoing somewhat detailed review of the properties and characteristics of diphenylamine and diphenylbenzidine was made because they have been used by numerous workers as oxidation-reduction indicators. Acquaintance with their properties was acquired by test determinations and the findings compared with the results of previous investigators. Diphenylamine is readily available since it is a commercial commodity but diphenylbenzidine must be prepared in the laboratory. This preparation was accomplished by oxidizing a sulfuric acid solution of diphenylamine with sodium dichromate followed by reduction with bisulfite. The authors of this procedure, Marqueyrol and Muraour (68), claim a 60% yield but actual experience, starting with 10 grams of diphenylamine, showed yields much below their figure. When recrystallized from toluene as recommended by them the product carried down considerable quantities of impurities. It was much more successfully recrystallized from boiling benzene from which the diphenylbenzidine sepatates in beautiful flaky silvery leaflets melting at 240°. Recorded M.P. 242°. In titrations using diphenylamine and diphenylbenzidine we found the endpoint with the latter to be sharper and more distinct because the green meriquinoid form seemed less noticeable. Therefore our attention was confined to diphenylbenzidine.

The determination of chromium in a chromite ore using diphenylbenzidine proved satisfactory. 0.5 grams of chromium ore of known chromium content (23.23%) was fused with 4 grams of sodium peroxide. After treating the fusion residue with water the iron precipitate was filtered off and the filtrate diluted to 250 cc. To 50 cc. portions of this solution acidified with 15 cc. of 6N sulfuric acid, 50 cc. of standard ferrous sulfate was added and the excess titrated with 0.1N dichromate in the presence of the usual retarder mixture (15 cc. phosphoric acid, density 1.7, 15 cc. sulfuric acid, density 1.84, diluted to 100 cc.). Using diphenylbenzidine 23.21% chromium was found as compared with 23.26% chromium using ferricyanide externally. These results show that diphenylbenzidine may be conviently accurately used for chromium determinations. The same chromium ore was analyzed by the above procedure with the modification that the iron precipitate was not filtered off but was dissolved in sulfuric acid, The object was to determine whether the presence of rather considerable quantities of iron would have any appreciable effect on the indicator. Under these conditions the determination in the presence of diphenylbenzidine gave 23.54% chromium, in the presence of ferricyanide, 23.26%. Therefore the presence of considerable ferric salts probably inhibits to a slight extent the color change of diphenylbenzidine.

A series of analyses was next run on an iron ore known to contain 59.51% iron. Various indicators were used: potassium ferricyanide, diphenylbenzidine, and permanganate. The standard stannous chloride method was followed and the results are given below under the heading %Fe.

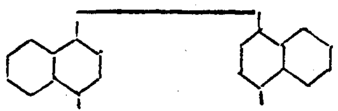
Table I

Titration of Iron Ore

0.1N $K_2Cr_2O_7$ (cc)	0.1N $KMnO_4$ (cc)	Indicator	% Fe	Corrected % Fe
31.98 31.95		$K_3Fe(CN)_6$	59.51%	59.51%
31.80 31.78		d.p.b. vol.= 500cc	59.19%	59.15%
31.90 31.88		d.p.b. vol.= 150cc	59.37%	59.51%
	31.88 31.86	$KMnO_4$ (alone)	58.75%	59.40%
	31.89 32.00	$KMnO_4$ d.p.b.	58.78%	59.62%

When 0.1N dichromate, standardized by direct weighing, was used to analyse this ore the Fe% found in the various trials differed considerably, so it was decided to standardize the dichromate and the permanganate against a standard iron ore. (Bureau of Standards #27, containing 69.2% Fe). This standardization was carried out five different times under exactly

the same conditions as the five analyses recorded above. The necessary corrections were then made for the iron values of the standard solutions and the corrected percentages appear in the table. Except in the analysis in which the diphenylbenzidine was used with dichromate in a volume of 500cc., the % Fe found agrees, within experimental error, with the true value. From these results it may be concluded that diphenylbenzidine ought not be used in a volume greater than 150 cc. and that the oxidizing agent should be standardized against a solution of known iron content and by the same procedure.

As has been shown by numerous workers, benzidine can be used with very satisfactory results in the titration of ferrous iron with dichromate but no record was found of attempts to use the analogous naphthalene derivative, naphthidine, 

. Like benzidine, this may be formed by treating the hydrazo compound with dilute acids when a rearrangement occurs as with hydrazo benzene. Naphthidine was first prepared by Nietzki and Goll (69) and later by Cummings and Steel (70). Nietzki and Goll state that oxidizing agents such as ferric chloride, chromic acid or chlorine produce, with a solution of naphthidine salts, a beautiful carmine red coloration. Because the other properties of naphthidine are similar to those of benzidine and because of this recorded action toward oxidizing agents it seemed logical to expect that naphthidine would serve as an oxidation-reduction indicator. It seemed to offer special promise because of its red oxidation product, since the change from the green of the chromic ions to the red coloration would be more striking and offer a greater contrast than does the change to the blue observed when benzidine is used. The difficulty due to the green meriquinoid form would also be avoided.

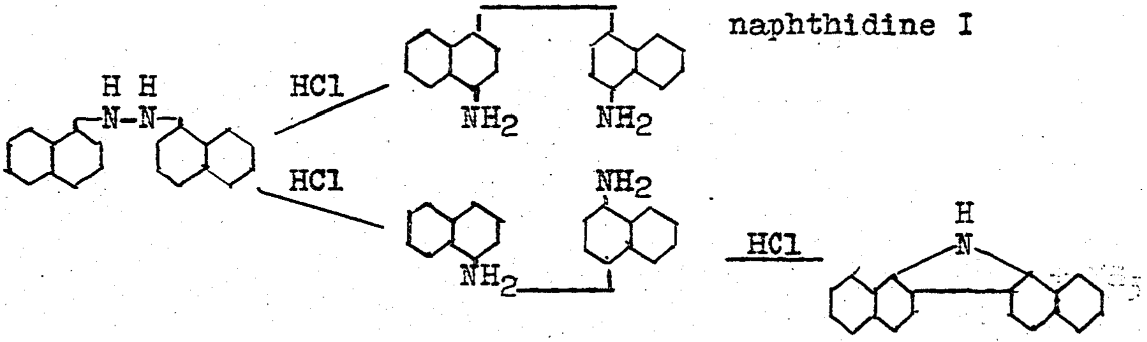
Nietzki and Goll prepared naphthidine by reducing azo naphthalene with zinc dust or with stannous chloride. The primary reduction product, hydrazo naphthalene, under the influence of hydrochloric acid undergoes the benzidine rearrangement, forming in part the isomeric diamino compound. The authors recommend the stannous chloride reduction because it gives a larger yield. Cummings and Steel prepared the compound by reduction of the azoxy-compound by means of stannous chloride. None of these writers state the actual yield of naphthidine obtained.

The α-α' azoxynaphthalene used in the present study was prepared according to the directions of Cummings and Steel. α-nitro-naphthalene was reduced with zinc dust in alcoholic solution, filtered, and the residue extracted with alcohol. The alcoholic filtrates were kept separate from the initial filtrate. Upon cooling the initial filtrate a crystalline mass of the yellow variety of α-azoxynaphthalene separated. The alcoholic extracts when cooled, gave a reddish brown precipitate which was undoubtedly the red variety of azoxynaphthalene. The yellow crystalline product after being treated with warm water to remove the water soluble impurities was extracted with alcohol and on evaporation a reddish brown product was obtained melting at 121°. As the pure compound melts at 127° the product was probably impure red azoxy naphthalene. The yellow variety could not be obtained pure because when recrystallized from alcohol only the red modification was deposited. After a second recrystallization the red crystals melted at 125°C. Twenty grams of α-nitro naphthalene yielded five grams of the α azoxynaphthalene. Cummings and Steel do not state their yield.

One part of the α-α' azoxynaphthalene was dissolved in 45 parts of glacial acetic acid. The red solution was treated with a stannous chloride solution (one part of stannous chloride, two parts of hydrochloric acid, two parts of water) until the color was almost discharged. Concentrated hydrochloric acid was then added and a precipitate, the hydrochloride of naphthidine, appeared. The hydrochloride which had a decided blue appearance, was recrystallized from hot water. It was then suspended in cold water and a concentrated solution of sodium hydroxide added. A flocculent gray white precipitate, the free base appeared. This was dissolved in hot ethyl alcohol in which it is fairly soluble and after complete solution hot water was added until the solution became turbid. This turbid solution was cleared by warming and then allowed to cool slowly. As the product from this recrystallization was grayish pink, attempts were made to recrystallize it from benzene. This was rather difficult because the base did not come out of solution until the solvent was removed by evaporation and the residue thus obtained was still pinkish. Methyl alcohol was then tried and this seems to be the best recrystallizing medium. Accordingly the base was dissolved in hot methyl alcohol and water carefully added to the cooled solution. A silvery crystalline precipitate separated which was quite pure and melted at 197°. Nietzki and Goll record 198°. The yield was 0.2 gram.

Another preparation of naphthidine was carried through the first stage but the azoxy compound was not recrystallized but dissolved directly in glacial acetic acid and reduced with stannous chloride solution. A large precipitate of the hydrochloride was produced on treatment with concentrated hydrochloric acid but its appearance indicated gross contamination. The product was dissolved in water, concentrated hydrochloric acid added in large excess, but the precipitate of the hydrochloride was considerably less than had been expected from the bulk of the crude product. The purified hydrochloride was then dissolved in water and the free base precipitated by sodium hydroxide. After recrystallizing as before from aqueous methyl alcohol the product came out in beautiful crystalline silvery flakes melting at 198°. Yield of about 0.15 gram.

This small yield of naphthidine is undoubtedly due to the complications which arise during the rearrangement of the hydrazo compound. Nietzki and Goll showed that in this rearrangement two isomers are obtained, one naphthidine I, insoluble in hydrochloric acid, and the other, which they called dinaphthyline II, soluble in hydrochloric acid. Upon heating dinaphthyline, ammonia is lost and there is formed dinaphthylcarbazol III, as shown by the structural scheme.



naphthidine I

dinaphthyline
II

III

Vesely (71) in his study of dinaphthylcarbazol and Jacobsen (72) in his general study of the rearrangement of hydrazo compounds found that this hydrazo compound has an equal chance of being transformed into 0,0, dinaphthyline rather than into the meta-para hypothetical structure II given above. According to Vesely, ammonia splits off leaving dinaphthylcarbazol of structure IV.

IV

0,0, dinaphthyline

The indicator characteristics of naphthidine were investigated. A 1% solution in concentrated sulfuric acid was prepared. Three drops of this added to 50 cc. of water, gave on addition of the 0.1N dichromate a pink color which deepened on standing. A few drops of 0.1N ferrous sulfate was then added and an intense red color appeared immediately. This showed that the oxidation of naphthidine by dichromate is catalyzed by the presence of ferrous iron and that this compound might possibly be used as an indicator in the titration of ferrous solutions with dichromate.

In order to determine any possible effect upon naphthidine of the ferric chloride which would be produced in the titration, 5 cc. of 0.1N ferric chloride was added to 50 cc. of water containing 4 drops of the indicator and 18 cc. of dilute hydrochloric acid. At first a pink appeared and after standing about three minutes the solution became deep red. Consequently ferric iron has an oxidation potential great enough to oxidize the naphthidine. However if the ferric chloride is added to 50 cc. of a solution containing 15 cc. of phosphoric-sulfuric acid mixture and four drops of indicator, no color is produced because the ferric ions are bound as complex phosphate ion. Therefore phosphoric-sulfuric acid mixture is essential in the titration of ferrous solutions with dichromate. Table II shows comparative titrations in which ferricyanide and naphthidine were used as indicators. Three drops of naphthidine was added to 50 cc. of water containing 18 cc. of dilute hydrochloric acid.

Table II

Comparison of Indicators

	$FeSO_4$	0.1N $K_2Cr_2O_7$ (cc)	Indicator
1.	20 20	19.87 19.88	$K_3Fe(CN)_6$
2.	20 20	19.90 19.89	naphthidine 15 cc H_3PO_4 H_2SO_4
3.	20 20	19-19.50 endpoint indefinite	naphthidine (alone)

A comparison of (1) and (2) shows that naphthidine may be used as an indicator in quantitative work since the volume of dichromate consumed agrees, within experimental error, w with the findings obtained when ferricyanide is used. The color change is quite definite and striking; near the end-point the red coloration appears but this fades very rapidly just as permanganate shows a fugitive coloration immediately preceding attainment of the equivalence point. However, the color change at the endpoint is deep red and persists at least 1 1/2 to 2 minutes and then gradually disappears. In carrying out the titrations in the presence of various acids and various concentrations it was found that sulfuric acid does not work so well as does hydrochloric acid and the best concentration is from 15-20 cc. of 6N hydrochloric acid in a total volume of 150-200 cc. The reaction is not sharply reversible but if the endpoint is overrun an excess of standard ferrous sulfate may be added and the equivalence point then established by adding dichromate.

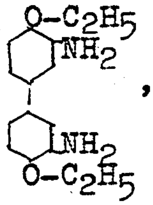
The effect of mercuric and mercurous chloride upon naphthidine was next investigated to determine whether the mercury chlorides which are always present when iron is determined by the stannous chloride method would interfere in any way. Ten cc. of saturated mercuric chloride solution was added to a solution containing 150 cc. water, 2 drops of stannous chloride, 3 drops of indicator, 18 cc. of 6N hydrochloric acid and 20 cc. of retarder. To this was added 5 cc. of saturated mercuric chloride and a measured volume of standard ferrous sulfate. The ratio of the ferrous solution to the dichromate thus obtained agreed within 0.02 cc. with that obtained when ferricyanide was used as an indicator. It was further noted that the color change from green to red is even more definite in the presence of the mercury salts than in their absence. This fact indicated that naphthidine could be used as an indicator in the determination of iron in its ores.

0.3 gram samples of iron ore were then analyzed according to the standard stannous chloride method using as indicators: potassium ferricyanide, diphenylbenzidine and naphthidine. The final volume in the case of the internal indicators was 150 cc. which included three drops of 1% indicator 15 cc. of retarder and 18 cc. of 6N hydrochloric acid. The results are shown in table III.

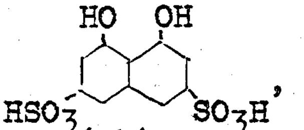
Table III

Analysis of iron ore using Naphthidine		
0.1N $K_2Cr_2O_7$ (cc)	Indicator	% Fe
35.28 35.27	$K_3Fe(CN)_6$	65.64
35.30 35.29	naphthidine	65.68
35.30 35.28	diphenyl-benzidine	65.67

These results show excellent agreement and either of the above internal indicators may be used with precision in this determination.

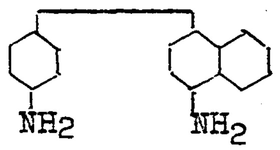
Ortho diamido diphenetol,  , was tried as a possible indicator because of its relation to paraphenetidin which has been recommended by Szebelledy (56). The hydrazo compound was prepared and rearranged according to the method of Schmitt and Mohlau (73). Using the rearranged compound as indicator a faint color change was observed in the vicinity of the endpoint. The green due to the chromic ion gave way to a deeper green but no distinct and striking change could be noted.

α naphthylamine, although used by Van Eck (74) in the colorimetric determination of chromium, proved unsuitable when tried as a titration indicator even in the presence of ferrous salts. When two drops of 0.1N dichromate was diluted to 50 cc., acidified, and two drops of a 1% solution of α naphthylamine was added, the solution became violet after about ten minutes. In this case it was quite evident that the violet color produced would not be dark enough to cover up the green of the chromic ions, and though the time required to develope this color is no disadvantage in colorimetric work, this factor excludes the use of α naphthylamine as an indicator.

Chromotropic acid, 

, another compound used successfully by Van Eck (74) in the colorimetric determination of chromium likewise proved unsuitable as a titration indicator. 1 cc. of a 1% solution of the chromotropic acid salt (obtained commercially) in a volume of 50 cc. of water and 10 cc. of 6N hydrochloric acid gave no color with four drops of 0.1N dichromate even on standing. However, 10 cc. of 0.1N ferrous solution, 50 cc. water, 10 cc. of retarder and 10 cc. of 6N hydrochloric acid, when treated with several drops of 0.1N dichromate in the presence of this indicator gave a beautiful cherry red whose intensity increased as the addition of dichromate proceeded. This showed definitely that the reaction between dichromate and chromotropic acid is catalyzed by the presence of ferrous iron. Since the dichromate may react with both the chromotropic acid and the ferrous iron, these reactions probably occur simultaneously and the colored compound resulting from the oxidation of the chromotropic acid seems to be stable and is not reduced by excess ferrous iron. Koenig (75) states that this compound may be used in determining the chromium content in plants by a colorimetric method because there is undoubtedly some ferrous iron present in plant ash and in its presence a red color is formed whose intensity increases proportionally to the chromate present.

The successful application of naphthidine and benzidine logically led to the belief that a similar compound containing one naphthalene and one benzene ring might also possess indicator properties. Phenyl α hydrazo naphthalene and the corresponding diamino compound was prepared by isolating the azo compound, reducing it and then rearranging it. The azo compound was prepared according to the directions of Bucherer and Sonnenburg (76) and then reduced to the hydrazo compound by ammoniacal hydrogen sulfide. It was rearranged by treatment with acid. Preliminary experiments with this compound, , showed that it had indicator possibilities but further study proved the material to be not suited to the requirements. When attempts were made to use it as an indicator, the first excess drop of dichromate produced a decided color change from green to red but after two or three reversals the intensity of the color diminished and eventually no change at all was observed. From these tests it was concluded that the erratic behavior of this substance precludes



its use as an indicator in these titrations.

Because of its structural similarity to diphenylamine a study of dinaphthlamine was begun. It was easily prepared according to a patent (77). β naphthylamine, in alcoholic solution was refluxed with bisulfite solution. After cooling a white crystalline mass separated which was filtered and washed with hot water and then extracted with hot dilute hydrochloric acid.to remove any unchanged β naphthylamine. Then it is extracted with boiling alcohol and the β dinaphthylamine remained as white plates. After recrystallization from boiling benzene it melted at 168°. The recorded melting point is 171°. To try its possibility as an indicator a 1% solution in sulfuric acid was made and several drops of this was used as an indicator in the titration of ferrous sulfate with dichromate. There was no evidence of color change.

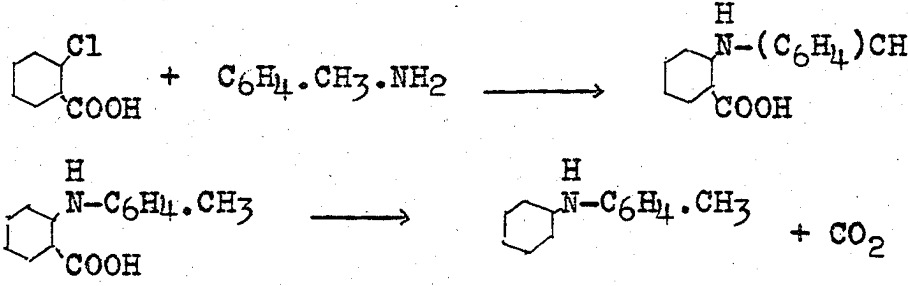
It was thought that a study of meta nitro diphenylamine might be enlightening since the possession of a nitro group makes this compound very soluble in dilute mineral acids. This amine was prepared according to the directions of Goldberg (78). Acetylated meta nitraniline was made by following Kaufman's (79) procedure. The stoichiometrical amount of acetic anhydride was added to 44 grams of meta nitraniline in 200 cc. of benzene. The solution became warm but after standing for two hours the acetylated compound separated, was filtered and dried. M.P. 149° Yield = 55 grams.

55 grams of this acetylated meta nitraniline was condensed with 96 grams of phenyl bromide by boiling for twelve hours in nitrobenzene in the presence of 22 grams of potassium iodide. The nitrobenzene was removed by steam distillation and 55 grams of a brown solid, acetyl meta-nitro diphenylamine was obtained. This was dissolved in alcohol and saponified by boiling for three hours with 50 grams of potassium hydroxide. Water was then added and a brown oil separated which later solidified. This was extrcated with ether and evaporation of the ether left a brick red solution of this meta-nitro diphenylamine crystalline compound. M. P. 110°. Recorded M.P. 112°. A 1% solution of this meta-nitro diphenylamine in concentrated sulfuric acid gave no evidence of indicator actiom.

A study of the next higher homologues of diphenylamine proved to be much more promising. An attempt to prepare phenyl p-toluidine was first begun according to the method of Goldberg (78). The acetyl p-toluidin, M.P. 147°, was prepared according to Kaufman by adding 40 grams of acetic anhydride to 42 grams of para-toluidin in 100 cc of benzene. 44 grams of this acet-p-toluidin was then mixed with 25 grams of potassium carbonate and added to 360 cc. of bromobenzene along with 3 grams of copper bronze and 3 grams of potassium iodide and boiled for several hours. After the excess of phenyl bromide was removed by steam distillation the brown crystalline residue was recrystallized from alcohol and it melted at 148°. The was undoubtedly the unchanged p-acetyl toluidin and the condensation had not taken place. Goldberg (80) patented another method for making compounds similar to this p-tolyl phenylamine by treating the substituted aniline and phenyl bromide dissolved in nitrobenzene with potassium hydroxide and cuprous iodide and then boiling for twenty hours. Wieland (81) in his preparation of the ditolylamines boiled the acetyl compound of the toluidin with bromotoluene, potassium hydroxide, copper bronze and a few crystals of iodine in nitrobenzene. A combination of both of these procedures was tried. Wieland's method was followed but the unacetylated compound was taken as the initial reagent. 50 grams of para-toluidin, 50 grams of bromobenzene, 23 grams of potassium hydroxide, 1.5 grams of copper bronze, and a few crystals of iodine were refluxed for twenty four hours in 200 cc. of dry nitrobenzene. After steam distillation a tarry mass was left as residue from which it was impossible to isolate any product of condensation.

It was next decided to treat ortho-acet-toluidin according to the directions of Goldberg to determine if the condensation could be accomplished. 55 grams of the ortho-acet-toluidin (M.P. 110°) obtained from ortho toluidin, was mixed with 27 grams of potassium carbonate, 150 cc. of bromobenzene and a small amount of copper and potassium iodides and boiled for twenty hours. Steam distillation left a brown residue that was extracted with ether and upon evaporation a compound was left which after recrystallization melted at 110°. This was the original ortho-acet-toluidin. These two attempts show that under these conditions para- and ortho- acet-toluidin cannot be condensed with phenylbromide.

Ullman's (82) method for the preparation of the phenyl toluidins proved more successful.



The ortho chlor benzoic acid used in this syntheais was prepared as described by Graebe (83). He recrystallized this ortho chlor benzoic acid from water but this is rather difficult since the solubility is 1-800. This acid may be more conveniently purified by dissolving it in alkali and then reprecipitating it with acid. M.P. = 138°. Recorded = 138°.

The ortho-, meta-, and para-tolyl anthranilic acids were prepared by treating 12 grams of ortho-chlor benzoic acid with 12 grams of potassium carbonate, 0.06 grams of natur kupfer, and 48 grams of the respective toluidins and boiling for 2-4 hours. The brown mass was then boiled with dilute hydrochloric acid to remove any untreated toluidin, filtered the residue then dissolved in sodium carbonate and the acid precipitated with hydrochloric acid.

Yields: ortho-tolyl anthranilic acid = 15 grams, M.P.= 180°
recorded M.P. = 182°
para-tolyl anthranilic acid = 14 grams, M.P. 180°
recorded M.P. = 190°
meta-tolyl anthranilic acid,= 14 grams, M.P. = 120°
recorded M.P. = 126°

These acids were not recrystallized because the next decomposition step does not require absolutely pure materials.

The para-tolyl anthranilic acid was heated for about two hours to 250° and a lively evolution of carbon dioxide took place. The temperature was then raised to or above the boiling point of para-tolyl phenylamine = 315°. This decomposition was carried out in a small distilling flask and because of its high boiling point the para-tolyl phenylamine was passed directly from the side arm of the flask into a test tube. It soldified easily. After recrystallization from dilute alcohol it melted at 85°. Recorded M.P. = 89°. The ortho- and meta-tolyl anthranilic acids were treated in the same way. The boiling point of the ortho-tolyl phenylamine was 303° while that of the meta-tolyl phenylamine was 313°. The ortho and meta compounds came over as oils which did not show any signs of solidifying until after standing two to three weeks. However, the boiling points are a sufficient indication of their purity.

A 1% solution of each of these compounds, ortho-, meta-para-tolyl phenylamines, was made in concentrated sulfuric acid and tried as indicators in the titration of ferrous sulfate with dichromate. There was a definite change with each of these possible indicators and back titration was accomplished in all cases. The meta and para compounds gave a sharp change to a blue while the ortho compound gave a red oxidation product. Unfortunately the endpoint change in the latter case is not distinct enough to make it practical as an indicator. A study of some of the derivatives of this compound might prove profitable. In obtaining the ratio of ferrous solution to dichromate with the meta- and para-tolyl amines as indicators in the presence of 50 cc. of water, 15 cc. of retarder solution, 15 cc. of dilute hydrochloric acid and three drops of indicator, there was a very sharp change from the green color of the chromium solution to a blue. However, when these indicators were tried with an iron ore it was found that mercury salts inhibited the action to a great extent. There was a change to a blue color but it was by no means definite and so these amines cannot be used in the analysis of iron ores by the standard stannous chloride method. In the analysis of chromium ores, however, the following results show that they may be used with confidence.

Insert Table IV.

The chromium ore was analysed by fusing a 0.5436 gram sample with sodium peroxide. After treating the fusion residue with water the iron oxide was filtered off and the filtrate diluted to exactly 250 cc. To 50 cc. portions of this solution

Table IV

Ratio of $FeSO_4$ to $K_2Cr_2O_7$

$FeSO_4$	$K_2Cr_2O_7$	Indicator
25 25	21.76 21.75	$K_3Fe(CN)_6$
25 25	21.80 21.82	meta-tolyl phenylamine
25 25	21.85 21.86	para-tolyl phenylamine

Analysis of Chromite

$FeSO_4$ (cc)	$K_2Cr_2O_7$ (cc)	Indicator	% Cr
25 25	8.93 8.94	$K_3Fe(CN)_6$	20.55
25 25	9.02 9.02	meta-tolyl phenylamine	20.49
25 25	9.04 9.06	para-tolyl phenylamine	20.52

100cc of water, 15 cc. of dilute sulfuric acid, 25 cc. of standard ferrous solution were added and the excess was titrated with 0.1006N dichromate. When the meta- and para-tolyl amines were used as indicators, 15 cc. of retarder solution was added. In obtaining the ratio of ferrous sulfate to dichromate the dichromate was added to a solution containing 100 cc. of water, 18 cc. of dilute hydrochloric acid 15 cc. of retarder and two drops of indicator.

The tolyl naphthylamines were next examined. Several compounds of this series have been prepared but not tested as indicators. Friedlander (84) prepared and described several derivatives of this type derived from α and β naphthol. Ullman and La Torre (85) and Bucherer and Seyde (86) also prepared compounds of this type. In 1914 Knoevenagel (87) carried out similar condensation reactions. The method described by Ullman for the preparation of ortho-tolyl β naphthylamine seemed the most simple and convenient. The following compounds were prepared according to his procedure: (1) para-tolyl β naphthylamine (2) ortho-tolyl β naphthylamine (3) meta-tolyl α naphthylamine (4) meta-tolyl β naphthylamine. Ullman did not prepare (3) and (4) but (4) was prepared by Bucherer and Seyde and (3) by Knoevenagel.

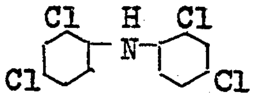
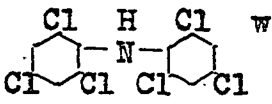
In this procedure the hydrochlorides of ortho-, meta-, and para-toluidin were used. These were prepared by dissolving the appropiate toluidins in carbon tetrachloride and passing hydrogen chloride gas through the solution and the hydrochloride precipitates. 25 grams of the respective three hydrochlorides were heated with 28 grams of β naphthol for 5 hours. Only one derivative of α naphthol, namely the meta-tolyl α naphthylamine was prepared. After cooling, the solutions were made alkaline with sodium hydroxide, steam distilled and the brown oil which remained was extracted with ether. After evaporation of the ether the residual tarry mass was heated in a distilling flask and the amines were distilled over. In the case of para-tolyl β naphthylamine a yellow oil came over which easily solidified. After recrystallization from alcohol it melted at 98°. Recorded M. P. = 102°. The other compounds: ortho-tolyl β naphthylamine meta-tolyl β naphthylamine, and meta-tolyl α naphthylamine came over as oils which did not crystallize. These oils were in an ice box for two months and finally the meta and ortho-tolyl naphthylamines showed signs of crystallization but the mass as a whole did not crystallize but formed a thick viscous mass. Sulfuric acid solutions of these compounds were trie d as indicators in titrating ferrous sulfate against dichromate. The ortho-, meta-, and para-tolyl β naphthylamines showed no color change and are therefore useless for the purpose in hand. The meta-tolyl α naphthylamine showed a slight change to a blue-green oxidation product but it was by no means sharp or distinct and had no possibilities as an indicator.

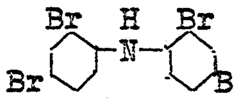
The next compounds to be tried were the ortho- and meta-tolidins $(NH_2.CH_3.C_6H_4)_2$. They offered some promise because of their structural similarity to compounds of the benzene type such as naphthidine and diphenylbenzidine whose satisfactory indicator properties have been described above.
The starting material for the preparation of ortho tolidin was ortho azo toluene which was prepared by the reduction of ortho nitro toluene, using a procedure develpoed by Fry (88). 68 grams of ortho nitro toluene was dissolved in 680 cc of methyl alcohol and 36 grams of magnesium turnings was added. As the magnesium was added the system had to be cooled with ice. After the reaction was complete the excess methyl

alcohol was distilled, the residue dried, placed in a Soxlet and extracted with ether. The ether extracts from duplicate reaction mixtures were combined and after condensation to a small volume this residue was subjected to steam distillation to remove any unchanged ortho-nitro toluene. This residue was then extracted with ether and after evaporation 35 grams of ortho azo toluene remained. M.P. = 55°. Recorded M.P. = 55°. This is equivalent to a 33% yield. This azo compound was reduced and rearranged according to Jacobsen's (72) method by suspending 12.5 grams in 40 cc. of alcohol, adding 23 grams of stannous chloride and then heating. The red color did not disappear entirely but it did get much lighter. After filtering, the filtrate was added to 100 cc. of 12% hydrochloric acid and a white crystalline precipitate of the tin double salts of ortho tolidin came down.almost immediately. After standing twelve hours it was filtered the tin double salt suspended in 100 cc. of water, warmed and hydrogen sulfide passed into this suspension to remove the tin. Sulfuric acid was added to the filtrate and the ortho tolidin sulfate separated as a white crystalline mass. The base was liberated by boiling with a solution of sodium carbonate, extracted with ether, dried, and recovered from the ether. M.P. = 126°. Recorded M.P. = 129°. This compound was found to give a yellow oxidation product and it is of no value as an oxidation-reduction indicator.

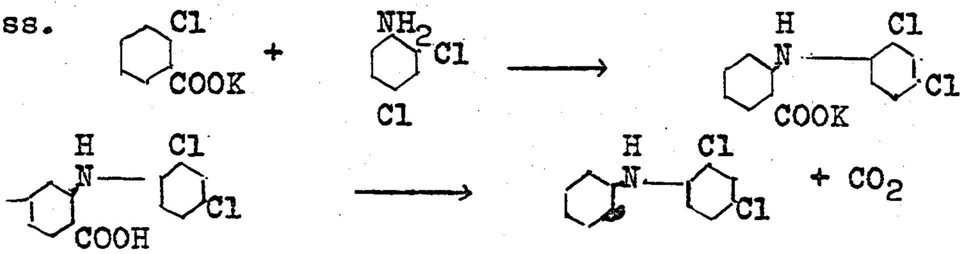
Attempts to prepare meta azo toluene in the same way as was used for the ortho compound produced a product melting at 35-40°, while the recorded melting point of this compound is 54°. Since meta azoxy toluene melts at 39° it seemed likely that the reduction product was the azoxy compound, and in fact when distilled with iron filings a red oil came over which gradually solidified. M.P. = 50°. Undoubtedly the azoxy compound had been produced in the original reduction and was reduced to the azo compound by this reductive distillation. This meta azo toluene was reduced according to the patent of Bodenstein (89): 10 grams of meta azo toluene was suspended in 50 cc. of concentrated hydrochloric acid and one gram of potassium iodide. The mixture turned deep blue at first. It was kept in a water bath at 40-50° and sulfur dioxide passed through it for ten hours and the precipitate became creamy yellow. The entire reaction mixture was then added to water, filtered, concentrated hydrochloric acid added, and upon standing the hydrochloride of meta tolidin, a white crystalline compound, precipitated. This was tried as an indicator and although it gives a faint red oxidation product, which is reversible with ferrous sulfate the color change is not very intense and the compound is useless as an indicator.

The tetra brom derivative of meta tolidin is said to give a red color on standing in air and so an investigation of this derivative was made. The bromination was carried out according to the directions of Schlenk (90). 9 grams of bromine was added to 5 grams of the hydrochloride of meta tolidin suspended in 100 cc. of concentrated hydrochloric acid. After standing the mixture first turned yellow and then creamy white. After filtration, the precipitate was added to a stannous chloride solution to remove the excess bromine. Any unbrominated tolidin was removed by dissolving it in boiling dilute hydrochloric acid. After recrystallization from toluene, the tetrabrom tolidin melted at 230° which agrees exactly with the recorded melting point. This compound dissolves in concentrated sulfuric acid forming a deep red solution but it does not function as a desirable indicator since it gives no evidence of a color change during a dichromate-iron titration.

The possible effect of halogen substitution upon the indicator properties of diphenylamine was investigated. 2,4,2',4', tetrachlor diphenylamine  was prepared according to the directions of Chapman (91) by passing gaseous chlorine for about two hours into a solution of 50 grams of diphenylamine dissolved in 250 grams of acetic acid. Recrystallized from alcohol the product melted at 141°. Recorded M.P. = 141-142°. The 2,4,6,2',4',6' hexachlor diphenylamine  was prepared by dissolving 50 grams of diphenylamine in 250 grams of glacial acetic acid and passing chlorine into the reaction mixture until there was a gain in weight of fifty grams as demanded by theory. A crystalline compound separated which after recrystallization from glacial acetic acid melted at 139°. Recorded M.P. = 139°.

2,4,2',4' tetrabrom diphenylamine  was prepared according to the procedure of Elson, Gibson and Johnson (92) by dissolving 21 grams of diphenylamine in 300 cc. of glacial acetic acid and heating with reflux. 25 cc. of bromine was dropped into the boiling solution. The crystals which separated on cooling, after recrystallization from glacial acetic acid melted at 180°. Recorded M.P. = 186°.

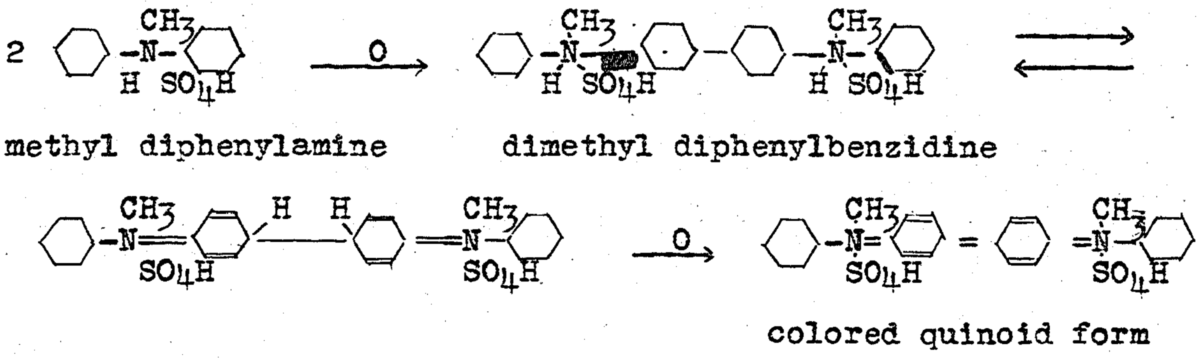
2,4 dichlor diphenylamine, described by Ullman (82), was prepared by refluxing for eight hours 25 grams of ortho-chlor potassium benzoate, 37.5 grams of dichlor aniline in 60 cc. of amyl alcohol in the presence of 0.5 grams of natur kupfer. The potassium salt of ortho-chlor benzoic acid was made by evaporation of a just alkaline solution of the acid to dryness.



After heating, the mixture was made alkaline with sodium hydroxide and steam distilled. Water was added to the steam distillation residue and the excess dichlor aniline removed by filtration. The filtrate was made acid with hydrochloric acid and a crystalline precipitate was formed. This was recrystallized from glacial acetic acid. M.P. = 230°. The recorded melting point for dichlor diphenylamine carbonic acid is 249°. Yield = 3 grams. This acid was heated to 285°

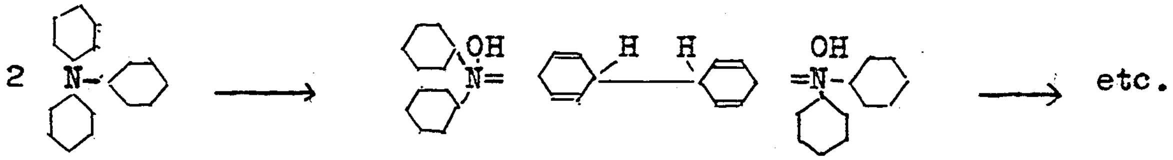
until the evolution of carbon dioxide ceased and the residue was extracted with aqueous ammonia to remove any undecomposed acid. The residue from the ammonia extraction was boiled with methyl alcohol and the solution treated with excess water. A crystalline compound separated. Recrystallized from dilute methyl alcohol. M.P. = 61°. Recorded melting point for dichlor diphenylamine = 64°. Since the yield by this preparation was very small another preparation was attempted with several modifications to determine whether the yield could not be increased and if the amine could be distilled as was the case with tolyl phenylamines. The reaction consisted of 20 grams of dichlor aniline, 13 grams of ortho-chlor potassium benzoate, 20 cc. of amyl alcohol and 0.3 gram of natur kupfer. The amount of amyl alcohol was reduced to see if this would have any effect upon the yield. The subsequent treatment was the same as before. The yiled of the acid was 13 grams as compared with 3 grams in the first attempt. This is interesting because it shows that too much amyl alcohol interferes with the course of the reaction. After splitting off the carbon dioxide by heating to 285° the amine was distilled. B.P. = 343° at atmospheric pressure. After recrystallization from dilute methyl alcohol. M.P. = 64.5°. All of these halogenated derivatives were tried as indicators without success.

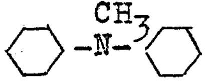
Marqueyrol and Muraour had criticized Wielands explanation of the oxidation of diphenylamine in which he postulated that the first step consisted in the removal of one hydrogen atom from a benzene nucleus with subsequent union of two such residues. Wieland replied to their criticism holding his ground and cited, in support of his views, experiments he had carried out on tertiary amines (93). In these compounds there is obviously no chance for union of the nitrogen atoms as is demanded by theory put forth by Marqueyrol and Muraour. Wieland represented the oxidation of methyl diphenylamine as follows:



This reaction mechanism was substantiated by Maitland and Tucker (94).

Since salt formation with acetic acid is obviously impossible in the case of triphenylamine, Wieland stated that the reaction in this case is best explained by addition of oxygen or hydroxyl.



In the course of this work Wieland noted that N,N' dimethyl, N,N' diphenylbenzidine gives a carmine red color with oxidizing agents. A thorough study of this and related compounds proved to be profitable as well as interesting. Methyl diphenylamine,  , was prepared by Wieland's method. 50 grams of technical diphenylamine and 40 grams of dimethyl sulfate were heated for one hour on the water bath and for one hour longer to 130° on the metal bath (thermometer) in the reaction mixture). 7.5 grams of sodium in 300 cc. of alcohol was added in order to bring all the diphenylamine into reaction. This cold sodium alcoholate seemed to have no effect upon the tarry mass on the bottom of the flask so the reaction mixture was boiled under reflux until a white precipitate had formed and the blackish material had been transformed. The white precipitate which is composed of a mixture of sodium sulfate and methyl diphenylamine sodium sulfonate was filtered off and treated as described below. The alcohol was distilled from the filtrate and the residue heated again with 40 grams of dimethyl sulfate. The resulting solution was made strongly alkaline with aqueous sodium hydroxide and boiled for three hours under reflux. The reaction mixture was then steam distilled and the methyl diphenylamine came over rather slowly as little drops of oil. About two liters of distillate was extracted with ether, dried over sodium sulfate and the ether removed by distillation. The residual methyl diphenylamine boiled at 290°. Recorded B.P. = 290-295°. The yield was 15 grams as compared with 24 grams obtained by Wieland from the same quantity of starting materials. The oxidation of methyl diphenylamine to the benzidine compound was unsuccessful when Wieland's directions were followed. 12 grams of methyl diphenylamine was treated with 150 cc. of glacial acetic acid, 50 cc. of absolute alcohol, and 10 cc. of concentrated sulfuric acid and cooled to 0^{o}. The amine was oxidized by slowly adding with constant stirring a cooled solution of 15 grams of sodium dichromate dissolved in a little water and 50 cc. of galcial acetic acid. The reaction mixture turned deep red almost black. After two minutes zinc dust was added in small portions with vigorous shaking and the reaction mixture turned greenish brown. The suspended solids were transfered to a filter and washed with water and alcohol. After thorough drying, this solid was extracted with ether in a soxlet. The ether yielded on evaporation a tarry residue from which we found it impossible to isolate the benzidine compound.

A further attempt to oxidize methyl diphenylamine required the preparation of more of the amine. The procedure of Wieland described above, was followed up to the point where a second 40 gram portion of dimethyl sulfate was added. This step was omitted. After distilling off the ethyl alcohol the mixture was made alkaline with sodium hydroxide and steam distilled. 15 grams of methyl diphenylamine was obtained so that the second treatment with methyl sulfate may be evidently omitted. The oxidation of the amine was successfully accomplished by the following directions of Maitland and Tucker (94). 15 grams of methyl diphenylamine was dissolved in 210 cc. of cold dilute sulfuric acid (60 cc. of concentrated sulfuric acid and 150 cc. of water). A pale yellow solution resulted. 4 grams of sodium dichromate, dissolved in 30 cc. of water, was added drop by drop with shaking. A purple color appeared immediately and remained during the addition of the dichromate. Solid sodium sulfite was then added, the purple color discharged and gave way to a green. The precipitate was filtered off, dried and extracted in a soxlet with benzene. The benzene solution deposited cream colored platelets. Portions of these were recrystallized from acetone, amyl alcohol, and benzene. The highest melting point = 165° was obtained after the benzidine was recrystallized three times from amyl alcohol and then washed with ether. Wieland records a melting point = 171°. This dimethyl diphenylbenzidine gives a pink color during a ferrous dichromate titration but it cannot be used as a titration indicator because the color of the oxidation product is not sufficiently intense and the color change is not sharply reversible.

Wieland had observed that the sulfonated methyl diphenylamine gives an intense color with oxidizing agents and as the sodium salt of this acid is obtained as a by-product when methyl diphenylamine is prepared as described above, the precipitate formed by the action of the sodium alcoholate was studied as this precipitate consists of a mixture of sodium sulfate and the desired sodium salt. The precipitate was dried and refluxed with ether to remove any diphenylamine or methyl diphenylamine. The extracted salt mixture was dissolved in water and 20% sodium hydroxide added until precipitation began. Mother of Pearl like crystals formed slowly and their quantity continued to increase for some time. After standing twelve hours the precipitate was filtered off and washed with alcohol. The crystals were again dissolved in water and the precipitation and washing repeated. The sodium content of the precipitate was determined as sulfate by the following procedure. 0.3-0.4 gram sample was heated to carbonization in a platinum crucible, a few crystals of ammonium sulfate (zur analyse) was added, followed by a few drops of water and the contents of the crucible ignited cautiously. After final strong heating the sodium sulfate was weighed. % Na found = 8.22%. Calculated % Na for $C_{13}H_{12}NSO_3Na$ = 8.07% Na. Therefore this compound is methyl diphenylamine sodium sulfonate.

Preliminary trials seemed to indicate that this salt had distinct possibilities. When ferrous sulfate was titrated with dichromate in the presence of two drops of a 1% solution of the salt and 15 cc. of retarder solution, the total volume being 100 cc., a slight excess of dichromate produced a beautiful strawberry red which was dispelled by an excess of ferrous solution. The addition of mercuric chloride to a solution containing this sodium salt did not interfere with these color changes. However, closer study disclosed the uselessness of this compound as an internal oxidation-reduction indicator because it shows at the equivalence point no sharp color change. It exhibits a series of intermediate colors which impart a straw color to the solution before a definite red is obtained.

Since dimethyl diphenylbenzidine and methyl diphenylamine sodium sulfonate give colored products with oxidizing agents it was decided to investigate the next higher homologues concentrating particularly on the sulfonated salts. In the preparation of methyl diphenylamine by Wieland's process it was found that the addition of a second portion of methyl sulfate was superfluous and so this omission was made in carrying out the procedure described on page 46 during an attempt to prepare ethyl diphenylamine. The final product was undoubtedly diphenylamine because the oily distillate solidified immediately and gave a blue coloration with dichromate. Gibson and Vining (95) report ethyl diphenylamine to be an oil, B.P. = 292-295°. The diphenylamine had not reacted and the additional portion of ethyl sulfate is necessary in preparing the ethyl diphenylamine by Wieland's method and another preparation which included the second addition of ethyl sulfate was in fact successful. 100 grams of diphenylamine, 100 grams of ethyl sulfate, and 15 grams of sodium dissolved in 400 cc. of alcohol, as reagents, produced 40 grams of a pale yellow oil (B.P. = 292-296°) i.e. ethyl diphenylamine.

Gibson and Vining had also prepared this amine, and a run was made using their directions in order to compare the relative merits of the two procedures. 34 grams of diphenylamine, 46 grams of ethyl sulfate and 75 cc. of benzene were refluxed for six hours. Two similar reaction mixtures were started that differed only in that toluene and xylene were used instead of benzene as the solvent. These were first heated on the water bath for two hours and then refluxed for four hours. The solvents were removed by steam distillation. After cooling an excess of aqueous sodium hydroxide was added to the steam distillation residues and then refluxed for 30 minutes. On cooling a crystalline compound settled out in each case. The solutions were then warmed to 50° and extracted with benzene. The benzene layers were washed and allowed to stand over night in contact with 50 cc. of concentrated hydrochloric acid. The hydrochloride of the unreacted diphenylamine precipitated and was removed by filtration. The filtrate, composed of benzene solution and concentrated hydrochloric, was made alkaline with sodium hydroxide and the benzene layer separated and dried over sodium sulfate. The benzene was then distilled off and the fraction boiling at 292-296° was collected. The weight of ethyl diphenylamine from each reaction mixture was: I (benzene) = 4.5 grams, II (toluene) = 0 grams, III (xylene) = 11 grams. This procedure using xylene as a solvent is therefore recommended in preference to Wieland's process. The absence of ethyl diphenylamine in case II is striking and only lack of time prevented a repetition to establish the validity of this finding.

As diethyl dipheynlbenzidine has never been prepared an attempt was made to do so using the procedure employed for the preparation of dimethyl diphenylbenzidine. Only a tar was obtained from which it was impossible to isolate any definite product.

The salt precipitate resulting from the treatment with sodium alcoholate of a reaction mixture in which ethyl sulfate and diphenylamine were carried through Wieland's procedure and presumably consisting of sodium sulfate and the ethyl diphenylamine sodium sulfonate was washed with ether. To remove any diphenylamine water was added to the residual solid and since it did not all dissolve the suspension was then warmed and filtered. An oil appeared in the filtrate and solidified on cooling. This was found to be diphenylamine so the solution was extracted with ether. The aqueous layer was separated and treated with excess sodium hydroxide which, by common ion effect, ought to cause the sodium salt of the sulfonated compound to precipitate as was the case in the methyl derivative. After three days a white crystalline compound appeared and when this was tried as an indicator with ferrous sulfate and dichromate it showed excellent promise of being practicable. This compound which was thought to be ethyl diphenylamine sodium sulfonate was filtered and attempts were made to purify it for analysis. The first sodium determination was made after two recrystallizations from amyl alcohol, the adhering solvent being removed by washing with ether. % Na found = 8.37. Further recrystallization from ethyl alcohol from whose saturated solution the salt precipitated rather slowly gave a material containing 8.42% Na. A Kjeldahl determination showed 3.60% nitrogen. Calculation gives for ethyl diphenylamine sodium sulfonate: 7.69% Na and 4.68% N. Since our analyses did not coincide with these values an attempt was made to prepare more of the compound but without avail. This failure will be discussed later.

Although the composition of the salt had not been recognizably established a 1% aqueous solution was prepared and a series of titrations was run to determine whether this compound had suitable indicator properties. The ratio of ferrous solution to dichromate as found under varying conditions is given in Table V.

Table V

$FeSO_4$ (cc)	$K_2Cr_2O_7$ (cc)	Conditions
20 20	17.85 17.88	$K_3fe(CN)_6$ as Indicator 100 cc H_2O 15 cc dilute HCl
20 20	17.95 17.95	1 drop of indicator solu. 15 cc dilute HCl 75 cc. H_2O 15 cc. retarder

In the case of the internal indicator the endpoint was very sharp and unmistakable, the color changing from the green of the chromic ions to the purple color of the oxidized indicator. The endpoint is very evident even when one drop of a 1% solution is used in a final volume of 400 cc.

In the next series of titrations mercuric, mercurous, and stannic ions were introduced to determine whether they would interfere with the indicator action of the compound. 100 cc. of water, 15 cc. of dilute hydrochloric acid, (omitted when ferricyanide was used) and 5 cc. of saturated mercuric chloride were placed in a 250 cc. beaker. Into this was rinsed 20 cc. of approximately 0.1N ferric chloride which had been decolorized by stannous chloride and which contained 10 cc. of concentrated hydrochloric acid. The solutions were titrated without delay and the results are given in Table VI.

Table VI

$FeCl_3$ (cc)	$K_2Cr_2O_7$ (cc)	Conditions
20 20	19.20 19.21	$K_3Fe(CN)_6$
20 20	19.28 19.25	1 drop of internal indicator

In this series of titrations it was noticed that the intensity of the purple color was lessened by the presence of the mercury and tin salts. However, the change is still unmistakable and the endpoint sharp, and check results are easily obtained as shown above. Tests were also made to determine whether it was the mercuric, mercurous, stannous, or stannic salts which caused this slight decrease in color intensity. Mercuric, stannous and stannic salts caused little if any diminution in the color intensity but mercurous chloride produced marked fading. There is a constant indicator error of about 0.08 cc. of dichromate but later analyses showed that when the dichromate is standardized with the aid of this indicator and the figures thus obtained used in the subsequent analyses, the errors arising from the indicator are eliminated.

A series of iron ore analyses was run using the new compound as indicator and comparing the values obtained with those found when ferricyanide was used. The iron values of the dichromate using the external indicator was obtained from a standard iron ore from the Bureau of Standards (#27 containing 69.2% Fe).

The ores were analysed by treating a 0.3 gram sample in a 100 cc. beaker with 15 cc. of concentrated hydrochloric acid and 3 cc. of stannous chloride and warming to decompose the ore. If the solution became permanently yellow it was decolorized with stannous chloride. The reduced solution was then rinsed into a 250 cc. beaker containing 100 cc. of water and 5 cc. of saturated mercuric chloride. When the internal indicator was used one drop of a 1% solution was used and also 15 cc. of retarder solution. The results are given in Tables VII, VIII, and IX.

Table VII

Iron value from Standard Ore

Indicator	$K_2Cr_2O_7$ (cc)	Fe value
$K_3Fe(CN)_6$	36.98 37.00	0.005611
Internal indicator	37.06 37.08	0.005601

Table VIII

Analysis of iron ore (a)

Indicator	$K_2Cr_2O_7$ (cc)	% Fe
$K_3Fe(CN)_6$	35.25 35.30	66.00
Internal indicator	35.35 35.40	66.04

Table IX Analysis of Ore (b)

Indicator	$K_2Cr_2O_7$ (cc)	% Fe
$K_3Fe(CN)_6$	31.10 31.11	58.19
Internal indicator	31.20 31.19	58.25

From these results we may conclude that this new indicator may be practically used in iron determinations by the stannous chloride method with great accuracy. The optimum volume of the solution being titrated is about 200 cc.

This new compound was used as an indicator in the determination of chromium in chromite with excellent results. The endpoint was exceedingly sharp and unmistakable. One drop of a 1% aqueous indicator solution is sufficient for a total optimum volume of 200-300 cc. In the first comparative series of chromium determinations an ore was analysed by the usual sodium peroxide procedure using ferricyanide and the internal indicator in the final titrations. The 50 cc. aliquot titrated was diluted with 200 cc. of water containing 15 cc. of dilute hydrochloric acid, 15 cc. of retarder solution and 25 cc. of ferrous solution, and the added excess ferrous iron immediately titrated with dichromate. The ratio of ferrous and dichromate solutions had previously been determined in the presence of each indicator.

Table X

Ratio of $FeSO_4$ to $K_2Cr_2O_7$

$FeSO_4$	$K_2Cr_2O_7$	Indicator	Conditions
25 25	22.11 22.13	$K_3Fe(CN)_6$	100cc H_2O 15 cc dil HCl
25 25	22.16 22.18	Internal indicator	100 cc H_2O 15 cc dil HCl 15 cc retard.

Table XI

Analysis of Ore (623)

$K_2Cr_2O_7$	Indicator	% Cr
9.68 9.67	$K_3Fe(CN)_6$	21.57
9.72 9.73	Internal indicator	21.57

Another series of comparative analyses was run on this chromium ore with a slight change in procedure. The samples were fused in the same way but after the fusion mass was disintegrated with water, concentrated hydrochloric acid was added in sufficient quantity to dissolve the hydrated ferric oxide. The solution was warmed slightly so that too large an excess of acid was not required. This acid solution was then made up to 250 cc. and aliquots taken for analysis. The idea leading to this modification was to determine whether an excess of ferric chloride interferes with the indicator action.

Table XII

Ratio $FeSO_4$ to $K_2Cr_2O_7$

$FeSO_4$ (cc)	$K_2Cr_2O_7$	Indicator
25 25	22.02 22.01	$K_3Fe(CN)_6$
25 25	22.08 22.08	Internal indicator

Table XIII

Analysis of Chrome Ore

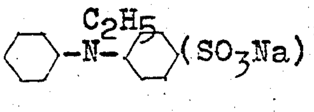
$K_2Cr_2O_7$	Indicator	% Cr
9.65 9.64	$K_3Fe(CN)_6$	21.44
9.72 9.70	Internal indicator	21.44

The above data shows that excellent agreement may be obtained between the external and internal indicator. It also shows that the hydrated ferric oxide may be dissolved without interfering with the action of the indicator.

Since the color changes exhibited by this new indicator are sharply reversible, ratios were run between ferrous and dichromate solutions by adding the indicator to a dichromate solution and then titrating with ferrous solution. In order to get approximately the same conditions as would be present in a chrome ore analysis the following procedure was followed. To a measured volume of dichromate was added 3.5 cc. of ferric chloride, 1.5 grams of sodium peroxide, the solution boiled the iron precipitate dissolved in hydrochloric acid, the solution diluted to 200 cc, 15 cc of retarder solution added and then titrated with ferrous solution. A very sharp endpoint was obtained and this ratio agreed with the ratio taken when ferrous solution was titrated with dichromate. However, some precautions were necessary. The purple color of the oxidized indicator does not develope in the presence of a large excess of dichromate but as the ferrous solution is slowly added the purple color appears and becomes rather pronounced several cc. before the endpoint and disappears sharply when the equivalence point is reached. It is better to delay the addition of the indicator until the endpoint is neared as can be qualitatively detected by the diminution of the orange color of the solution. The final change from the purple color to the green of the chromic ions is very sharp. Another series of ratios was taken between the dichromate and ferrous solution with the difference that the ferric oxide precipitate was filtered off. The ratio was the same as that obtained in the preceding series.

A chromium ore was then run using this direct method of titration with ferrous sulfate. A 0.1 gram sample was fused with 2 grams of sodium peroxide, the fusion residue treated with 100 cc. of water and boiled to decompose any peroxide. After cooling, the hydrated ferric oxide was dissolved in concentrated hydrochloric acid. 15 cc. of retarder was added the solution diluted to 250 cc. and titrated with ferrous sulfate in the presence of one drop of 1% indicator solution . % Cr found = 31.92%. When the ferric precipitate was removed by filtration the % Cr. = 32.23. The chromium content of this ore as determined by the standard procedure was found to be 32.10% Cr. The usual method involves addition of excess ferrous solution and back titration and establishment of exact ratios between these solutions. Therefore this simplified procedure seems worthy of further study.

Since this indicator worked so well a reaction mixture was established for the preparation of more of this compound. The directions which have been described earlier were followed but although numerous attempts have been made to repeat this preparation none have proved successful. A salt precipitate is obtained which gives slight indicator action but it is by no means satisfactory. All the products obtained subsequent to the first preparation give a red oxidation product but its developement during a titration is accompanied by a yellow -red intermediate stage which is objectionable. Possibly this difference in products may be due to the fact that in the first preparation an old lot of ethyl sulfate was used and this may have contained some material which served to catalyse that particular reaction and to direct the sulfonation along a particular line, the reaction taking a course which has never again been duplicated. This is the only explanation that can be offered at this time.

Since the identity of the compound prepared in the initial reaction could not be determined an analysis of the preparation obtained cocsistently in the subsequent attempts was made. The product was prepared by treating 100 grams of diphenylamine, 100 grams of ethyl sulfate on the water bath for two hours and then for two hours longer on the metal bath at 130°. The reaction mixture was then refluxed with a solution of sodium ethylate obtained by dissolving 15 grams of sodium in 400 cc. of alcohol. The white salt precipitate was filtered off, dissolved in water, the solution filtered and then extracted with ether. Air was blown through the solution to remove the ether and about 50 cc. of saturated sodium hydroxide solution was added. After standing over night the white salt precipitate composed of sodium sulfate and the sulfonated compound was filtered and dried. Various methods of separating the sulfonated compound from the sodium sulfate were tried. Alcohol dissolves the sulfonated compound but it is recovered from the alcoholic solution with great difficulty. Finally it was found that the best way to obtain the sulfonate compound free from sulfate was by fractional crystallization from water, the sulfonated compound being the less soluble. This sulfonated compound was repeatedly recrystallized from water until it was free from alkali and sulfate. It was analysed after being dried over phosphorus pentoxide and heated at 110° to constant weight. The % Na found = 7.66, 7.59, 7.73. Average % Na = 7.66. This analysis corresponds to the formula , ethyl diphenylamine sodium sulfonate, which gives a calculated % Na = 7.69. This compound as has been stated is not the same as the product obtained from the first preparation, differing not only in indicator action, but also in sodium content. Although the analytical data on the original indicator are not so informing as they might be it is believed that the compound is in all likelihood, an isomer of ethyl diphenylamine sodium sulfonate prepared in the latter runs.

The next attempts were directed toward the possible preparation of the original ethyl diphenylamine sodium sulfonate by the direct sulfonation of ethyl diphenylamine. The directions of Gibson and Vining (95) for the sulfonation of methyl diphenylamine were followed. These authors stated that they got no evidence of the formation of a sulfonated compound when they used ethyl sulfate in place of methyl sulfate. This is not true, and as will be shown later ethyl diphenylamine sodium sulfonate can be prepared by this procedure. 27 grams of ethyl diphenylamine and 20 grams of ethyl sulfate were heated on the water bath for twelve hours. After refluxing for two hours with aqueous sodium hydroxide the mixture was extracted with benzene at 50°. Saturated sodium hydroxide was added to the aqueous solution until the precipitation began. After standing over night the white crystalline precipitate was filtered and dried. It was expected that it would contain the sulfonated compound and sodium sulfate. The mixture was extracted several times with alcohol to dissolve out the sulfonated compound and the alcoholic solution was then evaporated to dryness. The residue was then recrystallized from alcohol. The difficulty of securing the material free from sulfate and alkali entailed such serious losses that another preparation was necessary to procure material sufficiently pure for analysis. A 1% aqueous solution of this admittedly contaminated product was tried as an indicator. It gives a rose oxidation product with a slight excess of dichromate and is much more satisfactory than the ethyl diphenylamine sodium sulfonate prepared according to Wieland's process. The latter gives a red oxidation product but in the present case during a titration there is no intermediate color change such as is observed with preparations obtained in the later duplications of Wieland's procedure.

Ratios between ferrous solutions and dichromate showed that the indicator error may be considered as 0.010 cc. Chromium analyses were run using this indicator and the following data show that it gives reliable results.

Table XIV

Ratio of $FeSO_4$ to $K_2Cr_2O_7$

$FeSO_4$	$K_2Cr_2O_7$	Indicator	Conditions
20 20 20	16.05 16.03 16.08	Internal Indicator	50 cc H_2O 30 cc retarder 15 cc dil HCl 1 drop of indicator
20 20	15.95 15.96	$K_3FE(CN)_6$	100 cc H_2O 15 cc dil HCl

Table XV

Analysis of Chrome Ore

$FeSO_4$	$K_2Cr_2O_7$	Indicator	Conditions	% Cr
25.00 25.00	7.02 7.03	Internal indicator	50 cc H_2O 30 cc retarder 15 cc dil HCl	22.50
25.00 25.00	6.92 6.95	$K_3Fe(CN)_6$	100 cc H_2O 15 cc dil HCl	22.49

Another preparation of this product from the direct sulfonation of the tertiary amine was begun. 31 grams of ethyl diphenylamine and 24 grams of ethyl sulfate formed the initial reagents. The procedure was that described above but the salt precipitate was handled differently. Instead of extracting with alcohol the salt was recrystallized from water as was done with the product from Wieland's preparation. It was dried over phosphorus pentoxide and heated to constant weight in the oven and then analysed. The sodium content is 7.48% and shows that this product is the ethyl diphenylamine sodium sulfonate and is identical with the product obtained from Wieland's process. Their indicator action is alike, both giving a red color with excess dichromate but this is preceded by a series of intermediate color changes which makes the material useless as an indicator.

These results indicate that by direct sulfonation of ethyl diphenylamine there is probably formed a mixture of isomers. In the first preparation the extraction of the salt mixture with alcohol removed one of the isomers which does function as a practicable indicator in chromium analyses. As yet not enough of this isomer has been obtained sufficiently pure. In the second preparation of this product by direct sulfonation of ethyl diphenylamine the recrystallization from water yielded a compound whose analysis corresponded to ethyl diphenylamine sodium sulfonate but which is not acceptable as an indicator.

Summary

(1) The history of internal oxidation-reduction indicators has been reviewed.

(2) A series of compounds of various types have been prepared and tested with respect to their possible use as oxidation-reduction indicators. The findings are grouped under the headings below.

(A) Compounds which give no colored oxidation products.

1. diamido diphenetol
2. α naphthylamine
3. chromotropic acid
4. β dinaphthylamine
5. meta nitro diphenylamine
6. ortho-, meta-, and para-tolyl β naphthylamine
7. meta-tolyl α naphthylamine
8. ortho-, and meta-tolidin
9. tetra brom meta tolidin
10. 2,4,2',4', tetrachlor diphenylamine
11. 2,4,6,2',4',6' hexachlor diphenylamine
12. 2,4,2',4' tetrabrom diphenylamine
13. 2,4, dichlor diphenylamine

(B) Compounds which give colored oxidation products but of too little merit to warrant use as oxidation-reduction indicators

1. ortho-tolyl phenylamine

2. phenyl hydrazo naphthalene
3. N,N, dimethyl N,N' diphenylbenzidine
4. methyl diphenylamine sodium sulfonate
5. ethyl diphenylamine sodium sulfonate

(C) Compounds which function satisfactorily in the determination of iron and chromium. Their action is not satisfactory in the presence of mercury salts.

1. para-tolyl phenylamine
2. meta-tolyl phenylamine
3. alcohol soluble sodium derivative of the action of ethyl sulfate on ethyl diphenylamine

(D) Compounds which function satisfactorily even in the presence of mercury salts.

1. naphthidine
2. one product of the action of ethyl sulfate on diphenylamine..

Bibliography

(1) Cazeneuve, P., Chem. Zeit., 24, 684, 557 (1900)
Bull. Soc. Chem., (3) 23, 592,701,769 (1900)
Bull. Soc. Chem., (3), 25, 758 (1901)

(2) Oddo, B., Gazz. Chim. ital., 33 II 134 (1903)
39 I 671 (1909)

(3) Brandt, L., Zeit. Anal. Chem., 45 95 (1906)
53 729 (1914)

(4) Barneby and Wilson, J.A.C.S. 35 156 (1913)

(5) Kolthoff, I.M., Chem. Weekblad 21 2 (1924)

(6) Feigl, F. Chem. Zeit. 44 689 (1920)

(7) Sierra, F. and Burriel, F., Anales soc. espan. fis. quim. 30 441 (1932)

(8) Haary, R.G. and Rudge, E.A., J.Soc. Chem. Ind., 51 64T (1932)

(9) Hofman, A.W., Ann. 132 165 (1864)

(10) Merz and Weith, Ber. 5 283 (1872)

(11) Kopp, E., Ber. 5 283(1872)

(12) Tillmans, J. and Sutthoff, W., Z. Anal. Chem., 50 473 (1911)

(13) Smith, L., Z. Anal. Chem. 56 28 (1917)

(14) Tillmans, J., Z. Anal. Chem. 56 509 (1917)

(15) Hinrichs, C.J., Bull. Soc. Chem., 33 1002 (1905)

(16) Meaurio, V.P., Anales soc. quim. Argentina 5 185 (1917)

(17) Knop, J., J.A.C.S. 46 263 (1924)
Zeit. Anal. Chem. 63 98 (1923)

(18) Baeyer, A.V., Ber. 38 583 (1905)

(19) Wieland, H., Ber. 39 1499, 3036 (1906)
41 3478 (1908)
43 3260 (1910)
45 494 (1912)
Ann. 381 200 (1911)

(20) Kehrmann and Micewicz, Ber. 45 2641 (1912)

(21) Kehrmann and Roy, Ber. 55 156 (1922)

(22) Schlenk, W., Ann. 363 313 (1908)

(23) Wieland, H., Ber. 46 3298 (1913)

(24) Marqueyrol and Muraour, Bull. Soc. Chem., 15 186 (1914)

(25) Wieland, H., Ber., 52 886 (1919)

(26) Madelung, W., Reiss, E., and Herr, E., Ann. 454 7 (1927)

(27) Kolthoff, I.M., and Sarver, L., Z. Electrochem., 36 139 (1930)

(28) Theil, A., Z. Electrochem., 35 274 (1929)

(29) Scott, W.W., J.A.C.S. 46 1396 (1924)

(30) Core, C.B., Chemist Analyst 20 14 (1931)

(31) Thomas, C.A., Chemist Ahalyst 17 18 (1928)

(32) Pichler, B.A., Zeit. Anal. Chem. 73 201 (1928)

(33) Mehlig, J.P., J.Chem.Ed. 3 824 (1926)

(34) Kolthoff, I.M., J.Chem.Ed. 6 1914 (1929)

(35) Watson, F.J., Chem.Eng.Mining Review 22 355 (1928)

(36) Kolthoff, I.M., and Sarver, L.A., J.A.C.S. 52 4179 (1930)

(37) Bennett, C.T., and Campbell, N.R., Quart. J. Pharm. Pharmacol 6 436 (1933)

(38) Furman, N. H., Ind. Eng. Chem. 17 314 (1925)

(39) Willard, H.H., and Young, P., Ind. Eng. Chem. 20 764 (1928)

(40) Willard, H.H., and Young, P., J.A.C.S. 50 1334 (1928)

(41) Furman, N.H., and Wallace, J.H., J.A.C.S. 52 2347 (1930)

(42) Willard, H.H., and Young, P., J.A.C.S. 51 139 (1929)

(43) Vanossi, R., and Ferramola, R., Anales asoc. quim. Argentina 20 96 (1932)

(44) Cone, W.H. and Cady, L.C., J.A.C.S. 49 356 (1927)

(45) Kolthoff, I.M., Chem. Weekblad 24 205 (1927)

(46) Kolthoff, I.M., Chem. Weekblad 26 298 (1929)

(47) Kolthoff, I.M. and Pearson, E.A., Ind. Eng. Chem., Anal. Ed. 4 147 (1932)

(48) Sarver, L.A., J.A.C.S. 49 1472 (1927)

(49) Schollenberger, C.J., J.A.C.S. 53 88 (1931)

(50) Druce, J.G.F., Chem. News 128 273 (1924)

(51) Saz, Eugenio, Quimica e Industria 3 33 (1926)
Chem. Zentralbl. 97 2725 (1926)

(52) Someya, K., Z. Anorg. Chem. 152 368 (1926)

(53) Lang, R. and Messinger, J., Ber. 63 1429 (1930)

(54) Gillis, J. and Cuelier, V., Naturw. Tydschr. 11 20 (1929)

(55) Furman, N.H. and Wallace, J.H., J.A.C.S. 52 1443 (1930)

(56) Szebelledy, L., Z. Anal. Chem. 81 97 (1930)

(57) Weeks, M.E., Trans. Kansas Acad. Sci. 34 158 (1931)

(58) Weeks, M.E., Ind. Eng. Chem., Anal. Ed. 4 127 (1932)

(59) Sarver, L.A. and Kolthoff, I.M., J.A.C.S. 53 2902 (1931)

(59) Sarver, L.A. and Kolthoff, I.M., J.A.C.S. 53 2906 (1931)

(60) Willard, H.H. and Young, P., Ind. Eng. Chem., Anal Ed. 5 154 (1933)

(61) Knop, J., Z. Anal. Chem. 85 253 (1931)

(62) Miyagi, Seikichi, J. Soc. Chem. Ind. Japan. 36 146 (1933)

(63) Szebelledy, L. and Schick, K., Magyar Gyogyszeresztud. Tarsasag Ertesitöze 9 449 (1933)

(64) Walden, G.H. and Hammett, L.P., and Chapman, R.P., J.A.C.S. 53 3908 (1931)
55 2649 (1933)

(65) Willard, H.H. and Young, P., J.A.C.S. 55 3260 (1933)

(66) Willard, H.H. and Young P., Ind. Eng. Chem., Anal. Ed. 6 48 (1934)

(67) Walden, G.H., Hammett, L.P., and Edmonds, S.M., J.A.C.S. 56 57 (1934)

(68) Marqueyrol and Muraour, Bull. Soc. Chem. 15 186 (1914)

(69) Nietzki and Goll, Ber. 18 3252 (1885)

(70) Cummings and Steel, J.C.S. 123 2464 (1923)

(71) Vesely, V., Ber. 38 136 (1905)

(72) Jacobsen, P., Ann. 428 77 (1922)

(73) Schmitt, R. and Möhlau, R., J. Prac. Chem. 18 198 (1878)

(74) Van Eck, Chem. Weekblad. 12 6 (1915)

(75) Koenig, P., Chem. Zeit. 35 277 (1911)

(76) Bucherer and Sonnenburg, J.Prac. Chem., 81 19 (1910)

(77) Patent, D.R.P. 114974 Friedlander VI 198

(78) Goldberg, I., Ber. 40 4543 (1907)

(79) Kaufmann, A., Ber. 42 3481 (1909)

(80) Goldberg, I., D.P.R. 187870 Friedlander IX 126

(81) Wieland, H., Ann. 392 176 (1912)

(82) Ullman, F., Ann. 355 323 (1907)

(83) Graebe, C., Ann. 276 54 (1893)

(84) Friedlander, E., Ber. 16 2075 (1883)

(85) Ullmann and La Torre, Ber. 37 2926 (1904)

(86) Bucherer and Seyde, J. Pr. Chem. (2) 75 269 (1907)

(87) Knoevenagel, E., J. Pr. Chem. (2) 89 22 (1914)

(88) Fry, H.S., PhD Thesis, University of Cincinnati, (1905)

(89) Bodenstein, M., D.R.P. 172569 Friedlander VIII 118

(90) Schlenk, W., Ann. 363 335 (1908)

(91) Chapman, A.W., J.C.S. 132 569 (1929)

(92) Elson, Gibson, and Johnson, J.C.S. 132 1085 (1929)

(93) Wieland, H., Ber. 52 890 (1919)

(94) Maitland and Tucker, J.C.S., 130 1390 (1927)

(95) Gibson and Vining, J.C.S. 123 831 (1923)

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